Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Palladium-Catalyzed Allylic Alkylation of Hydrazones with Hydroxy-Tethered Allyl Carbonates: Synthesis of Functionalized Hydrazones

Jiaqing Xu,[a] Min Liu,[a] Yimin Hu,[a] Lei Wang,[b] Wei Wang,[c] Yongjun Wu,[c] Hongchao Guo[a]*

[a] Department of Chemistry and Innovation Center of Pesticide Research, China Agricultural University, Beijing 100193, P. R. China. E-mail: hchguo@cau.edu.cn

[b] Nutrichem Co., LTD

[c] College of Public Health, Zhengzhou University, Zhengzhou 450001, P. R. China

Contents

1. General Information

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ using a 500 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Melting points were determined by an X-4 digital micro melting point apparatus. X-ray crystallographic data were collected using a Bruker D8 venture.

2. Preparation of Substrates

The hydroxy-tethered allylic carbonate **1**[1], 2-(2-Phenylhydrazine phenylene) ethyl acetates **2**[2], N'-benzylidene-4-methylbenzene-sulfonohydrazides **9**[2] and 2-Methylidenetrimethylene carbonate **7**[3] were synthesized using known literature procedures.

3. Experiment section

General Procedure for Palladium-Catalyzed C(sp^2)-H Allylic Alkylations

Under argon atmosphere, to a mixture of 2-methylidenetrimethylene carbonate **1** (0.15 mmol),

[1] Xu, J.; Shi, W.; Liu, M.; Liao, J.; Wang, W.; Wu, Y.; Guo, H. *Adv. Synth.Catal.* **2022***, 364,* 2060.

[2] Zhu, J.-N.; Wang, W.-K.; Jin, Z.-H.; Wang, Q.-K.; Zhao, S.-Y. *Org. Lett.* **2019**, *21*, 5046.

[3] R. Shintani, K. Moriya, T. Hayashi, *Chem. Commun.* **2011**, *47*, 3057.

hydrazones **2** (0.10 mmol) and catalyst $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%) /DpePhos (10.0 mol%) in a Schlenk tube, 2 mL of solvent was added at room temperature. The resulting mixture was stirred for 48 h and then was concentrated to dryness. The residue was purified through flash column chromatography to afford the corresponding allylic alkylation products **3**.

General Procedure for Further Cyclization

The allylation product **3** (0.2 mmol) and triethylamine (0.4 mmol) were dissolved in 3 mL of tetrahydrofuran in turn. The resulting solution was cooled to 0 °C, and NaH (0.3 mmol) was slowly added. The mixture was stirred at room temperature for 1 h, and then TsCl (0.4 mmol) was added into the reaction system. The resulting mixture was stirred at room temperature for 24 h, and then was concentrated to dryness. The residue was purified through flash column chromatography to afford the cyclization products **4**.

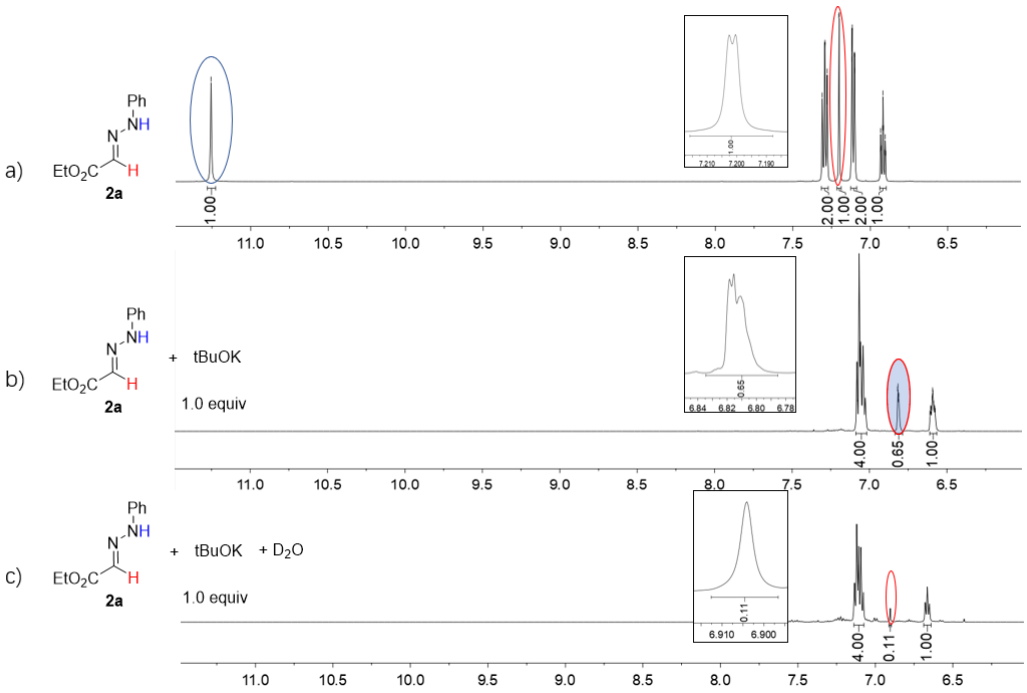
Further Transformation of 3aa

The allylic alkylation product **3aa** (0.1 mmol) was dissolved in 2 mL of CH_2Cl_2. Et_3N (0.2 mmol) and benzoyl chloride (0.2 mmol) were then added into the solution at 0 °C. The resulting mixture was warmed to room temperature and stirred for 12 h (monitored by TLC). The mixture was then concentrated to dryness. The residue was purified through flash column chromatography to afford the product **5**.

Allylic Alkylation Between 2-Methylidenetrimethylene Carbonate 7 and 2a

Under argon atmosphere, to a mixture of 2-methylidenetrimethylene carbonate **7** (0.15 mmol), hydrazones **2a** (0.10 mmol) and catalyst $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%) / BINAP (10.0 mol%) in a Schlenk tube, 2 mL of CH_2Cl_2 was added at room temperature. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography to afford the corresponding allylic alkylation products **8**.

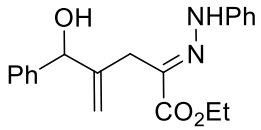
Scheme S1. Control Experiment with Hydrazone 2a for Exploration on Mechanism



^{1}H spectra were recorded in DMSO-d_6 using a 500 MHz NMR instrument (referenced internally to Me_4Si): a) Pure hydrazone **2a** (2.0 mmol); b) 2.0 mmol hydrazone **2a** with *t*BuOK (1.0 equiv.); c) 2.0 mmol of hydrazone **2a** and *t*BuOK (1.0 equiv.) with two drops of D_2O.

4. Characterization Data of the Compounds 3, 4, 5, 6, 8 and 10

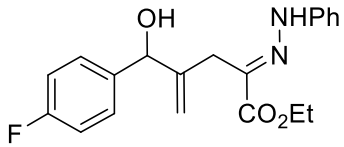
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3aa)



3aa

Prepared according to the general procedure as described above in 93% yield (31.4 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.45 – 7.40 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 3H), 7.37 – 7.30 (m, 1H), 7.27 (d, *J* = 9.9 Hz, 3H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 5.34 (d, *J* = 3.3 Hz, 1H), 5.16 (s, 1H), 4.99 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.28 (q, *J* = 16.6 Hz, 2H), 2.82 (d, *J* = 3.3 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.5, 143.3, 141.1, 133.0, 129.2, 128.7, 128.1, 126.1, 121.9, 114.1, 114.0, 77.7, 61.3, 26.5, 14.3; IR (film) ν_{max} 3428, 3254, 2980, 1698, 1604, 1566, 1496, 1242, 1192, 1169, 1098 cm^{-1};HRMS (ESI) calcd for $C_{20}H_{23}N_2O_3^+$ $[M+H]^+$ 339.1703; Found 339.1701.

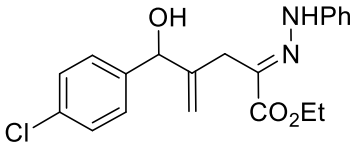
Ethyl (E)-4-((4-fluorophenyl)(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ba)



3ba

Prepared according to the general procedure as described above in 49% yield (17.5 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a white solid. mp = 89 – 91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.41 – 7.34 (m, 2H), 7.30 – 7.24 (m, 2H), 7.13 – 7.08 (m, 2H), 7.09 – 7.02 (m, 2H), 6.98 – 6.92 (m, 1H), 5.31 (d, *J* = 3.5 Hz, 1H), 5.12 (s, 1H), 5.02 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.30 (q, *J* = 16.5 Hz, 2H), 2.96 (d, *J* = 3.6 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 162.5 (C-F, $^{1}J_{C\text{-}F}$= 246.5 Hz), 144.7, 143.2, 136.80, 136.77, 132.9, 129.3, 127.9, 127.8, 122.0, 115.5 (C-F, $^{2}J_{C\text{-}F}$= 21.5 Hz), 114.6, 114.0, 77.0, 61.4, 26.7, 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.23; IR (film) ν_{max} 3420, 3255, 2926, 1698, 1604, 1567, 1498, 1242, 1193, 1170, 1098 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}FN_2O_3^+$ $[M+H]^+$ 357.1609; Found 357.1604.

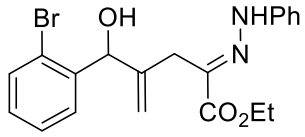
Ethyl (E)-4-((4-chlorophenyl)(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ca)



3ca

Prepared according to the general procedure as described above in 71% yield (26.5 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 103 – 105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.34 (s, 4H), 7.27 (s, 2H), 7.25 (d, *J* = 2.2 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.30 (d, *J* = 3.5 Hz, 1H), 5.11 (s, 1H), 5.01 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 4.6 Hz, 2H), 3.09 (d, *J* = 3.7 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 144.5, 143.2, 139.5, 133.8, 132.8, 129.3, 128.7, 127.5, 122.1, 114.8, 114.0, 77.0, 61.4, 26.5, 14.3; IR (film) ν_{max} 3420, 3257, 2925, 1698, 1604, 1567, 1497, 1243, 1194, 1169, 1097 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}ClN_2O_3^+$ $[M+H]^+$ 373.1313; Found 373.1306.

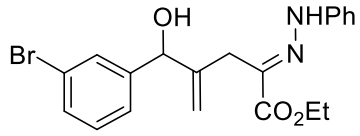
Ethyl (E)-4-((2-bromophenyl)(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3da)



3da

Prepared according to the general procedure as described above in 35% yield (14.7 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a white solid. mp = 82 – 84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 5.61 (d, *J* = 3.8 Hz, 1H), 5.04 (s, 1H), 4.98 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.52 (d, *J* = 16.7 Hz, 1H), 3.35 (d, *J* = 16.6 Hz, 1H), 2.95 (d, *J* = 4.0 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 143.3, 142.4, 140.1, 133.0, 132.9, 129.5, 129.3, 128.2, 127.8, 122.8, 122.0, 115.6, 114.0, 75.8, 61.4, 28.0, 14.4; IR (film) ν_{max} 3419, 3254, 2980, 1698, 1603, 1552, 1495, 1240, 1194, 1167, 1096 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_3^+$ $[M+H]^+$ 417.0808; Found 417.0802.

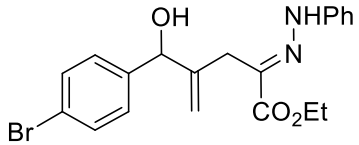
Ethyl (E)-4-((3-bromophenyl)(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ea)



3ea

Prepared according to the general procedure as described above in 73% yield (30.4 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a white solid. mp = 105 – 107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.58 (s, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.29 (d, *J* = 3.6 Hz, 1H), 5.14 (s, 1H), 5.02 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 16.6 Hz, 2H), 3.20 (d, *J* = 3.9 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 144.2, 143.5, 143.2, 132.7, 131.1, 130.2, 129.3, 129.1, 124.7, 122.8, 122.1, 115.0, 114.0, 77.0, 61.4, 26.4, 14.3; IR (film) ν_{max} 3420, 3256, 2980, 1698, 1604, 1568, 1497, 1243, 1192, 1170, 1098 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_3^+$ $[M+H]^+$ 417.0808; Found 417.0804.

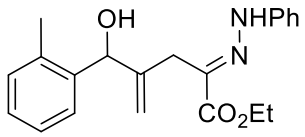
Ethyl (E)-4-((4-bromophenyl)(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3fa)



3fa

Prepared according to the general procedure as described above in 80% yield (33.4 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a white solid. mp = 119 – 121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 8.0, 2.9 Hz, 3H), 7.26 (s, 1H), 7.11 – 7.07 (m, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 5.29 (d, *J* = 3.5 Hz, 1H), 5.11 (s, 1H), 5.01 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 16.5 Hz, 2H), 3.06 (d, *J* = 3.6 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.4, 143.2, 140.1, 132.8, 131.7, 129.3, 127.9, 122.1, 122.0, 114.8, 114.0, 61.4, 26.4, 14.3; IR (film) ν_{max} 3420, 3257, 2926, 1698, 1604, 1559, 1497, 1243, 1194, 1169, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_3^+$ $[M+H]^+$ 417.0808; Found 417.0802.

Ethyl (E)-4-(hydroxy(o-tolyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ga)

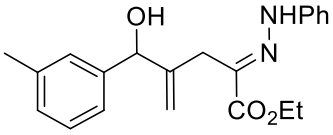


3ga

Prepared according to the general procedure as described above in 81% yield (28.7 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 88 – 90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.57 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.17 – 7.12 (m, 3H), 6.96 – 6.92 (m, 1H), 5.45 (d, *J* = 3.4 Hz, 1H), 5.00 (s, 1H), 4.96 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 16.4 Hz, 1H), 3.27 (d, *J* = 16.4 Hz, 1H), 2.77 (d, *J* = 3.4 Hz, 1H), 2.26 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 143.4, 143.2, 139.0, 135.5, 133.2, 130.7, 129.2, 128.0, 126.4, 125.7, 121.9, 114.8, 114.0, 74.4, 61.3, 27.2, 19.2, 14.4; IR (film) ν_{max} 3421, 3254, 2926, 1698, 1604, 1568, 1497, 1244, 1193, 1169, 1098 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3^+$ $[M+H]^+$ 353.1860; Found 353.1856.

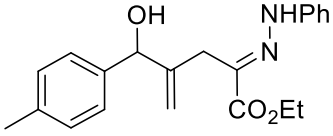
Ethyl (E)-4-(hydroxy(m-tolyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ha)



3ha

Prepared according to the general procedure as described above in 82% yield (28.7 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.31 – 7.25 (m, 3H), 7.28 – 7.24 (m, 3H), 7.23 (d, *J* = 7.1 Hz, 4H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 5.18 (s, 1H), 4.99 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.26 (q, *J* = 16.6 Hz, 2H), 2.73 (d, *J* = 3.2 Hz, 1H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.6, 143.3, 141.1, 138.4, 133.1, 129.2, 128.9, 128.6, 126.8, 123.1, 121.9, 114.0, 113.9, 77.7, 61.3, 26.6, 21.5, 14.34; IR (film) ν_{max} 3421, 3255, 2918, 1698, 1604, 1569, 1497, 1243, 1192, 1169, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3^+$ $[M+H]^+$ 353.1860; Found 353.1854.

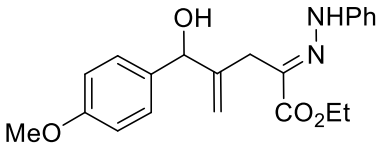
Ethyl (E)-4-(hydroxy(p-tolyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ia)



3ia

Prepared according to the general procedure as described above in 72% yield (25.4 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a white solid. mp = 79 – 81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 5.30 (d, *J* = 3.2 Hz, 1H), 5.17 (s, 1H), 4.98 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.36 (q, *J* = 16.6 Hz, 2H), 2.64 (d, *J* = 3.2 Hz, 1H), 2.37 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.7, 143.3, 138.2, 137.9, 133.1, 129.4, 129.2, 126.1, 121.9, 114.0, 113.8, 77.6, 61.3, 26.6, 21.2, 14.3; IR (film) ν_{max} 3447, 3255, 2924, 1698, 1604, 1569, 1497, 1244, 1194, 1170, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3^+$ $[M+H]^+$ 353.1860; Found 353.1854.

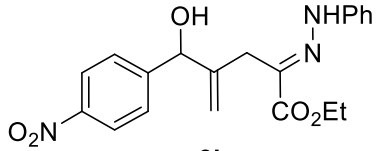
Ethyl (E)-4-(hydroxy(4-methoxyphenyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ja)



3ja

Prepared according to the general procedure as described above in 92% yield (33.8 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a yellow solid. mp = 100 – 102 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.10 – 7.07 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.23 (d, *J* = 3.2 Hz, 1H), 5.10 (s, 1H), 4.94 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.23 (q, *J* = 16.5 Hz, 2H), 3.15 (d, *J* = 3.4 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 159.4, 145.0, 143.4, 133.3, 133.1, 129.2, 127.4, 121.9, 114.0, 113.6, 77.1, 61.3, 55.3, 26.7, 14.3; IR (film) ν_{max} 3447, 3255, 2980, 1698, 1604, 1568, 1509, 1497, 1244, 1170, 1098 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4^+$ $[M+H]^+$ 369.1809; Found 369.1805.

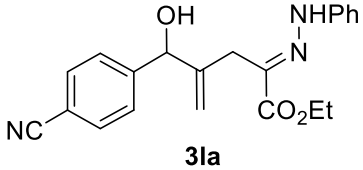
Ethyl (E)-4-(hydroxy(4-nitrophenyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ka)



3ka

Prepared according to the general procedure as described above in 54% yield (20.7 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a yellow solid. mp = 115 – 117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 5.44 (d, *J* = 4.0 Hz, 1H), 5.14 (s, 1H), 5.10 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.63 (d, *J* = 4.1 Hz, 1H), 3.26 (s, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 148.2, 147.5, 144.1, 143.1, 132.4, 129.3, 126.9, 123.7, 122.3, 116.2, 114.0, 76.9, 61.5, 26.4, 14.3; IR (film) ν_{max} 3256, 2926, 2854, 1698, 1604, 1559, 1521, 1497, 1243, 1170, 1100 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}N_3O_5^+$ $[M+H]^+$ 384.1554; Found 384.1551.

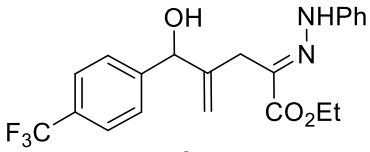
Ethyl (E)-4-((4-cyanophenyl)(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3la)



3la

Prepared according to the general procedure as described above in 77% yield (28.0 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.81 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 4.1 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 5.41 (d, *J* = 3.8 Hz, 1H), 5.12 (s, 1H), 5.05 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.69 (dd, *J* = 3.9, 2.2 Hz, 1H), 3.25 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 165.8, 148.0, 144.3, 143.2, 135.9, 132.6, 130.0, 129.3, 126.7, 122.1, 115.6, 114.0, 77.3, 61.4, 26.3, 14.3; IR (film) ν_{max} 3255, 2927, 1698, 1605, 1576, 1559, 1497, 1243, 1209, 1169, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}N_3O_3^+$ $[M+H]^+$ 364.1656; Found 364.1653.

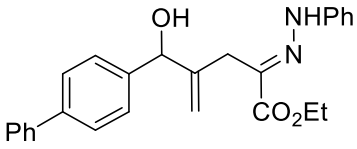
Ethyl (E)-4-(hydroxy(4-(trifluoromethyl)phenyl)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3ma)



3ma

Prepared according to the general procedure as described above in 78% yield (31.5 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a white solid. mp = 120 – 122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 6.97 – 6.93 (m, 1H), 5.39 (d, *J* = 3.7 Hz, 1H), 5.13 (s, 1H), 5.04 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.30 (d, *J* = 3.8 Hz, 1H), 3.26 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 145.0, 144.3, 143.1, 132.6, 130.2 (C-F, $^{2}J_{C\text{-}F}$= 32.3 Hz), 129.3, 126.4, 125.5 (C-F, $^{3}J_{C\text{-}F}$= 3.8 Hz), 124.1 (C-F, $^{1}J_{C\text{-}F}$= 272.2 Hz), 122.2, 115.3, 114.0, 77.1, 61.4, 26.4, 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.50; IR (film) ν_{max} 3255, 2927, 1698, 1559, 1497, 1324, 1243, 1167, 1123, 1110 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}F_3N_2O_3^+$ $[M+H]^+$ 407.1577; Found 407.1575

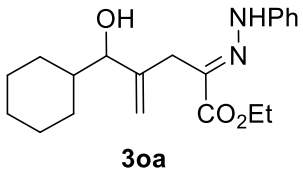
Ethyl (E)-4-([1,1'-biphenyl]-4-yl(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3na)



3na

Prepared according to the general procedure as described above in 70% yield (28.9 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.63 – 7.58 (m, 4H), 7.52 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.25 – 7.21 (m, 2H), 7.06 (dd, *J* = 8.6, 1.1 Hz, 2H), 6.93 (tt, *J* = 7.3, 1.2 Hz, 1H), 5.39 (d, *J* = 3.3 Hz, 1H), 5.22 (s, 1H), 5.02 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.31 (q, *J* = 16.6 Hz, 2H), 2.80 (d, *J* = 3.4 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.6, 143.3, 141.1, 140.5, 140.2, 133.0, 129.2, 128.9, 127.5, 127.4, 127.1, 126.6, 121.9, 114.2, 114.0, 77.5, 61.3, 26.6, 14.4; IR (film) ν_{max} 3254, 2924, 1698, 1684, 1604, 1559, 1497, 1243, 1193, 1170, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{27}N_2O_3^+$ $[M+H]^+$ 415.2016; Found 415.2019.

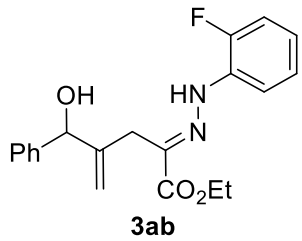
Ethyl (E)-4-(cyclohexyl(hydroxy)methyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (3oa)



3oa

Prepared according to the general procedure as described above in 82% yield (28.1 mg). It was purified by flash chromatography (6.7 % EtOAc/PE) to afford a yellow solid. mp = 85 – 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 4.96 (d, *J* = 2.2 Hz, 2H), 4.33 (qq, *J* = 7.2, 3.6 Hz, 2H), 3.89 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.57 (dt, *J* = 16.1, 2.4 Hz, 1H), 3.09 (d, *J* = 16.0 Hz, 1H), 2.51 (d, *J* = 3.5 Hz, 1H), 2.01 (d, *J* = 12.6 Hz, 1H), 1.84 – 1.79 (m, 1H), 1.74 (d, *J* = 15.3 Hz, 1H), 1.69 (d, *J* = 12.3 Hz, 1H), 1.59 (d, *J* = 13.0 Hz, 1H), 1.54 – 1.48 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.22 (m, 2H), 1.16 (ddd, *J* = 15.9, 8.0, 3.4 Hz, 1H), 1.04 – 0.96 (m, 1H), 0.92 – 0.84 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 143.6, 133.7, 129.2, 121.7, 115.2, 114.0, 82.6, 61.3, 40.6, 29.4, 29.3, 26.3, 25.9, 25.8, 25.1, 14.4; IR (film) ν_{max} 3245, 2925, 1698, 1605, 1569, 1559, 1497, 1240, 1192, 1169, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{29}N_2O_3^+$ $[M+H]^+$ 345.2173; Found 345.2169.

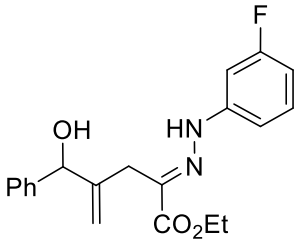
Ethyl (E)-2-(2-(2-fluorophenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ab)



3ab

Prepared according to the general procedure as described above in 87% yield (31.0 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 61 – 63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.6 Hz, 1H), 7.60 (td, *J* = 8.2, 1.7 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.35 – 7.32 (m, 2H), 7.29 – 7.26 (m, 1H), 7.10 – 7.06 (m, 1H), 7.01 (ddd, *J* = 11.6, 8.2, 1.4 Hz, 1H), 6.89 – 6.85 (m, 1H), 5.27 (d, *J* = 3.7 Hz, 1H), 5.16 (s, 1H), 5.02 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.30 (q, *J* = 16.4 Hz, 2H), 2.98 (d, *J* = 3.7 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 150.60 (C-F, $^{1}J_{C\text{-}F}$= 241.0 Hz), 144.4, 141.0, 135.4, 131.78 (C-F, $^{3}J_{C\text{-}F}$= 9.1 Hz), 128.6, 127.9, 126.5, 126.1, 124.89 (C-F, $^{3}J_{C\text{-}F}$= 3.3 Hz), 121.60 (C-F, $^{3}J_{C\text{-}F}$= 7.1 Hz), 115.74 (C-F, $^{3}J_{C\text{-}F}$= 2.1 Hz), 115.1, 115.0, 114.2, 77.1, 61.5, 27.3, 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.07; IR (film) ν_{max} 3447, 2981, 1699, 1624, 1577, 1489, 1283, 1256, 1189, 1105 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}FN_2O_3^+$ $[M+H]^+$ 357.1609; Found 357.1603.

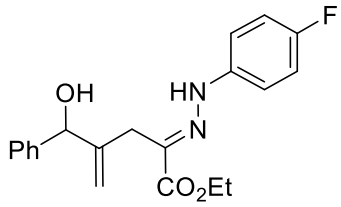
Ethyl (E)-2-(2-(3-fluorophenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ac)



3ac

Prepared according to the general procedure as described above in 87% yield (30.8 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a white solid. mp = 88 – 90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.42 (d, J = 7.3 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.33 (t, J = 6.8 Hz, 1H), 7.18 (q, J = 8.0 Hz, 1H), 6.89 (d, J = 10.8 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.64 – 6.58 (m, 1H), 5.35 (d, J = 3.3 Hz, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.28 (q, J = 16.5 Hz, 2H), 2.95 (d, J = 3.2 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 163.8 (C-F, $^{1}J_{C\text{-}F}$= 244.3 Hz), 145.2 (C-F, $^{2}J_{C\text{-}F}$= 10.6 Hz), 144.5, 141.0, 134.3, 130.4, 130.3, 128.7, 128.2, 126.0, 114.6, 109.6 (C-F, $^{3}J_{C\text{-}F}$= 2.8 Hz), 108.4 (C-F, $^{2}J_{C\text{-}F}$= 21.9 Hz), 101.4 (C-F, $^{2}J_{C\text{-}F}$= 26.3 Hz), 77.8, 61.5, 26.5, 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.04; IR (film) ν_{max} 3254, 2981, 1699, 1616, 1576, 1495, 1273, 1190, 1138, 1098 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}FN_2O_3^+$ $[M+H]^+$ 357.1609; Found 357.1604.

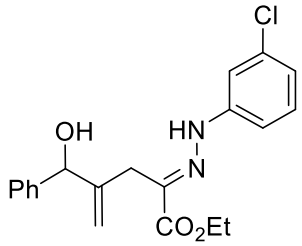
Ethyl (E)-2-(2-(4-fluorophenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ad)



3ad

Prepared according to the general procedure as described above in 85% yield (30.3 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 58 – 60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.41 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 7.05 – 7.01 (m, 2H), 6.95 – 6.91 (m, 2H), 5.31 (d, J = 3.4 Hz, 1H), 5.12 (s, 1H), 4.96 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.29 (d, J = 3.6 Hz, 1H), 3.22 (t, J = 16.0 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 158.3 (C-F, $^{1}J_{C\text{-}F}$= 239.7 Hz), 144.7, 141.2, 139.7 (C-F, $^{3}J_{C\text{-}F}$= 2.2 Hz), 133.1, 128.6, 128.0, 126.1, 115.9, 115.7, 115.12, 115.05, 114.2, 77.7, 61.4, 26.4, 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -122.20; IR (film) ν_{max} 3255, 2981, 1698, 1569, 1559, 1506, 1249, 1202, 1103 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}FN_2O_3^+$ $[M+H]^+$ 357.1609; Found 357.1604.

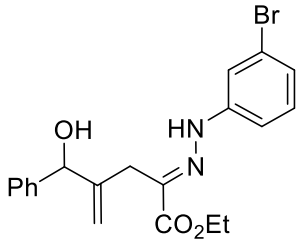
Ethyl (E)-2-(2-(3-chlorophenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ae)



3ae

Prepared according to the general procedure as described above in 81% yield (30.2 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 113 – 115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.43 – 7.40 (m, 2H), 7.37 (d, J = 7.7 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.15 (t, J = 8.1 Hz, 1H), 7.09 (t, J = 2.1 Hz, 1H), 6.95 (dd, J = 8.1, 2.2 Hz, 1H), 6.88 (dd, J = 8.0, 2.0 Hz, 1H), 5.34 (d, J = 3.2 Hz, 1H), 5.14 (s, 1H), 4.97 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.26 (q, J = 16.5 Hz, 2H), 3.07 (d, J = 3.3 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 144.6, 144.5, 141.0, 135.0, 134.5, 130.2, 128.7, 128.2, 126.0, 121.7, 114.6, 114.1, 112.1, 77.8, 61.5, 26.4, 14.3; IR (film) ν_{max} 3245, 2981, 1699, 1599, 1569, 1559, 1473, 1240, 1190, 1095 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}ClN_2O_3^+$ $[M+H]^+$ 373.1313; Found 373.1310.

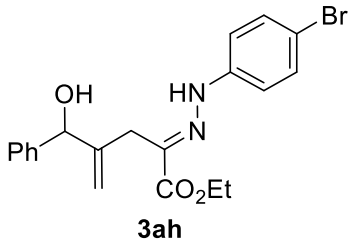
Ethyl (E)-2-(2-(3-bromophenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ag)



3ag

Prepared according to the general procedure as described above in 47% yield (19.6 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 98 – 100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.44 – 7.40 (m, 3H), 7.38 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.0 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 7.04 (s, 1H), 7.00 (d, J = 8.0 Hz, 1H), 5.34 (d, J = 3.2 Hz, 1H), 5.14 (s, 1H), 4.97 (s, 1H), 4.28 (d, J = 7.1 Hz, 2H), 3.26 (q, J = 16.5 Hz, 2H), 3.05 (d, J = 3.3 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 144.7, 144.5, 141.0, 134.5, 130.5, 128.7, 128.2, 126.0, 124.6, 123.1, 117.0, 114.5, 112.6, 77.8, 61.5, 26.4, 14.3; IR (film) ν_{max} 3246, 2926, 1699, 1596, 1570, 1559, 1473, 1236, 1190, 1101 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_3^+$ $[M+H]^+$ 417.0808; Found 417.0805.

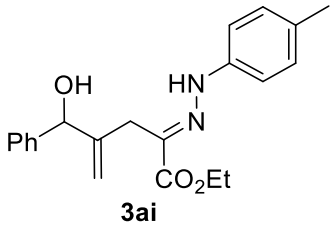
Ethyl (E)-2-(2-(4-bromophenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ah)



3ah

Prepared according to the general procedure as described above in 51% yield (21.3 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 144 – 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.44 – 7.41 (m, 2H), 7.41 – 7.38 (m, 2H), 7.38 – 7.35 (m, 2H), 7.34 (d, J = 3.2 Hz, 1H), 6.98 – 6.95 (m, 2H), 5.36 (d, J = 3.2 Hz, 1H), 5.16 (s, 1H), 5.00 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.32 (dt, J = 16.5, 1.7 Hz, 1H), 3.25 (d, J = 16.5 Hz, 1H), 2.73 (d, J = 3.5 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 144.4, 142.5, 141.0, 134.0, 132.0, 128.7, 128.2, 126.0, 115.6, 114.6, 114.0, 77.8, 61.4, 26.5, 14.3; IR (film) ν_{max} 3245, 2925, 1698, 1559, 1541, 1507, 1489, 1457, 1243, 1192 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_3^+$ $[M+H]^+$ 417.0808; Found 417.0804.

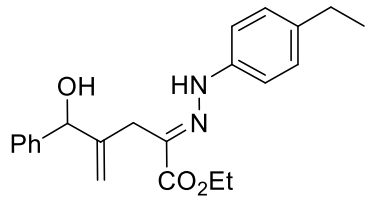
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(p-tolyl)hydrazineylidene)pent-4-enoate (3ai)



3ai

Prepared according to the general procedure as described above in 88% yield (31.1 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.45 – 7.39 (m, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.30 (s, 1H), 5.13 (s, 1H), 4.97 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 16.6 Hz, 2H), 2.94 (d, *J* = 3.3 Hz, 1H), 2.28 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.6, 141.2, 141.0, 132.3, 131.4, 129.7, 128.7, 128.1, 126.1, 114.0, 113.9, 77.6, 61.2, 26.6, 20.7, 14.4; IR (film) ν_{max} 3255, 2923, 1697, 1559, 1508, 1288, 1242, 1192, 1174, 1096 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3^+$ $[M+H]^+$ 353.1860; Found 353.1855.

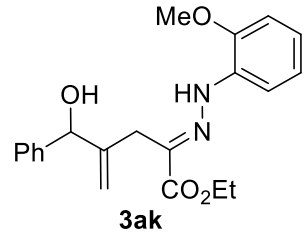
Ethyl (E)-2-(2-(4-ethylphenyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3aj)



3aj

Prepared according to the general procedure as described above in 90% yield (33.0 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.42 – 7.40 (m, 2H), 7.37 (dd, *J* = 8.3, 6.4 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.02 – 6.99 (m, 2H), 5.30 (d, *J* = 3.3 Hz, 1H), 5.12 (s, 1H), 4.95 (s, 1H), 4.26 (d, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 9.1 Hz, 2H), 3.09 (d, *J* = 3.4 Hz, 1H), 2.57 (d, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 144.7, 141.3, 141.2, 138.0, 132.3, 128.6, 128.5, 128.0, 126.1, 114.1, 113.9, 77.6, 61.3, 28.2, 26.5, 15.9, 14.4; IR (film) ν_{max} 3255, 2963, 2928, 1697, 1559, 1518, 1508, 1245, 1192, 1097 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_3^+$ $[M+H]^+$ 367.2016; Found 367.2012.

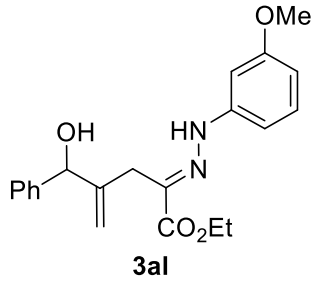
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(2-methoxyphenyl)hydrazineylidene)pent-4-enoate (3ak)



3ak

Prepared according to the general procedure as described above in 99% yield (36.5 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a yellow solid. mp = 77 – 79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.53 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.27 (m, 3H), 6.93 (dtd, *J* = 22.2, 7.5, 1.6 Hz, 2H), 6.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.25 (d, *J* = 3.9 Hz, 1H), 5.22 (s, 1H), 5.06 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.33 (s, 2H), 2.82 (d, *J* = 4.1 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 146.3, 144.5, 141.1, 133.5, 132.6, 128.4, 127.8, 126.3, 121.62, 121.59, 113.82, 113.79, 110.4, 76.7, 61.3, 55.8, 28.1, 14.3; IR (film) ν_{max} 3349, 2935, 1698, 1559, 1517, 1508, 1254, 1216, 1176, 1115 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4^+$ $[M+H]^+$ 369.1809; Found 369.1803.

