Palladium-catalysed asymmetric regioselective hydroamination of dienoates

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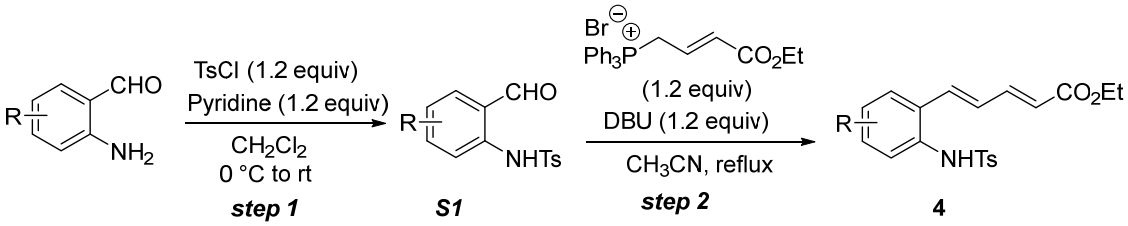
1. General methods

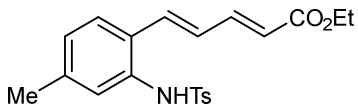
Unless otherwise noted, all reactions were carried out under ambient atmosphere; when the reaction requires heating, the source is oil bath. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (376 MHz) spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend^{TM} 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, tt = triple triplet, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). ESI-HRMS was recorded on a Waters SYNAPT G2. X-ray diffraction experiments were carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2427290 and 2427291). In each case, enantiomeric ratio was determined by HPLC (Agilent Technologies: 1220 Infinity II, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak IA Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm), Chiralpak ID Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm) or Chiralpak IE Column (250 × 4.6 mm). UV detection was monitored at 220 nm or 254 nm. The specific optical rotation was obtained from Rudolph Research Analytical Autopol I automatic polarimeter in $CHCl_3$ solution at 25 °C. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether or dichloromethane (CH_2Cl_2)/methanol (MeOH). TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether (60–90 °C), toluene and tetrahydrofuran (THF) were redistilled. The dienoates **1** were synthesized according to the literature procedures.[1] The known products were confirmed by NMR analysis compared to the reported data.

2. Typical procedure for the preparation of substrates 4

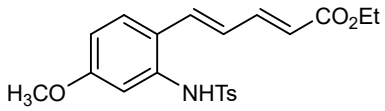


A solution of *p*-TsCl (5.5 mmol, 1.1 equiv) in DCM (5 mL) was added to a solution of 2-aminobenzaldehyde (5.0 mmol, 1.0 equiv) and pyridine (11.0 mmol, 1.2 equiv) in DCM (5 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. After completion (monitored by TLC), the reaction was quenched by adding H_2O (10 mL) and then extracted with DCM (3 × 10 mL). The organic layers were combined and dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/4) to give compound ***S1***.

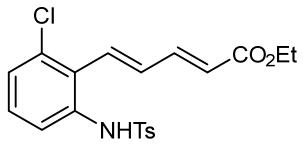
To a stirred solution of ***S1*** (5.0 mmol, 1.0 equiv) and triphenyl phosphonium bromide salt (5.5 mmol, 1.2 equiv) in CH_3CN (10 mL) was added DBU (6.0 mmol, 1.2 equiv). Then the reaction was heated to reflux for 12 h. After completion (monitored by TLC), the reaction was quenched by adding H_2O (20 mL) and then extracted with DCM (3 × 20 mL). The organic layers were combined and dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/4) to give **4**.



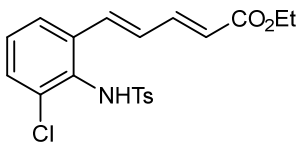
4a: 0.93 g, obtained as a white solid, 48% yield; mp = 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60–7.54 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24–7.20 (m, 2H), 7.19–7.09 (m, 2H), 7.04 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.54 (dd, *J* = 15.4, 10.4 Hz, 1H), 6.47 (s, 1H), 5.88 (d, *J* = 15.4 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.9, 144.3, 144.1, 140.2, 136.2, 134.1, 133.5, 129.7, 129.5, 128.4, 128.3, 127.7, 127.3, 126.3, 121.5, 60.5, 21.5, 21.3, 14.3; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{23}H_{16}NO_4SNa^+$ 408.1240; Found 408.1248.



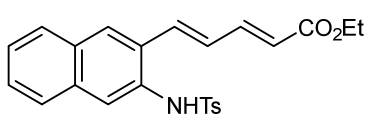
4b: 1.0 g, obtained as a white solid, 52% yield; mp = 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64–7.58 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.25–7.12 (m, 3H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.75 (s, 1H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.49 (dd, *J* = 15.6, 10.8 Hz, 1H), 5.87 (d, *J* = 15.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H), 1.32 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.1, 160.6, 144.5, 144.2, 136.1, 135.0, 133.9, 129.8, 127.5, 127.3, 126.6, 124.4, 120.9, 114.1, 111.6, 60.5, 55.5, 21.5, 14.3; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO_5SNa^+$ 424.1190; Found 424.1199.



4c: 0.73 g, obtained as a white solid, 36% yield; mp = 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64–7.56 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.29–7.14 (m, 4H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.57 (dd, *J* = 15.6, 10.8 Hz, 1H), 5.93 (d, *J* = 15.2 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 1H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.8, 144.5, 143.6, 135.9, 135.0, 134.6, 132.8, 130.4, 129.9, 129.3, 127.6, 127.4, 127.3, 126.8, 122.7, 60.6, 21.5, 14.3; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}{}^{35}ClNO_4SNa^+$ 428.0694; Found 428.0691; Calcd for $C_{20}H_{20}{}^{37}ClNO_4SNa^+$ 430.0665; Found 430.0665.

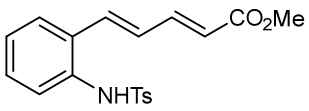


4d: 0.89 g, obtained as a white solid, 44% yield; mp = 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66–7.59 (m, 2H), 7.55–7.47 (m, 1H), 7.35–7.23 (m, 3H), 7.20–7.13 (m, 2H), 6.83–6.70 (m, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 11.2 Hz, 1H), 5.89 (d, *J* = 15.6 Hz, 1H), 4.25 (q, *J* = 7.2, 2H), 2.41 (s, 3H), 1.33 (t, *J* = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.5, 144.5, 142.8, 136.2, 135.4, 134.5, 134.0, 132.3, 129.9, 129.4, 128.0, 127.2, 126.5, 123.9, 121.0, 60.7, 21.6, 14.3; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}{}^{35}ClNO_4SNa^+$ 428.0694; Found 428.0700; Calcd for $C_{20}H_{20}{}^{37}ClNO_4SNa^+$ 430.0665; Found 430.0673.

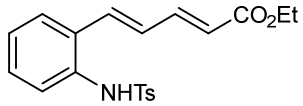


4e: 1.2 g, obtained as a white solid, 56% yield; mp = 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 (s, 1H), 7.82–7.70 (m, 3H), 7.64–7.56 (m, 2H), 7.49–7.44 (m, 2H), 7.31–7.22 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.71 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.62 (s, 1H), 5.96 (d, *J* =

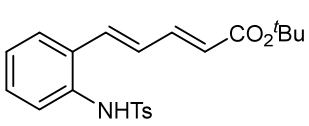
15.6 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.9, 144.2, 144.0, 136.3, 134.4, 133.5, 131.9, 131.2, 130.9, 129.8, 129.4, 127.9, 127.8, 127.3, 127.1, 126.8, 126.4, 125.5, 122.2, 60.6, 21.5, 14.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}NO_4S^+$ 422.1426; Found 422.1412.



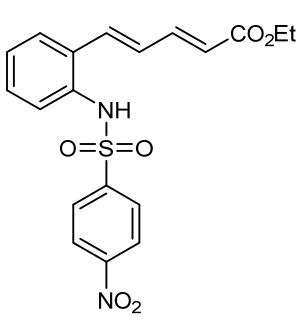
4f: 1.1 g, obtained as a white solid, 62% yield; mp = 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62–7.54 (m, 2H), 7.51–7.44 (m, 1H), 7.31–7.15 (m, 5H), 6.76 (d, J = 15.2 Hz, 1H), 6.66–6.55 (m, 2H), 5.93 (d, J = 15.4 Hz, 1H), 3.79 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.3, 144.4, 144.1, 136.1, 134.4, 133.7, 132.5, 129.8, 129.7, 128.6, 127.6, 127.4, 127.3, 126.6, 121.6, 51.7, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_4SNa^+$ 380.0927; Found 380.0925.



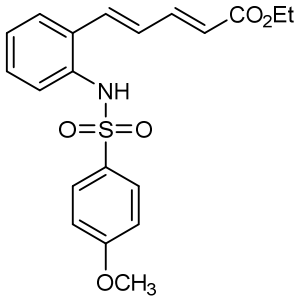
4g: 1.2 g, obtained as a white solid, 65% yield; mp = 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62–7.55 (m, 2H), 7.47 (dd, J = 6.8, 2.4 Hz, 1H), 7.31–7.14 (m, 6H), 6.71 (d, J = 15.2 Hz, 1H), 6.60 (dd, J = 15.6, 10.2 Hz, 1H), 6.40 (s, 1H), 5.92 (d, J = 15.2 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.8, 144.2, 144.0, 136.2, 134.1, 133.6, 132.5, 129.8, 129.6, 128.9, 127.5, 127.4, 127.3, 126.6, 122.2, 60.5, 21.5, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_4SNa^+$ 394.1084; Found 394.1077.



4h: 1.4 g, obtained as a white solid, 72% yield; mp = 172–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65–7.53 (m, 2H), 7.50–7.42 (m, 1H), 7.30–7.14 (m, 6H), 6.71 (d, J = 15.6 Hz, 1H), 6.59 (dd, J = 15.6, 10.8 Hz, 1H), 6.48 (s, 1H), 5.90 (d, J = 15.6 Hz, 1H), 5.17–5.06 (m, 1H), 2.36 (s, 3H), 1.30 (d, J = 6.0 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.4, 144.2, 143.7, 136.2, 133.9, 133.6, 132.5, 129.8, 129.6, 128.9, 127.5, 127.4, 127.3, 126.6, 122.7, 67.8, 22.0, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO_4SNa^+$ 408.1240; Found 408.1234.



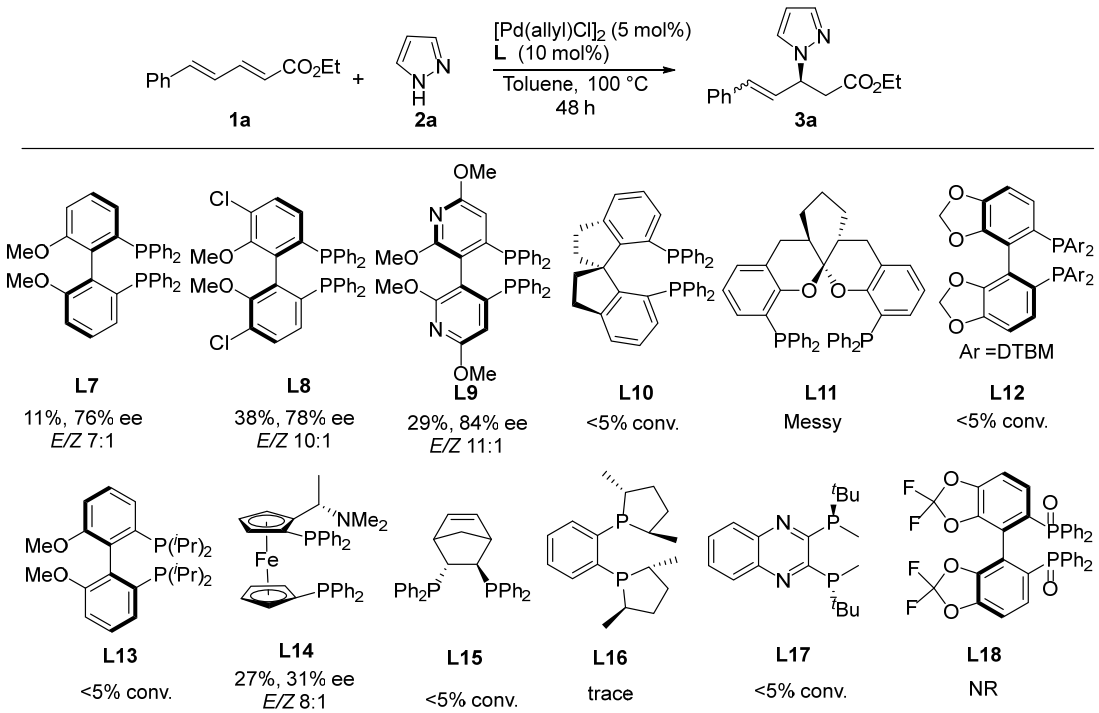
4i: 1.0 g, obtained as a white solid, 66% yield; mp = 166–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29–8.22 (m, 2H), 7.92–7.83 (m, 2H), 7.57–7.48 (m, 1H), 7.35–7.23 (m, 3H), 7.23–7.14 (m, 1H), 6.96 (s, 1H), 6.80 (d, *J* = 15.6, 1H), 6.59 (dd, *J* = 15.6, 11.2 Hz Hz, 1H), 5.92 (d, *J* = 15.6 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.9, 150.4, 144.8, 143.5, 133.7, 133.0, 132.5, 129.9, 129.2, 128.6, 128.3, 128.1, 126.9, 124.3, 122.8, 60.8, 14.3; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{18}N_2O_6SNa^+$ 425.0778; Found 425.0772.



4j: 1.3 g, obtained as a white solid, 65% yield; mp = 129–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66–7.59 (m, 2H), 7.52–7.46 (m, 1H), 7.28–7.19 (m, 4H), 6.91–6.85 (m, 2H), 6.84–6.73 (m, 2H), 6.61 (dd, *J* = 15.6, 11.2 Hz, 1H), 5.92 (d, *J* = 15.2 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.0, 163.2, 144.2, 134.4, 133.8, 132.6, 130.6, 129.6, 129.5, 128.6, 127.6, 127.3, 126.5, 122.1, 114.2, 60.5, 55.6, 14.3; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{23}NO_4S^+$ 388.1219; Found 388.1216.

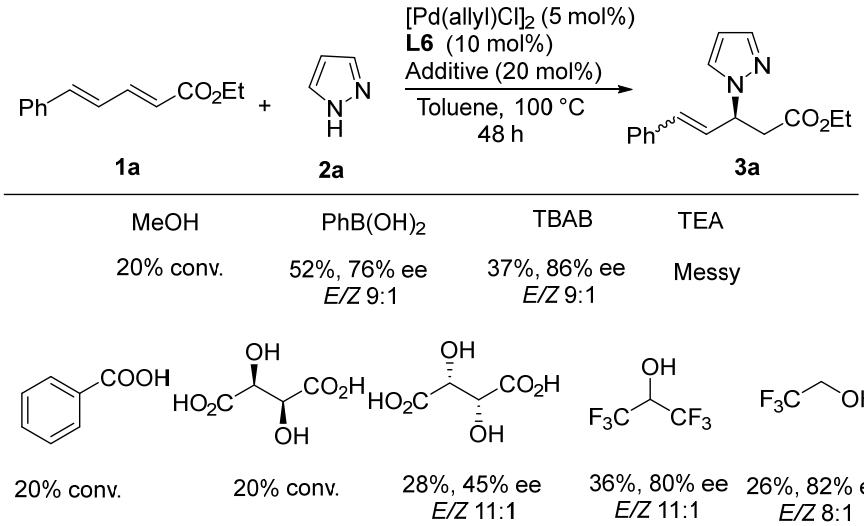
3. More screening conditions of the asymmetric hydroamination of dienoate 1a

3.1 Screenings of chiral ligands[a,b,c]



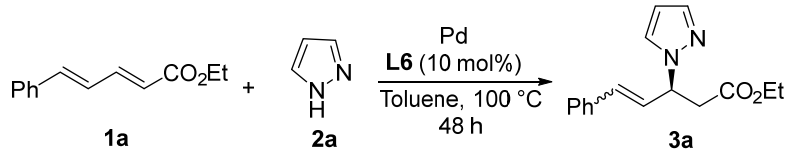
[a] Unless noted otherwise, reactions were performed with substrate **1a** (0.1 mmol), **2a** (0.05 mmol), $[Pd(allyl)Cl]_2$ (5 mol%), ligand **L** (10 mol%) in distilled toluene (0.2 mL) at 100 °C for 48 h. [b] Yield of the isolated product. [c] Ee was determined by HPLC analysis on a chiral stationary phase. [d] *Z/E* ratio was determined by ^{1}H NMR analysis.

3.2 Screenings of additives[a,b,c]



[a] Unless noted otherwise, reactions were performed with substrate **1a** (0.1 mmol), **2a** (0.05 mmol), $[Pd(allyl)Cl]_2$ (5 mol%), **L6** (10 mol%), additive (20 mol%) in distilled toluene (0.2 mL) at 100 °C for 48 h. [b] Yield of the isolated product. [c] Ee was determined by HPLC analysis on a chiral stationary phase. [d] *Z/E* ratio was determined by ^{1}H NMR analysis.

3.3 Screenings of palladium sources[a,b,c]

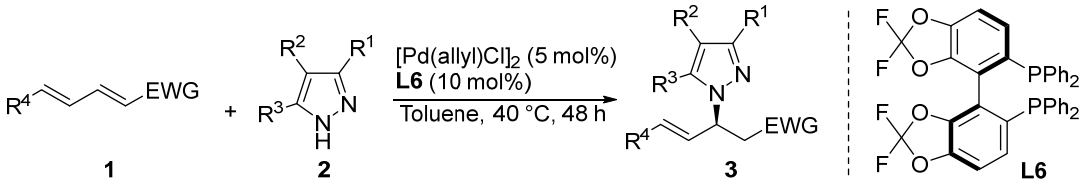


1a **2a** **3a**

$Pd(PPh_3)_4$ (10 mol%)	Pd_2dba_3 (5 mol%)	$Pd(OAc)_2$ (10 mol%)	$Pd(MeCN)_2Cl_2$ (10 mol%)
10% conv	<5%	21%, 83% ee *E/Z* 8:1	NR

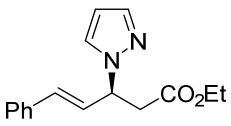
[a] Unless noted otherwise, reactions were performed with substrate **1a** (0.1 mmol), **2a** (0.05 mmol), [Pd] (5 mol%), **L6** (10 mol%), in distilled toluene (0.2 mL) at 100 °C for 48 h. [b] Yield of the isolated product. [c] Ee was determined by HPLC analysis on a chiral stationary phase. [d] *Z/E* ratio was determined by ^{1}H NMR analysis.

4. General procedure of the asymmetric hydroamination reaction of electron-deficient dienes with azoles

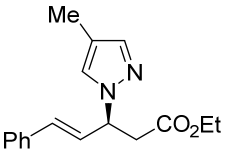


General procedure for the synthesis of 3: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), azole **2** (0.200 mmol, 1.0 equiv) and dienoate **1** (0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, product **3** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether).

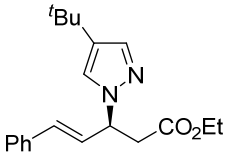
General procedure for the synthesis of racemic 3: The corresponding racemate **3** was obtained with (±)-**L1** as the ligand.



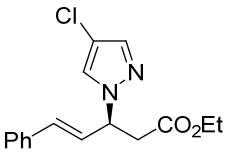
Synthesis of 3a: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3a** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 38.6 mg (0.143 mmol), as a colorless oil, 71% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –21.0 (*c* = 0.92 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 12.49 min, t (minor) = 16.65 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.39–7.18 (m, 5H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.43 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.39 (q, *J* = 6.8 Hz, 1H), 4.11 (q, *J* = 6.8 Hz, 2H), 3.28 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.98 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.19 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.3, 139.6, 135.9, 132.8, 128.8, 128.6, 128.2, 127.1, 126.7, 105.4, 60.9, 60.4, 40.0, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{18}N_2O_2Na^+$ 293.1261; Found 293.1261.



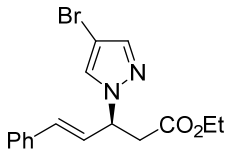
Synthesis of 3b: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-methyl-1*H*-pyrazole **2b** (16.4 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at rt for 48 h. After completion, pure **3b** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 48.6 mg (0.171 mmol), as a colorless oil, 85 % yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –9.4 (*c* = 1.05 in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 29.78 min, t (minor) = 50.52 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38–7.33 (m, 3H), 7.32–7.27 (m, 2H), 7.27–7.20 (m, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 15.2, 6.8 Hz, 1H), 5.30 (q, *J* = 7.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.25 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.95 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.06 (s, 3H), 1.20 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.4, 140.0, 136.0, 132.6, 128.6, 128.1, 127.5, 126.7, 115.9, 60.8, 60.2, 39.9, 14.1, 8.9; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{17}H_{20}N_2O_2Na^+$ 307.1417; Found 307.1414.



Synthesis of 3c: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-(*tert*-butyl)-1*H*-pyrazole **2c** (24.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at rt for 48 h. After completion, pure **3c** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 50.0 mg (0.153 mmol), as a colorless oil, 77% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –2.0 (*c* = 3.90 in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 9.74 min, t (minor) = 21.45 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45–7.39 (m, 1H), 7.39–7.33 (m, 2H), 7.32–7.27 (m, 2H), 7.26-7.20 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.42 (q, *J* = 7.6 Hz, 1H), 5.30 (q, *J* = 7.6 Hz, 1H), 4.11 (q, *J* = 6.8 Hz, 2H), 3.21 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.96 (dd, *J* = 16.0, 7.6 Hz, 1H), 1.24 (s, 9H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.4, 137.0, 136.0, 133.0, 132.6, 128.6, 128.1, 127.3, 126.7, 124.8, 60.8, 60.4, 40.1, 31.8, 29.4, 14.1; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{20}H_{28}N_2O_2^+$ 327.2068; Found 327.2058.

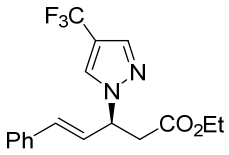


Synthesis of 3d: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-chloro-1*H*-pyrazole **2d** (20.5 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3d** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 48.9 mg (0.160 mmol), as a white solid, 80% yield; mp = 65–67 °C; *E*/*Z* = 15:1; $[\alpha]_D^{25}$ = +2.6 (*c* = 1.21 in $CHCl_3$); 87% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 8.95 min, t (minor) = 13.67 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (s, 1H), 7.47 (s, 1H), 7.39–7.22 (m, 5H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.36 (dd, *J* = 16.0, 7.6 Hz, 1H), 5.30 (q, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.25 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.94 (dd, *J* = 16.0, 6.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.0, 138.0, 135.6, 133.4, 128.7, 128.4, 126.9, 126.7, 126.2, 109.9, 61.1, 39.5, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{17}{}^{35}ClN_2O_2Na^+$ 327.0871; Found 327.0869; Calcd for $C_{16}H_{17}{}^{37}ClN_2O_2Na^+$ 329.0842; Found 329.0851.

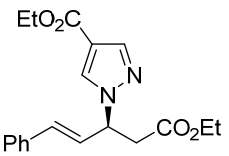


Synthesis of 3e: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-bromo-1*H*-pyrazole **2e** (29.4 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3e** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 53.7 mg (0.154 mmol), as a white solid, 77% yield; mp = 64–66 °C; *E*/*Z* = 13:1; $[\alpha]_D^{25}$ = +7.8 (*c* = 0.66 in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 9.18 min, t (minor) = 14.16 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (s, 1H), 7.50 (s, 1H), 7.40–7.20 (m, 5H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 7.6 Hz, 1H), 5.33 (q, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.94 (dd, *J* = 16.0, 6.0 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.0, 140.1, 135.6, 133.4, 129.1, 128.7,

128.4, 126.7, 126.2, 93.1, 61.0, 39.6, 14.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ $C_{16}H_{17}{}^{79}BrN_2O_2Na^+$ 371.0366; Found 371.0365; Calcd for $C_{16}H_{17}{}^{81}BrN_2O_2Na^+$ 373.0346; Found 373.0352.

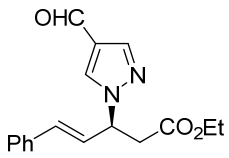


Synthesis of 3f: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-(trifluoromethyl)-1*H*-pyrazole **2f** (27.2 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3f** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 44.0 mg (0.130 mmol), as a colorless oil, 65% yield; *E/Z* = 19:1; $[\alpha]_D^{25}$ = +7.9 (*c* =1.62 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 7.83 min, t (major) = 8.66 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (s, 1H), 7.74 (s, 1H), 7.40–7.25 (m, 5H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.40 (dd, *J* = 16.0, 7.8 Hz, 1H), 5.42–5.33 (m, 1H), 4.12 (q, *J* = 7.8 Hz, 2H), 3.29 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.98 (dd, *J* = 16.4, 6.0 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 137.2 (q, *J* = 2.7 Hz, 1C), 135.4, 133.9, 128.7, 128.6, 128.3 (q, *J* = 3.6 Hz, 1C), 126.8, 125.7, 122.6 (q, *J* = 264.5 Hz, 1C), 113.4 (q, *J* = 38.1 Hz, 1C), 61.2, 61.1, 39.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –56.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{17}F_3N_2O_2Na^+$ 361.1135; Found 361.1134.

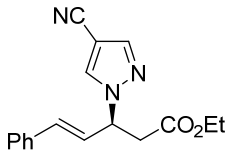


Synthesis of 3g: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), ethyl 1*H*-pyrazole-4-carboxylate **2g** (28.0 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3g** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 53.7 mg (0.154 mmol), as a colorless oil, 76% yield; *E/Z* = 18:1; $[\alpha]_D^{25}$ = +10.3 (*c* = 0.80 in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 14.14 min, t (minor) = 22.36 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00 (s, 1H), 7.95 (s, 1H), 7.39–7.19 (m, 5H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.40 (dd, *J* = 15.8, 7.6 Hz, 1H), 5.37 (q, *J* = 7.2

Hz, 1H), 4.28 (q, J = 7.2 Hz, 1H), 4.12 (q, J = 7.2 Hz, 1H), 3.29 (dd, J = 16.2, 8.0 Hz, 1H), 2.98 (dd, J = 16.2, 6.0 Hz, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 163.0, 141.3, 135.5, 133.7, 132.3, 128.7, 128.5, 126.8, 125.8, 115.0, 61.0, 60.2, 39.6, 14.4, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{22}N_2O_4Na^+$ 365.1472; Found 365.1462.

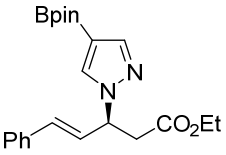


Synthesis of 3h: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole-4-carbaldehyde **2h** (19.2 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3h** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 38.5 mg (0.129 mmol), as a colorless oil, 65% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = +32.1 (*c* = 1.24 in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 22.41 min, t (major) = 24.54 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.85 (s, 1H), 8.06 (s, 1H), 8.01 (s, 1H), 7.40–7.27 (m, 5H), 6.60 (d, J = 16.0 Hz, 1H), 6.42 (dd, J = 16.0, 7.8 Hz, 1H), 5.44–5.36 (m, 1H), 4.15–4.12 (m, 2H), 3.31 (dd, J = 16.4, 8.4 Hz, 1H), 3.00 (dd, J = 16.4, 6.0 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 184.0, 169.8, 140.9, 135.4, 134.1, 132.7, 128.7, 128.6, 126.8, 125.4, 124.1, 61.3, 61.1, 39.5, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2O_3Na^+$ 321.1210; Found 321.1213.

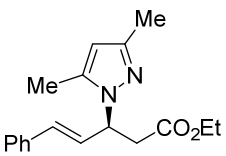


Synthesis of 3i: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole-4-carbonitrile **2i** (18.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3i** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 37.7 mg (0.128 mmol), as a colorless oil, 64% yield; *E*/*Z* = 15:1; $[\alpha]_D^{25}$ = +30.1 (*c* = 1.48 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 8.23 min, t (mnior) = 12.96 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (s, 1H), 7.83 (s, 1H), 7.40–

7.25 (m, 5H), 6.59 (d, J = 15.8 Hz, 1H), 6.38 (dd, J = 16.0, 7.8 Hz, 1H), 5.42–5.34 (m, 1H), 4.12 (d, J = 7.2 Hz, 2H), 3.29 (dd, J = 16.4, 8.4 Hz, 1H), 2.98 (dd, J = 16.8, 5.6 Hz, 1H), 1.21 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.7, 142.5, 135.2, 134.4, 134.2, 128.8, 128.7, 126.8, 125.1, 113.4, 92.2, 77.4, 77.1, 76.8, 61.5, 61.2, 39.4, 14.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{17}H_{17}F_3N_3O_2Na^+$ 318.1213; Found 318.1205.

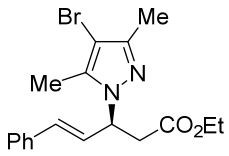


Synthesis of 3j: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole **2j** (38.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3j** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 43.9 mg (0.111 mmol), as a colorless oil, 55% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –27.0 (*c* = 1.92 in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.94 min, t (minor) = 9.93 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (s, 1H), 7.81 (s, 1H), 7.37–7.33 (m, 2H), 7.33–7.27 (m, 2H), 7.27–7.22 (m, 1H), 6.53 (d, J = 16.0 Hz, 1H), 6.40 (dd, J = 16.0, 7.6 Hz, 1H), 5.39 (q, J = 7.2 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.28 (dd, J = 16.0, 7.6 Hz, 1H), 2.98 (dd, J = 16.0, 6.8 Hz, 1H), 1.31 (s, 12H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1, 145.7, 135.8, 135.7, 133.2, 128.6, 128.2, 126.7, 126.6, 83.3, 60.9, 60.4, 39.9, 24.8, 14.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{22}H_{29}BrN_2O_4Na^+$ 419.2113; Found 419.2120.

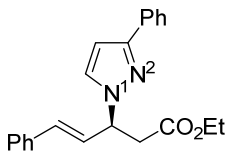


Synthesis of 3k: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 3,5-dimethyl-1*H*-pyrazole **2k** (19.2 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3k** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 34.8 mg (0.117 mmol), as a colorless oil, 58% yield; *E*/*Z* = 17:1; $[\alpha]_D^{25}$ = –47.3 (*c* = 0.83 in $CHCl_3$); 84% ee, determined by

HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.95 min, t (major) = 6.95 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35–7.31 (m, 2H), 7.30–7.24 (m, 2H), 7.24–7.18 (m, 1H), 6.37–6.35 (m, 2H), 5.78 (s, 1H), 5.26–5.19 (m, 1H), 4.09 (q, *J* = 6.8 Hz, 2H), 3.35 (dd, *J* = 16.0, 8.4 Hz, 1H), 2.97 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.8, 147.7, 139.1, 136.2, 131.5, 128.5, 128.1, 127.9, 126.6, 105.0, 60.7, 56.2, 39.6, 14.1, 13.7, 11.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{18}H_{22}N_2O_2Na^+$ 321.1574; Found 321.1574.

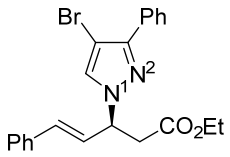


Synthesis of 3l: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-bromo-3,5-dimethyl-1*H*-pyrazole **2l** (35.0 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3l** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 54.5 mg (0.144 mmol), as a white solid, 72% yield; mp = 55–57 °C; *E*/*Z* = 18:1; $[\alpha]_D^{25}$ = +5.3 (*c* = 2.5 in $CHCl_3$); 73% ee, determined by HPLC analysis [Chiralpak IE, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 6.18 min, t (major) = 6.47 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36–7.19 (m, 5H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.32–5.22 (m, 1H), 4.10 (q, *J* = 7.8 Hz, 2H), 3.36 (dd, *J* = 16.4, 8.8 Hz, 1H), 2.93 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.5, 146.3, 137.3, 135.9, 132.0, 128.6, 128.1, 127.3, 126.7, 94.2, 60.8, 57.4, 39.2, 14.1, 12.5, 10.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{18}H_{21}{}^{79}BrN_2O_2Na^+$ 399.0679; Found 399.0683; Calcd for $C_{18}H_{21}{}^{81}BrN_2O_2Na^+$ 401.0659; Found 401.0663.

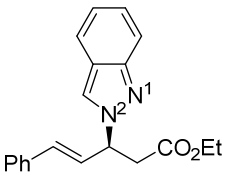


Synthesis of 3m: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 3-phenyl-1*H*-pyrazole **2m** (28.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3m** was obtained by

flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 48.0 mg (0.139 mmol), as a colorless oil, 69% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –89.3 (*c* = 0.91 in $CHCl_3$); N^1:N^2 >19:1; 92% ee (N^1), determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.36 min, t (minor) = 9.60 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87–7.78 (m, 2H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.41–7.34 (m, 4H), 7.34–7.21 (m, 4H), 6.61–6.53 (m, 2H), 6.47 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.40 (q, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.36 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.01 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.4, 151.5, 135.9, 133.7, 132.9, 130.1, 128.7, 128.6, 128.2, 127.6, 127.1, 126.7, 125.7, 102.8, 60.9, 60.7, 40.1, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_2^+$ 347.1775; Found 347.1760.

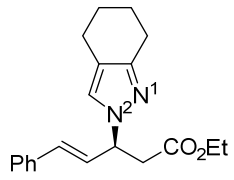


Synthesis of 3n: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-bromo-3-phenyl-1*H*-pyrazole **2n** (44.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3n** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 56.3 mg (0.132 mmol), as a colorless oil, 66% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –37.4 (*c* = 0.61 in $CHCl_3$); N^1:N^2 >19:1; 89% ee (N^1), determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 9.27 min, t (minor) = 10.48 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.88 (m, 2H), 7.59 (s, 1H), 7.46–7.22 (m, 8H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 7.6 Hz, 1H), 5.35 (q, *J* = 7.2 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.35 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.98 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1, 148.7, 135.7, 133.7, 132.2, 130.9, 128.7, 128.4, 128.3, 128.1, 127.6, 126.8, 126.2, 91.7, 61.3, 61.0, 39.6, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}{}^{79}BrN_2O_2Na^+$ 447.0679; Found 447.0676; Calcd for $C_{22}H_{21}{}^{81}BrN_2O_2Na^+$ 449.0658; Found 449.0658.

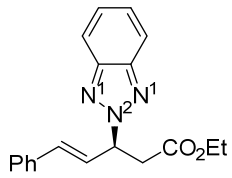


Synthesis of 3o: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-indazole **2o** (23.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0

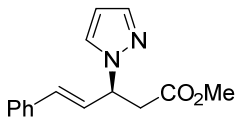
equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 72 h. After completion, pure **3o** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 31.8 mg (0.0993 mmol), as a semi-solid, 50% yield; *E/Z* = 5:1; $[\alpha]_D^{25}$ = +100.8 (*c* = 1.37 in $CHCl_3$); N^2:N^1 >19:1; 94% ee (N^2), determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.11 min, t (minor) = 8.77 min]; ^{1}H NMR (400 MHz, $CDCl_3$): for ***N*²**, δ (ppm) 8,10–8.02 (m, 1H), 7.75–7.10 (m, 1H), 7.58–7.51 (m, 1H), 7.41–7.35 (m, 1H), 7.34–7.29 (m, 2H), 7.29–7.23 (m, 2H), 7.24–7.17 (m, 1H), 7.17–7.11 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.46 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.80–5.73 (m, 1H), 4.08–3.98 (m, 2H), 3.44 (dd, *J* = 16.0 8.4 Hz, 1H), 3.14 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.5, 139.5, 136.0, 133.7, 132.2, 128.6, 128.1, 127.3, 126.7, 126.4, 124.1, 121.1, 120.8, 109.4, 60.8, 57.1, 39.6, 14.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2O_2Na^+$ 343.1417; Found 343.1419.



Synthesis of 3p: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4,5,6,7-tetrahydro-2*H*-indazole **2p** (24.4 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 72 h. After completion, pure **3p** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 38.1 mg (0.117 mmol), as a semi-solid, 59% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –19.2 (*c* = 0.62 in $CHCl_3$); N^2:N^1 = 2.4:1; 93% ee (N^2), determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 12.28 min, t (major) = 20.36 min]; ^{1}H NMR (400 MHz, $CDCl_3$): for ***N*²**, δ (ppm) 8,10–8.02 (m, 1H), 7.75–7.10 (m, 1H), 7.38–7.33 (m, 2H), 7.32–7.20 (m, 3H), 7.16 (s, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 7.6 Hz, 1H), 5.30–5.22 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.22 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.95 (dd, *J* = 16.0, 7.2 Hz, 1H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.57–2.43 (m, 2H), 1.86–1.76 (m, 2H), 1.75–1.66 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.5, 149.3, 136.1, 132.5, 128.6, 128.0, 127.5, 126.7, 125.7, 115.6, 60.7, 60.2, 40.1, 23.6, 23.5, 23.5, 20.6, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{24}N_2O_2Na^+$ 347.1730; Found 347.1728.

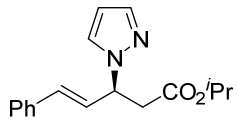


Synthesis of 3q: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-benzo[*d*][1,2,3]triazole **2q** (23.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1a** (80.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 72 h. After completion, pure **3q** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 43.1 mg (0.134 mmol), as a white solid, 67% yield; mp = 74–76 °C; *E*/*Z* = 13:1; $[\alpha]_D^{25}$ = –43.1 (*c* = 2.42 in $CHCl_3$); N^2:N^1 = 4.5:1; 60% ee (N^2), determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 13.42 min, t (major) = 16.81 min]; ^{1}H NMR (400 MHz, $CDCl_3$): for ***N*^{2}**, δ (ppm) 8.10–8.04 (m, 1H), 7.66–7.60 (m, 1H), 7.51–7.43 (m, 1H), 7.39–7.22 (m, 6H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.49 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.98–5.90 (m, 1H), 4.12–4.02 (m, 2H), 3.61 (dd, *J* = 16.4, 8.4 Hz, 1H), 3.28 (dd, *J* = 16.4, 6.4 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 146.1, 135.4, 133.6, 132.8, 128.7, 128.5, 127.4, 126.7, 125.7, 124.1, 120.1, 109.9, 61.1, 57.8, 39.5, 14.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{19}N_3O_2Na^+$ 344.1370; Found 344.1361.

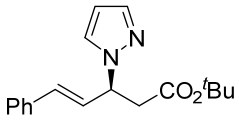


Synthesis of 3r: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and methyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1b** (75.3 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3r** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 29.6 mg (0.122 mmol), as a colorless oil, 61% yield; *E*/*Z* = 19:1; $[\alpha]_D^{25}$ = –27.9 (*c* = 0.45 in $CHCl_3$); 89% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 16.97 min, t (minor) = 21.80 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.38–7.33 (m, 2H), 7.33–7.27 (m, 2H), 7.27–7.23 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.43 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.26 (t, *J* = 2.4 Hz, 1H), 5.39 (q, *J* = 7.2 Hz, 1H), 3.65 (s, 1H), 3.31 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.00 (dd, *J* = 16.0, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)

170.8, 139.7, 135.9, 132.8, 128.8, 128.6, 128.2, 127.0, 126.7, 105.5, 60.3, 52.0, 39.7; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{15}H_{16}N_2O_2Na^+$ 279.1104; Found 279.1100.

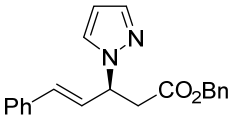


Synthesis of 3s: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and isopropyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1c** (75.3 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3s** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 36.3 mg (0.134 mmol), as a colorless oil, 67% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –16.0 (*c* = 0.53 in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak IH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 12.31 min, t (minor) = 14.03 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.38–7.33 (m, 2H), 7.33–7.27 (m, 2H), 7.27–7.19 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.43–5.33 (m, 1H), 5.01–4.91 (m, 1H), 3.24 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.95 (dd, *J* = 15.6, 6.4 Hz, 1H), 1.16 (dd, *J* = 6.4, 4.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.7, 139.6, 135.9, 132.7, 128.7, 128.6, 128.2, 127.1, 126.7, 105.4, 68.3, 60.5, 40.4, 21.7; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2O_2Na^+$ 307.1417; Found 307.1410.

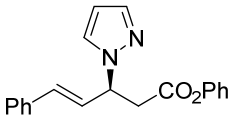


Synthesis of 3t: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and *tert*-butyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1d** (92.1 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3w** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 38.4 mg (0.135 mmol), as a colorless oil, 68% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –17.8 (*c* = 1.39 in $CHCl_3$); 82% ee, determined by HPLC analysis [Chiralpak ID *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 11.67 min, t (minor) = 16.80 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.37–7.33 (m, 2H), 7.32–7.26 (m, 2H), 7.27–7.19 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.34 (q, *J* = 7.2 Hz, 1H), 3.17 (dd, *J* = 15.6, 8.4 Hz, 1H),

2.90 (dd, J = 15.6, 7.2 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.4, 139.5, 136.0, 132.6, 128.6, 128.1, 127.3, 126.7, 105.3, 81.2, 60.7, 41.3, 28.0; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{18}H_{22}N_2O_2Na^+$ 321.1574; Found 321.1570.

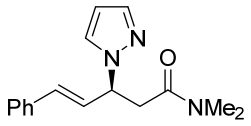


Synthesis of 3u: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and benzyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1e** (105.7 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3u** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 41.4 mg (0.130 mmol), as a colorless oil, 65% yield; *E*/*Z* = 19:1; $[\alpha]_D^{25}$ = –320.0 (*c* = 0.12 in $CHCl_3$); 88% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 15.04 min, t (minor) = 27.89 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, J = 1.6 Hz, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.37–7.17 (m, 10H), 6.49 (d, J = 16.0 Hz, 1H), 6.41 (dd, J = 16.0, 6.8 Hz, 1H), 6.24 (t, J = 2.0 Hz, 1H), 5.40 (q, J = 7.2 Hz, 1H), 5.14–5.04 (m, 2H), 3.35 (dd, J = 16.0, 8.0 Hz, 1H), 3.04 (dd, J = 16.0, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1, 139.7, 135.8, 135.6, 132.9, 128.8, 128.6, 128.6, 128.3, 128.2, 126.9, 126.7, 105.5, 66.7, 60.4, 40.0; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{21}H_{20}N_2O_2Na^+$ 355.1417; Found 355.1416.

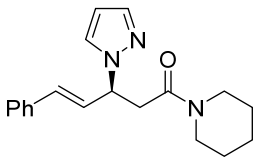


Synthesis of 3v: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and phenyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate **1f** (100.1 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at rt for 48 h. After completion, pure **3v** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 54.6 mg (0.176 mmol), as a colorless oil, 86% yield; *E*/*Z* = 19:1; $[\alpha]_D^{25}$ = –25.2 (*c* = 0.64 in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 11.56 min, t (major) = 13.10 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.42–7.36 (m, 2H), 7.36–7.14 (m, 6H), 6.96 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 16.0 Hz, 1H), 6.51

(dd, J = 16.0, 7.6 Hz, 1H), 6.29 (t, J = 2.0 Hz, 1H), 5.49 (q, J = 7.2 Hz, 1H), 3.56 (dd, J = 16.0, 8.4 Hz, 1H), 3.24 (dd, J = 16.0, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.0, 150.4, 139.8, 135.7, 133.2, 129.5, 129.0, 128.7, 128.4, 126.8, 126.6, 126.0, 121.5, 105.6, 60.5, 40.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2O_2Na^+$ 341.1261; Found 341.1265.

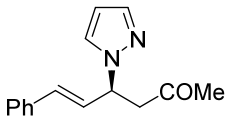


Synthesis of 3w: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and (2*E*,4*E*)-*N*,*N*-dimethyl-5-phenylpenta-2,4-dienamide **1g** (80.5 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 0 °C for 48 h. After completion, pure **3w** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 47.7 mg (0.177 mmol), as a semi-solid, 89% yield; E/Z >19:1; $[\alpha]_D^{25}$ = –2.5 (c = 0.32 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.46 min, t (minor) = 12.67 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.37–7.32 (m, 2H), 7.31–7.25 (m, 2H), 7.25–7.20 (m, 1H), 6.53 (dd, J = 16.0, 6.8 Hz, 1H), 6.44 (d, J = 16.0 Hz, 1H), 6.24 (t, J = 2.0 Hz, 1H), 5.59–5.49 (m, 1H), 3.38 (dd, J = 16.0, 8.0 Hz, 1H), 2.97 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5, 139.6, 136.2, 131.9, 129.8, 128.5, 128.3, 127.9, 126.6, 105.1, 60.7, 38.5, 37.2, 35.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{19}N_3ONa^+$ 292.1421; Found 292.1419.

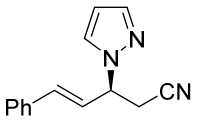


Synthesis of 3x: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and (2*E*,4*E*)-5-phenyl-1-(piperidin-1-yl)penta-2,4-dien-1-one **1h** (96.5 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 0 °C for 48 h. After completion, pure **3x** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 51.2 mg (0.165 mmol), as a semi-solid, 83% yield; E/Z >19:1; $[\alpha]_D^{25}$ = –12.2 (c = 0.59 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 33.05 min, t (minor) = 37.37 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 2.4

Hz, 1H), 7.39–7.31 (m, 2H), 7.31–7.25 (m, 2H), 7.25–7.19 (m, 1H), 6.53 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 5.60–5.50 (m, 1H), 3.62–3.30 (m, 5H), 2.91 (dd, *J* = 15.6, 6.0 Hz, 1H), 1.62–1.53 (m, 2H), 1.53–1.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.7, 139.7, 136.2, 131.8, 129.8, 128.5, 128.3, 127.9, 126.6, 105.0, 60.8, 46.8, 42.9, 38.2, 26.4, 25.5, 24.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{23}N_3ONa^+$ 332.1734; Found 332.1737.

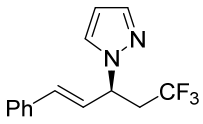


Synthesis of 3y: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and (3*E*,5*E*)-6-phenylhexa-3,5-dien-2-one **1i** (68.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3y** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 15.0 mg (0.0625 mmol), as a colorless oil, 31% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –25.3 (*c* = 0.43 in $CHCl_3$); 79% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 8.63 min, t (minor) = 16.64 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, *J* = 1.6 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.37–7.20 (m, 5H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.39 (dd, *J* = 16.0, 6.0 Hz, 1H), 6.24 (t, *J* = 2.0 Hz, 1H), 5.49–5.38 (m, 1H), 3.54 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.02 (dd, *J* = 17.2, 6.0 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.3, 139.5, 136.0, 132.2, 129.3, 128.6, 128.1, 127.7, 126.6, 105.4, 59.3, 47.8, 30.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{16}N_2ONa^+$ 263.1155; Found 263.1152.

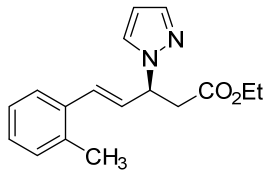


Synthesis of 3z: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and (2*E*,4*E*)-5-phenylpenta-2,4-dienenitrile **1j** (62.1 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3z** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 31.6 mg (0.125 mmol), as a colorless oil, 62% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –12.0 (*c* = 2.02 in $CHCl_3$); 88% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 9.15 min, t (minor) =

10.53 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.44–7.38 (m, 2H), 7.37–7.27 (m, 3H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.44 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.31 (t, *J* = 2.4 Hz, 1H), 5.22–5.14 (m, 1H), 3.24 (dd, *J* = 16.8, 6.8 Hz, 1H), 3.16 (dd, *J* = 16.8, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.5, 135.3, 135.1, 128.9, 128.8, 128.7, 126.9, 124.1, 116.5, 106.2, 60.0, 24.5; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{14}H_{13}N_3Na^+$ 246.1002; Found 246.1000.

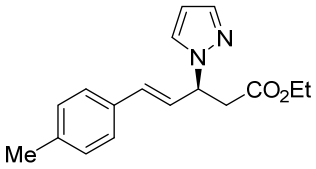


Synthesis of 3aa: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene **1k** (79.3 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3aa** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 30.0 mg (0.113 mmol), as a colorless oil, 56% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –2.9 (*c* = 0.42 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 7.86 min, t (minor) = 10.79 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 1.6 Hz, 1H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.38–7.24 (m, 5H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 1H), 5.19 (q, *J* = 6.8 Hz, 1H), 3.28–3.11 (m, 1H), 2.87–2.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.1, 135.5, 133.5, 128.7, 128.5, 126.8, 126.2, 125.5 (q, *J* = 275.5 Hz, 1C), 105.8, 58.5 (q, *J* = 3.2 Hz, 1C), 39.1 (q, *J* = 28.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –64.2 (t, *J* = 2.7 Hz); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{14}H_{13}F_3N_2Na^+$ 289.0924; Found 289.0926.

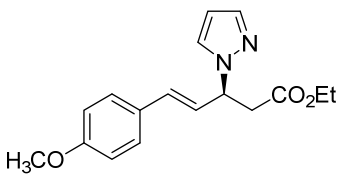


Synthesis of 3ab: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(*o*-tolyl)penta-2,4-dienoate **1l** (86.5 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ab** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 41.4 mg (0.146 mmol), as a colorless oil, 72% yield; *E*/*Z* = 13:1; $[\alpha]_D^{25}$ = –32.6 (*c* =

1.35 in $CHCl_3$); 87% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 9.06 min, t (minor) = 12.56 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, *J* = 1.6 Hz, 1H), 7.51 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.17–7.08 (m, 3H), 6.73 (d, *J* = 16.0, 1H), 6.31 (dd, *J* = 15.6, 7.2 Hz, 1H), 6.26 (t, *J* = 2.0 Hz, 1H), 5.46–5.37 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.29 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.99 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.30 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.3, 139.6, 135.7, 135.0, 130.7, 130.3, 128.7, 128.4, 128.1, 126.2, 125.8, 105.4, 60.9, 60.6, 40.1, 19.7, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2O_2Na^+$ 307.1417; Found 307.1416.

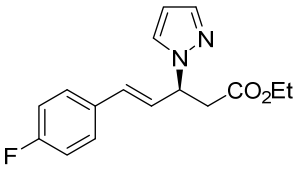


Synthesis of 3ac: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(*p*-tolyl)penta-2,4-dienoate **1m** (86.5 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ac** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 48.2 mg (0.170 mmol), as a colorless oil, 85% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –15.3 (*c* = 0.80 in $CHCl_3$); 80% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 19.94 min, t (minor) = 25.05 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 2.0 Hz, 1H), 7.52–7.46 (m, 1H), 7.28–7.23 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.42–5.33 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.27 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.97 (dd, *J* = 16.0, 6.4 Hz, 1H), 2.32 (s, 3H), 1.19 (t, *J* = 6,8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.3, 139.6, 138.1, 133.1, 132.7, 129.3, 128.7, 126.6, 126.0, 105.3, 60.8, 60.5, 40.1, 21.2, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2O_2Na^+$ 307.1417; Found 307.1409.

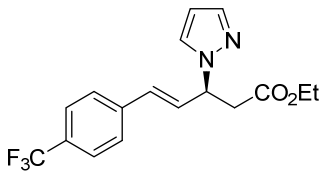


Synthesis of 3ad: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(4-methoxyphenyl)penta-2,4-dienoate **1n** (92.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by

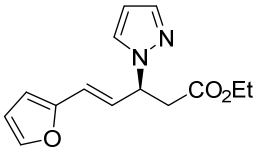
vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ad** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 34.7 mg (0.116 mmol), as a colorless oil, 58% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –7.7 (*c* = 1.38 in $CHCl_3$); 81% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 25.15 min, t (minor) = 31.39 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57–7.52 (m, 1H), 7.51–7.46 (m, 1H), 7.32–7.27 (m, 2H), 6.86–6.78 (m, 2H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.29 (dd, *J* = 15.6, 7.2 Hz, 1H), 6.24 (t, *J* = 2.4 Hz, 1H), 5.40–5.30 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.27 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.96 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.3, 159.7, 139.6, 132.3, 128.7, 128.6, 127.9, 124.8, 114.0, 105.3, 60.8, 60.5, 55.3, 40.1, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2O_3Na^+$ 323.1367; Found 323.1359.



Synthesis of 3ae: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(4-fluorophenyl)penta-2,4-dienoate **1o** (88.1 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at rt for 48 h. After completion, pure **3ae** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 46.1 mg (0.160 mmol), as a colorless oil, 77% yield; *E/Z* = 12:1; $[\alpha]_D^{25}$ = –1.8 (*c* = 0.11 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 18.11 min, t (minor) = 21.91 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57–7.55 (m, 1H), 7.49 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.34–7.29 (m, 2H), 6.98 (t, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.37 (q, *J* = 8.0 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.27 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.98 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.2, 163.9, 161.4, 139.7, 132.1 (d, *J* = 3.2 Hz, 1C), 131.5, 128.8, 128.3, 128.2, 126.9 (d, *J* = 2.2 Hz, 1C), 115.7, 115.4, 105.4, 60.9, 60.3, 40.0, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –113.4; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{17}FN_2O_2Na^+$ 311.1167; Found 311.1163.

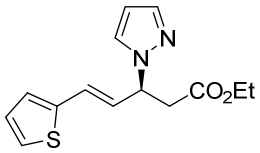


Synthesis of 3af: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(4-(trifluoromethyl) phenyl)penta-2,4-dienoate **1p** (108.1 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed toluene (0.8 mL) was added by syringe. The reaction was stirred at rt for 48 h. After completion, pure **3af** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 67.1 mg (0.198 mmol), as a colorless oil, 99% yield; *E/Z* = 16:1; $[\alpha]_D^{25} = -8.4$ (*c* = 1.91 in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 9.45 min, t (major) = 12.64 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60–7.52 (m, 3H), 7.52–7.49 (m, 1H), 7.47–7.41 (m, 2H), 6.60–6.42 (m, 2H), 6.29–6.26 (m, 1H), 5.42 (q, *J* = 6.4 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 1H), 3.28 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.01 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1, 139.9, 139.4, 131.2, 129.9, 128.9, 126.9, 125.6 (q, *J* = 4.0 Hz, 1C), 125.0 (q, *J* = 272.0 Hz, 1C), 105.5, 61.0, 60.1, 39.8, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −62.6; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{17}F_3N_2O_2Na^+$ 361.1135; Found 361.1136.

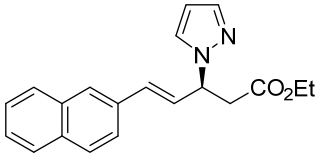


Synthesis of 3ag: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(3-methoxyphenyl)penta-2,4-dienoate **1q** (76.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ag** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 36.3 mg (0.139 mmol), as a colorless oil, 70% yield; *E/Z* >19:1; $[\alpha]_D^{25} = -7.7$ (*c* = 1.19 in $CHCl_3$); 81% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 9.54 min, t (major) = 10.44 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 2.0 Hz, 1H), 7.49–7.47 (m, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 6.39–6.31 (m, 2H), 6.29–6.22 (m, 3H), 5.43–5.32 (m, 1H), 4.16–4.06 (m, 2H), 3.26 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.96 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.2, 151.5, 142.4, 139.6, 128.8, 125.6, 120.8, 111.4,

109.2, 105.4, 60.9, 59.9, 39.8, 14.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{14}H_{16}N_2O_3Na^+$ 283.1054; Found 283.1053.

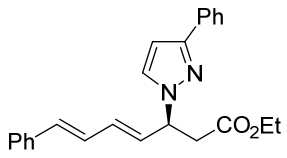


Synthesis of 3ah: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(thiophen-2-yl)penta-2,4-dienoate **1r** (83.3 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ah** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 30.9 mg (0.113 mmol), as a colorless oil, 57% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –8.2 (*c* = 1.25 in $CHCl_3$); 96% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.30 min, t (minor) = 12.97 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.20–7.13 (m, 1H), 6.98–6.91 (m, 2H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.30–6.19 (m, 2H), 5.40–5.30 (m, 1H), 4.16–4.04 (m, 2H), 3.26 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.96 (dd, *J* = 16.4, 6.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.2, 140.8, 139.7, 128.8, 127.4, 126.7, 126.4, 125.9, 125.1, 105.4, 60.9, 60.1, 39.9, 14.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{14}H_{16}N_2O_2SNa^+$ 299.0825; Found 299.0829.

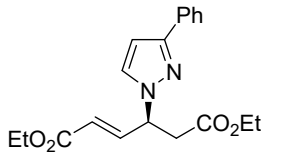


Synthesis of 3ai: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(naphthalen-2-yl)penta-2,4-dienoate **1s** (100.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ai** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 38.1 mg (0.119 mmol), as a white solid, 59% yield; mp = 56–58 °C; *E*/*Z* = 8:1; $[\alpha]_D^{25}$ = –224.0 (*c* = 0.15 in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 14.04 min, t (major) = 14.62 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.74 (m, 3H), 7.71 (s, 1H), 7.62–7.51 (m, 3H), 7.47–7.40 (m, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.56 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.27 (t, *J* = 2.0 Hz, 1H), 5.45 (q,

J = 7.2 Hz, 1H), 4.12 (q, J = 7.2 Hz, 1H), 3.31 (dd, J = 16.0, 8.0 Hz, 1H), 3.02 (dd, J = 16.0, 6.0 Hz, 1H), 1.19 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.3, 139.7, 133.5, 133.4, 133.2, 132.8, 128.9, 128.3, 128.1, 127.7, 127.4, 127.0, 126.4, 126.2, 123.5, 105.4, 60.9, 60.5, 40.1, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2O_2Na^+$ 343.1417; Found 343.1417.

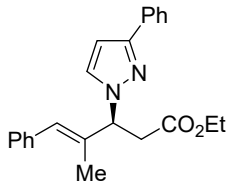


Synthesis of 3aj: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 3-phenyl-1*H*-pyrazole **2m** (28.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*,6*E*)-7-phenylhepta-2,4,6-trienoate **1t** (91.3 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3aj** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 28.6 mg (0.0768 mmol), as a colorless oil, 38% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –49.5 (*c* = 1.24 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 10.89 min, t (major) = 12.04 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.79 (m, 2H), 7.49 (d, J = 2.4 Hz, 1H), 7.42–7.35 (m, 5H), 7.33–7.28 (m, 3H), 6.75 (dd, J = 15.6, 10.6 Hz, 1H), 6.59–6.53 (m, 2H), 6.34 (dd, J = 15.2, 10.4 Hz, 1H), 6.07 (dd, J = 15.2, 7.2 Hz, 1H), 5.33 (q, J = 7.2 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.31 (dd, J = 16.0, 7.6 Hz, 1H), 2.97 (dd, J = 16.0, 6.8 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.6, 151.2, 139.1, 136.0, 130.3, 129.0, 128.2, 128.1, 126.9, 105.7, 65.3, 60.9, 37.7, 14.3, 14.1; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{26}N_2O_2^+$ 373.1911; Found 373.1904.

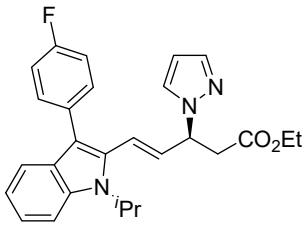


Synthesis of 3ak: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 3-phenyl-1*H*-pyrazole **2m** (28.8 mg, 0.200 mmol, 1.0 equiv), and diethyl (2*E*,4*E*)-hexa-2,4-dienedioate **1u** (79.3 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 0 °C for 48 h. After completion, pure **3ak** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 67.7 mg (0.198 mmol), as a colorless oil, 99% yield; *E*/*Z* >19:1; $[\alpha]_D^{25}$ = –69.4 (*c* = 0.94 in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t

(minor) = 13.94 min, t (major) = 15.79 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.76 (m, 2H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.43–7.34 (m, 2H), 7.34–7.25 (m, 1H), 7.12 (dd, *J* = 15.6, 6.0 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 5.78 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.45–5.35 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.11 (td, *J* = 7.2, 2.0 Hz, 2H), 3.33 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.98 (dd, *J* = 16.4, 6.0 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.8, 165.7, 152.0, 144.6, 133.4, 130.6, 128.6, 127.7, 125.7, 123.3, 103.1, 61.1, 60.8, 59.0, 38.7, 14.2, 14.1; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{19}H_{22}N_2O_4Na^+$ 365.1472; Found 365.1475.

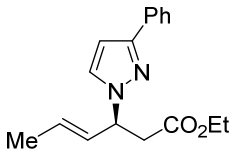


Synthesis of 3al: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 3-phenyl-1*H*-pyrazole **2m** (28.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-4-methyl-5-phenylpenta-2,4-dienoate **1v** (86.5 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3ao** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 33.9 mg (0.0940 mmol), as a colorless oil, 49% yield; *E*/*Z* = 3:1; $[\alpha]_D^{25}$ = –47.1 (*c* = 0.59 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.58 min, t (minor) = 7.42 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.78 (m, 2H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.39–7.22 (m, 8H), 6.58 (d, *J* = 2.4 Hz, 2H), 5.35 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.51 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.04 (dd, *J* = 16.0, 6.2 Hz, 1H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.7, 151.4, 150.8, 136.8, 135.9, 133.8, 130.4, 130.0, 129.0, 128.5, 128.2, 127.5, 127.0, 125.6, 103.1, 65.7, 60.9, 37.8, 14.3, 14.2; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{23}H_{24}N_2O_2Na^+$ 383.1730; Found 383.1730.



Synthesis of 3am: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 1*H*-pyrazole **2a** (13.6 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-5-(3-(4-fluorophenyl)-1-isopropyl-1*H*-indol-2-yl)penta-2,4-dienoate **1w** (151.0 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe.

The reaction was stirred at 40 °C for 48 h. After completion, pure **3am** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 64.8 mg (0.145 mmol), as a yellow oil, 73% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –20.7 (*c* = 1.65 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 5.20 min, t (major) = 7.03 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55–7.47 (m, 3H), 7.37–7.28 (m, 3H), 7.22–7.16 (m, 1H), 7.11–7.03 (m, 3H), 6.46 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.26 (t, *J* = 2.0 Hz, 1H), 5.87 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.33 (q, *J* = 7.2 Hz, 1H), 4.80–4.67 (m, 1H), 4.09 (q, *J* = 6.8 Hz, 2H), 3.17 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.82 (dd, *J* = 16.0, 6.8 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 6H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1, 162.7, 160.3, 139.6, 135.3, 133.8, 132.5, 131.9, 131.8, 131.2 (q, *J* = 3.2 Hz, 1C), 128.6, 128.1, 122.1 (q, *J* = 5.1 Hz, 1C), 119.8, 119.6, 115.5, 115.4, 115.3, 111.5, 105.6, 60.9, 60.2, 47.8, 39.3, 21.8, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −116.6; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{27}H_{28}FN_3O_2Na^+$ 468.2058; Found 468.2060.

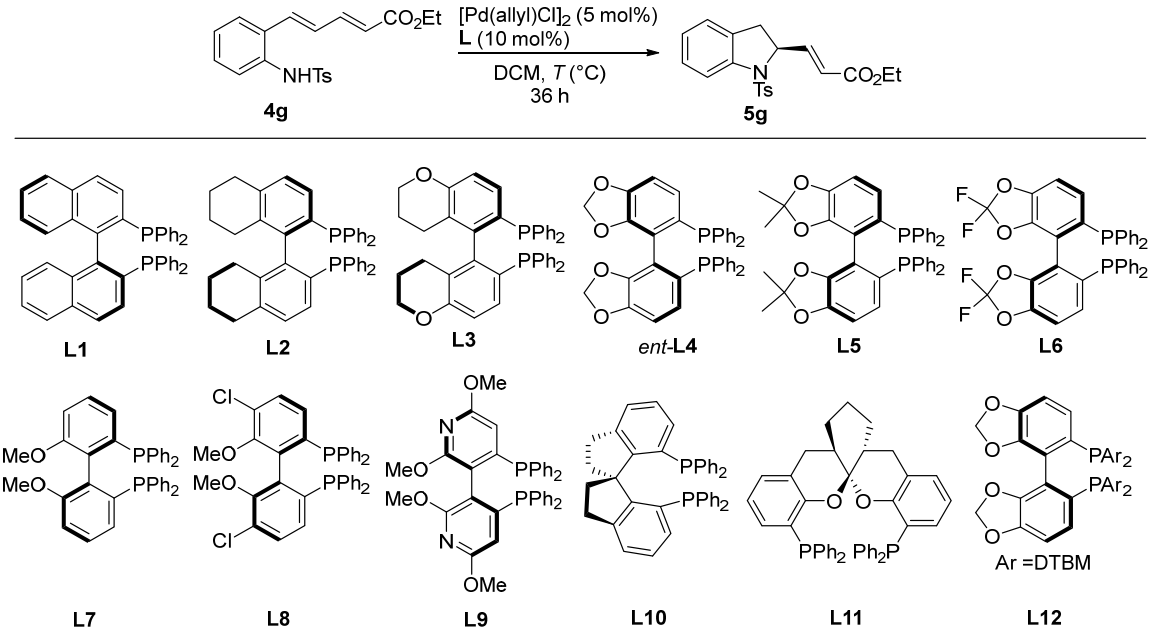


Synthesis of 3an: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol, 5 mol%), **L6** (13.7 mg, 0.0201 mmol, 10 mol%), 4-phenyl-1*H*-pyrazole **2m** (28.8 mg, 0.200 mmol, 1.0 equiv), and ethyl (2*E*,4*E*)-hexa-2,4-dienoate **1x** (56.9 mg, 0.400 mmol, 2.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed $PhCF_3$ (0.4 mL) was added by syringe. The reaction was stirred at 40 °C for 48 h. After completion, pure **3an** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10). For **3an**: 10.2 mg (0.0359 mmol), as a colorless oil, 18% yield; *E/Z* >19:1; $[\alpha]_D^{25}$ = –51.1 (*c* = 0.18 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 7.51 min, t (major) = 13.82 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 7.8 Hz, 2H), 7.47–7.42 (m, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.30–7.24 (m, 1H), 6.53–6.51 (m, 1H), 5.84–5.64 (m, 2H), 5.18 (q, *J* = 7.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.23 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.87 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.72 (d, *J* = 6.4 Hz, 3H), 1.0 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.5, 151.3, 133.8, 129.7, 129.5, 129.0, 128.5, 127.4, 125.6, 102.5, 60.7, 60.6, 40.1, 17.8, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_2^+$ 285.1598; Found 285.1595; for **3an′**: 25.4 mg (0.0893 mmol), as a colorless oil, 45% yield; *E/Z* = >19:1; $[\alpha]_D^{25}$ = –9.2 (*c* = 0.55 in $CHCl_3$); 62% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 6.65 min, t (major) = 8.04 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83–7.78 (m,

2H), 7.43 (d, J = 2.0 Hz, 1H), 7.41–7.35 (m, 2H), 7.31–7.24 (m, 1H), 6.55 (d, J = 2.0 Hz, 1H), 5.92–5.84 (m, 1H), 5.82–5.70 (m, 1H), 5.03–4.93 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.13–3.05 (m, 2H), 1.66 (d, J = 6.8 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 171.3, 151.1, 134.2, 133.8, 128.6, 128.3, 127.4, 125.6, 124.4, 102.7, 60.8, 59.0, 37.6, 20.7, 14.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_2^+$ 285.1598; Found 285.1604; for **3an″**: 15.0 mg (0.0528 mmol), as a colorless oil, 26% yield; E/Z = >19:1; $[\alpha]_D^{25}$ = −15.4 (c = 0.42 in $CHCl_3$); 68% ee, determined by HPLC analysis [Chiralpak AD, n-hexane/i-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 10.85 min, t (minor) = 11.78 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85–7.77 (m, 2H), 7.47–7.34 (m, 3H), 7.32–7.27 (m, 1H), 7.11 (dd, J = 15.6, 6.0 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 5.75 (dd, J = 15.6, 1.2 Hz, 1H), 4.87–4.16 (m, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.25–2.09 (m, 1H), 2.08–1.96 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 151.5, 146.1, 133.6, 129.3, 128.6, 127.6, 125.7, 122.5, 103.0, 64.8, 60.7, 27.6, 14.2, 10.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_2^+$ 285.1598; Found 285.1600.

5. More screening conditions of the intramolecular asymmetric hydroamination reaction of δ-aryl-functionalised dienoate 4g

5.1 Screenings of chiral ligands[a]

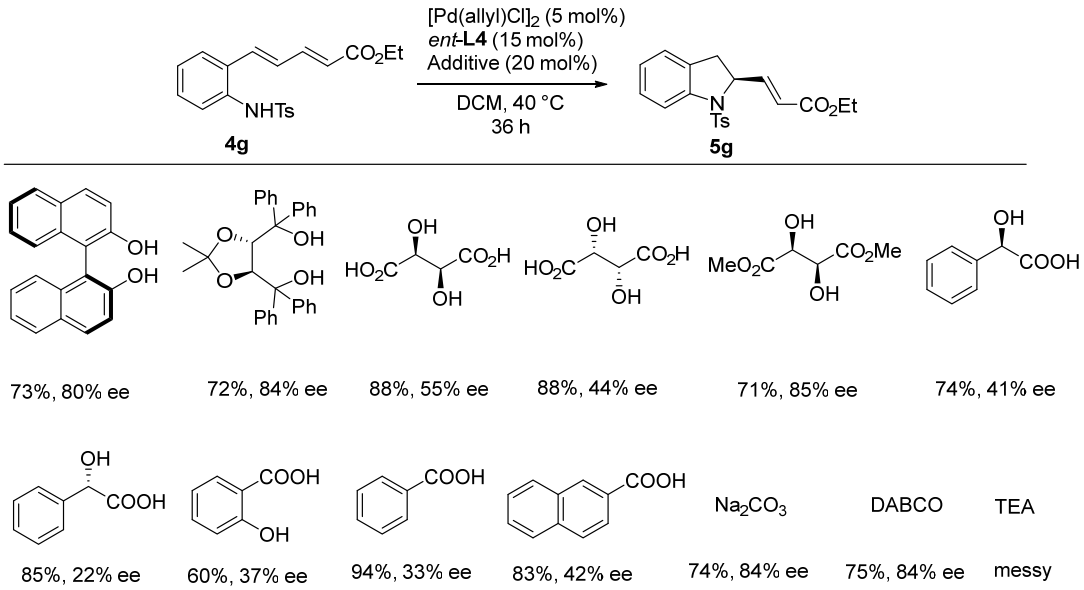


Entry	**L** (mol%)	*T* [°C]	Solvent	Yield (%)[b]	ee (%)[c]
1	**L6**	40	Toluene	24	–46
2	**L6**	40	$PhCF_3$	35	–57
3	**L6**	40	Xylene	27	–52
4	**L6**	40	DCM	60	–83
5	**L6**	40	$CHCl_3$	30	–49
6	**L6**	40	DCE	32	–56
7	**L6**	40	MeOH	<10	/
8	**L6**	40	CH_3CN	<10	/
9	**L6**	40	EtOAc	<10	/
10	**L6**	40	THF	<10	/
11	**L6**	20	DCM	25	–86
12	**L6**	60	DCM	76	–62
13	**L6**	80	DCM	71	–27
14	**L1**	40	DCM	69	78
15	**L2**	40	DCM	63	–71
16	**L3**	40	DCM	67	–80
17	*ent*-**L4**	40	DCM	72	84
18	**L5**	40	DCM	70	–81
19	**L6**	40	DCM	61	80
20	**L7**	40	DCM	60	–73
21	**L8**	40	DCM	62	–70
22	**L9**	40	DCM	41	54
23	**L10**	40	DCM	<10	/

24	**L11**	40	DCM	<10	/
25	**L12**	40	DCM	Messy	/
26[d]	**L4**	40	DCM	78	84
27[d,e]	**L4**	40	DCM	83	83

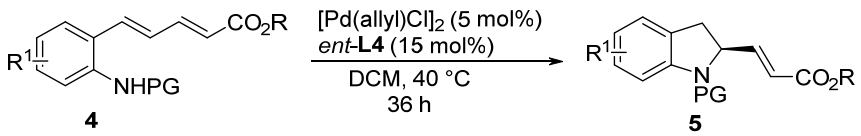
[a] Unless otherwise noted, the reactions were performed with **4g** (0.05 mmol, 1.0 equiv), $[Pd(allyl)Cl]_2$ (5 mol%) and ligand **L** (10 mol%) in distilled solvents (0.20 mL) at 40 °C for for 36 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] With 15 mol% of ligand. [e] At [0.5 M].

5.2 Screenings of additives[a,b,c]



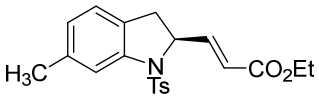
[a] Unless otherwise noted, the reactions were performed with **4g** (0.05 mmol, 1.0 equiv), [Pd(allyl)Cl] (5 mol%), *ent*-**L4** (15 mol%) and additive (20 mol%) in distilled solvents (0.10 mL) at 40 °C for 36 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

6. General procedure of the intramolecular asymmetric hydroamination reaction of δ-aryl-functionalised dienoates

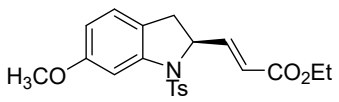


General procedure for the synthesis of 5: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%) and substrate **4** (0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, product **5** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether).

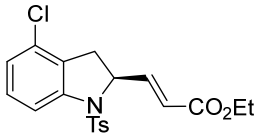
General procedure for the synthesis of racemic 5: The corresponding racemate **5** was obtained with (±)-**L4** as the ligand.



Synthesis of 5a: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(4-methyl-2-((4-methylphenyl)sulfonamido)phenyl)penta-2,4-dienoate **4a** (38.5 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5a** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 29.5 mg (0.0765 mmol), as a semi-solid, 77% yield; $[\alpha]_D^{25}$ = +107.7 (*c* = 0.51 in $CHCl_3$); 82% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 7.54 min, t (major) = 9.08 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59–7.53 (m, 2H), 7.52 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.93–6.81 (m, 3H), 6.15 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.91–4.81 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.91 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.61 (dd, *J* = 16.0, 3.2 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.2, 146.0, 144.1, 141.3, 138.2, 135.1, 129.7, 127.7, 127.1, 125.8, 124.7, 122.0, 117.9, 62.2, 60.5, 34.3, 21.6, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO_4SNa^+$ 408.1240; Found 408.1233.

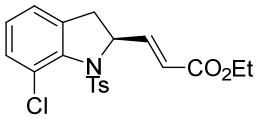


Synthesis of 5b: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(4-methoxy-2-((4-methylphenyl) sulfonamido)phenyl)penta-2,4-dienoate **4b** (40.1 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5b** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 20.2 mg (0.0503 mmol), as a semi-solid, 50% yield; $[\alpha]_D^{25}$ = +106.0 (*c* = 0.32 in $CHCl_3$); 78% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 14.29 min, t (major) = 20.04 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.22–7.18 (m, 2H), 6.93–6.85 (m, 2H), 6.59 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.15 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.94–4.84 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.98–2.85 (m, 1H), 2.59 (dd, *J* = 15.6, 2.8 Hz, 1H), 2.37 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.2, 160.0, 146.0, 144.2, 142.3, 135.0, 129.7, 127.1, 125.4, 122.4, 122.0, 111.2, 103.1, 62.8, 60.6, 55.7, 33.9, 21.6, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO_5SNa^+$ 424.1195; Found 424.1196.

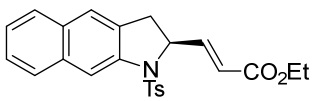


Synthesis of 5c: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(2-chloro-6-((4-methyl phenyl)sulfonamido)phenyl)penta-2,4-dienoate **4c** (40.6 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5c** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 31.2 mg (0.0769 mmol), as a semi-solid, 77% yield; $[\alpha]_D^{25}$ = +123.9 (*c* = 0.41 in $CHCl_3$); 78% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 14.20 min, t (major) = 16.09 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 15.6, 6.0 Hz, 1H), 6.14 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.94–4.81 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.97 (q, *J* = 10.0 Hz, 1H), 2.65 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.38 (s, 3H), 1.27 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 145.4, 144.6, 142.4, 134.7, 133.8, 129.9, 129.0, 127.1, 125.9,

125.0, 122.3, 117.2, 62.5, 60.7, 34.2, 21.6, 14.2; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{20}H_{20}{}^{35}ClNO_4SNa^+$ 428.0694; Found 428.0684; Calcd for $C_{20}H_{20}{}^{37}ClNO_4SNa^+$ 430.0665; Found 430.0665.

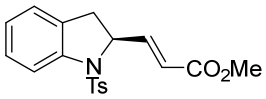


Synthesis of 5d: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(3-chloro-2-((4-methyl phenyl)sulfonamido)phenyl)penta-2,4-dienoate **4d** (40.6 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5d** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 27.3 mg (0.0673 mmol), as a semi-solid, 67% yield; $[\alpha]_D^{25}$ = +9.3 (*c* = 0.92 in $CHCl_3$); 64% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.80 min, t (mnior) = 6.35 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61–7.55 (m, 3H), 7.26–7.14 (m, 3H), 7.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.90 (dd, *J* = 15.6, 6.0 Hz, 1H), 6.16 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.96–4.84 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.03 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.78 (dd, *J* = 16.8, 3.6 Hz, 1H), 2.38 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 145.4, 144.6, 142.5, 134.7, 130.9, 129.9, 129.6, 129.1, 127.1, 124.8, 122.3, 115.0, 61.7, 60.7, 34.1, 21.6, 14.2; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{20}H_{20}{}^{35}ClNO_4SNa^+$ 428.0694; Found 428.0691; Calcd for $C_{20}H_{20}{}^{37}ClNO_4SNa^+$ 430.0665; Found 430.0661.

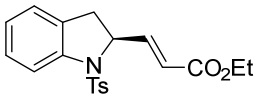


Synthesis of 5e: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added [Pd(allyl)Cl]$_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(3-((4-methyl phenyl)sulfonamido)naphthalen-2-yl)penta-2,4-dienoate **4e** (42.2 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5e** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 37.0 mg (0.0878 mmol), as a white soild, 88% yield; mp = 124–126 °C; $[\alpha]_D^{25}$ = +253.4 (*c* = 0.61 in $CHCl_3$); 82% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 17.98 min, t (major) = 26.84 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.06 (s, 1H), 7.85 (d, *J* =

8.4 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.65–7.60 (m, 2H), 7.50–7.42 (m, 2H), 7.41–7.35 (m, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.92 (dd, J = 15.6, 5.6 Hz, 1H), 6.17 (dd, J = 15.6, 1.6 Hz, 1H), 5.04–4.94 (m, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.15 (dd, J = 16.0, 10.0 Hz, 1H), 2.85 (dd, J = 16.4, 2.8 Hz, 1H), 2.33 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 145.7, 144.3, 139.3, 135.2, 133.6, 131.4, 130.8, 129.8, 127.9, 127.4, 127.0, 126.2, 125.2, 124.0, 122.3, 113.5, 62.3, 60.6, 34.3, 21.5, 14.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}NO_4SNa^+$ 444.1245; Found 444.1232.

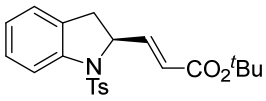


Synthesis of 5f: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and methyl (2*E*,4*E*)-5-(2-((4-methylphenyl)sulfonamido)phenyl) penta-2,4-dienoate **4f** (35.7 mg, 0.099 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5f** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 29.6 mg (0.0828 mmol), as a semi-solid, 83% yield; $[\alpha]_D^{25}$ = +59.0 (c = 0.80 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 15.98 min, t (major) = 19.85 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, J = 8.0 Hz, 1H), 7.58–7.52 (m, 2H), 7.28–7.21 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.07–7.01 (m, 2H), 6.91 (dd, J = 15.6, 6.0 Hz, 1H), 6.17 (dd, J = 15.6, 1.6 Hz, 1H), 4.92–4.82 (m, 1H), 3.71 (s, 3H), 2.99 (dd, J = 16.0, 10.0 Hz, 1H), 2.67 (dd, J = 16.0, 2.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.6, 146.2, 144.2, 141.1, 134.9, 130.6, 129.7, 128.1, 127.1, 125.2, 125.0, 121.6, 117.2, 61.9, 51.7, 34.6, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_4SNa^+$ 380.0927; Found 380.0924.

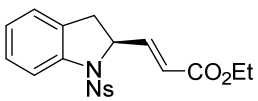


Synthesis of 5g: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(2-((4-methylphenyl)sulfonamido)phenyl) penta-2,4-dienoate **4g** (37.2 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5g** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 30.1 mg (0.0810 mmol), as a semi-solid, 81% yield; $[\alpha]_D^{25}$ = +49.0

(c = 0.40 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 14.88 min, t (major) = 18.22 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, J = 8.0 Hz, 1H), 7.58–7.54 (m, 2H), 7.26–7.21 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.05–7.02 (m, 2H), 6.89 (dd, J = 15.6, 6.4 Hz, 1H), 6.16 (dd, J = 15.6, 1.6 Hz, 1H), 4.93–4.82 (m, 1H), 4.17 (q, J = 7.2 Hz, 2H), 2.99 (dd, J = 16.0, 10.4 Hz, 1H), 2.67 (dd, J = 16.0, 2.8 Hz, 1H), 2.36 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.1, 145.9, 144.2, 141.2, 134.9, 130.6, 129.7, 128.1, 127.1, 125.2, 125.0, 122.1, 117.2, 61.9, 60.6, 34.6, 21.6, 14.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{21}NO_4SNa^+$ 394.1084; Found 394.1075.

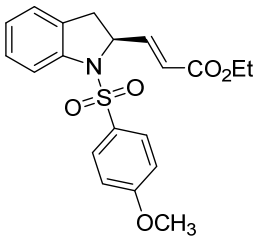


Synthesis of 5h: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and *tert*-butyl (2*E*,4*E*)-5-(2-((4-methylphenyl)sulfonamido)phenyl) penta-2,4-dienoate **4h** (40.0 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5h** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 27.7 mg (0.0693 mmol), as a semi-solid, 69% yield; $[\alpha]_D^{25}$ = +54.2 (c = 0.47 in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 11.51 min, t (major) = 17.00 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, J = 8.4 Hz, 1H), 7.58–7.53 (m, 2H), 7.26–7.21 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.05–7.01 (m, 2H), 6.78 (dd, J = 15.6, 5.6 Hz, 1H), 6.08 (dd, J = 15.2, 1.6 Hz, 1H), 4.93–4.80 (m, 1H), 2.97 (dd, J = 16.0, 10.0 Hz, 1H), 2.66 (dd, J = 16.0, 2.8 Hz, 1H), 2.36 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.4, 144.7, 144.2, 141.2, 135.0, 130.8, 129.7, 128.1, 127.1, 125.2, 125.0, 123.8, 117.3, 80.7, 61.9, 34.6, 28.1, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{25}NO_4SNa^+$ 422.1397; Found 422.1394.



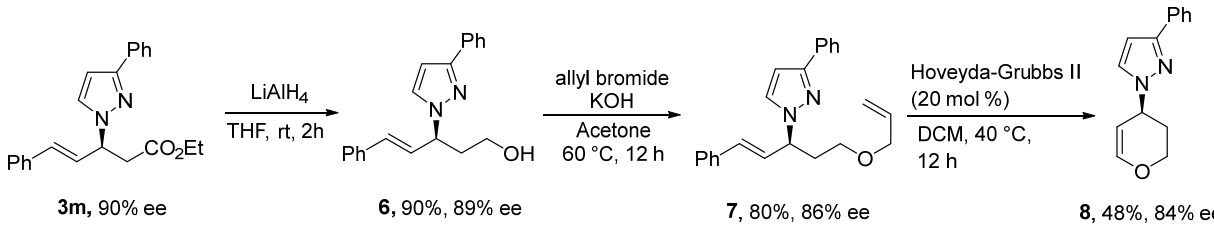
Synthesis of 5i: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(2-((4-nitrophenyl)sulfonamido)phenyl)penta-2,4-dienoate **4i** (40.2 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5i** was obtained by flash chromatography on silica gel

(EtOAc/petroleum ether = 1/10): 28.3 mg (0.0703 mmol), as a white soild, 70% yield; mp = 145–147 °C; $[\alpha]_D^{25}$ = +50.9 (*c* = 0.41 in $CHCl_3$); 75% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 27.30 min, t (major) = 34.95 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28–8.23 (m, 2H), 7.92–7.86 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.34–7.24 (m, 1H), 7.13–7.06 (m, 2H), 6.86 (dd, *J* = 15.6, 6.0 Hz, 1H), 6.16 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.00–4.88 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.04 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.74 (dd, *J* = 16.0, 2.8 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.9, 150.4, 144.8, 143.6, 140.1, 130.4, 128.5, 128.3, 125.7, 125.7, 124.3, 122.6, 116.8, 62.3, 60.8, 34.6, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{18}N_2O_6SNa^+$ 425.0778; Found 425.0773.



Synthesis of 5j: A flame-dried 10 mL Schlenk tube equipped with a magnetic stirring bar were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.049 mmol, 5 mol%), *ent*-**L4** (9.2 mg, 0.015 mmol, 15 mol%), and ethyl (2*E*,4*E*)-5-(2-((4-methoxyphenyl) sulfonamido)phenyl)penta-2,4-dienoate **4j** (38.8 mg, 0.100 mmol, 1.0 equiv). The mixture was degassed five times by vacuum/argon cycles. Then degassed DCM (0.2 mL) was added by syringe. The reaction was stirred at 40 °C for 36 h. After completion, pure **5j** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10): 29.7 mg (0.0767 mmol), as a semi-solid, 77% yield; $[\alpha]_D^{25}$ = +46.4 (*c* = 1.03 in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 11.65 min, t (major) = 13.47 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, *J* = 8.0 Hz, 1H), 7.64–7.58 (m, 2H), 7.27–7.19 (m, 1H), 7.07–7.01 (m, 2H), 6.94–6.81 (m, 3H), 6.16 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.92–4.80 (m, 1H), 4.17 (q, *J* = 6.8 Hz, 2H), 3.81 (s, 3H), 3.00 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.68 (dd, *J* = 16.4, 3.2 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.2, 163.4, 146.0, 141.3, 130.7, 129.5, 129.2, 128.1, 125.2, 125.0, 122.0, 117.3, 114.2, 61.9, 60.6, 55.6, 34.6, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{21}NO_5SNa^+$ 410.1033; Found 410.1025.

7. Synthetic transformations of diverse products



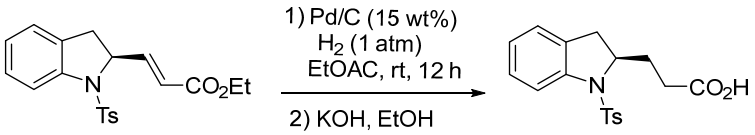
3m, 90% ee **6,** 90%, 89% ee **7**, 80%, 86% ee **8,** 48%, 84% ee

To a solution of compound **3m** (34.6 mg, 0.0999 mmol, 1.0 equiv) in dry THF (1.0 mL) was added $LiAlH_4$ (7.6 mg, 0.20 mmol, 2.0 equiv) at 0 °C. After stirred at room temperature for 2 h, the solvent was quenched with aqueous HCl (1M, 2 mL) and stirred at rt for 30 min. The mixture was extracted with EtOAc (3 × 2 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography (petroleum ether/EtOAc = 10/1) to give product **6**: 27.4 mg (0.0900 mmol), as a white solid, 90% yield; mp = 57–69 °C; $[\alpha]_D^{25}$ = +28.4 (*c* = 0.40 in $CHCl_3$); 89% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 6.51 min, t (minor) = 7.04 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.75 (m, 2H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.44–7.35 (m, 4H), 7.36–7.19 (m, 4H), 6.65–6.53 (m, 2H), 6.49 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.26–5.18 (m, 1H), 3.78–3.68 (m, 1H), 3.63–3.53 (m, 1H), 3.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 136.1, 133.3, 132.6, 129.8, 128.7, 128.2, 127.7, 126.7, 125.7, 103.0, 61.6, 58.9, 37.8; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2ONa^+$ 327.1468; Found 327.1472.

To a solution of **6** (30.4 mg, 0.0999 mmol, 1.0 equiv) in acetone (0.5 mL) was added KOH (22.4 mg, 0.400 mmol, 4.0 equiv) and 3-bromopropylene (34.6 μL, 0.400 mmol, 4.0 equiv). The mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC analysis), the solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give product **7**: 27.6 mg (0.0801 mmol), as a colorless oil, 80% yield; $[\alpha]_D^{25}$ = +31.4 (*c* = 0.33 in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 10/10, 1.0 mL/min, λ = 254 nm, t (major) = 5.37 min, t (minor) = 5.75 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91–7.78 (m, 2H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.44–7.34 (m, 4H), 7.33–7.18 (m, 4H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 6.0 Hz, 2H), 5.98–5.83 (m, 1H), 5.30–5.22 (m, 1H), 5.20–5.09 (m, 2H), 3.93 (dt, *J* = 6.0, 1.6 Hz, 2H), 3.53–3.43 (m, 1H), 3.32–3.25 (m, 1H), 2.54–2.44 (m, 1H), 2.33–2.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 136.4,

134.8, 133.9, 132.0, 129.9, 128.7, 128.6, 128.6, 127.9, 127.5, 126.6, 125.7, 117.0, 102.4, 72.0, 66.3, 61.3, 35.3; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O^+$ 345.1961; Found 345.1963.

Then an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the *o*-allyl product **7** (34.4 mg, 0.0999 mmol, 1.0 equiv) and Hoveyda-Grubbs catalyst (12.6 mg, 0.0201 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed DCM (1.0 mL) was added via syringe. The mixture was stirred at 40 °C for 12 h. After completion, the mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give product **8**: 10.9 mg (0.0482 mmol), as a colorless oil, 48% yield; $[\alpha]_D^{25}$ = +49.8 (*c* = 0.27 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 7.18 min, t (minor) = 10.35 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83–7.76 (m, 2H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.43–7.35 (m, 2H), 7.31–7.24 (m, 1H), 6.72 (dd, *J* = 6.4, 1.2 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 5.01–4.96 (m, 1H), 4.96–4.90 (m, 1H), 4.16–4.08 (m, 1H), 3.85 (td, *J* = 10.8, 3.6 Hz, 1H), 2.35–2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.9, 148.7, 133.7, 129.6, 128.6, 127.6, 125.6, 102.1, 97.9, 62.1, 51.3, 30.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2ONa^+$ 249.0998; Found 249.1005.

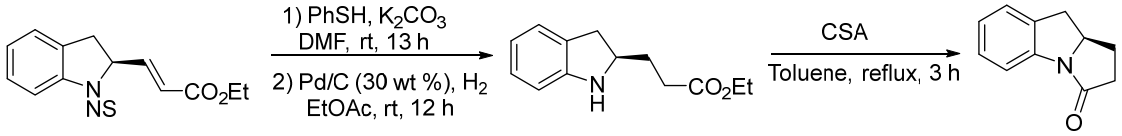


5g, 84 % ee

9, 68%, 84 % ee

To a solution of **5g** (37.2 mg, 0.100 mmol) in EtOAc (1.0 mL) was added Pd/C (5.6 mg, 15% wt). The mixture was evacuated and back-filled with H_2 (balloon). After stirred at room temperature for 12 h, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give the product: 37.2 mg (0.0996 mmol), as a white solid, 99% yield. Then the solution of hydrogenated product (37.4 mg, 0.100 mmol, 1.0 equiv) and KOH (16.8 mg, 0.299 mmol, 3.0 equiv) in EtOH (2.0 mL) was heated under reflux for 12 h. After completion, the solvent was removed under reduced pressure, and the residue was acidified with 1 M HCl, and extracted with DCM (3 × 3 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo to give the crude product, which was further purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1) to give product **9**: 23.4 mg (0.0677 mmol), as a white solid, 68% yield; mp = 94–96 °C; $[\alpha]_D^{25}$ = +195.9 (*c* = 0.15 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) =10.43 min, t

(major) = 12.03 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.26–7.20 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08–6.99 (m, 2H), 4.38–4.29 (m, 1H), 2.80–2.53 (m, 3H), 2.39 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.34 (s, 3H), 1.90 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 178.2, 143.9, 141.1, 134.9, 132.8, 129.5, 127.8, 127.1, 125.3, 125.1, 61.4, 34.8, 30.8, 29.6, 21.5; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{18}H_{19}NO_4SNa^+$ 368.0927; Found 368.0922.



5i
recrystallization
81% ee

10
55%, 82% ee
(two steps)

11
88%, 81% ee

To a solution of **5i** (26.2 mg, 0.0999 mmol, 1.0 equiv) in DMF (2.0 mL) was added K_2CO_3 (20.7 mg, 0.150 mmol, 1.5 equiv) and PhSH (12.3 μL, 0.120 mmol, 1.2 equiv). The mixture was stirred at room temperature for 13 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 6/1) to give the product (14.1 mg, 0.0649 mmol, 65% yield). To a solution of intermediate (21.7 mg, 0.0999 mmol) in EtOAc (1.0 mL) was added Pd/C (5.6 mg, 30% wt). The mixture was evacuated and back-filled with H_2 (balloon). After stirred at room temperature for 12 h, the mixture was filtered and evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give product **10**: 18.8 mg (0.0857 mmol), as a colorless oil, 56% yield (two steps); $[\alpha]_D^{25}$ = –5.2 (*c* = 0.93 in $CHCl_3$); 82% ee, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 7.88 min, t (minor) = 8.87 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.08–7.04 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.72–6.65 (m, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.96–3.82 (m, 1H), 3.14 (dd, *J* = 15.2, 8.4 Hz, 1H), 2.69 (dd, *J* = 15.2, 8.4 Hz, 1H), 2.46–2.35 (m, 2H), 2.02–1.86 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.4, 150.8, 128.5, 127.4, 124.7, 118.7, 109.2, 60.5, 59.0, 35.8, 31.7, 31.2, 14.2; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{13}H_{17}NO_2Na^+$ 242.1151; Found 242.1160.

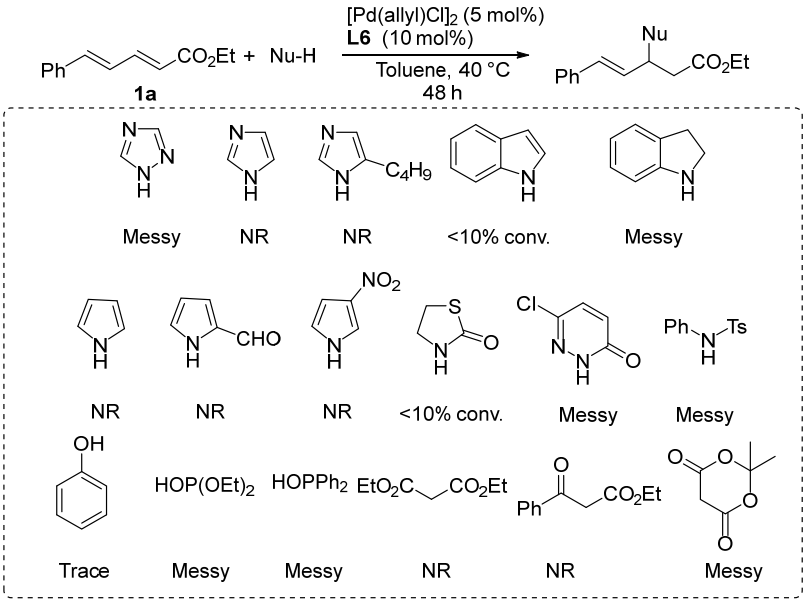
To a solution of **10** (21.9 mg, 0.0999 mmol, 1.0 equiv) in toluene (0.7 mL) was added CSA (4.6 mg, 0.020 mmol, 0.2 equiv), and the solution was heated to reflux for 3 h. After completion and concentration, the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1) gave the product **11**: 15.2 mg (0.0878 mmol), as a white solid, 88% yield; mp = 122–124 °C;

$[\alpha]_D^{25}$ = +14.0 (*c* = 0.39 in $CHCl_3$); 81% ee, determined by HPLC analysis [Chiralpak IF, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 19.07 min, t (minor) = 20.74 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 7.6 Hz, 1H), 7.24–7.15 (m, 2H), 7.08–6.97 (m, 1H), 4.71–4.58 (m, 1H), 3.17 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.94–2.79 (m, 2H), 2.66–2.54 (m, 1H), 2.53–2.43 (m, 1H), 2.08–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 171.7, 139.2, 134.2, 127.7, 125.3, 124.2, 114.8, 63.0, 36.4, 35.8, 29.4; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{11}H_{11}NONa^+$ 196.0733; Found 196.0732.

8. More investigation on substrate scope

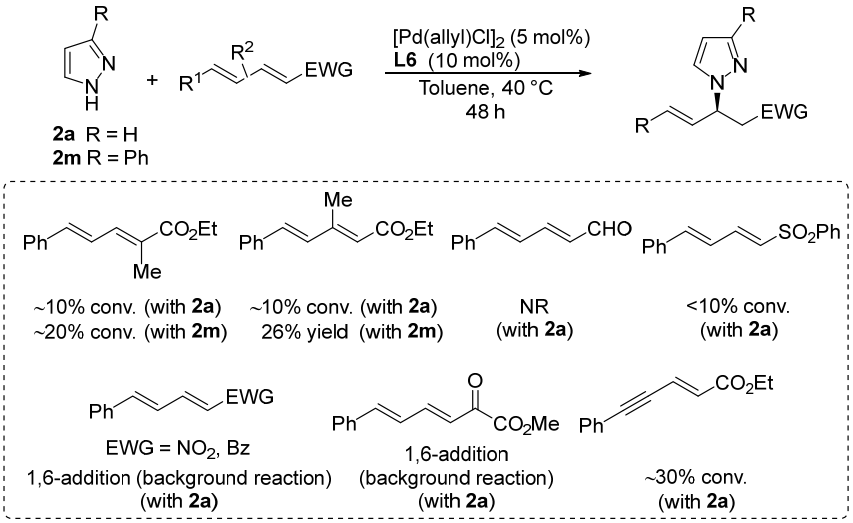
8.1 Other nucleophiles

Dienoate **1a** was subjected to the reaction with various nucleophiles (listed as below) under the standard conditions; however, no desired products were observed.



8.2 Other electron-deficient dienes

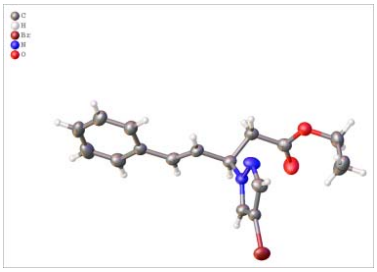
Additionally, various dienes were tested with pyrazole **2a** or **2m** under the standard conditions. However, most of them exhibited poor reactivity, while some dienes with strong electron-withdrawing groups underwent uncatalysed 1,6-addition reactions even in the absence of the catalyst.

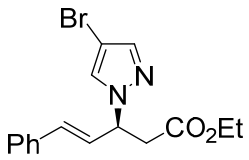


9. X-ray crystallographic data and structural refinement

9.1 Crystal data and structural refinement for enantiopure 3e

Preparation of the single crystals of enantiopure **3e**: Compound **3e** (30.0 mg, 85% ee) was dissolved in EtOAc (1.0 mL) in a 10 mL tube, and petroleum ether (3.0 mL) was added. The tube was sealed by a piece of weighing paper with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After 7 days, the crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of **3e**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (K = 0.71073 Å) at 220 K. CCDC 2427290 (**3e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





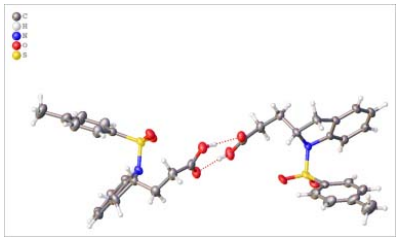
3e

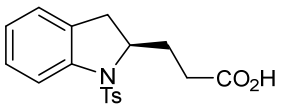
Identification code	**3e**
Empirical formula	$C_{16}H_{17}BrN_2O_2$
Formula weight	349.22
Temperature/K	220.0
Crystal system	triclinic
Space group	P1
a/Å	5.6253(3)
b/Å	6.9311(5)
c/Å	10.2824(7)
α/°	84.979(3)
β/°	81.399(2)
γ/°	80.650(2)
Volume/Å^3	390.31(4)
Z	1
ρ_{calc}g/cm^3	1.486

μ/mm^{-1}	2.639
F(000)	178.0
Crystal size/mm^3	0.32 × 0.21 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.97 to 55.11
Index ranges	$-7 \le h \le 7$, $-9 \le k \le 9$, $-13 \le l \le 13$
Reflections collected	11374
Independent reflections	3541 [R_{int} = 0.0390, R_{sigma} = 0.0568]
Data/restraints/parameters	3541/3/191
Goodness-of-fit on F^2	0.865
Final R indexes [I>=2σ (I)]	R_1 = 0.0243, wR_2 = 0.0493
Final R indexes [all data]	R_1 = 0.0275, wR_2 = 0.0509
Largest diff. peak/hole / e Å^{-3}	0.17/–0.27
Flack parameter	0.019(5)

9.2 Crystal data and structural refinement for enantiopure 9

Preparation of the single crystals of enantiopure **9**: Compound **9** (25.0 mg, 84% ee) was dissolved in EtOAc (1.0 mL) in a 10 mL tube, and petroleum ether (3.0 mL) was added. The tube was sealed by a piece of weighing paper with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After 7 days, the crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of **9**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (K = 0.71073 Å) at 152 K. CCDC 2427291 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





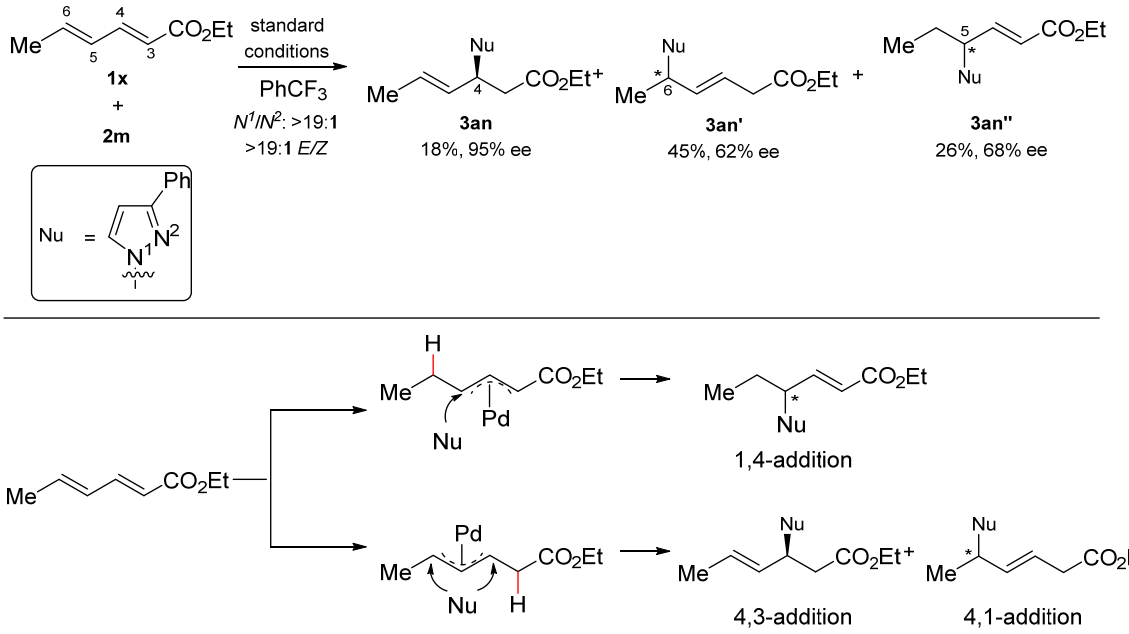
9

Identification code	**9**
Empirical formula	$C_{18}H_{19}NO_4S$

Formula weight	345.40
Temperature/K	152.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.8672(12)
b/Å	12.4115(18)
c/Å	15.622(2)
α/°	90
β/°	101.092(5)
γ/°	90
Volume/Å^3	1687.2(4)
Z	4
ρ_{calc}g/cm^3	1.360
μ/mm^{-1}	0.213
F(000)	728.0
Crystal size/mm^3	0.5 × 0.39 × 0.34
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.222 to 55.244
Index ranges	$-11 \leq h \leq 11$, $-16 \leq k \leq 16$, $-20 \leq l \leq 20$
Reflections collected	51615
Independent reflections	7793 [R_{int} = 0.0615, R_{sigma} = 0.0364]
Data/restraints/parameters	7793/1/437
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0715
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0743
Largest diff. peak/hole / e Å^{-3}	0.18/–0.23
Flack parameter	0.014(19)

10. Mechanism studies

10.1 Diverse selectivity for alkyl-substituted dienoate

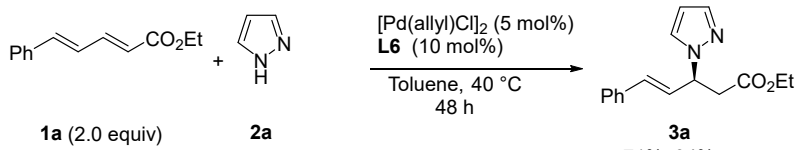


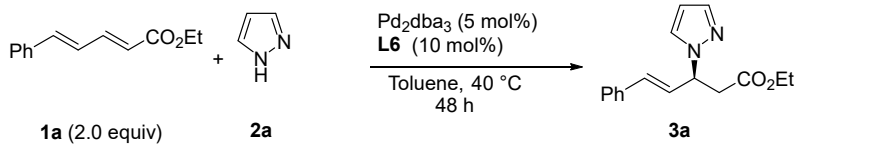
It was found that three regioisomers were produced when alkyl-substituted dienoate **1x** was employed. These isomers likely arise from protonation and subsequent allylic alkylation occurring at different sites. Previous studies have demonstrated that the regioselectivity was significantly influenced by the electronic and steric properties of the diene substrates.[2,3]

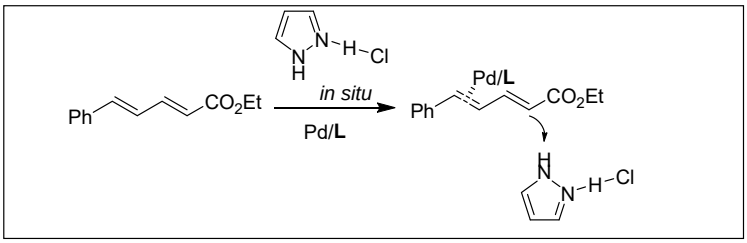
10.2 Control experiment

10.2.1 Pd source & acid additive

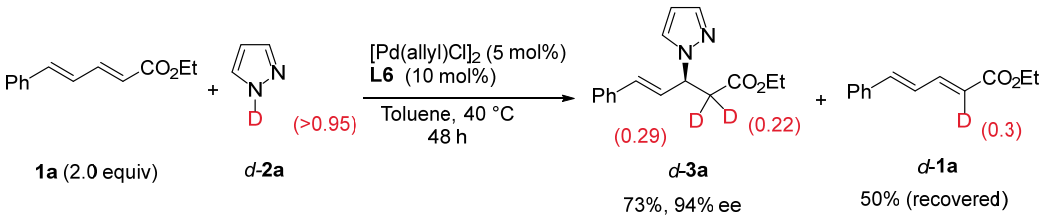
Under standard conditions, $[Pd(allyl)Cl]_2$ could promote the hydroamination reaction of pyrazole **2a** and **1a** in 71% yield after 48 h. In contrast, when the reaction was carried out with Pd_2dba_3, poor conversion was observed. Nevertheless, the addition of HCl was beneficial for the reaction, and the yield was improved significantly. The results indicated that HCl additive play an important role in the reaction. It was proposed that $[Pd(allyl)Cl]_2$ might be converted to Pd^0 and HCl under the standard condition, and in situ formed pyrazole hydrochloride would be the active proton substrate.

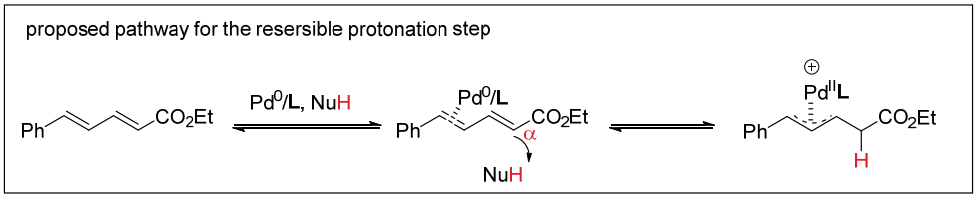


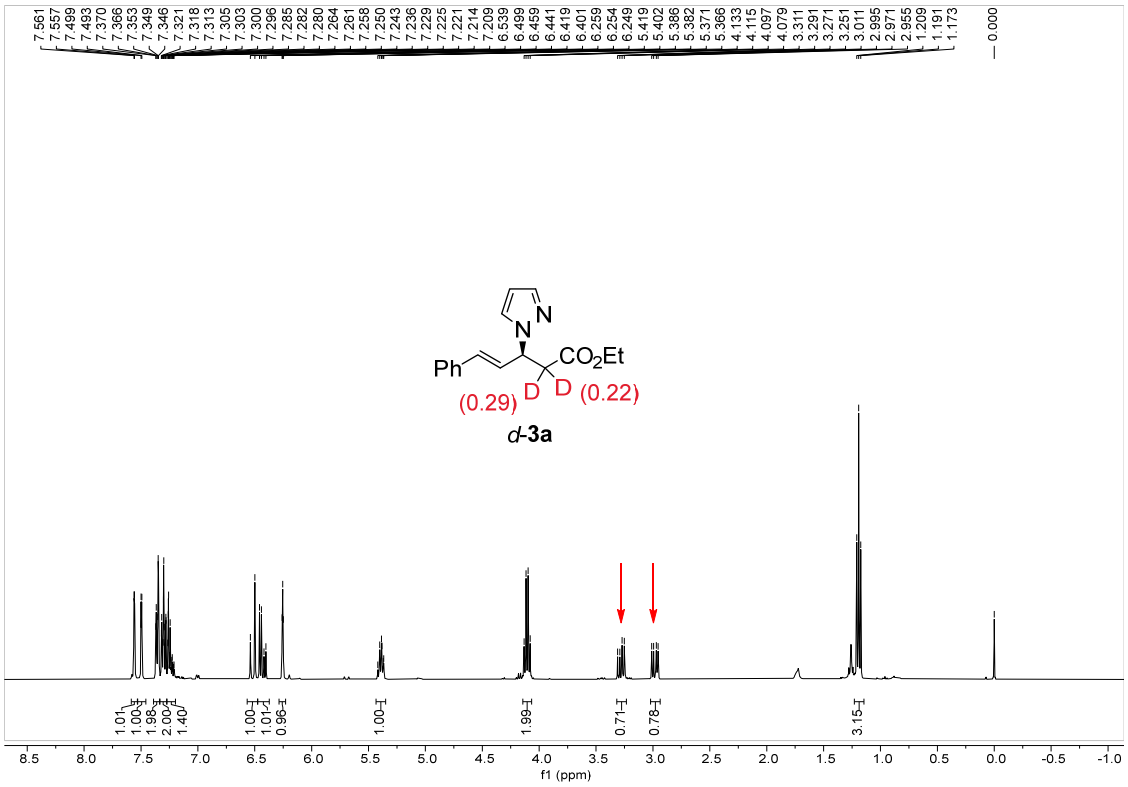




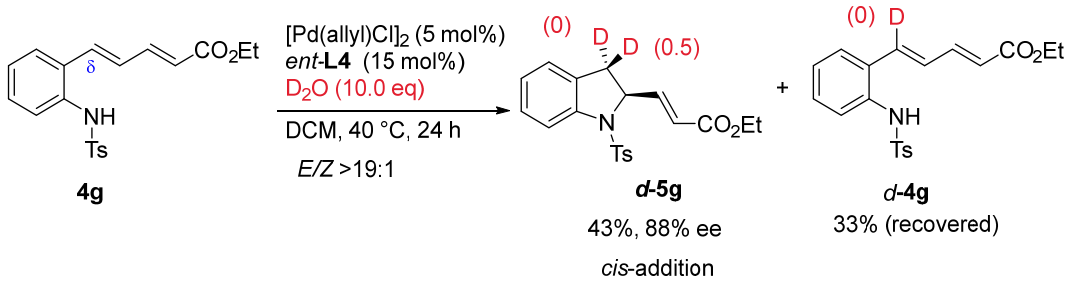
10.2.2 Deuterium-labeling experiments



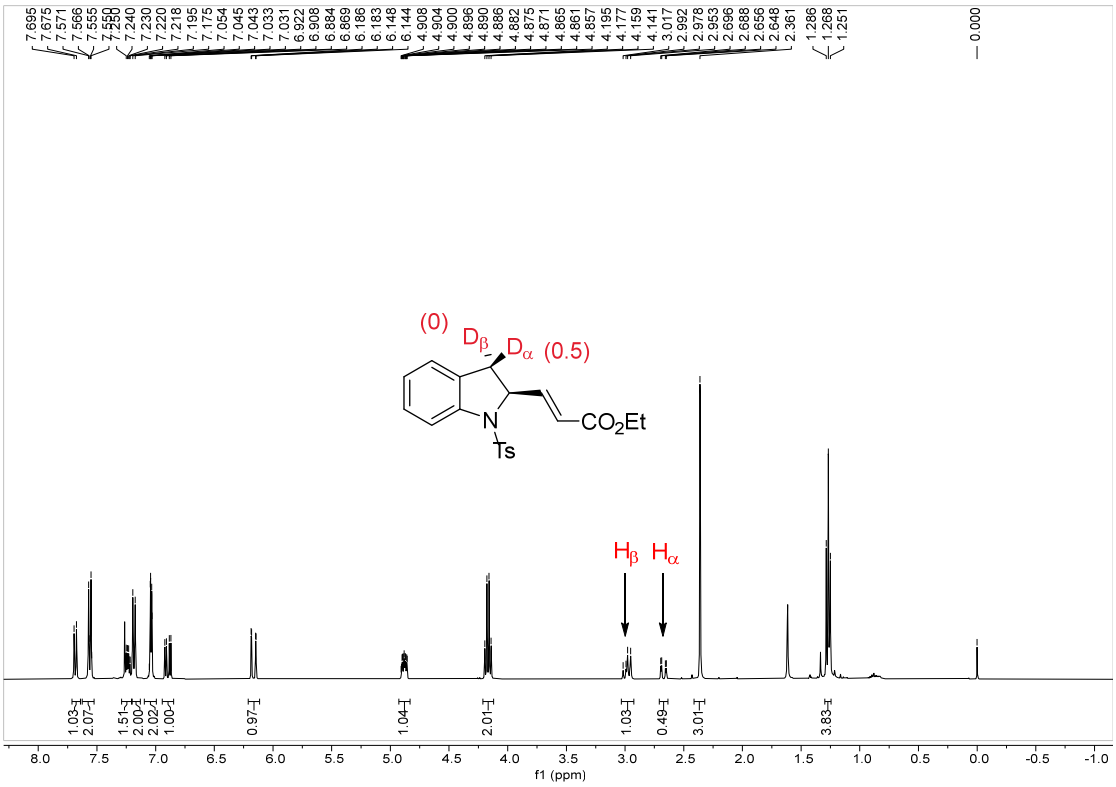




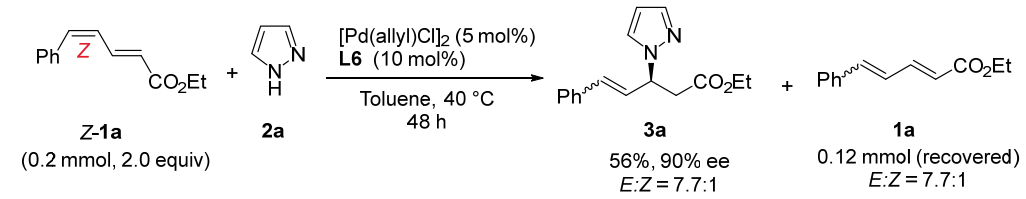
Deuterium-labeled pyrazole *d*-**2a** was applied to the reaction with **1a** under the standard conditions. *d*-**3a** was obtained with deuteration at both α-CHs, and **1a** was recovered with deuterium incorporation at the α-position. The findings suggested that the protonation (or hydropalladation) occurred specifically at the α-site of the dienoate, and this process was reversible. The results also implied that Pd-hydride species would be likely not involved, as they usually exhibit poor regioselectivity during the migratory insertion process.

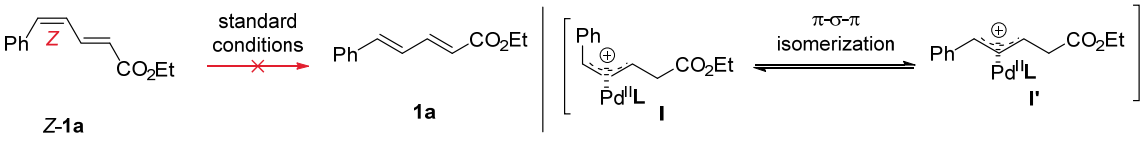


D_2O was applied to the reaction with **4g** under the catalysis of Pd/*ent*-**L4**. *d*-**5g** was obtained and only H_α at δ-protonation was deuterium-labeled. The findings suggested that the protonation (or hydropalladation) occurred exclusively at the δ-position of the dienoate in a stereospecific *cis*-addition manner. Furthermore, this process was found to be irreversible.



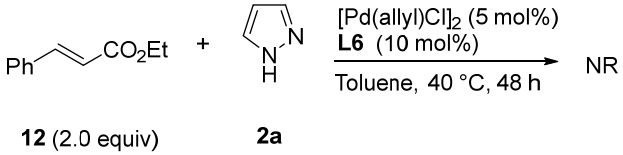
10.2.3 Diene geometry study





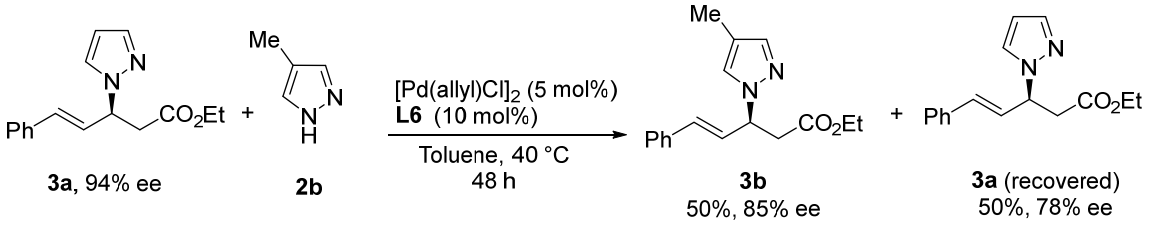
Z-**1a** was employed for the asymmetric hydroamination reaction under the standard catalytic conditions. After 48 h, *E*-configured product **3a** as the major product, along with recovered **1a** mainly in *E*-configuration, was obtained. In contrast, *Z*-**1a** could not be converted to *E*-**1a** in the absence of pyrazole under the standard conditions. The observations further supported that the nucleophile might trigger the formation of active catalyst Pd(0). The double bond isomerisation might be attributed to the π-σ-π isomerisation of the *in situ* formed π-allylpalladium intermediate.

10.2.4 Ethyl cinnamate as substrate



Ethyl cinnamate **12** was inert in the reaction, demonstrating the importance of the diene moiety.

10.2.5 Crossover study



3a, 94% ee **2b** **3b** 50%, 85% ee **3a** (recovered) 50%, 78% ee

3a was applied to the reaction with **2b** under the standard conditions, **3b** was obtained in 50% yield and **3a** was recovered with apparent ee losses, indicating the allylic allylation is reversible as well.

10.3 DFT calculations

10.3.1 Computational details

In this work all geometry optimizations and single-point energy calculations were carried out using Gaussian 09.[4] Geometries of intermediates and transition states were optimized using the ωb97XD functional[5] with a mixed basis set of SDD for Pd and 6-31G(d) for other atoms in the gas phase. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure, as well as deriving the thermochemical corrections for the enthalpies and free energies. Solvation energy corrections were calculated in toluene solvent with the SMD continuum solvation model[6] based on the gas-phase optimized geometries. To gain more accurate results, the ωb97XD with large basis set of SDD for Pd and 6-311++G(d,p) for other atoms was used for solvation single-point energy calculations. The integration grids defined by the Int=Ultrafine keyword were used for all calculations.

10.3.2 Calculated results

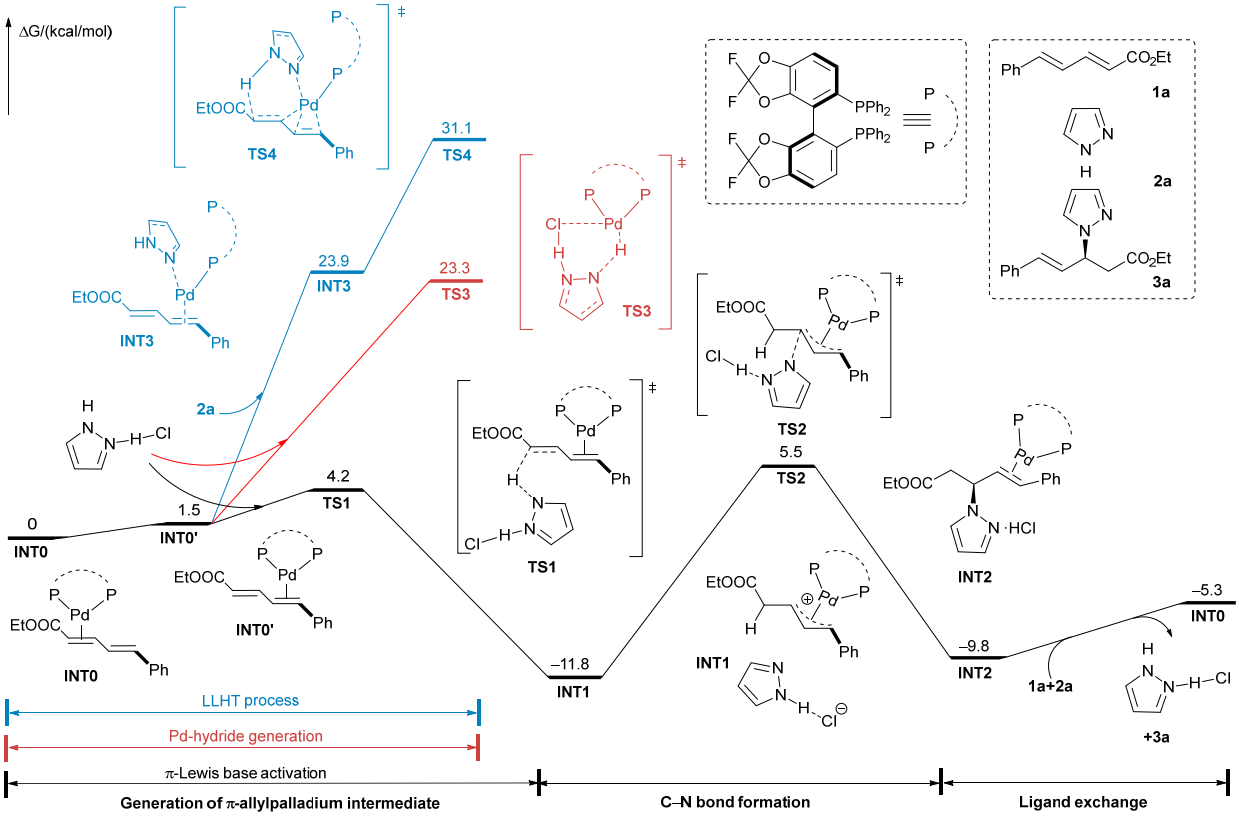


Figure S1 Reaction energy profile for the hydroamination reaction of 1a and 2a.

Furthermore, density functional theory (DFT) calculations were conducted to rationalise the process. As shown in **Figure S1**, the whole catalytic cycle can be divided into two parts: 1) the generation of π-allylpalladium intermediate, and 2) the C-N bond construction via reductive elimination. Starting from Pd^0 complex **INT0**, three possible pathways were considered after facile conversion to **INT0′**: π-Lewis base activation (black line), Pd-hydride migratory insertion (red line), and ligand-to-ligand hydrogen transfer (LLHT) process (blue line).

The generation of Pd-H species via **TS3** has an energy barrier of 23.3 kcal/mol, and the LLHT process via **TS4** also would be highly disfavored (31.1 kcal/mol). In contrast, the π-Lewis base promoted protonation pathway via **TS1** can directly provide Pd^{II}-π-allyl complex **INT1**, with an energy barrier of only 4.2 kcal/mol, suggesting the cooperative Pd^0 π-Lewis base and acid catalysis would be preferred. This information is also consistent with the reversible α-protonation observed in section 10.2.2. The C-N bond is formed via **TS2**, with an energy barrier of 17.3 kcal/mol. The results show that nucleophilic attack is the rate-determining as well as the enantioselectivity-determining step in the catalytic cycle.

10.3.3 Pd as a π-Lewis base catalyst and the rationality of the coordination site (due to the reversibility of the two coordination sites, the lower energy is selected as the potential energy zero)

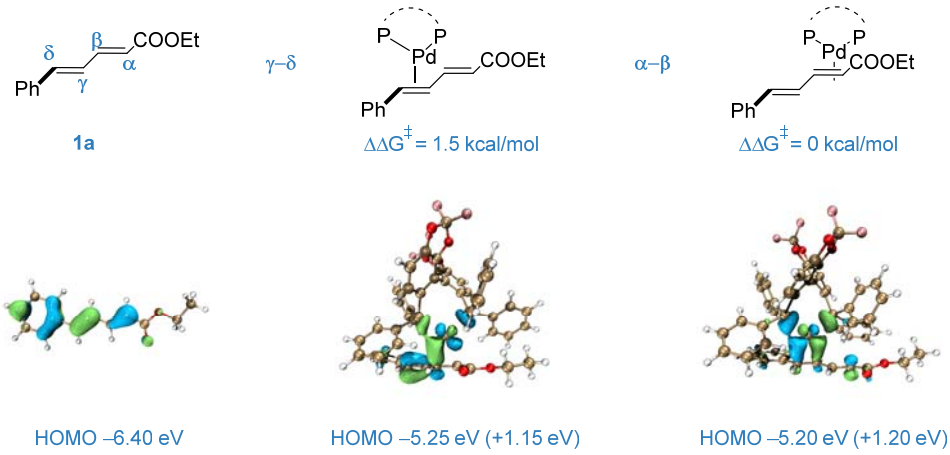


Figure S2 The molecular orbitals and energies of the complexes at different coordination sites

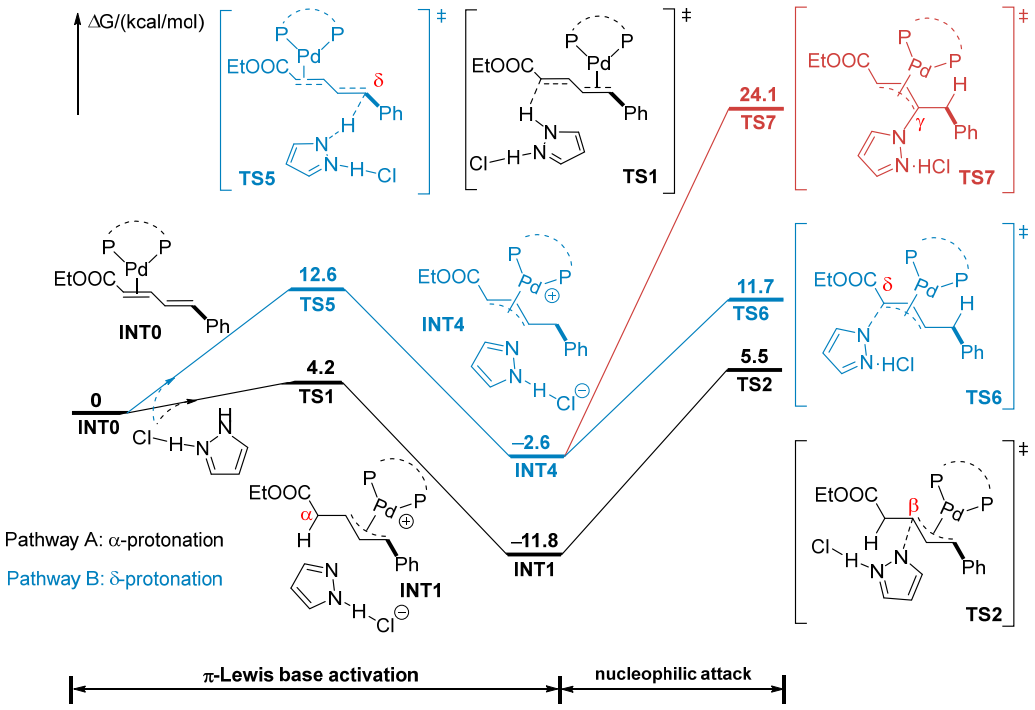


Figure S3 Comparison of pathways of complexes with different coordination sites

Pd as a π-Lewis base catalyst might coordinate to the α,β- or γ,δ-double bond of **1a**. After conformational search, both coordination sites of **1a** were identified capable of binding with Pd^0 to facilitate the reaction (**Figure S2**). When Pd^0 coordinates to the γ,δ-double bond (**INT0'**), the HOMO energy of **1a** is increased with 1.15 eV, whereas an increase of 1.20 eV occurs when Pd^0 coordinates to the α,β-double bond (**INT0**). To elucidate the mechanism, the α- and δ-protonation processes,

initiated from **INT0** and **INT0'**, respectively, were compared. Due to the reversibility of the two coordination sites, the lower energy state was selected as the reference point (potential energy zero).

Based on the DFT calculation results, pathway A (α-protonation) is energetically favored over pathway B (δ-protonation), owing to the significantly lower energy barrier in both the protonation and allylic alkylation steps (**Figure S3**).

10.3.4 Proton source investigation

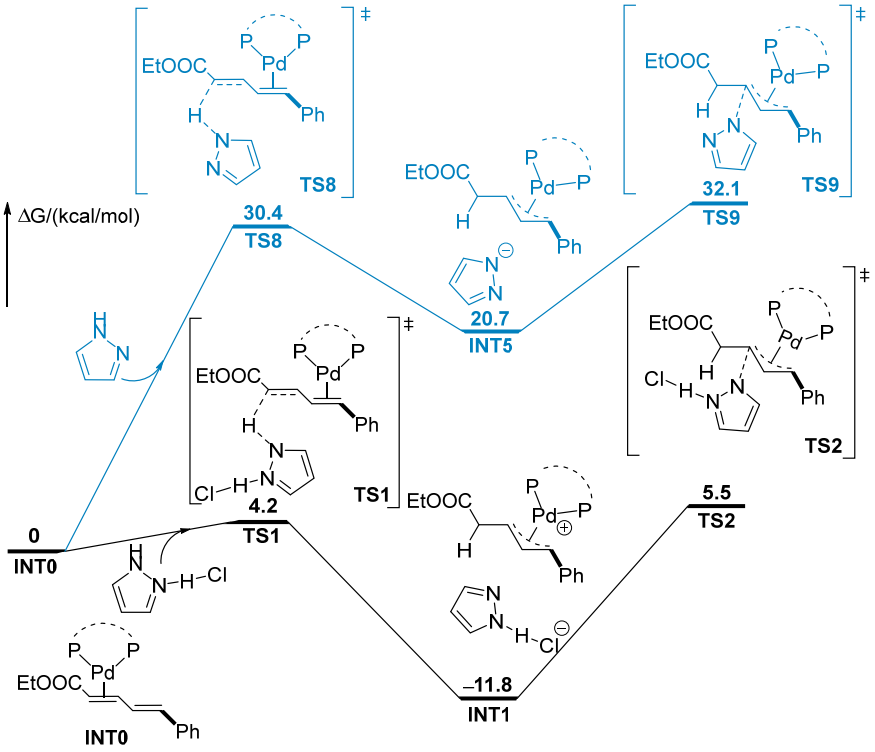


Figure S4 Comparison of paths of different proton sources

In 2021, the Dong group reported the hydroamination reaction of diene with pyrazole.[7] The work indicated that the hydrogen of pyrazole was transferred to the diene via a LLHT process. Based on this work, we also investigated the proton donor in the current work. Two pathways were considered: 1) **Pathway 1:** pyrazole hydrochloride as the proton donor; 2) **Pathway 2:** pyrazole as the proton source. As shown in Figure S4, the latter has a much higher energy barrier compared the former (**TS1** *vs* **TS8**), indicating that pyrazole hydrochloride might be the proton donor. This is consistent with the control experiment (Scheme 6a in the manuscript), which demonstrated the crucial role of HCl as the additive.

10.3.5 Enantioselectivity

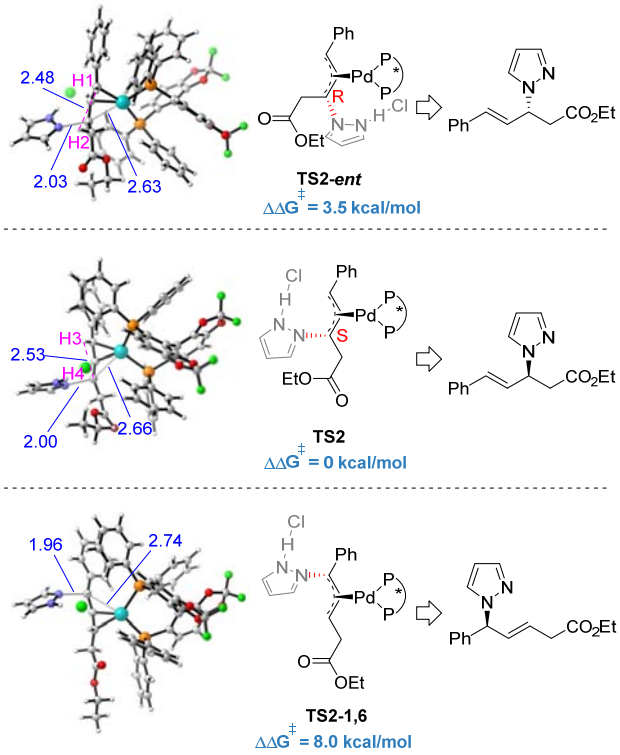
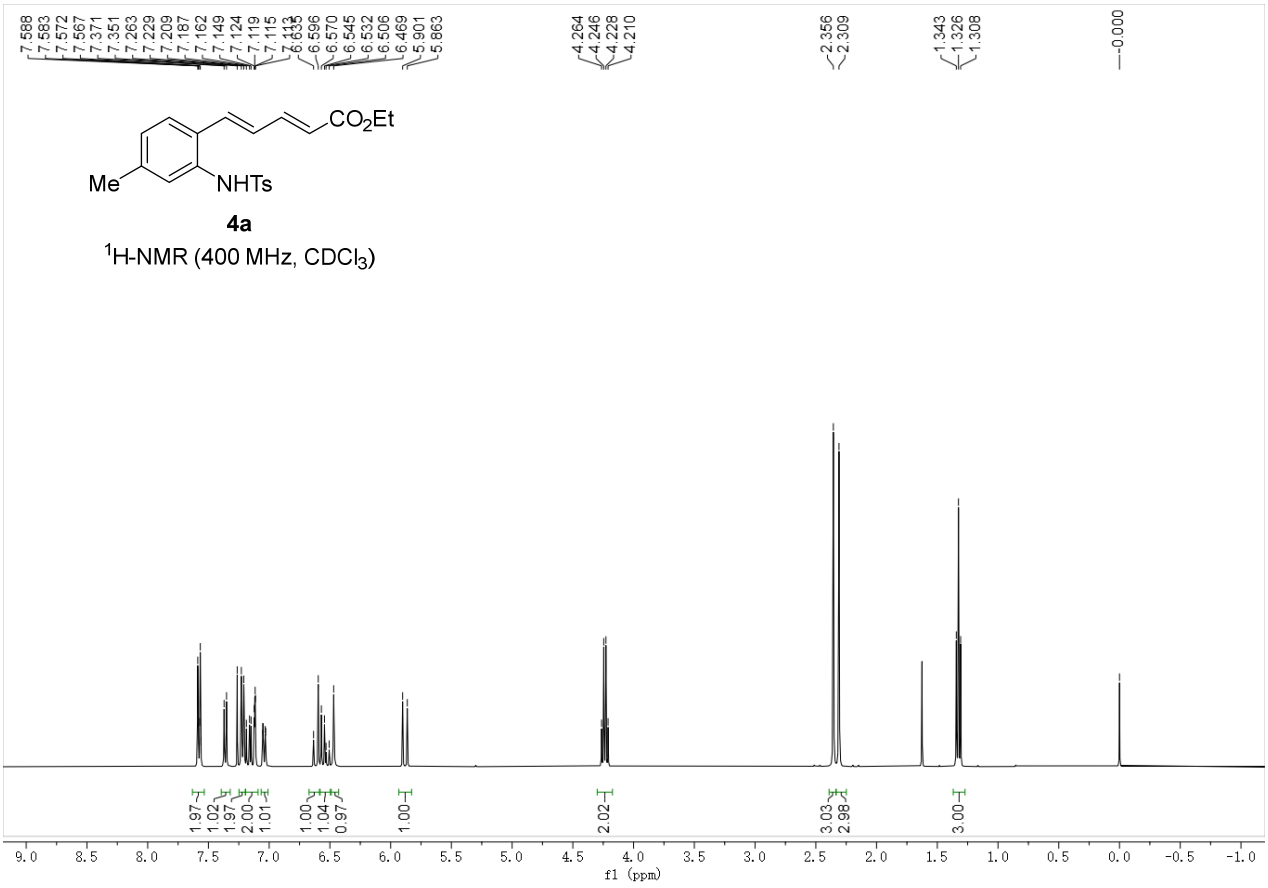


Figure S5 Stereoselective source analysis

Geometry analysis indicates the distance between H^3 and H^4 in **TS2** (2.53 Å) is longer than that between H^1 and H^2 in **TS2-*ent*** (2.48 Å), indicating a significant 1,3-strain between adjacent H atom and CH_2 moiety in **TS2-*ent***, which leads to its high relative free energy (**Figure S5**).

In addition, the regional selectivity of allylic alkylation process was compared, and the transition state of 1,6-selective products was also studied. In fact, the 1,6-selective product would be less favored since a higher energy (8.0 kcal/mol) was observed in transition state **TS2-1,6** in comparison with that of **TS2**.

11. NMR, HRMS spectra and HPLC chromatograms



4a

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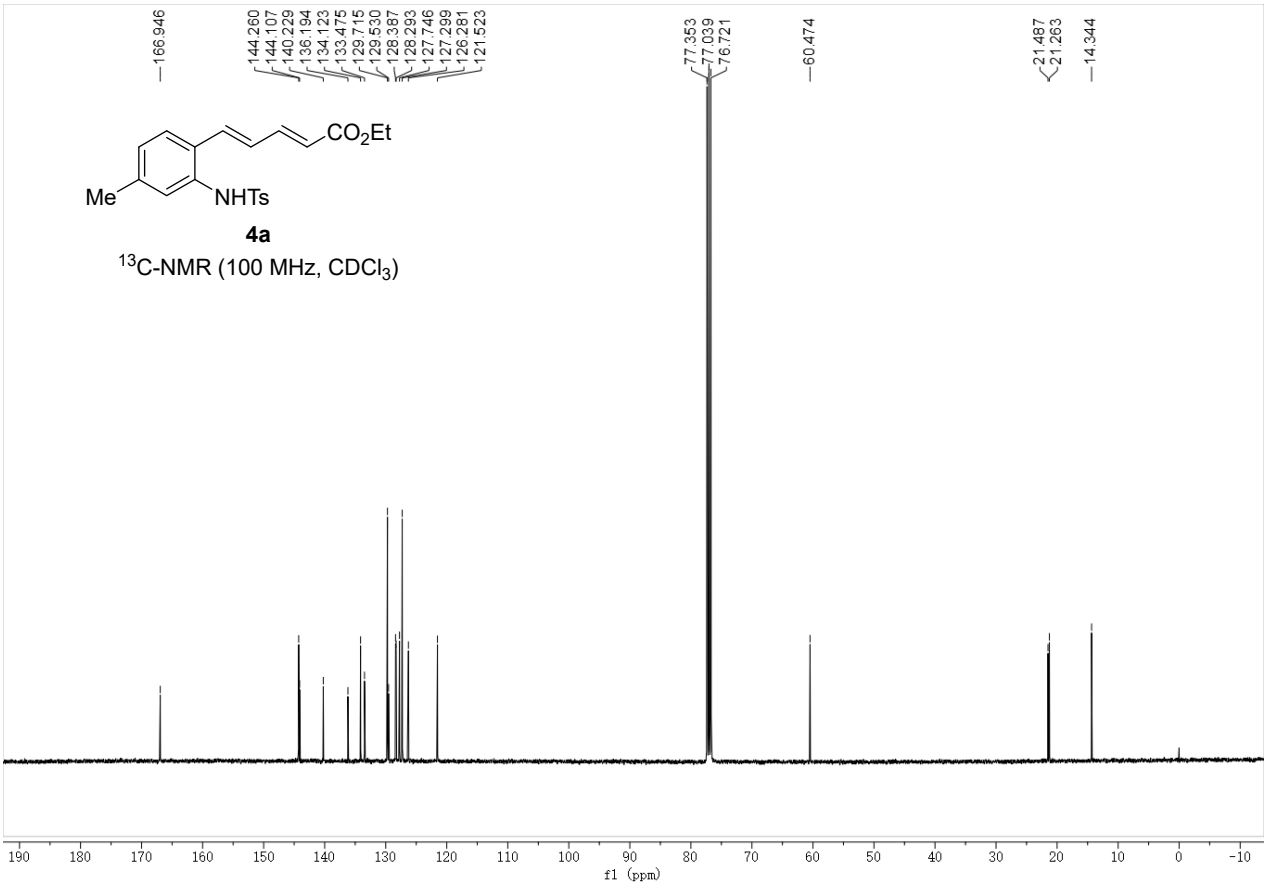
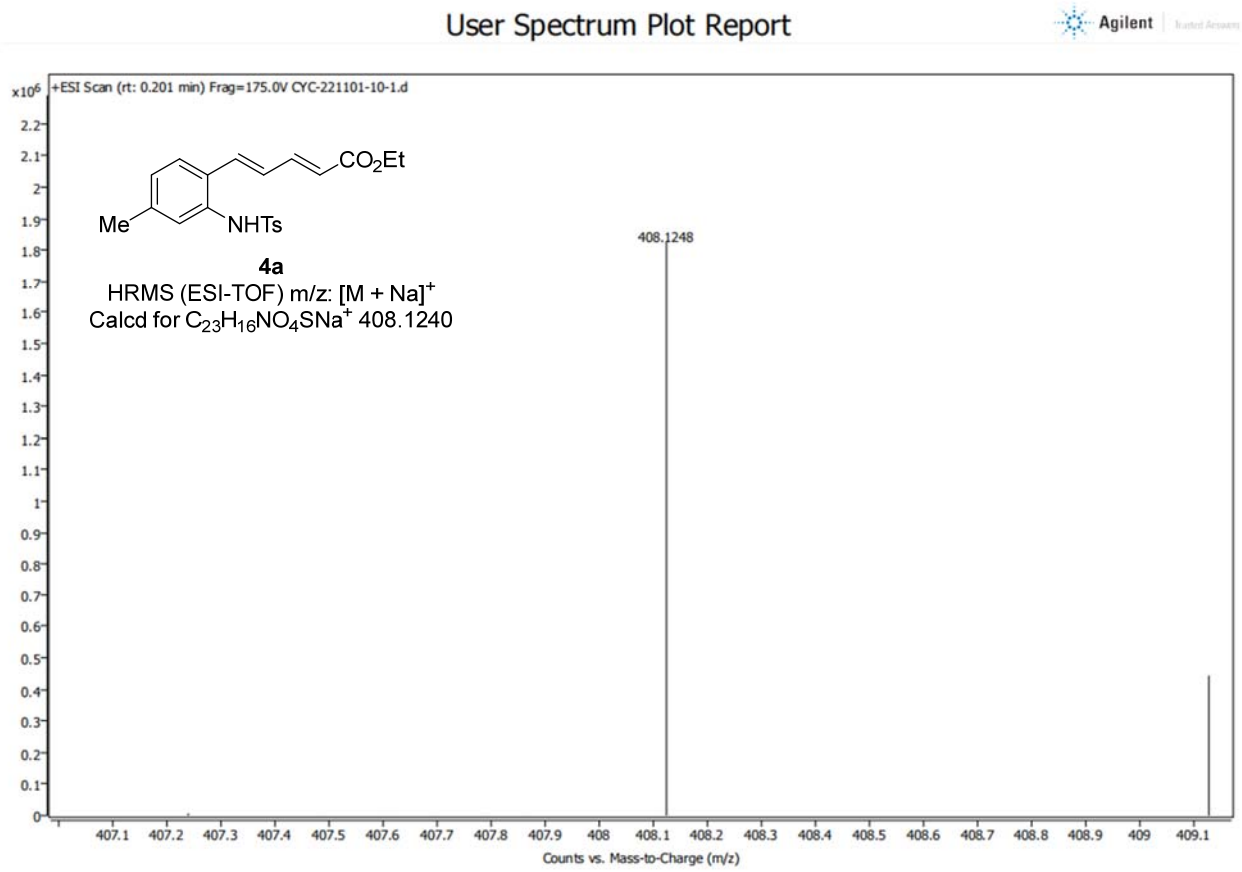


4a

^{13}C-NMR (100 MHz, $CDCl_3$)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Me
NHTs
4a
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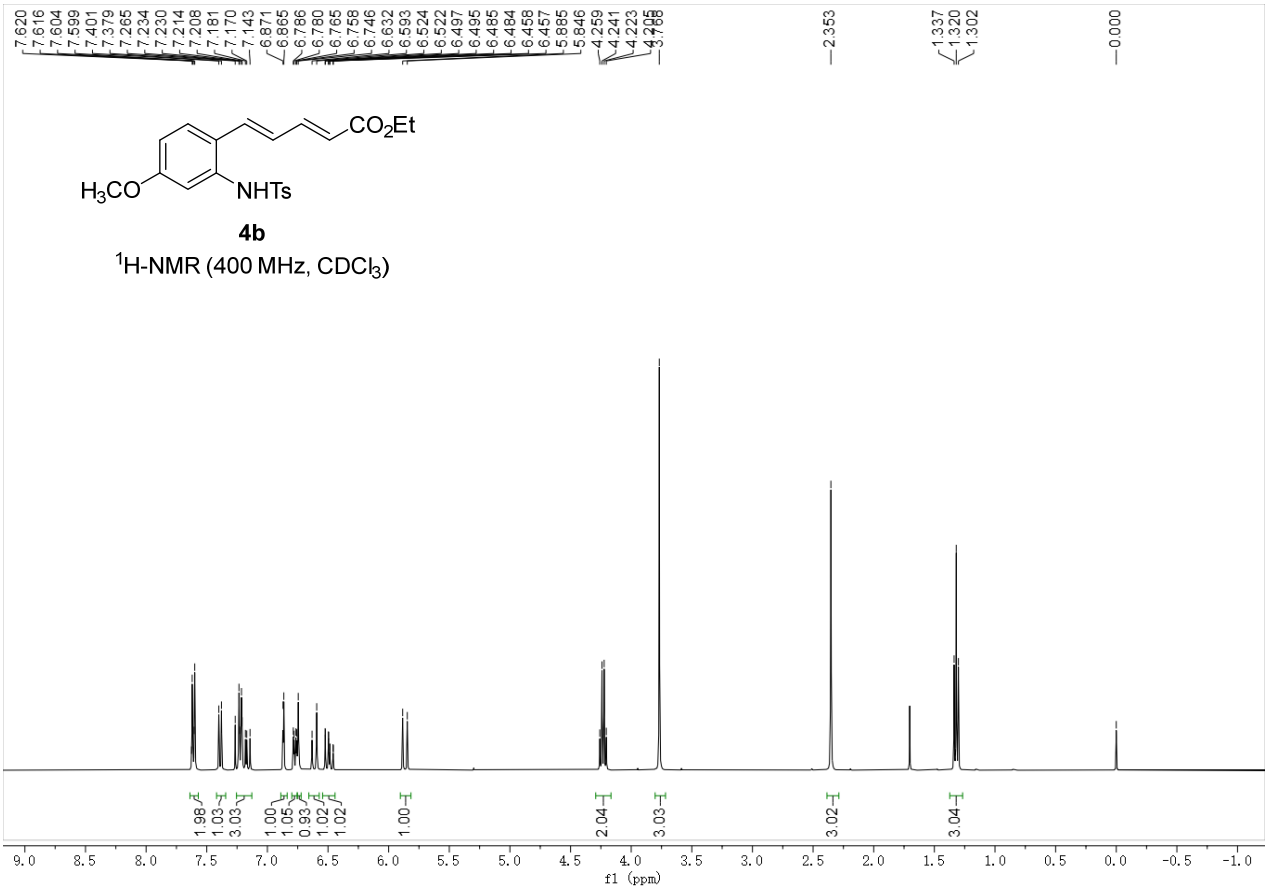
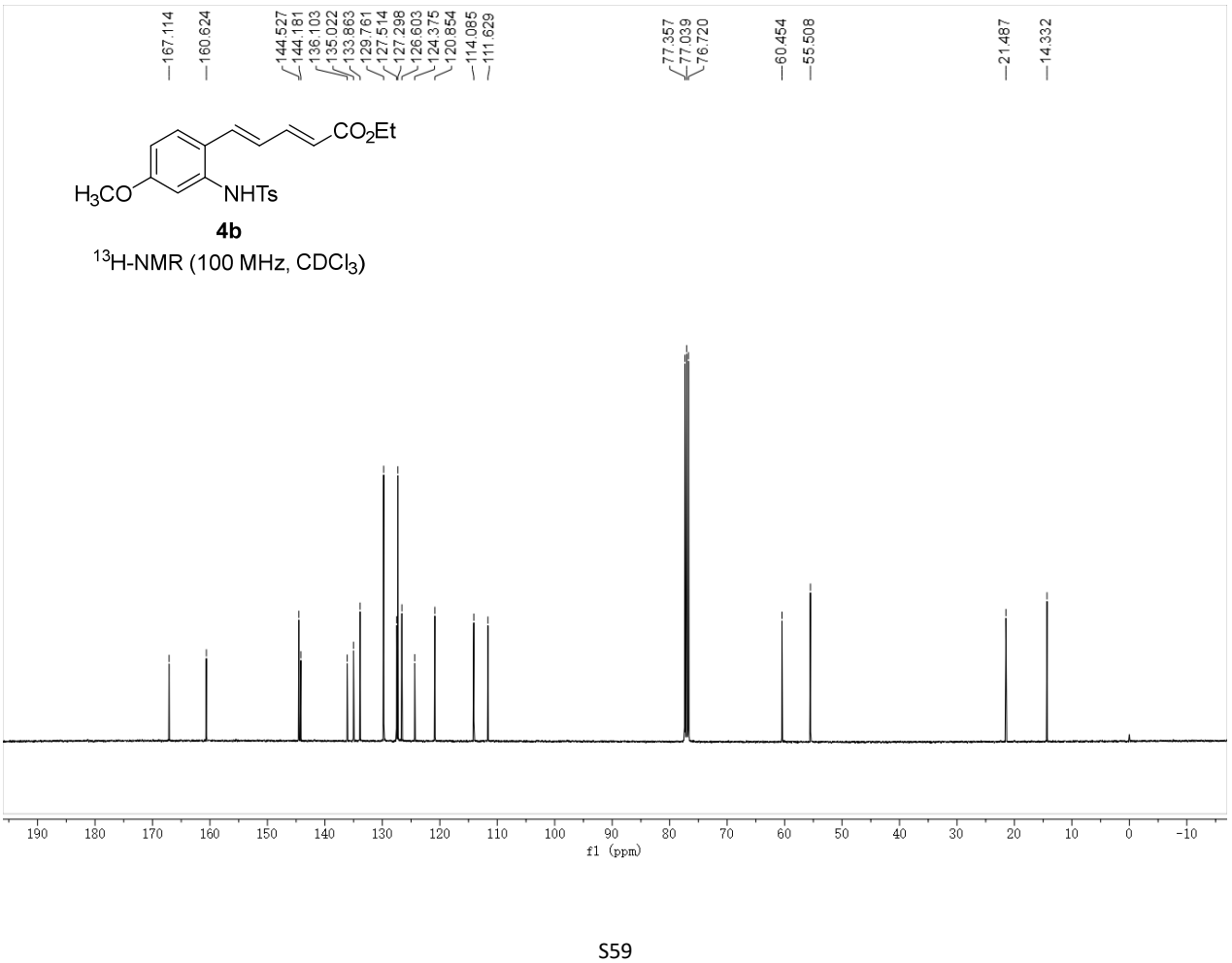
Counts vs. Mass-to-Charge (m/z)



4b

^{1}H-NMR (400 MHz, $CDCl_3$)



4b

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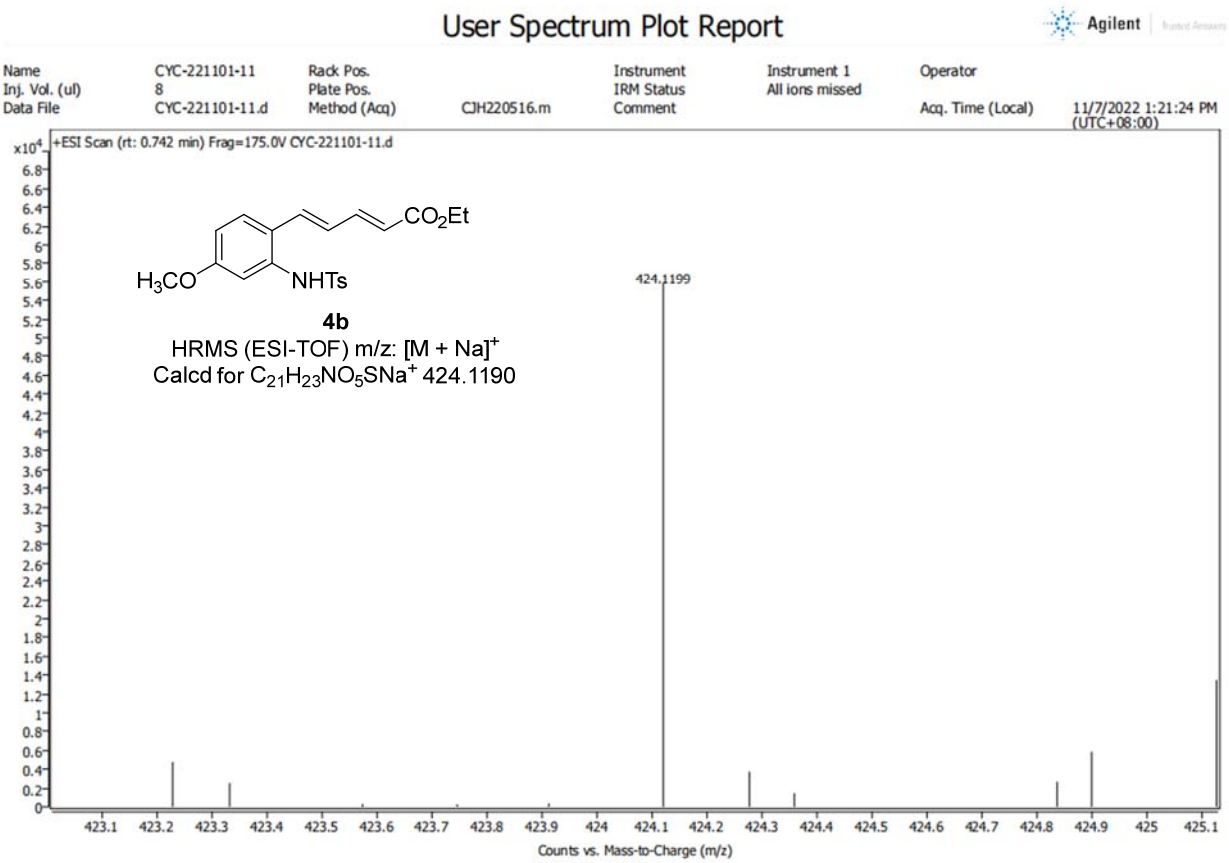
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Instrument
IRM Status
Comment
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Operator
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4b
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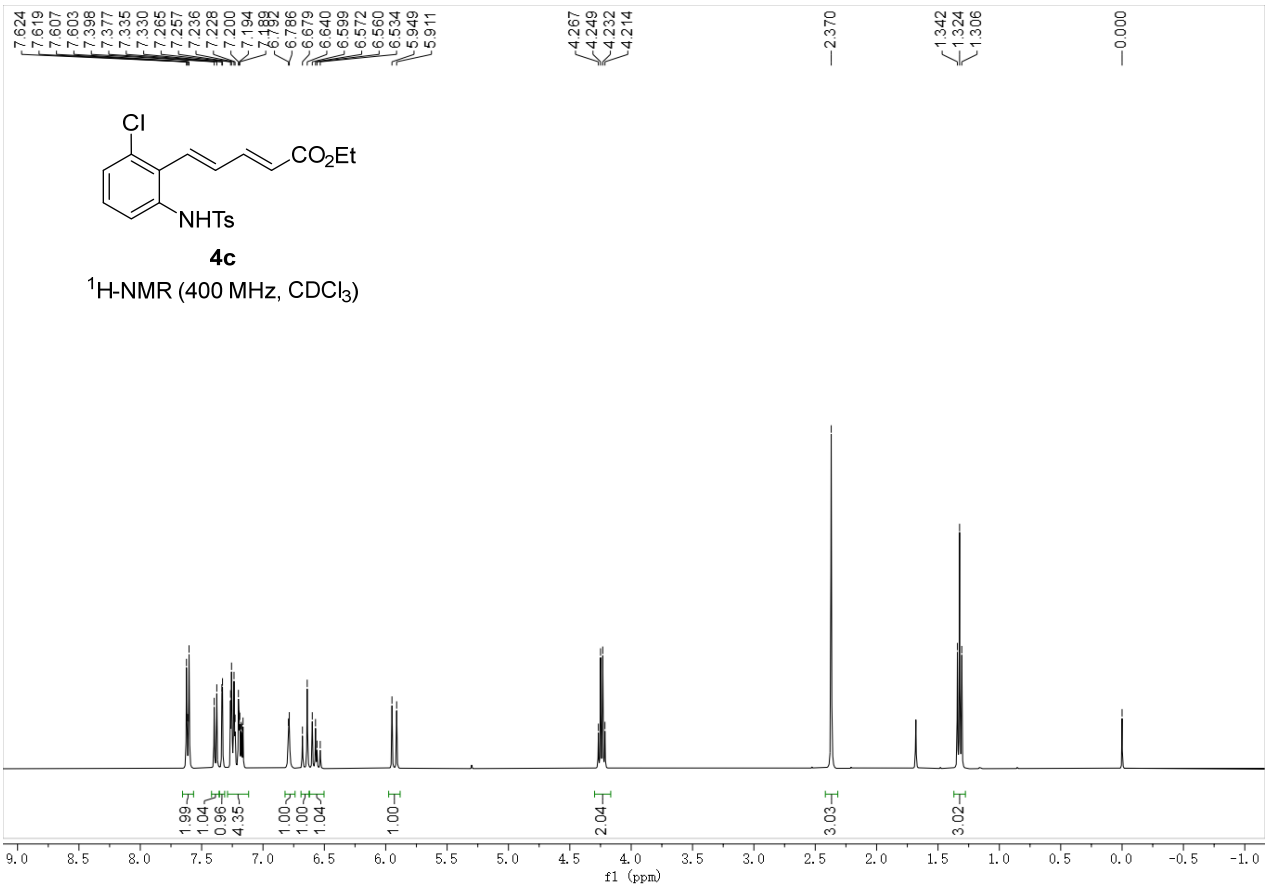
Counts vs. Mass-to-Charge (m/z)



4c

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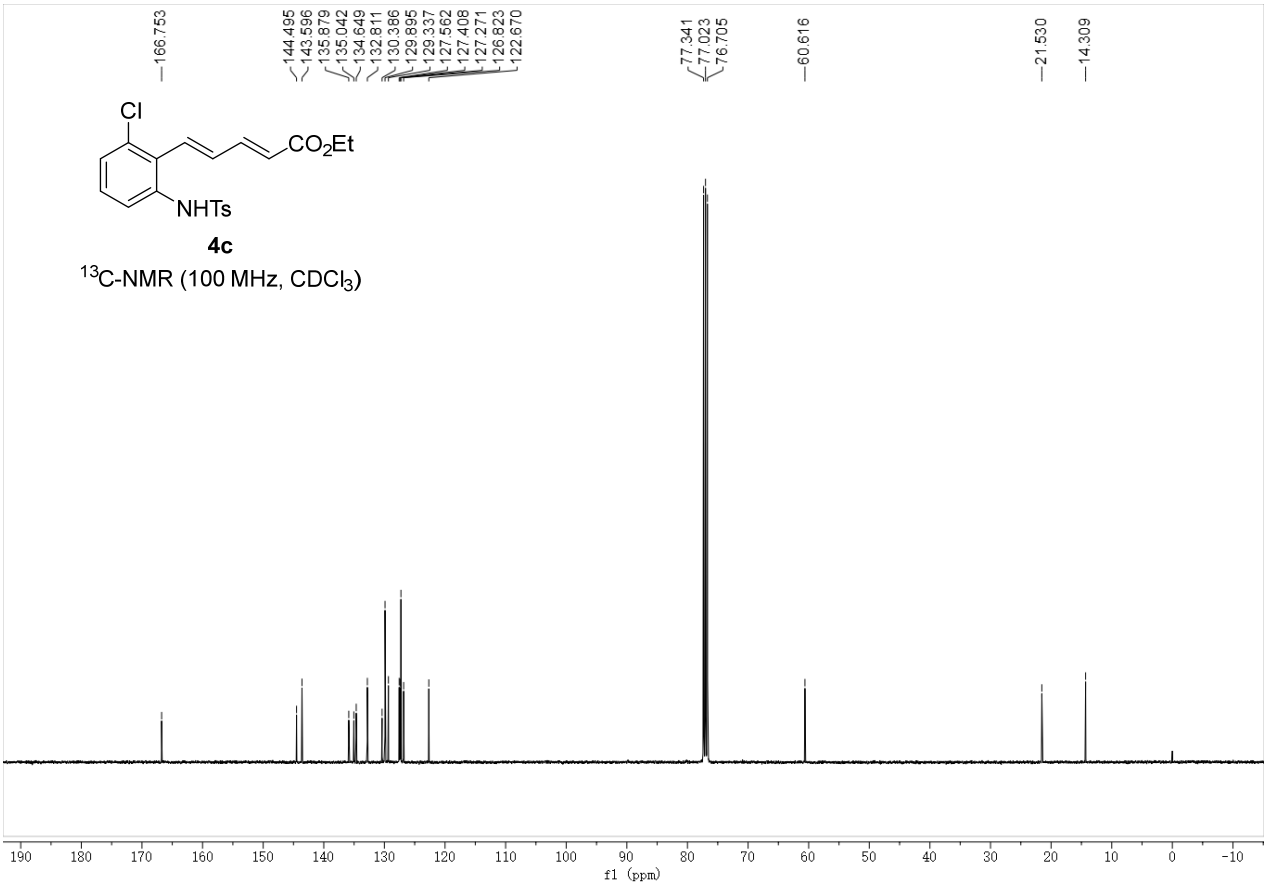
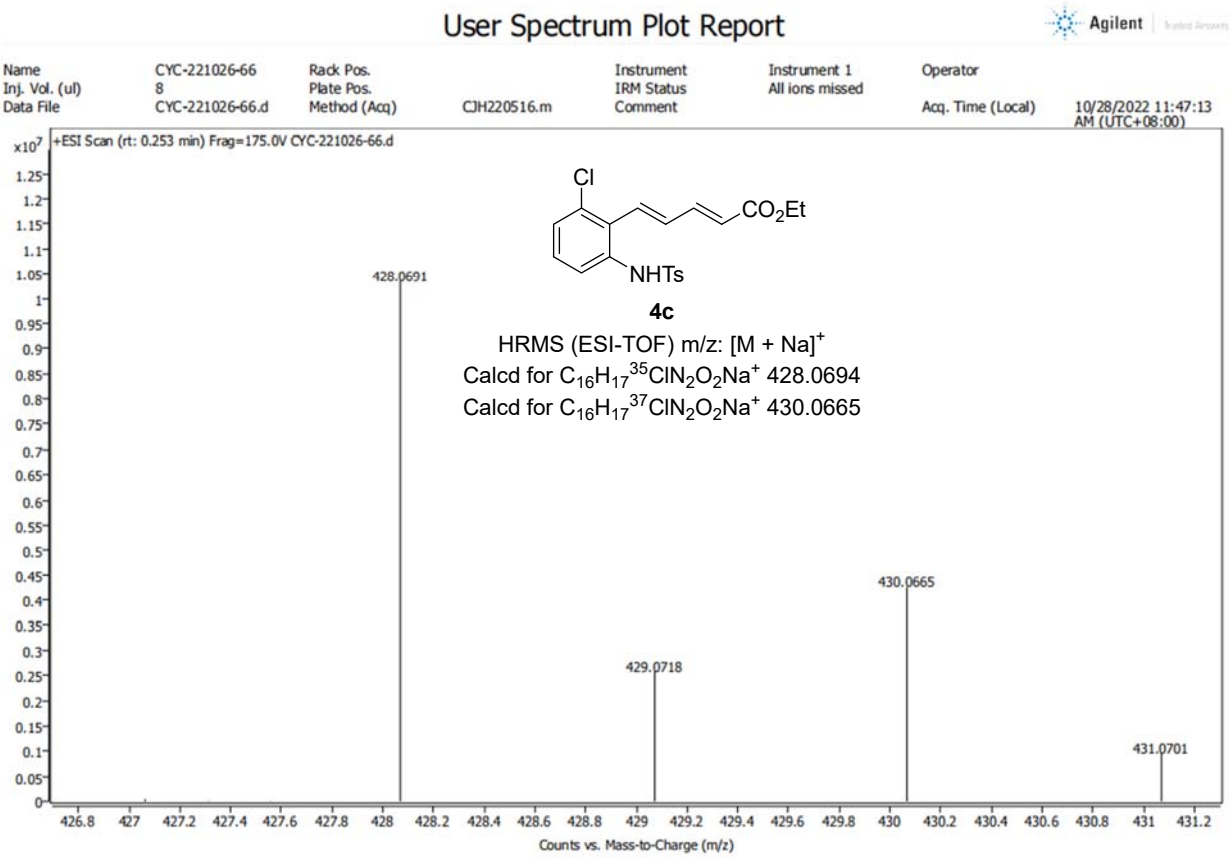


4c

^{13}C-NMR (100 MHz, $CDCl_3$)