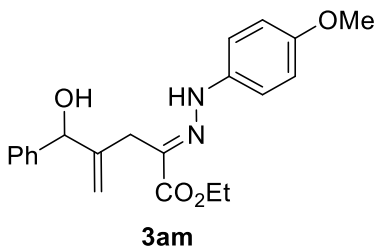
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(3-methoxyphenyl)hydrazineylidene)pent-4-enoate (3al)



3al

Prepared according to the general procedure as described above in 91% yield (33.5 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.42 (d, J = 6.7 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.14 (d, J = 8.1 Hz, 1H), 6.73 (t, J = 2.3 Hz, 1H), 6.63 (dd, J = 8.0, 2.1 Hz, 1H), 6.50 (dd, J = 8.1, 2.5 Hz, 1H), 5.33 (d, J = 3.1 Hz, 1H), 5.15 (s, 1H), 4.98 (s, 1H), 4.27 (t, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.27 (d, J = 14.2 Hz, 2H), 2.86 (d, J = 3.2 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 160.7, 144.7, 144.6, 141.2, 133.2, 130.0, 128.7, 128.1, 126.1, 114.2, 107.6, 106.7, 99.8, 77.7, 61.3, 55.3, 26.5, 14.3; IR (film) ν_{max} 3255, 2930, 1698, 1601, 1569, 1496, 1285, 1200, 1152, 1100 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4^+$ $[M+H]^+$ 369.1809; Found 369.1805.

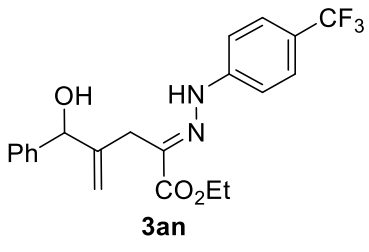
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)pent-4-enoate (3am)



3am

Prepared according to the general procedure as described above in 86% yield (31.8 mg). It was purified by flash chromatography (10.0 – 12.5% EtOAc/PE) to afford a red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.42 (d, J = 7.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.02 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 5.33 – 5.31 (m, 1H), 5.15 (s, 1H), 4.98 (s, 1H), 4.26 (t, J = 7.1 Hz, 2H), 3.76 (s, 3H), 3.25 (d, J = 14.4 Hz, 2H), 2.93 (d, J = 3.2 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 155.0, 144.7, 141.3, 137.3, 131.8, 128.6, 128.0, 126.1, 115.1, 114.6, 113.9, 77.6, 61.2, 55.6, 26.5, 14.4; IR (film) ν_{max} 3255, 2932, 1697, 1559, 1508, 1231, 1196,1179, 1096, 1035 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4^+$ $[M+H]^+$ 369.1809; Found 369.1802.

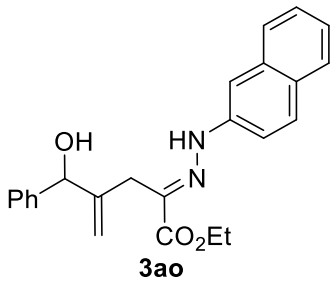
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(4-(trifluoromethyl)phenyl)hydrazineylidene) pent-4-enoate (3an)



3an

Prepared according to the general procedure as described above in 47% yield (19.1 mg). It was purified by flash chromatography (10.0% EtOAc/PE) to afford a yellow solid. mp = 133 – 135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.42 – 7.37 (m, 4H), 7.35 – 7.31 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 5.35 (d, J = 3.2 Hz, 1H), 5.13 (s, 1H), 4.99 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.27 (q, J = 16.3 Hz, 2H), 3.16 (d, J = 3.4 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 146.1, 144.5, 141.0, 135.4, 128.7, 128.2, 127.7, 126.5 (C-F, $^1J_{C\text{-}F}$= 3.7 Hz), 126.0, 125.6, 123.5 (C-F, $^2J_{C\text{-}F}$= 32.4 Hz), 123.4, 123.1, 121.3, 114.8, 113.7, 61.6, 26.5, 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.54; IR (film) ν_{max} 3255, 2929, 1699, 1617, 1323, 1251, 1173, 1111, 1064 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}F_3N_2O_3^+$ $[M+H]^+$ 407.1577; Found 407.1574.

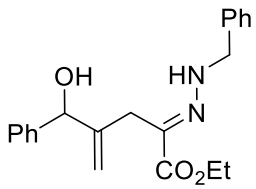
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(naphthalen-2-yl)hydrazineylidene)pent-4-enoate (3ao)



3ao

Prepared according to the general procedure as described above in 88% yield (34.2 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a red solid. mp = 78 – 80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.75 – 7.69 (m, 3H), 7.45 – 7.37 (m, 6H), 7.35 – 7.28 (m, 3H), 5.36 (s, 1H), 5.16 (s, 1H), 5.02 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.32 (q, *J* = 16.6 Hz, 2H), 2.99 (d, *J* = 3.3 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.6, 141.2, 141.0, 134.3, 133.5, 129.8, 129.3, 128.7, 128.1, 127.8, 126.9, 126.6, 126.1, 123.8, 115.7, 114.3, 109.1, 77.8, 61.4, 26.6, 14.4; IR (film) ν_{max} 3255, 2981, 1698, 1632, 1559, 1541, 1508, 1253, 1179, 1096 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}N_2O_3^+$ $[M+H]^+$ 389.1860; Found 389.1853.

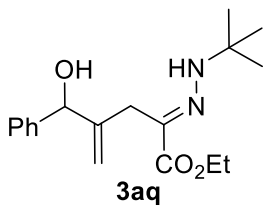
Ethyl (E)-2-(2-benzylhydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3ap)



3ap

Prepared according to the general procedure as described above in 67% yield (23.6 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 6.7 Hz, 1H), 7.27 (dd, *J* = 6.9, 2.9 Hz, 2H), 7.22 (d, *J* = 5.7 Hz, 4H), 6.21 (t, *J* = 4.9 Hz, 1H), 5.17 (d, *J* = 3.4 Hz, 1H), 5.14 (s, 1H), 4.89 (s, 1H), 4.52 (d, *J* = 4.8 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 2H), 2.53 (d, *J* = 3.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 144.4, 141.2, 138.0, 131.6, 128.6, 128.5, 128.0, 127.9, 127.6, 126.1, 112.6, 61.2, 55.4, 27.1, 14.4; IR (film) ν_{max} 3308, 2928, 1716, 1698, 1684, 1559, 1541, 1507, 1457 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3^+$ $[M+H]^+$ 353.1860; Found 353.1854.

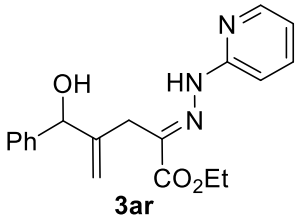
Ethyl (E)-2-(2-(tert-butyl)hydrazineylidene)-4-(hydroxy(phenyl)methyl)pent-4-enoate (3aq)



3aq

Prepared according to the general procedure as described above in 78% yield (24.7 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a yellow solid. mp = 85 – 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.28 (m, 1H), 5.90 (s, 1H), 5.22 (d, *J* = 3.1 Hz, 1H), 5.18 (s, 1H), 4.87 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.08 (s, 2H), 2.72 (d, *J* = 3.7 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 144.7, 141.6, 130.0, 128.6, 127.9, 126.2, 111.9, 77.1, 60.7, 54.8, 28.7, 27.0, 14.3; IR (film) ν_{max} 3447, 2966, 2926, 1698, 1684, 1559, 1541, 1457, 1198, 1107 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{27}N_2O_3^+$ $[M+H]^+$ 319.2016; Found 319.2012.

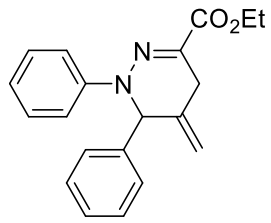
Ethyl (E)-4-(hydroxy(phenyl)methyl)-2-(2-(pyridin-2-yl)hydrazineylidene)pent-4-enoate (3ar)



3ar

Prepared according to the general procedure as described above in 66% yield (22.5 mg). It was purified by flash chromatography (6.7 – 10.0% EtOAc/PE) to afford a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (ddd, *J* = 5.1, 2.0, 0.9 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.65 (ddd, *J* = 8.7, 7.0, 1.9 Hz, 1H), 7.35 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 6.94 (ddd, *J* = 7.0, 5.0, 1.1 Hz, 1H), 6.81 (s, 1H), 5.23 (d, *J* = 4.2 Hz, 1H), 5.11 (s, 1H), 5.01 – 4.96 (m, 2H), 4.70 (d, *J* = 17.2 Hz, 1H), 4.65 (d, *J* = 4.4 Hz, 1H), 4.28 (t, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 156.7, 146.7, 143.5, 140.7, 138.4, 128.3, 127.6, 126.2, 124.7, 118.2, 114.6, 111.5, 74.8, 60.9, 46.2, 14.3; IR (film) ν_{max} 3447, 2927, 1716, 1705, 1593, 1559, 1466, 1439, 1161, 1142 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{22}N_3O_3^+$ $[M+H]^+$ 340.1656; Found 340.1653.

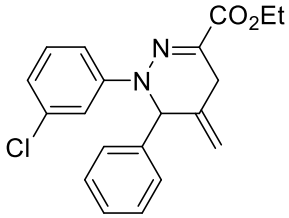
Ethyl 5-methylene-1,6-diphenyl-1,4,5,6-tetrahydropyridazine-3-carboxylate (4a)



4a

Prepared according to the general procedure as described above in 71% yield (45.5 mg). It was purified by flash chromatography (3.3 % EtOAc/PE) to afford a white solid. mp = 101 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.30 (d, *J* = 1.4 Hz, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 7.25 (d, *J* = 3.0 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.98 (tt, *J* = 7.0, 1.3 Hz, 1H), 5.58 (s, 1H), 5.36 (d, *J* = 2.6 Hz, 1H), 5.10 (d, *J* = 2.5 Hz, 1H), 4.36 – 4.27 (m, 2H), 3.27 (dd, *J* = 19.5, 2.1 Hz, 1H), 2.81 (dt, *J* = 19.4, 2.6 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 145.6, 138.6, 136.5, 130.4, 129.1, 129.0, 127.8, 125.7, 122.2, 115.3, 112.2, 64.9, 61.1, 27.5, 14.4; IR (film) ν_{max} 2924, 2854, 2360, 1717, 1698, 1559, 1541, 1522, 1507, 1457 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}N_2O_2^+$ $[M+H]^+$ 321.1598; Found 321.1595.

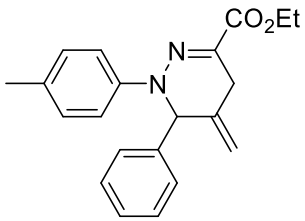
Ethyl 1-(3-chlorophenyl)-5-methylene-6-phenyl-1,4,5,6-tetrahydropyridazine-3-carboxylate (4b)



4b

Prepared according to the general procedure as described above in 59% yield (41.9 mg). It was purified by flash chromatography (3.3 % EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 2.2 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 7.19 – 7.14 (m, 3H), 7.12 (ddd, *J* = 8.4, 2.3, 1.1 Hz, 1H), 6.94 (ddd, *J* = 7.8, 2.0, 1.1 Hz, 1H), 5.54 (s, 1H), 5.38 (d, *J* = 2.5 Hz, 1H), 5.12 (d, *J* = 2.4 Hz, 1H), 4.37 – 4.28 (m, 2H), 3.28 (dd, *J* = 19.6, 2.0 Hz, 1H), 2.80 (dt, *J* = 19.6, 2.6 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 146.6, 138.0, 136.1, 135.0, 131.7, 130.0, 129.1, 128.0, 125.6, 122.1, 115.5, 113.1, 112.6, 64.7, 61.3, 27.4, 14.4; IR (film) ν_{max} 2923, 2850, 2362, 1716, 1699, 1588, 1569, 1559,1480 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{20}ClN_2O_2^+$ $[M+H]^+$ 355.1208; Found 355.1202.

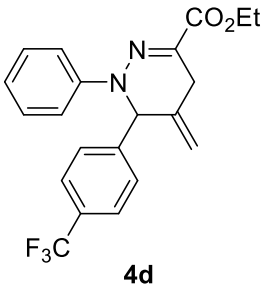
Ethyl 5-methylene-6-phenyl-1-(p-tolyl)-1,4,5,6-tetrahydropyridazine-3-carboxylate (4c)



4c

Prepared according to the general procedure as described above in 33% yield (21.9 mg). It was purified by flash chromatography (3.3 % EtOAc/PE) to afford a yellow solid. mp = 154 – 156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.20 (d, *J* = 2.1 Hz, 4H), 7.19 (s, 4H), 7.06 (d, *J* = 8.6 Hz, 2H), 5.55 (d, *J* = 2.0 Hz, 1H), 5.34 (d, *J* = 1.5 Hz, 1H), 5.09 (d, *J* = 2.5 Hz, 1H), 4.37 – 4.25 (m, 2H), 3.25 (dd, *J* = 19.4, 2.0 Hz, 1H), 2.80 (dt, *J* = 19.4, 2.6 Hz, 1H), 2.27 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 143.4, 138.8, 136.6, 131.7, 129.7, 129.6, 129.0, 127.8, 125.7, 115.3, 112.1, 65.0, 61.0, 27.4, 20.6, 14.4; IR (film) ν_{max} 2923, 2359, 1697, 1569, 1559, 1509, 1248, 1159, 1098 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_2^+$ $[M+H]^+$ 335.1754; Found 335.1752.

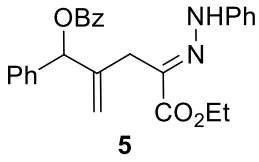
Ethyl 5-methylene-1-phenyl-6-(4-(trifluoromethyl)phenyl)-1,4,5,6-tetrahydropyridazine-3-carboxylaten (4d)



4d

Prepared according to the general procedure as described above in 71% yield (55.1 mg). It was purified by flash chromatography (3.3 % EtOAc/PE) to afford a yellow solid. mp = 102 – 104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 3.8 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.03 – 6.97 (m, 1H), 5.63 (d, *J* = 2.0 Hz, 1H), 5.41 (d, *J* = 2.6 Hz, 1H), 5.17 (d, *J* = 2.5 Hz, 1H), 4.38 – 4.27 (m, 2H), 3.30 (dd, *J* = 19.7, 2.0 Hz, 1H), 2.75 (dt, *J* = 19.7, 2.6 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 145.3, 135.8, 130.8, 130.3 (C-F, $^{2}J_{C\text{-}F}$= 32.4 Hz), 129.2, 126.2, 126.1 (C-F, $^{3}J_{C\text{-}F}$= 3.7 Hz), 122.5, 115.2, 113.2, 64.4, 61.2, 27.4, 14.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.59; IR (film) ν_{max} 2981, 2359, 1698, 1575, 1497, 1323, 1249, 1152, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}F_3N_2O_2^+$ $[M+H]^+$ 389.1471; Found 389.1471.

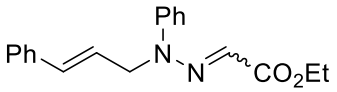
(E)-2-methylene-1,4-diphenyl-4-(2-tosylhydrazineylidene)butyl benzoate (5)



5

Prepared according to the general procedure as described above in 52% yield (22.9 mg). It was purified by flash chromatography (10.0 – 12.5 % EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.01 (s, 1H), 7.61 – 7.58 (m, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.53 (s, 1H), 7.50 – 7.46 (m, 2H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.41 – 7.38 (m, 1H), 7.29 – 7.27 (m, 1H), 7.15 – 7.12 (m, 2H), 6.97 – 6.94 (m, 1H), 6.38 (s, 1H), 5.38 (s, 1H), 4.98 (t, *J* = 1.6 Hz, 1H), 4.30 – 4.26 (m, 2H), 3.53 (dt, *J* = 17.6, 2.0 Hz, 1H), 3.35 (d, *J* = 17.7 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.2, 143.2, 140.3, 137.6, 133.5, 131.6, 129.8, 129.8, 129.2, 129.0, 128.8, 128.6, 127.0, 122.1, 114.1, 113.1, 78.9, 61.3, 28.8, 14.3; IR (film) ν_{max} 2926, 2360, 1717, 1698, 1559, 1541, 1522, 1507, 1457 1246, 1102 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{27}N_2O_4^+$ $[M+H]^+$ 443.1965; Found 443.1965.

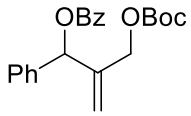
Ethyl (2E,4E(z))-5-phenyl-2-(2-phenylhydrazineylidene)pent-4-enoate (5-2)



5-2

Prepared according to the general procedure as described above in 85% yield (25.9 mg). It was purified by flash chromatography (10.0 % EtOAc/PE) to afford a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.27 (dd, J = 7.0, 1.8 Hz, 2H), 7.23 (dd, J = 4.0, 1.2 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.17 – 7.15 (m, 1H), 6.99 (tt, J = 7.3, 1.1 Hz, 1H), 6.74 (s, 1H), 6.32 (dt, J = 16.1, 2.0 Hz, 1H), 6.07 (dd, J = 16.1, 4.3 Hz, 1H), 4.56 (dd, J = 4.4, 2.0 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 146.4, 136.0, 132.1, 129.3, 128.7, 128.1, 126.5, 123.5, 121.8, 119.6, 116.9, 114.1, 60.7, 49.9, 14.4; IR (film) ν_{max} 3028, 2980, 1695, 1550, 1493, 1314, 1266, 1236, 1137, 1096 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{21}N_2O_2^+$ $[M+H]^+$ 309.1598; Found 309.1596.

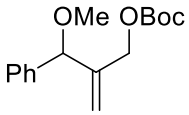
2-(((tert-butoxycarbonyl)oxy)methyl)-1-phenylallyl benzoate (6)



6

Prepared according to the general procedure as described above in 50% yield (185.3 mg). It was purified by flash chromatography (3.3% EtOAc/PE) to afford a white solid. mp = 89 – 91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.09 (m, 2H), 7.59 – 7.55 (m, 1H), 7.47 – 7.43 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.29 (m, 1H), 6.59 (s, 1H), 5.44 (s, 1H), 5.41 (s, 1H), 4.62 (d, *J* = 13.4 Hz, 1H), 4.51 (d, *J* = 13.4 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 153.2, 141.9, 137.8, 133.2, 130.1, 129. 8, 128.6, 128.5, 128.4, 127.2, 115.9, 82.3, 76.1, 66.4, 27.7; IR (film) ν_{max} 2980, 2359, 1743, 1724, 1457, 1255, 1159, 1106 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}NaO_5^+$ $[M+Na]^+$ 391.1516; Found 391.1512.

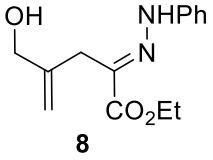
***tert*-butyl (2-(methoxy(phenyl)methyl)allyl) carbonate (6-1)**



6-1

To a 50 mL round-bottom flask charged with NaH (60% in mineral oil, 1.8 equiv) at 0 °C was added a solution of hydroxy-tethered allylic carbonate **1a** (528.6 mg, 2 mmol, 1 equiv) in dry THF (20 mL). The suspension was stirred at 0 °C for over 1 h, and MeI (2.5 equiv) was added. The reaction was allowed to warm up to room temperature, the starting material was monitored by TLC until its complete consumption. The crude product was purified by flash chromatography (3.3% EtOAc/PE) to afford a colorless oil. Prepared according to the general procedure as described above in 30% yield (166.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 3.7 Hz, 4H), 7.22 – 7.18 (m, 1H), 5.21 (dp, J = 3.5, 1.2 Hz, 2H), 4.66 (s, 1H), 4.49 (d, J = 13.7 Hz, 1H), 4.29 (d, J = 13.7 Hz, 1H), 3.26 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 143.6, 139.4, 128.4, 127.8, 126.9, 114.4, 84.1, 82.1, 66.2, 56.8, 27.8; IR (film) ν_{max} 2980, 2935, 1742, 1454, 1394, 1369, 1275, 1254, 1161, 1094 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}O_4^+$ $[M+H]^+$ 279.1591; Found 279.1593.

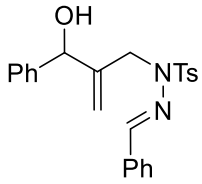
Ethyl (E)-4-(hydroxymethyl)-2-(2-phenylhydrazineylidene)pent-4-enoate (8)



8

Prepared according to the general procedure as described above in 59% yield (15.5 mg). It was purified by flash chromatography (10.0 – 12.5 % EtOAc/PE) to afford a white solid. mp = 91 – 93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.31 – 7.27 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 5.14 (s, 1H), 5.08 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.13 (d, *J* = 5.3 Hz, 2H), 3.48 (s, 2H), 2.34 (t, *J* = 5.5 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 143.3, 142.7, 132.6, 129.3, 122.0, 114.8, 114.0, 66.2, 61.4, 28.6, 14.3; IR (film) ν_{max} 2927, 2359, 1698, 1559, 1541, 1507, 1497, 1240, 1188, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_3^+$ $[M+H]^+$ 263.139; Found 263.1385.

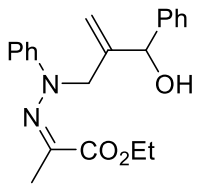
(E)-N'-(3-(hydroxy(phenyl)methyl)-1-phenylbut-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (10)



10

Prepared according to the general procedure as described above in 98% yield (41.2 mg). It was purified by flash chromatography (12.5 – 20.0% EtOAc/PE) to afford a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 4.2 Hz, 2H), 7.39 (s, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.29 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.09 (s, 1H), 5.37 (s, 1H), 5.34 (s, 1H), 5.16 (s, 1H), 4.33 (d, *J* = 17.5 Hz, 1H), 4.11 (d, *J* = 17.6 Hz, 1H), 2.55 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 144.1, 143.6, 141.2, 134.7, 134.1, 129.9, 129.6, 128.7, 128.6, 128.11, 128.08, 127.3, 126.3, 113.2, 75.7, 48.5, 21.6; IR (film) ν_{max} 3503, 918, 1355, 1186, 1166, 1090, 1059, 923 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}N_2O_3S^+$ $[M+H]^+$ 421.1580; Found 421.1575.

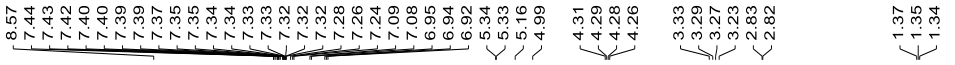
Ethyl (Z)-2-(2-(2-(hydroxy(phenyl)methyl)allyl)-2-phenylhydrazineylidene)propanoate (12)

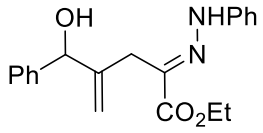


12

Prepared according to the general procedure as described above in 24% yield (8.6 mg). It was purified by flash chromatography (10.0% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.3 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.21 – 7.16 (m, 3H), 6.99 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 7.6 Hz, 2H), 5.25 (d, J = 3.9 Hz, 1H), 5.15 (s, 1H), 4.82 (s, 1H), 4.66 (d, J = 5.1 Hz, 1H), 4.26 (p, J = 7.0 Hz, 2H), 4.13 (d, J = 15.1 Hz, 1H), 4.00 (d, J = 15.0 Hz, 1H), 1.59 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 148.1, 146.6, 144.1, 142.7, 129.1, 128.2, 127.2, 126.3, 124.4, 122.0, 117.6, 76.4, 61.7, 60.8, 16.6, 14.3; IR (film) ν_{max} 3392, 2980, 2924, 1702, 1593, 1577, 1490, 1273, 1129, 1025 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3^+$ $[M+H]^+$ 353.1860; Found 353.1860.

5. ^{1}H, ^{13}C and ^{19}F NMR Spectra of All Products





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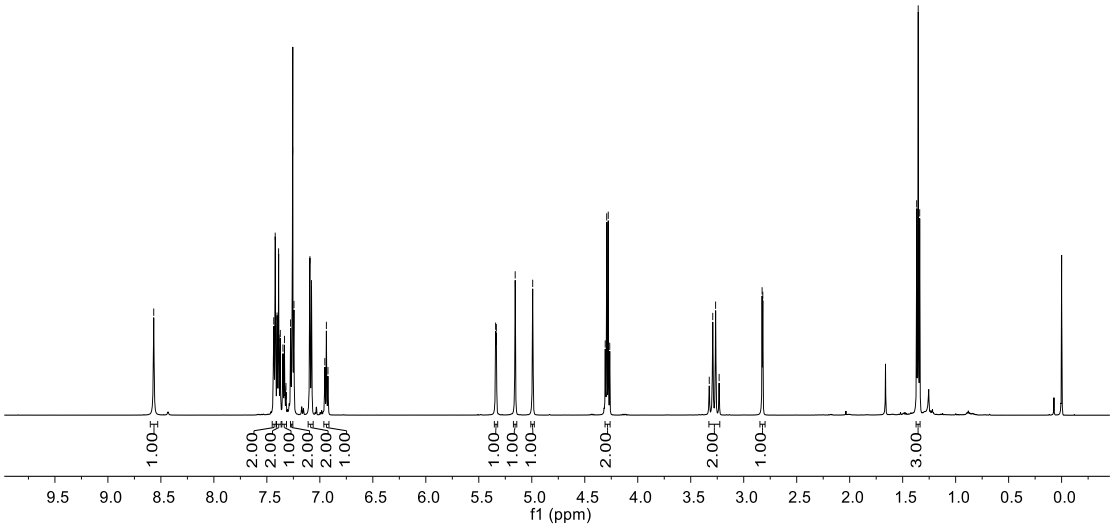

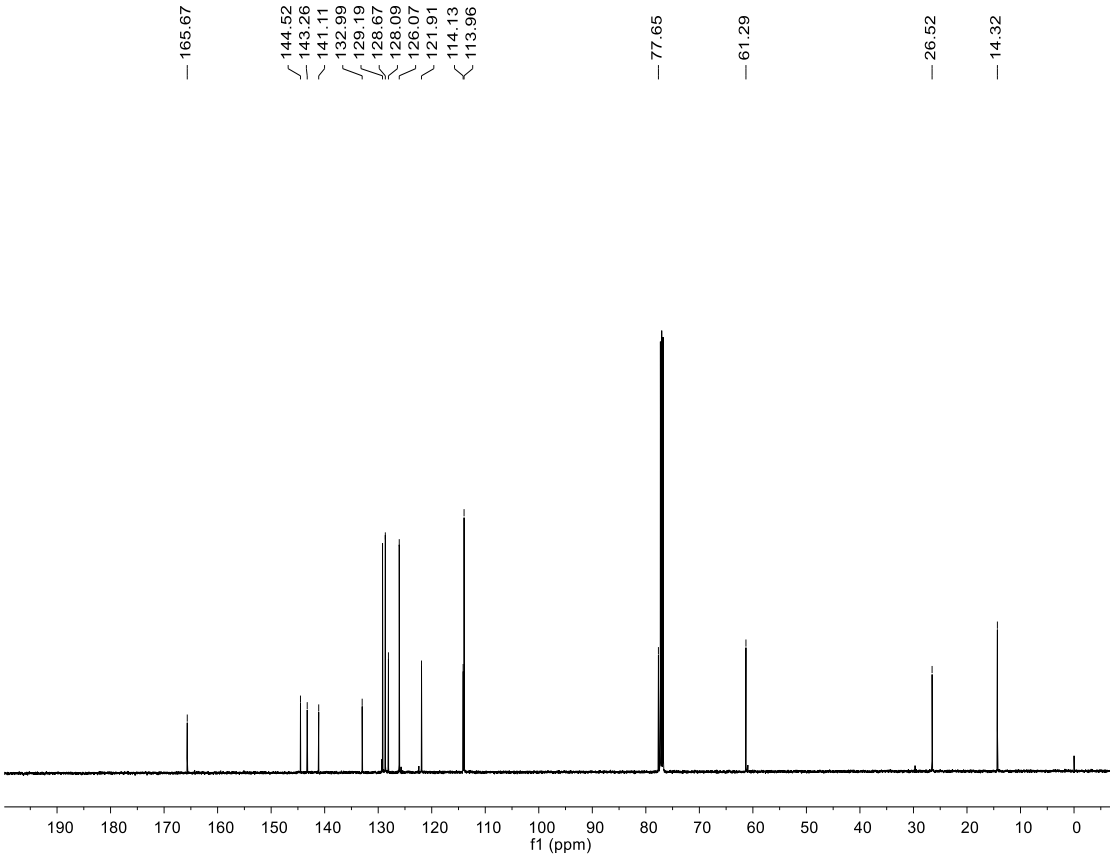


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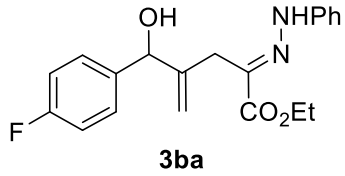
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F