4c

HRMS (ESI-TOF) m/z: $[M + Na]^+$

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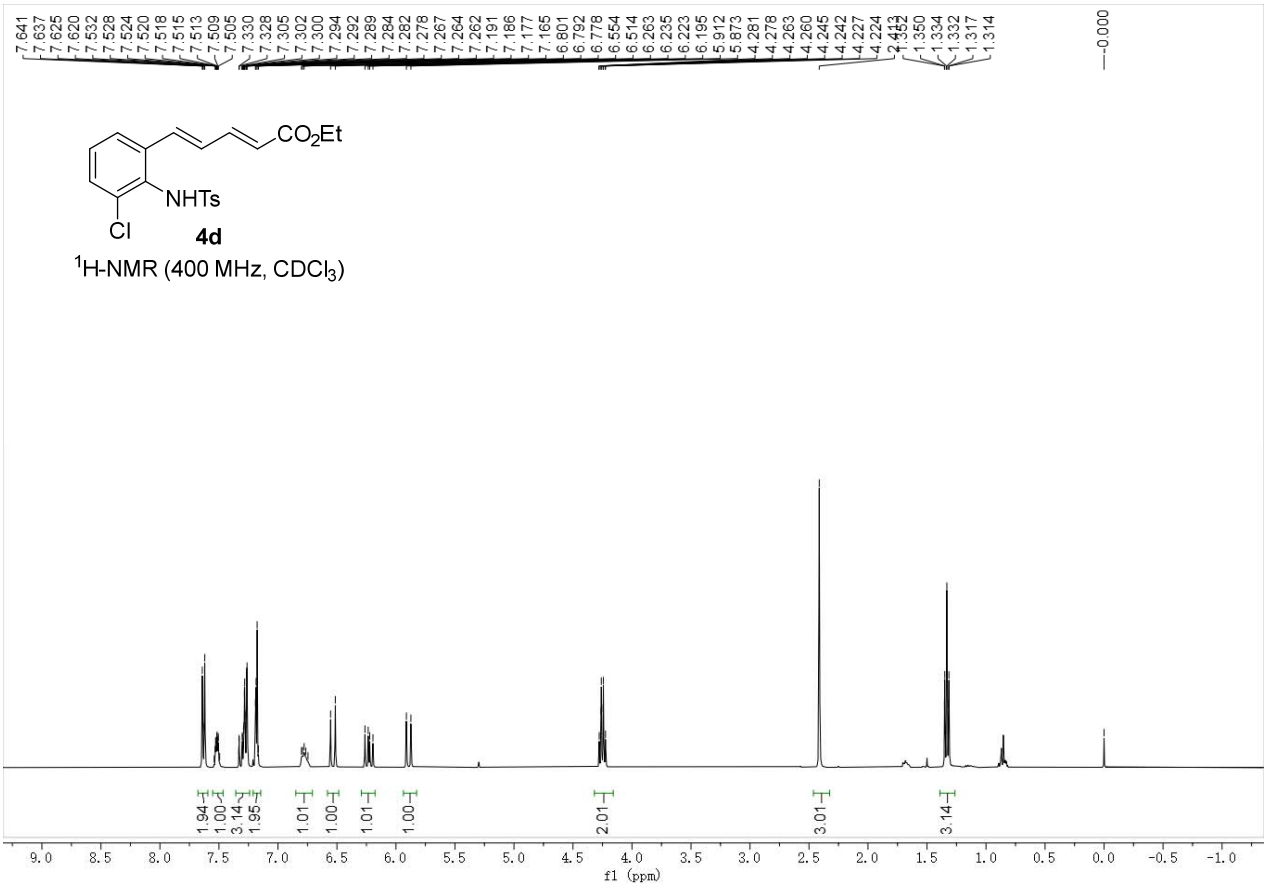
Calcd for $C_{16}H_{17}{}^{37}ClN_2O_2Na^+$ 430.0665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7.505
7.330
7.328
7.305
7.302
7.300
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7.289
7.284
7.282
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7.267
7.264
7.262
7.191
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7.177
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6.792
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6.235
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4.278
4.263
4.260
4.245
4.242
4.227
4.224
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1.334
1.332
1.317
1.314
0.000
CO2Et
NHTs
Cl
4d
1H-NMR (400 MHz, CDCl3)
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1.00
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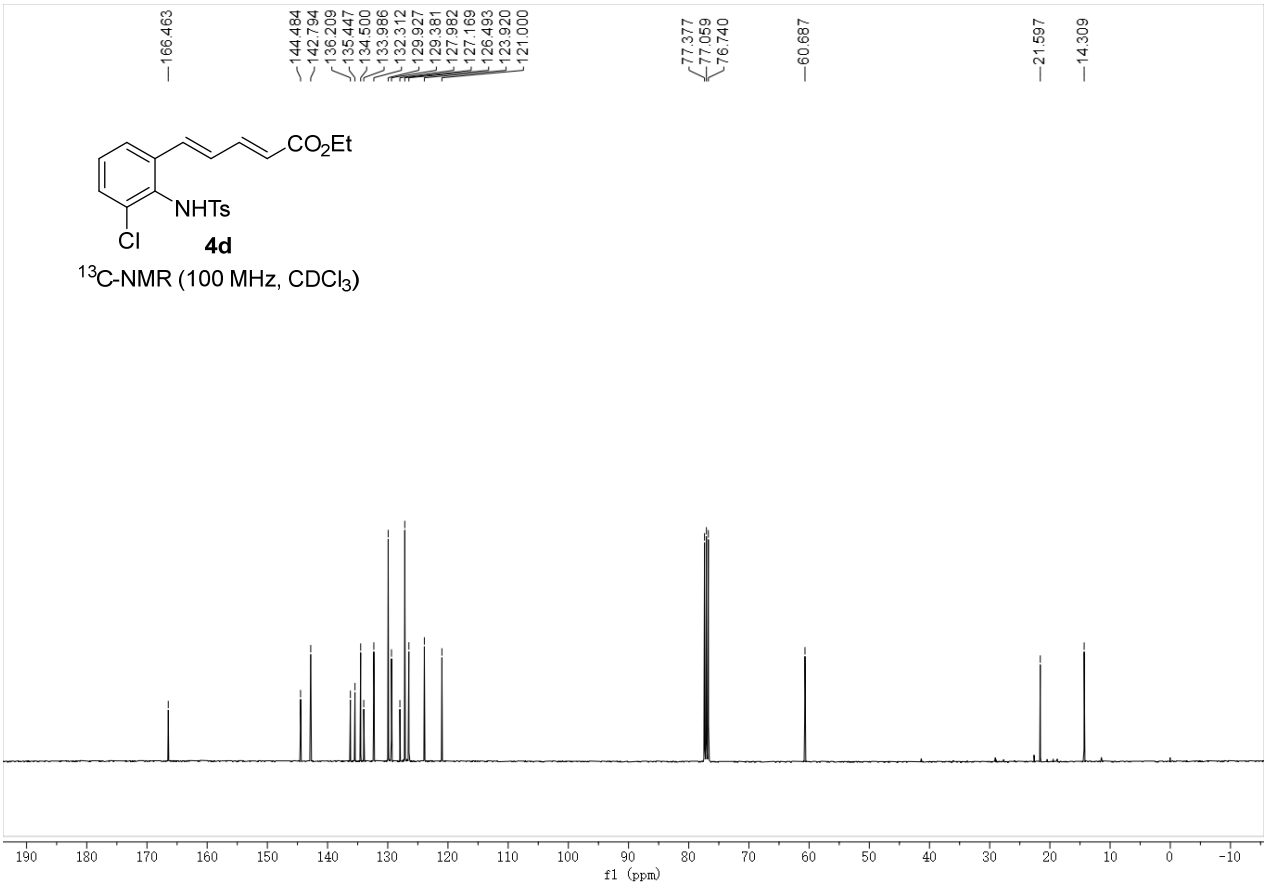
1.95
1.01
1.00
1.01
1.00
2.01
3.01
3.14
f1 (ppm)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121.000
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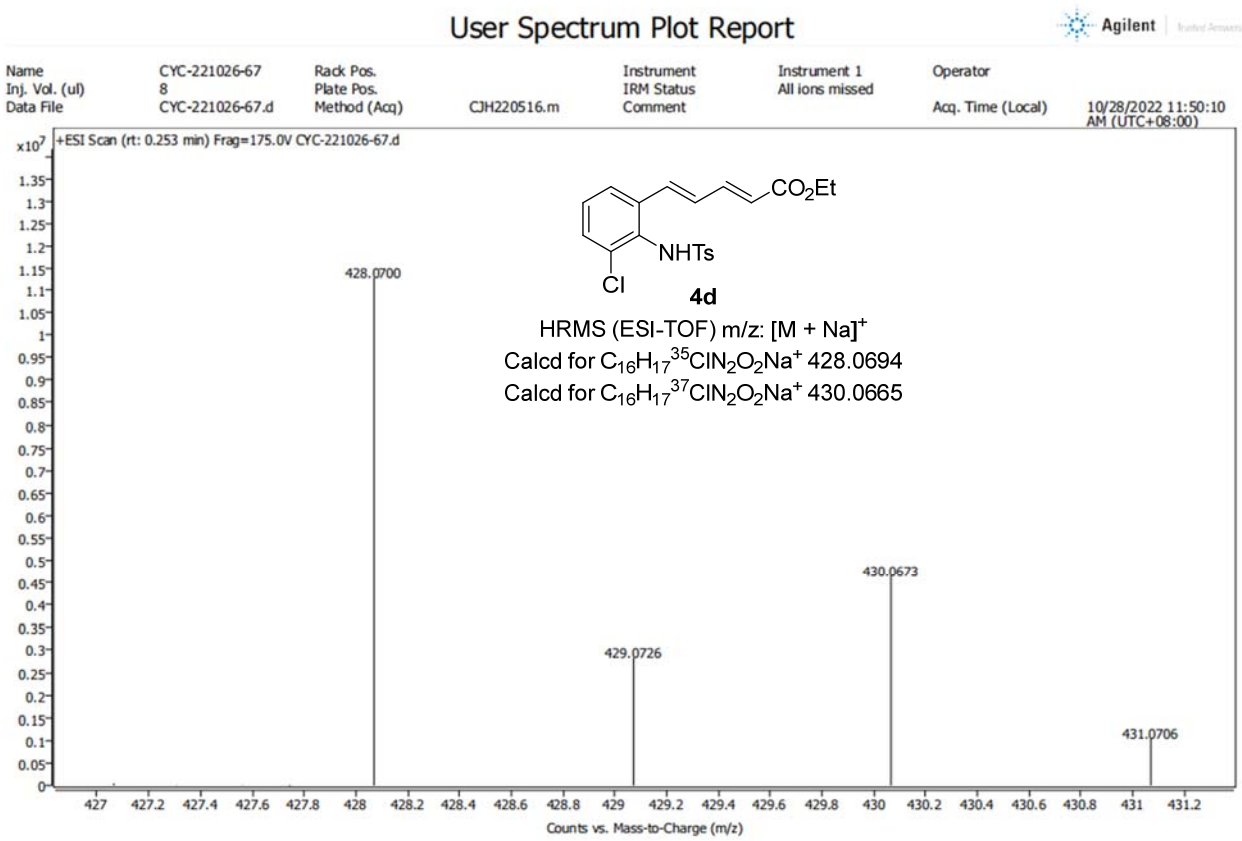
f1 (ppm)

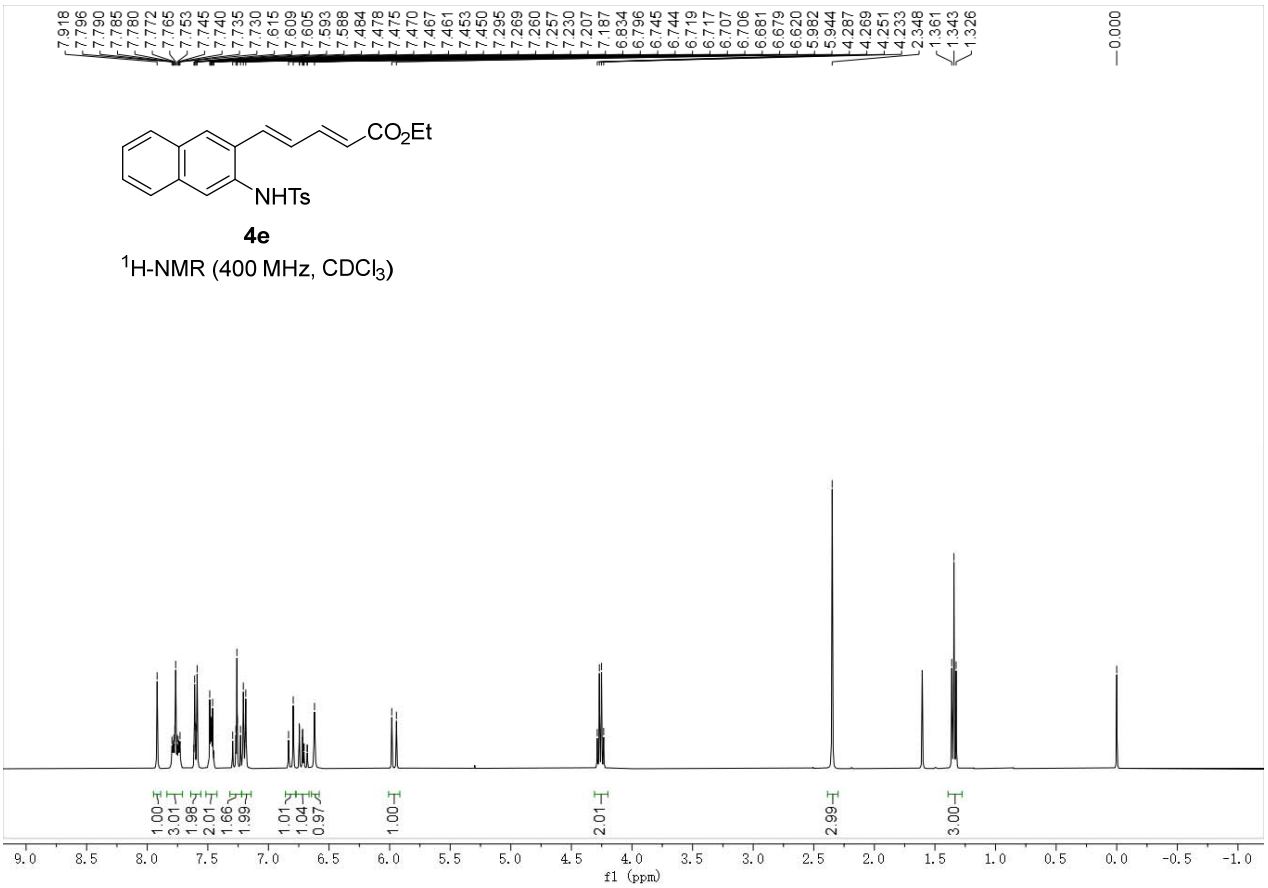


4d

HRMS (ESI-TOF) m/z: $[M + Na]^+$

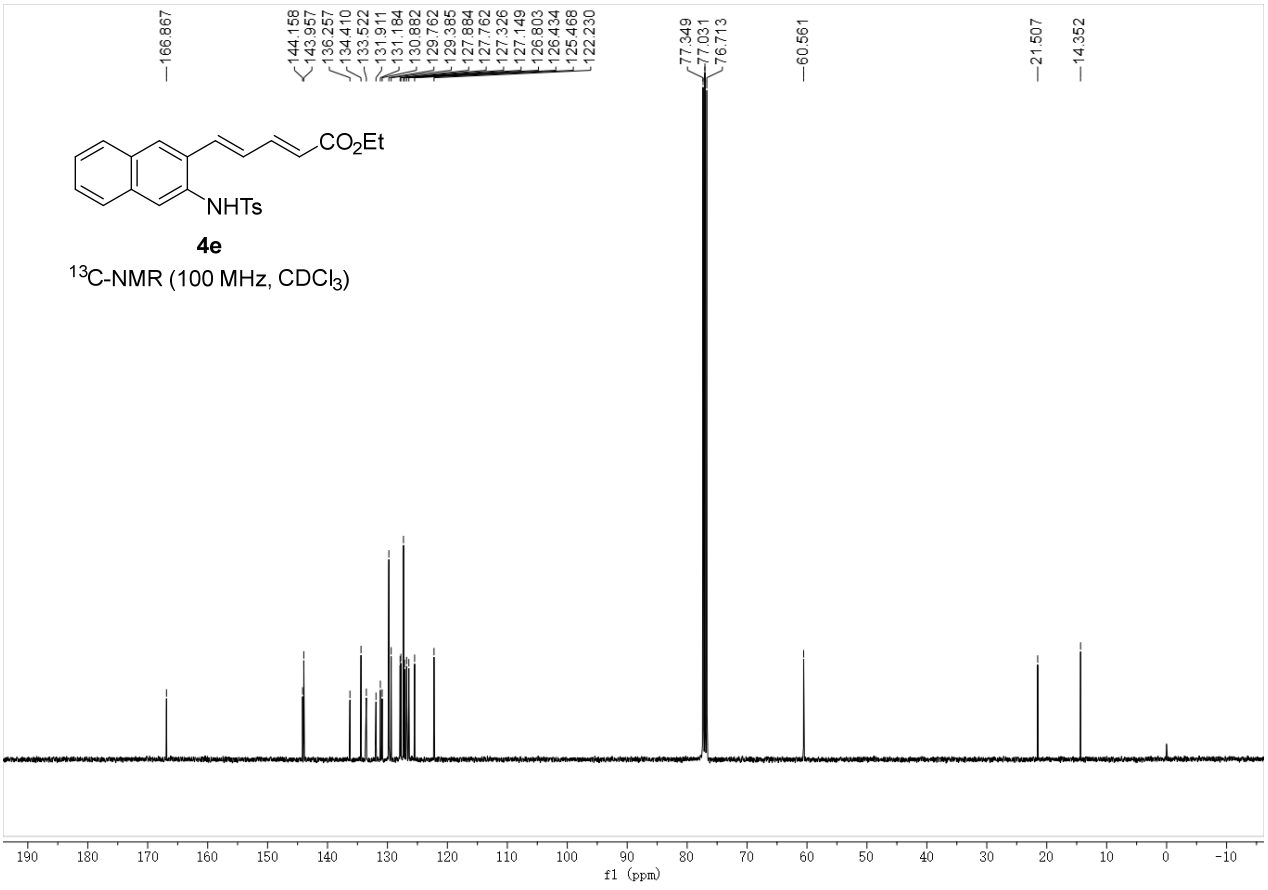
Calcd for $C_{16}H_{17}{}^{35}ClN_2O_2Na^+$ 428.0694

Calcd for $C_{16}H_{17}{}^{37}ClN_2O_2Na^+$ 430.0665



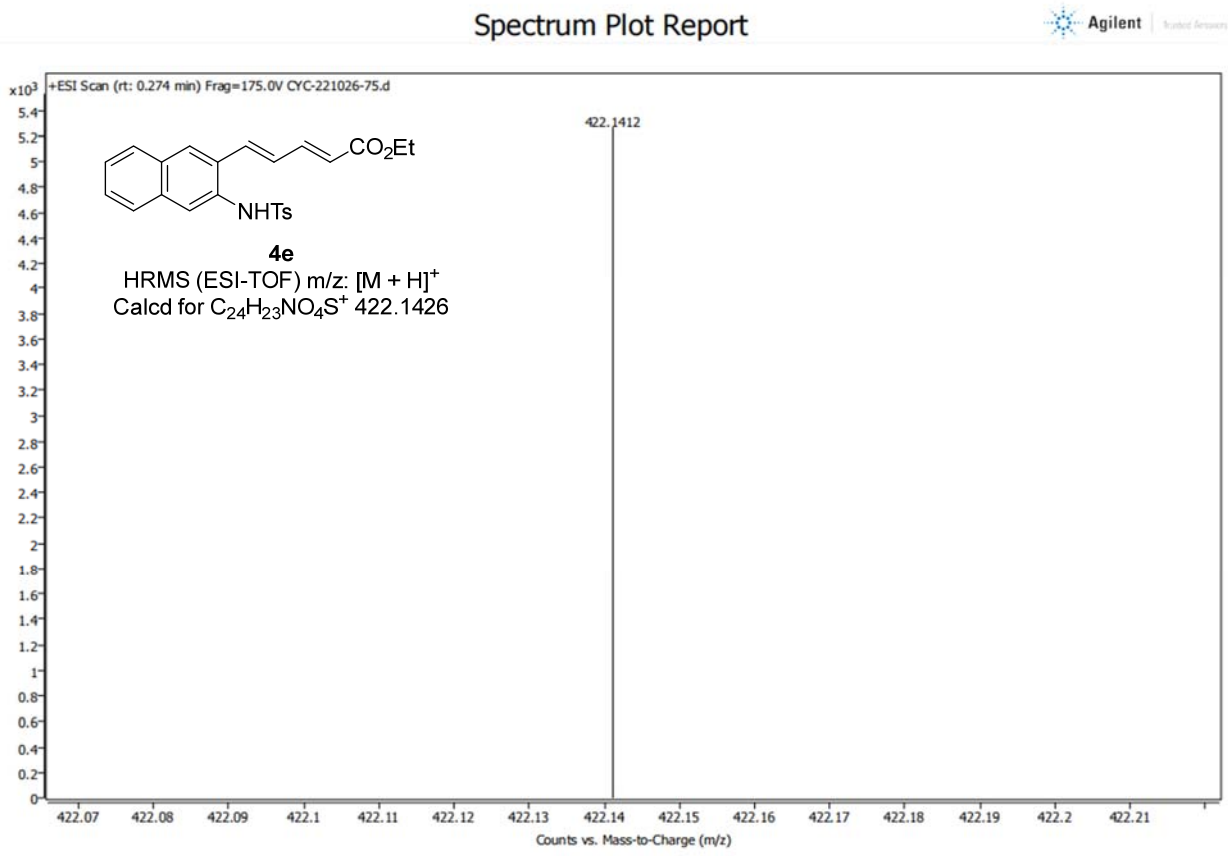
4e

^{1}H-NMR (400 MHz, $CDCl_3$)



4e

^{13}C-NMR (100 MHz, $CDCl_3$)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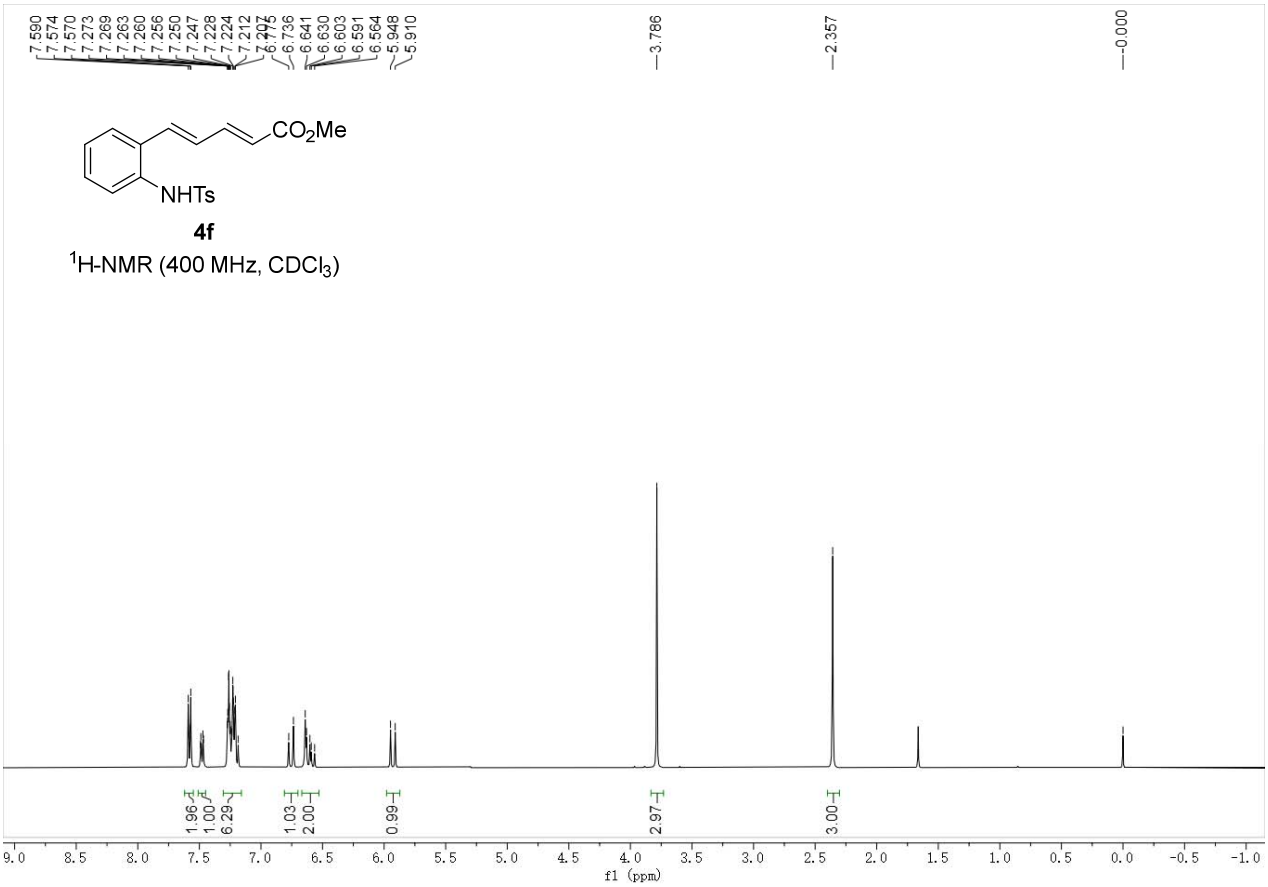
Counts vs. Mass-to-Charge (m/z)



4f

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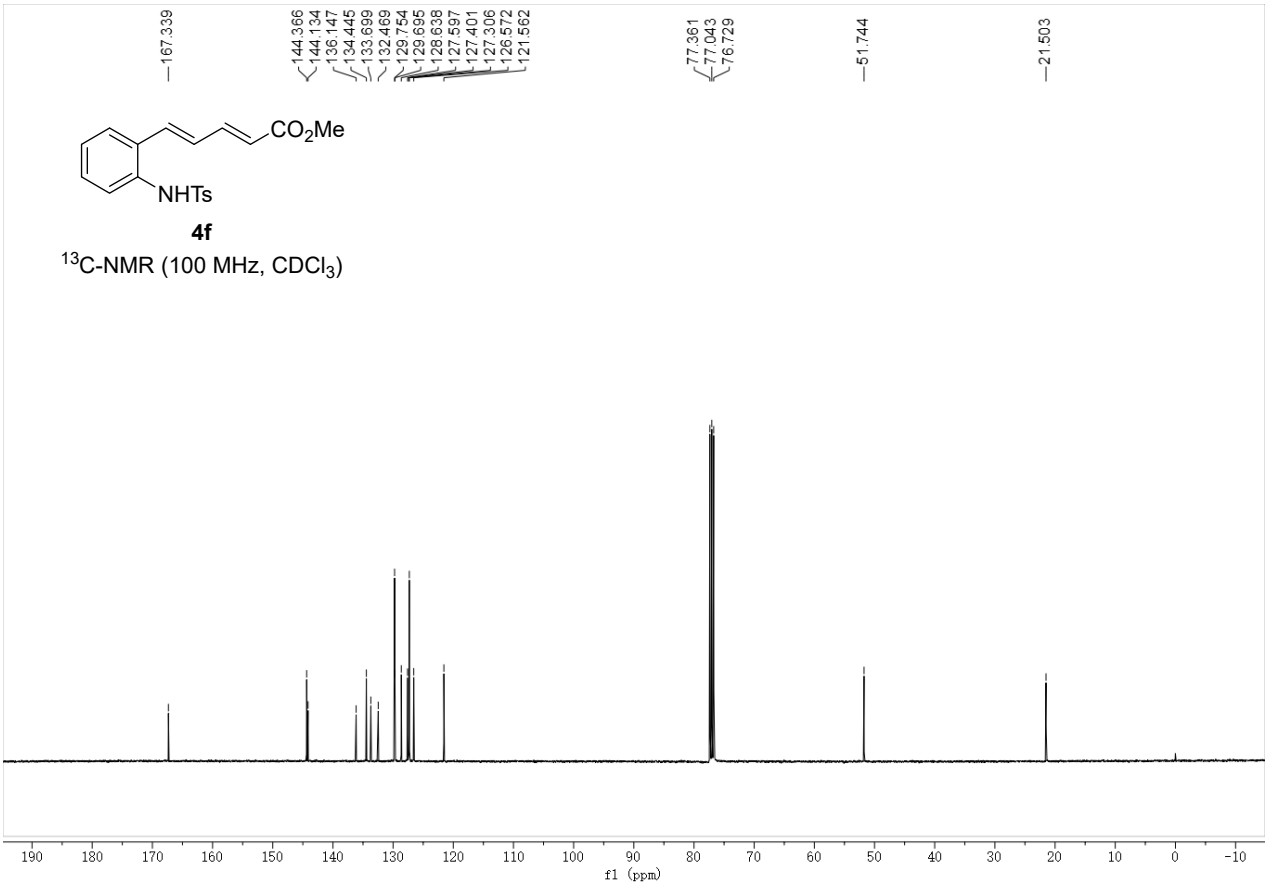
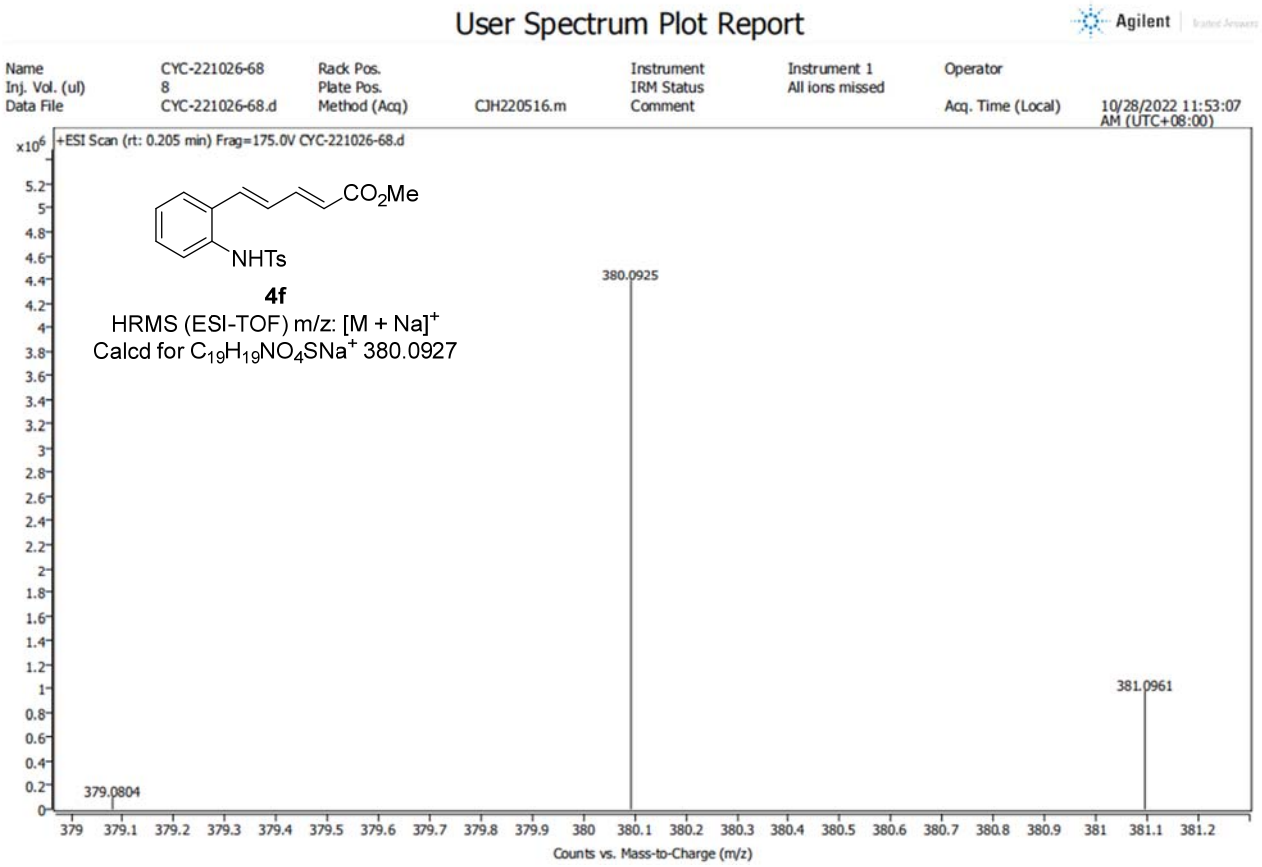


4f

^{13}C-NMR (100 MHz, $CDCl_3$)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IRM Status
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Operator
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NHTs
4f
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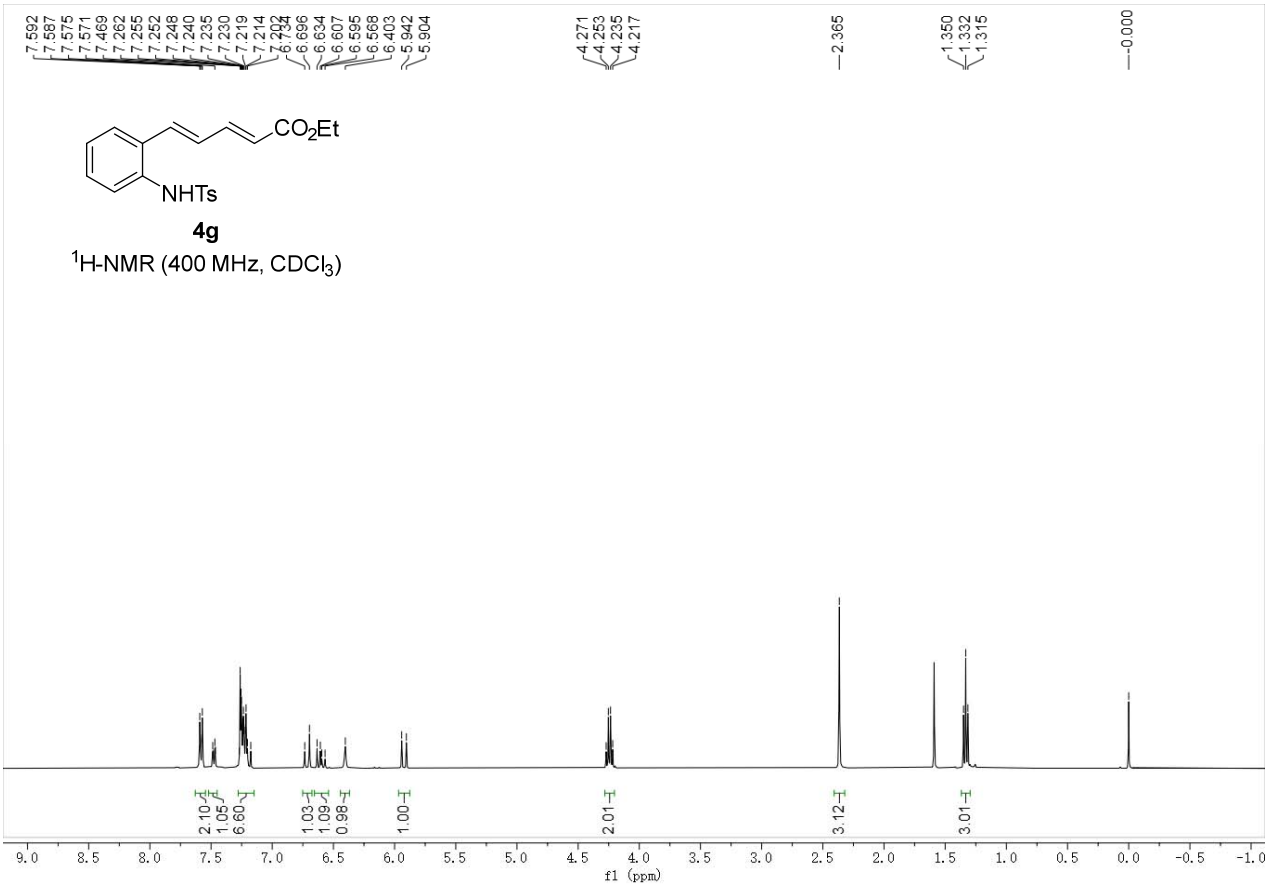
Counts vs. Mass-to-Charge (m/z)



4g

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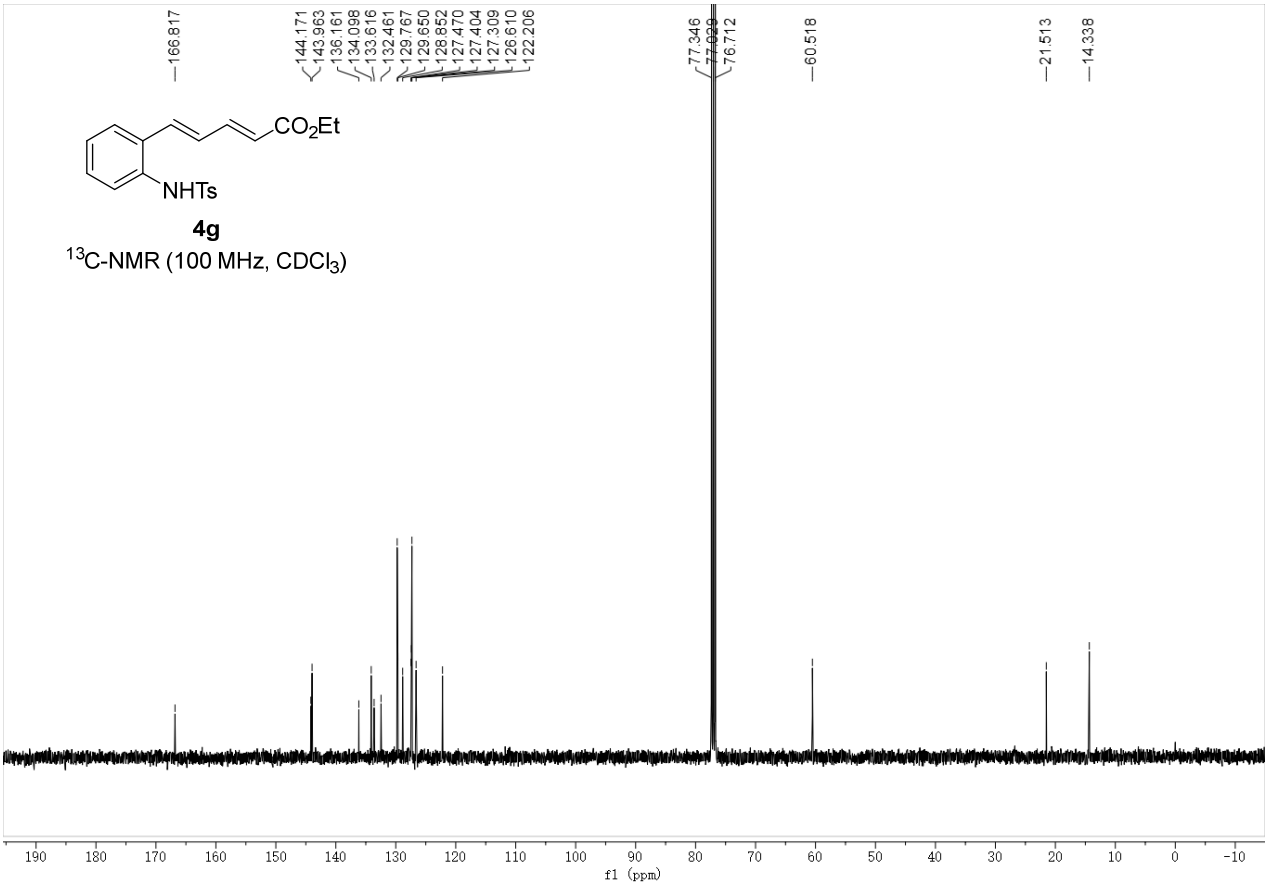
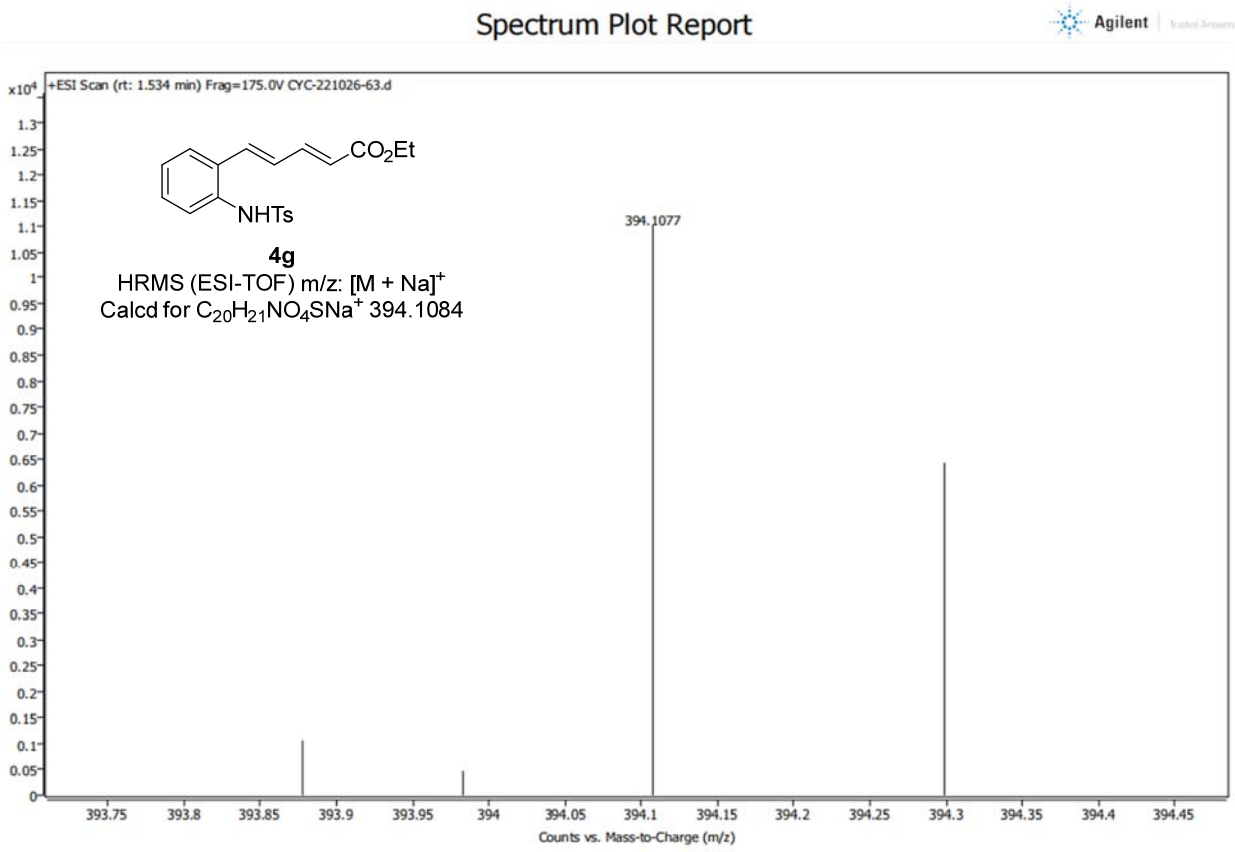


4g

^{13}C-NMR (100 MHz, $CDCl_3$)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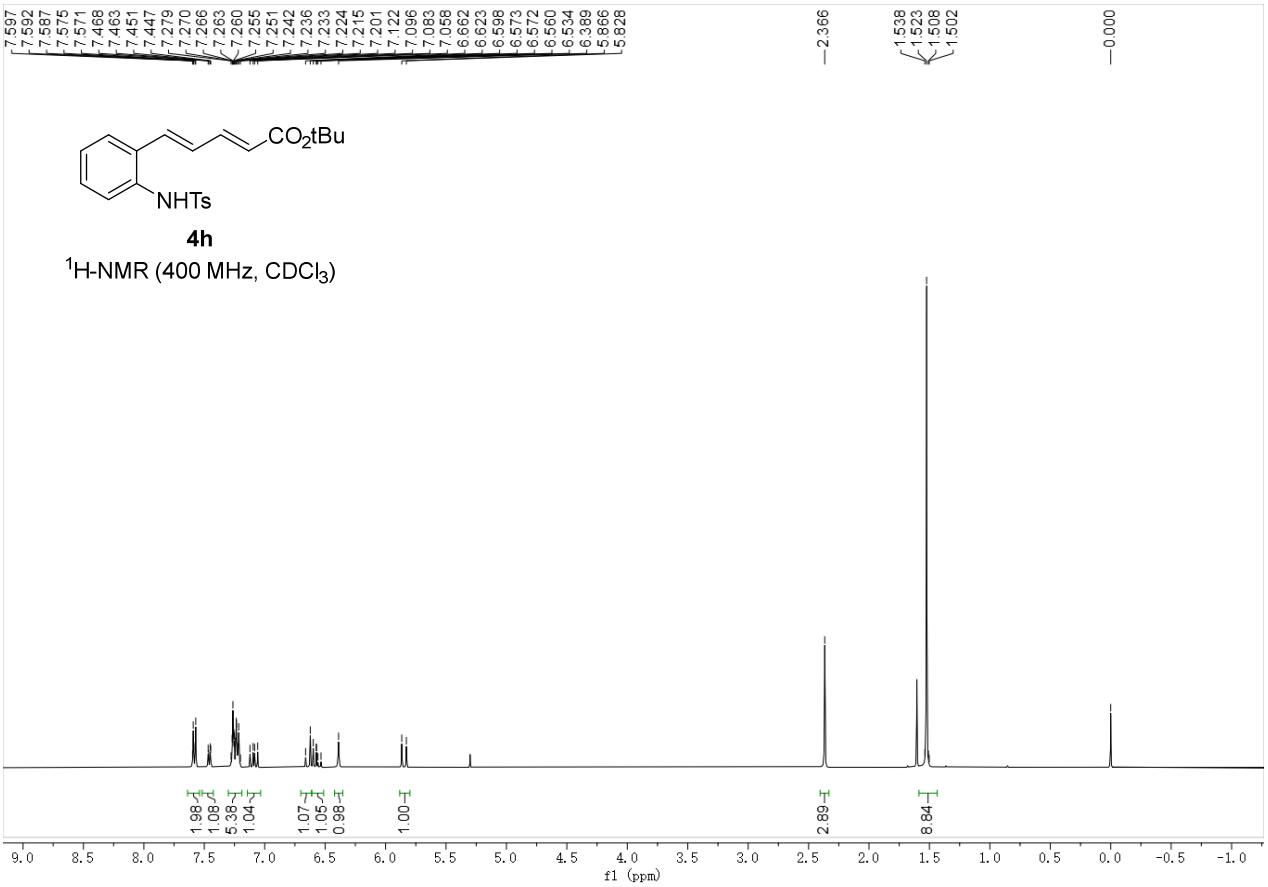
Counts vs. Mass-to-Charge (m/z)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NHTs
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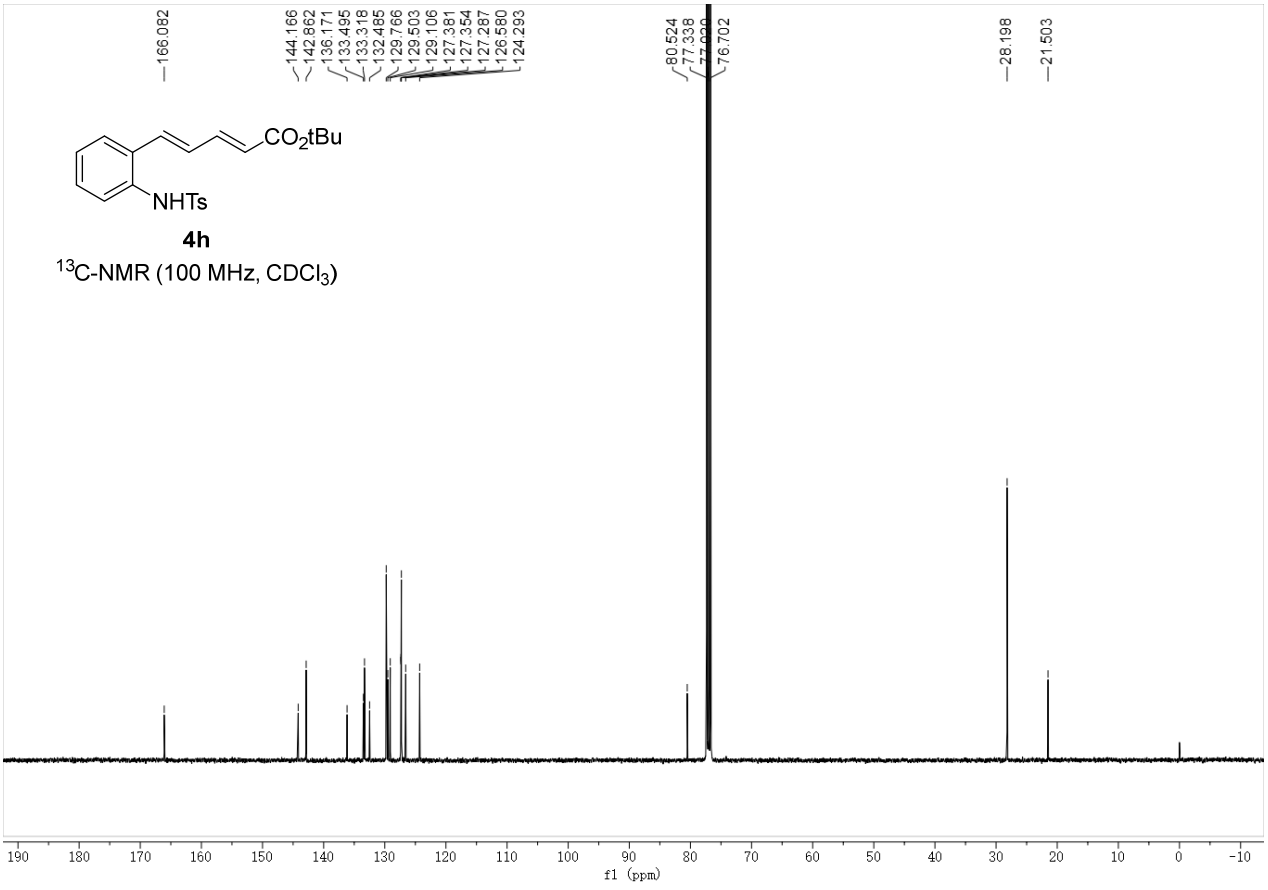
f1 (ppm)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4h
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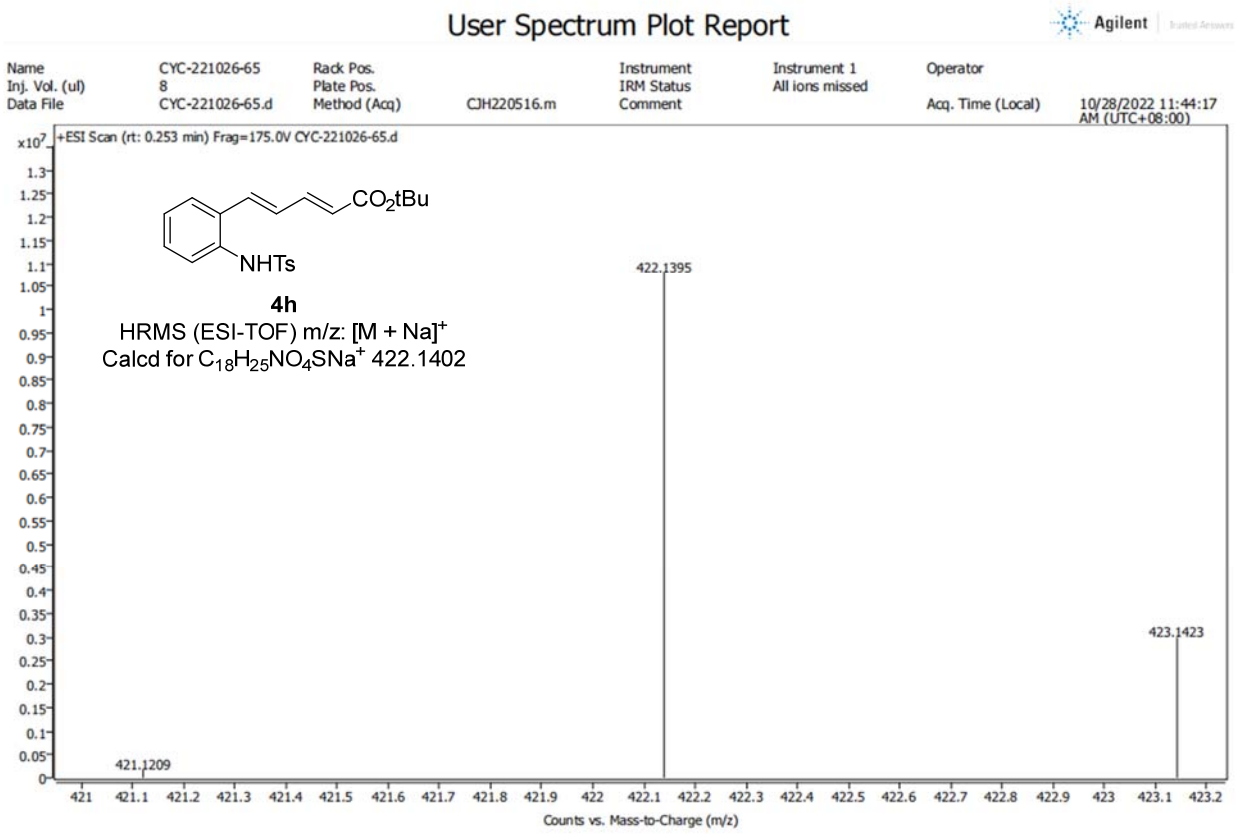
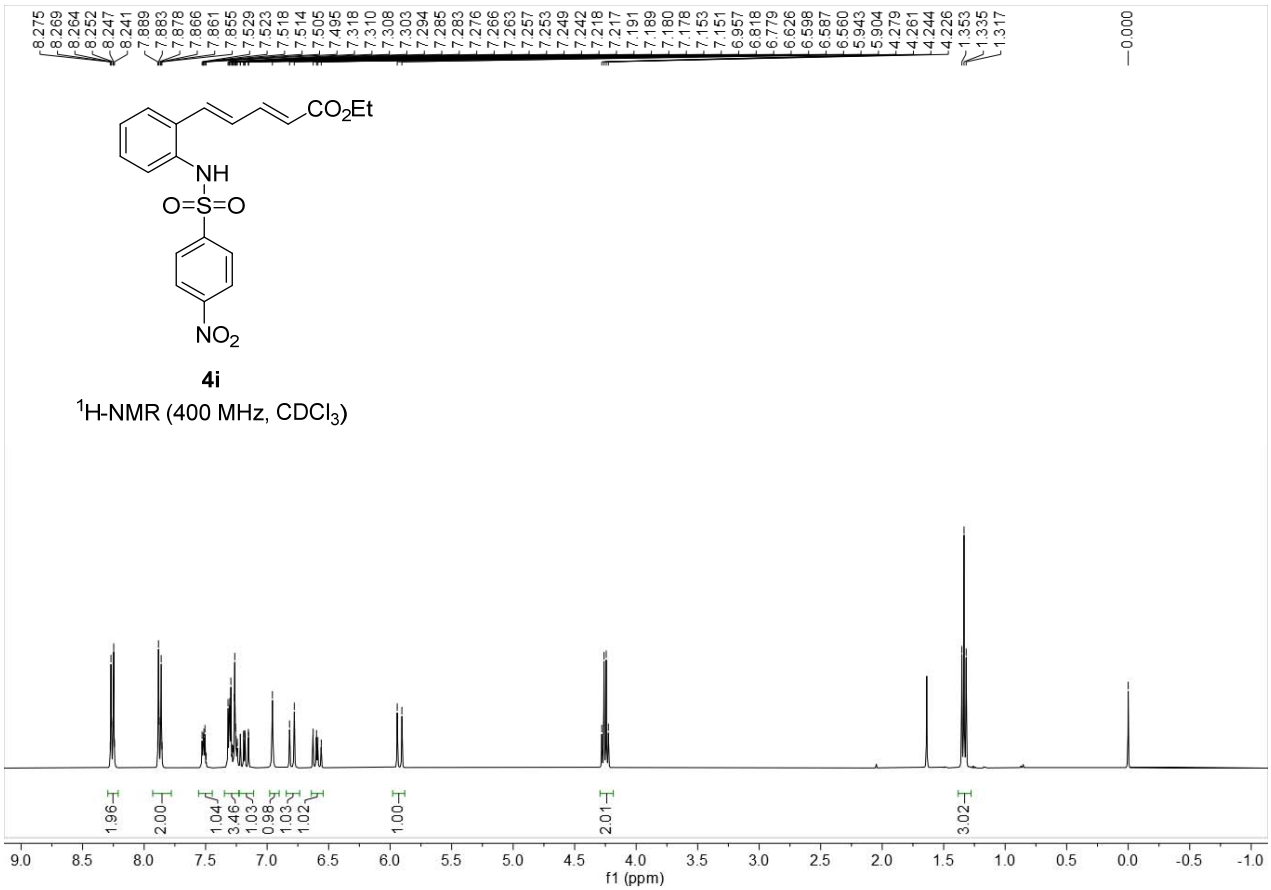
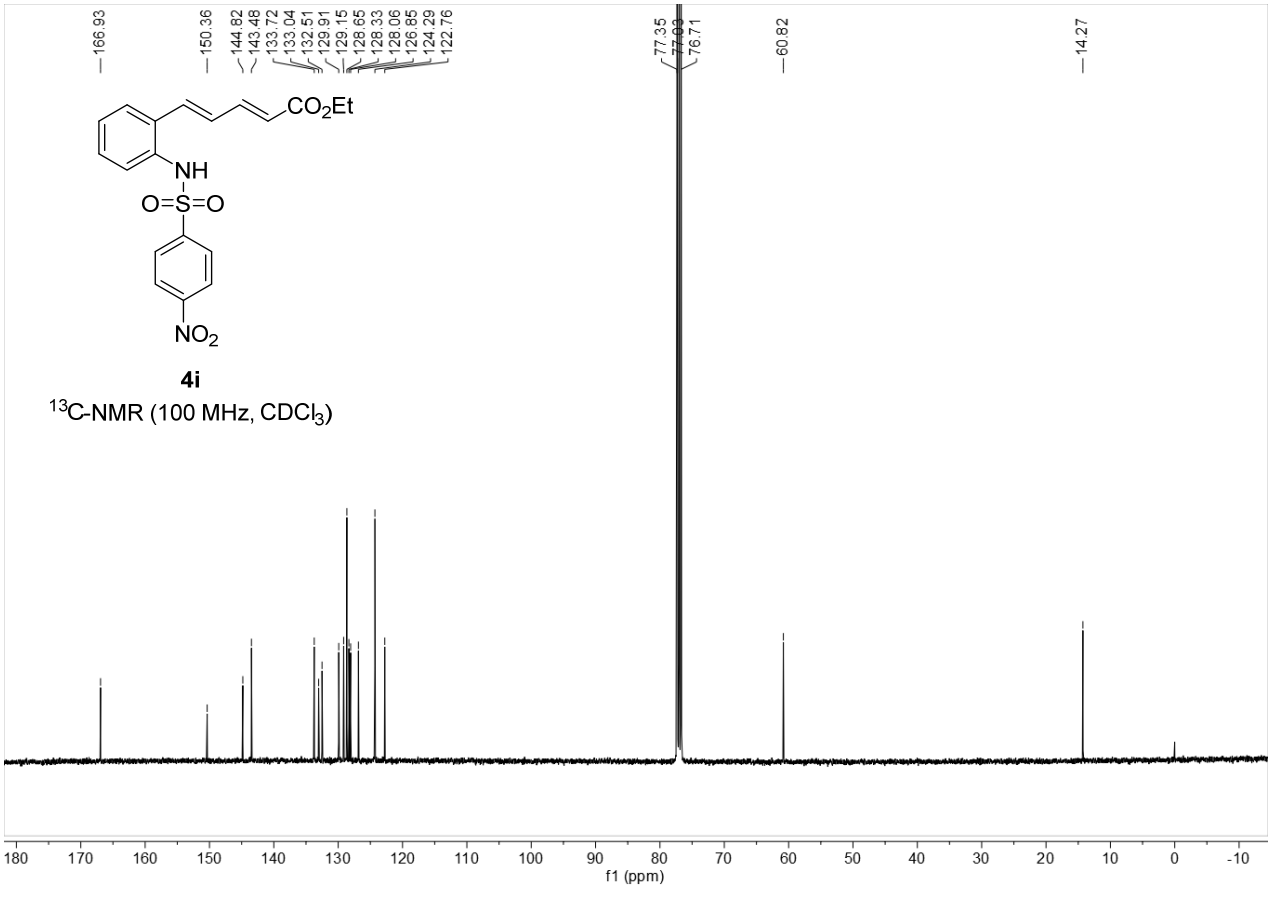
f1 (ppm)


User Spectrum Plot Report
Agilent
Name CYC-221026-65
Inj. Vol. (ul) 8
Data File CYC-221026-65.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 10/28/2022 11:44:17 AM (UTC+08:00)
+ESI Scan (rt: 0.253 min) Frag=175.0V CYC-221026-65.d
x10^7
CO2tBu
NHTs
4h
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C18H25NO4SNa+ 422.1402
422.1395
423.1423
421.1209
Counts vs. Mass-to-Charge (m/z)



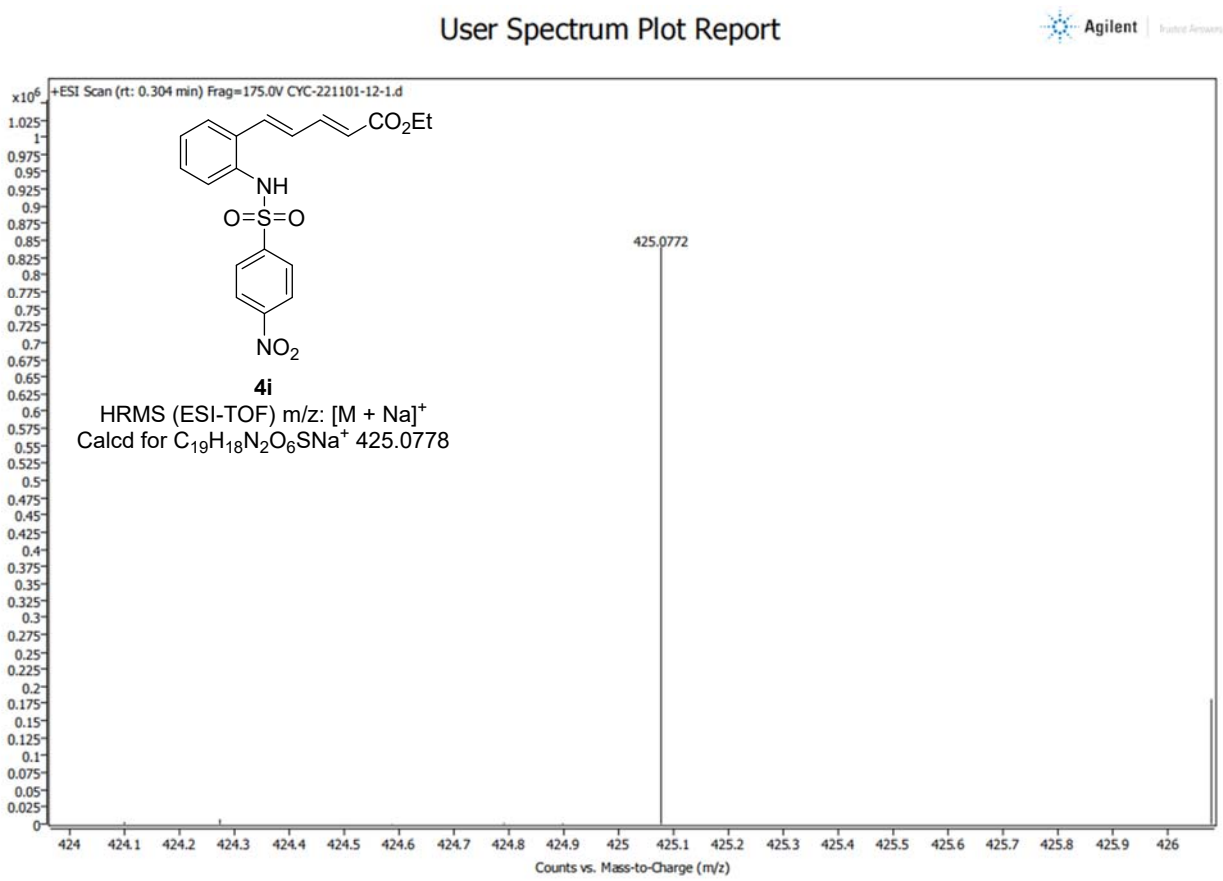
4i

^{1}H-NMR (400 MHz, $CDCl_3$)



4i

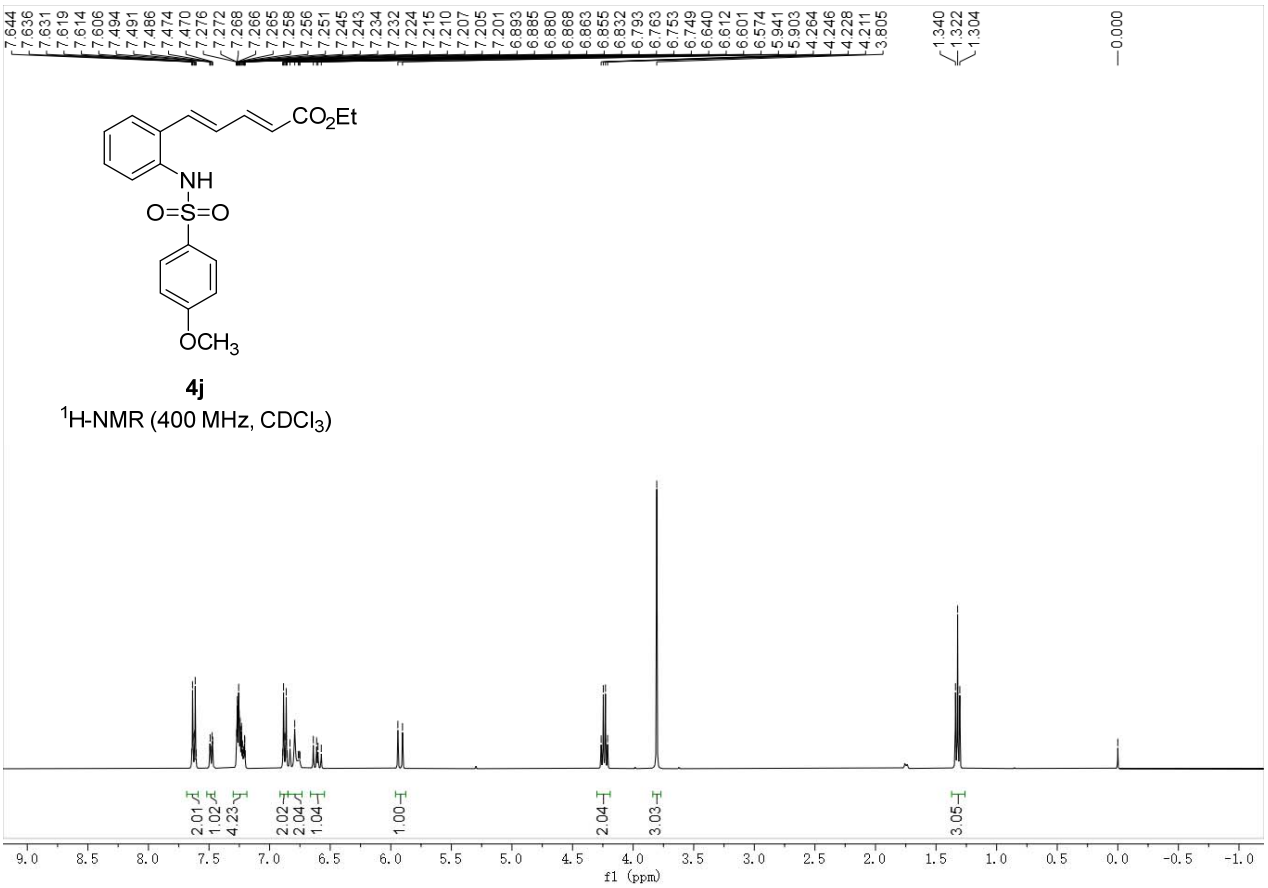
^{13}C-NMR (100 MHz, $CDCl_3$)



4i

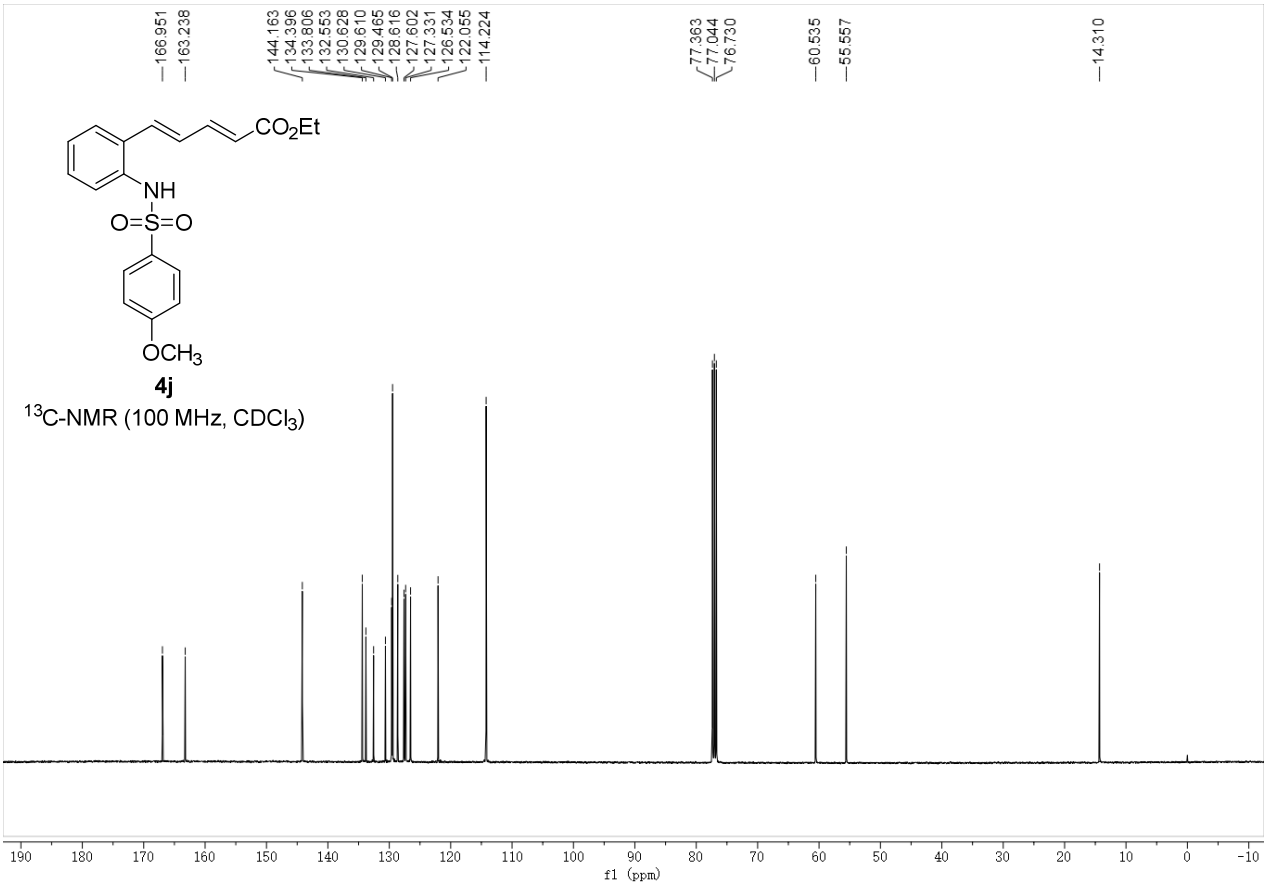
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{19}H_{18}N_2O_6SNa^+$ 425.0778



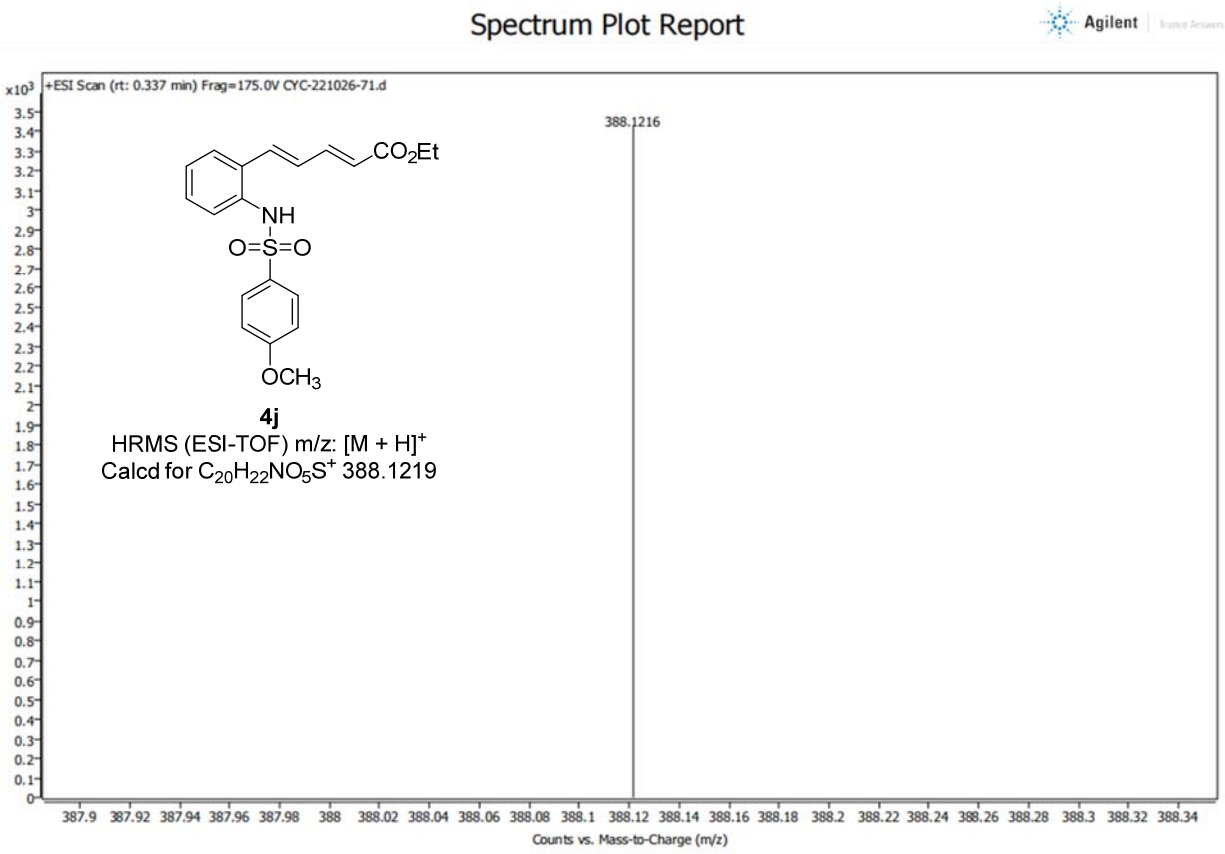
4j

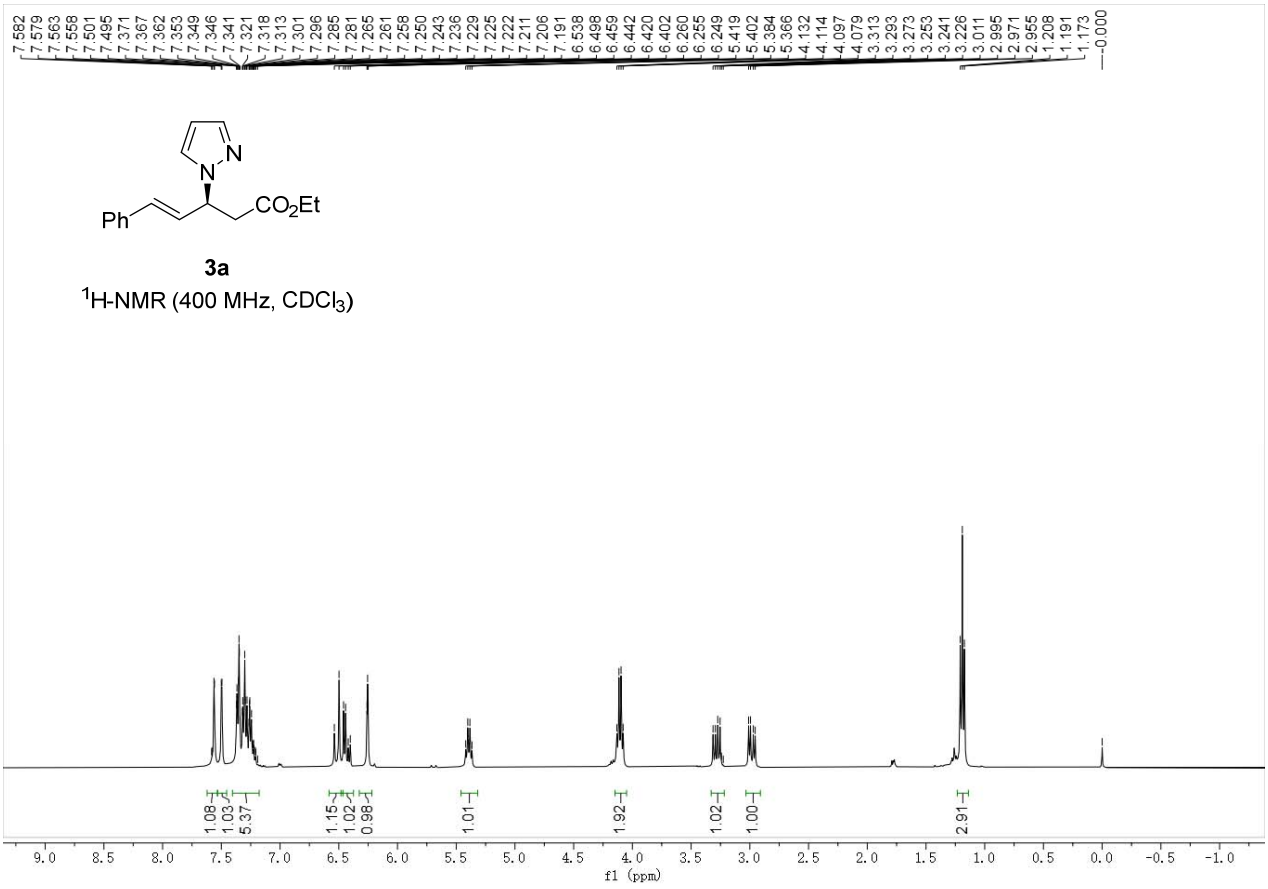
^{1}H-NMR (400 MHz, $CDCl_3$)



4j

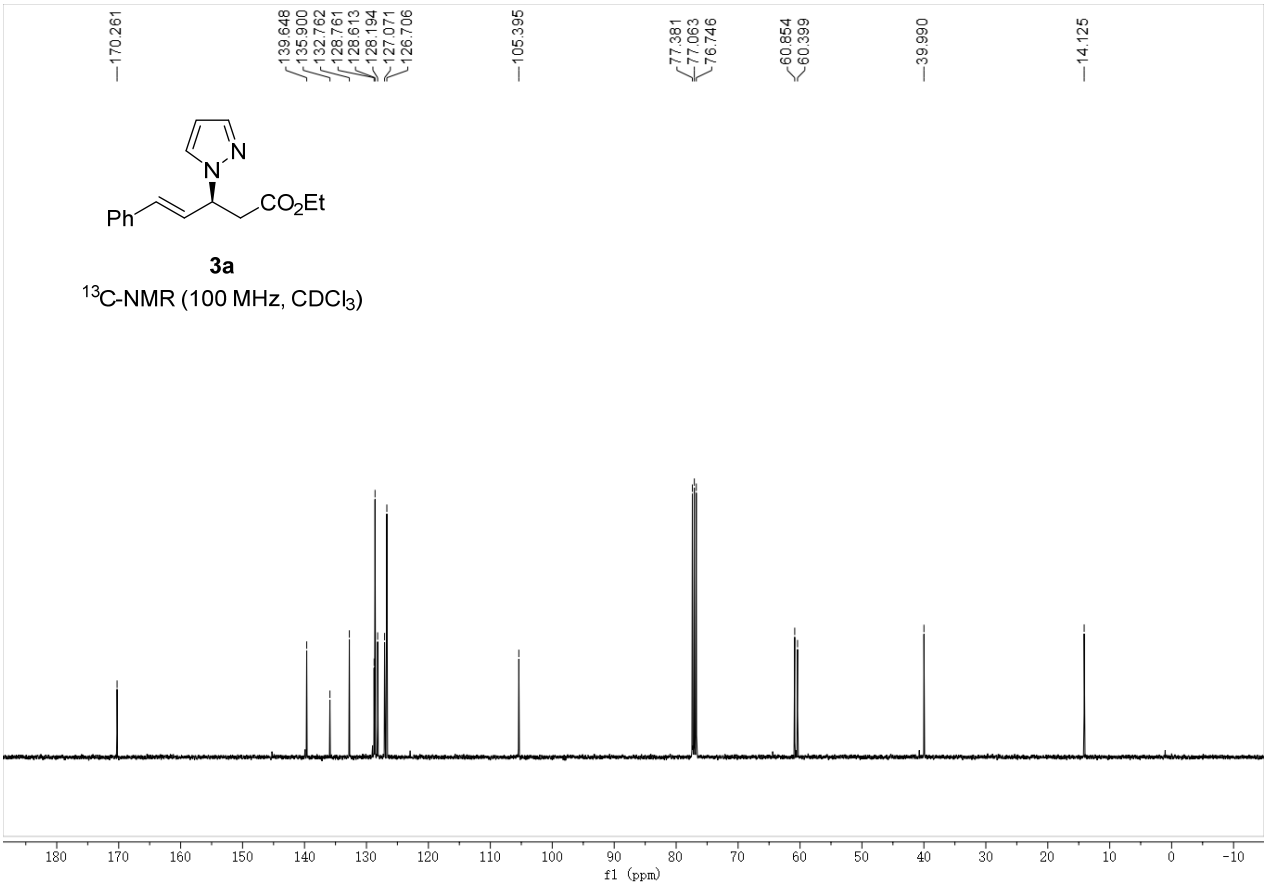
^{13}C-NMR (100 MHz, $CDCl_3$)


Spectrum Plot Report
Agilent
+ESI Scan (rt: 0.337 min) Frag=175.0V CYC-221026-71.d
388.1216
CO2Et
NH
O=S=O
OCH3
4j
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C20H22NO5S+ 388.1219
Counts vs. Mass-to-Charge (m/z)



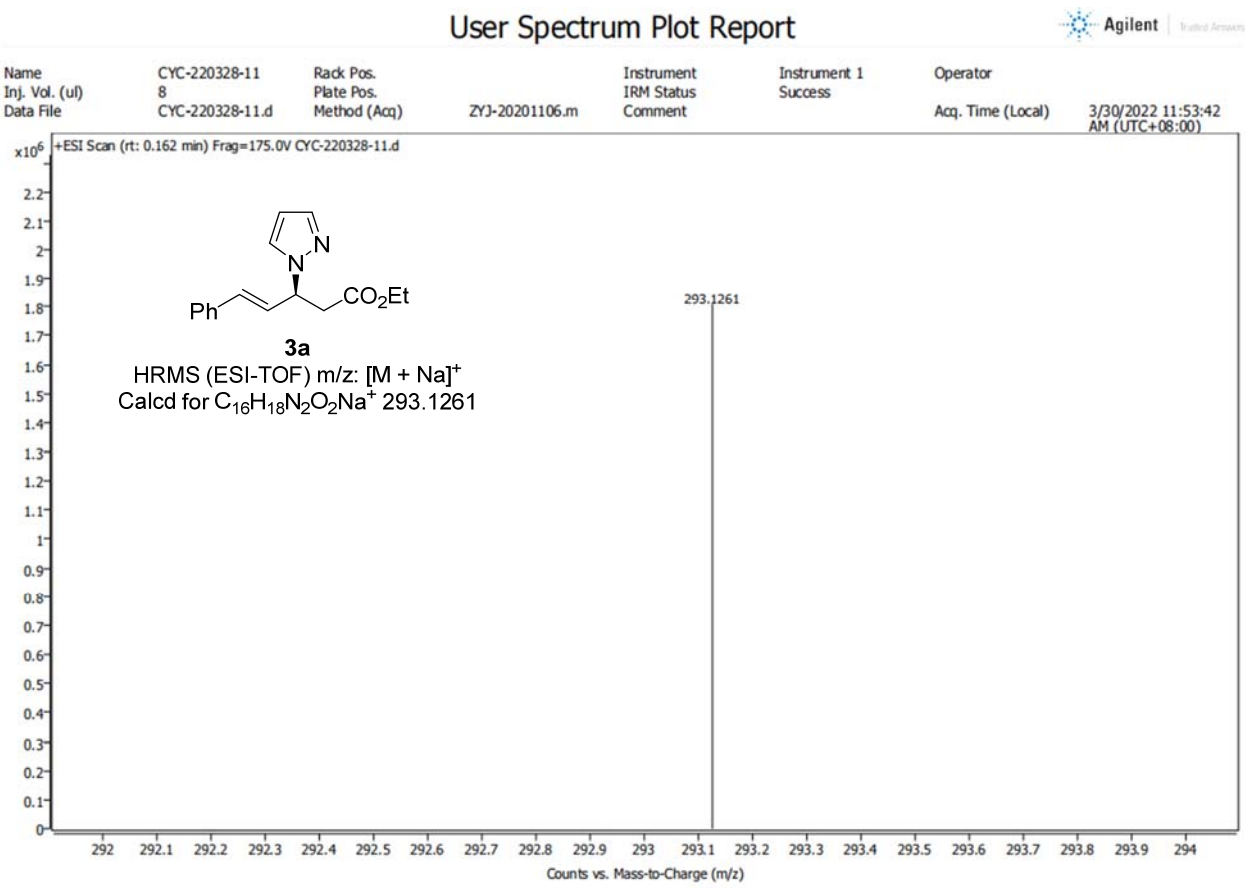
3a

^{1}H-NMR (400 MHz, $CDCl_3$)



3a

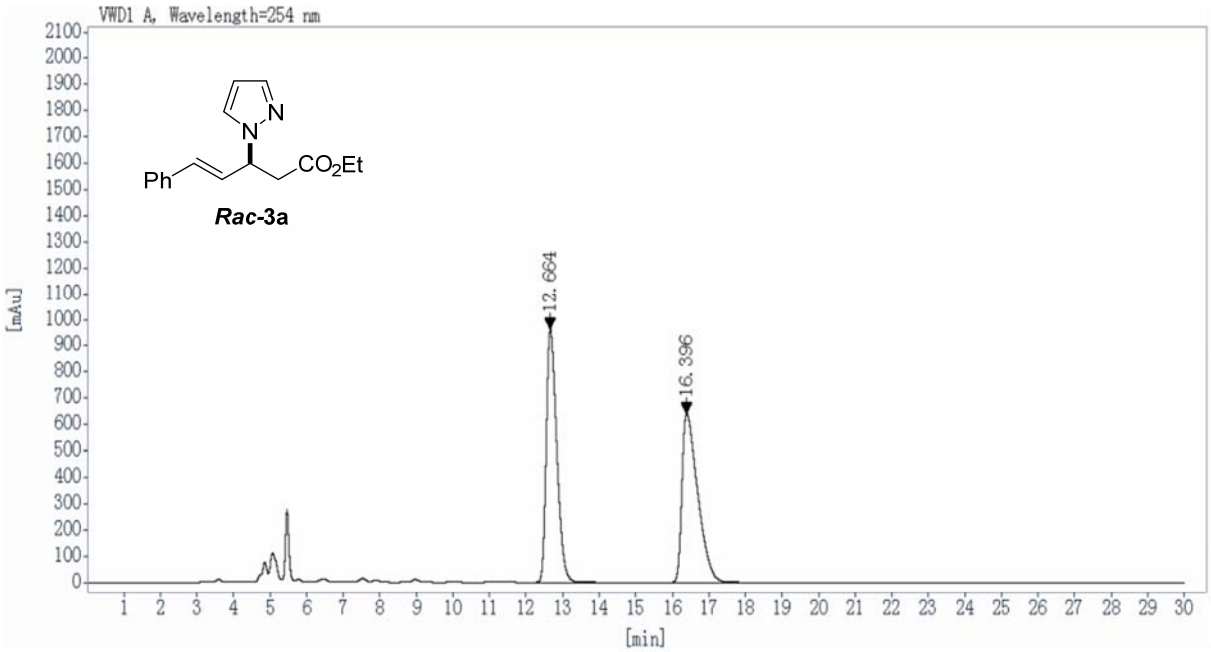
^{13}C-NMR (100 MHz, $CDCl_3$)



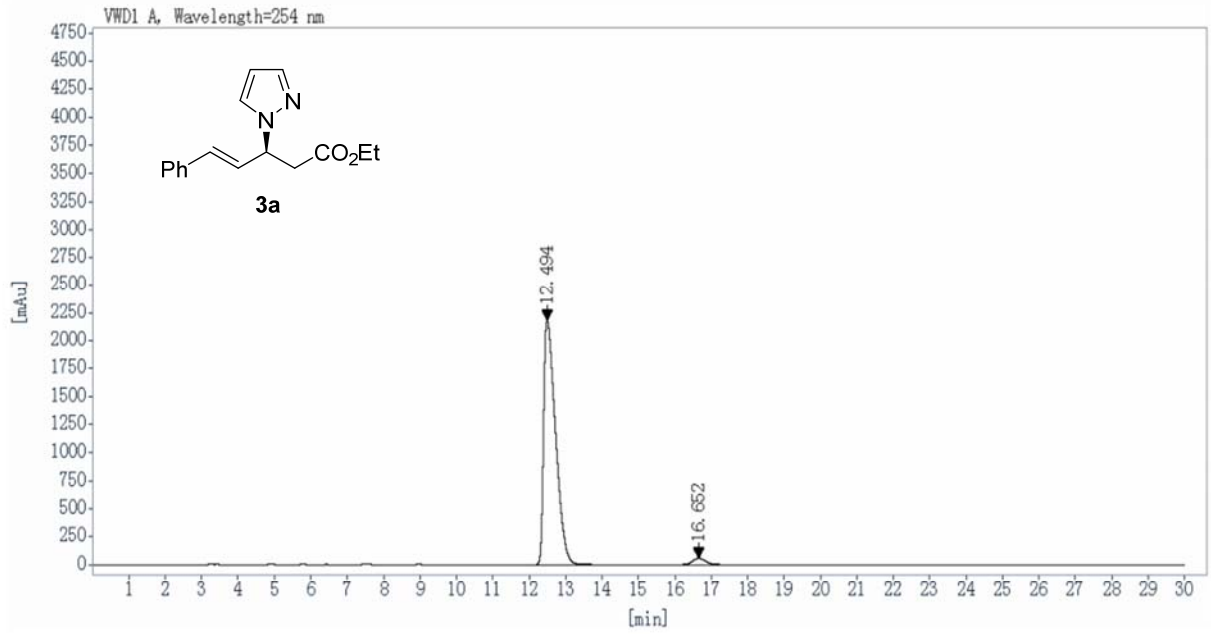
3a

HRMS (ESI-TOF) m/z: $[M + Na]^+$

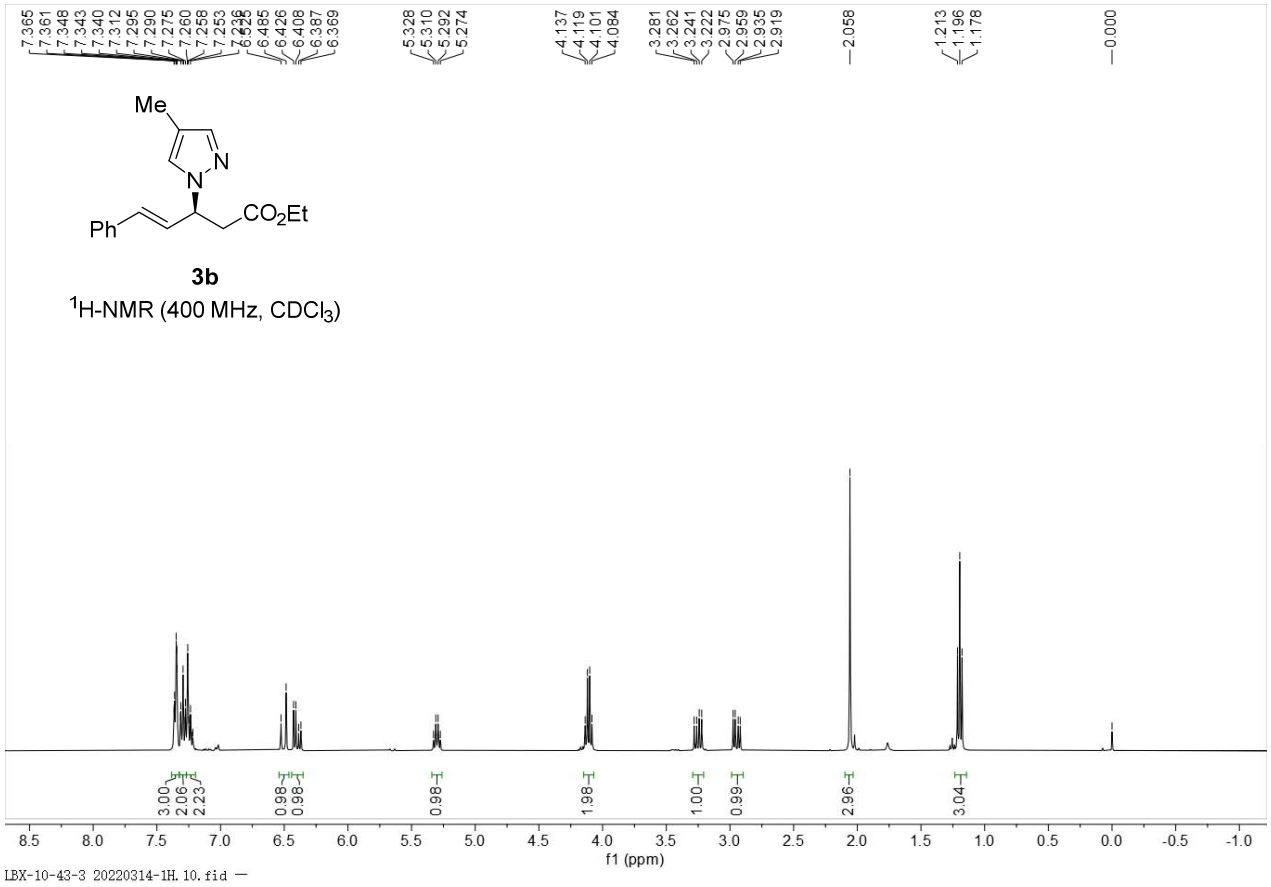
Calcd for $C_{16}H_{18}N_2O_2Na^+$ 293.1261



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.664	BB	0.31	964.4125	19105.8164	49.9709
16.396	BBA	0.45	640.9527	19128.0508	50.0291
			Totals:	38233.8672	100.0000

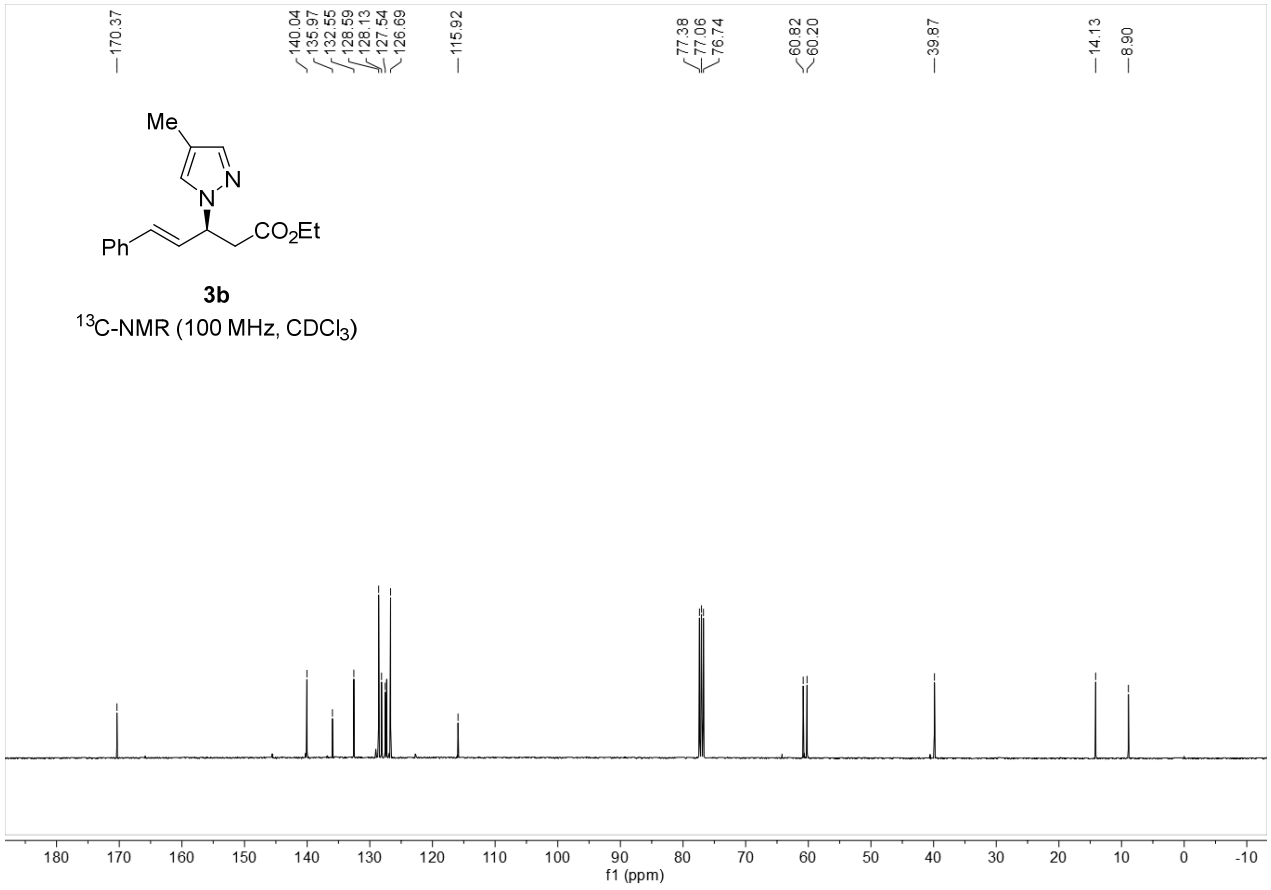


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.494	BB	0.35	2181.9866	49551.6484	97.2259
16.652	BBA	0.40	54.8063	1413.8533	2.7741
			Totals:	50965.5017	100.0000



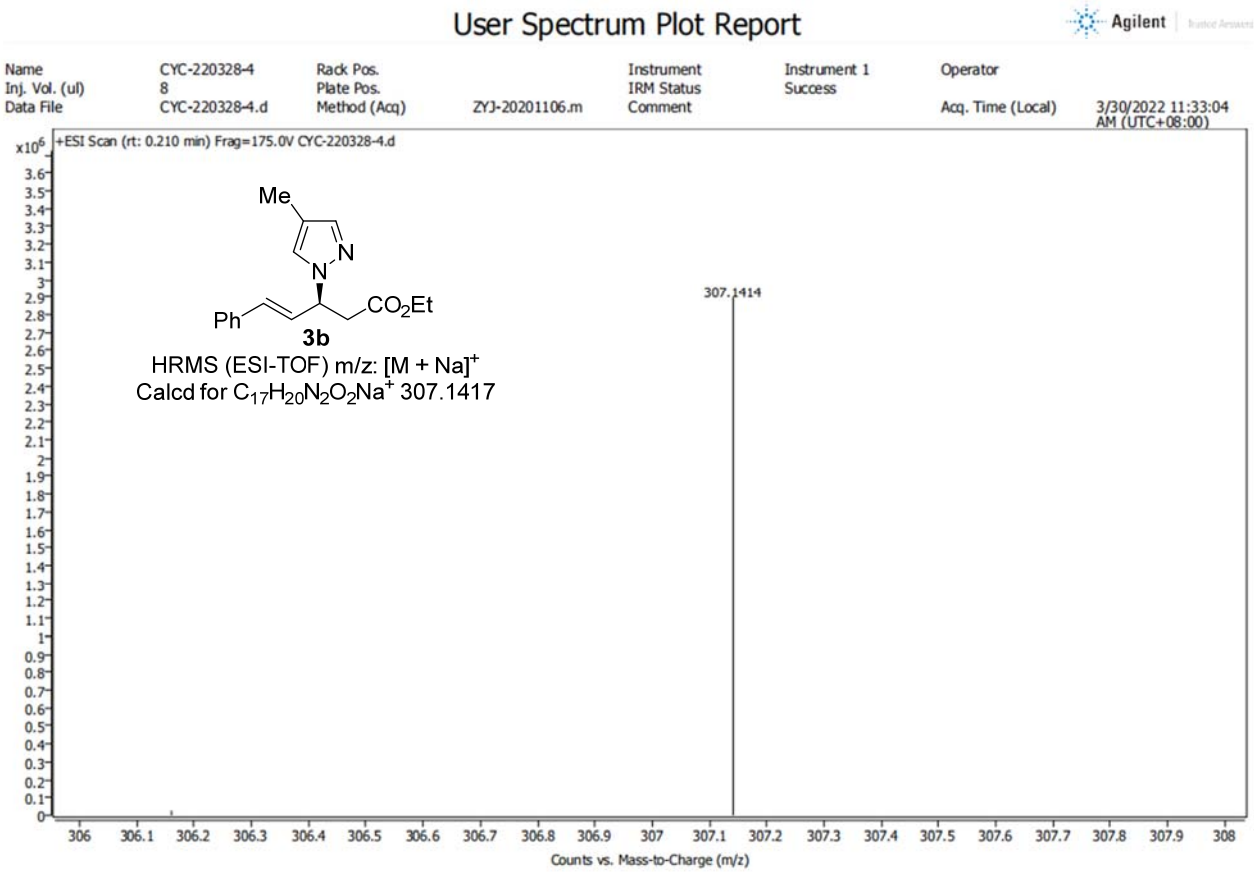
3b

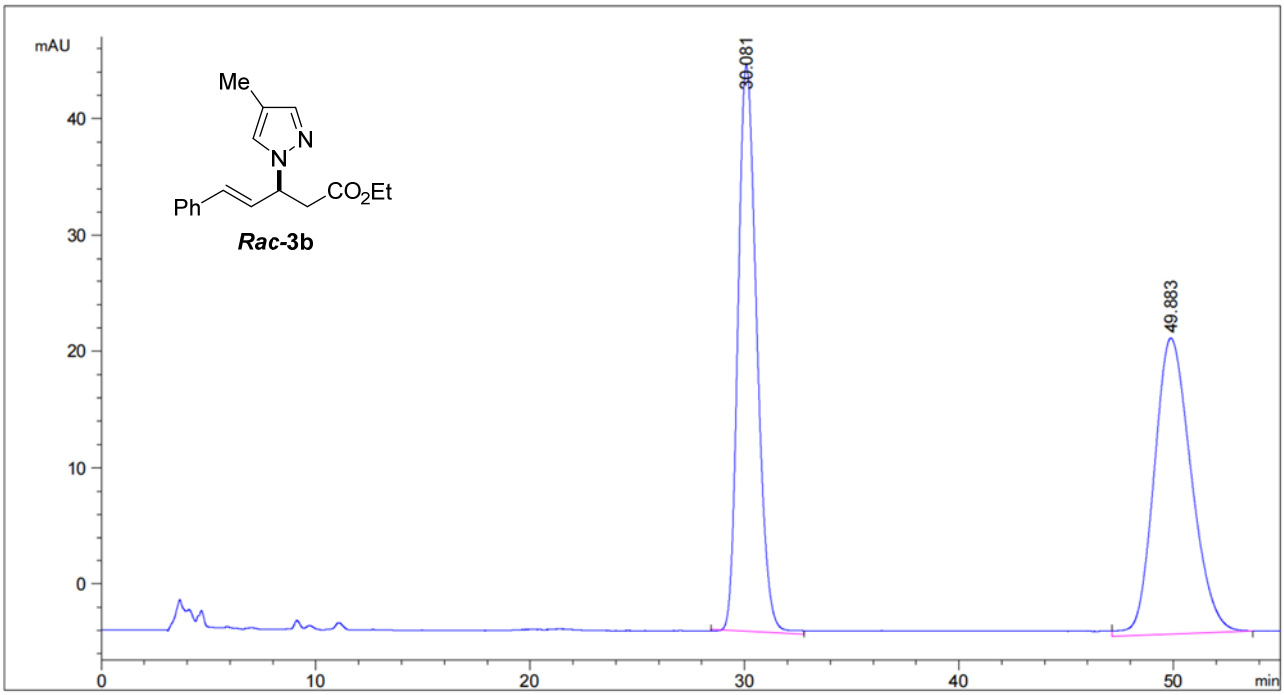
^{1}H-NMR (400 MHz, $CDCl_3$)



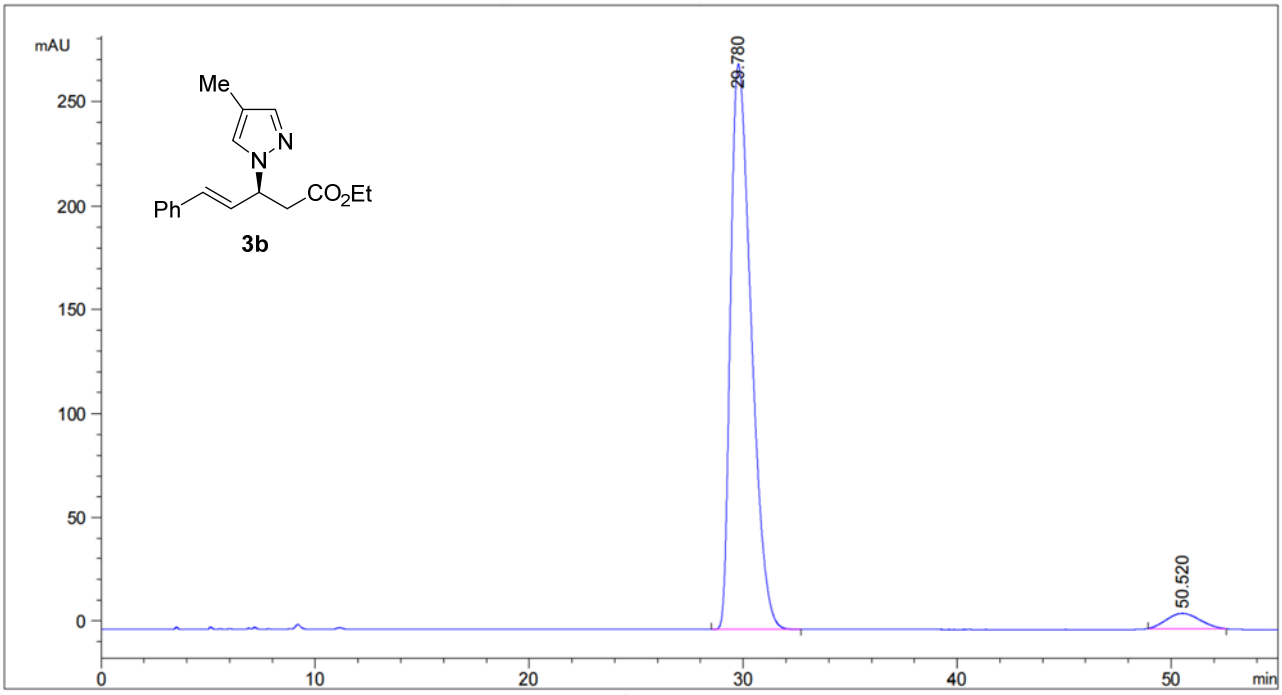
3b

^{13}C-NMR (100 MHz, $CDCl_3$)

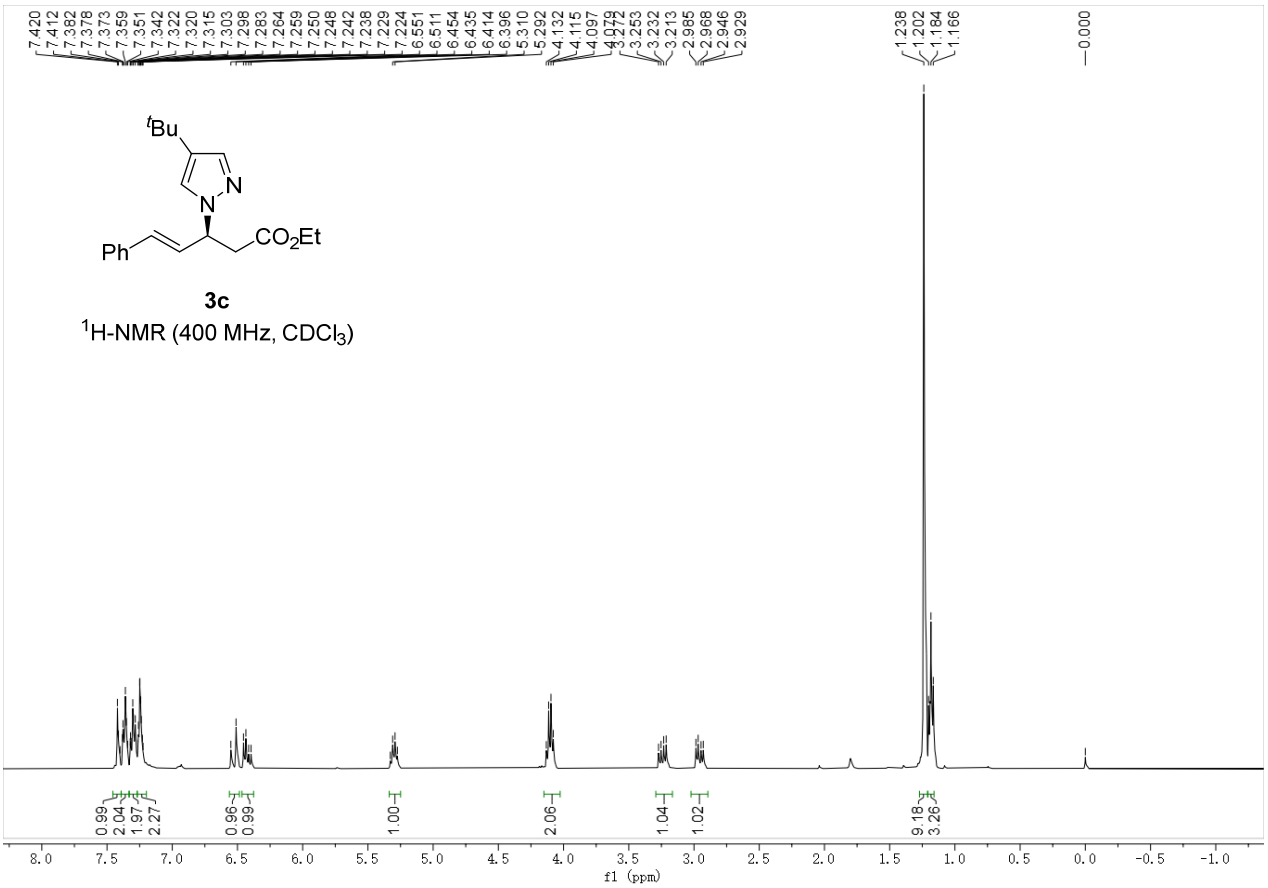

User Spectrum Plot Report
Agilent
Name CYC-220328-4
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
Success
Data File CYC-220328-4.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 3/30/2022 11:33:04 AM (UTC+08:00)
+ESI Scan (rt: 0.210 min) Frag=175.0V CYC-220328-4.d
x10^6
Me
N
N
Ph
CO2Et
3b
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C17H20N2O2Na+ 307.1417
307.1414
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.081	MM T	1.0138	2961.38208	48.68360	49.1610
2	49.883	MM T	2.3190	3062.45654	25.43376	50.8390

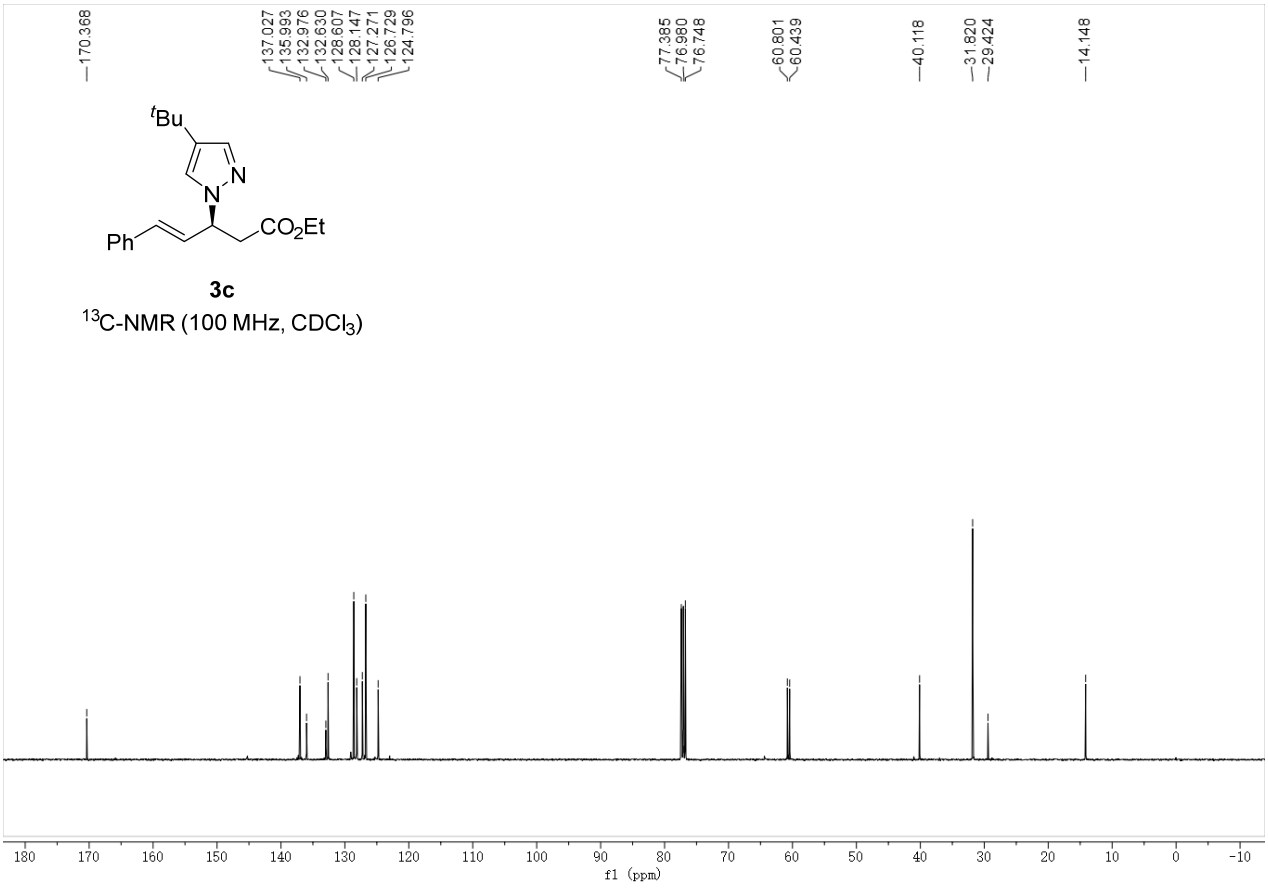


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.780	BB	1.0377	1.82175e4	271.97906	95.8795
2	50.520	BBA	1.2639	782.90668	7.29408	4.1205



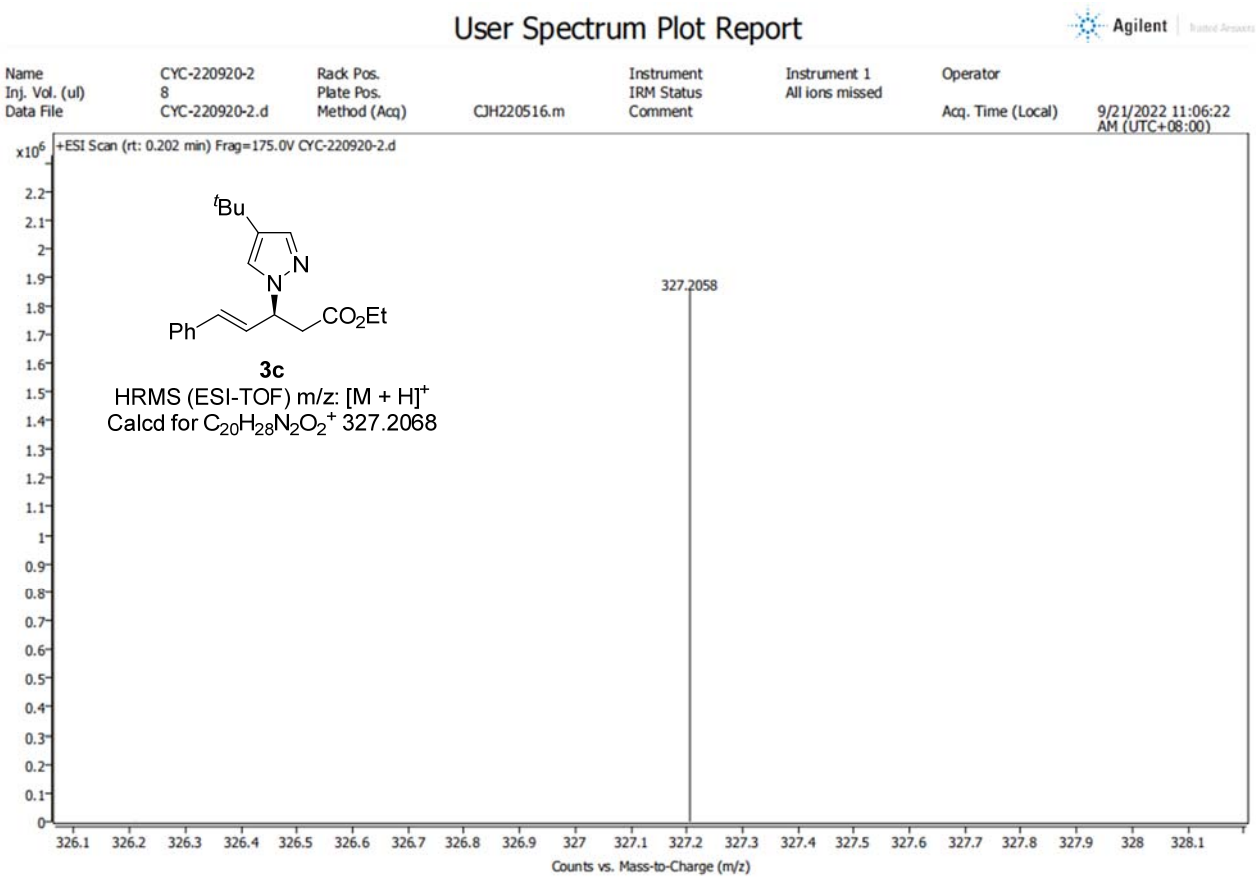
3c

^{1}H-NMR (400 MHz, $CDCl_3$)



3c

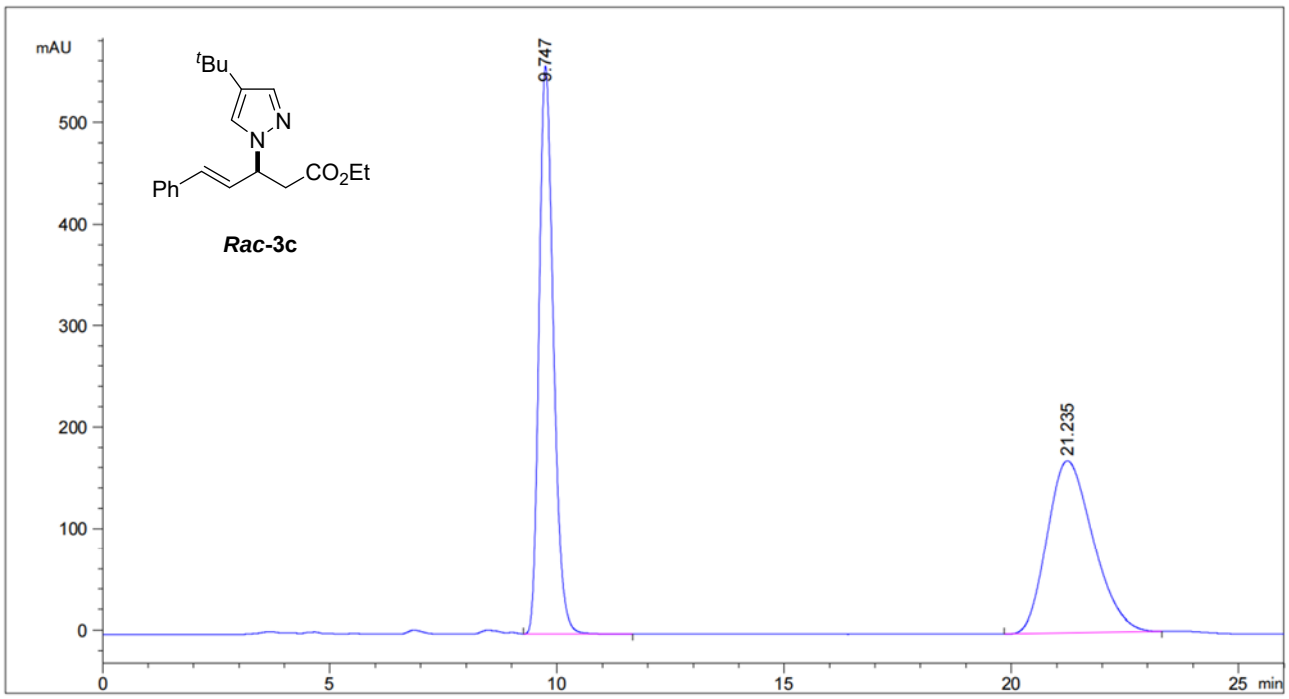
^{13}C-NMR (100 MHz, $CDCl_3$)



3c

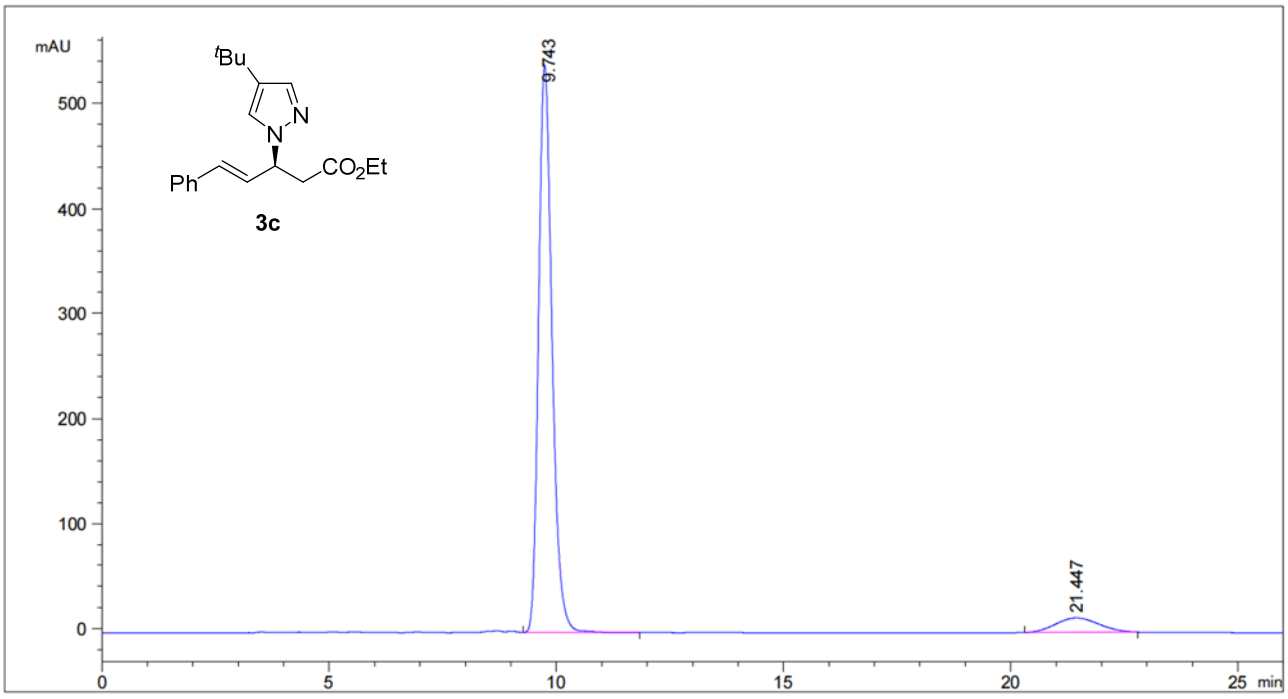
HRMS (ESI-TOF) m/z: $[M + H]^+$

Calcd for $C_{20}H_{28}N_2O_2^+$ 327.2068



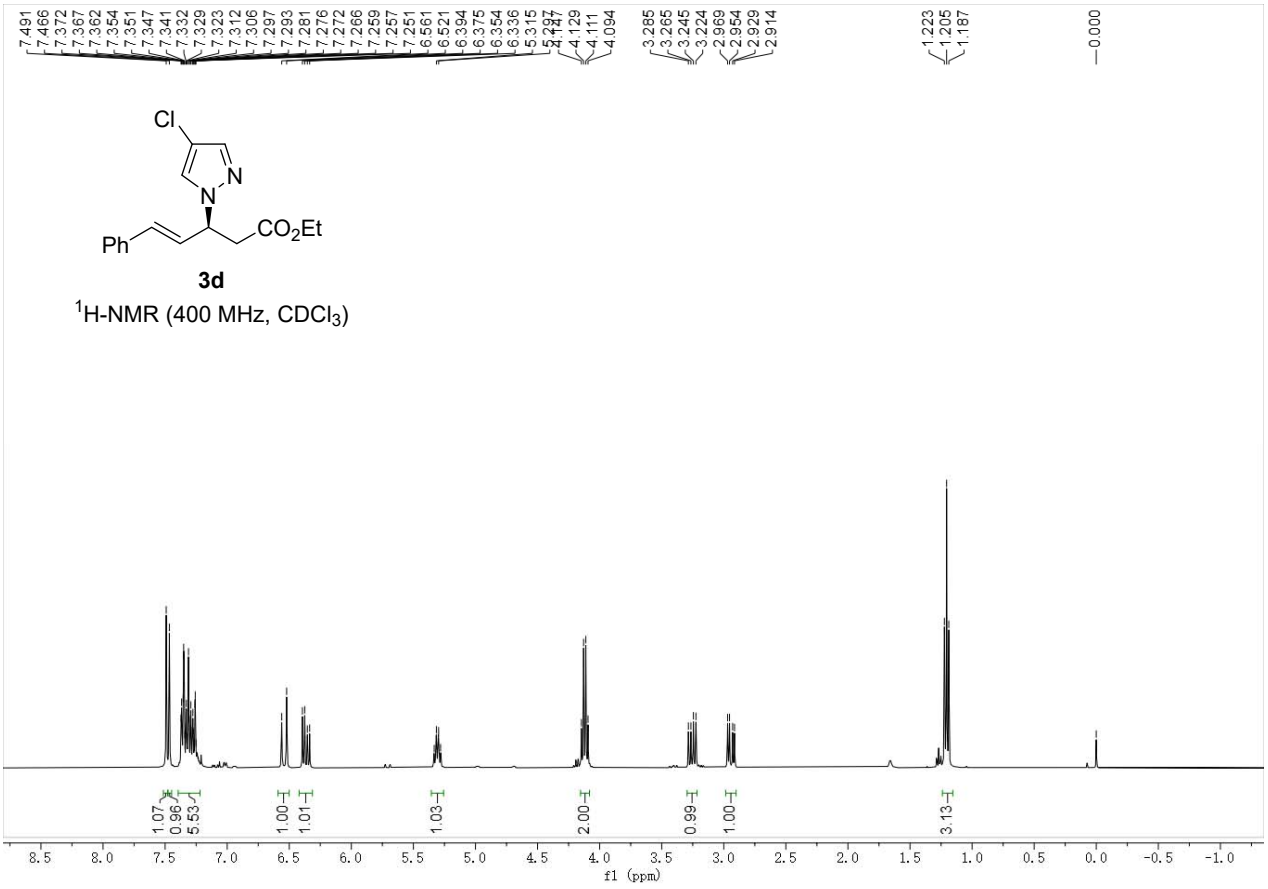
***Rac*-3c**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.747	BB	0.3418	1.23206e4	558.45197	50.8160
2	21.235	BB	1.0792	1.19249e4	169.66229	49.1840



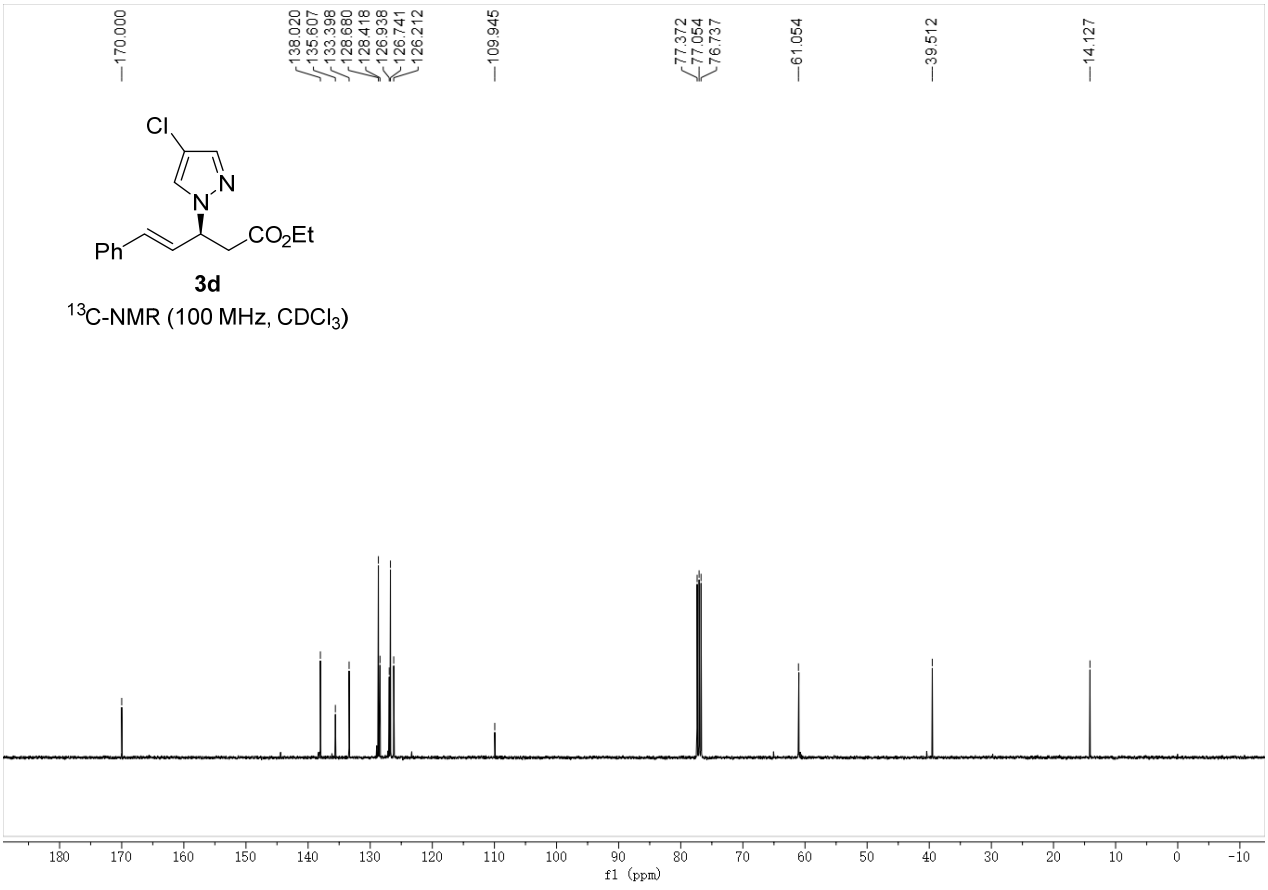
3c

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.743	BBA	0.3179	1.11477e4	540.18048	92.5546
2	21.447	BBA	1.0222	896.75964	13.58104	7.4454



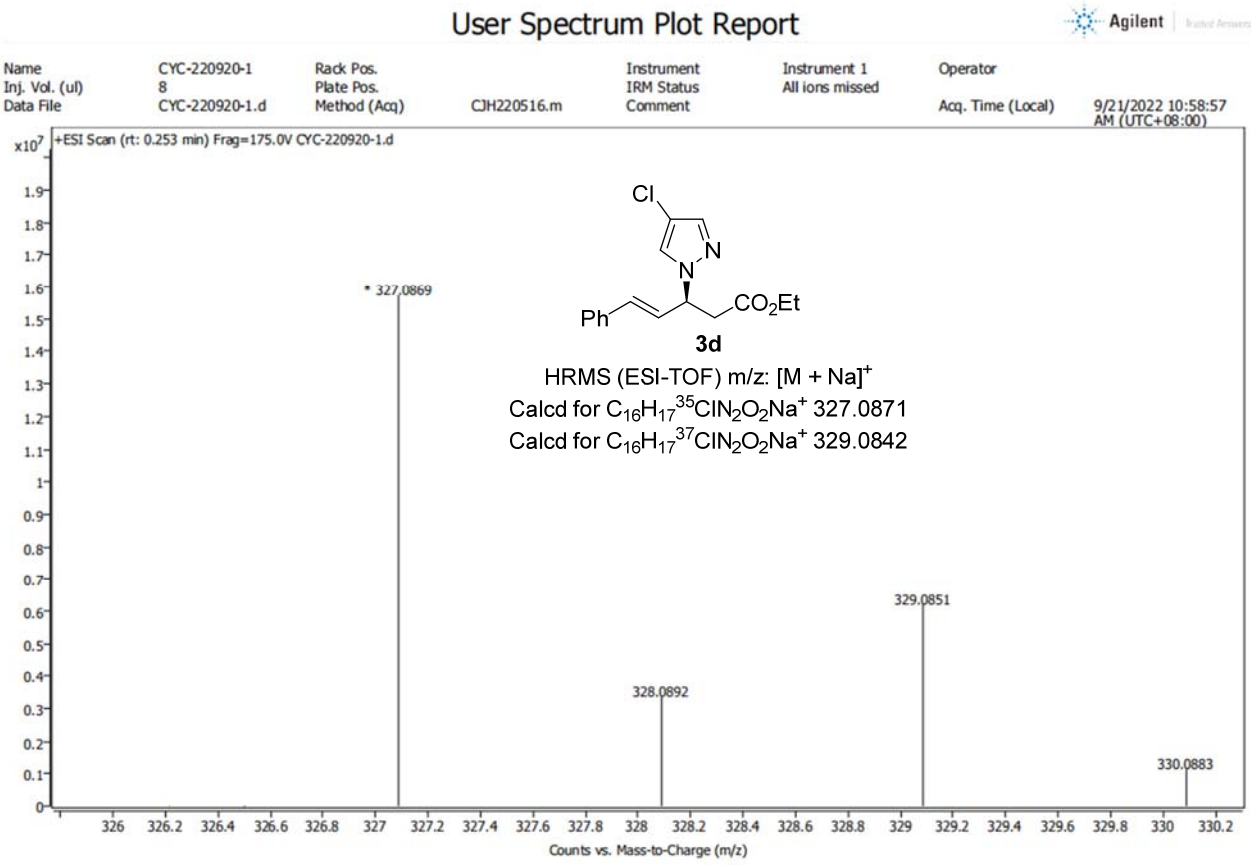
3d

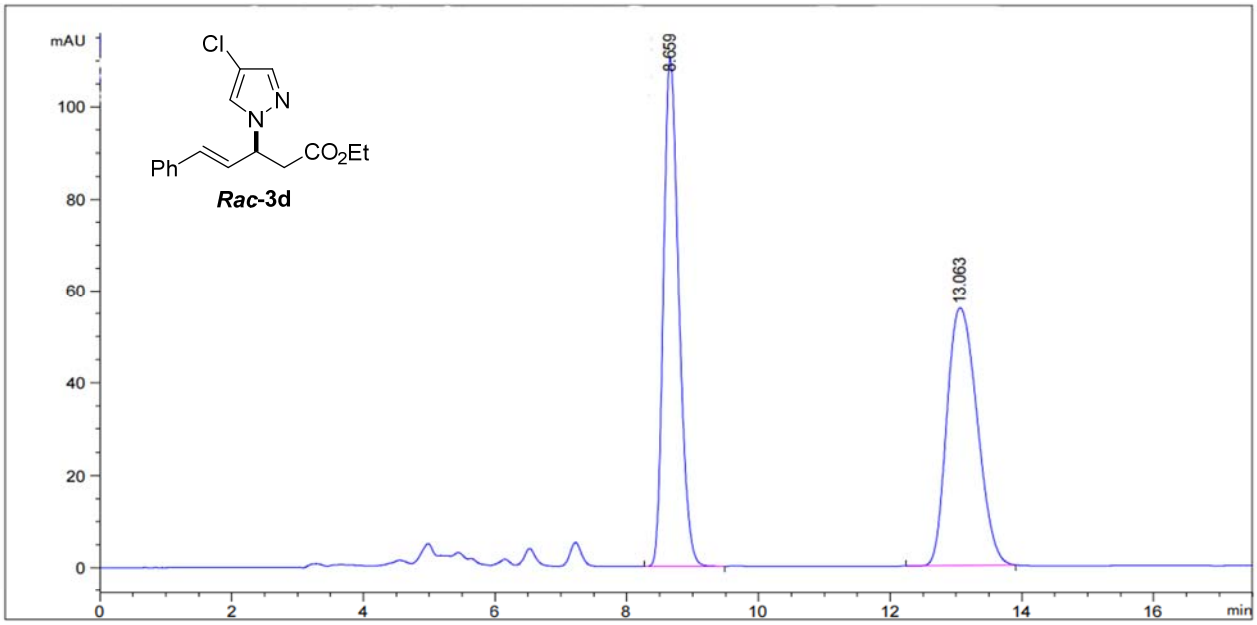
^{1}H-NMR (400 MHz, $CDCl_3$)



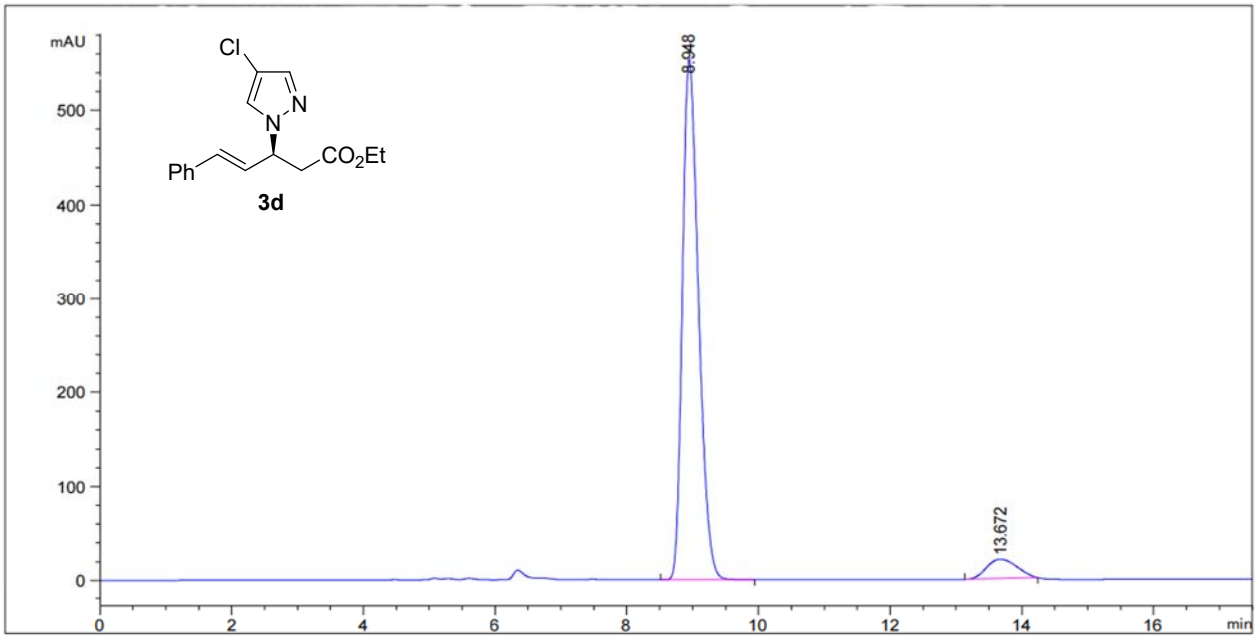
3d

^{13}C-NMR (100 MHz, $CDCl_3$)

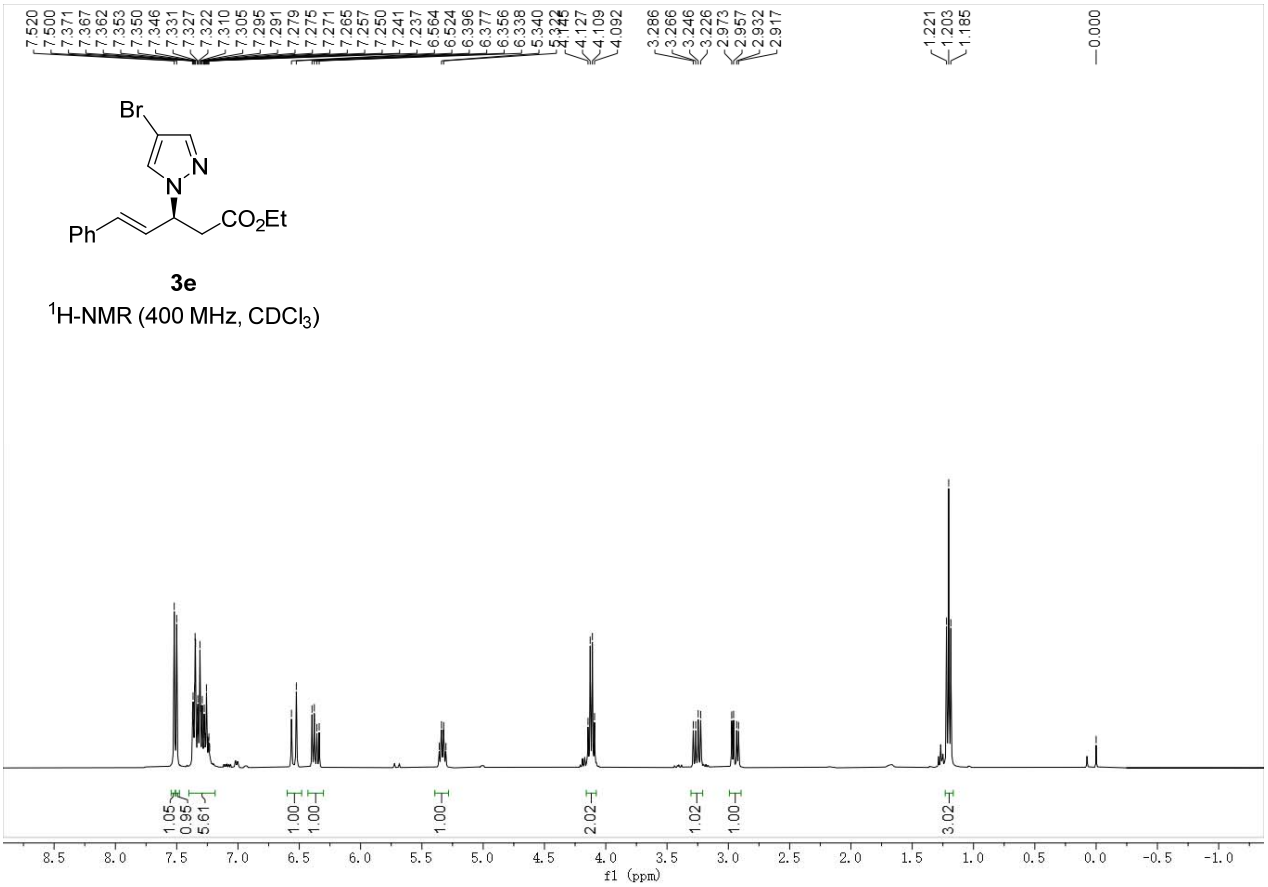

User Spectrum Plot Report
Agilent
Name CYC-220920-1
Inj. Vol. (ul) 8
Data File CYC-220920-1.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 9/21/2022 10:58:57 AM (UTC+08:00)
+ESI Scan (rt: 0.253 min) Frag=175.0V CYC-220920-1.d
x10^7
* 327.0869
328.0892
329.0851
330.0883
Counts vs. Mass-to-Charge (m/z)
Cl
N
N
Ph
CO2Et
3d
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C16H17 35ClN2O2Na+ 327.0871
Calcd for C16H17 37ClN2O2Na+ 329.0842



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.659	BB	0.2501	1785.79834	110.26414	50.1526
2	13.063	BBA	0.5128	1774.93030	55.73080	49.8474

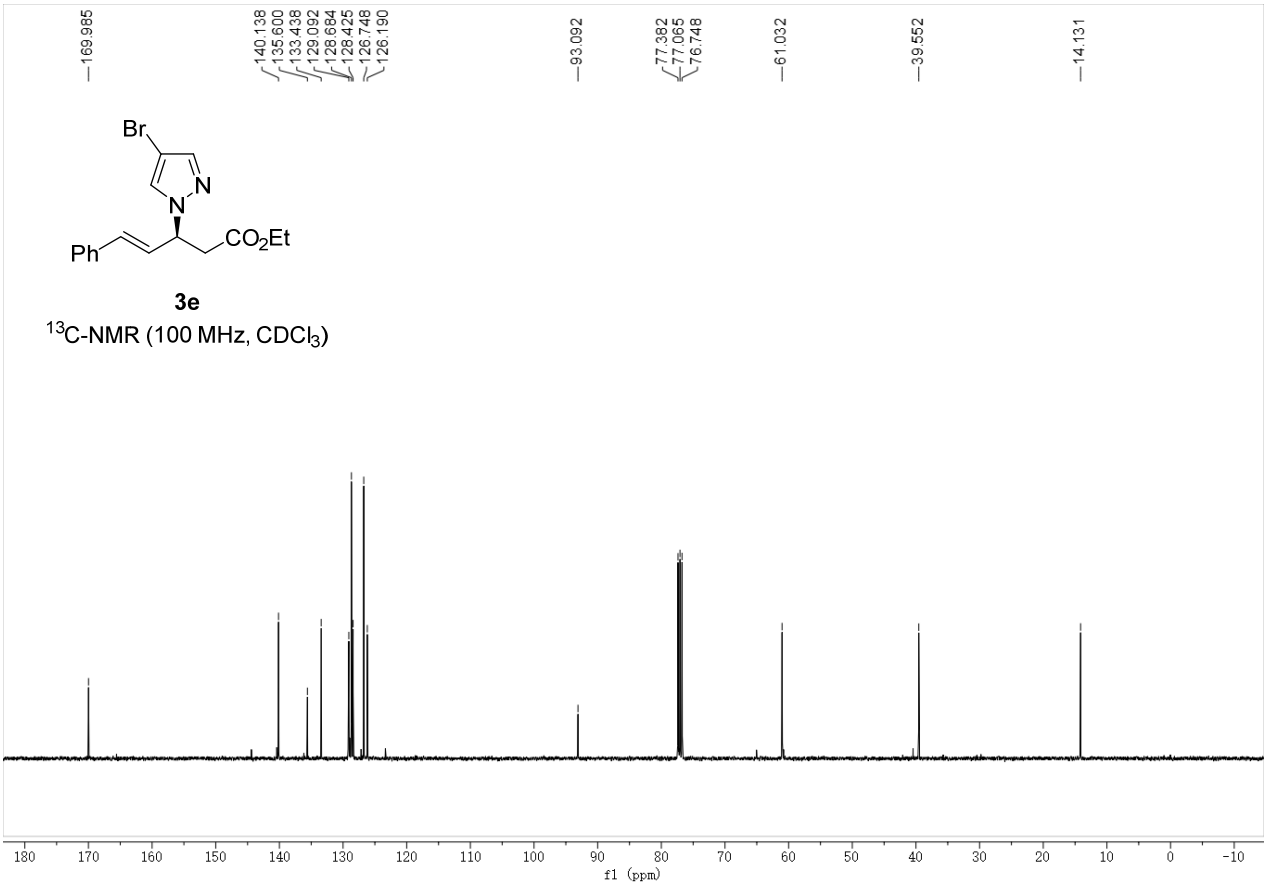


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.948	BBA	0.2622	9395.85254	553.21509	93.4509
2	13.672	BBA	0.5261	658.46814	20.58255	6.5491



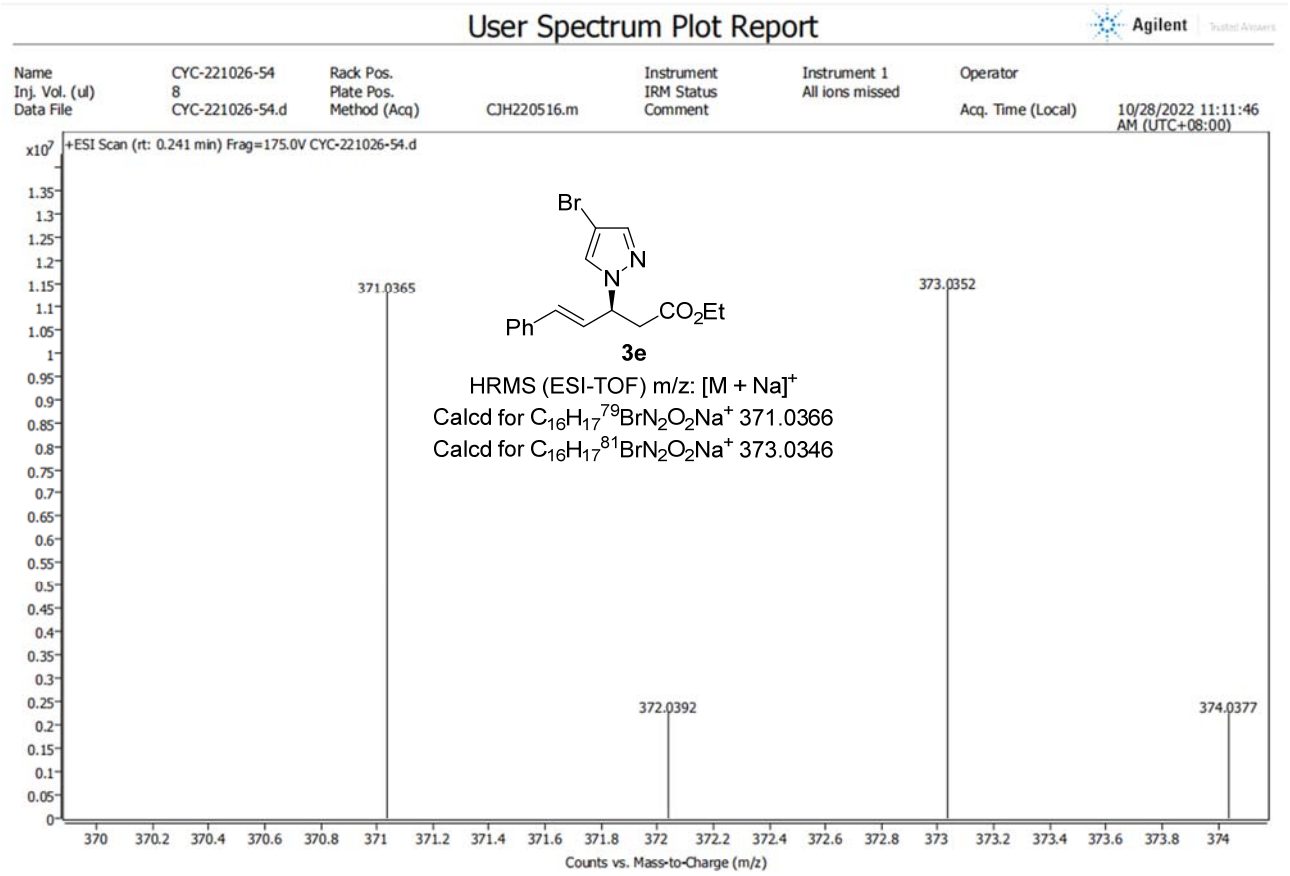
3e

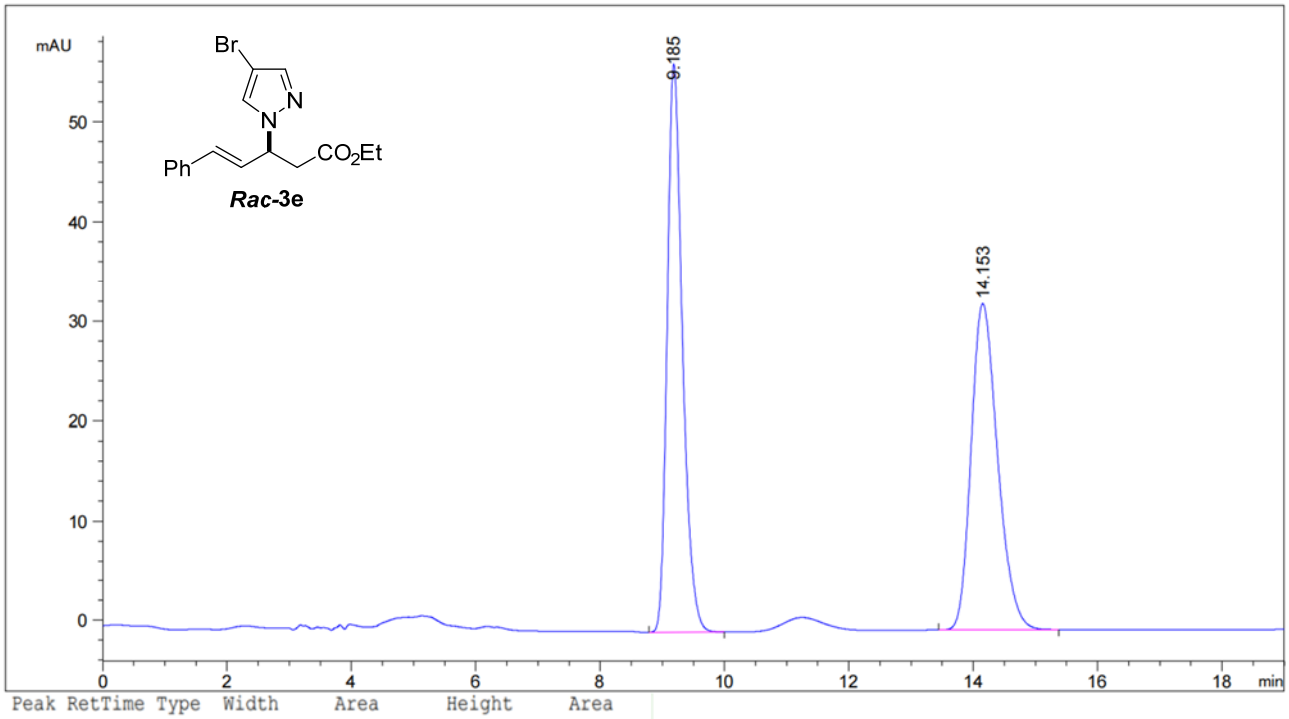
^{1}H-NMR (400 MHz, $CDCl_3$)



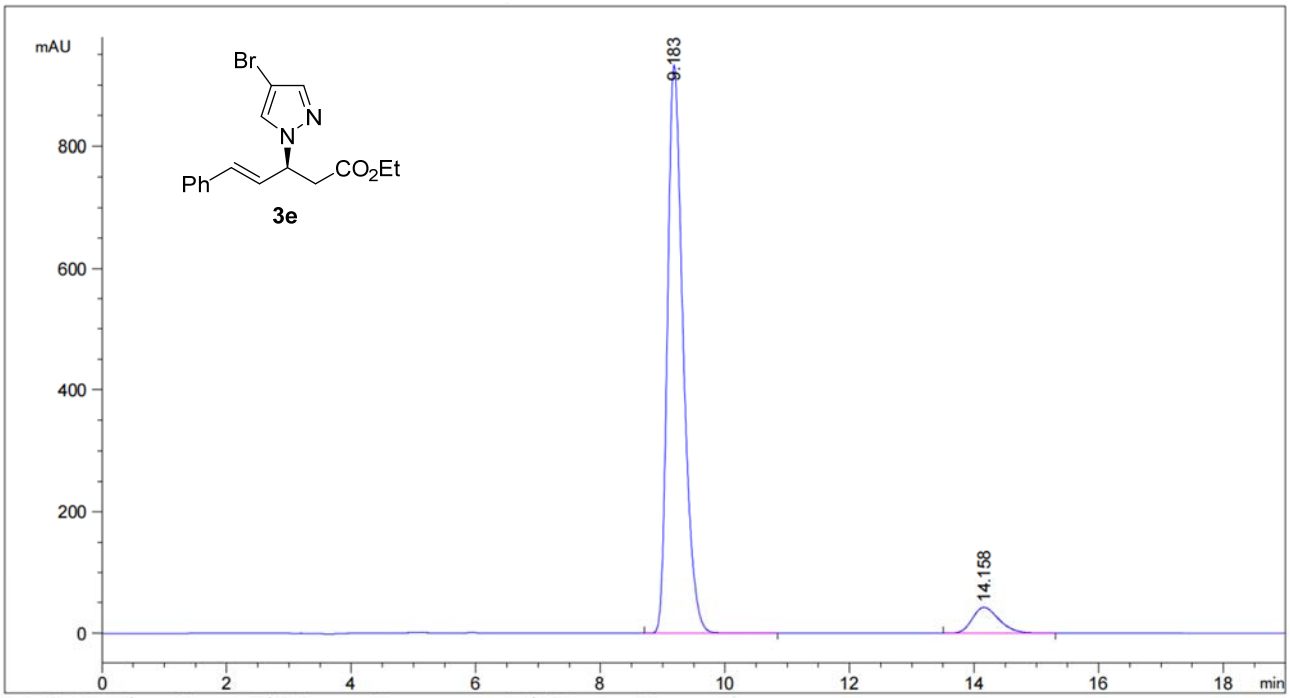
3e

^{13}C-NMR (100 MHz, $CDCl_3$)

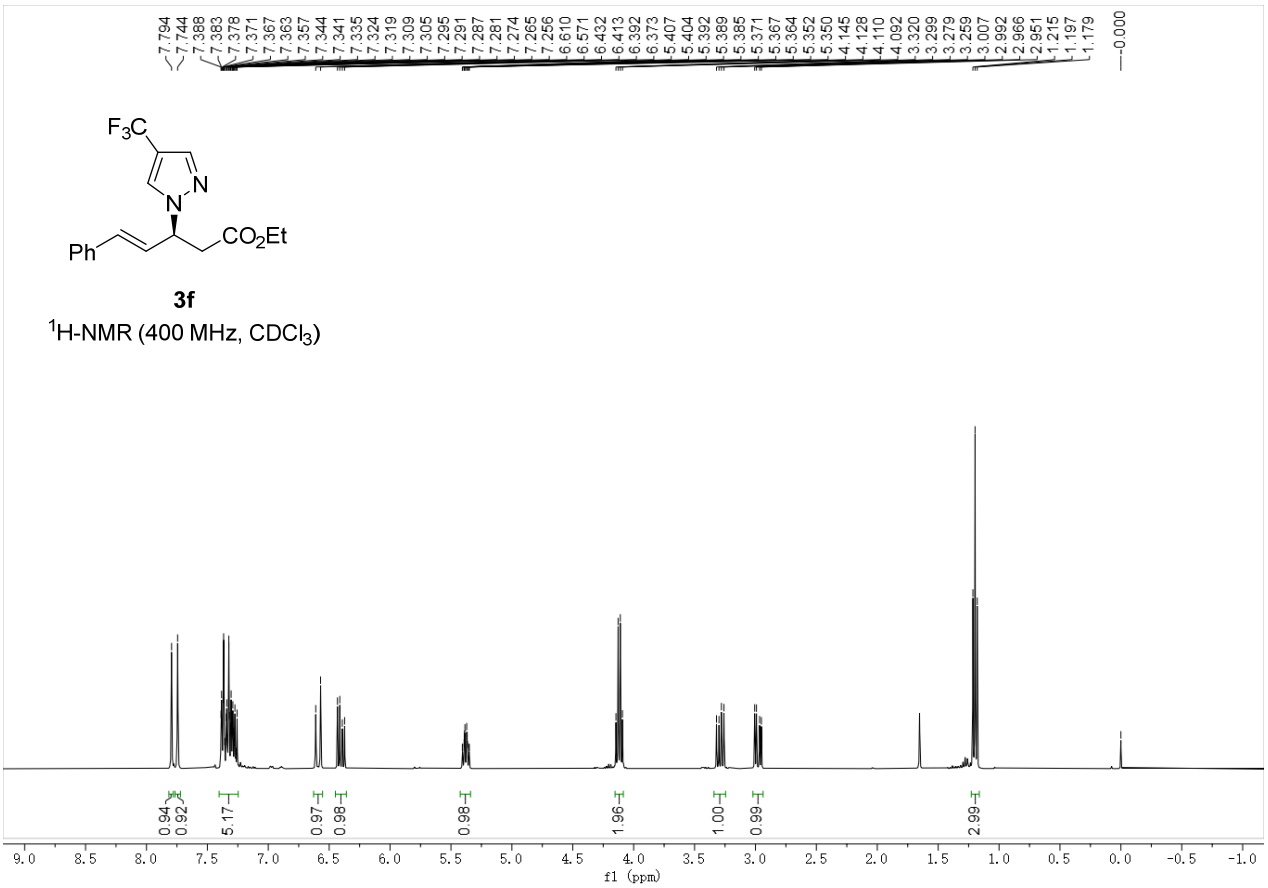

User Spectrum Plot Report
Agilent
Name CYC-221026-54
Inj. Vol. (ul) 8
Data File CYC-221026-54.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 10/28/2022 11:11:46 AM (UTC+08:00)
+ESI Scan (rt: 0.241 min) Frag=175.0V CYC-221026-54.d
x10^7
371.0365
372.0392
373.0352
374.0377
Counts vs. Mass-to-Charge (m/z)
Br
N
N
Ph
CO2Et
3e
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C16H17 79BrN2O2Na+ 371.0366
Calcd for C16H17 81BrN2O2Na+ 373.0346



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.185	BB	0.2588	972.19519	56.96394	50.0378
2	14.153	BB	0.4567	970.72461	32.72650	49.9622

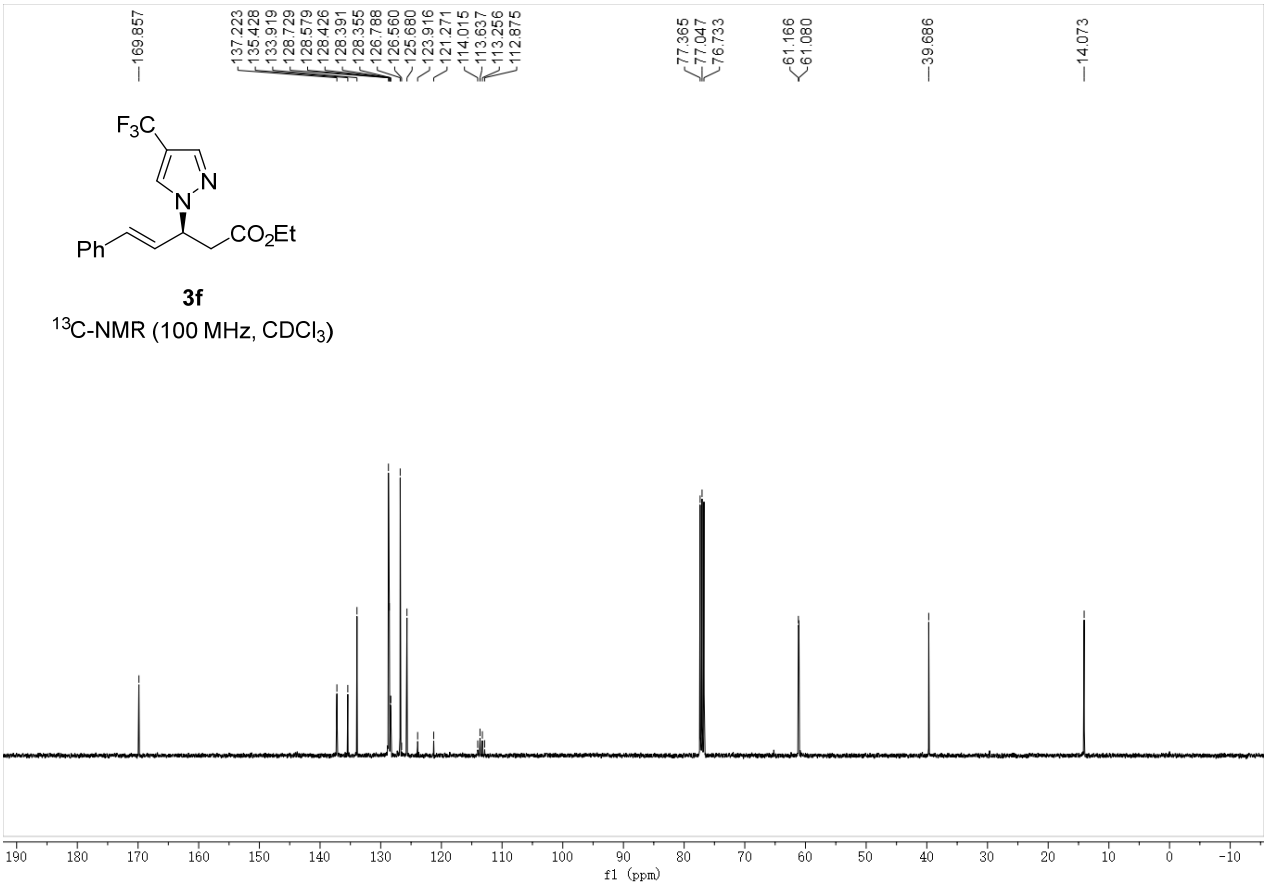


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.183	BB	0.2670	1.63462e4	932.81177	92.8798
2	14.158	BB	0.4572	1253.10498	42.19164	7.1202



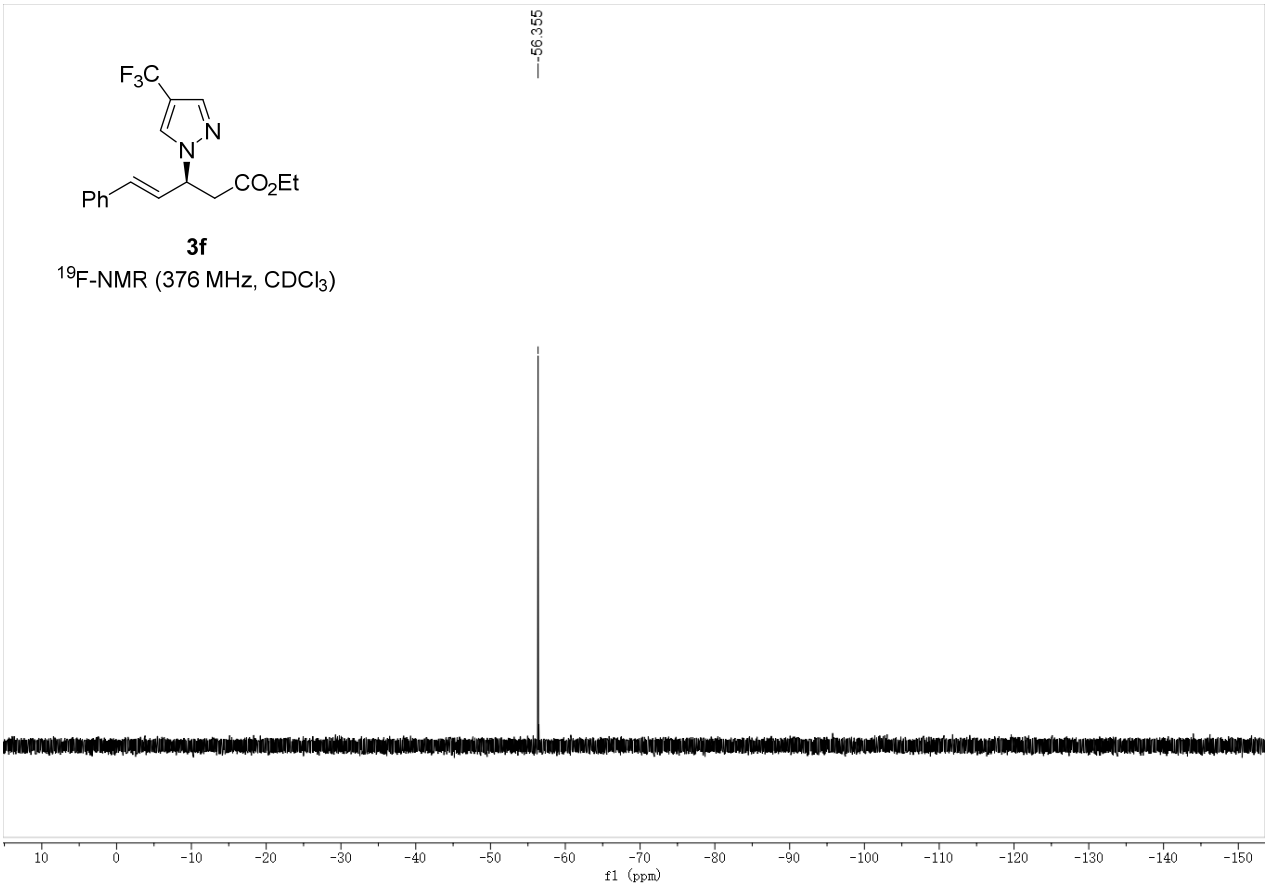
3f

^{1}H-NMR (400 MHz, $CDCl_3$)



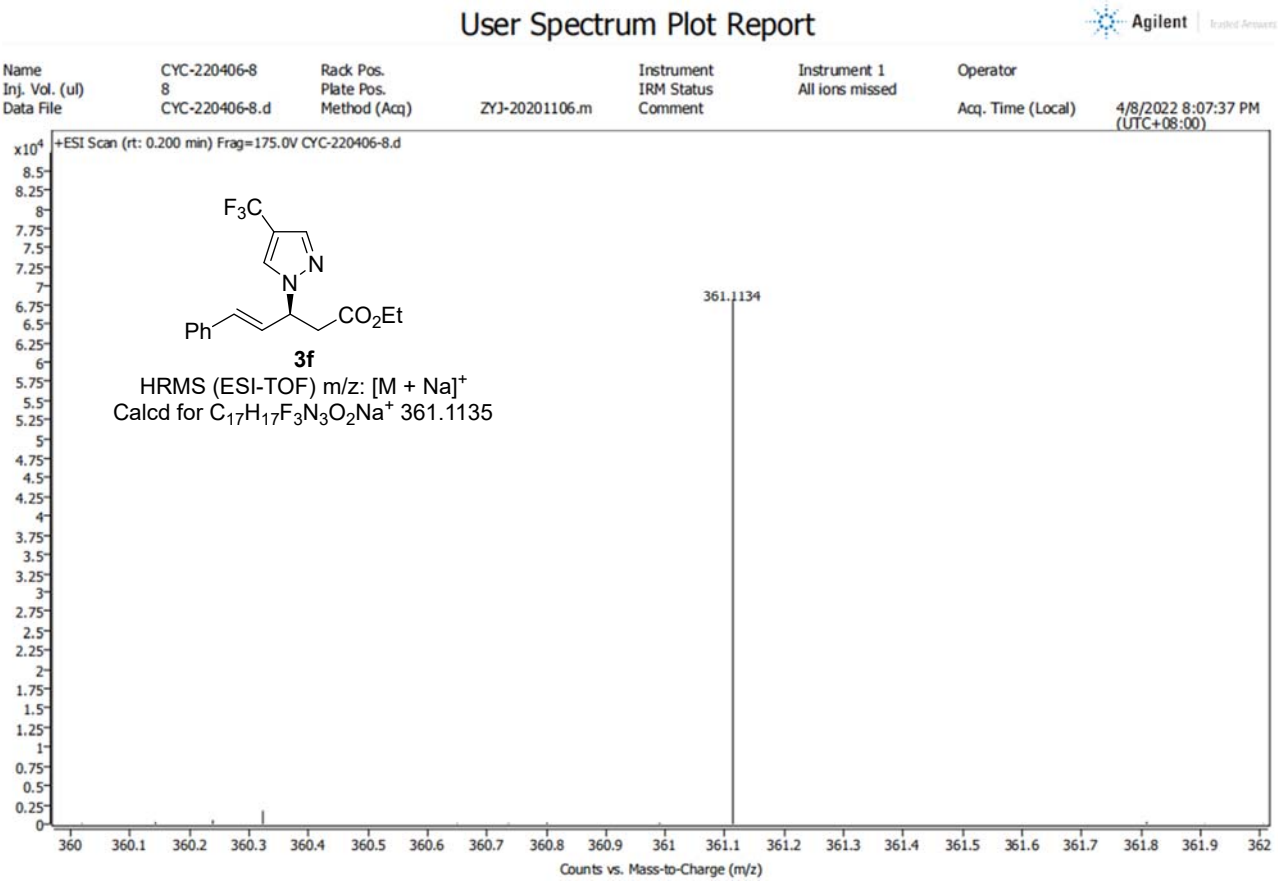
3f

^{13}C-NMR (100 MHz, $CDCl_3$)



3f

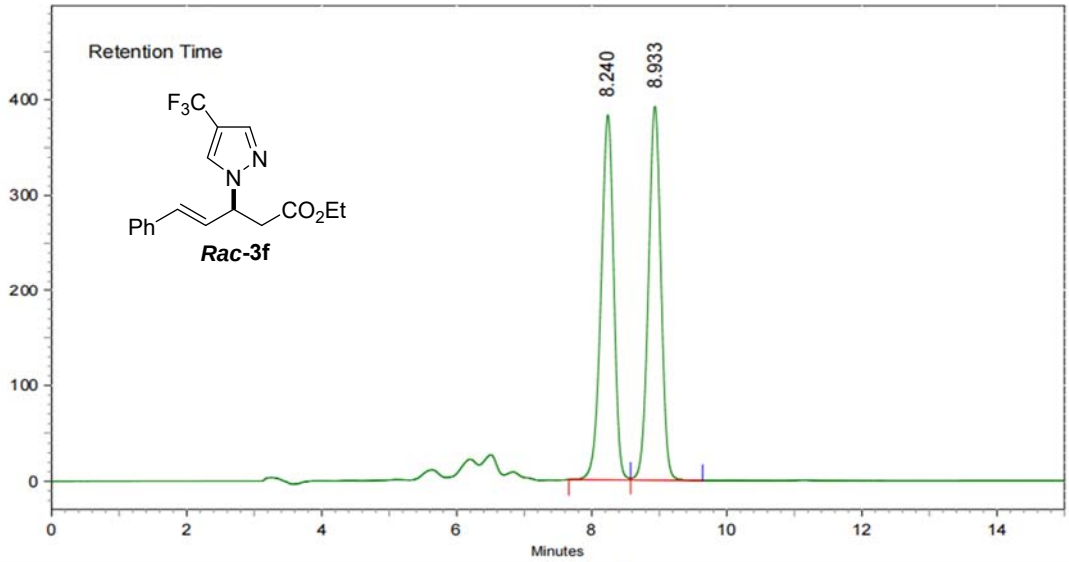
^{19}F-NMR (376 MHz, $CDCl_3$)



3f

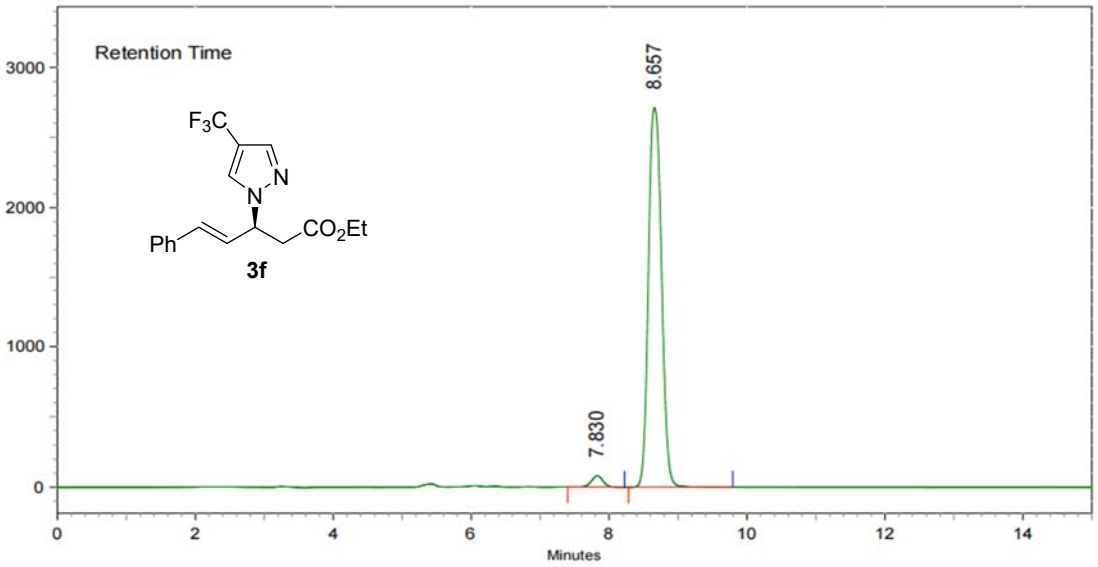
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{17}H_{17}F_3N_3O_2Na^+$ 361.1135



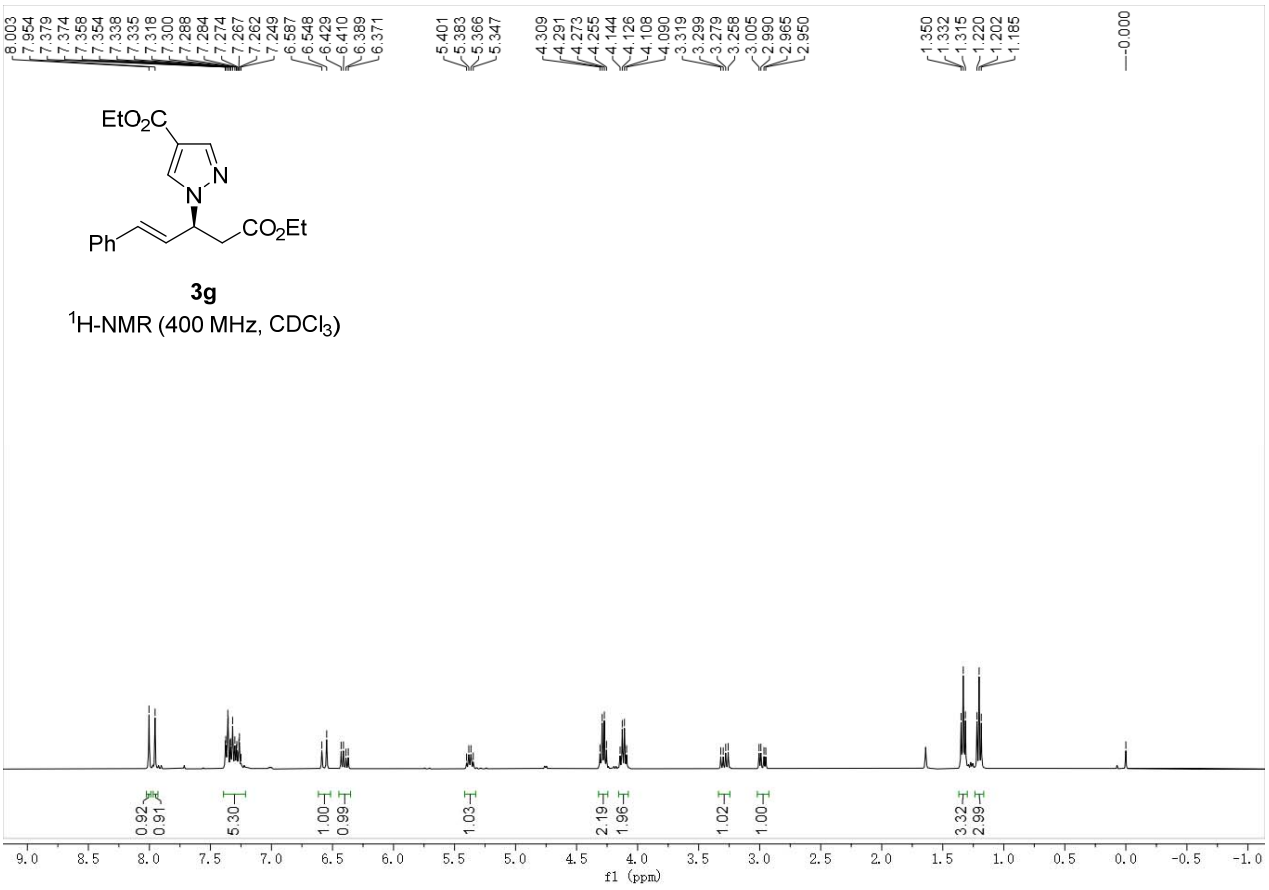
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.240	0.913	6414608	84025682	49.8297
2	8.933	1.067	6572790	84600183	50.1703
Totals			12987398	168625865	100.0000



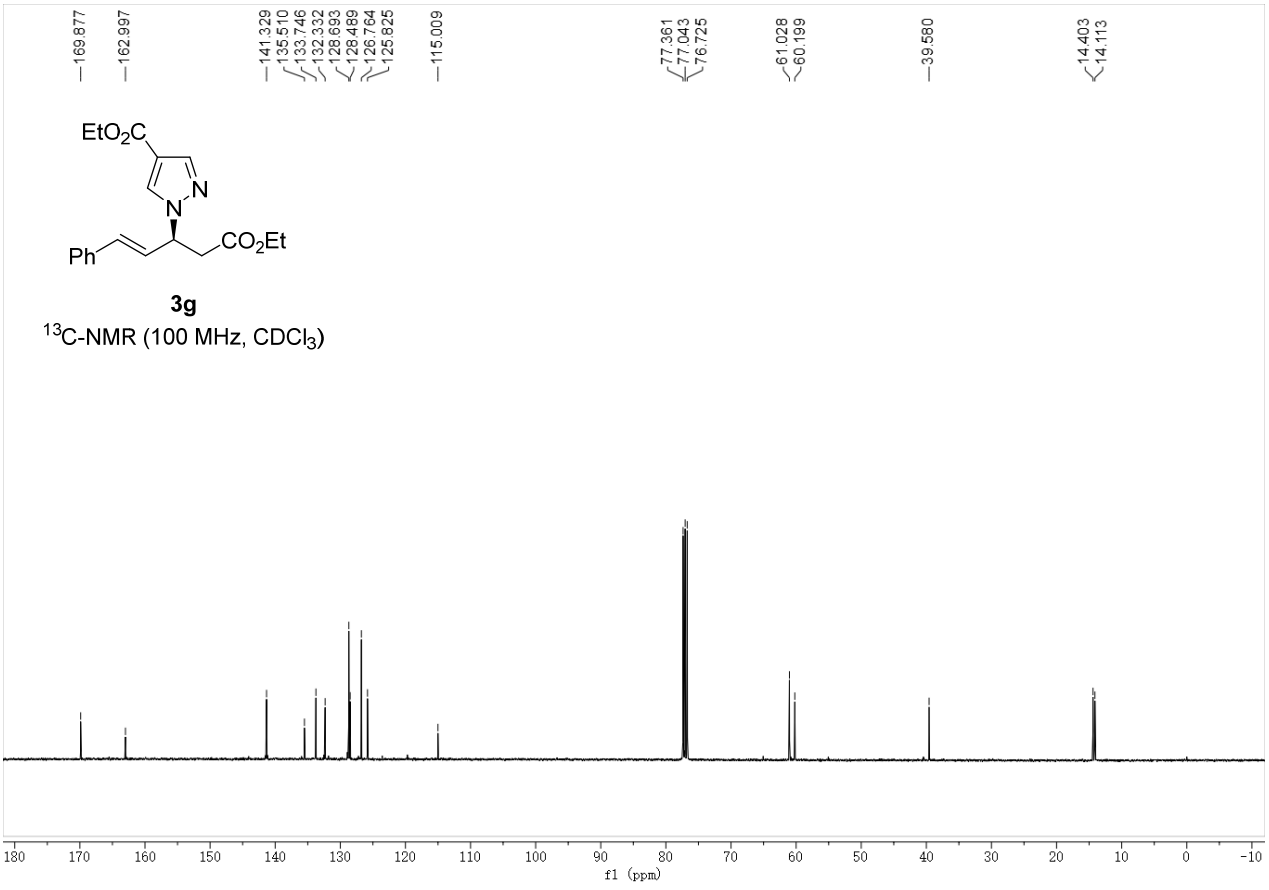
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.830	0.823	1351305	15320843	2.4971
2	8.657	1.510	45483774	598227512	97.5029
Totals			46835079	613548355	100.0000



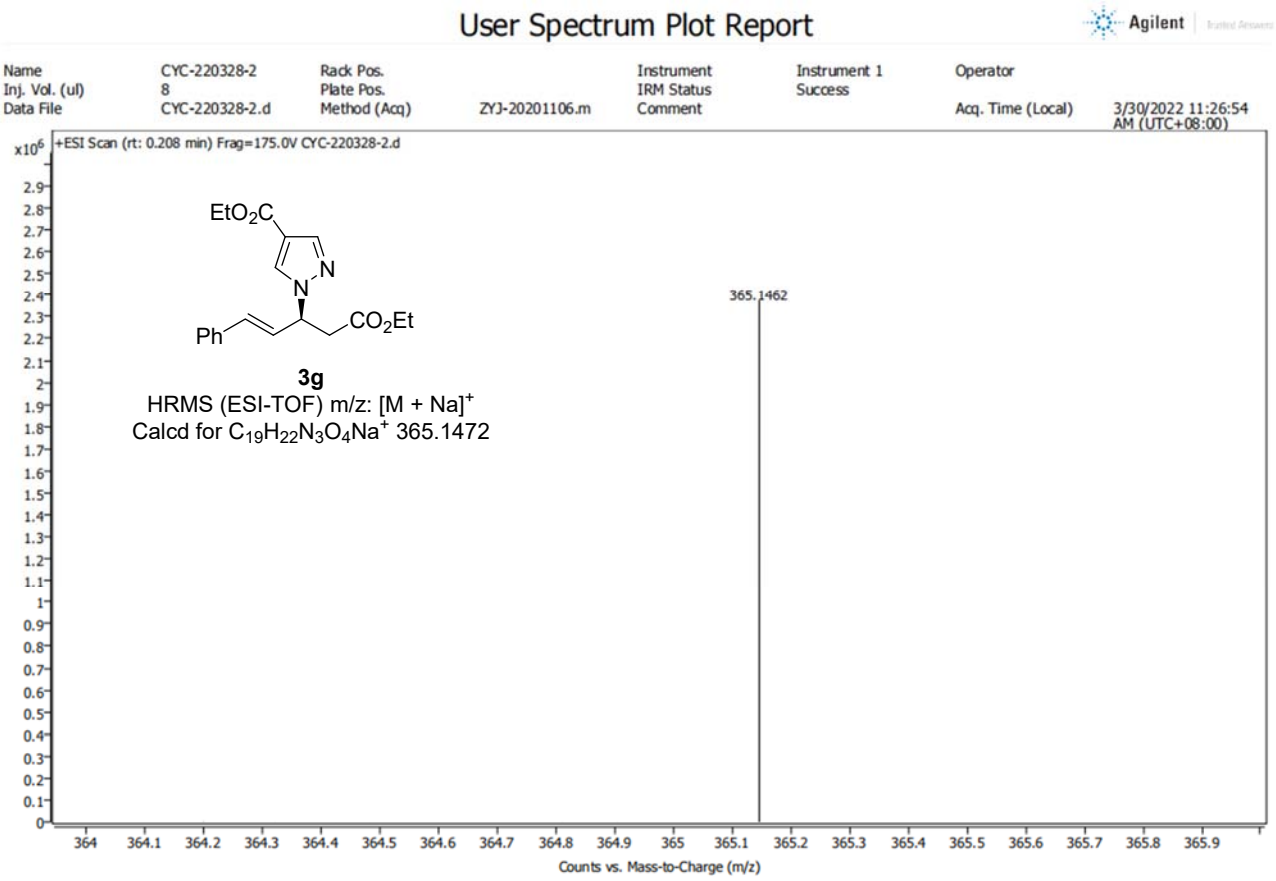
3g

^{1}H-NMR (400 MHz, $CDCl_3$)



3g

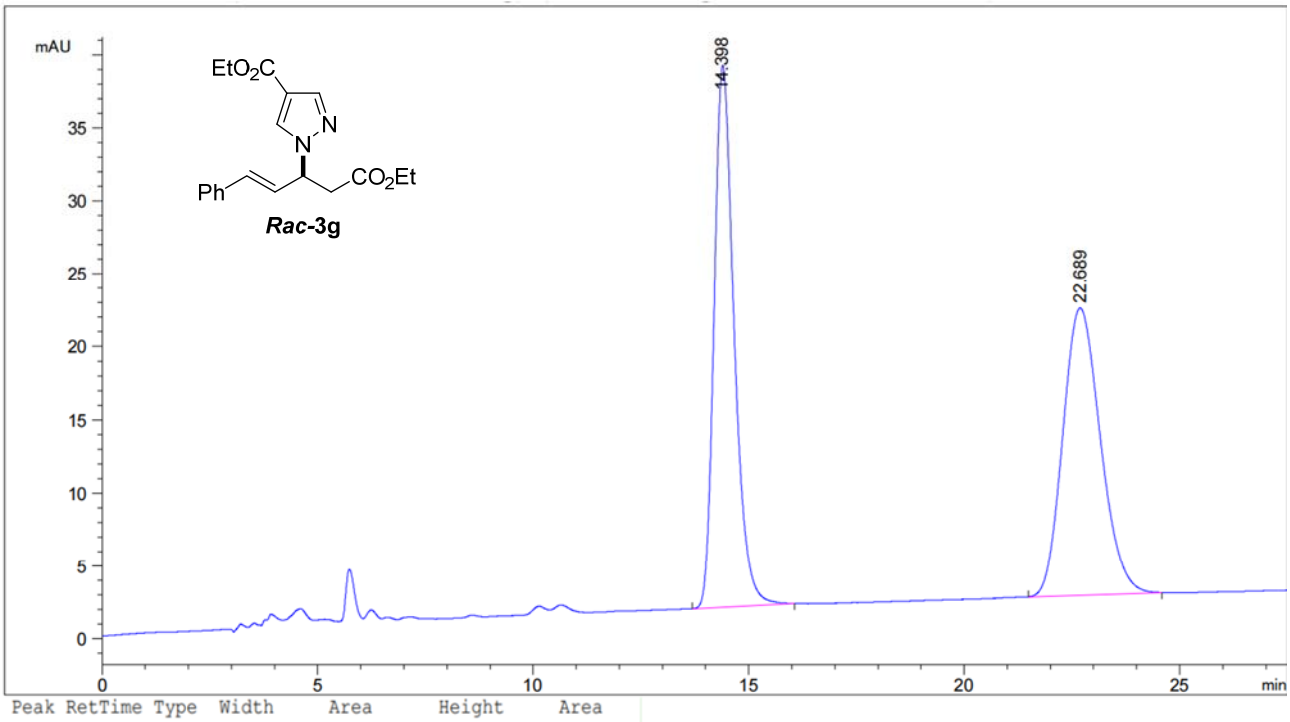
^{13}C-NMR (100 MHz, $CDCl_3$)



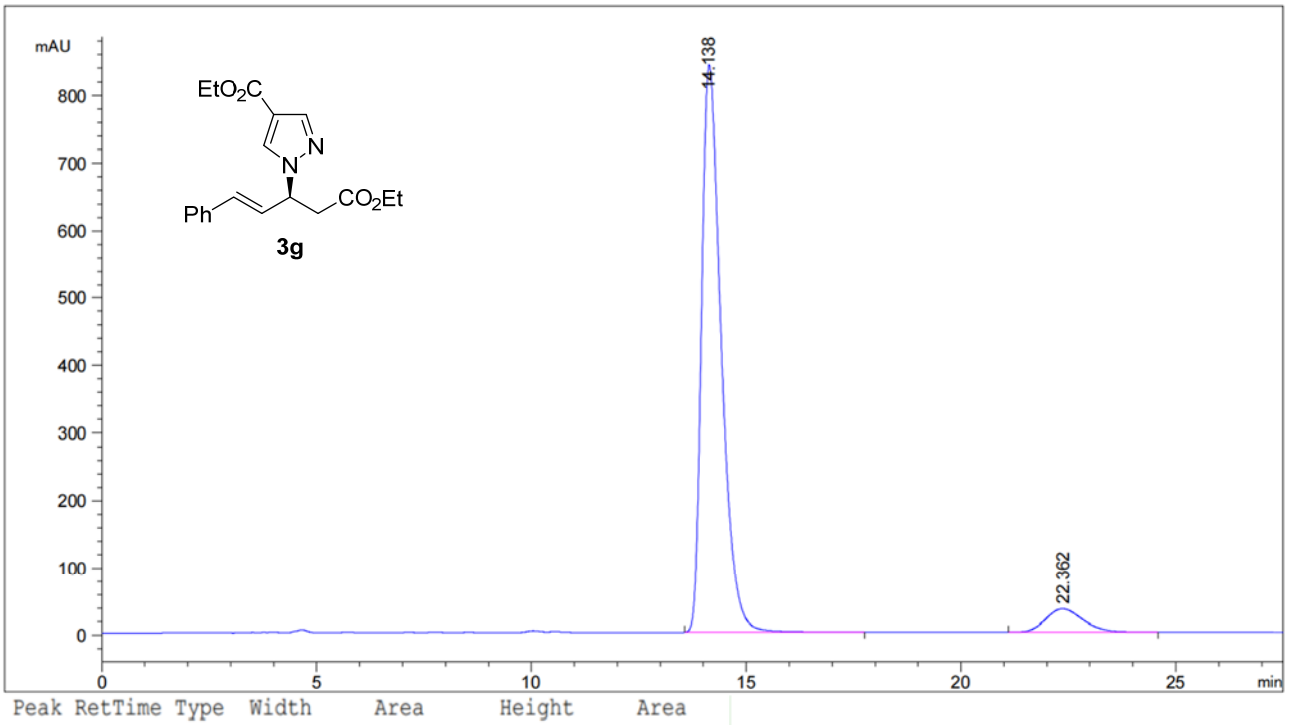
3g

HRMS (ESI-TOF) m/z: $[M + Na]^+$

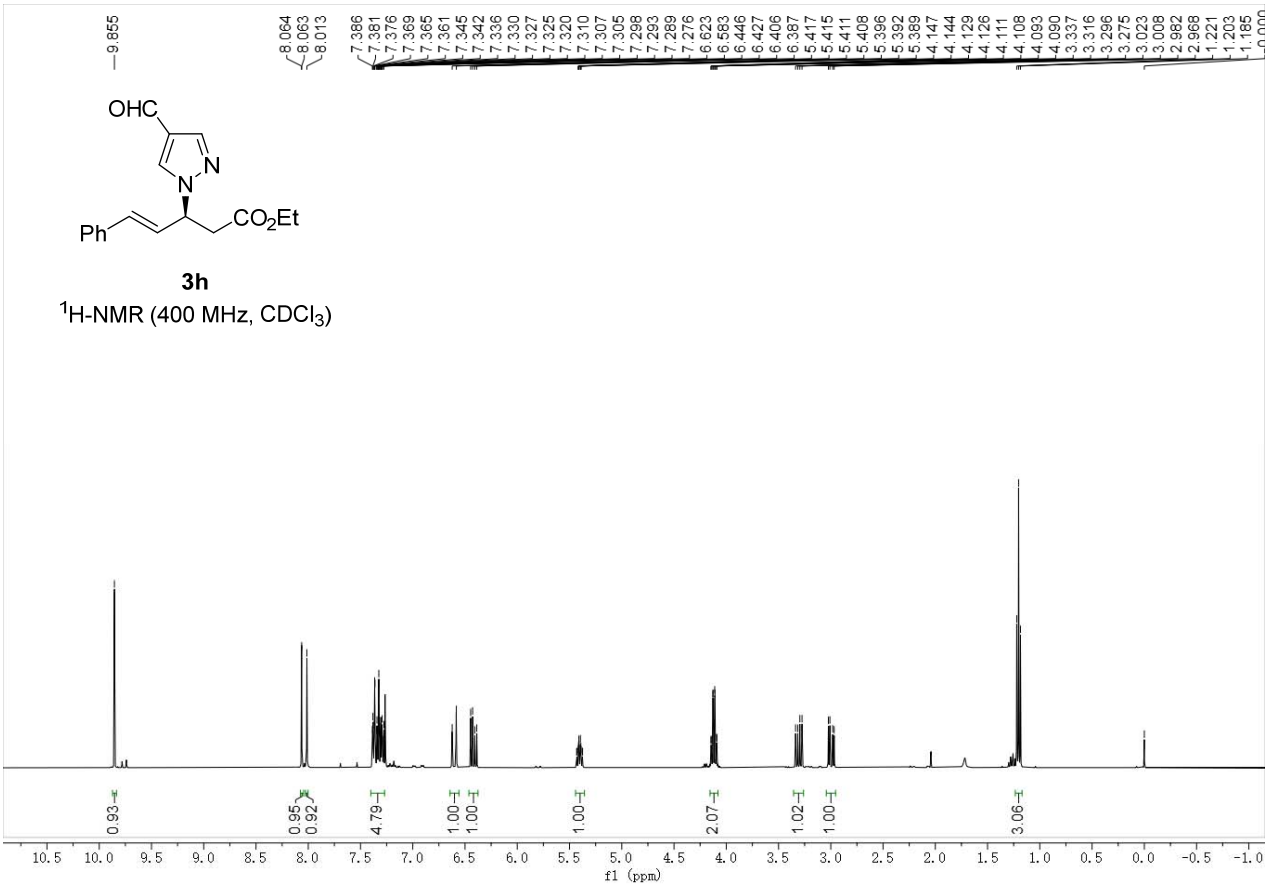
Calcd for $C_{19}H_{22}N_3O_4Na^+$ 365.1472



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.398	BB	0.4911	1196.47620	37.11380	50.0782
2	22.689	BBA	0.9221	1192.74170	19.65389	49.9218

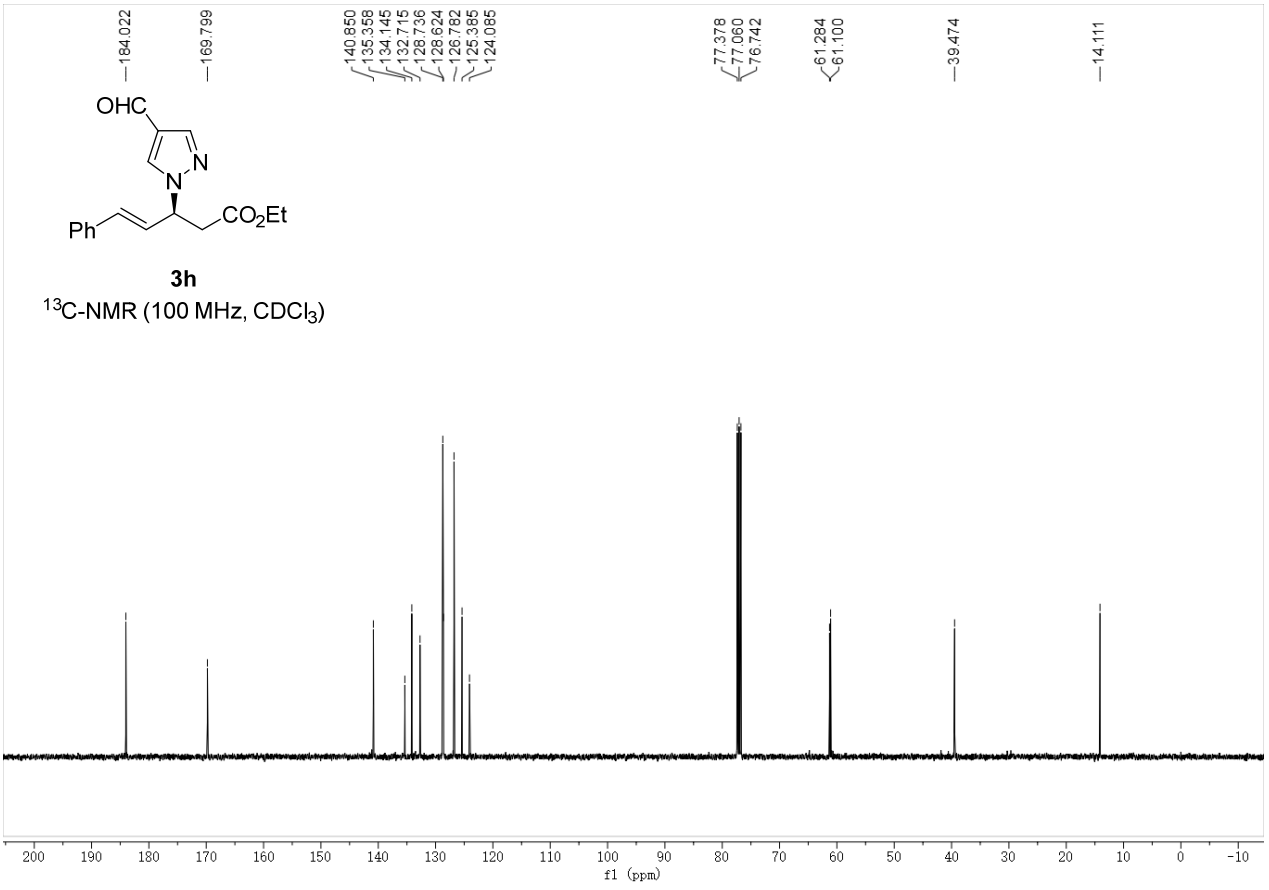


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.138	BB	0.4867	2.66602e4	840.24585	92.8895
2	22.362	BBA	0.9215	2040.77832	34.21685	7.1105



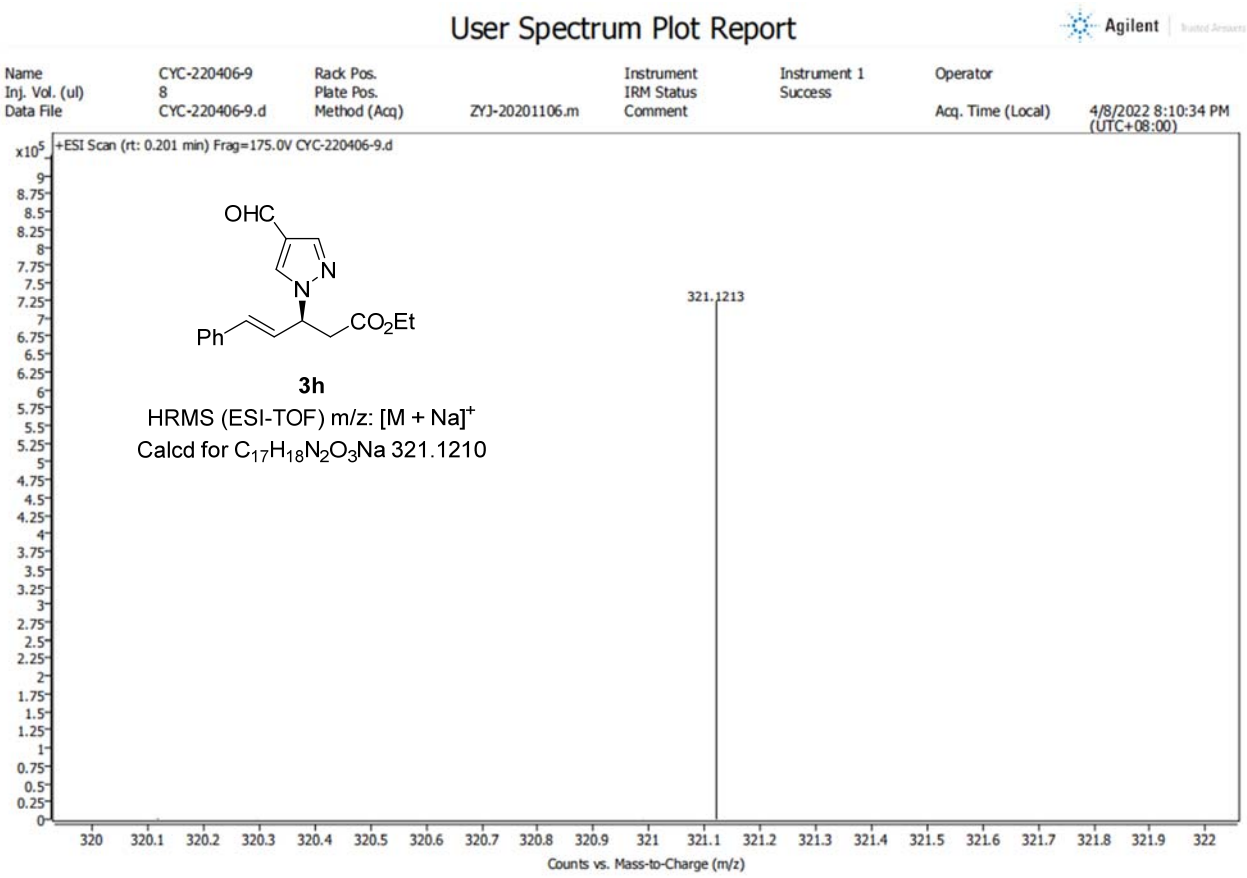
3h

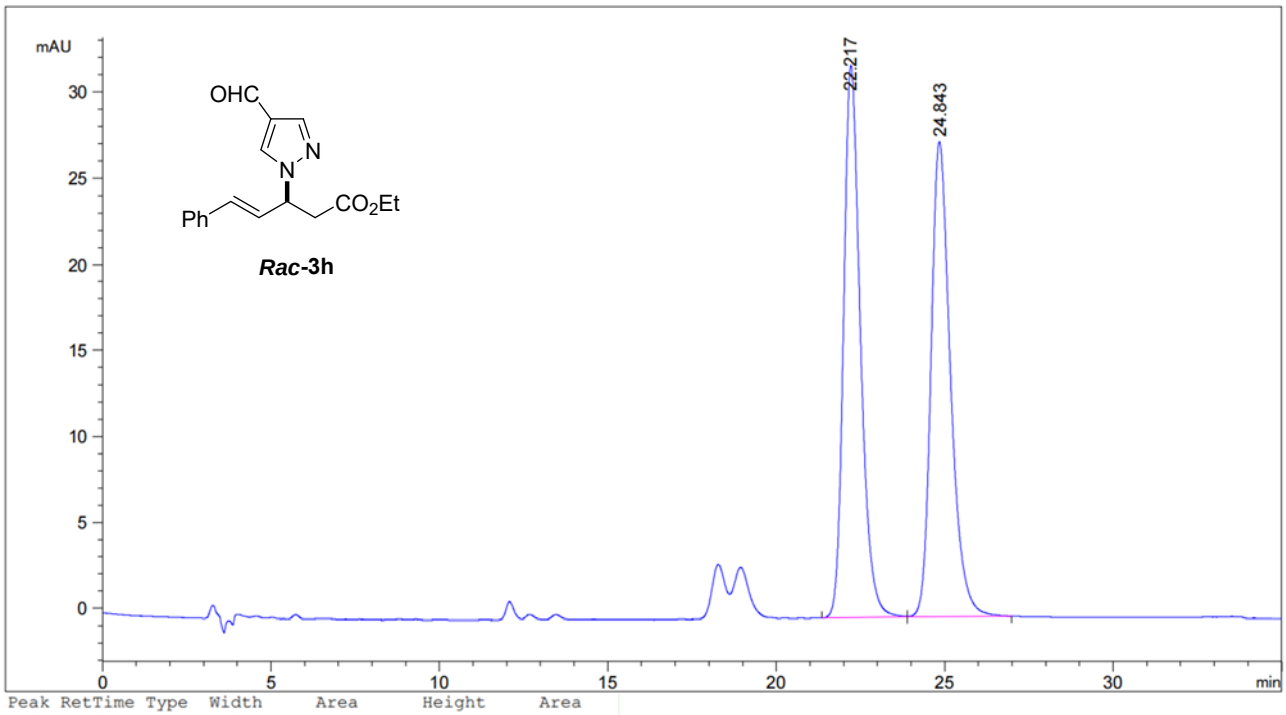
^{1}H-NMR (400 MHz, $CDCl_3$)



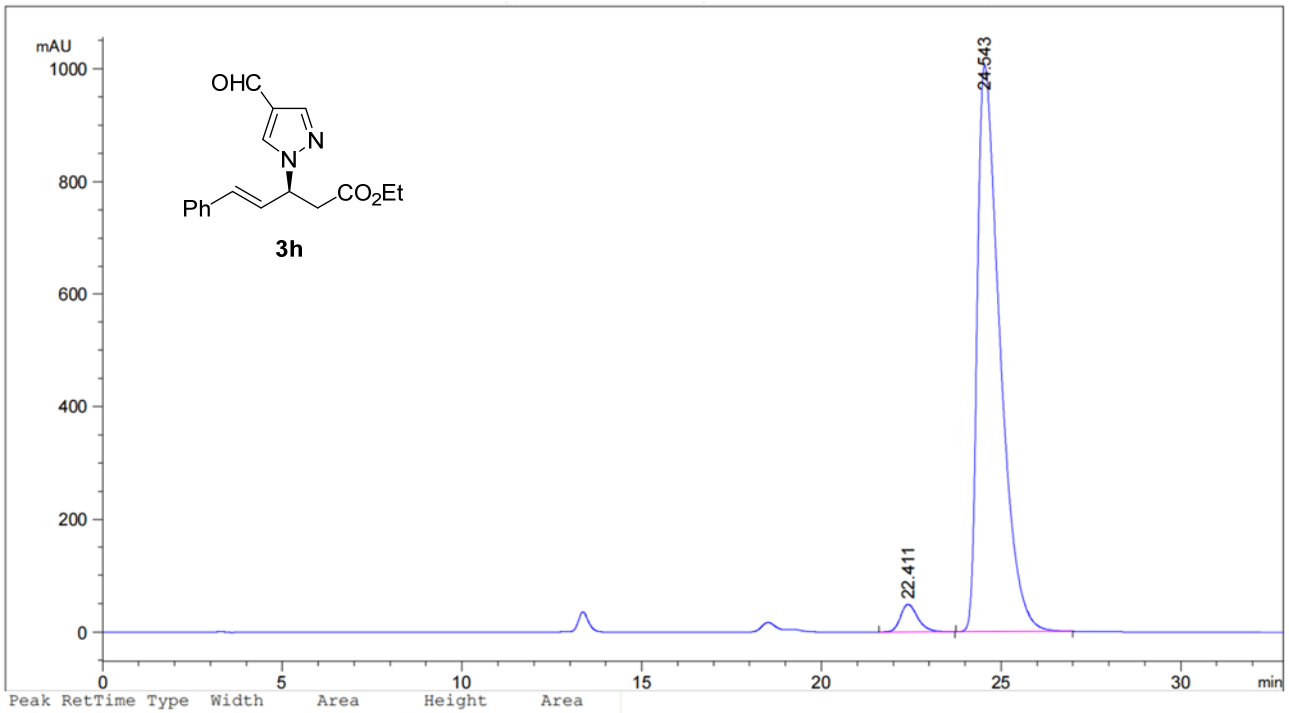
3h

^{13}C-NMR (100 MHz, $CDCl_3$)

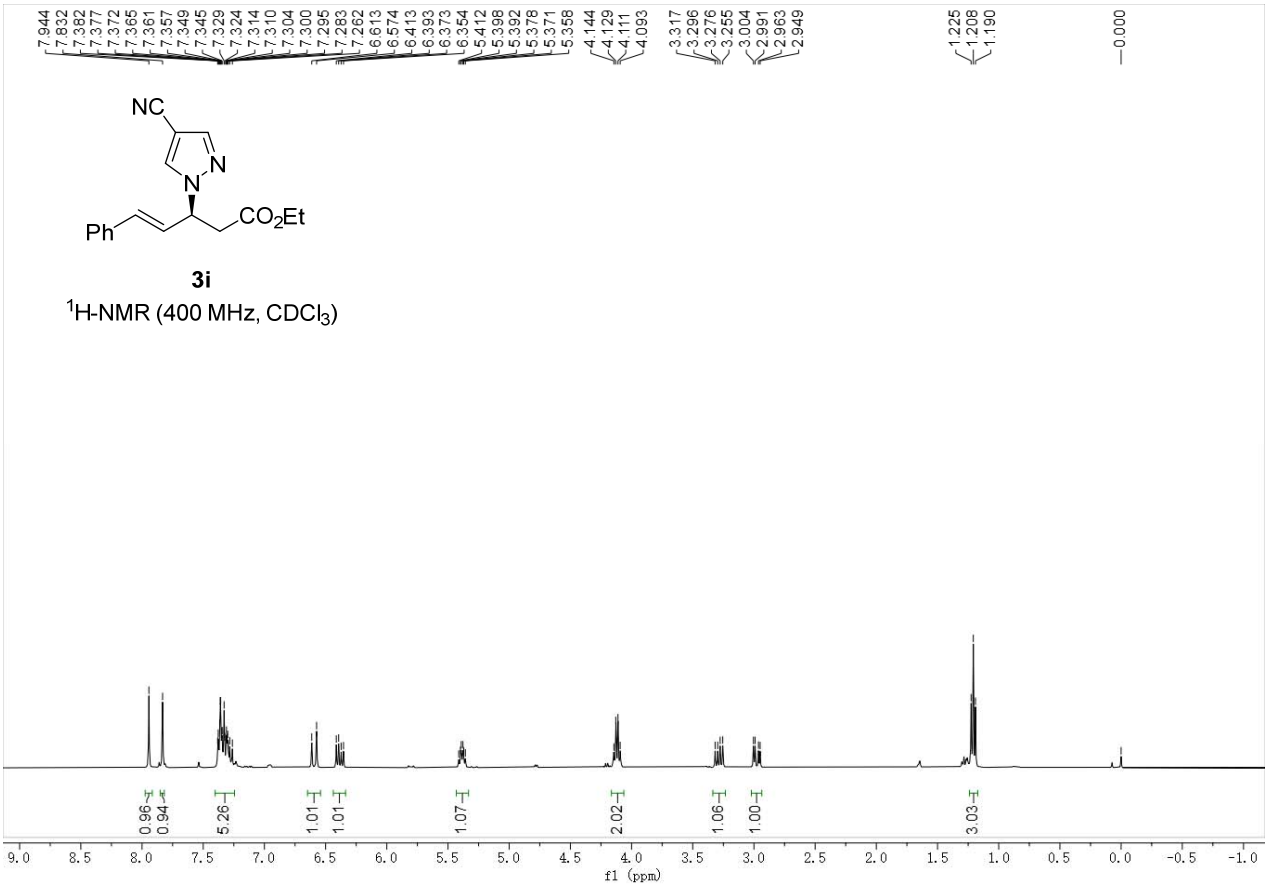

User Spectrum Plot Report
Agilent
Name CYC-220406-9
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
Success
Data File CYC-220406-9.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 4/8/2022 8:10:34 PM (UTC+08:00)
+ESI Scan (rt: 0.201 min) Frag=175.0V CYC-220406-9.d
x10^5
OHC
N
N
Ph
CO2Et
3h
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C17H18N2O3Na 321.1210
321.1213
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.217	BB	0.5287	1112.90869	32.06647	50.1111
2	24.843	BBA	0.6050	1107.97253	27.61088	49.8889

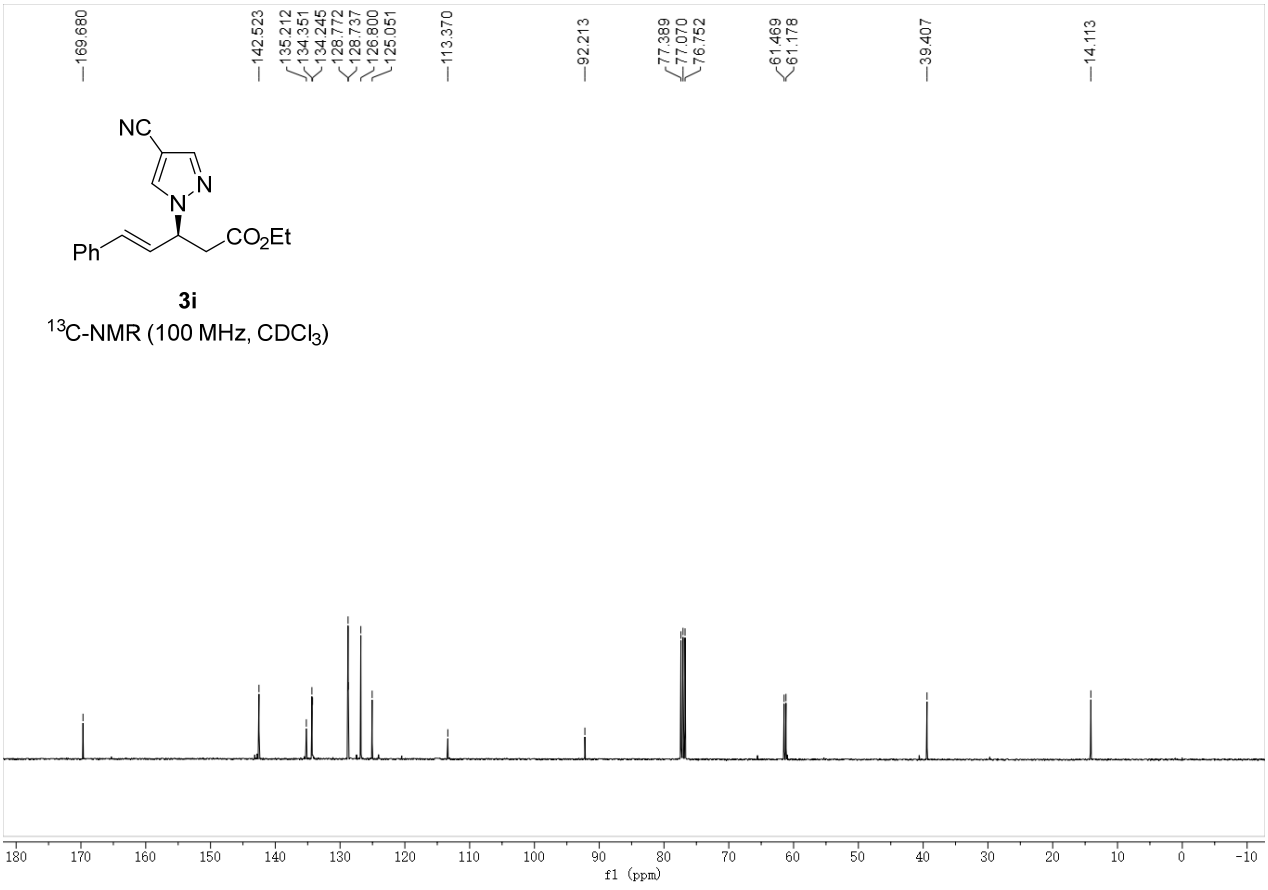


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.411	BB	0.5150	1604.05420	47.65371	3.5335
2	24.543	BBA	0.6436	4.37912e4	1005.28326	96.4665



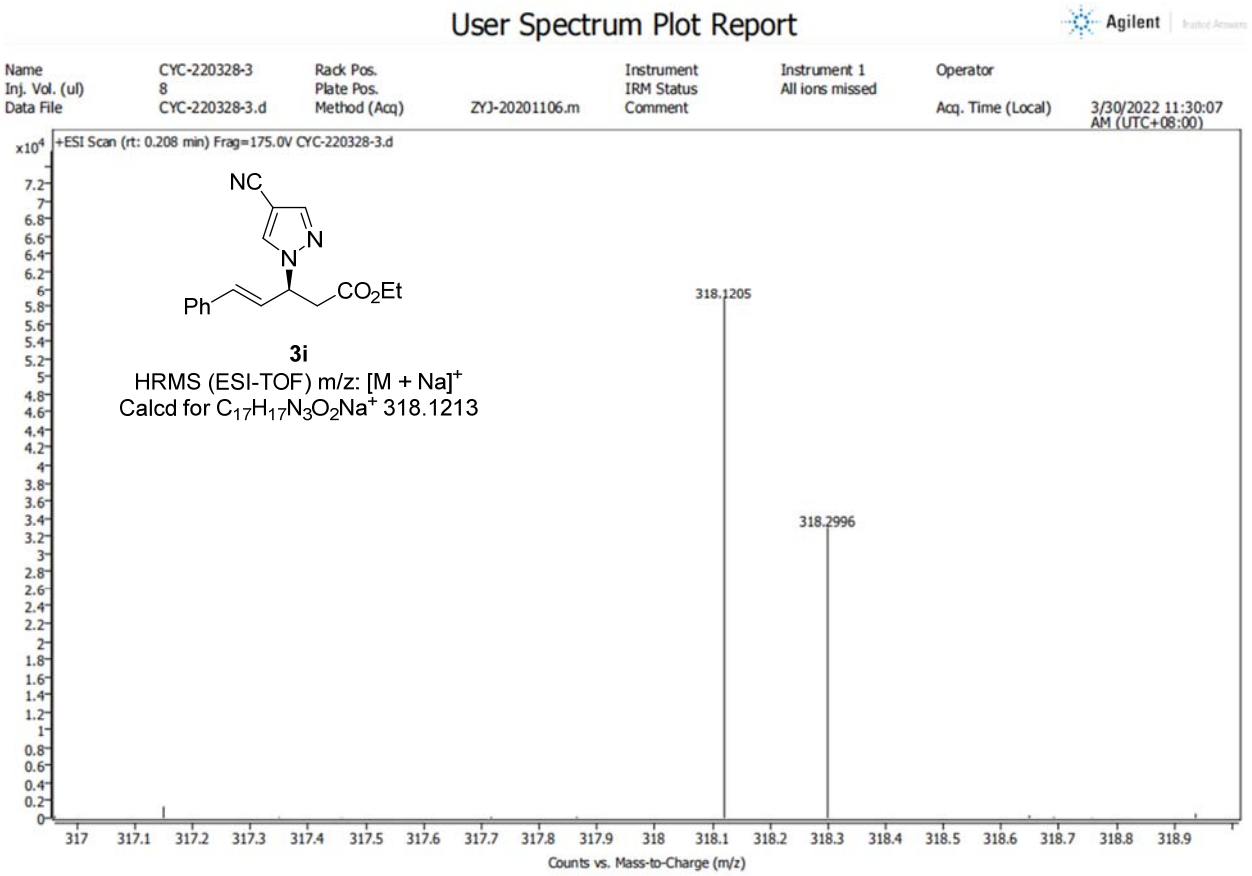
3i

^{1}H-NMR (400 MHz, $CDCl_3$)



3i

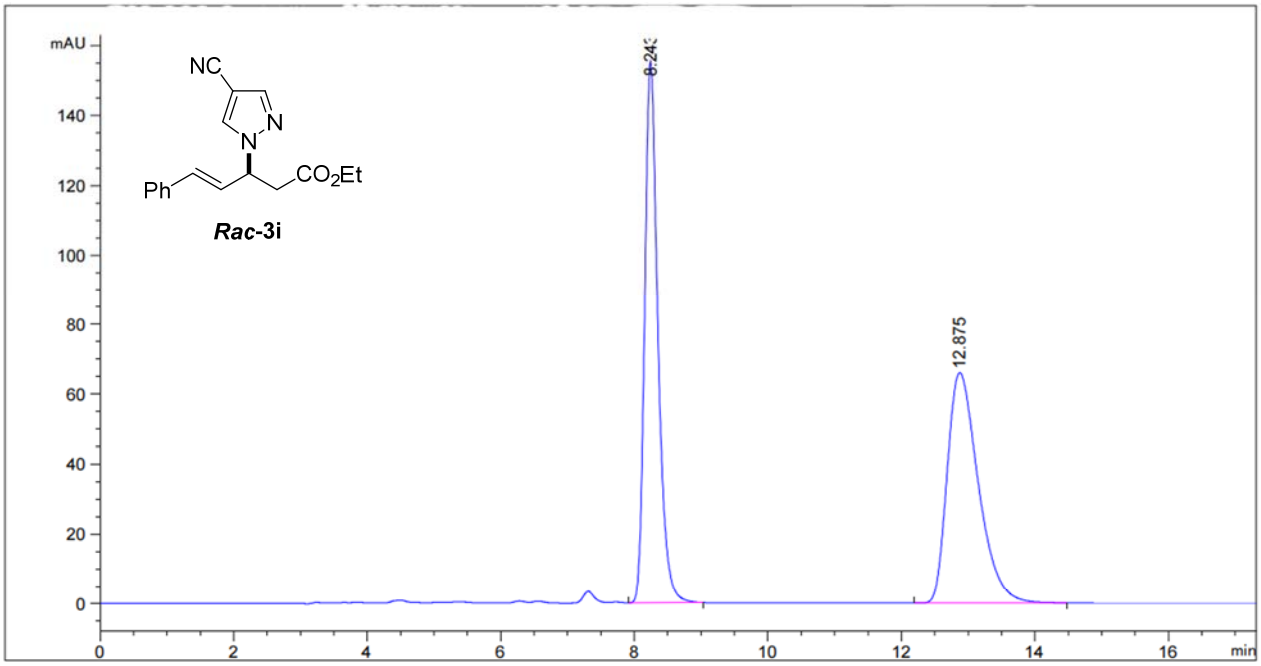
^{13}C-NMR (100 MHz, $CDCl_3$)



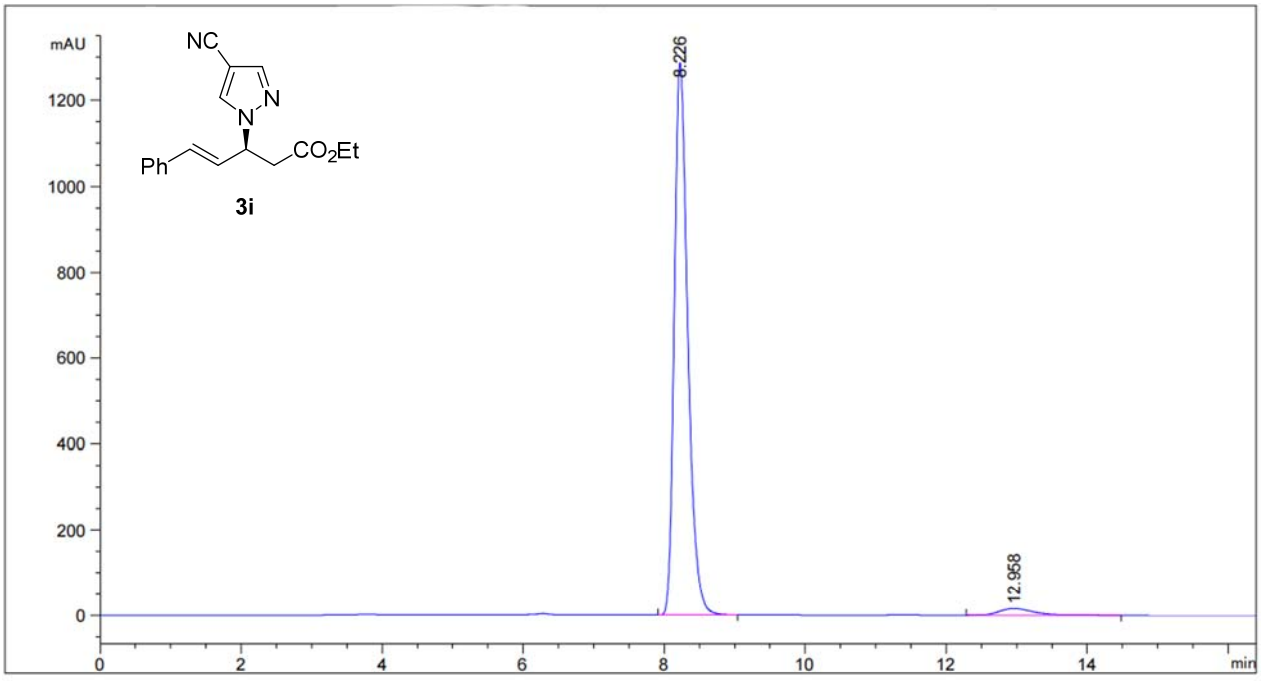
3i

HRMS (ESI-TOF) m/z: $[M + Na]^+$

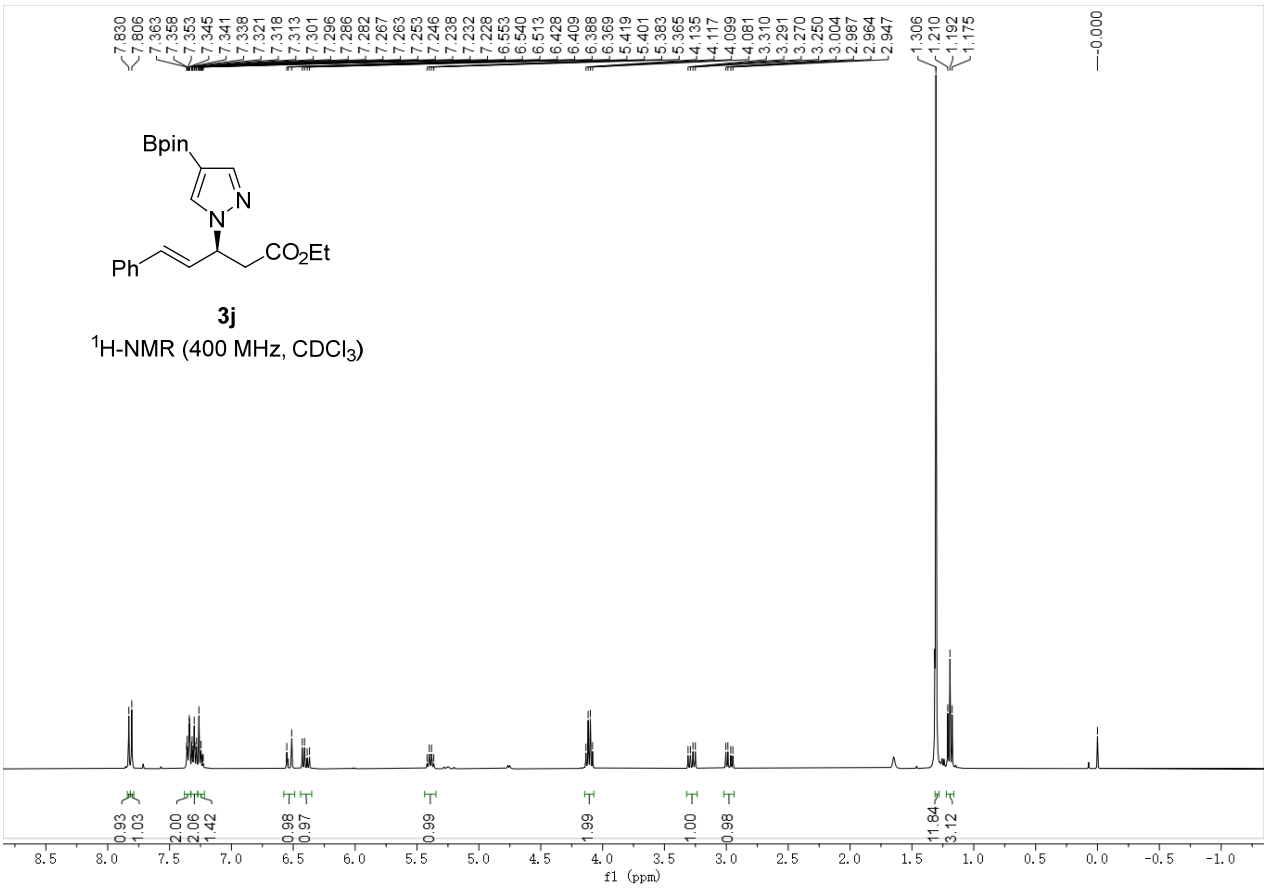
Calcd for $C_{17}H_{17}N_3O_2Na^+$ 318.1213



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.243	BBA	0.2086	2136.41333	155.24393	49.9547
2	12.875	BBA	0.4961	2140.29004	66.02816	50.0453

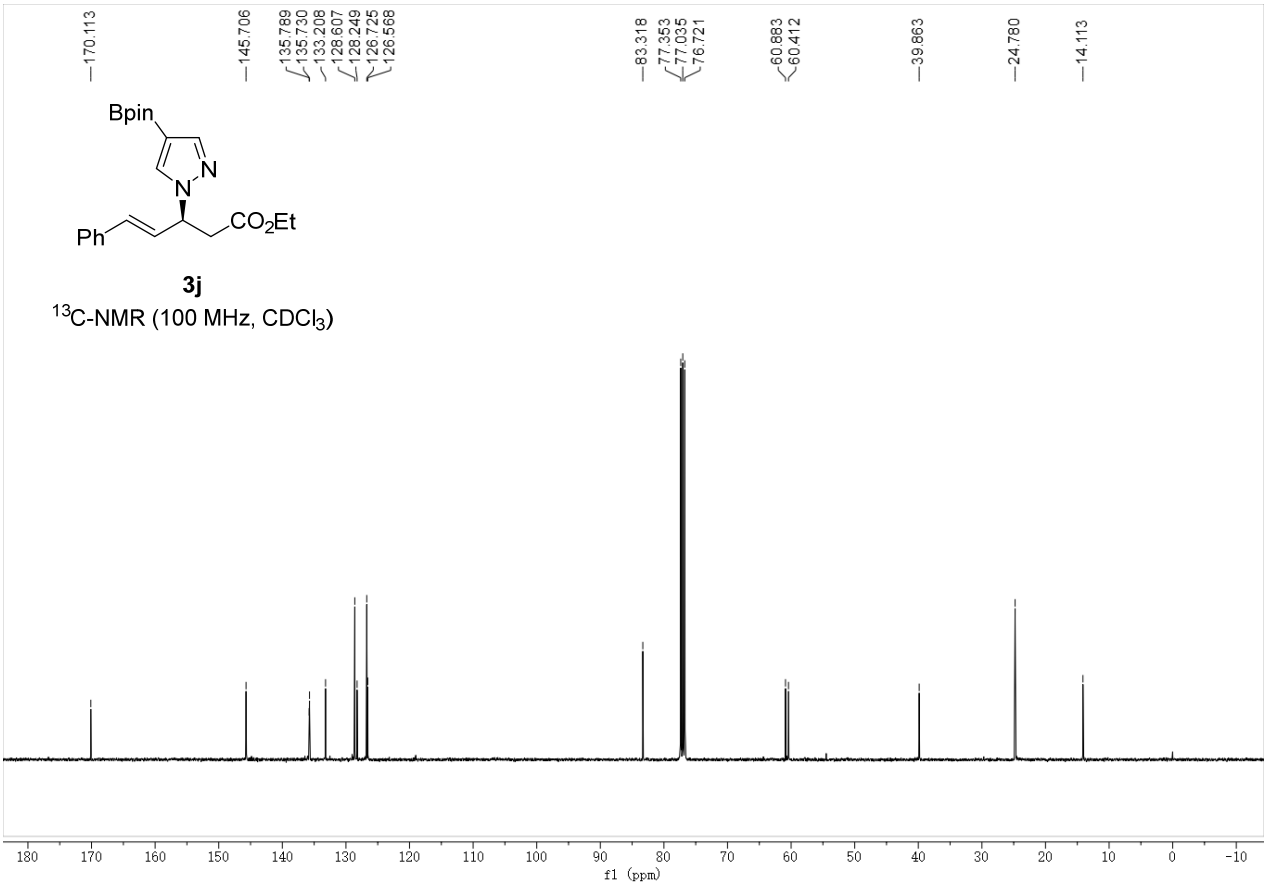


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.226	BBA	0.2036	1.71365e4	1285.32996	97.1574
2	12.958	BBA	0.5010	501.37439	15.44579	2.8426



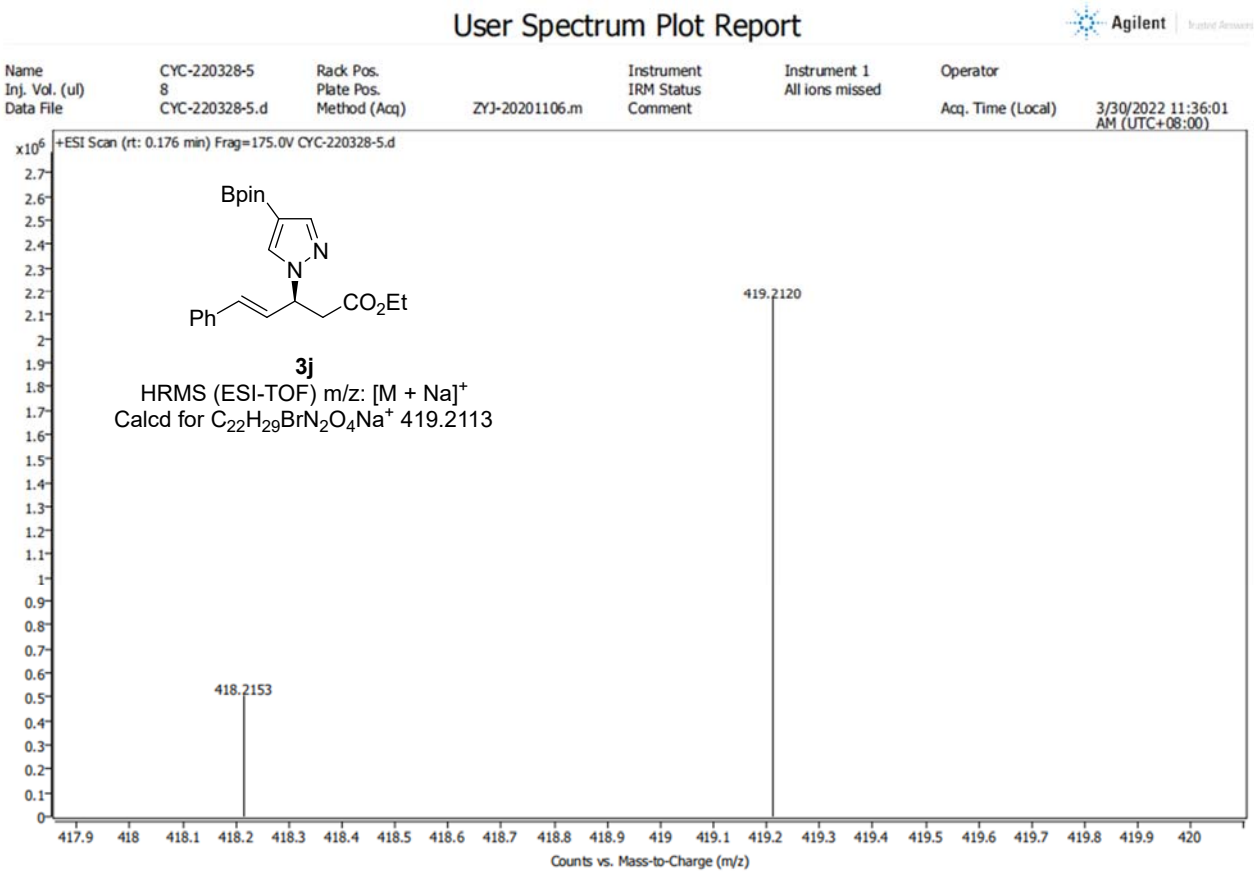
3j

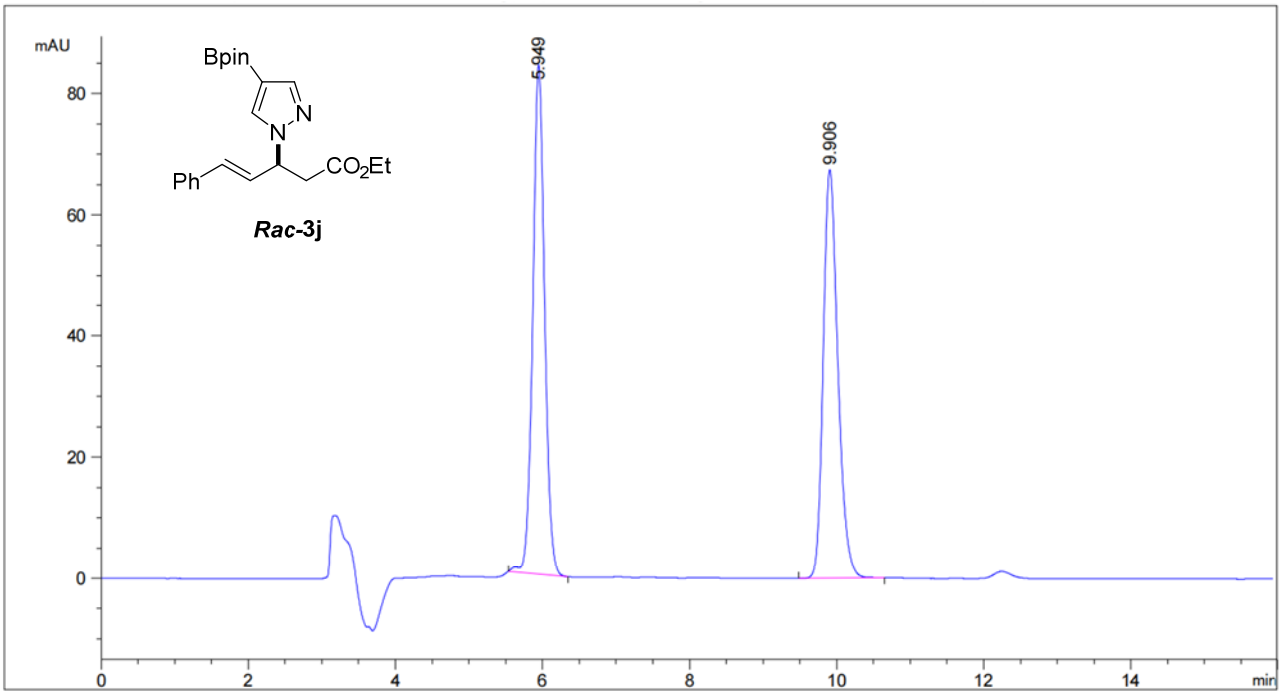
^{1}H-NMR (400 MHz, $CDCl_3$)



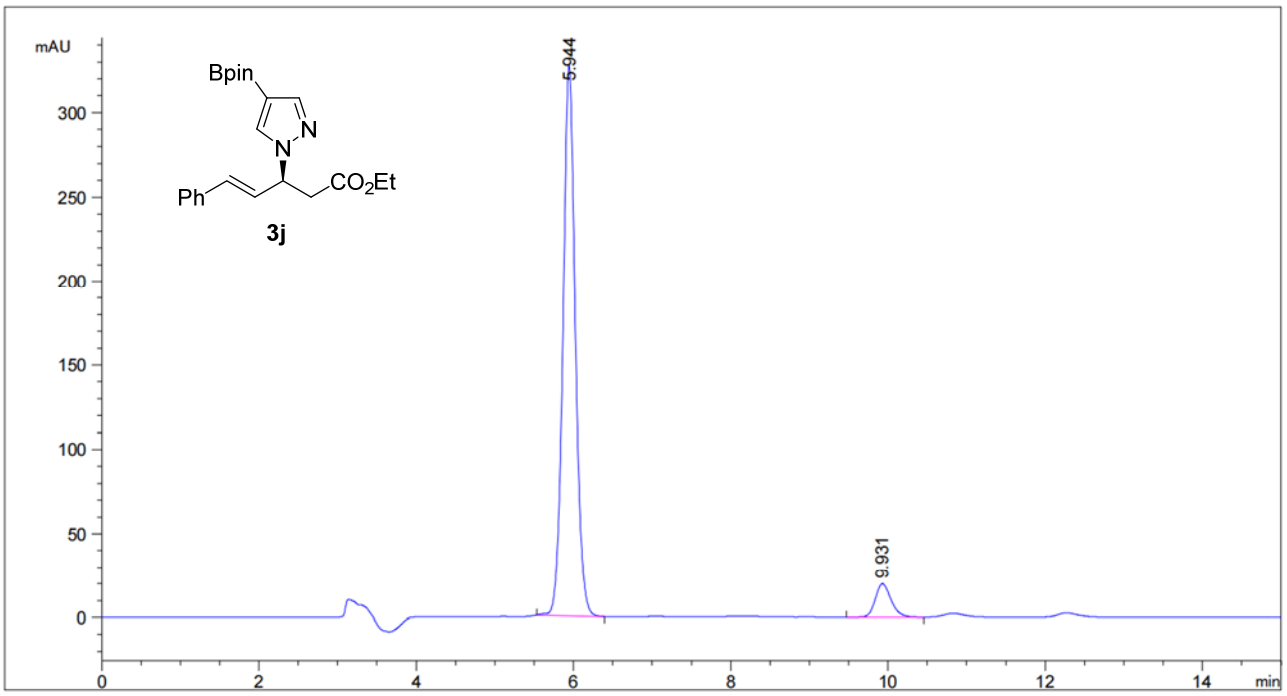
3j

^{13}C-NMR (100 MHz, $CDCl_3$)

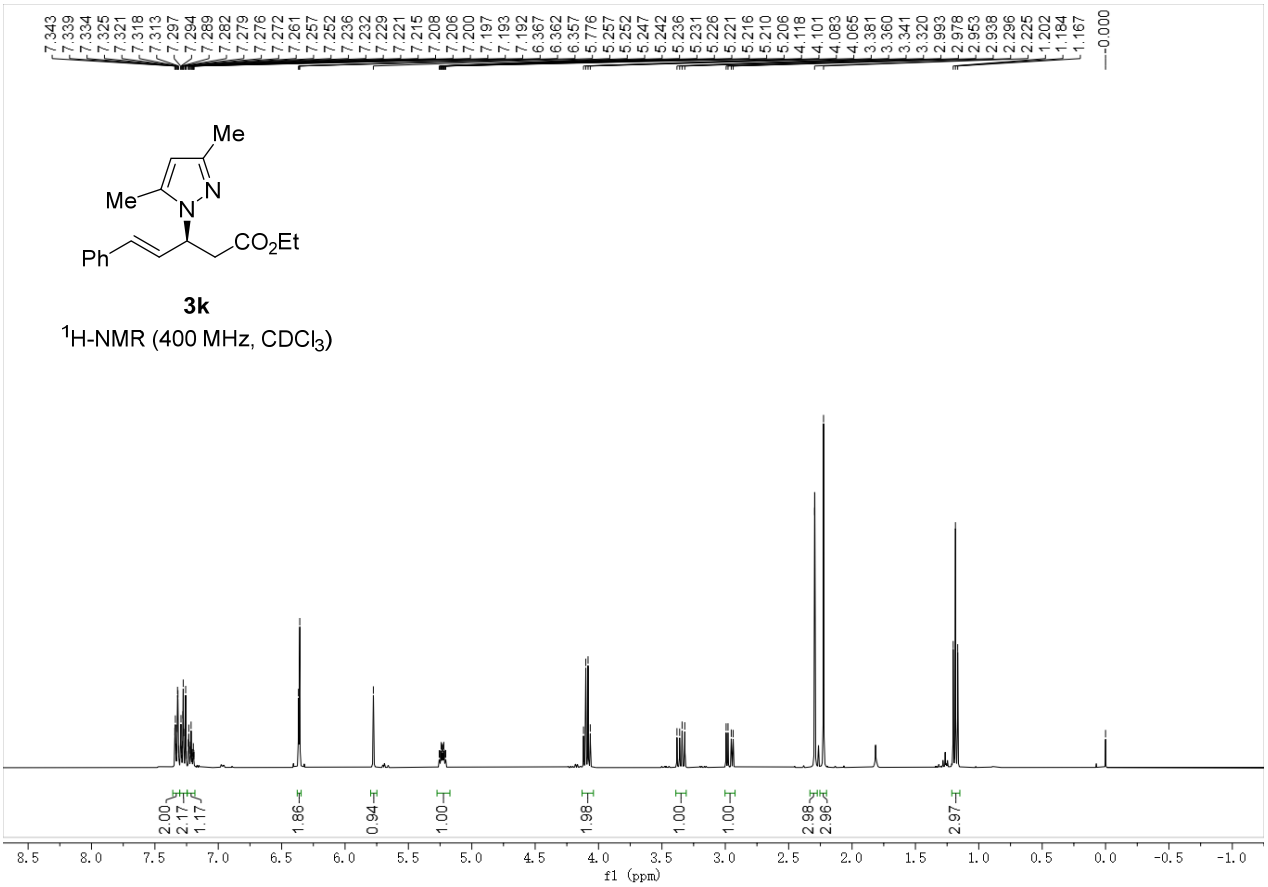

User Spectrum Plot Report
Agilent
Name CYC-220328-5
Inj. Vol. (ul) 8
Data File CYC-220328-5.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/30/2022 11:36:01 AM (UTC+08:00)
+ESI Scan (rt: 0.176 min) Frag=175.0V CYC-220328-5.d
x10^6
Bpin
N
N
CO2Et
Ph
3j
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C22H29BrN2O4Na+ 419.2113
419.2120
418.2153
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.949	BBA	0.1709	937.05402	84.01639	49.8923
2	9.906	BBA	0.2151	941.09955	67.47408	50.1077

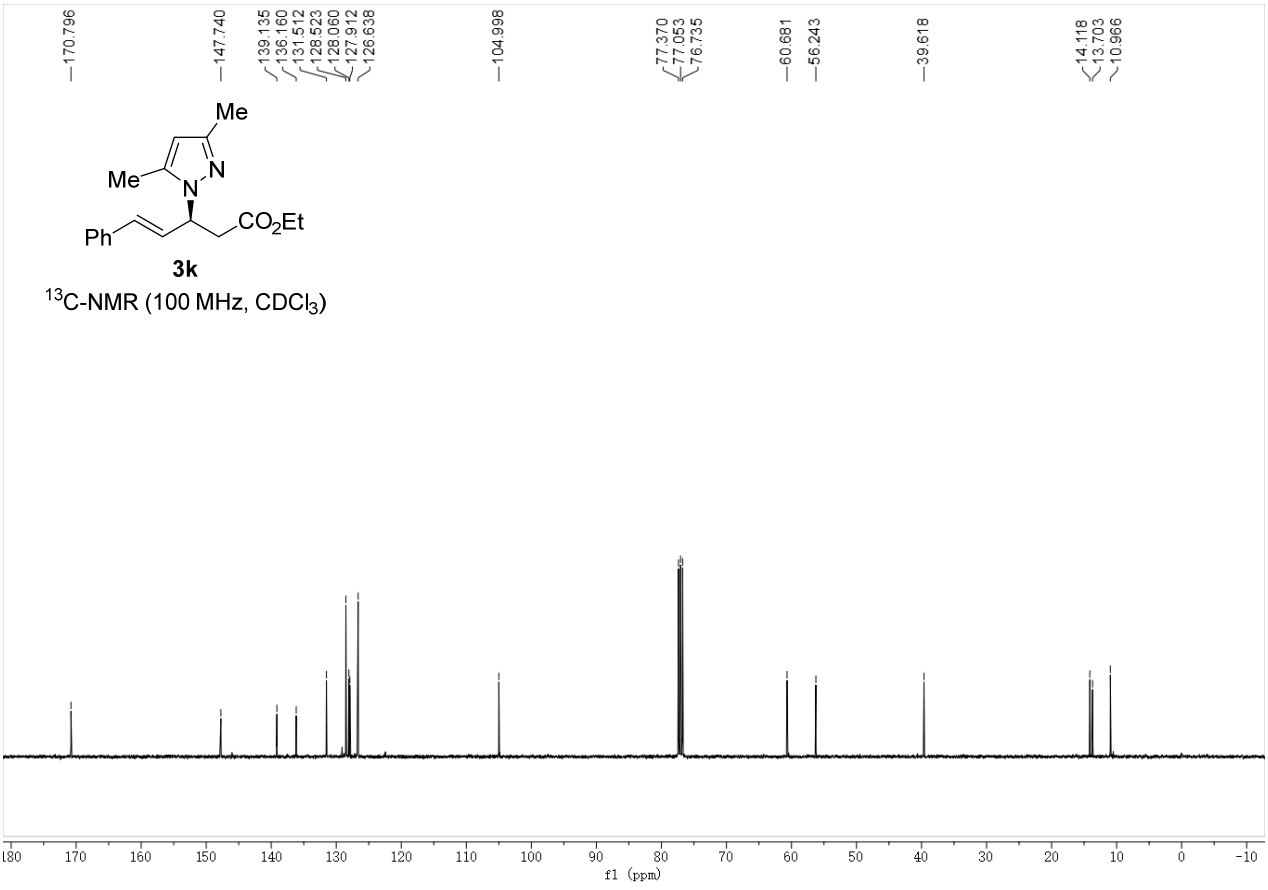


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.944	BBA	0.1652	3567.46777	326.86575	92.8635
2	9.931	BB	0.2138	274.15854	19.81794	7.1365



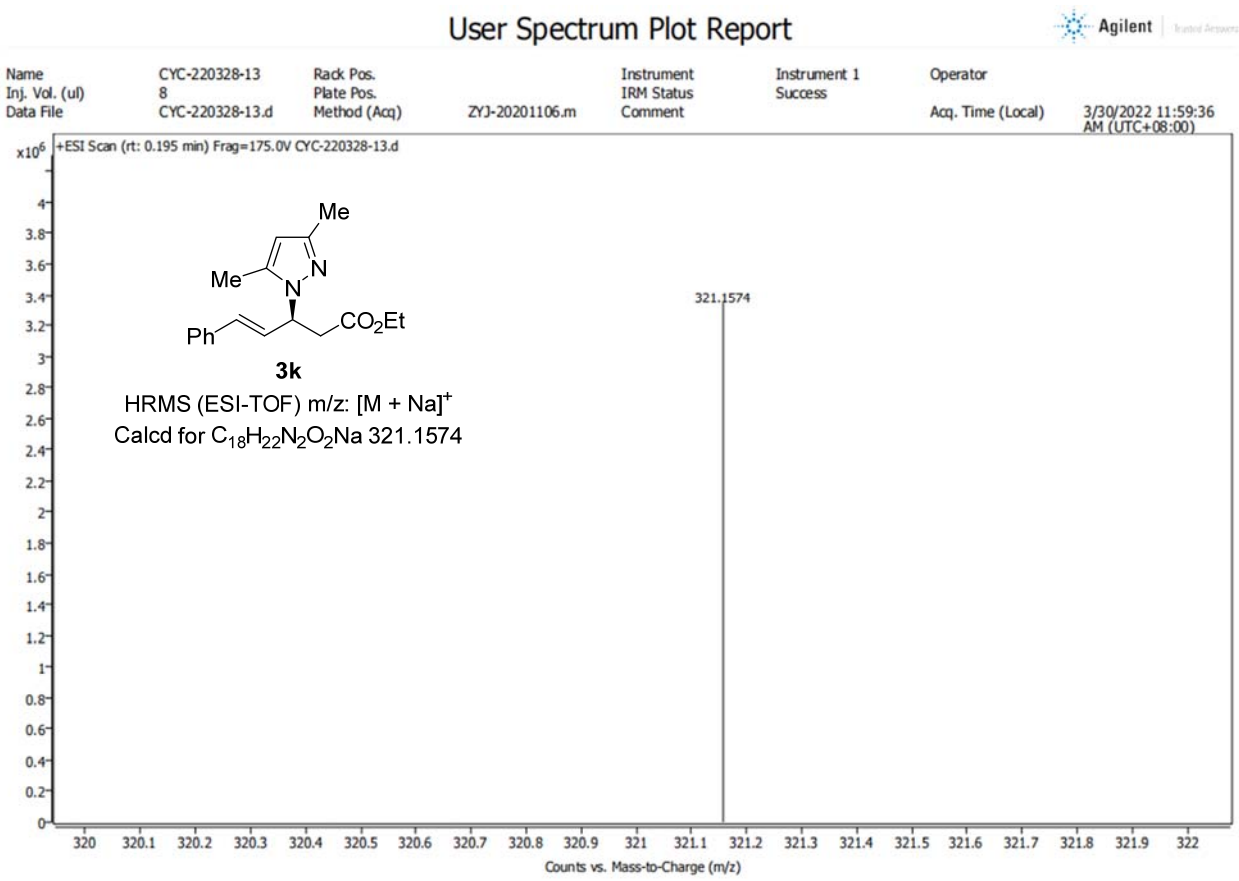
3k

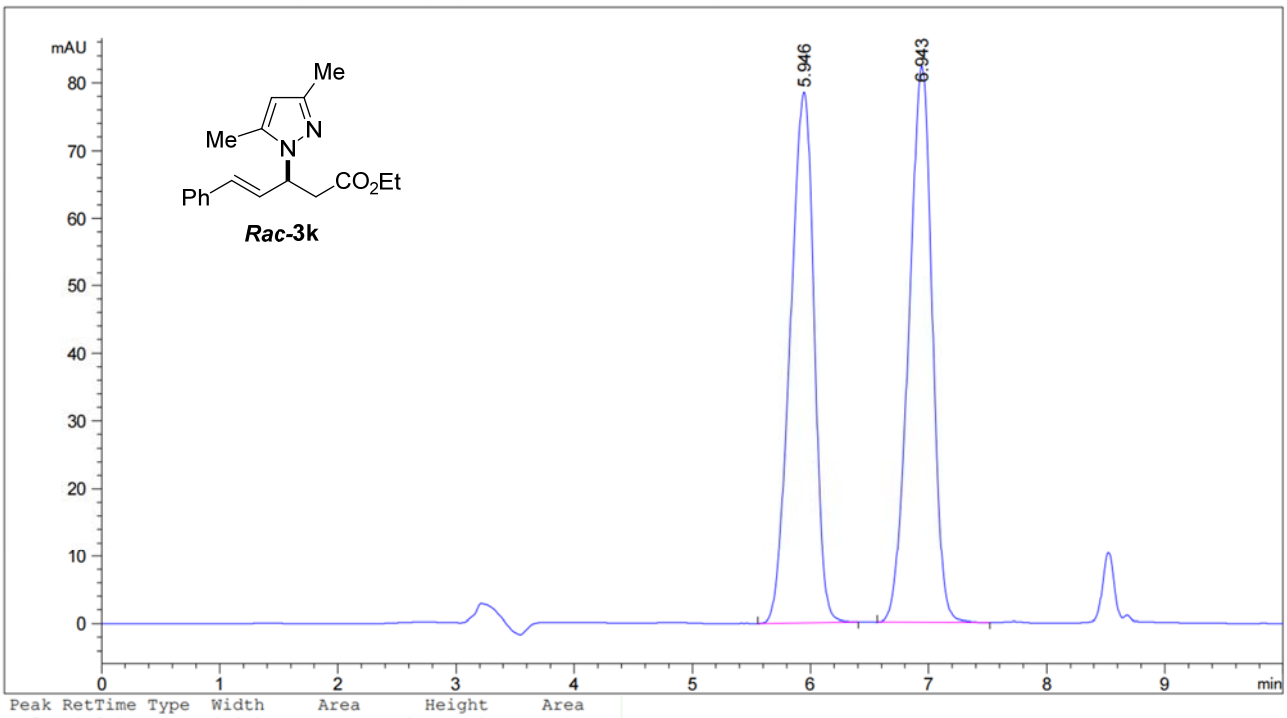
^{1}H-NMR (400 MHz, $CDCl_3$)



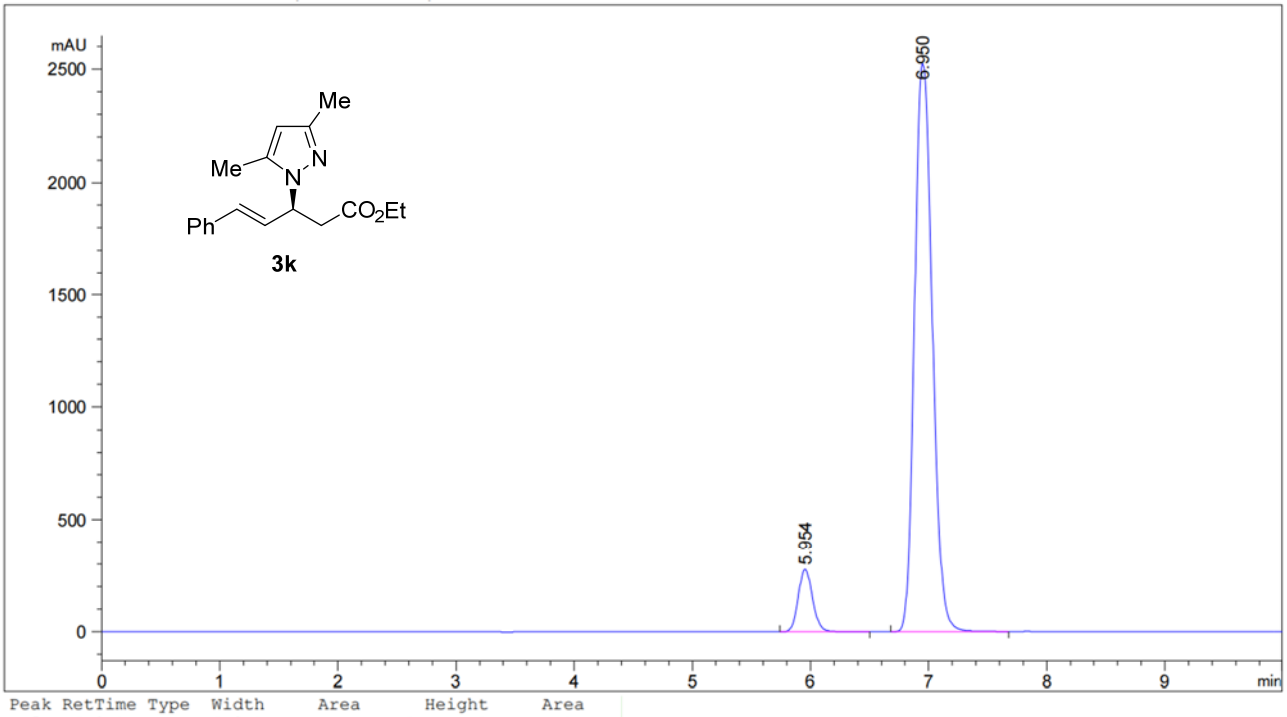
3k

^{13}C-NMR (100 MHz, $CDCl_3$)

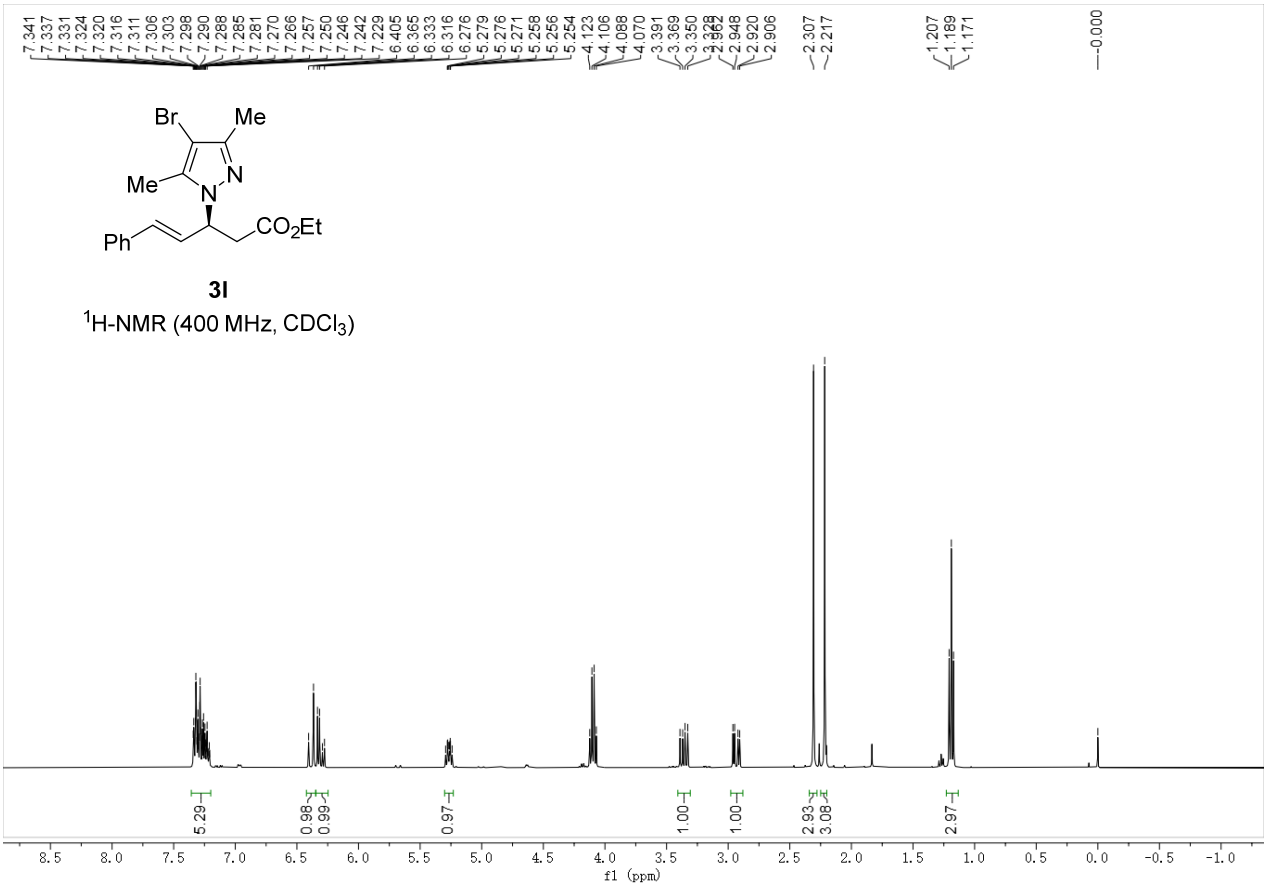

User Spectrum Plot Report
Agilent
Name CYC-220328-13
Inj. Vol. (ul) 8
Data File CYC-220328-13.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
Success
Operator
Acq. Time (Local) 3/30/2022 11:59:36 AM (UTC+08:00)
+ESI Scan (rt: 0.195 min) Frag=175.0V CYC-220328-13.d
x10^6
Me
Me
N
N
Ph
CO2Et
3k
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C18H22N2O2Na 321.1574
321.1574
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.946	BB	0.2201	1098.37927	78.48659	49.3410
2	6.943	BB	0.2109	1127.71887	82.25845	50.6590

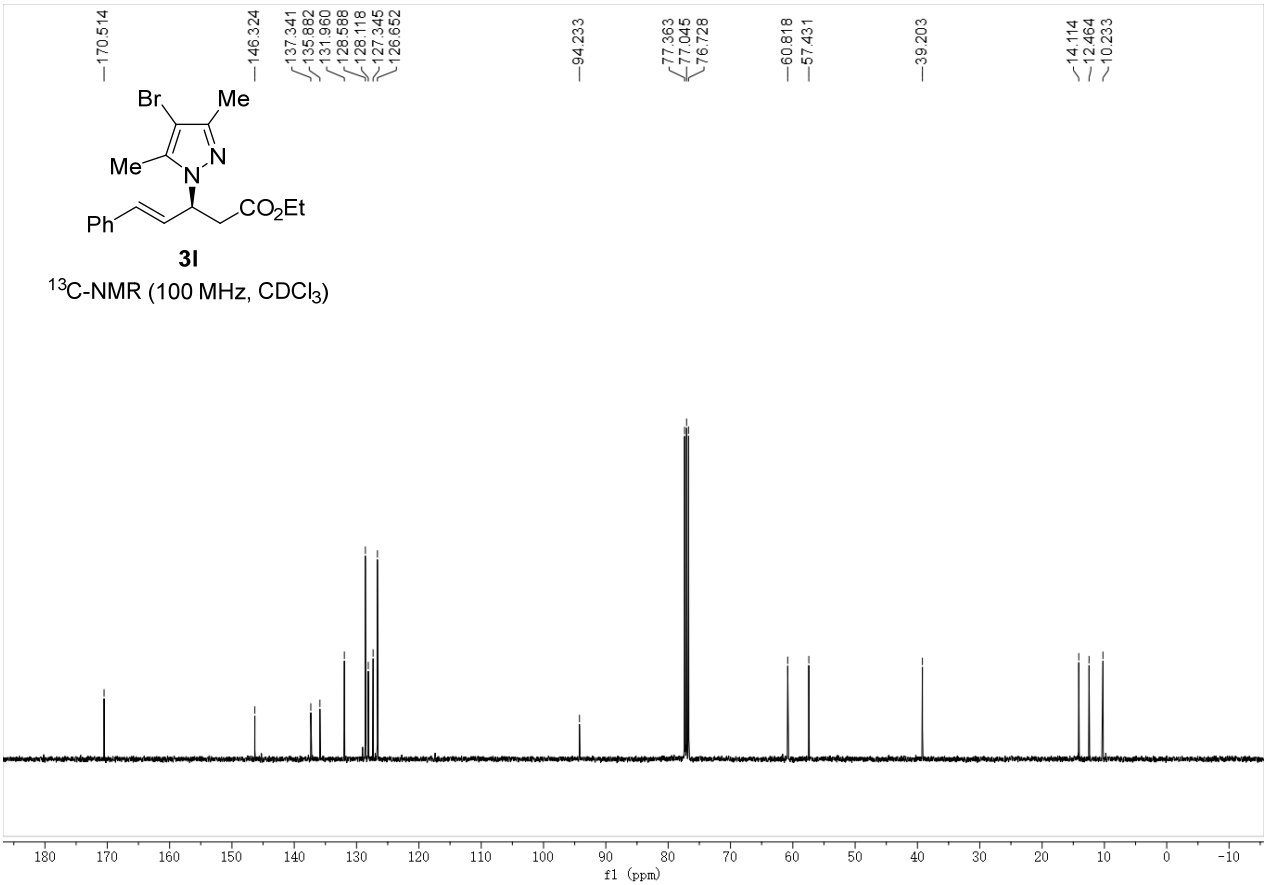


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.954	VB	0.1306	2331.44336	275.84317	8.1209
2	6.950	BBA	0.1656	2.63778e4	2523.33301	91.8791



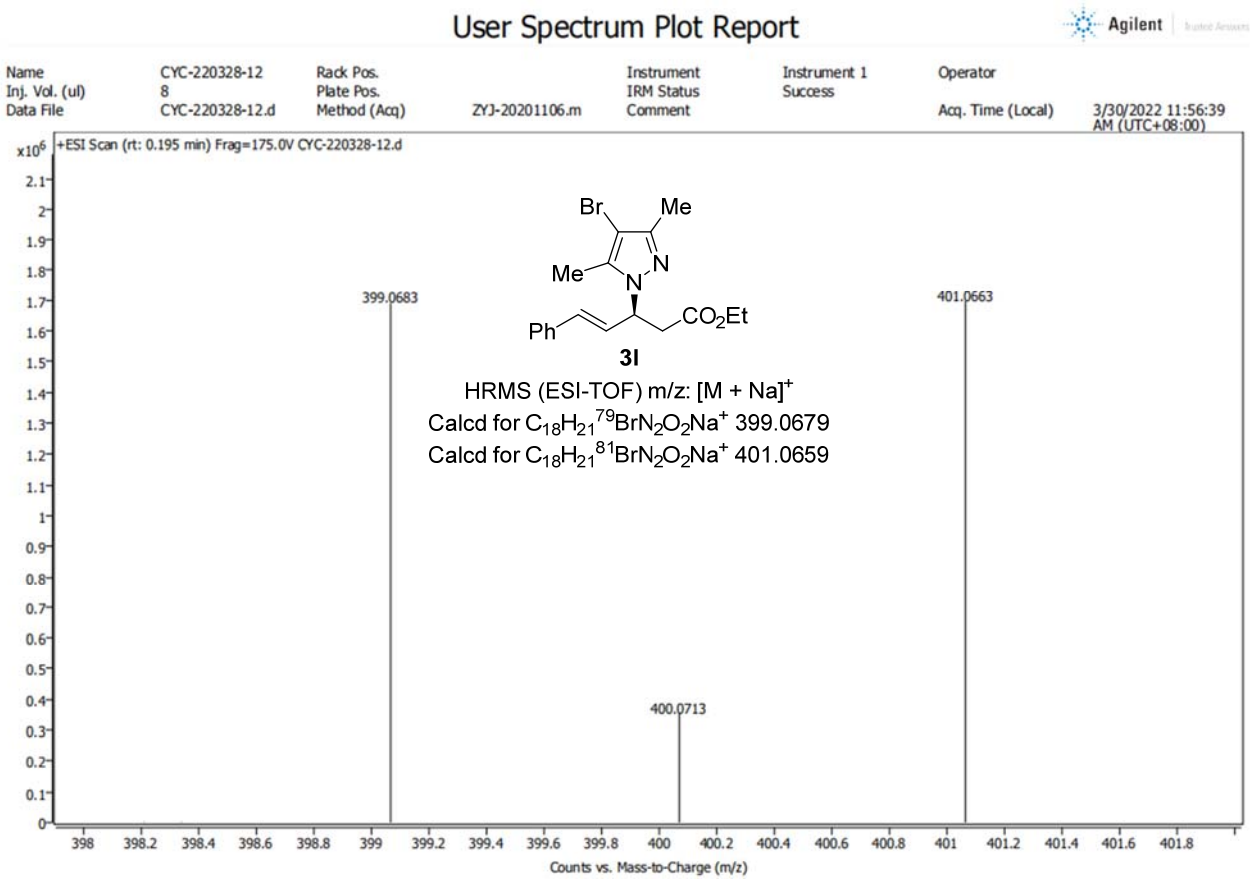
3l

^{1}H-NMR (400 MHz, $CDCl_3$)



3l

^{13}C-NMR (100 MHz, $CDCl_3$)

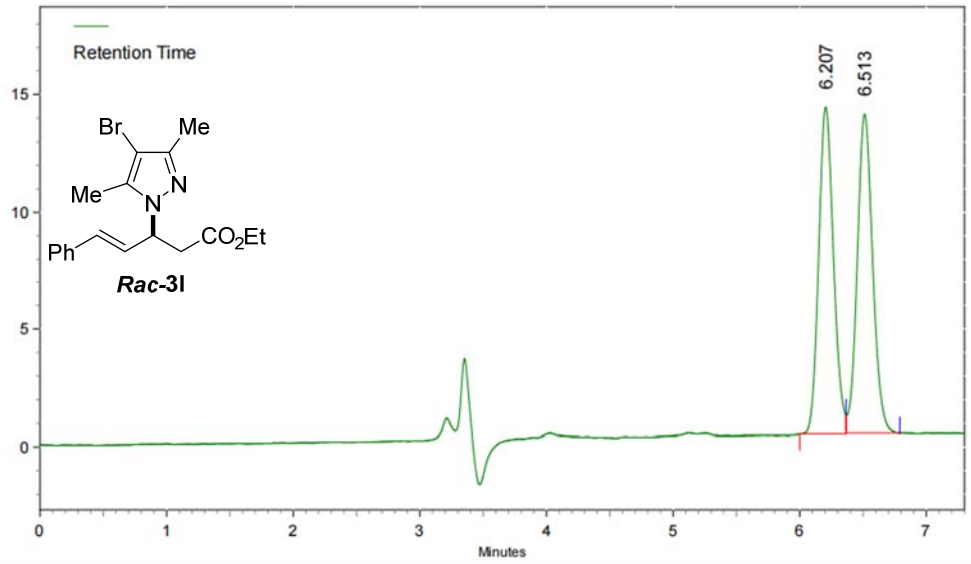


3l

HRMS (ESI-TOF) m/z: $[M + Na]^+$

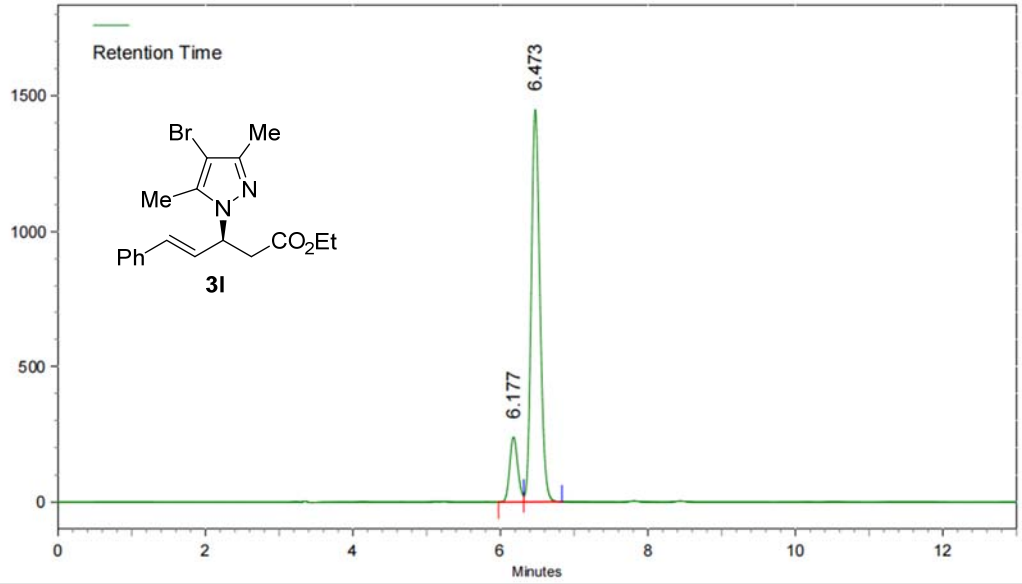
Calcd for $C_{18}H_{21}{}^{79}BrN_2O_2Na^+$ 399.0679

Calcd for $C_{18}H_{21}{}^{81}BrN_2O_2Na^+$ 401.0659



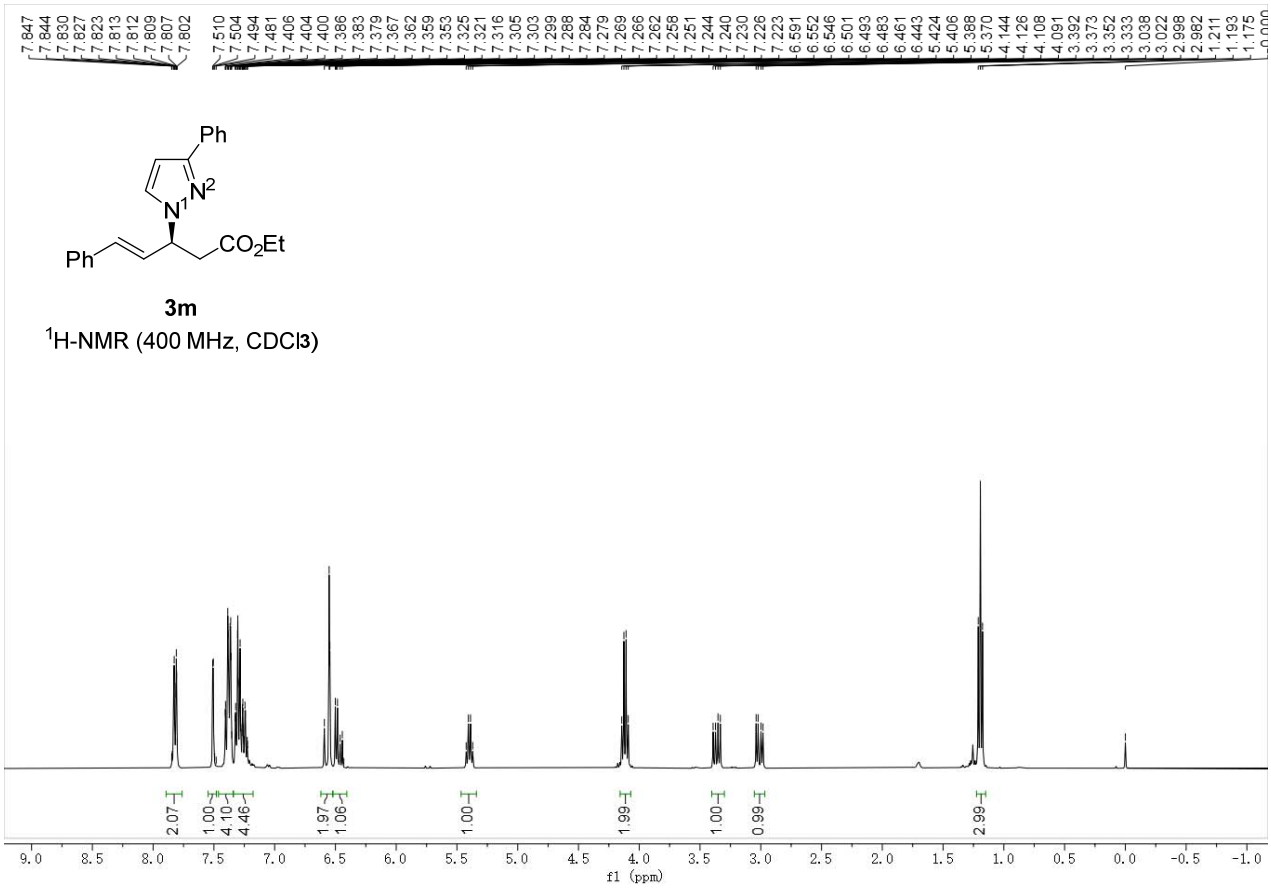
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.207	0.367	233428	1896017	49.6296
2	6.513	0.425	227800	1924319	50.3704
Totals			461228	3820336	100.0000



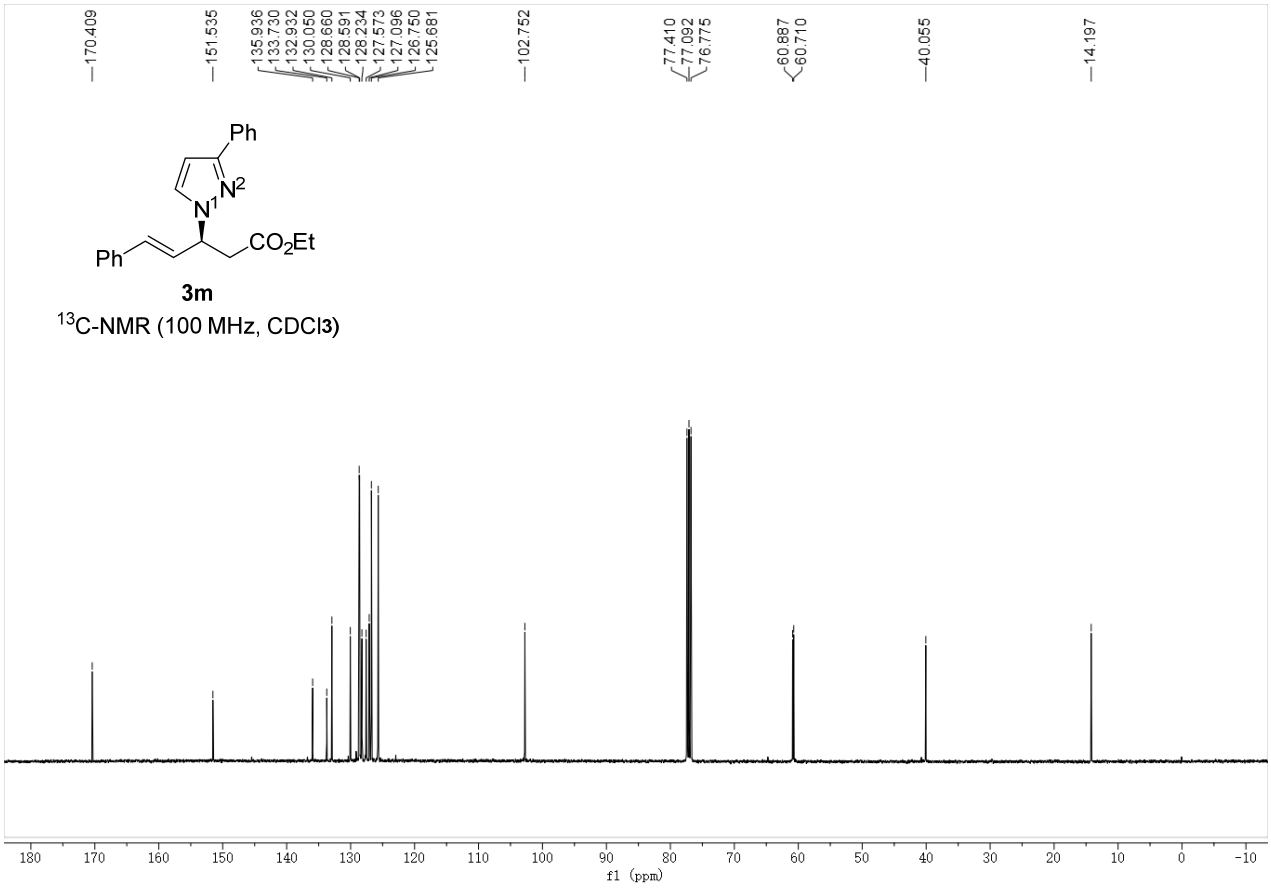
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.177	0.343	3987181	30736017	13.4132
2	6.473	0.517	24271114	198411045	86.5868
Totals			28258295	229147062	100.0000



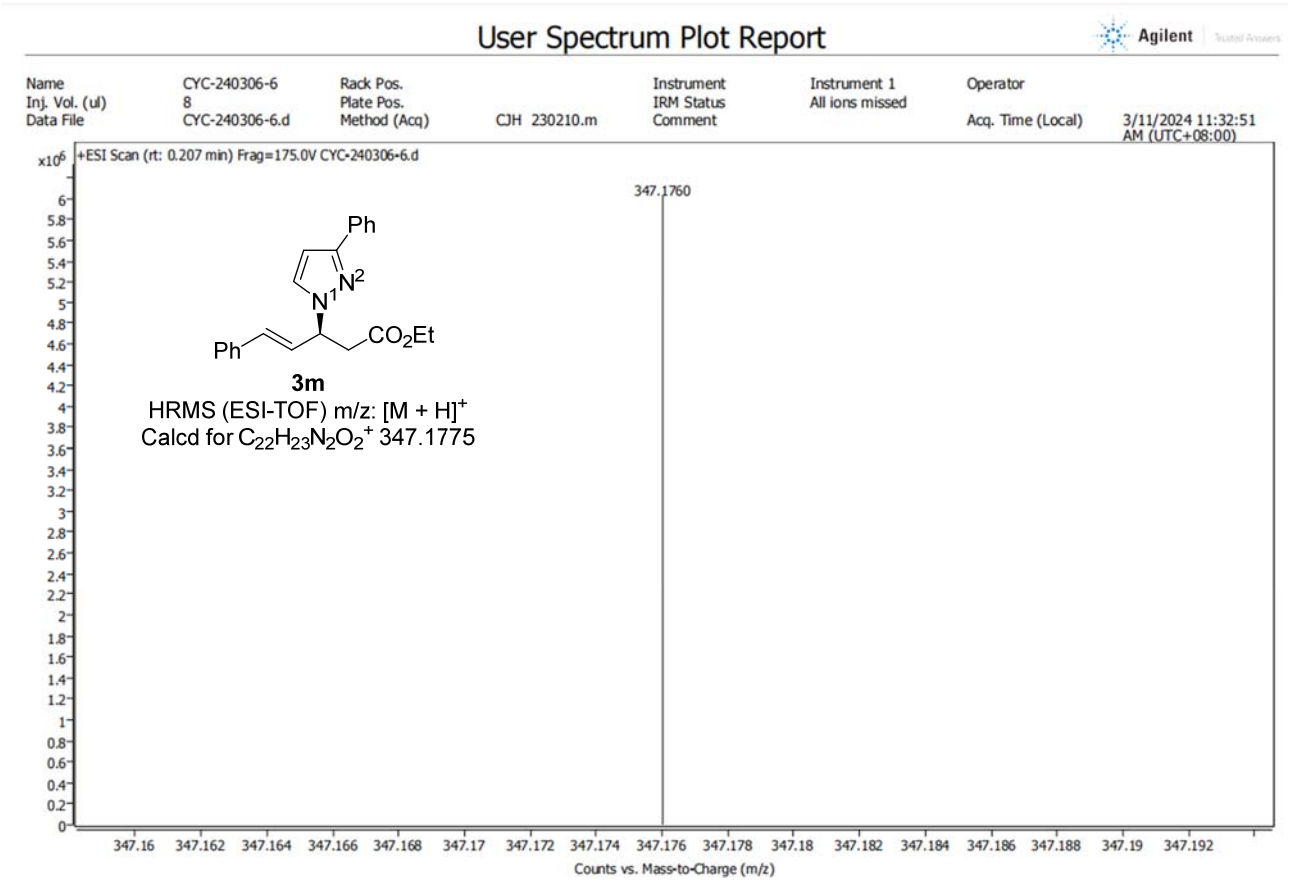
3m

^{1}H-NMR (400 MHz, CDCl3)



3m

^{13}C-NMR (100 MHz, CDCl3)


User Spectrum Plot Report
Agilent
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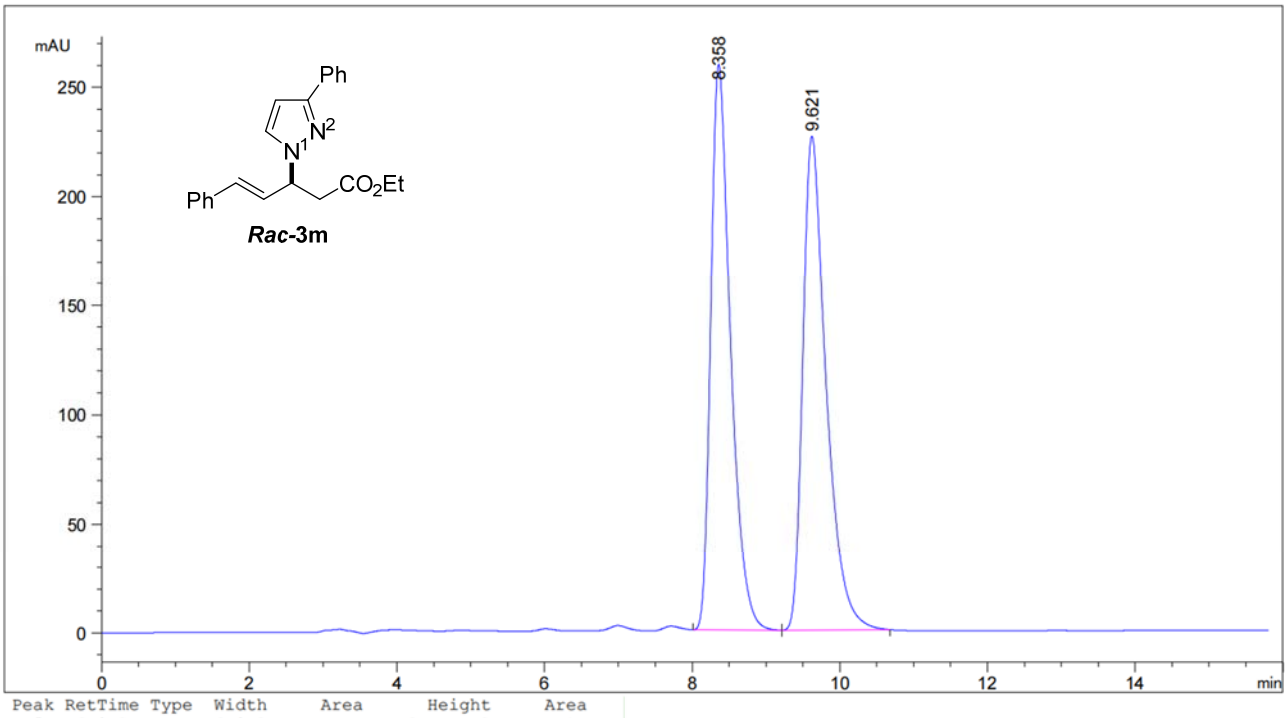
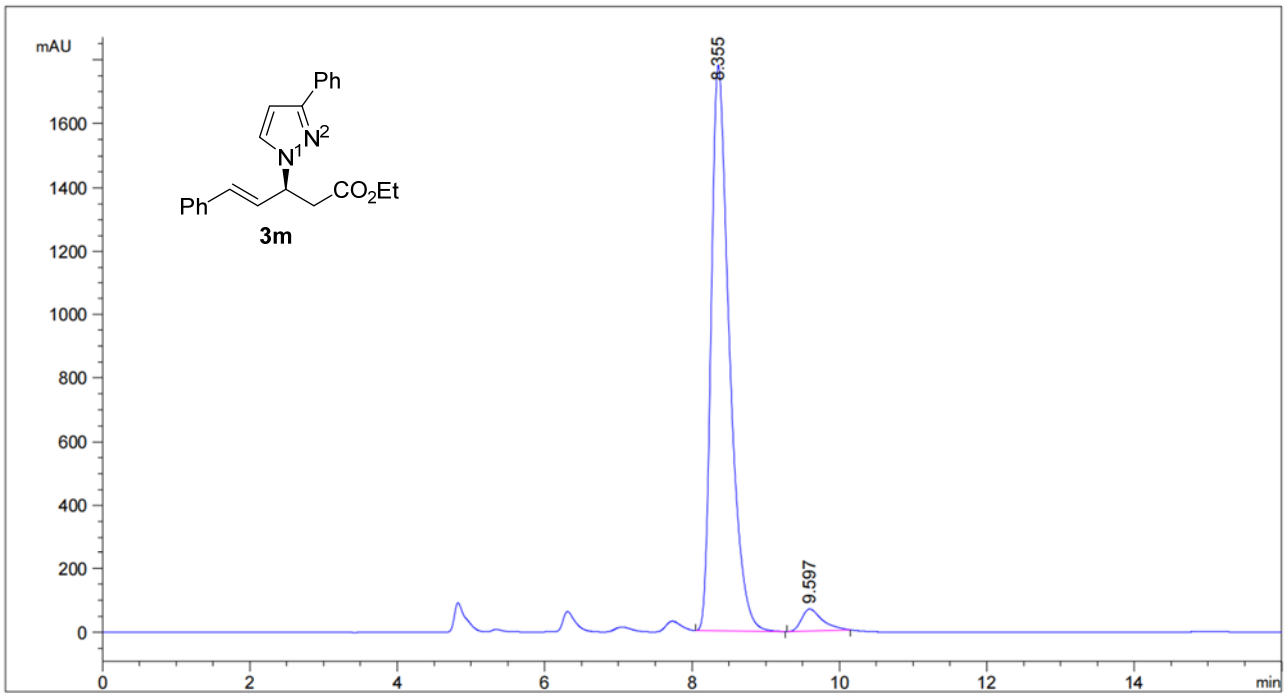
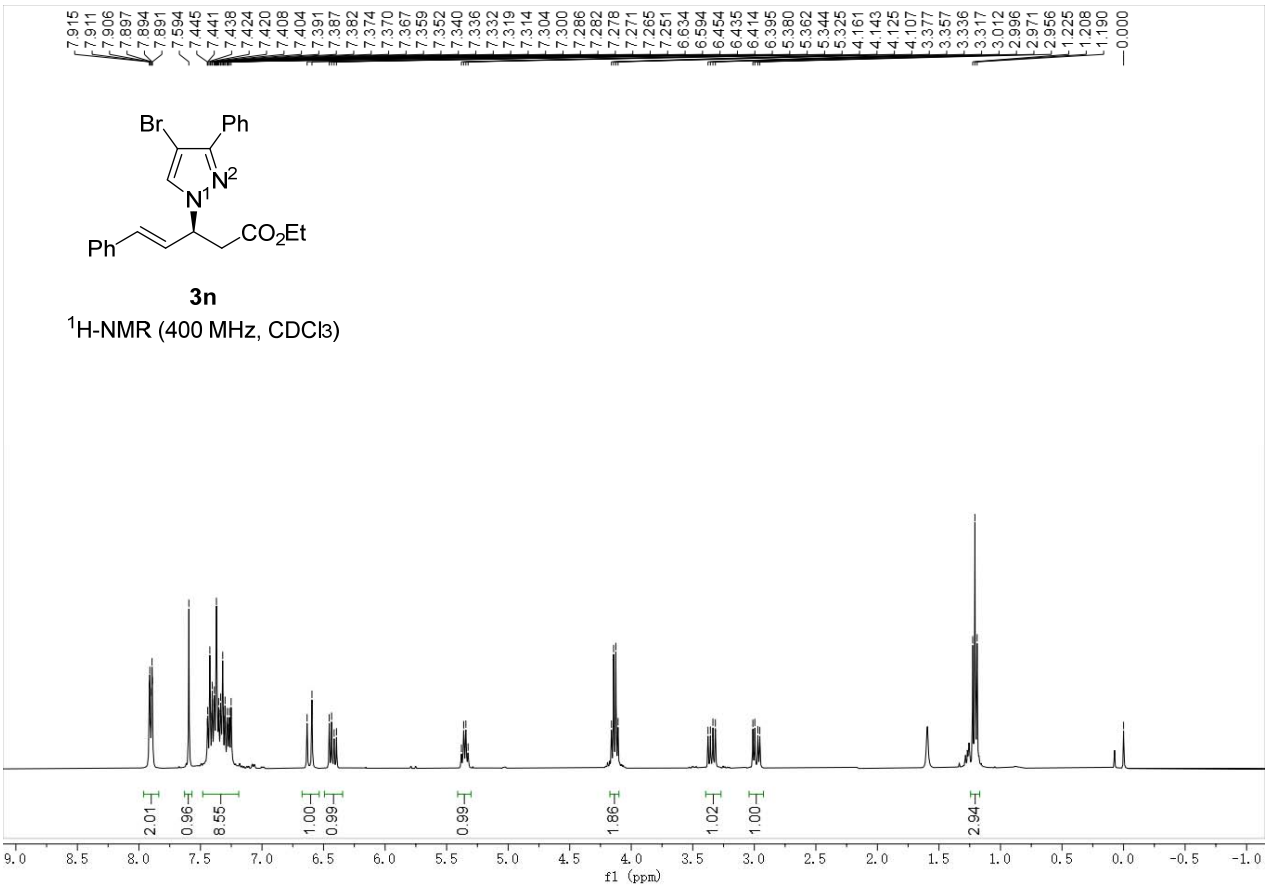
Inj. Vol. (ul) 8
Data File CYC-240306-6.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:32:51 AM (UTC+08:00)
+ESI Scan (rt: 0.207 min) Frag=175.0V CYC-240306-6.d
x10^6
347.1760
Ph
N2
N1
CO2Et
Ph
3m
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C22H23N2O2+ 347.1775
347.16 347.162 347.164 347.166 347.168 347.17 347.172 347.174 347.176 347.178 347.18 347.182 347.184 347.186 347.188 347.19 347.192
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.358	BB	0.2799	4824.40967	259.00995	49.2537
2	9.621	BBA	0.3261	4970.61865	226.35707	50.7463

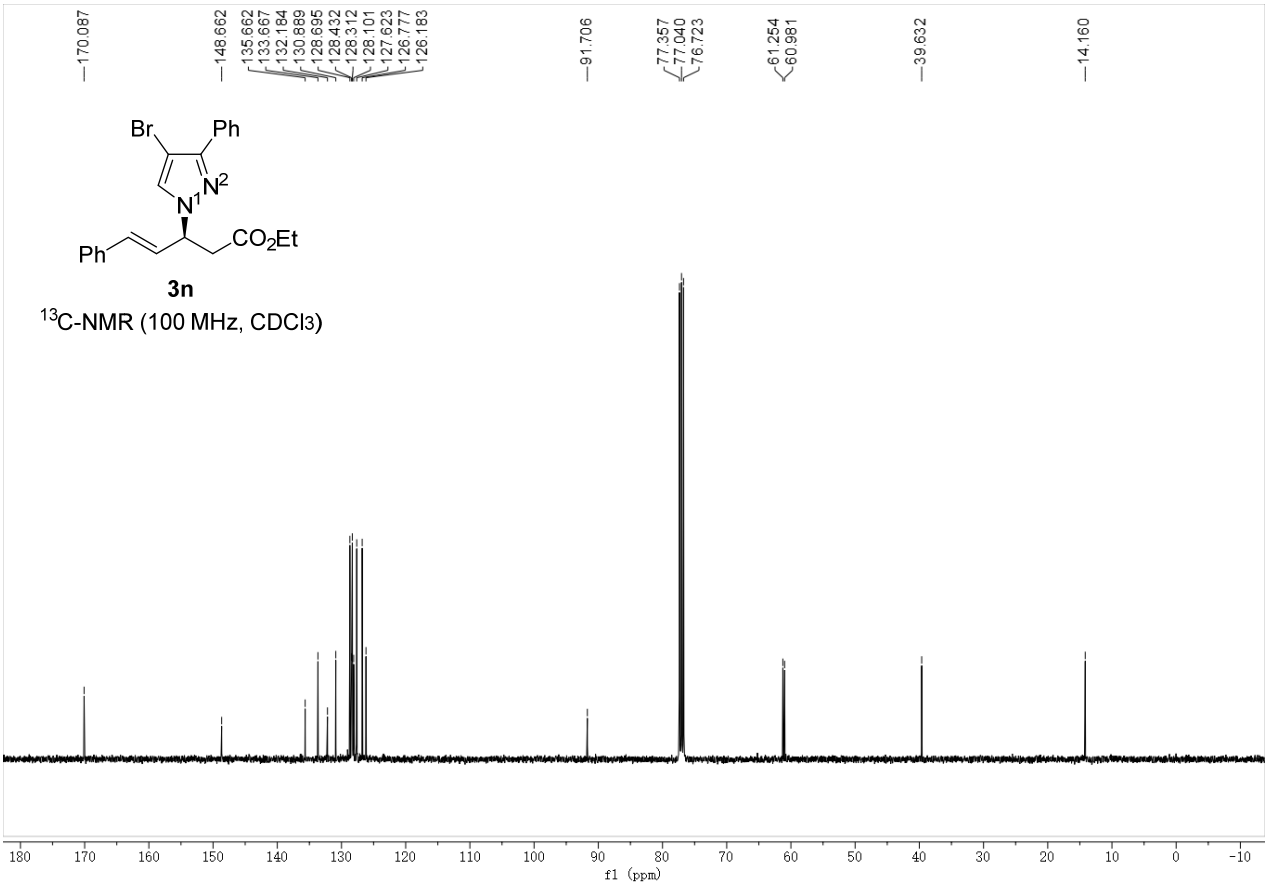


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.355	BB	0.2574	3.05841e4	1778.55798	95.8240
2	9.597	BBA	0.2899	1332.83826	68.42090	4.1760



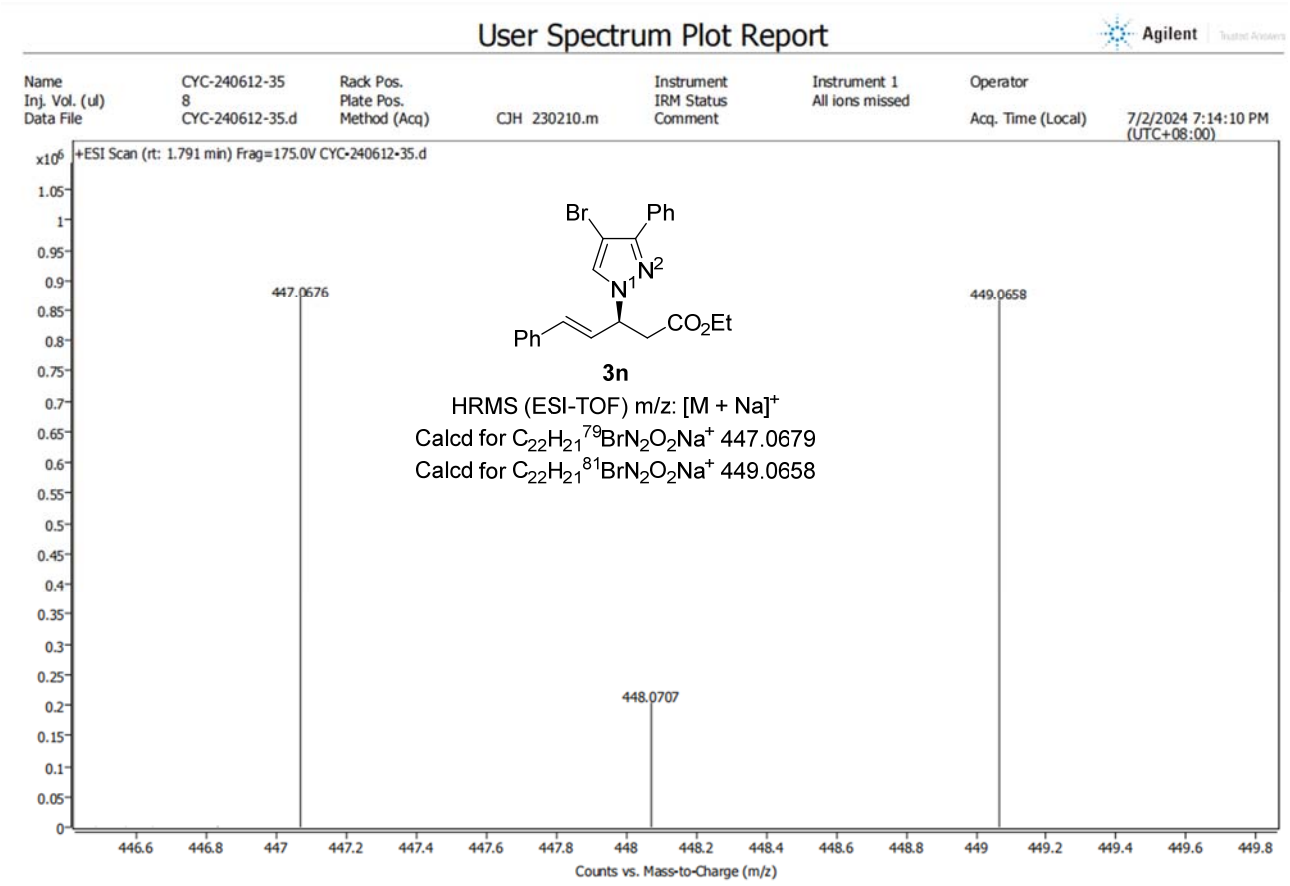
3n

^{1}H-NMR (400 MHz, $CDCl_3$)



3n

^{13}C-NMR (100 MHz, $CDCl_3$)

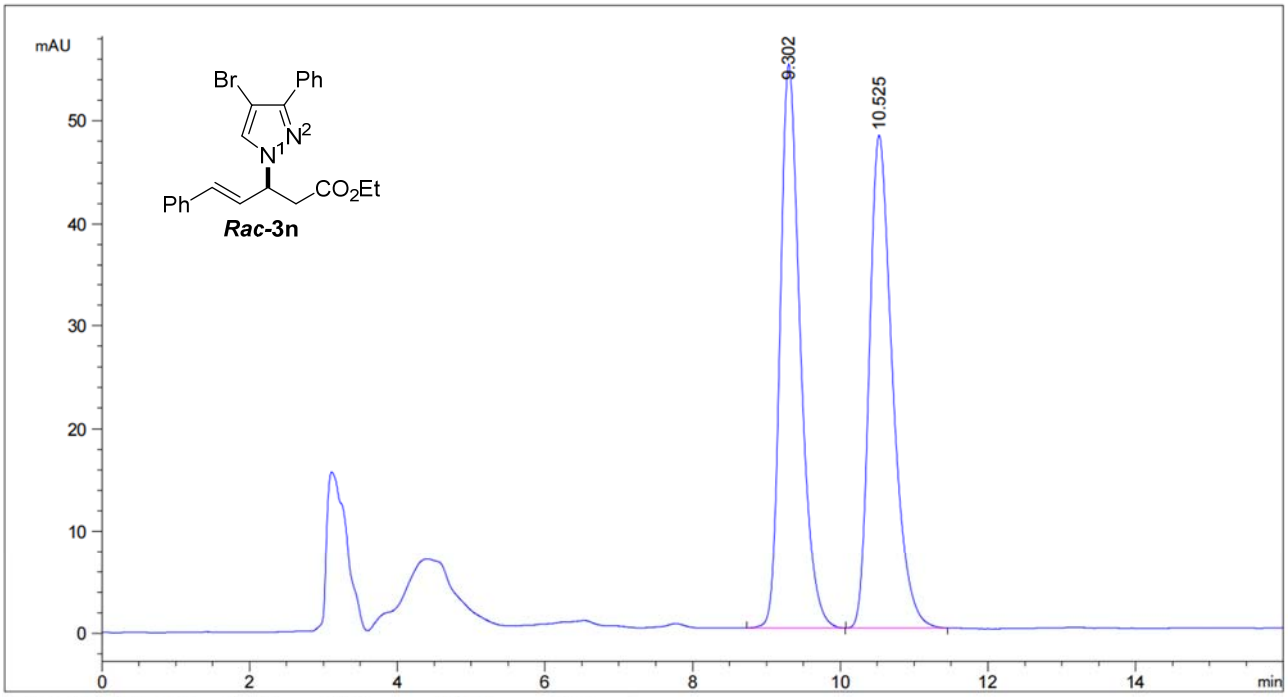


3n

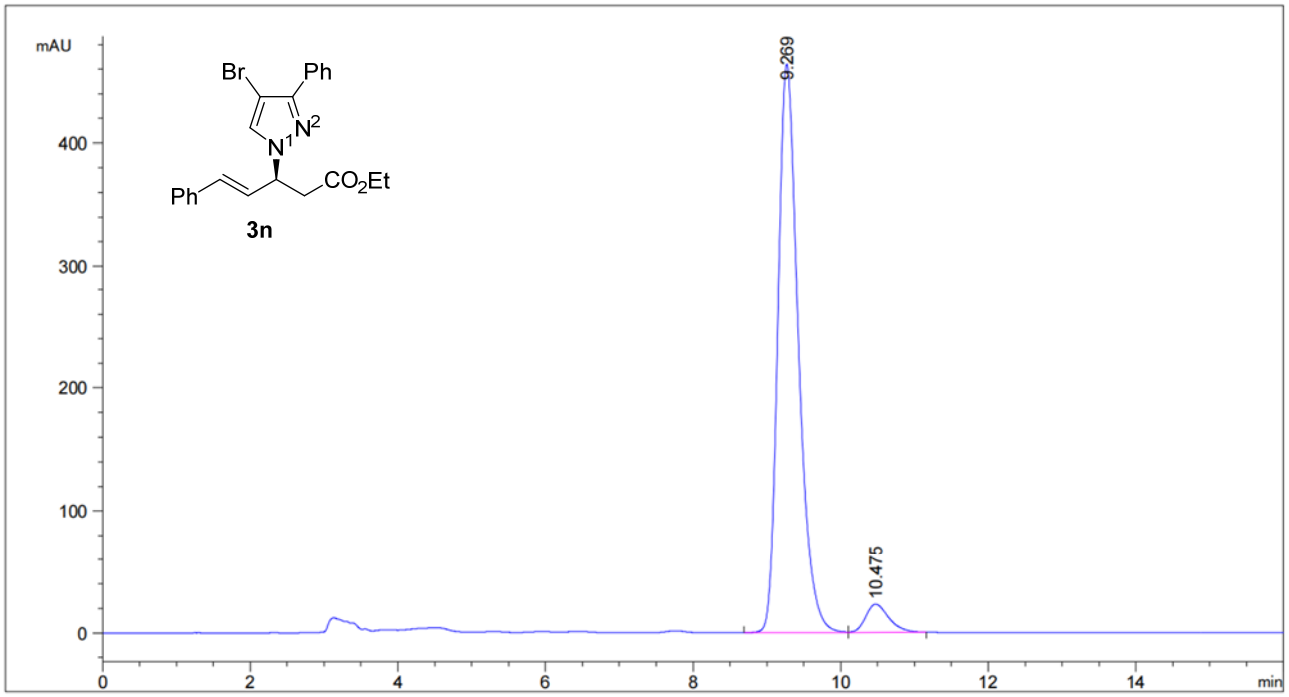
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{22}H_{21}{}^{79}BrN_2O_2Na^+$ 447.0679

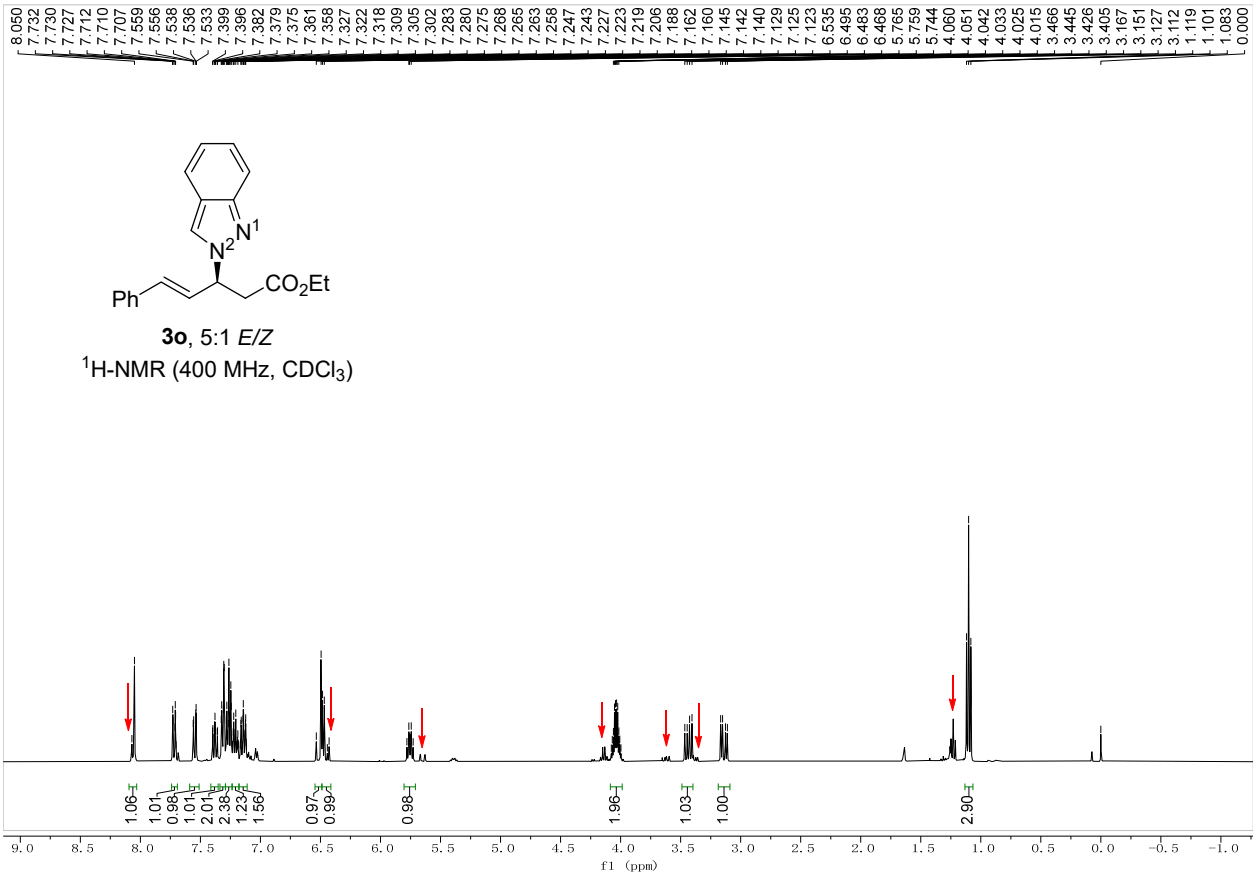
Calcd for $C_{22}H_{21}{}^{81}BrN_2O_2Na^+$ 449.0658



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.302	BB	0.2880	1042.46033	55.01510	49.8713
2	10.525	BB	0.3313	1047.84167	48.09887	50.1287

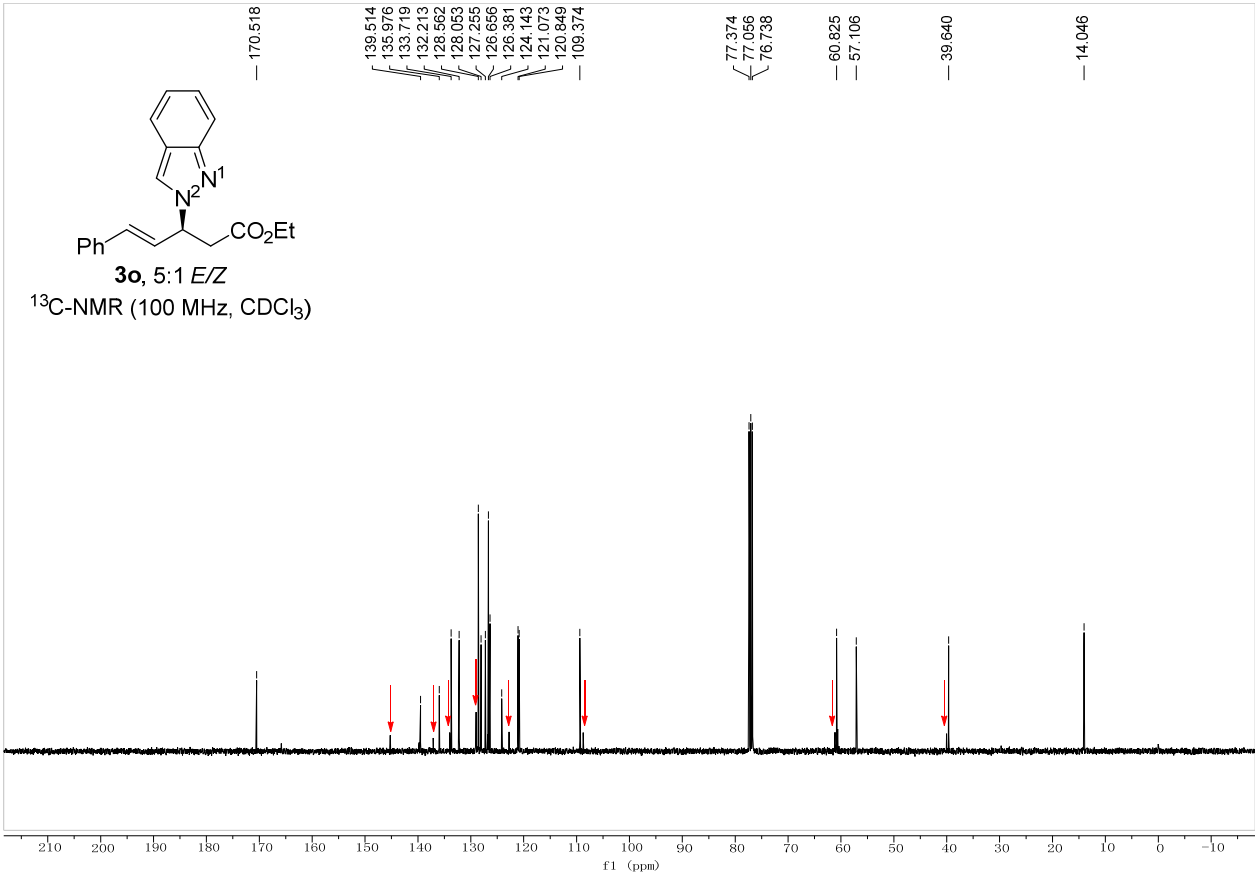


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.269	BV	0.2944	8919.68262	463.48798	94.6827
2	10.475	VBA	0.3329	500.92084	23.11647	5.3173



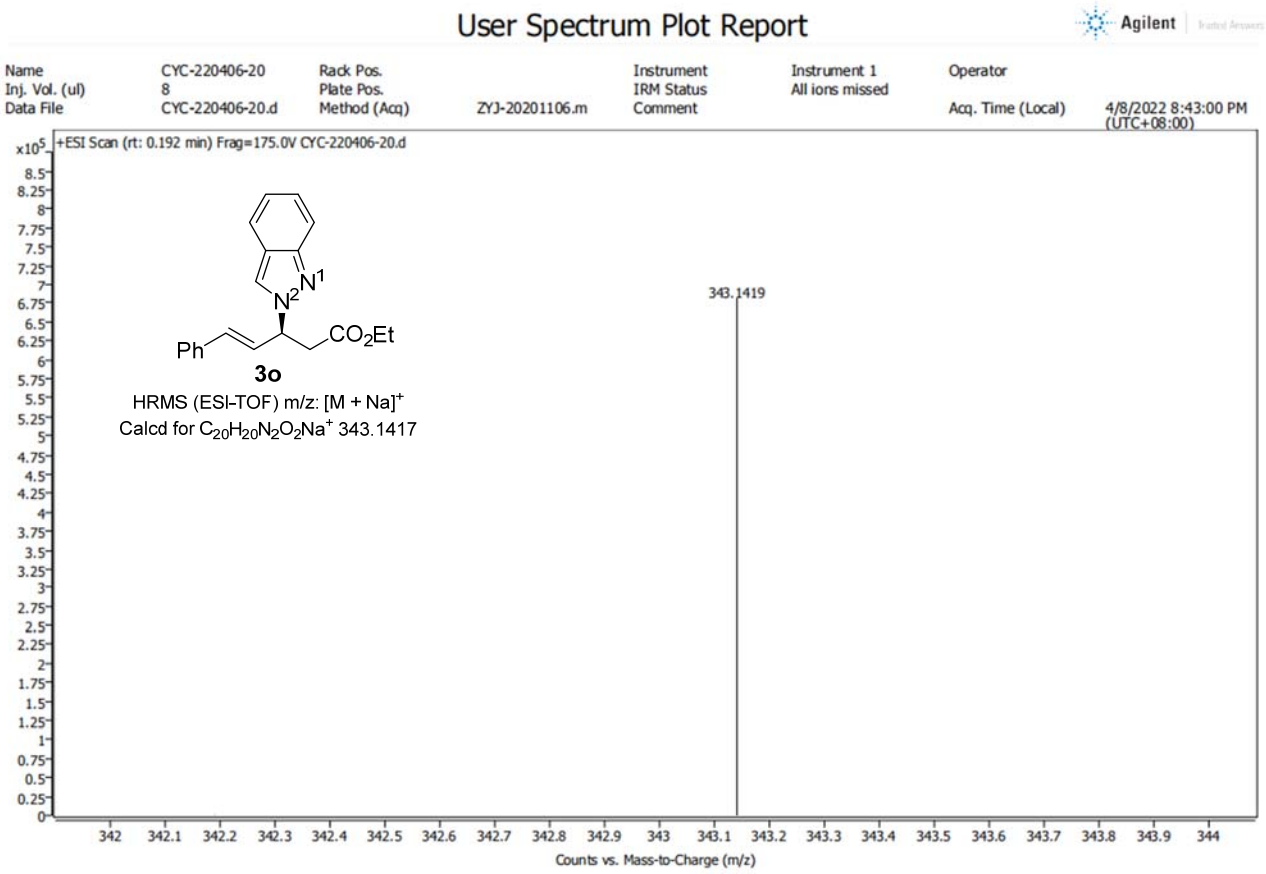
3o, 5:1 *E/Z*

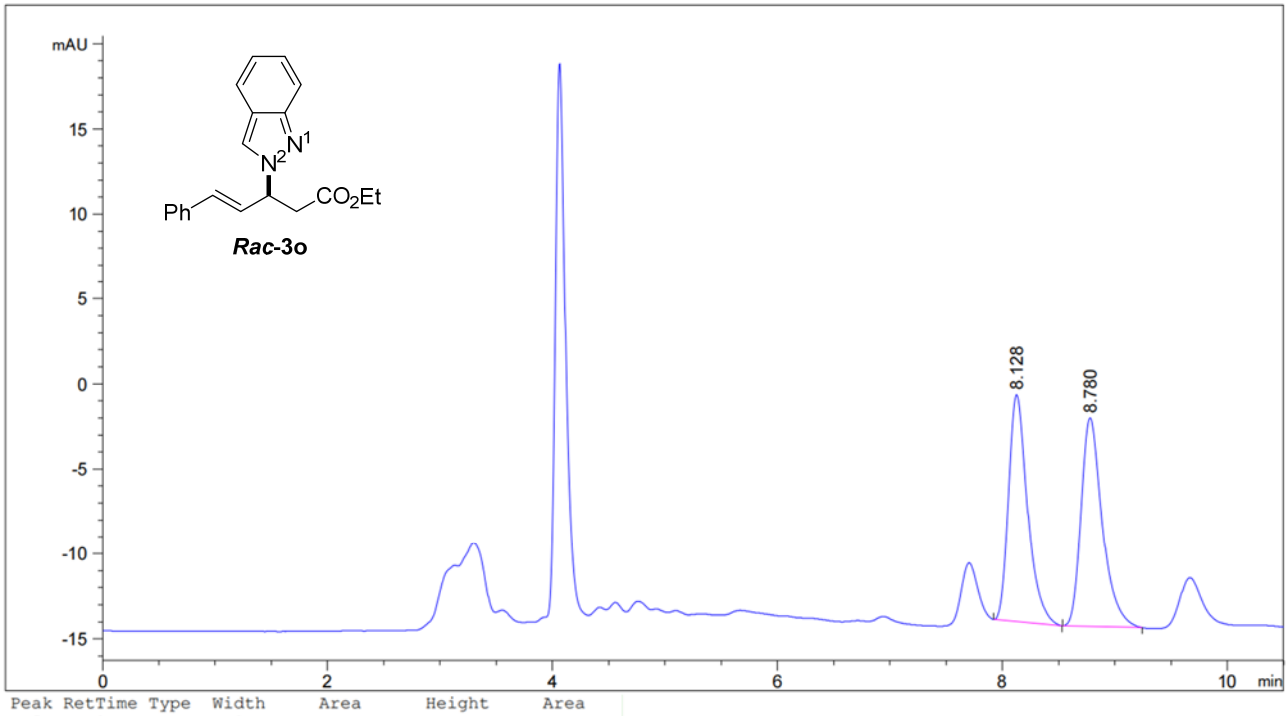
^{1}H-NMR (400 MHz, $CDCl_3$)



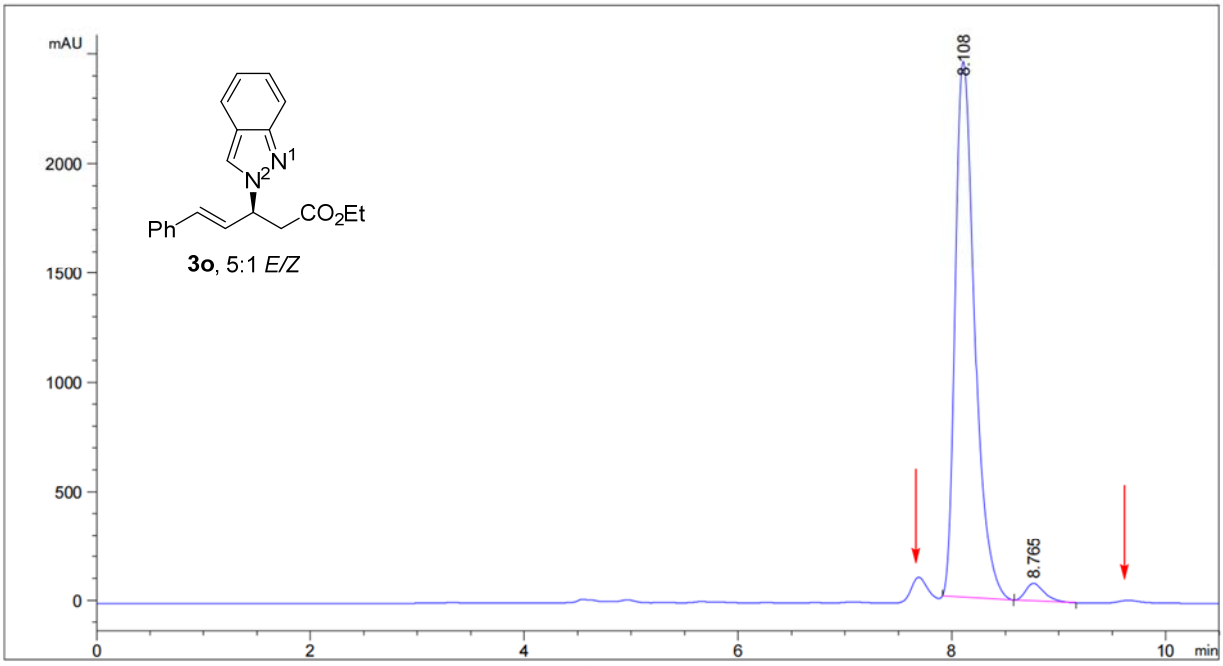
3o, 5:1 *E/Z*

^{13}C-NMR (100 MHz, $CDCl_3$)

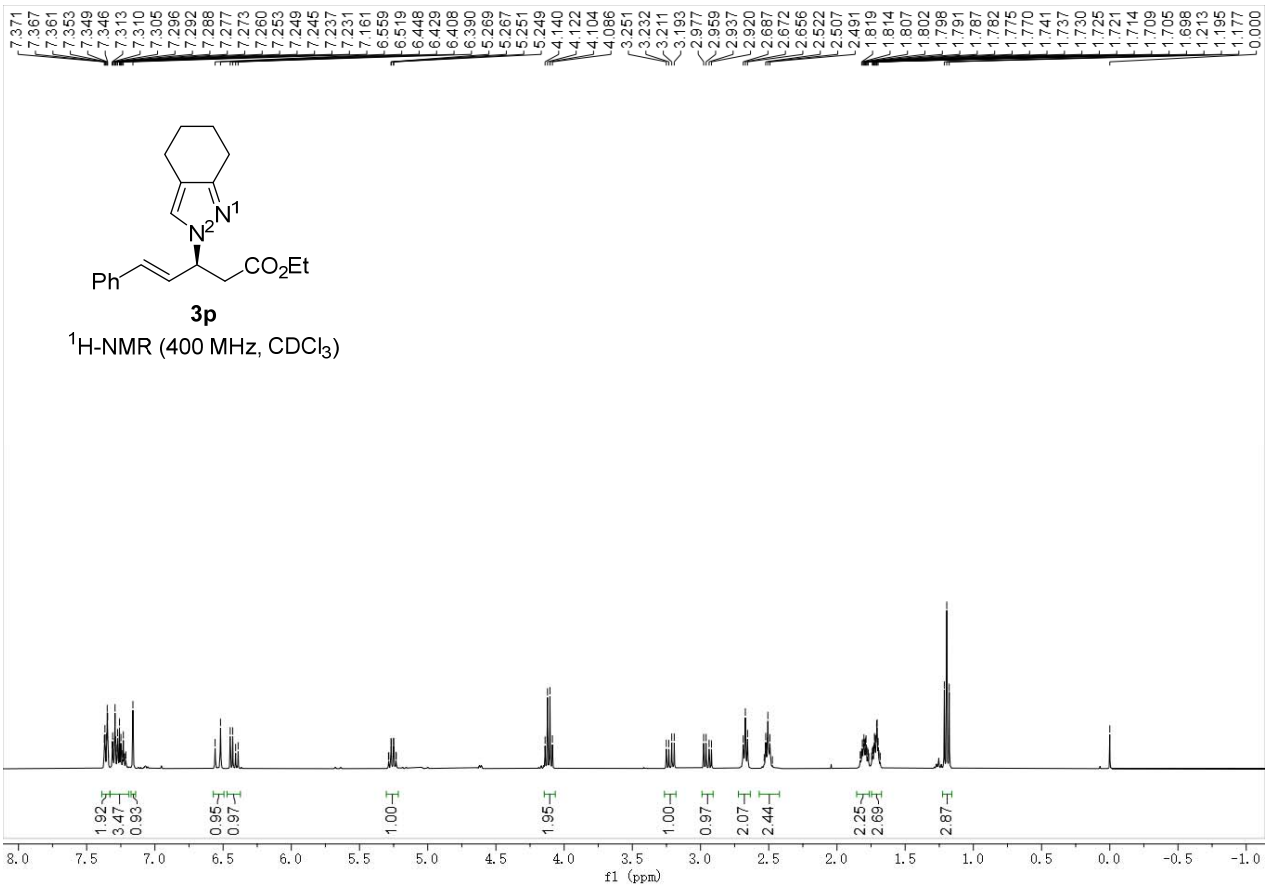

User Spectrum Plot Report
Agilent
Name CYC-220406-20
Inj. Vol. (ul) 8
Data File CYC-220406-20.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 4/8/2022 8:43:00 PM (UTC+08:00)
+ESI Scan (rt: 0.192 min) Frag=175.0V CYC-220406-20.d
x10^5
343.1419
Ph
CO2Et
N1
N2
3o
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C20H20N2O2Na+ 343.1417
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.128	BB	0.1782	157.16757	13.34072	49.2205
2	8.780	BBA	0.1992	162.14575	12.27789	50.7795

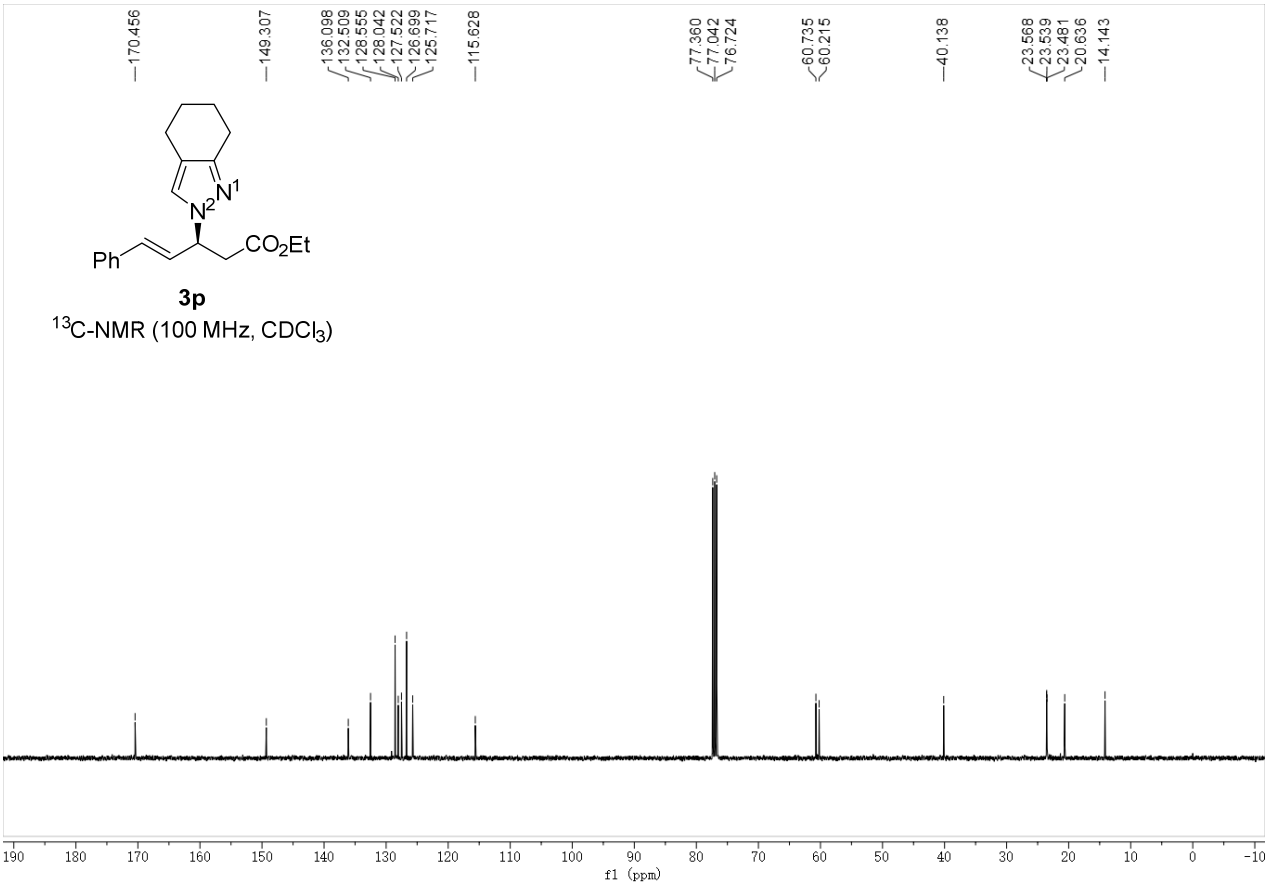


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.108	BB	0.1954	3.12643e4	2450.79834	96.9988
2	8.765	BBA	0.1865	967.34888	79.83965	3.0012



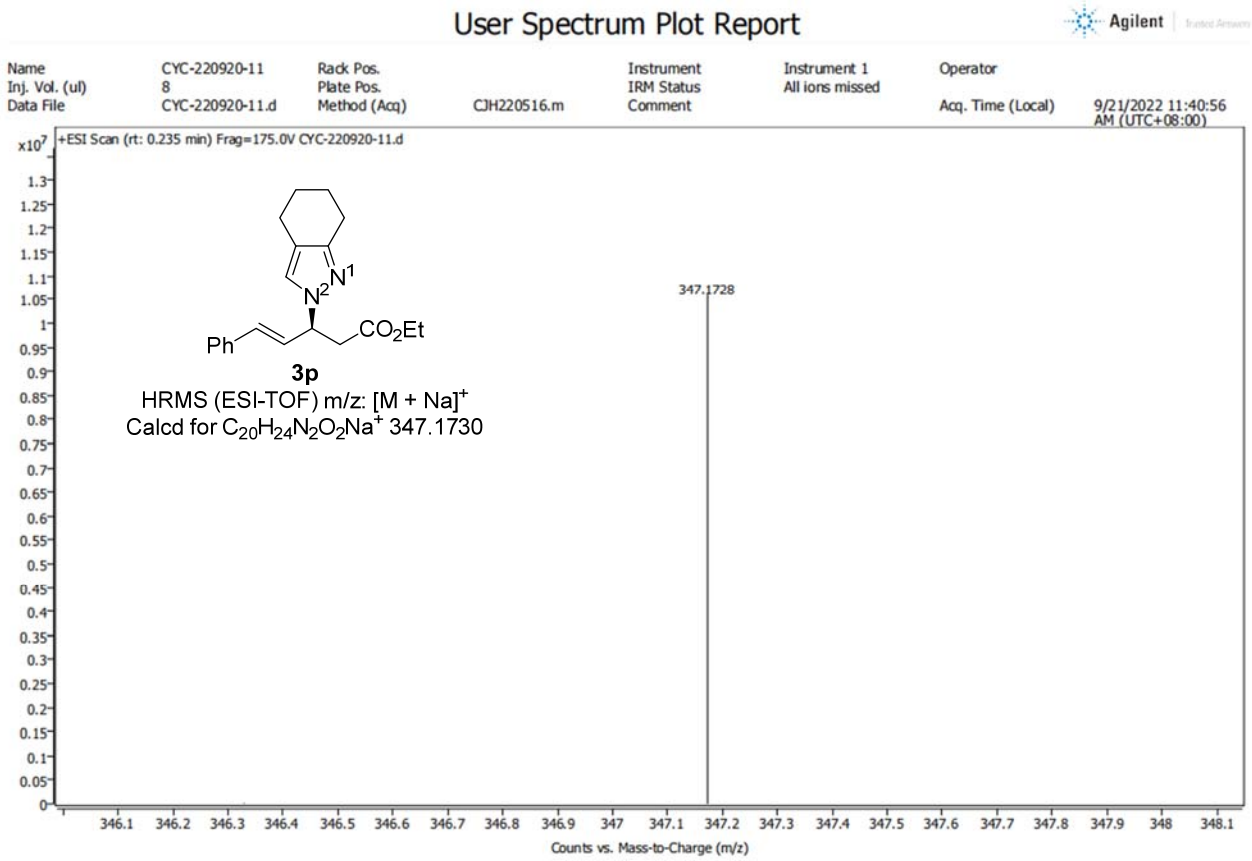
3p

^{1}H-NMR (400 MHz, $CDCl_3$)