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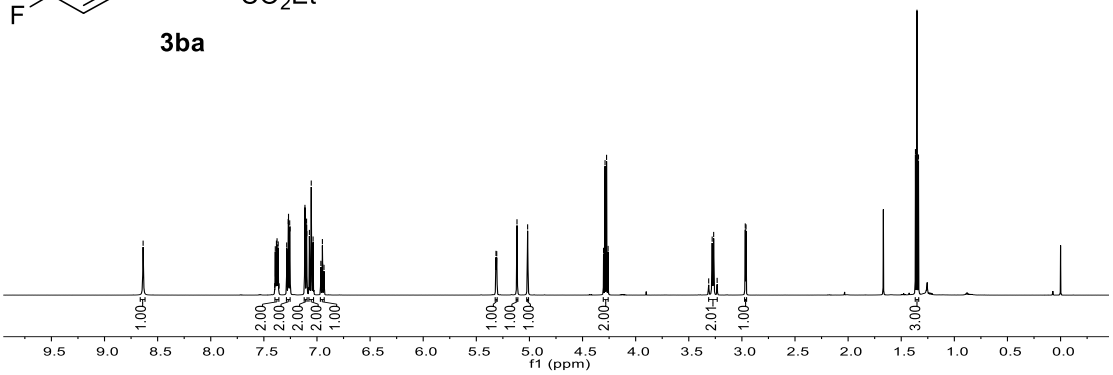
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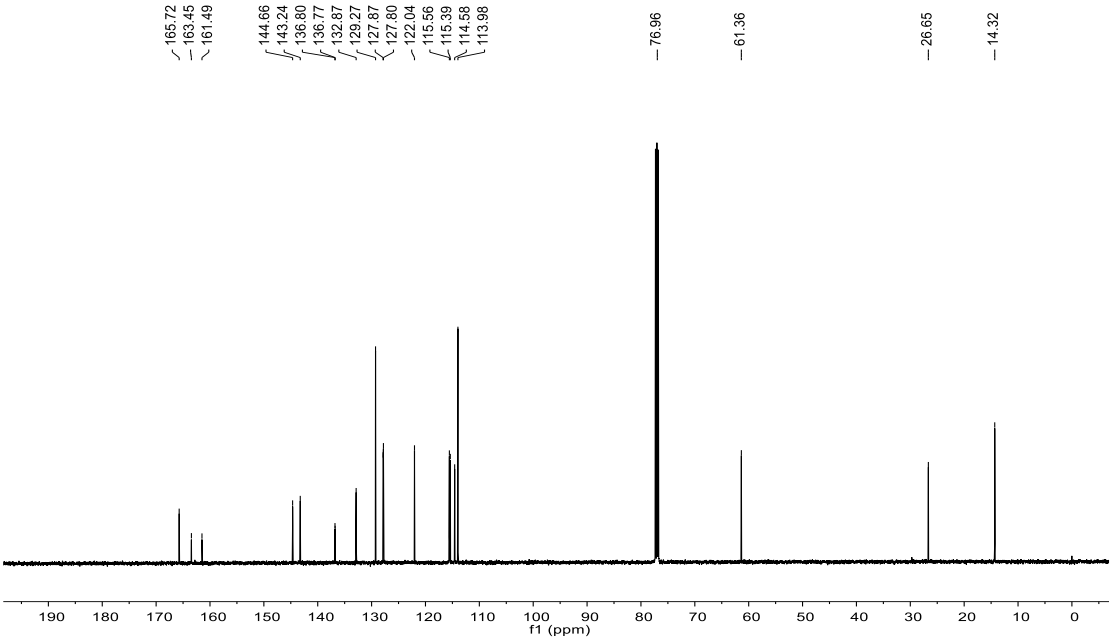
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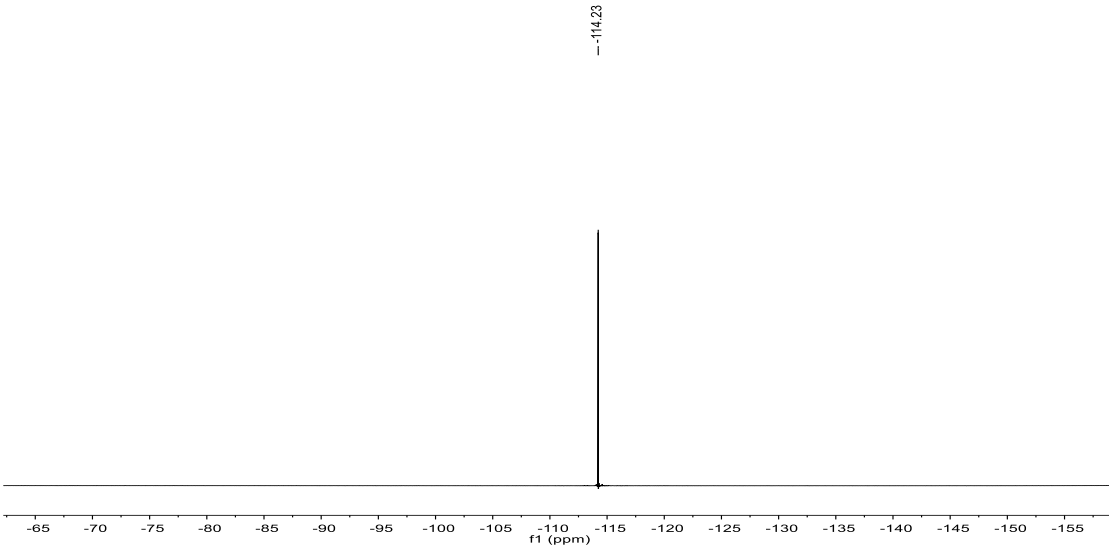
f1 (ppm)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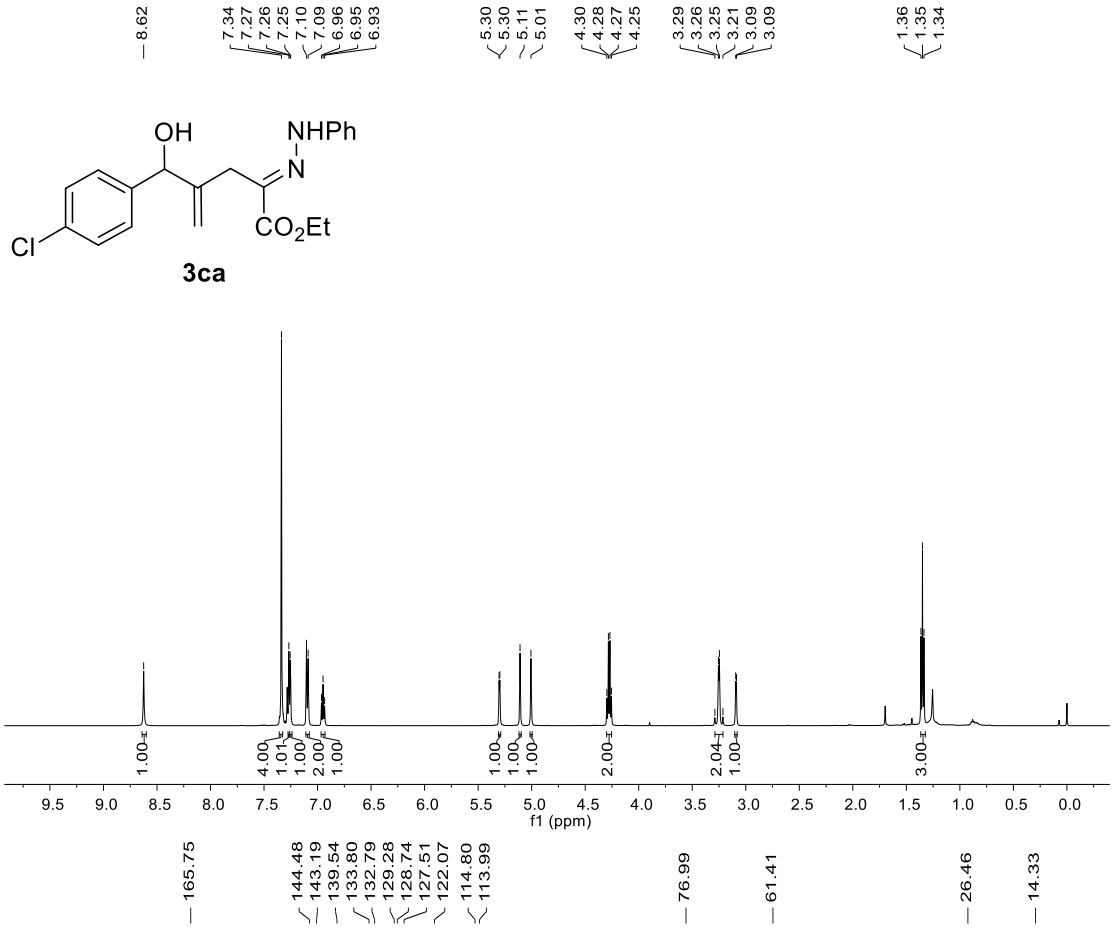
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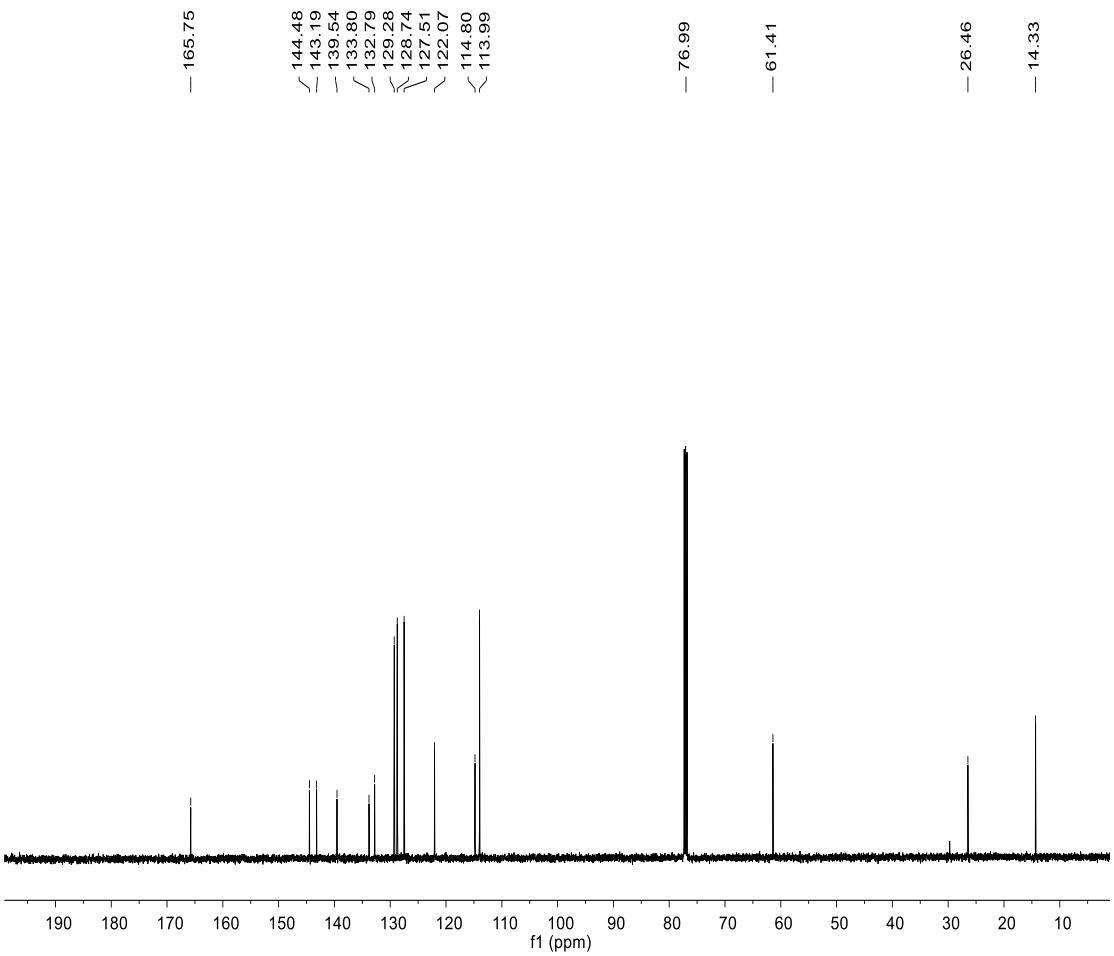
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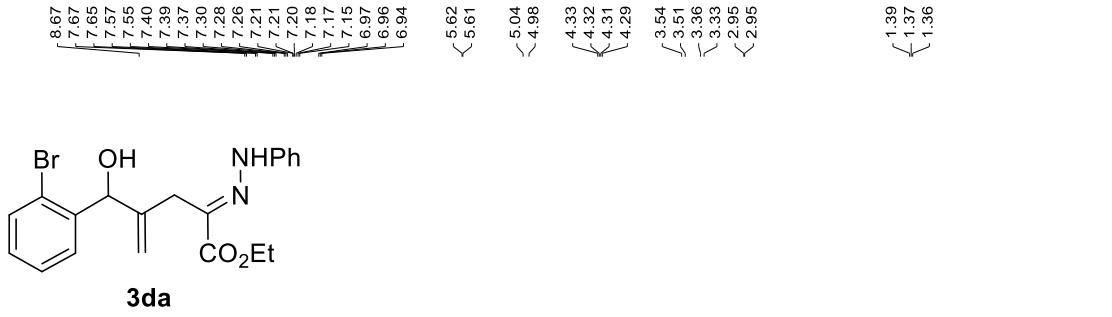
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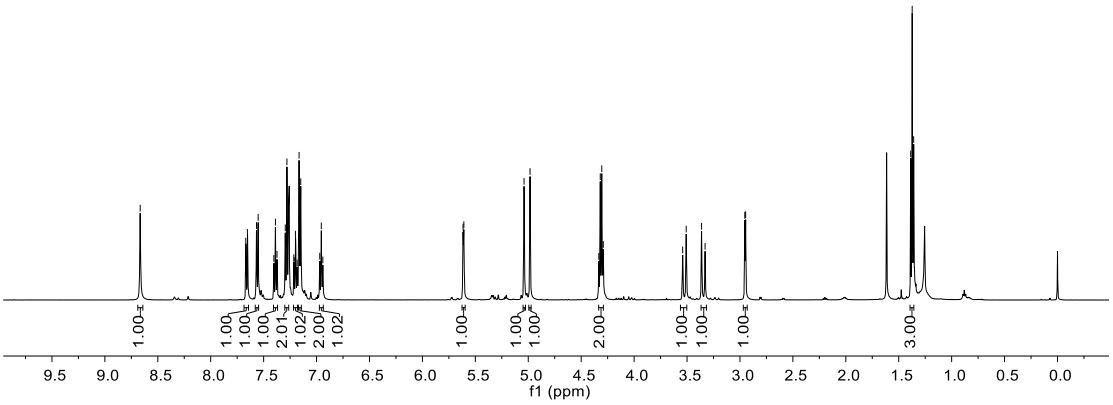
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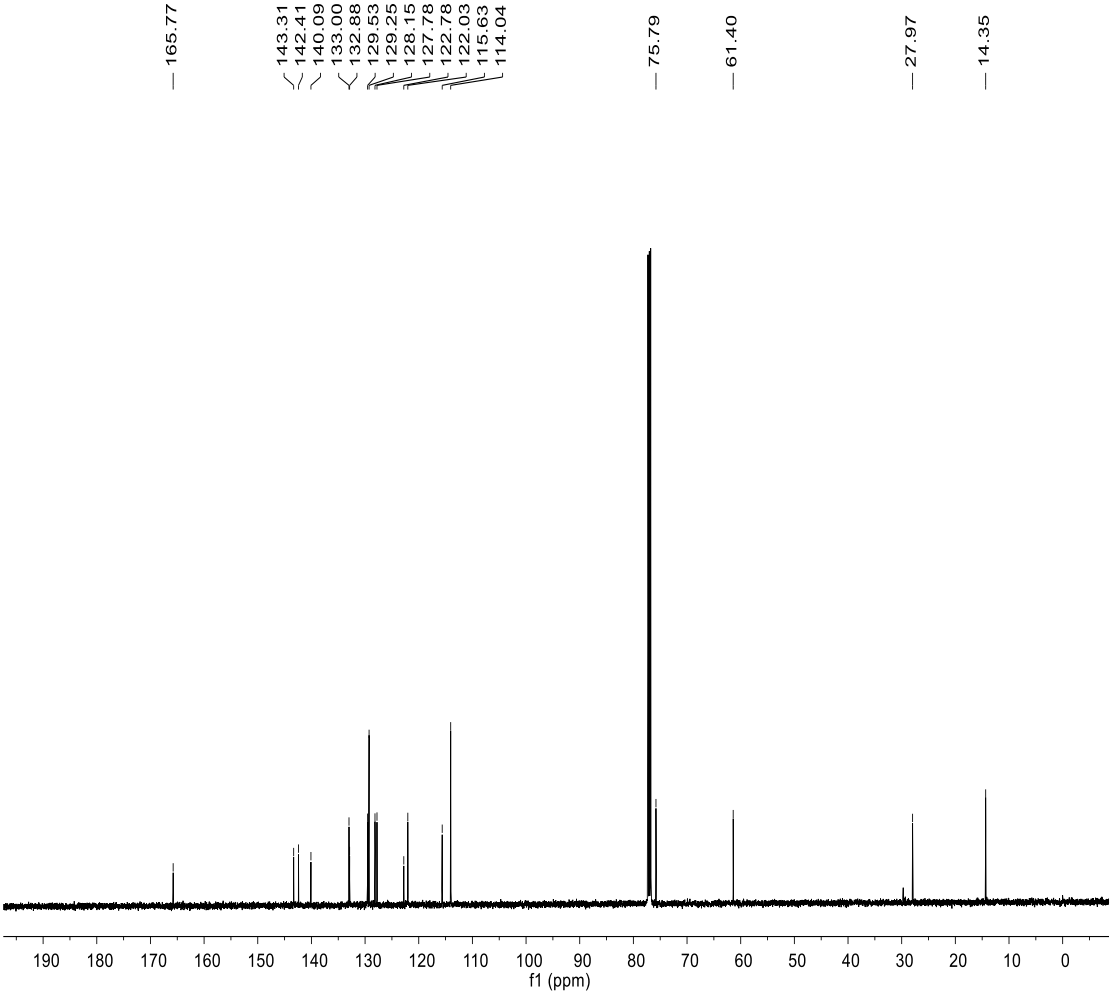
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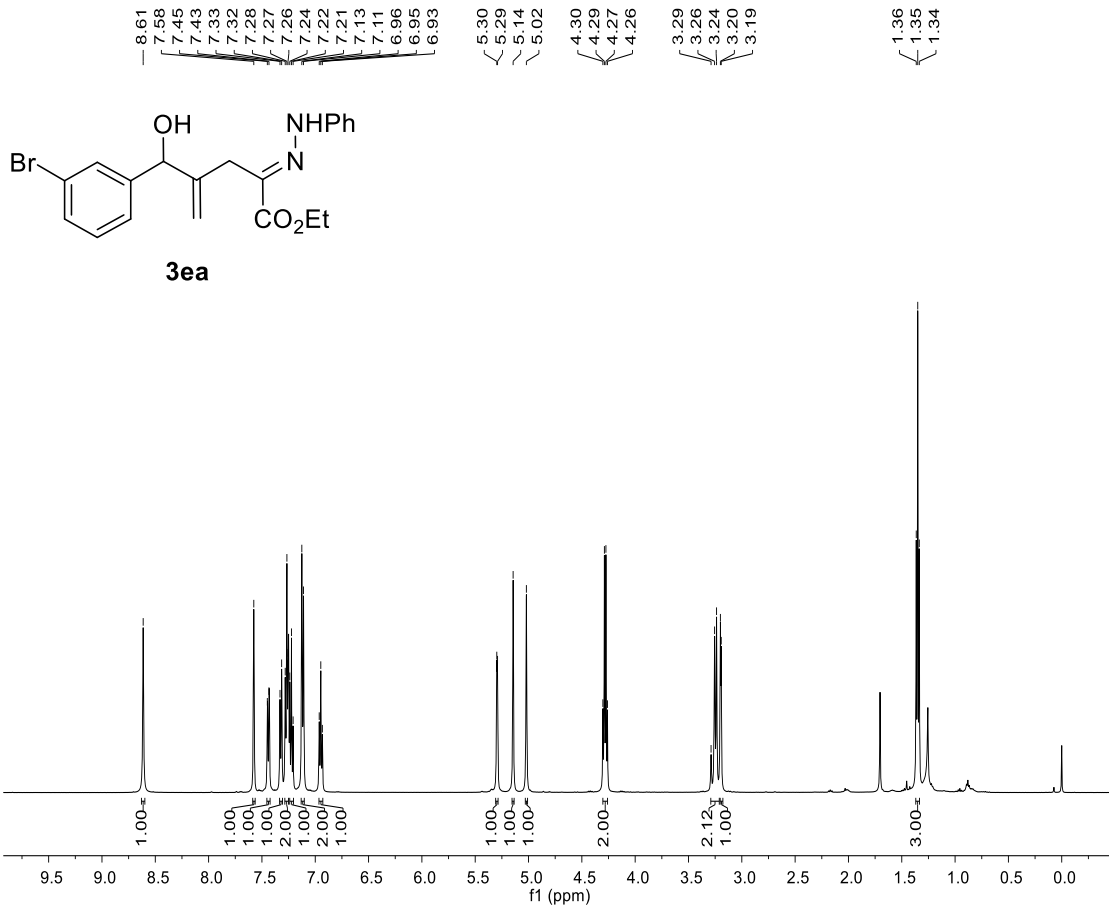
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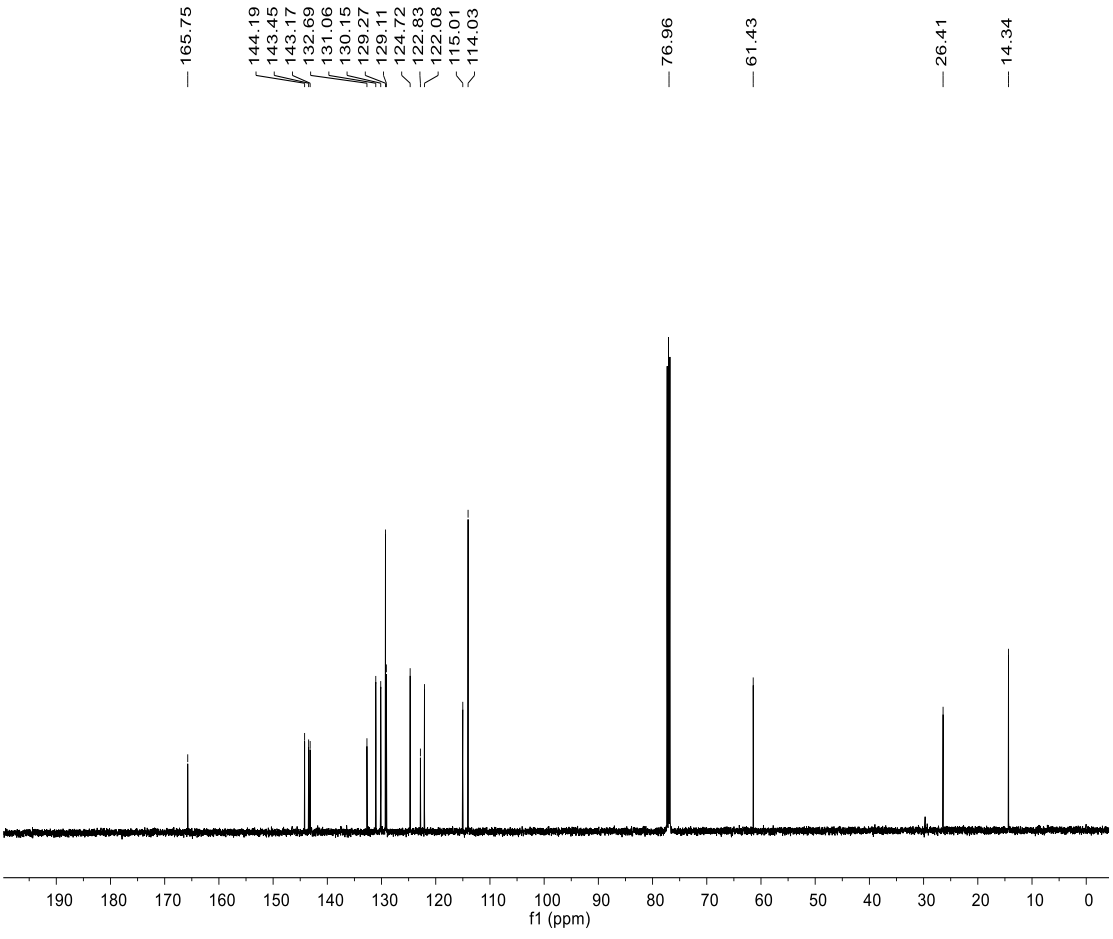
1.00
1.00
1.00
2.00
2.12
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ea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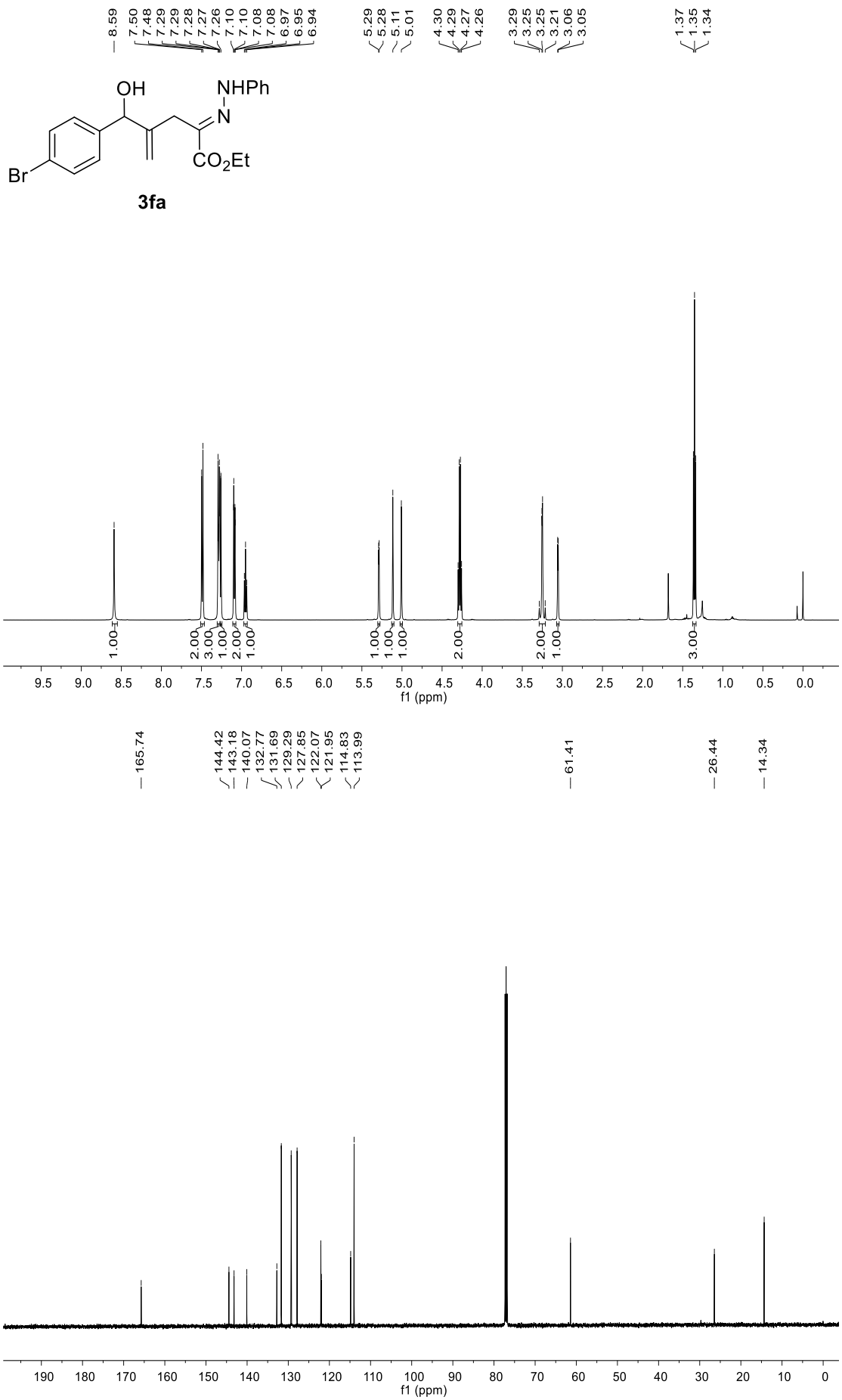
144.19
143.45
143.17
132.69
131.06
130.15
129.27
129.11
124.72
122.83
122.08
115.01
114.03
76.96
61.43
26.41
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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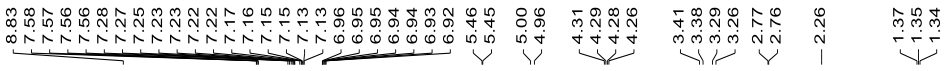
7.27
7.26
7.10
7.10
7.08
7.08
6.97
6.95
6.94
5.29
5.28
5.11
5.01
4.30
4.29
4.27
4.26
3.29
3.25
3.25
3.21
3.06
3.05
1.37
1.35
1.34
OH
NHPh
N
CO2Et
Br
3fa
1.00
2.00
3.00
1.00
2.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.74
144.42
143.18
140.07
132.77
131.69
129.29
127.85
122.07
121.95
114.83
113.99
61.41
26.44
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.25
7.23
7.23
7.22
7.22
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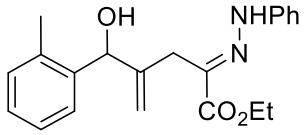
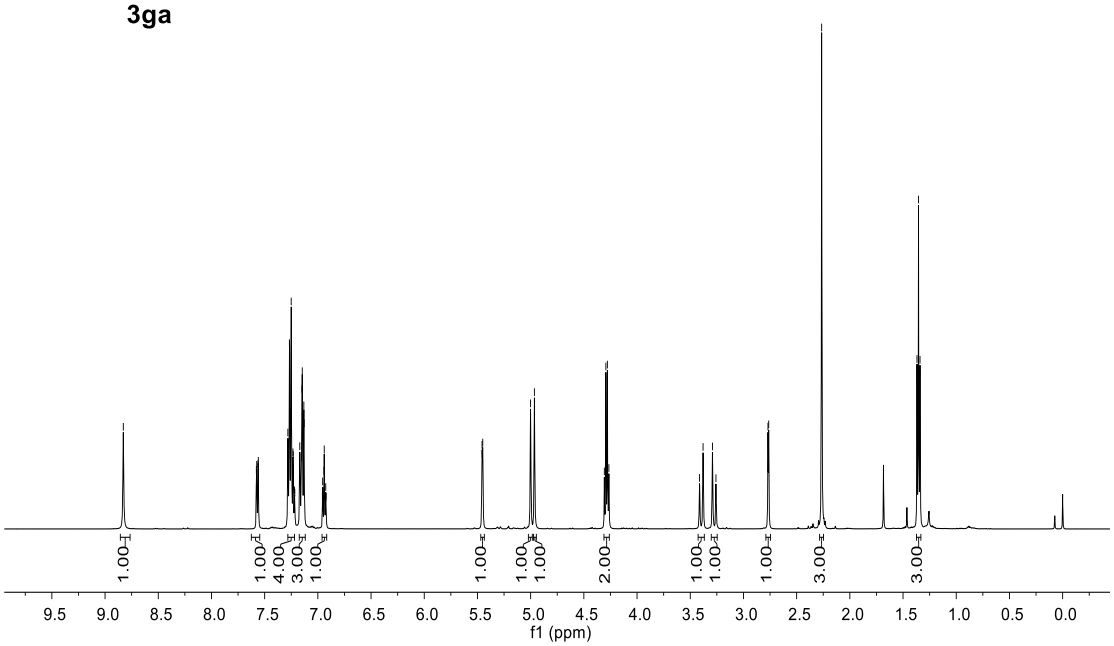
7.16
7.15
7.15
7.13
7.13
6.96
6.95
6.95
6.94
6.94
6.93
6.92
5.46
5.45
5.00
4.96
4.31
4.29
4.28
4.26
3.41
3.38
3.29
3.26
2.77
2.76
2.26
1.37
1.35
1.34