3p

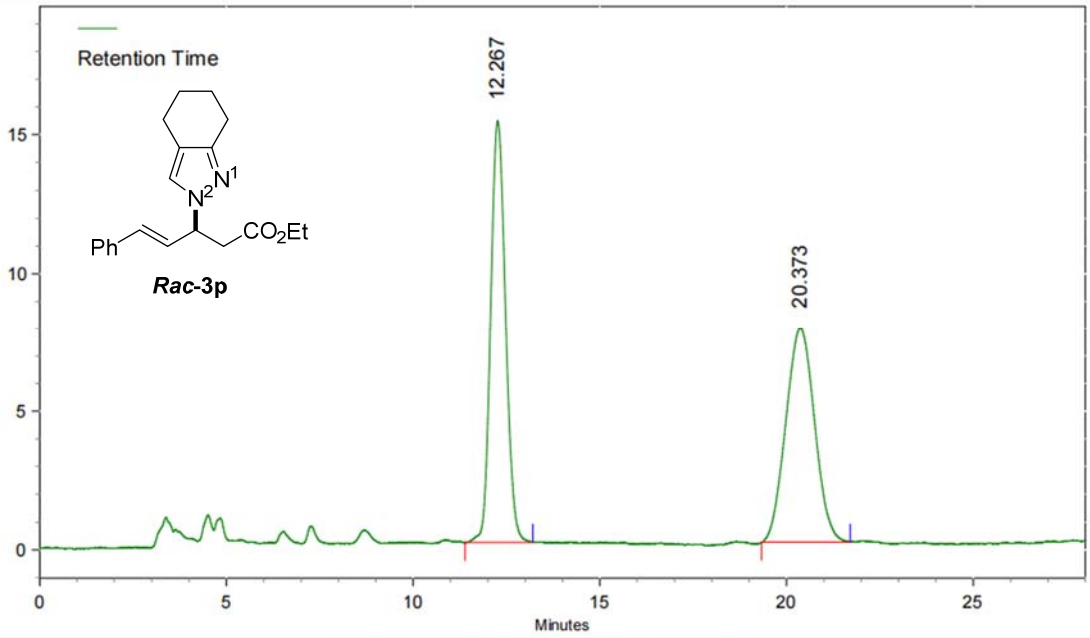
^{13}C-NMR (100 MHz, $CDCl_3$)



3p

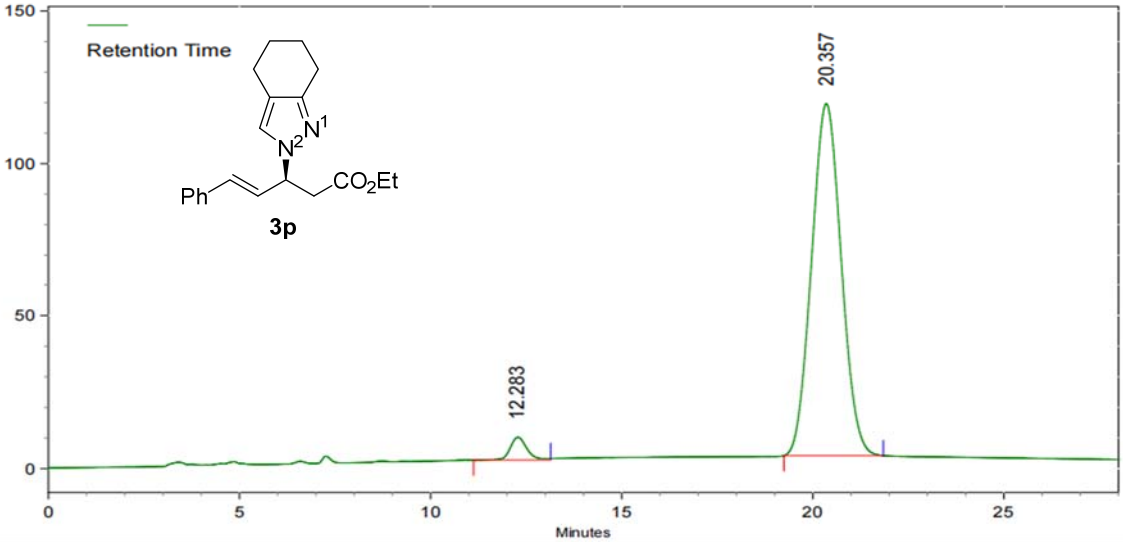
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{20}H_{24}N_2O_2Na^+$ 347.1730



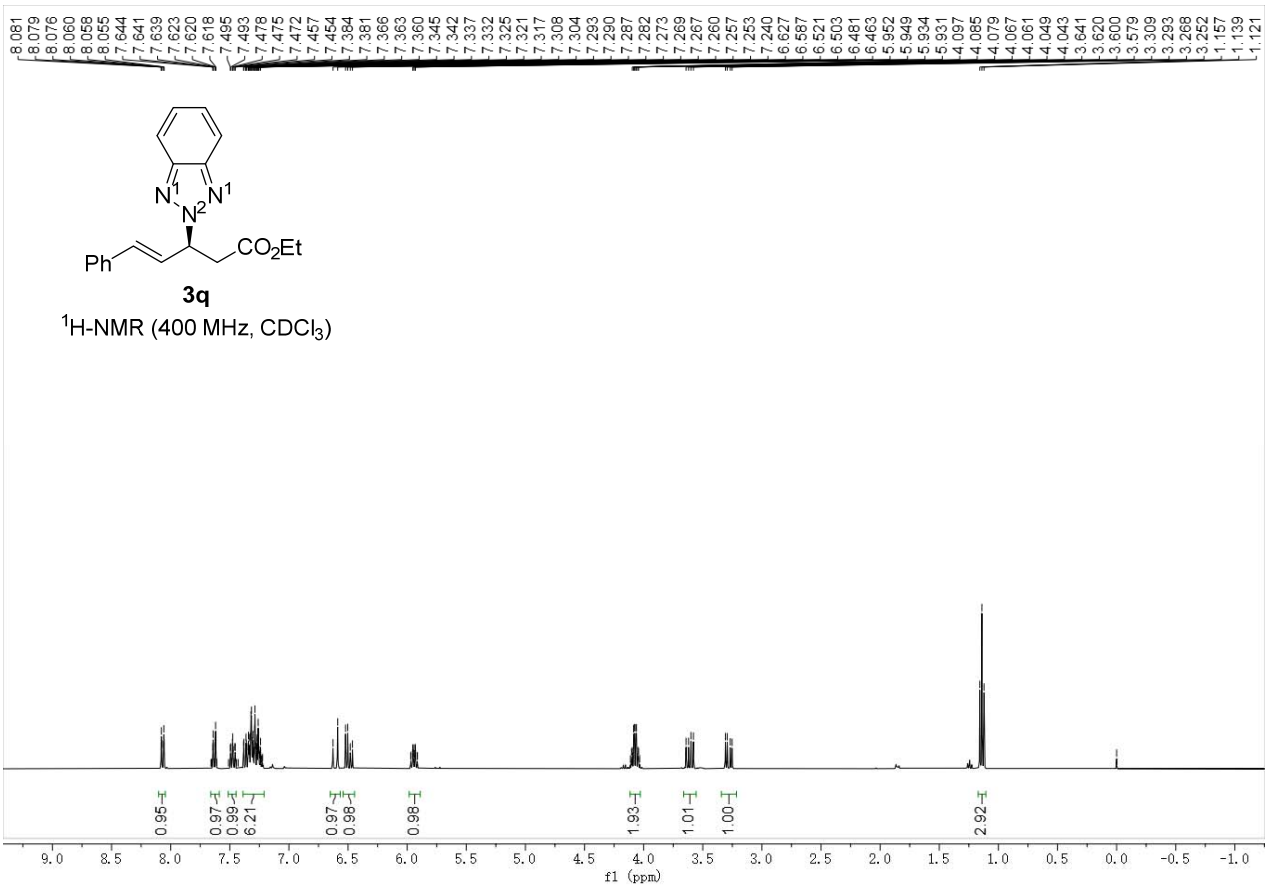
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.267	1.813	255514	7091329	50.5544
2	20.373	2.370	129835	6935809	49.4456
Totals			385349	14027138	100.0000



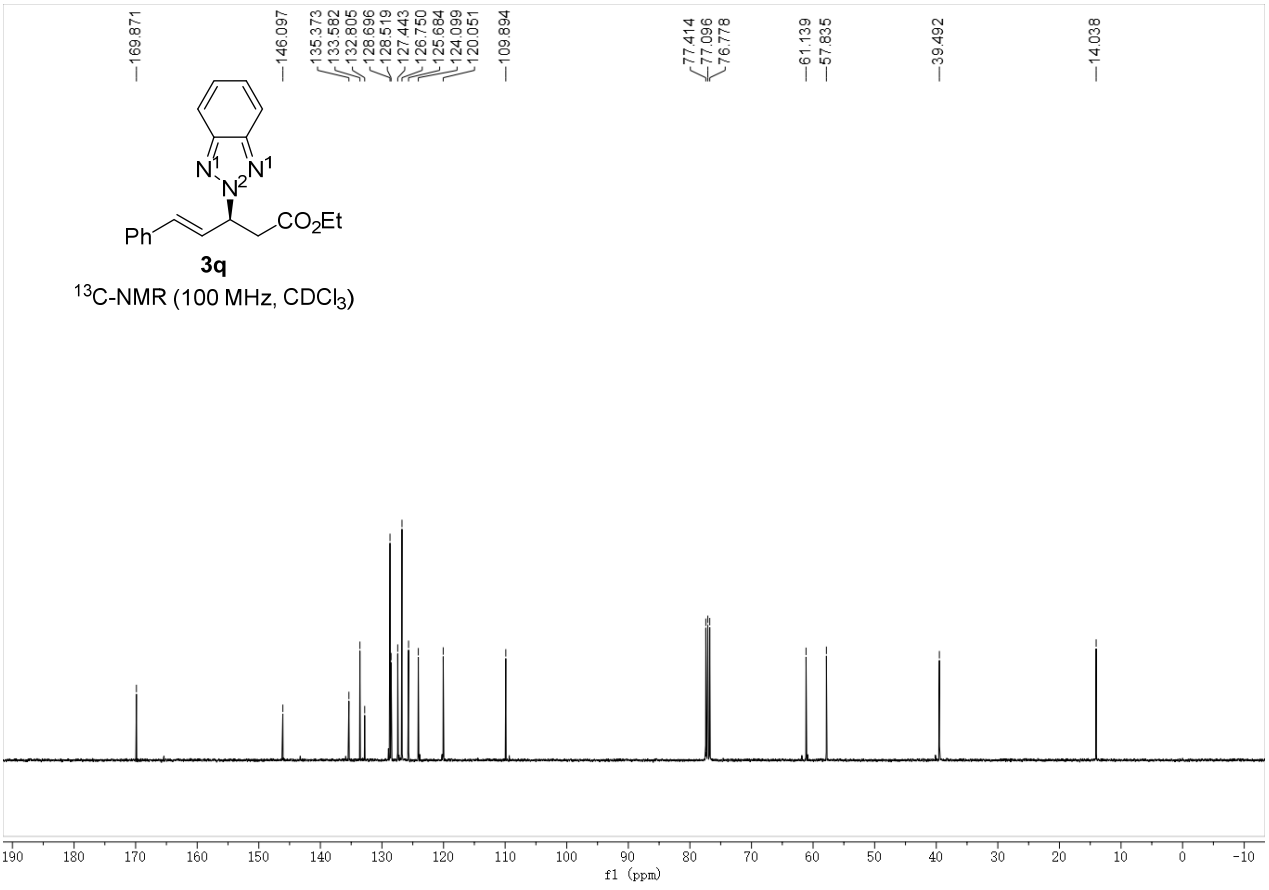
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.283	2.013	125160	3870265	3.5778
2	20.357	2.600	1936163	104304628	96.4222
Totals			2061323	108174893	100.0000



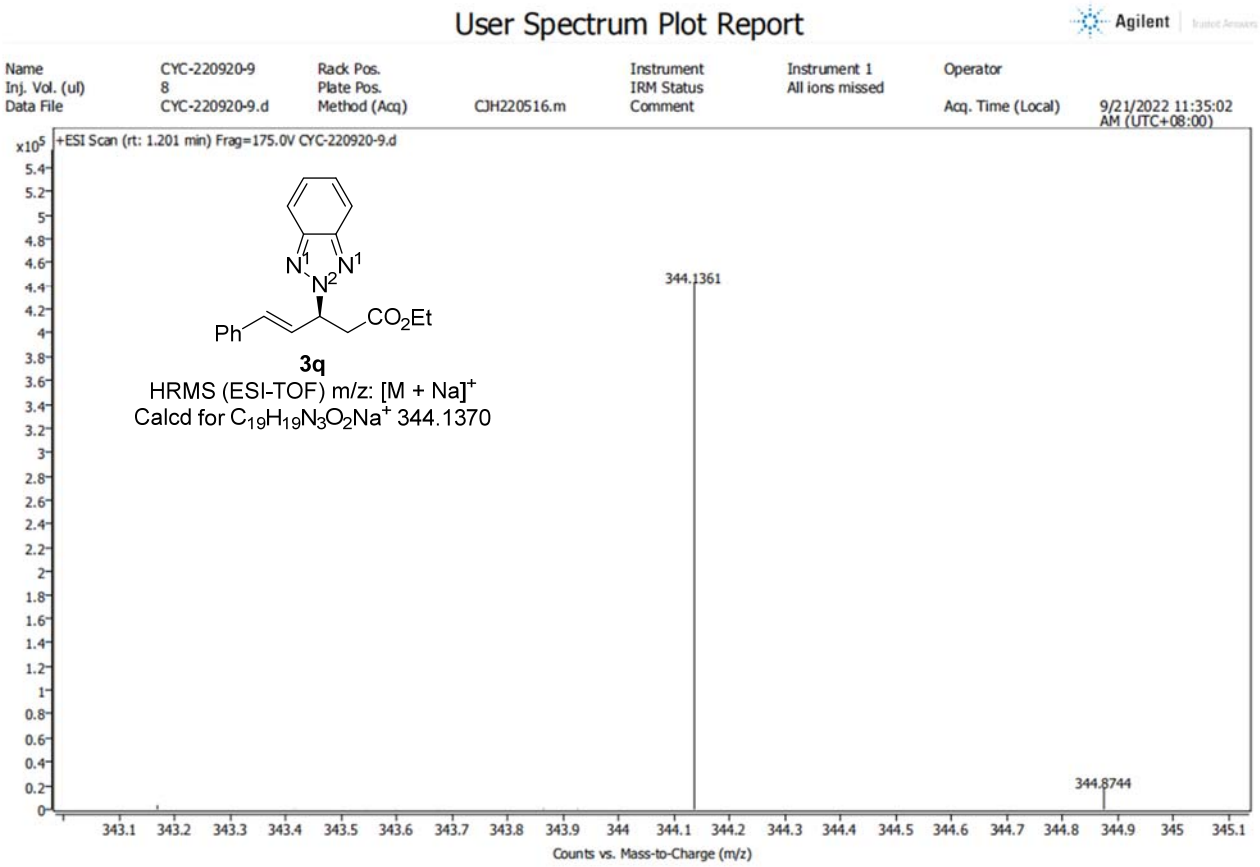
3q

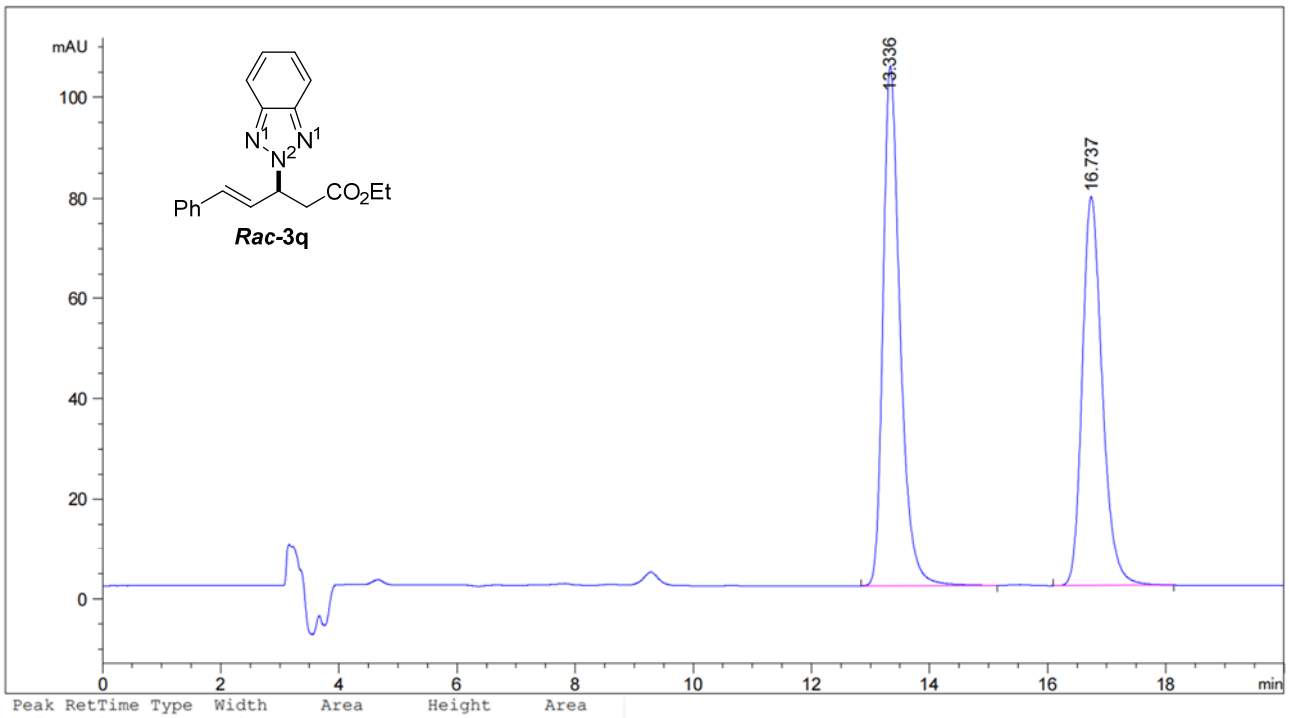
^{1}H-NMR (400 MHz, $CDCl_3$)



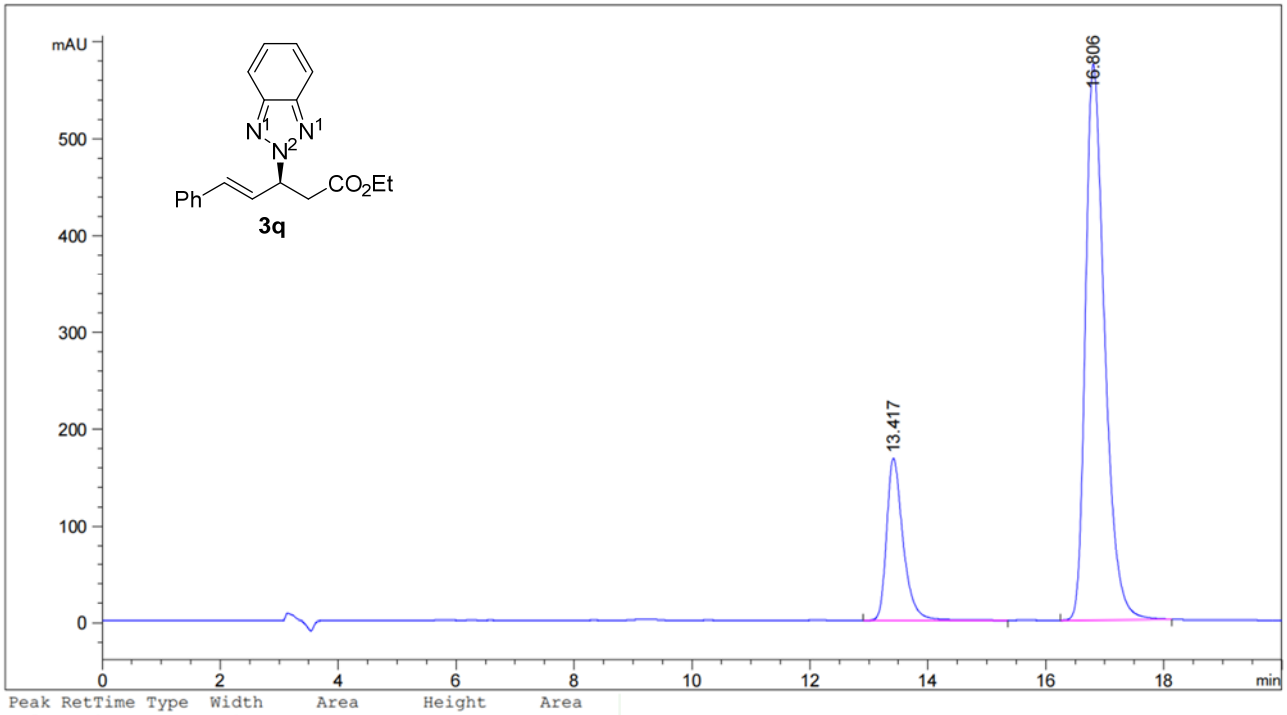
3q

^{13}C-NMR (100 MHz, $CDCl_3$)

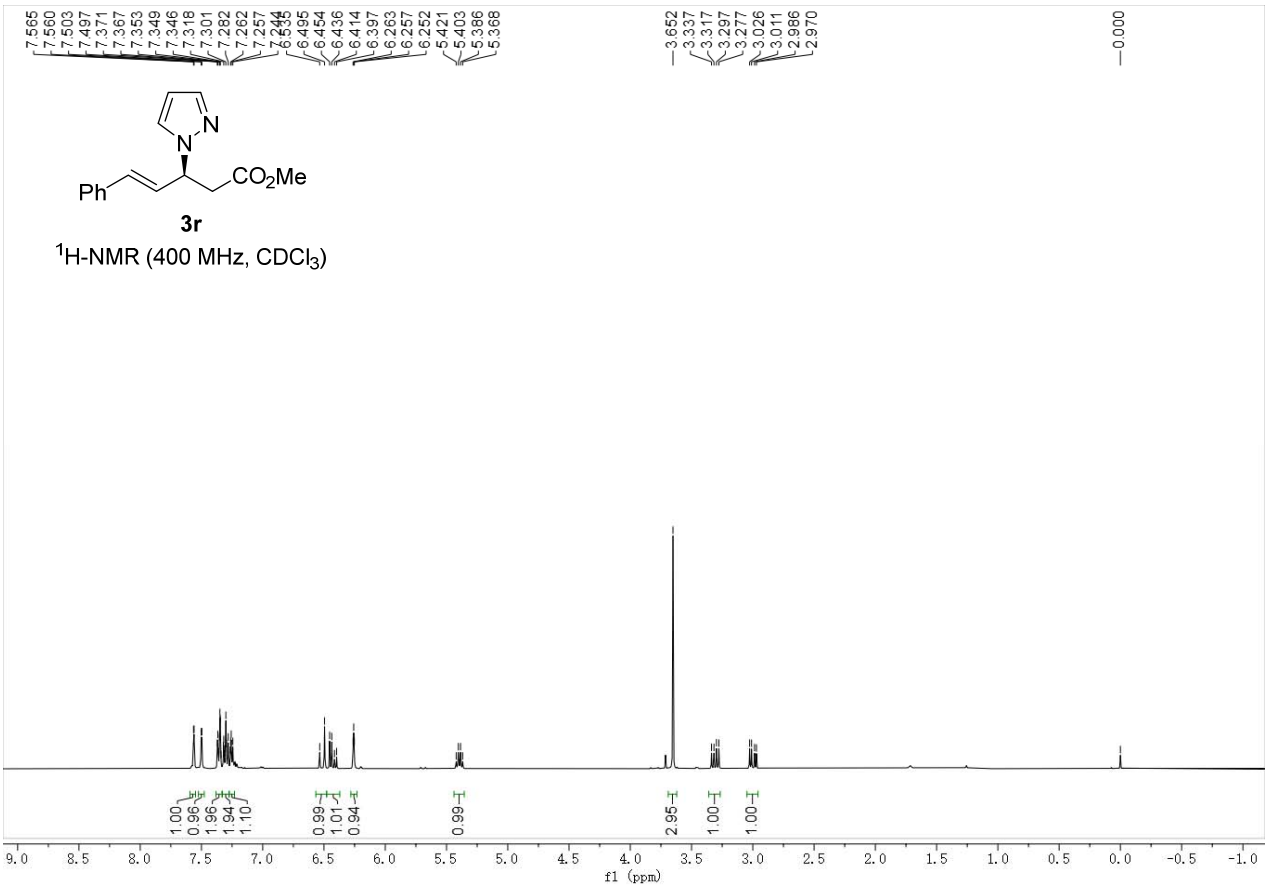

User Spectrum Plot Report
Agilent
Name CYC-220920-9
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
All ions missed
Data File CYC-220920-9.d
Method (Acq) CJH220516.m
Comment
Acq. Time (Local) 9/21/2022 11:35:02 AM (UTC+08:00)
+ESI Scan (rt: 1.201 min) Frag=175.0V CYC-220920-9.d
x10^5
344.1361
344.8744
Counts vs. Mass-to-Charge (m/z)
3q
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C19H19N3O2Na+ 344.1370



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.336	BB	0.3038	2091.53125	103.65214	53.2812
2	16.737	BBA	0.3610	1833.92603	77.78006	46.7188

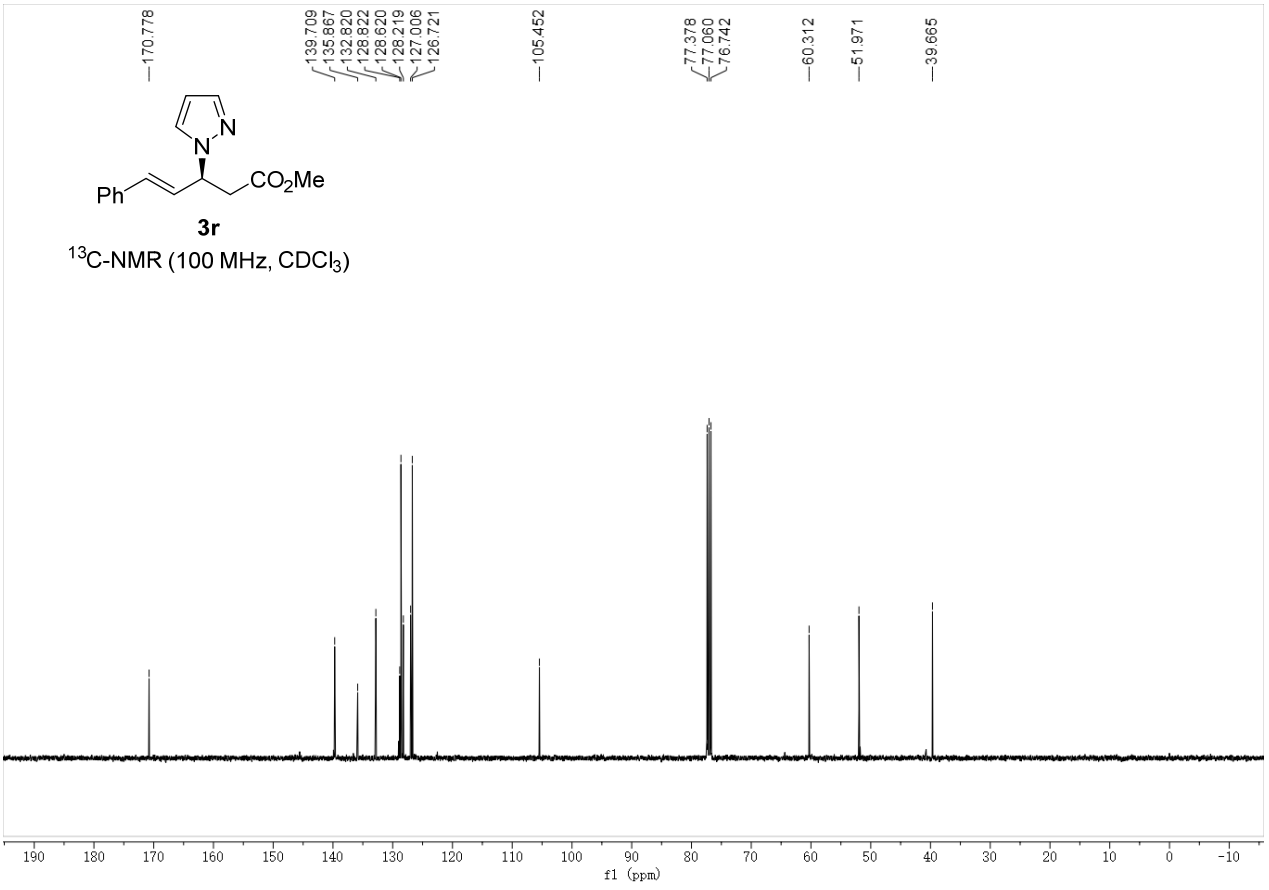


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.417	BB	0.2923	3239.41138	167.72394	19.9326
2	16.806	BBA	0.3458	1.30124e4	574.46667	80.0674



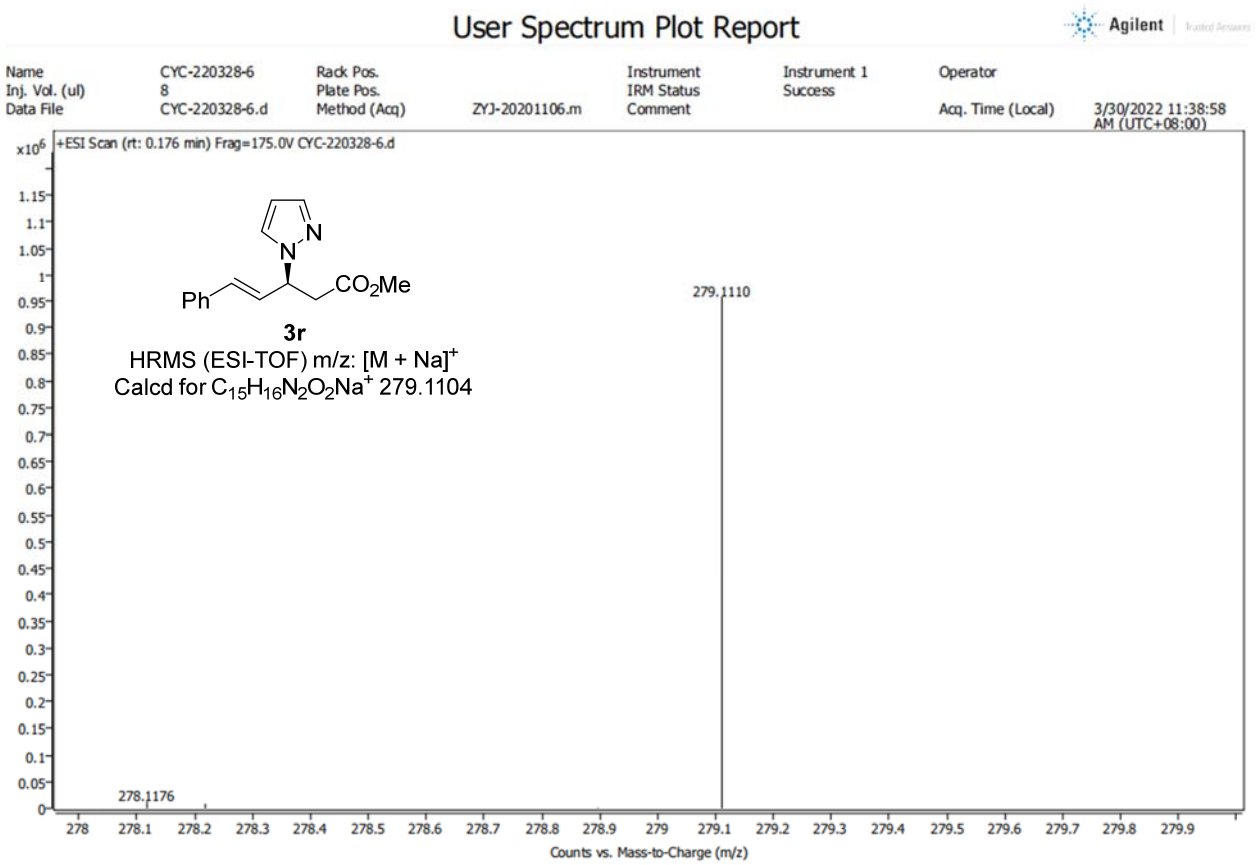
3r

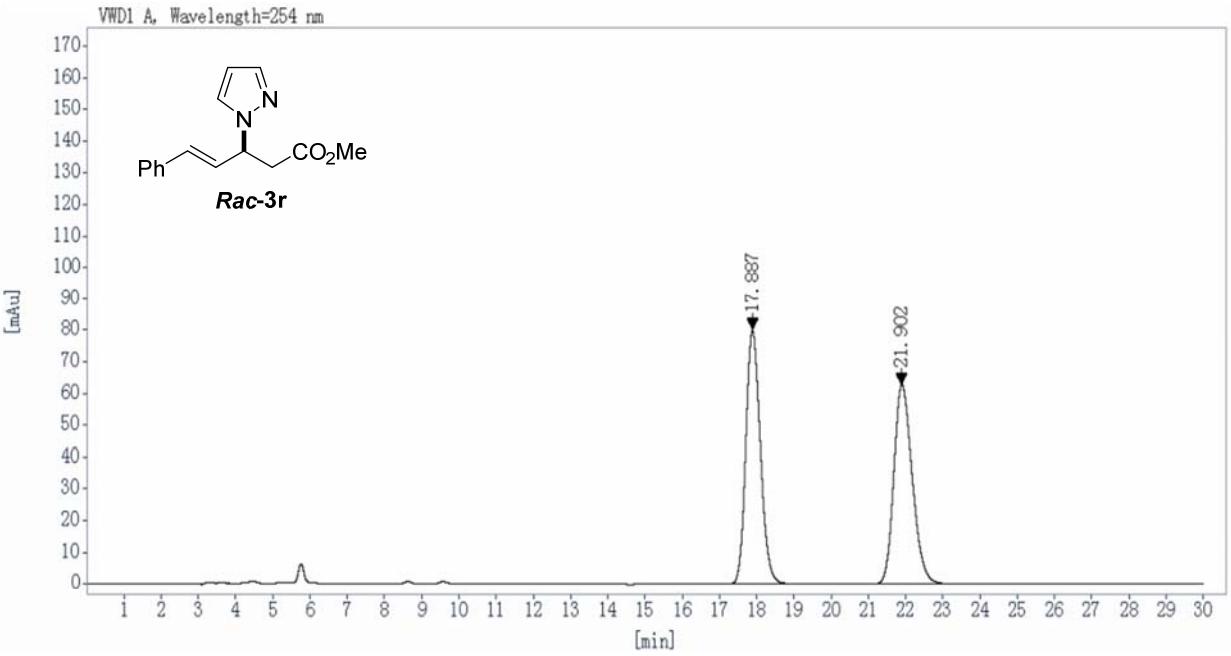
^{1}H-NMR (400 MHz, $CDCl_3$)



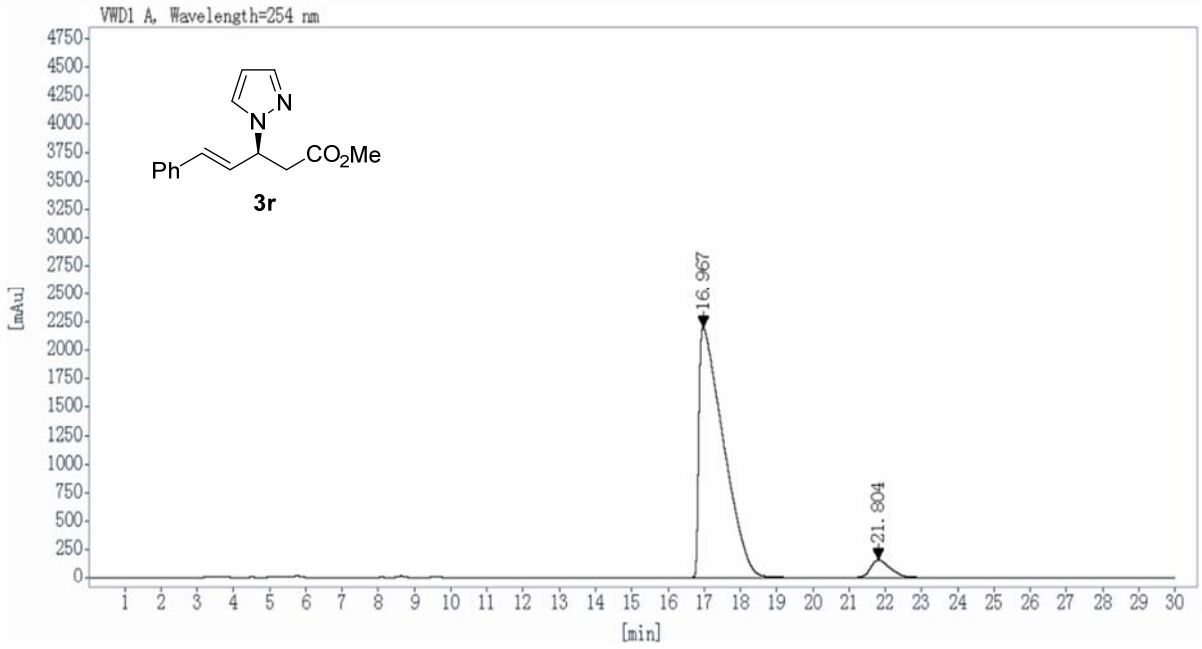
3r

^{13}C-NMR (100 MHz, $CDCl_3$)

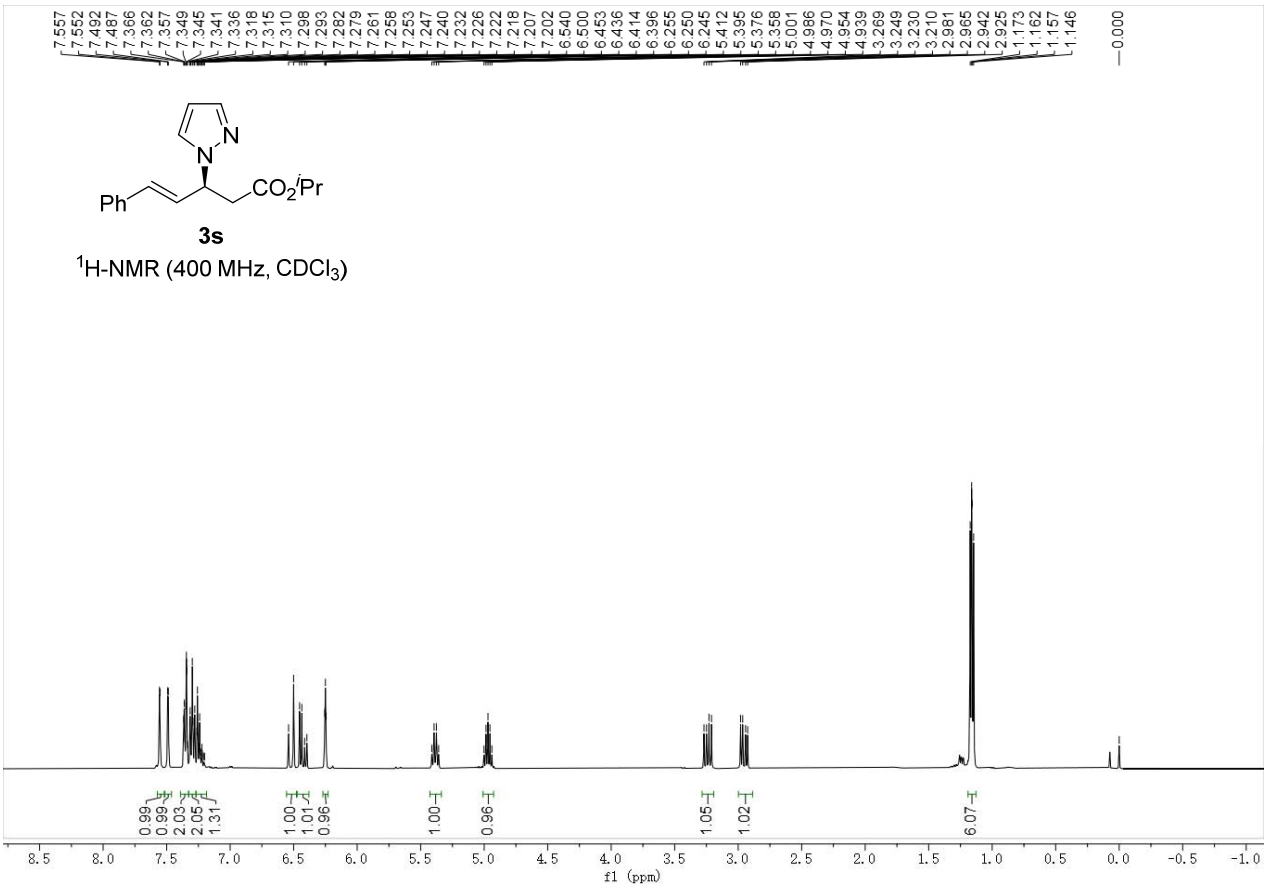

User Spectrum Plot Report
Agilent
Name CYC-220328-6
Inj. Vol. (ul) 8
Data File CYC-220328-6.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
Success
Operator
Acq. Time (Local) 3/30/2022 11:38:58 AM (UTC+08:00)
+ESI Scan (rt: 0.176 min) Frag=175.0V CYC-220328-6.d
x10^6
Ph
CO2Me
3r
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C15H16N2O2Na+ 279.1104
279.1110
278.1176
Counts vs. Mass-to-Charge (m/z)

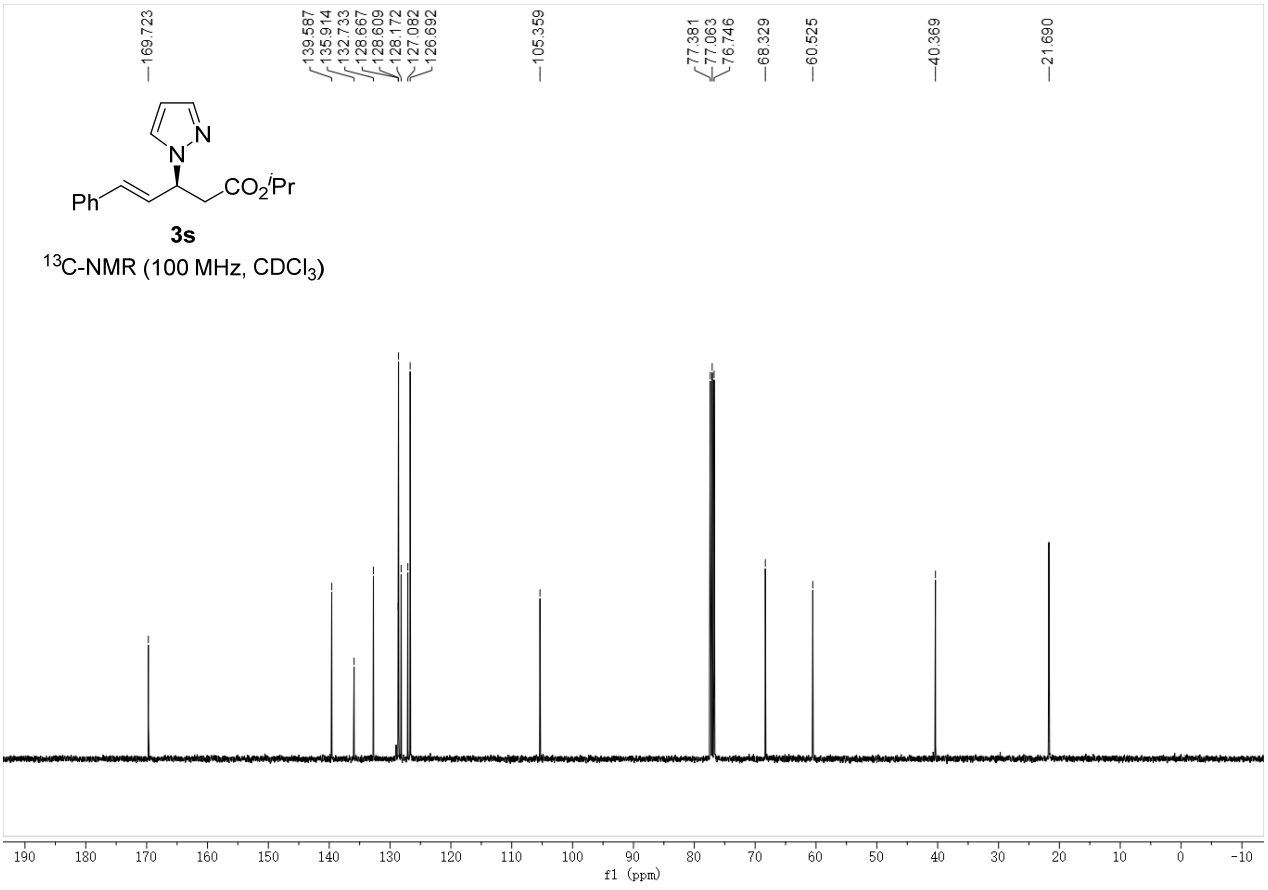


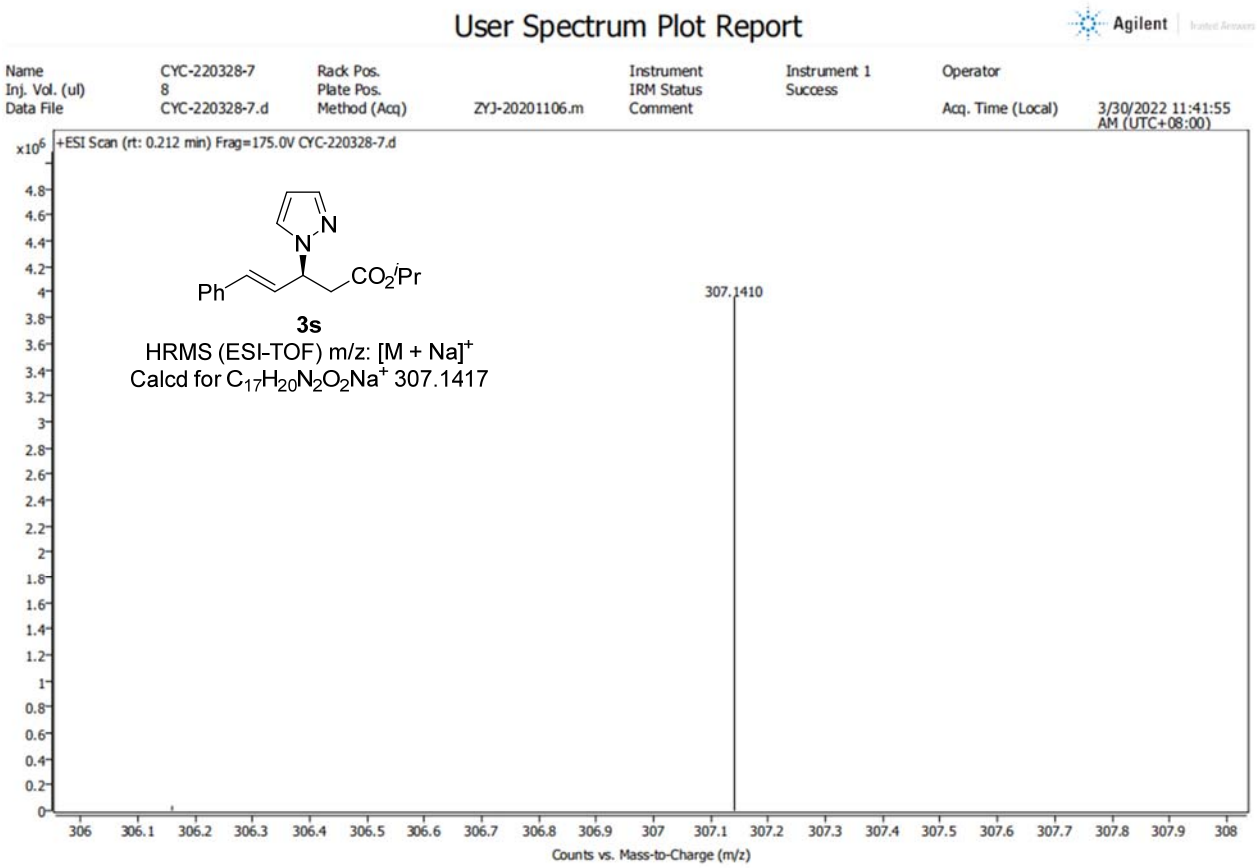
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
17.887	BB	0.42	79.9914	2164.8281	50.0175
21.902	BBA	0.53	62.8045	2163.3159	49.9825
			Totals:	4328.1440	100.0000

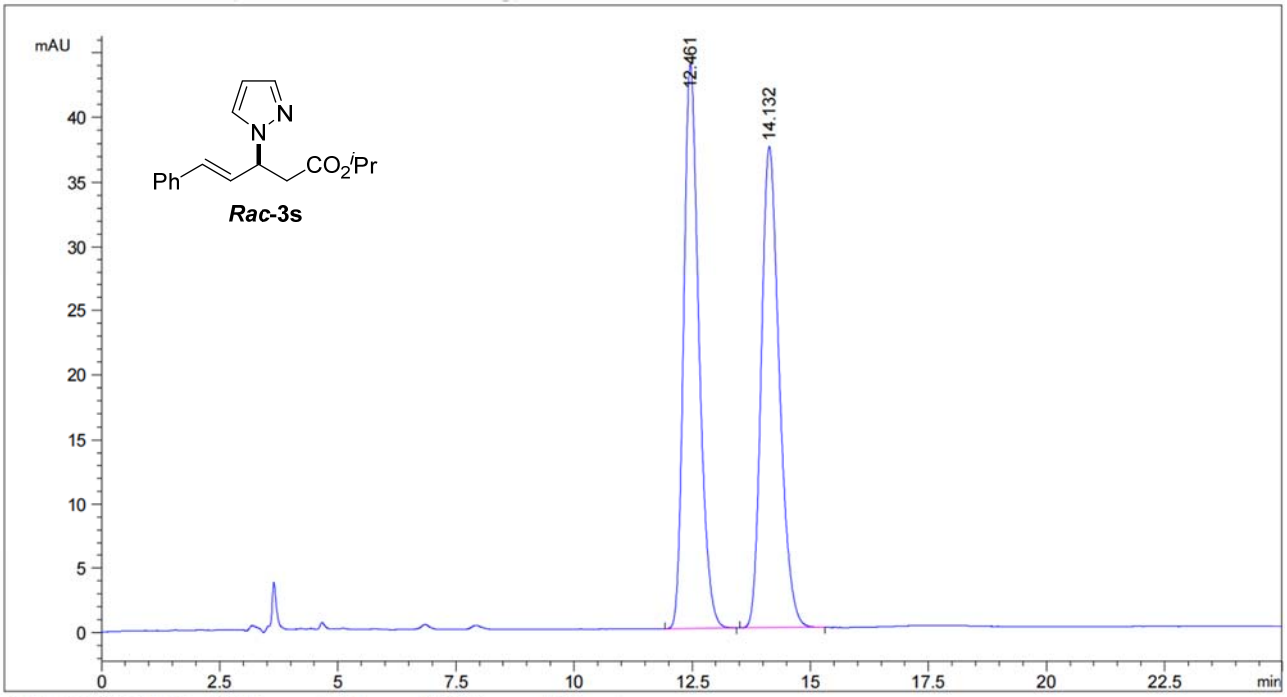


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.967	BB	0.70	2206.9880	102825.3672	94.7371
21.804	BBA	0.58	152.5006	5712.2661	5.2629
			Totals:	108537.6333	100.0000

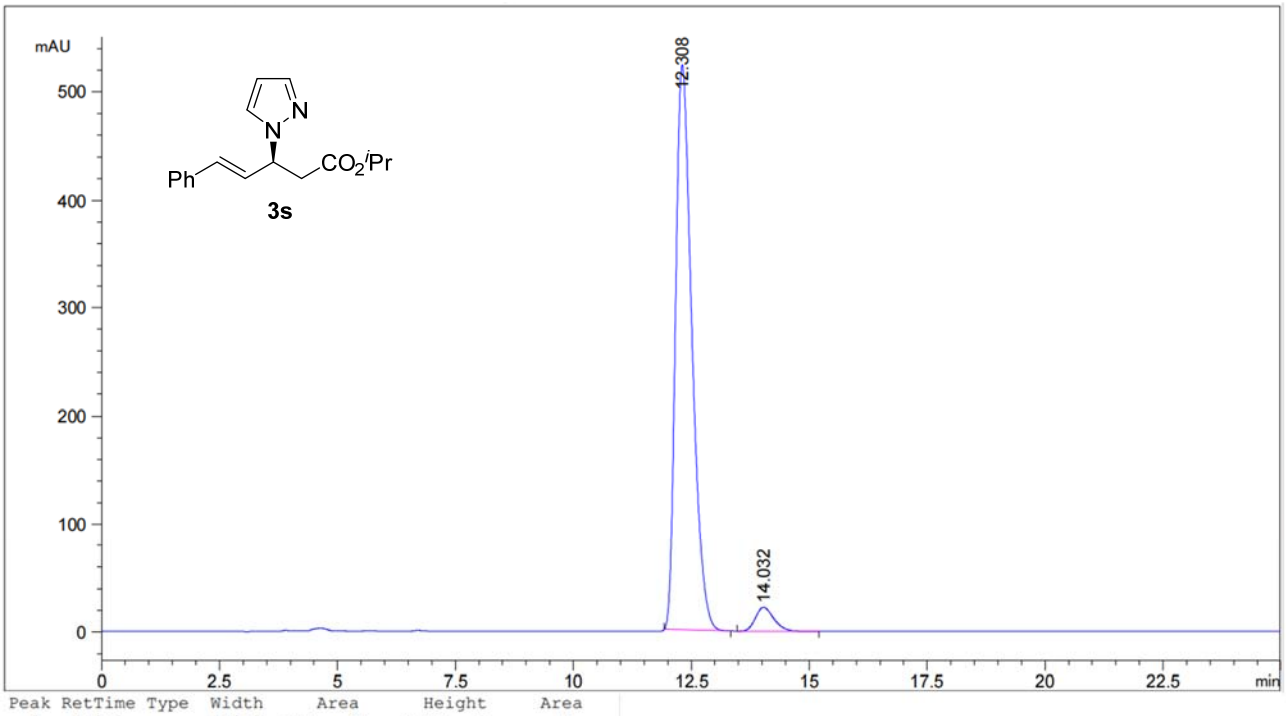

7.557
7.552
7.492
7.487
7.366
7.362
7.357
7.349
7.345
7.341
7.336
7.318
7.315
7.310
7.298
7.293
7.282
7.279
7.261
7.258
7.253
7.247
7.240
7.232
7.226
7.222
7.218
7.207
7.202
6.540
6.500
6.453
6.436
6.414
6.396
6.255
6.250
6.245
5.412
5.395
5.376
5.358
5.001
4.986
4.970
4.954
4.939
3.269
3.249
3.230
3.210
2.981
2.965
2.942
2.925
1.173
1.162
1.157
1.146
0.000
N
N
Ph
CO2iPr
3s
1H-NMR (400 MHz, CDCl3)
0.99
0.99
2.03
2.05
1.31
1.00
1.01
0.96
1.00
0.96
1.05
1.02
6.07
f1 (ppm)


169.723
139.587
135.914
132.733
128.667
128.609
128.172
127.082
126.692
105.359
77.381
77.063
76.746
68.329
60.525
40.369
21.690
N
N
Ph
CO2iPr
3s
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

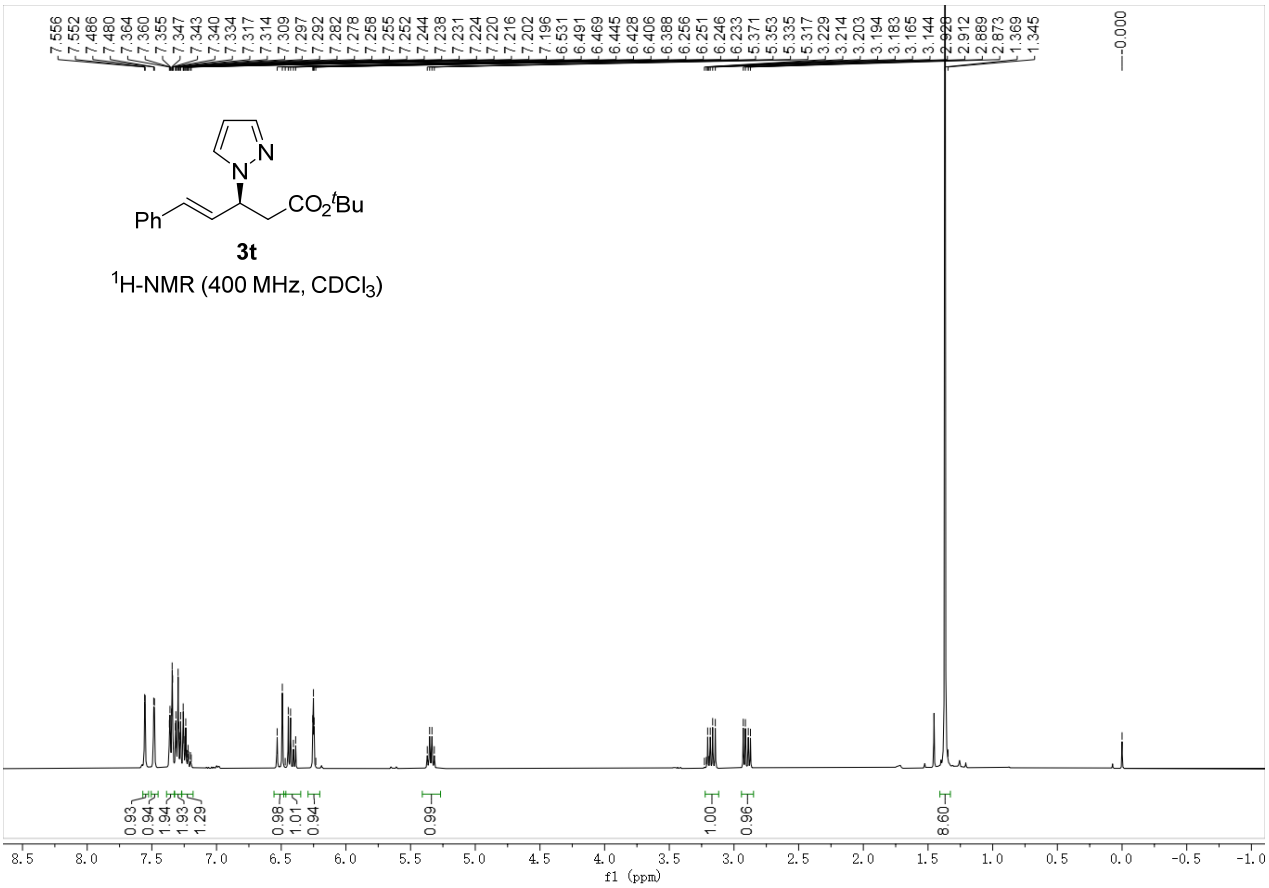

User Spectrum Plot Report
Agilent
Name CYC-220328-7
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
Success
Data File CYC-220328-7.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 3/30/2022 11:41:55 AM (UTC+08:00)
+ESI Scan (rt: 0.212 min) Frag=175.0V CYC-220328-7.d
x10^6
307.1410
Ph
CO2iPr
3s
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C17H20N2O2Na+ 307.1417
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.461	BB	0.3423	985.01605	43.82821	49.7945
2	14.132	BB	0.4058	993.14624	37.41253	50.2055

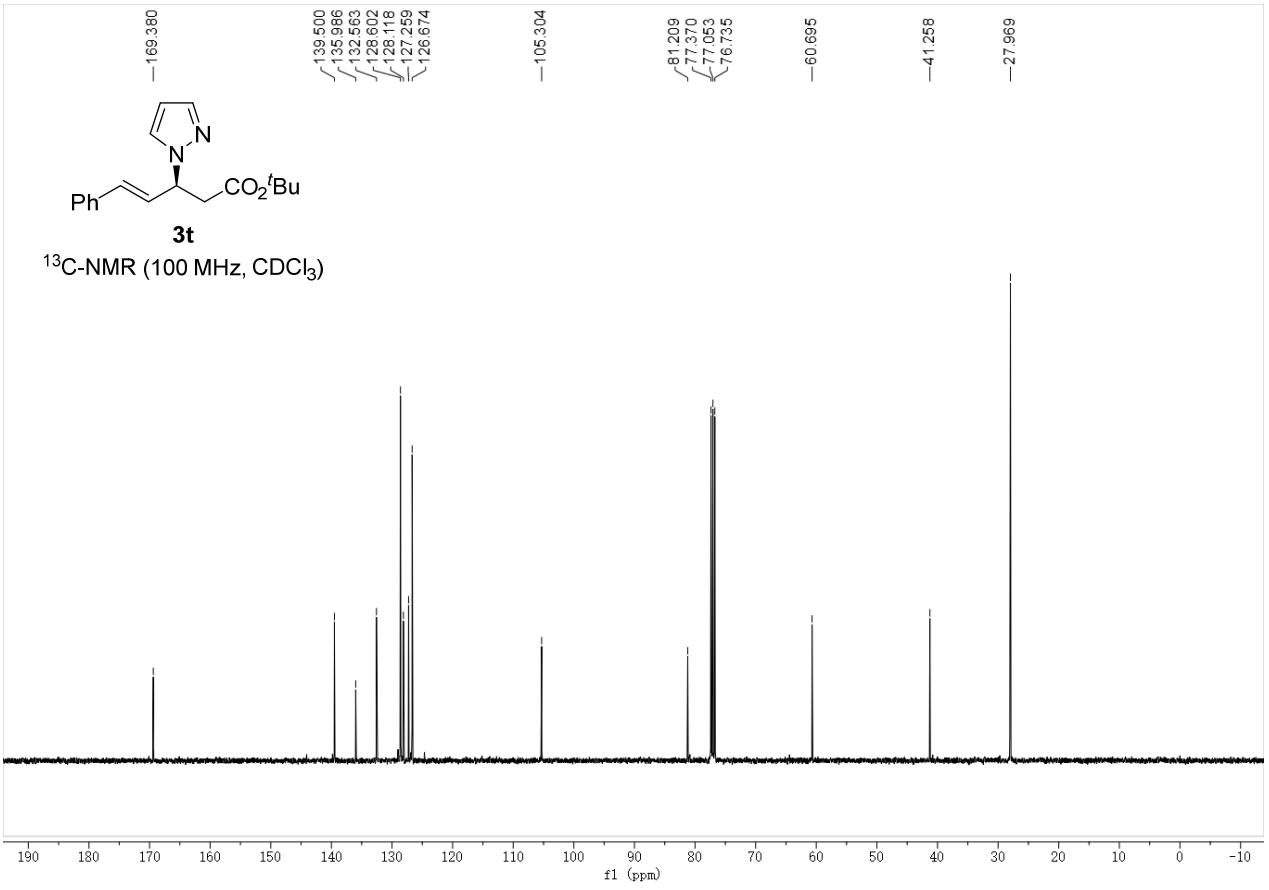


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.308	BB	0.3700	1.25267e4	522.49249	95.4538
2	14.032	BB	0.4160	596.60968	22.05907	4.5462



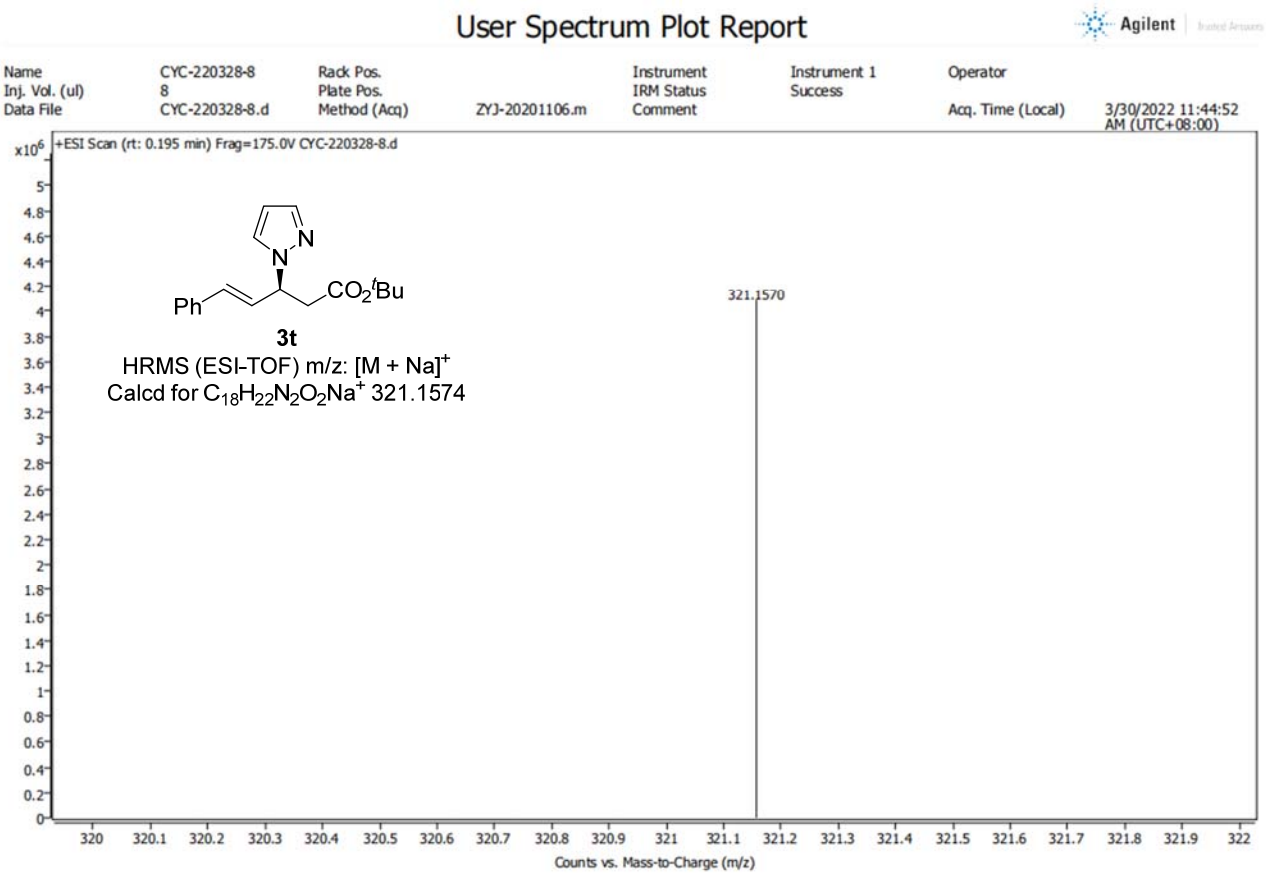
3t

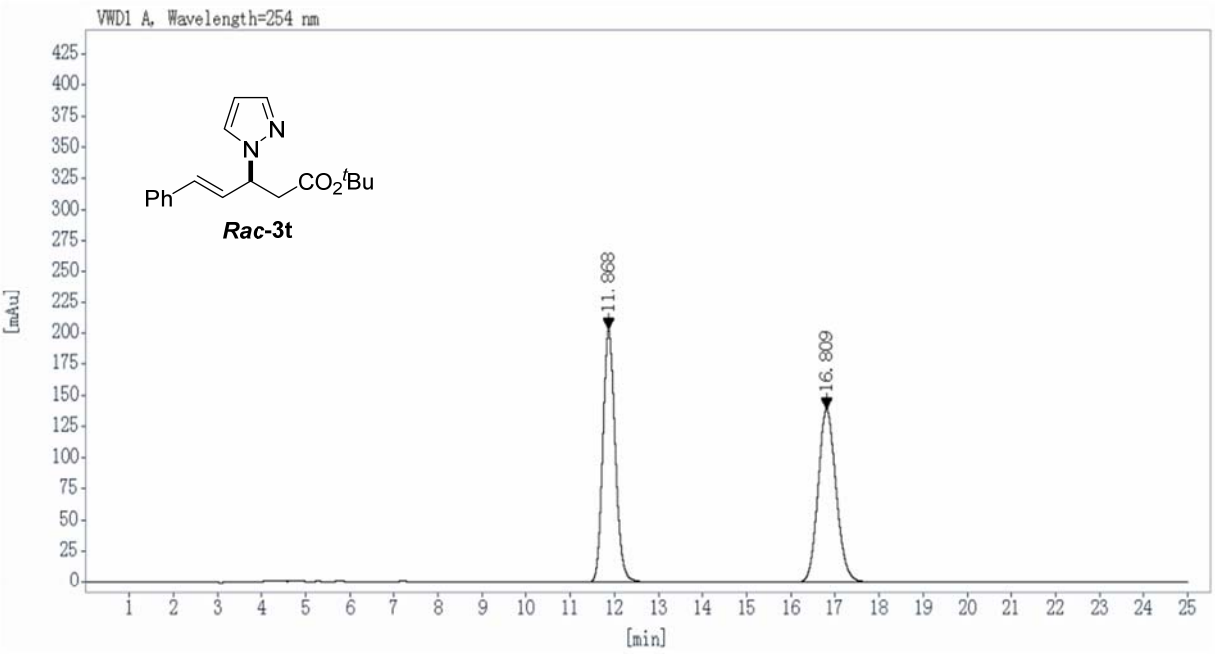
^{1}H-NMR (400 MHz, $CDCl_3$)



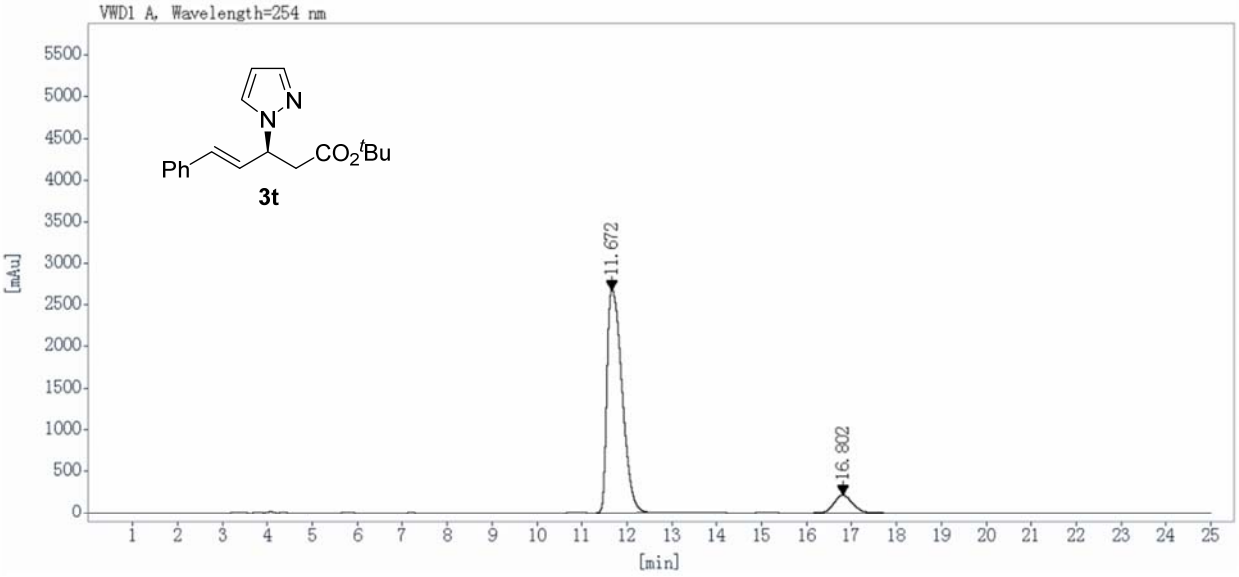
3t

^{13}C-NMR (100 MHz, $CDCl_3$)

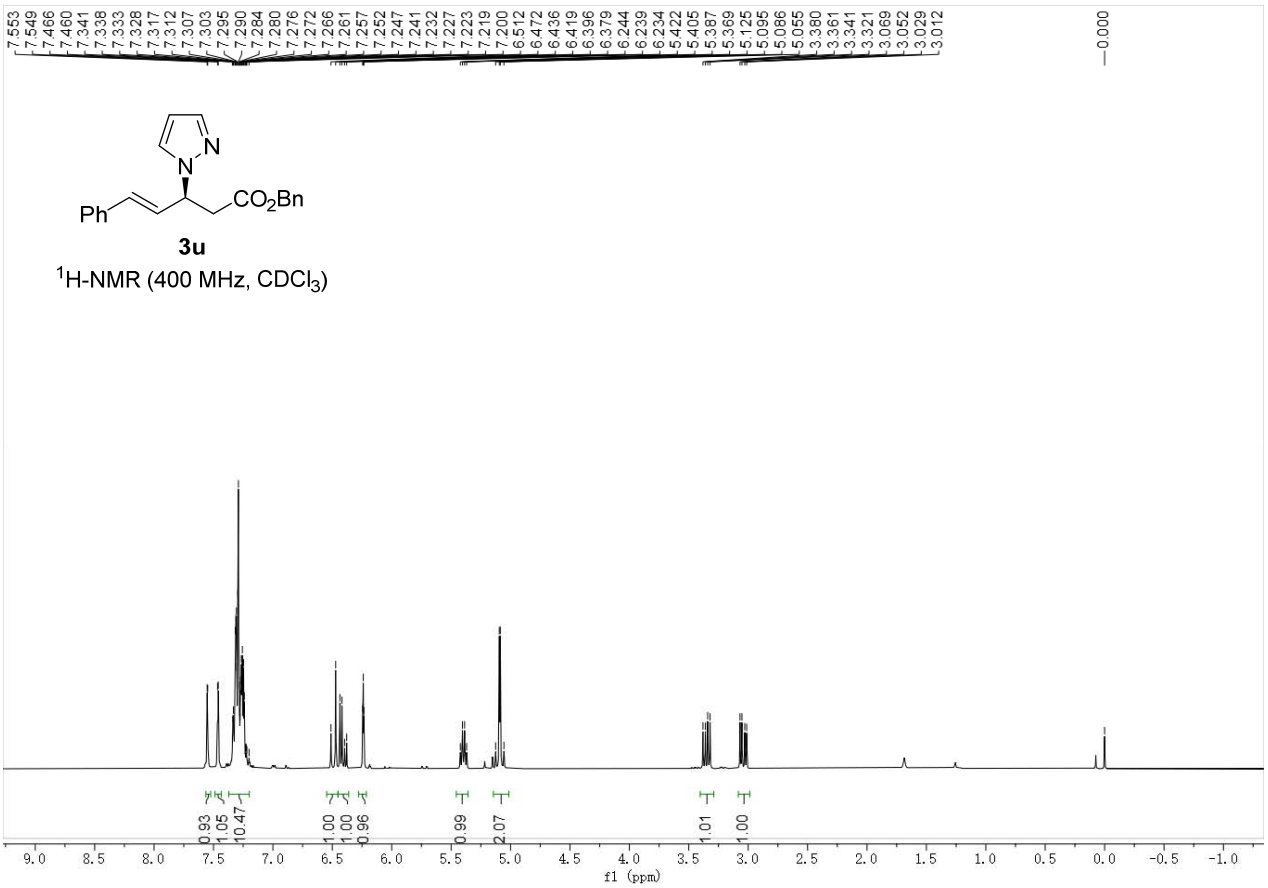

User Spectrum Plot Report
Agilent
Name CYC-220328-8
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
Success
Data File CYC-220328-8.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 3/30/2022 11:44:52 AM (UTC+08:00)
+ESI Scan (rt: 0.195 min) Frag=175.0V CYC-220328-8.d
x10^6
Ph
CO2tBu
3t
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C18H22N2O2Na+ 321.1574
321.1570
Counts vs. Mass-to-Charge (m/z)



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
11.868	BB	0.30	202.1230	3954.3215	50.0521
16.809	BBA	0.44	138.3933	3946.0952	49.9479
			Totals:	7900.4167	100.0000

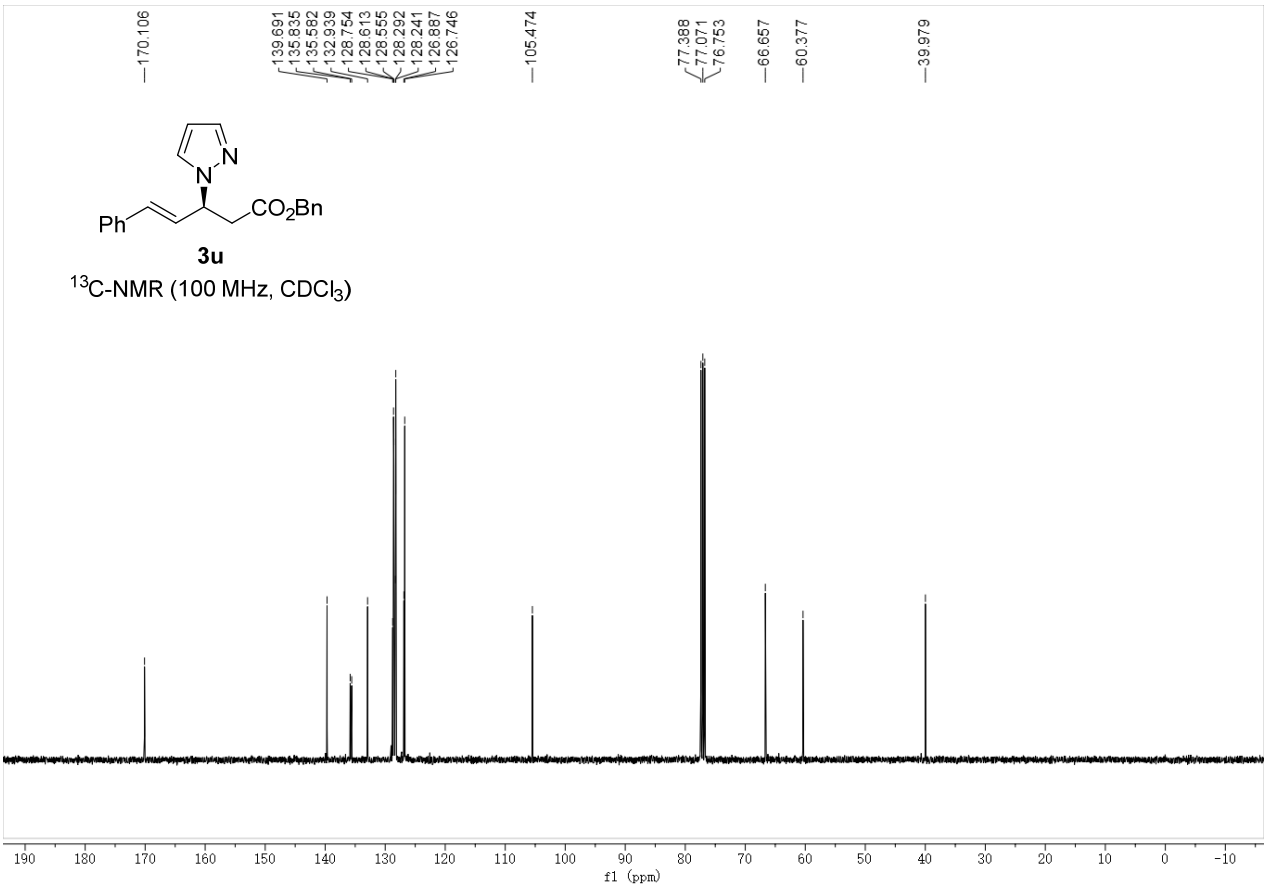


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
11.672	BB	0.37	2673.4663	62479.7109	91.0481
16.802	BBA	0.44	215.3783	6143.0596	8.9519
			Totals:	68622.7705	100.0000



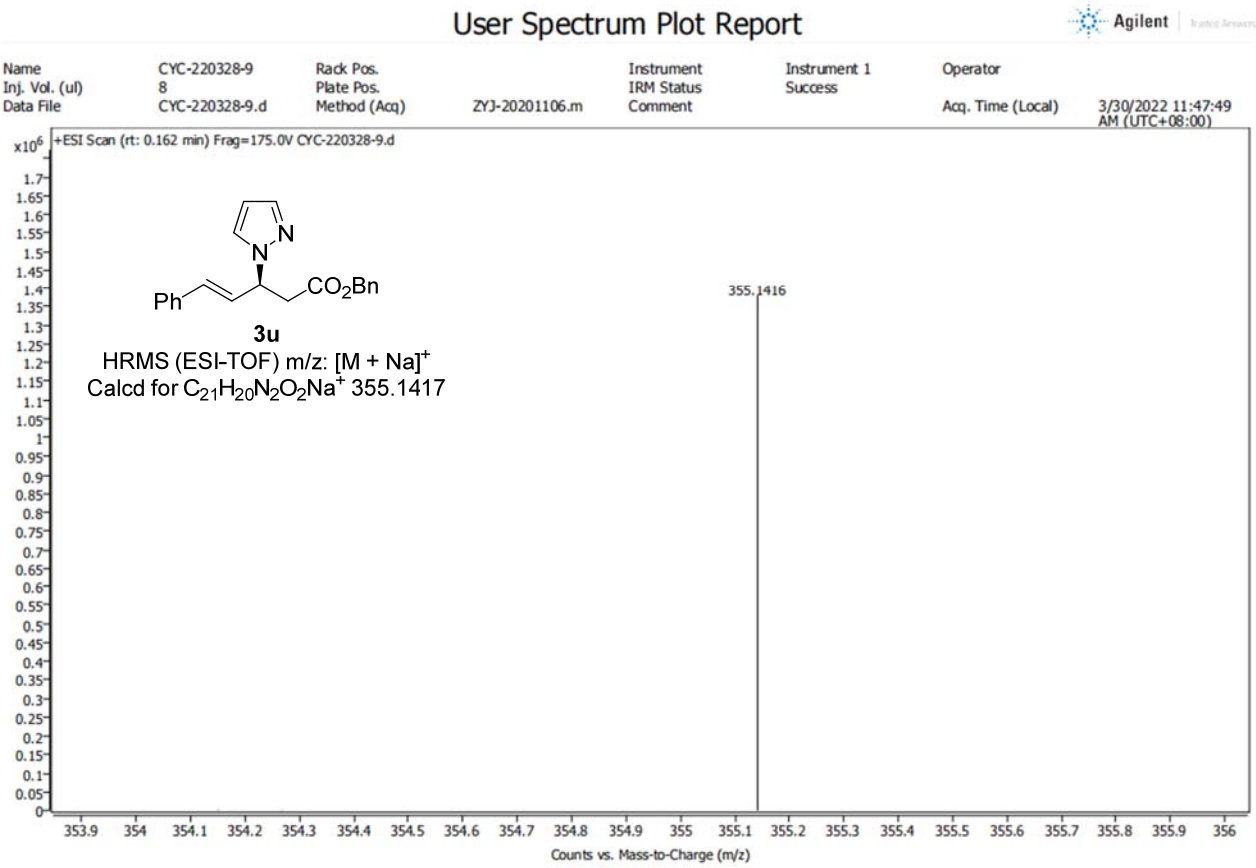
3u

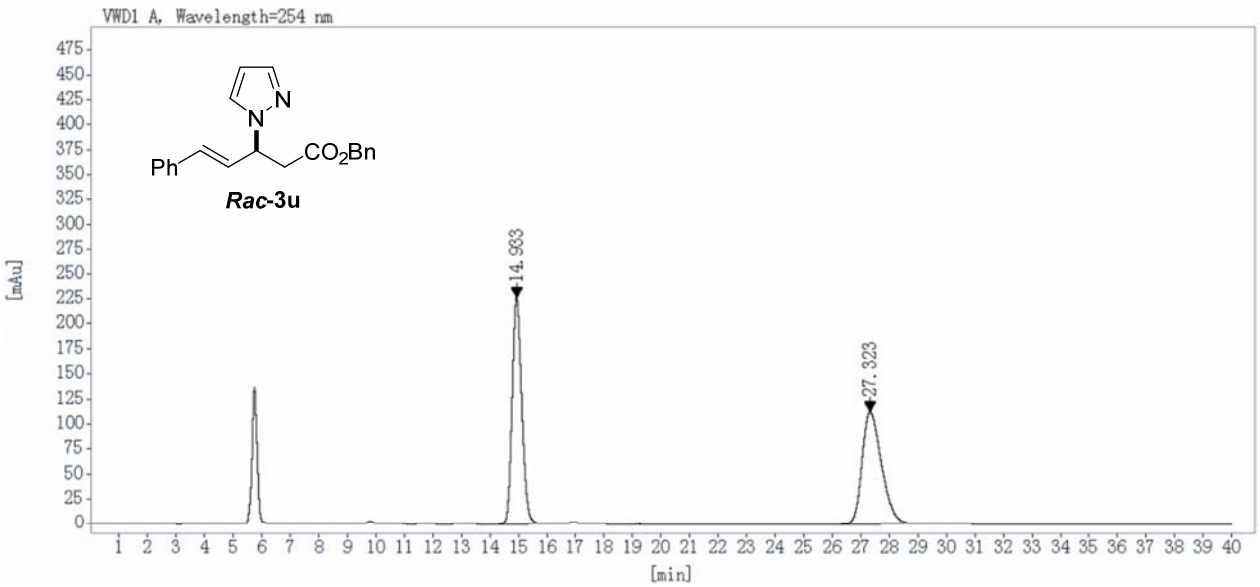
^{1}H-NMR (400 MHz, $CDCl_3$)



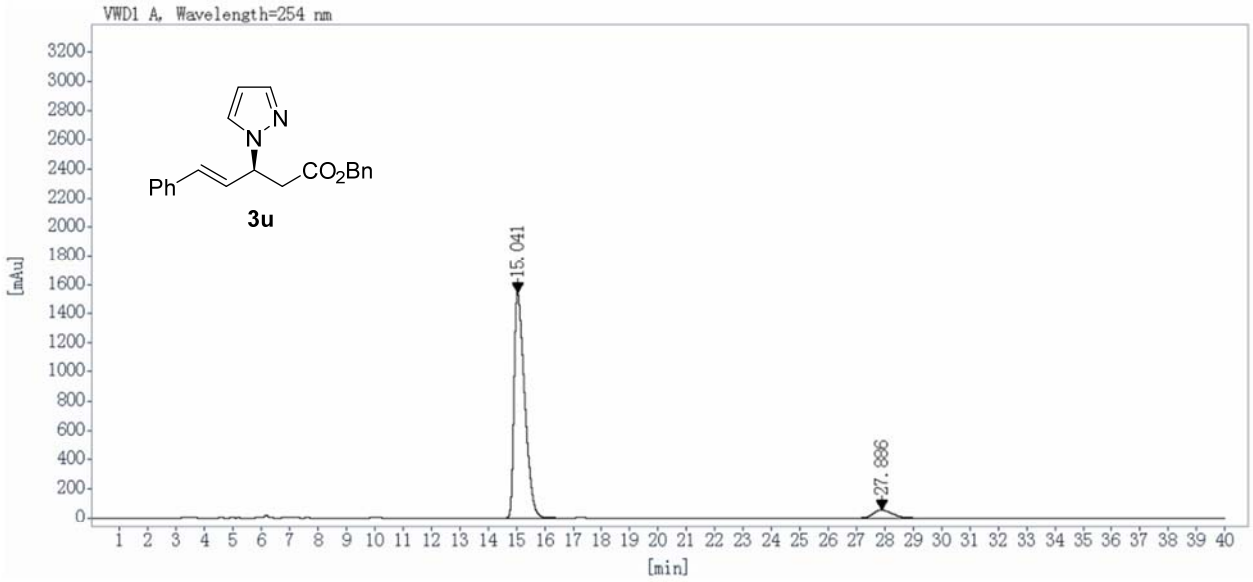
3u

^{13}C-NMR (100 MHz, $CDCl_3$)

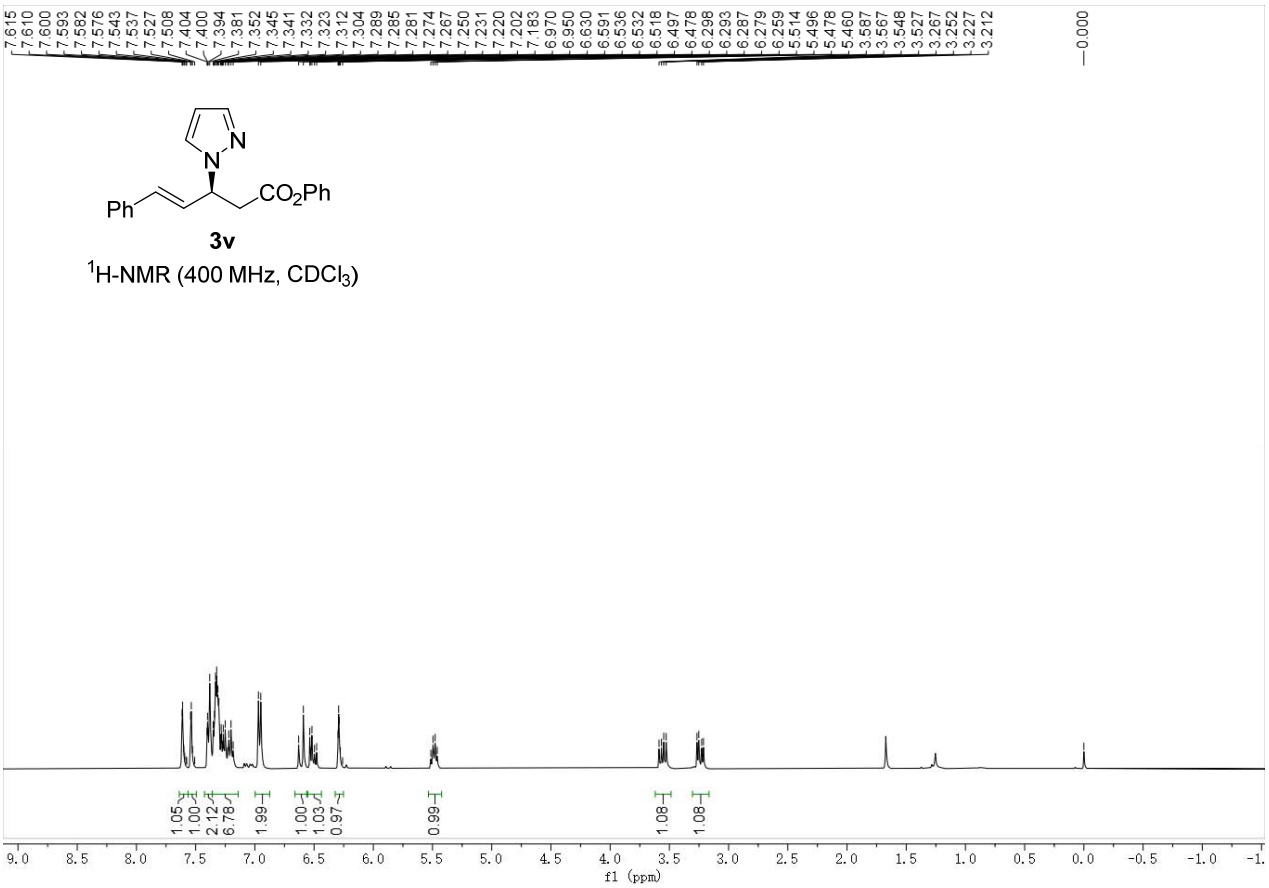

User Spectrum Plot Report
Agilent
Name CYC-220328-9
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status Success
Data File CYC-220328-9.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 3/30/2022 11:47:49 AM (UTC+08:00)
+ESI Scan (rt: 0.162 min) Frag=175.0V CYC-220328-9.d
x10^6
355.1416
Counts vs. Mass-to-Charge (m/z)
Ph
CO2Bn
3u
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C21H20N2O2Na+ 355.1417



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.933	BB	0.36	226.4614	5284.1123	49.9810
27.323	BBA	0.73	112.1682	5288.1387	50.0190
			Totals:	10572.2510	100.0000

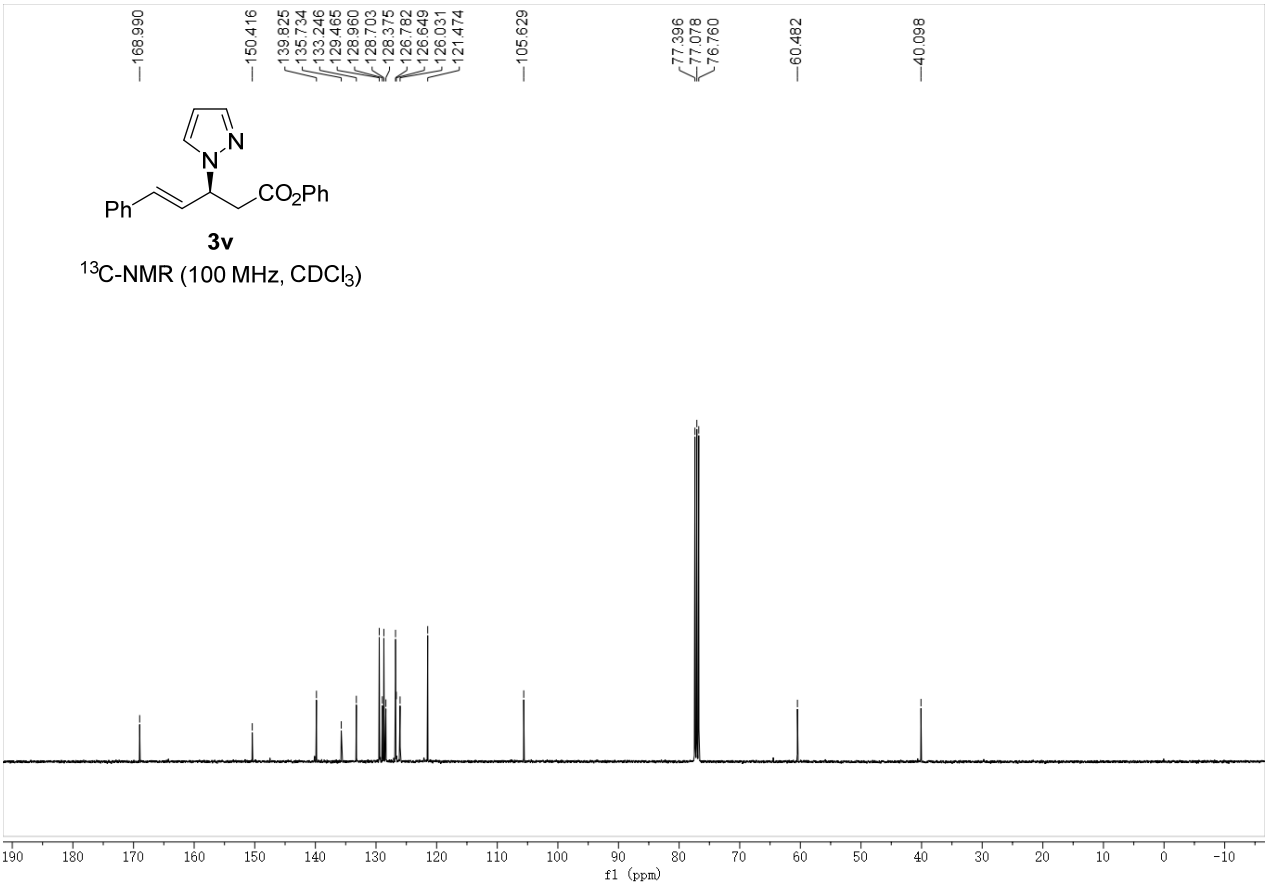


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.041	BB	0.40	1543.3091	40184.6719	94.1638
27.886	BBA	0.71	54.5138	2490.6360	5.8362
			Totals:	42675.3079	100.0000



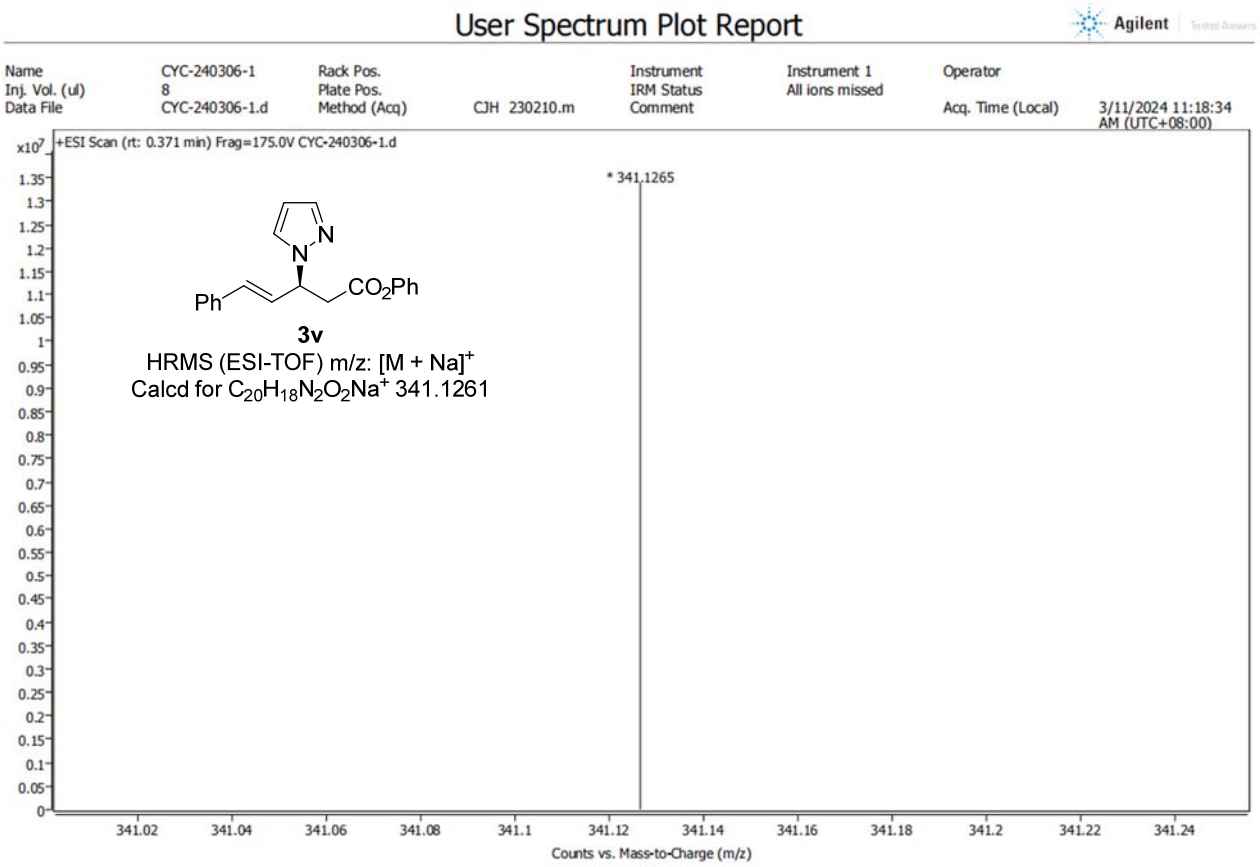
3v

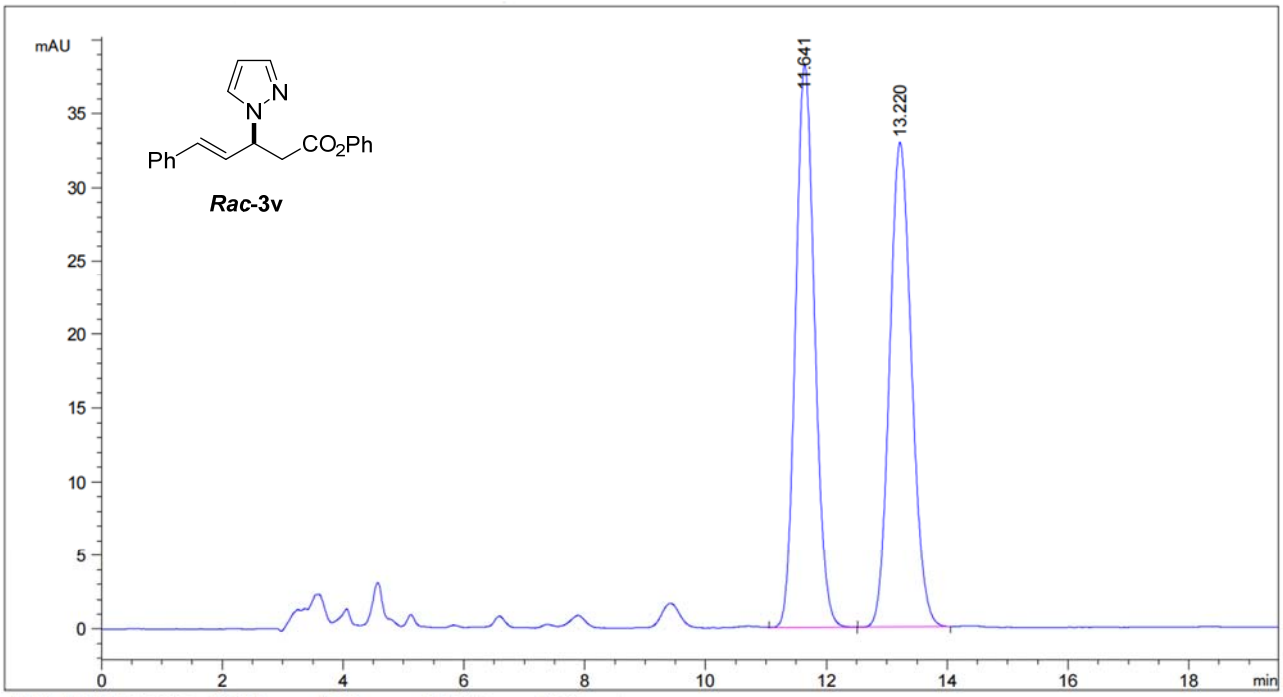
^{1}H-NMR (400 MHz, $CDCl_3$)



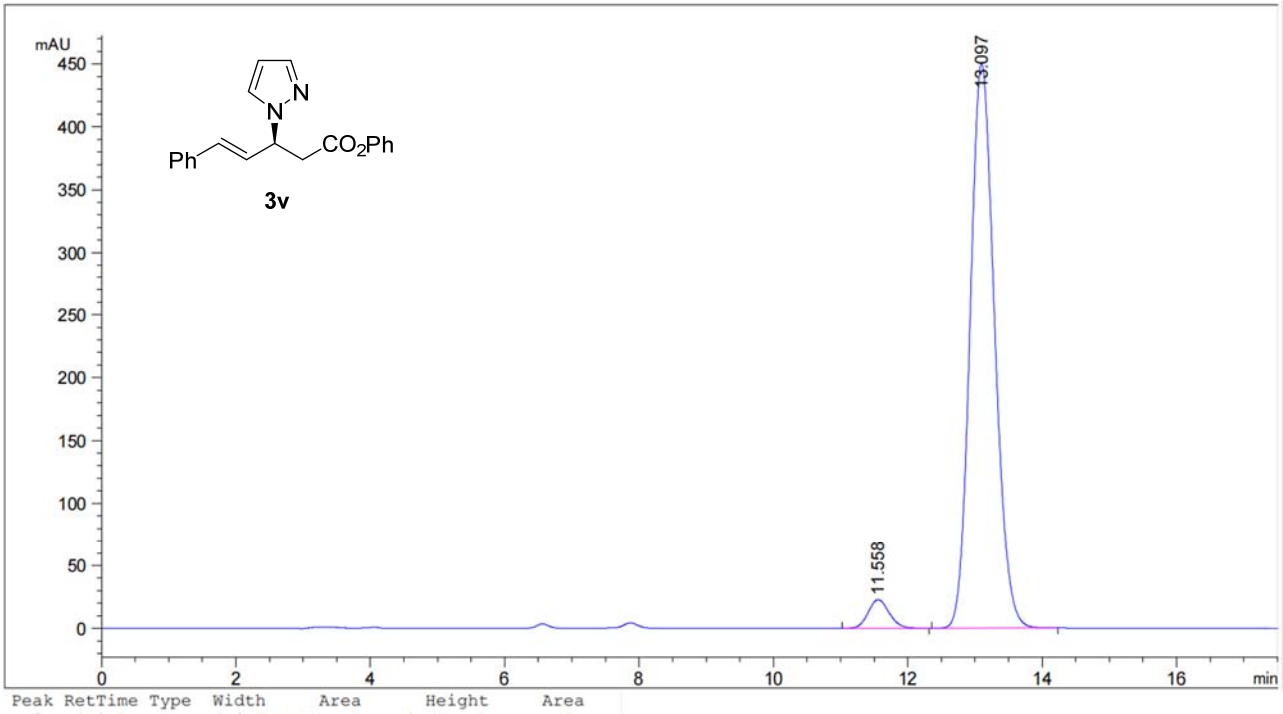
3v

^{13}C-NMR (100 MHz, $CDCl_3$)

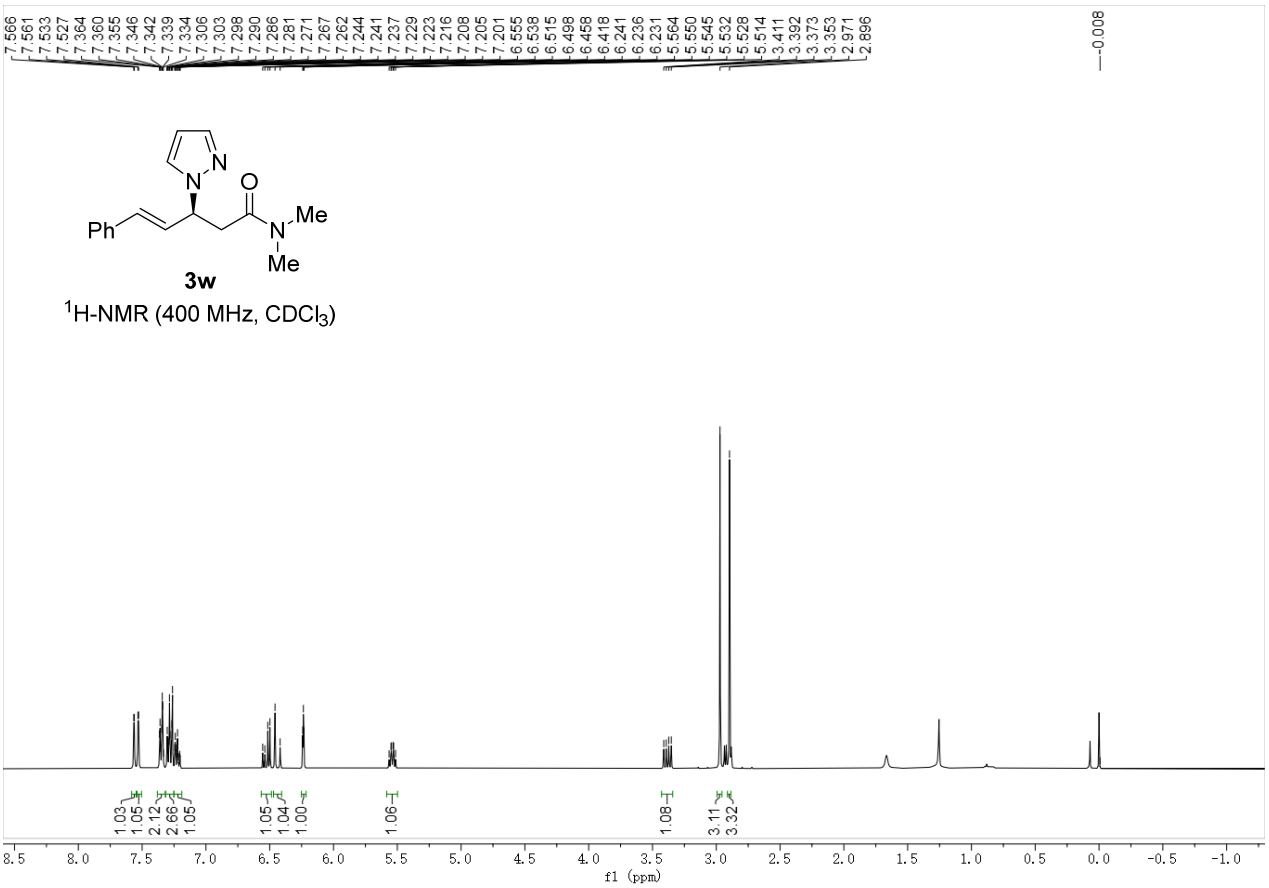

User Spectrum Plot Report
Agilent
Name CYC-240306-1
Inj. Vol. (ul) 8
Data File CYC-240306-1.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:18:34 AM (UTC+08:00)
+ESI Scan (rt: 0.371 min) Frag=175.0V CYC-240306-1.d
x10^7
* 341.1265
Ph
CO2Ph
3v
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C20H18N2O2Na+ 341.1261
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.641	BB	0.3407	839.29968	38.20576	50.2211
2	13.220	BB	0.3911	831.90948	32.90385	49.7789

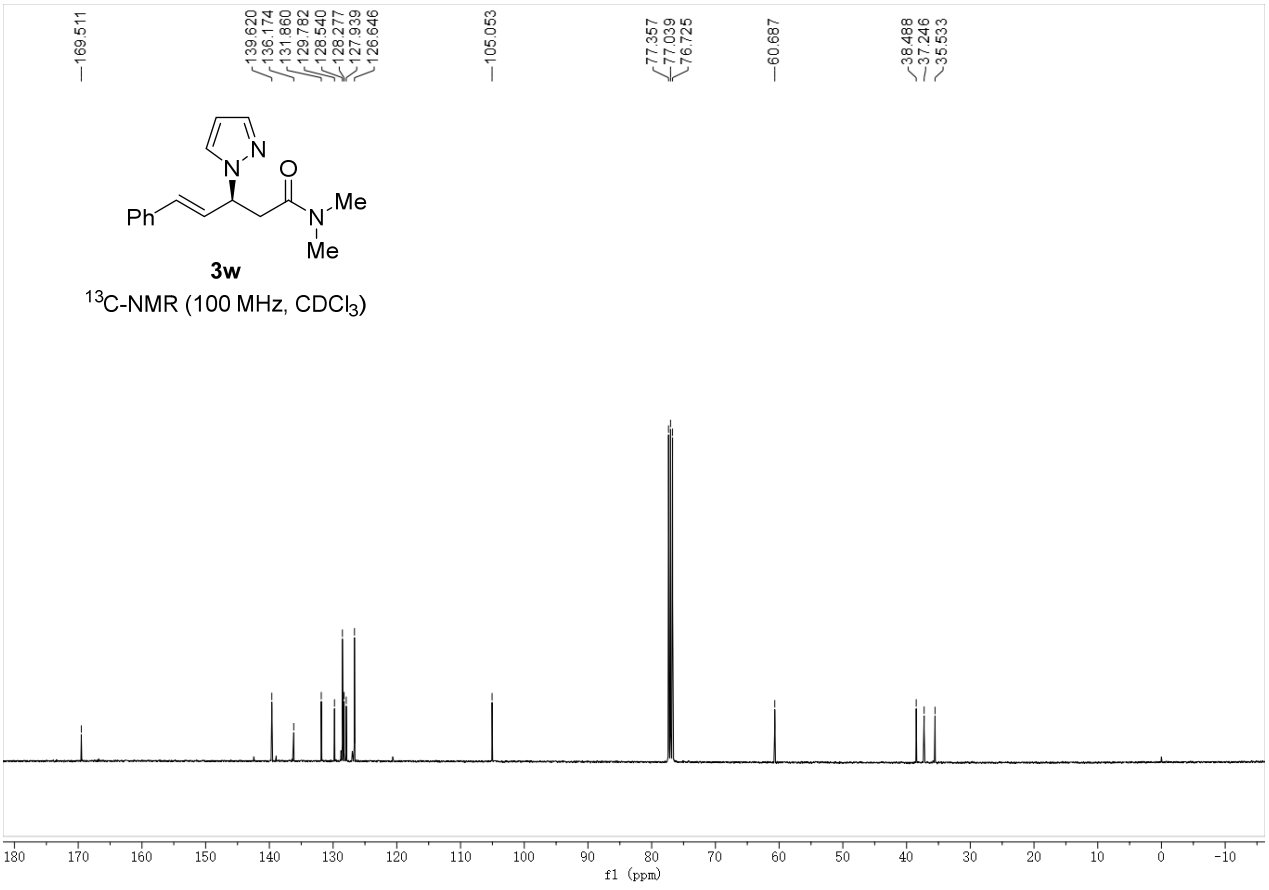


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.558	BB	0.3379	495.45862	22.81002	4.1828
2	13.097	BBA	0.3917	1.13496e4	450.10721	95.8172



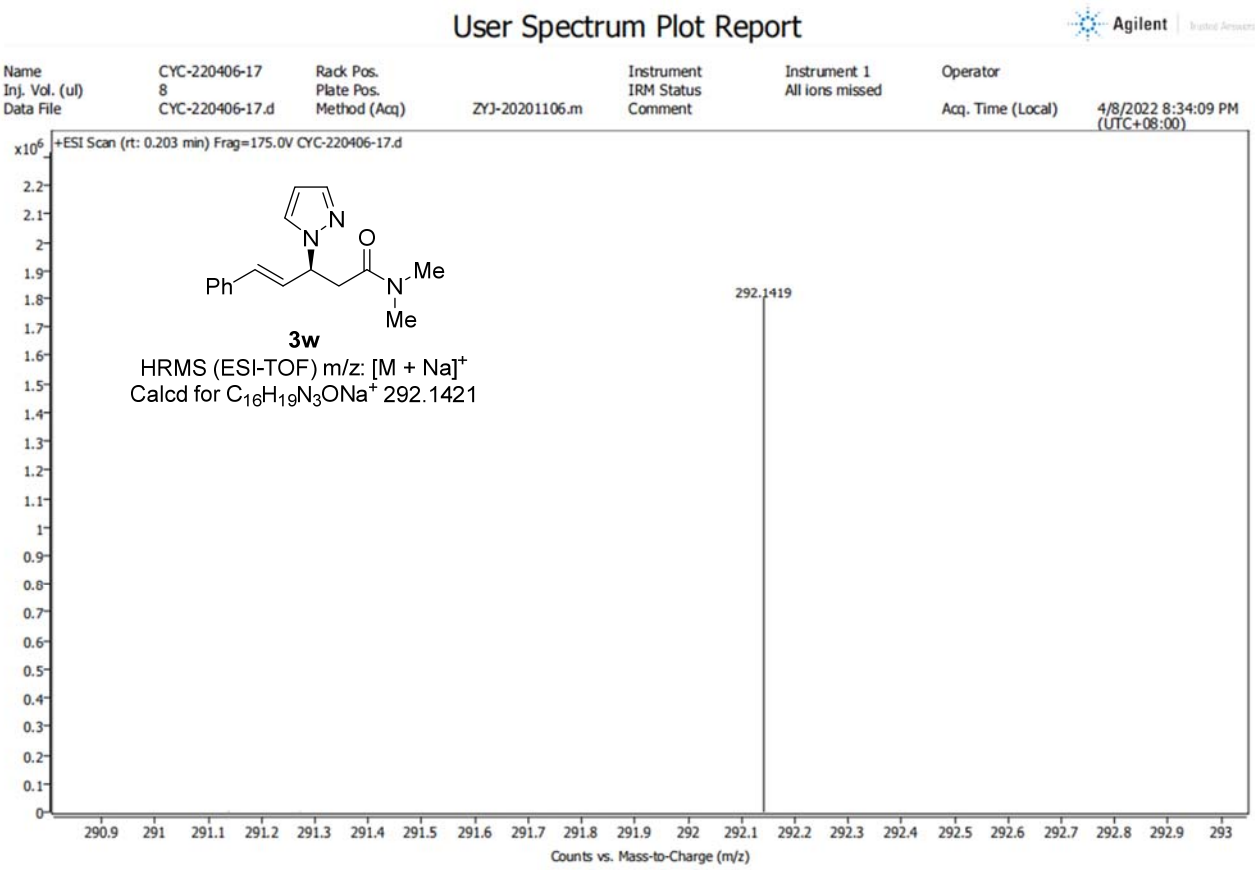
3w

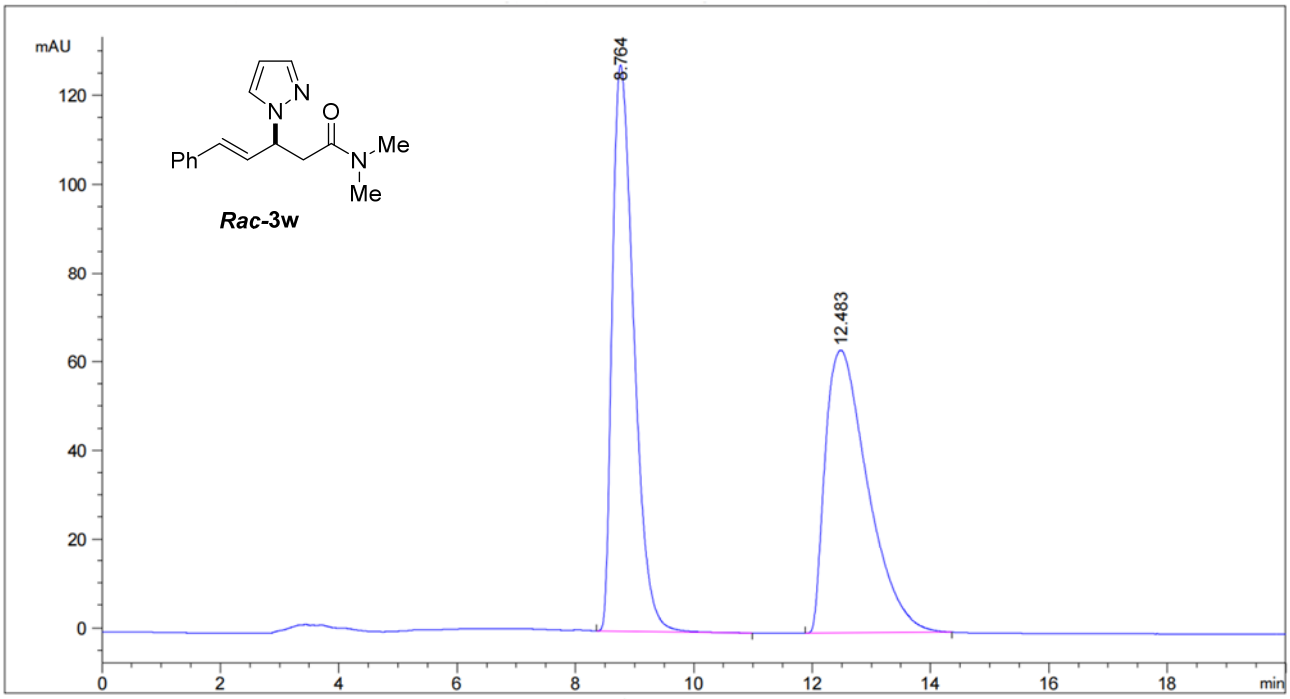
^{1}H-NMR (400 MHz, $CDCl_3$)



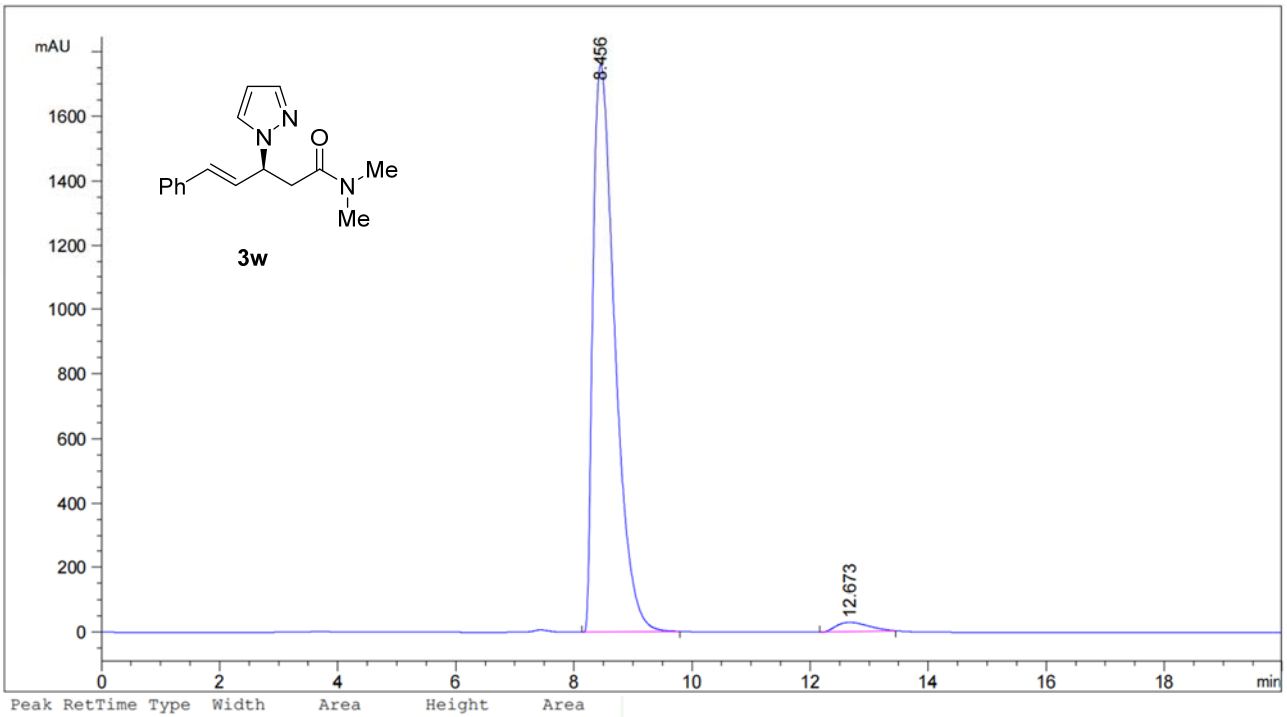
3w

^{13}C-NMR (100 MHz, $CDCl_3$)

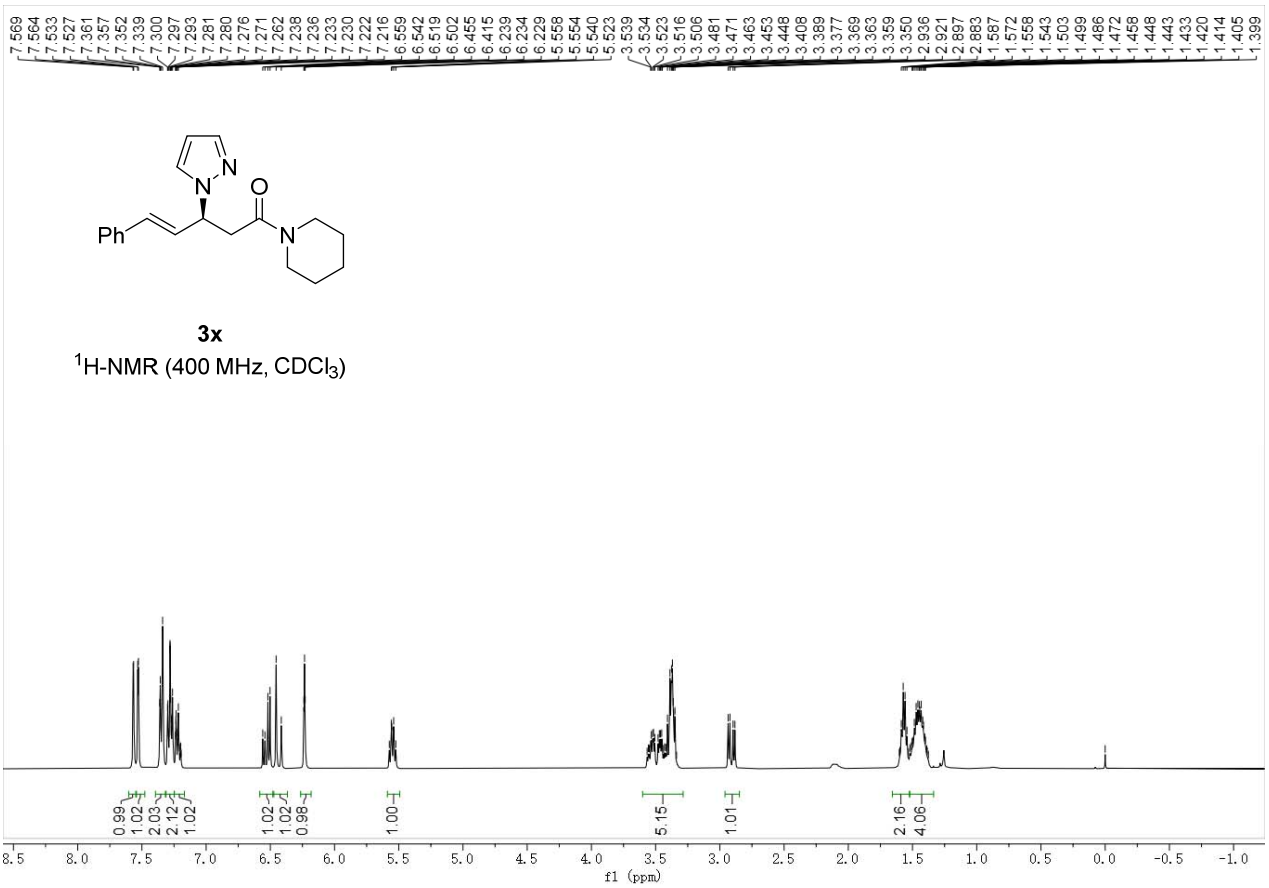

User Spectrum Plot Report
Agilent
Name CYC-220406-17
Inj. Vol. (ul) 8
Data File CYC-220406-17.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 4/8/2022 8:34:09 PM (UTC+08:00)
+ESI Scan (rt: 0.203 min) Frag=175.0V CYC-220406-17.d
x10^6
292.1419
Counts vs. Mass-to-Charge (m/z)
3w
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C16H19N3ONa+ 292.1421



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.764	BB	0.4001	3225.83691	127.44935	50.4075
2	12.483	BBA	0.7739	3173.68359	63.65538	49.5925

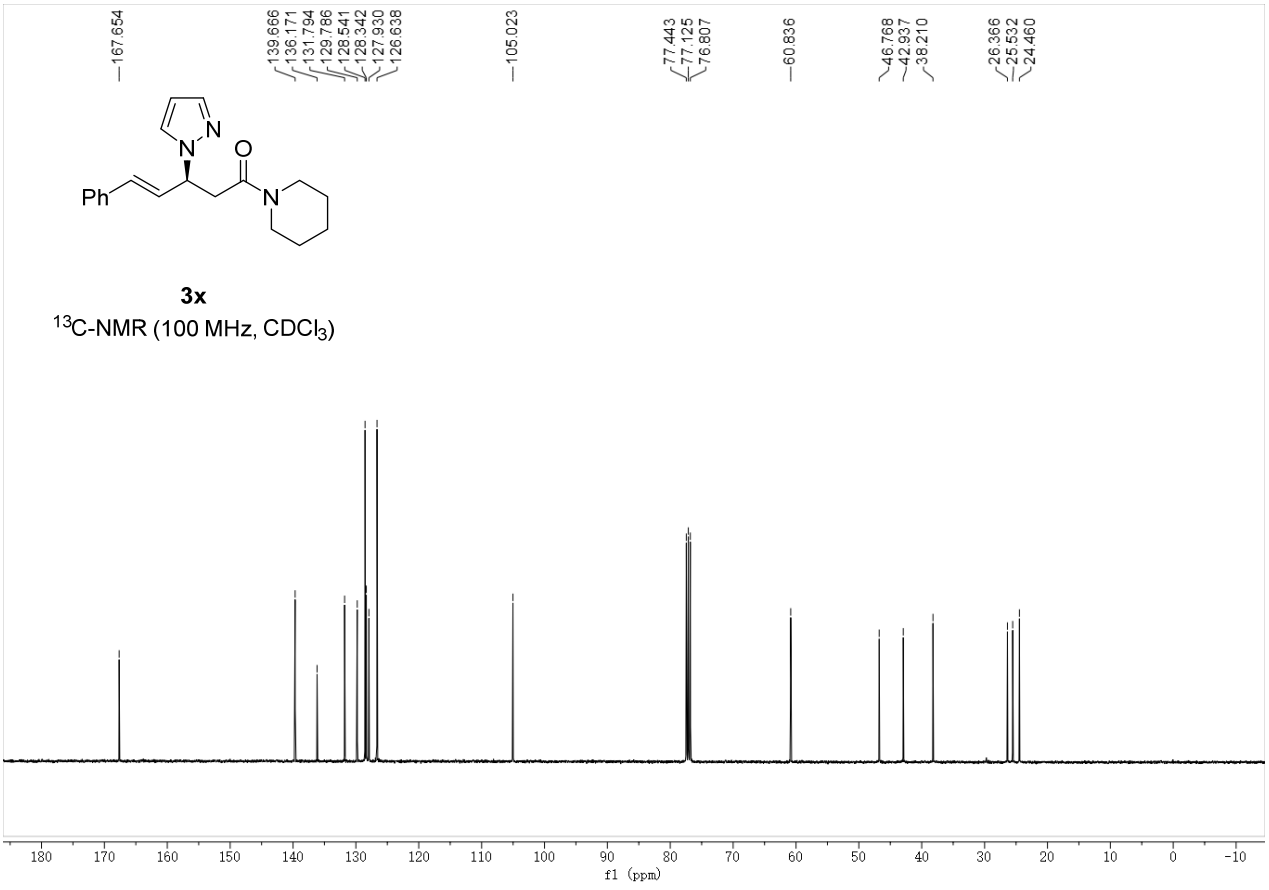


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.456	BBA	0.3992	4.52708e4	1759.20935	97.6331
2	12.673	BBA	0.6125	1097.48523	28.86231	2.3669



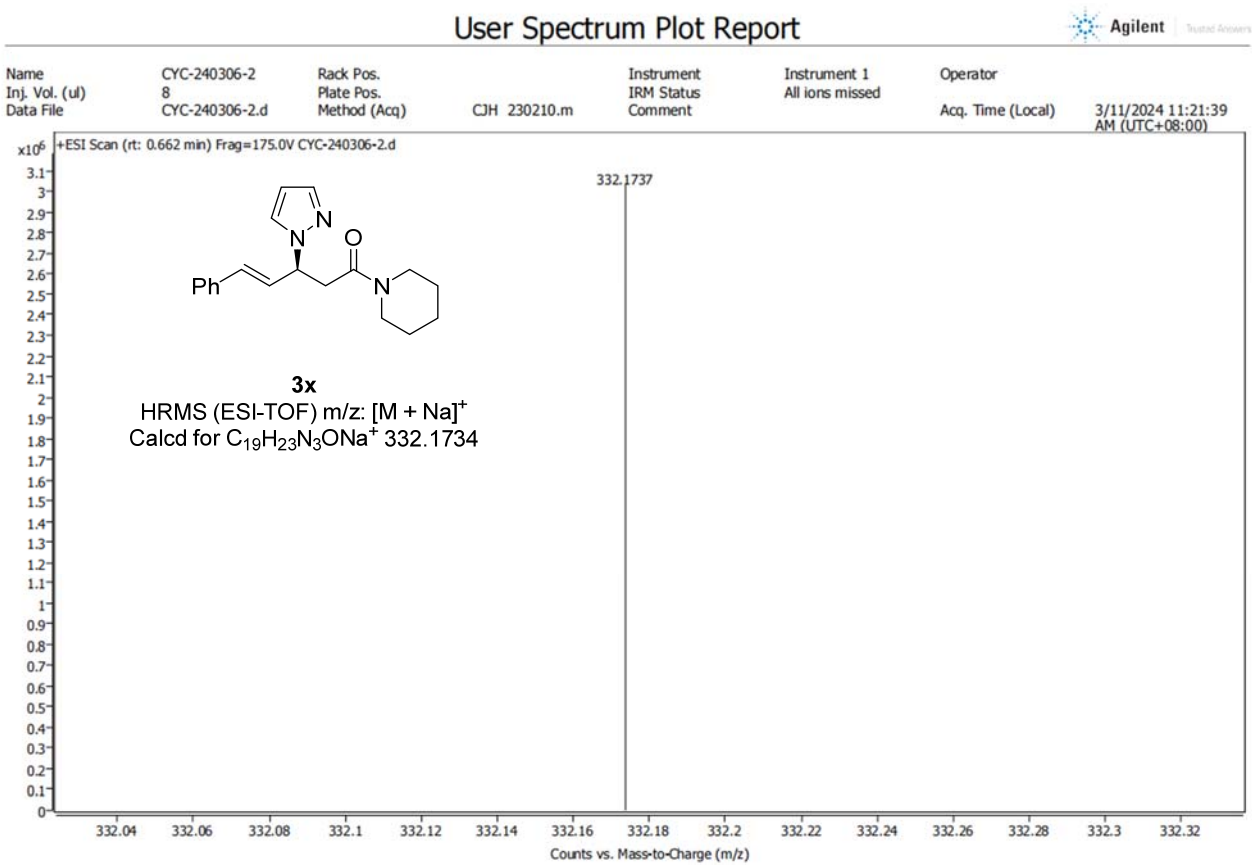
3x

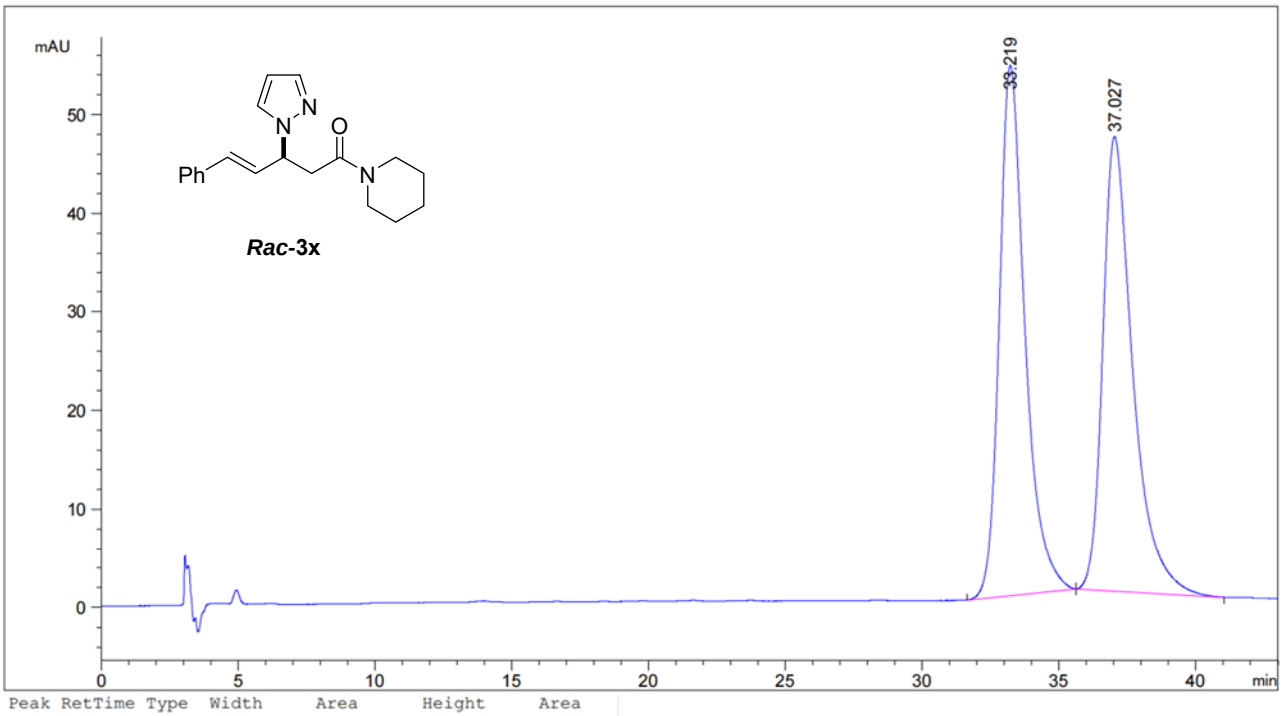
^{1}H-NMR (400 MHz, $CDCl_3$)



3x

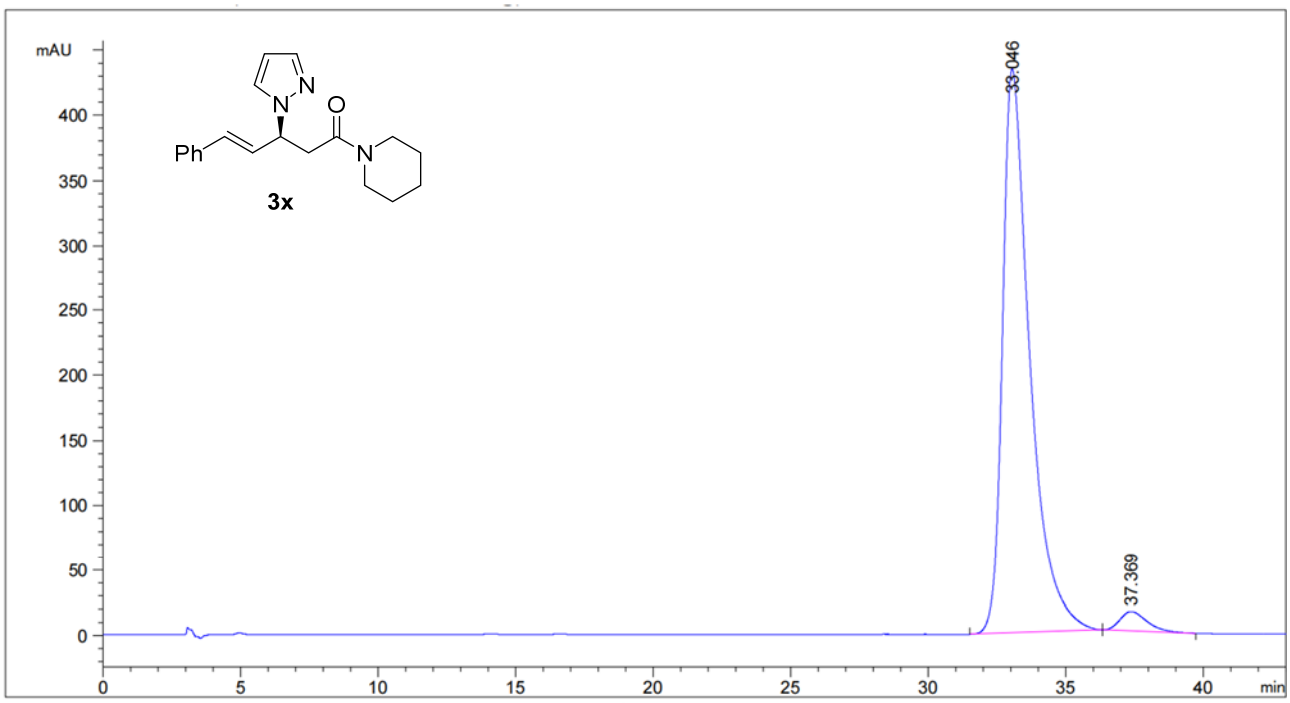
^{13}C-NMR (100 MHz, $CDCl_3$)


User Spectrum Plot Report
Agilent
Name CYC-240306-2
Inj. Vol. (ul) 8
Data File CYC-240306-2.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:21:39 AM (UTC+08:00)
+ESI Scan (rt: 0.662 min) Frag=175.0V CYC-240306-2.d
x10^6
332.1737
Ph
N
O
N
3x
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C19H23N3ONa+ 332.1734
Counts vs. Mass-to-Charge (m/z)



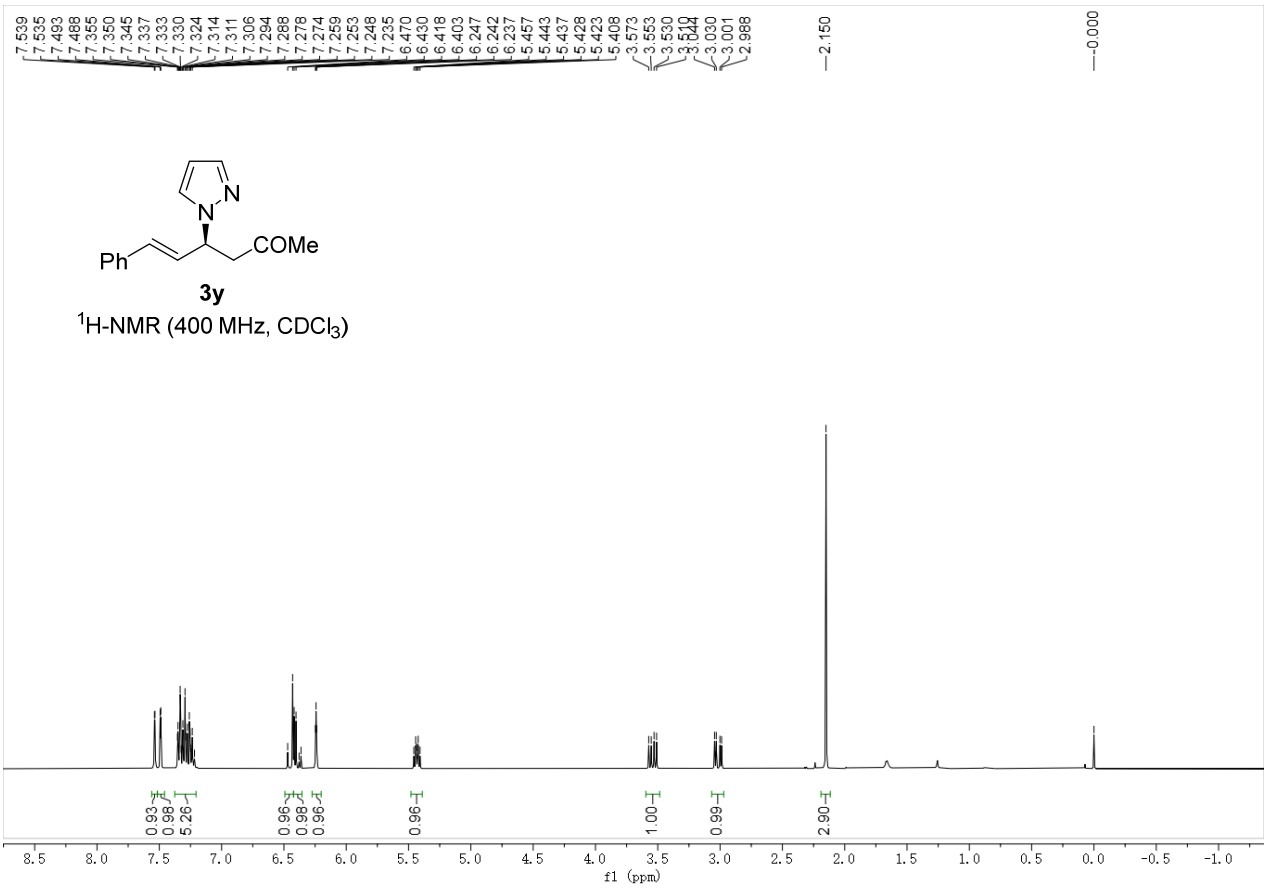
***Rac*-3x**

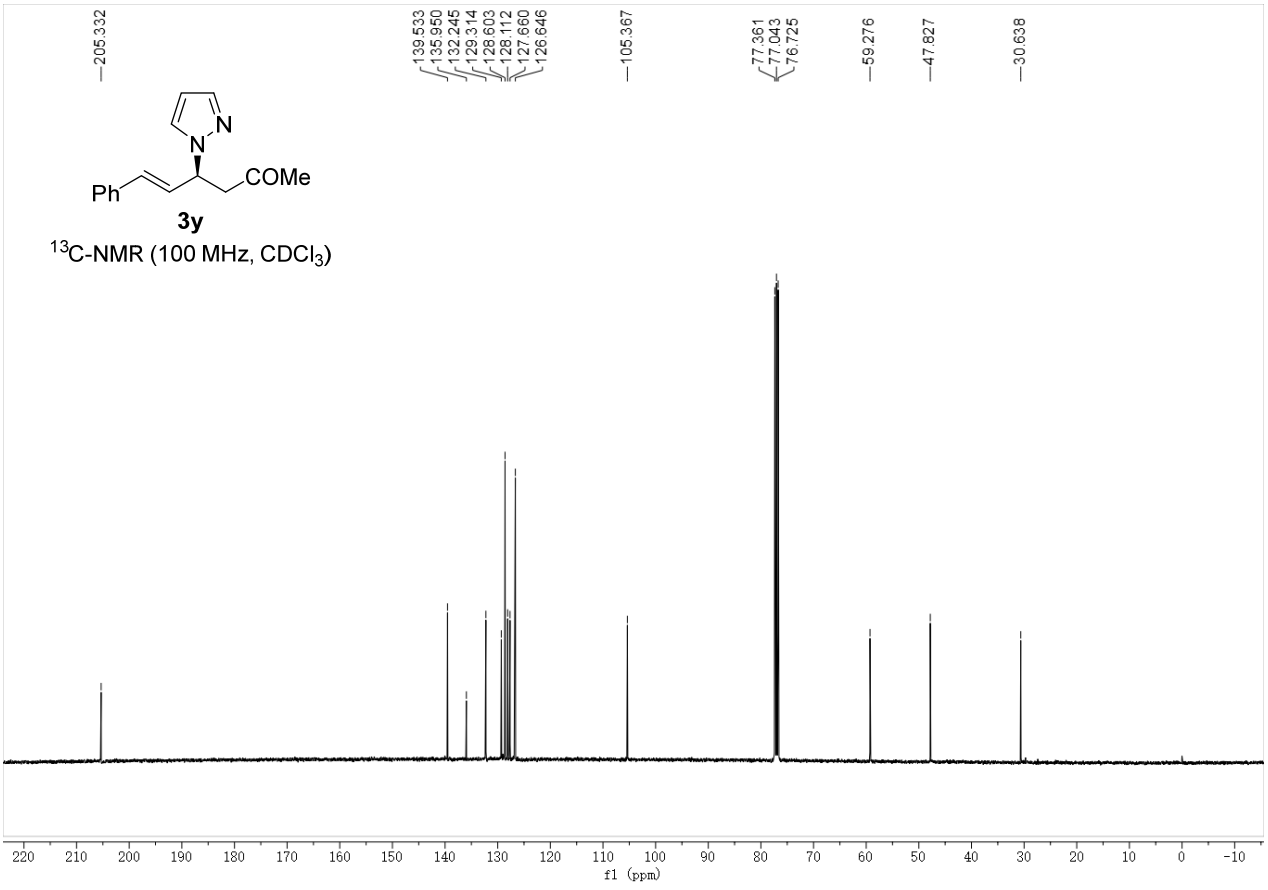
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.219	BB	0.9750	3516.99878	53.81386	49.9152
2	37.027	BB	1.1322	3528.95435	46.15652	50.0848

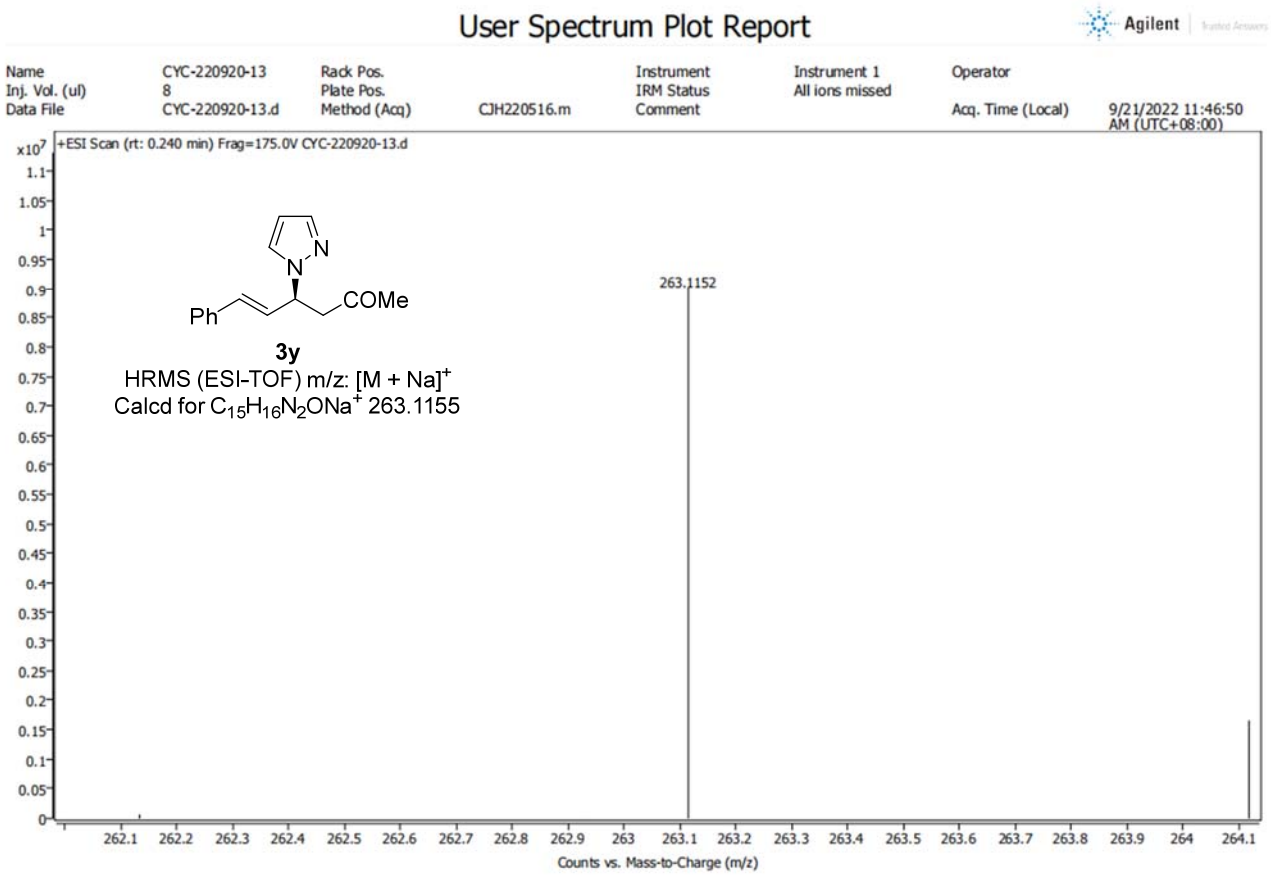


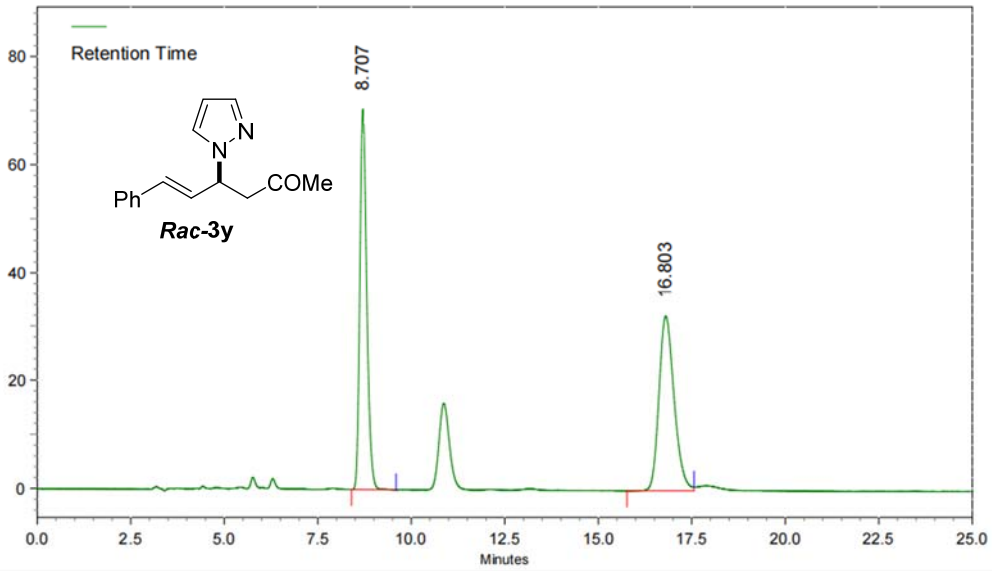
3x

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.046	BB	1.0205	2.99147e4	433.54422	96.7291
2	37.369	BBA	1.0289	1011.55884	14.85357	3.2709


7.539
7.535
7.493
7.488
7.355
7.350
7.345
7.337
7.333
7.330
7.324
7.314
7.311
7.306
7.294
7.288
7.278
7.274
7.259
7.253
7.248
7.235
6.470
6.430
6.418
6.403
6.247
6.242
6.237
5.457
5.443
5.437
5.428
5.423
5.408
3.573
3.553
3.530
3.044
3.030
3.001
2.988
2.150
-0.000
N
N
Ph
COMe
3y
1H-NMR (400 MHz, CDCl3)
0.93
0.98
5.26
0.96
0.98
0.96
0.96
1.00
0.99
2.90
f1 (ppm)

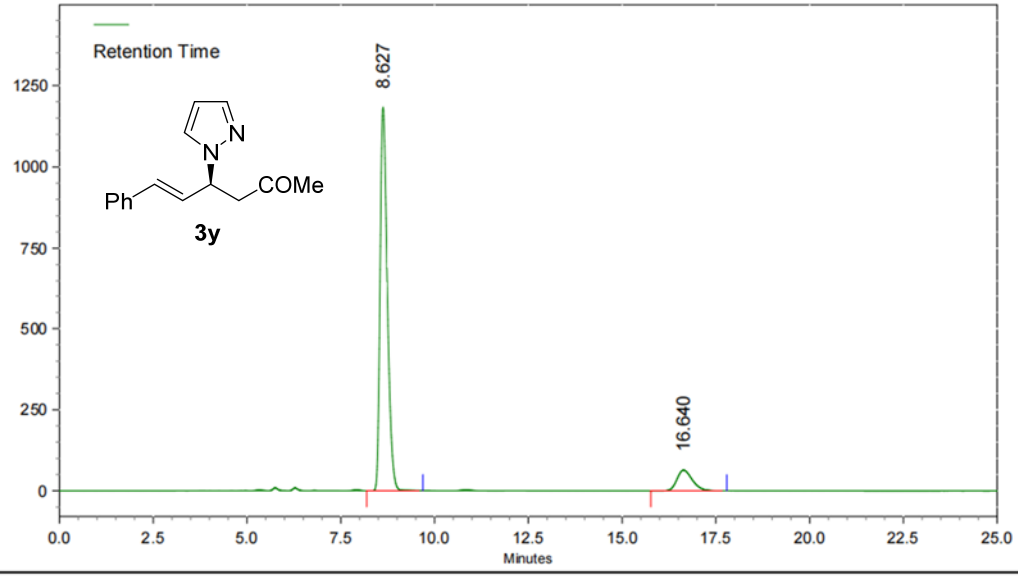

205.332
139.533
135.950
132.245
129.314
128.603
128.112
127.660
126.646
105.367
77.361
77.043
76.725
59.276
47.827
30.638
N
N
Ph
COMe
3y
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


User Spectrum Plot Report
Agilent
Name CYC-220920-13
Inj. Vol. (ul) 8
Data File CYC-220920-13.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 9/21/2022 11:46:50 AM (UTC+08:00)
+ESI Scan (rt: 0.240 min) Frag=175.0V CYC-220920-13.d
x10^7
263.1152
Ph
COMe
N
N
3y
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C15H16N2ONa+ 263.1155
Counts vs. Mass-to-Charge (m/z)



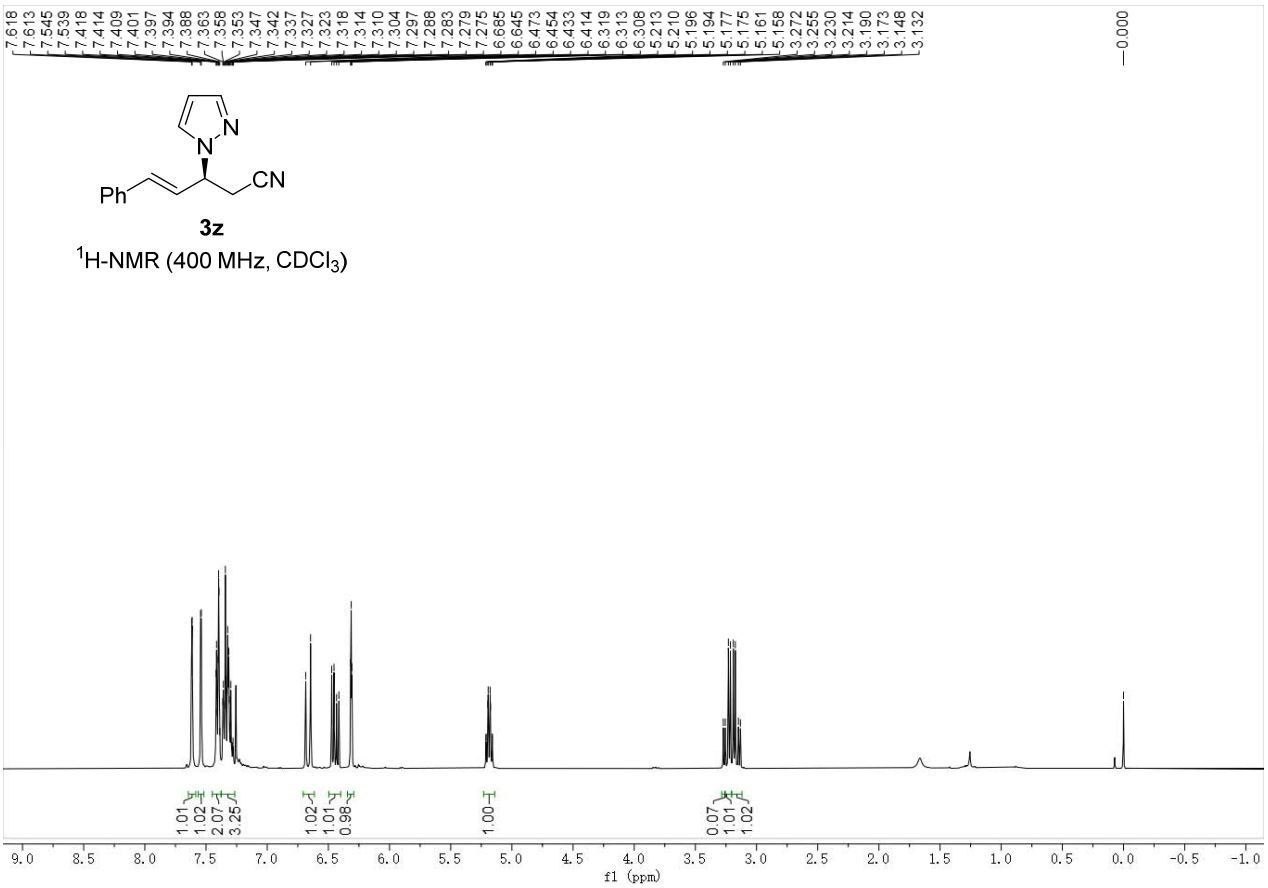
AREA PERCENT REPORT

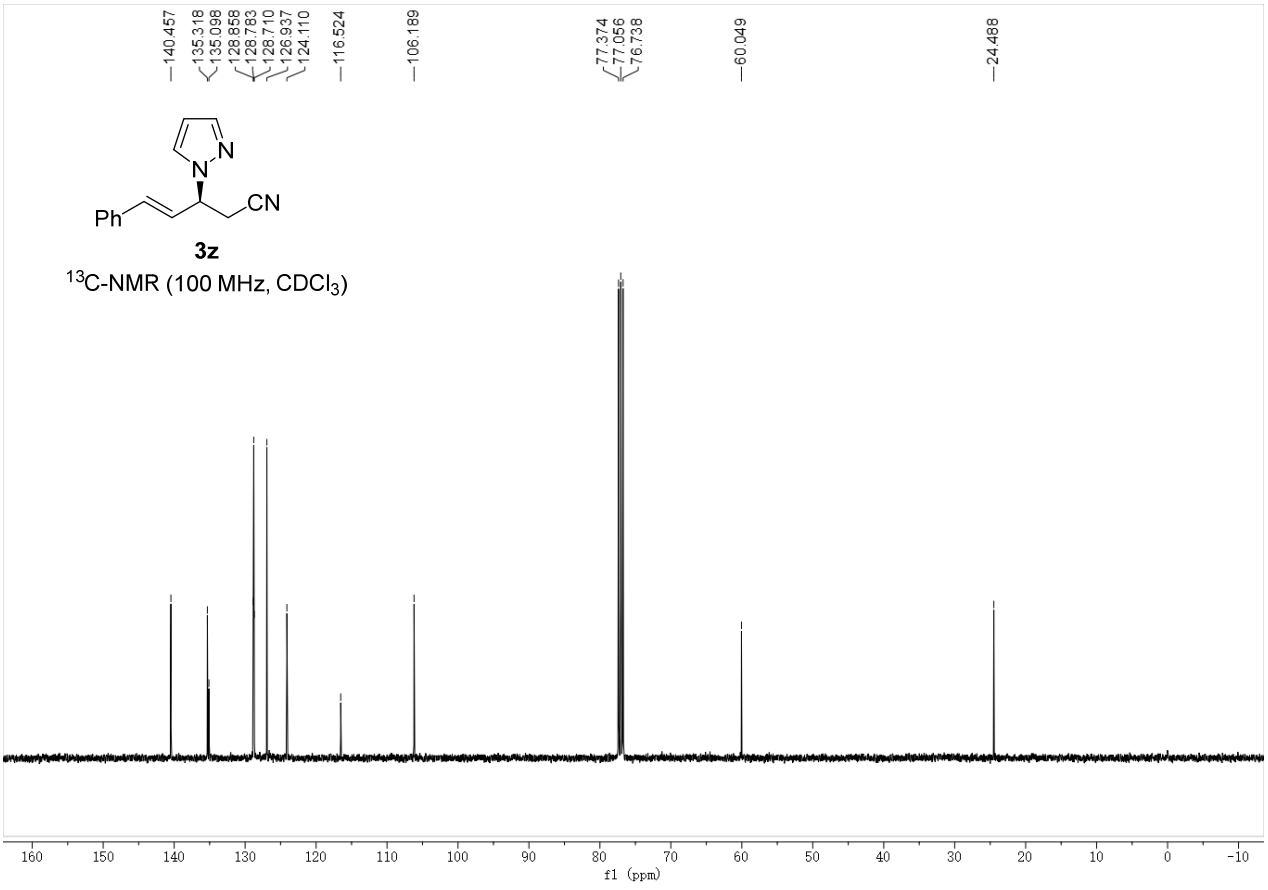
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.707	1.190	1182739	15150974	49.7621
2	16.803	1.797	542133	15295824	50.2379
Totals			1724872	30446798	100.0000

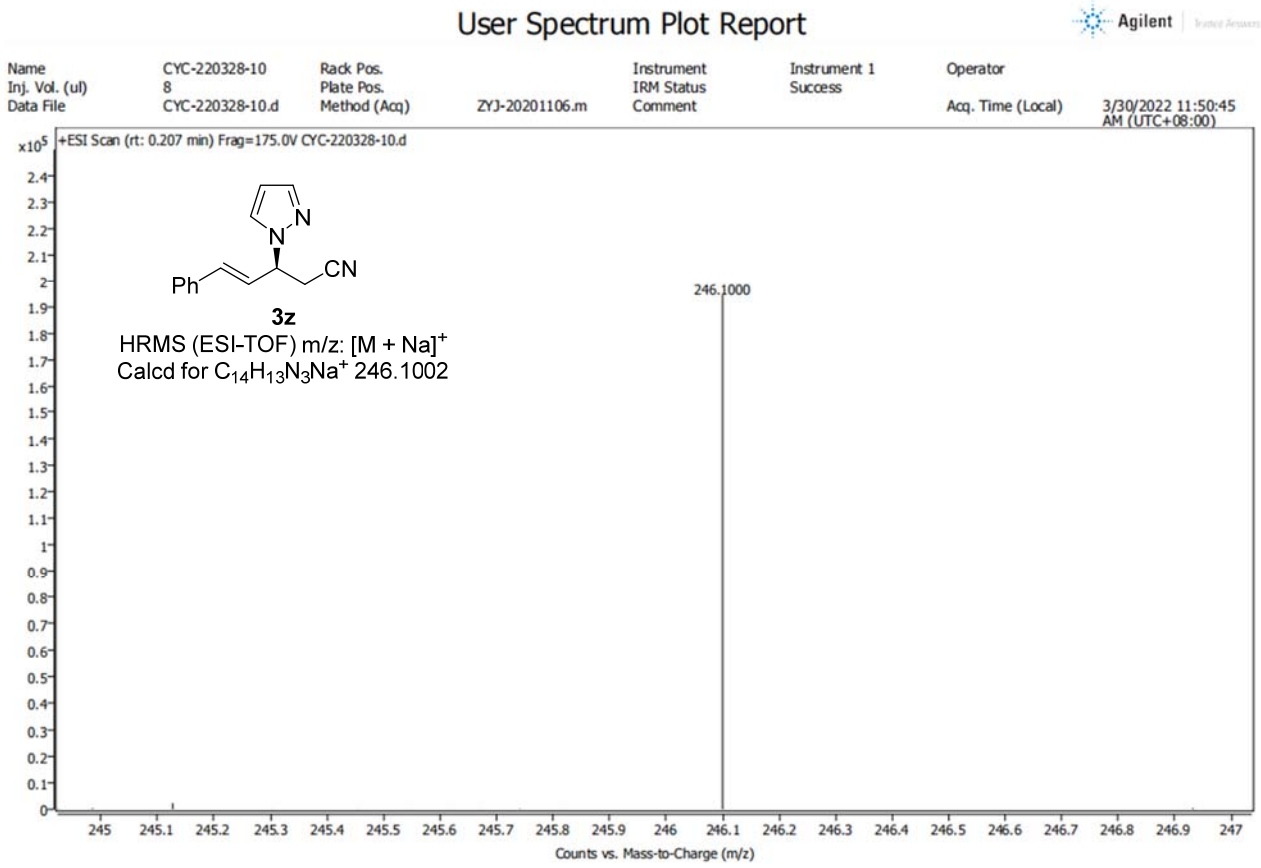


AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.627	1.493	19837492	264859980	89.6950
2	16.640	2.027	1070636	30429481	10.3050
Totals			20908128	295289461	100.0000

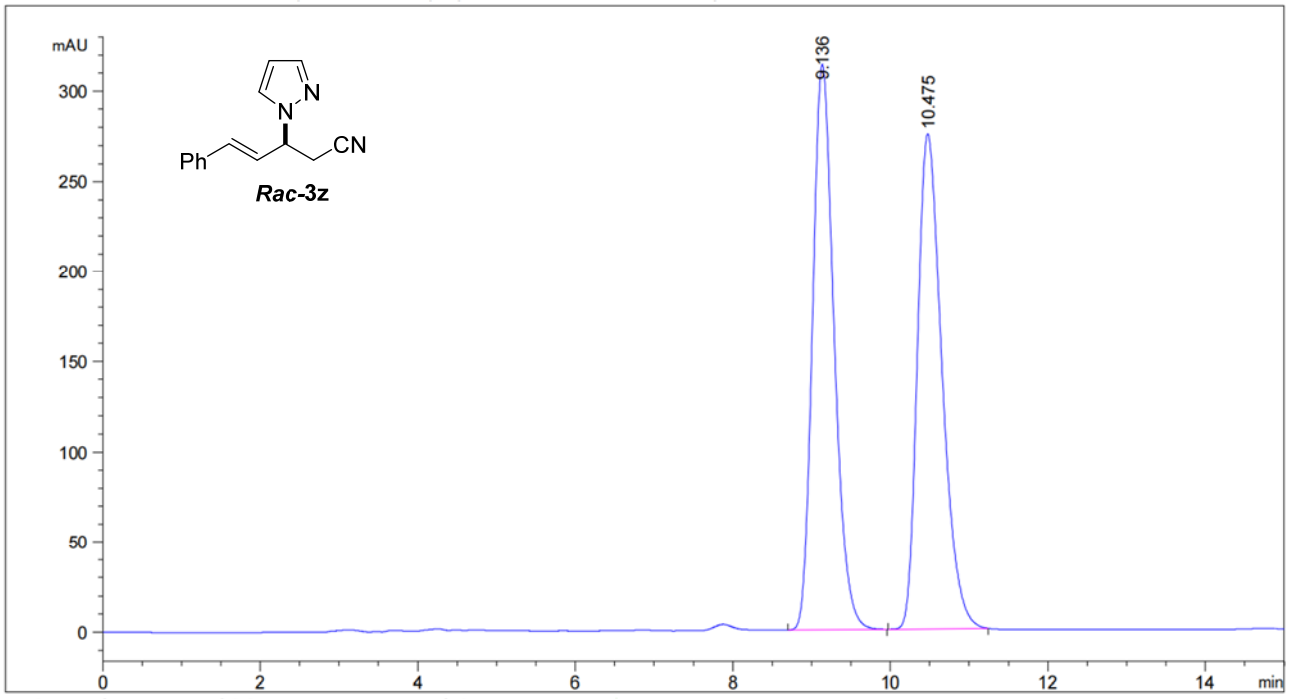

7.618
7.613
7.545
7.539
7.418
7.414
7.409
7.401
7.397
7.394
7.388
7.363
7.358
7.353
7.347
7.342
7.337
7.327
7.323
7.318
7.314
7.310
7.304
7.297
7.288
7.283
7.279
7.275
6.685
6.645
6.473
6.454
6.433
6.414
6.319
6.313
6.308
5.213
5.210
5.196
5.194
5.177
5.175
5.161
5.158
3.272
3.255
3.230
3.214
3.190
3.173
3.148
3.132
0.000
N
N
Ph
CN
3z
1H-NMR (400 MHz, CDCl3)
1.01
1.02
2.07
3.25
1.02
1.01
0.98
1.00
0.07
1.01
1.02
f1 (ppm)


140.457
135.318
135.098
128.858
128.783
128.710
126.937
124.110
116.524
106.189
77.374
77.056
76.738
60.049
24.488
N
N
Ph
CN
3z
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

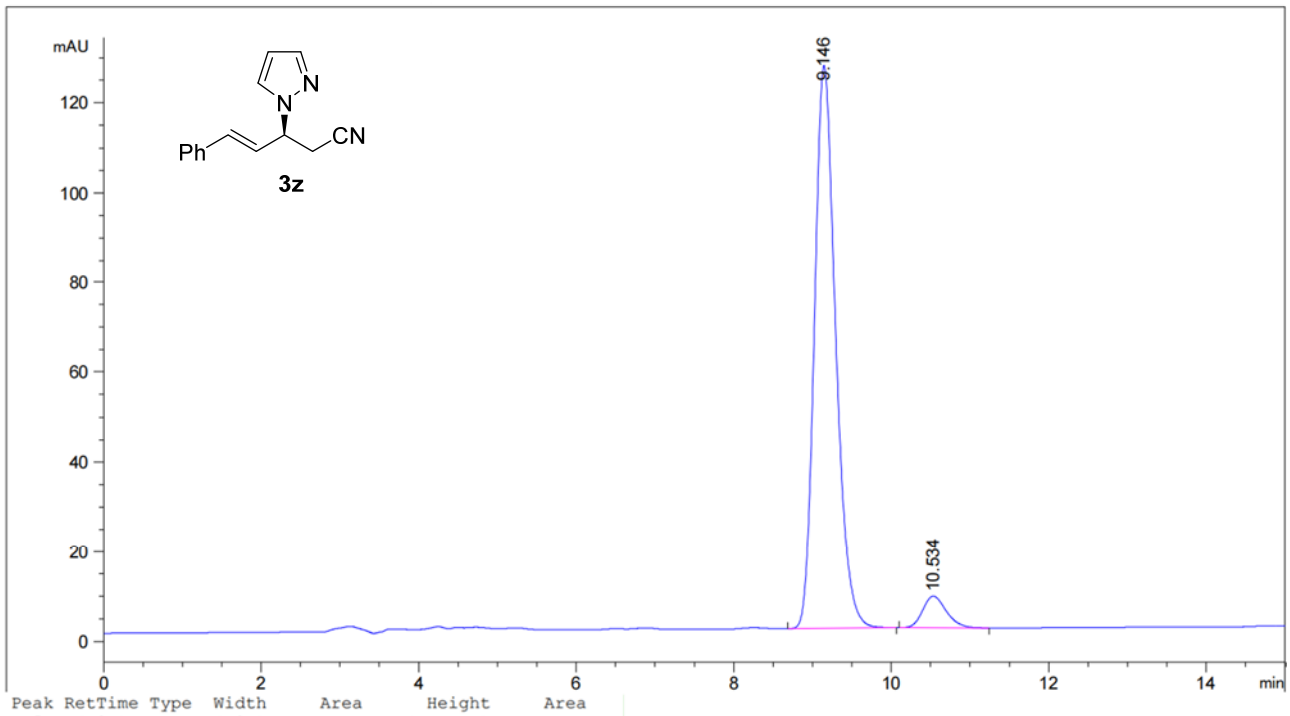


3z

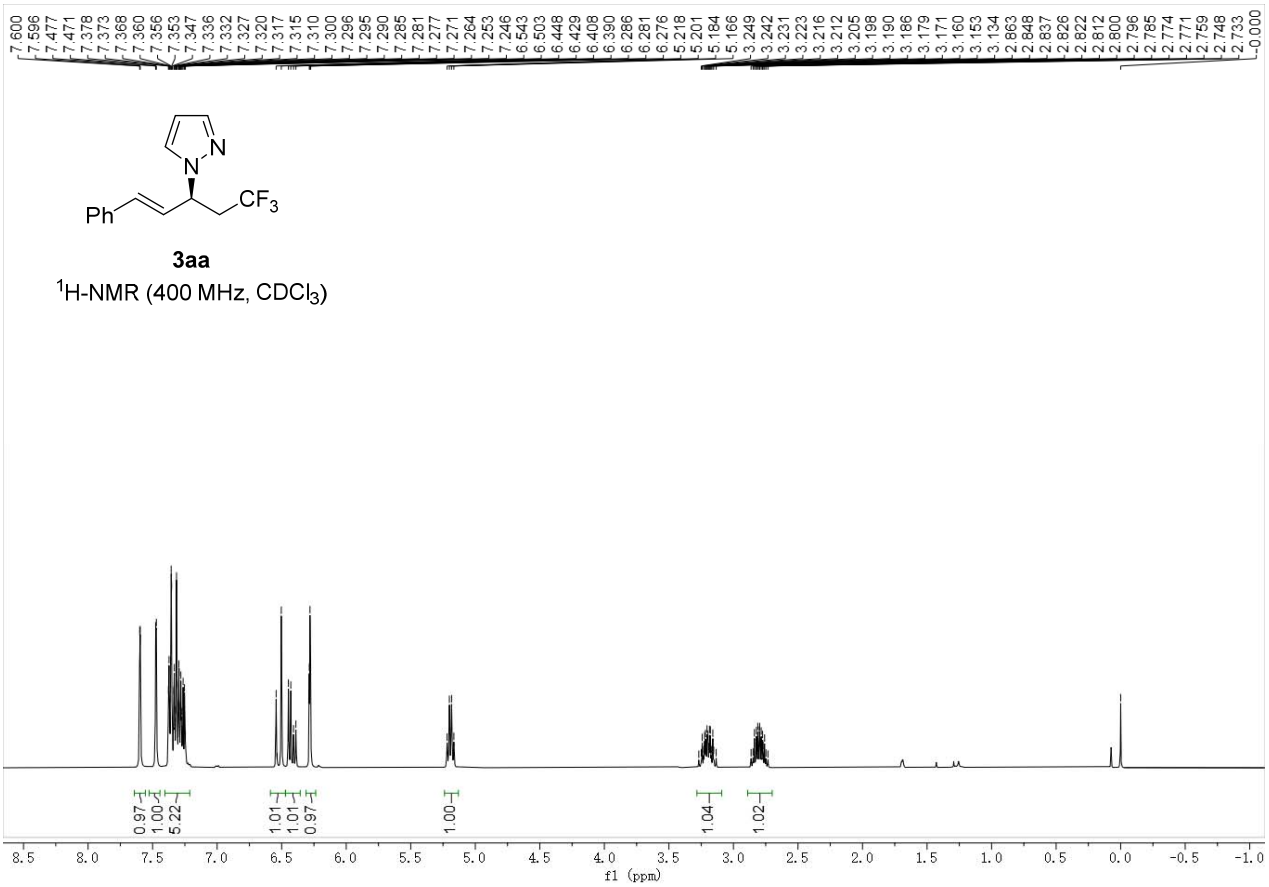
HRMS (ESI-TOF) m/z: $[M + Na]^+$
Calcd for $C_{14}H_{13}N_3Na^+$ 246.1002



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.136	BB	0.2910	5938.52197	313.34711	50.0799
2	10.475	BBA	0.3331	5919.56885	274.57425	49.9201

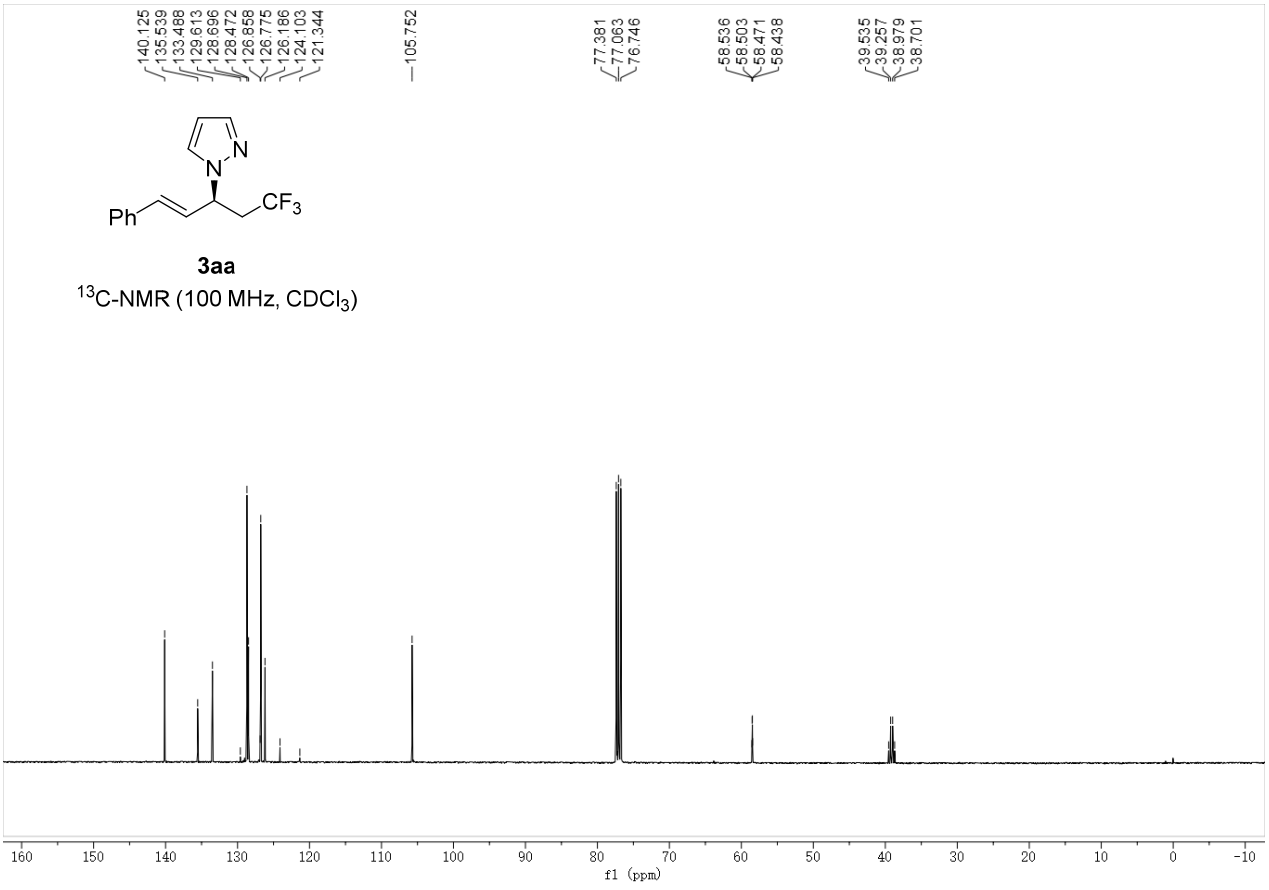


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.146	BB	0.2862	2340.21631	125.36149	94.1546
2	10.534	BBA	0.3208	145.28661	7.00055	5.8454



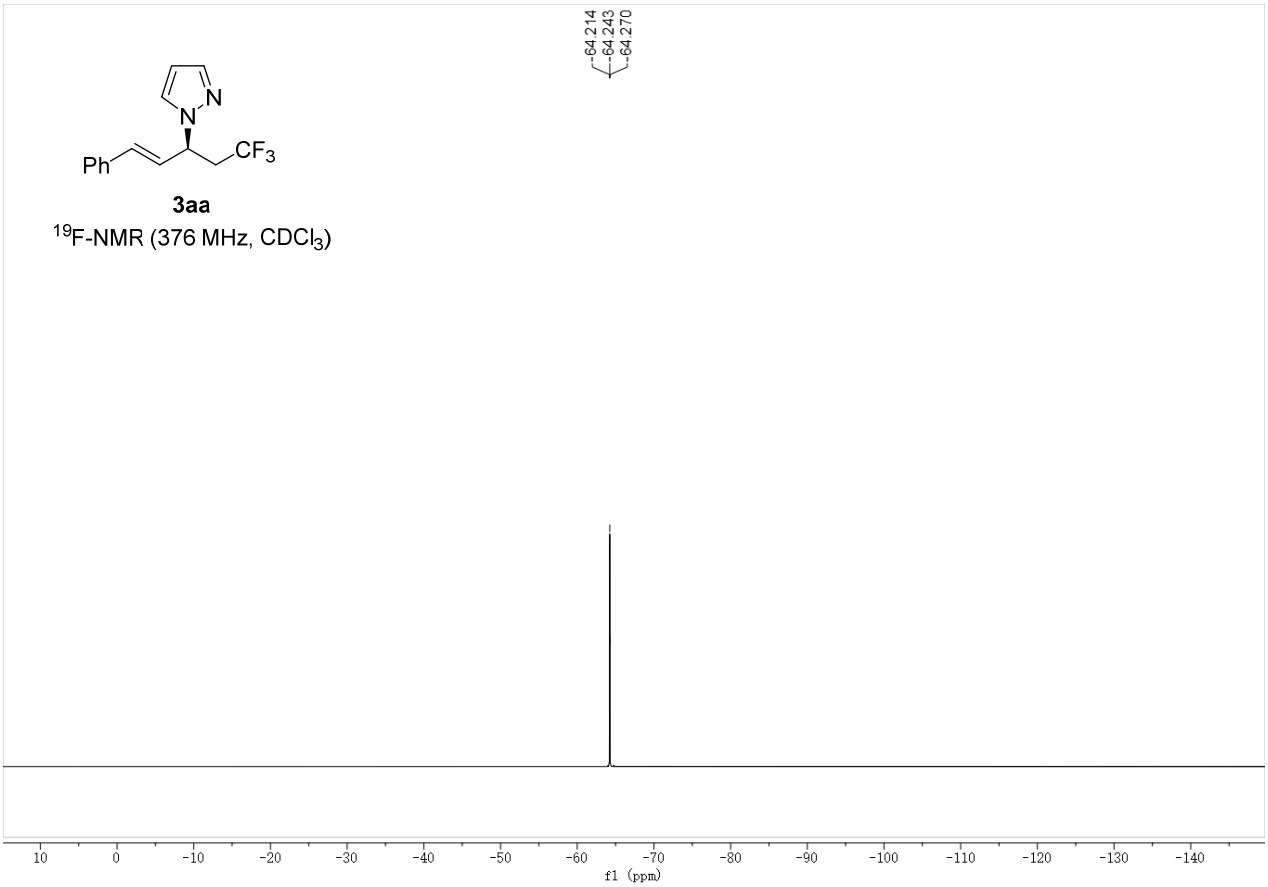
3aa

^{1}H-NMR (400 MHz, $CDCl_3$)



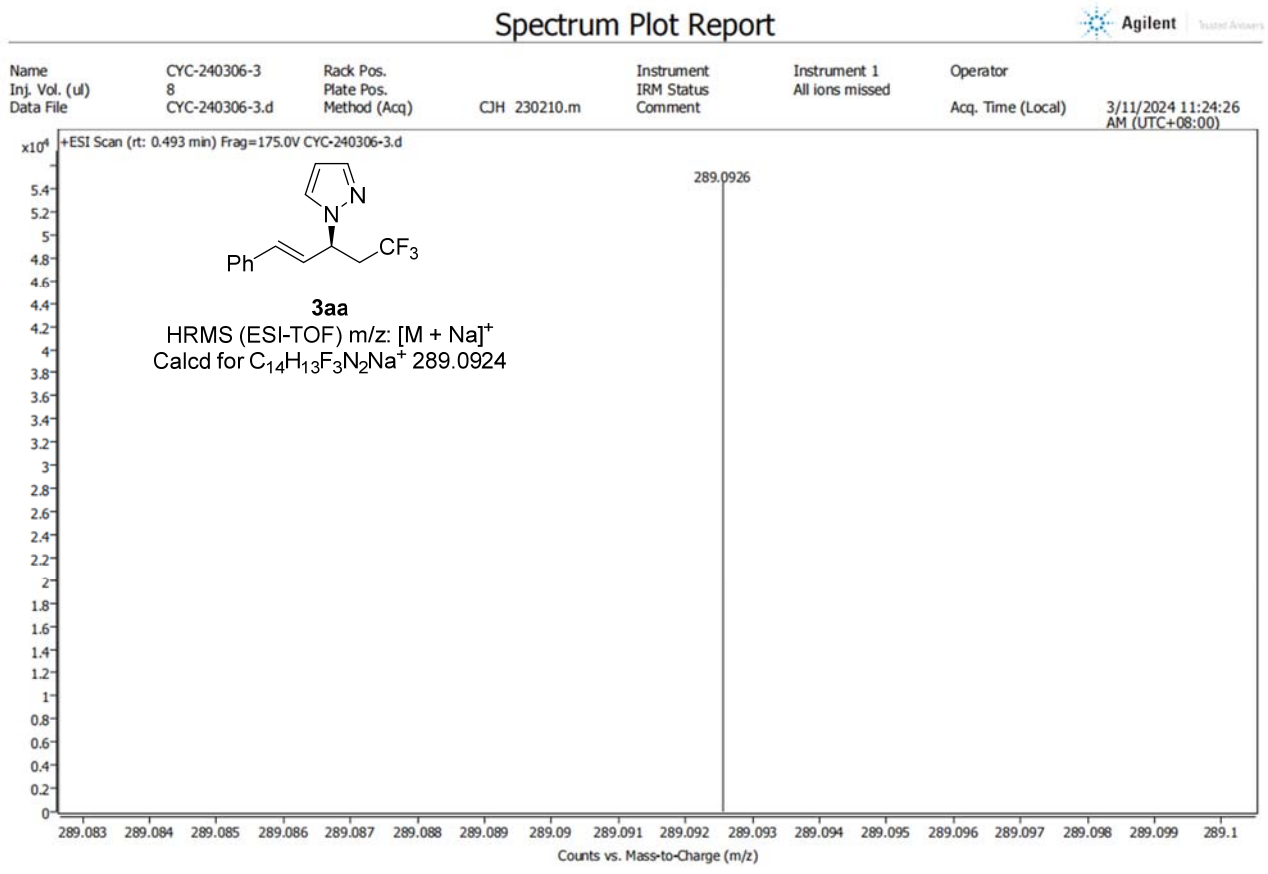
3aa

^{13}C-NMR (100 MHz, $CDCl_3$)



3aa

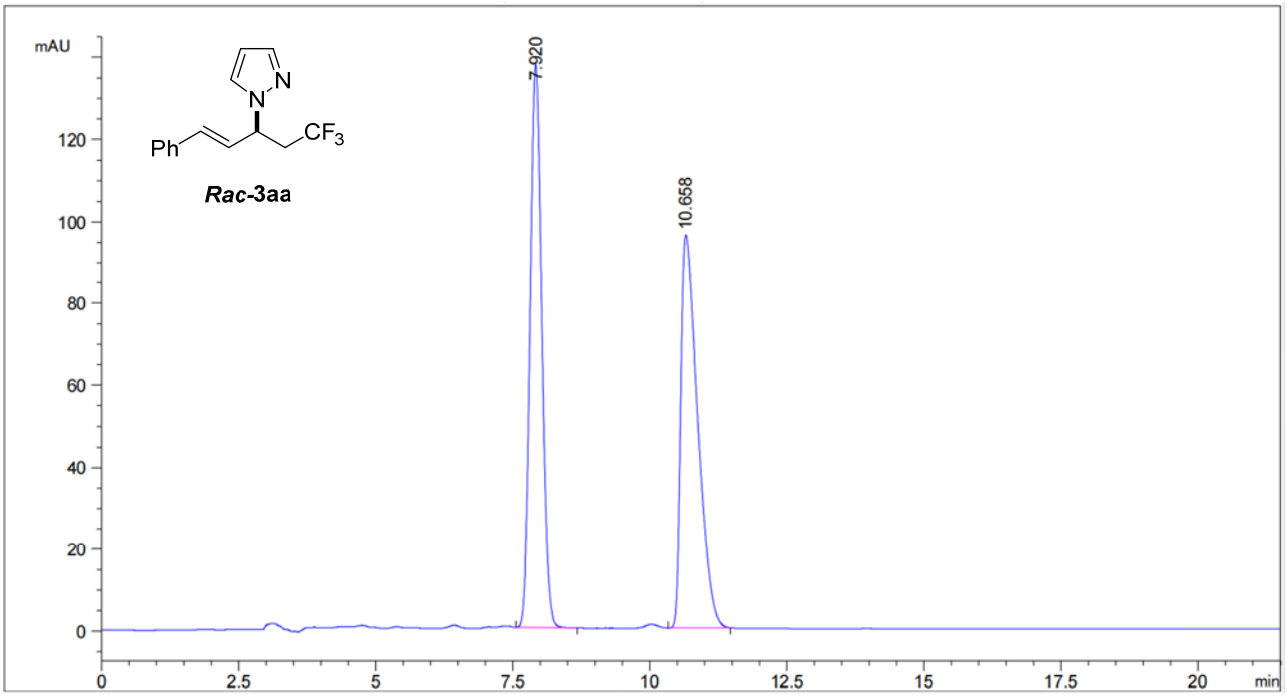
^{19}F-NMR (376 MHz, $CDCl_3$)



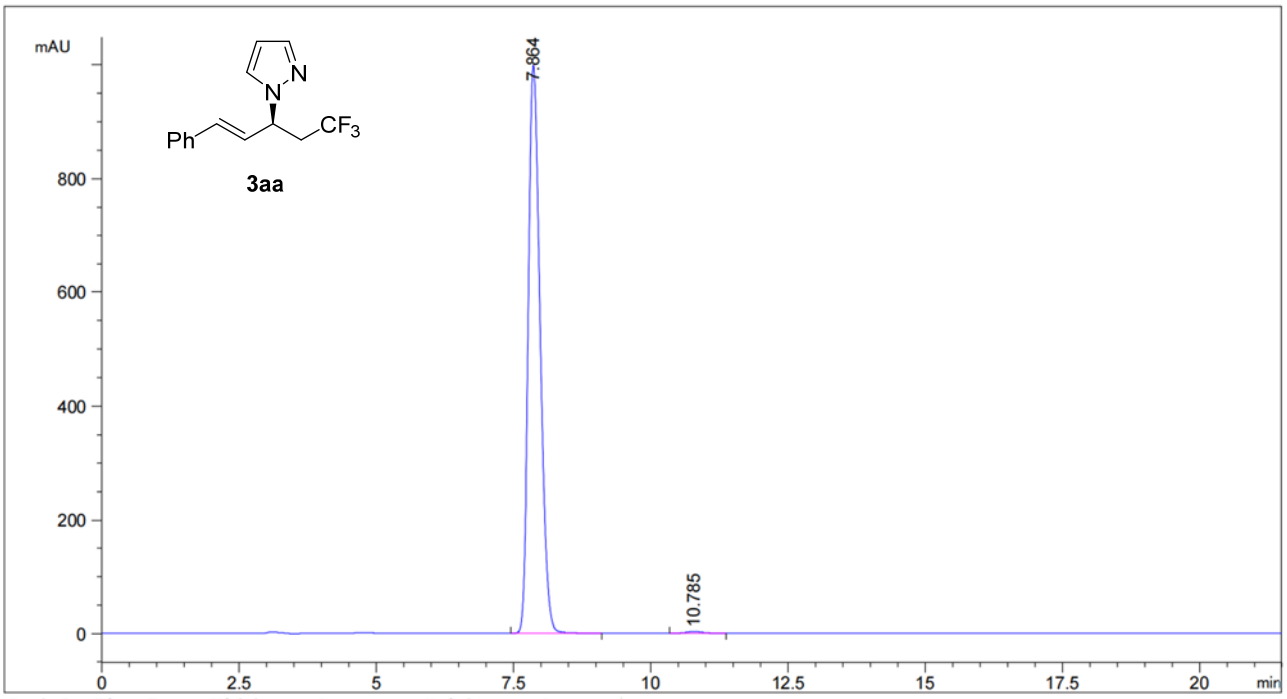
3aa

HRMS (ESI-TOF) m/z: $[M + Na]^+$

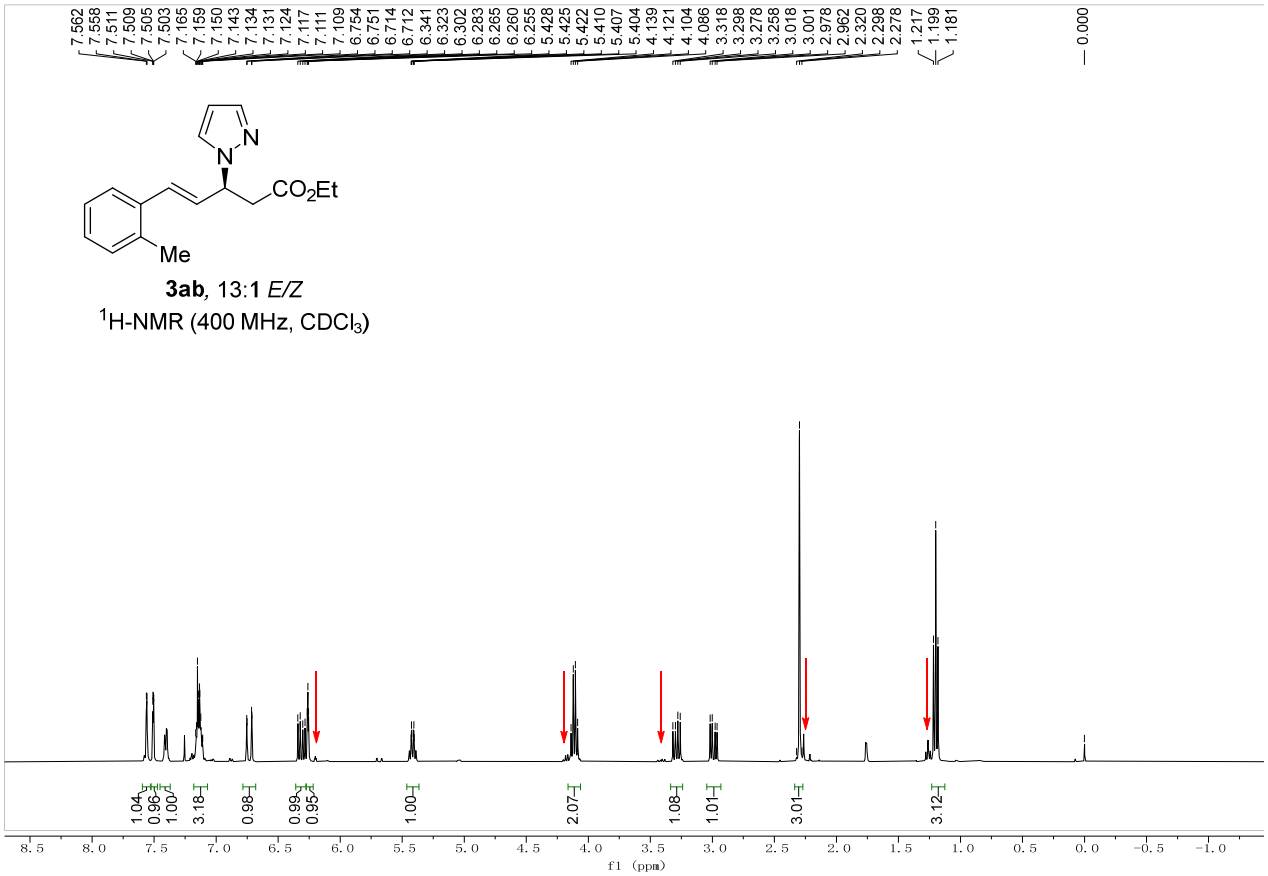
Calcd for $C_{14}H_{13}F_3N_2Na^+$ 289.0924



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.920	BV	0.2303	2025.96570	137.33609	49.6844
2	10.658	BBA	0.3235	2051.70313	96.05376	50.3156

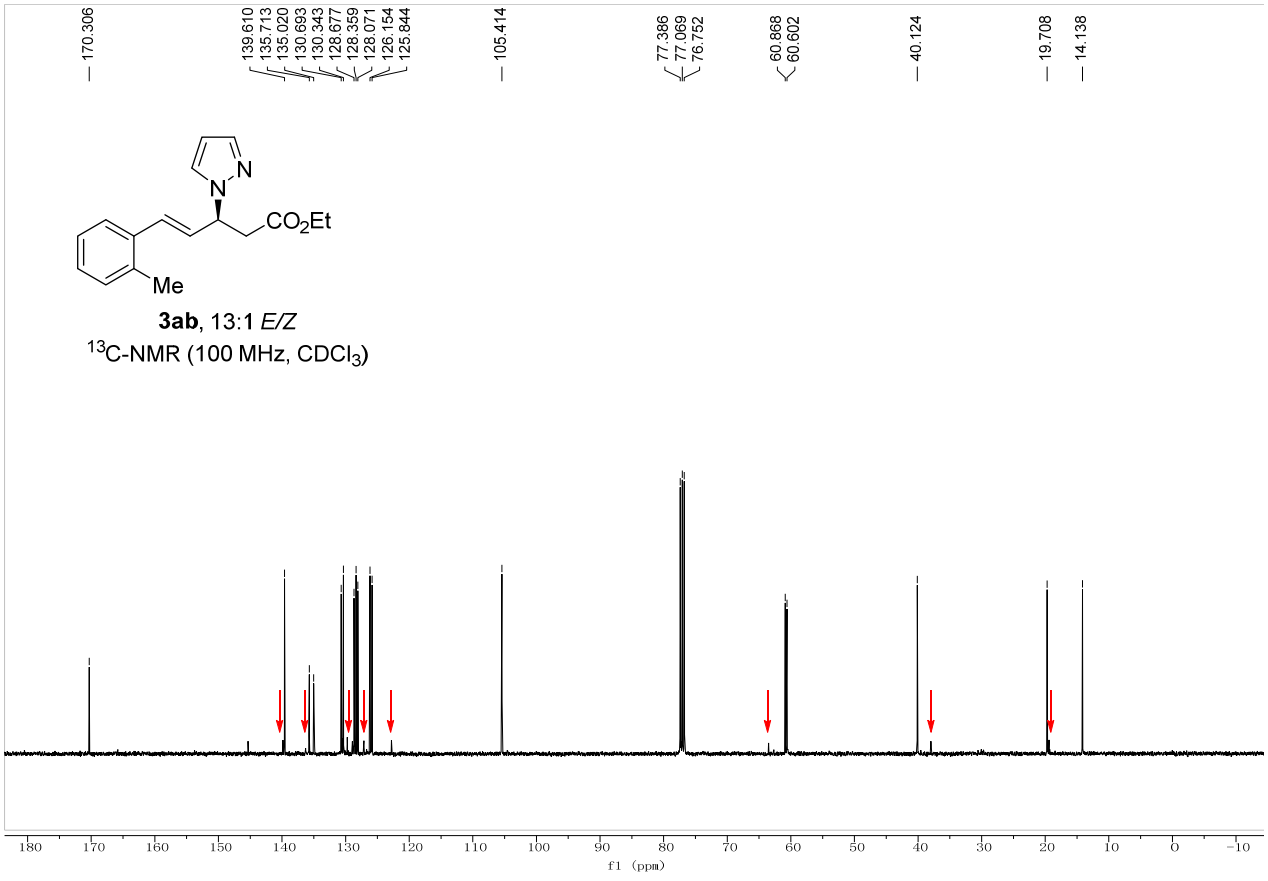


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.864	BB	0.2337	1.48875e4	998.22754	99.6211
2	10.785	BB	0.3071	56.62261	2.87288	0.3789



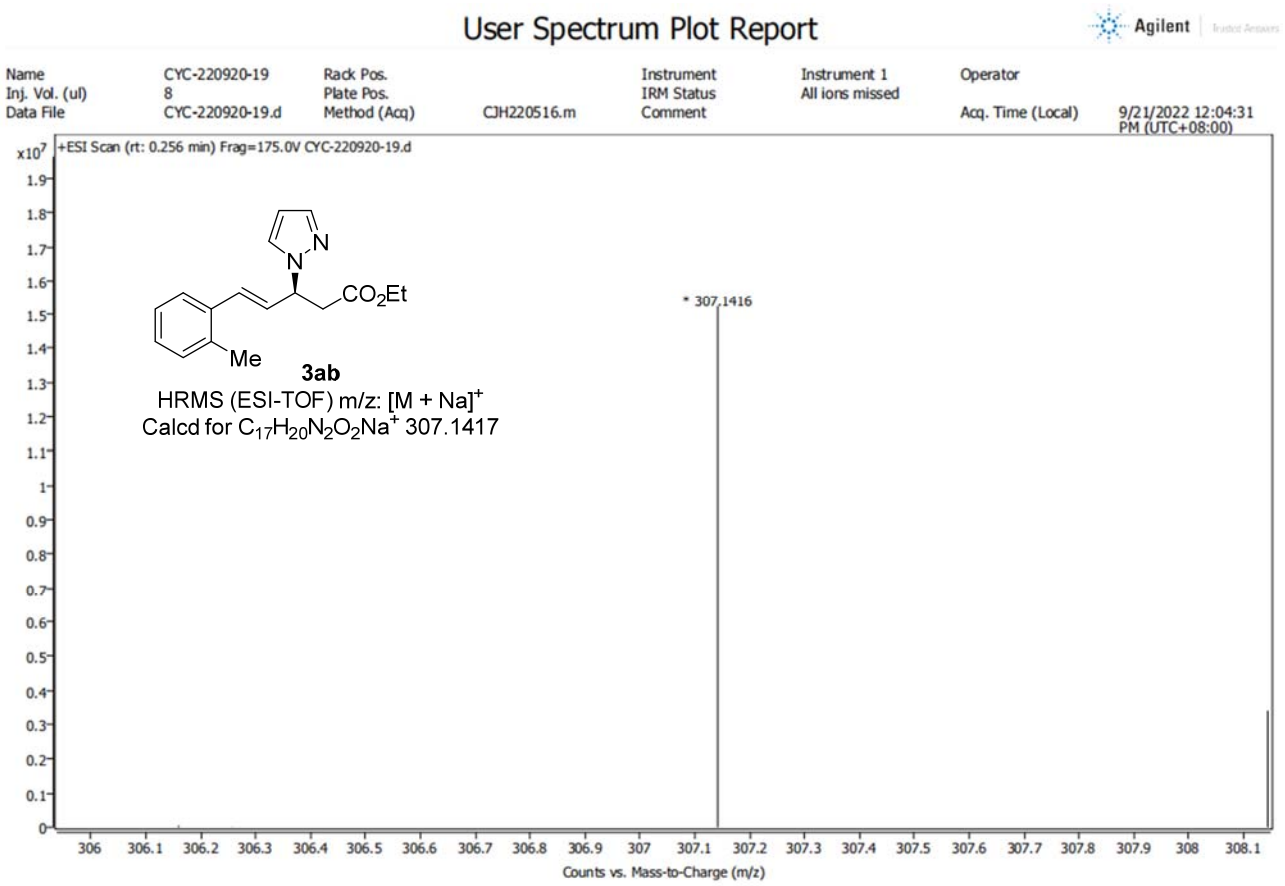
3ab, 13:1 *E/Z*

^{1}H-NMR (400 MHz, $CDCl_3$)



3ab, 13:1 *E/Z*

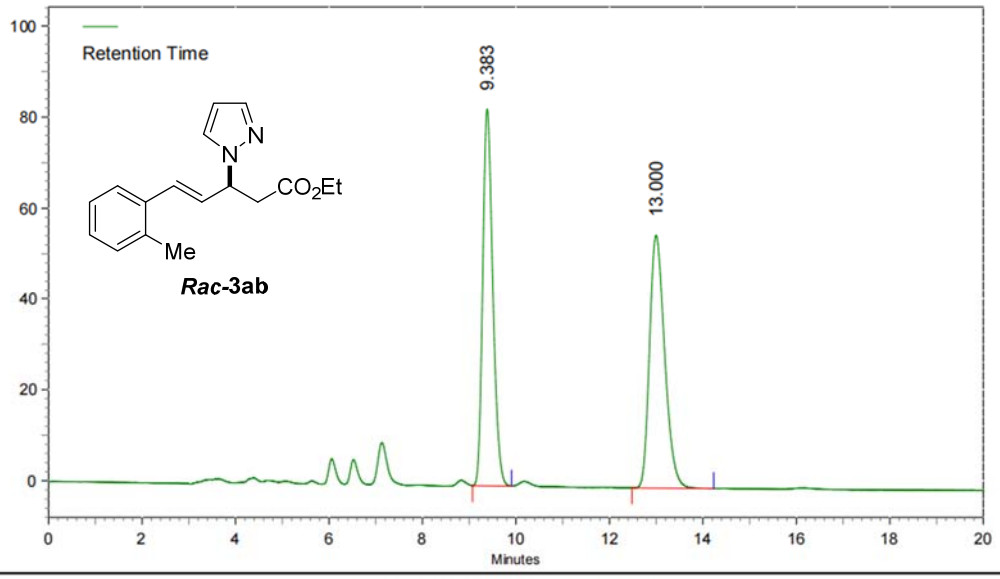
^{13}C-NMR (100 MHz, $CDCl_3$)



3ab

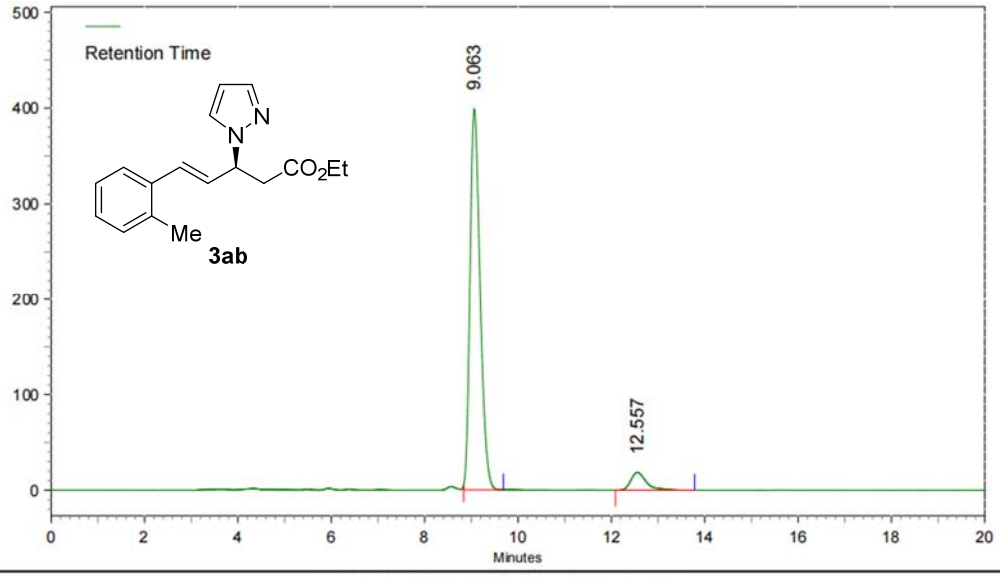
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{17}H_{20}N_2O_2Na^+$ 307.1417



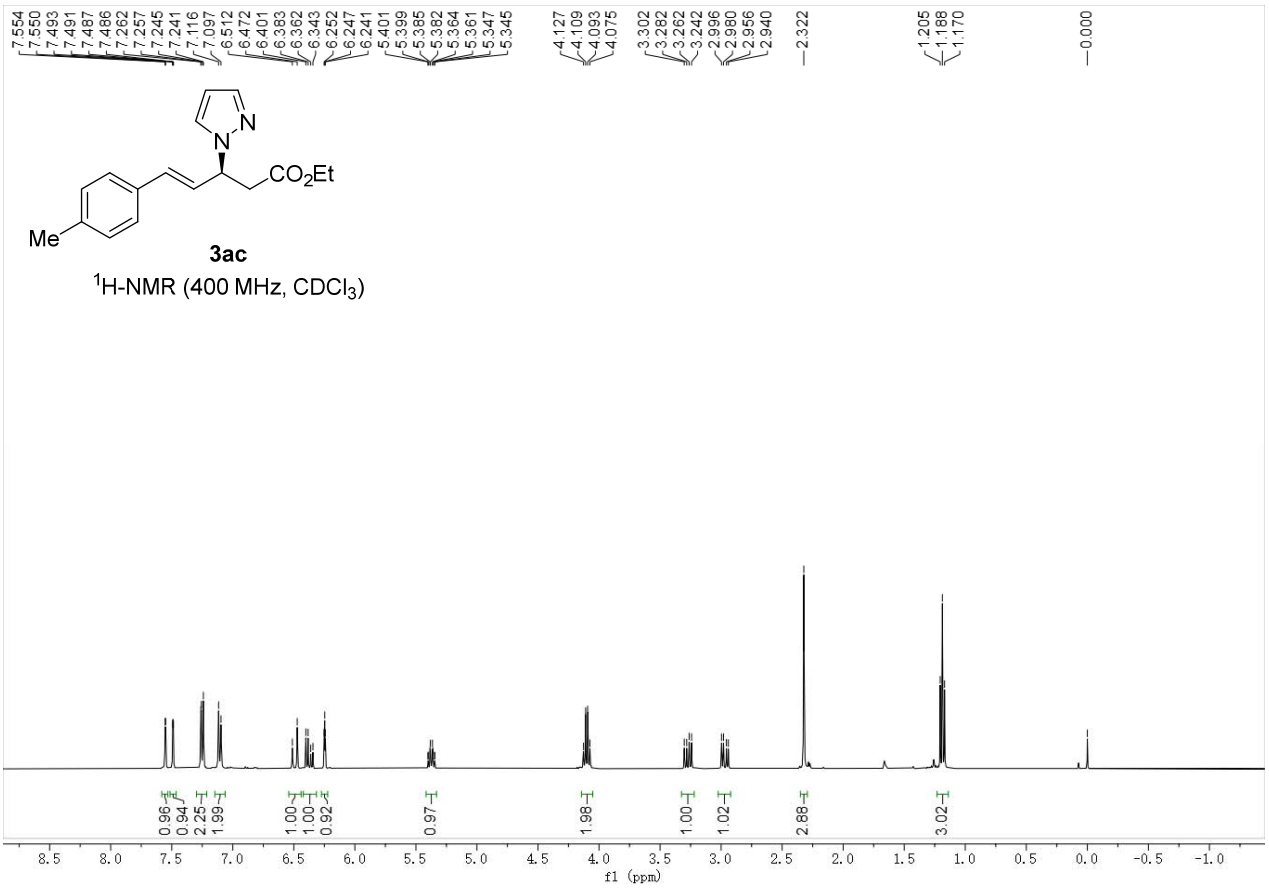
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.383	0.837	1390087	20801676	49.7532
2	13.000	1.750	933979	21008043	50.2468
Totals			2324066	41809719	100.0000



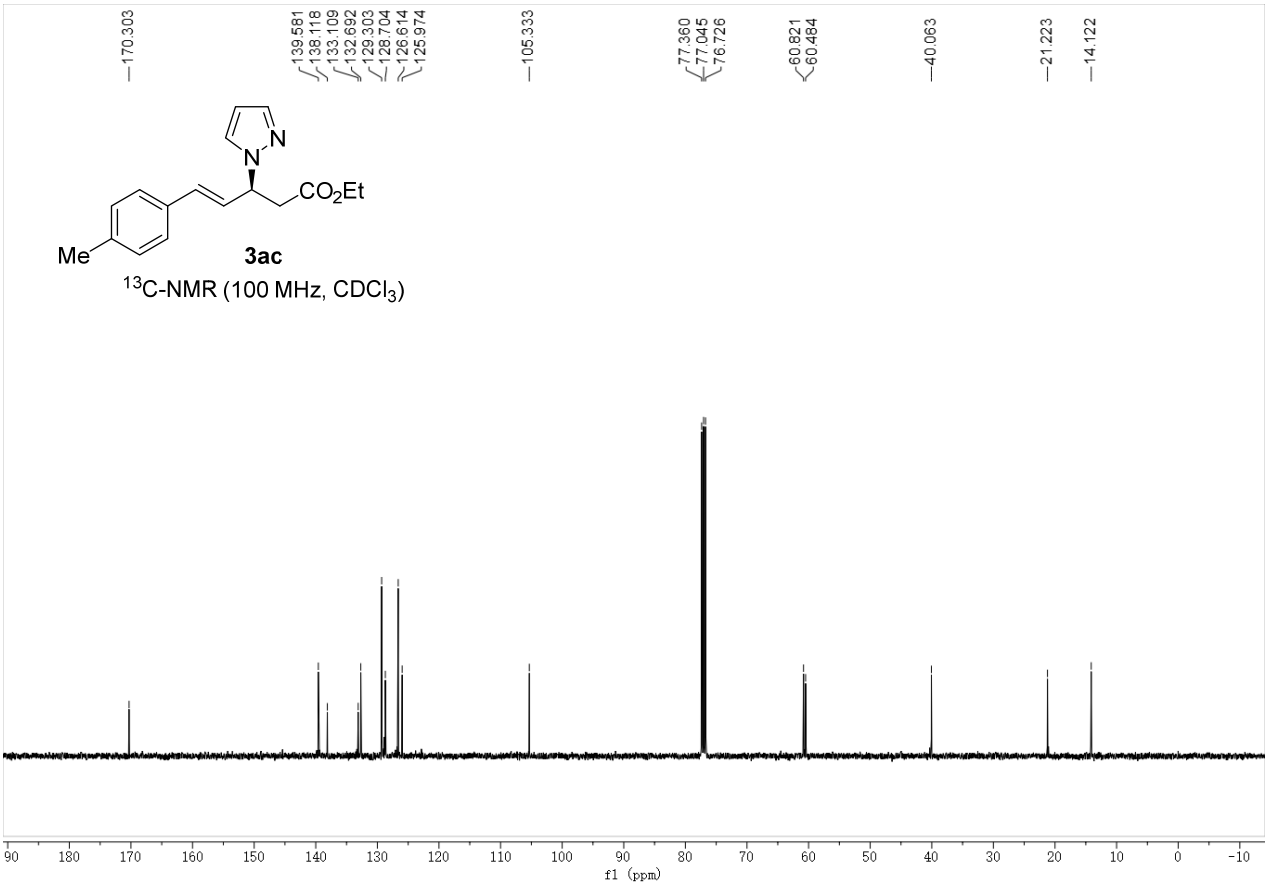
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.063	0.853	6694178	100045182	93.3290
2	12.557	1.697	311601	7151073	6.6710
Totals			7005779	107196255	100.0000



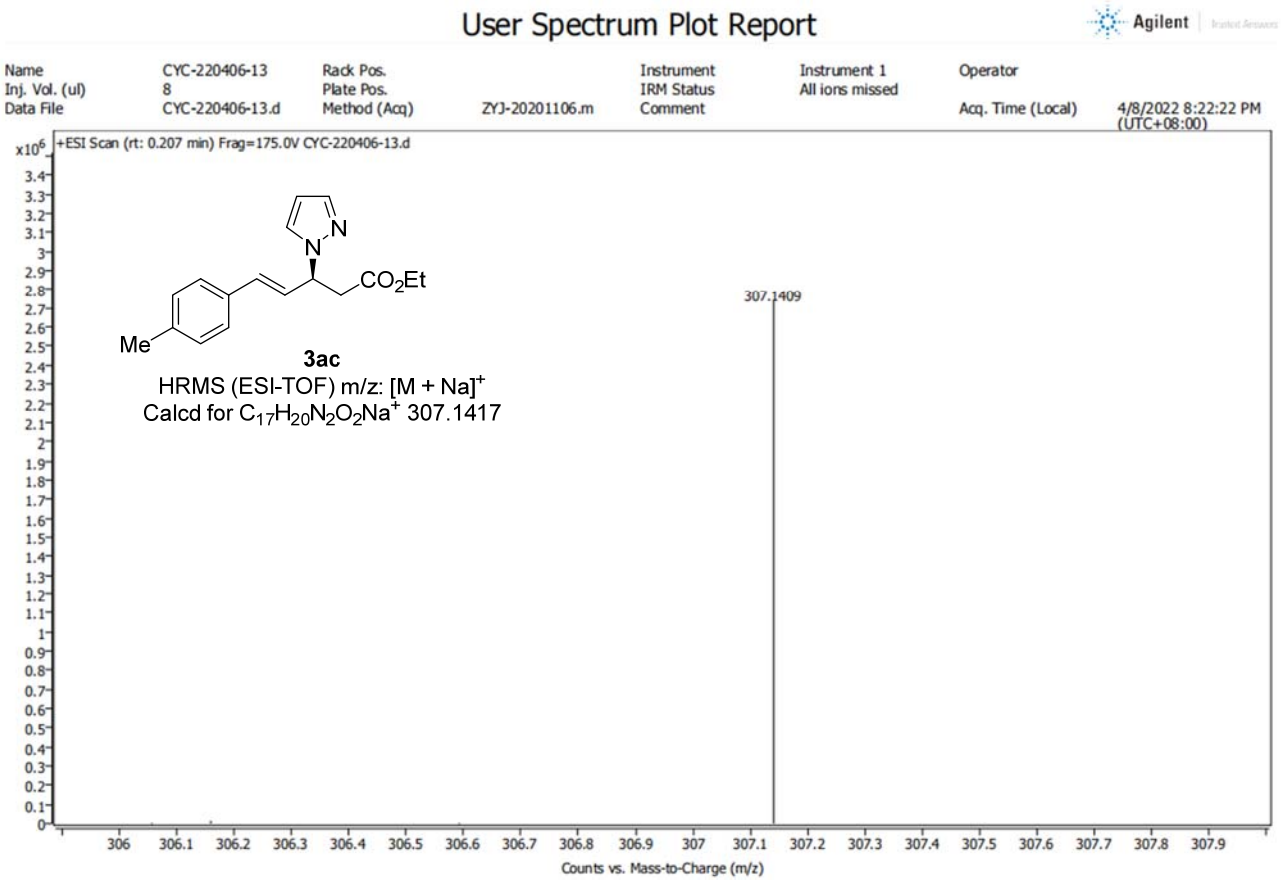
3ac

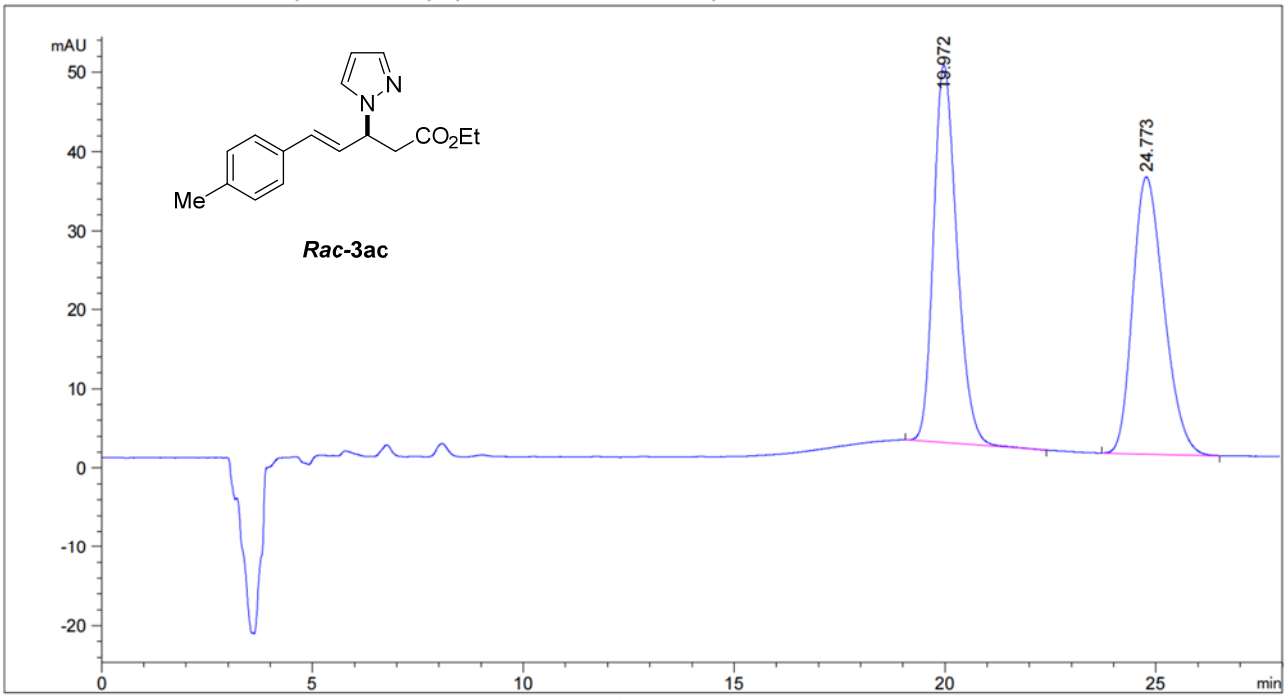
^{1}H-NMR (400 MHz, $CDCl_3$)



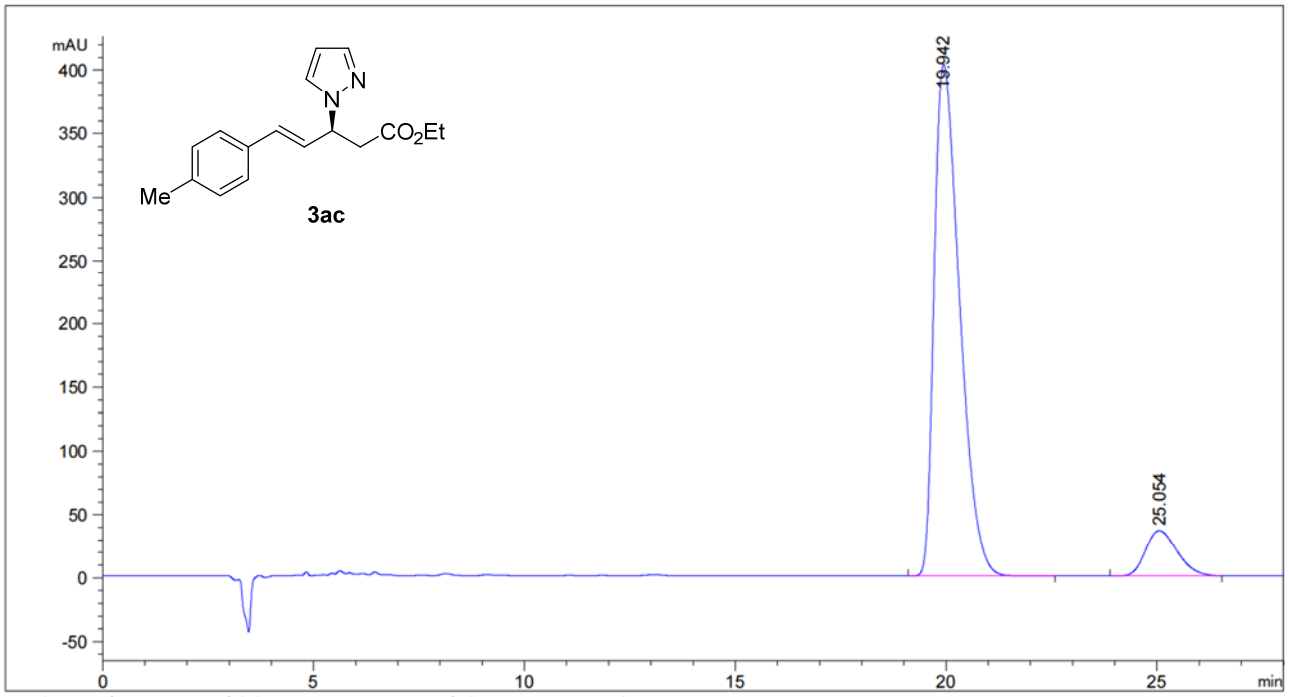
3ac

^{13}C-NMR (100 MHz, $CDCl_3$)

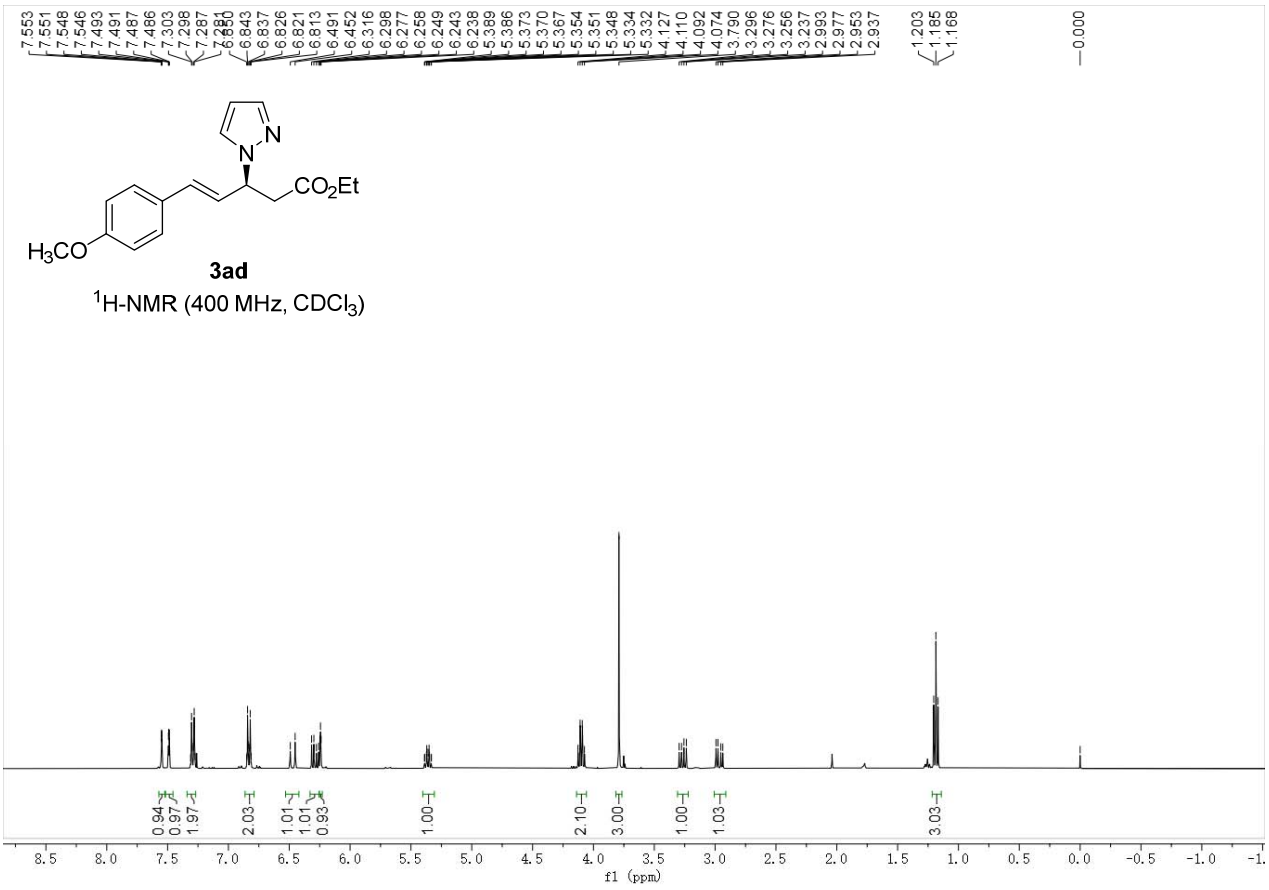

User Spectrum Plot Report
Agilent
Name CYC-220406-13
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
All ions missed
Data File CYC-220406-13.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 4/8/2022 8:22:22 PM (UTC+08:00)
+ESI Scan (rt: 0.207 min) Frag=175.0V CYC-220406-13.d
x10^6
307.1409
Me
CO2Et
3ac
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C17H20N2O2Na+ 307.1417
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.972	BB	0.5885	1836.52185	47.74617	50.4717
2	24.773	BB	0.7933	1802.19250	35.06365	49.5283

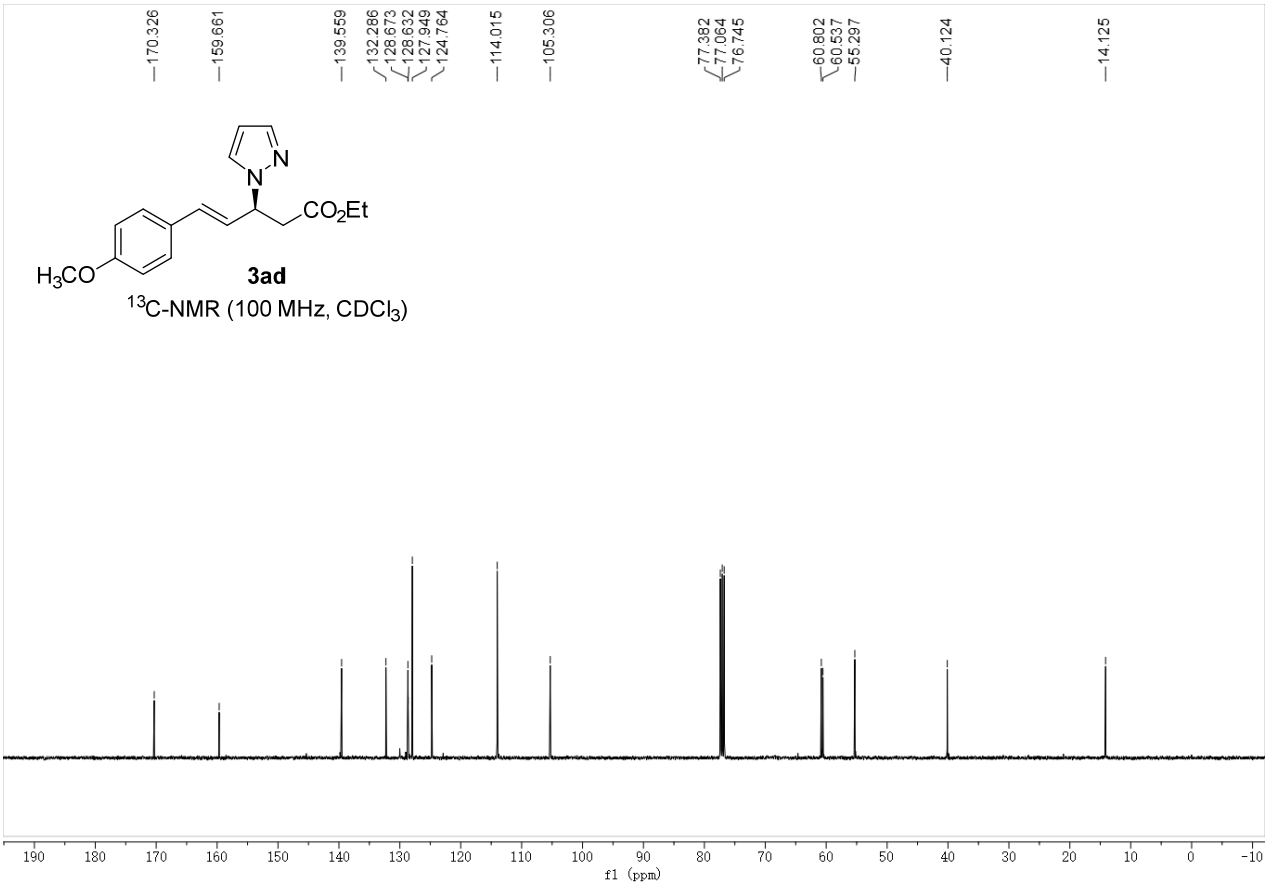


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.942	BB	0.6525	1.69162e4	403.22864	90.0020
2	25.054	BBA	0.8135	1879.15796	36.04363	9.9980



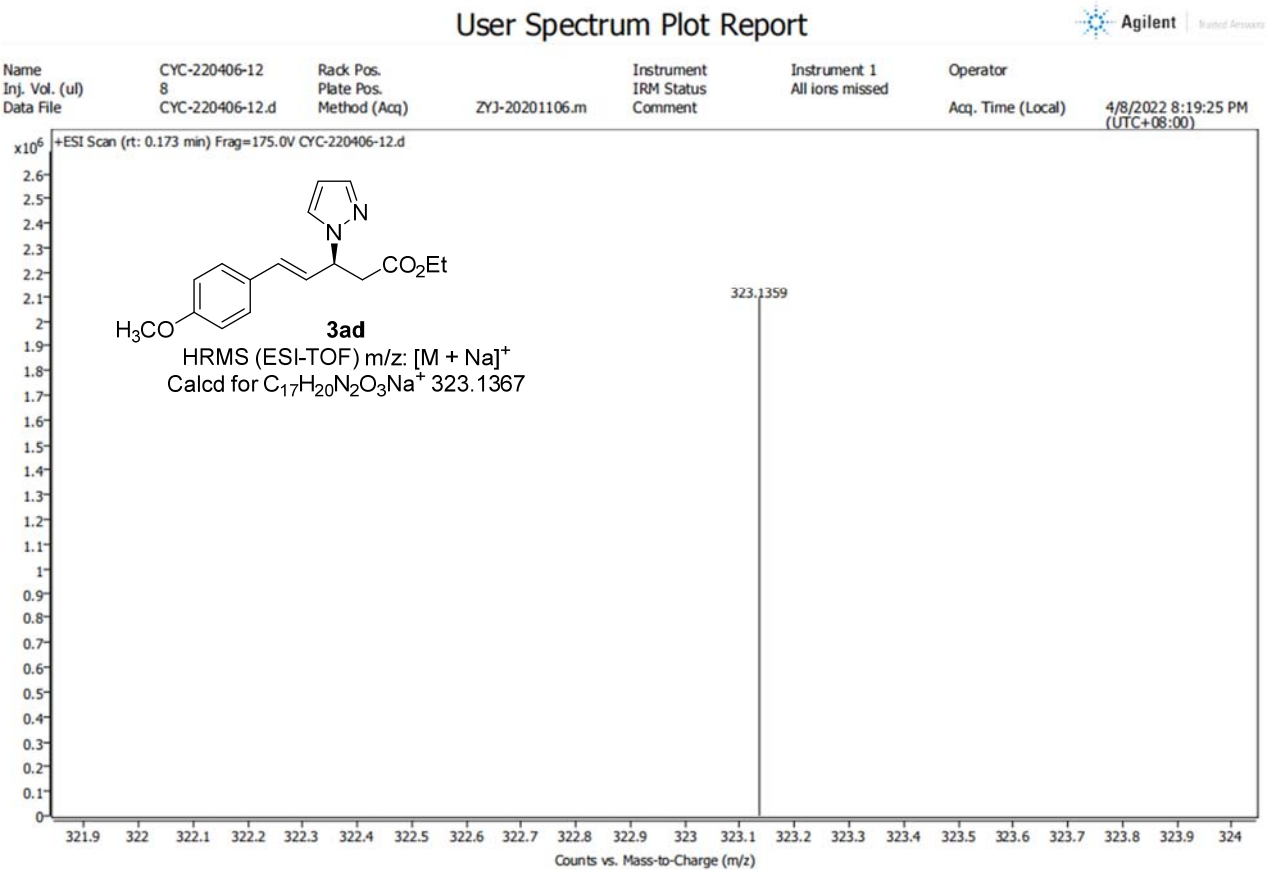
3ad

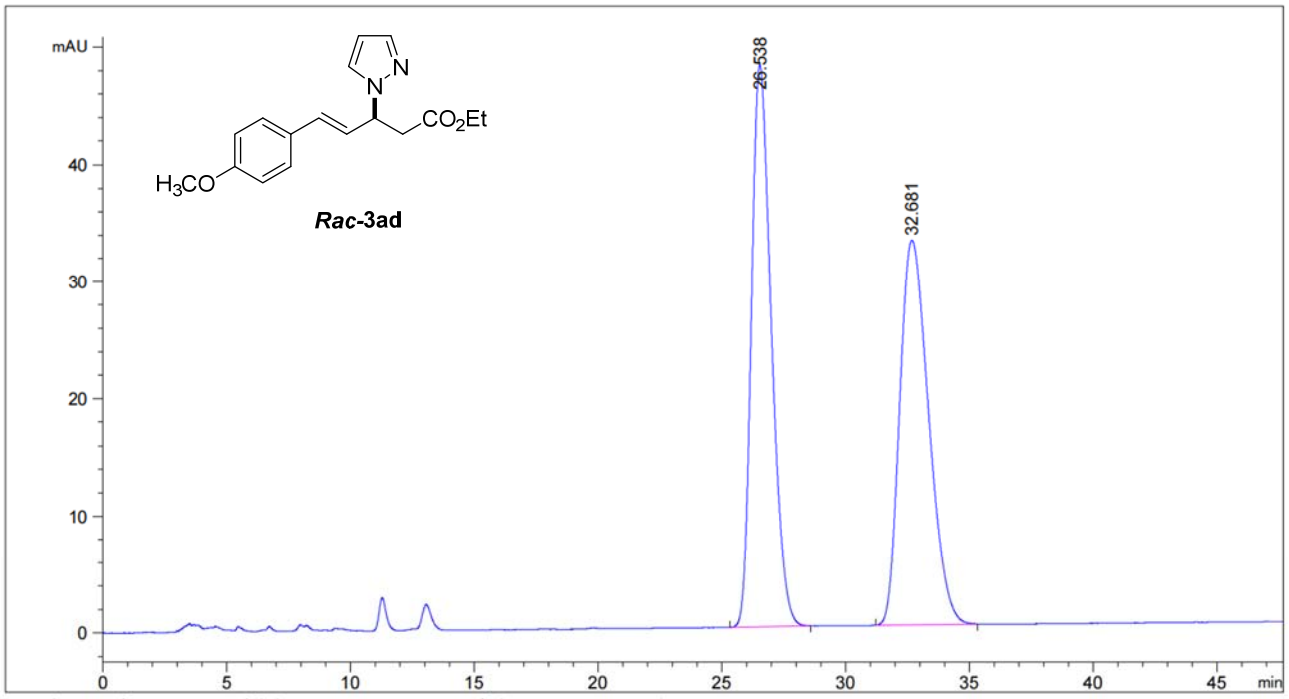
^{1}H-NMR (400 MHz, $CDCl_3$)



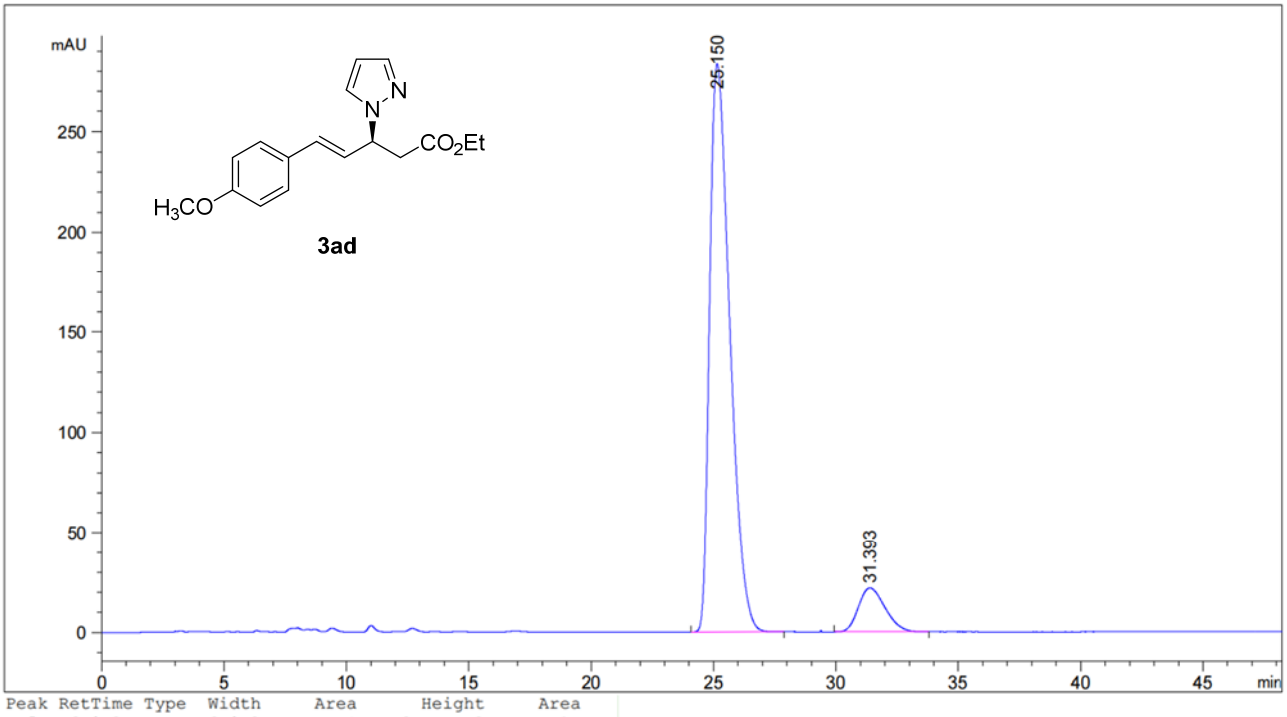
3ad

^{13}C-NMR (100 MHz, $CDCl_3$)

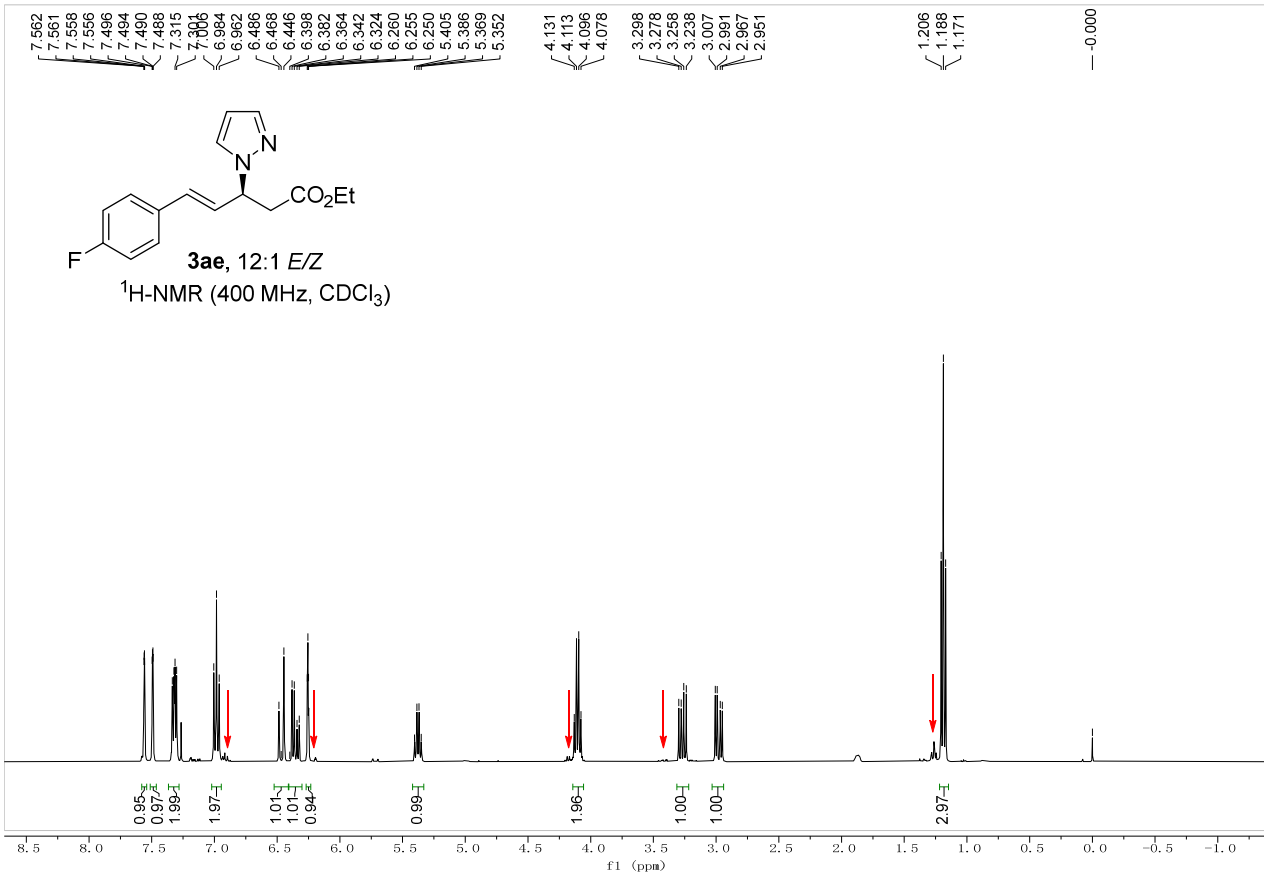

User Spectrum Plot Report
Agilent
Name CYC-220406-12
Inj. Vol. (ul) 8
Data File CYC-220406-12.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 4/8/2022 8:19:25 PM (UTC+08:00)
+ESI Scan (rt: 0.173 min) Frag=175.0V CYC-220406-12.d
x10^6
323.1359
3ad
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C17H20N2O3Na+ 323.1367
Counts vs. Mass-to-Charge (m/z)

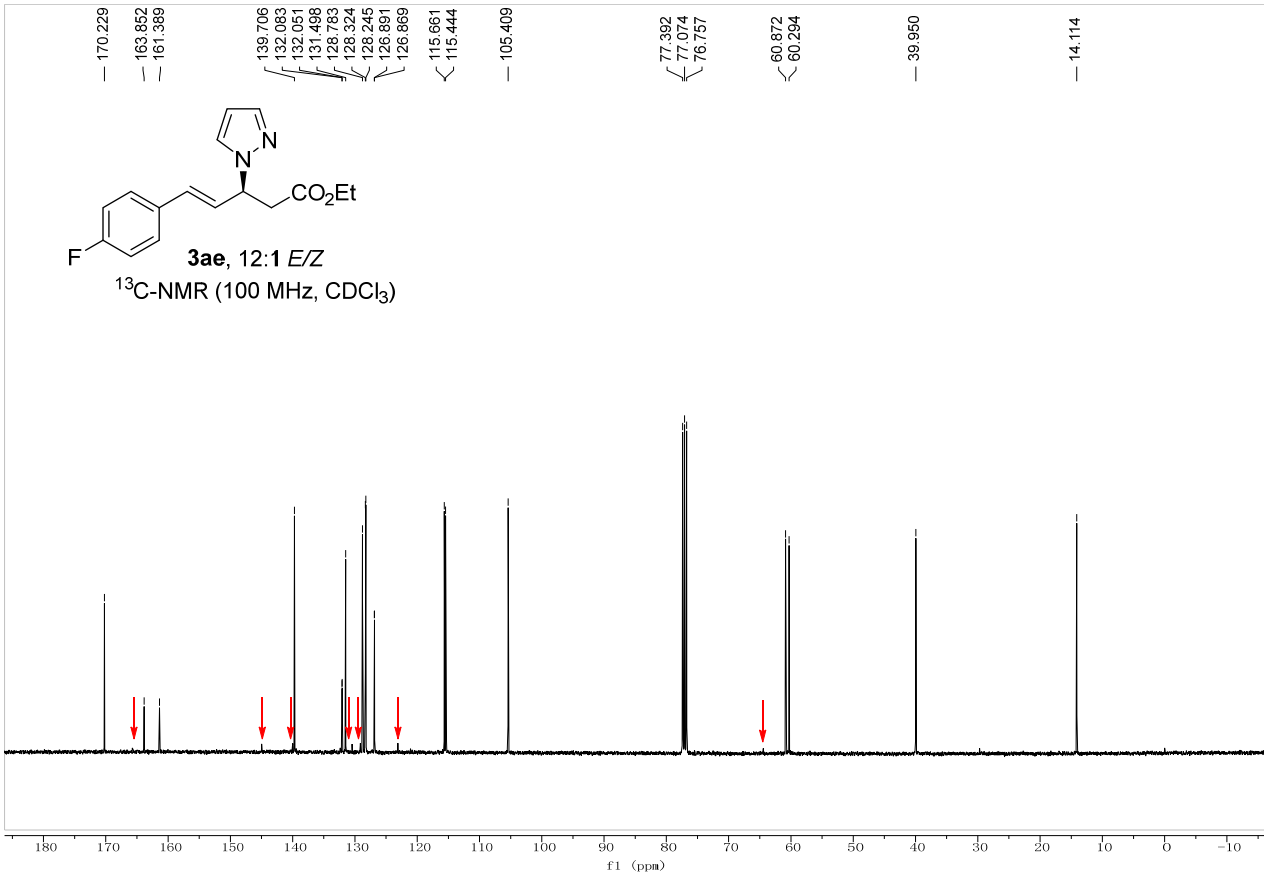


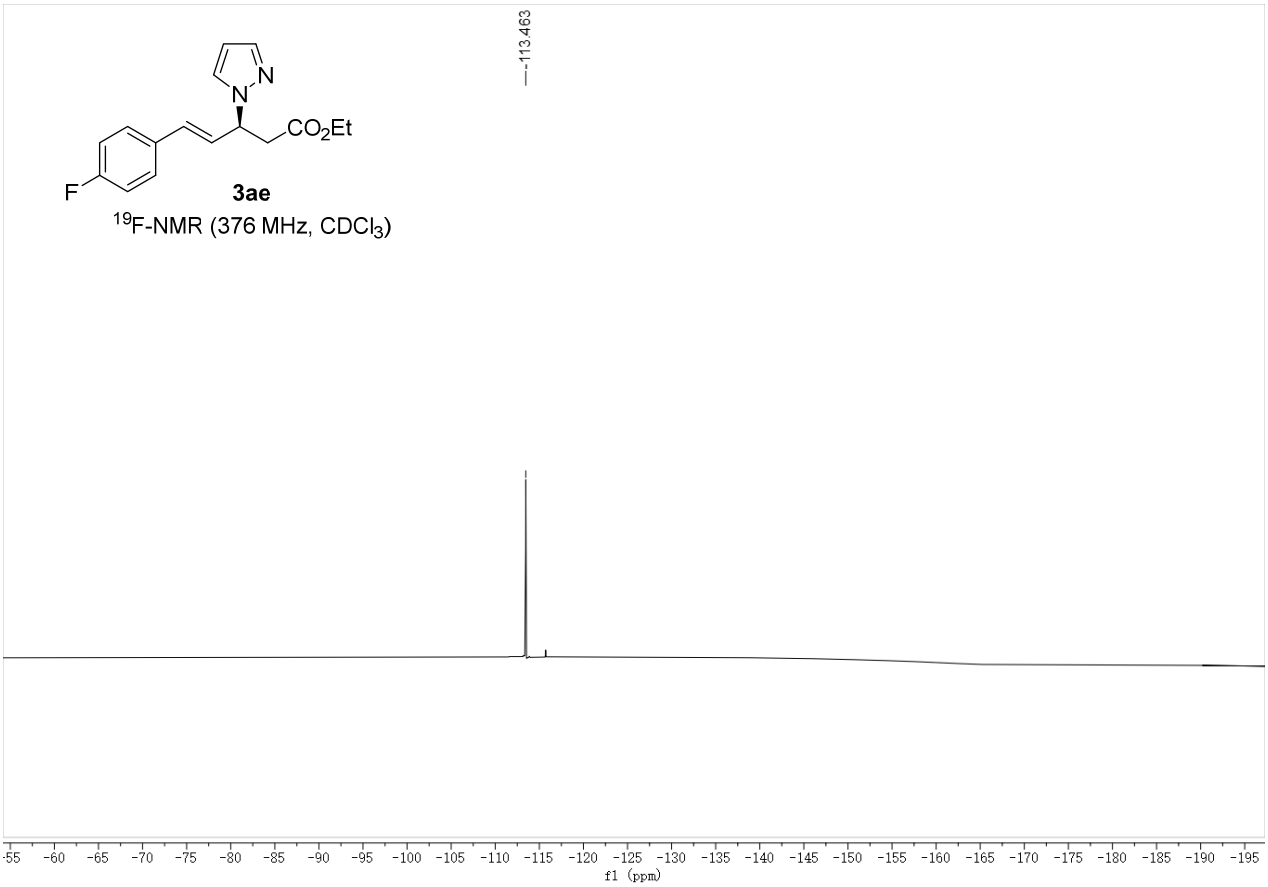
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.538	BB	0.8559	2673.46265	47.94024	50.0690
2	32.681	BB	1.2484	2666.09912	32.89600	49.9310

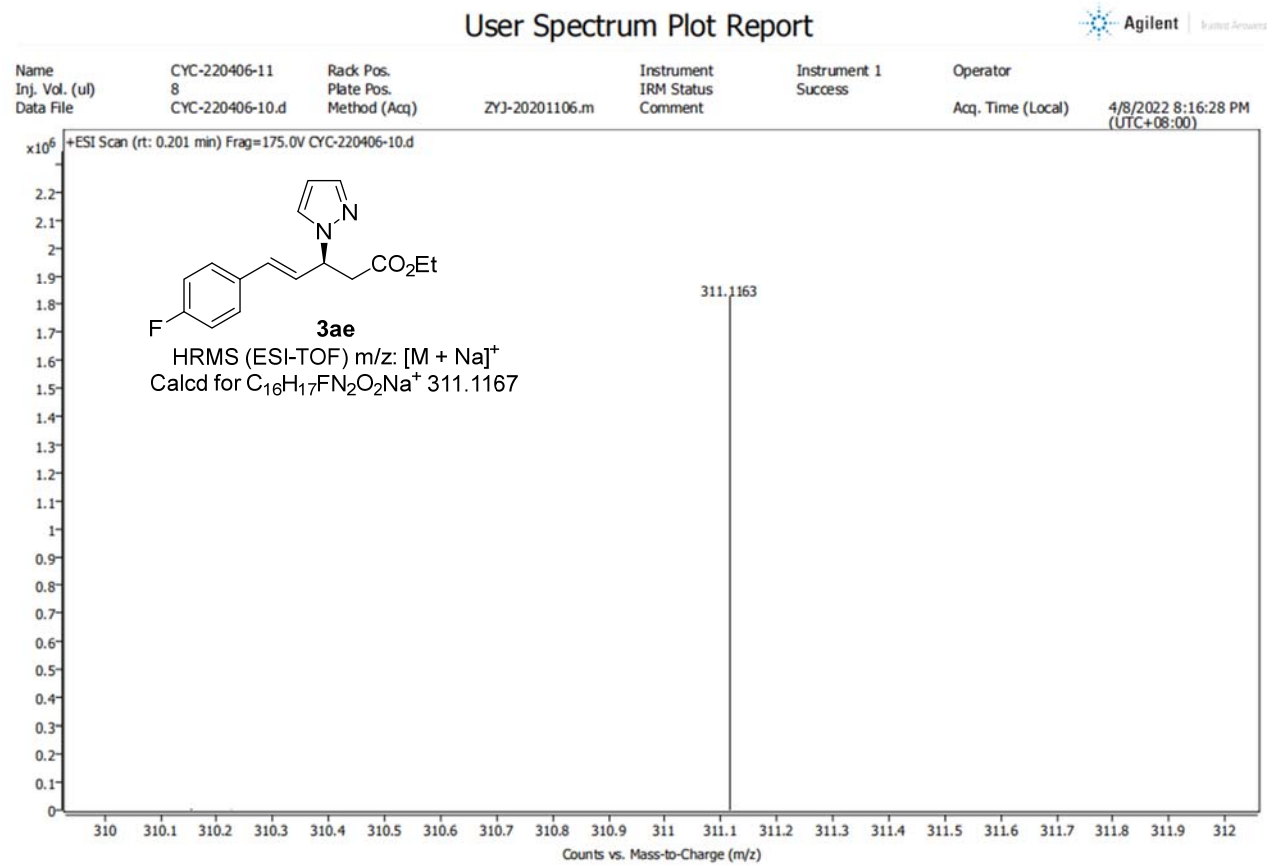


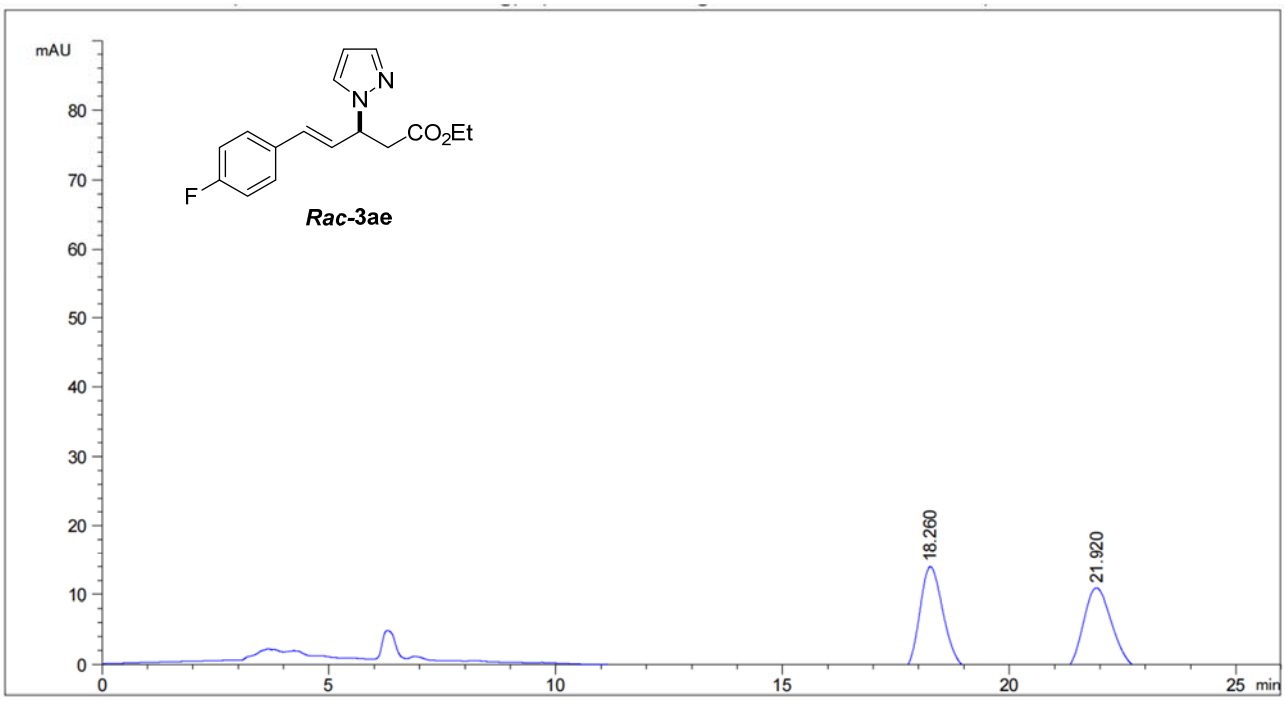
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.150	BB	0.8916	1.62088e4	283.36151	90.7389
2	31.393	BB	1.1312	1654.31494	21.87821	9.2611


7.562
7.561
7.558
7.556
7.496
7.494
7.490
7.488
7.315
7.304
7.300
6.984
6.962
6.486
6.468
6.446
6.398
6.382
6.364
6.342
6.324
6.260
6.255
6.250
5.405
5.386
5.369
5.352
4.131
4.113
4.096
4.078
3.298
3.278
3.258
3.238
3.007
2.991
2.967
2.951
1.206
1.188
1.171
-0.000
N
N
CO2Et
F
3ae, 12:1 E/Z
1H-NMR (400 MHz, CDCl3)
0.95
0.97
1.99
1.97
1.01
1.01
0.94
0.99
1.96
1.00
1.00
2.97
f1 (ppm)

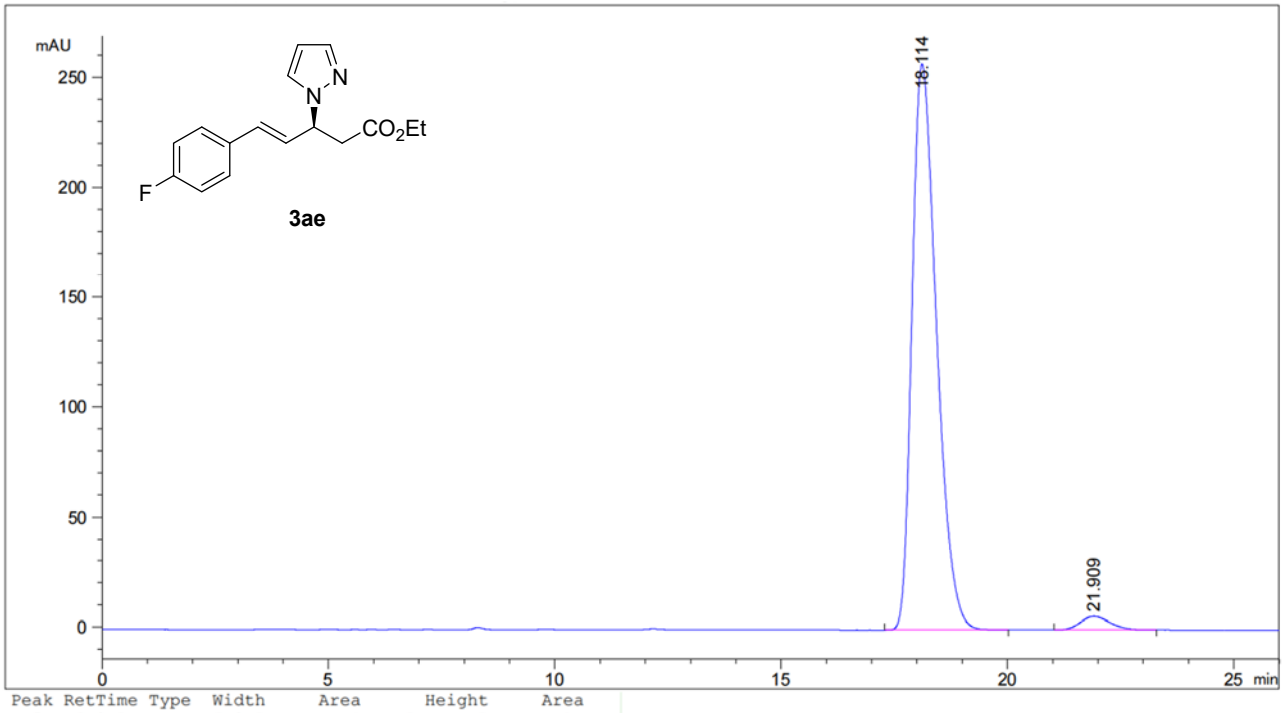

170.229
163.852
161.389
139.706
132.083
132.051
131.498
128.783
128.324
128.245
126.891
126.869
115.661
115.444
105.409
77.392
77.074
76.757
60.872
60.294
39.950
14.114
N
N
CO2Et
F
3ae, 12:1 E/Z
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


-113.463
CO2Et
F
3ae
19F-NMR (376 MHz, CDCl3)
f1 (ppm)

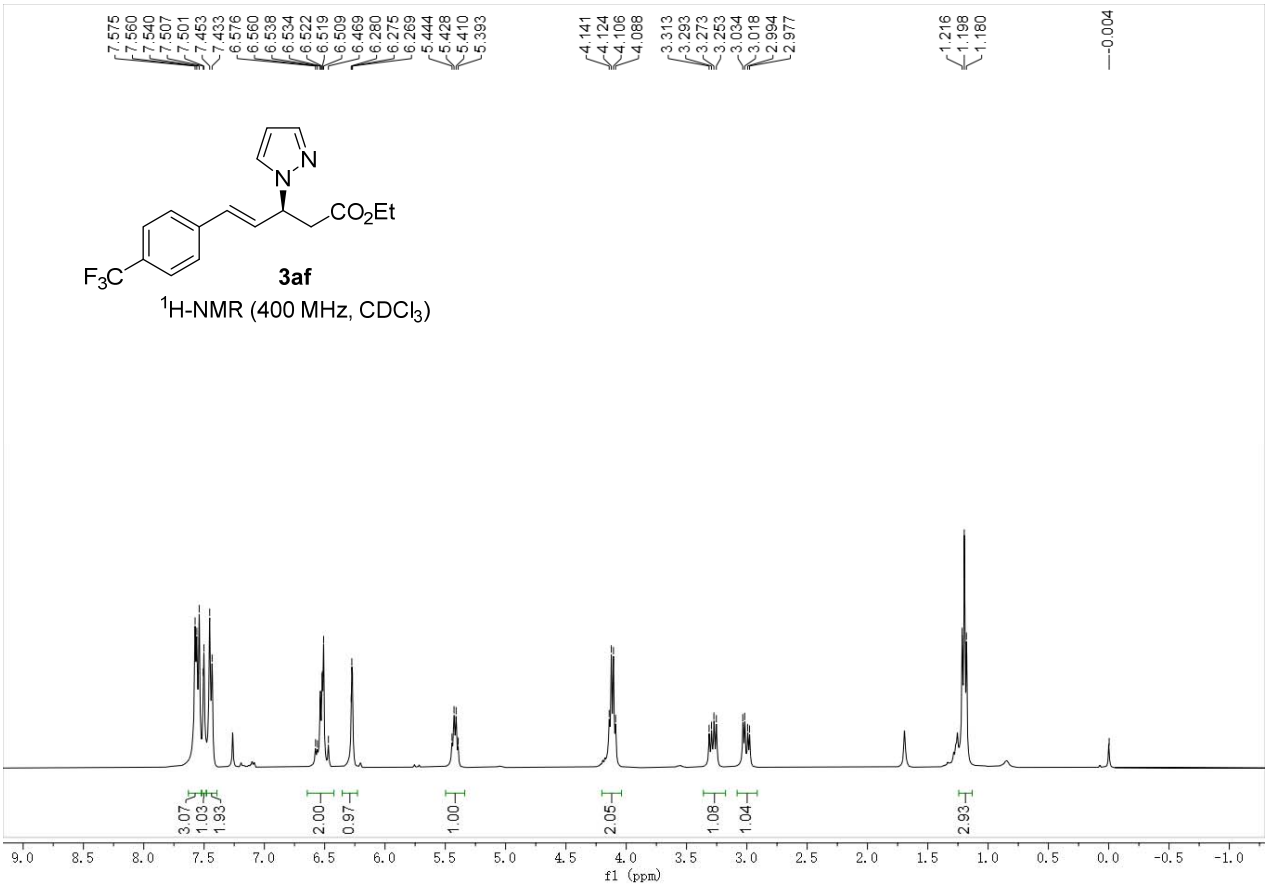

User Spectrum Plot Report
Agilent
Name CYC-220406-11
Inj. Vol. (ul) 8
Data File CYC-220406-10.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
Success
Operator
Acq. Time (Local) 4/8/2022 8:16:28 PM (UTC+08:00)
+ESI Scan (rt: 0.201 min) Frag=175.0V CYC-220406-10.d
x10^6
CO2Et
F
3ae
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C16H17FN2O2Na+ 311.1167
311.1163
Counts vs. Mass-to-Charge (m/z)

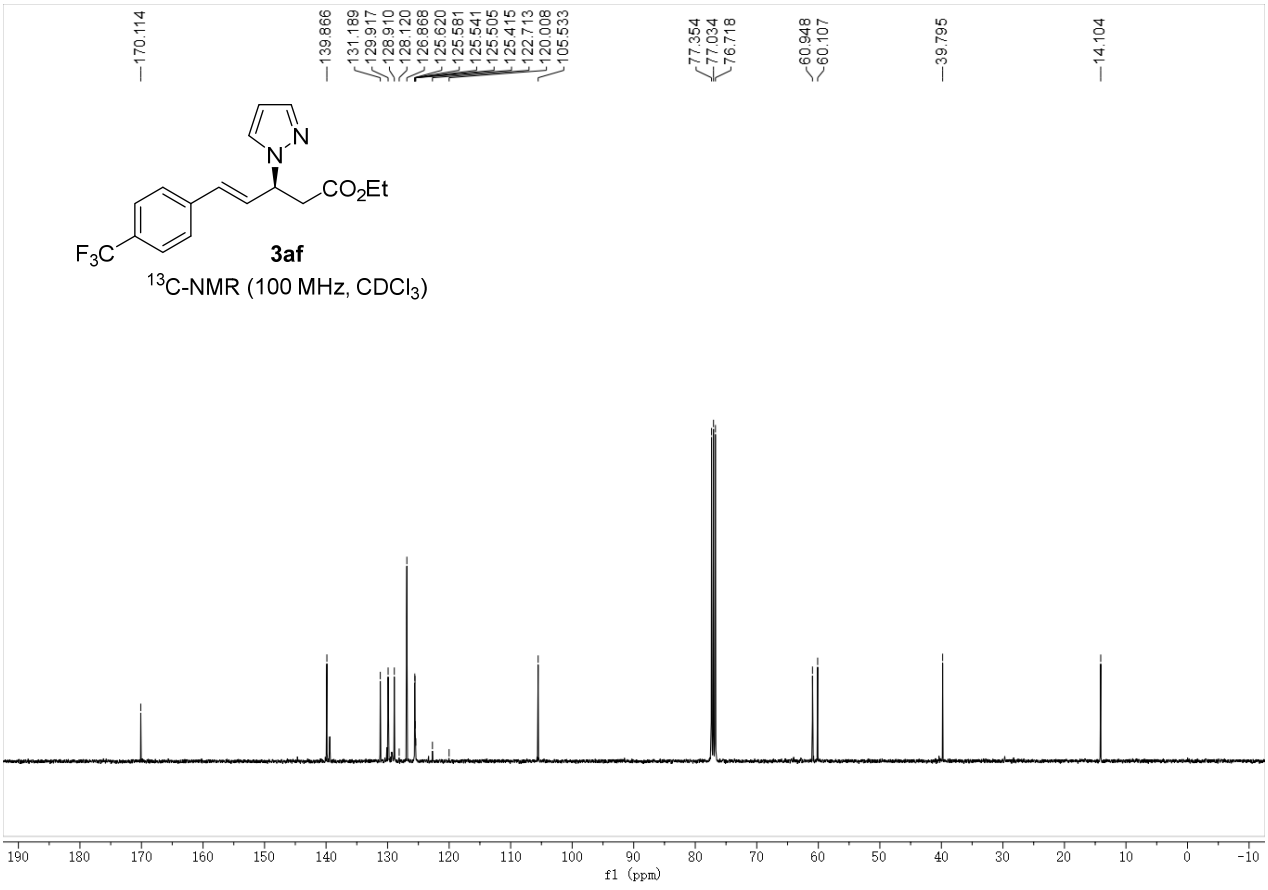


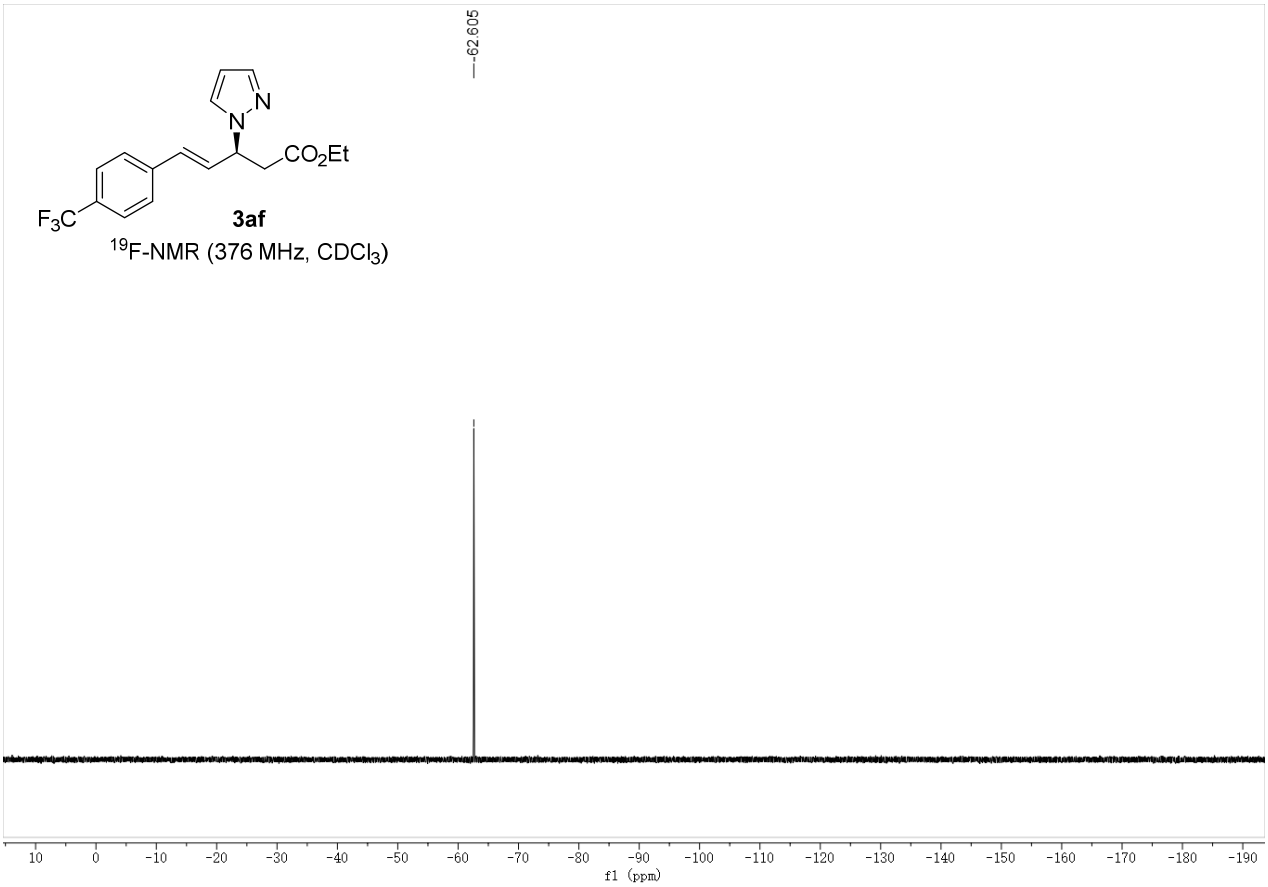
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.260	BB	0.5718	553.97113	14.95879	49.6690
2	21.920	BB	0.7135	561.35498	12.08918	50.3310

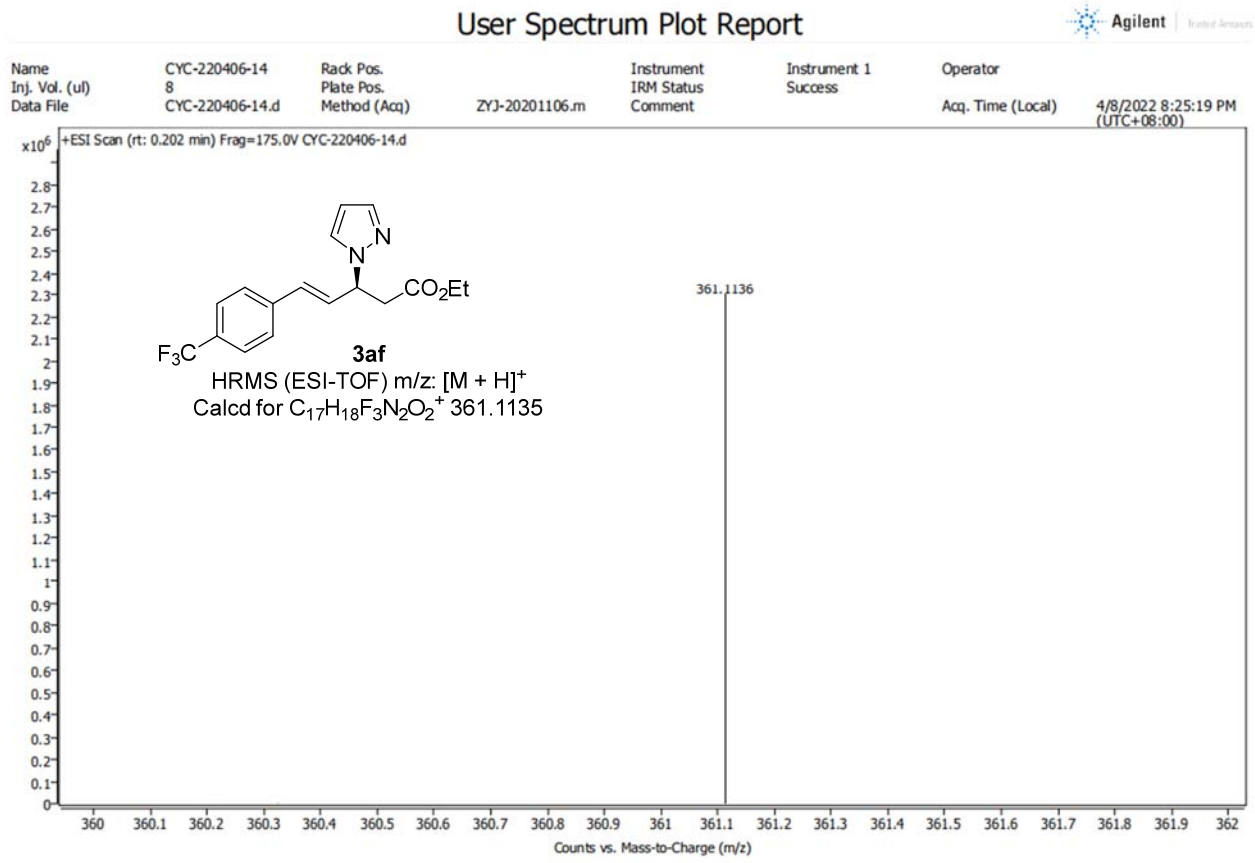


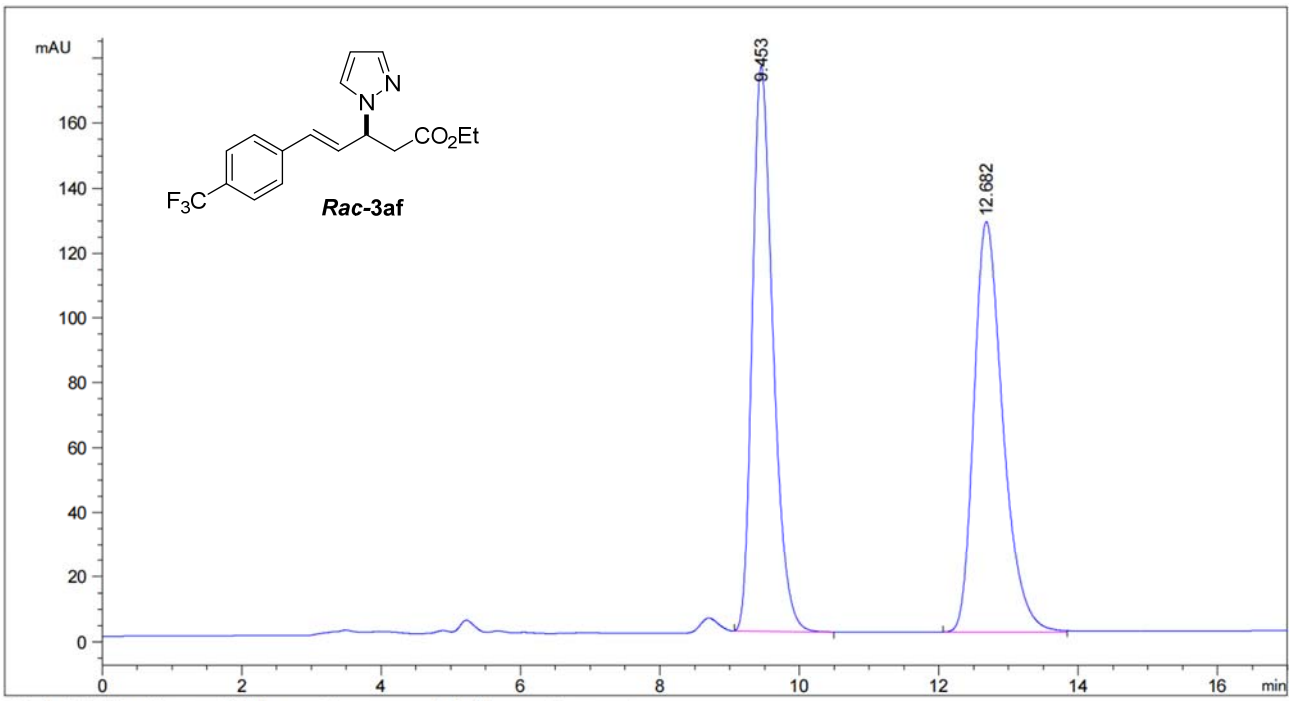
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.114	BB	0.5832	9686.78711	257.39569	97.2323
2	21.909	BB	0.6961	275.73199	6.06822	2.7677


7.575
7.560
7.540
7.507
7.501
7.453
7.433
6.576
6.560
6.538
6.534
6.522
6.519
6.509
6.469
6.280
6.275
6.269
5.444
5.428
5.410
5.393
4.141
4.124
4.106
4.088
3.313
3.293
3.273
3.253
3.034
3.018
2.994
2.977
1.216
1.198
1.180
0.004
CO2Et
F3C
3af
1H-NMR (400 MHz, CDCl3)
3.07
1.03
1.93
2.00
0.97
1.00
2.05
1.08
1.04
2.93
f1 (ppm)

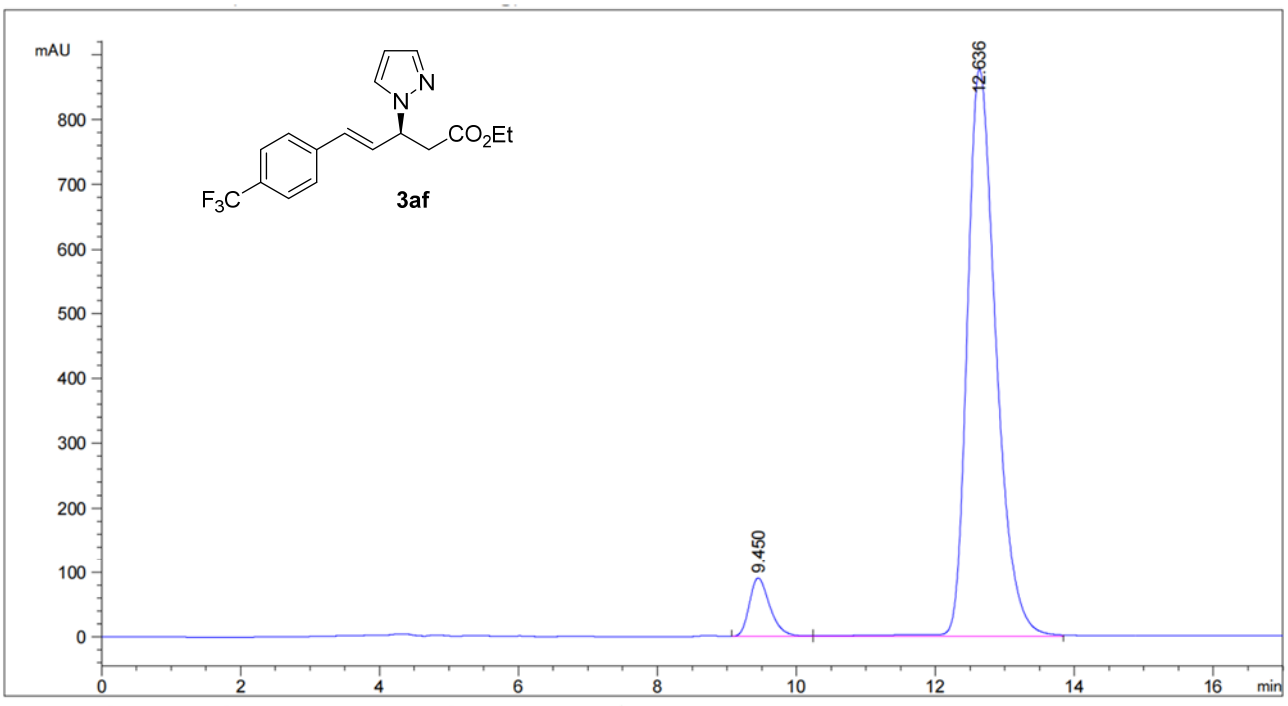

170.114
139.866
131.189
129.917
128.910
128.120
126.868
125.620
125.581
125.541
125.505
125.415
122.713
120.008
105.533
77.354
77.034
76.718
60.948
60.107
39.795
14.104
CO2Et
F3C
3af
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


-62.605
N
N
CO2Et
F3C
3af
19F-NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

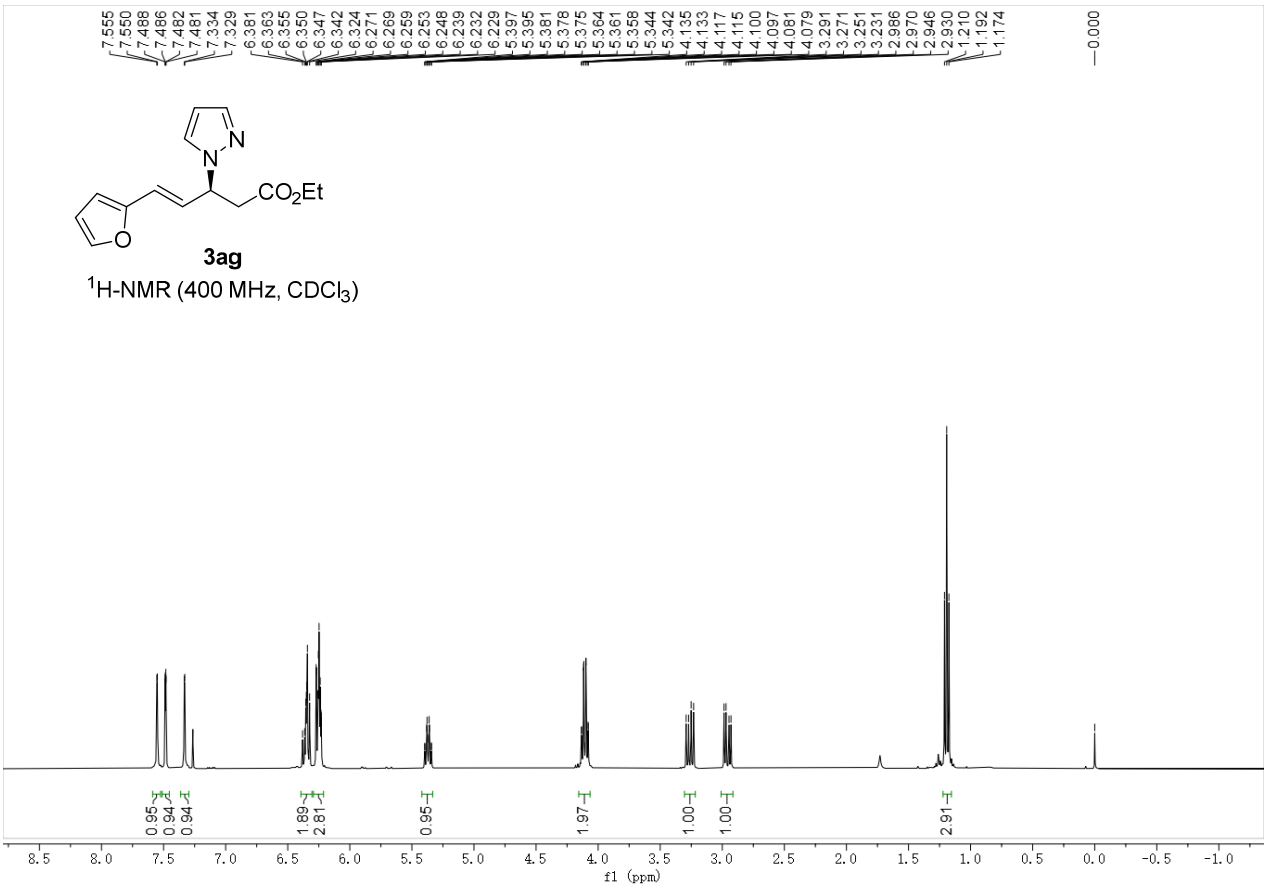

User Spectrum Plot Report
Agilent
Name CYC-220406-14
Inj. Vol. (ul) 8
Data File CYC-220406-14.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
Success
Operator
Acq. Time (Local) 4/8/2022 8:25:19 PM (UTC+08:00)
x10^6
+ESI Scan (rt: 0.202 min) Frag=175.0V CYC-220406-14.d
N
N
CO2Et
F3C
3af
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C17H18F3N2O2+ 361.1135
361.1136
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
360 360.1 360.2 360.3 360.4 360.5 360.6 360.7 360.8 360.9 361 361.1 361.2 361.3 361.4 361.5 361.6 361.7 361.8 361.9 362
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.453	BB	0.3174	3606.25830	174.11229	49.6218
2	12.682	BBA	0.4388	3661.22314	126.78777	50.3782

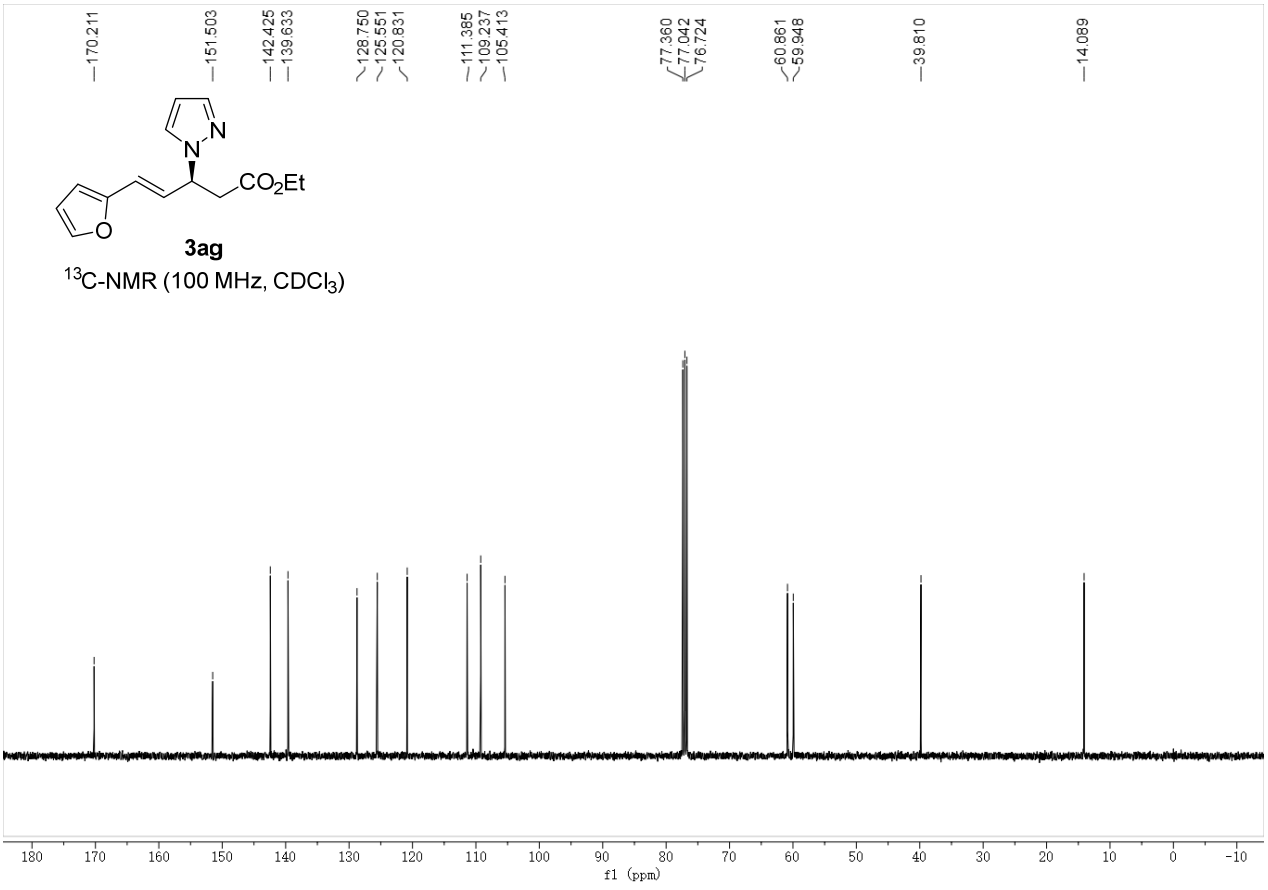


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.450	BV	0.3161	1864.84216	90.51836	6.8534
2	12.636	VBA	0.4419	2.53455e4	877.36853	93.1466



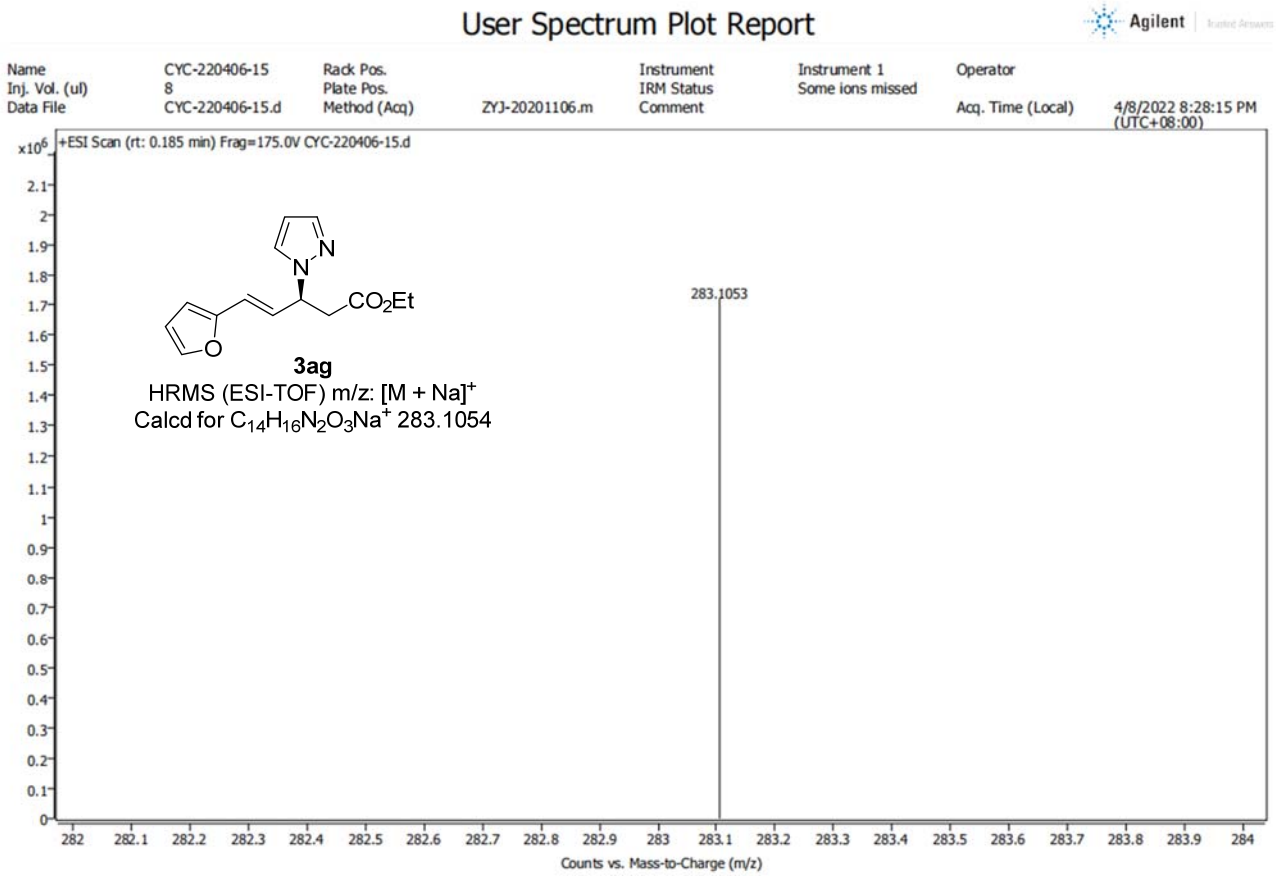
3ag

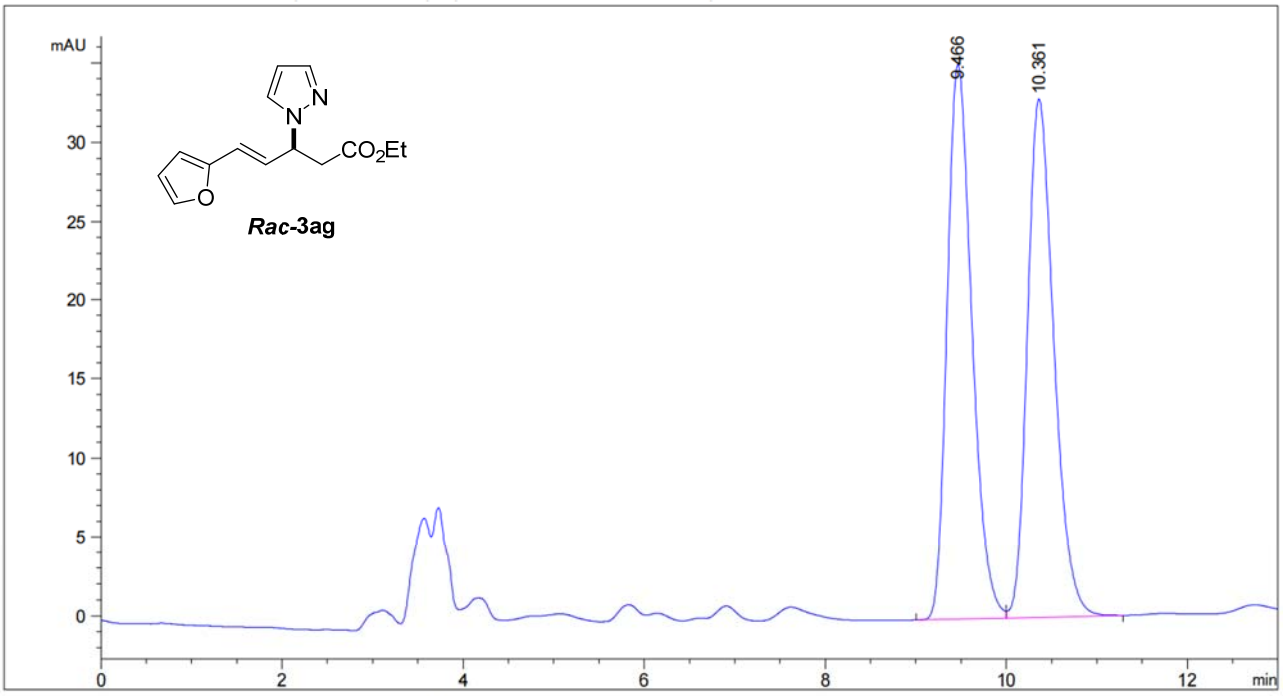
^{1}H-NMR (400 MHz, $CDCl_3$)



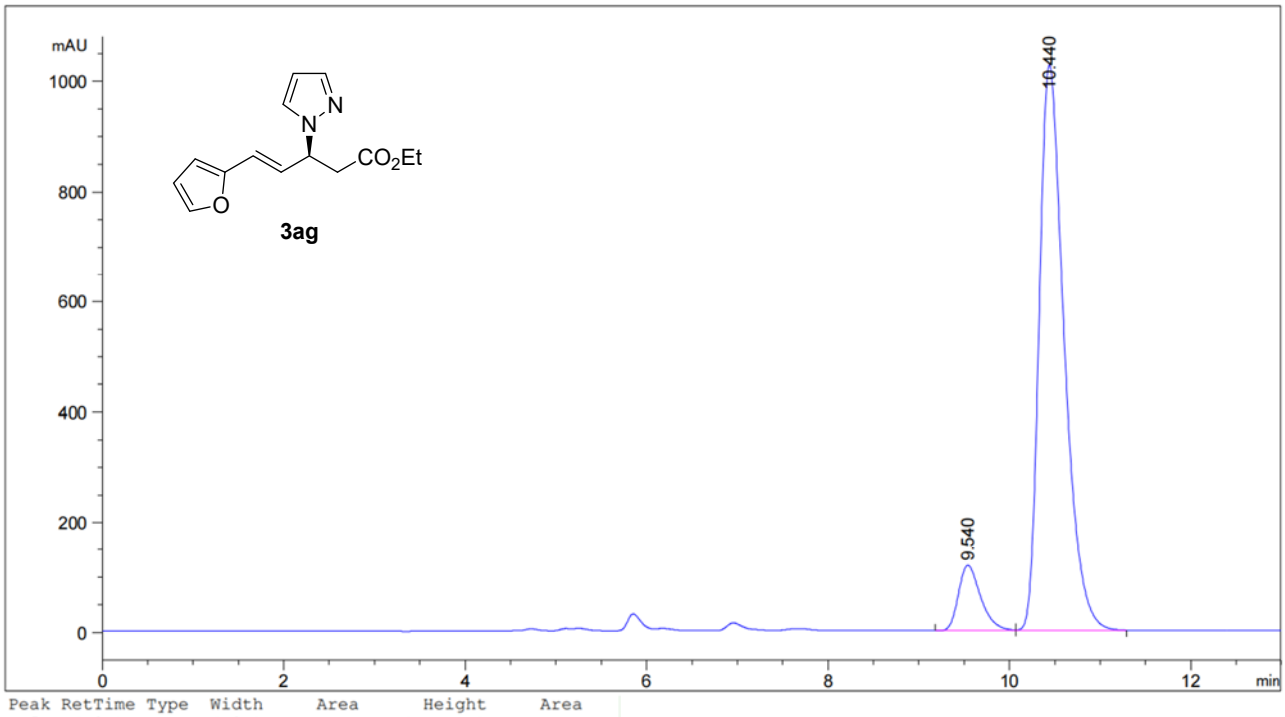
3ag

^{13}C-NMR (100 MHz, $CDCl_3$)

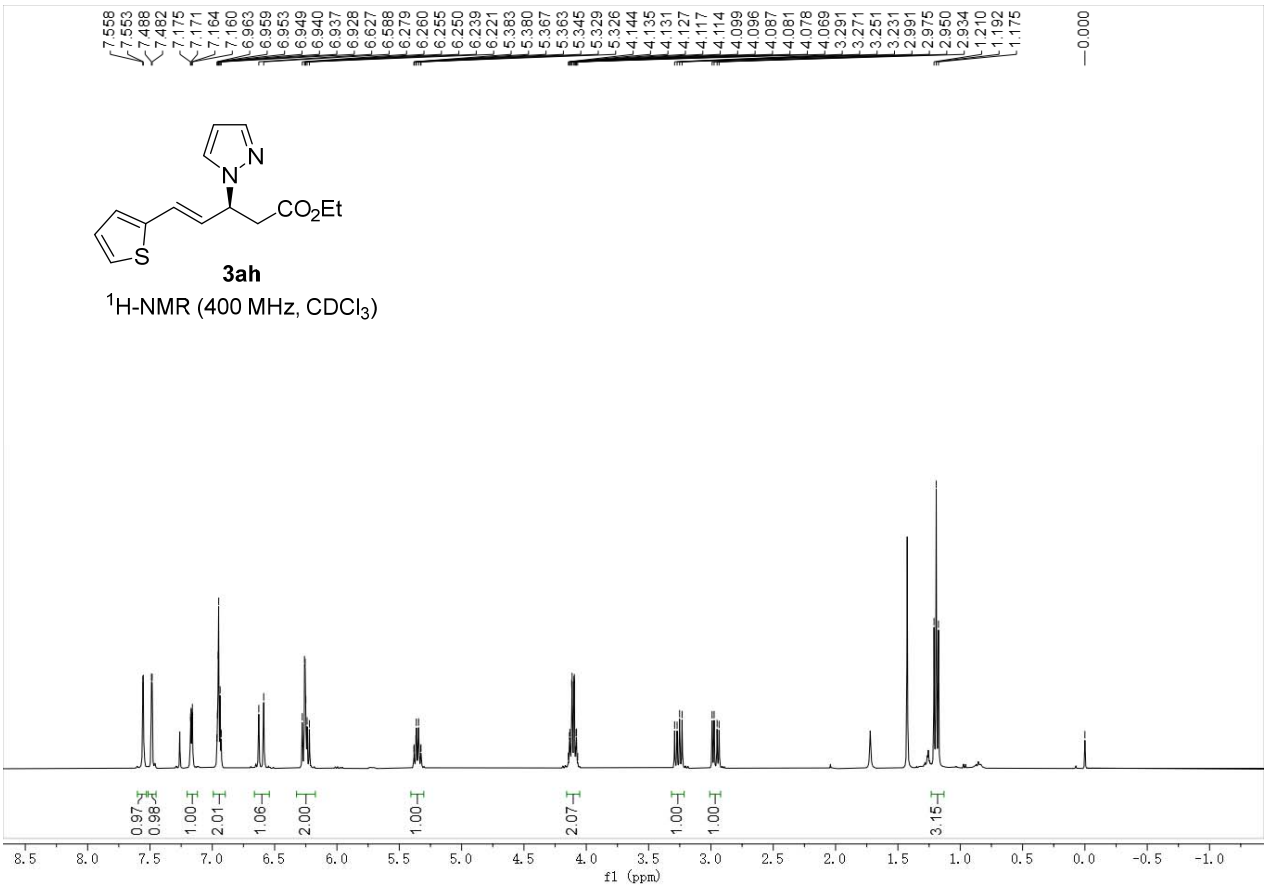

User Spectrum Plot Report
Agilent
Name CYC-220406-15
Inj. Vol. (ul) 8
Data File CYC-220406-15.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
Some ions missed
Operator
Acq. Time (Local) 4/8/2022 8:28:15 PM (UTC+08:00)
+ESI Scan (rt: 0.185 min) Frag=175.0V CYC-220406-15.d
x10^6
283.1053
3ag
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C14H16N2O3Na+ 283.1054
Counts vs. Mass-to-Charge (m/z)

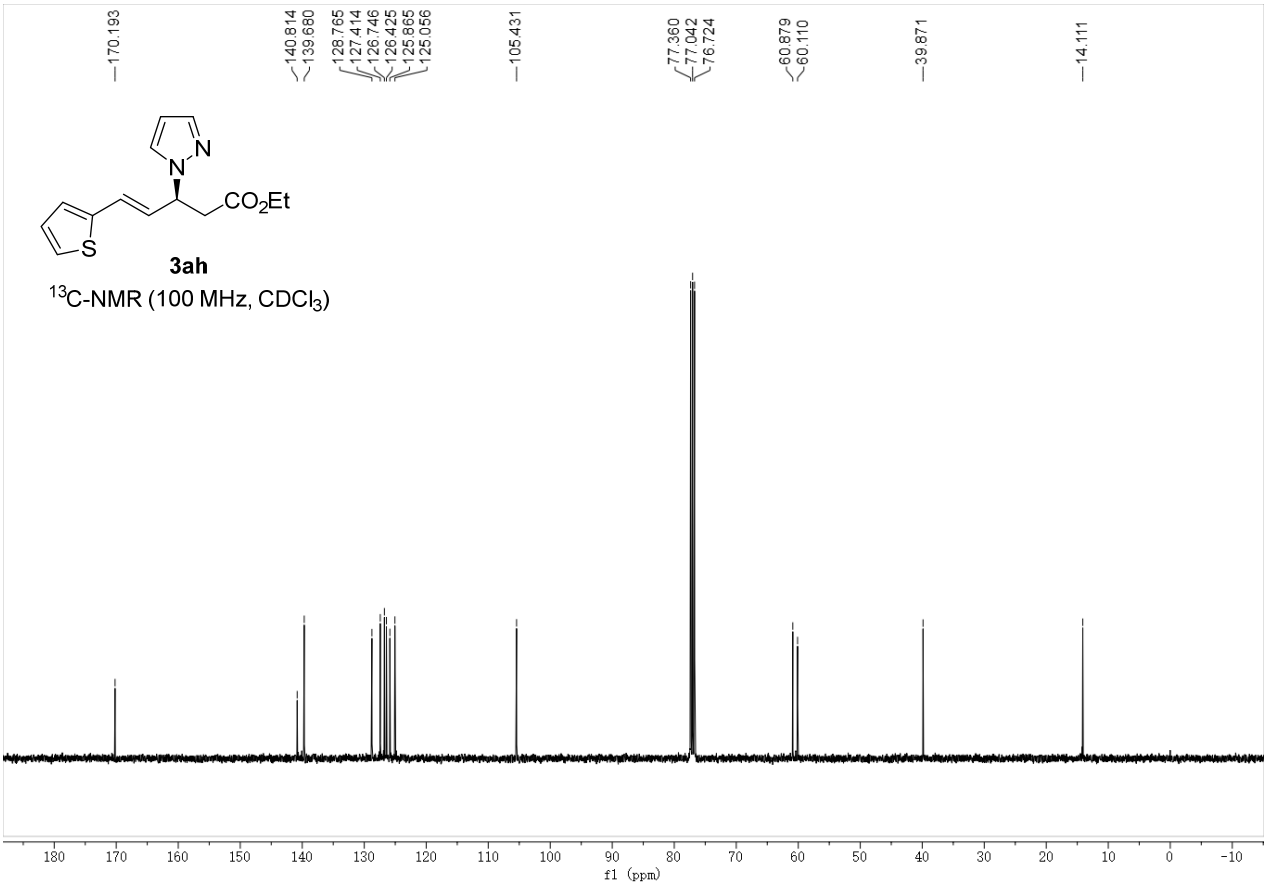


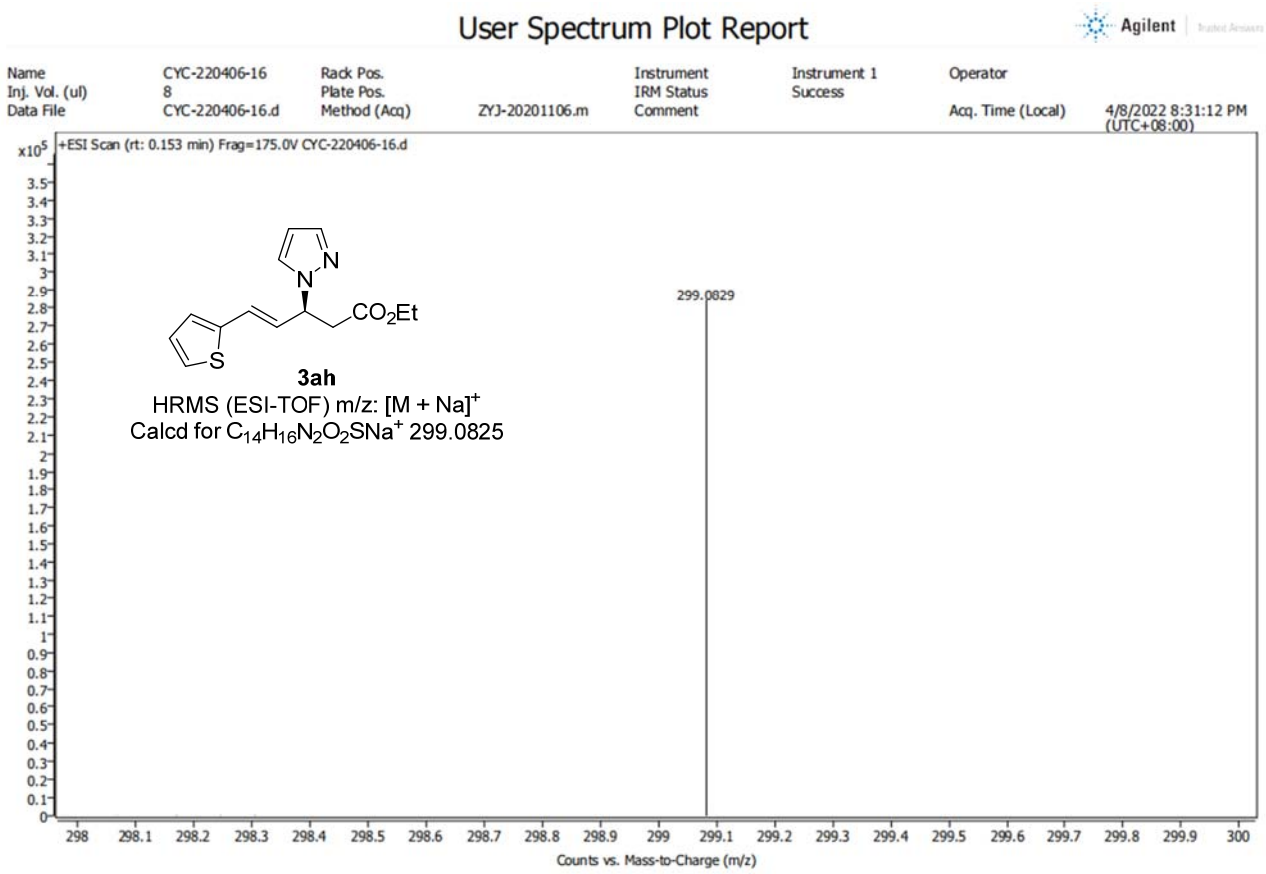
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.466	BV	0.2944	667.07007	35.11298	50.0139
2	10.361	VBA	0.3129	666.69830	32.79888	49.9861

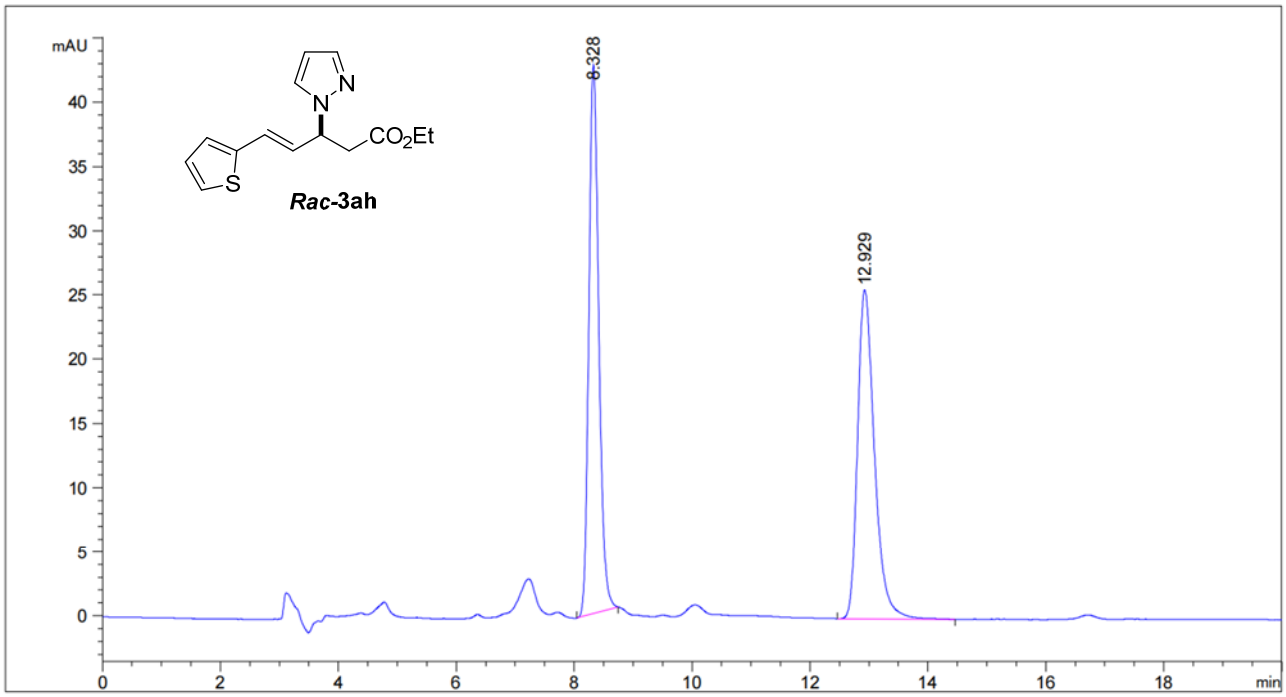


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.540	BV	0.2594	2009.31396	118.24461	9.2959
2	10.440	VBA	0.2927	1.96057e4	1026.59070	90.7041

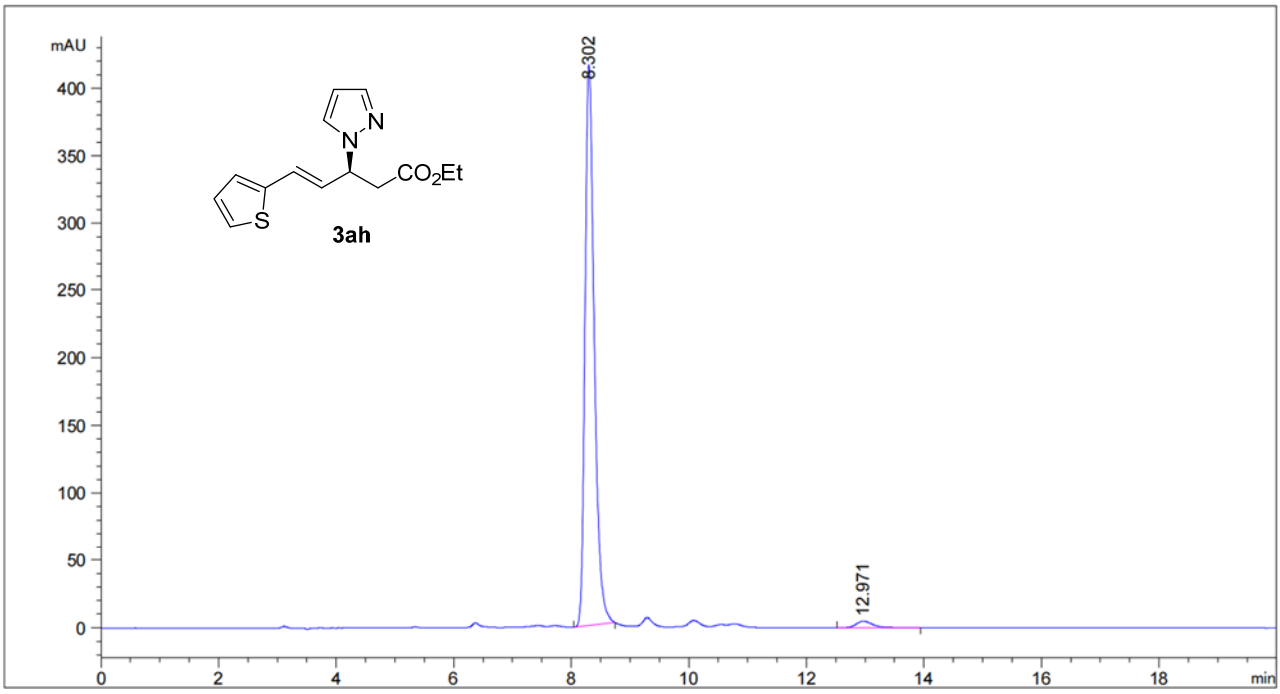

7.558
7.553
7.488
7.482
7.175
7.171
7.164
7.160
6.963
6.959
6.953
6.949
6.940
6.937
6.928
6.627
6.588
6.279
6.260
6.255
6.250
6.239
6.221
5.383
5.380
5.367
5.363
5.345
5.329
5.326
4.144
4.135
4.131
4.127
4.117
4.114
4.099
4.096
4.087
4.081
4.078
4.069
3.291
3.271
3.251
3.231
2.991
2.975
2.950
2.934
1.210
1.192
1.175
0.000
N
N
CO2Et
S
3ah
1H-NMR (400 MHz, CDCl3)
0.97
0.98
1.00
2.01
1.06
2.00
1.00
2.07
1.00
1.00
3.15
f1 (ppm)


170.193
140.814
139.680
128.765
127.414
126.746
126.425
125.865
125.056
105.431
77.360
77.042
76.724
60.879
60.110
39.871
14.111
N
N
CO2Et
S
3ah
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

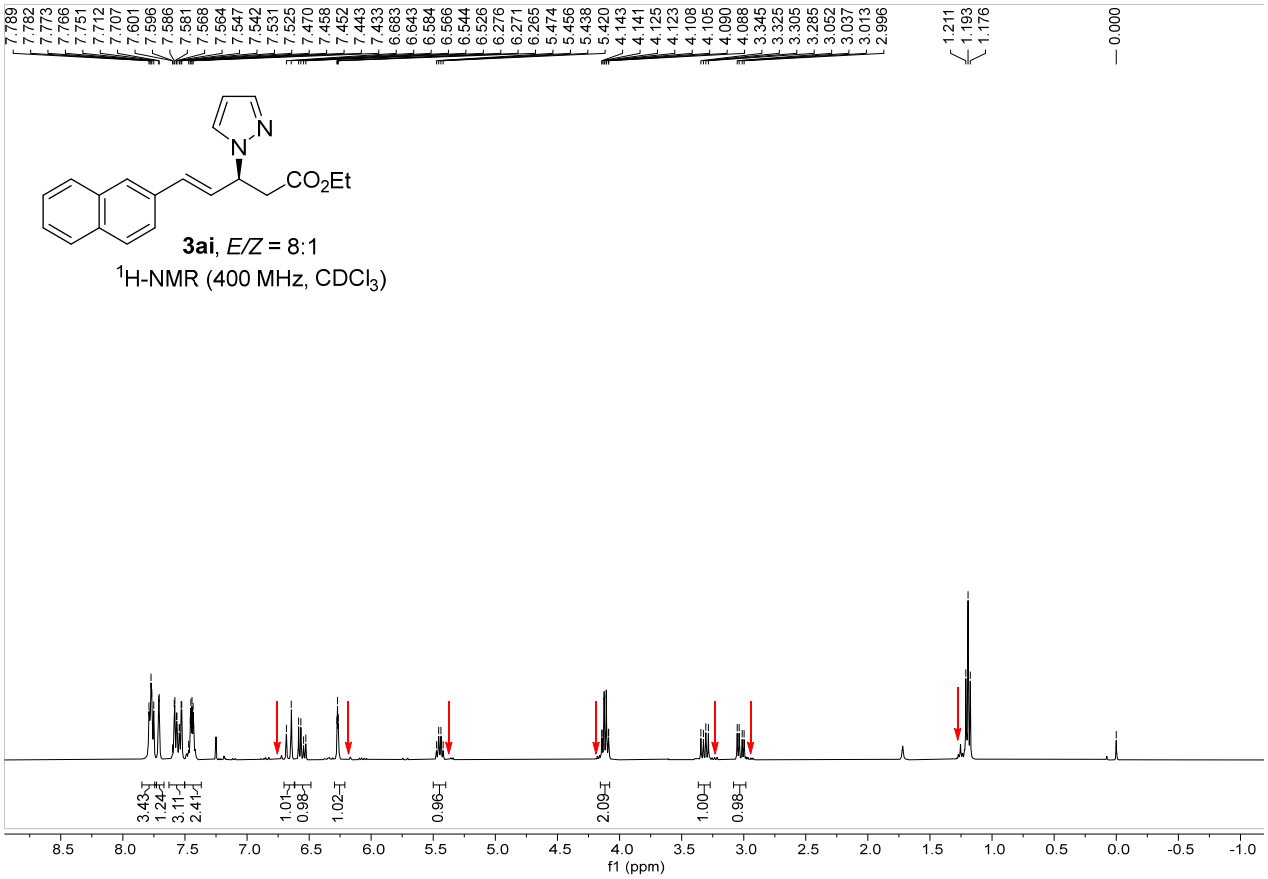

User Spectrum Plot Report
Agilent
Name CYC-220406-16
Inj. Vol. (ul) 8
Data File CYC-220406-16.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument
IRM Status
Comment
Instrument 1
Success
Operator
Acq. Time (Local) 4/8/2022 8:31:12 PM (UTC+08:00)
+ESI Scan (rt: 0.153 min) Frag=175.0V CYC-220406-16.d
x10^5
299.0829
CO2Et
3ah
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C14H16N2O2SNa+ 299.0825
Counts vs. Mass-to-Charge (m/z)

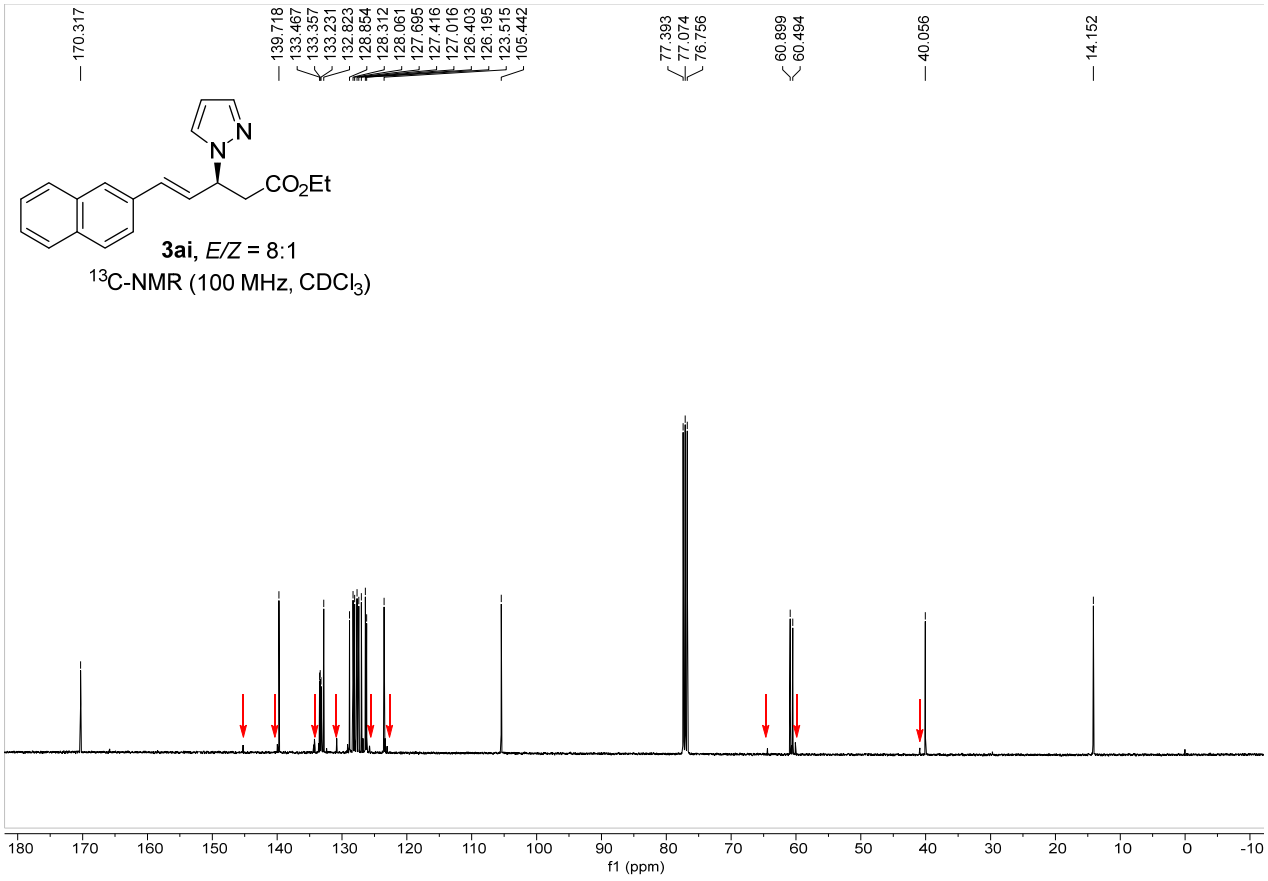


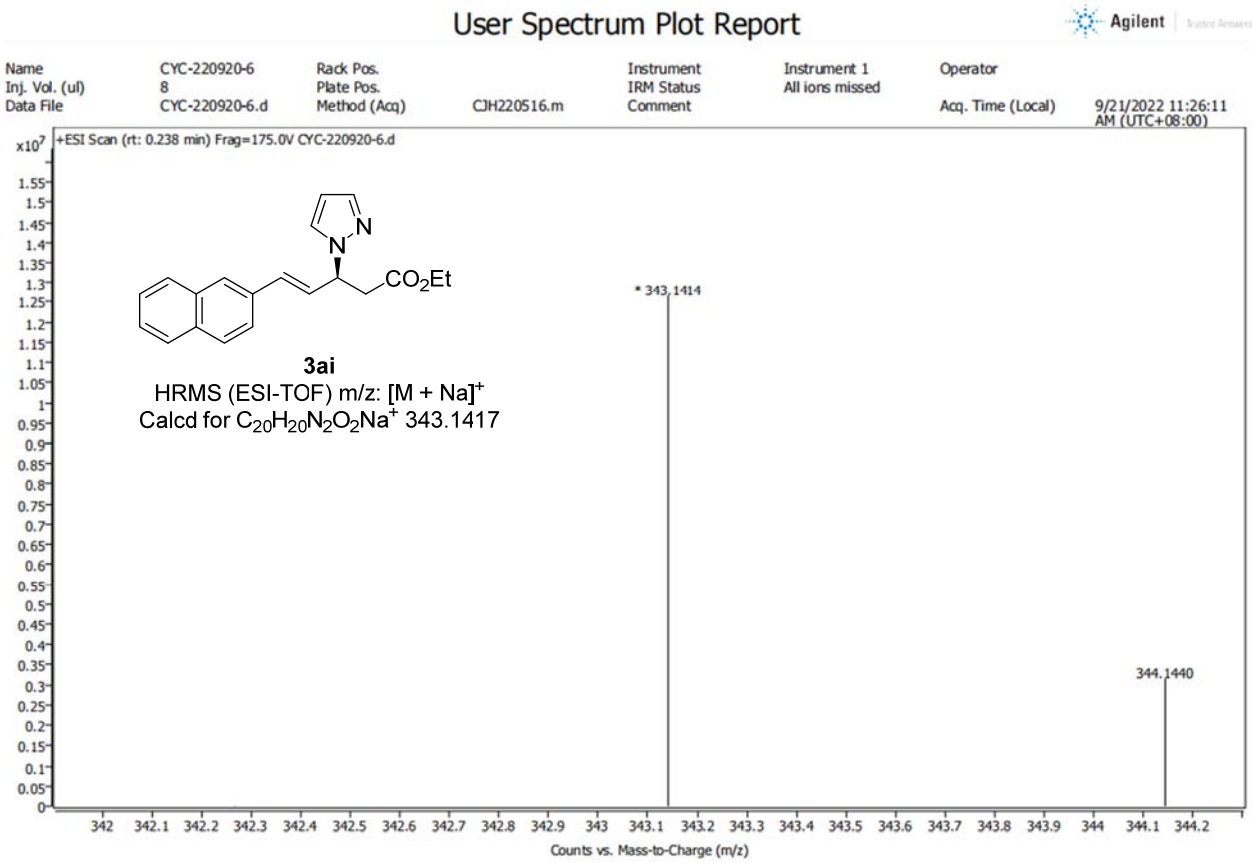
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.328	BBA	0.1836	499.59299	42.55075	49.4411
2	12.929	BB	0.3028	510.88797	25.59109	50.5589

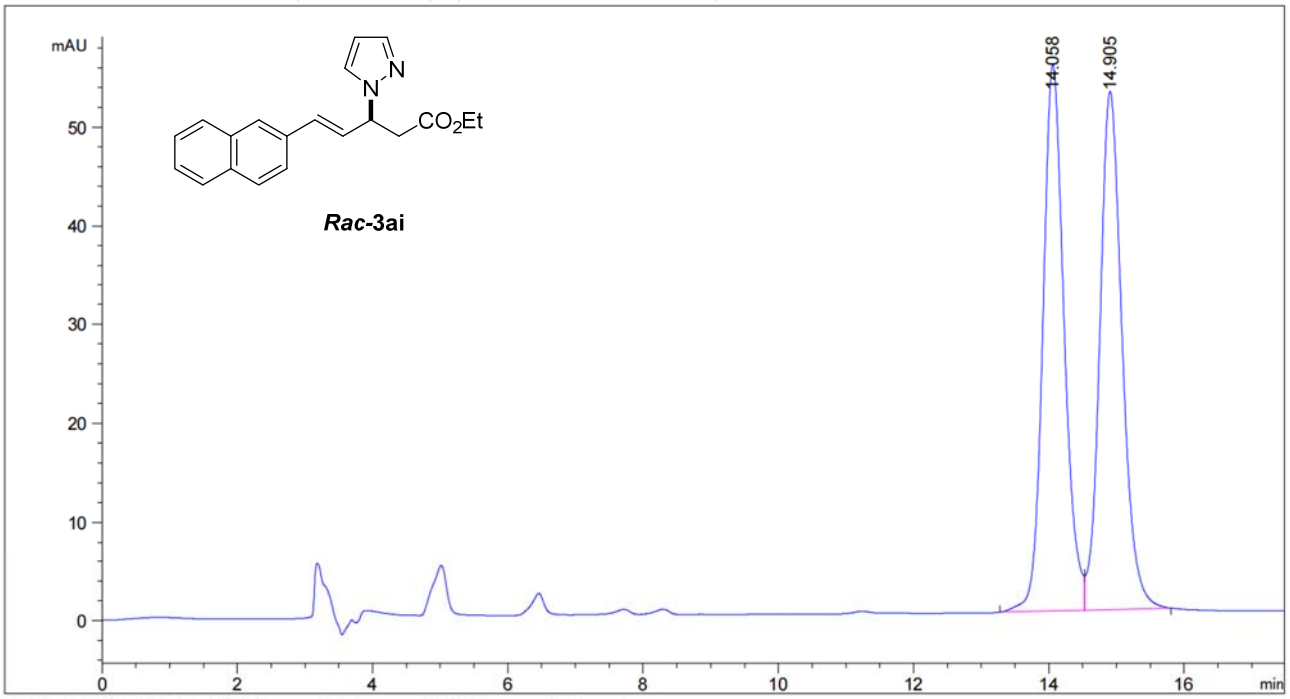


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.302	BBA	0.1684	4540.01953	415.01700	97.9782
2	12.971	BB	0.2955	93.68615	4.84513	2.0218


7.789 7.782 7.773 7.766 7.751 7.712 7.707 7.601 7.596 7.586 7.581 7.568 7.564 7.547 7.542 7.531 7.525 7.470 7.458 7.452 7.443 7.433 6.683 6.643 6.584 6.566 6.544 6.526 6.276 6.271 6.265 5.474 5.456 5.438 5.420 4.143 4.141 4.125 4.123 4.108 4.105 4.090 4.088 3.345 3.325 3.305 3.285 3.052 3.037 3.013 2.996
1.211 1.193 1.176
0.000
N
N
CO2Et
3ai, E/Z = 8:1
1H-NMR (400 MHz, CDCl3)
3.43 1.24 3.11 2.41 1.01 0.98 1.02 0.96 2.09 1.00 0.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