OH
NHPh
N
CO2Et

3ga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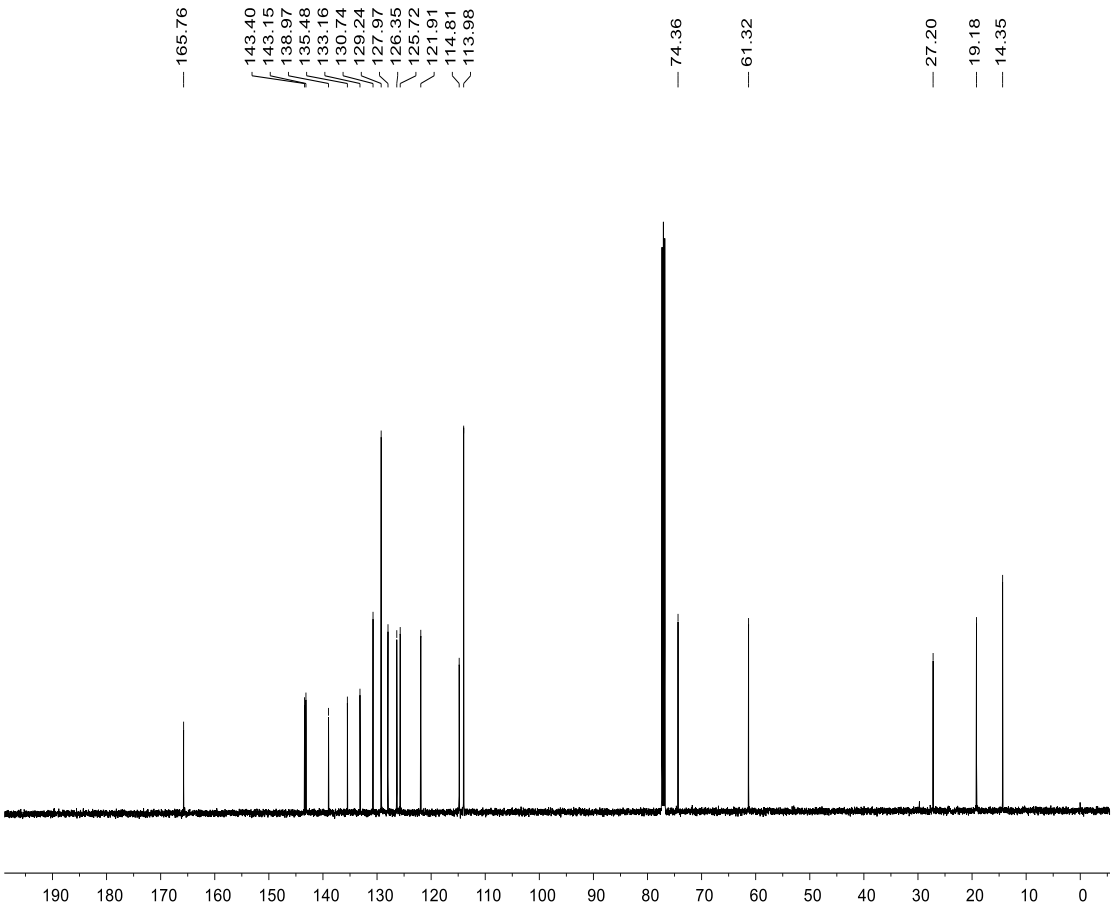
1.00
4.00
3.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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143.40
143.15
138.97
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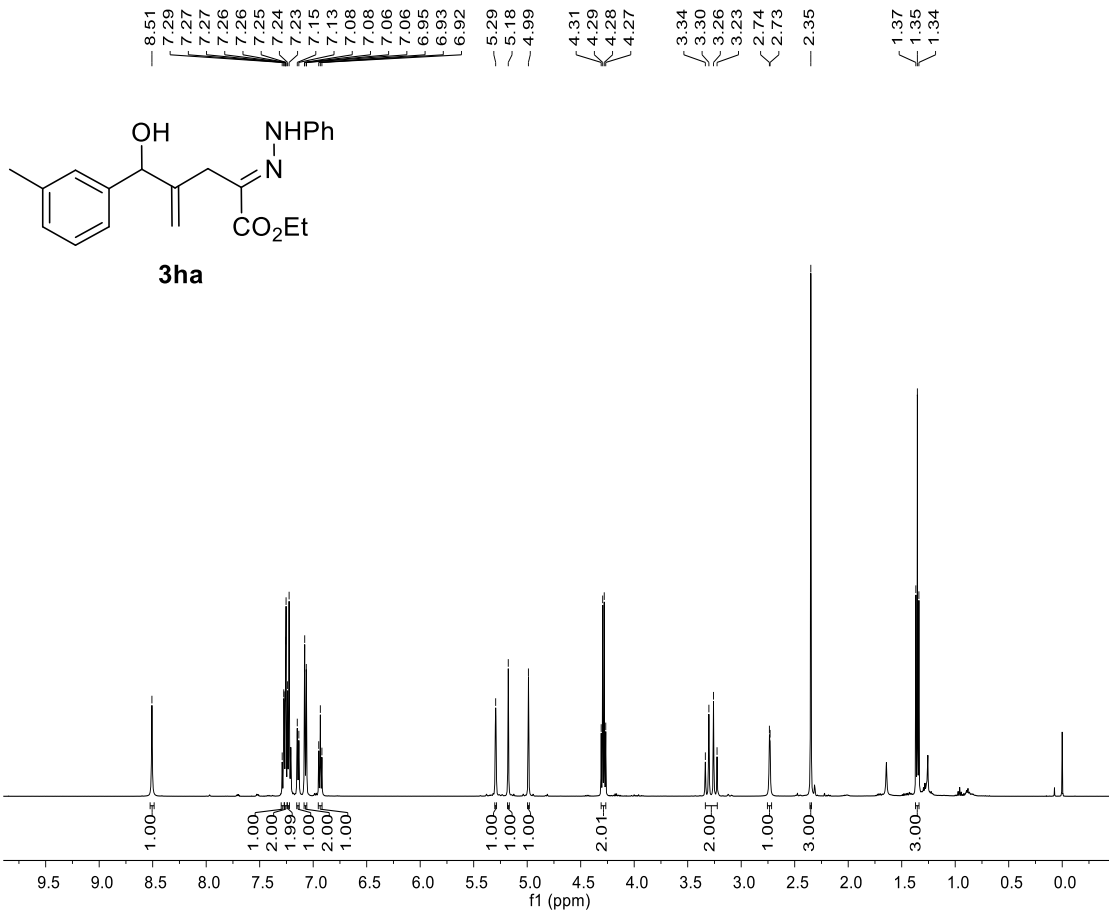
133.16
130.74
129.24
127.97
126.35
125.72
121.91
114.81
113.98
74.36
61.32
27.20
19.18
14.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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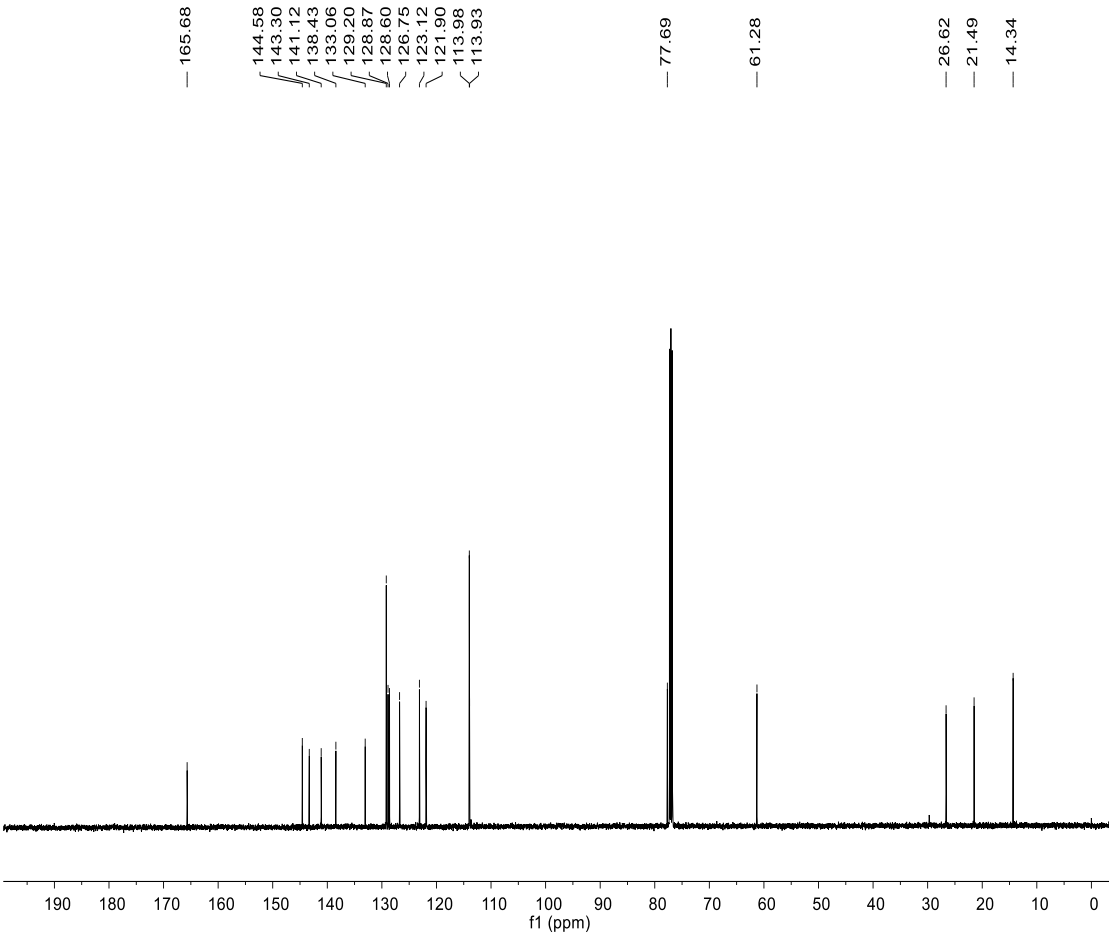
7.25
7.24
7.23
7.15
7.13
7.08
7.08
7.06
7.06
6.95
6.93
6.92
5.29
5.18
4.99
4.31
4.29
4.28
4.27
3.34
3.30
3.26
3.23
2.74
2.73
2.35
1.37
1.35
1.34
OH
NHPh
N
CO2Et
3ha
1.00
2.00
1.99
1.00
2.00
1.00
1.00
1.00
1.00
2.01
2.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.58
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141.12
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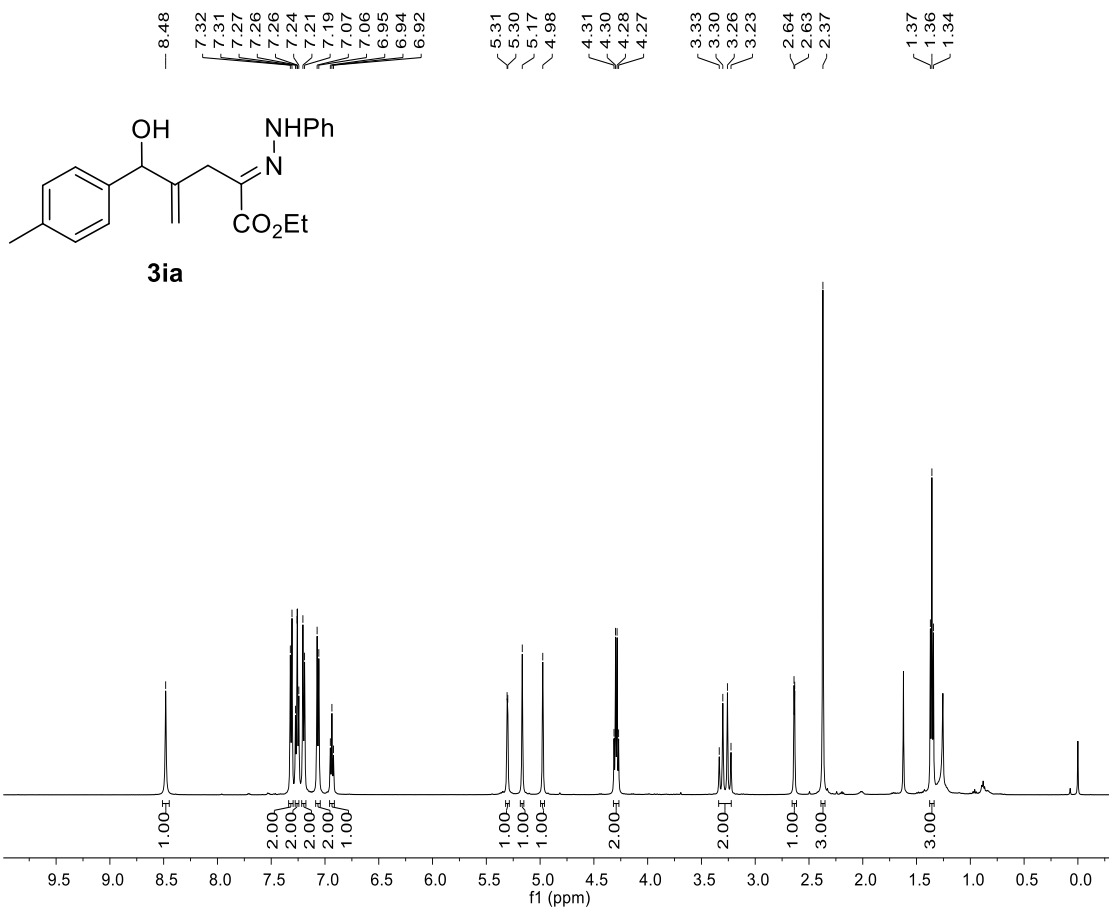
133.06
129.20
128.87
128.60
126.75
123.12
121.90
113.98
113.93
77.69
61.28
26.62
21.49
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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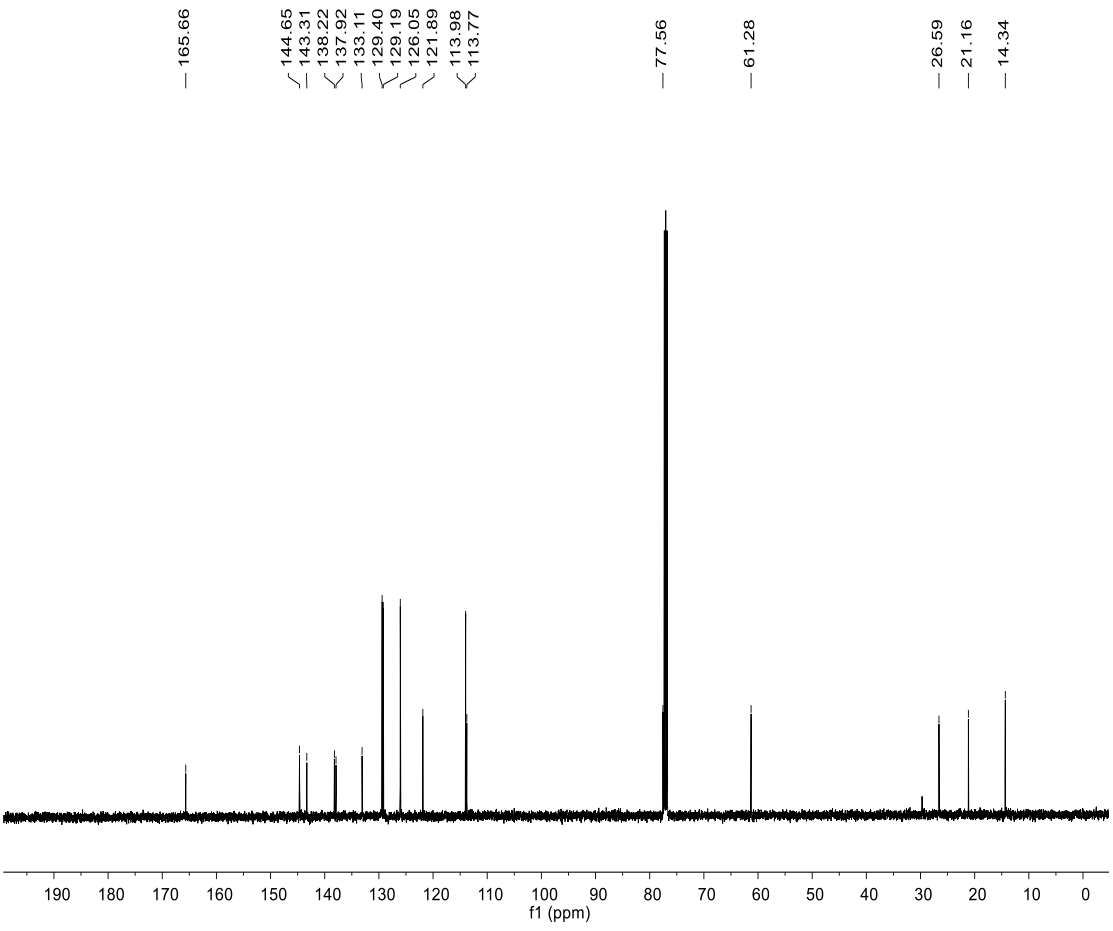
7.32
7.31
7.27
7.26
7.26
7.24
7.21
7.19
7.07
7.06
6.95
6.94
6.92
5.31
5.30
5.17
4.98
4.31
4.30
4.28
4.27
3.33
3.30
3.26
3.23
2.64
2.63
2.37
1.37
1.36
1.34
OH
NHPh
N
CO2Et
1.00
2.00
2.00
2.00
2.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ia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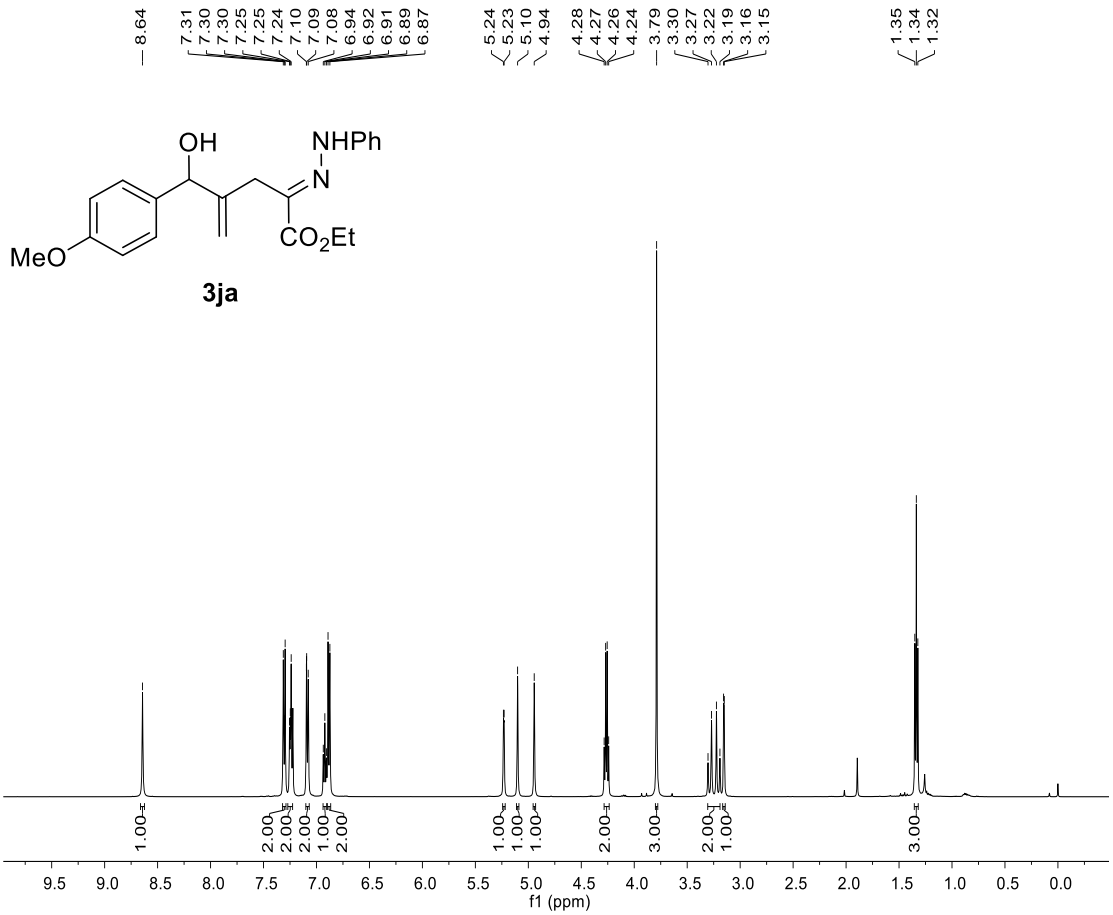
144.65
143.31
138.22
137.92
133.11
129.40
129.19
126.05
121.89
113.98
113.77
77.56
61.28
26.59
21.16
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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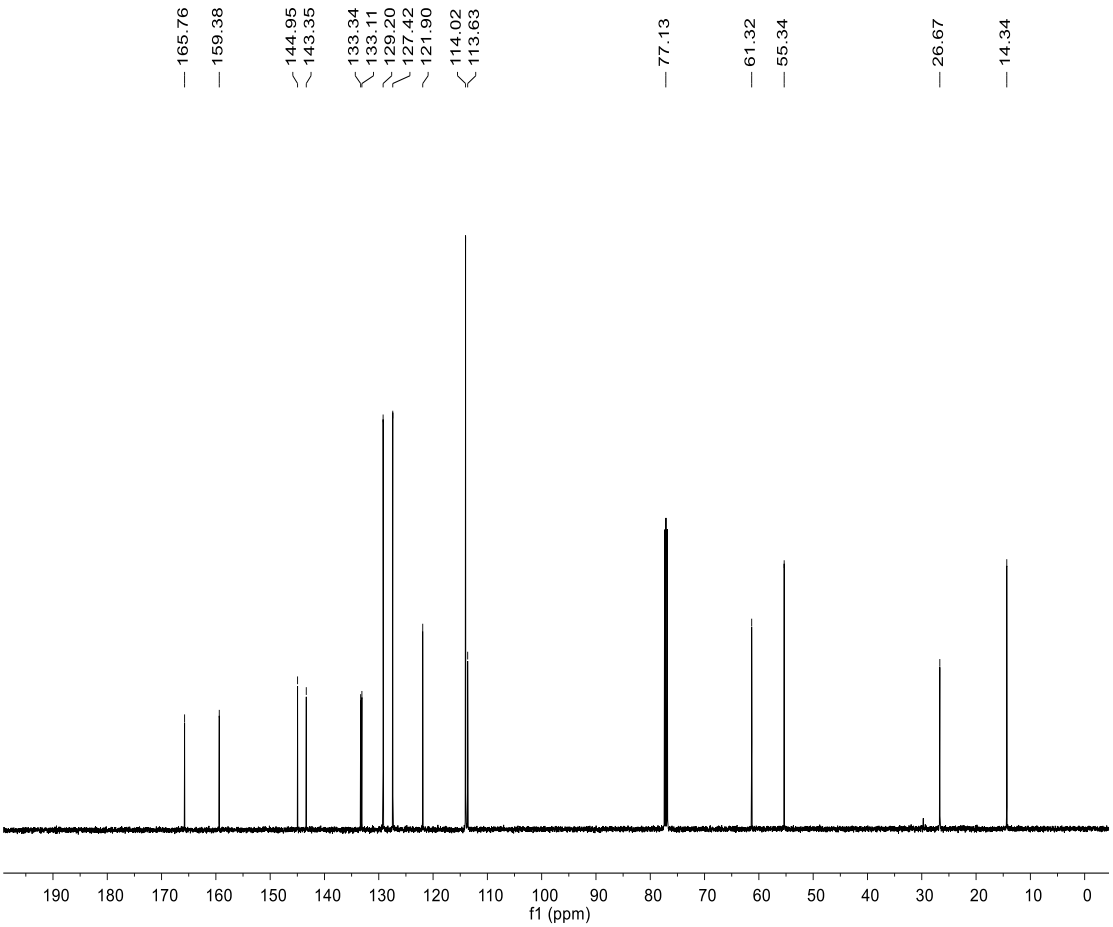
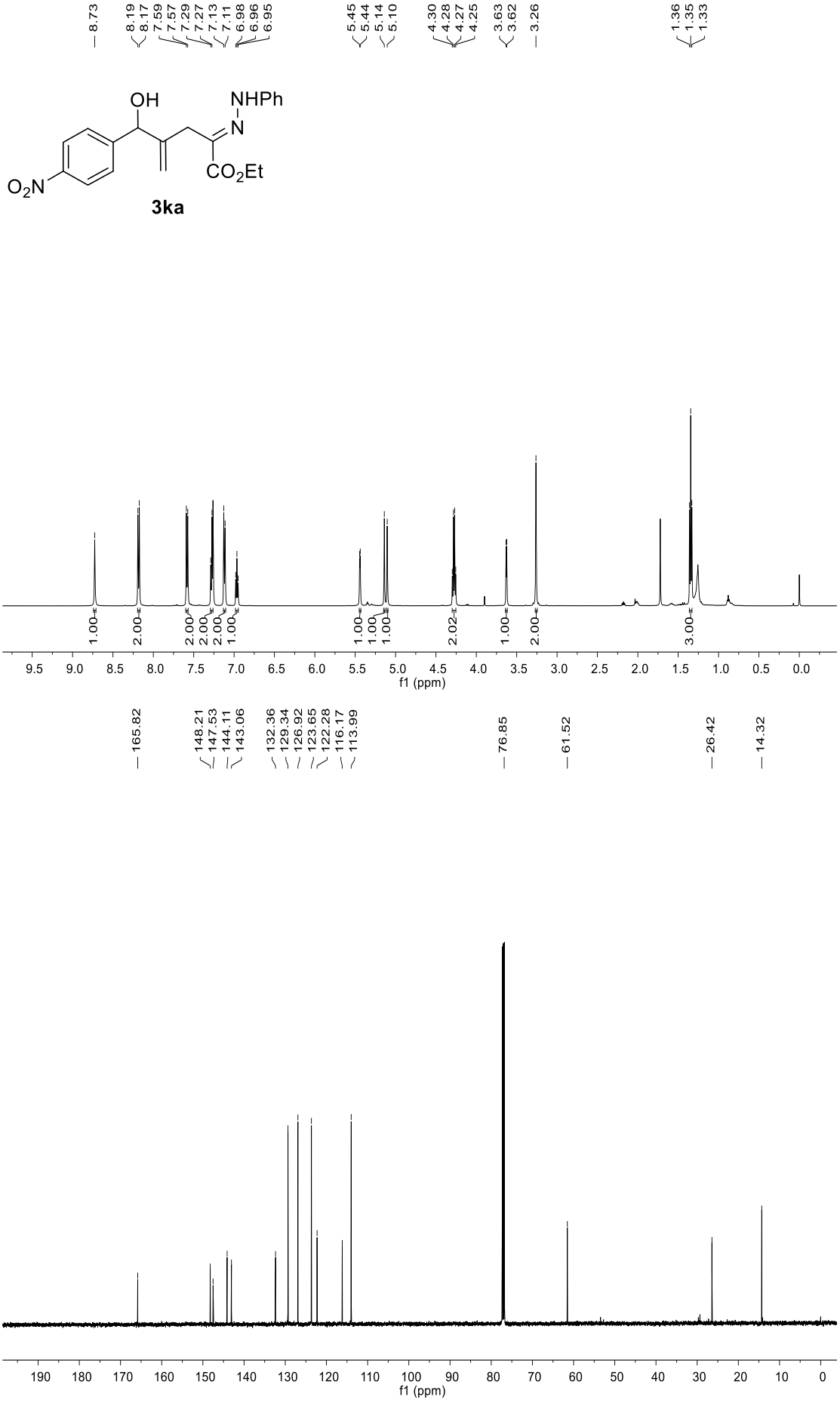
7.31
7.30
7.30
7.25
7.25
7.24
7.10
7.09
7.08
6.94
6.92
6.91
6.89
6.87
5.24
5.23
5.10
4.94
4.28
4.27
4.26
4.24
3.79
3.30
3.27
3.22
3.19
3.16
3.15
1.35
1.34
1.32
OH
NHPh
N
CO2Et
MeO
1.00
2.00
2.00
2.00
1.00
2.00
1.00
1.00
1.00
2.00
3.00
2.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ja


165.76
159.38
144.95
143.35
133.34
133.11
129.20
127.42
121.90
114.02
113.63
77.13
61.32
55.34
26.67
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.17
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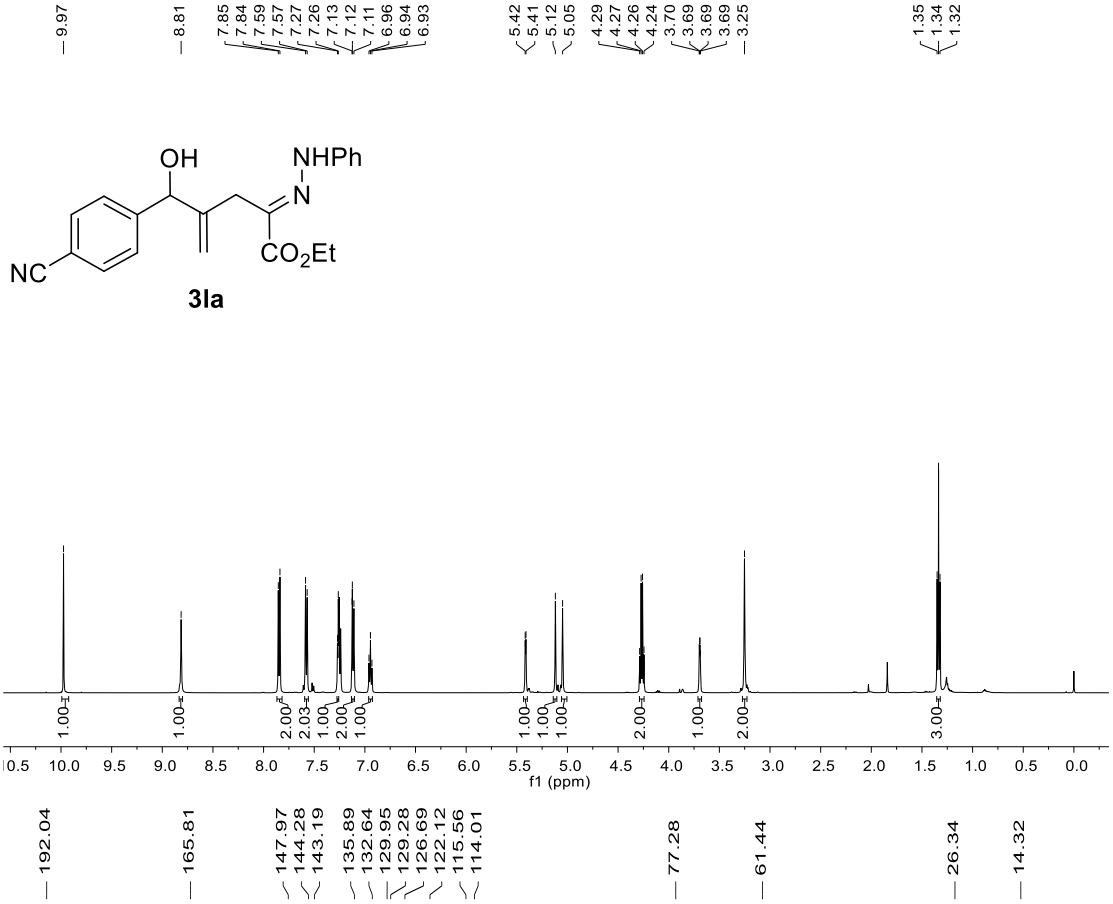
7.57
7.29
7.27
7.13
7.11
6.98
6.96
6.95
5.45
5.44
5.14
5.10
4.30
4.28
4.27
4.25
3.63
3.62
3.26
1.36
1.35
1.33
OH
NHPh
N
CO2Et
O2N
3ka
1.00
2.00
2.00
2.00
1.00
1.00
1.00
2.02
1.00
2.00
3.00
f1 (ppm)
165.82
148.21
147.53
144.11
143.06
132.36
129.34
126.92
123.65
122.28
116.17
113.99
76.85
61.52
26.42
14.32
f1 (ppm)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7.84
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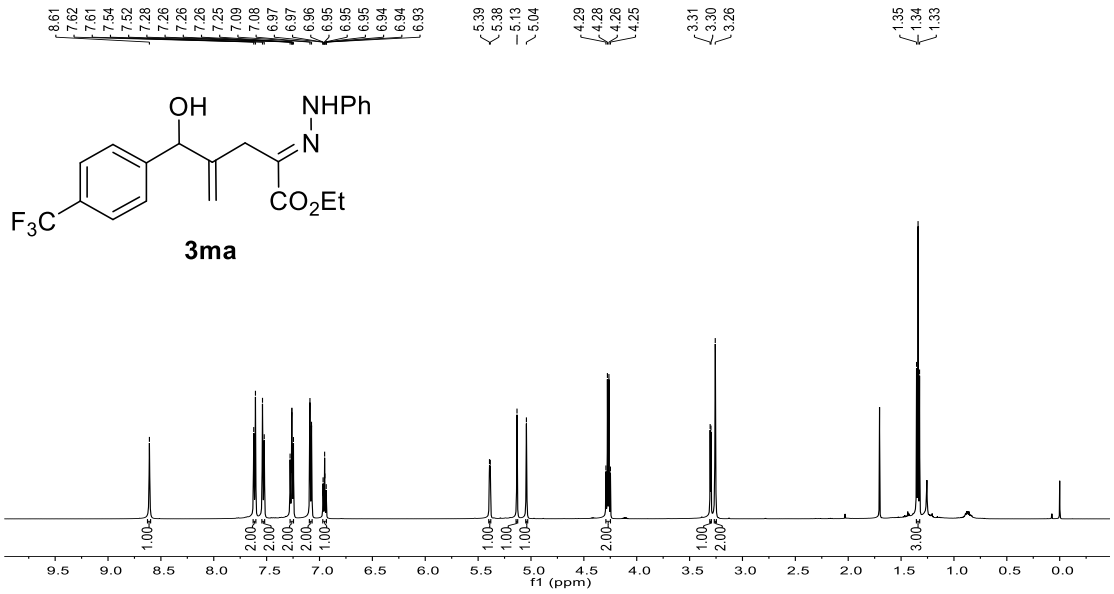
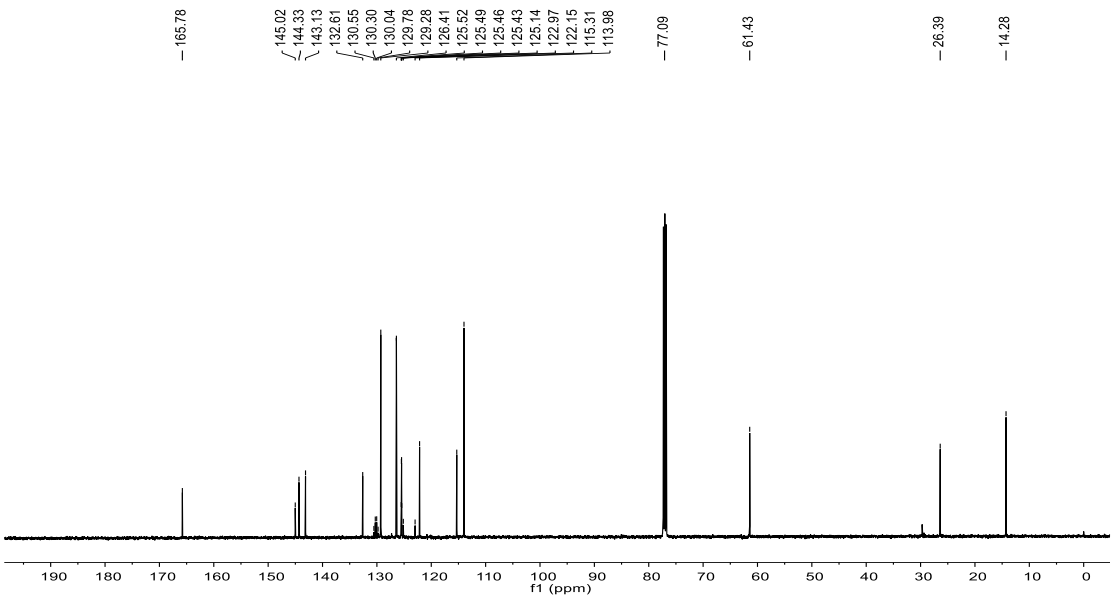
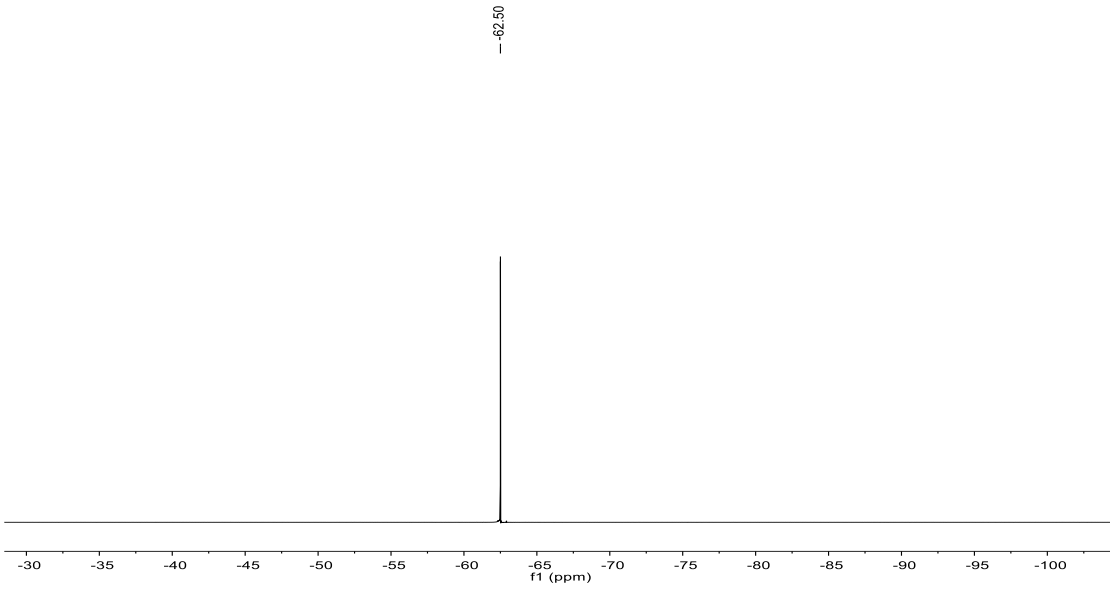
7.57
7.27
7.26
7.13
7.12
7.11
6.96
6.94
6.93
5.42
5.41
5.12
5.05
4.29
4.27
4.26
4.24
3.70
3.69
3.69
3.69
3.25
1.35
1.34
1.32
OH
NHPh
N
CO2Et
NC
1.00
1.00
2.00
2.03
1.00
2.00
1.00
1.00
1.00
1.00
2.00
1.00
2.00
3.00
f1 (ppm)
192.04
165.81
147.97
144.28
143.19
135.89
132.64
129.95
129.28
126.69
122.12
115.56
114.01
77.28
61.44
26.34
14.32
f1 (ppm)

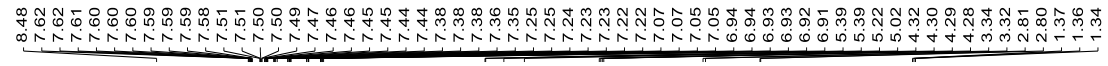
3la



3ma



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7.59
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7.51
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7.45
7.45
7.44
7.44
7.38
7.38
7.38
7.36
7.35
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.07
7.07
7.05
7.05
6.94
6.94
6.93
6.93
6.92
6.91
5.39
5.39
5.22
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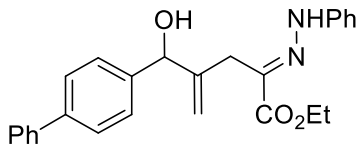
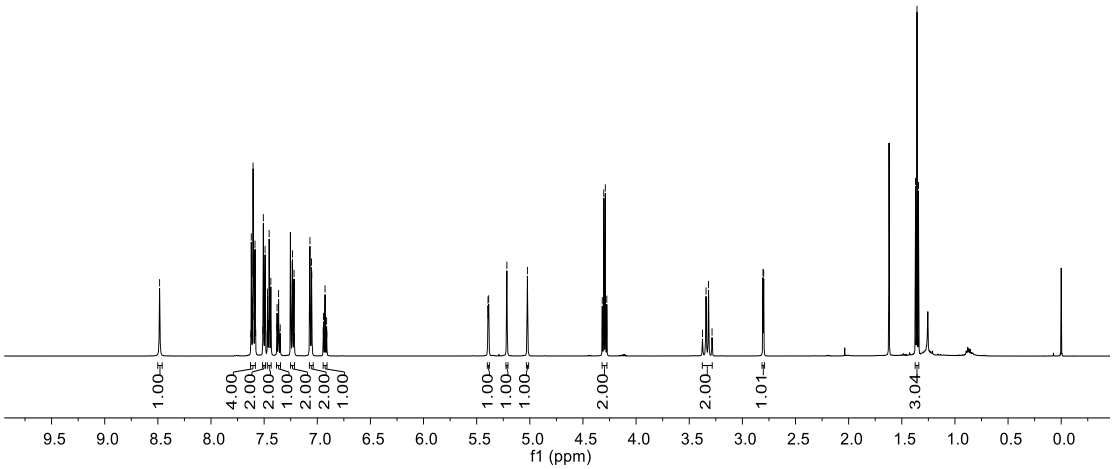
3.32
2.81
2.80
1.37
1.36
1.34


OH
NHPh
N
CO2Et
Ph

3na


1.00
4.00
2.00
2.00
1.00
2.00
1.00
1.00
1.00
1.00
2.00
2.00
1.01
3.04
9.5 9.0 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
f1 (ppm)