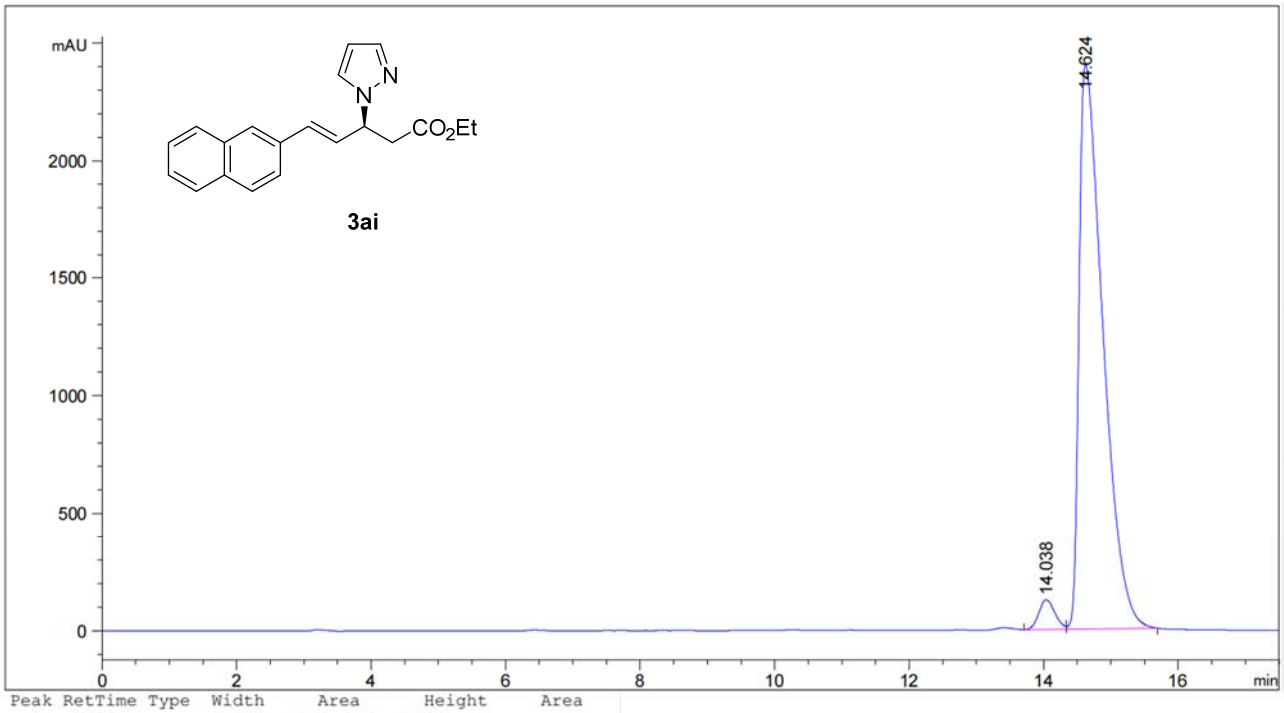

170.317
139.718 133.467 133.357 133.231 132.823 128.854 128.312 128.061 127.695 127.416 127.016 126.403 126.195 123.515 105.442
77.393 77.074 76.756
60.899 60.494
40.056
14.152
N
N
CO2Et
3ai, E/Z = 8:1
13C-NMR (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


User Spectrum Plot Report
Agilent
Name CYC-220920-6
Inj. Vol. (ul) 8
Data File CYC-220920-6.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 9/21/2022 11:26:11 AM (UTC+08:00)
+ESI Scan (rt: 0.238 min) Frag=175.0V CYC-220920-6.d
x10^7
* 343.1414
344.1440
Counts vs. Mass-to-Charge (m/z)
3ai
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C20H20N2O2Na+ 343.1417



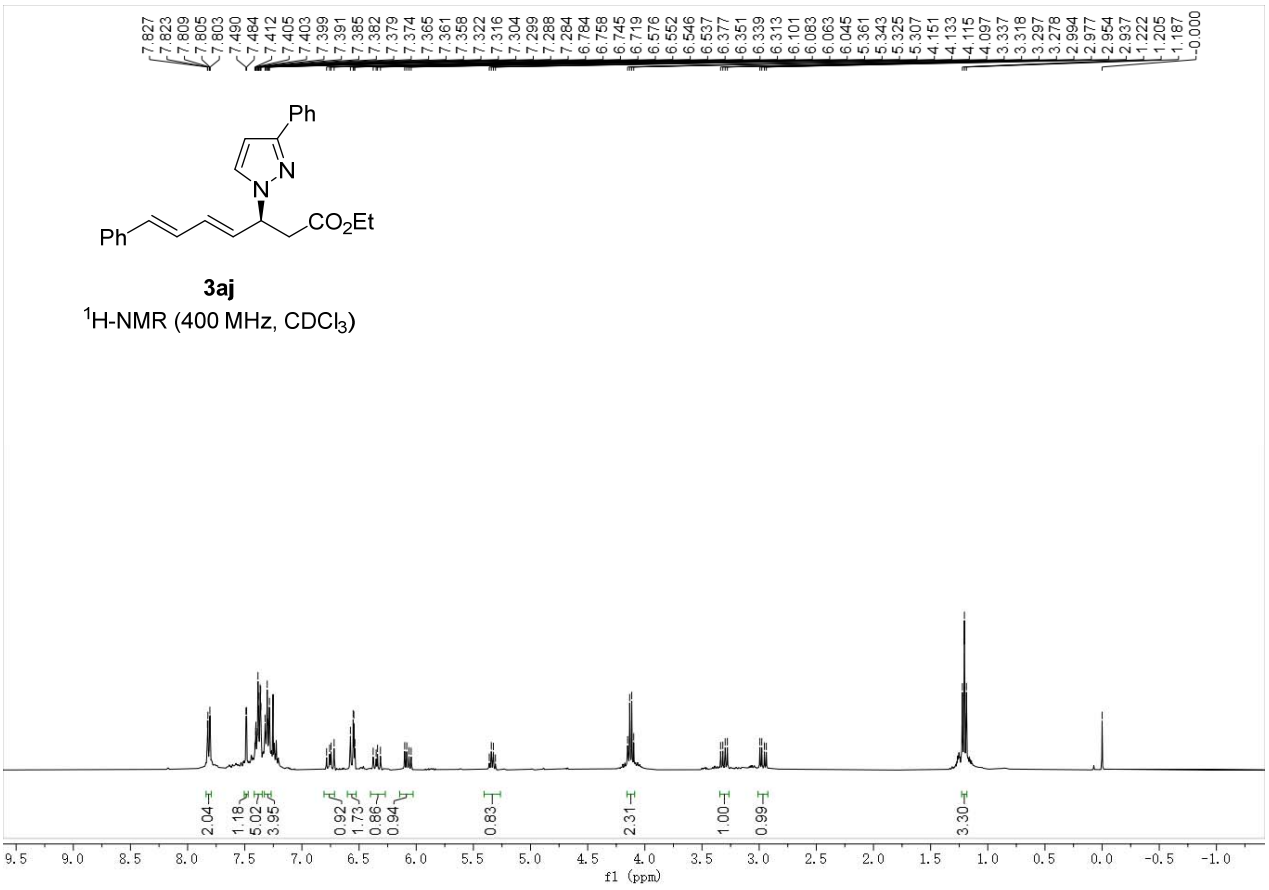
***Rac*-3ai**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.058	BV	0.3335	1208.09070	55.30421	50.0736
2	14.905	VBA	0.3493	1204.53784	52.48270	49.9264



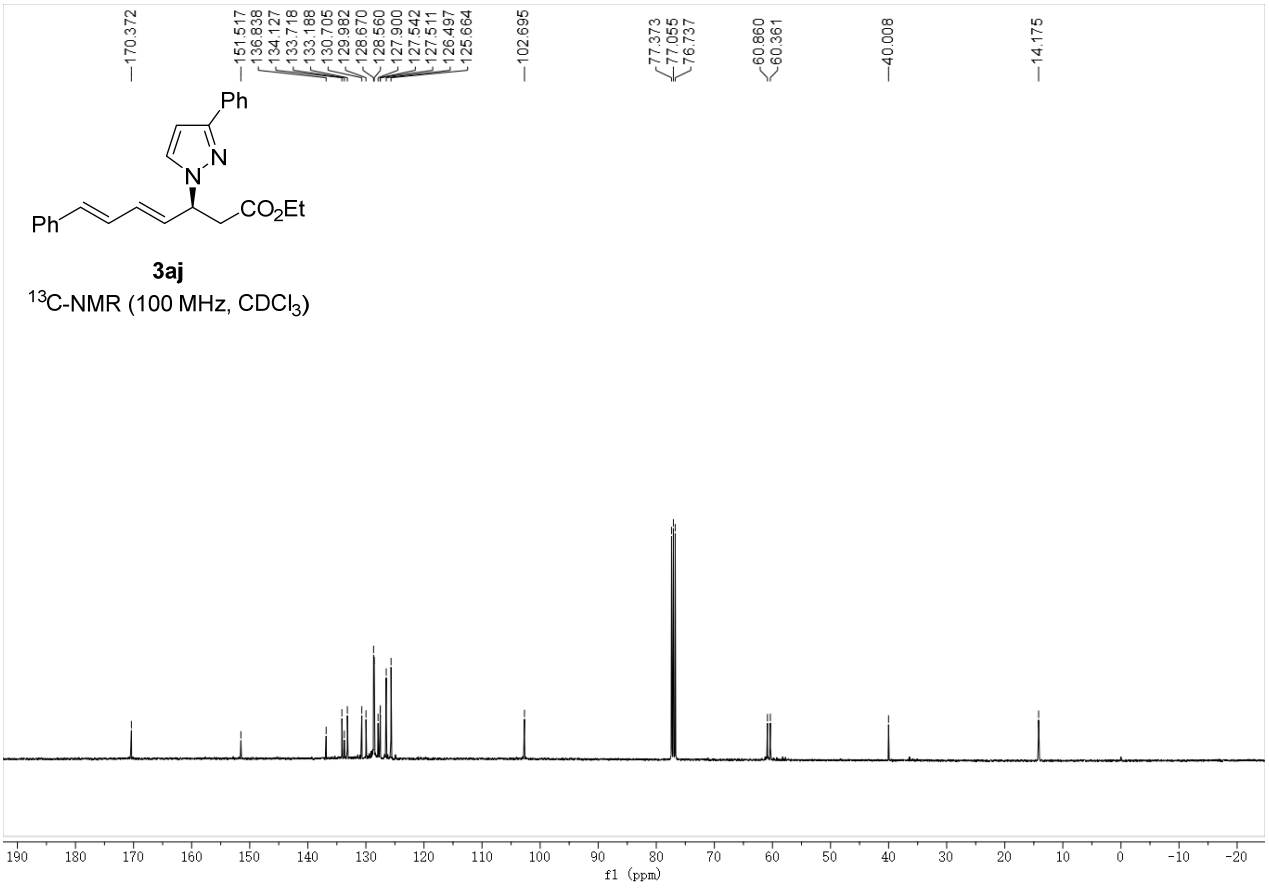
3ai

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.038	BV	0.2636	2076.23291	123.21645	3.3850
2	14.624	VBA	0.3768	5.92598e4	2400.45605	96.6150



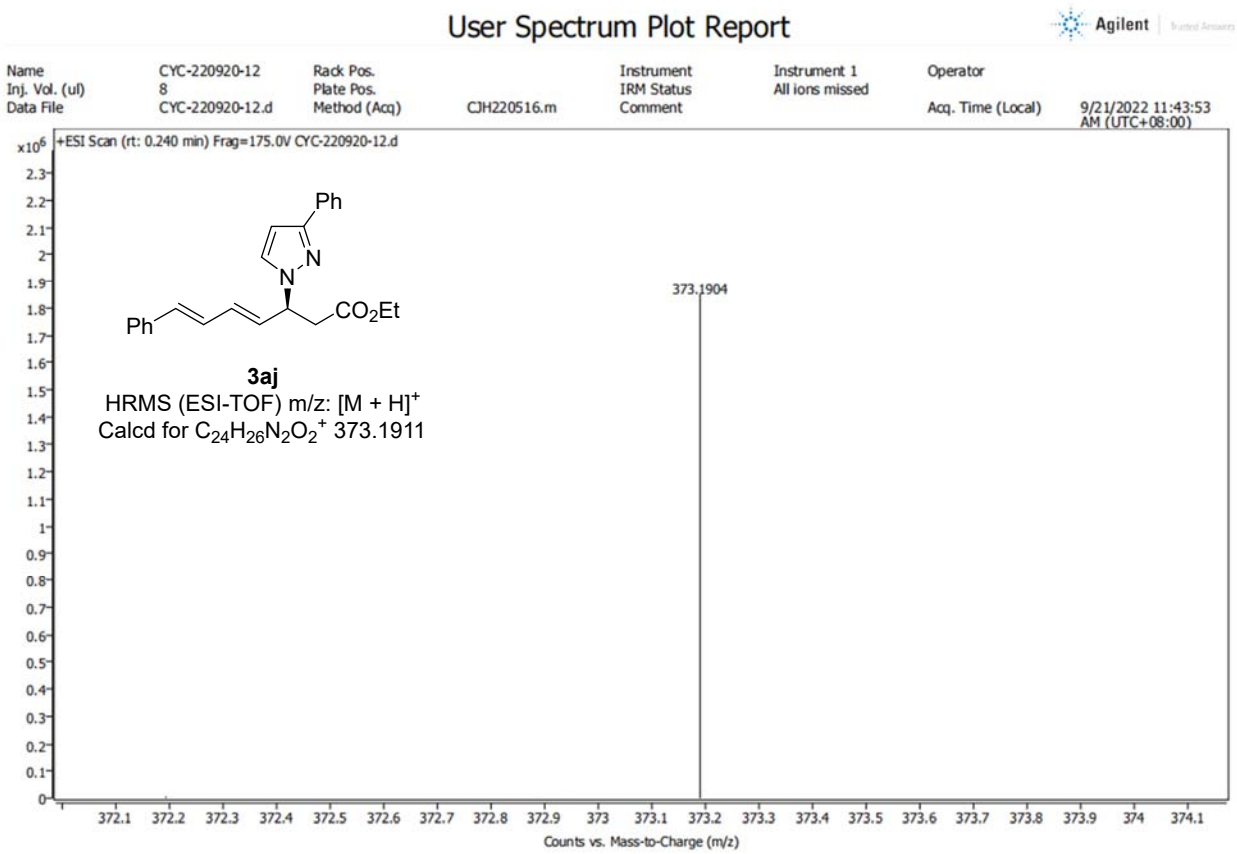
3aj

^{1}H-NMR (400 MHz, $CDCl_3$)



3aj

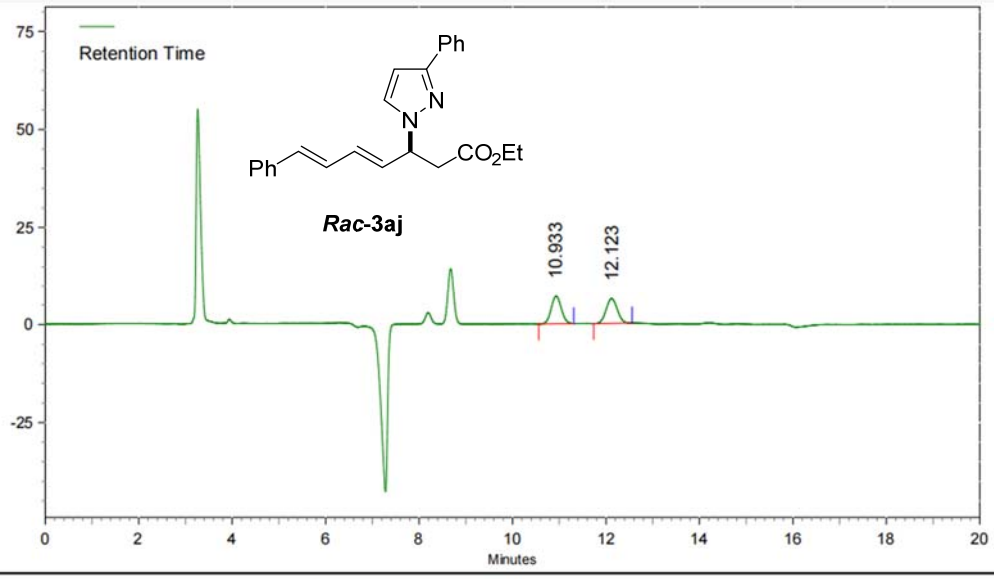
^{13}C-NMR (100 MHz, $CDCl_3$)



3aj

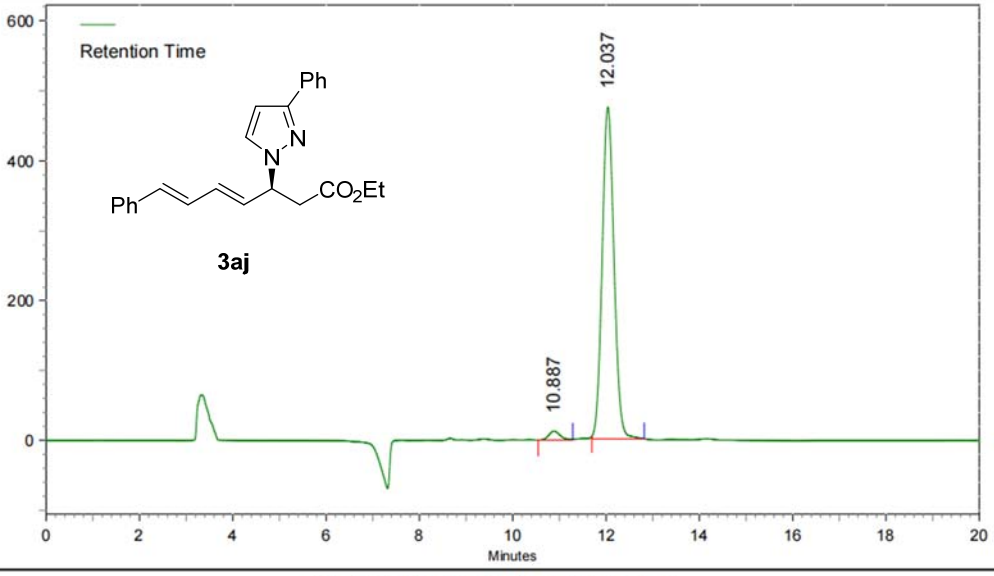
HRMS (ESI-TOF) m/z: $[M + H]^+$

Calcd for $C_{24}H_{26}N_2O_2^+$ 373.1911



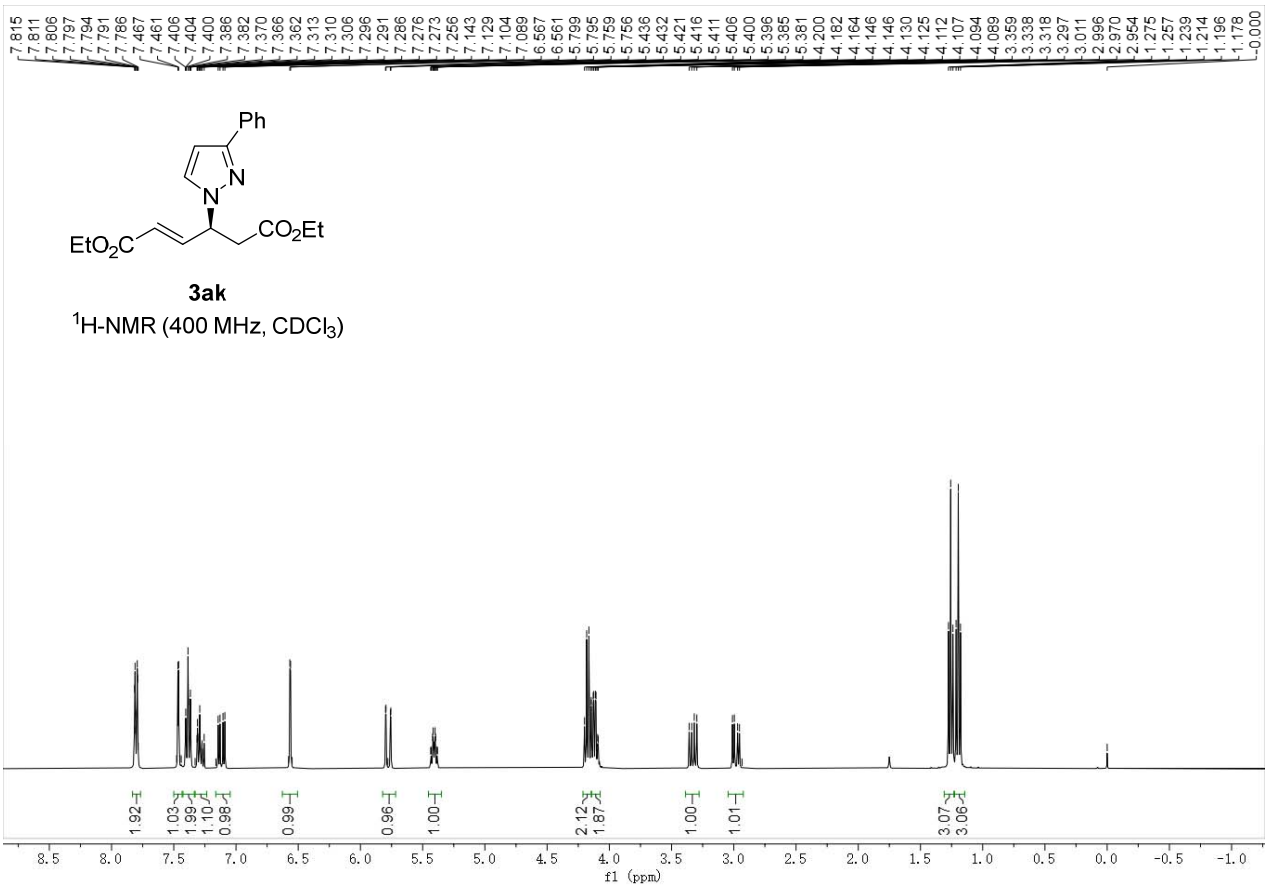
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.933	0.750	118611	1783733	50.3710
2	12.123	0.823	106216	1757458	49.6290
Totals			224827	3541191	100.0000



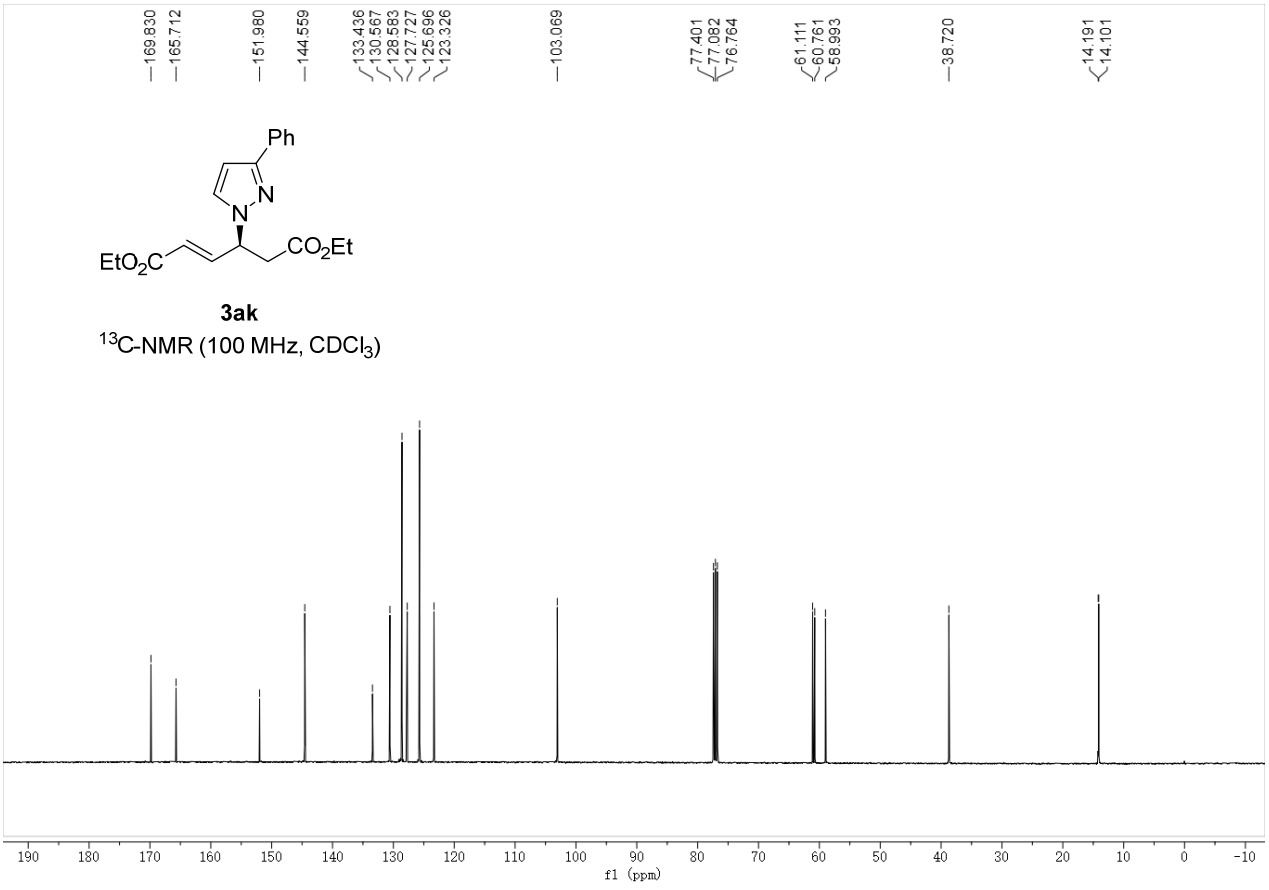
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.887	0.740	216025	3745800	2.5994
2	12.037	1.127	7962120	140355782	97.4006
Totals			8178145	144101582	100.0000



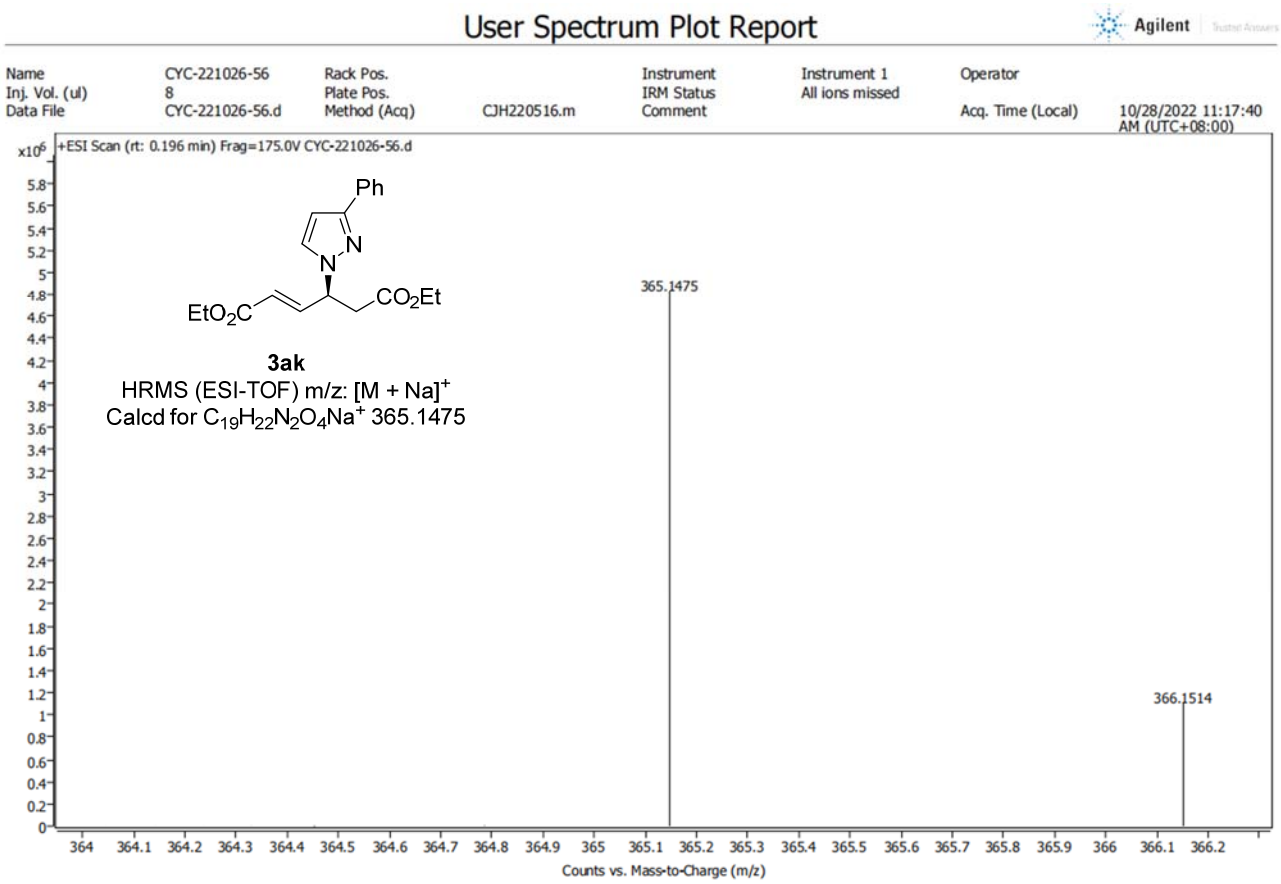
3ak

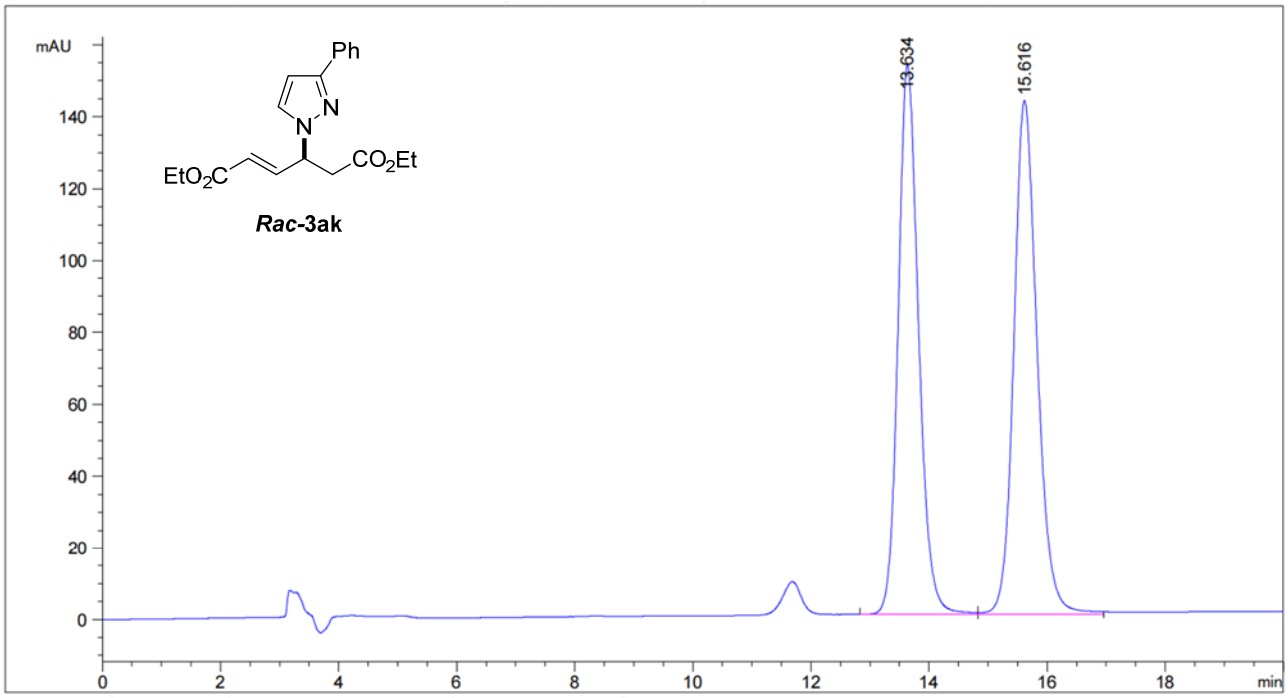
^{1}H-NMR (400 MHz, $CDCl_3$)



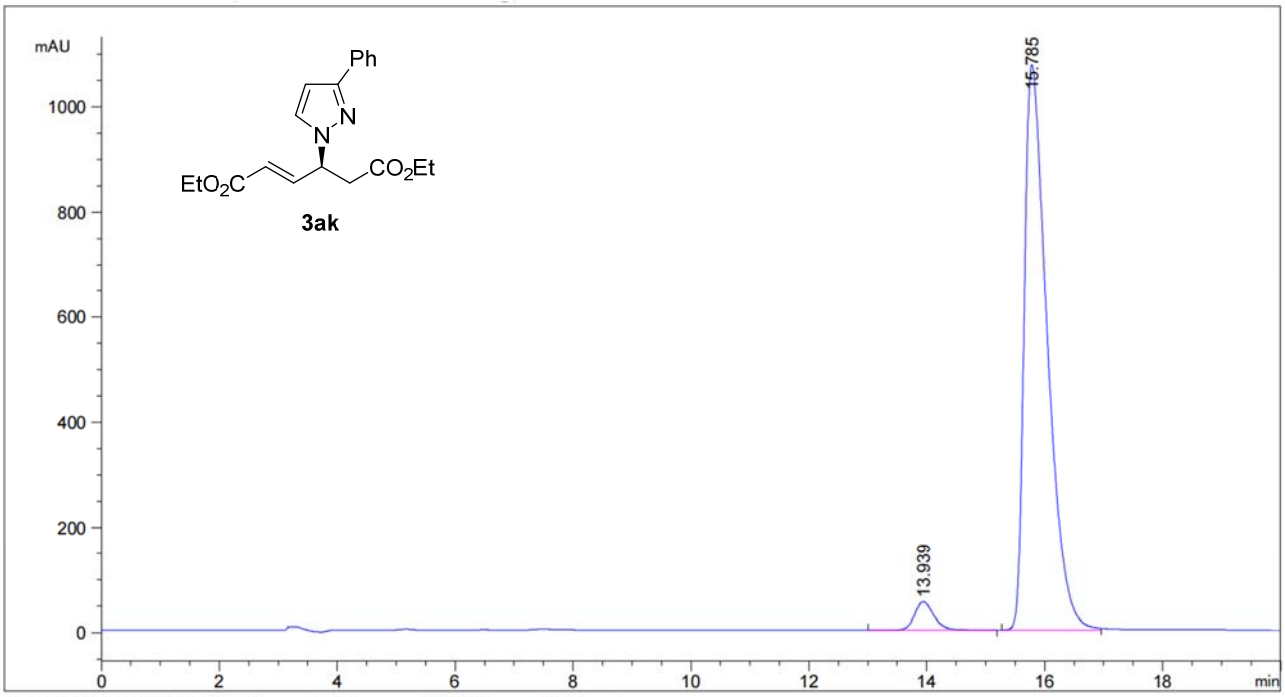
3ak

^{13}C-NMR (100 MHz, $CDCl_3$)

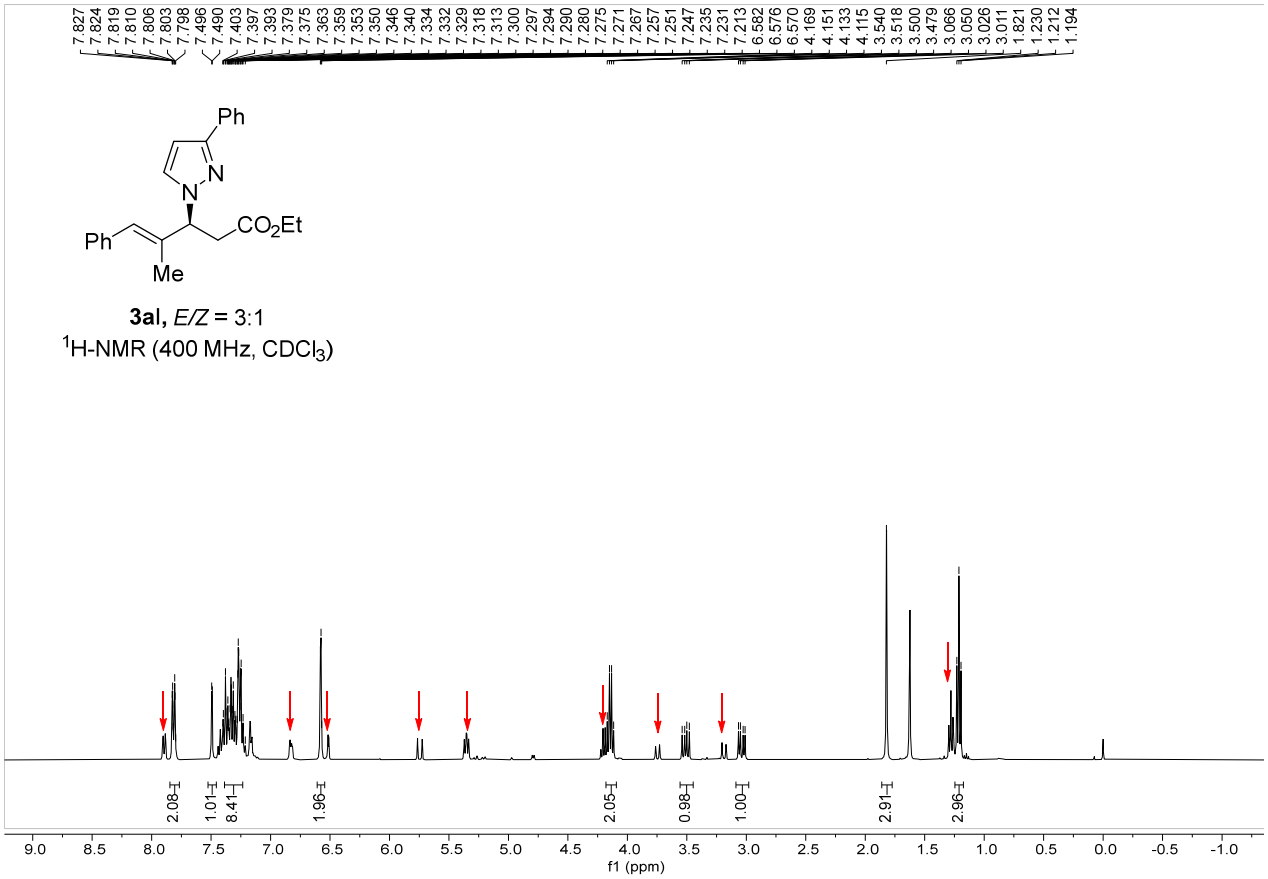

User Spectrum Plot Report
Agilent
Name CYC-221026-56
Inj. Vol. (ul) 8
Data File CYC-221026-56.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 10/28/2022 11:17:40 AM (UTC+08:00)
+ESI Scan (rt: 0.196 min) Frag=175.0V CYC-221026-56.d
x10^6
Ph
N
N
EtO2C
CO2Et
3ak
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C19H22N2O4Na+ 365.1475
365.1475
366.1514
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.634	BV	0.3683	3683.21826	152.93556	48.3478
2	15.616	VBA	0.4169	3934.94556	143.08698	51.6522

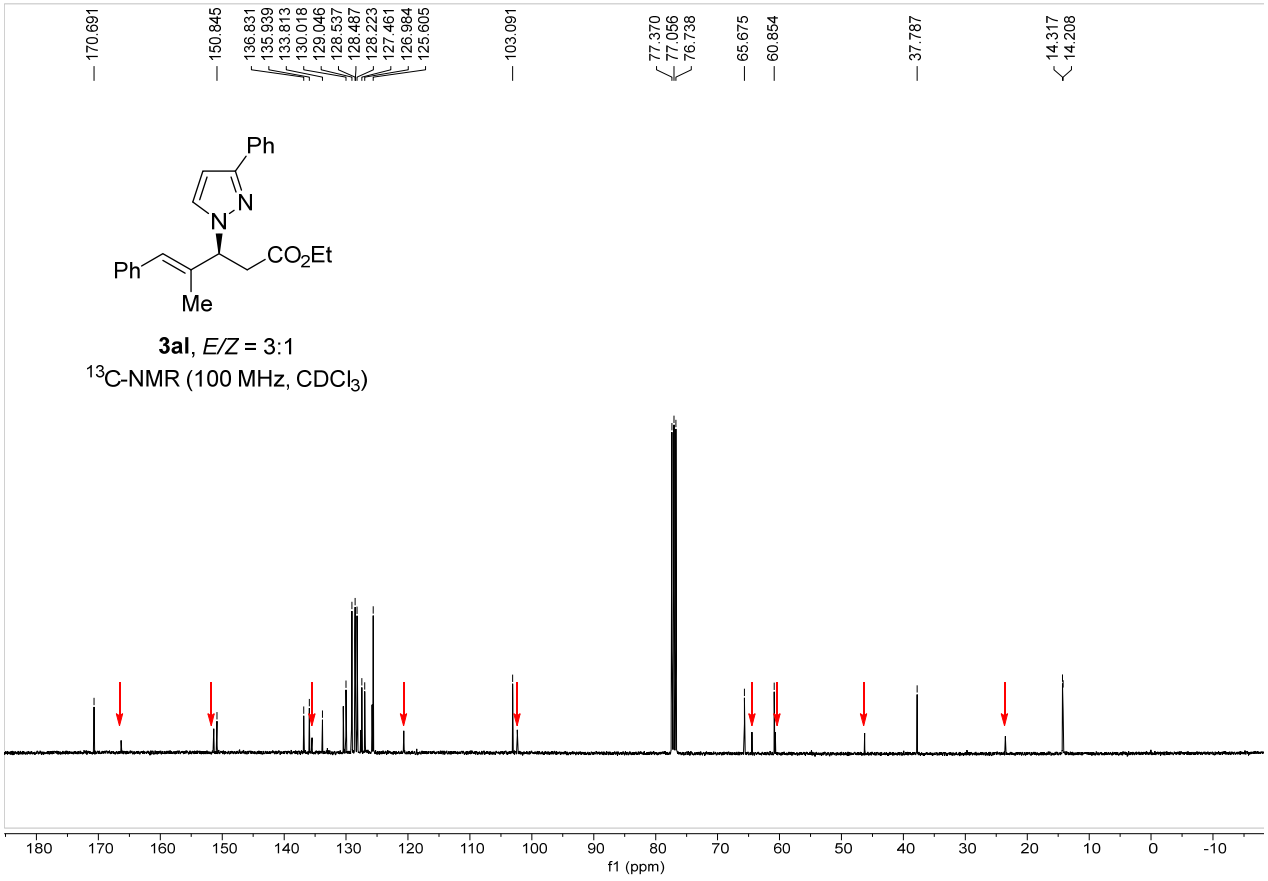


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.939	BB	0.3478	1197.45471	53.05260	3.9595
2	15.785	BBA	0.4116	2.90452e4	1074.01660	96.0405



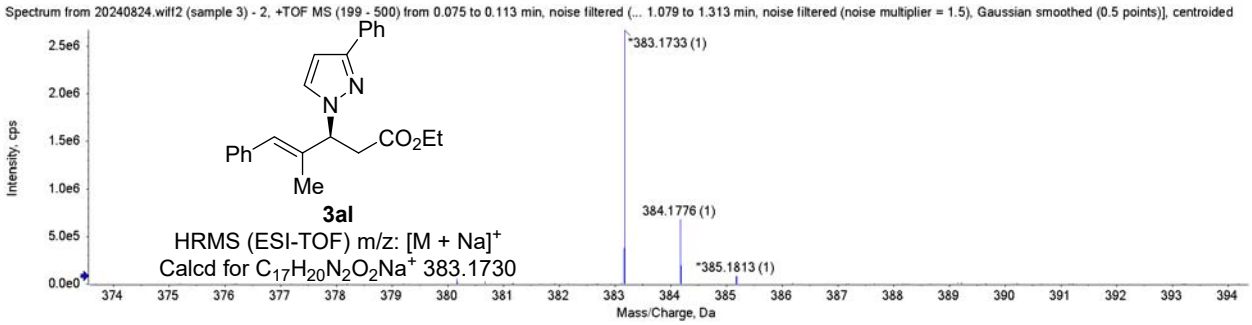
3al, *E*/*Z* = 3:1

^{1}H-NMR (400 MHz, $CDCl_3$)



3al, *E*/*Z* = 3:1

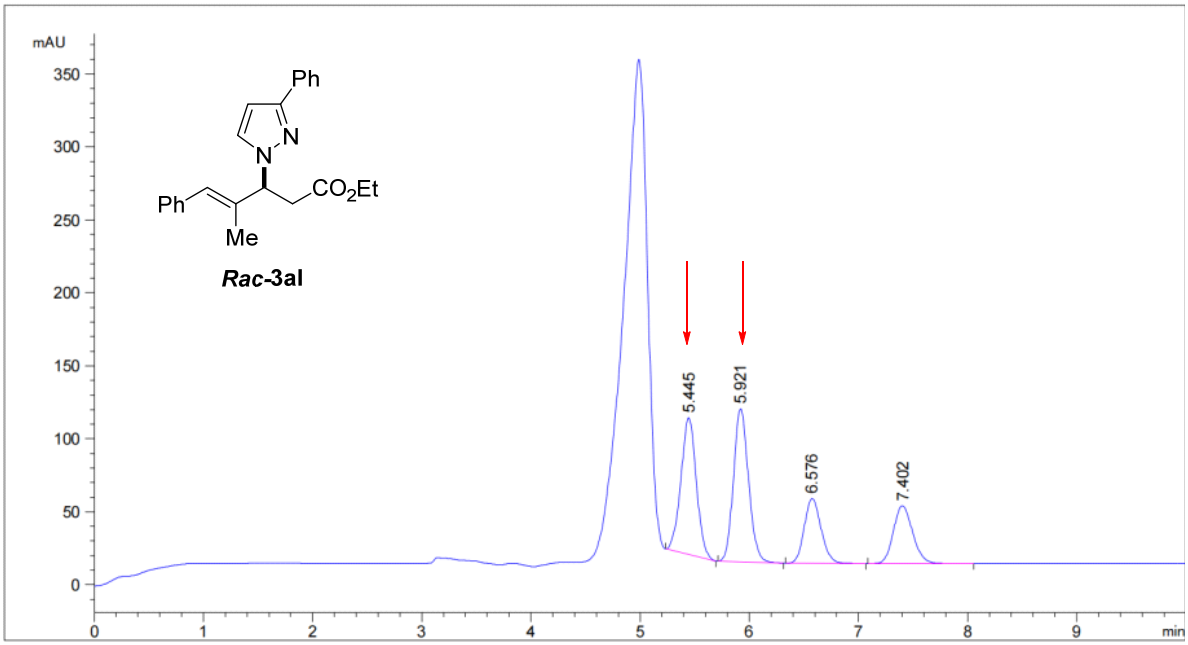
^{13}C-NMR (100 MHz, $CDCl_3$)



3al

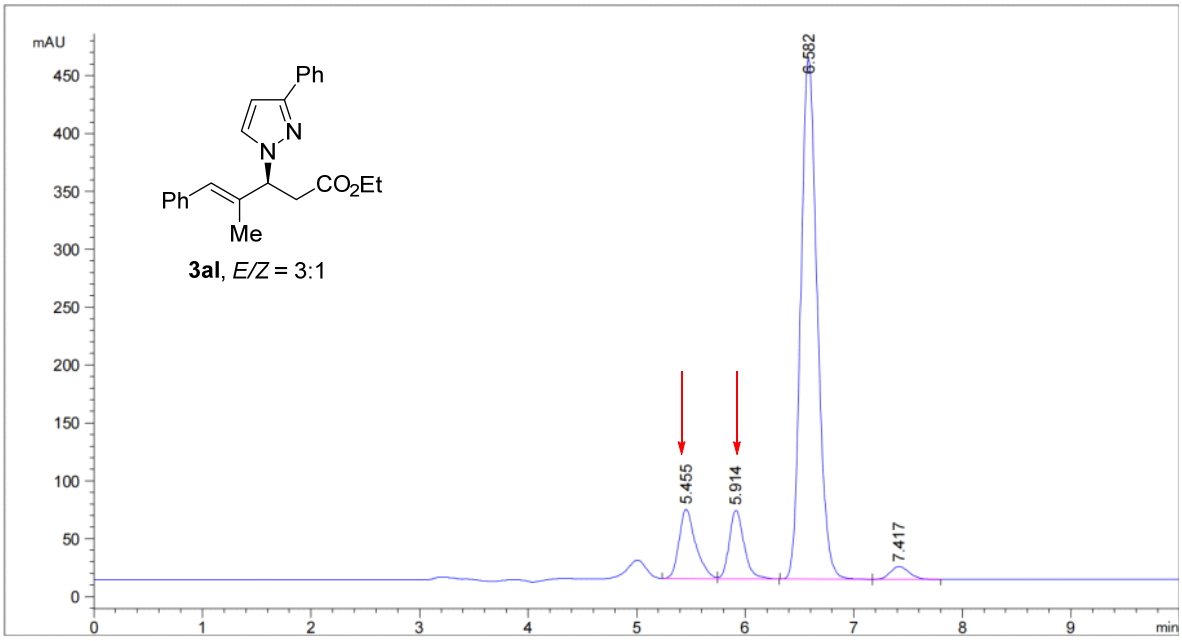
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{17}H_{20}N_2O_2Na^+$ 383.1730



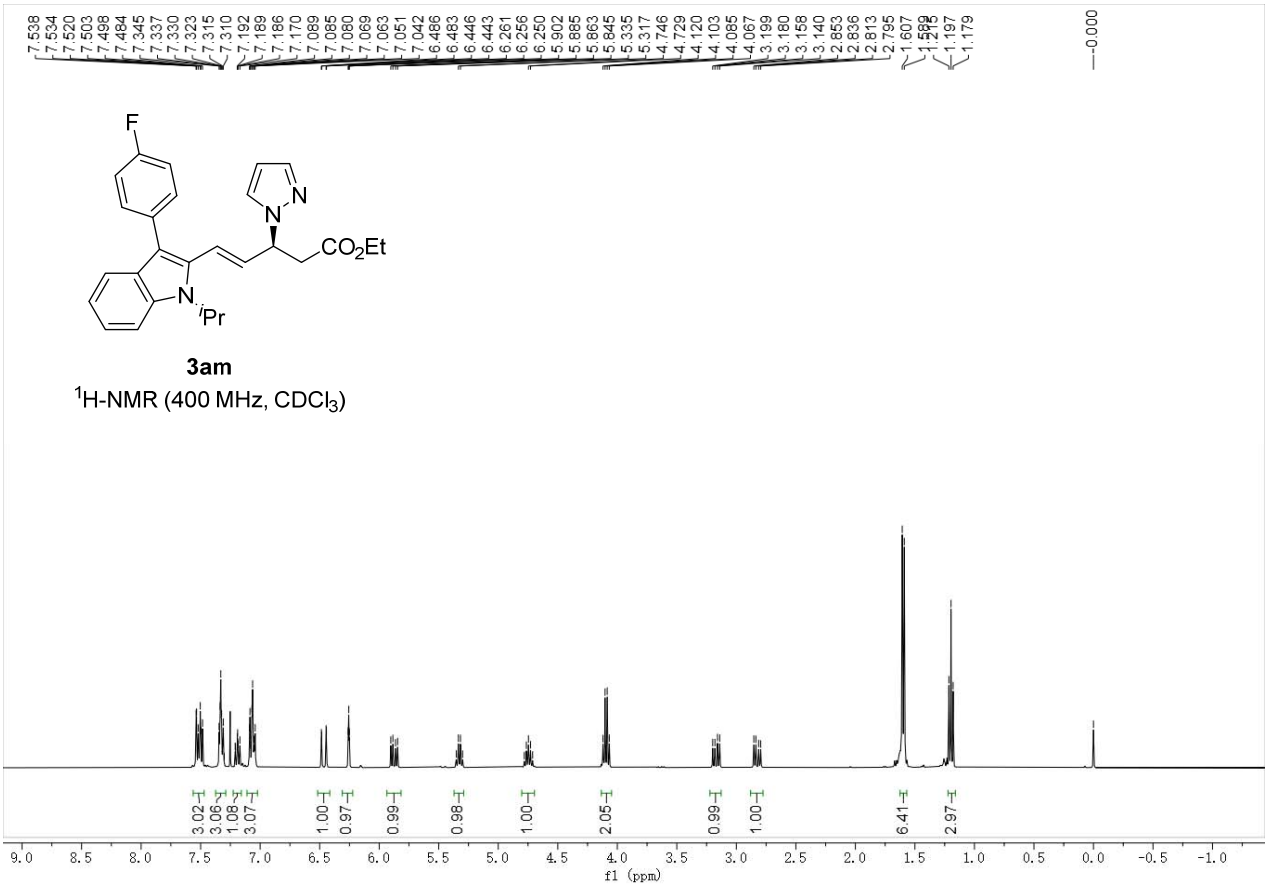
***Rac*-3al**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.445	BB	0.1494	920.06287	93.74937	31.8913
2	5.921	BB	0.1482	1004.50519	104.78314	34.8183
3	6.576	BB	0.1672	474.49509	44.27723	16.4470
4	7.402	BB	0.1912	485.93274	39.60023	16.8434



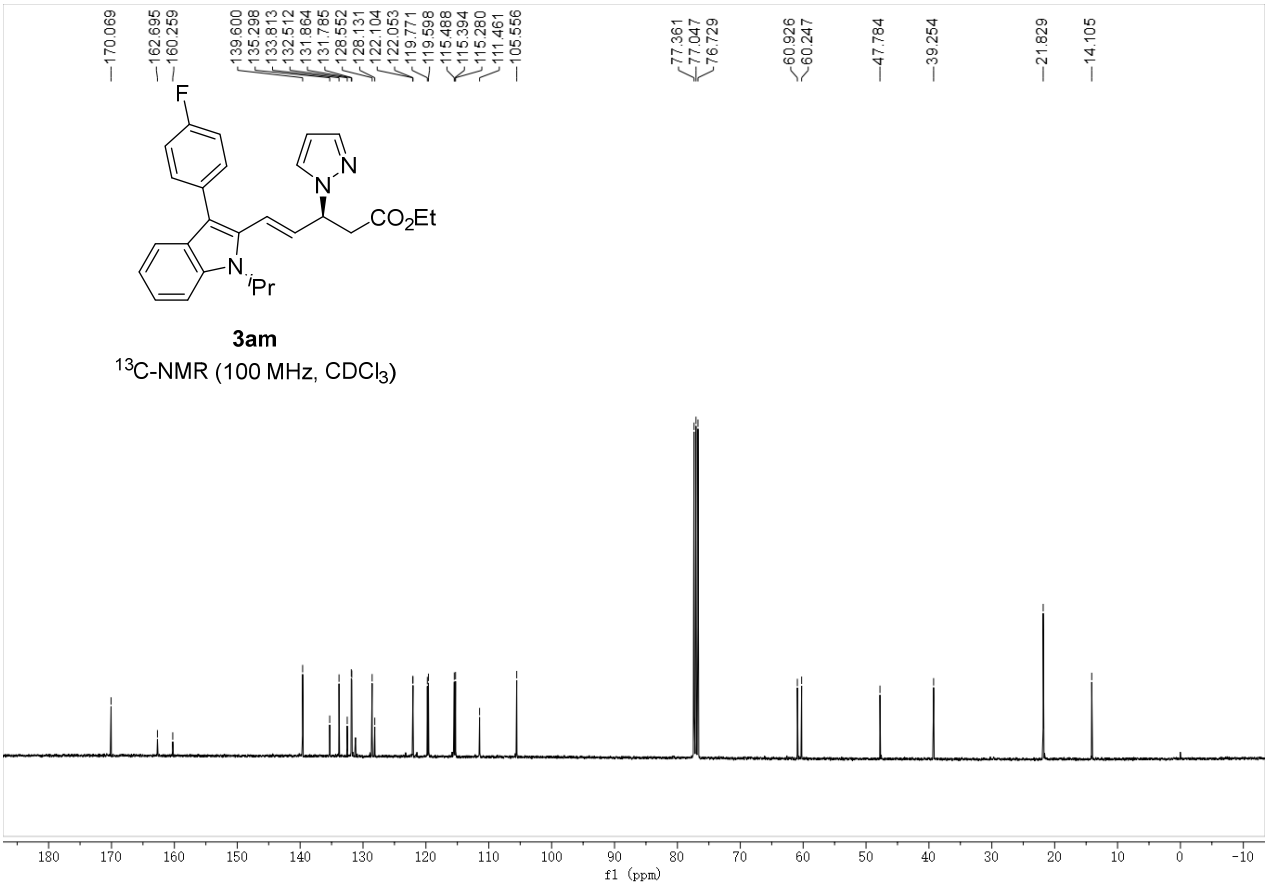
3al, *E*/*Z* = 3:1

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.455	BV	0.1580	638.51282	59.80757	10.5455
2	5.914	VB	0.1455	560.68030	59.18485	9.2600
3	6.582	BV	0.1635	4722.61572	448.99335	77.9972
4	7.417	VB	0.1861	133.04492	11.12957	2.1973



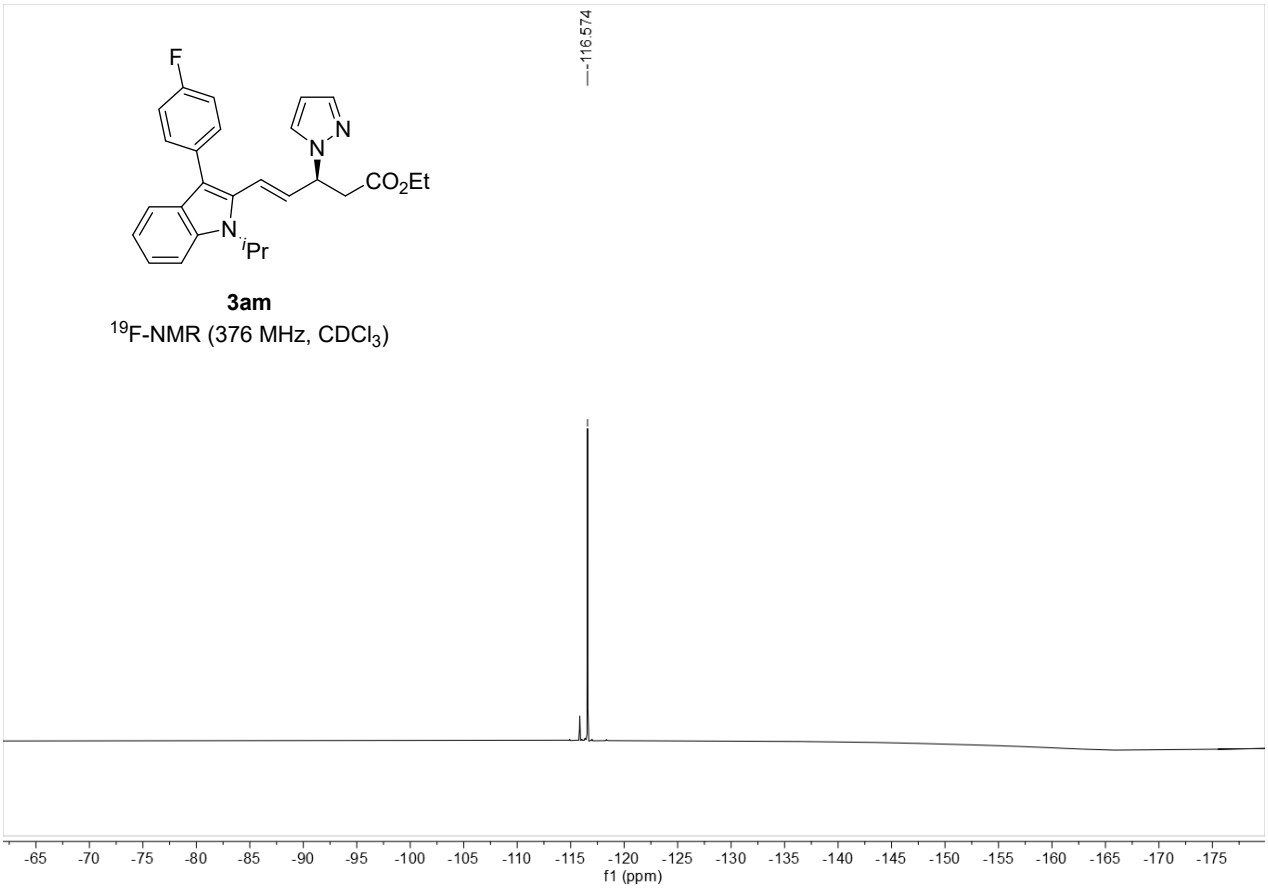
3am

^{1}H-NMR (400 MHz, $CDCl_3$)



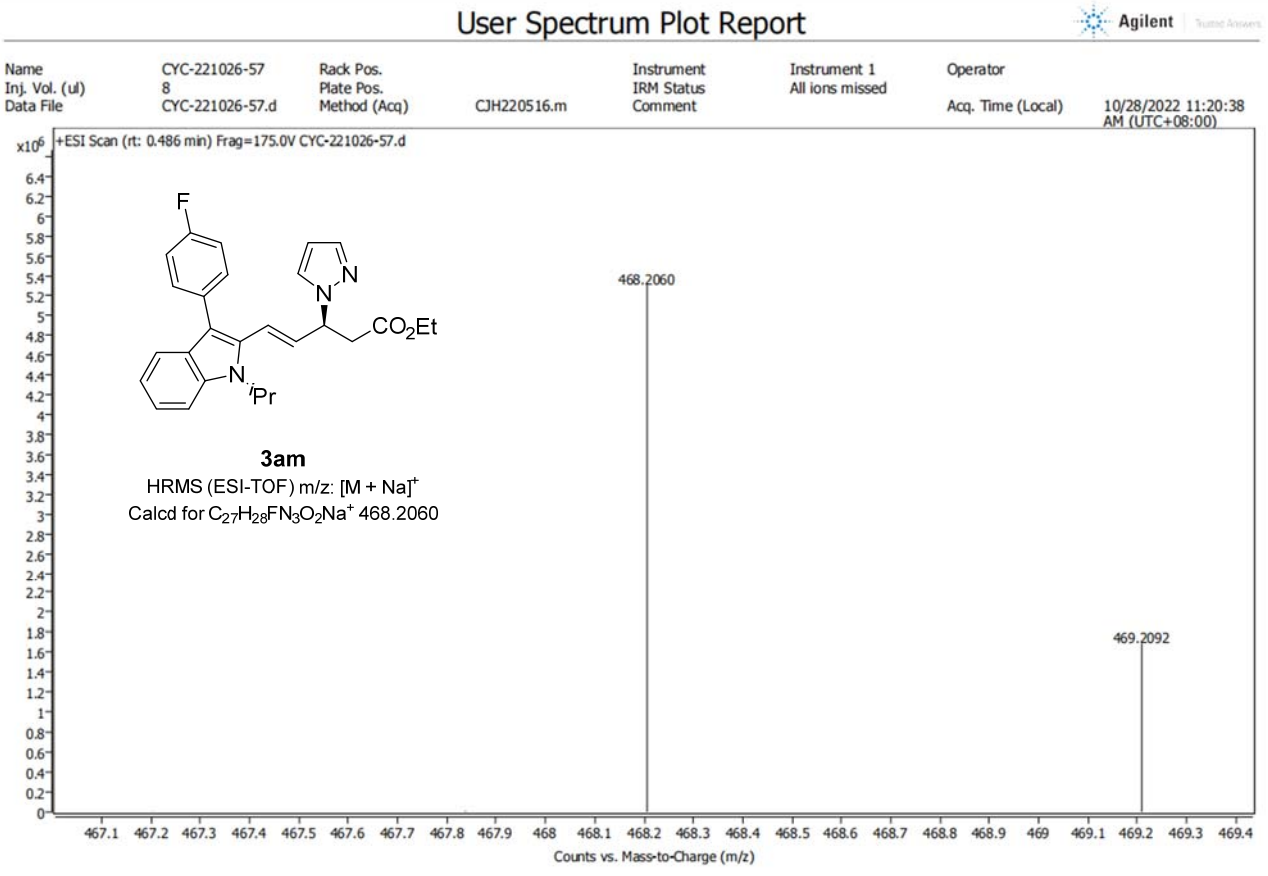
3am

^{13}C-NMR (100 MHz, $CDCl_3$)



3am

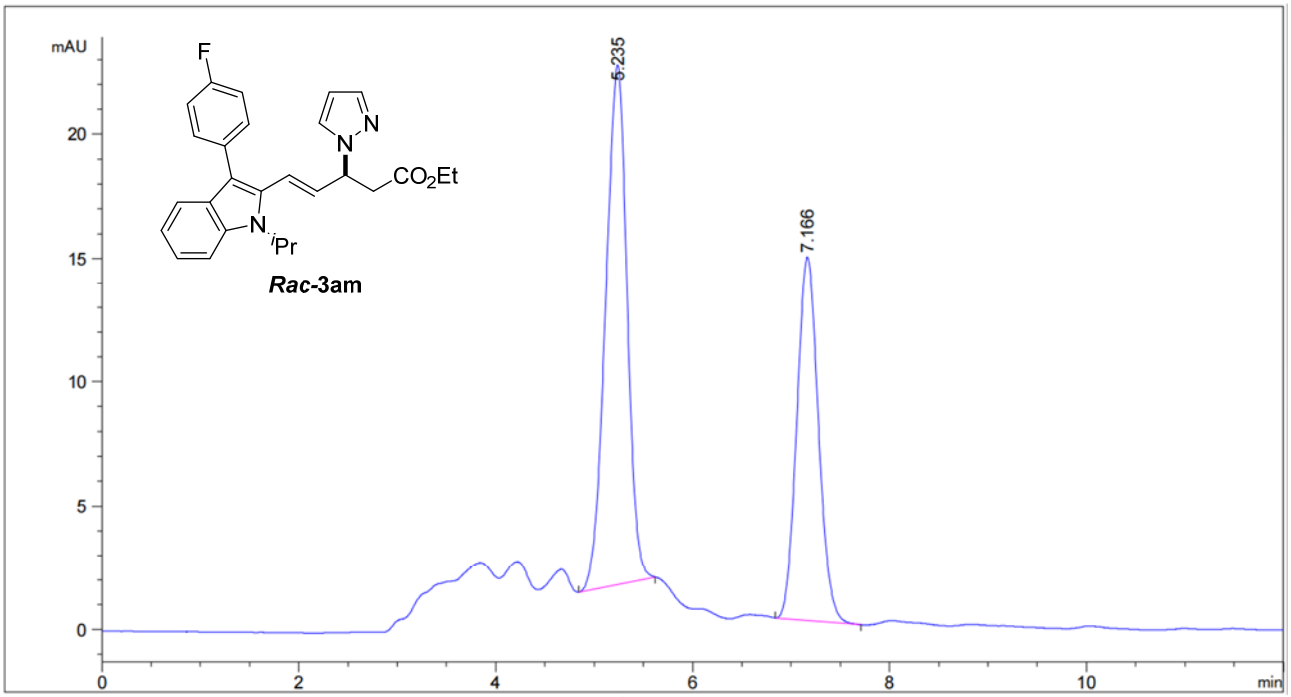
^{19}F-NMR (376 MHz, $CDCl_3$)



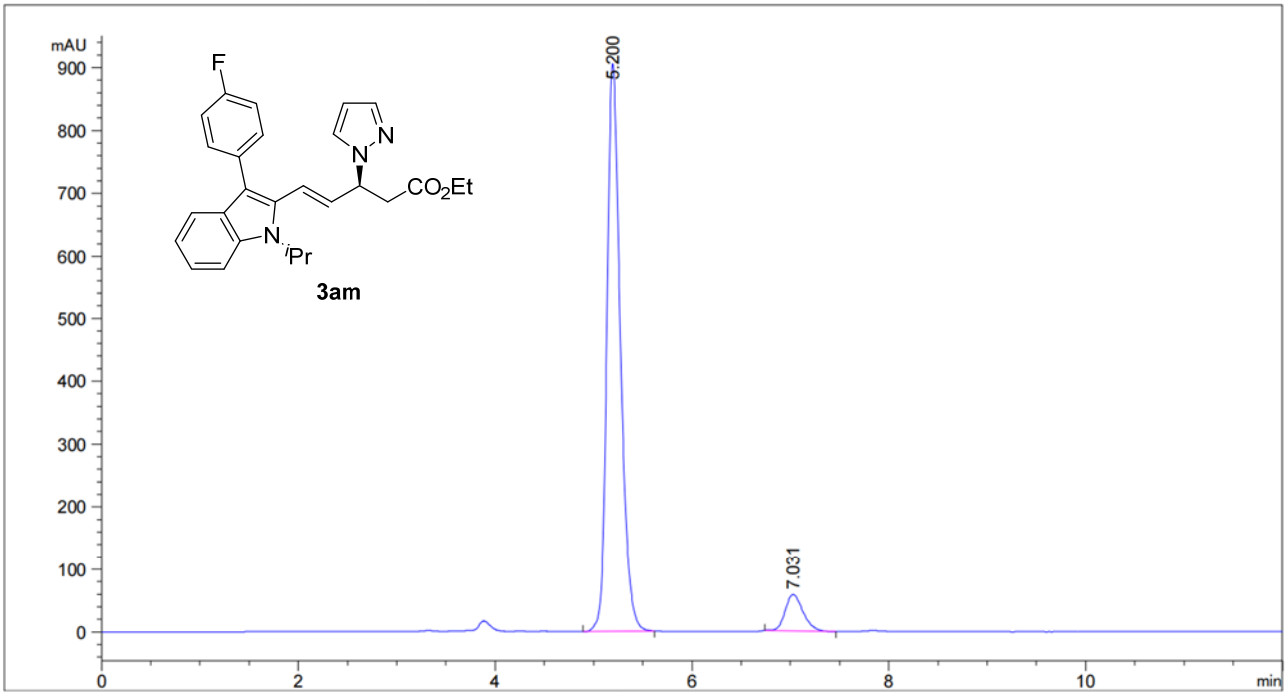
3am

HRMS (ESI-TOF) m/z: $[M + Na]^+$

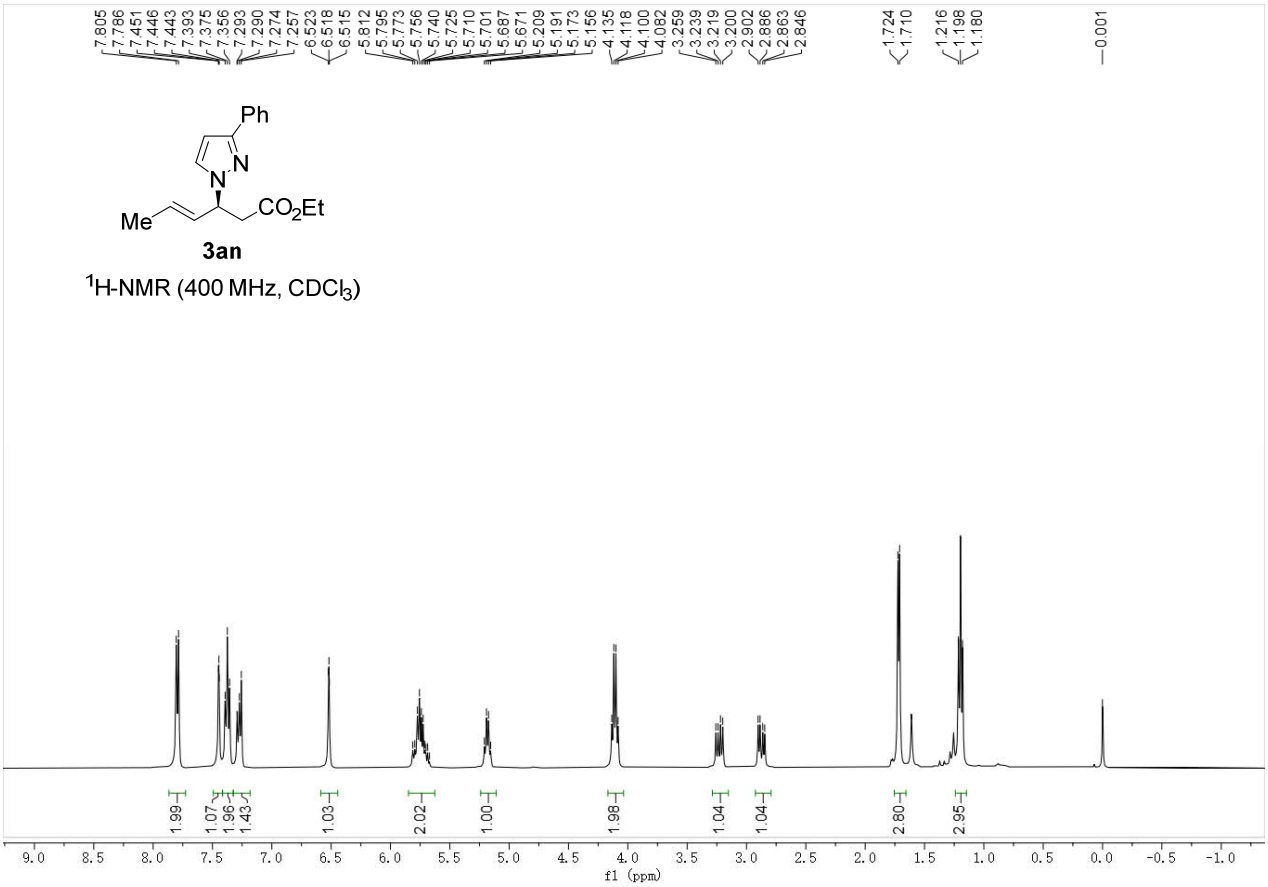
Calcd for $C_{27}H_{28}FN_3O_2Na^+$ 468.2060



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.235	BBA	0.2417	317.83011	20.87578	58.6503
2	7.166	BB	0.2365	224.07663	14.66684	41.3497

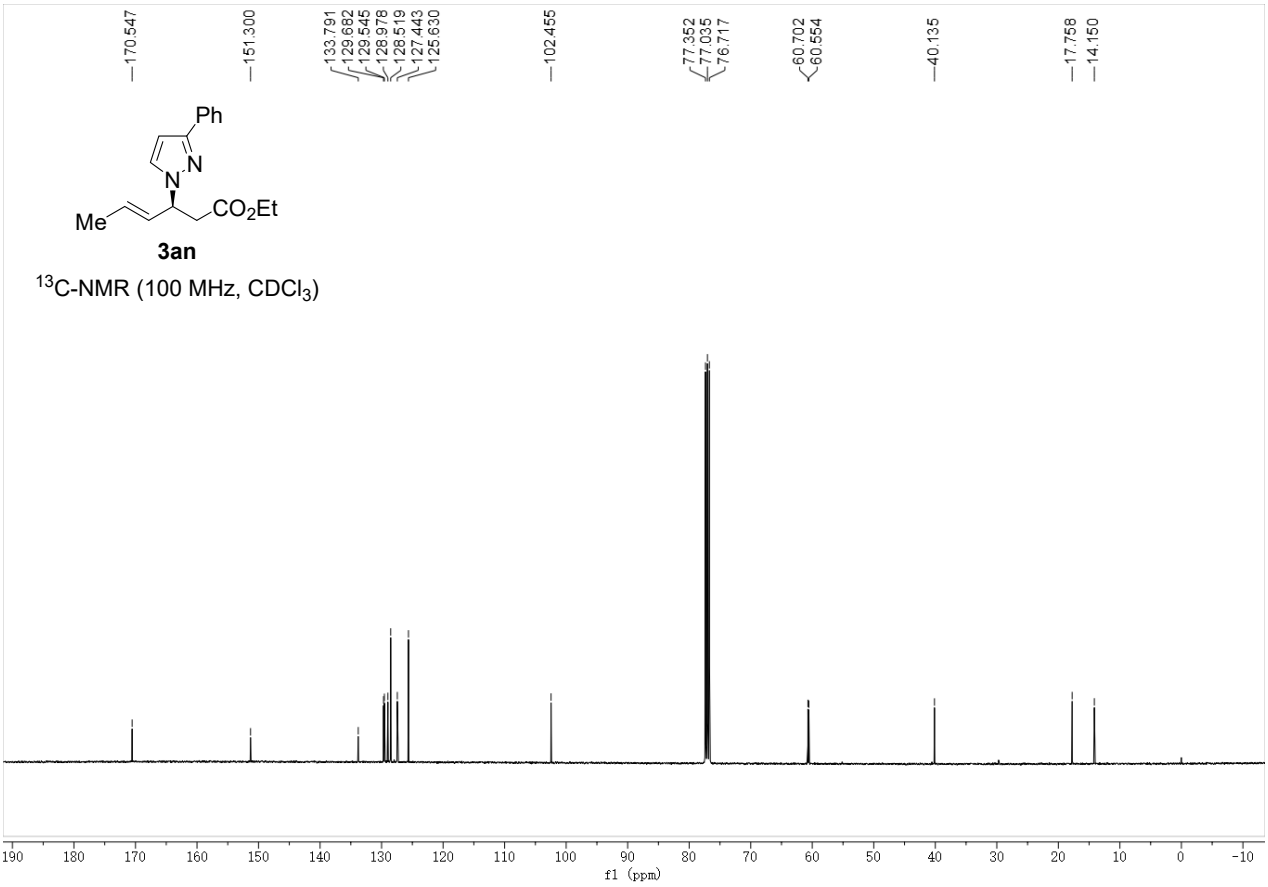


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.200	BBA	0.1456	8588.90234	905.51373	92.1842
2	7.031	BB	0.1999	728.20483	57.58732	7.8158



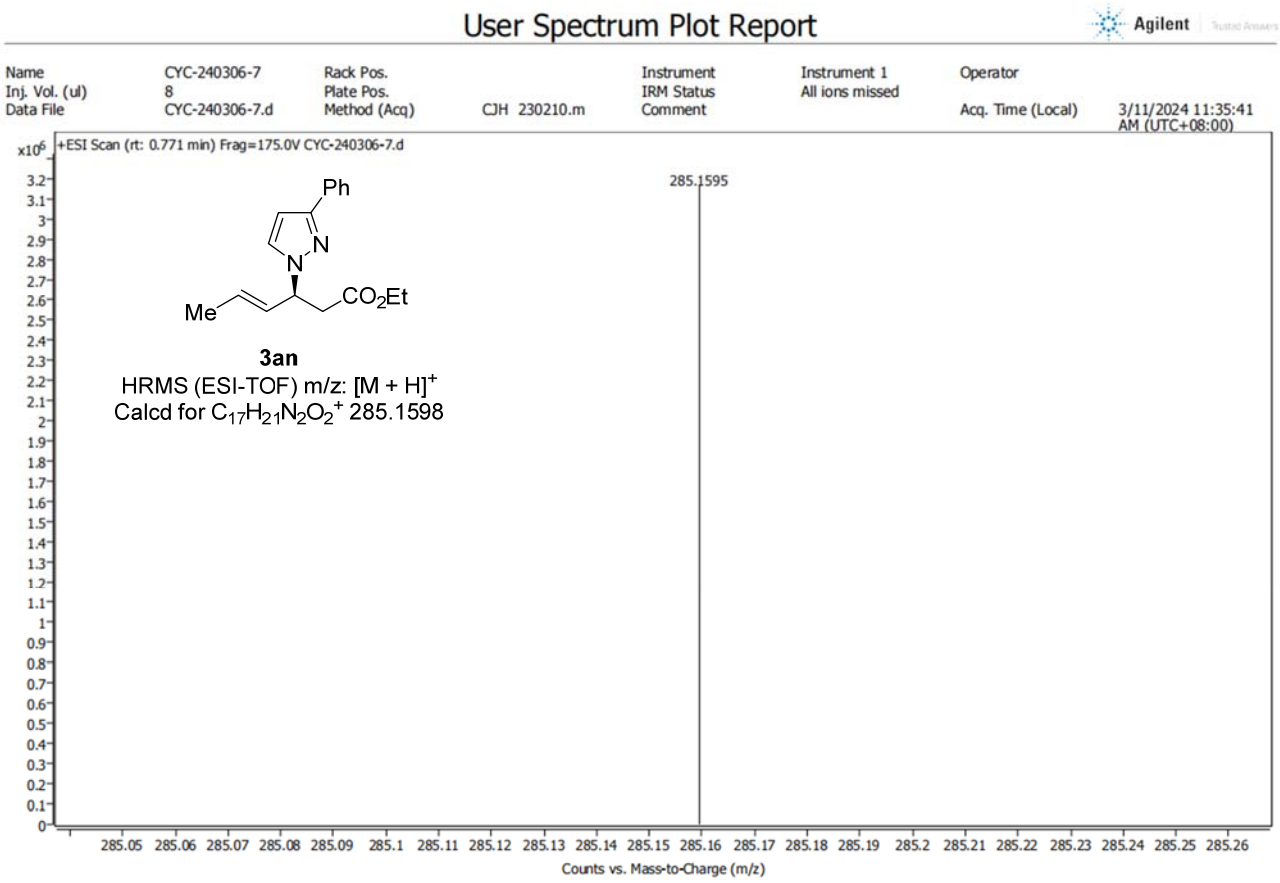
3an

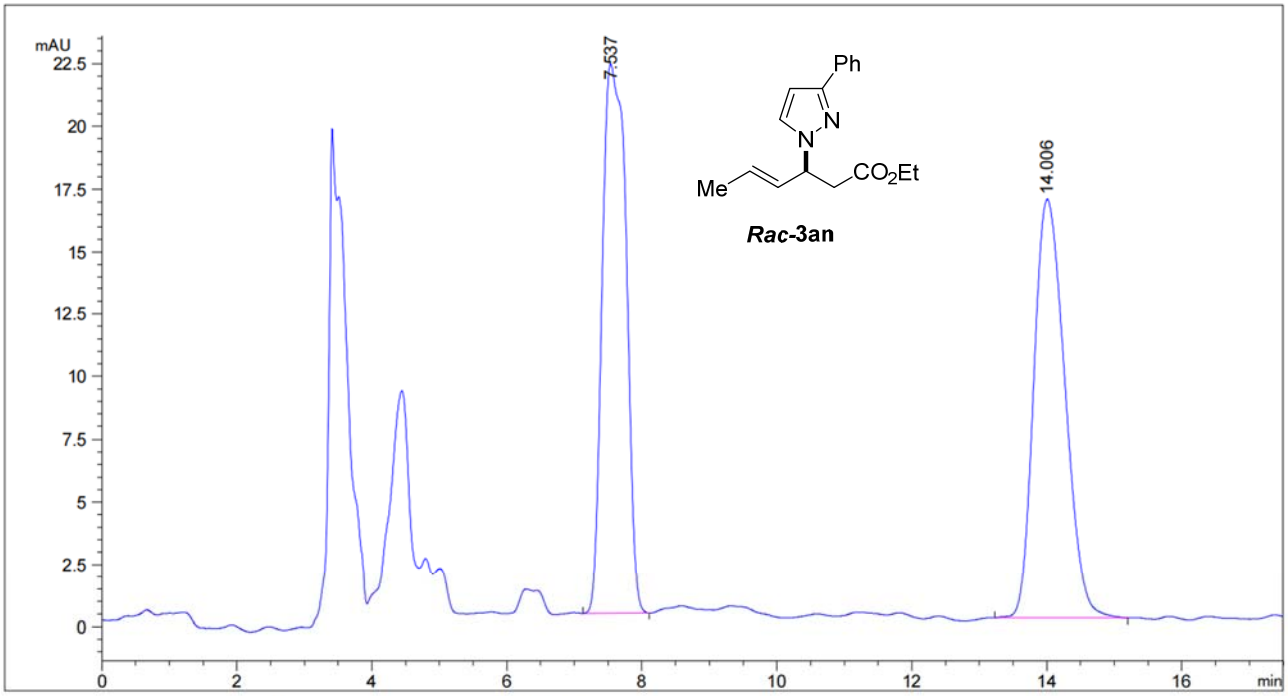
^{1}H-NMR (400 MHz, $CDCl_3$)



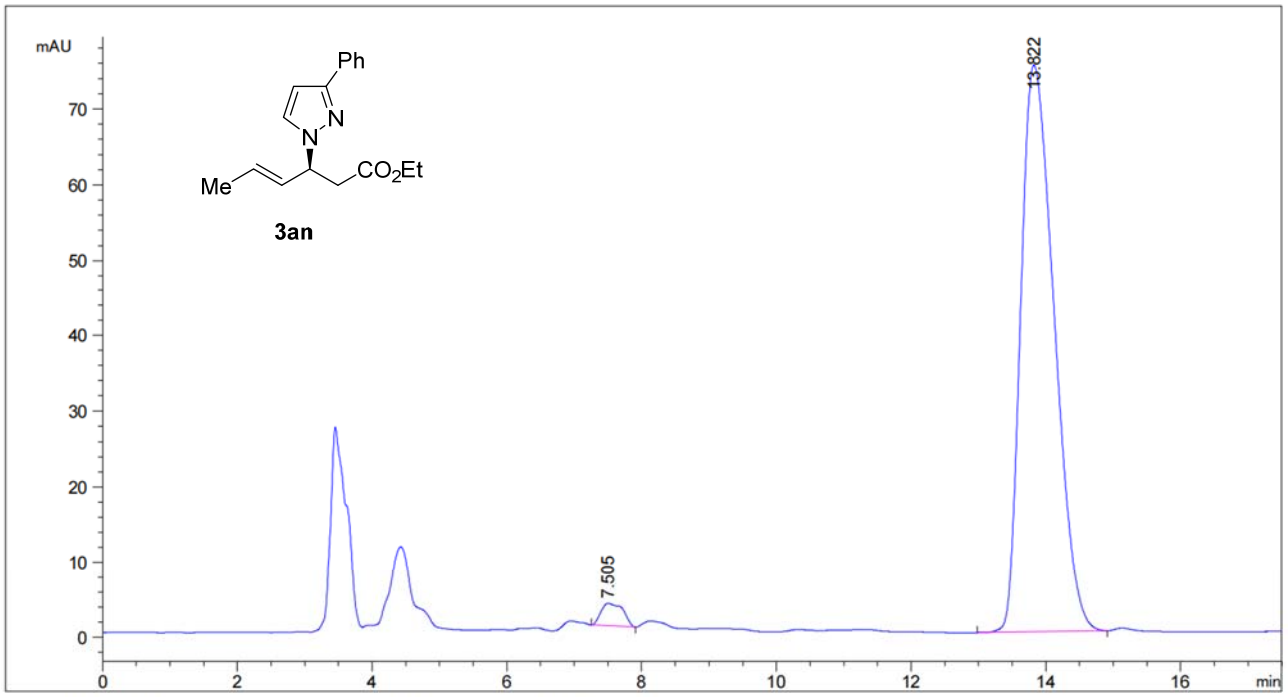
3an

^{13}C-NMR (100 MHz, $CDCl_3$)

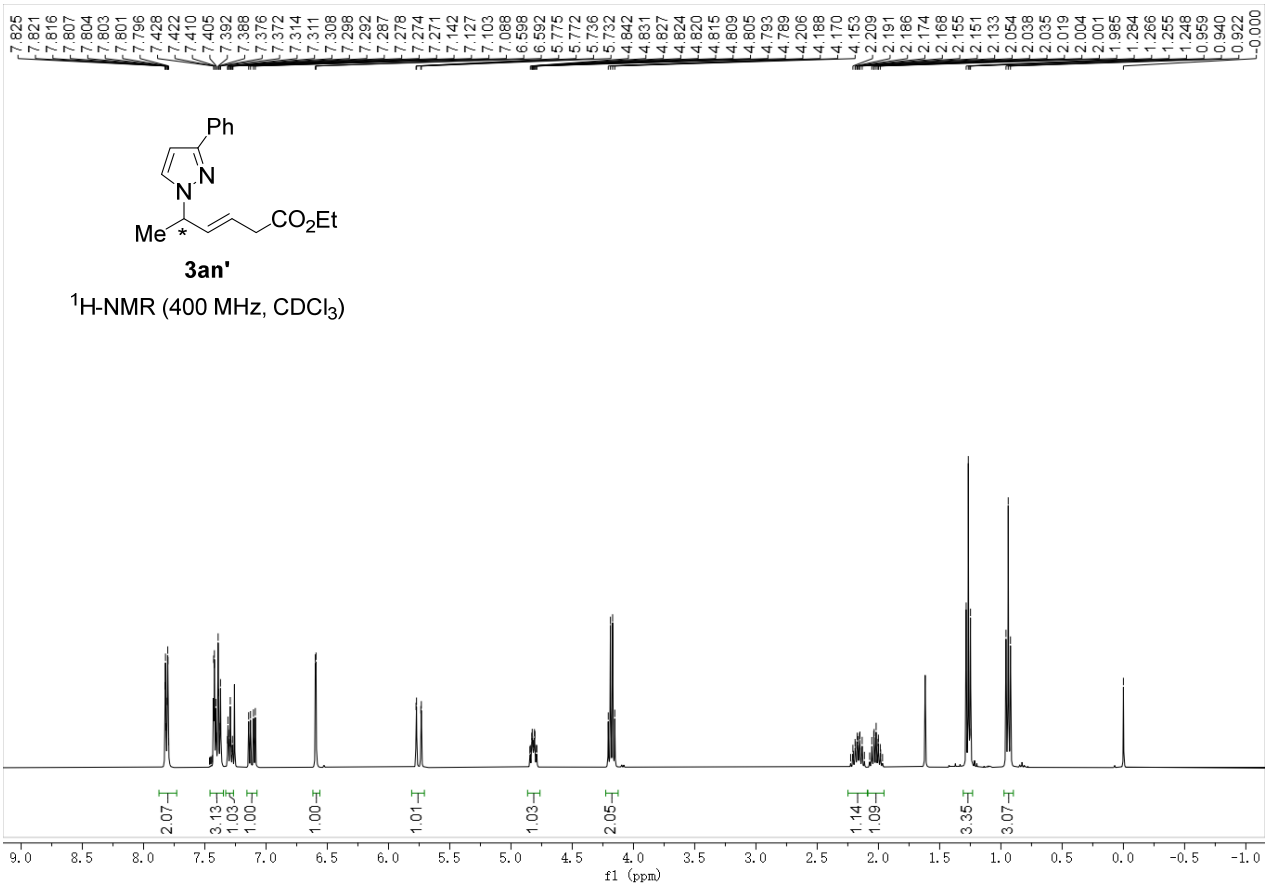

User Spectrum Plot Report
Agilent
Name CYC-240306-7
Inj. Vol. (ul) 8
Data File CYC-240306-7.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:35:41 AM (UTC+08:00)
+ESI Scan (rt: 0.771 min) Frag=175.0V CYC-240306-7.d
x10^6
285.1595
Ph
N
N
Me
CO2Et
3an
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C17H21N2O2+ 285.1598
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.537	BB	0.3419	539.30811	21.95664	50.1390
2	14.006	BB	0.5042	536.31824	16.76857	49.8610



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.505	BB	0.3177	68.07534	2.99396	2.5683
2	13.822	BB	0.5454	2582.55249	75.08834	97.4317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7.816
7.807
7.804
7.803
7.801
7.796
7.428
7.422
7.410
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7.392
7.388
7.376
7.372
7.314
7.311
7.308
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7.292
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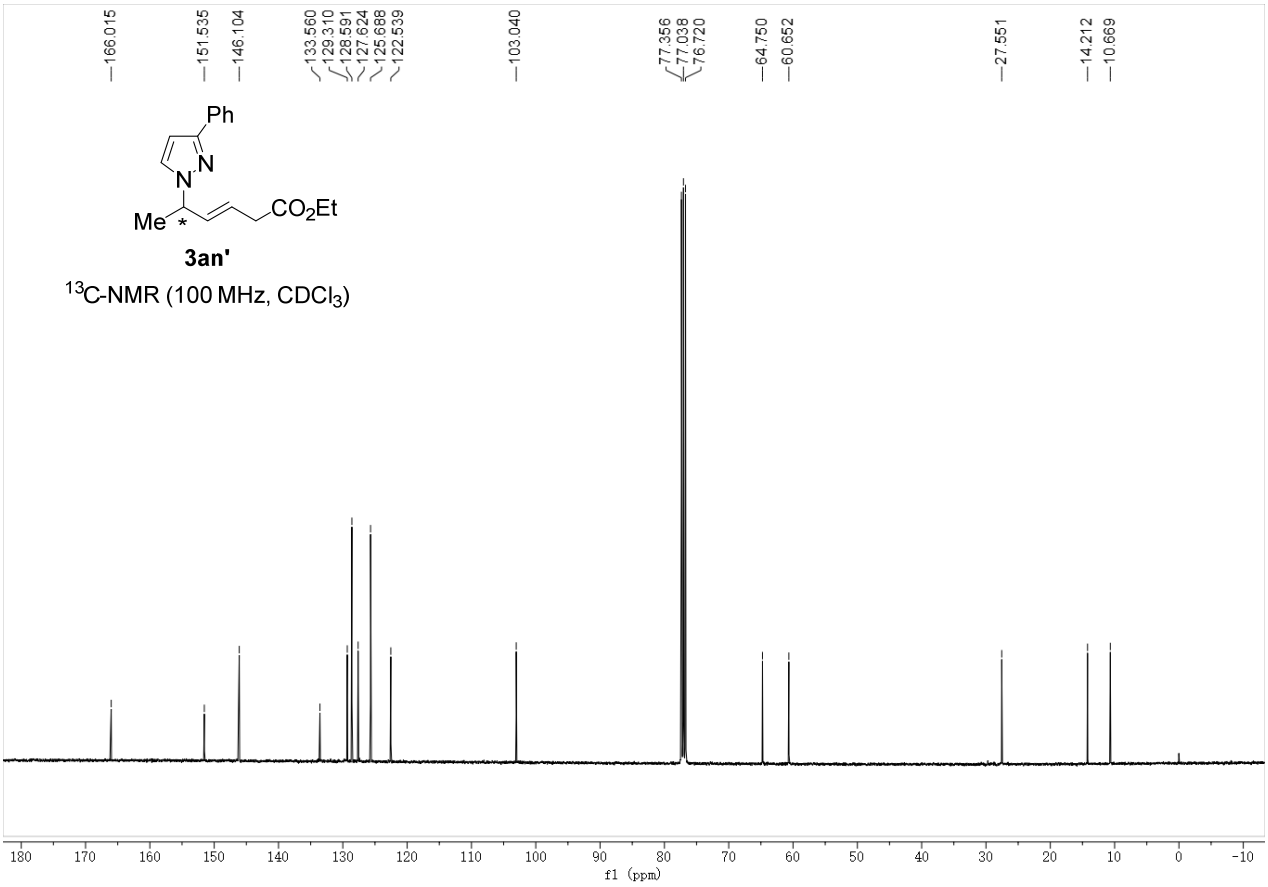
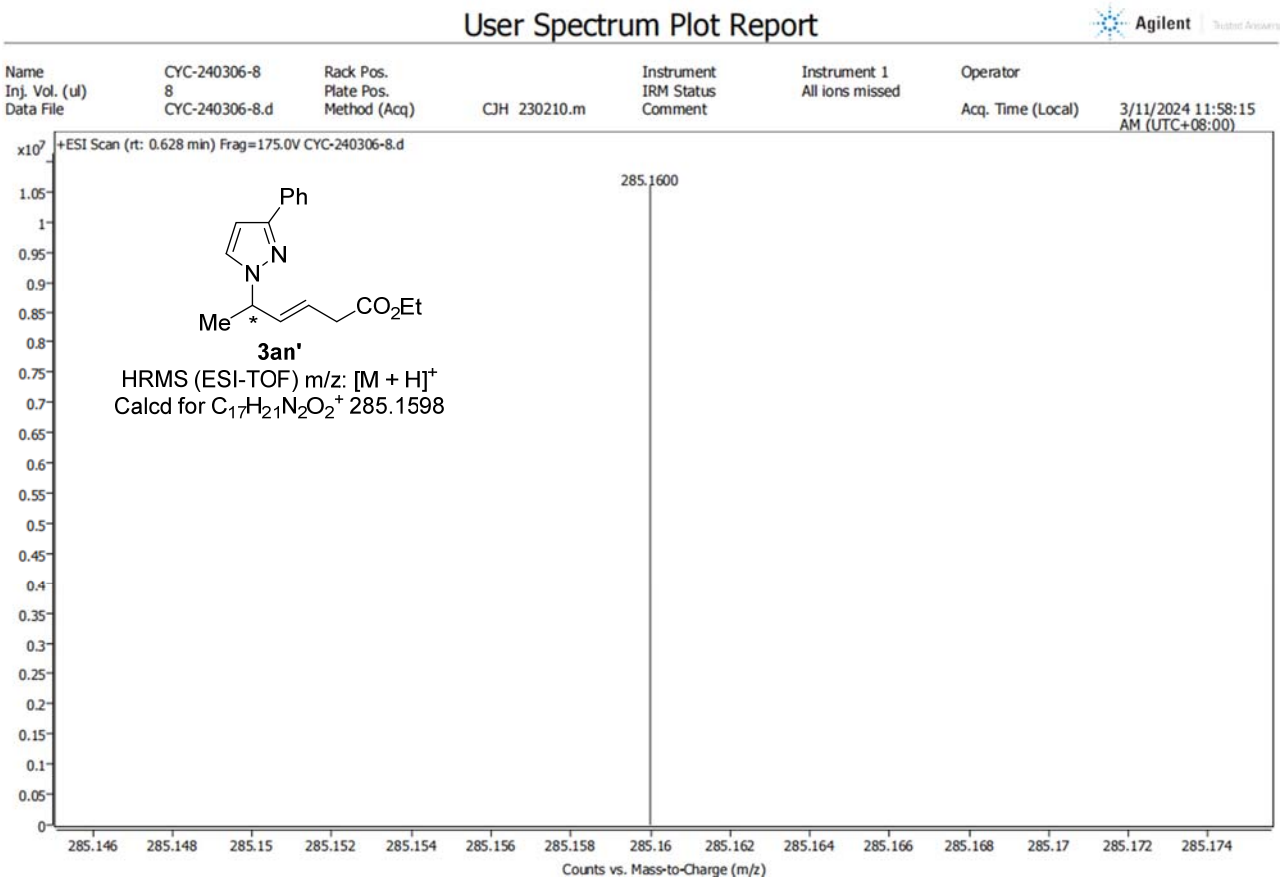
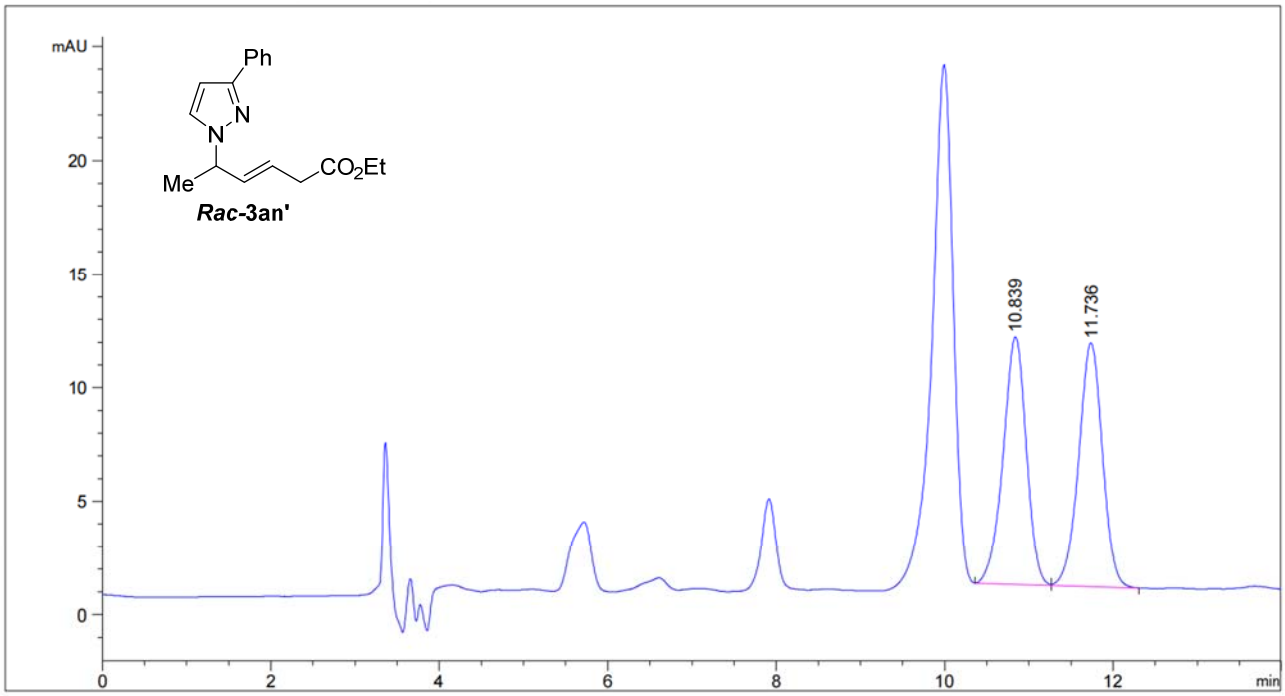
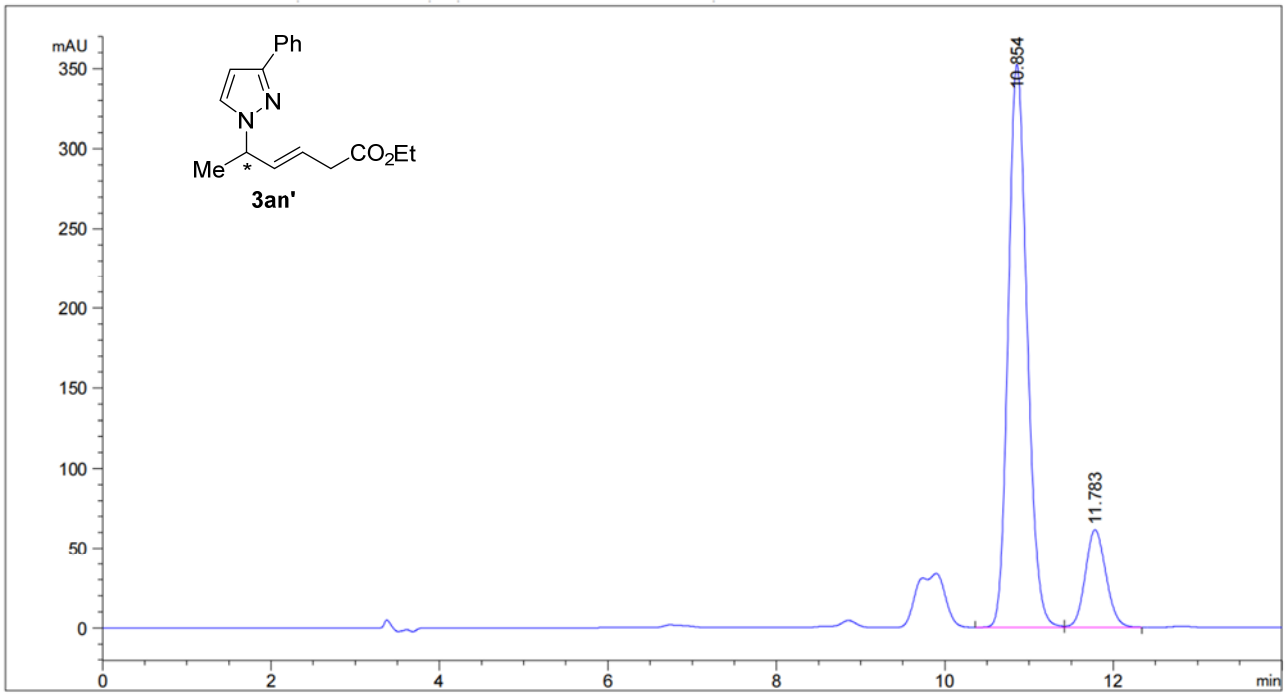
4.824
4.820
4.815
4.809
4.805
4.793
4.789
4.206
4.188
4.170
4.153
2.209
2.191
2.186
2.174
2.168
2.155
2.151
2.133
2.054
2.038
2.035
2.019
2.004
2.001
1.985
1.284
1.266
1.255
1.248
0.959
0.940
0.922
-0.000
Ph
N
N
Me
*
CO2Et
3an'
1H-NMR (400 MHz, CDCl3)
2.07
3.13
1.03
1.00
1.00
1.01
1.03
2.05
1.14
1.09
3.35
3.07
f1 (ppm)


166.015
151.535
146.104
133.560
129.310
128.591
127.624
125.688
122.539
103.040
77.356
77.038
76.720
64.750
60.652
27.551
14.212
10.669
Ph
N
N
Me
*
CO2Et
3an'
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

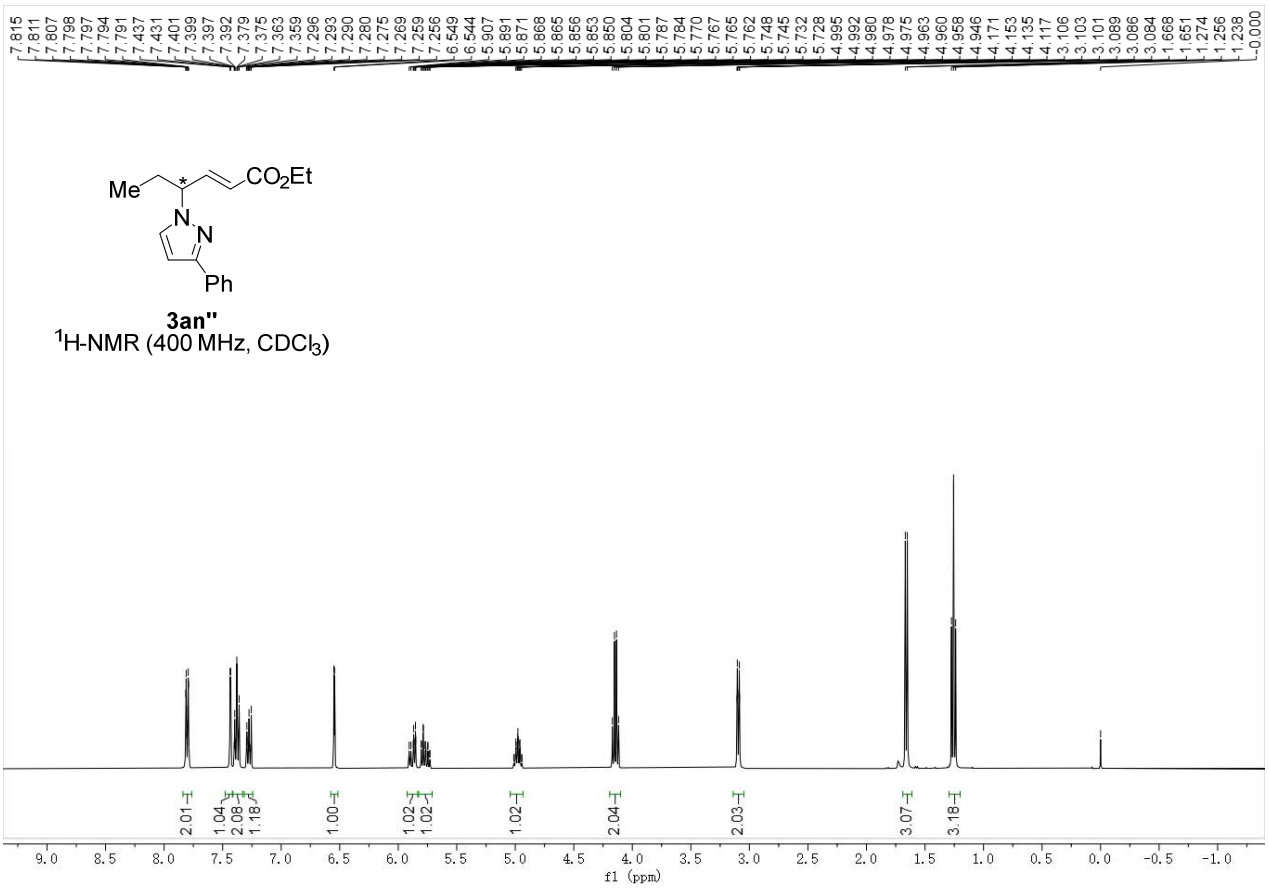

User Spectrum Plot Report
Agilent
Name CYC-240306-8
Inj. Vol. (ul) 8
Data File CYC-240306-8.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:58:15 AM (UTC+08:00)
+ESI Scan (rt: 0.628 min) Frag=175.0V CYC-240306-8.d
x10^7
285.1600
Ph
N
N
Me
*
CO2Et
3an'
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C17H21N2O2+ 285.1598
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.839	BV	0.2934	208.91907	10.90627	49.7683
2	11.736	VBA	0.3017	210.86427	10.74806	50.2317

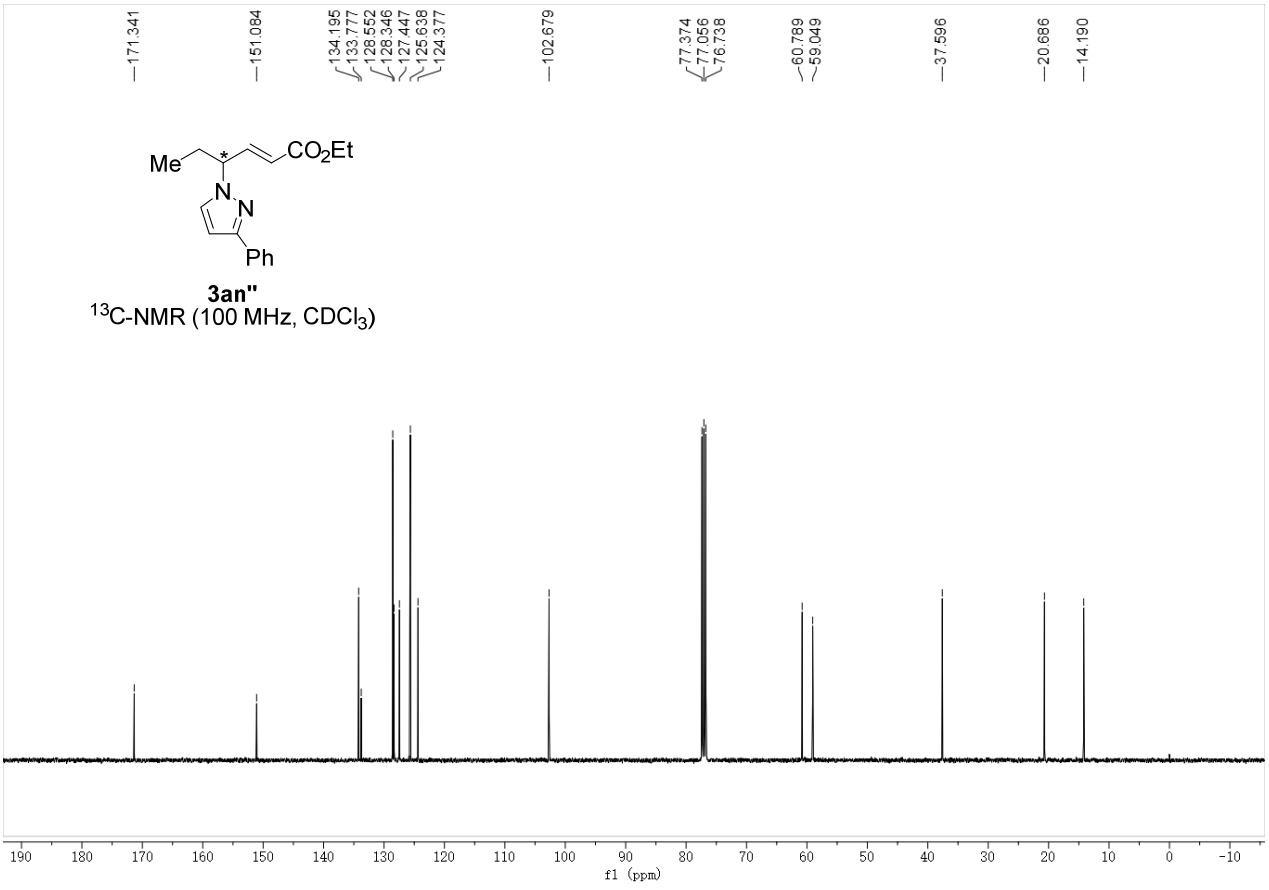


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.854	BV	0.2420	5504.70264	352.19736	84.1084
2	11.783	VBA	0.2632	1040.07153	61.38700	15.8916



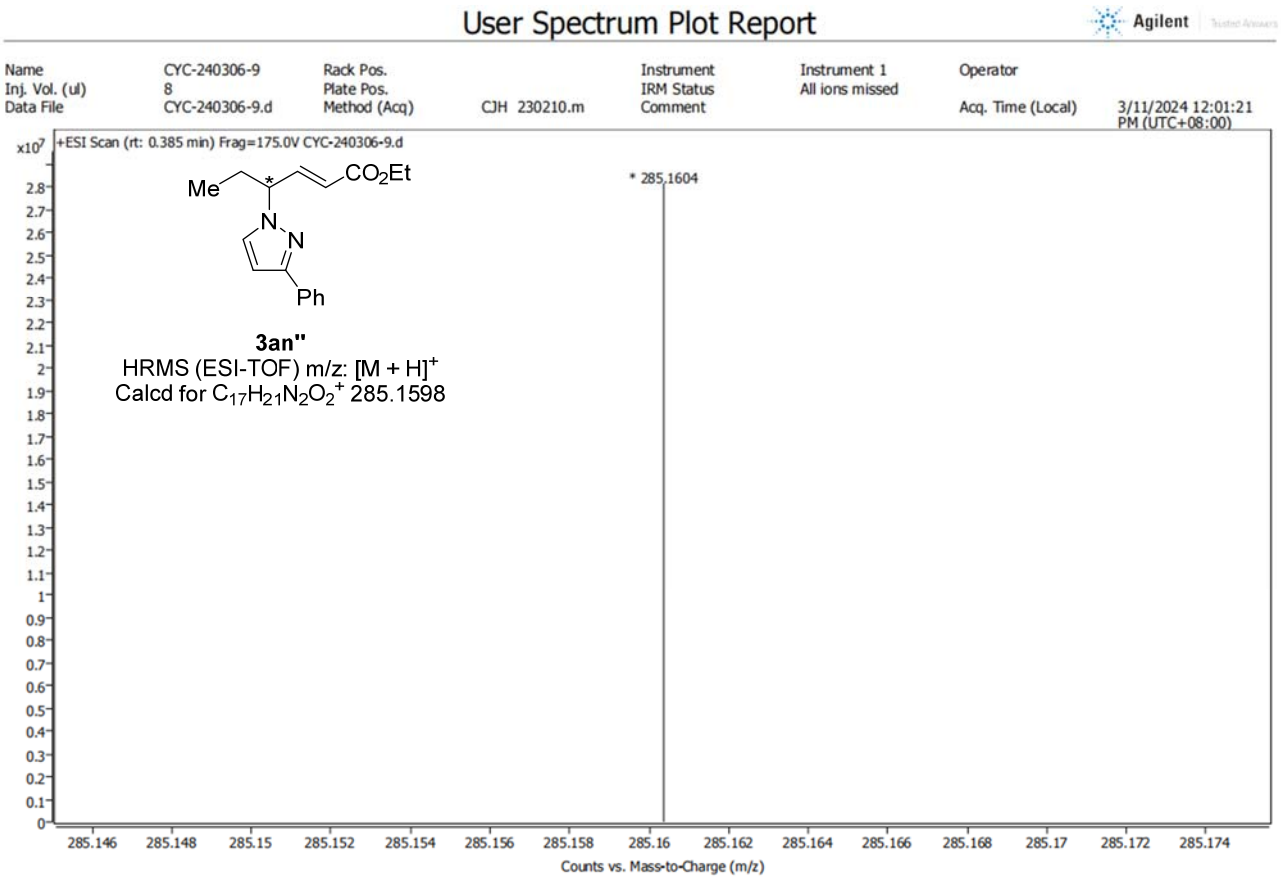
3an"

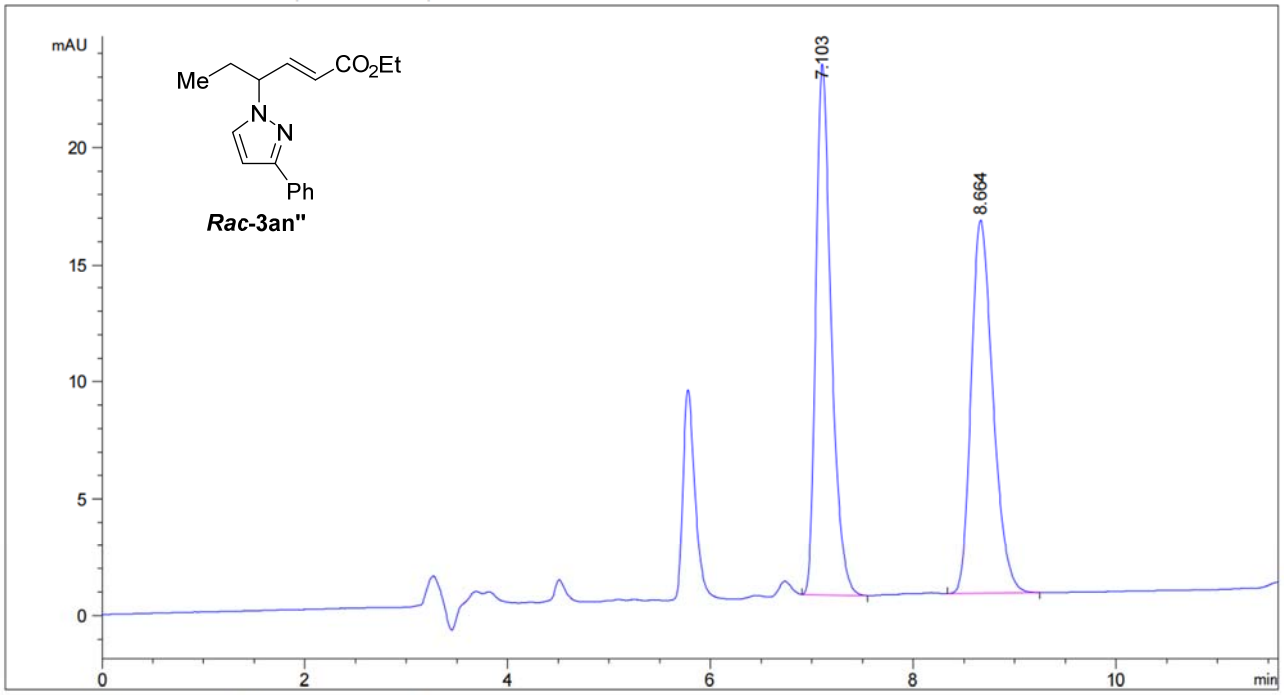
^{1}H-NMR (400 MHz, $CDCl_3$)



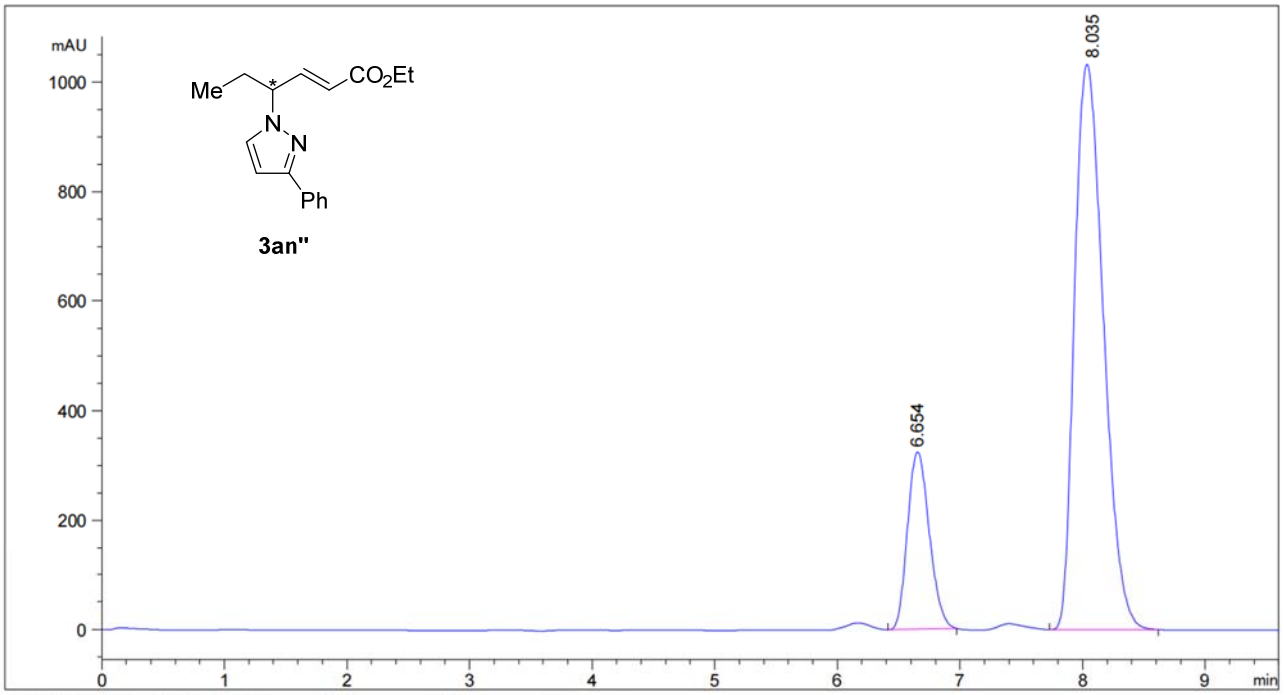
3an"

^{13}C-NMR (100 MHz, $CDCl_3$)

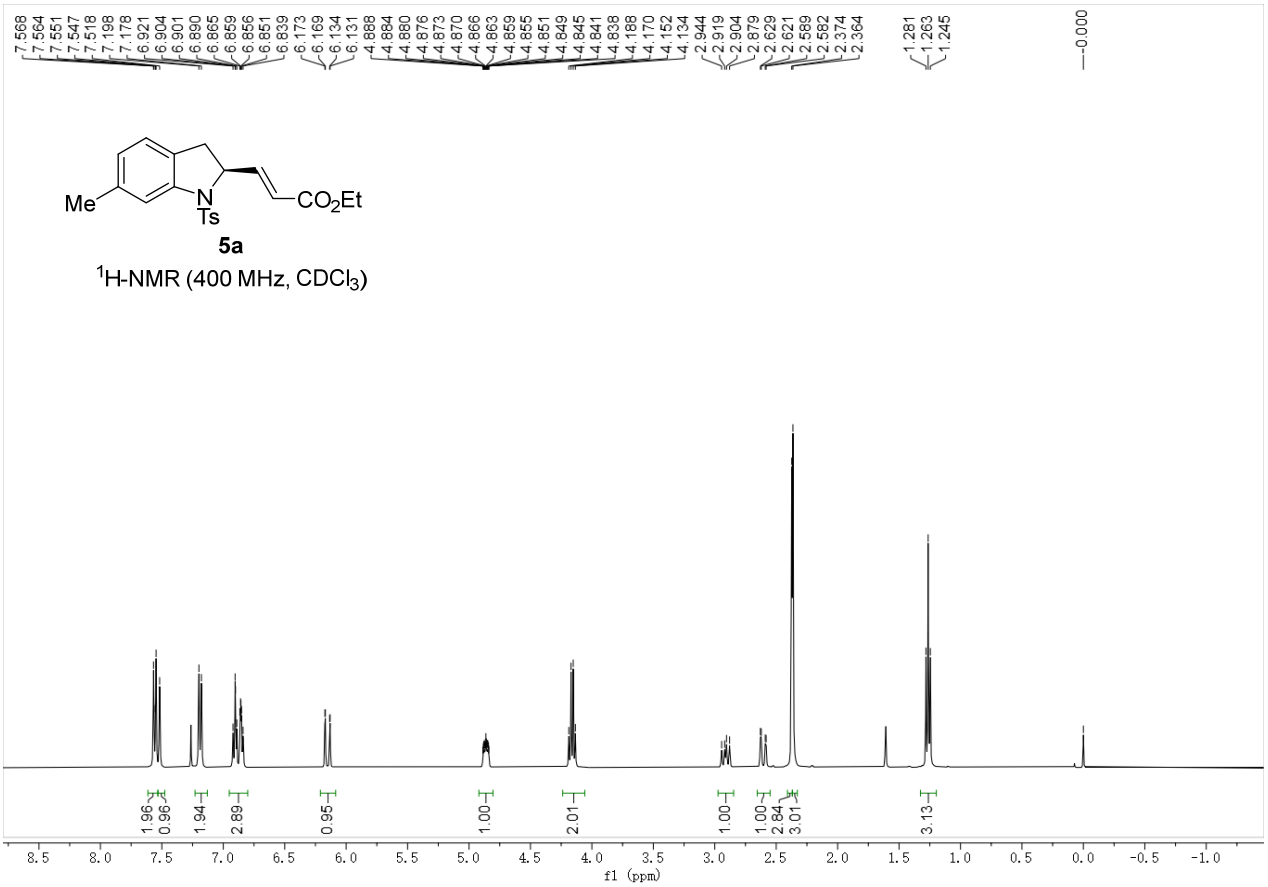

User Spectrum Plot Report
Agilent
Name CYC-240306-9
Inj. Vol. (ul) 8
Data File CYC-240306-9.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 12:01:21 PM (UTC+08:00)
+ESI Scan (rt: 0.385 min) Frag=175.0V CYC-240306-9.d
x10^7
* 285.1604
Me
CO2Et
N
N
Ph
3an"
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C17H21N2O2+ 285.1598
285.146
285.148
285.15
285.152
285.154
285.156
285.158
285.16
285.162
285.164
285.166
285.168
285.17
285.172
285.174
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.103	BB	0.1595	239.07616	22.66597	50.1258
2	8.664	BB	0.2277	237.87596	15.96473	49.8742



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.654	BBA	0.1934	3994.32129	323.75461	19.1122
2	8.035	BBA	0.2610	1.69050e4	1031.88953	80.8878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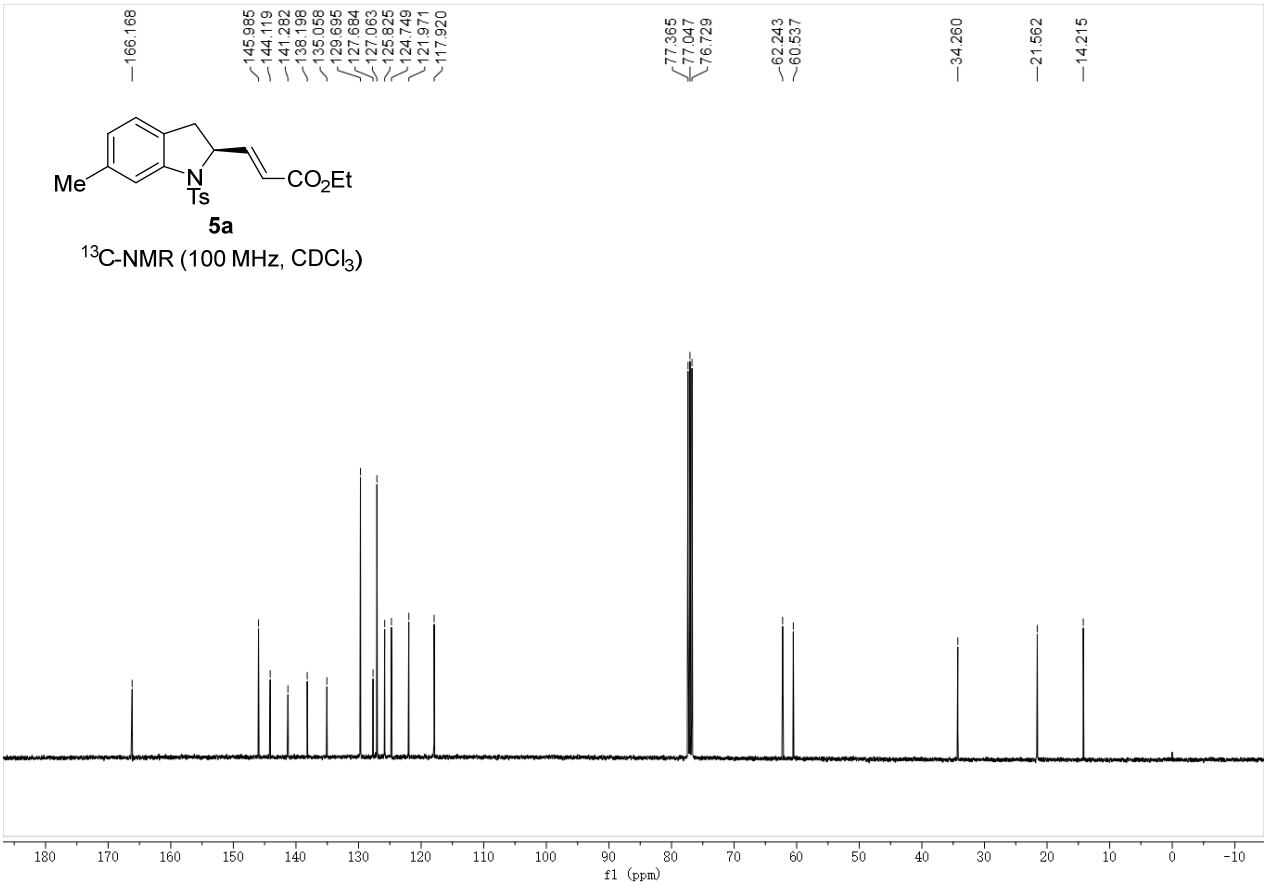
7.547
7.518
7.198
7.178
6.921
6.904
6.901
6.890
6.865
6.859
6.856
6.851
6.839
6.173
6.169
6.134
6.131
4.888
4.884
4.880
4.876
4.873
4.870
4.866
4.863
4.859
4.855
4.851
4.849
4.845
4.841
4.838
4.188
4.170
4.152
4.134
2.944
2.919
2.904
2.879
2.629
2.621
2.589
2.582
2.374
2.364
1.281
1.263
1.245
0.000
Me
N
Ts
CO2Et
5a
1H-NMR (400 MHz, CDCl3)
1.96
0.96
1.94
2.89
0.95
1.00
2.01
1.00
1.00
2.84
3.01
3.13
f1 (ppm)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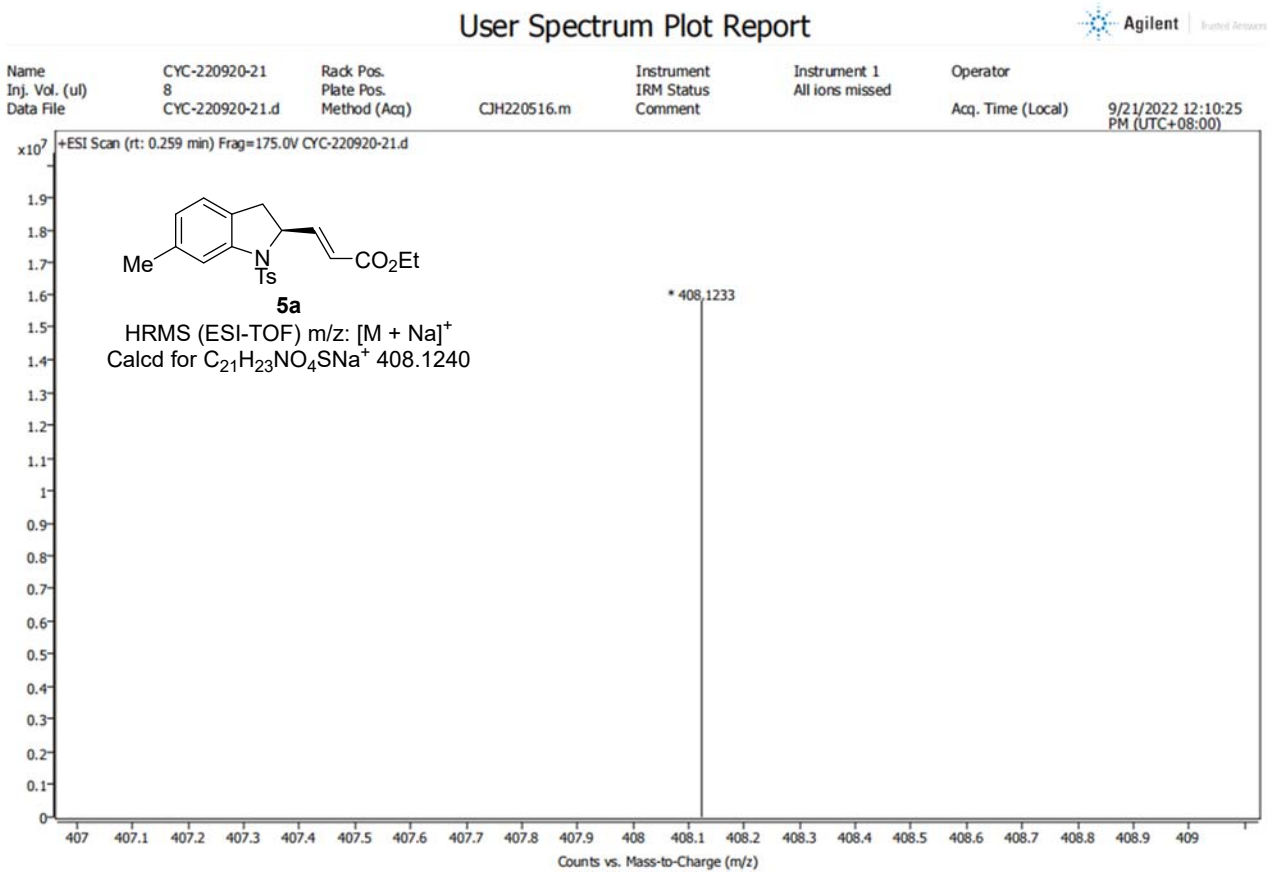
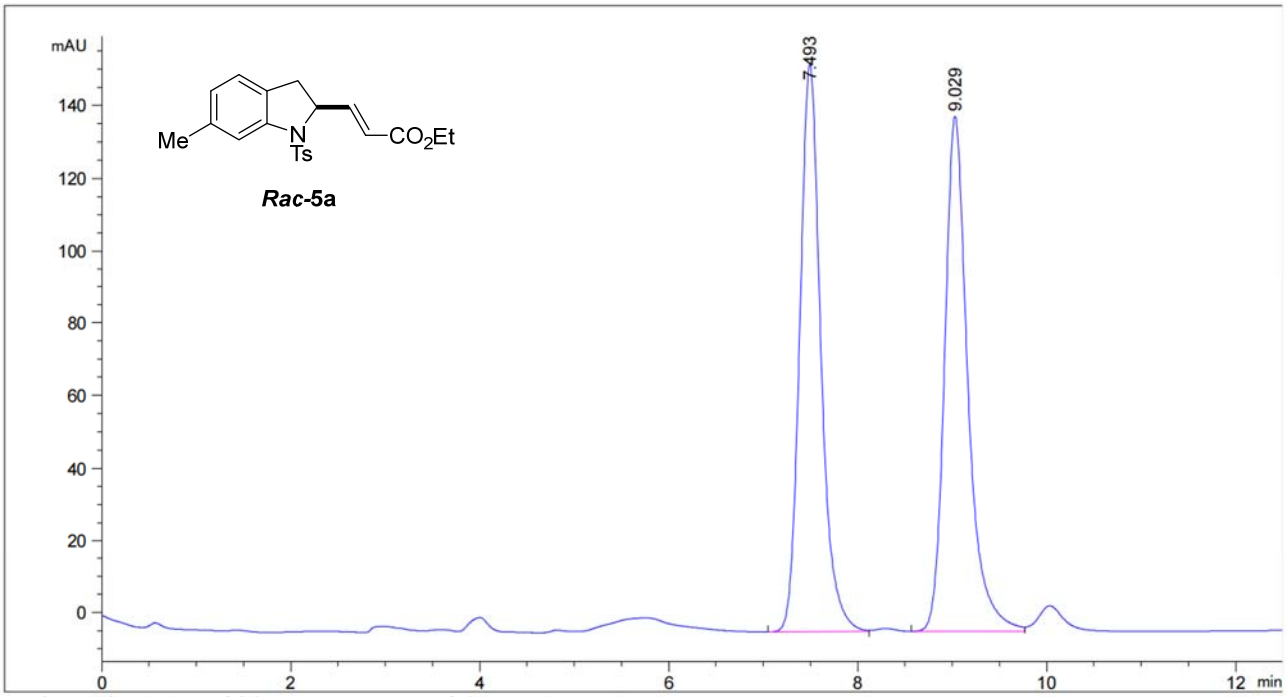
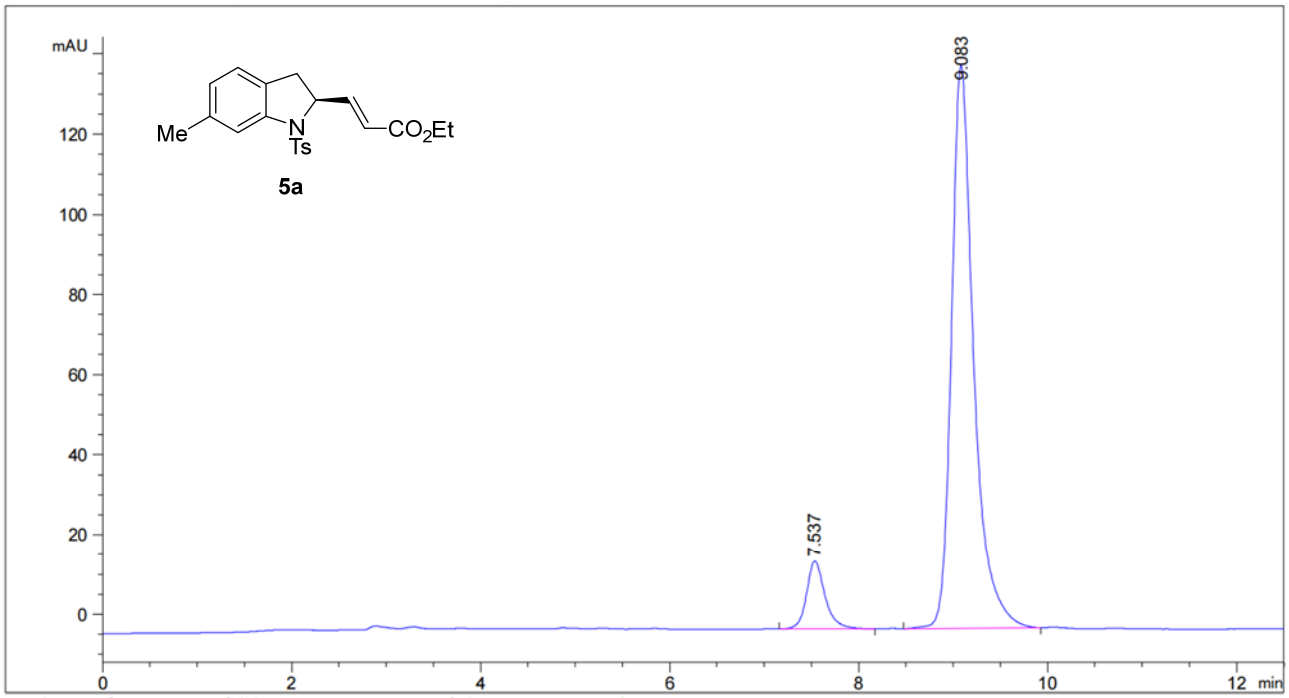
144.119
141.282
138.198
135.058
129.695
127.684
127.063
125.825
124.749
121.971
117.920
77.365
77.047
76.729
62.243
60.537
34.260
21.562
14.215
Me
N
Ts
CO2Et
5a
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


User Spectrum Plot Report
Agilent
Name CYC-220920-21
Inj. Vol. (ul) 8
Data File CYC-220920-21.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 9/21/2022 12:10:25 PM (UTC+08:00)
+ESI Scan (rt: 0.259 min) Frag=175.0V CYC-220920-21.d
x10^7
Me
N
Ts
CO2Et
5a
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C21H23NO4SNa+ 408.1240
* 408.1233
Counts vs. Mass-to-Charge (m/z)



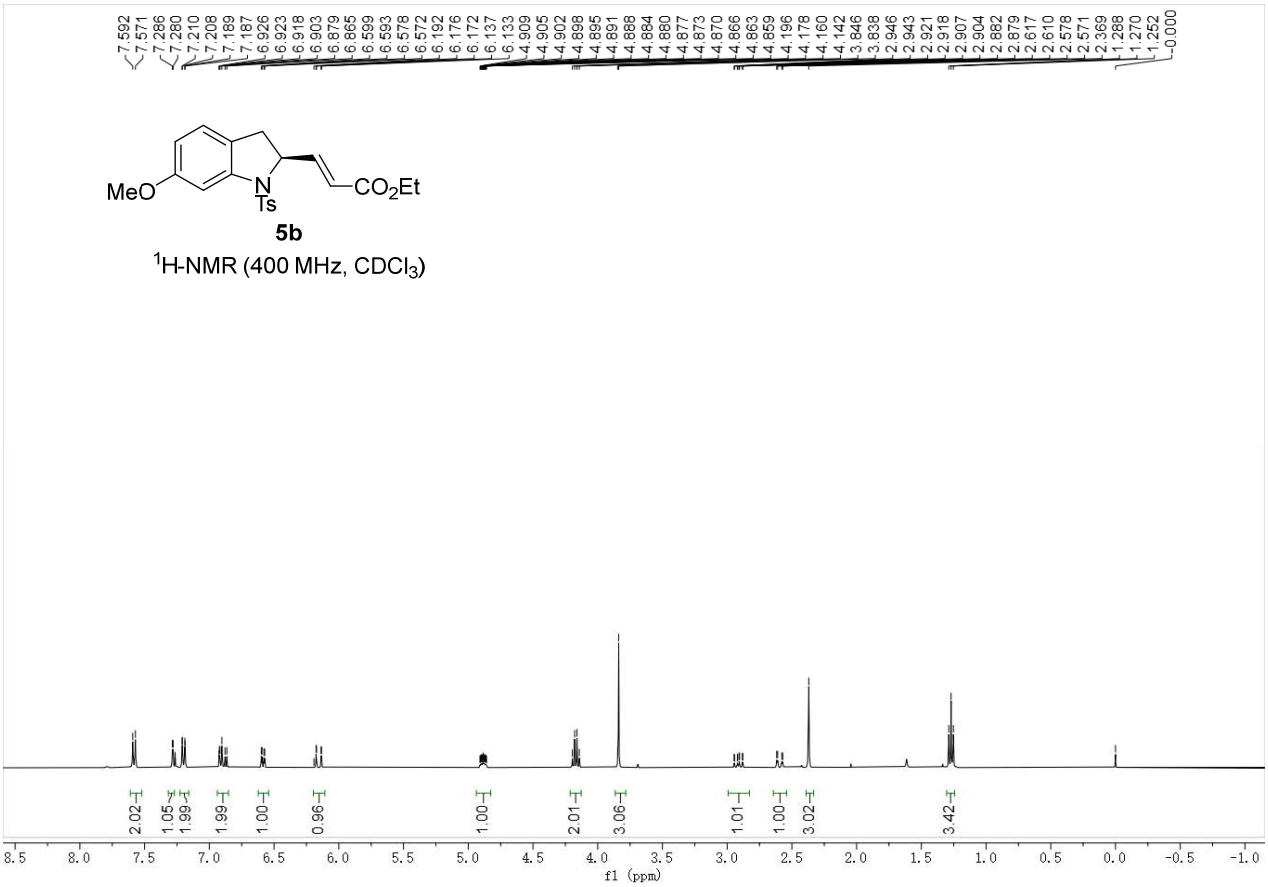
***Rac*-5a**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.493	BV	0.2344	2422.20117	156.54553	49.8904
2	9.029	BV	0.2564	2432.83911	142.15891	50.1096



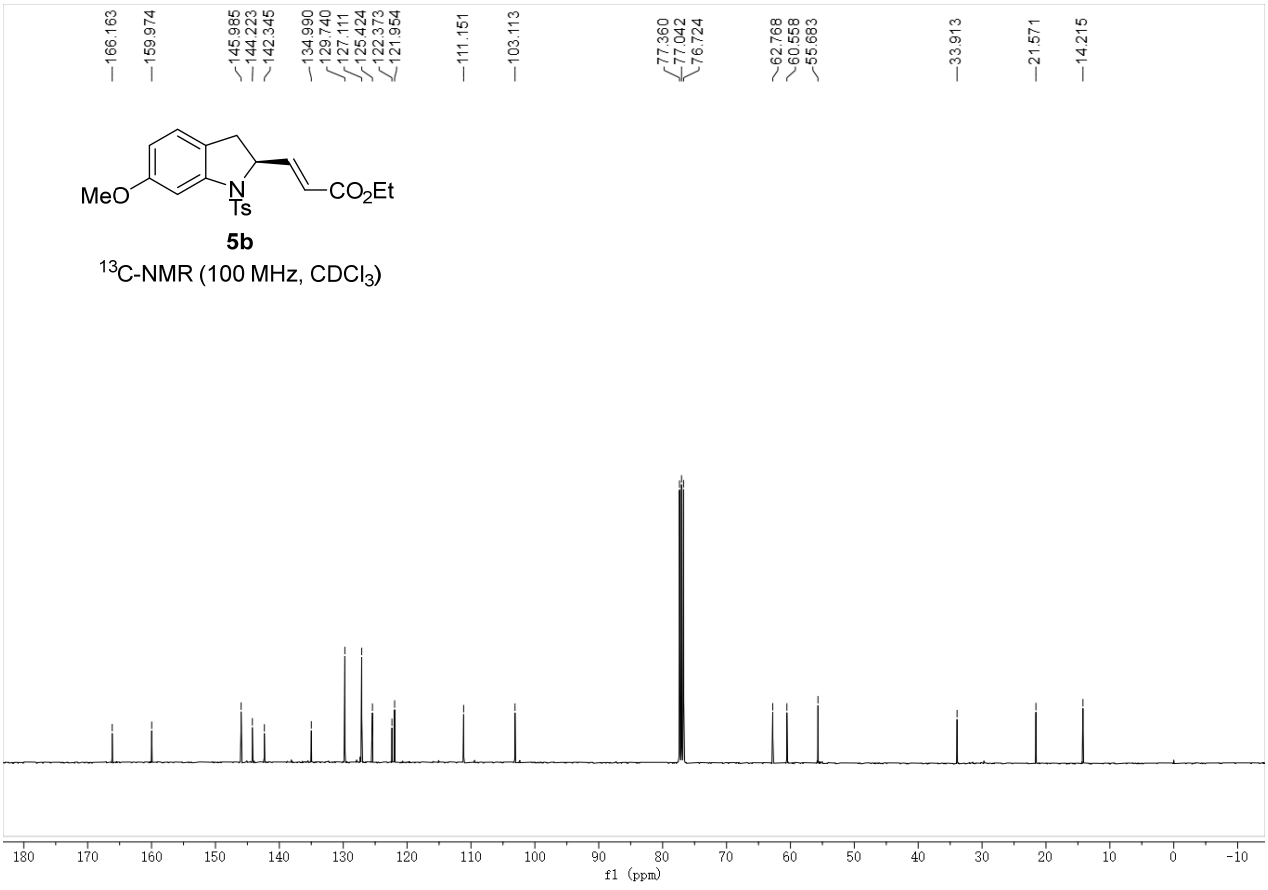
5a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.537	BB	0.2028	231.96300	17.00843	9.1499
2	9.083	BB	0.2449	2303.17163	140.66490	90.8501



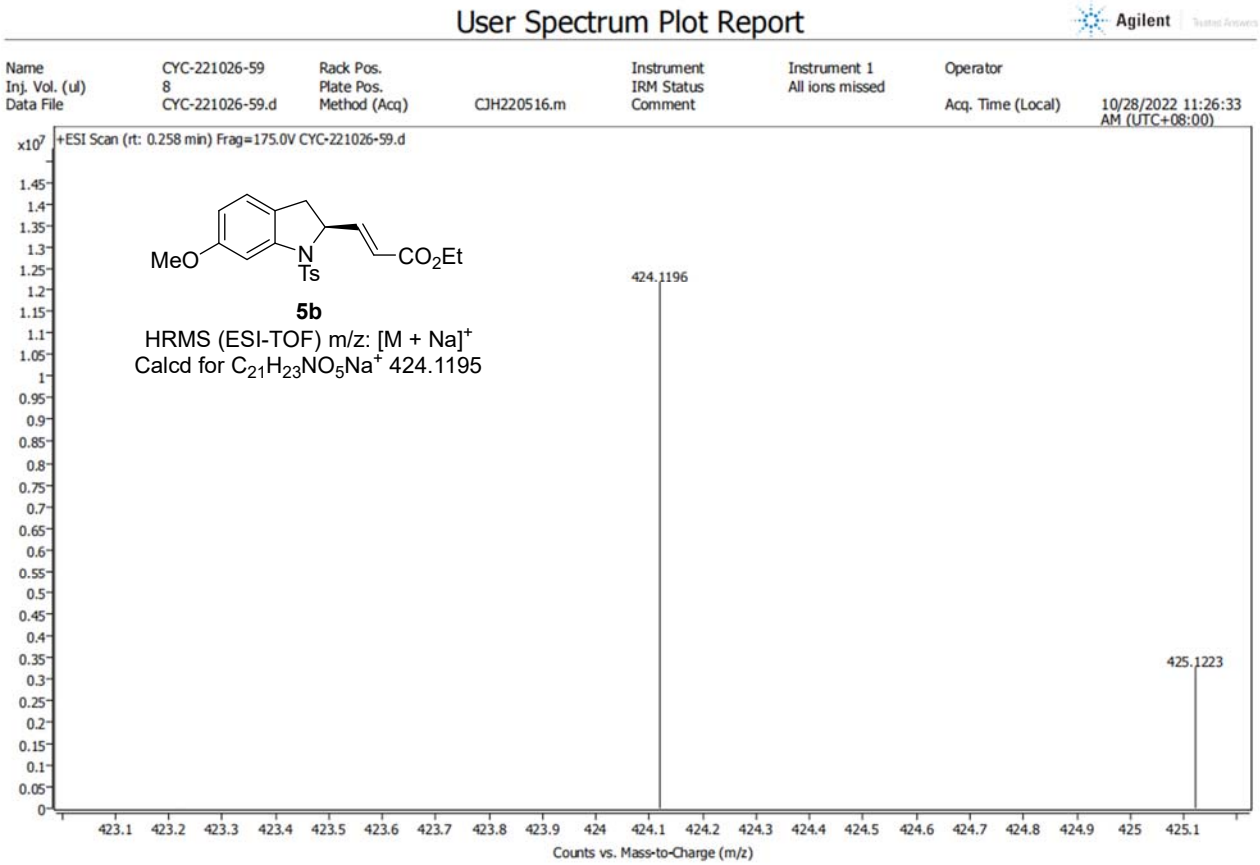
5b

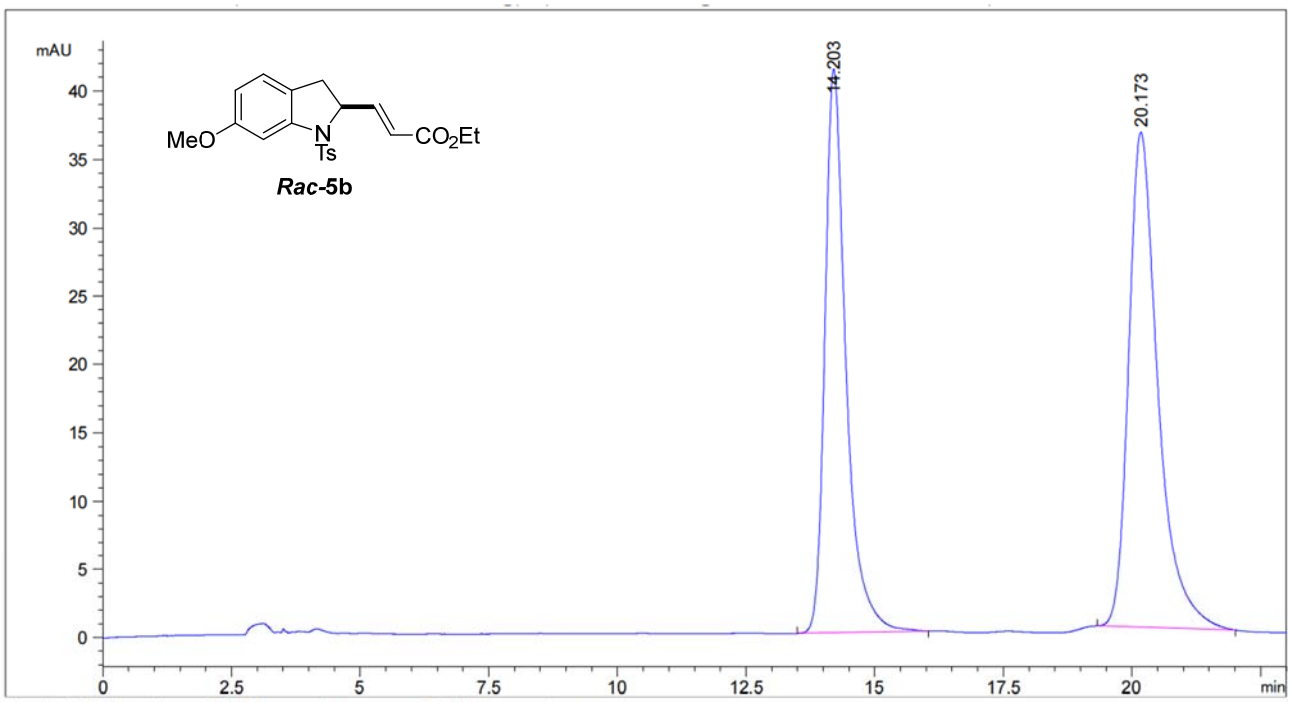
^{1}H-NMR (400 MHz, $CDCl_3$)



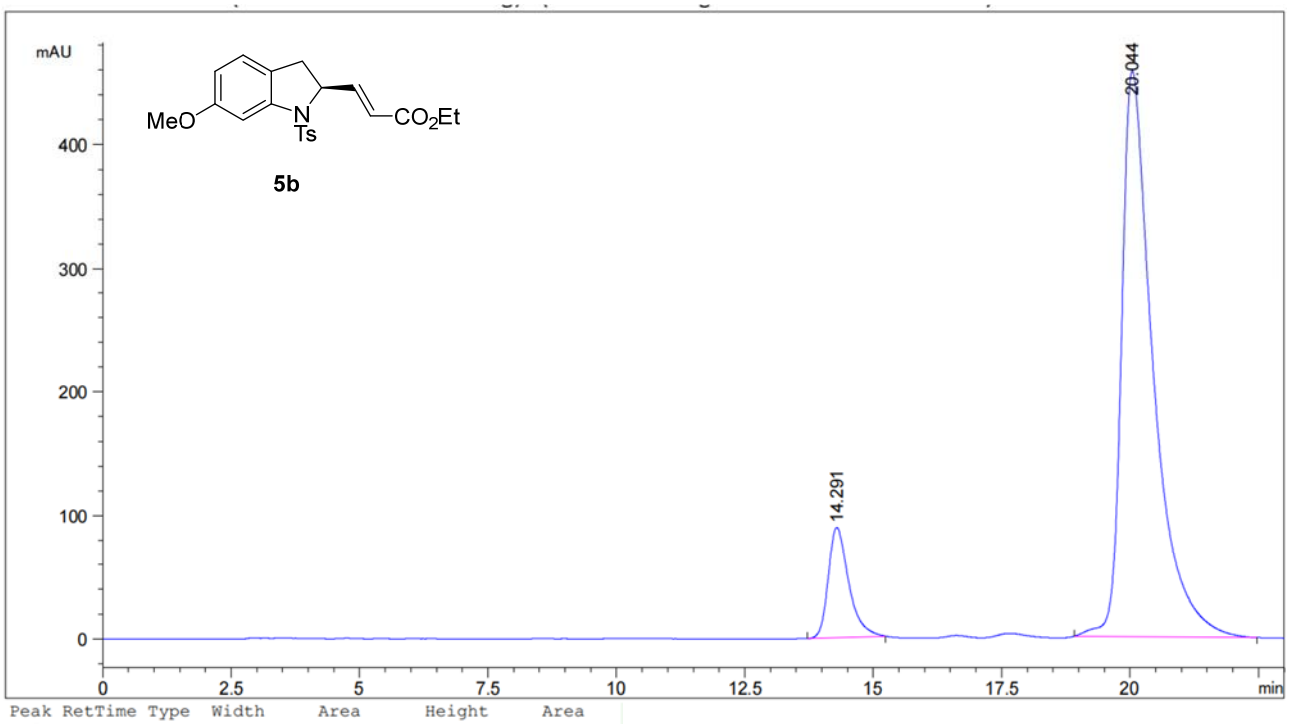
5b

^{13}C-NMR (100 MHz, $CDCl_3$)

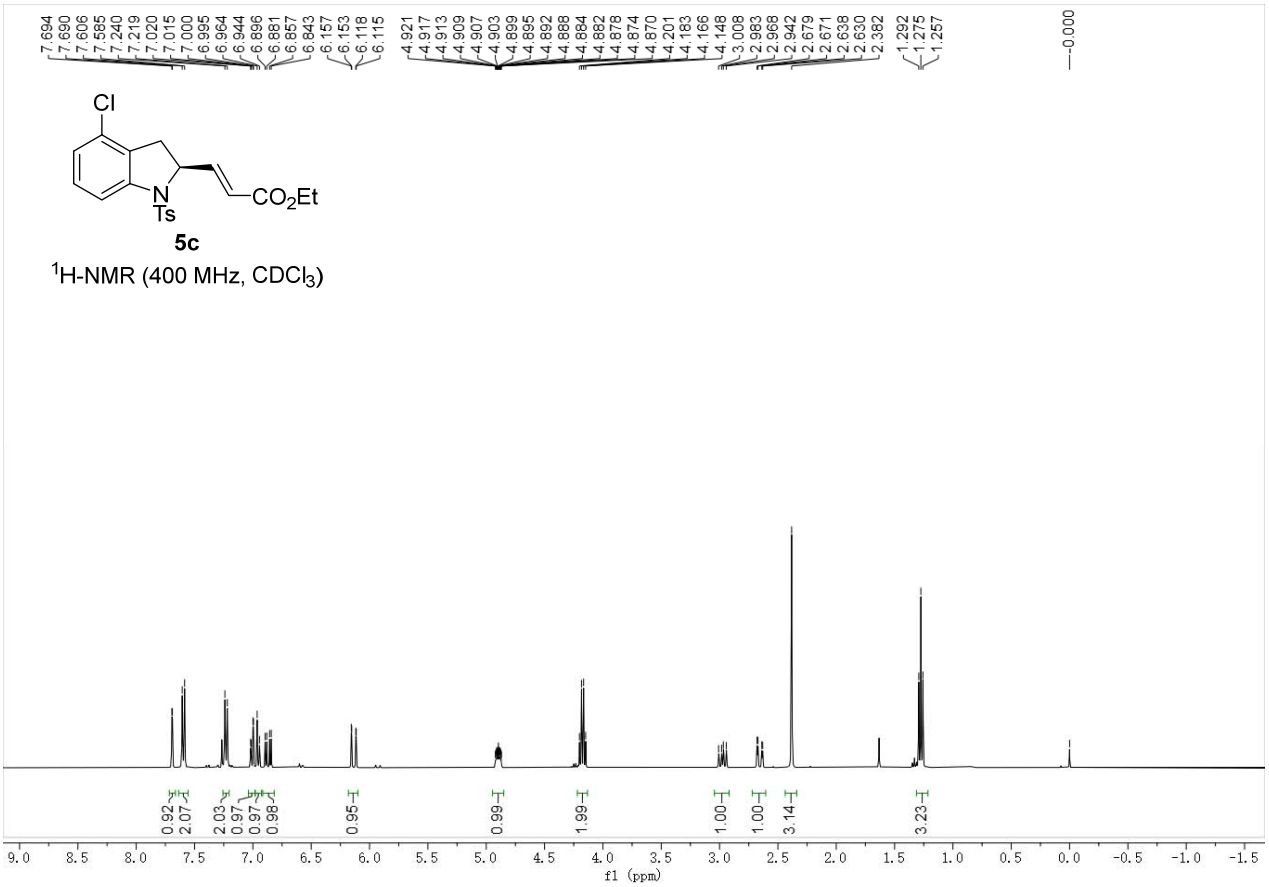

User Spectrum Plot Report
Agilent
Name CYC-221026-59
Inj. Vol. (ul) 8
Data File CYC-221026-59.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 10/28/2022 11:26:33 AM (UTC+08:00)
+ESI Scan (rt: 0.258 min) Frag=175.0V CYC-221026-59.d
x10^7
MeO
N
Ts
CO2Et
5b
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C21H23NO5Na+ 424.1195
424.1196
425.1223
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.203	BB	0.4280	1178.74146	41.25382	45.0061
2	20.173	BBA	0.5962	1440.33130	36.23800	54.9939

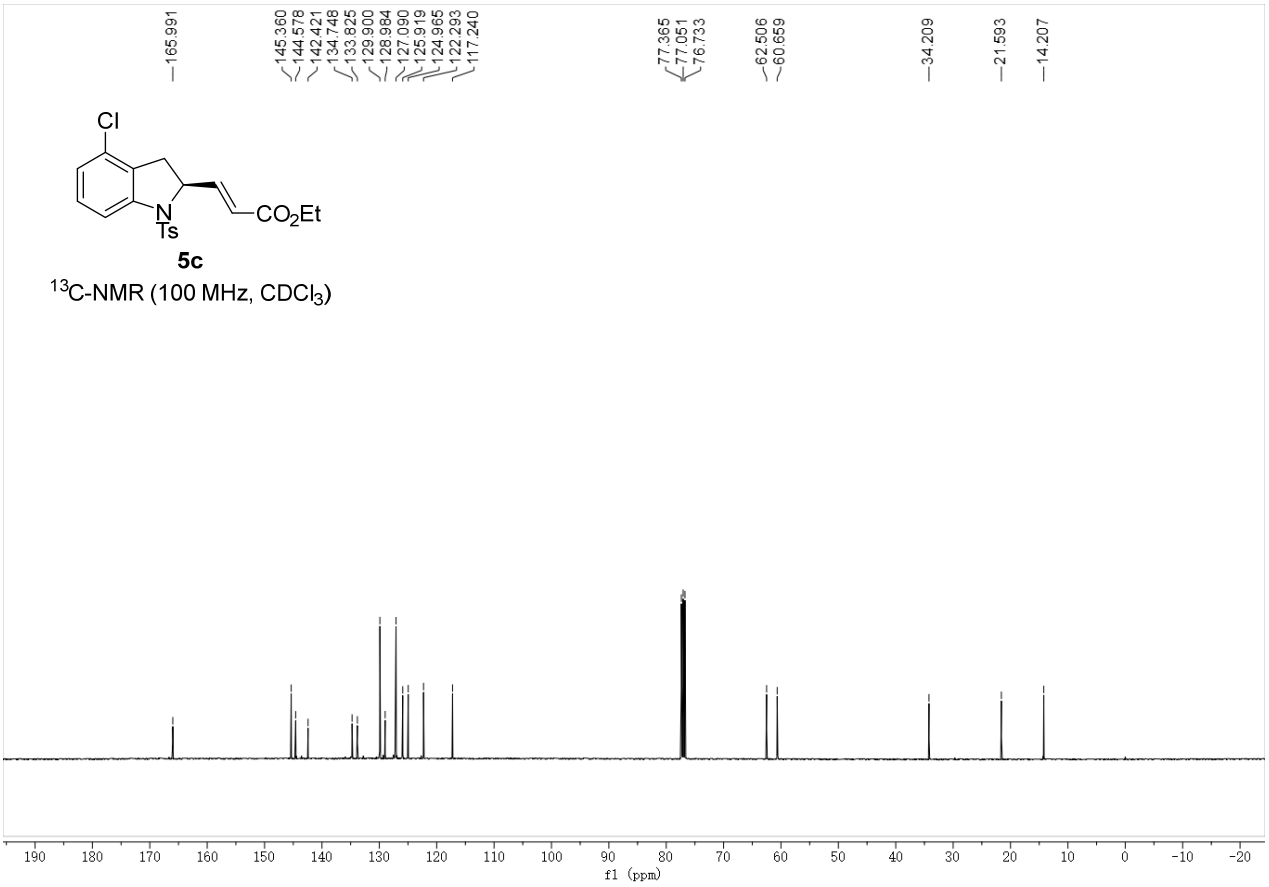


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.291	BBA	0.4145	2464.46509	89.49551	11.1603
2	20.044	BBA	0.6300	1.96179e4	457.40317	88.8397



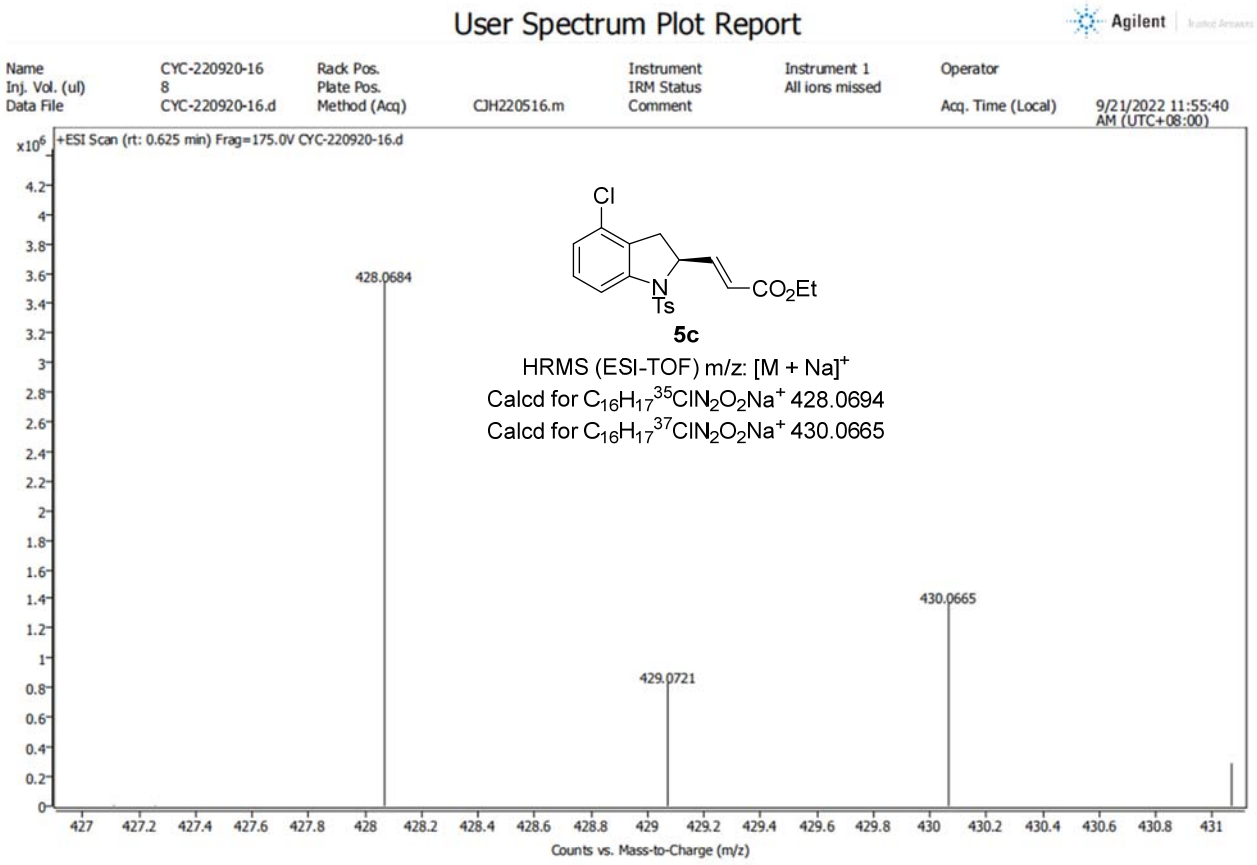
5c

^{1}H-NMR (400 MHz, $CDCl_3$)



5c

^{13}C-NMR (100 MHz, $CDCl_3$)