165.71
144.61
143.26
141.08
140.54
140.15
133.00
129.22
128.86
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127.41
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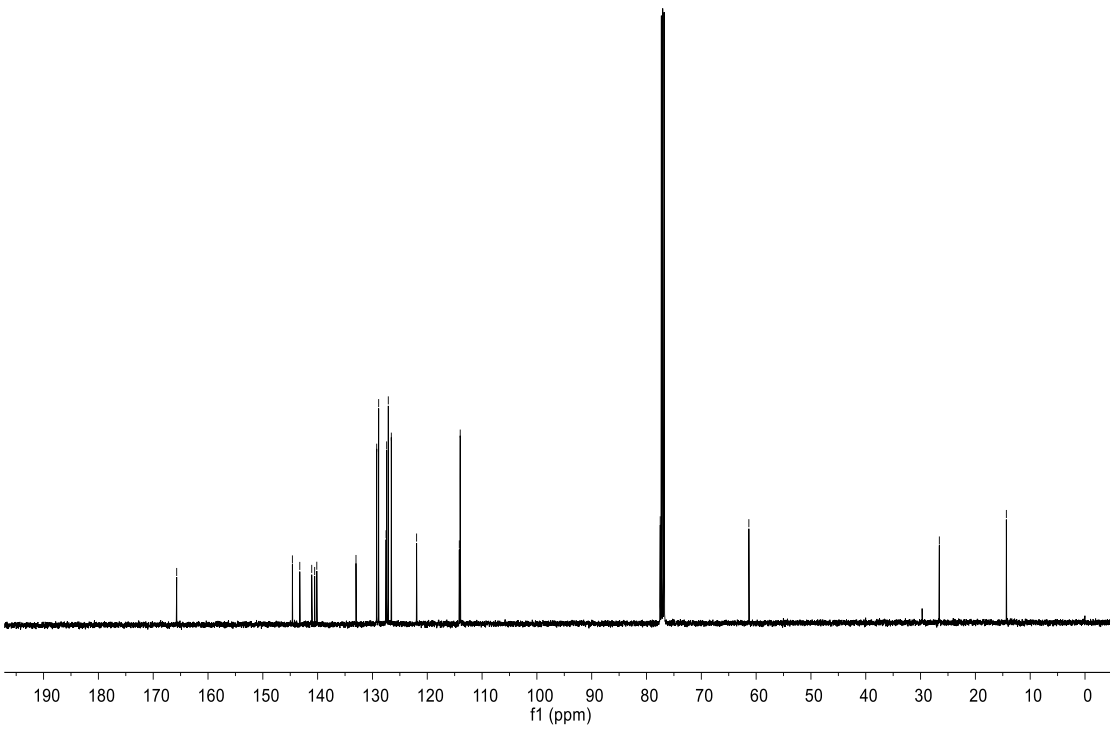
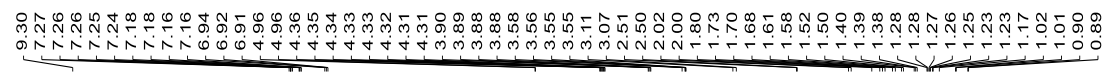
114.16
113.99
77.50
61.33
26.58
14.35


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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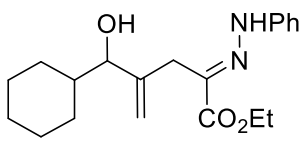
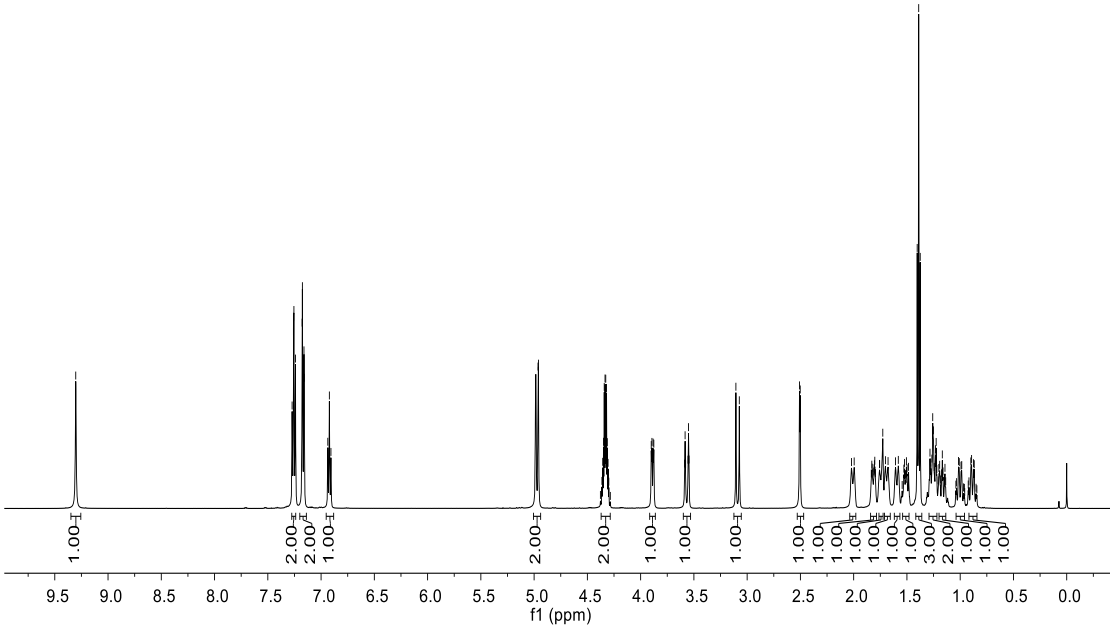
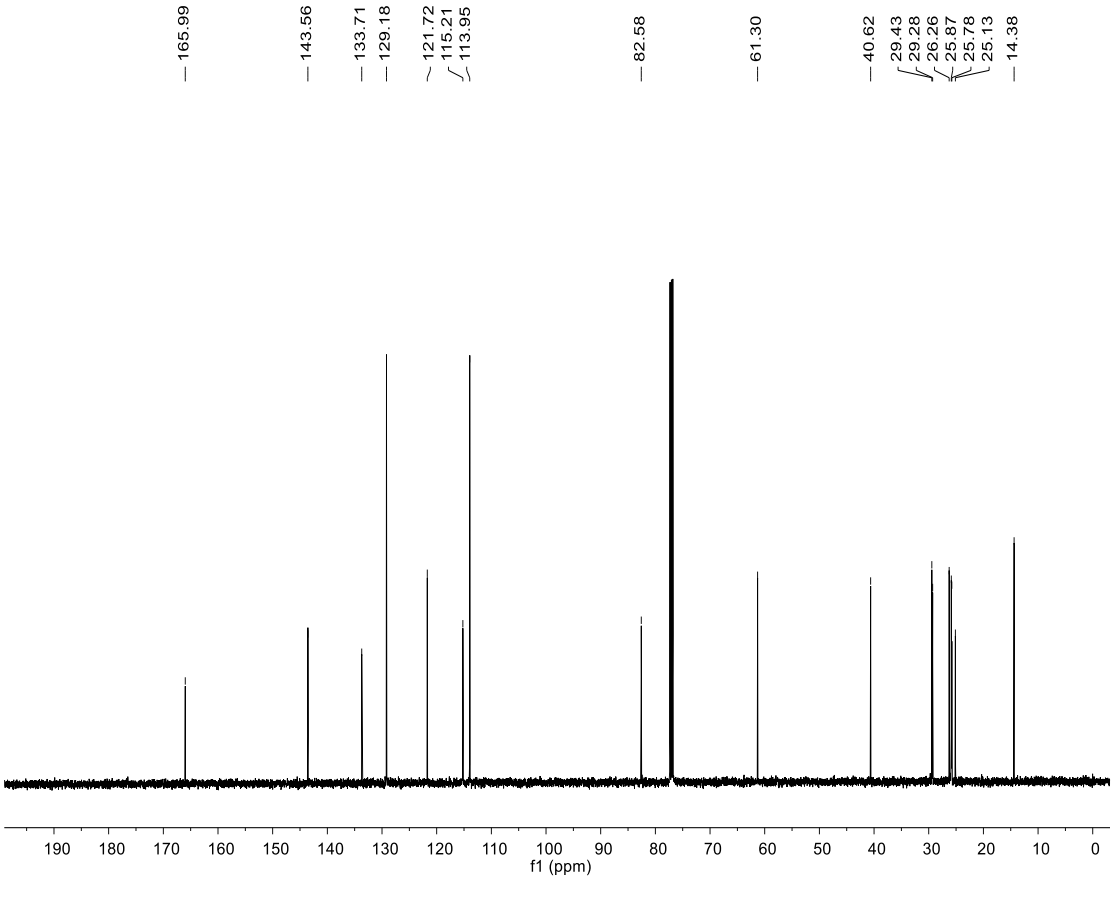
7.24
7.18
7.18
7.16
7.16
6.94
6.92
6.91
4.96
4.96
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.31
3.90
3.89
3.88
3.88
3.58
3.56
3.55
3.55
3.11
3.07
2.51
2.50
2.02
2.00
1.80
1.73
1.70
1.68
1.61
1.58
1.52
1.50
1.40
1.39
1.38
1.28
1.28
1.27
1.26
1.25
1.23
1.23
1.17
1.02
1.01
0.90
0.89


OH
NHPh
N
CO2Et

3oa


1.00
2.00
2.00
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
2.00
1.00
1.00
1.00
9.5 9.0 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
f1 (ppm)


165.99
143.56
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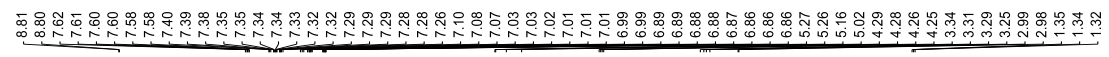
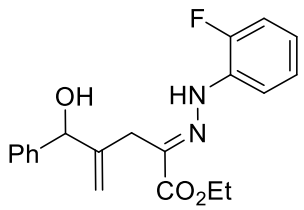
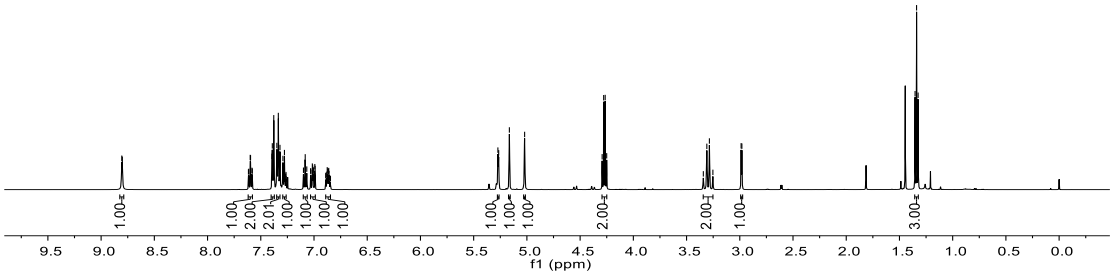
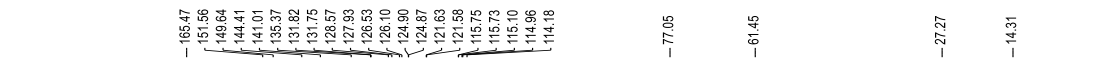
129.18
121.72
115.21
113.95
82.58
61.30
40.62
29.43
29.28
26.26
25.87
25.78
25.13
14.38
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

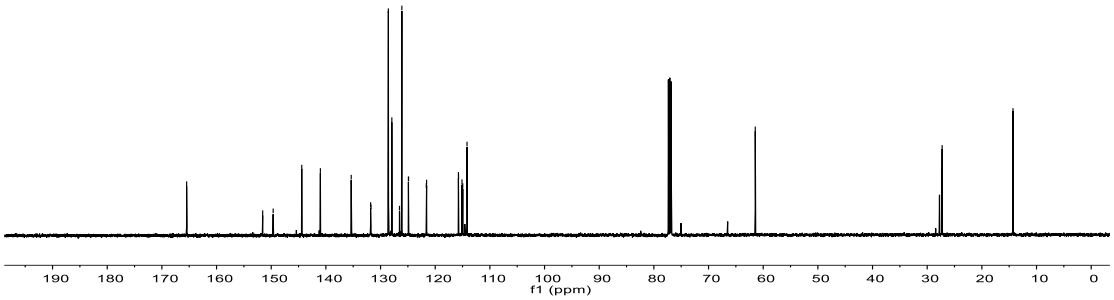


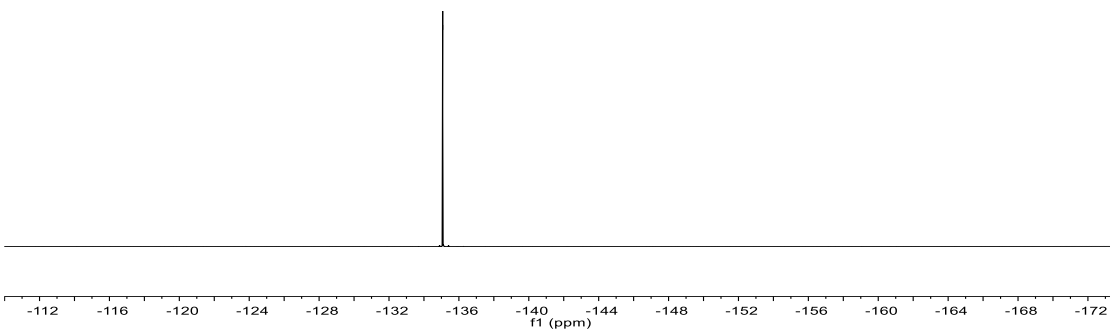


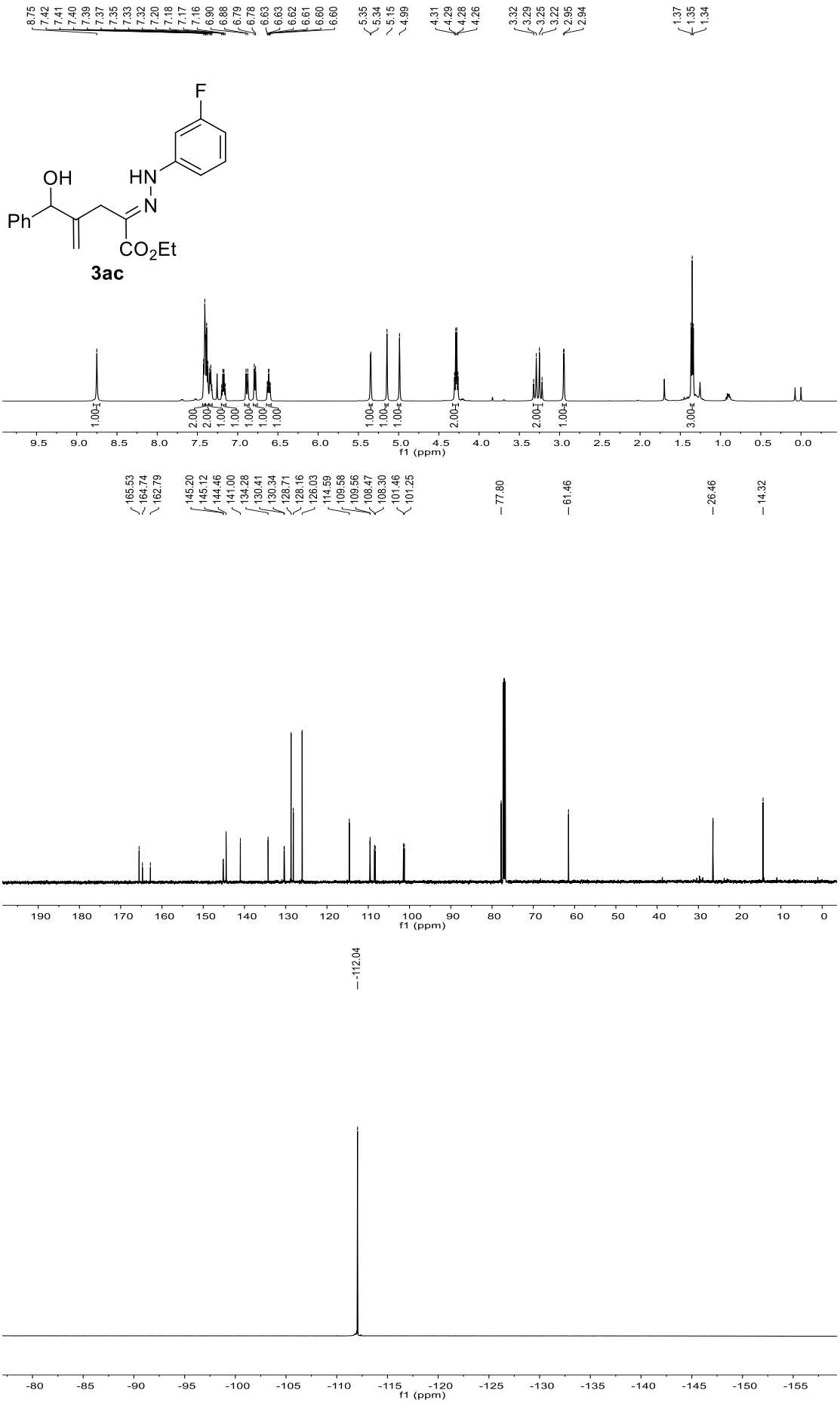
3ab







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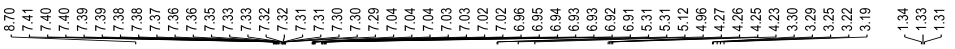
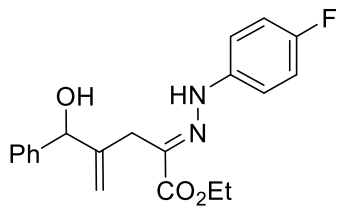
7.16
6.90
6.88
6.79
6.78
6.63
6.63
6.62
6.61
6.60
6.60
5.35
5.34
5.15
4.99
4.31
4.29
4.28
4.26
3.32
3.29
3.25
3.22
2.95
2.94
1.37
1.35
1.34
F
OH
HN
N
Ph
CO2Et
3ac
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.53
164.74
162.79
145.20
145.12
144.46
141.00
134.28
130.41
130.34
128.71
128.16
126.03
114.59
109.58
109.56
108.47
108.30
101.46
101.25
77.80
61.46
26.46
14.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
-112.04
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)





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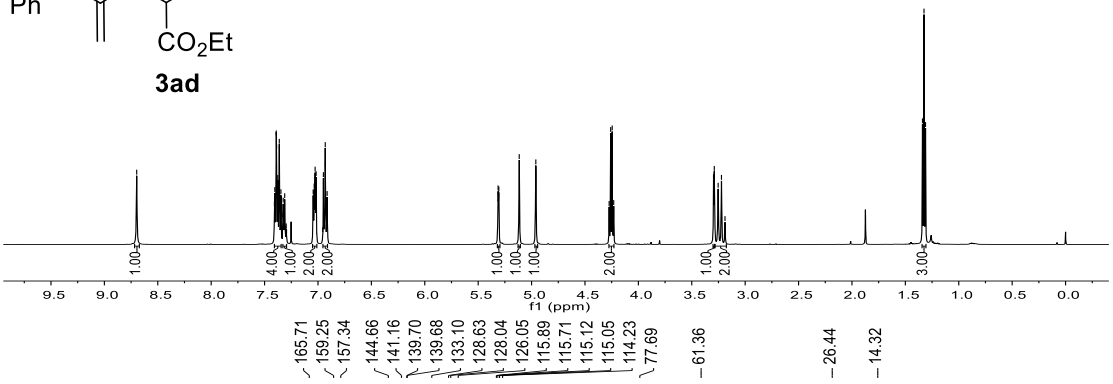

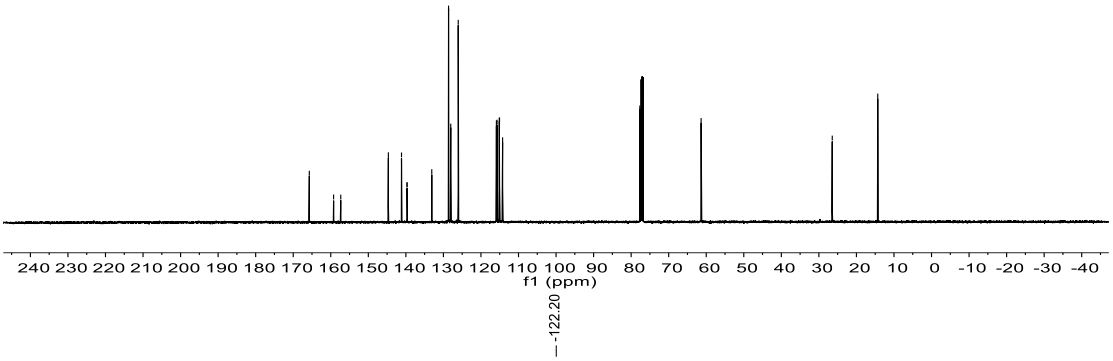

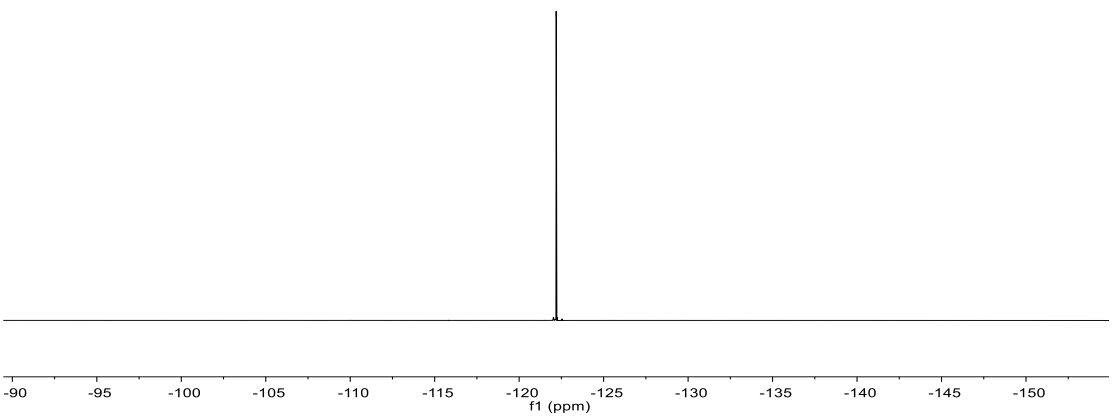

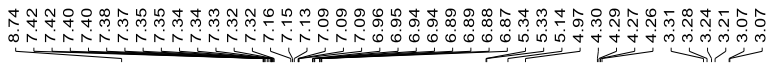
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7.15
7.13
7.09
7.09
7.09
6.96
6.95
6.94
6.94
6.89
6.89
6.88
6.87
5.34
5.33
5.14
4.97
4.30
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3.31
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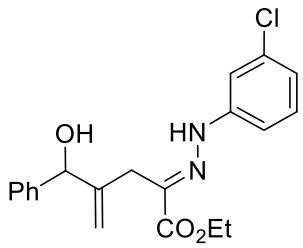
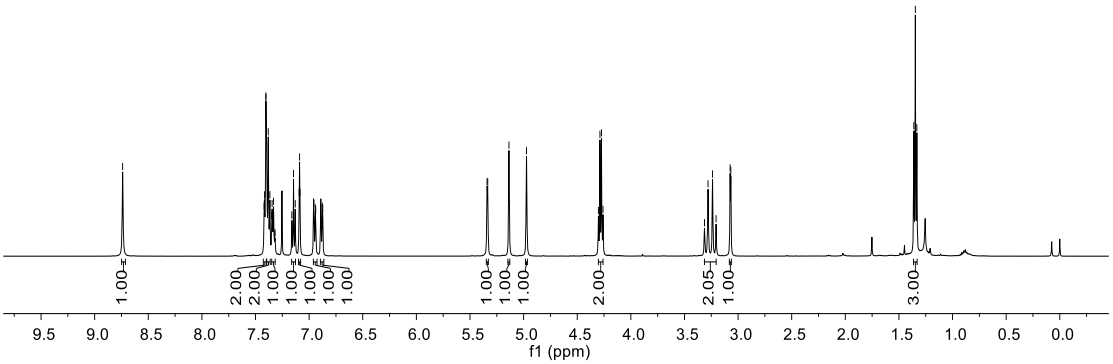
3.24
3.21
3.07
3.07
1.36
1.35
1.33


Cl
OH
HN
N
Ph
CO2Et

3ae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1.00
1.00
1.00
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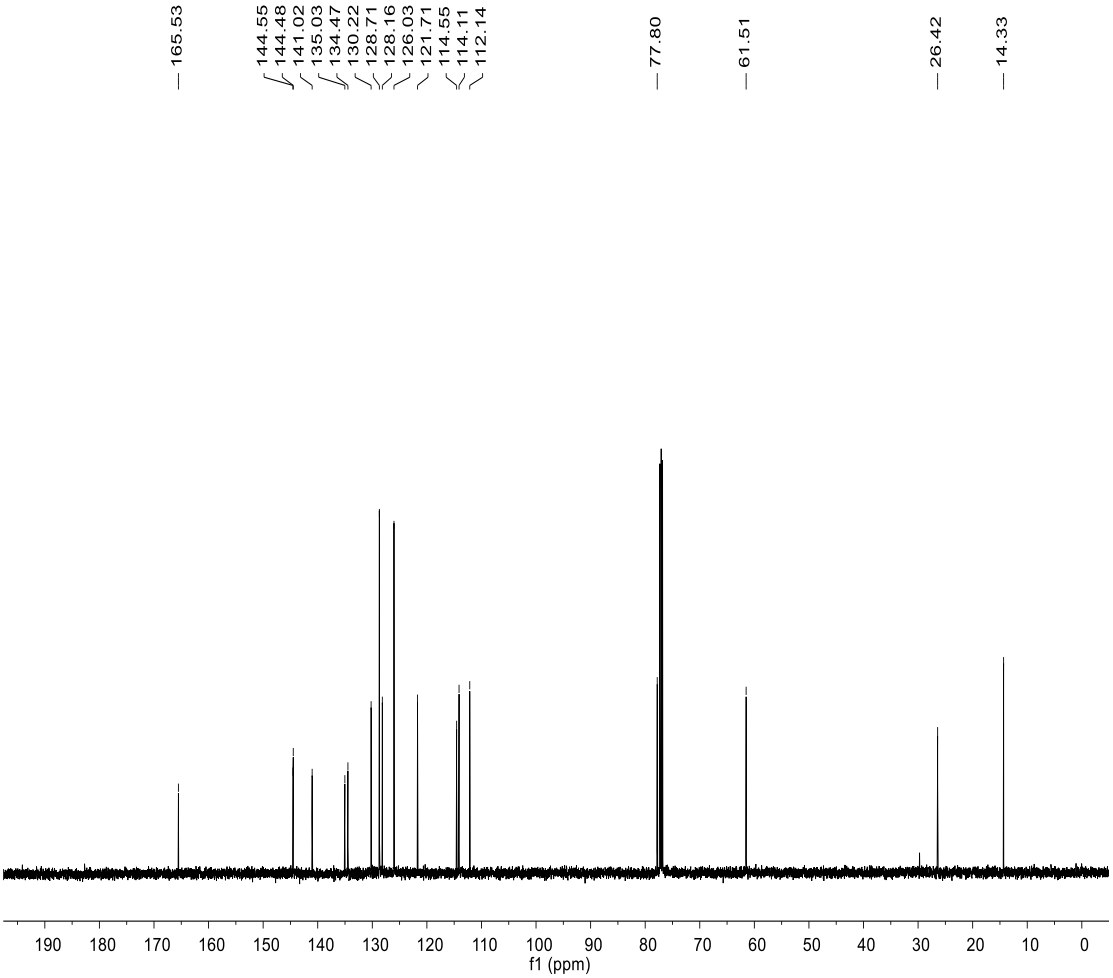
1.00
2.00
2.05
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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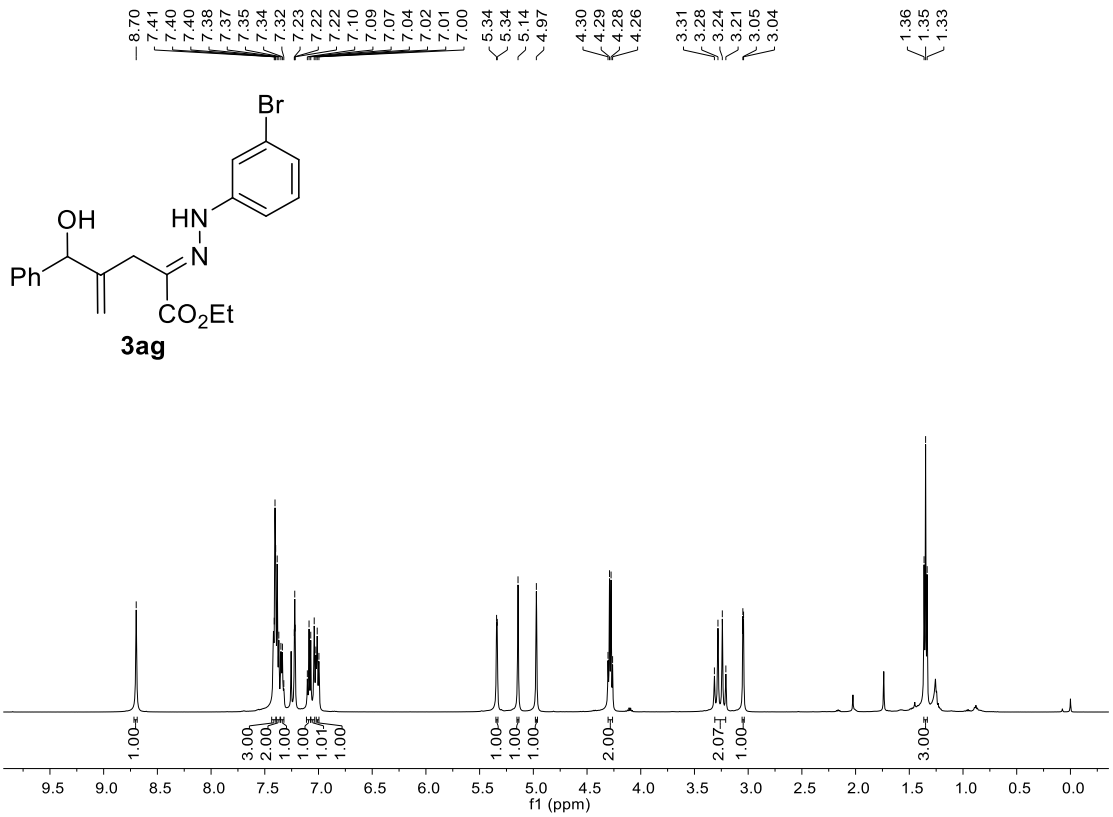
144.48
141.02
135.03
134.47
130.22
128.71
128.16
126.03
121.71
114.55
114.11
112.14
77.80
61.51
26.42
14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.32
7.23
7.22
7.22
7.10
7.09
7.07
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7.02
7.01
7.00
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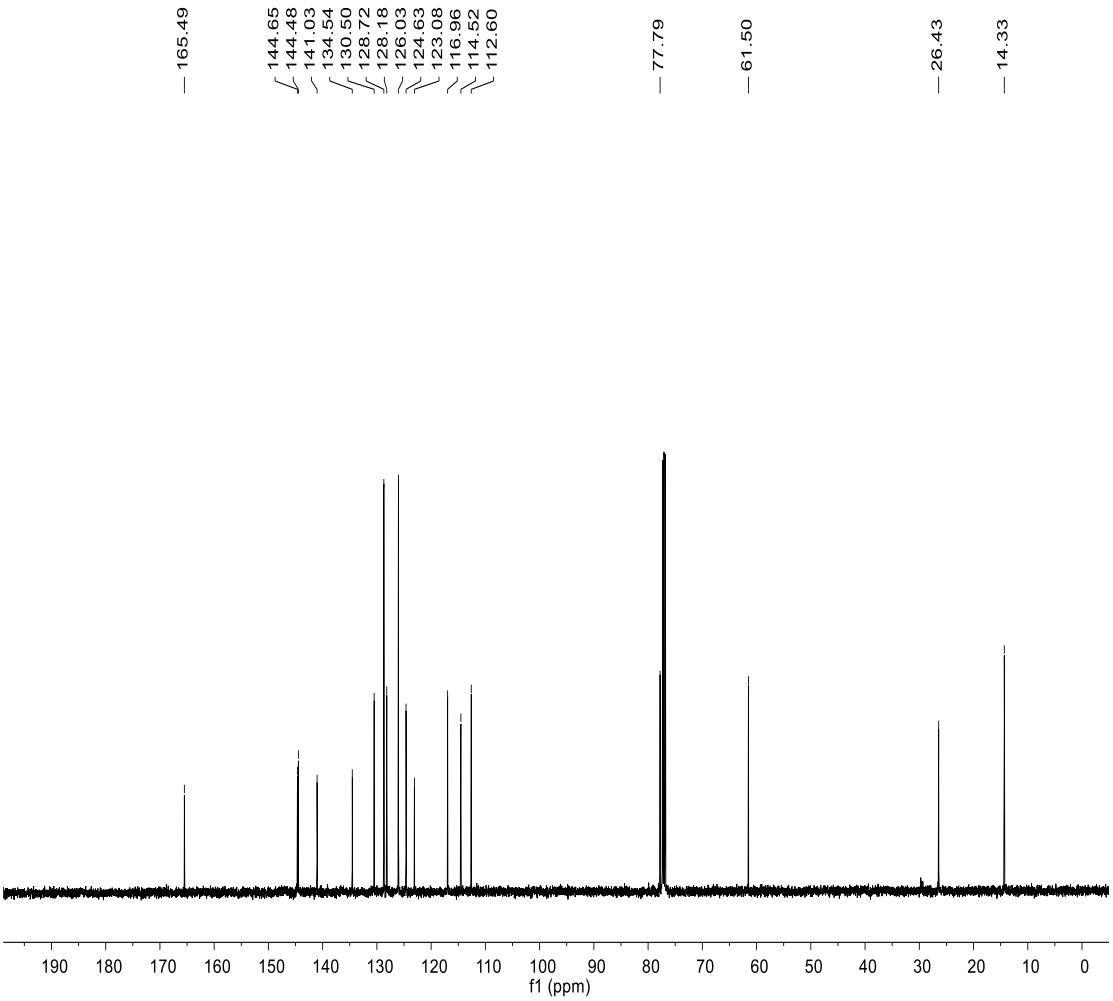
4.30
4.29
4.28
4.26
3.31
3.28
3.24
3.21
3.05
3.04
1.36
1.35
1.33
Br
OH
HN
N
Ph
CO2Et
3ag
1.00
3.00
2.00
1.00
1.01
1.00
1.00
1.00
1.00
2.00
2.07
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.50
128.72
128.18
126.03
124.63
123.08
116.96
114.52
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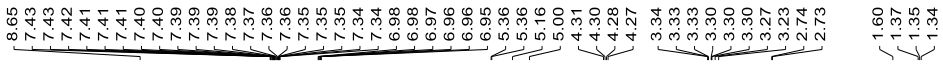
77.79
61.50
26.43
14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.36
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6.96
6.95
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2.73
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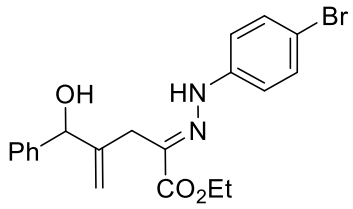
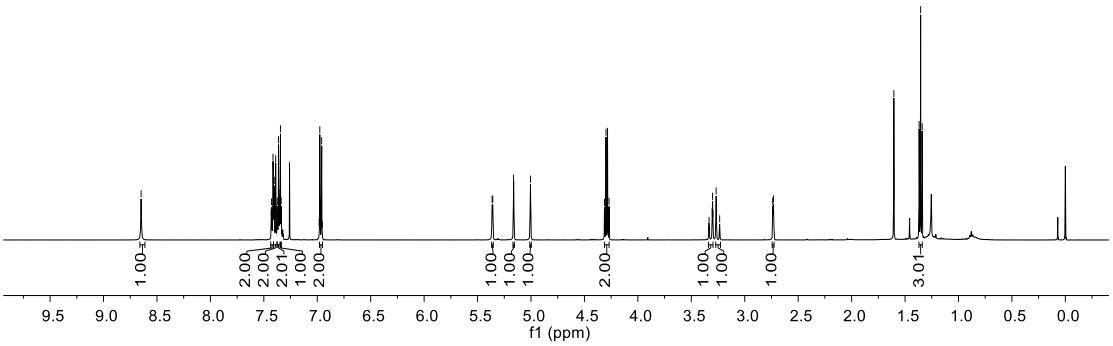
1.37
1.35
1.34


Br
OH
HN
N
Ph
CO2Et

3ah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2.00
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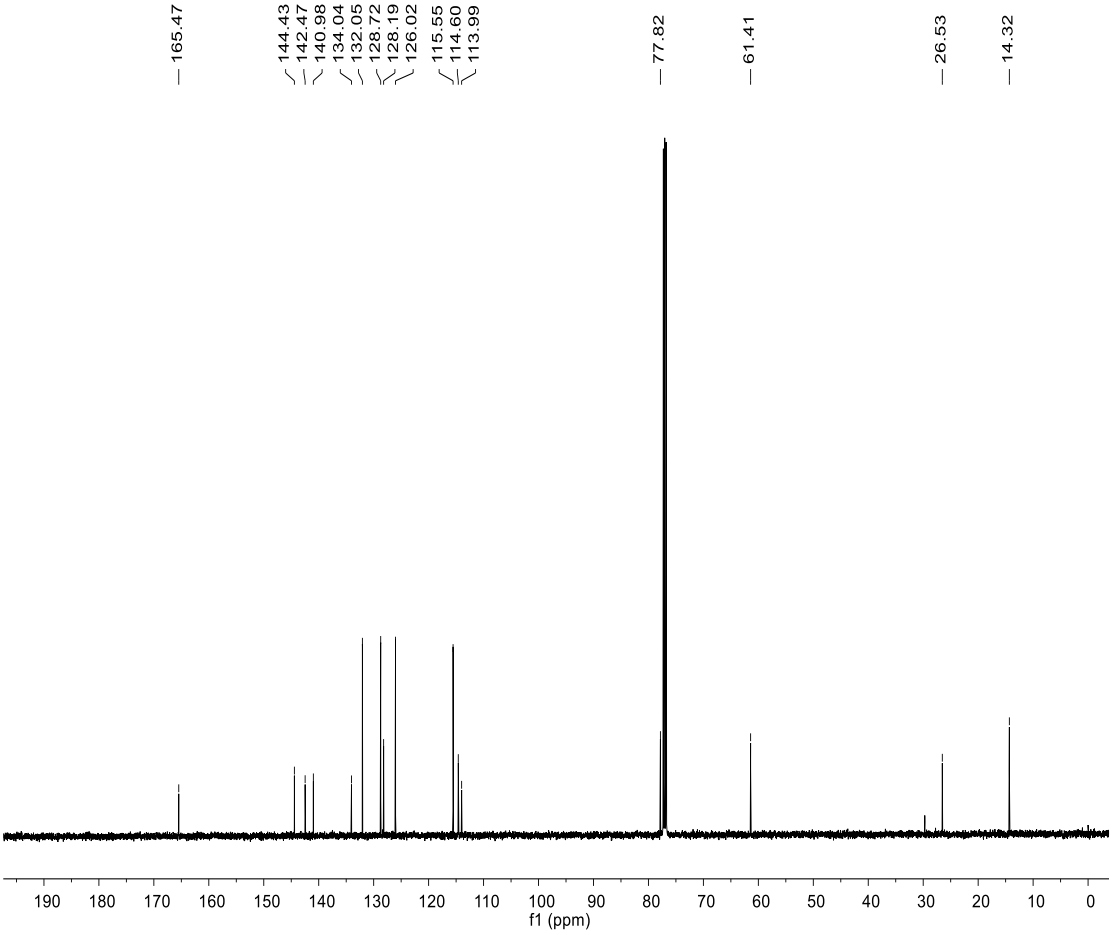
1.00
1.00
2.00
1.00
1.00
1.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.05
128.72
128.19
126.02
115.55
114.60
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77.82
61.41
26.53
14.32
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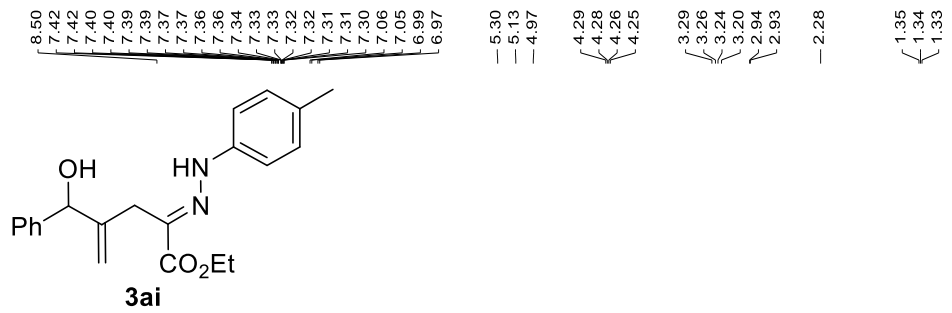
f1 (ppm)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7.33
7.32
7.32
7.31
7.31
7.30
7.06
7.05
6.99
6.97
5.30
5.13
4.97
4.29
4.28
4.26
4.25
3.29
3.26
3.24
3.20
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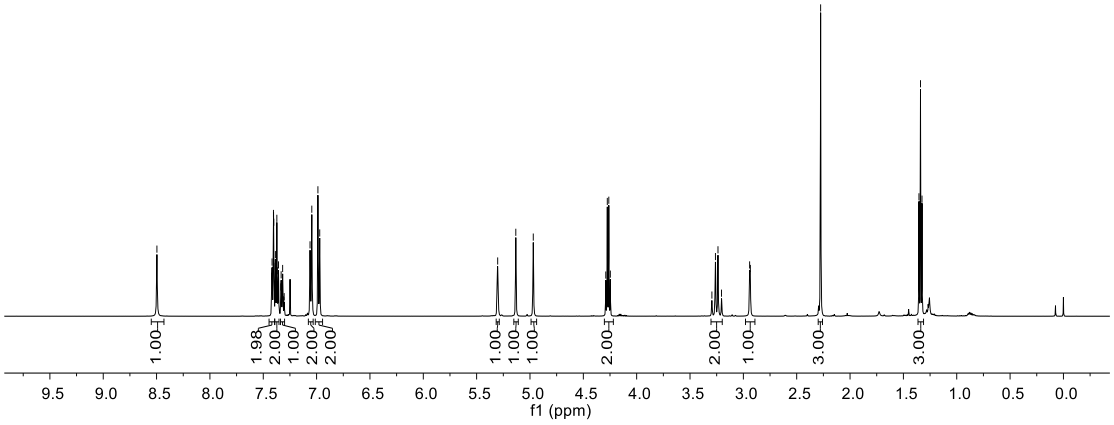
2.93
2.28
1.35
1.34
1.33
OH
HN
N
Ph
CO2Et

3ai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1.00
1.00
2.00
2.00
1.00
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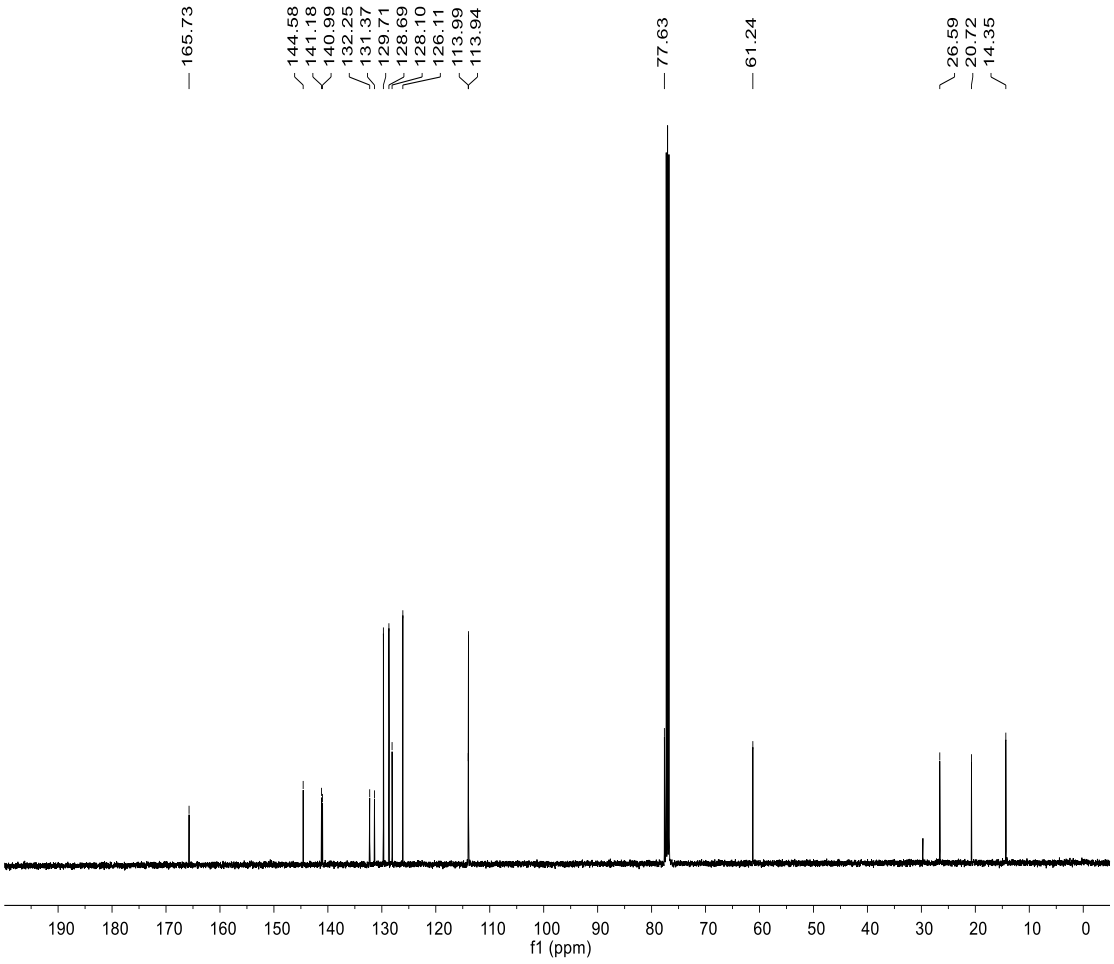
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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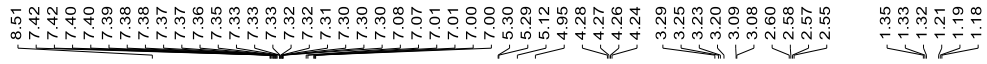
131.37
129.71
128.69
128.10
126.11
113.99
113.94
77.63
61.24
26.59
20.72
14.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.01
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7.00
5.30
5.29
5.12
4.95
4.28
4.27
4.26
4.24
3.29
3.25
3.23
3.20
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3.08
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2.55
1.35
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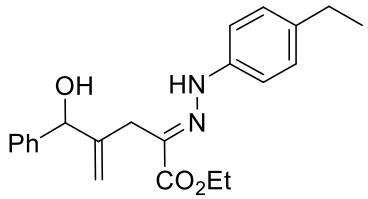
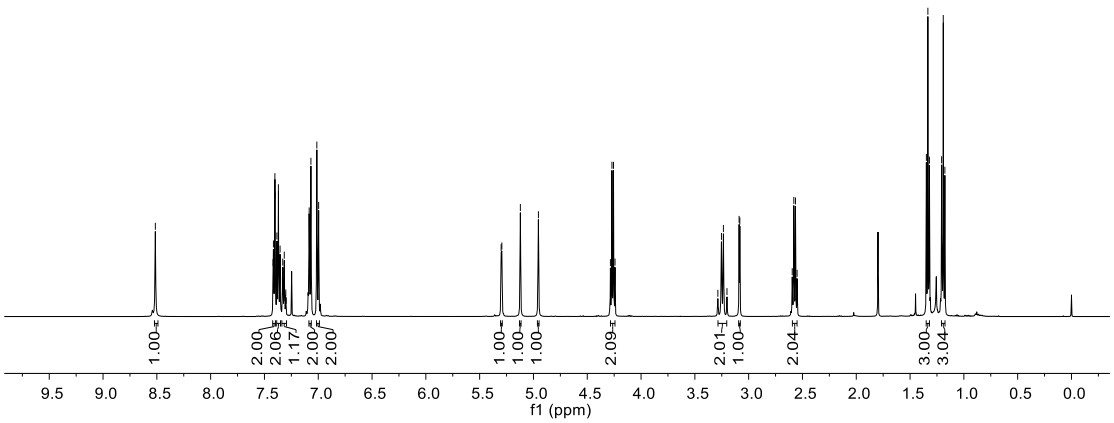
1.19
1.18


OH
HN
N
Ph
CO2Et

3aj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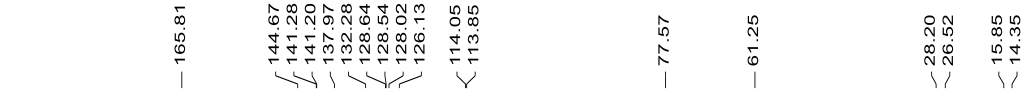
1.00
1.00
1.00
2.09
2.01
1.00
2.04
3.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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113.85
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61.25
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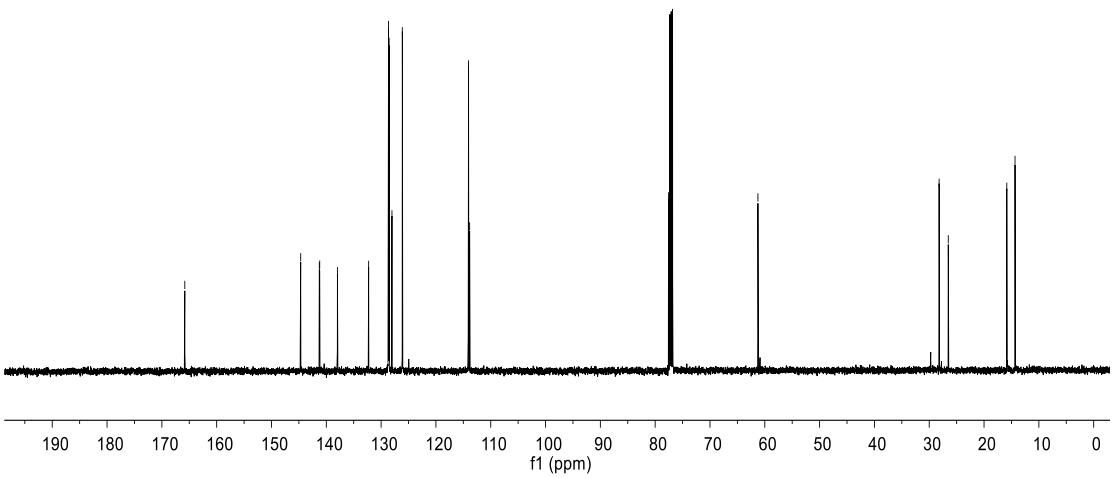
26.52
15.85
14.35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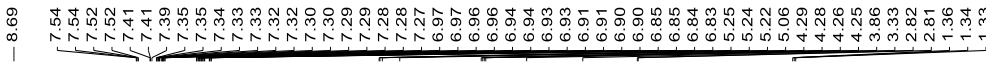
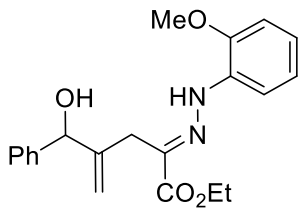
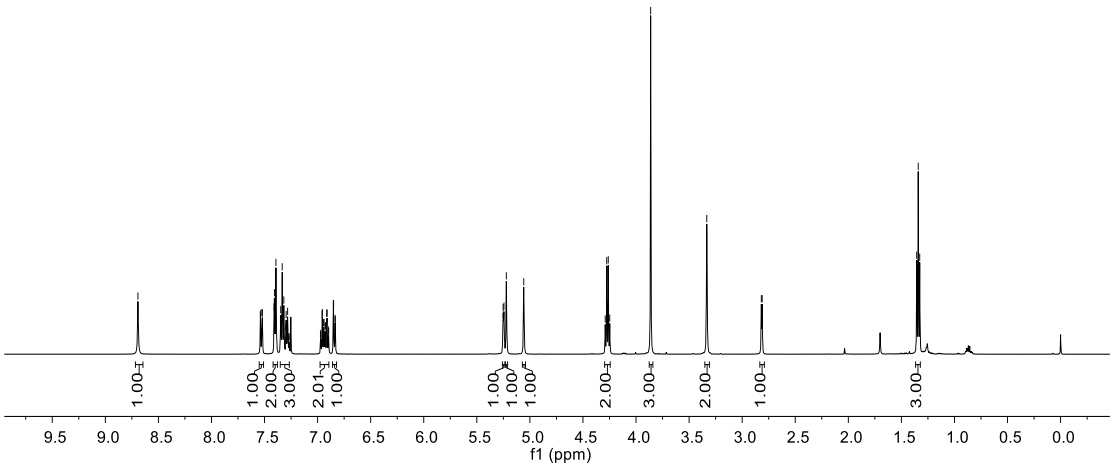
f1 (ppm)




MeO
HN
OH
N
Ph
CO2Et

3ak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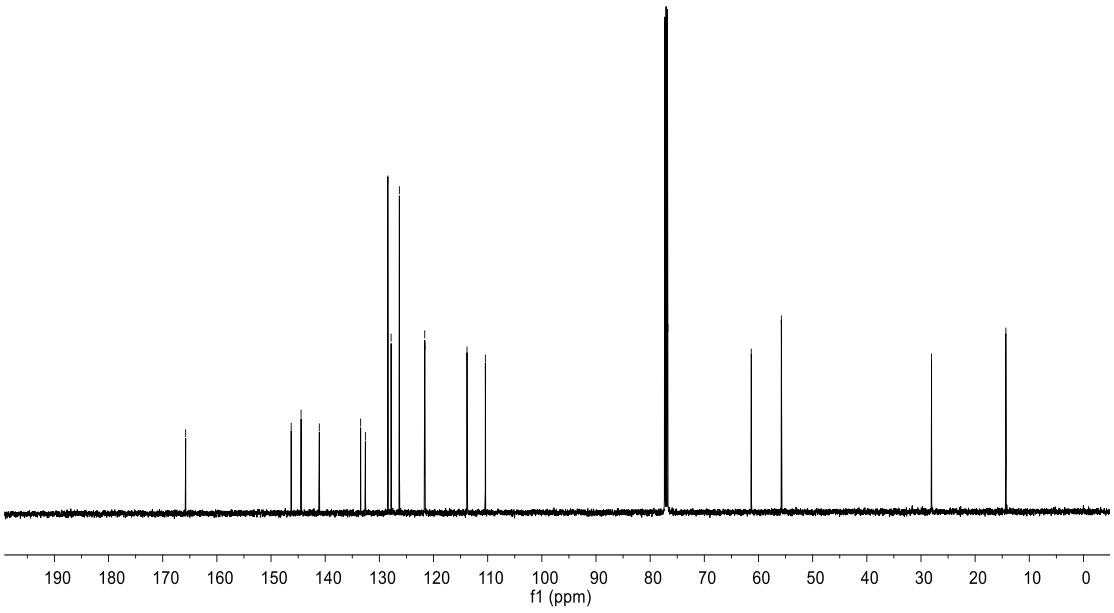
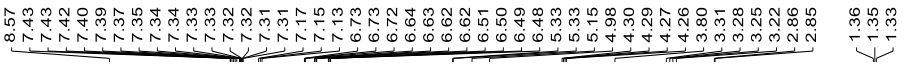
1.00
2.00
3.00
2.00
1.00
3.00
f1 (ppm)


f1 (ppm)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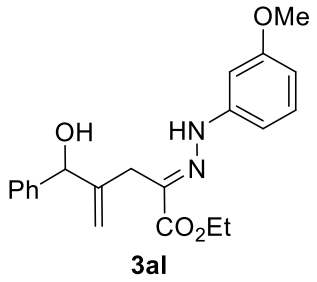
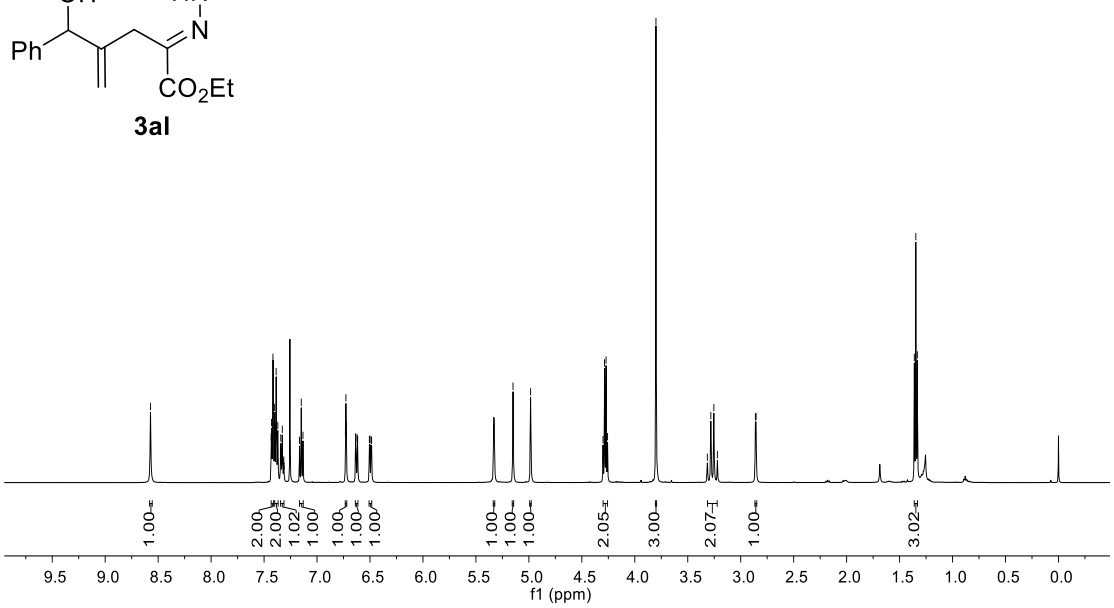
1.33


OMe
HN
N
OH
Ph
CO2Et

3al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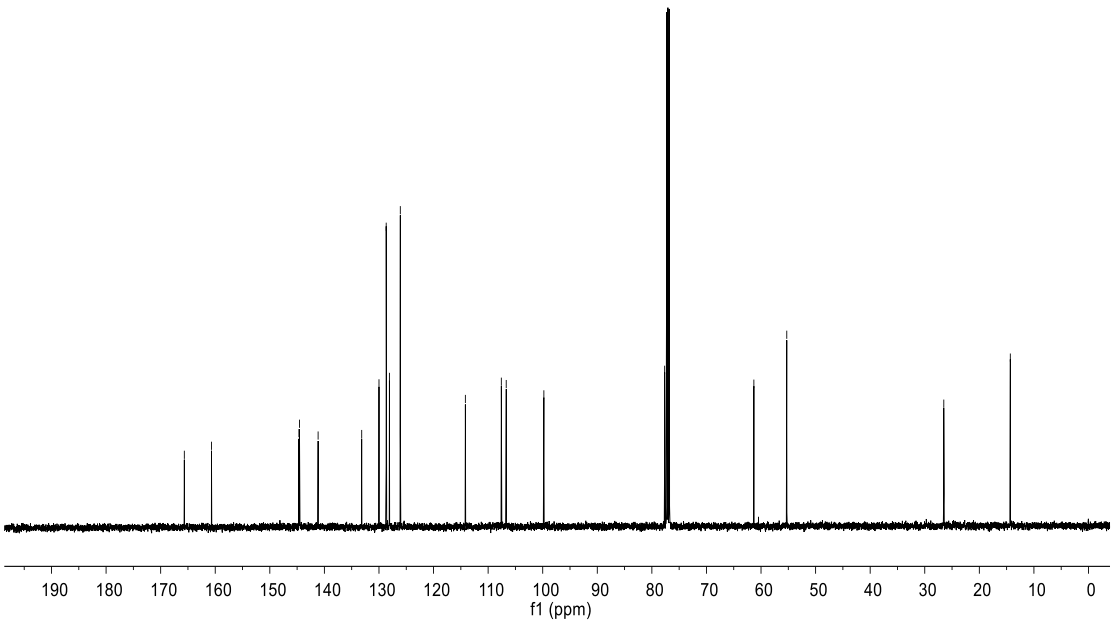
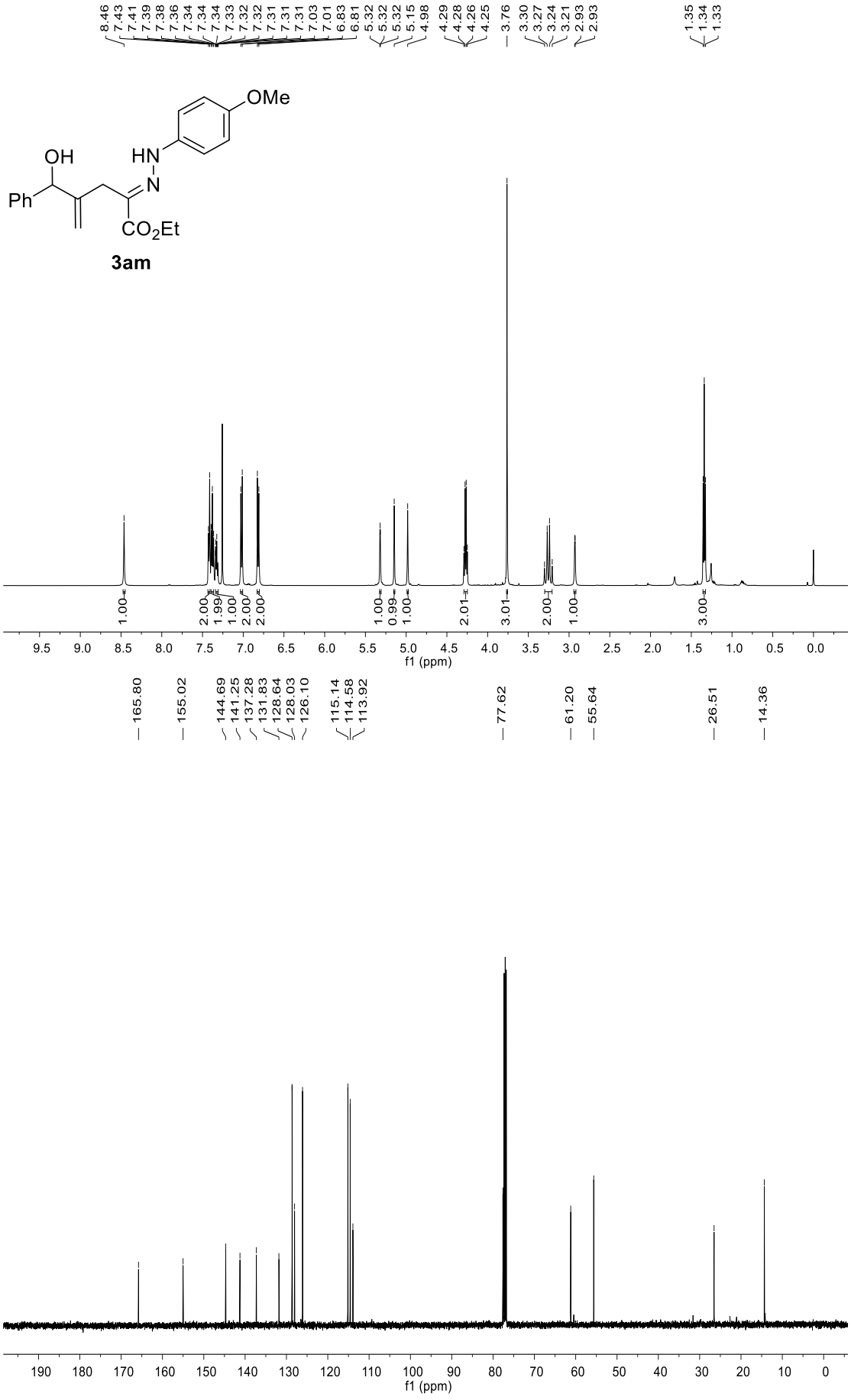
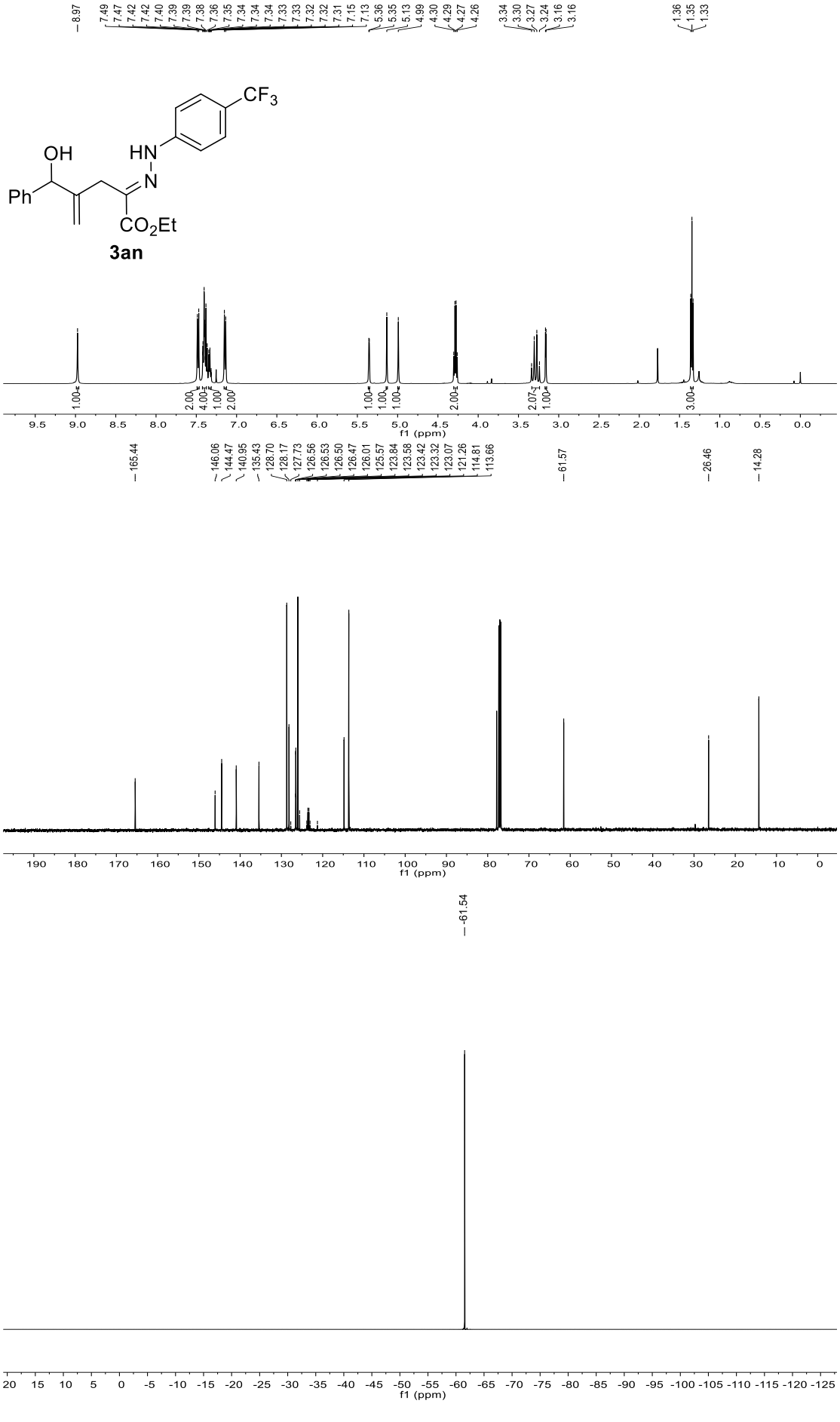
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.05
3.00
2.07
1.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

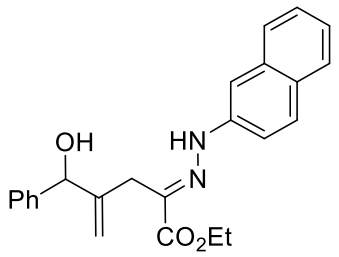

165.66
160.69
144.67
144.56
141.15
133.16
130.00
128.68
128.09
126.09
114.17
107.58
106.68
99.79
77.66
61.31
55.28
26.51
14.32