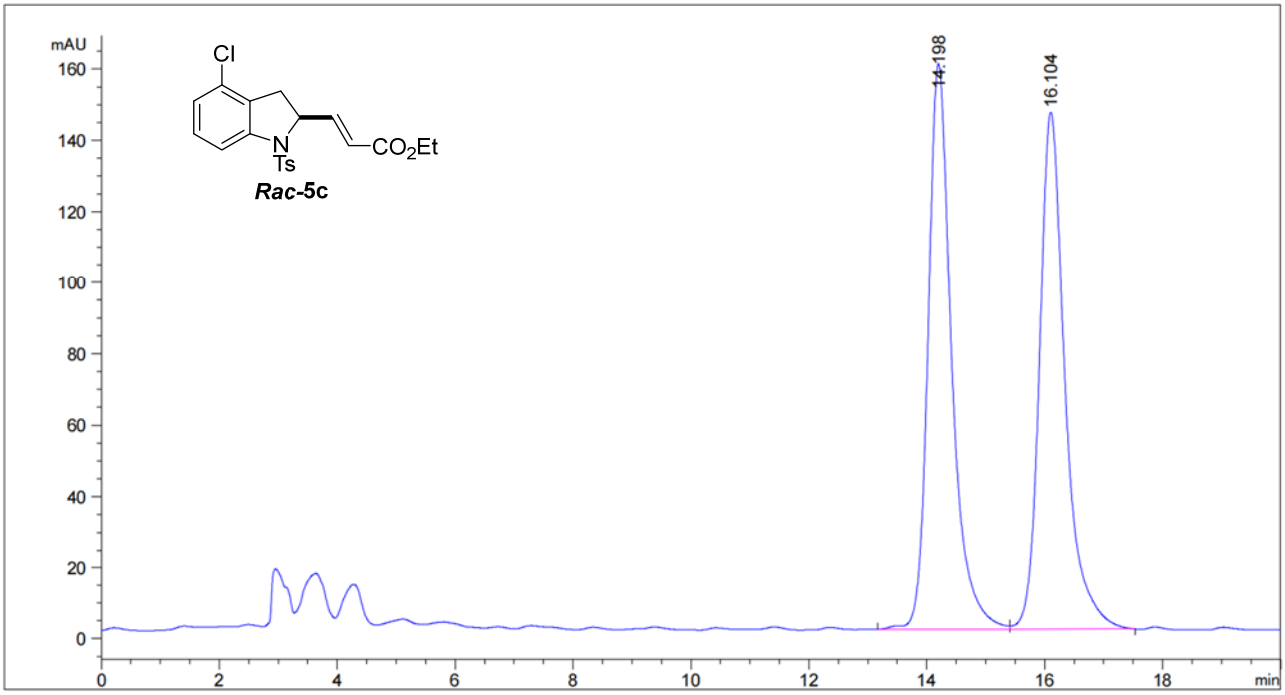


5c

HRMS (ESI-TOF) m/z: $[M + Na]^+$

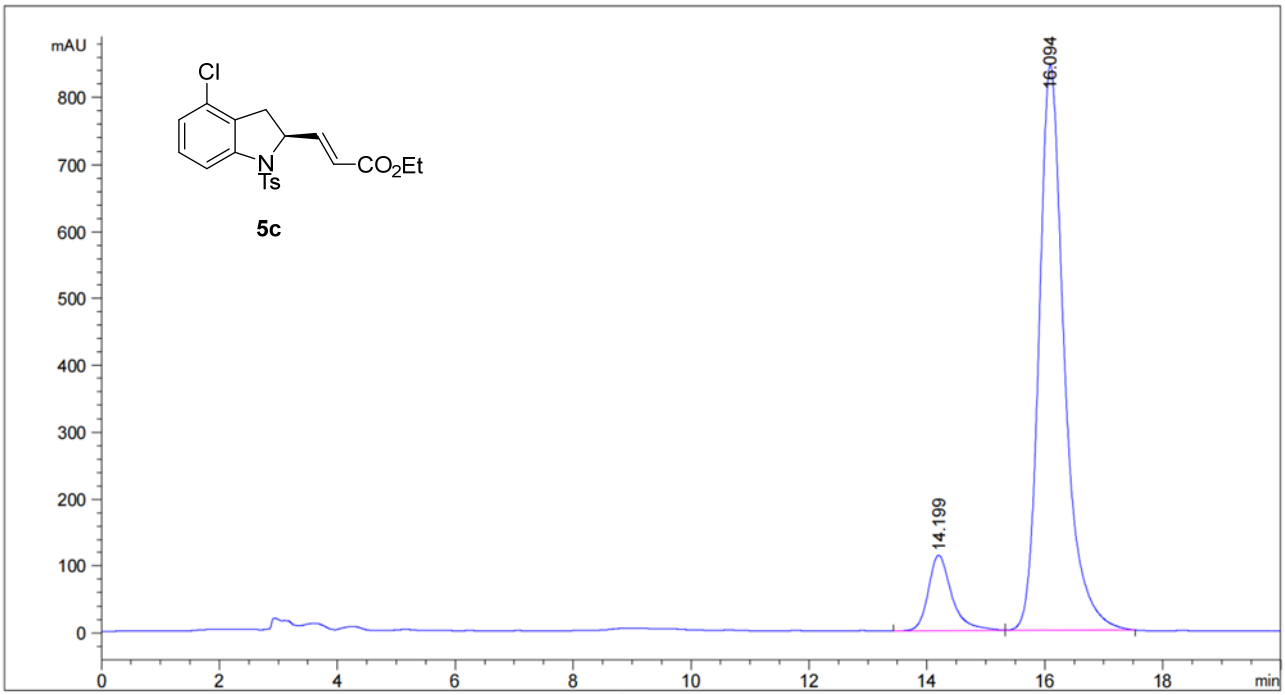
Calcd for $C_{16}H_{17}{}^{35}ClN_2O_2Na^+$ 428.0694

Calcd for $C_{16}H_{17}{}^{37}ClN_2O_2Na^+$ 430.0665



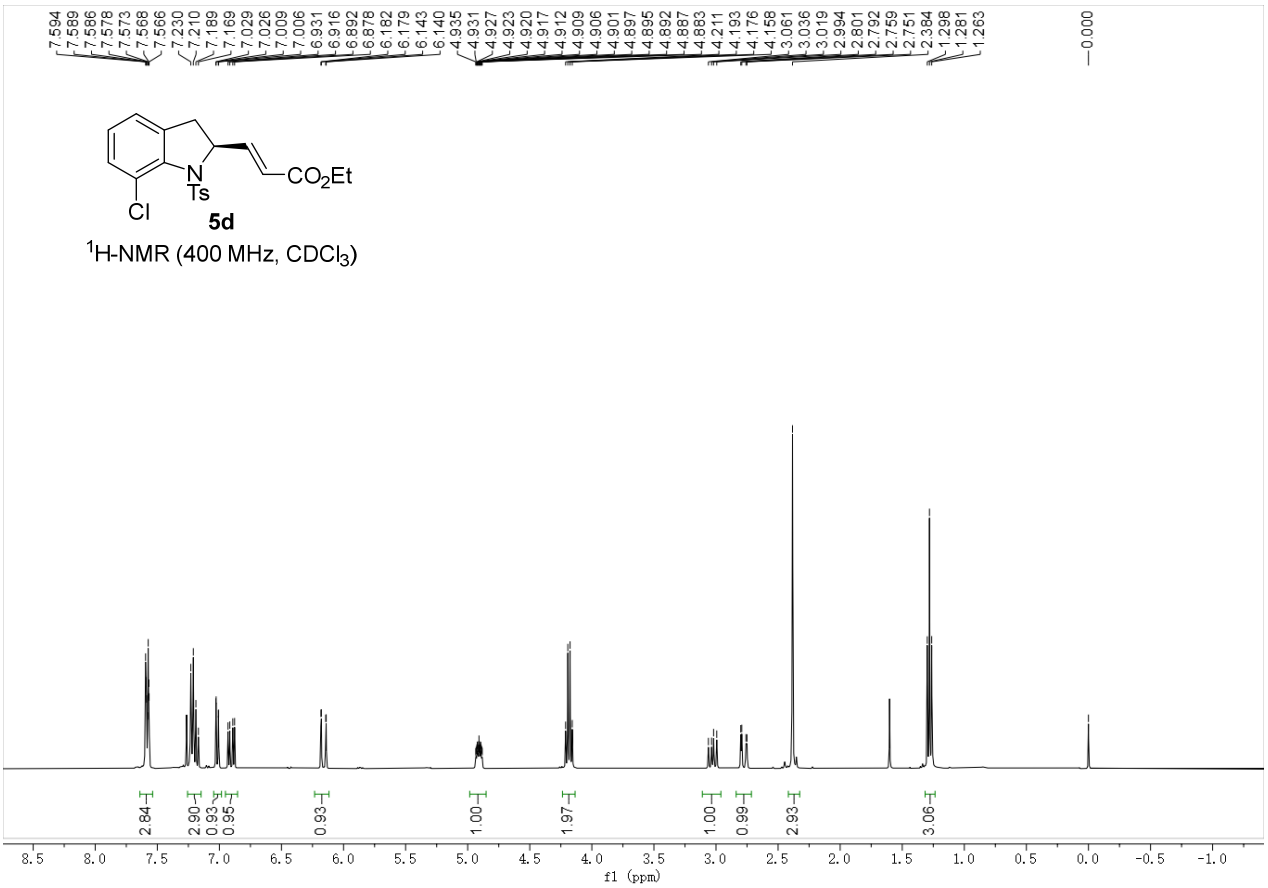
***Rac*-5c**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.198	BV	0.4158	4413.30566	158.86833	50.2898
2	16.104	VBA	0.4495	4362.44336	145.22653	49.7102



5c

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.199	BV	0.4136	3110.39722	112.21831	10.9802
2	16.094	VBA	0.4486	2.52170e4	845.07550	89.0198


7.594
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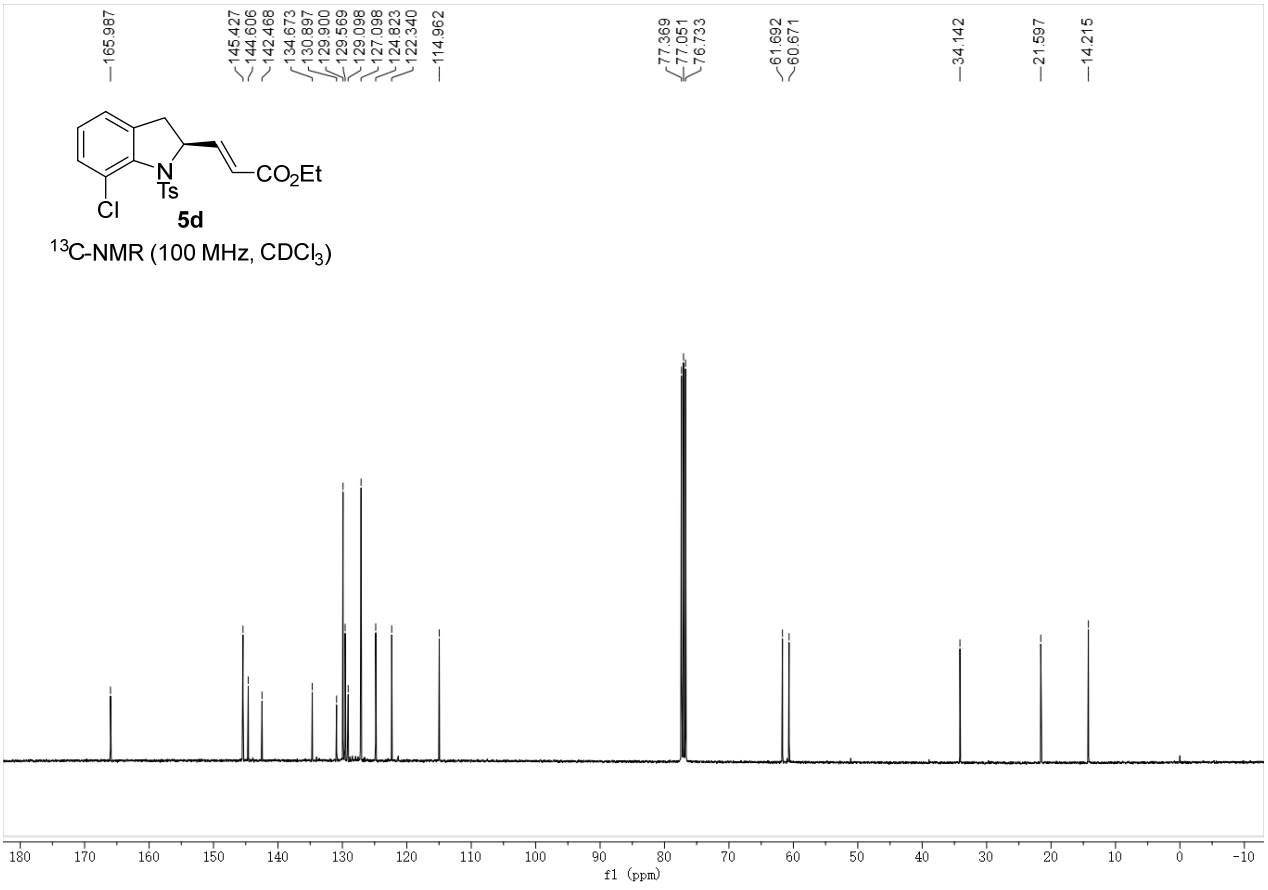
7.586
7.578
7.573
7.568
7.566
7.230
7.210
7.189
7.169
7.029
7.026
7.009
7.006
6.931
6.916
6.892
6.878
6.182
6.179
6.143
6.140
4.935
4.931
4.927
4.923
4.920
4.917
4.912
4.909
4.906
4.901
4.897
4.895
4.892
4.887
4.883
4.211
4.193
4.176
4.158
3.061
3.036
3.019
2.994
2.801
2.792
2.759
2.751
2.384
1.298
1.281
1.263
0.000
N
Ts
Cl
CO2Et
5d
1H-NMR (400 MHz, CDCl3)
2.84
2.90
0.93
0.95
0.93
1.00
1.97
1.00
0.99
2.93
3.06
f1 (ppm)


165.987
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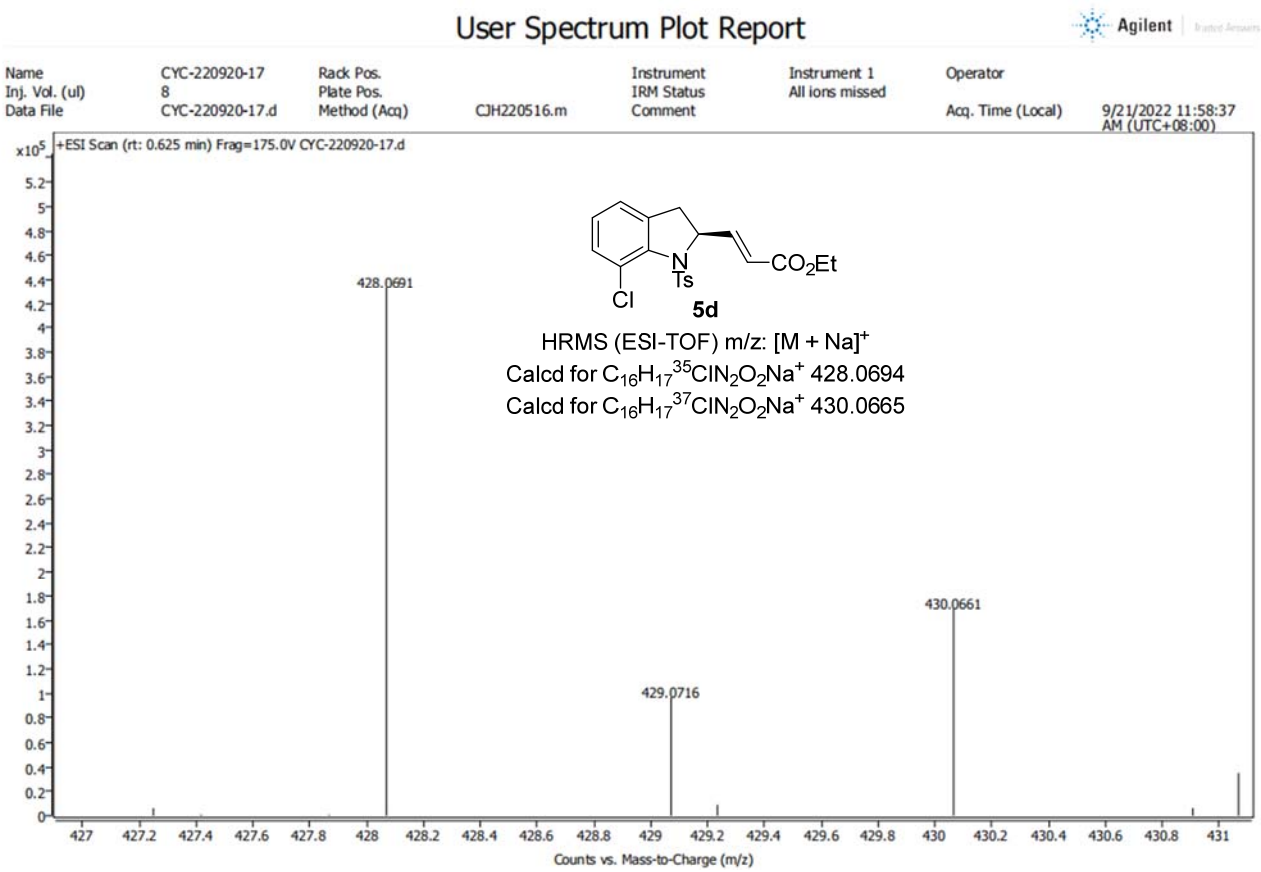
129.900
129.569
129.098
127.098
124.823
122.340
114.962
77.369
77.051
76.733
61.692
60.671
34.142
21.597
14.215
N
Ts
Cl
CO2Et
5d
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

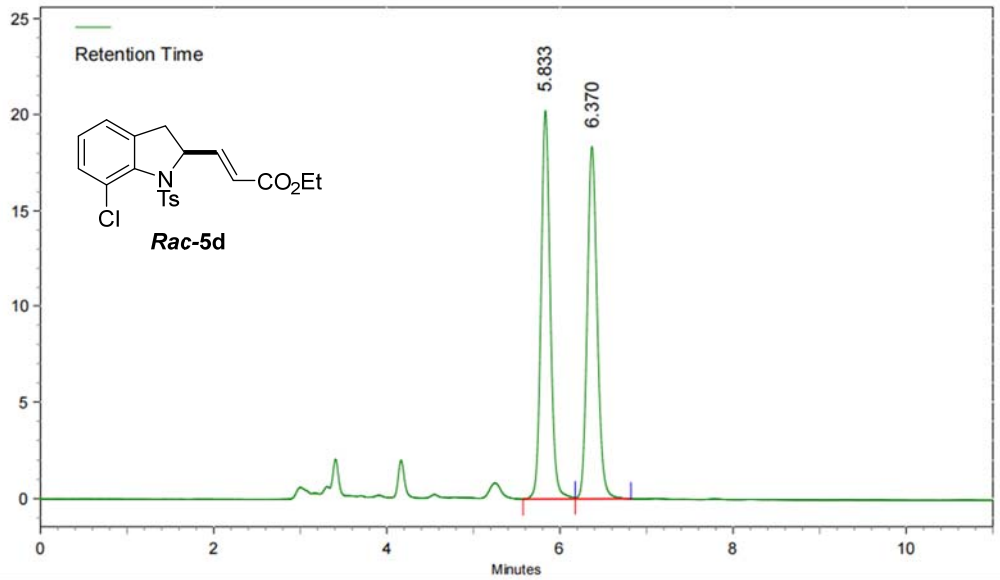


5d

HRMS (ESI-TOF) m/z: $[M + Na]^+$

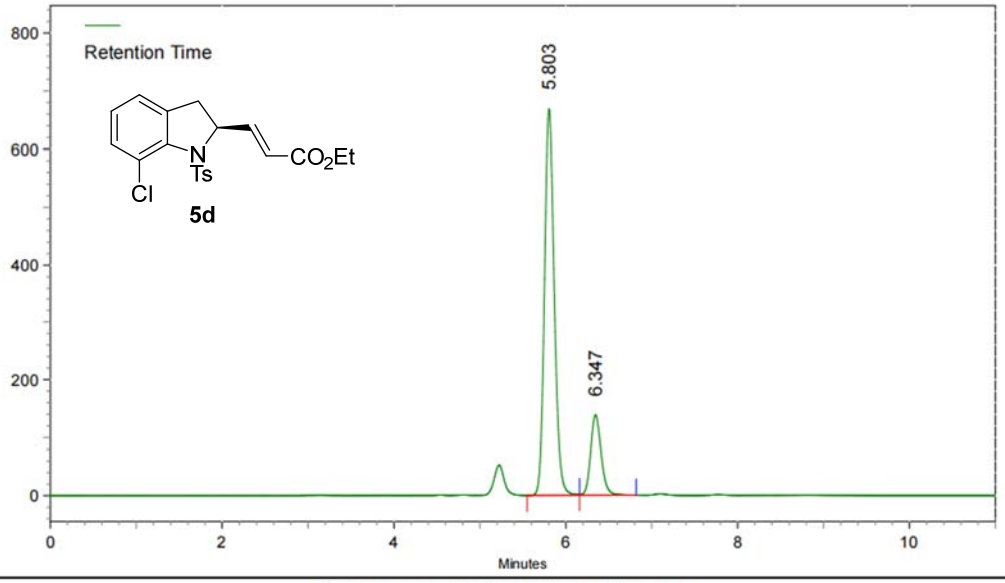
Calcd for $C_{16}H_{17}{}^{35}ClN_2O_2Na^+$ 428.0694

Calcd for $C_{16}H_{17}{}^{37}ClN_2O_2Na^+$ 430.0665



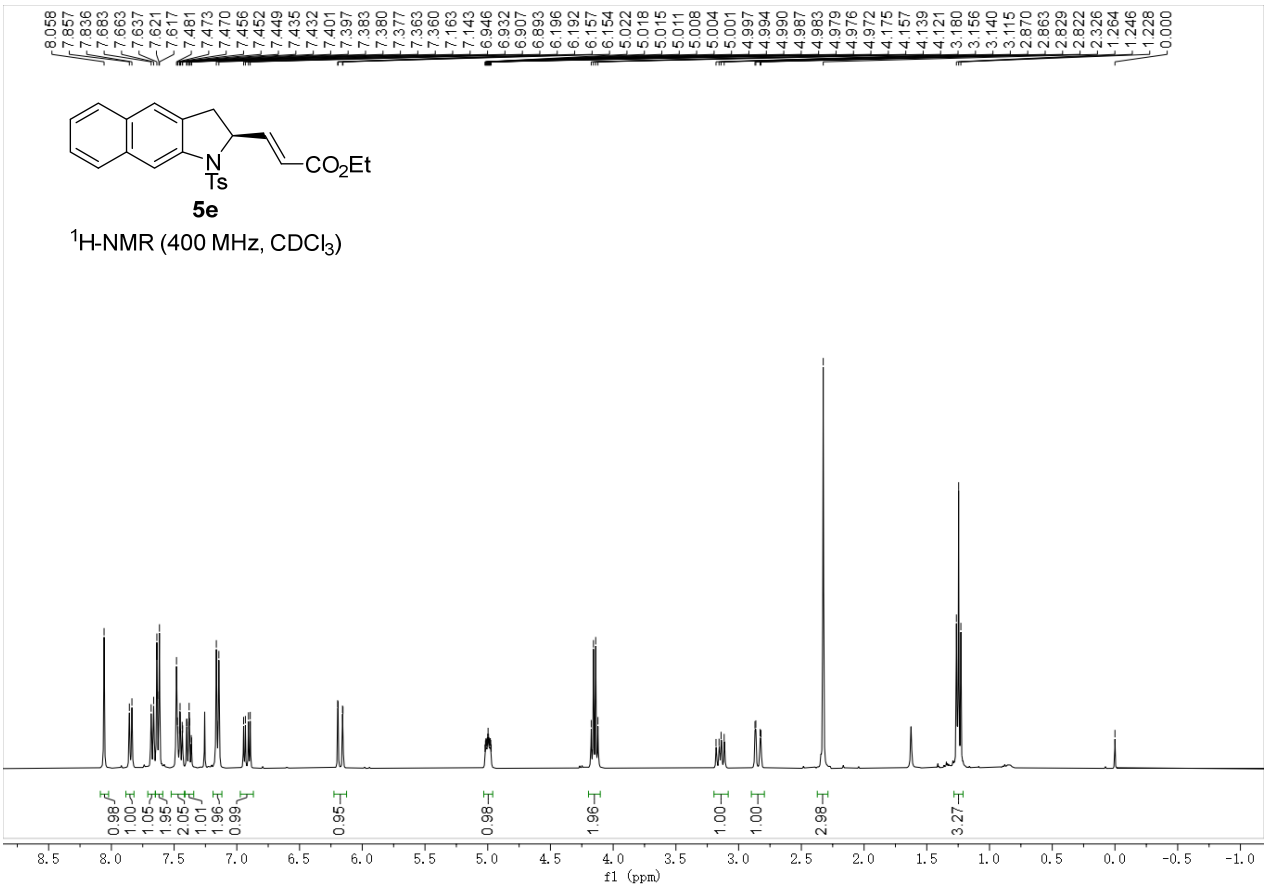
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.833	0.603	338894	2506249	50.4464
2	6.370	0.643	307554	2461894	49.5536
Totals			646448	4968143	100.0000



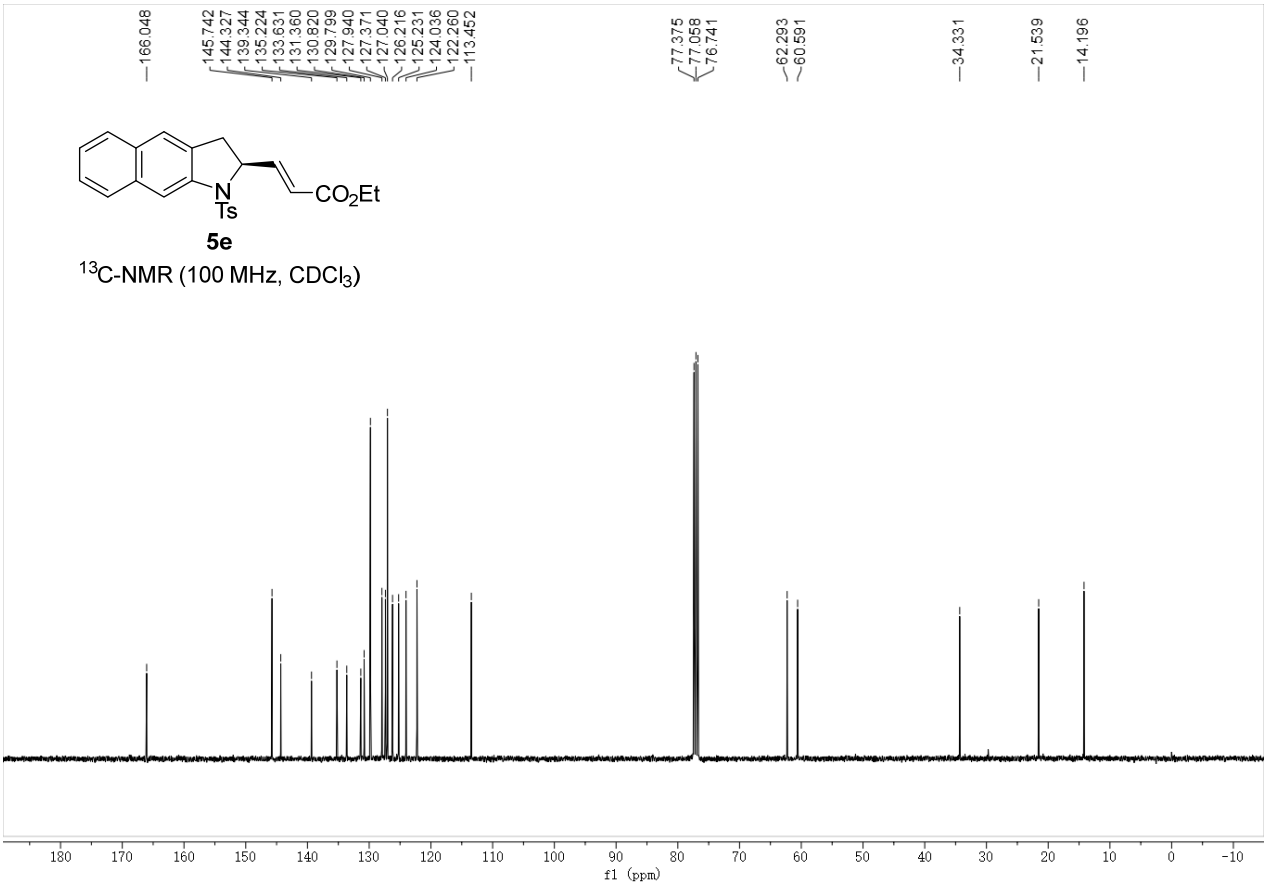
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.803	0.610	11217328	88505873	81.7817
2	6.347	0.660	2319735	19716220	18.2183
Totals			13537063	108222093	100.0000



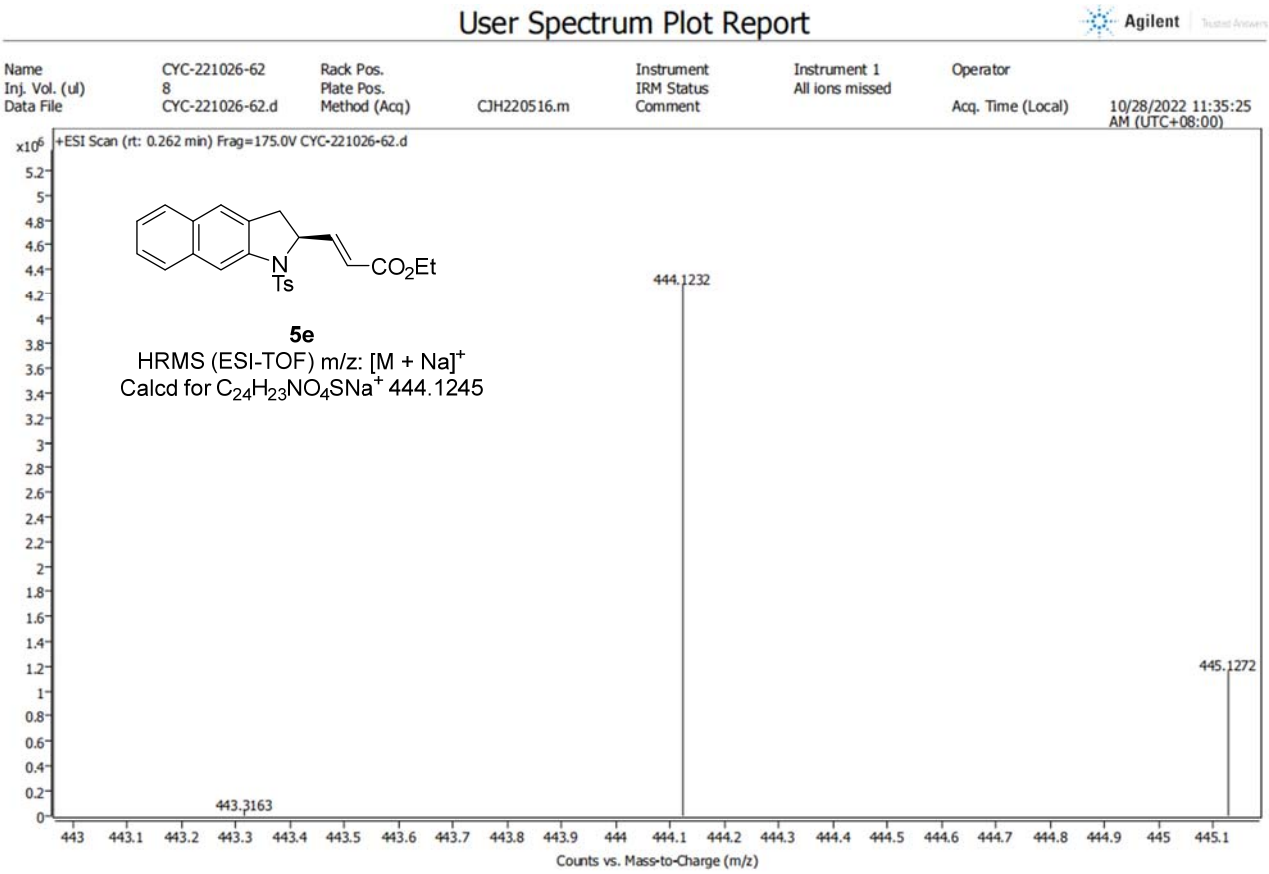
5e

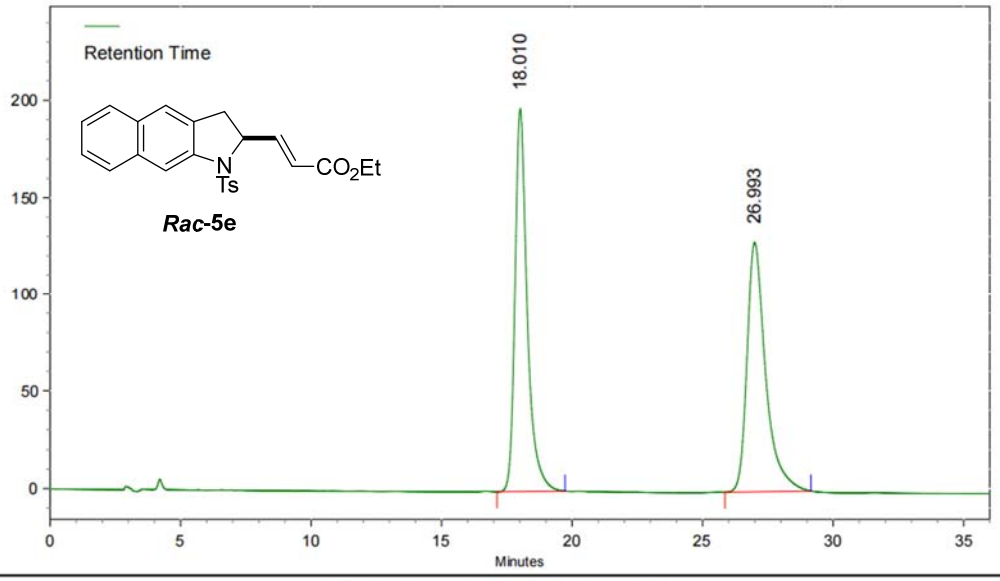
^{1}H-NMR (400 MHz, $CDCl_3$)



5e

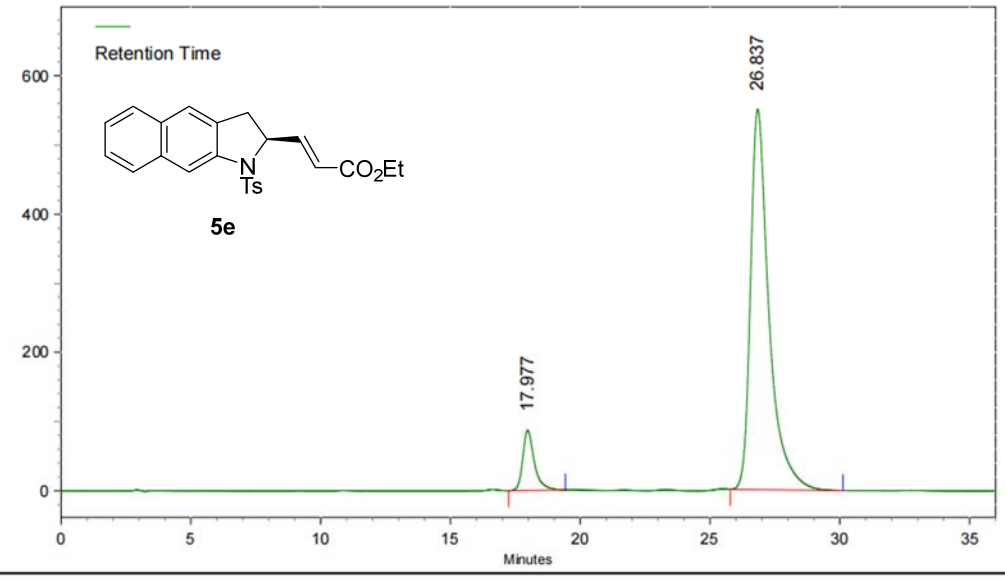
^{13}C-NMR (100 MHz, $CDCl_3$)


User Spectrum Plot Report
Agilent
Name CYC-221026-62
Inj. Vol. (ul) 8
Data File CYC-221026-62.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 10/28/2022 11:35:25 AM (UTC+08:00)
+ESI Scan (rt: 0.262 min) Frag=175.0V CYC-221026-62.d
x10^6
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
N
Ts
CO2Et
5e
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C24H23NO4SNa+ 444.1245
444.1232
445.1272
443.3163
443
443.1
443.2
443.3
443.4
443.5
443.6
443.7
443.8
443.9
444
444.1
444.2
444.3
444.4
444.5
444.6
444.7
444.8
444.9
445
445.1
Counts vs. Mass-to-Charge (m/z)



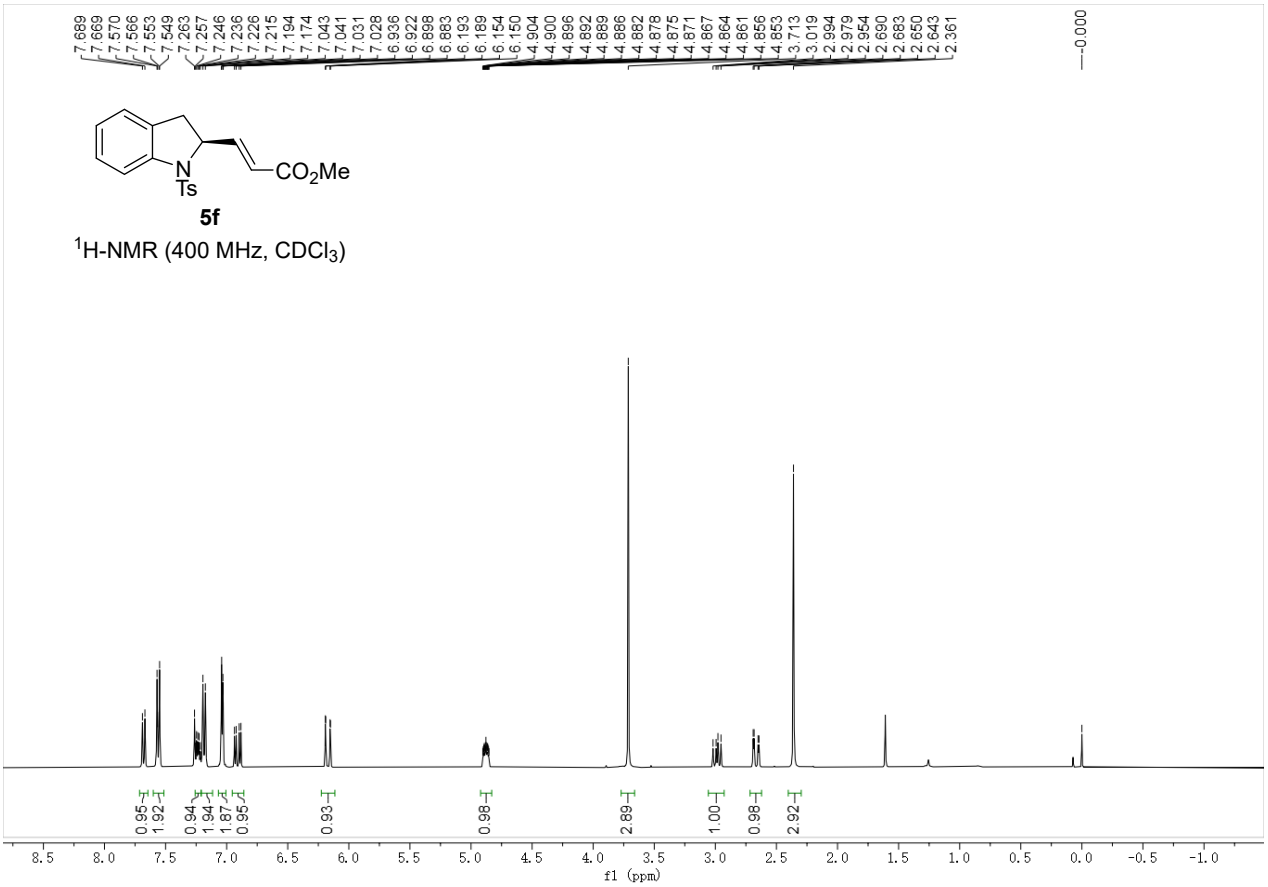
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	18.010	2.603	3307487	107474946	50.2112
2	26.993	3.293	2157971	106571025	49.7888
Totals			5465458	214045971	100.0000



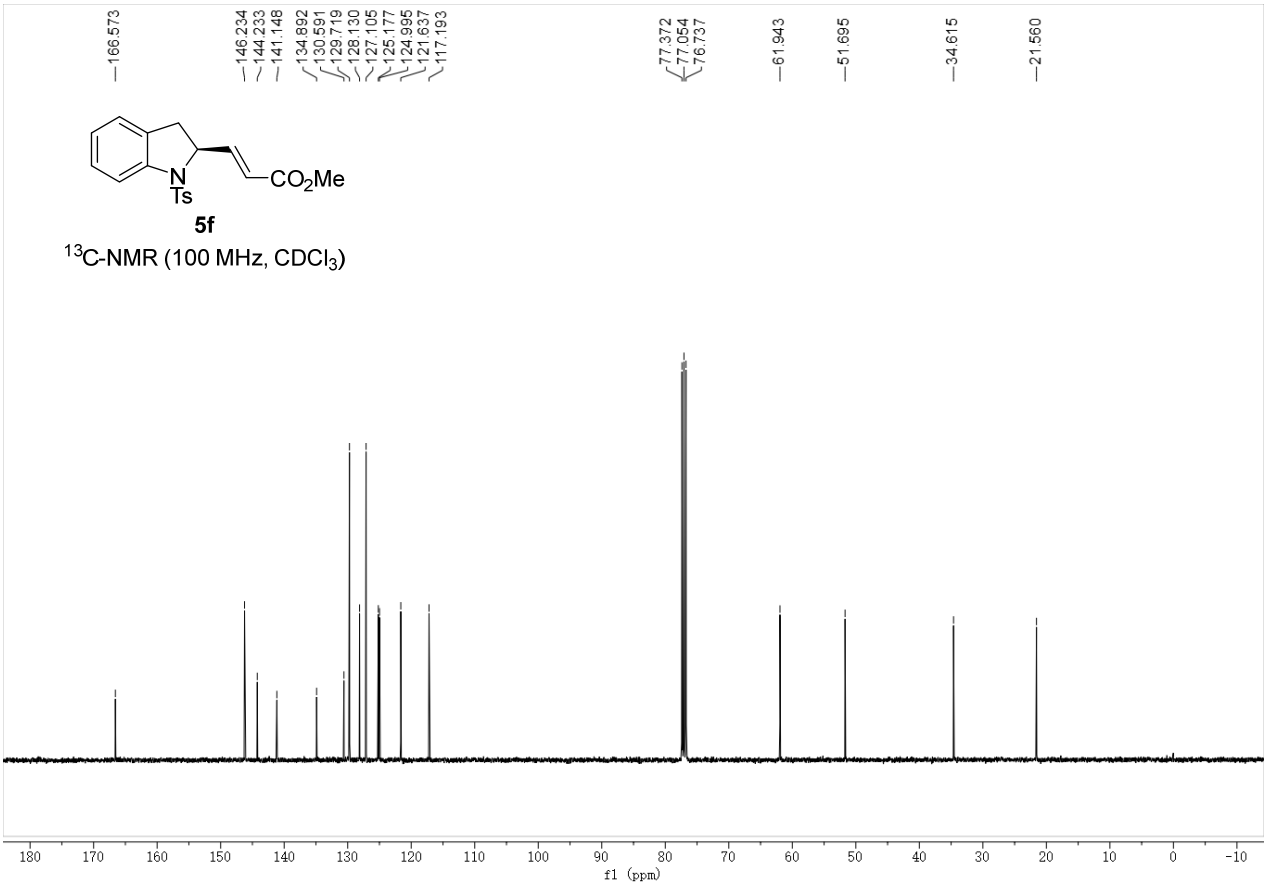
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.977	2.180	1455602	45148595	9.0050
2	26.837	4.343	9227459	456222698	90.9950
Totals			10683061	501371293	100.0000



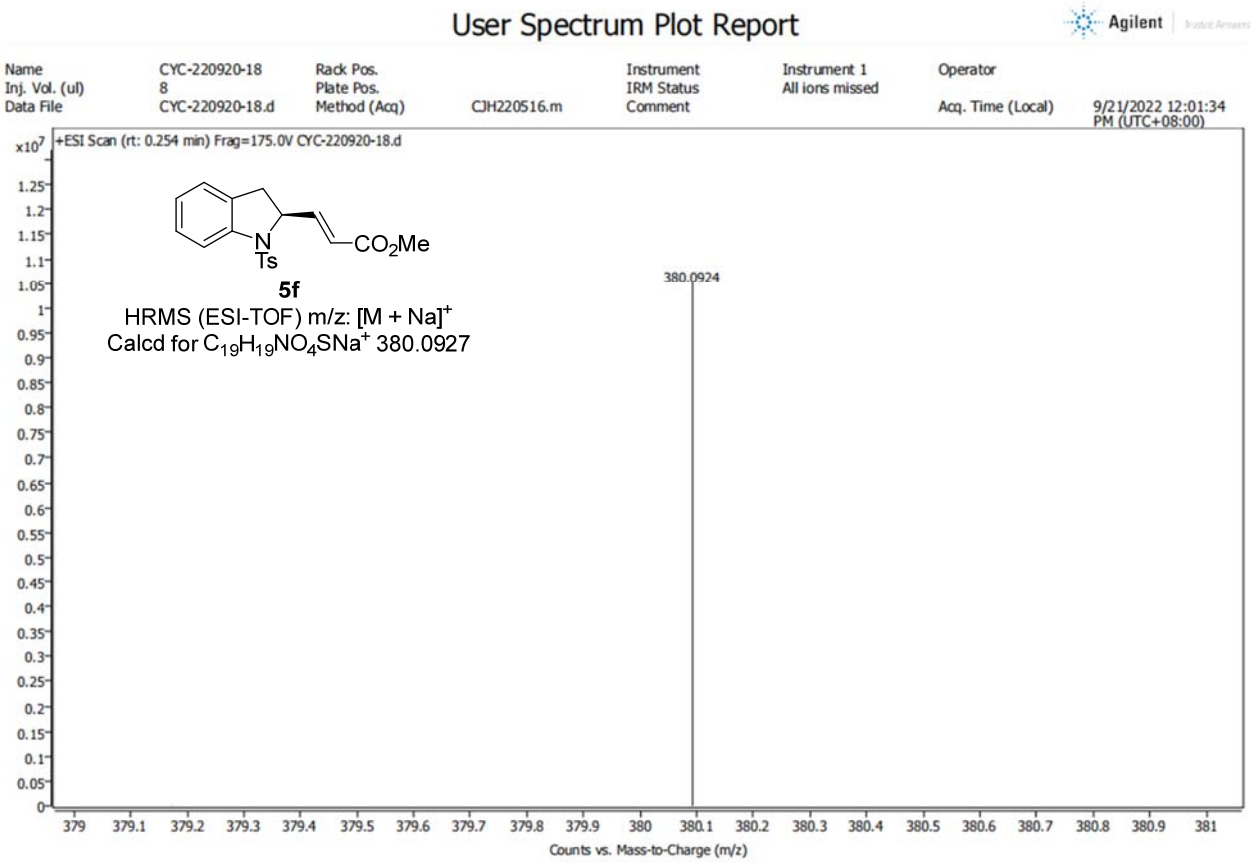
5f

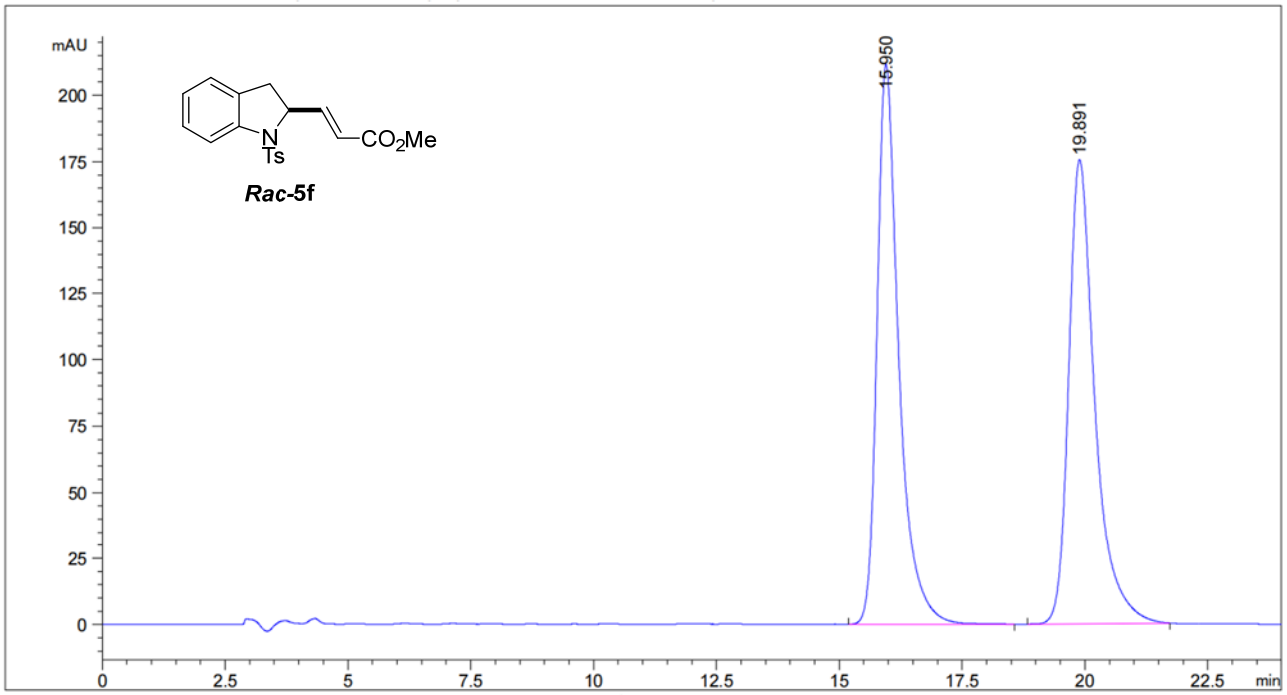
^{1}H-NMR (400 MHz, $CDCl_3$)



5f

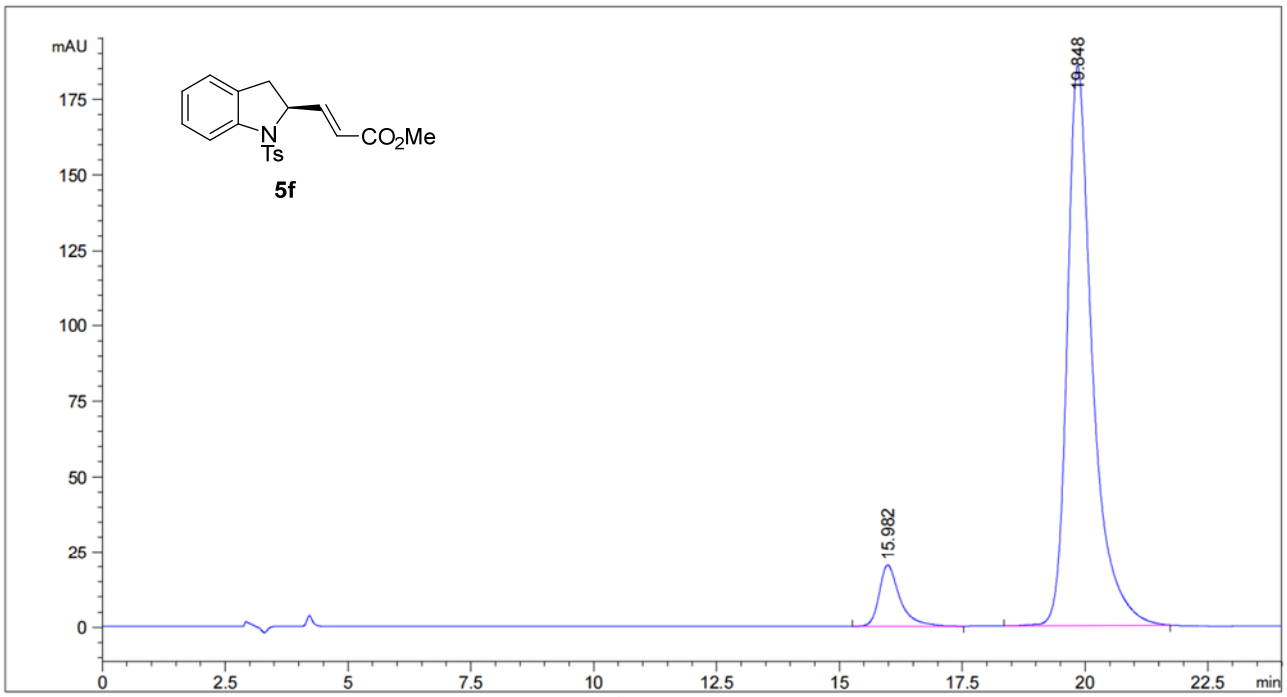
^{13}C-NMR (100 MHz, $CDCl_3$)


User Spectrum Plot Report
Agilent
Name CYC-220920-18
Inj. Vol. (ul) 8
Data File CYC-220920-18.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 9/21/2022 12:01:34 PM (UTC+08:00)
+ESI Scan (rt: 0.254 min) Frag=175.0V CYC-220920-18.d
x10^7
CO2Me
N
Ts
5f
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C19H19NO4SNa+ 380.0927
380.0924
Counts vs. Mass-to-Charge (m/z)



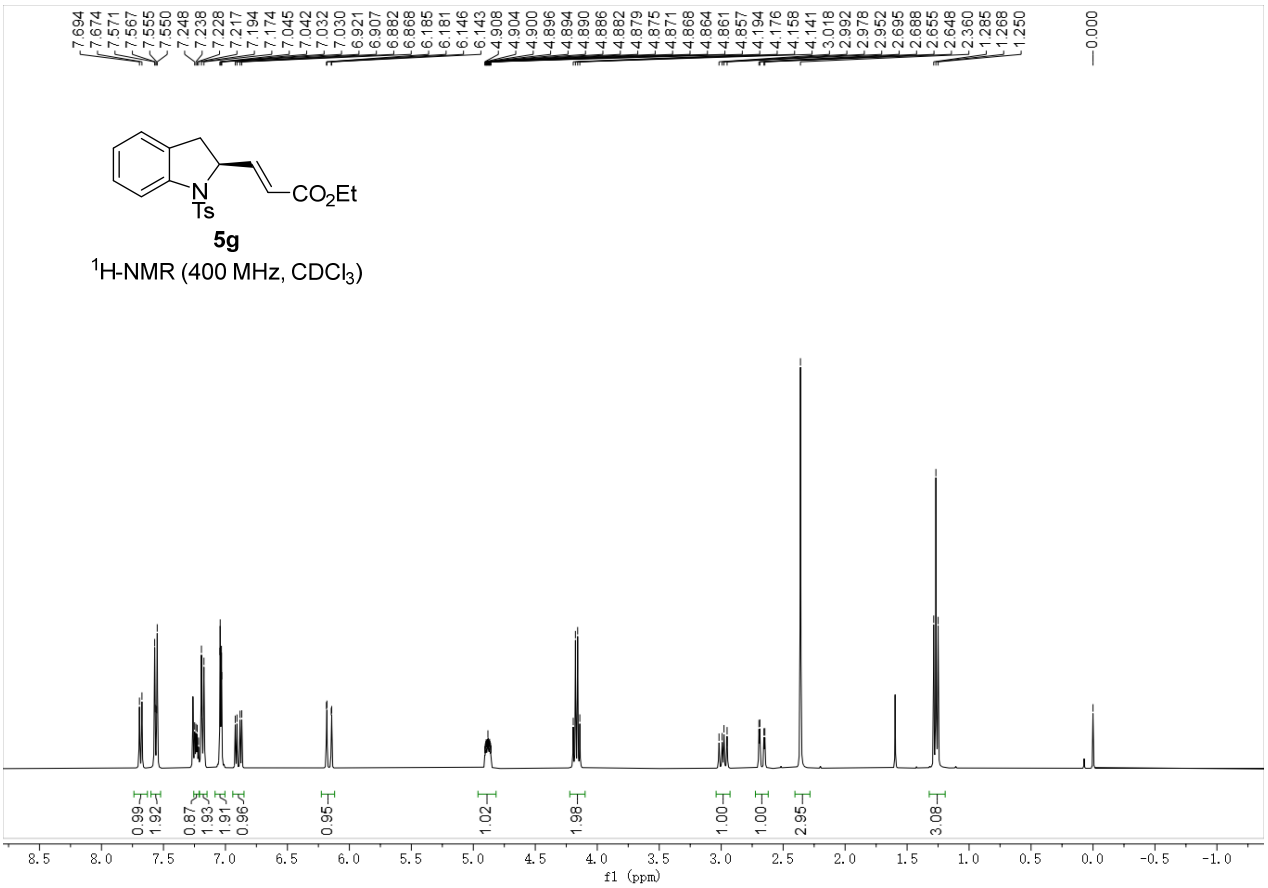
***Rac*-5f**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.950	BB	0.4615	6546.88428	211.56723	50.1254
2	19.891	BBA	0.5538	6514.13135	175.53539	49.8746



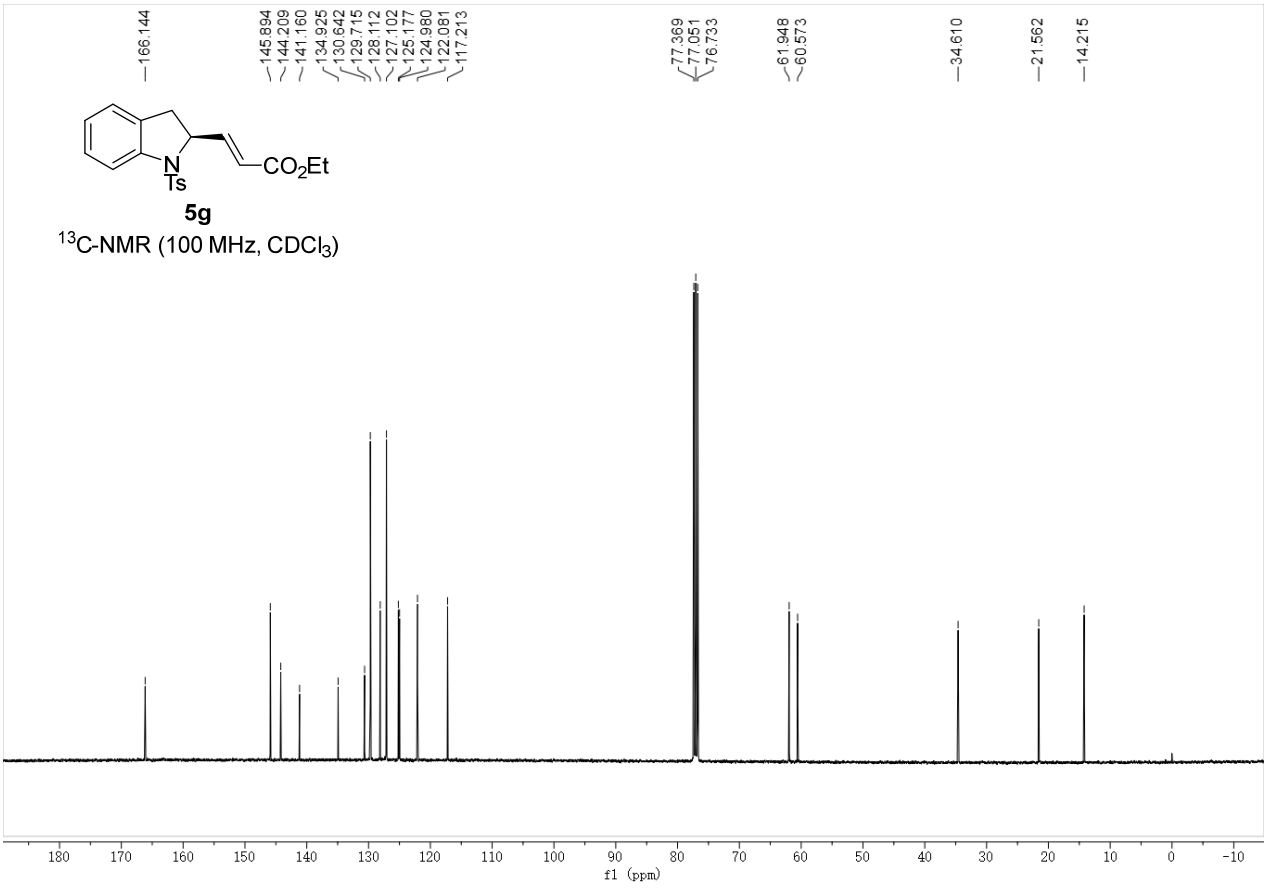
5f

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.982	BB	0.4334	588.33850	20.17315	8.1351
2	19.848	BBA	0.5328	6643.78467	185.54453	91.8649



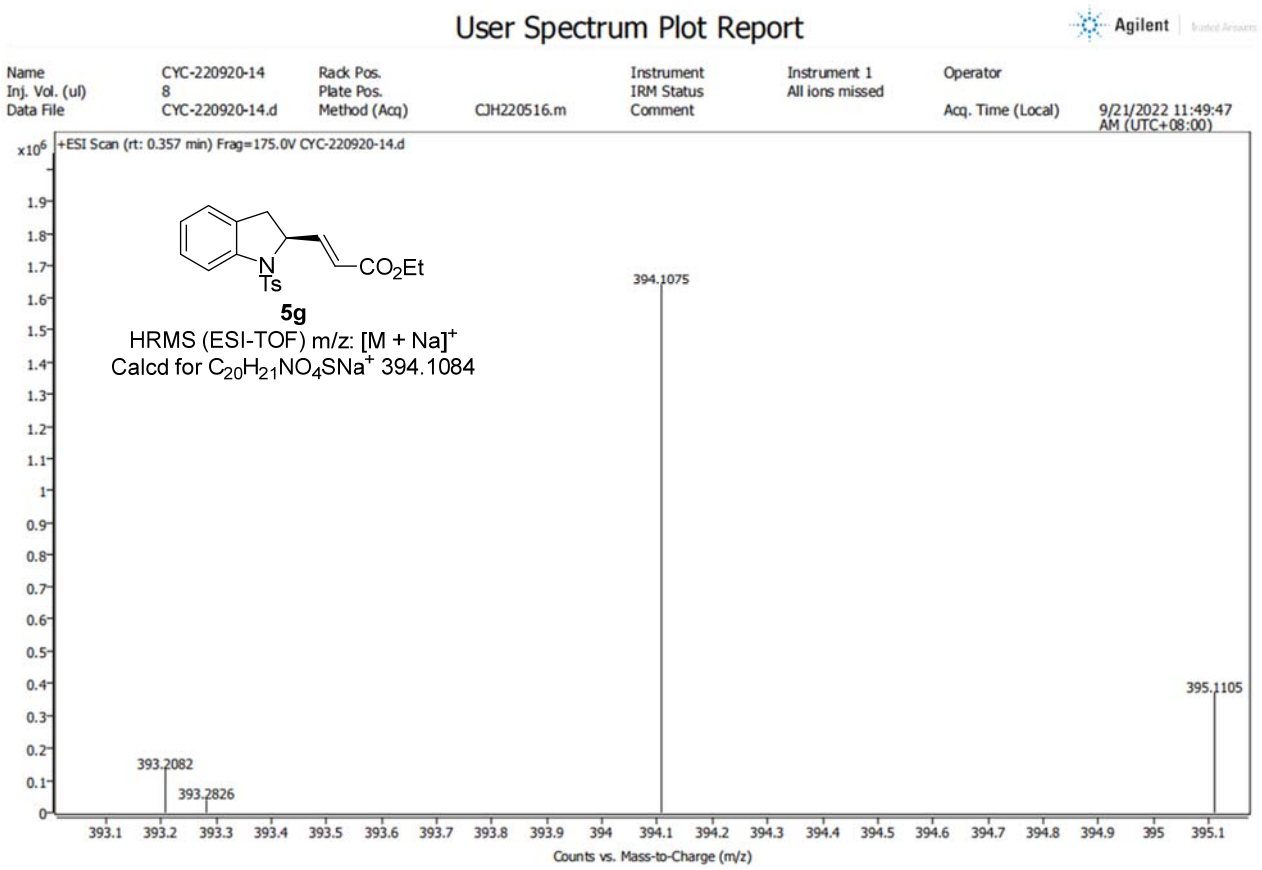
5g

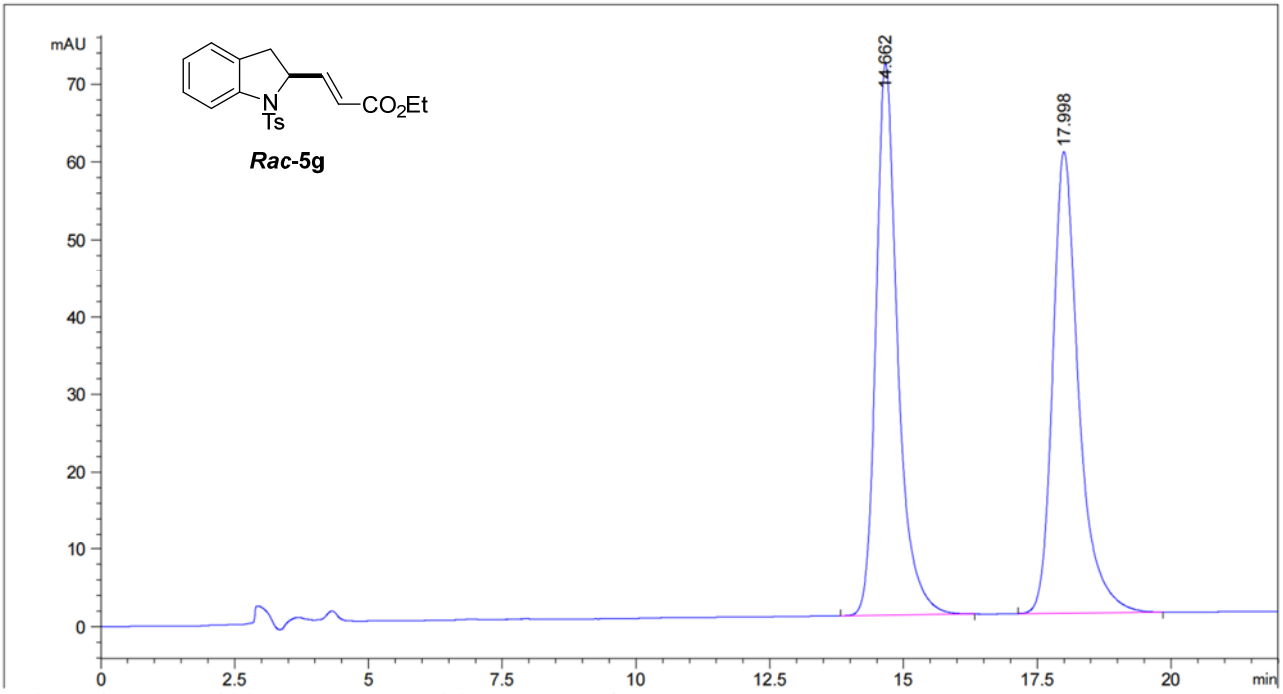
^{1}H-NMR (400 MHz, $CDCl_3$)



5g

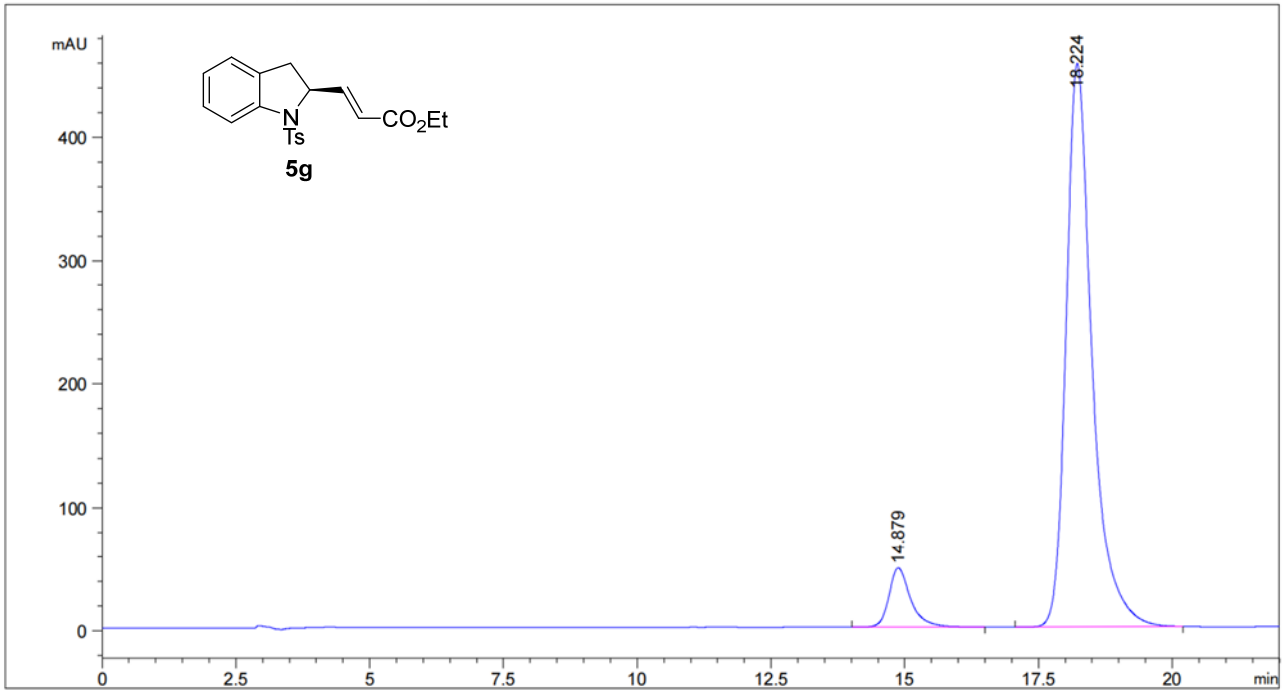
^{13}C-NMR (100 MHz, $CDCl_3$)


User Spectrum Plot Report
Agilent
Name CYC-220920-14
Inj. Vol. (ul) 8
Data File CYC-220920-14.d
Rack Pos.
Plate Pos.
Method (Acq) CJH220516.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 9/21/2022 11:49:47 AM (UTC+08:00)
+ESI Scan (rt: 0.357 min) Frag=175.0V CYC-220920-14.d
x10^6
N
Ts
CO2Et
5g
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C20H21NO4SNa+ 394.1084
394.1075
395.1105
393.2082
393.2826
Counts vs. Mass-to-Charge (m/z)



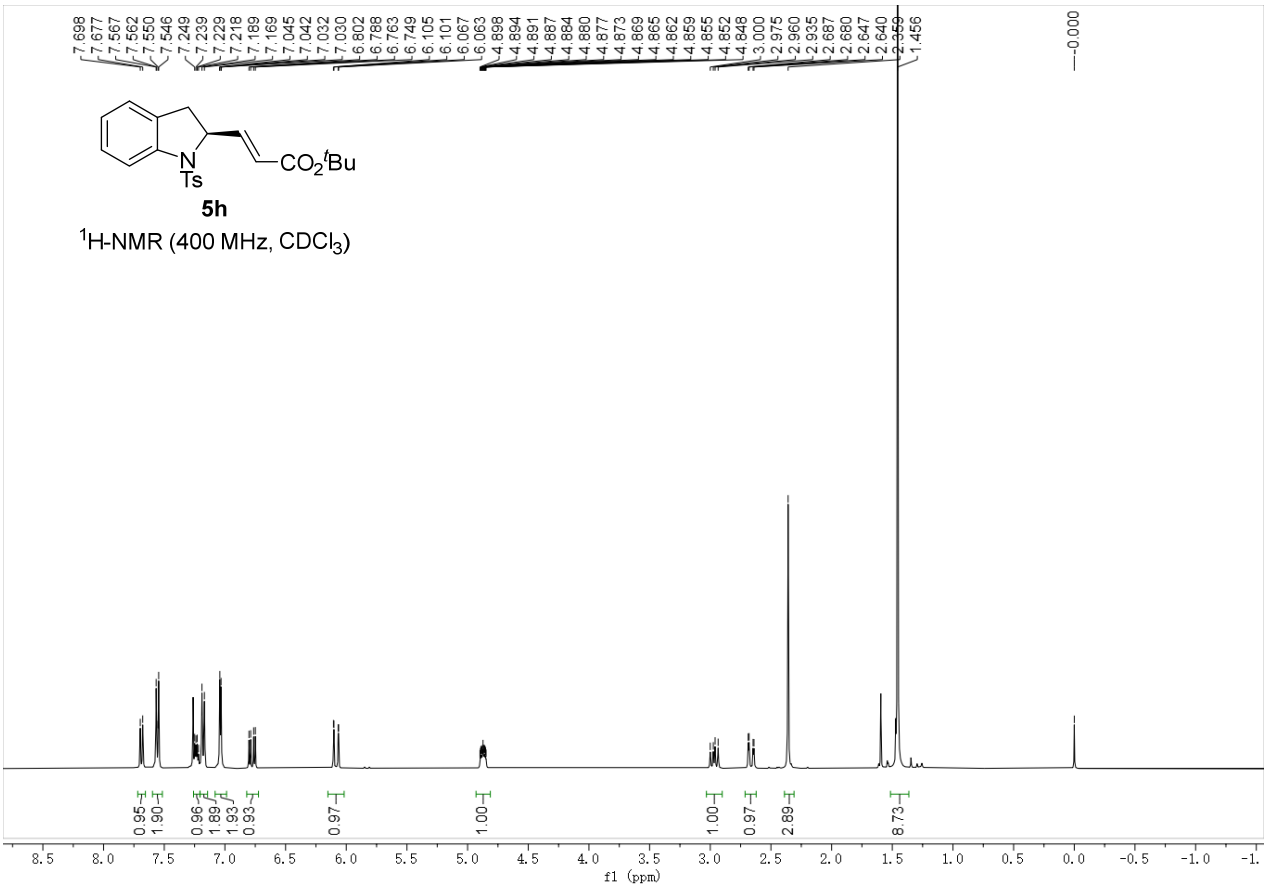
***Rac*-5g**

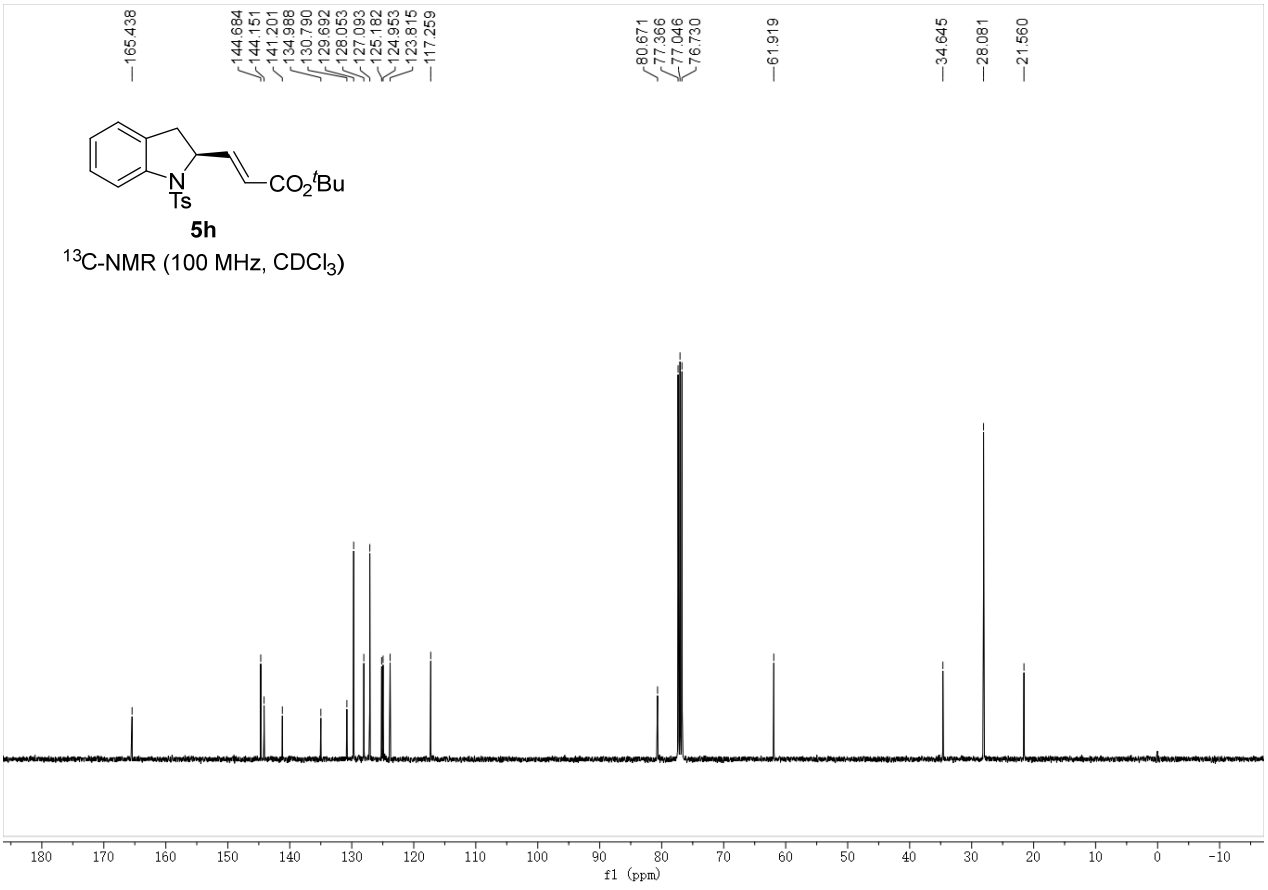
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.662	BB	0.4238	2017.04102	71.16637	50.0325
2	17.998	BB	0.5066	2014.42236	59.58206	49.9675

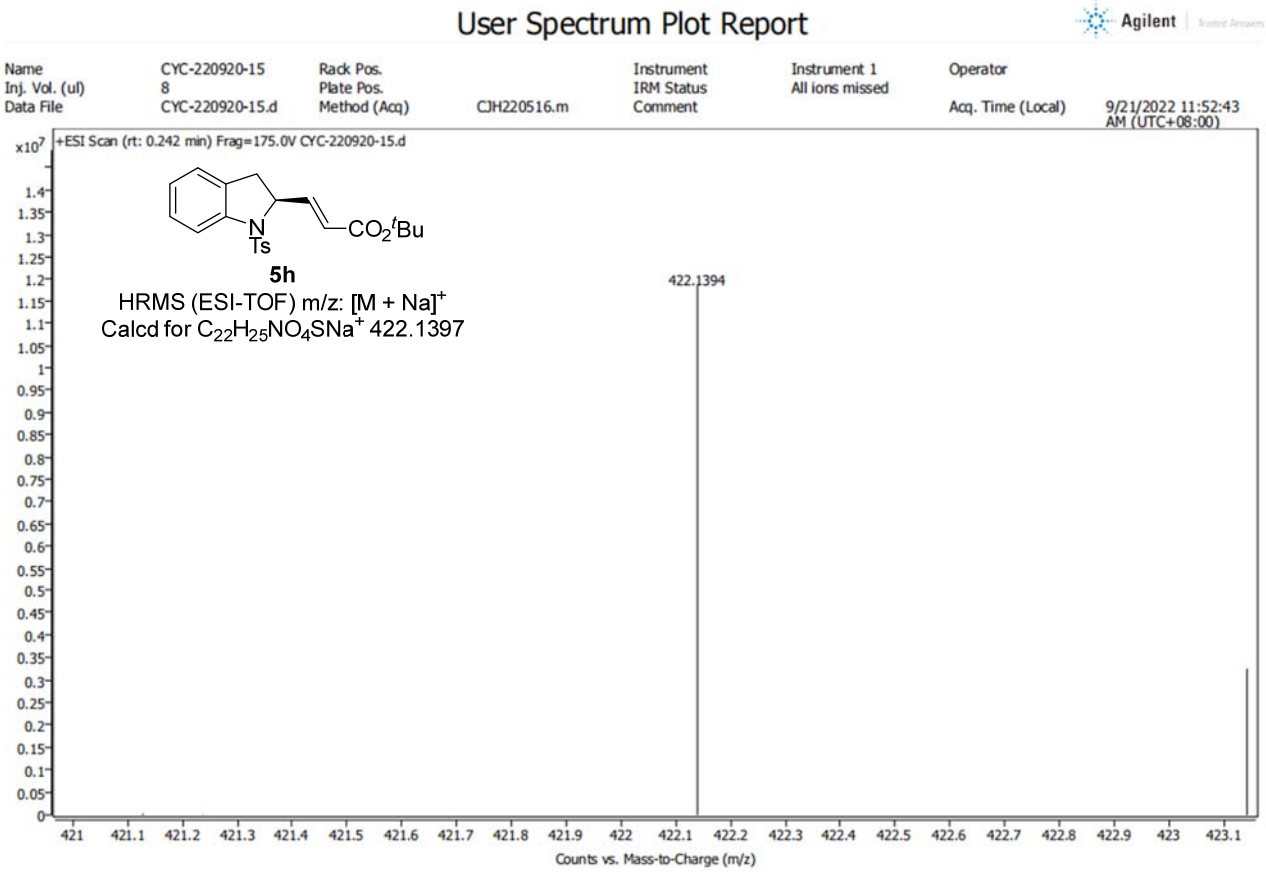


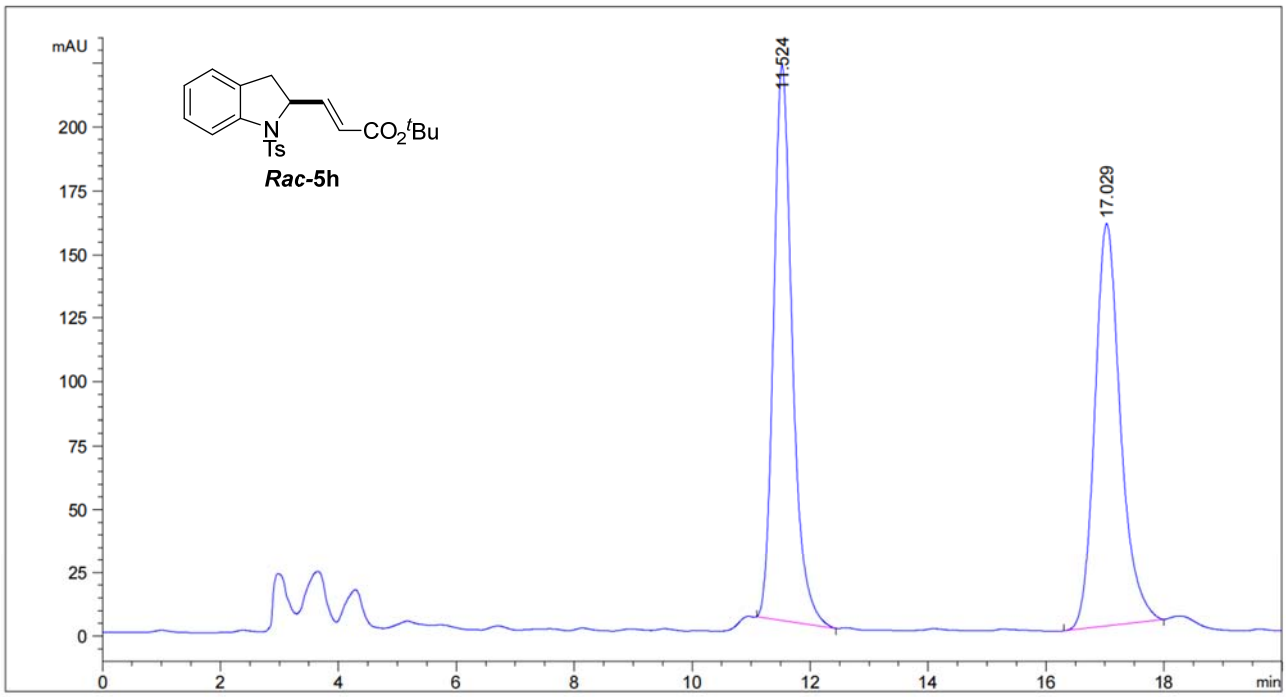
5g

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.879	BB	0.4208	1356.53137	48.09257	8.0849
2	18.224	BBA	0.5062	1.54221e4	456.56467	91.9151

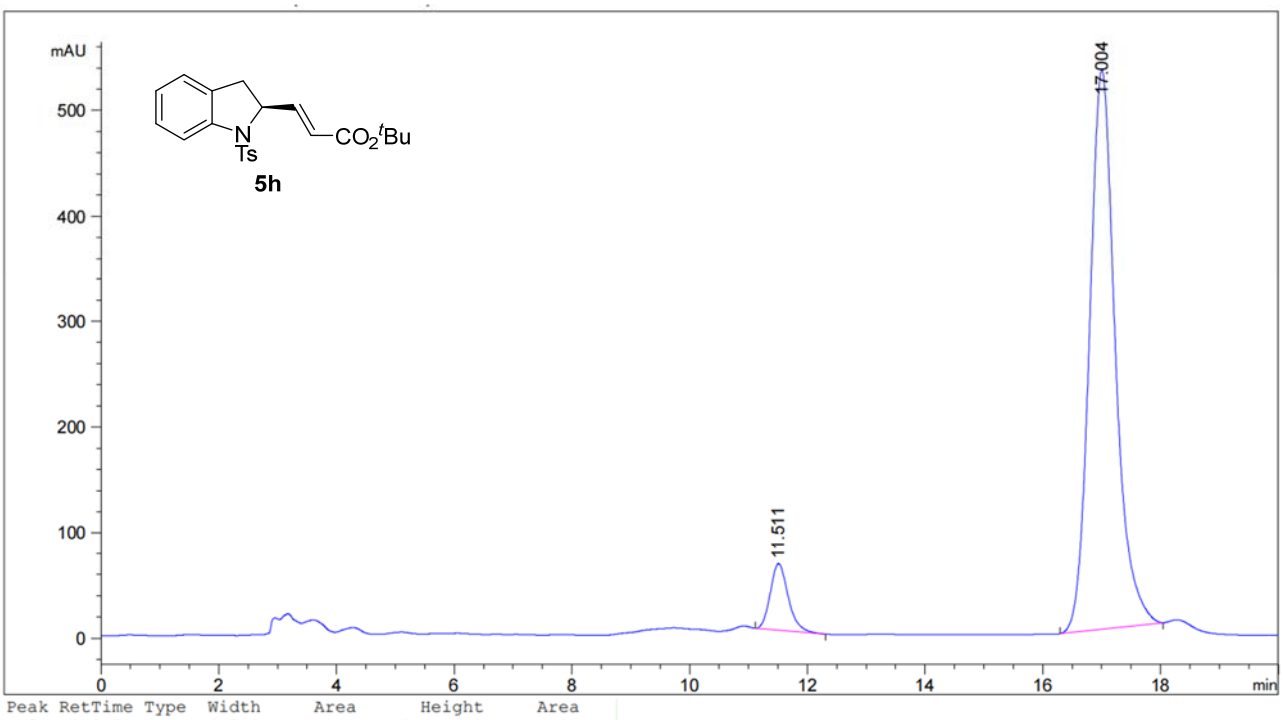

7.698
7.677
7.567
7.562
7.550
7.546
7.249
7.239
7.229
7.218
7.189
7.169
7.045
7.042
7.032
7.030
6.802
6.788
6.763
6.749
6.105
6.101
6.067
6.063
4.898
4.894
4.891
4.887
4.884
4.880
4.877
4.873
4.869
4.865
4.862
4.859
4.855
4.852
4.848
3.000
2.975
2.960
2.935
2.687
2.680
2.647
2.640
2.359
1.456
0.000
N
Ts
CO2tBu
5h
1H-NMR (400 MHz, CDCl3)
0.95
1.90
0.96
1.89
1.93
0.93
0.97
1.00
1.00
0.97
2.89
8.73
f1 (ppm)


165.438
144.684
144.151
141.201
134.988
130.790
129.692
128.053
127.093
125.182
124.953
123.815
117.259
80.671
77.366
77.046
76.730
61.919
34.645
28.081
21.560
N
Ts
CO2tBu
5h
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

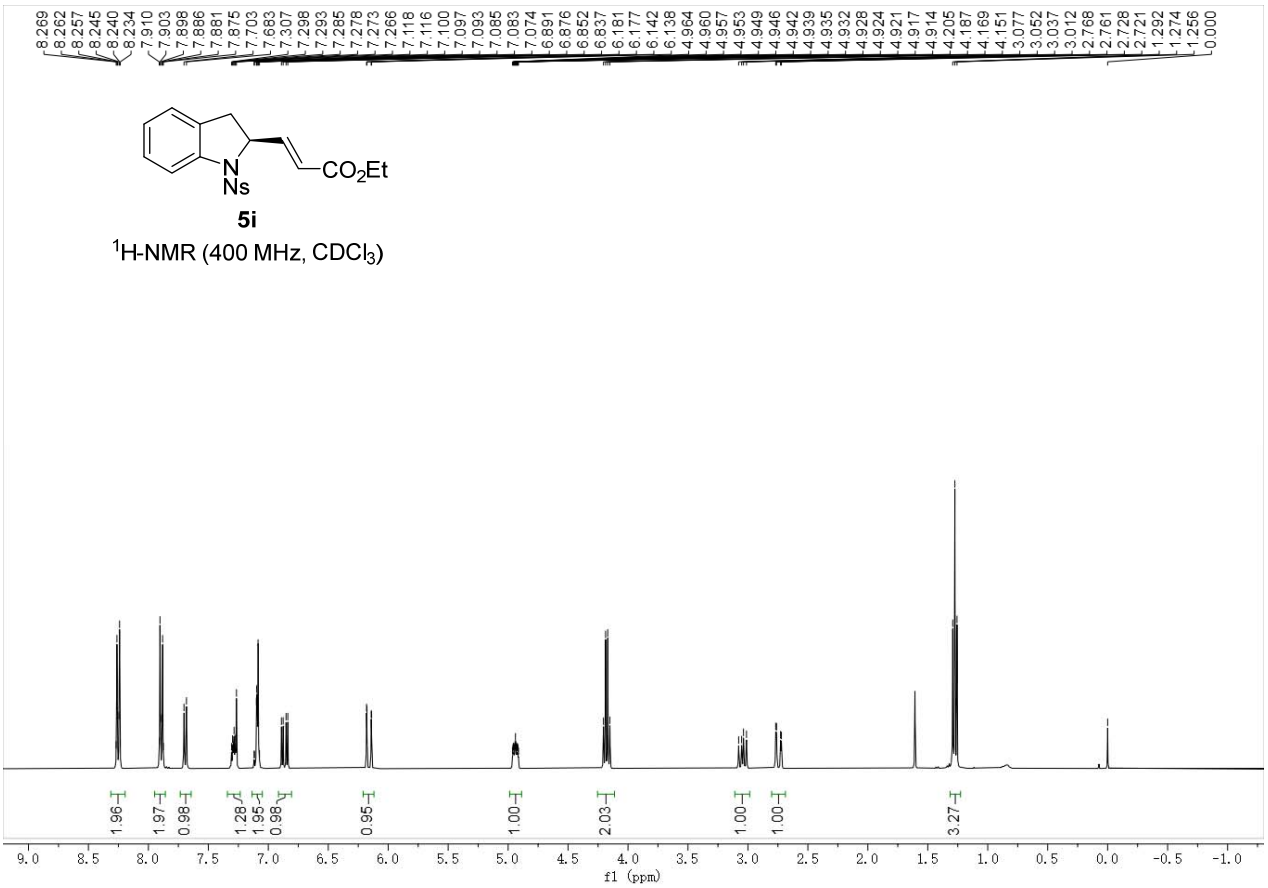

User Spectrum Plot Report
Agilent
Name CYC-220920-15
Rack Pos.
Instrument
Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status
All ions missed
Data File CYC-220920-15.d
Method (Acq) CJH220516.m
Comment
Acq. Time (Local) 9/21/2022 11:52:43 AM (UTC+08:00)
+ESI Scan (rt: 0.242 min) Frag=175.0V CYC-220920-15.d
x10^7
N
Ts
CO2tBu
5h
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C22H25NO4SNa+ 422.1397
422.1394
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.524	BBA	0.3360	4806.57715	217.89729	50.1140
2	17.029	BB	0.4574	4784.70752	158.32251	49.8860

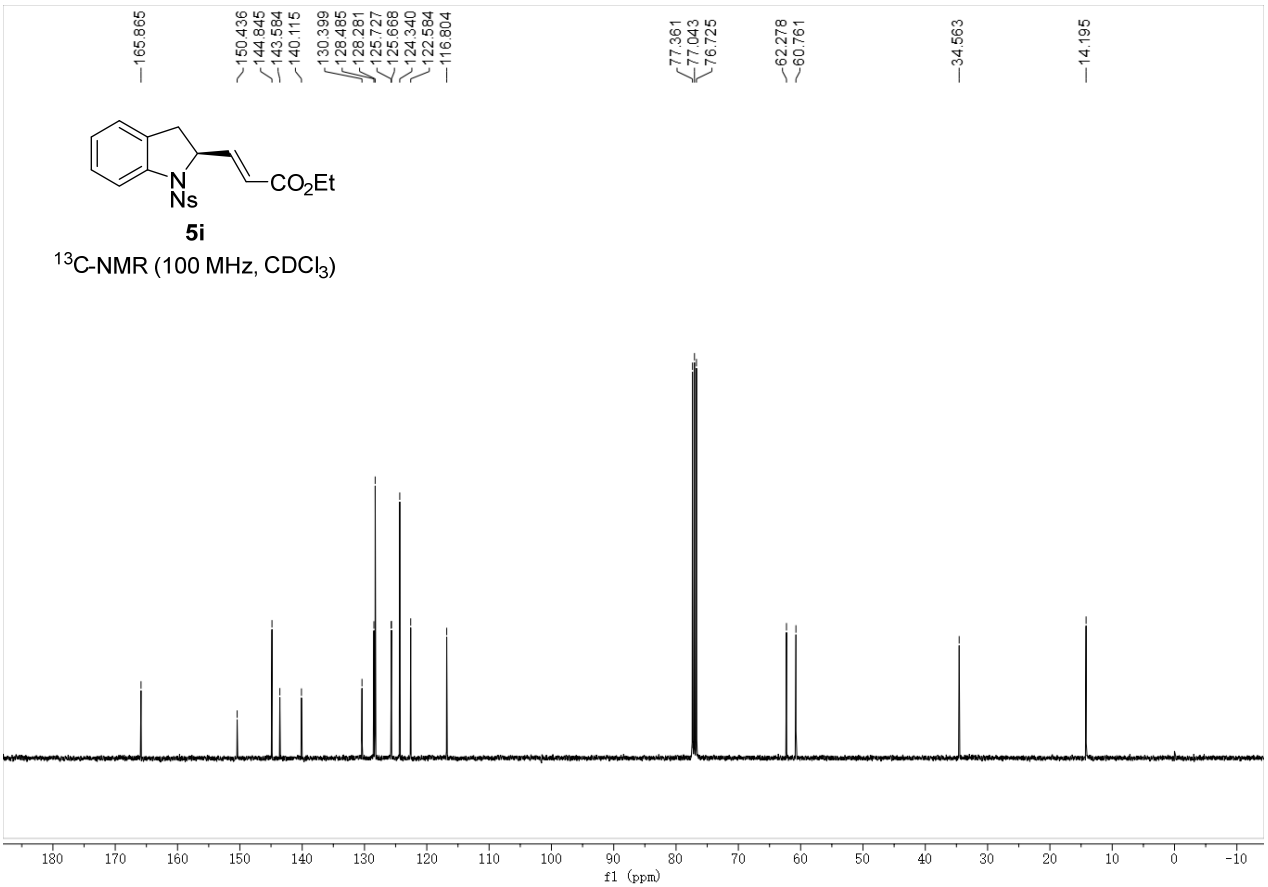


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.511	BBA	0.3225	1325.65137	62.66241	7.6134
2	17.004	BB	0.4636	1.60865e4	529.55481	92.3866



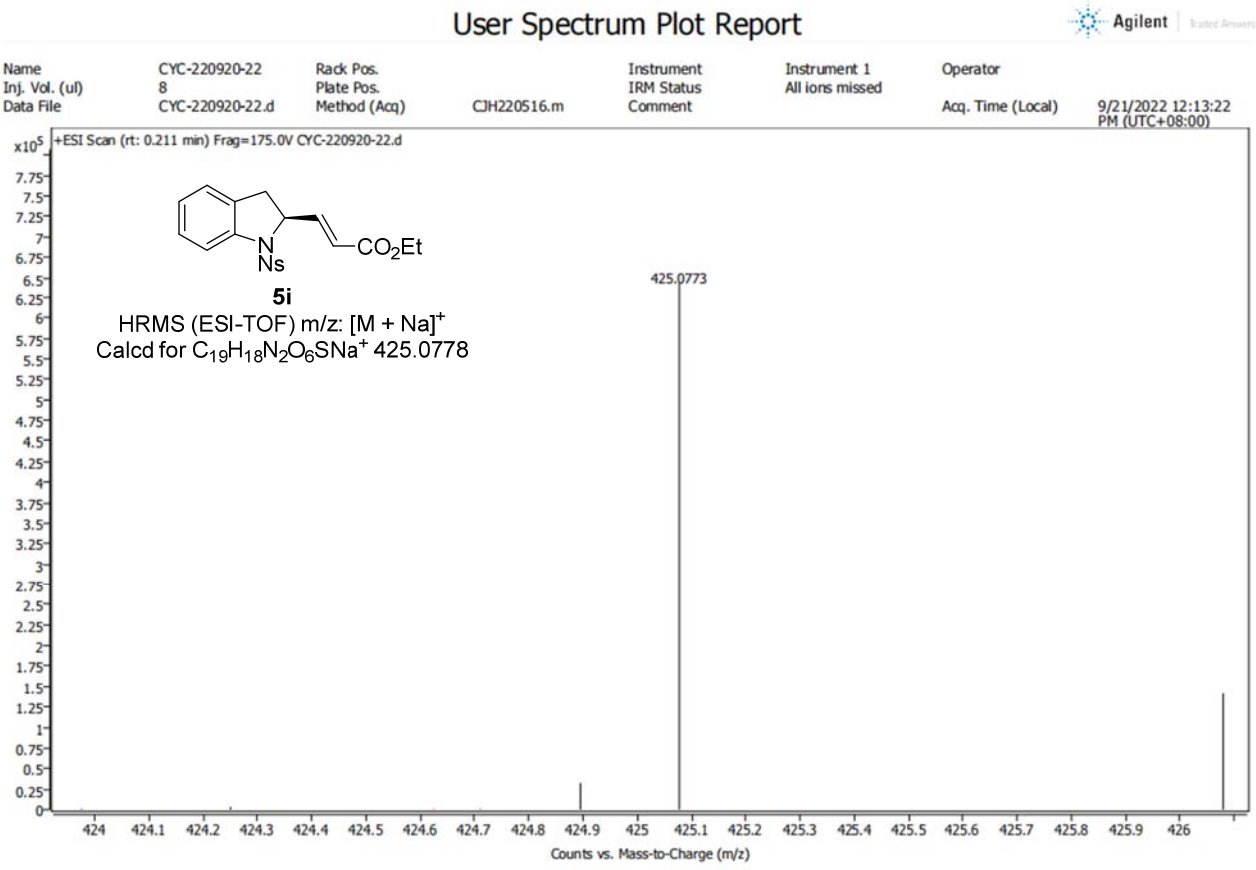
5i

^{1}H-NMR (400 MHz, $CDCl_3$)



5i

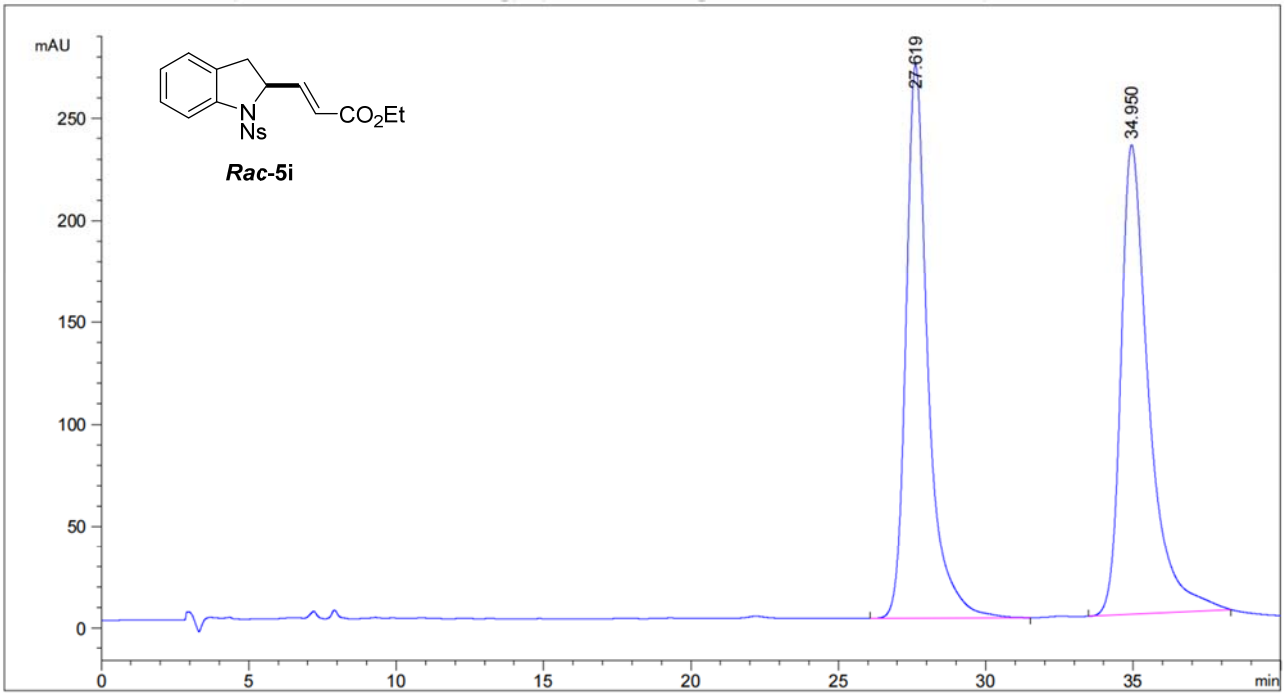
^{13}C-NMR (100 MHz, $CDCl_3$)



5i

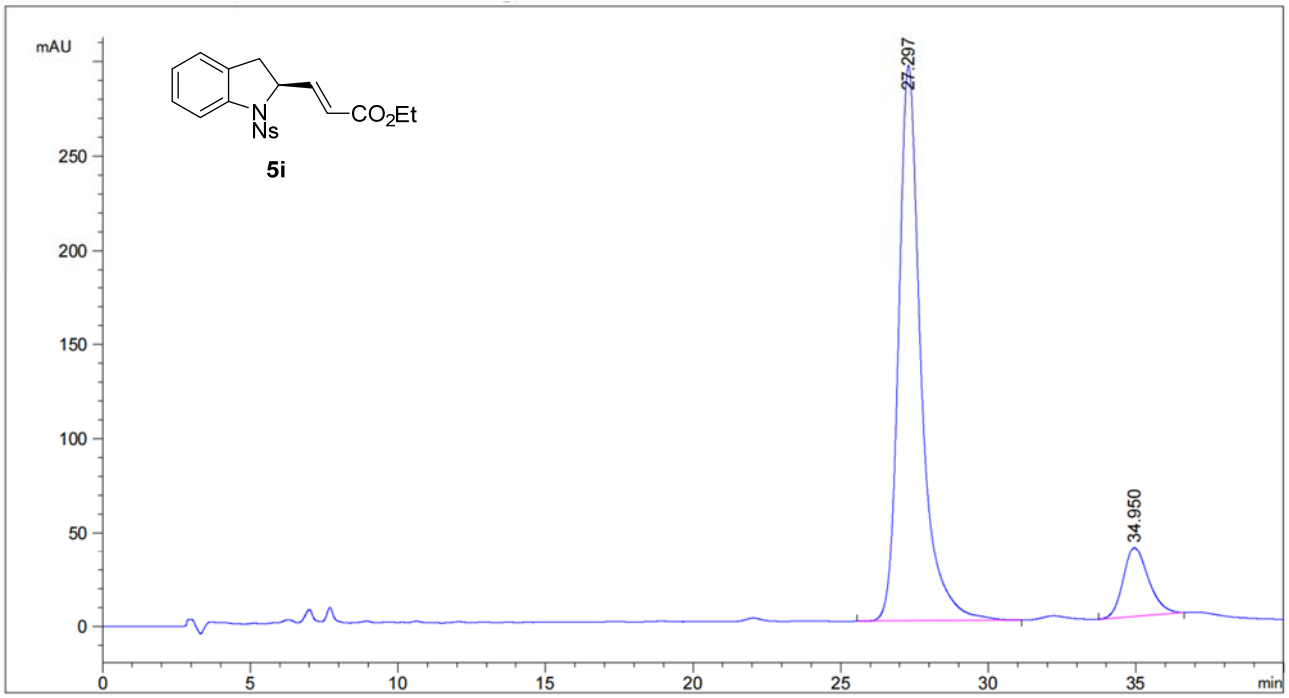
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{19}H_{18}N_2O_6SNa^+$ 425.0778



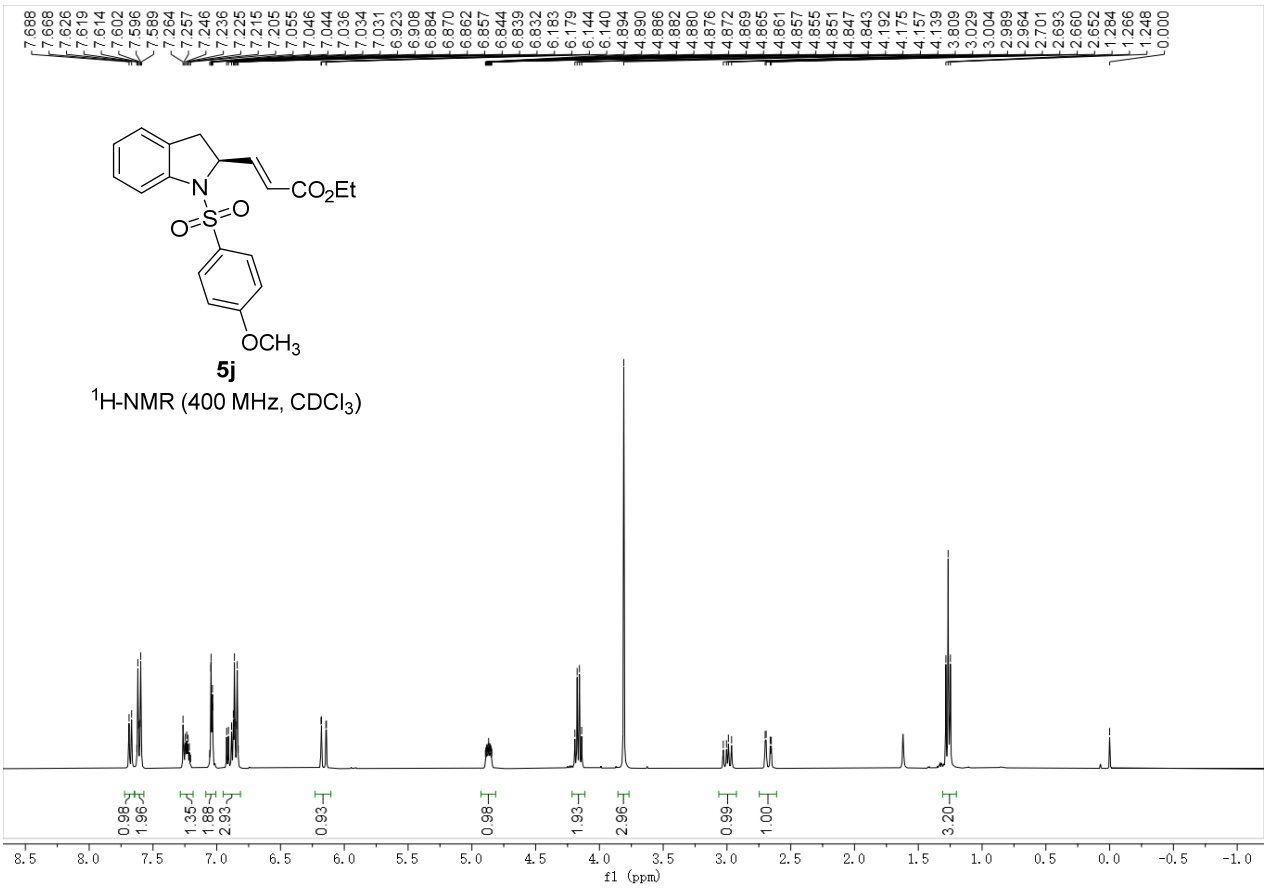
***Rac*-5i**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.619	BBA	0.7739	1.41571e4	271.70267	48.2393
2	34.950	BBA	0.9691	1.51906e4	230.70750	51.7607



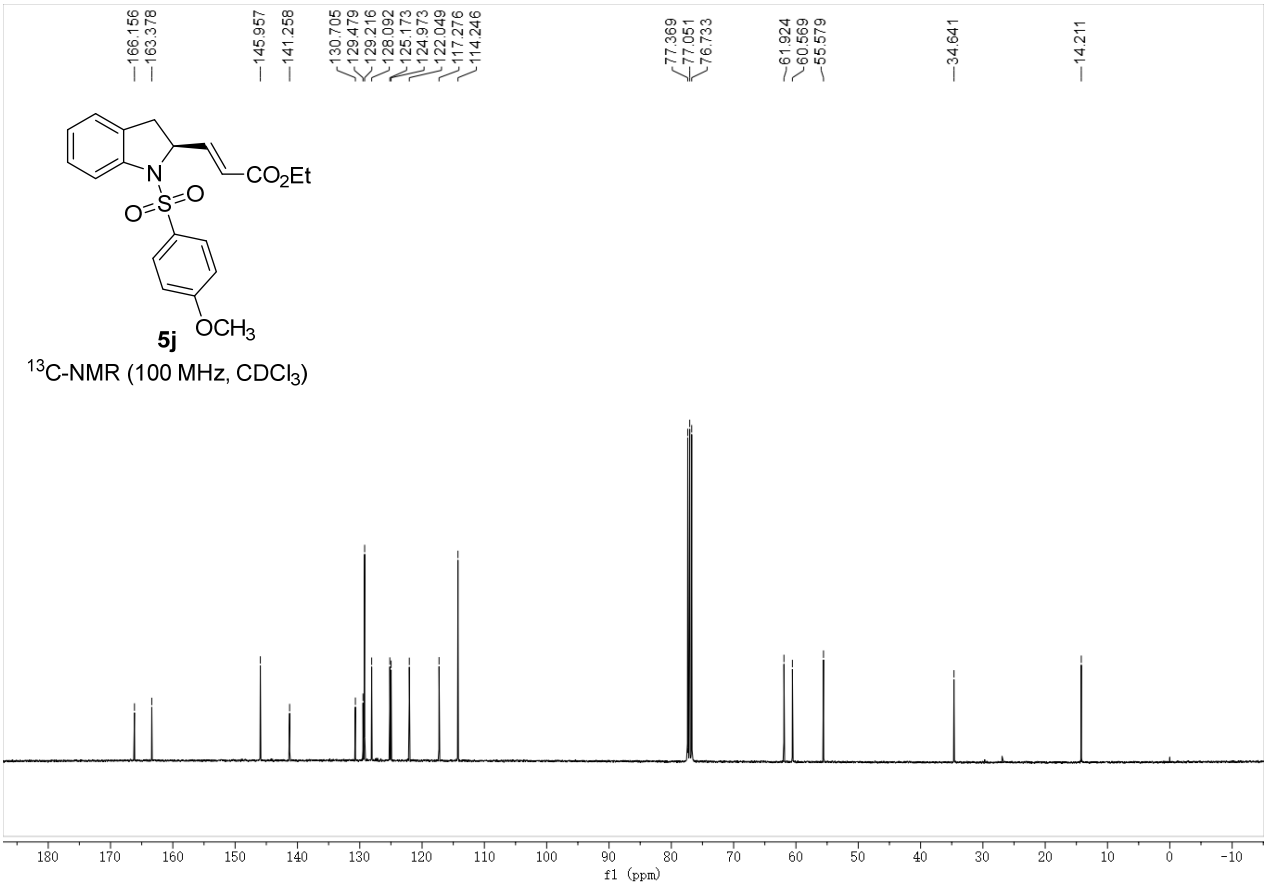
5i

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.297	BB	0.7849	1.55349e4	294.93097	87.6813
2	34.950	BB	0.9045	2182.55542	36.87736	12.3187



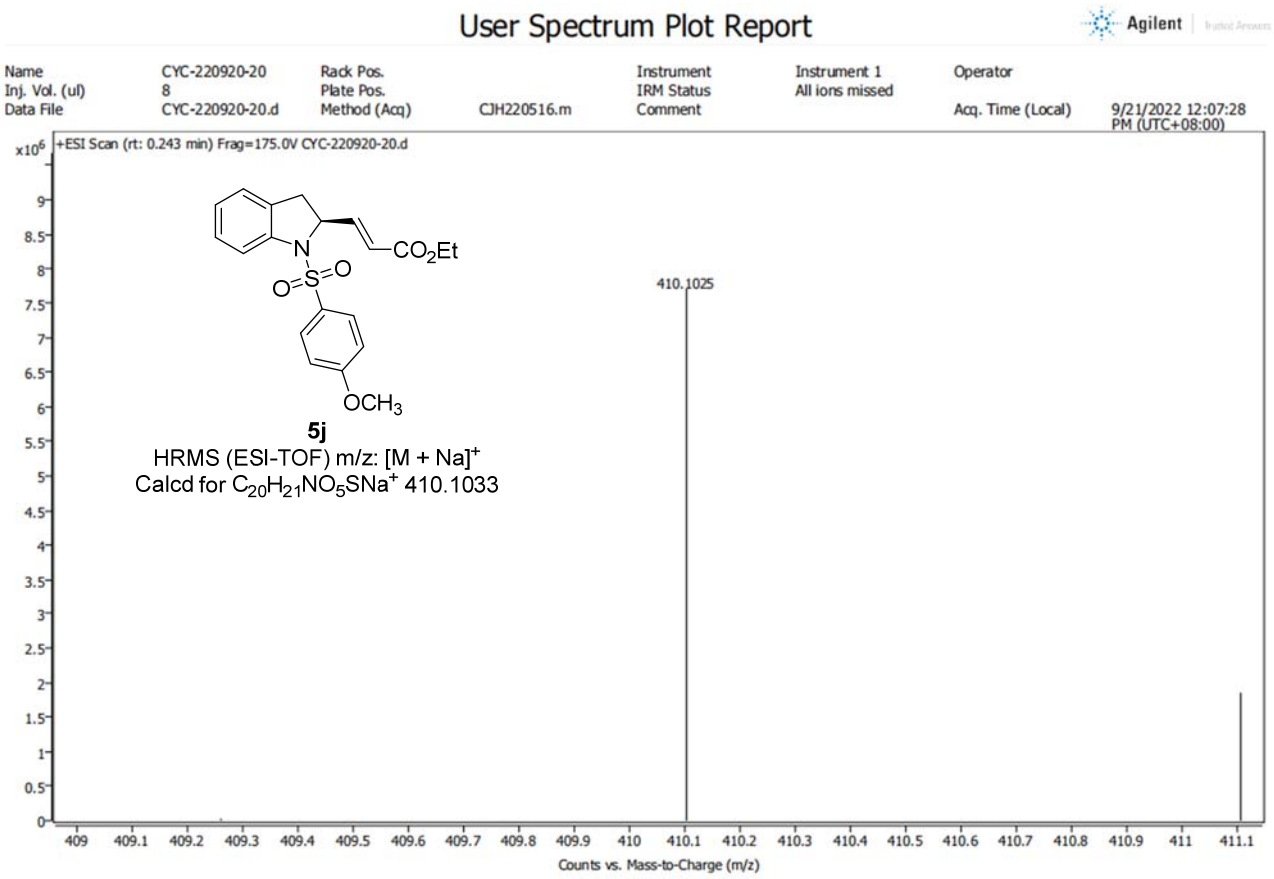
5j

^{1}H-NMR (400 MHz, $CDCl_3$)



5j

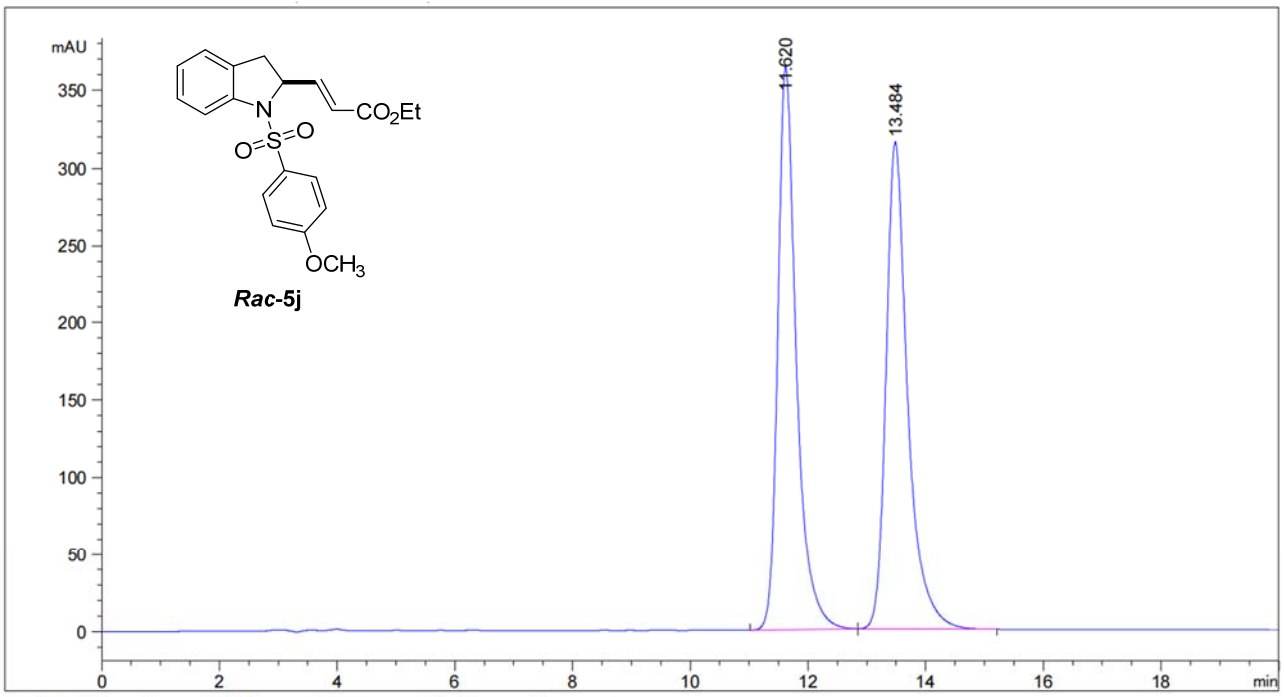
^{13}C-NMR (100 MHz, $CDCl_3$)



5j

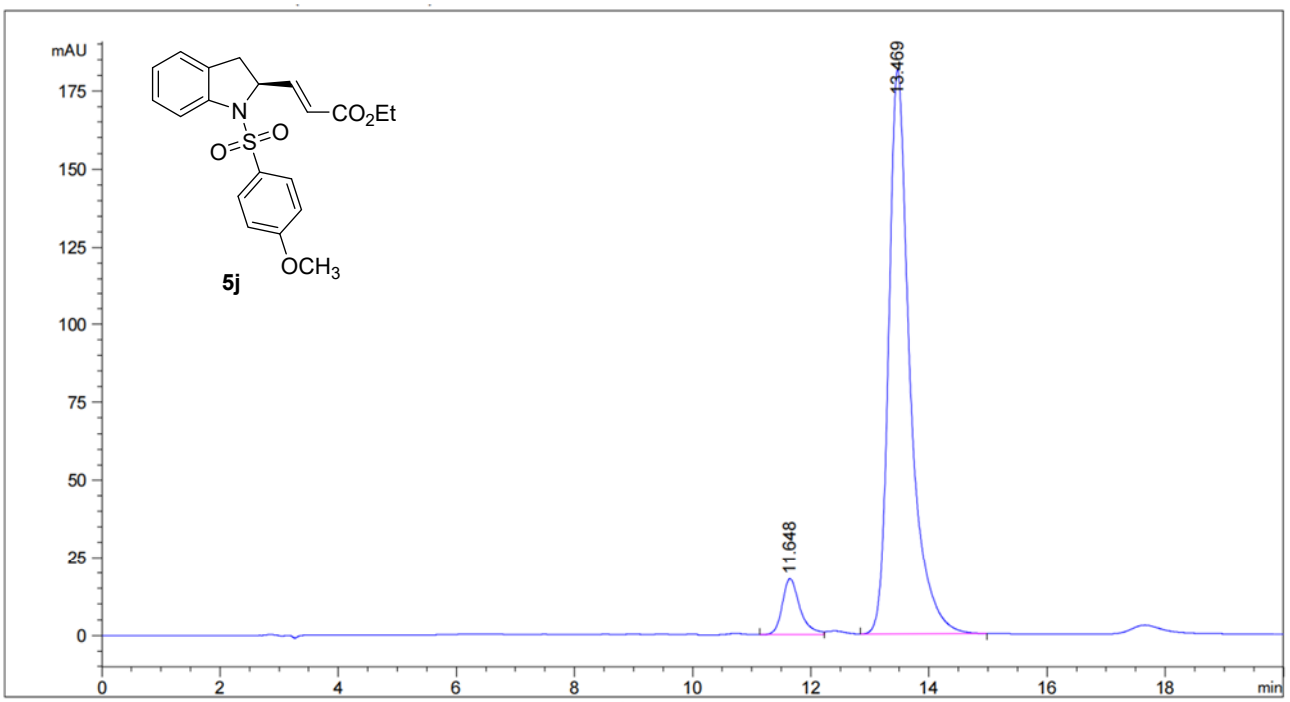
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{20}H_{21}NO_5SNa^+$ 410.1033



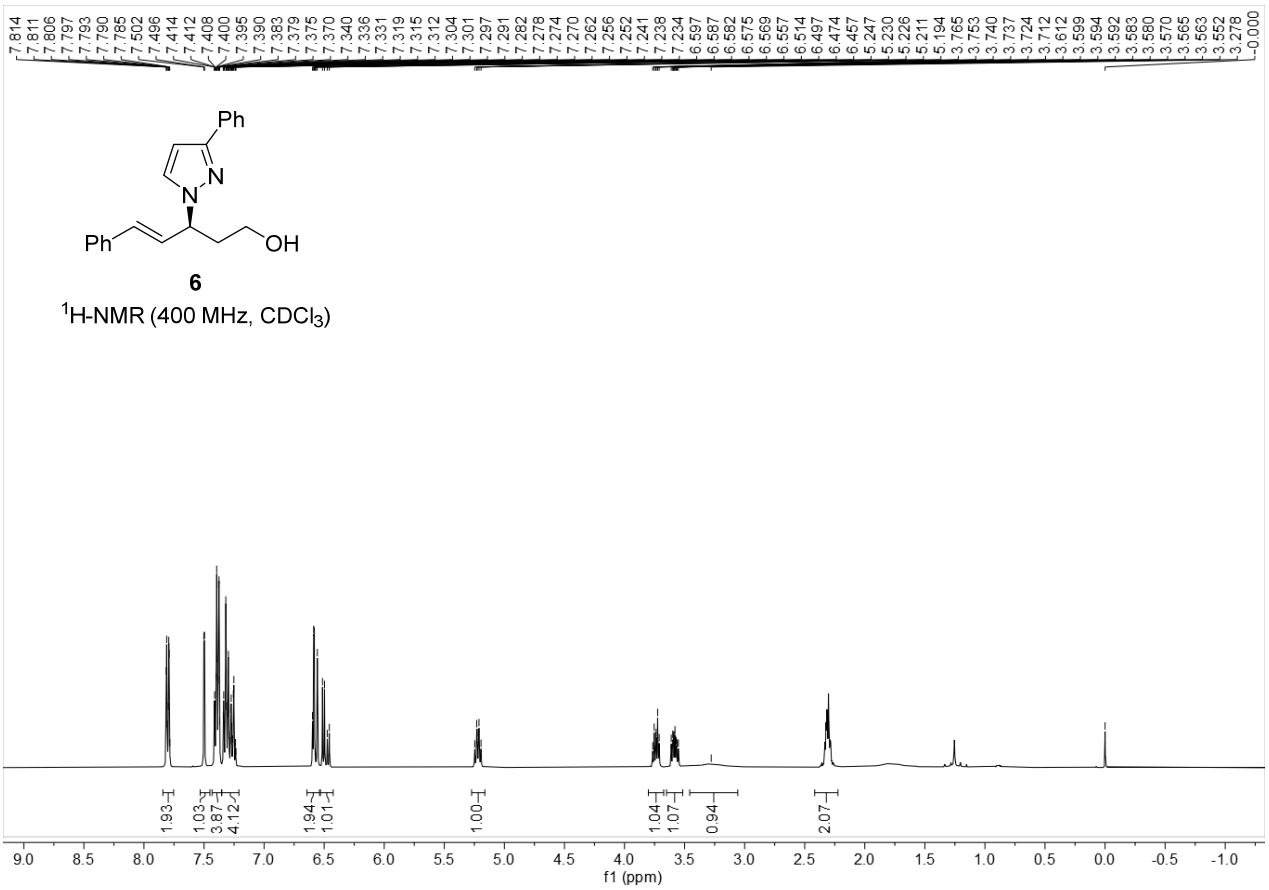
***Rac*-5j**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.620	BB	0.3275	7995.81641	364.19144	49.7747
2	13.484	BBA	0.3834	8068.19092	314.89407	50.2253



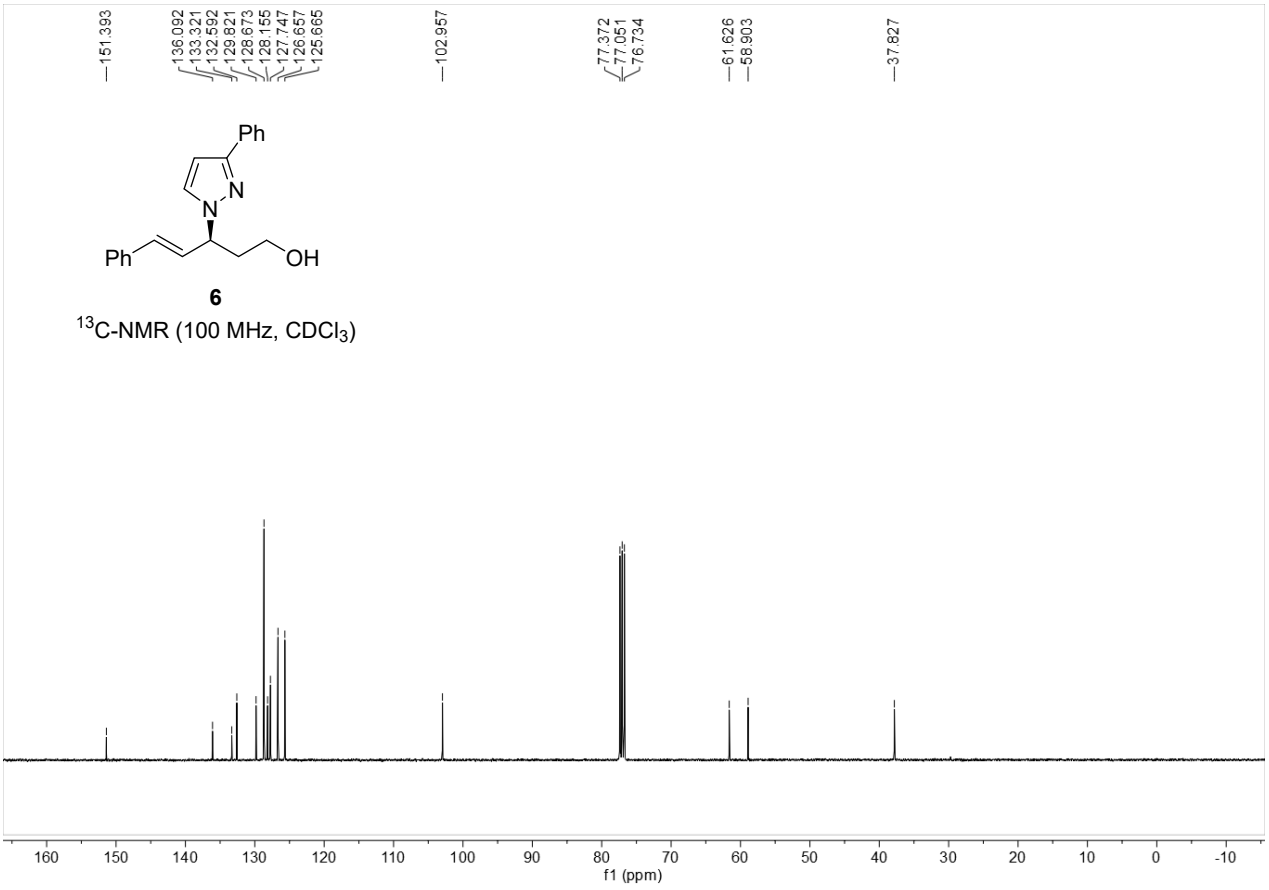
5j

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.648	BV	0.3084	368.57791	17.81234	7.5126
2	13.469	VB	0.3720	4537.56934	181.32797	92.4874



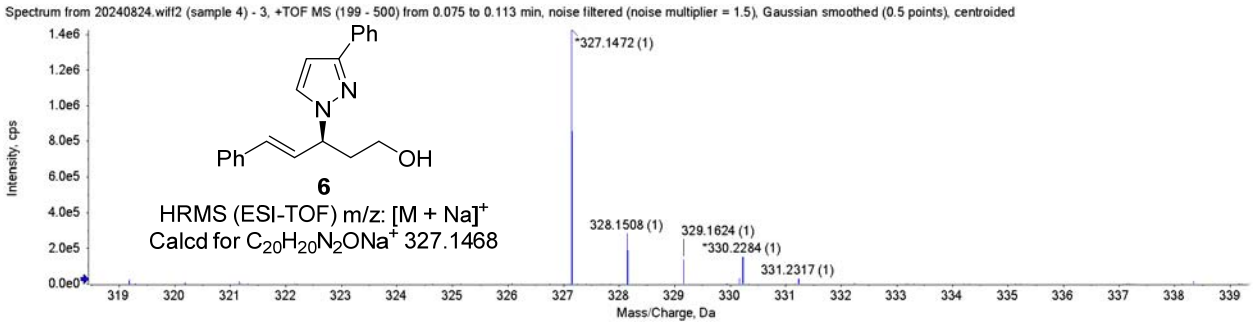
6

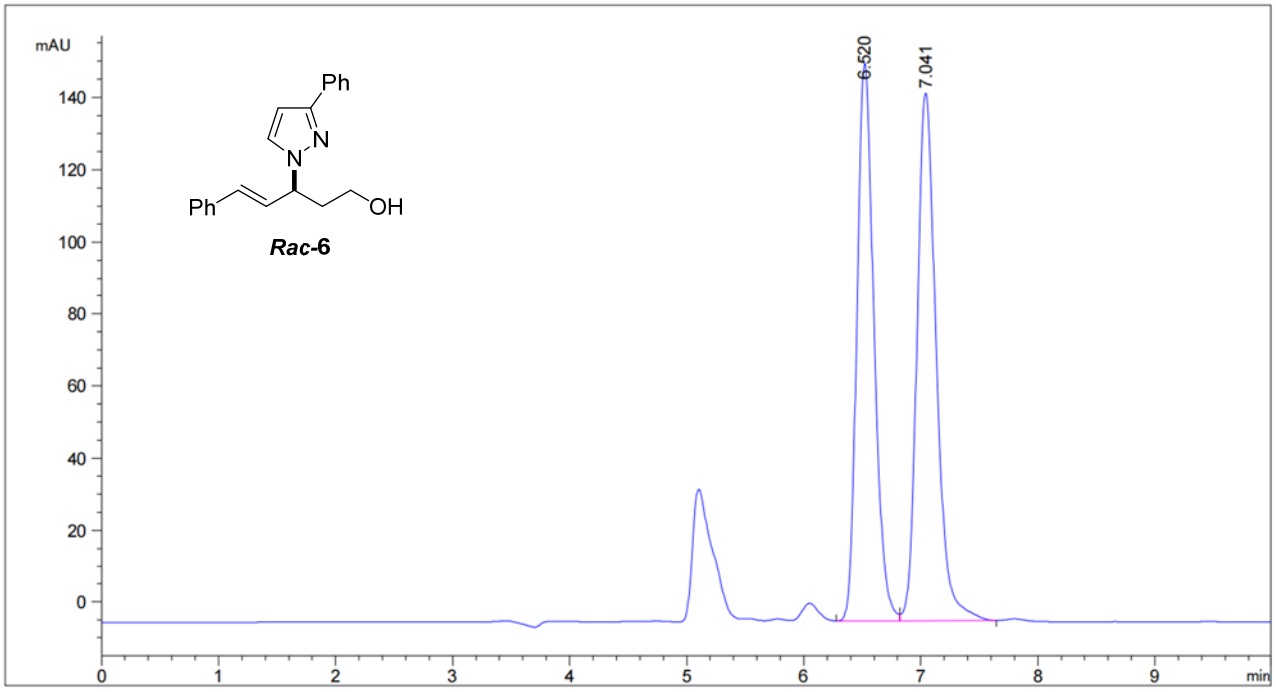
^{1}H-NMR (400 MHz, $CDCl_3$)



6

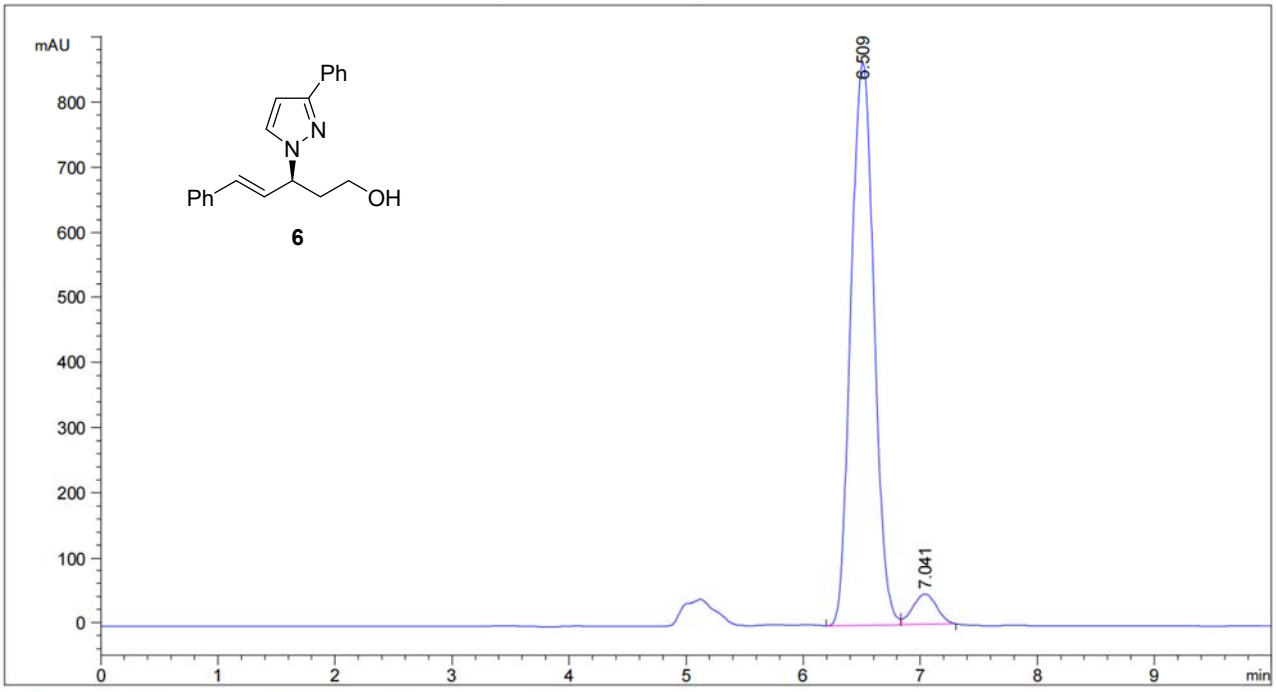
^{13}C-NMR (100 MHz, $CDCl_3$)


Spectrum from 20240824.wiff2 (sample 4) - 3, +TOF MS (199 - 500) from 0.075 to 0.113 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points), centroided
Intensity, cps
Mass/Charge, Da
*327.1472 (1)
328.1508 (1)
329.1624 (1)
*330.2284 (1)
331.2317 (1)
Ph
N
N
Ph
OH
6
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C20H20N2ONa+ 327.1468



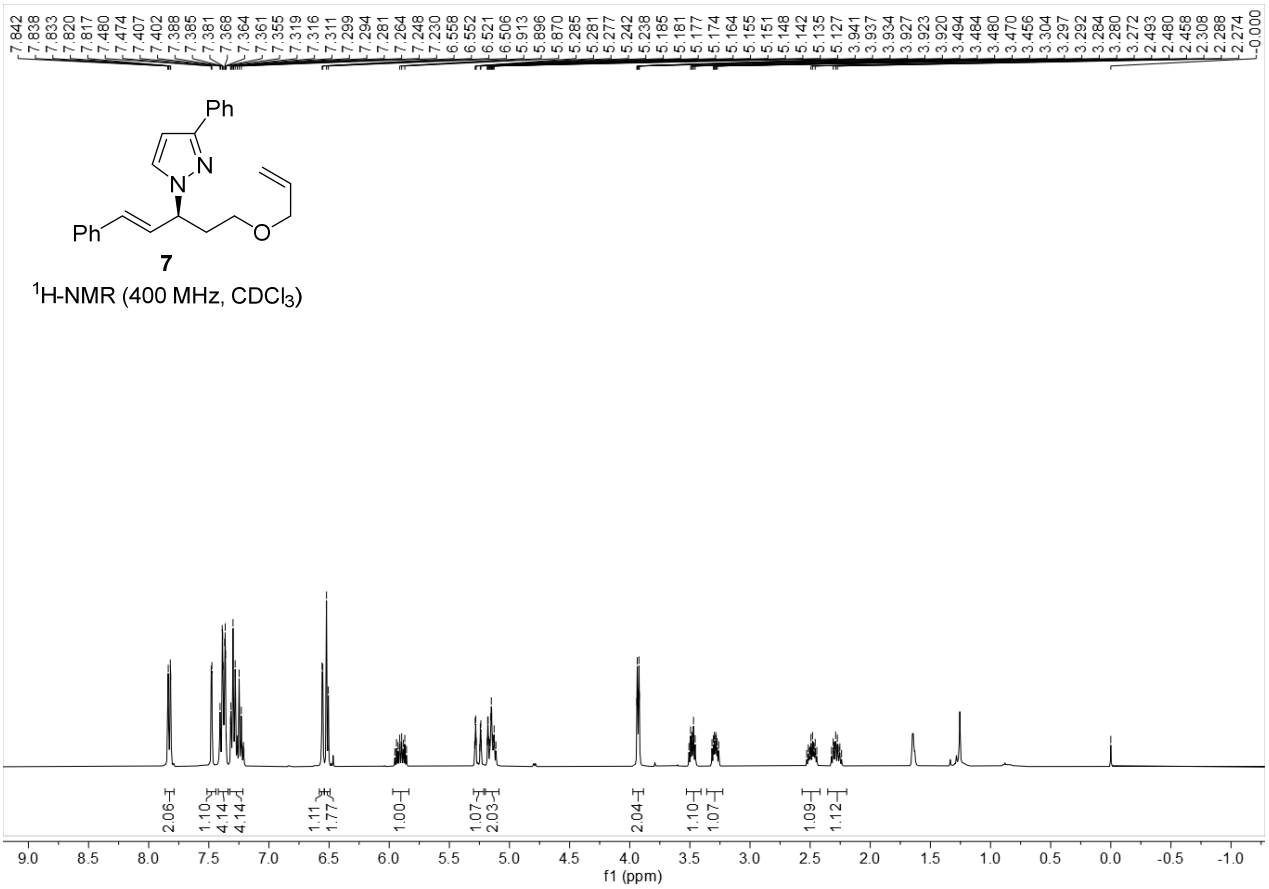
***Rac*-6**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.520	BV	0.1559	1565.16736	154.65277	48.3200
2	7.041	VB	0.1756	1674.00317	146.44867	51.6800



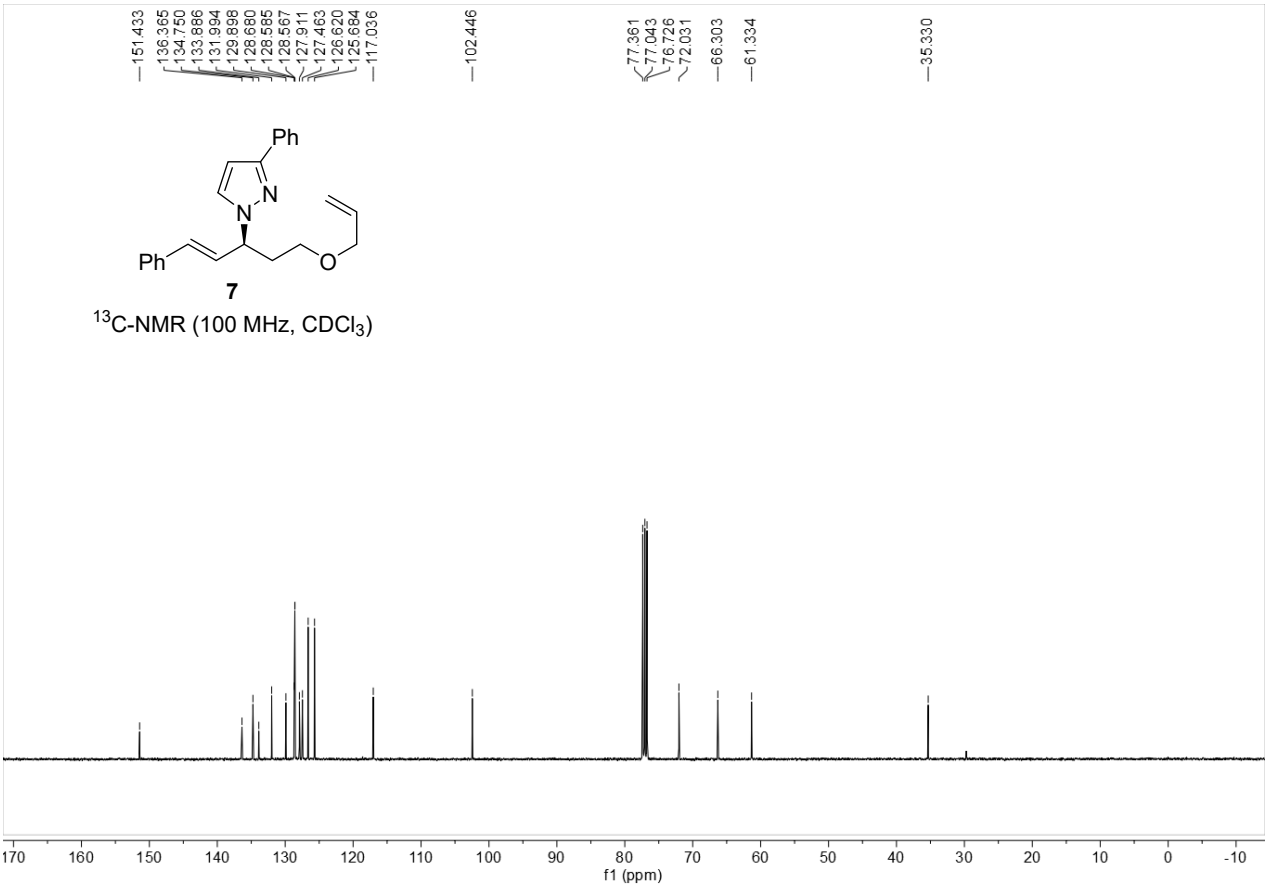
6

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.509	BV	0.2213	1.18438e4	862.65228	94.7209
2	7.041	VBA	0.2255	660.09924	46.43443	5.2791



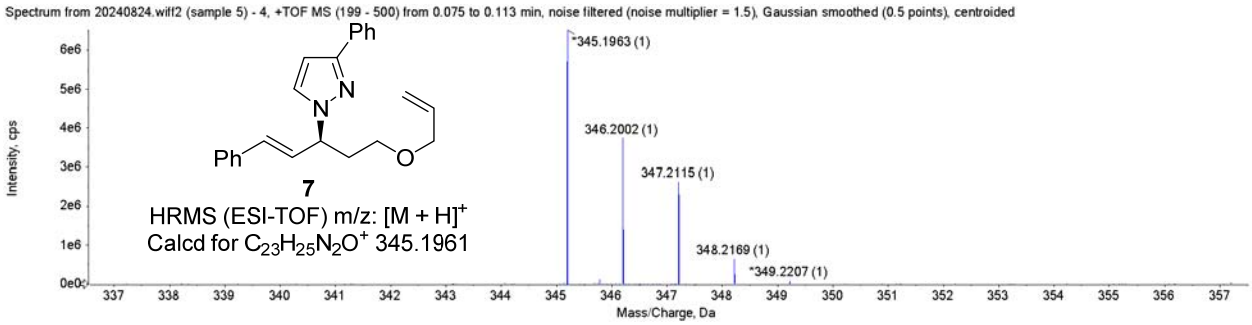
7

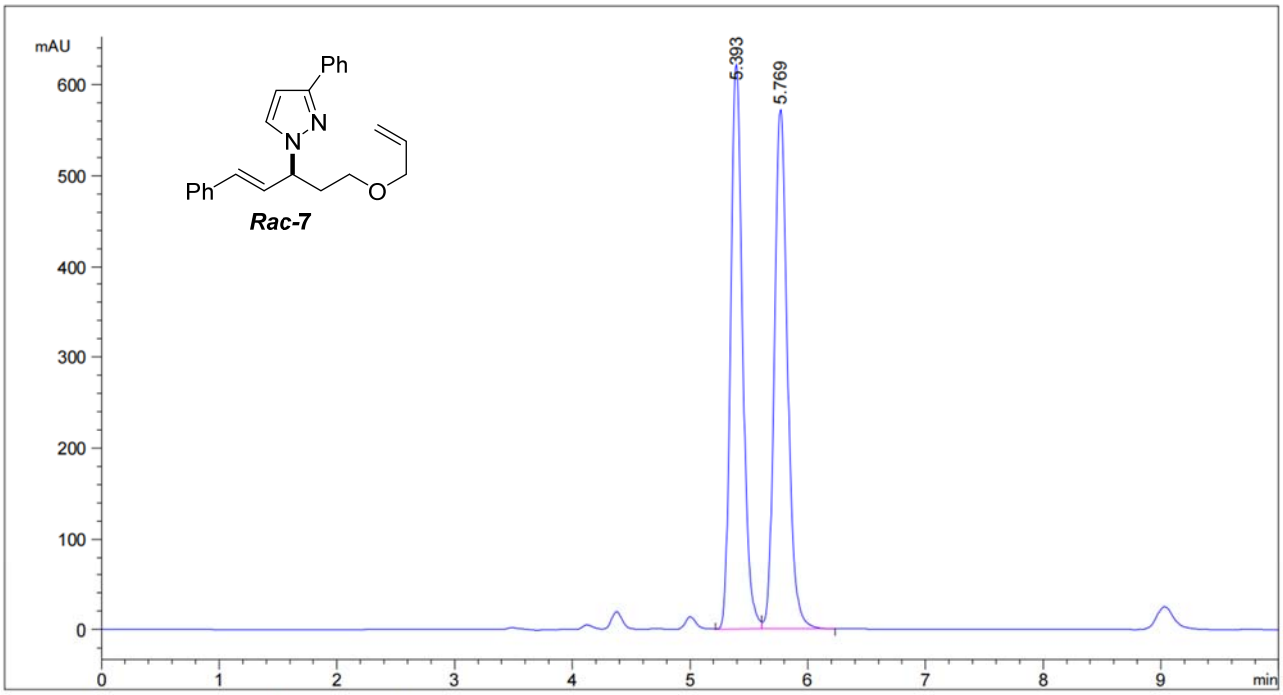
^{1}H-NMR (400 MHz, $CDCl_3$)



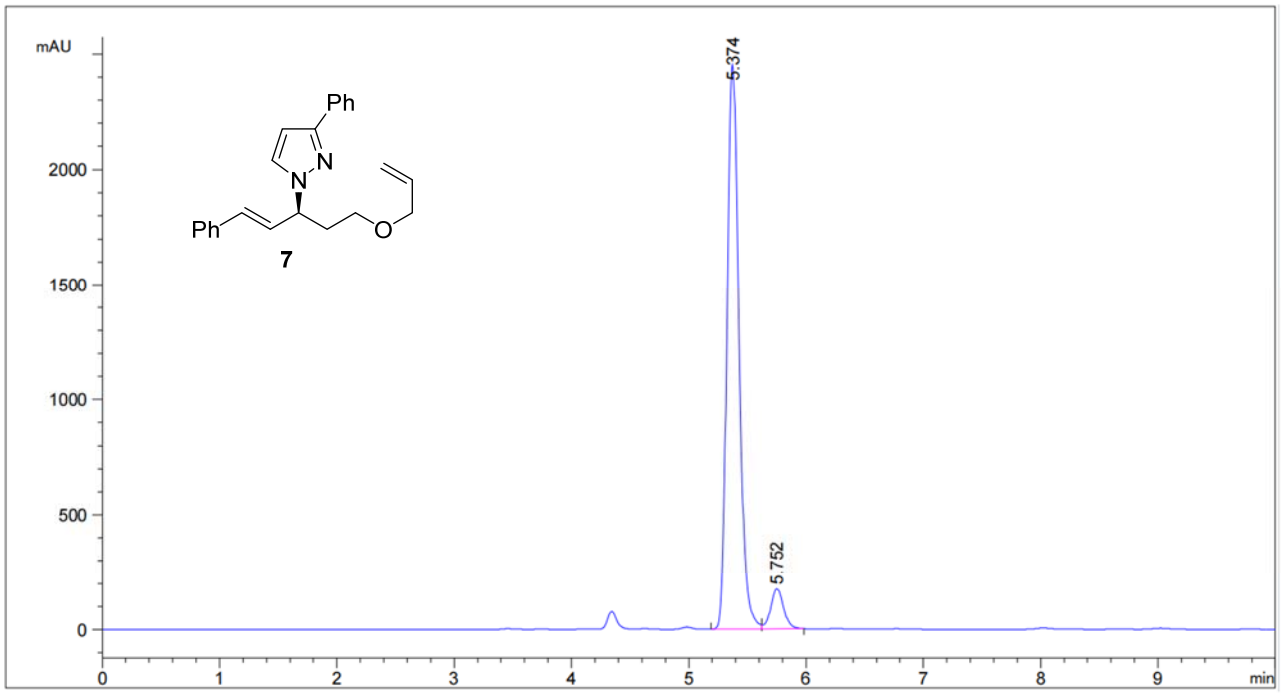
7

^{13}C-NMR (100 MHz, $CDCl_3$)

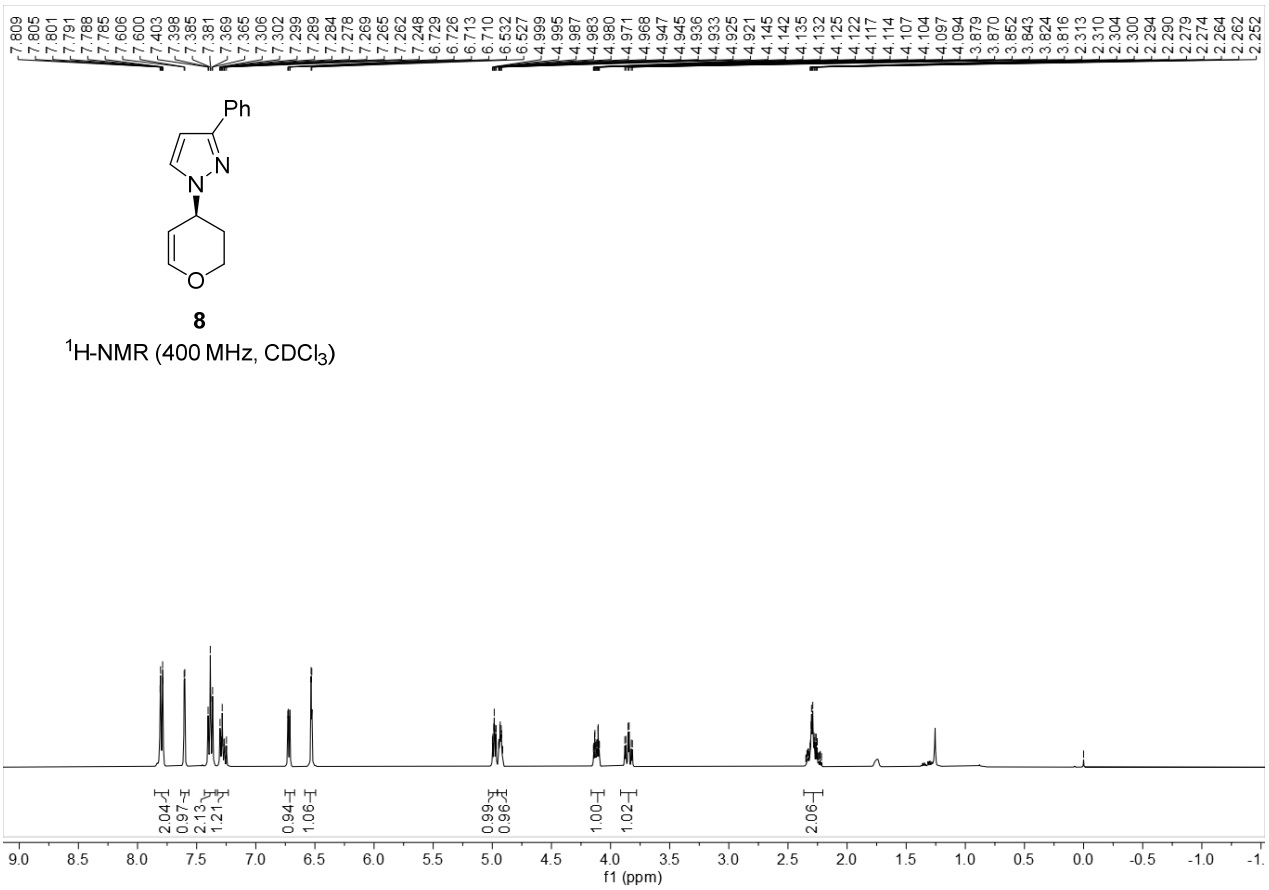

Spectrum from 20240824.wiff2 (sample 5) - 4, +TOF MS (199 - 500) from 0.075 to 0.113 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points), centroided
Intensity, cps
6e6
5e6
4e6
3e6
2e6
1e6
0e0
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
Mass/Charge, Da
345.1963 (1)
346.2002 (1)
347.2115 (1)
348.2169 (1)
349.2207 (1)
Ph
N
N
Ph
O
7
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C23H25N2O+ 345.1961



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.393	BV	0.1118	4399.40332	620.64410	49.7210
2	5.769	VBA	0.1228	4448.76953	571.74030	50.2790

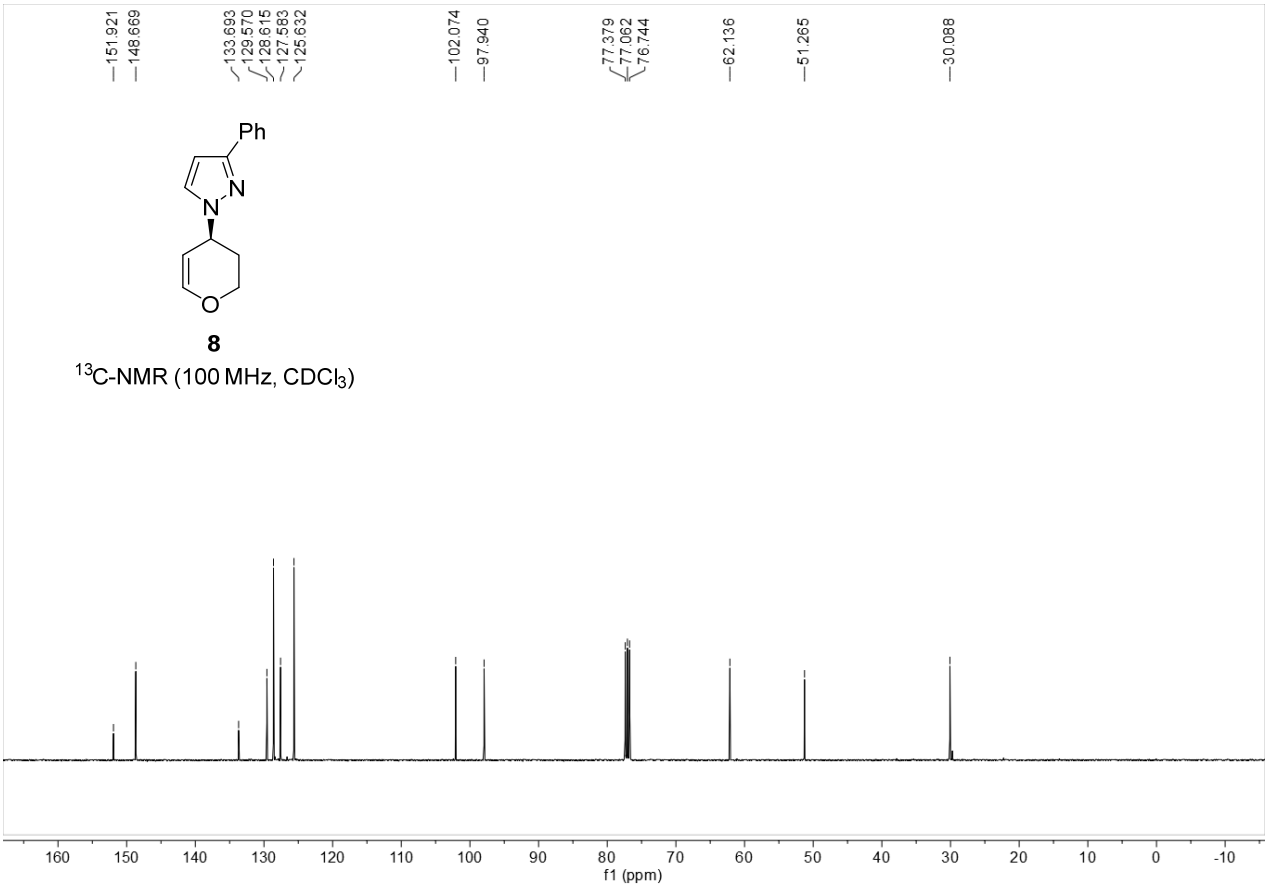


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.374	BV	0.1123	1.74606e4	2450.44214	92.8866
2	5.752	VBA	0.1188	1337.15369	173.88777	7.1134



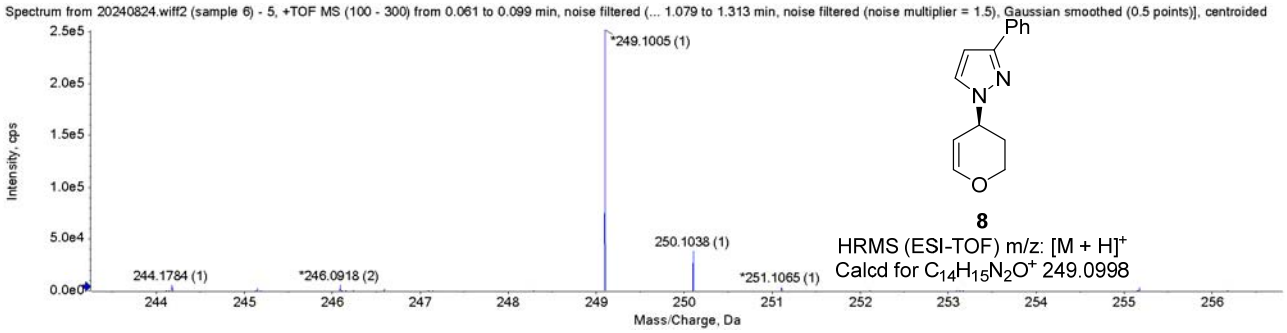
8

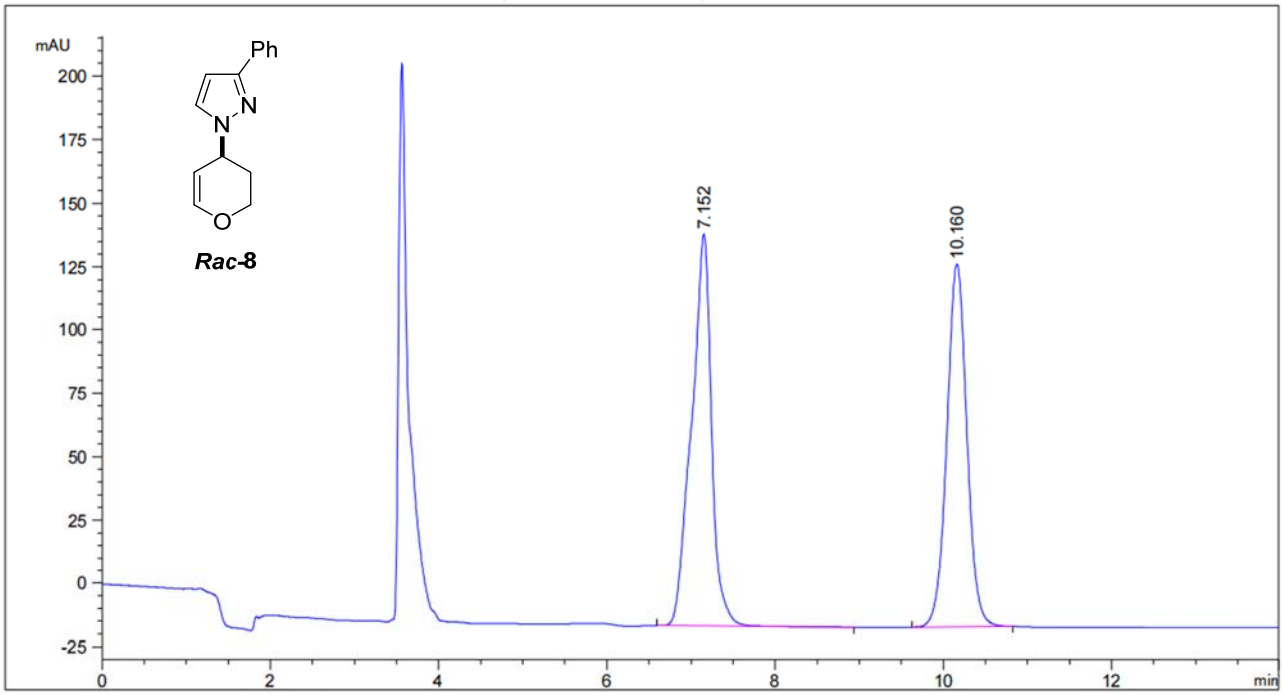
^{1}H-NMR (400 MHz, $CDCl_3$)



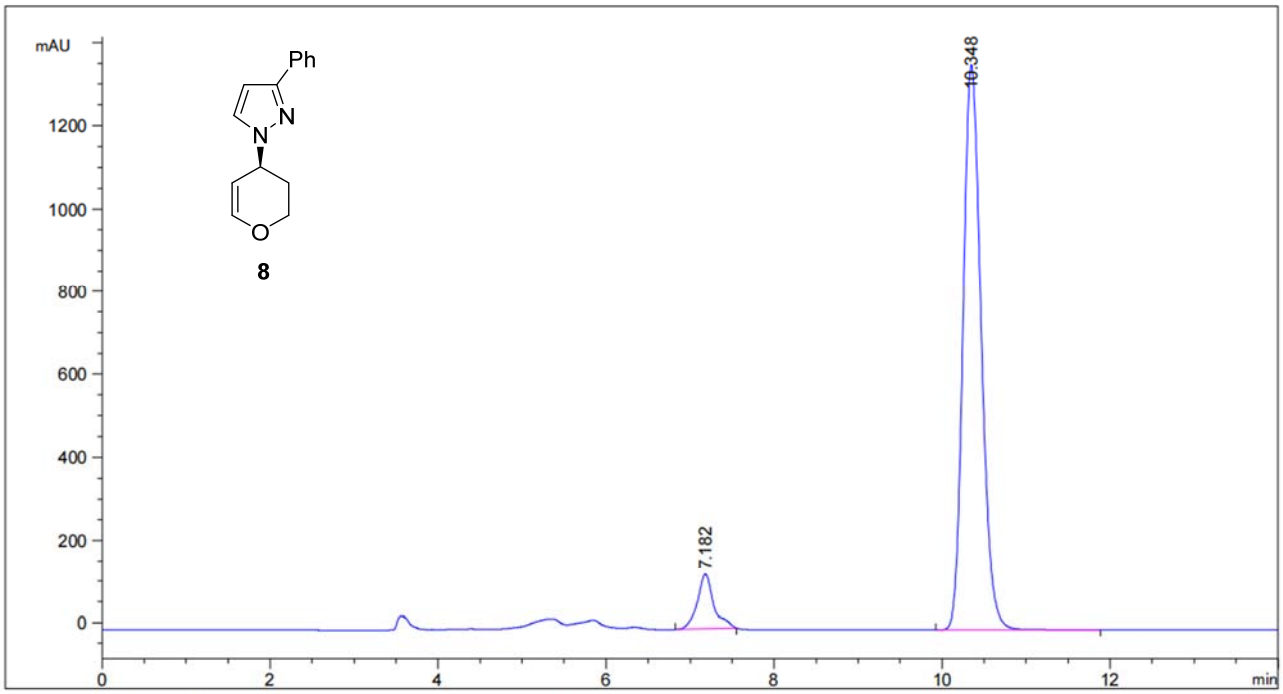
8

^{13}C-NMR (100 MHz, $CDCl_3$)

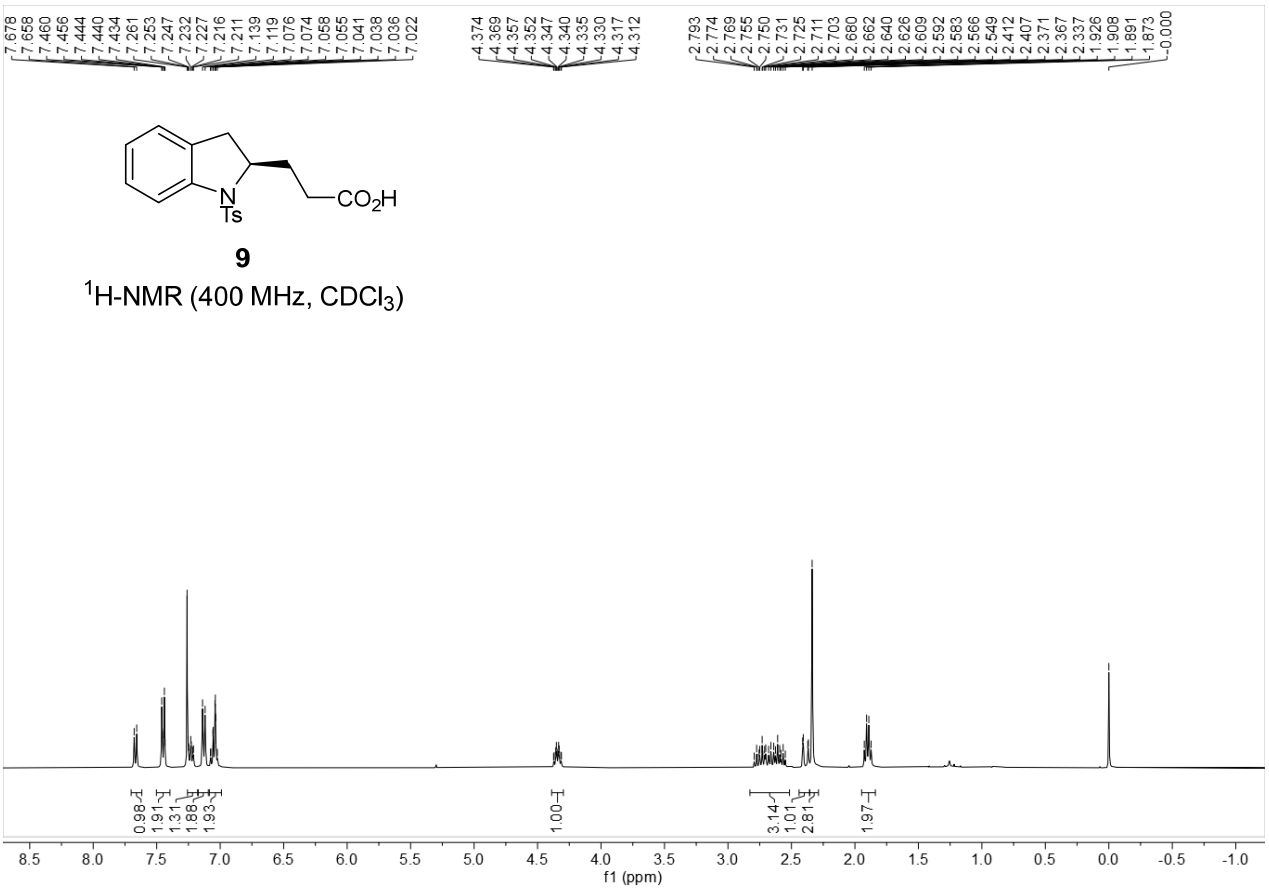

Spectrum from 20240824.wiff2 (sample 6) - 5, +TOF MS (100 - 300) from 0.061 to 0.099 min, noise filtered (... 1.079 to 1.313 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points)], centroided
Intensity, cps
2.5e5
2.0e5
1.5e5
1.0e5
5.0e4
0.0e0
*249.1005 (1)
250.1038 (1)
244.1784 (1)
*246.0918 (2)
*251.1065 (1)
244
245
246
247
248
249
250
251
252
253
254
255
256
Mass/Charge, Da
Ph
N
N
O
8
HRMS (ESI-TOF) m/z: [M + H]+
Calcd for C14H15N2O+ 249.0998