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

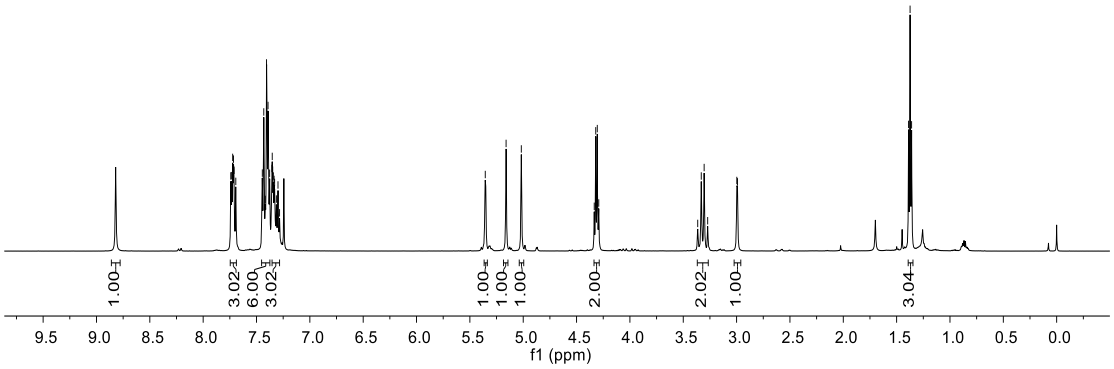

8.46
7.43
7.41
7.39
7.38
7.36
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.03
7.01
6.83
6.81
5.32
5.32
5.32
5.15
4.98
4.29
4.28
4.26
4.25
3.76
3.30
3.27
3.24
3.21
2.93
2.93
1.35
1.34
1.33
OMe
HN
N
OH
Ph
CO2Et
3am
1.00
2.00
1.99
1.00
2.00
2.00
1.00
0.99
1.00
2.01
3.01
2.00
1.00
3.00
9.5 9.0 8.5 8.0 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
f1 (ppm)
165.80
155.02
144.69
141.25
137.28
131.83
128.64
128.03
126.10
115.14
114.58
113.92
77.62
61.20
55.64
26.51
14.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.97
7.49
7.47
7.42
7.42
7.42
7.40
7.39
7.39
7.38
7.36
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.15
7.13
5.36
5.35
5.13
4.99
4.30
4.29
4.27
4.26
3.34
3.30
3.27
3.24
3.16
3.16
1.36
1.35
1.33
CF3
OH
HN
N
Ph
CO2Et
3an
1.00
2.00
4.00
1.00
2.00
1.00
1.00
1.00
2.00
2.07
1.00
3.00
f1 (ppm)
165.44
146.06
144.47
140.95
135.43
128.70
128.17
127.73
126.56
126.53
126.50
126.47
126.01
125.57
123.84
123.58
123.42
123.32
123.07
121.26
114.81
113.66
61.57
26.46
14.28
f1 (ppm)
-61.54
f1 (ppm)


7.74
7.73
7.72
7.72
7.71
7.69
7.45
7.43
7.42
7.41
7.39
7.39
7.38
7.36
7.35
7.35
7.34
7.34
7.33
7.31
7.30
7.28
5.36
5.16
5.02
4.33
4.32
4.31
4.29
3.36
3.33
3.30
3.27
3.00
2.99
1.39
1.37
1.36


OH
HN
N
Ph
CO2Et

3ao


1.00
3.02
6.00
3.02
1.00
1.00
1.00
2.00
2.02
1.00
3.04
9.5 9.0 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
f1 (ppm)


165.68
144.63
141.16
140.97
134.29
133.54
129.83
129.25
128.72
128.13
127.82
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126.12
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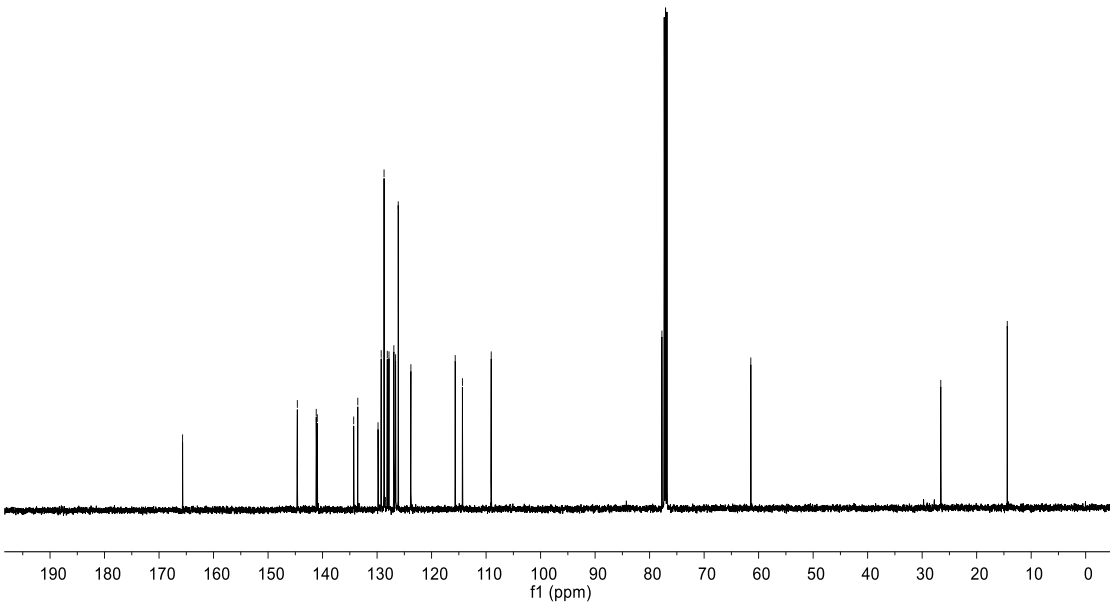
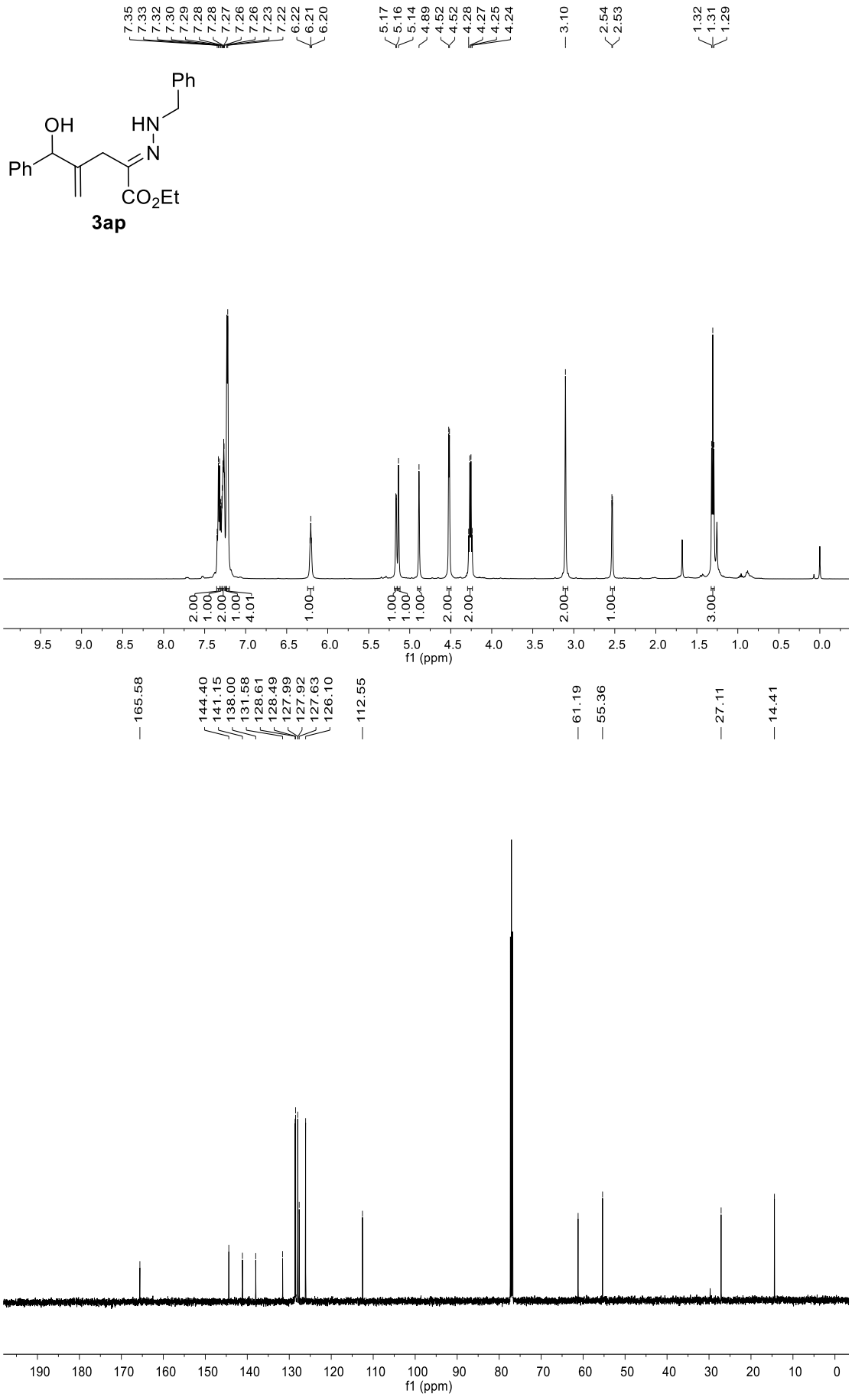
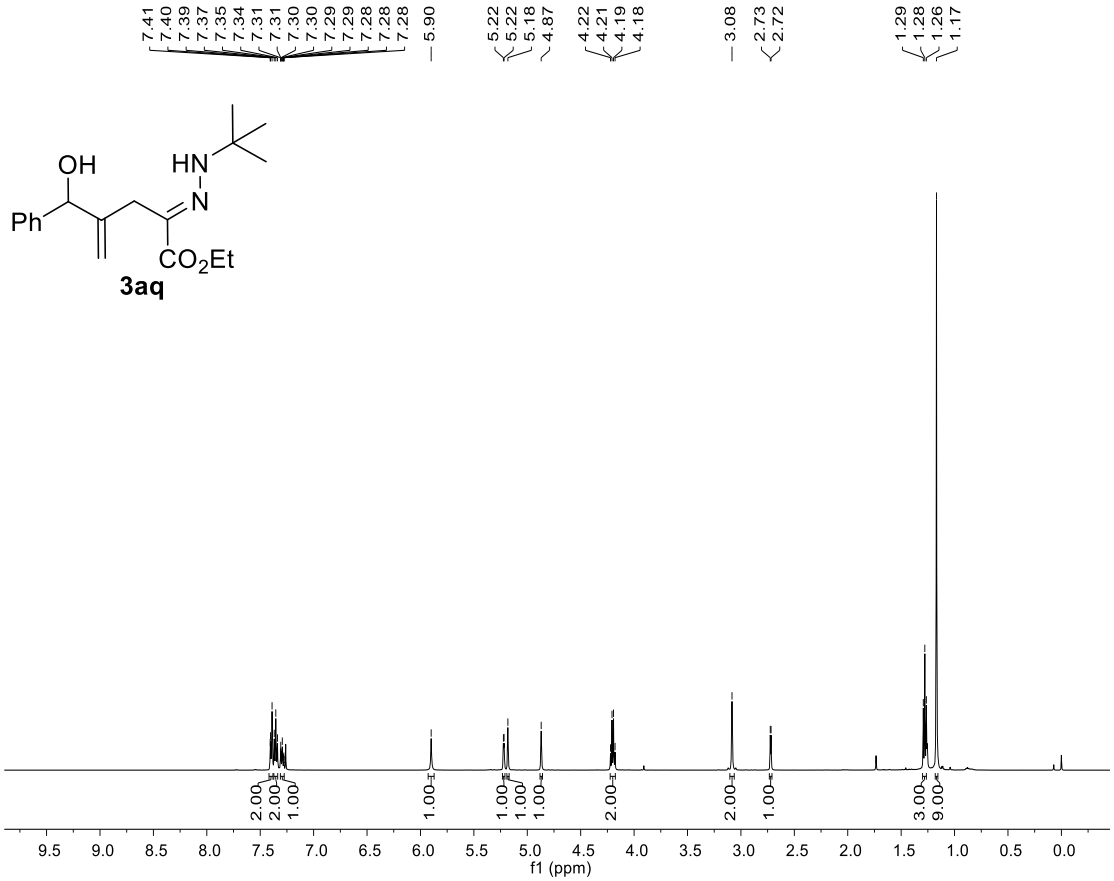
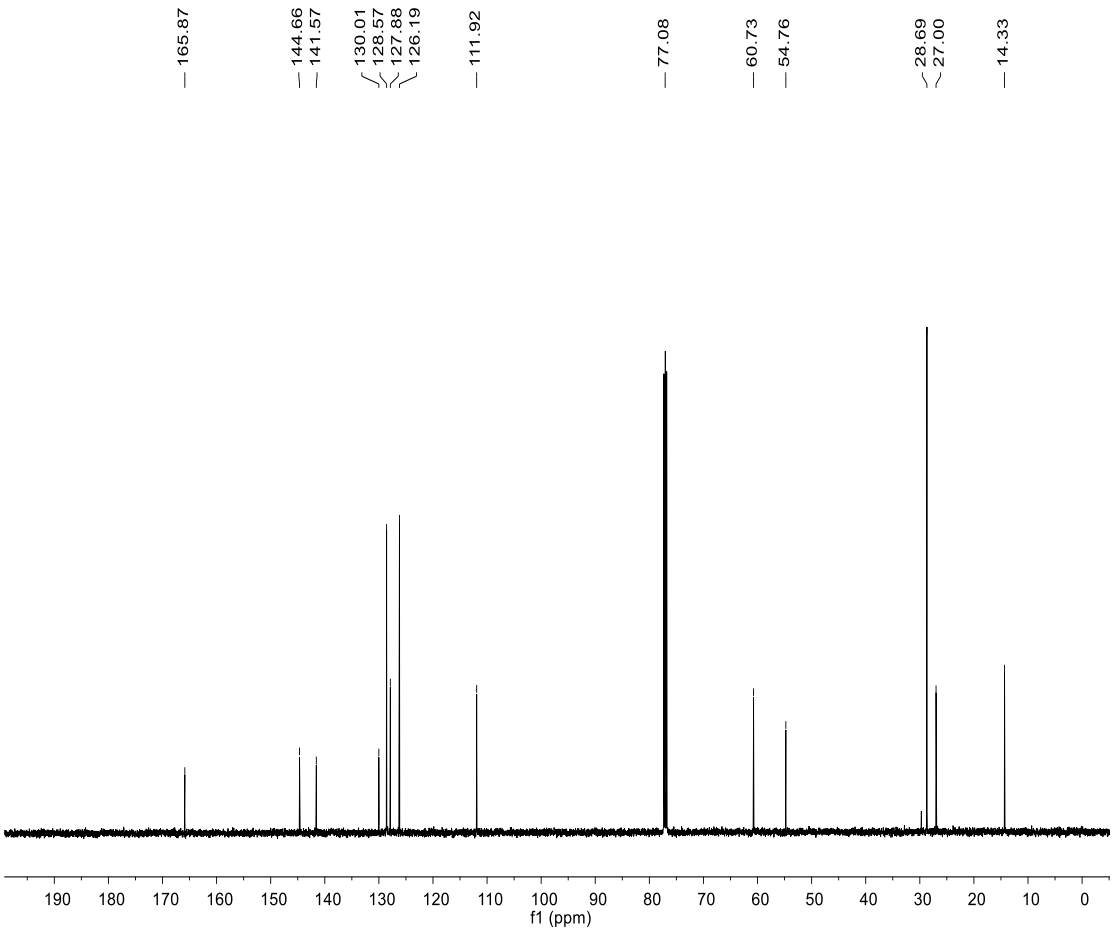
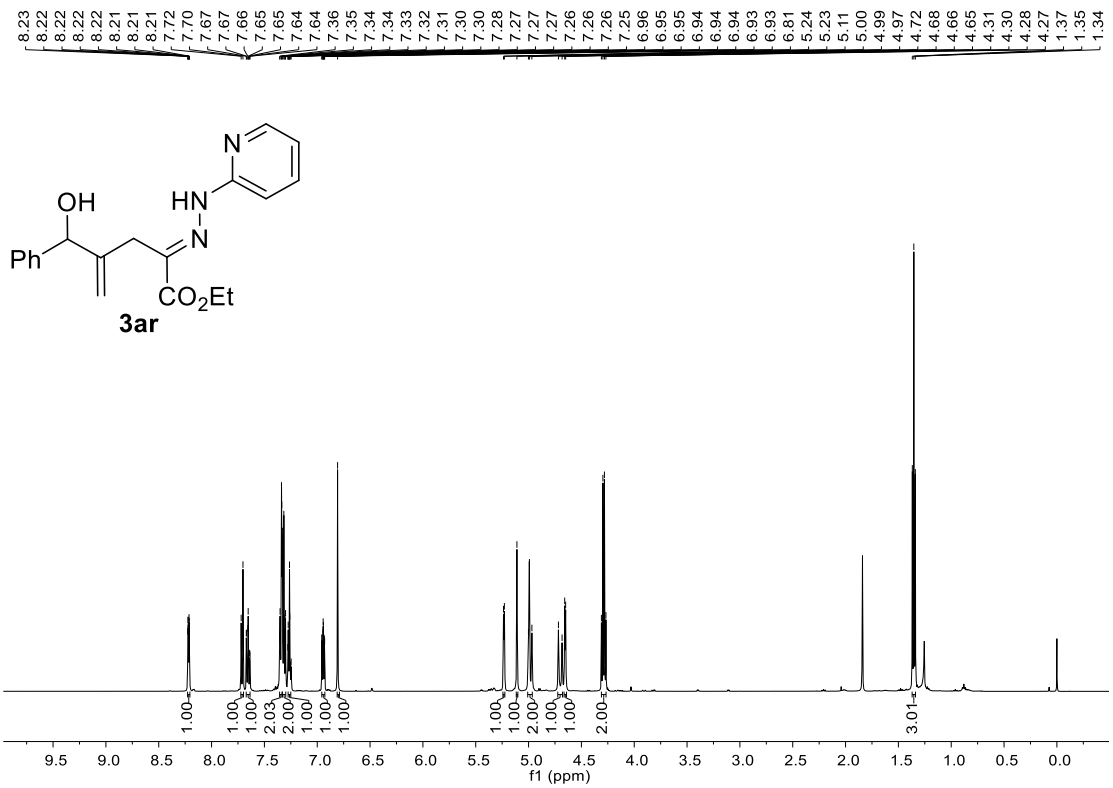
114.34
109.06
77.75
61.43
26.58
14.39

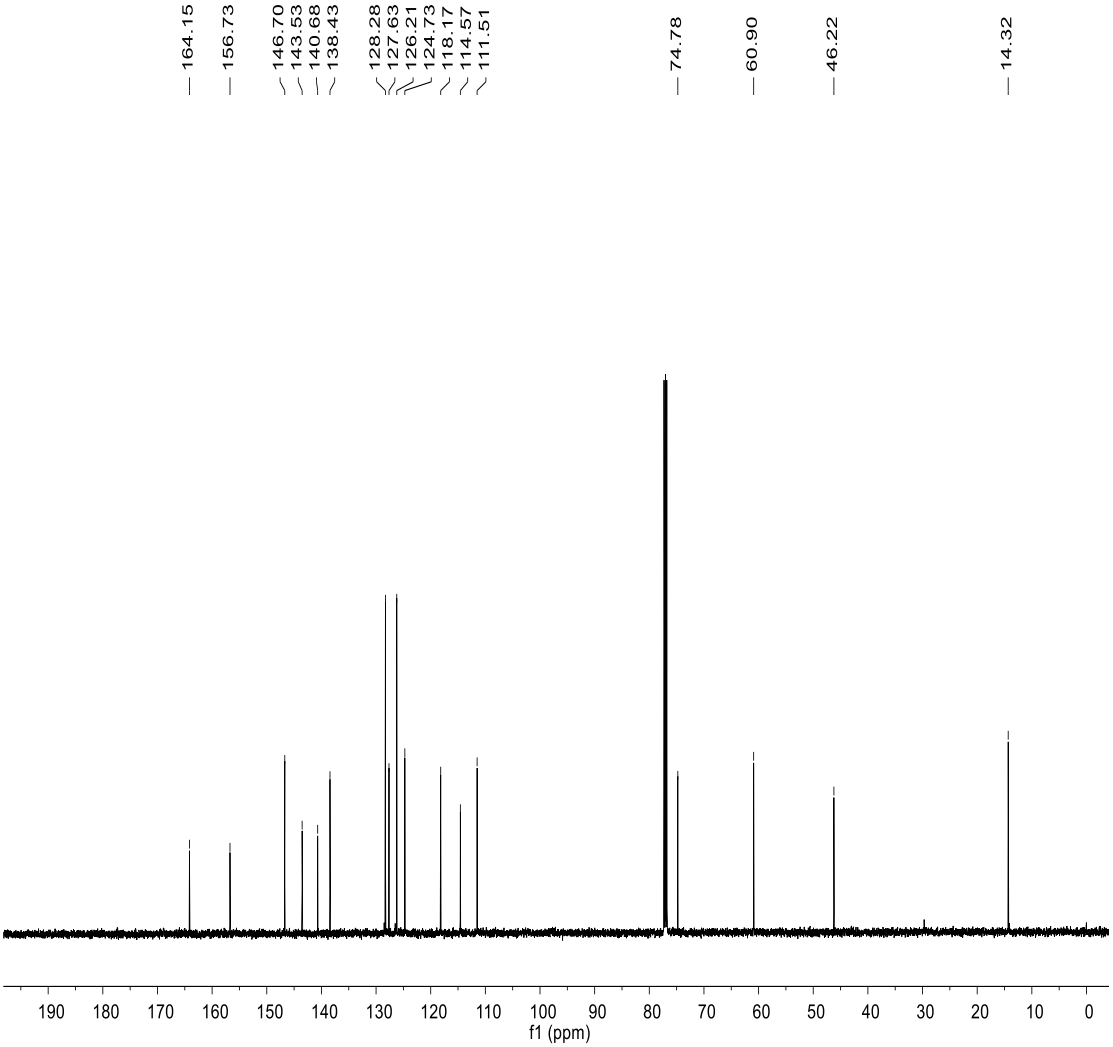

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

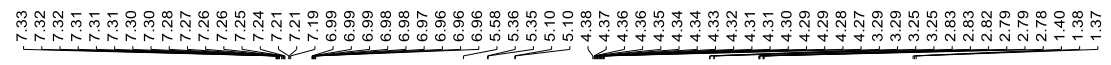

7.35
7.33
7.32
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.23
7.22
6.22
6.21
6.20
5.17
5.16
5.14
4.89
4.52
4.52
4.28
4.27
4.25
4.24
3.10
2.54
2.53
1.32
1.31
1.29
Ph
OH
HN
N
Ph
CO2Et
3ap
2.00
1.00
2.00
1.00
4.01
1.00
1.00
1.00
1.00
2.00
2.00
2.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.58
144.40
141.15
138.00
131.58
128.61
128.49
127.99
127.92
127.63
126.10
112.55
61.19
55.36
27.11
14.41
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.41
7.40
7.39
7.37
7.35
7.34
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
5.90
5.22
5.22
5.18
4.87
4.22
4.21
4.19
4.18
3.08
2.73
2.72
1.29
1.28
1.26
1.17
OH
HN
N
Ph
CO2Et
3aq
2.00
2.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
3.00
9.00
9.5 9.0 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
f1 (ppm)


165.87
144.66
141.57
130.01
128.57
127.88
126.19
111.92
77.08
60.73
54.76
28.69
27.00
14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.23 8.22 8.22 8.22 8.22 8.21 8.21 8.21 7.72 7.70 7.67 7.67 7.66 7.65 7.65 7.64 7.64 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.30 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 6.96 6.95 6.95 6.94 6.94 6.94 6.93 6.93 6.81 5.24 5.23 5.11 5.00 4.99 4.97 4.72 4.68 4.66 4.65 4.31 4.30 4.28 4.27 1.37 1.35 1.34
OH
HN
N
N
Ph
CO2Et
3ar
1.00 1.00 1.00 2.03 2.00 1.00 1.00 1.00 1.00 1.00 2.00 1.00 1.00 2.00 3.01
9.5 9.0 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
f1 (ppm)


164.15 156.73 146.70 143.53 140.68 138.43 128.28 127.63 126.21 124.73 118.17 114.57 111.51 74.78 60.90 46.22 14.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.33
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7.32
7.31
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7.31
7.30
7.30
7.28
7.27
7.26
7.26
7.25
7.24
7.21
7.21
7.19
6.99
6.99
6.99
6.98
6.98
6.97
6.96
6.96
6.96
5.58
5.36
5.35
5.10
5.10
4.38
4.37
4.36
4.36
4.35
4.34
4.34
4.33
4.32
4.31
4.31
4.30
4.29
4.29
4.28
4.27
3.29
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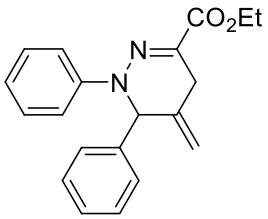
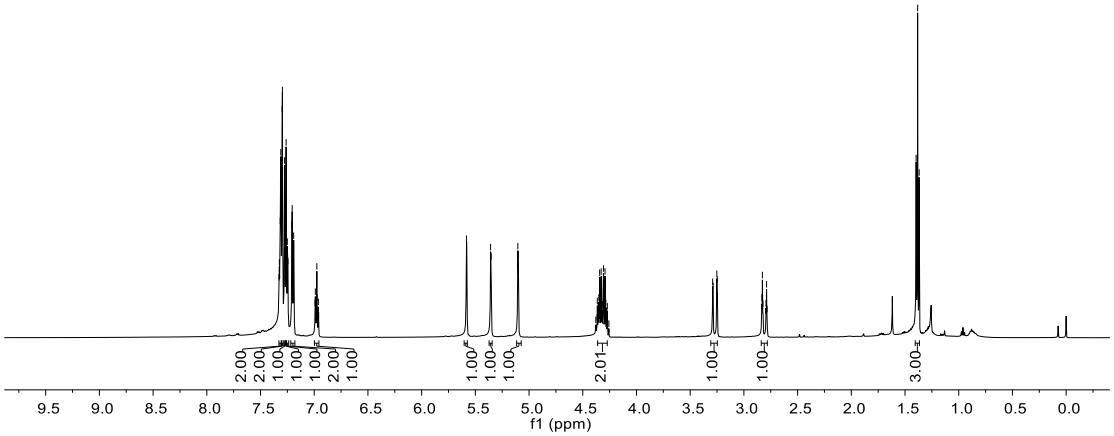
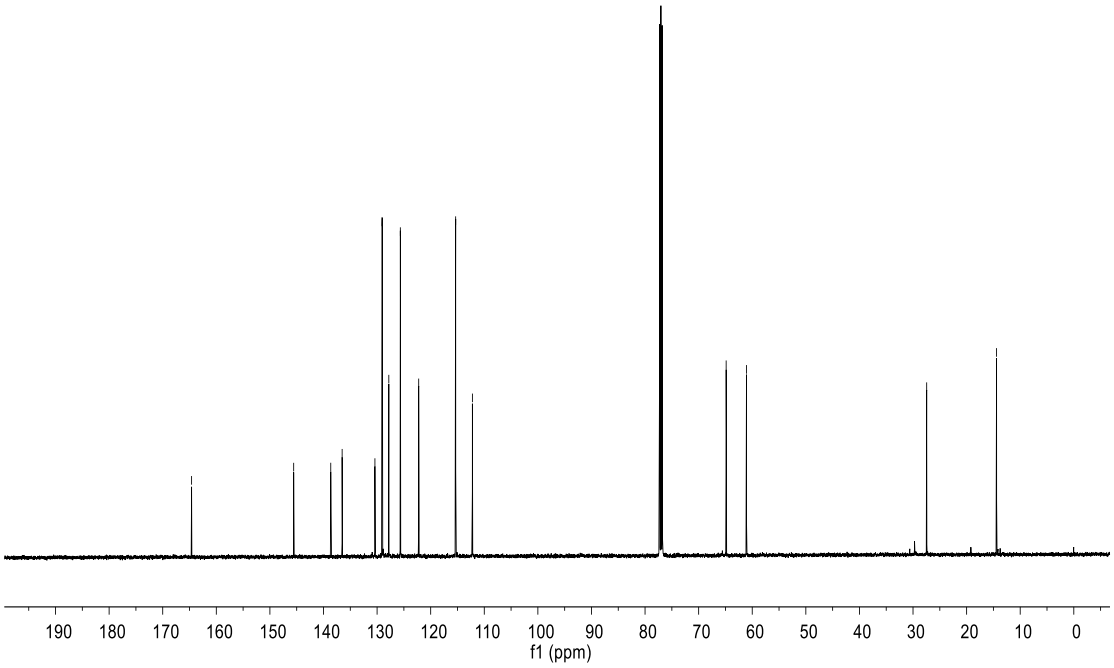
2.79
2.79
2.78
1.40
1.38
1.37

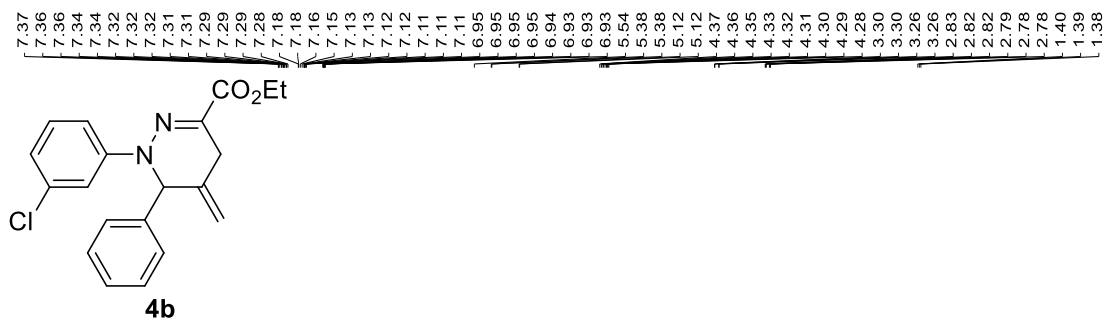

CO2Et
N
N

4a


2.00
2.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
2.01
1.00
1.00
3.00
9.5
9.0
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
f1 (ppm)

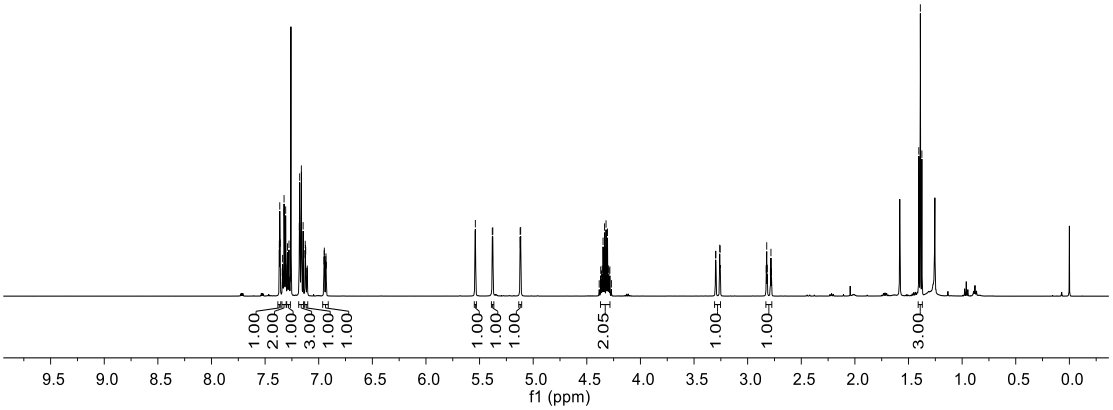

164.61
145.56
138.64
136.52
130.41
129.08
129.02
127.81
125.66
122.24
115.34
112.21
64.87
61.07
27.45
14.41

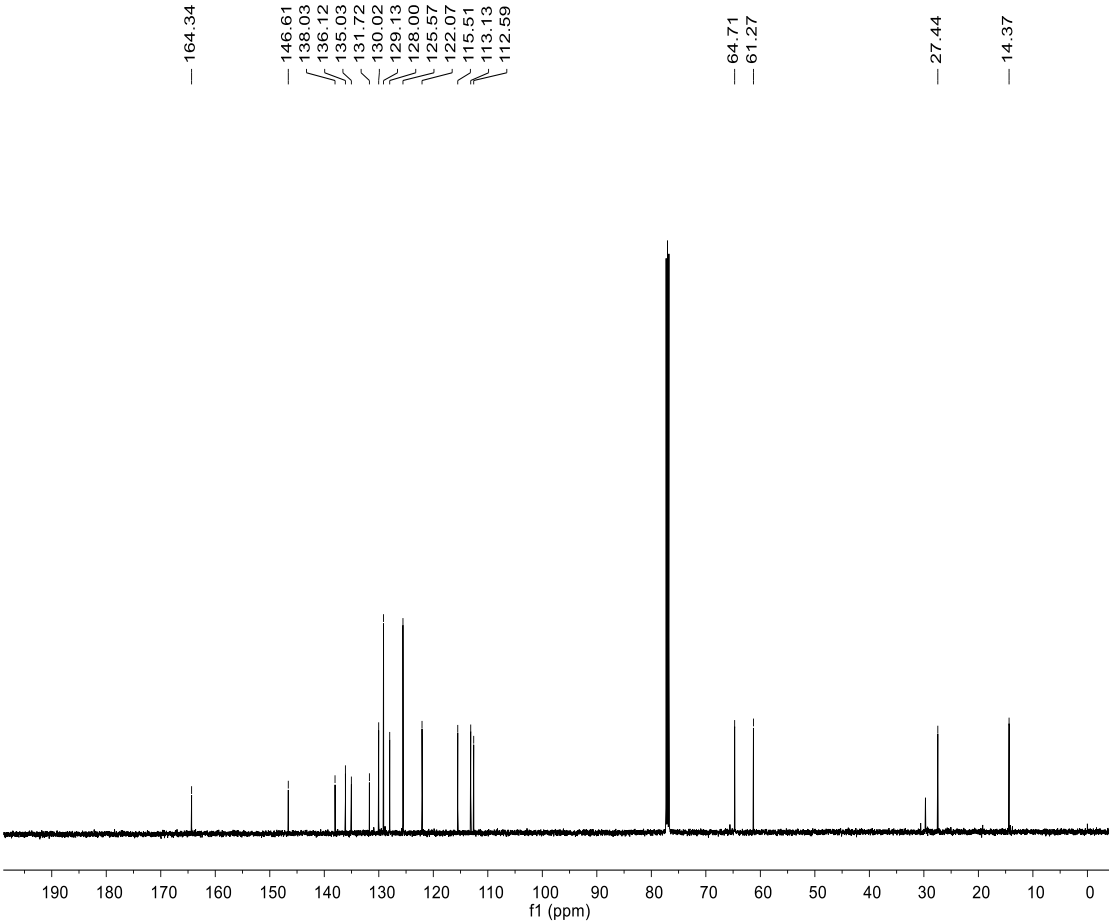

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37 7.36 7.36 7.34 7.34 7.32 7.32 7.32 7.31 7.31 7.29 7.29 7.29 7.28 7.18 7.18 7.16 7.15 7.13 7.13 7.12 7.12 7.11 7.11 7.11 6.95 6.95 6.95 6.94 6.93 6.93 6.93 5.54 5.38 5.38 5.12 5.12 4.37 4.36 4.35 4.33 4.32 4.31 4.30 4.29 4.28 3.30 3.30 3.26 3.26 2.83 2.82 2.82 2.79 2.78 2.78 1.40 1.39 1.38