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.152	BB	0.2367	2560.12085	154.71696	51.9667
2	10.160	BBA	0.2567	2366.34644	143.28116	48.0333

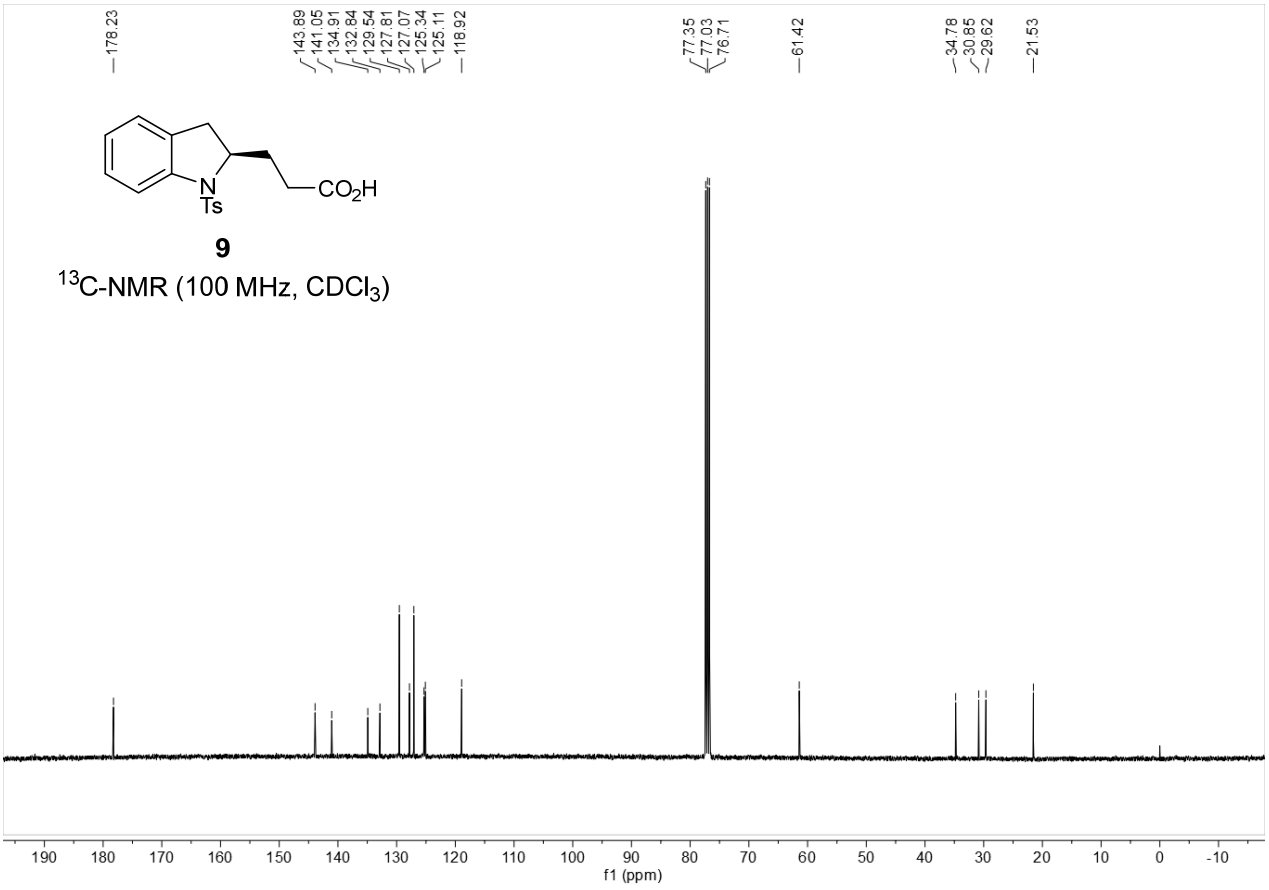


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.182	BBA	0.1996	1790.95618	131.56111	8.0944
2	10.348	BBA	0.2323	2.03348e4	1363.06482	91.9056



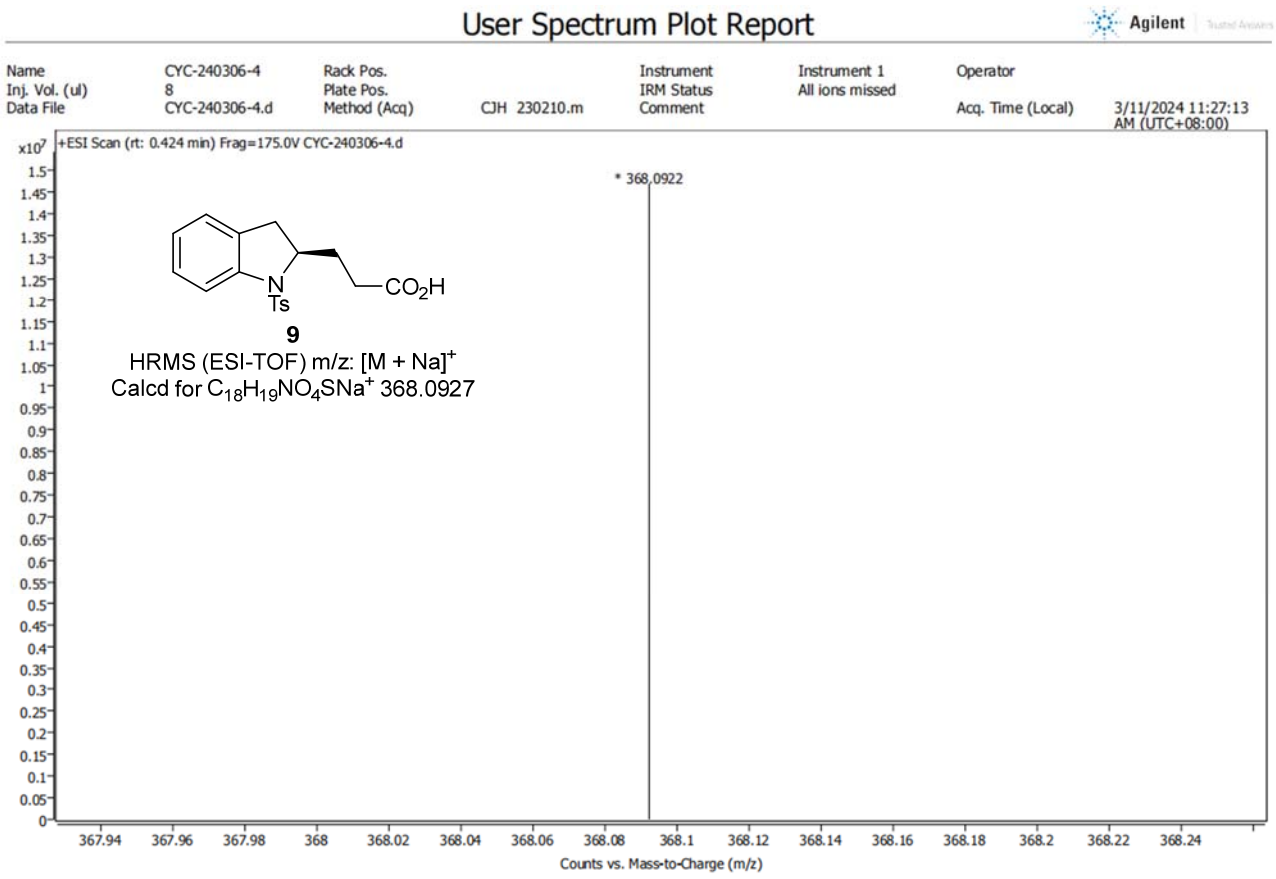
9

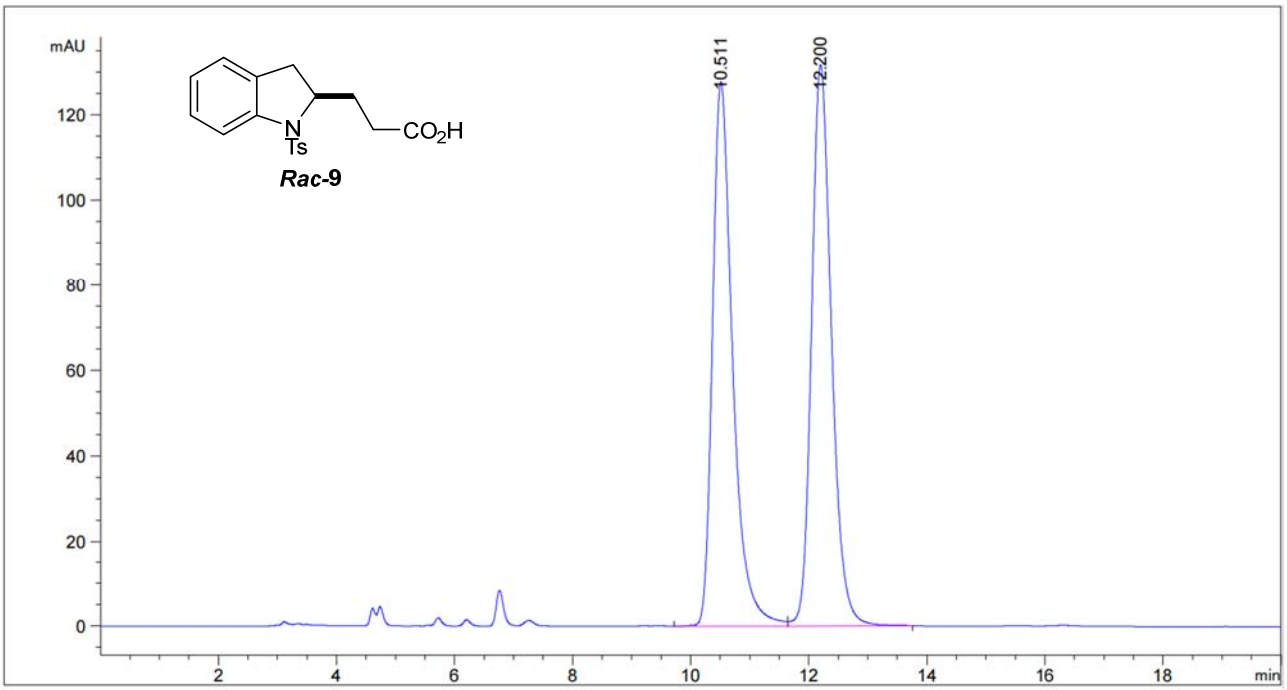
^{1}H-NMR (400 MHz, $CDCl_3$)



9

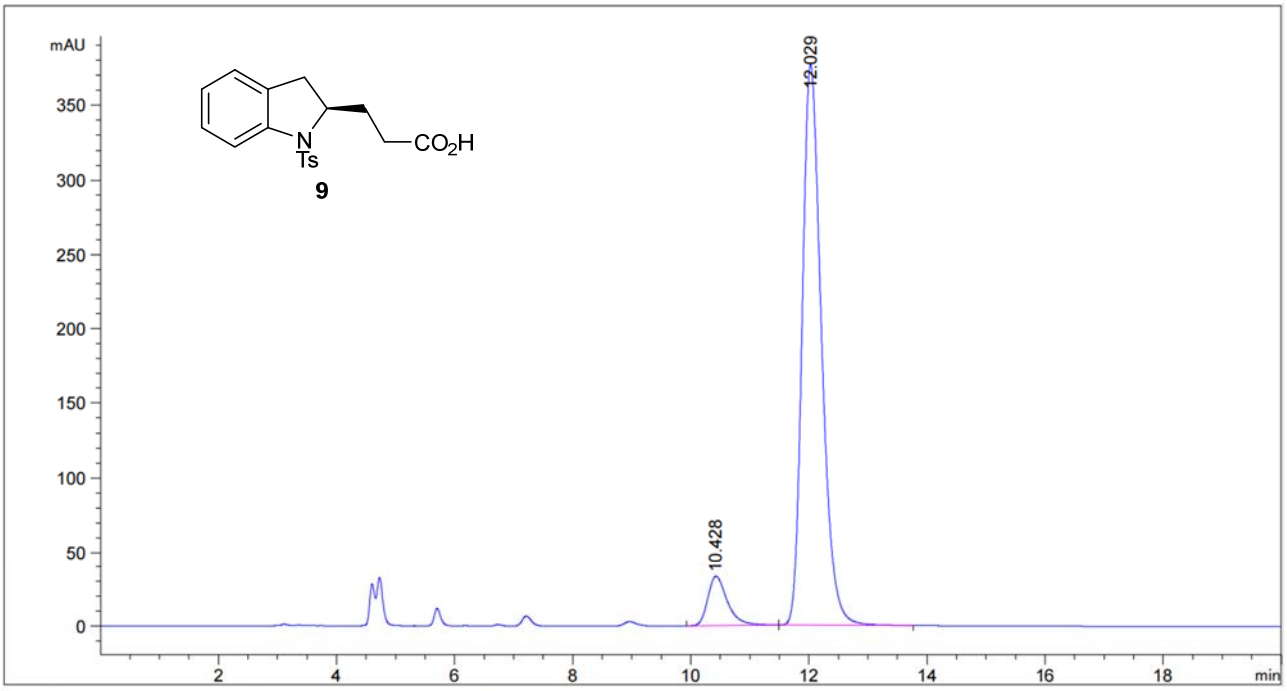
^{13}C-NMR (100 MHz, $CDCl_3$)


User Spectrum Plot Report
Agilent
Name CYC-240306-4
Inj. Vol. (ul) 8
Data File CYC-240306-4.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:27:13 AM (UTC+08:00)
+ESI Scan (rt: 0.424 min) Frag=175.0V CYC-240306-4.d
x10^7
* 368.0922
N
Ts
CO2H
9
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C18H19NO4SNa+ 368.0927
Counts vs. Mass-to-Charge (m/z)



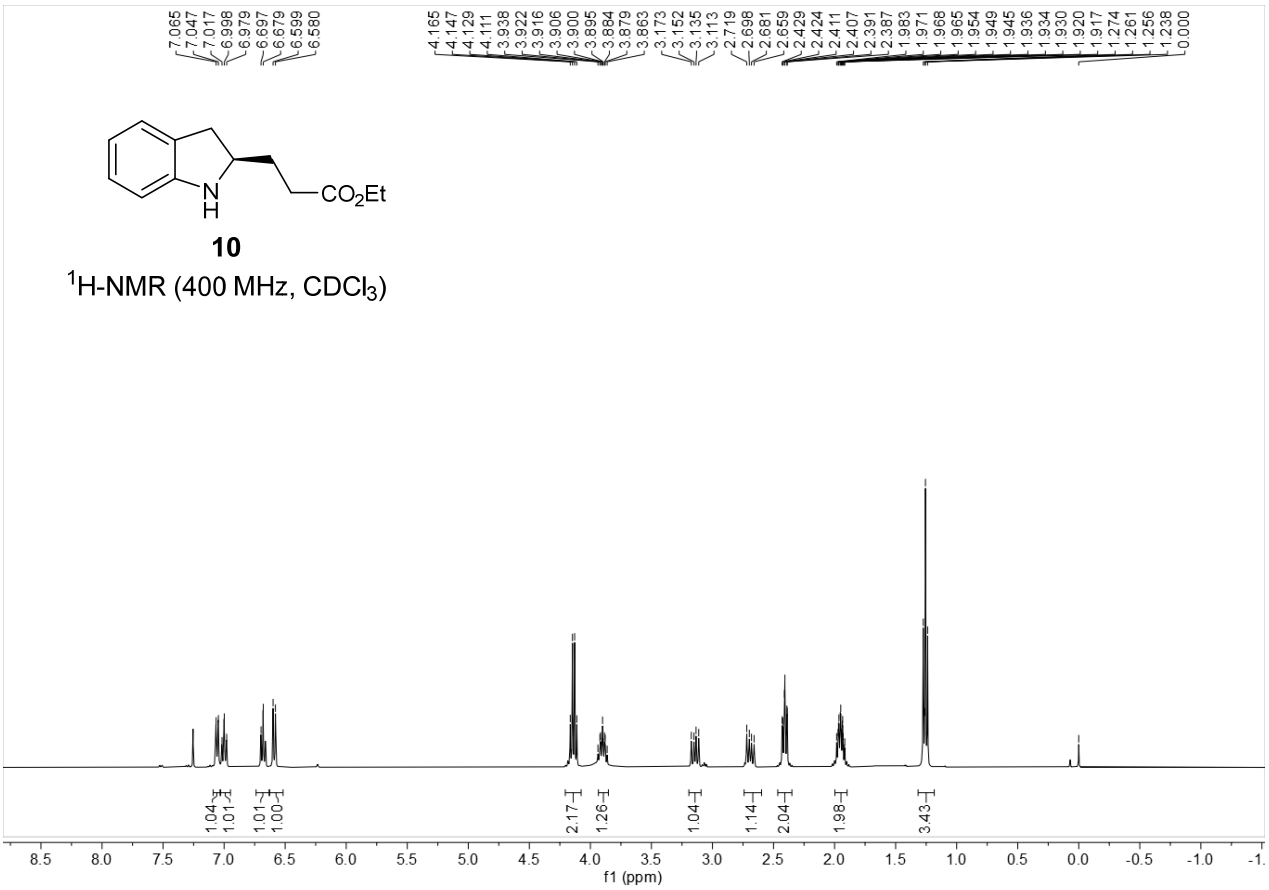
***Rac*-9**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.511	BV	0.3574	3027.03516	127.75760	49.4707
2	12.200	VBA	0.3589	3091.80981	131.70956	50.5293



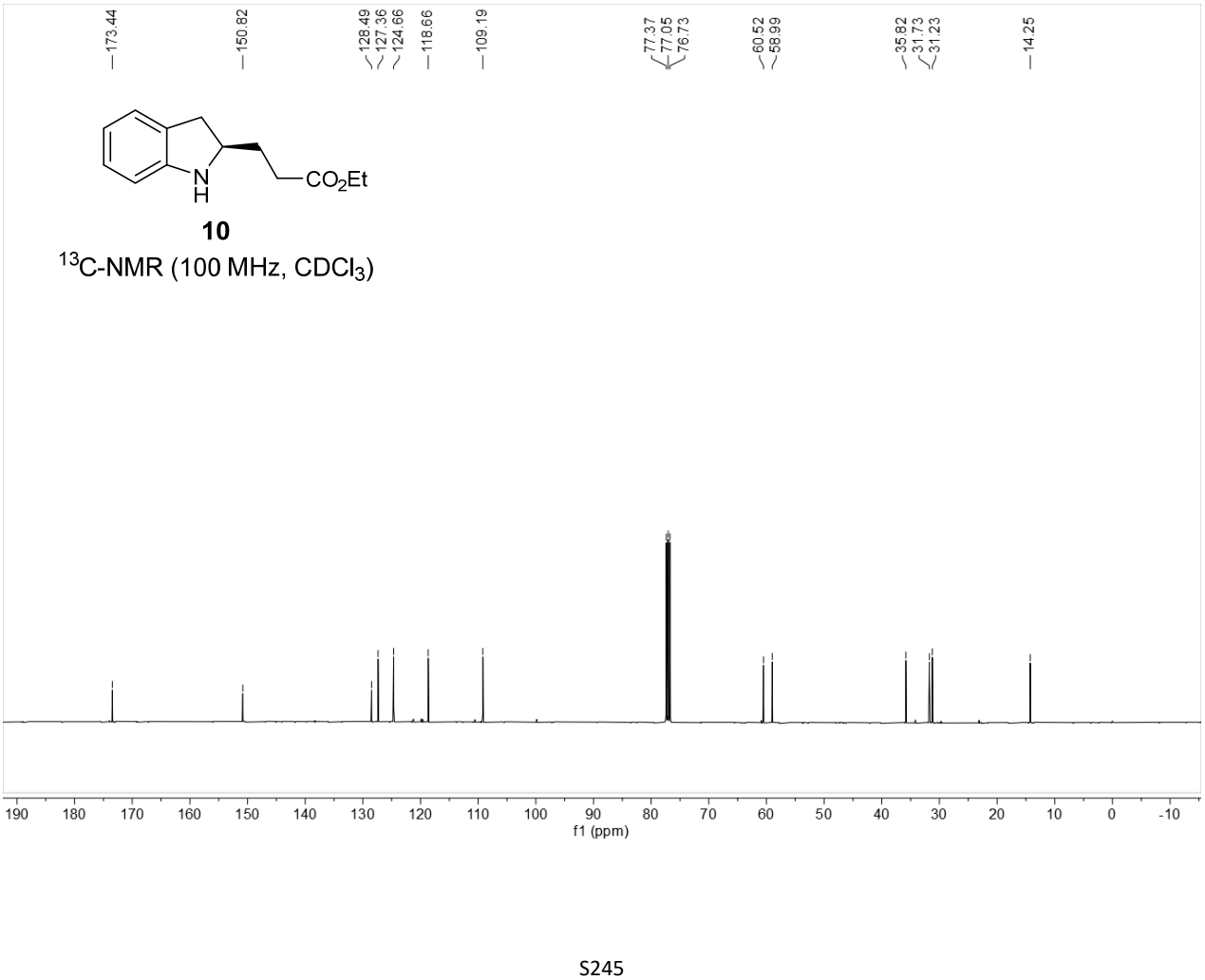
9

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.428	BB	0.3479	762.60590	33.21193	8.2096
2	12.029	BBA	0.3470	8526.56152	376.86188	91.7904



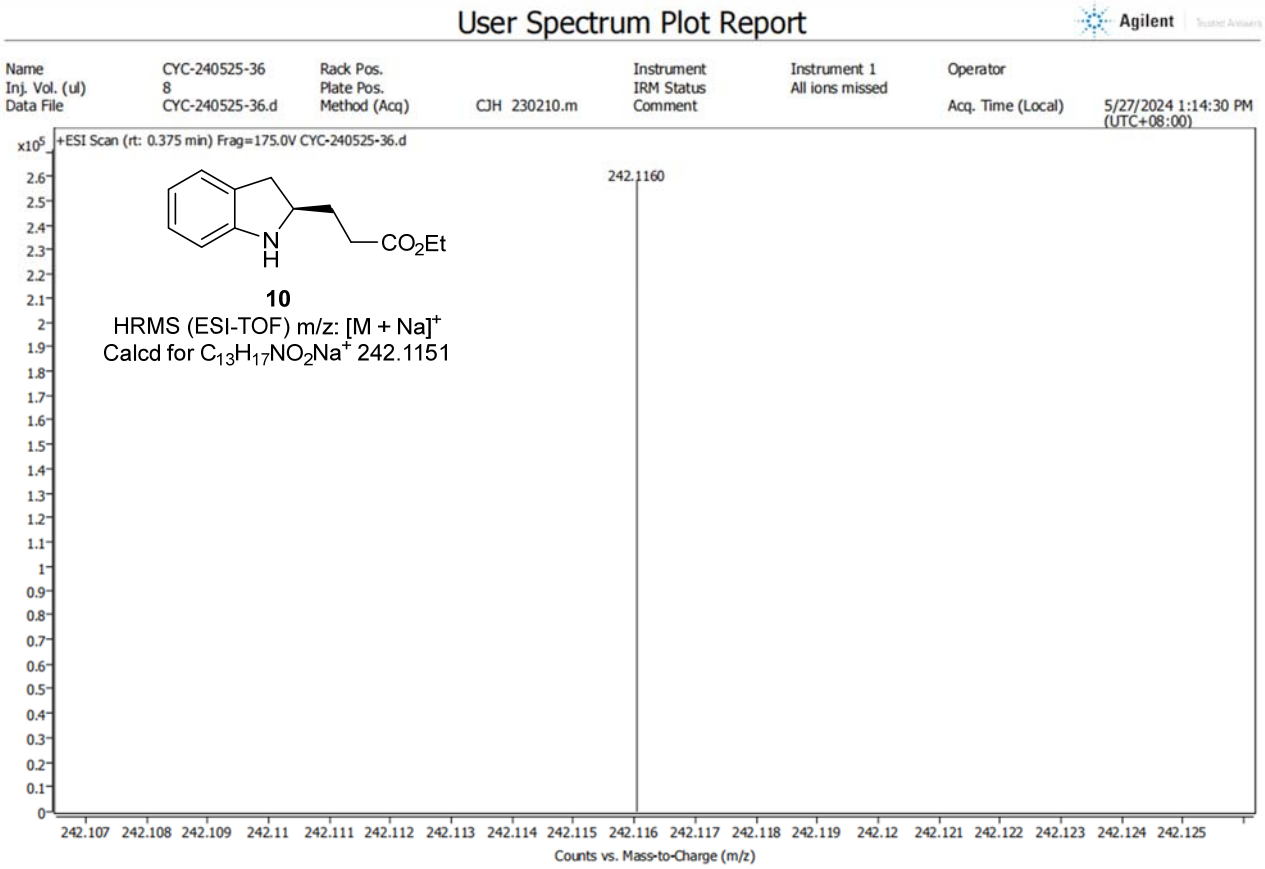
10

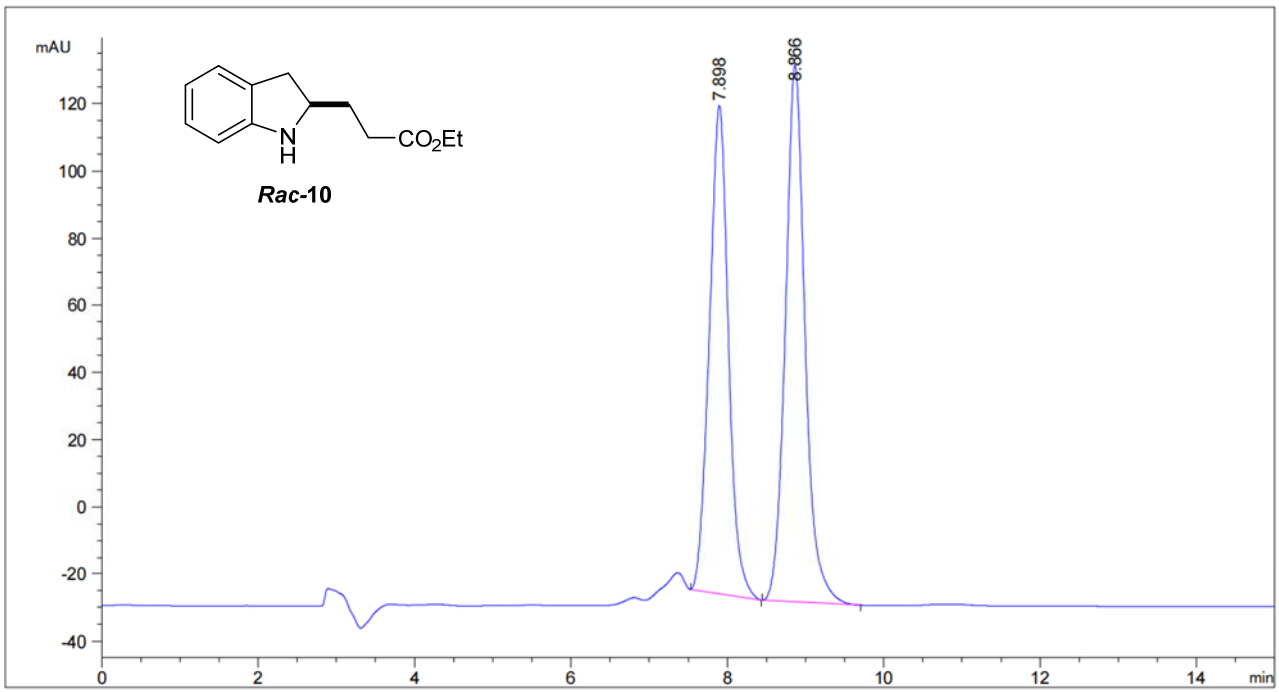
^{1}H-NMR (400 MHz, $CDCl_3$)



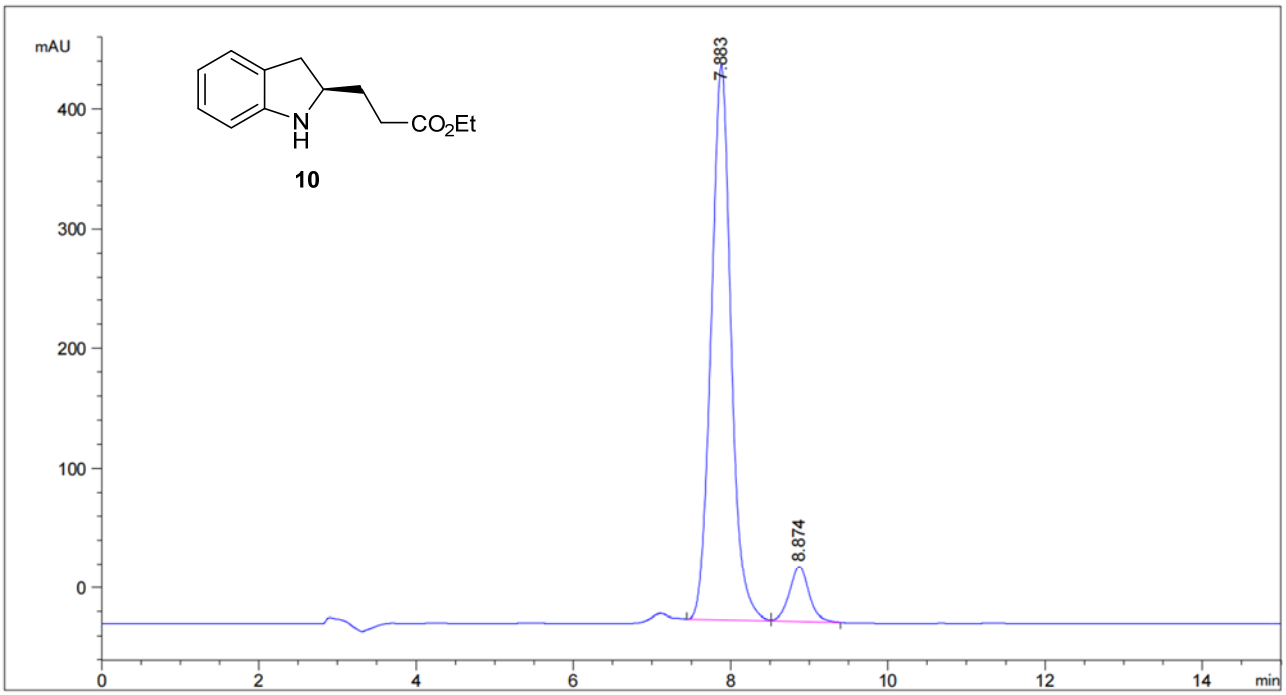
10

^{13}C-NMR (100 MHz, $CDCl_3$)

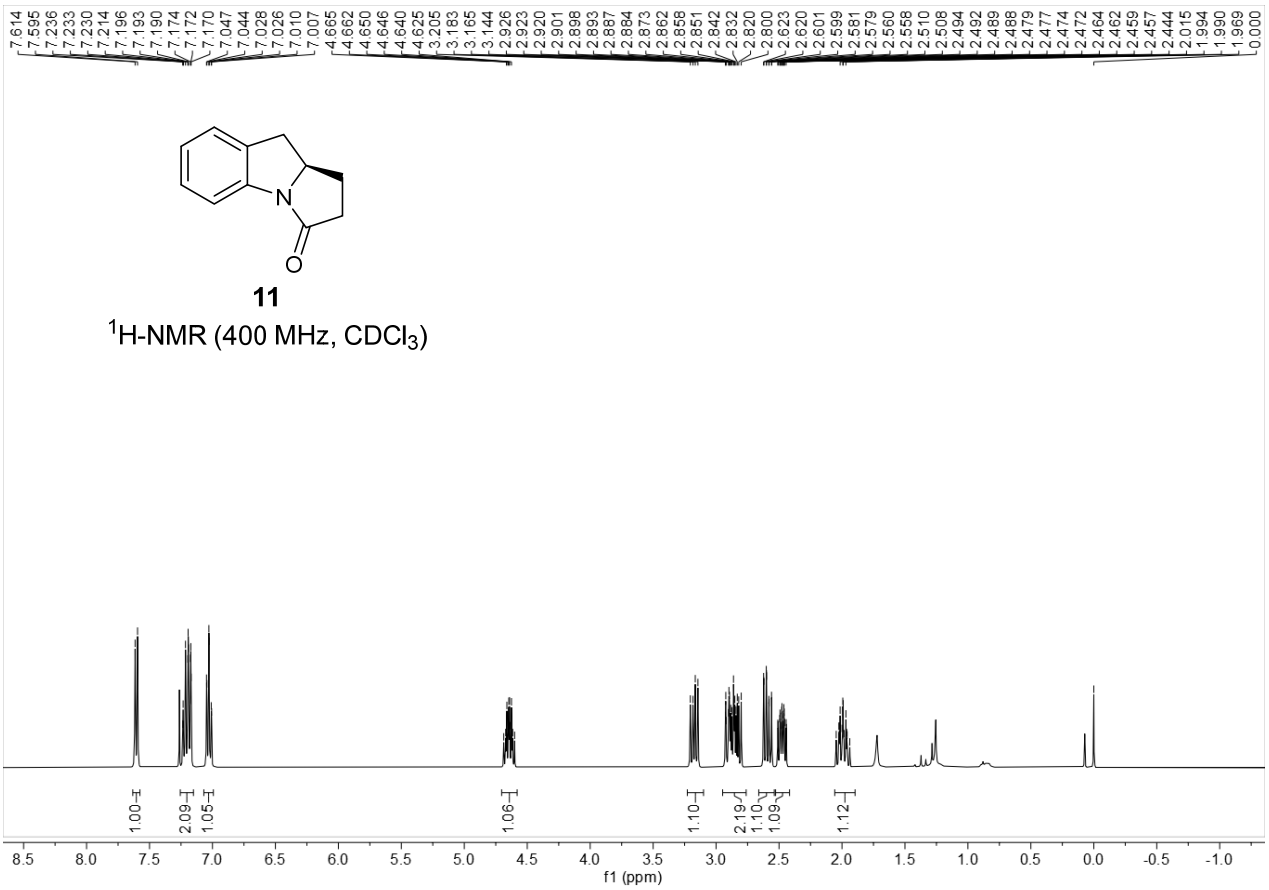

User Spectrum Plot Report
Agilent
Name CYC-240525-36
Inj. Vol. (ul) 8
Data File CYC-240525-36.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 5/27/2024 1:14:30 PM (UTC+08:00)
+ESI Scan (rt: 0.375 min) Frag=175.0V CYC-240525-36.d
x10^5
242.1160
CO2Et
N
H
10
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C13H17NO2Na+ 242.1151
Counts vs. Mass-to-Charge (m/z)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.898	BB	0.2530	2464.70239	145.46916	46.8553
2	8.866	BBA	0.2624	2795.53906	159.73091	53.1447

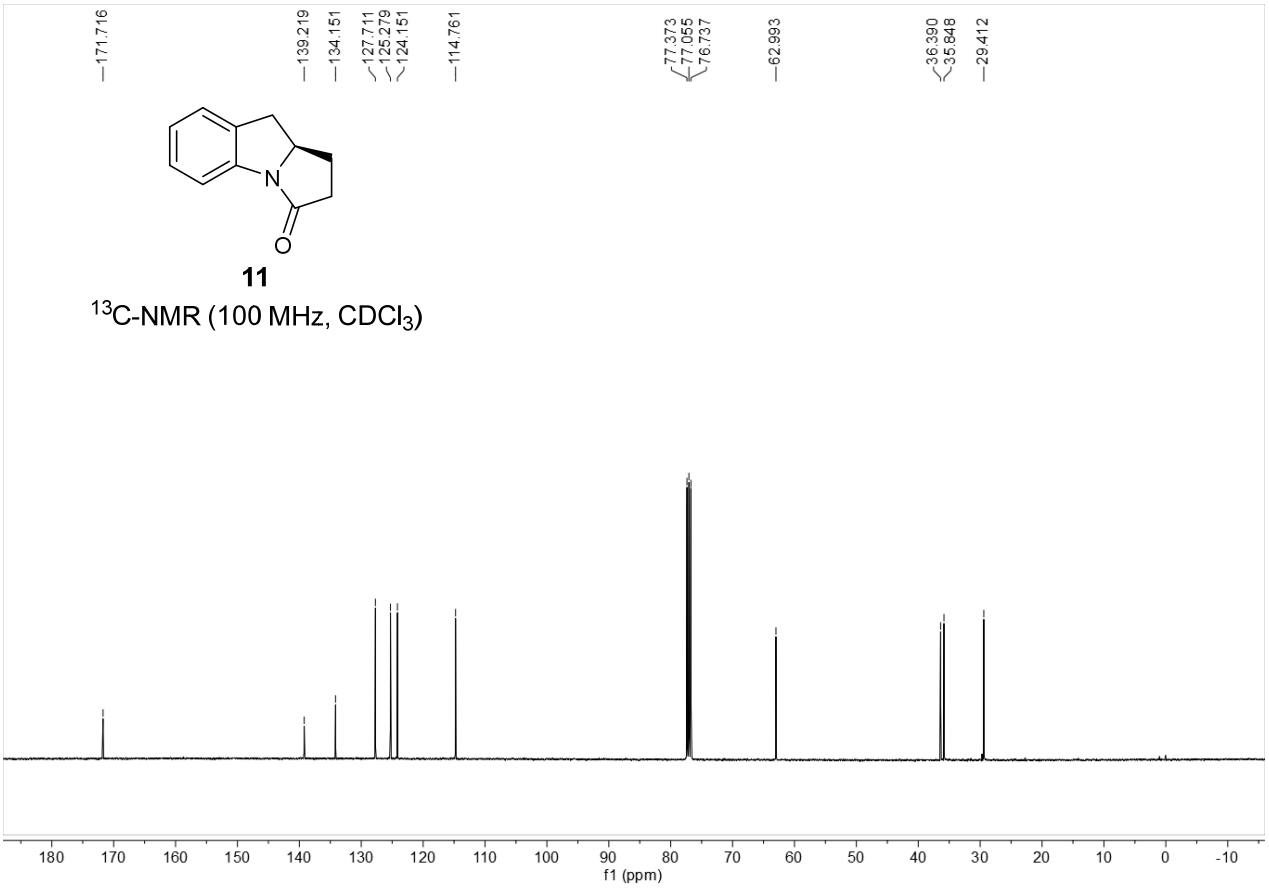


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.883	BV	0.2644	8131.67871	463.37805	91.1803
2	8.874	VBA	0.2602	786.56110	45.77396	8.8197



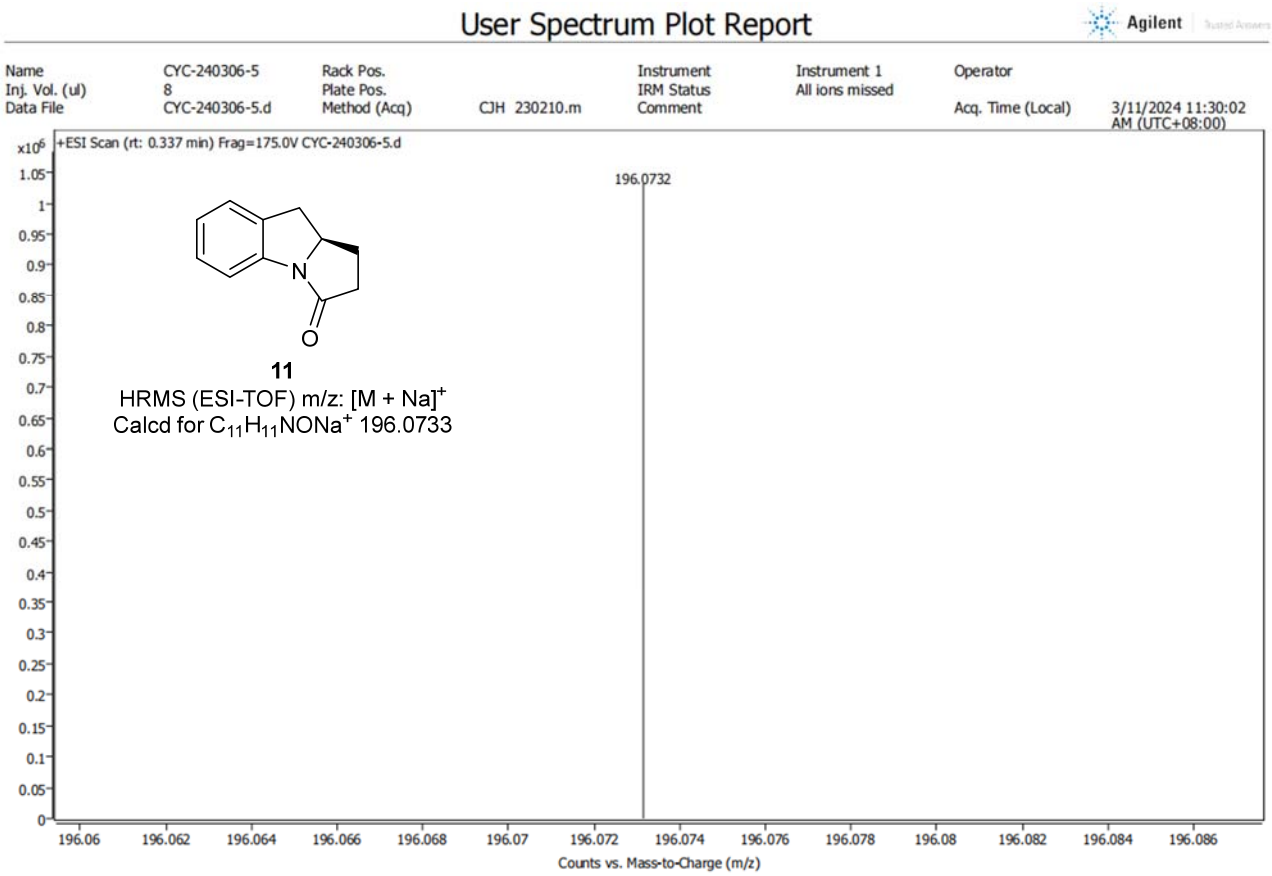
11

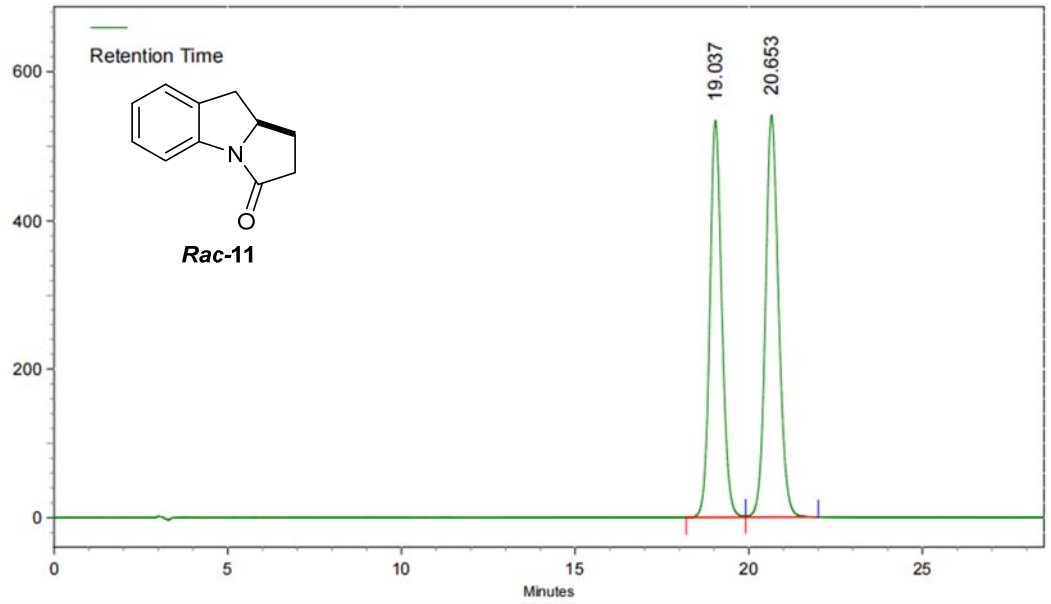
^{1}H-NMR (400 MHz, $CDCl_3$)



11

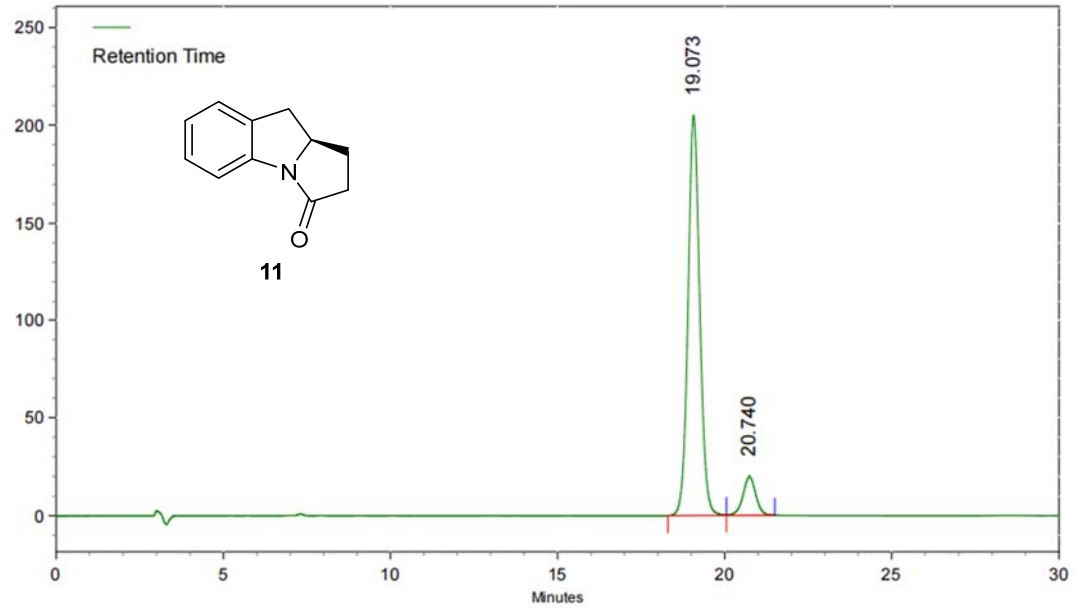
^{13}C-NMR (100 MHz, $CDCl_3$)


User Spectrum Plot Report
Agilent
Name CYC-240306-5
Inj. Vol. (ul) 8
Data File CYC-240306-5.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument
IRM Status
Comment
Instrument 1
All ions missed
Operator
Acq. Time (Local) 3/11/2024 11:30:02 AM (UTC+08:00)
+ESI Scan (rt: 0.337 min) Frag=175.0V CYC-240306-5.d
x10^6
196.0732
N
O
11
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C11H11NONa+ 196.0733
Counts vs. Mass-to-Charge (m/z)



AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	19.037	1.710	8967282	214709734	47.3910
2	20.653	2.090	9081177	238350389	52.6090
Totals			18048459	453060123	100.0000



AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	19.073	1.753	3438314	83702476	90.3931
2	20.740	1.447	331321	8895854	9.6069
Totals			3769635	92598330	100.0000

12. DFT computational calculation data

Absolute Calculation Energies, Enthalpies, and Free Energies

Geometry	$E_{(elec\text{-}wB97XD)}$[1]	$G_{(corr\text{-}wB97XD)}$[2]	$H_{(corr\text{-}wB97XD)}$[3]	$E_{(solv,\ wB97XD)}$[4]	IF[5]
1a	-654.024448	0.200128	0.256849	-654.217741	-
2a	-226.118688	0.046271	0.077152	-226.191478	-
2a-HCl	-686.910728	0.0492	0.089028	-687.025654	-
3a	-880.178393	0.266815	0.338084	-880.43399	-
INT0	3626.821861	0.686516	0.837818	3627.644217	-
INT0′	3626.817335	0.685895	0.837852	-3627.64116	-
INT1	4313.789663	0.769914	0.933405	4314.718756	-
INT2	4313.779793	0.767015	0.933058	4314.712596	-
INT1-*ent*	4313.781141	0.768649	0.934126	4314.712476	-
INT2-*ent*	4313.779793	0.767016	0.933059	4314.712594	-
INT3	-3852.92067	0.752094	0.917025	3853.812776	-
INT4	4313.765021	0.767031	0.933255	4314.701188	-
INT5	3852.933667	0.759872	0.916779	3853.825608	-
TS1	4313.748836	0.76016	0.927094	4314.683524	1221.03
TS2	4313.759842	0.767356	0.932013	4314.688531	315.47
TS1-*ent*	4313.745544	0.763145	0.927464	4314.679564	957.8
TS2-*ent*	4313.751435	0.767147	0.932165	4314.682656	346.5
TS3	3659.665016	0.533805	0.665938	-3660.41322	819.67
TS4	3852.908191	0.74923	0.911386	3853.798392	1302.67
TS5	4313.734092	0.759587	0.92637	4314.669545	1383.98
TS6	4313.745718	0.767434	0.931957	4314.678787	274.27
TS7	-4313.72495	0.766439	0.931241	4314.658005	420.06
TS8	3852.907183	0.750999	0.911519	3853.801288	1087.35
TS9	3852.906198	0.7548	0.915209	3853.802347	242.06

[1] The electronic energy calculated by ωB97XD in gas phase. [2] The thermal correction to Gibbs free energy calculated by ωB97XD in gas phase. [3] The thermal correction to enthalpy calculated by ωB97XD in gas phase. [4] The electronic energy calculated by ωB97XD in toluene solvent. [5] The ωB97XD calculated imaginary frequencies for the transition states.

Geometries for All Optimized Structures

1a

C	1.70191000	-0.65340500	-0.00000400
C	0.59532100	0.11022000	0.00010200
C	-0.73804100	-0.45733400	0.00010200
C	-1.87085700	0.26211400	0.00020800
C	3.09828700	-0.20239000	-0.00001900
C	4.11573800	-1.16591700	-0.00013900
C	5.45615900	-0.79600100	-0.00015900
C	5.80578000	0.55089600	-0.00006000
C	4.80511100	1.52203700	0.00006000
C	3.46722800	1.15117800	0.00008000
C	-3.18247100	-0.41523300	0.00021600
O	-3.35653600	-1.61574000	-0.00005900
O	-4.18671500	0.47911500	0.00009900
C	-6.48374200	1.08838400	-0.00017700
C	-5.50918400	-0.07103800	-0.00013300
H	1.56762200	-1.73541200	-0.00009100
H	0.66557100	1.19639000	0.00019100
H	-0.82707800	-1.54315900	0.00001500
H	-1.86709200	1.34814100	0.00029700
H	3.84838800	-2.21981500	-0.00021700
H	6.22714300	-1.56066100	-0.00025300
H	6.85108200	0.84475700	-0.00007500
H	5.07032100	2.57514200	0.00013900
H	2.70475800	1.92417500	0.00017500
H	-7.51086700	0.71025400	-0.00035600
H	-6.34480800	1.71257500	0.88747900
H	-6.34455300	1.71272200	-0.88769000
H	-5.63083000	-0.70652000	-0.88305900
H	-5.63107800	-0.70666400	0.88265500

2a

N	0.07127500	-1.20188800	0.00039200
C	0.68110000	0.98566300	0.00036900
C	-0.69454200	0.91643300	-0.00022500
N	-1.00521500	-0.40111000	-0.00004300
H	1.29217100	1.87532800	0.00067600
H	-1.45712000	1.68117200	-0.00038100
H	-1.92095900	-0.81971900	-0.00008300
C	1.09946300	-0.36233100	-0.00047400
H	2.10735400	-0.75439000	-0.00066900

2a-HCl

C	-2.48473100	0.43334500	-0.00016900
C	-2.10092400	-0.89129800	-0.00013800
N	-0.75097600	-0.89891000	0.00020600
H	-3.49069100	0.82331500	-0.00032800
H	-2.67209400	-1.80739300	-0.00025800
H	-0.12582400	-1.69050100	0.00031300
N	-0.23040600	0.33598500	0.00021000
H	1.52641400	0.32137900	0.00006400
Cl	2.81876300	-0.00619700	-0.00008400
C	-1.27567500	1.15394400	0.00007200
H	-1.11912300	2.22307300	0.00013700

3a

C	-1.10086700	-0.58764200	0.69999100
C	-0.02640000	-0.77297400	-0.07053400
C	1.38111600	-0.57348200	0.41863600
C	1.99548400	0.69198300	-0.18883700
C	-2.50823800	-0.69584700	0.27948200
C	-3.49982200	-0.11275600	1.07728000
C	-4.84069300	-0.17538000	0.71244500
C	-5.21503800	-0.83276500	-0.45573500
C	-4.23944900	-1.42980100	-1.25255000
C	-2.90058900	-1.36483100	-0.88762900
C	1.35524300	1.92664300	0.40075800
O	0.89584000	2.00460300	1.51812100
O	1.38509600	2.94887700	-0.46170000
C	0.96491000	5.19965600	-1.10328100
C	0.84258200	4.18898300	0.01744800
H	-0.94124500	-0.29108200	1.73606300
H	-0.12378100	-1.01757000	-1.12817200
H	1.37781800	-0.45673500	1.50742900
H	1.89741600	0.69864900	-1.27786900
H	-3.21131900	0.40311600	1.98969700
H	-5.59356900	0.28817100	1.34304500
H	-6.26124200	-0.88722100	-0.74137100
H	-4.52475000	-1.95547000	-2.15907500
H	-2.15490700	-1.85364900	-1.50820800
H	0.56120800	6.16355700	-0.77807700
H	2.01187300	5.34066300	-1.38718000
H	0.40771000	4.87073200	-1.98530800
H	-0.19886800	4.02783100	0.31187500
H	1.39652400	4.49742100	0.90943200
H	3.06698800	0.71514900	0.03598100
N	3.53199800	-1.62607100	-0.05740000
C	2.90852100	-3.79842600	-0.21369800
C	1.78580300	-3.02917200	0.00144600
N	2.19968800	-1.74015100	0.07691900
H	2.95516400	-4.86974800	-0.33793100
H	0.74323300	-3.28947400	0.10838500
C	3.96442300	-2.86781700	-0.24115400

H	5.02054300	-3.04685400	-0.39110700

INT0

C	4.72134300	1.06327600	0.37855200
C	3.82773400	1.89070200	-0.19268200
C	2.77262700	2.59831400	0.52872000
C	1.89831400	3.50930400	-0.10818900
C	5.61480000	0.15505000	-0.35047400
C	6.08792200	-0.99461000	0.29787700
C	6.84903900	-1.94109200	-0.37856500
C	7.16635200	-1.75576000	-1.72146500
C	6.72408000	-0.60606100	-2.37459800
C	5.96203500	0.33903600	-1.69777800
C	0.99555300	4.35675200	0.68590900
O	0.86152100	4.33376700	1.89860900
O	0.25846000	5.15895300	-0.11158200
C	-1.65949100	6.47610300	-0.57861400
C	-0.81942600	5.85458500	0.51786900
H	4.70090600	0.94560400	1.46204300
H	3.79375700	1.97655500	-1.27984400
H	2.85917000	2.64220400	1.61303000
H	2.04793500	3.80247100	-1.14431700
H	5.82854700	-1.15161100	1.34173500
H	7.19221600	-2.82940500	0.14425600
H	7.76132700	-2.49304000	-2.25224500
H	6.98263500	-0.43978100	-3.41680700
H	5.64355700	1.23737300	-2.21919800
H	-2.48252400	7.04729700	-0.13667600
H	-1.05830100	7.15313500	-1.19318900
H	-2.08117300	5.70218200	-1.22668100
H	-1.40426600	5.14536600	1.11306000
H	-0.41336500	6.60810700	1.20110200
P	1.11468100	-0.55227200	0.91950100
P	-1.25728400	1.49705900	-0.74032300
O	-1.69731000	-3.84007200	-3.33213600
O	-1.61967400	-3.78334800	-1.07590500
O	-4.16649600	-2.49194900	2.85434300
O	-3.89667600	-2.21024300	0.63075800
C	1.73900300	-1.86556000	-0.18649900
C	2.68329200	-1.49719600	-1.14956300
H	2.96806000	-0.45498600	-1.24928300
C	3.27600100	-2.46011900	-1.95955400
H	4.03534100	-2.16197000	-2.67599500
C	2.90249800	-3.79550600	-1.83541300
H	3.35607000	-4.54859400	-2.47309100
C	1.94641000	-4.16815400	-0.89269900
H	1.64364600	-5.20608000	-0.80248300
C	1.37496300	-3.20958500	-0.06143400
H	0.63883600	-3.50934900	0.67889300
C	2.25689100	-0.63204200	2.35309500
C	2.24895400	0.44655700	3.24745900
H	1.55476400	1.26986500	3.09164900
C	3.13652700	0.48372300	4.31712600
H	3.12201800	1.32812800	4.99947500
C	4.05432600	-0.55009700	4.49666200
H	4.75852200	-0.51537700	5.32260300
C	4.06940000	-1.62375600	3.61112900
H	4.78378500	-2.43100900	3.74539800
C	3.17359900	-1.66763200	2.54441700
H	3.20574800	-2.50235100	1.85127400
C	-1.54483100	-0.12735600	-1.56566900
C	-1.60678200	-0.18058700	-2.96107900
H	-1.62038700	0.74696700	-3.52252600
C	-1.65271900	-1.38290600	-3.67908800
H	-1.70358800	-1.40252100	-4.76097900
C	-1.63909400	-2.53015100	-2.92776300
C	-1.71594200	-4.60916800	-2.18199600
C	-1.58613500	-2.49437600	-1.54764900
C	-1.52203300	-1.33179800	-0.81029200
C	-1.54791600	-1.45420600	0.67708600
C	-0.46912700	-1.22824200	1.57177400
C	-0.64725300	-1.42134300	2.94417700
H	0.18717500	-1.24632800	3.61321000
C	-1.86192200	-1.83687100	3.50526300
H	-1.98200200	-1.97602600	4.57275300
C	-2.88224600	-2.06842500	2.61877700
C	-4.76549800	-2.64183000	1.61644300
C	-2.71622300	-1.89497200	1.25880000
C	-2.52659600	1.58339000	0.57404500
C	-2.18781200	2.25885900	1.75136600
H	-1.19968900	2.70195500	1.85975000
C	-3.10793900	2.35597900	2.79211600
H	-2.83382400	2.88014900	3.70268300
C	-4.36578000	1.77272300	2.66899500
H	-5.07898600	1.83883400	3.48534800
C	-4.70833900	1.09507200	1.50059900
H	-5.68030300	0.62299000	1.40775000
C	-3.79271400	1.00105600	0.45773700
H	-4.05430900	0.44091900	-0.43653200
C	-1.82269400	2.72248600	-1.98496700
C	-0.83830200	3.36434700	-2.74221400
H	0.20654400	3.14146000	-2.54620000
C	-1.18742100	4.29339100	-3.71805300

H	-0.41165200	4.78772700	-4.29469100
C	-2.52692500	4.60270800	-3.93459600
H	-2.80203300	5.33593500	-4.68696900
C	-3.51497400	3.98024100	-3.17369700
H	-4.56068200	4.22648800	-3.33233300
C	-3.16621200	3.04311600	-2.20609600
H	-3.94464600	2.57189700	-1.61452600
Pd	0.92515300	1.59940000	0.05517000
F	-2.84307900	-5.32313100	-2.12357300
F	-0.70550200	-5.48242100	-2.19581800
F	-5.09163100	-3.92162400	1.41403600
F	-5.90326900	-1.94287500	1.56630000

INT0′

C	-1.59084100	3.57553300	0.44164500
C	-2.61174500	2.83456200	-0.20791600
C	-3.60234400	2.07929900	0.53652900
C	-4.58224700	1.31724700	0.00349600
C	-0.66507600	4.51489000	-0.23077500
C	0.31238500	5.17011600	0.53517900
C	1.27873800	5.96842400	-0.06259100
C	1.28551800	6.15169600	-1.44447700
C	0.30481200	5.53227900	-2.21538400
C	-0.65798800	4.72406300	-1.61783300
C	-5.30872500	0.38322300	0.86080900
O	-5.23858100	0.31112500	2.07598300
O	-6.04814500	-0.47804700	0.12730600
C	-7.24262000	-2.50405500	-0.16348700
C	-6.67318300	-1.53567600	0.85346700
H	-1.67591200	3.72012700	1.51950500
H	-2.80408400	2.96028800	-1.27205900
H	-3.49514900	2.05874300	1.62213500
H	-4.74480100	1.25276000	-1.06811100
H	0.33046000	5.01794600	1.61163400
H	2.03396700	6.44589100	0.55517500
H	2.04108100	6.77509900	-1.91304500
H	0.28801500	5.67613700	-3.29240700
H	-1.40472200	4.24142900	-2.24145300
H	-7.75605300	-3.32595600	0.34562800
H	-7.95838300	-2.00180900	-0.82136200
H	-6.44257200	-2.92695800	-0.77965700
H	-5.93005200	-2.01835500	1.49632400
H	-7.45331400	-1.12132300	1.50125100
P	1.25533500	1.31026500	0.94902500
P	-1.23014800	-0.52159800	-0.82138700
O	3.90216800	-2.32558300	-3.21290200
O	3.77597500	-2.19226400	-0.96235100
O	1.69925400	-4.30186700	2.87363600
O	1.54681700	-3.96689200	0.64569300
C	2.61604400	1.58293000	-0.23721500
C	2.40422800	2.52336700	-1.25059800
H	1.45349800	3.04573700	-1.31685300
C	3.40931800	2.79449500	-2.17365300
H	3.23475500	3.53203400	-2.95118900
C	4.62497300	2.11962200	-2.09973200
H	5.40537500	2.32191300	-2.82753500
C	4.84186200	1.18179700	-1.09211200
H	5.78420800	0.64770500	-1.03635400
C	3.84353400	0.91858000	-0.15939800
H	4.01570600	0.18151600	0.62013500
C	1.67812500	2.40352900	2.35916700
C	0.66621400	2.67087100	3.29052500
H	-0.30404400	2.19231700	3.17503800
C	0.88515100	3.55526100	4.34048900
H	0.09268200	3.75154900	5.05648400
C	2.11344600	4.20462100	4.45673600
H	2.28157800	4.90962800	5.26541900
C	3.12019000	3.95298100	3.52951200
H	4.07661500	4.46053400	3.61335000
C	2.90770300	3.05196000	2.48805400
H	3.69726200	2.86941200	1.76588600
C	0.28825100	-1.18749900	-1.61759900
C	0.37673300	-1.29370000	-3.00743600
H	-0.50330000	-1.09067400	-3.60718300
C	1.55589500	-1.66003000	-3.67018600
H	1.60554900	-1.74177300	-4.74922800
C	2.63645200	-1.92304900	-2.86777000
C	4.58606700	-2.53826200	-2.02918900
C	2.55963900	-1.83557800	-1.49076600
C	1.42407000	-1.45911900	-0.80731900
C	1.46765600	-1.50127800	0.68583500
C	1.52552600	-0.39917500	1.58243800
C	1.63793600	-0.62437700	2.95707500
H	1.68578100	0.22610000	3.62735500
C	1.69443100	-1.90589800	3.52092000
H	1.78171600	-2.05803300	4.58985600
C	1.64389500	-2.95178900	2.63574100
C	1.68641800	-4.92216900	1.63687200
C	1.54696500	-2.74551500	1.27317200
C	-1.77261200	-1.84629700	0.31075900
C	-2.50545300	-1.46912500	1.43943300
H	-2.69893200	-0.41904900	1.63558600
C	-3.00679900	-2.43504200	2.30736300

H	-3.59222600	-2.12339400	3.16661000
C	-2.75776400	-3.78307200	2.06376700
H	-3.13764000	-4.53861000	2.74531700
C	-2.01877400	-4.16591100	0.94527100
H	-1.81511700	-5.21491700	0.75868100
C	-1.53490500	-3.20246200	0.06612700
H	-0.96083900	-3.50612200	-0.80500000
C	-2.51828800	-0.51076700	-2.12441800
C	-2.48913900	0.54050700	-3.05184700
H	-1.66825700	1.25459700	-3.02430000
C	-3.50942100	0.69236000	-3.98199700
H	-3.47277400	1.50888800	-4.69713700
C	-4.59180700	-0.18784600	-3.97673000
H	-5.40252800	-0.05700800	-4.68717100
C	-4.63674000	-1.22248700	-3.04934700
H	-5.48702700	-1.89694700	-3.02627200
C	-3.60208500	-1.38963600	-2.13087100
H	-3.65991400	-2.19014200	-1.40074300
Pd	-0.88348400	1.58565400	0.10023300
F	4.95084300	-3.81946300	-1.93138200
F	5.70911700	-1.81519100	-2.01007300
F	2.81731200	-5.60959500	1.45483800
F	0.68498000	-5.80325700	1.57362900

INT1

C	2.15168700	2.42262100	-1.73165300
C	3.14004200	1.51999500	-1.26036100
C	3.16677200	0.23196600	-1.80528800
C	4.16316900	-0.80864500	-1.39884500
C	1.89017300	3.74376700	-1.12525600
C	1.38820600	4.77463400	-1.92705200
C	1.10239800	6.02133300	-1.38111000
C	1.31089700	6.25170200	-0.02387400
C	1.80897200	5.22881400	0.78173200
C	2.09985100	3.98412800	0.23871000
C	3.75563100	-2.19667300	-1.82654500
O	2.78990200	-2.46500400	-2.51000900
O	4.62609800	-3.10594000	-1.38599100
C	5.43818000	-5.31958500	-1.11896500
C	4.35775000	-4.46734100	-1.74858400
H	1.88173400	2.34629500	-2.78630200
H	3.71764600	1.71844500	-0.35669000
H	2.74731600	0.08654100	-2.80403200
H	4.37293600	-0.78418700	-0.32742000
H	1.20757100	4.59287900	-2.98410900
H	0.70914800	6.80919300	-2.01731300
H	1.08017800	7.22211600	0.40620100
H	1.95914900	5.38602400	1.84537200
H	2.44080800	3.19027300	0.90081100
H	5.26783000	-6.37384600	-1.35906800
H	6.42663900	-5.03425400	-1.49079700
H	5.43054000	-5.20124700	-0.03169600
H	3.36187100	-4.73651700	-1.38579900
H	4.35278000	-4.54980900	-2.84020700
P	-1.03333500	1.51965500	-1.02205500
P	0.53604500	-1.39392100	0.05549100
O	-3.37893800	0.21142500	4.23557700
O	-4.14165900	0.00618300	2.12022500
O	-5.12596800	-2.73261100	-1.75764300
O	-4.08808600	-2.59692100	0.24358700
C	-1.63700000	2.37316800	0.46028900
C	-0.75177200	2.56692200	1.51902400
H	0.28314700	2.24064500	1.46534600
C	-1.20491500	3.13405200	2.70763600
H	-0.50108800	3.24657100	3.52627500
C	-2.53673400	3.51208400	2.83407900
H	-2.89617600	3.93942400	3.76546900
C	-3.42479000	3.32437500	1.77258900
H	-4.46855900	3.60024900	1.87987800
C	-2.98162100	2.74700400	0.59084900
H	-3.68368100	2.56186200	-0.21838300
C	-1.22608200	2.67629100	-2.42704300
C	-0.71247800	2.29014000	-3.67277700
H	-0.24462500	1.31340800	-3.78287700
C	-0.78841900	3.14392000	-4.76640100
H	-0.38984500	2.82999800	-5.72639500
C	-1.36568100	4.40567000	-4.62330800
H	-1.41851800	5.07871300	-5.47368200
C	-1.86172300	4.80204200	-3.38648800
H	-2.29638000	5.78932400	-3.26420800
C	-1.79254300	3.94345200	-2.29090500
H	-2.15787600	4.27677600	-1.32586500
C	-0.65873300	-0.97268600	1.39431700
C	-0.20020300	-0.83187700	2.70448100
H	0.84217700	-1.01062800	2.93265800
C	-1.02742000	-0.41968600	3.75645400
H	-0.63878700	-0.28305000	4.75746800
C	-2.33794000	-0.18236000	3.43315600
C	-4.50518000	0.24492000	3.43388900
C	-2.80557300	-0.30983400	2.13866300
C	-2.00914600	-0.66746900	1.07419600
C	-2.61750400	-0.68744100	-0.28387100
C	-2.32506800	0.23697300	-1.32104000

C	-2.98455600	0.14928500	-2.54820100
H	-2.76324100	0.87158000	-3.32466900
C	-3.94913300	-0.82938900	-2.82236700
H	-4.45367700	-0.88423800	-3.77927400
C	-4.22841800	-1.69875100	-1.79944500
C	-5.08968100	-3.23450800	-0.46616900
C	-3.59179900	-1.61502800	-0.57492200
C	-0.35629900	-2.63536600	-0.93662100
C	-0.35853400	-2.52144500	-2.32749600
H	0.21374400	-1.72906600	-2.79966100
C	-1.08845600	-3.41946400	-3.10024700
H	-1.09591800	-3.31788100	-4.18111900
C	-1.80568100	-4.44409500	-2.48898400
H	-2.38032800	-5.14085000	-3.09182600
C	-1.79155500	-4.57471200	-1.10163300
H	-2.35804500	-5.36469200	-0.62134600
C	-1.07907500	-3.66692500	-0.32732000
H	-1.10856700	-3.74336000	0.75636300
C	1.89282800	-2.29445200	0.88732500
C	2.86362400	-1.53812600	1.55516500
H	2.78065400	-0.45281400	1.60597300
C	3.93097100	-2.16826900	2.18849100
H	4.67854900	-1.56664600	2.69621200
C	4.03964100	-3.55500800	2.15550000
H	4.87558300	-4.04624800	2.64509100
C	3.07816100	-4.31216800	1.49087100
H	3.16036500	-5.39511200	1.46025300
C	2.01067500	-3.68766600	0.85334900
H	1.28193700	-4.28962300	0.32145500
Pd	1.14280000	0.62934200	-0.96550200
F	-5.38531900	-0.67897400	3.83862800
F	-5.11437800	1.42656300	3.54014600
F	-6.26878500	-3.04633100	0.13188800
F	-4.87502100	-4.55107900	-0.49232300
N	5.17164700	1.03366800	2.41203900
C	7.18546200	0.16809500	2.48596100
C	6.70204900	0.26015400	1.16855800
N	5.47708300	0.78347600	1.13282000
H	8.14029200	-0.20574200	2.82378700
H	7.18914600	-0.03063300	0.24710100
H	5.12504200	-0.59058800	-1.88578800
H	4.22021500	1.37067700	2.64550000
Cl	2.20584800	1.66659500	2.97630300
C	6.15739900	0.67903000	3.25795300
H	6.05411300	0.81806500	4.32392100

INT2

C	-2.51545300	2.08779000	0.59261800
C	-3.05341100	0.93859500	-0.03659600
C	-4.02870900	0.05004200	0.69142100
C	-4.15541600	-1.33846500	0.07622700
C	-2.15750000	3.33831000	-0.12429400
C	-1.52358600	4.37308900	0.57950000
C	-1.08889400	5.52134900	-0.07002500
C	-1.29505000	5.67267500	-1.44007400
C	-1.95962200	4.67034600	-2.14261100
C	-2.39216700	3.51536200	-1.49588500
C	-4.98091200	-2.27928300	0.91603700
O	-5.35768900	-2.05786300	2.04861700
O	-5.21769000	-3.41829200	0.26443300
C	-6.04233200	-5.63415300	0.06950200
C	-5.94039800	-4.42948900	0.98103500
H	-2.70014900	2.22181200	1.66152400
H	-3.22664500	0.95381600	-1.11155700
H	-3.77302000	-0.03700700	1.75025100
H	-3.15272400	-1.76684900	-0.01499700
H	-1.34673400	4.25821900	1.64618600
H	-0.58274700	6.29816600	0.49646000
H	-0.95325400	6.56804900	-1.95100600
H	-2.15267500	4.78514600	-3.20566100
H	-2.92324800	2.75773100	-2.06702900
H	-6.58163500	-6.44025100	0.57658100
H	-6.57889700	-5.38015500	-0.84910000
H	-5.04645200	-5.99690600	-0.20123800
H	-5.40428900	-4.65984100	1.90689300
H	-6.92465100	-4.03610200	1.25365100
P	1.03832800	1.54864400	1.03119300
P	-0.12735900	-1.36504000	-0.56225700
O	4.76701100	0.27400100	-3.53142300
O	4.89401400	0.18538400	-1.27889800
O	4.89606200	-2.69054400	2.62038800
O	4.37832600	-2.50194600	0.43089200
C	1.94998700	2.50652500	-0.22995600
C	1.24003700	2.98270600	-1.33467800
H	0.17409800	2.79358100	-1.41813700
C	1.89529900	3.69945200	-2.33162000
H	1.33007200	4.06519500	-3.18316700
C	3.26210400	3.94127900	-2.23324000
H	3.77618900	4.49071600	-3.01636600
C	3.97536500	3.47499700	-1.12997400
H	5.04302100	3.65155800	-1.05575300
C	3.32305500	2.75882500	-0.13300200
H	3.88871900	2.37396200	0.71155800

C	0.88405000	2.68982300	2.45906800
C	-0.05152900	2.35445000	3.44590200
H	-0.61691300	1.42980800	3.34946700
C	-0.28268500	3.20276400	4.52280100
H	-1.01029300	2.92941900	5.28130100
C	0.40353900	4.41269200	4.61322400
H	0.21268200	5.08607100	5.44350600
C	1.32626600	4.75945800	3.63089100
H	1.85696900	5.70492200	3.69222100
C	1.57092000	3.90094100	2.56121500
H	2.28151500	4.19009100	1.79384100
C	1.39515700	-0.95883300	-1.52631700
C	1.33636500	-0.90684600	-2.92084600
H	0.42247900	-1.20712100	-3.42094400
C	2.41251900	-0.48917600	-3.71455300
H	2.34758000	-0.45651200	-4.79532700
C	3.55436100	-0.14032100	-3.03983500
C	5.60926600	0.40600900	-2.44236200
C	3.63048700	-0.19284600	-1.66147100
C	2.58292000	-0.56948900	-0.84875000
C	2.82197200	-0.59549300	0.62488300
C	2.28790300	0.31043900	1.57978000
C	2.62794700	0.18934400	2.92875900
H	2.21422100	0.89369600	3.64173000
C	3.49469500	-0.80125000	3.40953900
H	3.74920200	-0.88091500	4.45949600
C	4.01411900	-1.65049800	2.46648700
C	5.17811200	-3.15795000	1.34856100
C	3.69521500	-1.53533300	1.12673500
C	0.48477300	-2.61727200	0.62405600
C	0.11940200	-2.48975400	1.96638400
H	-0.53016400	-1.66932900	2.26342600
C	0.61233500	-3.37795800	2.91863800
H	0.33617700	-3.25981200	3.96214500
C	1.46724300	-4.40658800	2.53324400
H	1.86050100	-5.09485300	3.27536800
C	1.82855000	-4.54784600	1.19456300
H	2.50660500	-5.33881100	0.89369200
C	1.34762600	-3.65206700	0.24663400
H	1.66797600	-3.73964000	-0.78820700
C	-1.19089800	-2.29859500	-1.73014500
C	-2.01379600	-1.54509200	-2.57860000
H	-1.98641600	-0.45859900	-2.54595400
C	-2.91842300	-2.16719000	-3.43188700
H	-3.56691700	-1.55178600	-4.04678800
C	-3.02472500	-3.55592700	-3.43210400
H	-3.74564900	-4.04489400	-4.08064900
C	-2.22394700	-4.31419000	-2.58278000
H	-2.31388300	-5.39671800	-2.56985200
C	-1.30887500	-3.69215600	-1.73715600
H	-0.70686800	-4.29885900	-1.06934400
Pd	-0.98950000	0.62039300	0.31621400
F	6.61807800	-0.46755800	-2.53182500
F	6.15611500	1.62345500	-2.42738200
F	6.46802600	-2.95703700	1.06034800
F	4.97155300	-4.47550300	1.28660800
H	-4.54462900	-1.28442400	-0.94734800
N	-5.93767600	1.16889300	-0.40792400
C	-7.31568100	1.58732900	1.27344800
C	-6.18556900	0.93234600	1.74590100
N	-5.37242000	0.69485300	0.70936500
H	-8.16462800	1.92230400	1.84756300
H	-5.91333000	0.59424300	2.73323800
C	-7.11382000	1.71108800	-0.09861900
H	-7.72328900	2.14458500	-0.87694500
H	-5.49175800	1.04693100	-1.40852800
Cl	-4.89390400	0.81182800	-3.10035400

INT1-*ent*

C	-2.60132000	1.64021300	-1.31528100
C	-3.27114900	0.54690900	-0.73211000
C	-3.07099200	-0.74927700	-1.22935800
C	-3.70990000	-1.92461100	-0.55254500
C	-2.63399500	2.99453700	-0.71909600
C	-2.73699600	4.11138400	-1.55116600
C	-2.76088000	5.39515600	-1.01575400
C	-2.67123400	5.57717300	0.36096200
C	-2.56890900	4.46684300	1.19849300
C	-2.55570500	3.18329200	0.66693500
C	-5.14032800	-2.12929800	-1.00884600
O	-5.68983600	-1.53291600	-1.90662200
O	-5.71546800	-3.09373900	-0.28461000
C	-7.57009600	-4.37382800	0.45434400
C	-7.12155800	-3.27131800	-0.48177700
H	-2.42554700	1.60987300	-2.39214800
H	-3.71735100	0.66184100	0.25102200
H	-2.85775500	-0.86432600	-2.29402500
H	-3.15689400	-2.85031000	-0.74264200
H	-2.78689600	3.97419300	-2.62797900
H	-2.83778900	6.25262300	-1.67800300
H	-2.67905800	6.57884400	0.78105900
H	-2.49176300	4.59776100	2.27401900
H	-2.47249900	2.32337400	1.33003500

H	-8.64615800	-4.54204100	0.34441900
H	-7.36513100	-4.09847900	1.49277700
H	-7.04814800	-5.30971300	0.23202600
H	-7.31293900	-3.51930900	-1.53068300
H	-7.62230800	-2.32483400	-0.25657500
P	0.73726700	1.58736700	-0.70266700
P	0.10739300	-1.77979900	-0.06259200
O	4.01620200	0.05331500	4.03420400
O	4.49187100	0.48305400	1.86865700
O	5.70430200	-1.17782500	-2.46424800
O	4.86419800	-1.69581500	-0.43273700
C	1.24836500	2.28029500	0.89926300
C	0.47554500	2.00824800	2.02776700
H	-0.43480100	1.41534900	1.96366400
C	0.89800900	2.45238000	3.27857400
H	0.29422100	2.21297200	4.14828000
C	2.08372800	3.16852300	3.40247000
H	2.42049100	3.50185900	4.37958700
C	2.85556200	3.44664300	2.27322200
H	3.78975600	3.98939900	2.37118400
C	2.44593700	2.99677300	1.02534400
H	3.06828200	3.18104900	0.15327300
C	0.50102100	3.00083900	-1.84008300
C	0.06306200	2.73051000	-3.14374000
H	-0.11700500	1.70150300	-3.44914300
C	-0.14413600	3.76304400	-4.04975400
H	-0.47505900	3.53834000	-5.05931700
C	0.05880200	5.08465100	-3.65418800
H	-0.11174700	5.89466200	-4.35686700
C	0.46208800	5.36153000	-2.35324300
H	0.59648300	6.38936300	-2.03101000
C	0.68548000	4.32601700	-1.44803200
H	0.97997900	4.55893200	-0.43077300
C	1.32682800	-1.30495100	1.23746900
C	1.04711800	-1.56015400	2.58119600
H	0.14730100	-2.09615000	2.84873900
C	1.87934400	-1.13927300	3.62515500
H	1.63313700	-1.33686600	4.66087500
C	3.01317700	-0.46300800	3.25541800
C	4.96197400	0.57286800	3.16735400
C	3.30347300	-0.20087200	1.93088500
C	2.49007500	-0.57104300	0.88231500
C	2.91861300	-0.18150200	-0.48970500
C	2.29564500	0.79999800	-1.30386300
C	2.83829000	1.12368600	-2.54884000
H	2.36778400	1.89089800	-3.15110700
C	3.99073400	0.51174600	-3.05937800
H	4.39883500	0.77712300	-4.02701800
C	4.57695300	-0.42906500	-2.25269700
C	5.91594700	-1.90919200	-1.30605700
C	4.06125700	-0.74594400	-1.01004600
C	1.15854200	-2.46638300	-1.39027000
C	0.97174200	-2.04052400	-2.70622800
H	0.19503900	-1.31218300	-2.92748300
C	1.79340300	-2.51985700	-3.72304700
H	1.65238700	-2.17075200	-4.74138100
C	2.79776800	-3.43784200	-3.43083400
H	3.44459300	-3.80638000	-4.22112500
C	2.97752900	-3.88265700	-2.12190500
H	3.76456100	-4.59154800	-1.89003700
C	2.16663800	-3.39412900	-1.10509300
H	2.32780900	-3.72107200	-0.08147400
C	-0.80494100	-3.23435600	0.57548200
C	-1.70115500	-3.05952600	1.63801000
H	-1.84635800	-2.07548300	2.08589700
C	-2.46815100	-4.12791700	2.08979100
H	-3.16201300	-3.96898400	2.90923600
C	-2.37513400	-5.37181000	1.47285200
H	-2.98790900	-6.19979000	1.81656500
C	-1.50702000	-5.54461500	0.39886300
H	-1.43726800	-6.50734600	-0.09864000
C	-0.72309600	-4.48465400	-0.04908400
H	-0.06012300	-4.64085300	-0.89255300
Pd	-1.11636700	0.13094200	-0.67424800
F	6.11140600	-0.10050000	3.28452200
F	5.22607500	1.84225000	3.47916200
F	7.06740500	-1.54542200	-0.73753800
F	6.02015600	-3.20748600	-1.59696400
H	-3.73006900	-1.77855800	0.53042900
N	-5.33943600	0.65866500	1.90638700
C	-6.54501400	2.04079200	0.70679700
C	-6.73295100	0.70069200	0.31465100
N	-5.99245700	-0.13375900	1.03934300
H	-7.00793800	2.92802200	0.30227000
H	-7.35430300	0.30743500	-0.47834300
C	-5.62435600	1.96688000	1.73223900
H	-5.14615700	2.72723500	2.33110900
H	-4.55617600	0.28580200	2.45094000
Cl	-2.33909400	0.11841600	2.79837300

INT2-*ent*

C	2.51543200	2.08774100	0.59263900
C	3.05340500	0.93857300	-0.03661700

C	4.02876800	0.05004500	0.69134000
C	4.15553600	-1.33844000	0.07611200
C	2.15746800	3.33828000	-0.12423200
C	1.52366700	4.37308900	0.57962300
C	1.08898800	5.52138100	-0.06985200
C	1.29503800	5.67270900	-1.43991900
C	1.95949300	4.67034700	-2.14252000
C	2.39203400	3.51533500	-1.49583700
C	4.98098400	-2.27927600	0.91594700
O	5.35784100	-2.05783800	2.04849200
O	5.21763200	-3.41834500	0.26438000
C	6.04171000	-5.63442700	0.06965600
C	5.94024400	-4.42959500	0.98102000
H	2.70017500	2.22174200	1.66153900
H	3.22659200	0.95382500	-1.11158700
H	3.77310500	-0.03703200	1.75017600
H	3.15286600	-1.76684600	-0.01524400
H	1.34691100	4.25822900	1.64632600
H	0.58292800	6.29821700	0.49668400
H	0.95324800	6.56810600	-1.95081600
H	2.15247000	4.78514600	-3.20558400
H	2.92301800	2.75767600	-2.06703400
H	6.58093900	-6.44057500	0.57673300
H	6.57813000	-5.38069000	-0.84910300
H	5.04568600	-5.99698800	-0.20081100
H	5.40425900	-4.65966000	1.90701800
H	6.92464300	-4.03638900	1.25336700
P	-1.03827700	1.54858100	1.03124400
P	0.12735200	-1.36510600	-0.56222300
O	-4.76680600	0.27445300	-3.53145400
O	-4.89392400	0.18559200	-1.27895000
O	-4.89621800	-2.69048100	2.62025300
O	-4.37845200	-2.50182300	0.43077000
C	-1.94997100	2.50650500	-0.22986000
C	-1.24003500	2.98276800	-1.33455500
H	-0.17409000	2.79368300	-1.41802600
C	-1.89532400	3.69952100	-2.33147600
H	-1.33010600	4.06531200	-3.18300900
C	-3.26214400	3.94127200	-2.23310700
H	-3.77624700	4.49070200	-3.01622500
C	-3.97539200	3.47490300	-1.12986800
H	-5.04306000	3.65140200	-1.05564700
C	-3.32305500	2.75872800	-0.13291600
H	-3.88872200	2.37379600	0.71161000
C	-0.88397600	2.68970600	2.45916300
C	0.05167400	2.35435300	3.44593400
H	0.61711300	1.42975200	3.34942700
C	0.28281900	3.20263300	4.52286400
H	1.01048600	2.92931100	5.28131600
C	-0.40349800	4.41250100	4.61338100
H	-0.21264700	5.08585400	5.44368500
C	-1.32631400	4.75923900	3.63111900
H	-1.85709400	5.70465400	3.69253000
C	-1.57095400	3.90075600	2.56141300
H	-2.28162500	4.18987900	1.79410000
C	-1.39509100	-0.95871200	-1.52632000
C	-1.33623600	-0.90659000	-2.92083800
H	-0.42233800	-1.20685300	-3.42092500
C	-2.41233600	-0.48880000	-3.71456100
H	-2.34734100	-0.45601100	-4.79532700
C	-3.55420200	-0.13999300	-3.03985500
C	-5.60913400	0.40625800	-2.44243000
C	-3.63039300	-0.19265900	-1.66150000
C	-2.58287500	-0.56940300	-0.84876200
C	-2.82197200	-0.59548300	0.62485300
C	-2.28786300	0.31037300	1.57979300
C	-2.62791500	0.18924200	2.92876600
H	-2.21413700	0.89353400	3.64177000
C	-3.49472100	-0.80132200	3.40950700
H	-3.74922400	-0.88102800	4.45946100
C	-4.01420700	-1.65048600	2.46640600
C	-5.17824000	-3.15786000	1.34841100
C	-3.69528600	-1.53528100	1.12666200
C	-0.48491600	-2.61739500	0.62394800
C	-0.11957400	-2.49001300	1.96630100
H	0.53002300	-1.66964400	2.26343000
C	-0.61256900	-3.37828300	2.91846000
H	-0.33642900	-3.26025800	3.96198500
C	-1.46751700	-4.40683800	2.53294500
H	-1.86082300	-5.09515600	3.27499300
C	-1.82880300	-4.54795200	1.19424300
H	-2.50688000	-5.33886400	0.89328400
C	-1.34781100	-3.65210800	0.24640800
H	-1.66811500	-3.73958300	-0.78845700
C	1.19092500	-2.29862900	-1.73012100
C	2.01379800	-1.54512000	-2.57859000
H	1.98636100	-0.45862500	-2.54599600
C	2.91850500	-2.16720900	-3.43180000
H	3.56696200	-1.55181500	-4.04674900
C	3.02493000	-3.55593700	-3.43191300
H	3.74592100	-4.04488400	-4.08039700
C	2.22417900	-4.31420400	-2.58256500

H	2.31421400	-5.39672300	-2.56954300
C	1.30901800	-3.69218500	-1.73702700
H	0.70701800	-4.29889100	-1.06921400
Pd	0.98953500	0.62028800	0.31625700
F	-6.61784600	-0.46742000	-2.53204000
F	-6.15612200	1.62363400	-2.42735400
F	-6.46815200	-2.95697100	1.06018800
F	-4.97165900	-4.47541200	1.28642700
H	4.54485400	-1.28434500	-0.94742200
N	5.93766500	1.16909700	-0.40796900
C	7.31568800	1.58740700	1.27343100
C	6.18559600	0.93235200	1.74584000
N	5.37244700	0.69492400	0.70928400
H	8.16462300	1.92238300	1.84756200
H	5.91337600	0.59414100	2.73314500
C	7.11380300	1.71127400	-0.09862600
H	7.72325700	2.14486400	-0.87691400
H	5.49176300	1.04711100	-1.40863500
Cl	4.89397300	0.81191500	-3.10034500

INT3

C	3.91359700	2.01836200	0.33092500
C	4.83963000	1.02397100	0.77095500
C	5.70693700	0.33145400	-0.14334400
C	6.67921300	-0.56119200	0.19131400
C	3.39187800	3.07580400	1.23614600
C	3.40017500	4.41148600	0.82015300
C	2.85380700	5.41437100	1.61574200
C	2.27813900	5.09839000	2.84366600
C	2.27583200	3.77366800	3.27828900
C	2.83582100	2.77781000	2.48720300
C	7.45920200	-1.22496100	-0.85243300
O	7.31860300	-1.09067000	-2.05330700
O	8.38096200	-2.06012300	-0.31646400
C	10.17032000	-3.61355900	-0.46691800
C	9.20533400	-2.75239400	-1.25642900
H	4.00096700	2.34292700	-0.70855900
H	5.08145100	0.95798700	1.83241500
H	5.55555400	0.51179400	-1.20855700
H	6.94125700	-0.75991200	1.22770700
H	3.81823700	4.66134900	-0.15146100
H	2.86686400	6.44390900	1.26840100
H	1.83405200	5.87682400	3.45724400
H	1.81762700	3.50859300	4.22678000
H	2.79849700	1.74370600	2.81815000
H	10.82502300	-4.16381000	-1.15020200
H	10.79280400	-2.99706900	0.18834200
H	9.63023000	-4.33690200	0.15181200
H	8.57339700	-3.35327900	-1.91913000
H	9.73113700	-2.02313700	-1.88104800
P	0.66367400	0.69981200	-0.03191600
P	-3.18235300	-0.85770400	1.96988300
O	-4.01389400	3.60626900	-1.90656800
O	-2.60757800	1.96915400	-2.57199900
O	-2.48182300	-3.17048500	-3.29464300
O	-3.67196000	-1.52041900	-2.31684000
C	-0.12199500	1.06904300	1.58639000
C	0.33254100	0.31652200	2.67777500
H	1.08023600	-0.45758100	2.51777100
C	-0.12998100	0.57182900	3.96335900
H	0.23255100	-0.02352700	4.79593700
C	-1.04678200	1.59698100	4.17891900
H	-1.40360000	1.80766200	5.18287000
C	-1.50445700	2.35177000	3.10285900
H	-2.22450100	3.14914100	3.26091600
C	-1.04974900	2.08714500	1.81509300
H	-1.42768300	2.67887700	0.98783900
C	0.48900800	2.20647400	-1.06108000
C	0.46490700	2.07075700	-2.45450600
H	0.38053000	1.08572900	-2.90416000
C	0.54563500	3.18842000	-3.27542600
H	0.51652100	3.06520500	-4.35371800
C	0.64615600	4.46093100	-2.71849400
H	0.70034400	5.33459300	-3.36103100
C	0.67314900	4.60499100	-1.33604200
H	0.76542600	5.58929600	-0.88668100
C	0.60616900	3.48623800	-0.51006300
H	0.67245100	3.62063400	0.56441500
C	-3.44674500	0.45690200	0.68876600
C	-4.29492200	1.50023700	1.09055600
H	-4.79522500	1.42790900	2.05056100
C	-4.54879400	2.63249300	0.31260700
H	-5.22525200	3.41360700	0.63825300
C	-3.91162300	2.67720800	-0.90333900
C	-3.27703800	3.11329700	-2.97110100
C	-3.04604600	1.67948000	-1.30412600
C	-2.74606200	0.56897200	-0.53711400
C	-1.81586100	-0.44778400	-1.10241600
C	-0.40949000	-0.52395600	-0.91747400
C	0.31171700	-1.55049500	-1.53964700
H	1.38584600	-1.58632900	-1.38656200
C	-0.27543400	-2.52317300	-2.35973700
H	0.30682900	-3.30867400	-2.82563600

C	-1.62908900	-2.40512700	-2.54223000
C	-3.72051500	-2.55382200	-3.23323200
C	-2.35649200	-1.39565000	-1.93971900
C	-2.83579700	-2.44068300	1.08587600
C	-3.77153100	-3.17230300	0.34692900
H	-4.77355600	-2.78516200	0.19828400
C	-3.43173700	-4.40294300	-0.20534700
H	-4.16584300	-4.95433500	-0.78276200
C	-2.15214400	-4.92231300	-0.02579700
H	-1.88913700	-5.88261500	-0.45929000
C	-1.21645500	-4.21163200	0.71824200
H	-0.22184100	-4.62095300	0.86922200
C	-1.56036700	-2.98267200	1.27521300
H	-0.83985000	-2.43098300	1.87490300
C	-4.91636500	-1.16413700	2.51924500
C	-6.04802700	-1.07497800	1.69718500
H	-5.94321800	-0.74914700	0.66588600
C	-7.31012500	-1.38262500	2.19289500
H	-8.17707000	-1.30847300	1.54280700
C	-7.46284400	-1.78629700	3.51839200
H	-8.44935100	-2.02620700	3.90400100
C	-6.34871700	-1.87356000	4.34647400
H	-6.46121000	-2.17974300	5.38233600
C	-5.08549800	-1.55848300	3.84996600
H	-4.21892500	-1.61696700	4.50372400
Pd	2.91309400	0.16852000	0.34046800
F	-4.08889300	2.82798300	-3.99744100
F	-2.42202300	4.03656000	-3.39953800
F	-4.05738000	-2.08343800	-4.43964000
F	-4.66169800	-3.43427300	-2.88912000
N	3.08096800	-2.02223900	0.64753400
C	2.90464300	-4.19888500	1.20279500
C	4.23498800	-3.89827600	0.97940200
N	4.29134300	-2.59442900	0.65316700
H	2.48673500	-5.15289200	1.48570500
H	5.12840200	-4.50280300	1.02444500
H	5.10496200	-2.01978400	0.42534900
C	2.22882100	-2.98866800	0.97999300
H	1.17388000	-2.76427100	1.02317000

INT4

C	-3.66456300	2.57008700	0.01264100
C	-3.23758100	1.21992200	-0.48069900
C	-3.44898300	0.01975800	0.19087200
C	-3.07825500	-1.16705400	-0.49742700
C	-2.99313900	3.70481900	-0.72562200
C	-2.25953600	4.67334200	-0.04075600
C	-1.60573300	5.69331400	-0.72786300
C	-1.69025400	5.77179800	-2.11413800
C	-2.44812500	4.83052900	-2.80851400
C	-3.09280900	3.80860000	-2.11836600
C	-3.18767900	-2.47734900	0.19590900
O	-3.00278400	-2.66034100	1.37984500
O	-3.50790100	-3.44919700	-0.66838500
C	-4.29729100	-5.63453000	-1.16258300
C	-3.64136000	-4.76328500	-0.11318800
H	-3.55725300	2.64684400	1.09766800
H	-3.11331300	1.15490100	-1.56569700
H	-3.71365100	0.02284600	1.25241000
H	-3.23326200	-1.21120100	-1.57339200
H	-2.20324700	4.63008500	1.04190600
H	-1.02903500	6.42704600	-0.17213500
H	-1.17927700	6.56612800	-2.65035200
H	-2.54509500	4.89764500	-3.88886100
H	-3.69943300	3.09224300	-2.66916800
H	-4.40342500	-6.65626700	-0.78456400
H	-5.29149000	-5.25265900	-1.41283100
H	-3.69519000	-5.65878700	-2.07515400
H	-2.64409900	-5.12879700	0.15607500
H	-4.23706700	-4.70477100	0.80162500
P	0.28958800	1.55592400	0.56865900
P	0.22441500	-1.70275600	-0.66068600
O	5.11462400	0.63630200	-3.10202000
O	4.81008100	0.91070500	-0.88043500
O	4.57188500	-1.44914500	3.41022400
O	4.56374000	-1.54495200	1.15366600
C	1.12912000	2.53431900	-0.71749000
C	0.41888700	2.82143900	-1.88506000
H	-0.60114400	2.46575900	-2.00146500
C	1.00395500	3.58597300	-2.88956000
H	0.43673900	3.81391200	-3.78619500
C	2.30284400	4.06074200	-2.73656400
H	2.76276700	4.65099800	-3.52347000
C	3.01477300	3.78267300	-1.57113800
H	4.02939400	4.14576200	-1.45035100
C	2.43023000	3.02405200	-0.56349000
H	2.99786800	2.79553300	0.33436800
C	-0.29706200	2.75216900	1.80838400
C	-1.40700000	2.41514300	2.58566900
H	-1.95111600	1.48380300	2.44108500
C	-1.87650700	3.29494200	3.55948200
H	-2.76671300	3.01196300	4.11364100
C	-1.22956400	4.51014400	3.76061000

H	-1.59887000	5.20301500	4.51094100
C	-0.11430400	4.84801100	2.99145100
H	0.38606400	5.79980600	3.14424300
C	0.35315300	3.97433100	2.01761200
H	1.20519600	4.25634300	1.40737600
C	1.74437400	-1.04799300	-1.47017000
C	1.95103100	-1.21920600	-2.84054800
H	1.24398900	-1.80316500	-3.41745000
C	3.05605200	-0.68073400	-3.51337400
H	3.20452700	-0.82558500	-4.57642700
C	3.94512800	0.02296700	-2.74162300
C	5.67821100	1.13335700	-1.93724900
C	3.75749800	0.19095500	-1.38224300
C	2.67088700	-0.30192000	-0.69596300
C	2.59442000	-0.10746400	0.77639700
C	1.64148600	0.68097200	1.46914100
C	1.66096700	0.73139700	2.86592800
H	0.92191300	1.33134000	3.38340800
C	2.59952700	0.03762900	3.63978900
H	2.59175600	0.08299600	4.72185400
C	3.53132800	-0.68953200	2.94409400
C	5.25667700	-1.90779200	2.29746300
C	3.52797500	-0.74502600	1.56347400
C	0.83764200	-2.65340800	0.76276700
C	0.17086500	-2.53873200	1.98497400
H	-0.72166300	-1.92489000	2.06832100
C	0.64806400	-3.22462100	3.09903800
H	0.12975600	-3.12692900	4.04742800
C	1.78024700	-4.02659500	2.99424000
H	2.15455700	-4.55416800	3.86627800
C	2.43936100	-4.15411400	1.77172600
H	3.32659400	-4.77218100	1.69129200
C	1.97439200	-3.46427400	0.65933200
H	2.50998400	-3.53598200	-0.28383800
C	-0.43702500	-2.92816100	-1.84673800
C	-1.14400400	-2.45376300	-2.95910400
H	-1.27665500	-1.38272300	-3.09708800
C	-1.68641400	-3.33853100	-3.88193400
H	-2.23165400	-2.95768800	-4.73980100
C	-1.54329000	-4.71180700	-3.69401500
H	-1.97402700	-5.40599900	-4.40923700
C	-0.85928400	-5.19119400	-2.58177800
H	-0.75625600	-6.26061200	-2.42462100
C	-0.30526400	-4.30507900	-1.66050900
H	0.21834700	-4.69330000	-0.79338700
Pd	-1.29929200	-0.01023800	-0.17696200
F	6.84800000	0.53761200	-1.70237700
F	5.92297200	2.43774300	-2.06612100
F	6.48761200	-1.39080200	2.26934700
F	5.39336900	-3.23268900	2.35347800
C	-6.59978600	-1.67513600	-0.48620700
C	-6.66036800	-0.45234500	-1.18427200
N	-6.45926600	0.58743800	-0.37613100
H	-6.72815400	-2.67462100	-0.87415500
H	-6.85191600	-0.28311600	-2.23599300
H	-4.75072100	2.58811100	-0.17591000
N	-6.28688700	0.04345300	0.83674700
H	-5.96719400	0.61237000	1.63662300
Cl	-4.58737700	1.13899300	3.23168100
C	-6.34823900	-1.30268500	0.82133900
H	-6.19146500	-1.87175300	1.72576100

INT5

C	-2.74441900	2.55974700	-0.23994100
C	-3.45695300	1.55529200	-0.93748200
C	-3.73790500	0.34340100	-0.29577800
C	-4.51033100	-0.74382300	-0.97857800
C	-2.24646800	3.78163900	-0.90607000
C	-2.11134400	4.95315100	-0.15436500
C	-1.63072900	6.12126300	-0.73681400
C	-1.27406200	6.13901800	-2.08159700
C	-1.40529300	4.97862500	-2.84340100
C	-1.88707300	3.81394200	-2.26054600
C	-4.30471500	-2.11410800	-0.37171600
O	-3.55224900	-2.38520400	0.53294000
O	-5.09121600	-3.01259500	-0.98039200
C	-5.77511100	-5.23736800	-1.44910500
C	-5.01822000	-4.35426900	-0.48041400
H	-2.92432300	2.61929600	0.84318100
H	-3.60913300	1.63210900	-2.01531800
H	-3.78110300	0.32527200	0.79404800
H	-4.30288300	-0.80549400	-2.05189600
H	-2.37113900	4.93653000	0.89994200
H	-1.52419700	7.01562200	-0.13022300
H	-0.89148500	7.04859200	-2.53524200
H	-1.12241700	4.98065300	-3.89225100
H	-1.96303600	2.90953200	-2.85990800
H	-5.75128400	-6.27581900	-1.10387800
H	-6.81979900	-4.92356700	-1.53113200
H	-5.32022800	-5.18862500	-2.44341700
H	-3.96853900	-4.64700800	-0.39715400
H	-5.45313600	-4.37873300	0.52406200
P	0.47819700	1.74698100	0.41233200

P	-0.59420800	-1.38480500	-0.63812700
O	4.85247600	-0.68932400	-2.96744800
O	4.58962400	-0.29093800	-0.75978000
O	3.62058500	-2.17081200	3.60422000
O	3.57394500	-2.44146100	1.36260900
C	1.63263700	2.20281100	-0.92552200
C	1.20113400	2.13419600	-2.25061800
H	0.17954400	1.83261300	-2.46120200
C	2.08055000	2.41938900	-3.29073800
H	1.74100800	2.34886500	-4.31967500
C	3.39496200	2.78158900	-3.01095800
H	4.08556300	2.99374700	-3.82147300
C	3.82990600	2.86310400	-1.68925800
H	4.85703500	3.13243200	-1.46890600
C	2.95498500	2.56810000	-0.65070700
H	3.30685600	2.59863800	0.37694800
C	0.27927700	3.24319200	1.43544200
C	-0.65576700	3.17009700	2.47393000
H	-1.21760900	2.25480400	2.65404200
C	-0.89974700	4.28471500	3.26919200
H	-1.64771400	4.21011900	4.05179800
C	-0.22062300	5.47684700	3.02961500
H	-0.41684500	6.34996200	3.64562100
C	0.69830400	5.55495900	1.98540400
H	1.21585500	6.48780100	1.78161100
C	0.94733500	4.44425700	1.18433500
H	1.64054700	4.53091200	0.35480400
C	1.08186900	-1.22837400	-1.41402000
C	1.26602400	-1.48013800	-2.77587400
H	0.42994900	-1.82610300	-3.37079000
C	2.49853800	-1.32253800	-3.42307800
H	2.61929900	-1.52472700	-4.48041000
C	3.54257800	-0.91366900	-2.63423400
C	5.50985500	-0.37158600	-1.78957000
C	3.38025100	-0.67098400	-1.28383000
C	2.17729800	-0.79140400	-0.62386600
C	2.14005700	-0.50173000	0.83514900
C	1.48214500	0.59596600	1.44700500
C	1.52430200	0.75255400	2.83347300
H	1.00965600	1.58890000	3.28918100
C	2.20895600	-0.13185100	3.67609900
H	2.22492000	0.00252100	4.75062800
C	2.85941200	-1.16930800	3.05858700
C	4.11961900	-2.90901100	2.54509000
C	2.82962000	-1.33513100	1.68752700
C	-0.25615100	-2.44257900	0.80091300
C	-0.71572400	-2.00491400	2.04424900
H	-1.29637500	-1.08761900	2.12166000
C	-0.39253300	-2.72535100	3.19051000
H	-0.74114700	-2.36981500	4.15520100
C	0.37919800	-3.88008900	3.09821000
H	0.63848500	-4.43509700	3.99491100
C	0.83851400	-4.31836400	1.85659100
H	1.45991400	-5.20466400	1.78621700
C	0.53372100	-3.59423800	0.71050900
H	0.94116000	-3.90673400	-0.24777400
C	-1.49406700	-2.38263400	-1.88462700
C	-2.02707000	-1.70414200	-2.98734200
H	-1.91195500	-0.62364200	-3.05472400
C	-2.70678500	-2.39303000	-3.98679900
H	-3.11340000	-1.85214600	-4.83607300
C	-2.87790100	-3.77123100	-3.88528700
H	-3.41615700	-4.31176200	-4.65796200
C	-2.36396900	-4.45137700	-2.78500800
H	-2.50452200	-5.52461600	-2.69492500
C	-1.67461900	-3.76352200	-1.78968200
H	-1.30120700	-4.30205500	-0.92559700
Pd	-1.53899100	0.72188300	-0.21962800
F	6.42888500	-1.30042700	-1.51276900
F	6.15866900	0.78635000	-1.92454000
F	5.45271300	-2.81008900	2.50401800
F	3.83510200	-4.20182200	2.70944900
H	-5.58158600	-0.51600500	-0.88771200
N	-3.42025400	1.83118900	2.71127100
C	-4.84282600	0.18258800	3.29853200
C	-3.54369300	-0.30637100	3.16370000
N	-2.69778200	0.68053500	2.80509500
H	-5.73655100	-0.35478400	3.58626000
H	-3.19126100	-1.32352100	3.28997000
C	-4.69779100	1.54184100	3.00058100
H	-5.44935100	2.32401300	2.99329600

TS1

C	-2.49651700	2.13414200	0.96390000
C	-3.22843300	1.08613600	0.33704300
C	-3.32848900	-0.17341500	0.95103800
C	-3.98016500	-1.31457900	0.39901800
C	-2.27044300	3.44906300	0.32159700
C	-1.70874400	4.48692500	1.07629700
C	-1.37705800	5.70083700	0.48563800
C	-1.62308200	5.90858700	-0.86906900
C	-2.21906100	4.89704700	-1.62035700
C	-2.53934100	3.67574200	-1.03751800

C	-3.76612800	-2.57265700	1.11215100
O	-3.30901900	-2.68475200	2.24096800
O	-4.17421400	-3.63438500	0.38417500
C	-2.59669000	-5.46490100	0.67494700
C	-3.98497000	-4.92362300	0.97172800
H	-2.45554400	2.14688800	2.05469700
H	-3.61855400	1.19298600	-0.67628900
H	-3.06200400	-0.25811700	2.00768400
H	-4.00897300	-1.39694600	-0.68790200
H	-1.51726300	4.33335300	2.13517000
H	-0.92710600	6.48501100	1.08801000
H	-1.36518700	6.85604900	-1.33322000
H	-2.43945700	5.05515100	-2.67212000
H	-3.00408000	2.90597300	-1.64980300
H	-2.48991900	-6.47354600	1.08932200
H	-2.42847100	-5.50896400	-0.40481400
H	-1.83175800	-4.82434400	1.12301100
H	-4.15702100	-4.85852800	2.04903300
H	-4.75697000	-5.55147000	0.51965600
P	0.92876800	1.59830700	1.05242600
P	-0.16749300	-1.31961600	-0.57095700
O	4.53310900	0.66289700	-3.63899300
O	4.76112400	0.46595500	-1.40080300
O	4.97025400	-2.54485500	2.42349400
O	4.41098900	-2.29439600	0.24982900
C	1.75497600	2.60995500	-0.21761500
C	0.99990700	3.04249700	-1.30986800
H	-0.05404100	2.78997100	-1.37590800
C	1.59643200	3.79821900	-2.31481100
H	1.00049300	4.12888100	-3.15958200
C	2.94732900	4.12214900	-2.23376200
H	3.41614000	4.70218900	-3.02299100
C	3.70361300	3.70017900	-1.14105000
H	4.75880000	3.94334000	-1.08123200
C	3.11140900	2.94382100	-0.13680300
H	3.71018200	2.59280300	0.69955000
C	0.76920000	2.68614100	2.51526300
C	-0.05688900	2.25010300	3.55947800
H	-0.53170500	1.27297700	3.49574700
C	-0.29072200	3.06172400	4.66341200
H	-0.93350000	2.71163100	5.46533900
C	0.28482200	4.33006500	4.72697200
H	0.09076900	4.97286400	5.58022000
C	1.10146300	4.77245500	3.69083500
H	1.54586600	5.76227800	3.73258800
C	1.34680500	3.95447500	2.59012400
H	1.96729700	4.32017100	1.77899000
C	1.29858600	-0.79745500	-1.56256700
C	1.17489400	-0.67340400	-2.94911800
H	0.24967600	-0.97700200	-3.42551200
C	2.19970600	-0.17362900	-3.76278200
H	2.08414200	-0.08359400	-4.83599800
C	3.35955000	0.17783500	-3.12012800
C	5.41895600	0.76687300	-2.58128600
C	3.49855100	0.05712400	-1.75109400
C	2.49860600	-0.39689800	-0.91880900
C	2.77702400	-0.46979000	0.54255000
C	2.21587800	0.37254100	1.53767900
C	2.57967800	0.21393300	2.87680300
H	2.14894900	0.86922300	3.62476200
C	3.49630800	-0.75524700	3.30551300
H	3.76645900	-0.86594000	4.34858500
C	4.04229700	-1.54093400	2.32285000
C	5.25001300	-2.95479200	1.13048300
C	3.69953800	-1.38713300	0.99304800
C	0.46236100	-2.62171300	0.53961000
C	-0.08419100	-2.70258600	1.82288600
H	-0.87051800	-2.01641100	2.12390900
C	0.35336500	-3.68396100	2.70879500
H	-0.08666000	-3.74429000	3.69916000
C	1.34000900	-4.58472300	2.31954400
H	1.68526700	-5.34677600	3.01192100
C	1.88679300	-4.51127500	1.03925300
H	2.66229700	-5.20586400	0.73587700
C	1.45168400	-3.53249200	0.15320900
H	1.90127400	-3.46158600	-0.83382100
C	-1.22872500	-2.18109500	-1.78043000
C	-2.18602700	-1.41899600	-2.45834600
H	-2.31795000	-0.36076800	-2.24120700
C	-3.01661400	-2.00757800	-3.40764800
H	-3.76489000	-1.38824200	-3.89262200
C	-2.89817100	-3.36713200	-3.67999500
H	-3.55150300	-3.83323200	-4.41182000
C	-1.95190000	-4.13495500	-3.00394900
H	-1.86415100	-5.19829700	-3.20855000
C	-1.11957200	-3.54748900	-2.05709200
H	-0.39942200	-4.16042100	-1.52485100
Pd	-1.08902100	0.60211700	0.43191400
F	6.44699800	-0.06907400	-2.75759000
F	5.92901700	1.99850300	-2.52675600
F	6.52557500	-2.69383700	0.83198400
F	5.08932200	-4.27455000	1.02077100

N	-6.52079600	-0.45794200	0.32662800
C	-8.65702000	0.16208100	0.40520600
C	-8.05977200	0.68017500	-0.73794200
N	-6.78326000	0.28629800	-0.75063200
H	-9.67995400	0.28402600	0.72525200
H	-8.44671300	1.29645300	-1.53522900
H	-6.03443400	0.51297700	-1.47296700
H	-5.38404400	-0.91342500	0.47696800
Cl	-4.75687600	1.04293300	-2.83322100
C	-7.64099600	-0.55008900	1.04427400
H	-7.65100200	-1.11631400	1.96397300

TS2

C	2.79784200	1.98771400	0.21226900
C	3.22901600	0.97578400	1.12670200
C	3.57583100	-0.32788200	0.67876800
C	3.75677300	-1.43000800	1.69835400
C	2.56530400	3.39199700	0.62080400
C	2.58207300	4.40399400	-0.34639800
C	2.28961200	5.72137600	-0.00975600
C	1.98326100	6.05970500	1.30484000
C	1.97204000	5.06456400	2.28123300
C	2.25604700	3.74739900	1.94318400
C	3.67801700	-2.84759500	1.16395400
O	3.44423300	-3.80751300	1.86298500
O	3.91950900	-2.90926500	-0.14179000
C	4.29876500	-4.04254200	-2.19065700
C	3.84612500	-4.20632700	-0.75636600
H	3.05906600	1.84947200	-0.83809300
H	3.42139300	1.21605900	2.17120900
H	3.25478800	-0.62055900	-0.31789800
H	3.00122100	-1.34263800	2.48299100
H	2.80532300	4.14929100	-1.37835200
H	2.29631400	6.48299800	-0.78406300
H	1.75324700	7.08772100	1.56853000
H	1.73341400	5.31586400	3.31108600
H	2.21409900	2.98005300	2.71236700
H	4.19832300	-4.99534300	-2.72081500
H	3.69936900	-3.27865600	-2.69588300
H	5.34808500	-3.73295000	-2.23054700
H	4.47751600	-4.89831100	-0.19113700
H	2.81145600	-4.55619300	-0.68981600
P	-0.50503900	1.68161400	-0.78756600
P	-0.11880500	-1.04656900	1.39188900
O	-5.80781700	0.58047000	1.98142800
O	-4.98983800	0.33326100	-0.10885400
O	-3.24885800	-2.95492600	-3.31189900
O	-3.73772100	-2.49424900	-1.15597900
C	-1.82553500	2.59017200	0.08575900
C	-1.62323000	2.94826400	1.42038900
H	-0.67700800	2.70908400	1.89923100
C	-2.63137000	3.59091800	2.13347300
H	-2.47252300	3.85425900	3.17483100
C	-3.84141100	3.88879200	1.51319800
H	-4.63212300	4.38139400	2.07108800
C	-4.04136900	3.55368600	0.17499300
H	-4.98537800	3.77941100	-0.30848800
C	-3.03983300	2.90170100	-0.53460300
H	-3.20954300	2.61320200	-1.56850800
C	0.08056000	2.83042800	-2.08436000
C	1.15332200	2.41658200	-2.88532600
H	1.58741900	1.42286500	-2.77117500
C	1.69476900	3.27997100	-3.83160400
H	2.51720500	2.93413100	-4.45046200
C	1.19911800	4.57575200	-3.96344900
H	1.63124700	5.25472400	-4.69296200
C	0.15355600	5.00046500	-3.14886700
H	-0.23002500	6.01283000	-3.23596600
C	-0.40838600	4.13265400	-2.21536100
H	-1.21548100	4.48410800	-1.58160500
C	-1.89427700	-0.62453100	1.64973100
C	-2.41861100	-0.48302500	2.93589800
H	-1.79353100	-0.71265200	3.79106500
C	-3.73420800	-0.06599200	3.17863200
H	-4.12719400	0.03617100	4.18291600
C	-4.49704700	0.18669700	2.06753900
C	-6.12646500	0.59611500	0.63384900
C	-3.99481100	0.03724700	0.78857800
C	-2.69981900	-0.34255300	0.51443500
C	-2.29294700	-0.50763400	-0.91140400
C	-1.41482000	0.32985200	-1.65168700
C	-1.12568900	0.03245700	-2.98488500
H	-0.43873100	0.66303800	-3.53462400
C	-1.67647400	-1.06548300	-3.65717000
H	-1.42689800	-1.28402100	-4.68798700
C	-2.54354200	-1.84088600	-2.93153500
C	-4.03971700	-3.30768900	-2.23324300
C	-2.84147000	-1.55907000	-1.61254800
C	-0.19156400	-2.50563400	0.30335400
C	0.58599300	-2.49622200	-0.85710200
H	1.24938400	-1.66671600	-1.09072300
C	0.48157700	-3.53832400	-1.77540500
H	1.07537000	-3.49314600	-2.68344900

C	-0.38722700	-4.59730500	-1.53112100
H	-0.48000500	-5.40445800	-2.25173200
C	-1.15763600	-4.61653100	-0.36761300
H	-1.84791200	-5.43325800	-0.18514700
C	-1.07028700	-3.56973900	0.54134200
H	-1.70489700	-3.56572300	1.42394900
C	0.46577900	-1.62437000	3.02653200
C	0.77510500	-0.63760100	3.97605600
H	0.60560900	0.40996600	3.73394700
C	1.31448700	-0.98513800	5.20767300
H	1.54211500	-0.21269500	5.93636100
C	1.58464700	-2.32371800	5.49434900
H	2.02610600	-2.59675800	6.44810800
C	1.30794900	-3.30321400	4.54834000
H	1.54614400	-4.34216600	4.75114300
C	0.74350700	-2.95905000	3.32105100
H	0.56319900	-3.73278700	2.58339800
Pd	1.13745000	0.73595600	0.55566600
F	-7.06690200	-0.31687000	0.37364300
F	-6.63760800	1.78222000	0.29682400
F	-5.33343400	-3.18336800	-2.55140800
F	-3.84447900	-4.58936300	-1.91726200
H	4.72466700	-1.32560900	2.20123000
N	5.54476600	-0.39080700	-1.38901200
C	7.57463500	0.01984700	-0.64971200
C	6.65542900	-0.03594500	0.40661500
N	5.43689100	-0.29018000	-0.06377600
H	8.63671600	0.20265300	-0.59519800
H	6.81334600	0.09400500	1.46834400
C	6.81383900	-0.21053400	-1.78487200
H	7.07860400	-0.25705500	-2.83035900
H	4.68462700	-0.54366100	-1.96556500
Cl	2.88068200	-0.64847200	-2.89009400

TS1-*ent*

C	3.01890000	1.53474800	0.67919100
C	3.16947700	0.59478800	1.73236800
C	3.16506700	-0.80533500	1.53218600
C	3.49952400	-1.56875900	0.37426500
C	2.98907900	2.99588400	0.92312400
C	3.60038100	3.85556600	0.00657400
C	3.55679200	5.23457300	0.18392600
C	2.90426200	5.77904400	1.28554400
C	2.29335000	4.93270300	2.20924800
C	2.33417200	3.55612700	2.02761600
C	3.35101200	-3.01532900	0.51890300
O	3.30127100	-3.62926200	1.57350900
O	3.32603200	-3.63386900	-0.68431200
C	1.82942100	-5.54847500	-0.39053400
C	3.24239500	-5.05919200	-0.66311600
H	3.35641800	1.24384400	-0.31964300
H	3.12273700	0.94604400	2.76179000
H	3.08063200	-1.40286800	2.43978500
H	3.28309600	-1.16879200	-0.61875300
H	4.09539700	3.43442300	-0.86366100
H	4.02412800	5.88428200	-0.55005200
H	2.86274100	6.85584800	1.42060100
H	1.77097800	5.34749900	3.06669300
H	1.82471900	2.90540100	2.73419500
H	1.79094900	-6.64047300	-0.47592400
H	1.52842500	-5.26637600	0.62073100
H	1.12469300	-5.11779100	-1.10771600
H	3.57973700	-5.36522900	-1.65642400
H	3.93525500	-5.44982000	0.08828800
P	-0.26828500	1.77009100	-0.35504200
P	-0.28846400	-1.40111800	1.13580500
O	-5.75185600	0.72969100	2.11305700
O	-4.92179700	0.89914500	0.01982500
O	-3.62343000	-1.62106100	-3.91518700
O	-4.05719400	-1.67571700	-1.70009500
C	-1.49496800	2.58431400	0.72918200
C	-1.35474700	2.49443600	2.11540900
H	-0.50252000	1.96271100	2.53073300
C	-2.31872800	3.04292700	2.95635400
H	-2.21183800	2.95026700	4.03291800
C	-3.42356100	3.69514200	2.41641400
H	-4.18214900	4.11392700	3.07071100
C	-3.56252300	3.80276900	1.03385600
H	-4.42827300	4.29965500	0.61002600
C	-2.60728500	3.24291900	0.19398700
H	-2.73712400	3.29810200	-0.88346200
C	0.45732600	3.11543500	-1.35601000
C	1.45772300	2.76534500	-2.26999100
H	1.80279000	1.73636100	-2.36289200
C	2.05673100	3.73808200	-3.06231100
H	2.82248300	3.43580900	-3.77032100
C	1.69567100	5.07497200	-2.91875500
H	2.17069700	5.83852300	-3.52829800
C	0.73972500	5.43411100	-1.97282100
H	0.47386200	6.47791200	-1.83433600
C	0.11660400	4.46092600	-1.19606100
H	-0.62164700	4.76076400	-0.46050300
C	-2.01488800	-0.84883300	1.46301300

C	-2.54726800	-0.95780200	2.74987100
H	-1.97165400	-1.46149900	3.51821800
C	-3.80580500	-0.45119900	3.09793300
H	-4.20557600	-0.54716700	4.10014700
C	-4.50478300	0.15986500	2.08843700
C	-6.03025300	1.12482200	0.81529100
C	-3.99465400	0.26542500	0.80856700
C	-2.75124300	-0.19866800	0.43770200
C	-2.34304100	-0.04979100	-0.98970700
C	-1.34266100	0.81399100	-1.51170800
C	-1.09532200	0.84443200	-2.88581700
H	-0.32838400	1.50271400	-3.27336600
C	-1.79637700	0.05498200	-3.80539300
H	-1.58016800	0.08851600	-4.86602500
C	-2.76863600	-0.75620000	-3.28022600
C	-4.46636000	-2.12724900	-2.94200600
C	-3.03254300	-0.78975500	-1.92494200
C	-0.44789600	-2.41538000	-0.37437000
C	0.43352000	-2.17769300	-1.43257500
H	1.22589500	-1.44069700	-1.34619700
C	0.28671100	-2.86130400	-2.63619700
H	0.97820200	-2.64898800	-3.44514200
C	-0.73549900	-3.79311700	-2.78623500
H	-0.85700400	-4.32258600	-3.72661600
C	-1.61439000	-4.04304000	-1.73157500
H	-2.42276700	-4.75587200	-1.85216900
C	-1.47954200	-3.34894500	-0.53541100
H	-2.20472600	-3.50489300	0.25914400
C	0.09029300	-2.53964400	2.51738100
C	0.62995400	-1.97358500	3.67830000
H	0.81060800	-0.90103700	3.71475500
C	0.95494000	-2.77012900	4.76994800
H	1.37462300	-2.31809600	5.66362300
C	0.76462100	-4.14817800	4.70395000
H	1.03620800	-4.77576300	5.54732200
C	0.24071200	-4.72013600	3.54936400
H	0.10488400	-5.79549100	3.48689700
C	-0.10226100	-3.92072300	2.46299200
H	-0.49326300	-4.38391100	1.56401400
Pd	1.19596000	0.39125900	0.82045800
F	-7.08018100	0.44646300	0.34371400
F	-6.36404200	2.41731600	0.79100400
F	-5.72508000	-1.74153100	-3.17768700
F	-4.46126500	-3.46140300	-2.97503600
N	6.02132100	-0.88329400	-0.23505000
C	8.10424900	-0.26063700	-0.68871300
C	7.26953300	0.08507700	-1.74584100
N	6.02987600	-0.30451600	-1.43752100
H	9.16690400	-0.09312400	-0.60920300
H	7.47095300	0.57458000	-2.68647800
H	5.12321100	-0.20393400	-1.99081700
H	4.97105300	-1.27480300	0.16321900
Cl	3.44295400	0.01093000	-2.90838800
C	7.26551900	-0.87162700	0.24389900
H	7.47961900	-1.29674400	1.21303800

TS2-*ent*

C	-2.66767000	2.04189500	0.74063400
C	-3.20297500	1.01678700	-0.07855400
C	-3.64488000	-0.24914100	0.38256600
C	-3.63718000	-0.66522900	1.83941000
C	-2.38285900	3.40462000	0.22838000
C	-1.84063300	4.35646000	1.10171100
C	-1.46076400	5.61266000	0.64437800
C	-1.63740700	5.95112900	-0.69485600
C	-2.21574700	5.02715700	-1.56277800
C	-2.58795700	3.76455700	-1.11238000
C	-3.86443000	-2.15158600	2.00035500
O	-4.68163000	-2.65897500	2.73225400
O	-3.01138100	-2.82796100	1.22304700
C	-4.25694600	-4.61513400	0.16083700
C	-3.16055100	-4.25535200	1.14510100
H	-2.81643500	1.99085700	1.82060200
H	-3.32065000	1.17641500	-1.15066000
H	-3.60330500	-1.05141800	-0.34361700
H	-2.65913700	-0.42908300	2.27690000
H	-1.69785100	4.10012400	2.14843400
H	-1.02616400	6.32651600	1.33851400
H	-1.34080100	6.93151700	-1.05601400
H	-2.38448000	5.28697100	-2.60388000
H	-3.04044200	3.06868200	-1.81579400
H	-4.30607200	-5.70212700	0.03885500
H	-5.22759500	-4.26400000	0.52194900
H	-4.05303600	-4.16577800	-0.81553200
H	-2.18229300	-4.60491500	0.80971900
H	-3.36649600	-4.64512600	2.14503500
P	0.83735400	1.52762000	1.08131300
P	-0.22222100	-1.39593700	-0.59021800
O	4.41817700	0.70348400	-3.66354000
O	4.65306400	0.50958300	-1.42582500
O	4.96000000	-2.56436900	2.34714300
O	4.36792600	-2.29748900	0.18432700
C	1.66441900	2.59843900	-0.14091800

C	0.91575600	3.07256300	-1.22039100
H	-0.13544000	2.81668400	-1.30825900
C	1.51470300	3.87468000	-2.18708200
H	0.92186800	4.23709000	-3.02086700
C	2.86283400	4.20292800	-2.08194700
H	3.33386700	4.81917100	-2.84188400
C	3.61363600	3.73763400	-1.00325900
H	4.66720700	3.98333500	-0.92535100
C	3.01867800	2.93551900	-0.03679900
H	3.61415400	2.55260200	0.78782500
C	0.63424000	2.56148700	2.57801000
C	-0.23542900	2.09616200	3.57223100
H	-0.71842700	1.12887600	3.44927200
C	-0.50601400	2.86775100	4.69616200
H	-1.18307600	2.49550100	5.45907600
C	0.07543600	4.12812200	4.82803200
H	-0.14804600	4.74164500	5.69550300
C	0.93457900	4.60105400	3.84090100
H	1.38279100	5.58550300	3.93553100
C	1.21783500	3.82094600	2.72192000
H	1.87192100	4.20950700	1.94849000
C	1.23004000	-0.85391600	-1.59029300
C	1.10088100	-0.73125000	-2.97559600
H	0.18266600	-1.05692900	-3.45159300
C	2.11105100	-0.20121600	-3.78882200
H	1.99260300	-0.11245700	-4.86179800
C	3.25882900	0.18511000	-3.14482400
C	5.29996400	0.83571800	-2.60589300
C	3.40173700	0.06776200	-1.77532800
C	2.41786800	-0.41910500	-0.94244000
C	2.71170800	-0.49995200	0.51821000
C	2.15190000	0.32048700	1.53327000
C	2.53651800	0.15278700	2.86507700
H	2.10396600	0.79343400	3.62512900
C	3.47433700	-0.80627700	3.27028000
H	3.76228300	-0.92450700	4.30780800
C	4.01707600	-1.57212100	2.27052500
C	5.23265200	-2.95019700	1.04524500
C	3.65385100	-1.40814900	0.94683600
C	0.49091100	-2.64087500	0.54313700
C	0.12756700	-2.60427400	1.89106400
H	-0.57199700	-1.84699100	2.23201200
C	0.67002400	-3.51461300	2.79313300
H	0.38840200	-3.47047900	3.84089100
C	1.57876700	-4.47293400	2.35252600
H	2.00813900	-5.17995900	3.05584900
C	1.94722800	-4.51769200	1.00951400
H	2.66892300	-5.25031800	0.66586800
C	1.41313800	-3.60033000	0.11129700
H	1.73881000	-3.61153700	-0.92549700
C	-1.26978300	-2.34724900	-1.75303000
C	-2.20557600	-1.62244700	-2.50031800
H	-2.29504000	-0.54230400	-2.40249600
C	-3.05904300	-2.26692600	-3.39140800
H	-3.77480800	-1.66213700	-3.94070500
C	-2.98644600	-3.64905800	-3.54074600
H	-3.65400600	-4.15879200	-4.22931700
C	-2.06129700	-4.38060100	-2.79745300
H	-2.00711200	-5.46023500	-2.90455000
C	-1.20719200	-3.73655800	-1.90686300
H	-0.50513900	-4.32571200	-1.32674600
Pd	-1.13699700	0.56295800	0.32382500
F	6.35586700	0.03540100	-2.78359900
F	5.76747700	2.08375500	-2.54869100
F	6.49826000	-2.65688000	0.73470700
F	5.10037500	-4.27195200	0.92021100
N	-5.66374100	-0.28216900	0.14074500
C	-7.89347600	-0.48411700	0.08924600
C	-7.45041400	0.05863300	-1.10669600
N	-6.11598300	0.16212000	-1.03566200
H	-8.91000600	-0.70442200	0.37669000
H	-7.97649100	0.37572400	-1.99451000
H	-5.46511900	0.49989600	-1.79177300
H	-4.39115900	-0.11936700	2.40943300
Cl	-4.32853700	1.07420900	-3.34156000
C	-6.72761600	-0.68378200	0.83895500
H	-6.60130000	-1.10891400	1.82547300

TS3

P	-1.16710900	-0.06234300	1.69382700
P	1.85604500	-1.39462400	0.04844400
O	-1.78104200	0.89917300	-4.04815700
O	-1.42112200	2.11831300	-2.18266800
O	2.36729600	4.52287900	0.30621800
O	1.85107800	3.05489100	-1.32967400
C	-2.83592600	0.59738900	1.30907000
C	-3.93279700	-0.22361200	1.60222600
H	-3.76818800	-1.19792200	2.05610800
C	-5.22314000	0.18941300	1.29623200
H	-6.06476600	-0.45566400	1.52898200
C	-5.43274500	1.41717600	0.66765200
H	-6.43987800	1.73250100	0.41184600
C	-4.34742500	2.23209900	0.36176600

H	-4.50136400	3.18390500	-0.13716200
C	-3.05335800	1.82964400	0.69064000
H	-2.21769600	2.47722900	0.44839300
C	-1.17842300	-0.13622800	3.52656600
C	-0.32767900	-1.05226500	4.15394200
H	0.27725300	-1.72173100	3.54688900
C	-0.27531000	-1.12816300	5.54248300
H	0.38521900	-1.84682200	6.01807200
C	-1.08194900	-0.29843900	6.31699600
H	-1.04750000	-0.36325700	7.40049100
C	-1.94356500	0.60557300	5.70008300
H	-2.58212700	1.24681500	6.30037900
C	-1.99265900	0.68726600	4.31148800
H	-2.66944000	1.39208600	3.83649100
C	0.95044400	-0.59289700	-1.35279100
C	0.71481700	-1.33414700	-2.51561900
H	1.22340900	-2.28331400	-2.64294300
C	-0.18856000	-0.92978700	-3.50709600
H	-0.36481900	-1.52223100	-4.39648900
C	-0.84924600	0.24927000	-3.27419500
C	-2.16500900	2.02309500	-3.34327500
C	-0.62706700	0.99488800	-2.13267200
C	0.24851700	0.62588200	-1.13783100
C	0.45241200	1.53822300	0.02375600
C	-0.07328400	1.37988300	1.33142700
C	0.24787800	2.30327900	2.33015000
H	-0.15013200	2.16068700	3.32789500
C	1.07723100	3.40888100	2.10878500
H	1.33035900	4.10443500	2.89958500
C	1.54763100	3.55646700	0.82834400
C	2.48487700	4.25074100	-1.04676300
C	1.22963300	2.65819200	-0.17121100
C	2.99970200	-0.09482300	0.66882400
C	3.08922200	0.05859800	2.05448600
H	2.47542200	-0.56304200	2.70138200
C	3.93747700	1.01330100	2.61076700
H	3.98981400	1.12554200	3.68962900
C	4.70735300	1.82371500	1.78349600
H	5.36742800	2.57156000	2.21289600
C	4.62267100	1.68297100	0.39911700
H	5.20770600	2.32544200	-0.24991000
C	3.77027400	0.73434700	-0.15404000
H	3.67999600	0.66834400	-1.23393900
C	2.97529200	-2.59620800	-0.76504900
C	3.84473200	-2.28028500	-1.81711400
H	3.86037300	-1.27701500	-2.23123200
C	4.68226400	-3.25025200	-2.35338700
H	5.35224800	-2.99462200	-3.16912800
C	4.66141800	-4.54889700	-1.84435000
H	5.31659900	-5.30631900	-2.26498900
C	3.79565100	-4.87413100	-0.80651600
H	3.76351700	-5.88696700	-0.41709100
C	2.95188700	-3.90289600	-0.27049400
H	2.25010600	-4.16477900	0.51529700
Pd	-0.49540800	-1.98584800	0.73613000
F	-2.00009300	3.11628700	-4.08824000
F	-3.47311200	1.95609200	-3.04498100
F	1.94004000	5.24059500	-1.76169500
F	3.77092500	4.18690900	-1.39598700
N	-2.70804500	-2.90977300	-1.82598400
C	-3.85950100	-1.45959200	-3.00592100
C	-3.62679700	-0.97624200	-1.71185800
N	-2.93697000	-1.87698100	-1.01197700
H	-4.38590700	-0.96431700	-3.80660800
H	-3.92195500	-0.04095400	-1.26037200
H	-2.03014000	-1.87182500	0.07042700
H	-2.07826700	-3.64367000	-1.46535600
Cl	-0.57596000	-4.28692700	-0.09244000
C	-3.24490700	-2.70107100	-3.03732100
H	-3.15786800	-3.43871100	-3.82075600

TS4

C	3.89722100	2.20412200	-0.26950200
C	4.88410800	1.31909100	0.28144400
C	5.21484000	0.14260200	-0.40038600
C	5.95402600	-0.98250600	0.11511800
C	3.47676500	3.42855700	0.45852700
C	3.41864400	4.65613200	-0.20673800
C	2.98627800	5.80499400	0.44951000
C	2.58817200	5.74239000	1.78191600
C	2.64300000	4.52421600	2.45879500
C	3.09044600	3.38257400	1.80497700
C	6.54307800	-1.86325600	-0.90173000
O	6.19279100	-1.93754100	-2.06593500
O	7.48520000	-2.67284200	-0.36517300
C	7.09209500	-4.90195100	-1.25834600
C	8.00745500	-3.68915800	-1.22518300
H	3.87951500	2.30319900	-1.35680300
H	5.24667400	1.47309300	1.29731800
H	4.97299200	0.08229300	-1.46390000
H	6.56265800	-0.81715800	1.00458500
H	3.69961200	4.70681600	-1.25528300
H	2.94742500	6.74839700	-0.08761400

H	2.23625900	6.63499500	2.29066500
H	2.32326400	4.45862200	3.49466600
H	3.10067400	2.43104200	2.33034400
H	7.53791000	-5.69524300	-1.86806500
H	6.93150800	-5.29066500	-0.24764700
H	6.12564500	-4.63271000	-1.69271000
H	8.14608700	-3.27848100	-2.22840500
H	8.98229200	-3.93935800	-0.79961700
P	0.66497600	0.93111200	-0.06275500
P	-2.16245600	-1.51678400	1.69613400
O	-4.74113900	3.18278600	-0.91306200
O	-3.15493500	2.05404100	-2.06149600
O	-2.08241700	-2.71536700	-3.82076800
O	-3.42707900	-1.36870600	-2.60625100
C	-0.03154300	1.36678700	1.58140200
C	0.64388600	0.87671100	2.70600600
H	1.48001200	0.19509200	2.57828100
C	0.26551000	1.26445600	3.98731300
H	0.80215100	0.87415100	4.84673800
C	-0.79150200	2.15451200	4.16188400
H	-1.08246500	2.46703900	5.16076900
C	-1.47576800	2.64080200	3.05088000
H	-2.30692100	3.32791100	3.17598800
C	-1.09729200	2.25133400	1.77091900
H	-1.63116600	2.65335100	0.91707200
C	0.28868400	2.38423300	-1.12131000
C	0.04408400	2.21456300	-2.48981100
H	-0.00442600	1.21944300	-2.91976000
C	-0.15430600	3.31555900	-3.31490500
H	-0.35573000	3.16282400	-4.37076500
C	-0.11093400	4.60300100	-2.78808400
H	-0.27943500	5.46170000	-3.43085700
C	0.14796900	4.78184300	-1.43377400
H	0.20182000	5.78019500	-1.01075500
C	0.35768200	3.68334600	-0.60596800
H	0.58150500	3.84943600	0.44309100
C	-3.09611300	-0.10384200	0.94092100
C	-4.09291300	0.59204500	1.62665800
H	-4.39711100	0.24960900	2.60926100
C	-4.71984000	1.73203900	1.10182900
H	-5.49247900	2.26146600	1.64670900
C	-4.30986600	2.13000600	-0.14621700
C	-3.99960600	3.15011400	-2.08466700
C	-3.33424700	1.44390100	-0.84721100
C	-2.68410500	0.34126400	-0.34319800
C	-1.68321900	-0.39698200	-1.15340200
C	-0.27877900	-0.39084600	-0.94750400
C	0.53104600	-1.26230000	-1.68517800
H	1.60058000	-1.26216900	-1.50191800
C	0.03302100	-2.12315800	-2.67335000
H	0.68212400	-2.78692200	-3.23105700
C	-1.31546400	-2.04484700	-2.90657600
C	-3.36035300	-2.18828200	-3.71916200
C	-2.13661200	-1.21379200	-2.16407800
C	-2.65397200	-2.90453300	0.60066000
C	-3.94691900	-3.06629100	0.08878900
H	-4.72045400	-2.34628800	0.34287600
C	-4.24145600	-4.12684800	-0.75967000
H	-5.24448300	-4.23691900	-1.15920300
C	-3.24215900	-5.02797000	-1.12307000
H	-3.46937800	-5.84325100	-1.80318700
C	-1.95160600	-4.87147100	-0.62736800
H	-1.16707300	-5.56421300	-0.91658300
C	-1.65899600	-3.81600000	0.23311300
H	-0.64338100	-3.68815600	0.59774900
C	-3.10097000	-1.81689400	3.24743300
C	-4.05717200	-2.82113200	3.42371600
H	-4.30781800	-3.48503200	2.60283900
C	-4.68859800	-2.98647100	4.65446300
H	-5.42630100	-3.77414300	4.77707500
C	-4.37997100	-2.14796400	5.72147500
H	-4.87629900	-2.27804800	6.67866900
C	-3.42345500	-1.14835900	5.55869100
H	-3.16799500	-0.49597100	6.38874600
C	-2.78003200	-0.99382100	4.33558700
H	-2.02301800	-0.22291300	4.21843400
Pd	2.93307000	0.37411900	0.15459800
F	-4.81119900	3.08034400	-3.13996900
F	-3.29320100	4.27631600	-2.20649100
F	-3.65122500	-1.48459200	-4.82127200
F	-4.25803200	-3.16547700	-3.63757000
N	2.73394200	-1.63921900	0.86546600
C	2.17739600	-3.57208500	1.84509400
C	3.53901900	-3.55084700	1.54822400
N	3.83739300	-2.38558700	0.96470100
H	1.60986200	-4.35815800	2.32173300
H	4.30676400	-4.29429400	1.71292300
H	4.95406200	-1.78495900	0.56944700
C	1.71516900	-2.33635700	1.39311100
H	0.71872400	-1.91404600	1.43159800

TS5

C	4.18479400	-0.90405800	-0.12180700

C	3.46407200	0.21185700	-0.59002600
C	3.10625400	1.36537100	0.14732200
C	2.37293600	2.40004600	-0.50274200
C	4.09716800	-2.17649100	-0.88363400
C	3.84871600	-3.37876900	-0.21047500
C	3.70462600	-4.57275400	-0.90892500
C	3.81881400	-4.59675900	-2.29663900
C	4.09479700	-3.41321500	-2.97792000
C	4.23788900	-2.21892400	-2.27798400
C	1.95768300	3.60561000	0.25037400
O	1.90381600	3.70355800	1.45858700
O	1.57490600	4.58477700	-0.58933900
C	0.83250600	6.79329600	-1.05097800
C	0.97603600	5.73399900	0.02074100
H	4.21285600	-1.00882700	0.96549200
H	3.24277900	0.23993400	-1.66087700
H	3.39834600	1.44680100	1.19616900
H	2.46192500	2.53877700	-1.57875900
H	3.75037700	-3.36845300	0.87132700
H	3.49329800	-5.48796100	-0.36315800
H	3.70279600	-5.52893600	-2.84149900
H	4.20893500	-3.42080300	-4.05889600
H	4.46937200	-1.30577000	-2.82387700
H	0.34993100	7.68237400	-0.63241300
H	1.81321500	7.08261700	-1.44047600
H	0.22453000	6.42183700	-1.88058100
H	0.00392700	5.43867700	0.43329200
H	1.60433500	6.07058800	0.84962900
P	0.20547200	-1.25335000	0.63397000
P	-1.04801800	1.69506200	-0.78837400
O	-4.67003200	-2.55703200	-2.83908500
O	-4.24871000	-2.51437700	-0.62093500
O	-4.85424100	-0.05636800	3.53104700
O	-4.92914300	-0.03692800	1.27434400
C	-0.18117600	-2.49397700	-0.64728600
C	0.61571700	-2.50211500	-1.79468800
H	1.40957100	-1.76946800	-1.90772100
C	0.41286300	-3.45836900	-2.78469500
H	1.05337500	-3.46407800	-3.66061100
C	-0.59801600	-4.40369800	-2.64169700
H	-0.76315900	-5.14587900	-3.41711300
C	-1.39889000	-4.40093600	-1.50126100
H	-2.19400300	-5.12996800	-1.38949600
C	-1.18779900	-3.45396400	-0.50483900
H	-1.82261900	-3.45286100	0.37720500
C	1.23617100	-2.16330100	1.83538900
C	2.19251200	-1.45263200	2.56451000
H	2.33895200	-0.38656400	2.40739700
C	3.00456300	-2.10669700	3.48999700
H	3.76338900	-1.52833000	4.00821500
C	2.85834800	-3.47560400	3.68962900
H	3.49589700	-3.99015300	4.40274000
C	1.90385200	-4.19213400	2.96598500
H	1.79398100	-5.26220600	3.11668500
C	1.09676800	-3.54166400	2.04100900
H	0.37369700	-4.11205500	1.46700400
C	-2.20405200	0.43233300	-1.47281100
C	-2.47966100	0.39776500	-2.84198200
H	-2.05839500	1.16000500	-3.48702400
C	-3.29491200	-0.57879500	-3.42896400
H	-3.49731600	-0.59157300	-4.49296000
C	-3.83231300	-1.50532900	-2.57231600
C	-4.97163600	-3.14203400	-1.62065400
C	-3.57445500	-1.47771900	-1.21532900
C	-2.75107500	-0.55411100	-0.61085900
C	-2.56591000	-0.62331300	0.86515700
C	-1.37189400	-0.97399000	1.54727000
C	-1.34335200	-0.98419300	2.94506300
H	-0.42098900	-1.24554600	3.45109300
C	-2.45876100	-0.67279900	3.73219000
H	-2.41492500	-0.68229400	4.81437500
C	-3.60946400	-0.37151500	3.04888100
C	-5.68379500	0.06620200	2.43047400
C	-3.65478500	-0.36108100	1.66845900
C	-1.99858400	2.45238000	0.57204600
C	-1.32472600	2.77556700	1.75357200
H	-0.25537000	2.60330700	1.84189300
C	-2.02577700	3.31836800	2.82780200
H	-1.49516400	3.55967100	3.74337100
C	-3.39574100	3.54091700	2.72770500
H	-3.94269800	3.95455900	3.56960800
C	-4.07069300	3.22681700	1.54896600
H	-5.14066100	3.38585300	1.47323100
C	-3.37686500	2.67815400	0.47733600
H	-3.91469000	2.39628400	-0.42416000
C	-0.97346600	2.96388000	-2.10741700
C	-0.02649100	2.78643100	-3.12265600
H	0.64148800	1.92894900	-3.08618100
C	0.06842600	3.69558800	-4.16984400
H	0.80762200	3.54545500	-4.95070500
C	-0.77557000	4.80312800	-4.20688800
H	-0.69846800	5.51932600	-5.01932700

C	-1.71030300	4.99511900	-3.19348900
H	-2.36378600	5.86218600	-3.21219900
C	-1.81012100	4.08113500	-2.14728500
H	-2.53634500	4.24936800	-1.35905900
Pd	1.01026000	0.81426400	-0.14806600
F	-6.27951100	-3.04228200	-1.37371800
F	-4.68121000	-4.44469700	-1.65069800
F	-6.62096100	-0.88652100	2.45154200
F	-6.32323800	1.23669500	2.46299400
C	8.89277500	0.45266500	-0.32426600
C	7.79106500	-0.10542700	-0.97644400
N	6.72843700	-0.05521100	-0.17184200
H	9.89810500	0.56304700	-0.70020100
H	7.70583600	-0.53866500	-1.96232300
H	5.49610800	-0.43649900	-0.25559200
N	7.11182600	0.51241000	0.97333000
H	6.40304900	0.62185100	1.76567400
Cl	5.03305200	0.71340900	3.09893800
C	8.40825000	0.83237800	0.92218000
H	8.89098000	1.30163400	1.76596900

TS6

C	4.17501000	-2.02570900	-0.00295800
C	3.91511600	-0.60957800	-0.44587900
C	3.41172900	0.41029900	0.38950700
C	2.92443600	1.61359600	-0.21098700
C	3.40780600	-3.05251600	-0.81288200
C	2.73131300	-4.08406500	-0.15972200
C	2.06296900	-5.06917300	-0.88126900
C	2.07110700	-5.04656200	-2.27211200
C	2.75839000	-4.03346300	-2.93655100
C	3.42020300	-3.04627800	-2.21191600
C	2.68723800	2.81077600	0.62730500
O	2.62367100	2.82659300	1.83940600
O	2.49135400	3.90084000	-0.13683800
C	2.16193000	6.23322100	-0.44282400
C	2.12717500	5.09907900	0.55948500
H	3.97356800	-2.11763600	1.06630800
H	3.79814700	-0.45674900	-1.51641500
H	3.60593100	0.34833900	1.46103100
H	3.15885500	1.82685200	-1.25290100
H	2.73942000	-4.12150200	0.92487800
H	1.53302300	-5.85364100	-0.34914500
H	1.54565300	-5.81184600	-2.83540500
H	2.78726600	-4.01550800	-4.02270200
H	3.97738700	-2.28055300	-2.74741700
H	1.86504200	7.16799300	0.04338200
H	3.16987200	6.35834300	-0.84947500
H	1.47752000	6.03583900	-1.27287300
H	1.12653500	4.96411900	0.98560400
H	2.82504400	5.26025700	1.38568400
P	-0.04014000	-1.48268700	0.70676200
P	-0.45333500	1.63388000	-0.82242900
O	-4.98406100	-1.62522700	-2.86653200
O	-4.63823500	-1.58217700	-0.63530900
O	-4.64614500	1.14375500	3.41719700
O	-4.68263200	1.06319900	1.16060400
C	-0.81064300	-2.56335700	-0.54563100
C	-0.25912800	-2.57680400	-1.82711600
H	0.63260600	-1.99112100	-2.03405000
C	-0.84126300	-3.34053100	-2.83446200
H	-0.40207700	-3.34257000	-3.82718100
C	-1.97179200	-4.10452700	-2.56463700
H	-2.42938300	-4.69792200	-3.35059200
C	-2.52246600	-4.10535600	-1.28396100
H	-3.41201400	-4.68817500	-1.07261400
C	-1.95209200	-3.32930400	-0.28240600
H	-2.42248000	-3.28920100	0.69642300
C	0.69782400	-2.58299700	1.96499600
C	1.80195900	-2.10417000	2.67660600
H	2.19733700	-1.11004200	2.48880200
C	2.45016600	-2.90918900	3.61107400
H	3.33546700	-2.51799600	4.10364500
C	1.98823800	-4.20104600	3.84279300
H	2.49884500	-4.83908500	4.55800100
C	0.87972700	-4.68354900	3.14607900
H	0.52283200	-5.69430800	3.32171500
C	0.23581900	-3.88108600	2.21133500
H	-0.60151600	-4.28475900	1.65308600
C	-1.86347400	0.67619700	-1.51911100
C	-2.09251500	0.64623500	-2.89579400
H	-1.46485500	1.23879800	-3.55139900
C	-3.11700300	-0.11294900	-3.47674400
H	-3.28356700	-0.12722200	-4.54691900
C	-3.90560600	-0.82091600	-2.60638600
C	-5.48390400	-2.02496200	-1.63787800
C	-3.69361600	-0.79362200	-1.24037700
C	-2.67536700	-0.08795700	-0.64015600
C	-2.54452500	-0.13007200	0.84349700
C	-1.48988400	-0.73744800	1.57525300
C	-1.48204600	-0.67849400	2.97116500
H	-0.66443900	-1.14051200	3.51325100
C	-2.49184500	-0.05103700	3.71198700

H	-2.46745600	-0.01349900	4.79421700
C	-3.51747700	0.49636900	2.98398300
C	-5.39921200	1.42140700	2.28982500
C	-3.53985800	0.44567900	1.60321000
C	-1.26862300	2.68424600	0.42688400
C	-0.67486800	2.82180600	1.68430600
H	0.27759700	2.34625200	1.89824100
C	-1.31065100	3.56409000	2.67689300
H	-0.84516500	3.65763100	3.65292300
C	-2.53642700	4.17039800	2.41957500
H	-3.03740100	4.73762400	3.19805800
C	-3.13039200	4.03989000	1.16506600
H	-4.09430800	4.49609400	0.96767400
C	-2.50475000	3.29203400	0.17559100
H	-2.99443400	3.15385200	-0.78486300
C	0.04464300	2.74482300	-2.18940800
C	0.95462700	2.23968100	-3.12601900
H	1.33621000	1.22740100	-3.00912800
C	1.38037500	3.02160200	-4.19340900
H	2.08532600	2.61653900	-4.91303900
C	0.91394900	4.32749200	-4.32735400
H	1.25320100	4.94470600	-5.15360500
C	0.01920100	4.84122000	-3.39392400
H	-0.34110600	5.86128400	-3.48879900
C	-0.41568500	4.05496100	-2.32939600
H	-1.10082300	4.47563600	-1.60107300
Pd	1.29276000	0.30440500	-0.05359600
F	-6.70989200	-1.52668200	-1.45693100
F	-5.59584400	-3.35307500	-1.59705500
F	-6.55405500	0.75003200	2.33038000
F	-5.70849100	2.71855000	2.25072500
C	7.72723800	1.38856800	-0.93465800
C	6.65060300	0.72717000	-1.54120600
N	5.94789600	0.05196600	-0.63155700
H	8.48012500	2.00309800	-1.40409000
H	6.35740200	0.70149800	-2.58197800
H	5.24521900	-2.22142100	-0.11991300
N	6.53999600	0.27660600	0.54604800
H	6.13226400	-0.12273100	1.43343000
Cl	5.26176500	-0.82614000	3.08836500
C	7.61134300	1.07091800	0.40992900
H	8.20600300	1.34416800	1.26851500

TS7

C	-3.19491100	3.02515900	-0.15194100
C	-3.01051700	1.59684500	-0.59364500
C	-3.39883800	0.48968700	0.16974200
C	-3.70545600	-0.76786000	-0.41192000
C	-2.30839400	4.01119000	-0.87757100
C	-1.53401300	4.92382400	-0.15999200
C	-0.70957400	5.83539100	-0.81429100
C	-0.65783100	5.86116800	-2.20421900
C	-1.44473800	4.97325600	-2.93476000
C	-2.26030100	4.05817500	-2.27544200
C	-3.50309800	-2.01698000	0.40105400
O	-3.30302800	-2.04272100	1.59151300
O	-3.58835200	-3.09708600	-0.38152300
C	-3.89842000	-5.43671000	-0.67112800
C	-3.38121900	-4.36465800	0.26273200
H	-3.08192500	3.11059400	0.92978400
H	-3.01807300	1.46133000	-1.68131700
H	-3.57692600	0.61095400	1.23789900
H	-3.64583700	-0.89618000	-1.48746000
H	-1.58161100	4.92144200	0.92452400
H	-0.10571500	6.52523700	-0.23181200
H	-0.01307400	6.56978900	-2.71571200
H	-1.42729900	4.99599700	-4.02114800
H	-2.88009600	3.38256100	-2.86124500
H	-3.72334000	-6.42457700	-0.23364100
H	-4.97375000	-5.31796100	-0.83569600
H	-3.38829700	-5.38522900	-1.63694600
H	-2.30876900	-4.47174400	0.45944800
H	-3.90502000	-4.36507400	1.22172900
P	0.49626900	1.63935600	0.62935700
P	-0.02005800	-1.61047500	-0.73117100
O	5.16410300	0.32089800	-2.93916000
O	4.85169600	0.45911500	-0.70641900
O	4.17403000	-2.11328000	3.44717000
O	4.22690900	-2.09150600	1.18972100
C	1.64303000	2.58607700	-0.42746700
C	1.20487000	2.93810400	-1.70517800
H	0.19734000	2.67855000	-2.01802200
C	2.04875200	3.62843500	-2.57000500
H	1.69485800	3.90097900	-3.55945200
C	3.33497000	3.96986000	-2.16376400
H	3.99827500	4.49921500	-2.84133500
C	3.77577500	3.62952100	-0.88603500
H	4.78166500	3.88436000	-0.57010800
C	2.93618300	2.93567100	-0.02285900
H	3.29813400	2.64136700	0.95865600
C	-0.06067300	2.79054000	1.93874000
C	-1.26358100	2.49067300	2.58718400
H	-1.82126600	1.59627900	2.32327500

C	-1.78854600	3.34652200	3.55130100
H	-2.75079700	3.10893900	3.99515500
C	-1.09767000	4.50841500	3.88554500
H	-1.50726600	5.18908800	4.62591300
C	0.11387800	4.80515600	3.26108000
H	0.65138500	5.71278800	3.52009400
C	0.63144200	3.95340700	2.29002400
H	1.55628200	4.21453700	1.78573100
C	1.58741600	-1.07858600	-1.47596600
C	1.79925900	-1.16404100	-2.85341400
H	1.03937700	-1.61529400	-3.48087800
C	2.96946900	-0.70247100	-3.47231800
H	3.12008600	-0.78079200	-4.54219200
C	3.91952400	-0.16918200	-2.63974000
C	5.76457100	0.63674800	-1.73167300
C	3.72615000	-0.08169200	-1.27343200
C	2.57543200	-0.49354800	-0.63927900
C	2.48148700	-0.37911200	0.84206500
C	1.63297300	0.50904000	1.55302400
C	1.61157700	0.48137600	2.94986000
H	0.95428300	1.16000800	3.48077100
C	2.41399700	-0.38223800	3.70751300
H	2.38062300	-0.39016700	4.79018300
C	3.25689500	-1.19757200	2.99653600
C	4.83475800	-2.59007300	2.32883300
C	3.28991900	-1.18269100	1.61532100
C	0.49549600	-2.77859000	0.57231300
C	-0.14703400	-2.70159700	1.81085900
H	-0.94930400	-1.98572600	1.96289200
C	0.24591800	-3.53891400	2.85242000
H	-0.25287000	-3.46659400	3.81379200
C	1.27673700	-4.45404300	2.66193500
H	1.58981500	-5.09883100	3.47756400
C	1.91861000	-4.53706700	1.42687100
H	2.73388000	-5.23727700	1.28176500
C	1.53701300	-3.69604700	0.38888600
H	2.07165900	-3.73029000	-0.55693000
C	-0.76352200	-2.64707400	-2.05358700
C	-1.52365000	-1.98844600	-3.02853100
H	-1.64479700	-0.90799800	-2.96914700
C	-2.12311200	-2.69623700	-4.06375600
H	-2.70553100	-2.16892600	-4.81340100
C	-1.98136400	-4.08070500	-4.13131400
H	-2.45350600	-4.63858700	-4.93432200
C	-1.23581800	-4.74561800	-3.16264800
H	-1.12463800	-5.82514300	-3.20713500
C	-0.62939000	-4.03455000	-2.12892400
H	-0.06112600	-4.57106000	-1.37645100
Pd	-1.26224000	0.32595300	-0.24323000
F	6.83229900	-0.14221500	-1.53271500
F	6.20291200	1.89556700	-1.75235800
F	6.11963800	-2.22015000	2.36095900
F	4.81914500	-3.92379800	2.31763200
C	-7.82933600	-1.30646300	-0.54101100
C	-6.54491600	-1.64410800	-0.97719700
N	-5.64446800	-0.89646400	-0.33740500
H	-8.77004700	-1.72347800	-0.86607400
H	-6.21841400	-2.37726600	-1.70097100
H	-4.25089700	3.27221900	-0.33952500
N	-6.30861100	-0.09413800	0.49936100
H	-5.83774700	0.58336000	1.17495100
Cl	-5.26967500	1.86795800	2.55403000
C	-7.62555800	-0.31224000	0.40684700
H	-8.31036200	0.25170500	1.02224300

TS8

C	-2.87752000	1.90812200	1.02375600
C	-3.54132500	0.81420300	0.40647000
C	-3.48403300	-0.45687000	0.99468800
C	-4.07905500	-1.64695300	0.42106400
C	-2.77343900	3.24288400	0.39289400
C	-2.24482400	4.30794600	1.13283400
C	-2.02393500	5.54743800	0.54381900
C	-2.35142700	5.75452800	-0.79354100
C	-2.92138700	4.71587700	-1.52771700
C	-3.13016600	3.47109200	-0.94469500
C	-3.88554100	-2.86763300	1.22286600
O	-3.46715200	-2.91413100	2.36911600
O	-4.22376200	-3.96638500	0.52212300
C	-2.58144400	-5.72175200	0.83156200
C	-3.98585300	-5.23112300	1.14268300
H	-2.80727200	1.91064900	2.11239000
H	-3.96961000	0.89164100	-0.58994900
H	-3.22331400	-0.52582900	2.05427600
H	-3.84497600	-1.82154800	-0.62887500
H	-1.99253700	4.15657500	2.17873500
H	-1.59680300	6.35279200	1.13435400
H	-2.18043200	6.72207500	-1.25593300
H	-3.20935700	4.87501000	-2.56295000
H	-3.58546500	2.68033800	-1.53341900
H	-2.42852200	-6.72352900	1.24789100
H	-2.42447200	-5.76300600	-0.25070200
H	-1.83600300	-5.04948100	1.26616400

H	-4.14405300	-5.14266100	2.22008300
H	-4.74060600	-5.89835900	0.71965400
P	0.58245700	1.60916600	1.02976900
P	-0.32822700	-1.38009700	-0.57770300
O	4.18295100	0.89465000	-3.72377500
O	4.45026700	0.74397600	-1.48603000
O	4.93480800	-2.22675100	2.33924300
O	4.32424000	-2.02393300	0.17420800
C	1.30792300	2.70054300	-0.23561000
C	0.47658000	3.16585300	-1.25698000
H	-0.56948600	2.87578500	-1.28107700
C	0.98523900	4.00695900	-2.24196900
H	0.32919600	4.36625700	-3.02858100
C	2.32547400	4.38075200	-2.21478500
H	2.72565300	5.02850900	-2.98895900
C	3.15827300	3.92308200	-1.19475700
H	4.20514700	4.20551600	-1.17674500
C	2.65256500	3.08581100	-0.20713500
H	3.31003500	2.71510100	0.57462500
C	0.36459100	2.66806700	2.50575100
C	-0.41673700	2.16952400	3.55628600
H	-0.82724100	1.16381900	3.49122500
C	-0.68653900	2.95457700	4.67122100
H	-1.29520800	2.55711000	5.47750200
C	-0.19066700	4.25589200	4.74031600
H	-0.41363200	4.87699100	5.60243900
C	0.58472600	4.75823400	3.69971900
H	0.96887200	5.77265200	3.74764700
C	0.86573000	3.96814000	2.58725500
H	1.45428200	4.37820500	1.77338000
C	1.08563500	-0.76370100	-1.58868300
C	0.93768600	-0.66818400	-2.97527600
H	0.03202900	-1.04672000	-3.43536100
C	1.91540300	-0.10932100	-3.80837900
H	1.78320100	-0.04515200	-4.88154500
C	3.05409000	0.33373900	-3.18461500
C	5.07016900	1.08169900	-2.67773800
C	3.21707200	0.24125900	-1.81577200
C	2.26290400	-0.27385500	-0.96576800
C	2.56759300	-0.32197700	0.49055900
C	1.96046000	0.47811500	1.49277300
C	2.35614200	0.35021600	2.82629400
H	1.89000500	0.97320800	3.58035100
C	3.34856700	-0.54742100	3.24170800
H	3.64165400	-0.63553300	4.28068600
C	3.93578700	-1.29319200	2.25173300
C	5.22121600	-2.62269300	1.04302700
C	3.56186900	-1.16826400	0.92724700
C	0.38287300	-2.64188200	0.52861300
C	-0.18965300	-2.78930000	1.79492800
H	-1.03862100	-2.17717100	2.08672300
C	0.30427600	-3.74632100	2.67781600
H	-0.15719400	-3.86042200	3.65353400
C	1.37365900	-4.55425500	2.30315200
H	1.76276000	-5.29654400	2.99364000
C	1.94580600	-4.41439500	1.03965100
H	2.78364000	-5.03766000	0.74737900
C	1.45265400	-3.46205300	0.15494300
H	1.91721300	-3.34177400	-0.82027900
C	-1.34836800	-2.30540600	-1.77546000
C	-2.40125000	-1.62760300	-2.39863100
H	-2.61106500	-0.58923400	-2.15233800
C	-3.24440900	-2.28821000	-3.28665200
H	-4.10185900	-1.75568000	-3.68285000
C	-3.02647100	-3.63242700	-3.57089500
H	-3.69108300	-4.15745400	-4.25034400
C	-1.97535300	-4.31470100	-2.96065200
H	-1.81306400	-5.36769300	-3.17186100
C	-1.14321300	-3.65945800	-2.05941500
H	-0.34987900	-4.21088100	-1.56512800
Pd	-1.37543600	0.46016600	0.45522500
F	6.15829400	0.32834900	-2.85672700
F	5.47922000	2.35091400	-2.64233500
F	6.47014800	-2.27694300	0.72250500
F	5.14722100	-3.95033700	0.93984600
N	-5.48977900	-0.20184100	-1.90970400
C	-6.80675800	1.58114000	-1.45647900
C	-6.88412900	0.64597600	-0.42859200
N	-6.10782300	-0.41262900	-0.72669200
H	-7.32038900	2.52886300	-1.53920500
H	-7.45297900	0.67123300	0.49248300
H	-5.25584700	-1.26411500	0.10477500
C	-5.91677700	0.98732600	-2.36155100
H	-5.57579300	1.35819000	-3.32237000

TS9

C	3.12320900	-1.62133700	-0.35247300
C	3.61597800	-0.38373200	-0.85019300
C	3.76488000	0.69911800	0.02077800
C	4.23419700	2.03285700	-0.46482400
C	2.89801200	-2.81046100	-1.19874900
C	2.70676500	-4.05109800	-0.57672200
C	2.39538600	-5.18164100	-1.32275900

C	2.28969800	-5.10108300	-2.70929700
C	2.50839100	-3.87993400	-3.34380800
C	2.80420300	-2.74579200	-2.59595100
C	3.46831100	3.19274200	0.12379400
O	2.70634400	3.13064100	1.06182900
O	3.76751700	4.33040700	-0.51099000
C	3.58522500	6.67174200	-0.86557800
C	3.15293000	5.51710000	0.01180100
H	3.36914200	-1.82658400	0.68923000
H	3.88423300	-0.25047800	-1.89648100
H	3.48129400	0.61504900	1.06299700
H	4.22821500	2.11075400	-1.55615500
H	2.79819300	-4.11893300	0.50380400
H	2.23853300	-6.13048300	-0.81821100
H	2.04750600	-5.98457300	-3.29230600
H	2.44128000	-3.80878700	-4.42592900
H	2.94169900	-1.79566000	-3.10543100
H	3.13374000	7.60146900	-0.50501800
H	4.67298600	6.78645400	-0.85123700
H	3.26713100	6.50617400	-1.89911700
H	2.06761000	5.38310700	0.00672400
H	3.46985900	5.65036100	1.05088900
P	-0.09477100	-1.65940500	0.66443700
P	0.08812900	1.61229600	-0.60204100
O	-4.70731700	-0.90461400	-3.07789800
O	-4.48659900	-1.05264100	-0.83498100
O	-4.42717500	1.33680700	3.41701500
O	-4.32965400	1.45848400	1.16422900
C	-1.05825500	-2.69934600	-0.48450800
C	-0.60726300	-2.84025300	-1.79755300
H	0.31567000	-2.36032700	-2.10425500
C	-1.33881300	-3.59020300	-2.71335100
H	-0.97568900	-3.69414800	-3.73112300
C	-2.52730600	-4.19952500	-2.32320200
H	-3.10623700	-4.77453500	-3.03955900
C	-2.98188000	-4.06545900	-1.01230800
H	-3.91592900	-4.52667800	-0.70950200
C	-2.25429700	-3.31453400	-0.09711100
H	-2.63067700	-3.18544000	0.91419900
C	0.63340000	-2.78610800	1.90461400
C	1.67900500	-2.28838700	2.69319400
H	2.05224600	-1.27558700	2.55802600
C	2.29971700	-3.10425200	3.63284900
H	3.11260800	-2.69969200	4.22650400
C	1.89729200	-4.42964600	3.77846000
H	2.39385700	-5.07239300	4.49923000
C	0.86840100	-4.93458200	2.98680100
H	0.56044500	-5.97098700	3.08847400
C	0.23418600	-4.11689800	2.05568000
H	-0.55364200	-4.52687300	1.43243300
C	-1.42440700	0.92221300	-1.41072400
C	-1.57870500	1.00912600	-2.79570400
H	-0.85041100	1.56607900	-3.37466900
C	-2.64699600	0.41494500	-3.48143100
H	-2.75348400	0.49570400	-4.55642000
C	-3.55793700	-0.25642600	-2.70678600
C	-5.31369500	-1.33347900	-1.90891100
C	-3.42126500	-0.34786100	-1.33411900
C	-2.36832400	0.19735500	-0.63241700
C	-2.34086400	0.03090900	0.84930900
C	-1.42210900	-0.76956700	1.57755500
C	-1.49702200	-0.84054200	2.96937900
H	-0.78388400	-1.45590200	3.50605400
C	-2.46717200	-0.15336100	3.71111000
H	-2.51216900	-0.21492800	4.79158600
C	-3.36431400	0.58651200	2.98426100
C	-5.06980400	1.80166600	2.28239700
C	-3.30391300	0.66126400	1.60489300
C	-0.61123600	2.56654800	0.78599500
C	-0.03538900	2.42748900	2.05043600
H	0.84898400	1.81119700	2.17356100
C	-0.59376800	3.08027500	3.14520700
H	-0.14636700	2.95885200	4.12670800
C	-1.71928800	3.88305200	2.98204000
H	-2.15701900	4.38721300	3.83837700
C	-2.29340000	4.03248500	1.72108800
H	-3.18133600	4.64173200	1.59345000
C	-1.74995600	3.36518600	0.62980700
H	-2.23805000	3.43624100	-0.33892900
C	0.71639600	2.84290600	-1.81083800
C	1.62821500	2.38428000	-2.76976100
H	1.93458500	1.34034500	-2.75474800
C	2.15508500	3.24935800	-3.72294200
H	2.86266500	2.87753400	-4.45783300
C	1.78669900	4.59191000	-3.72056600
H	2.20370300	5.27288500	-4.45641300
C	0.88945100	5.06029300	-2.76492000
H	0.60598300	6.10864000	-2.75192900
C	0.35582100	4.19275100	-1.81549800
H	-0.32825900	4.57866700	-1.06755500
Pd	1.49758900	-0.22409500	-0.24439400
F	-6.49109300	-0.72144100	-1.75141000

F	-5.56350800	-2.64154000	-1.97394300
F	-6.29518900	1.27412000	2.19945800
F	-5.22345800	3.12476300	2.34955200
H	5.27411100	2.13462700	-0.13244500
N	4.85274200	-0.78206100	2.20976500
C	6.70641700	-1.93329500	1.61611900
C	6.64893300	-0.71200100	0.94779300
N	5.55206400	-0.02960500	1.32204500
H	7.46941200	-2.69788300	1.55917900
H	7.34859700	-0.28479600	0.23744400
C	5.54667600	-1.91542800	2.40025200
H	5.18703900	-2.67364900	3.08772200

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