CO2Et
N
N
Cl

4b


1.00 2.00 1.00 3.00 1.00 1.00 1.00 1.00 2.05 1.00 1.00 3.00
9.5 9.0 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
f1 (ppm)


164.34
146.61
138.03
136.12
135.03
131.72
130.02
129.13
128.00
125.57
122.07
115.51
113.13
112.59
64.71
61.27
27.44
14.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.27
7.27
7.27
7.26
7.25
7.25
7.20
7.20
7.19
7.07
7.05
5.55
5.55
5.34
5.34
5.09
5.09
4.37
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.31
4.30
4.29
4.29
4.28
4.27
4.26
4.25
3.28
3.27
3.24
3.23
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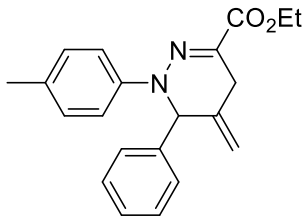
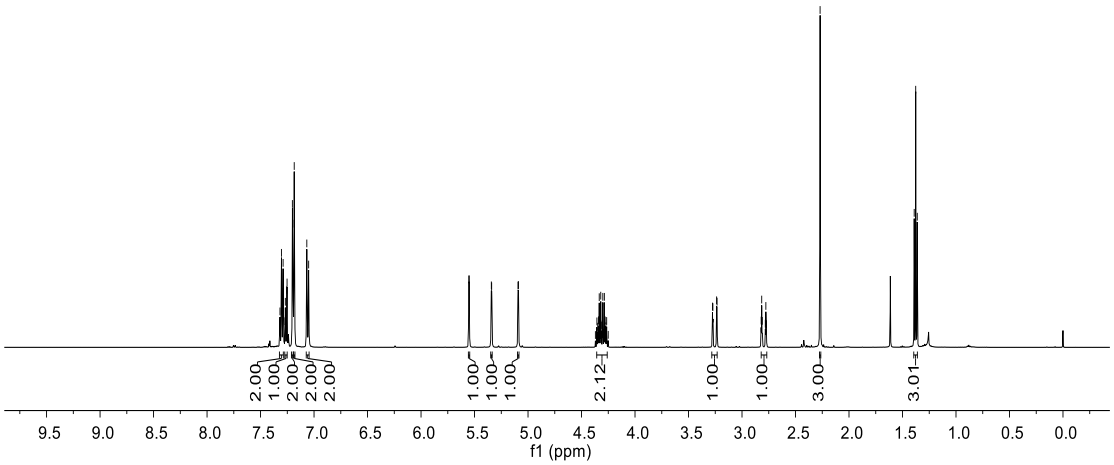
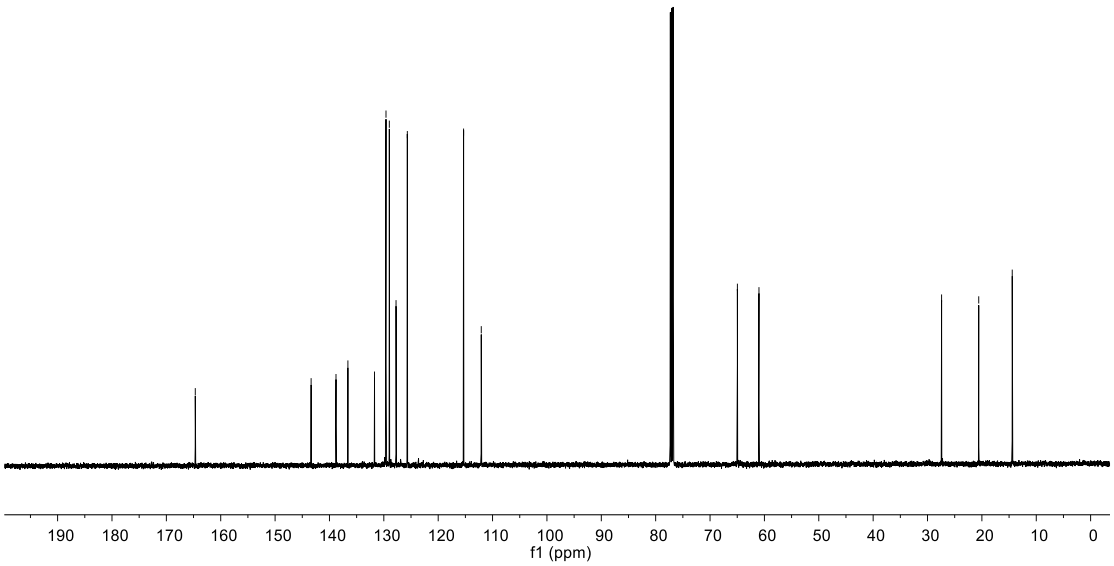
2.82
2.81
2.78
2.78
2.77
2.27
1.39
1.38
1.36

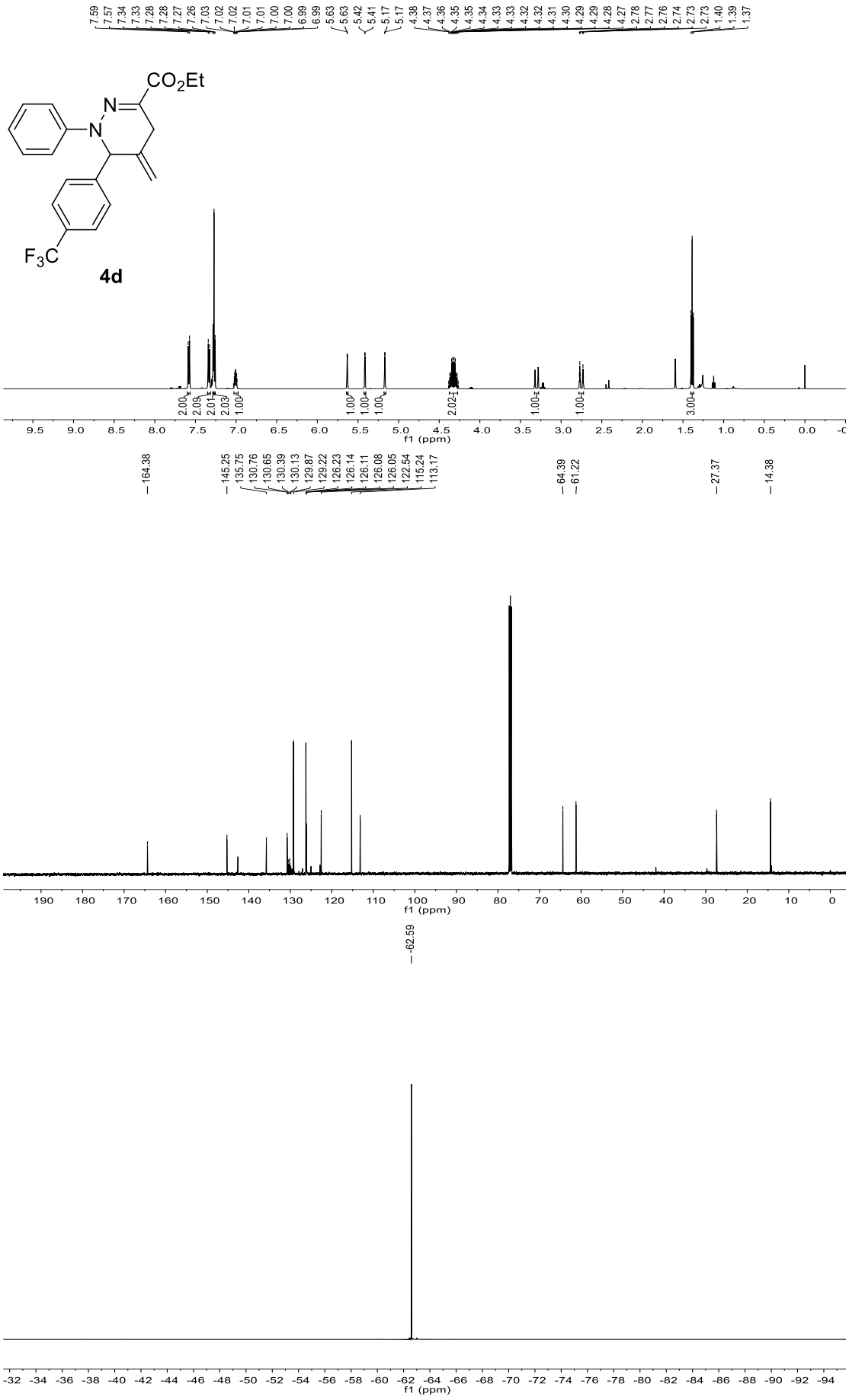

CO2Et
N
N

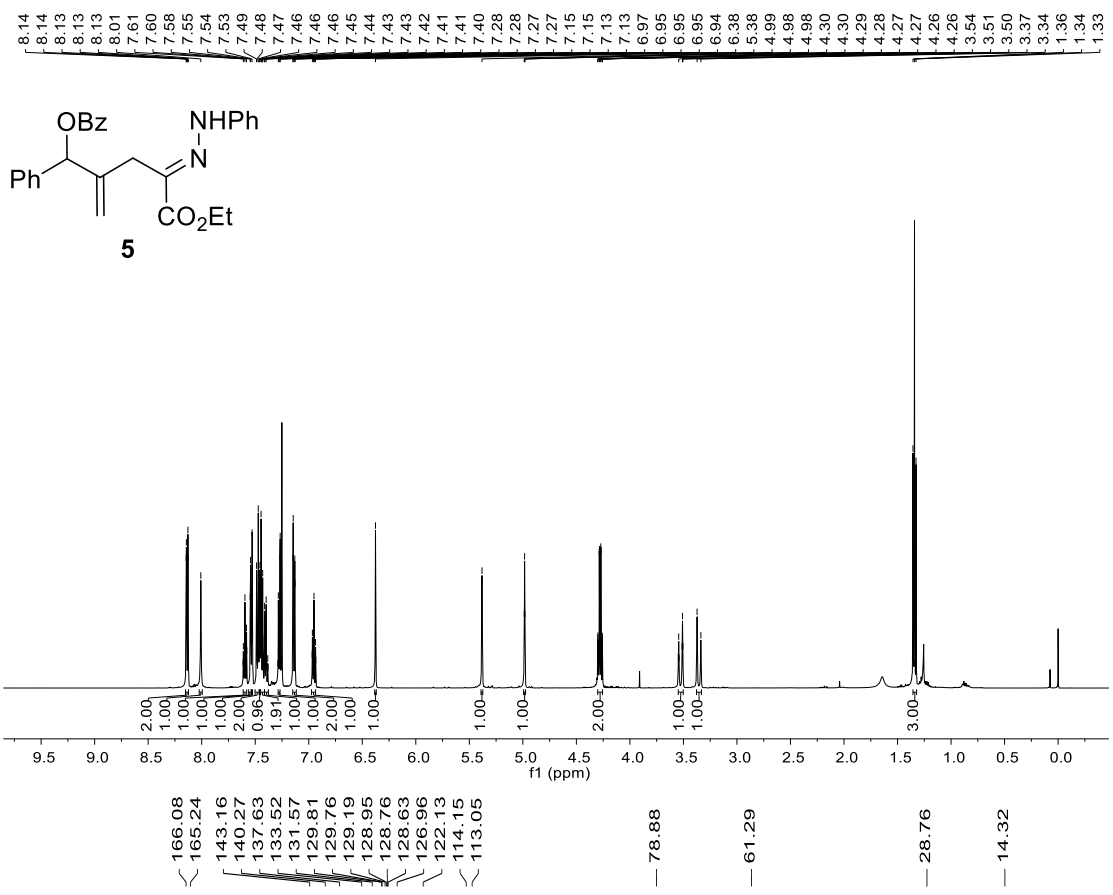
4c

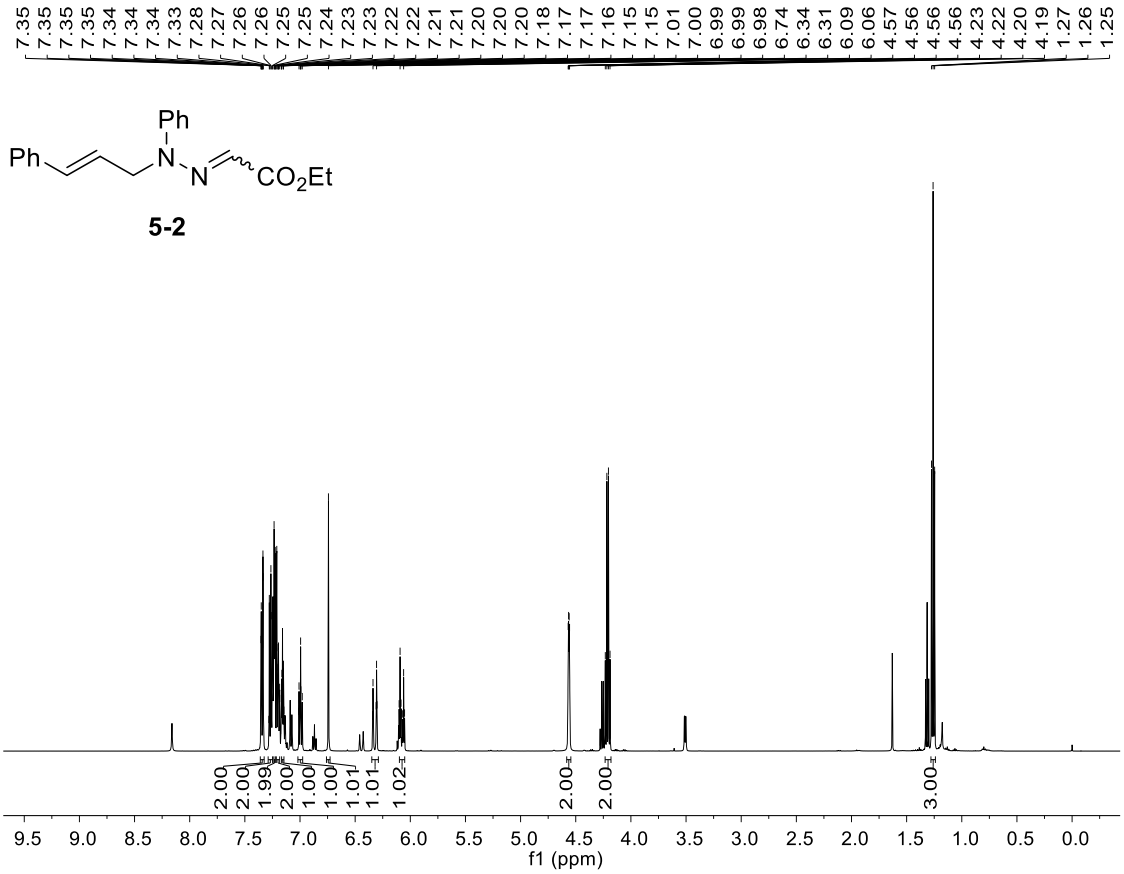

2.00
1.00
2.00
2.00
2.00
1.00
1.00
1.00
2.12
1.00
1.00
3.00
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.68
143.37
138.80
136.61
131.71
129.68
129.60
128.99
127.75
125.68
115.33
112.08
64.97
61.00
27.41
20.58
14.42


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.59
7.57
7.34
7.33
7.28
7.28
7.27
7.26
7.03
7.02
7.02
7.01
7.01
7.00
7.00
6.99
6.99
5.63
5.63
5.42
5.41
5.17
5.17
4.38
4.37
4.36
4.35
4.35
4.34
4.33
4.33
4.32
4.32
4.31
4.30
4.29
4.29
4.28
4.27
2.78
2.77
2.76
2.74
2.73
2.73
1.40
1.39
1.37
CO2Et
N
N
F3C
4d
2.00
2.09
2.01
2.03
1.00
1.00
1.00
1.00
2.02
1.00
1.00
3.00
f1 (ppm)
164.38
145.25
135.75
130.76
130.65
130.39
130.13
129.87
129.22
126.23
126.14
126.11
126.08
126.05
122.54
115.24
113.17
64.39
61.22
27.37
14.38
f1 (ppm)
-62.59
f1 (ppm)


8.14 8.14 8.13 8.13 8.13 8.01 7.61 7.60 7.58 7.55 7.54 7.53 7.49 7.48 7.47 7.46 7.46 7.46 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.40 7.28 7.28 7.27 7.27 7.15 7.15 7.13 7.13 6.97 6.95 6.95 6.95 6.94 6.38 5.38 4.99 4.98 4.98 4.30 4.30 4.29 4.28 4.27 4.27 4.26 4.26 3.54 3.51 3.50 3.37 3.34 1.36 1.34 1.33
OBz
NHPh
N
Ph
CO2Et
5
2.00 1.00 1.00 1.00 1.00 2.00 0.96 1.91 1.00 1.00 2.00 1.00 1.00 1.00 1.00 2.00 1.00 1.00 3.00
9.5 9.0 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
f1 (ppm)
166.08 165.24 143.16 140.27 137.63 133.52 131.57 129.81 129.76 129.19 128.95 128.76 128.63 126.96 122.13 114.15 113.05 78.88 61.29 28.76 14.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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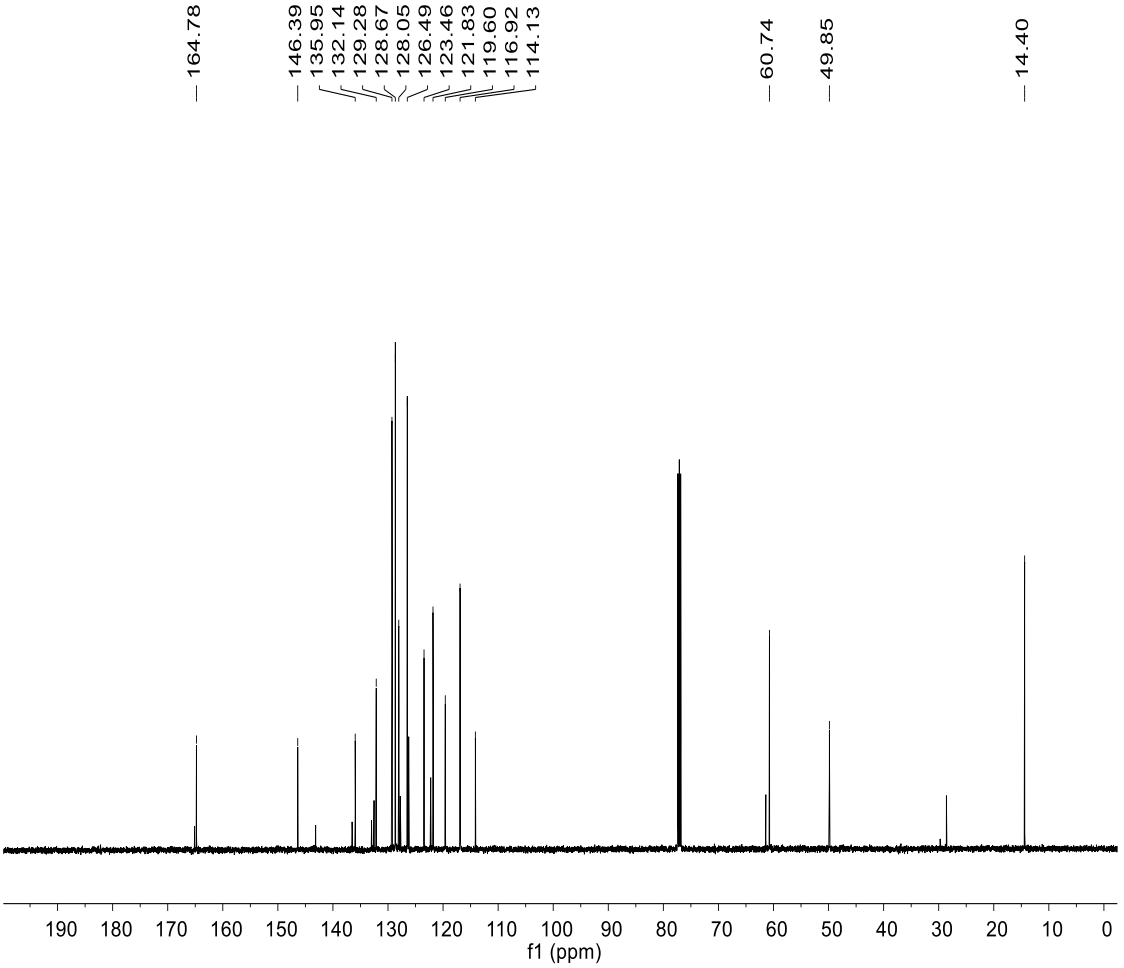
Ph
N
N
CO2Et
Ph
5-2
2.00 2.00 1.99 2.00 1.00 1.00 1.01 1.01 1.02 2.00 2.00 3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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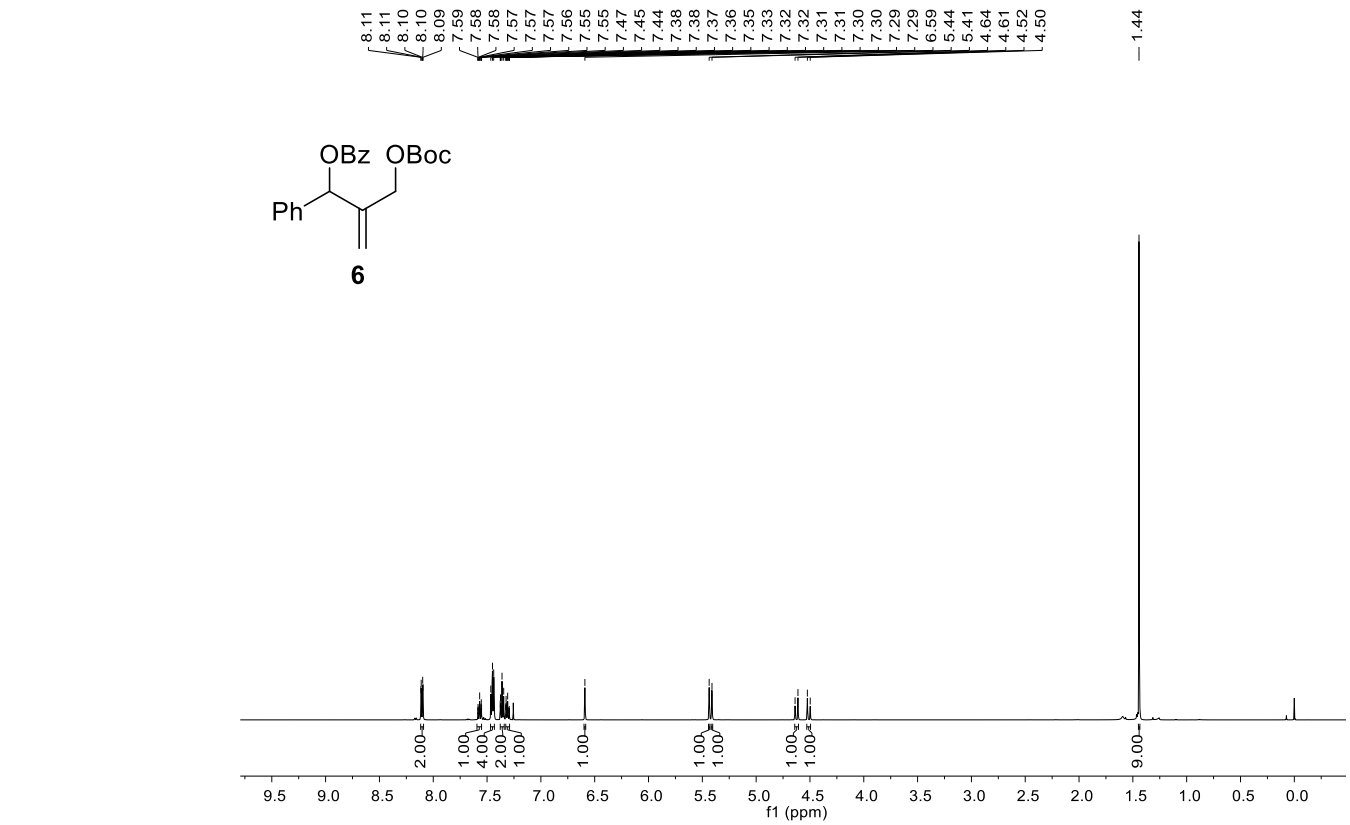
146.39
135.95
132.14
129.28
128.67
128.05
126.49
123.46
121.83
119.60
116.92
114.13
60.74
49.85
14.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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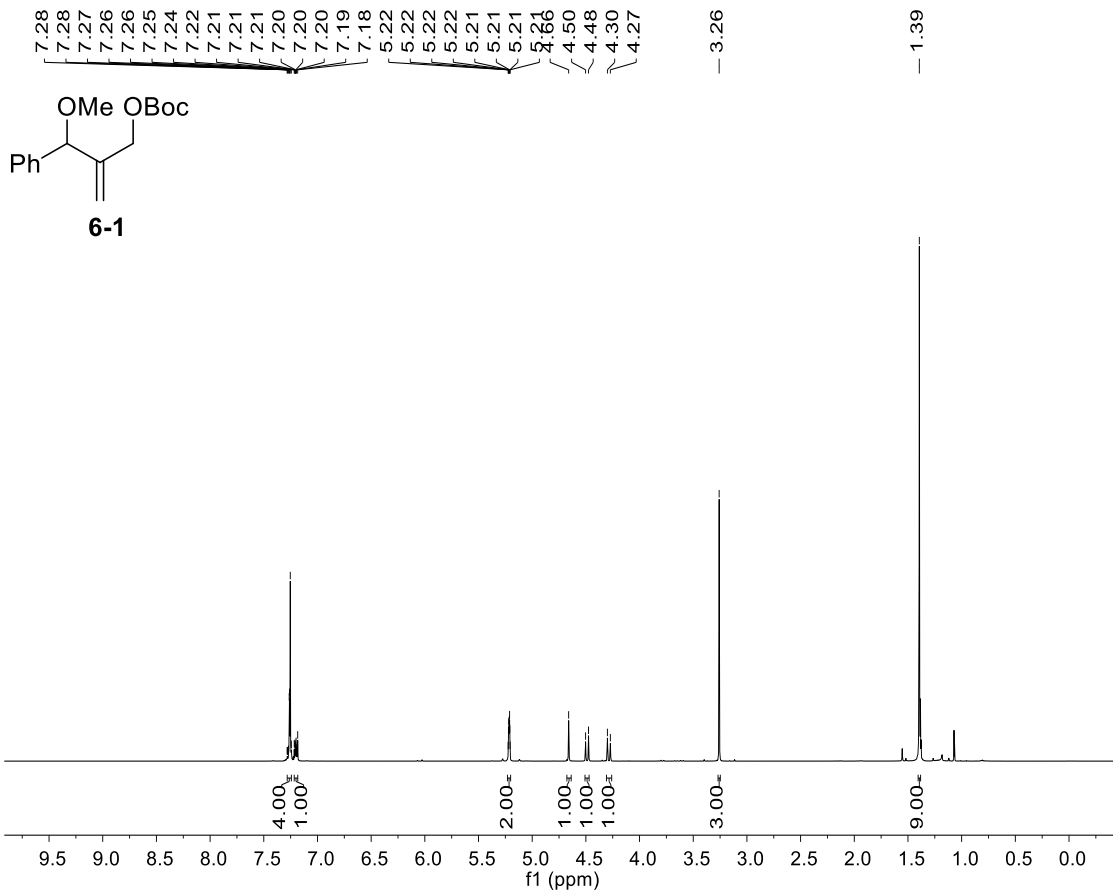
8.11
8.10
8.10
8.09
7.59
7.58
7.58
7.57
7.57
7.57
7.56
7.55
7.55
7.47
7.45
7.44
7.38
7.38
7.37
7.36
7.35
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
6.59
5.44
5.41
4.64
4.61
4.52
4.50
1.44
OBz
OBoc
Ph
6
2.00
1.00
4.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.21
153.18
141.94
137.75
133.17
130.08
129.78
128.63
128.46
128.38
127.16
115.93
82.27
76.14
66.39
27.73
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.24
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7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.18
5.22
5.22
5.22
5.21
5.21
5.21
4.66
4.50
4.48
4.30
4.27
3.26
1.39
OMe OBoc
Ph
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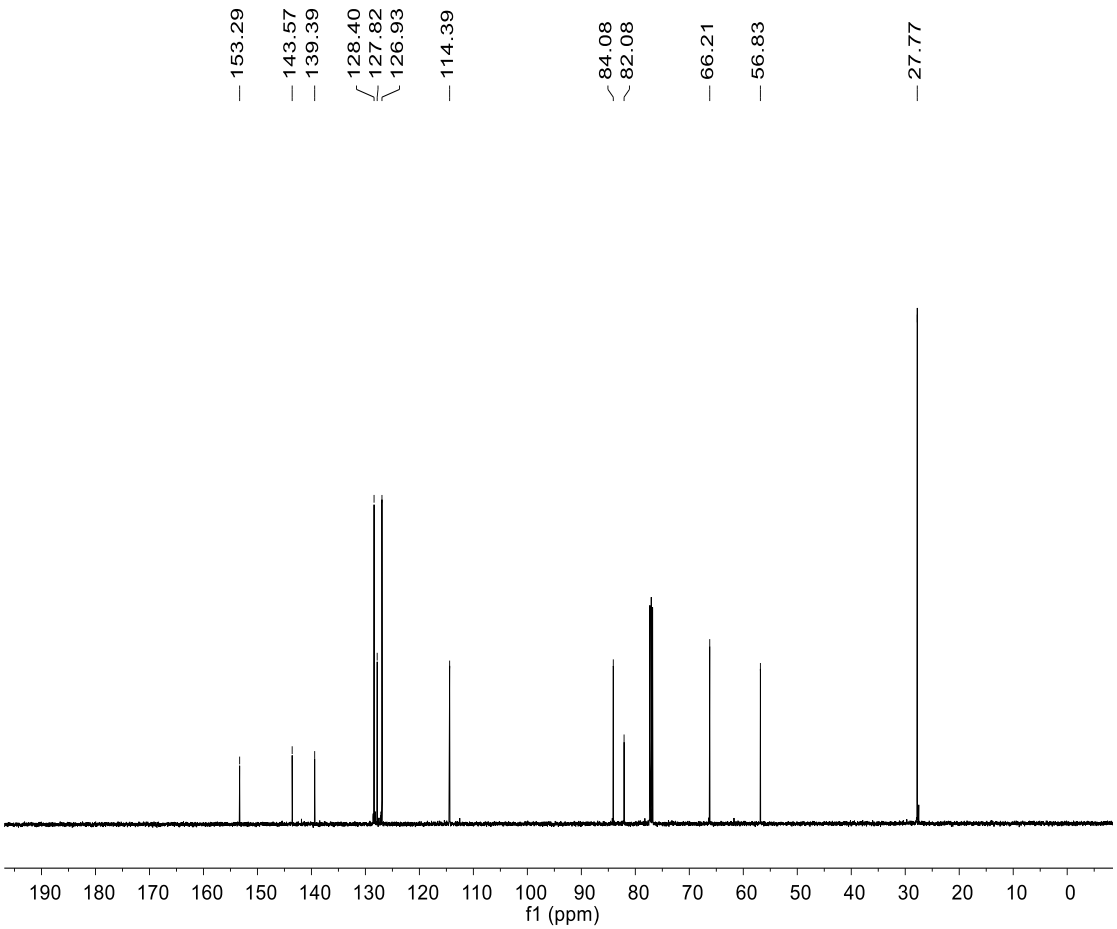
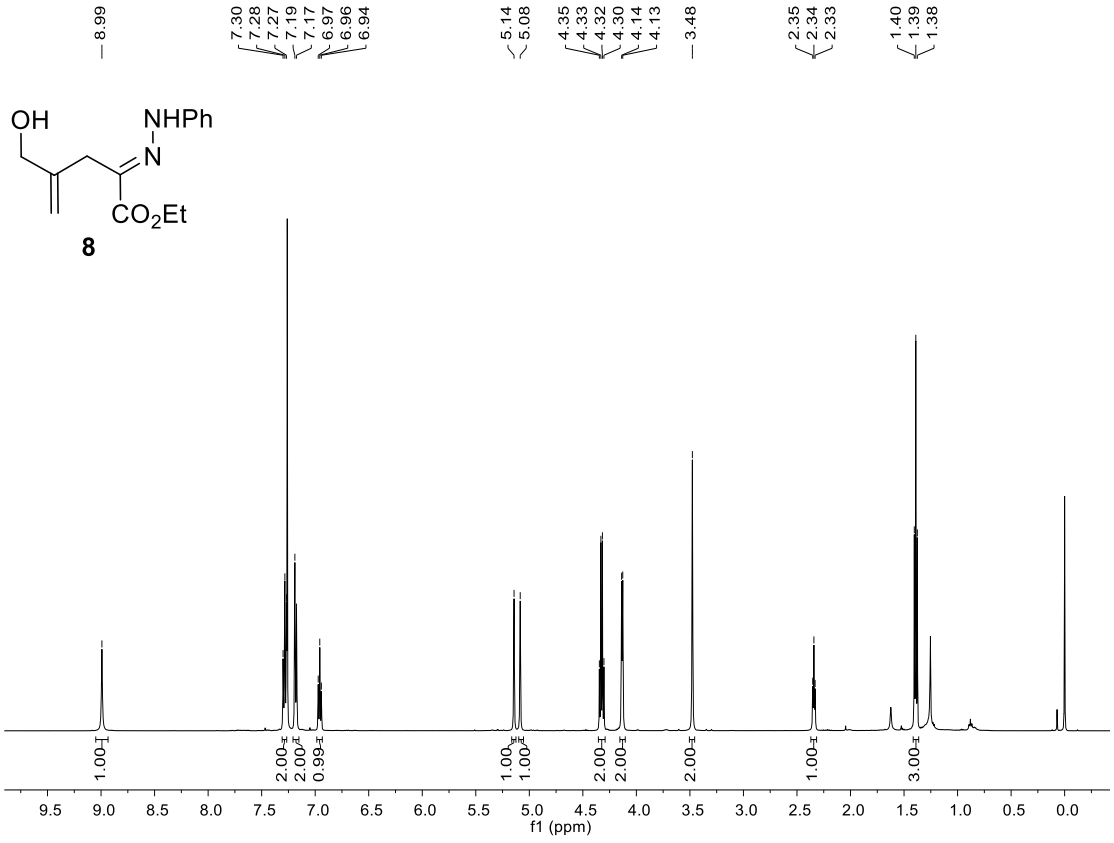
1.00
2.00
1.00
1.00
1.00
3.00
9.00
f1 (ppm)

6-1


153.29
143.57
139.39
128.40
127.82
126.93
114.39
84.08
82.08
66.21
56.83
27.77
f1 (ppm)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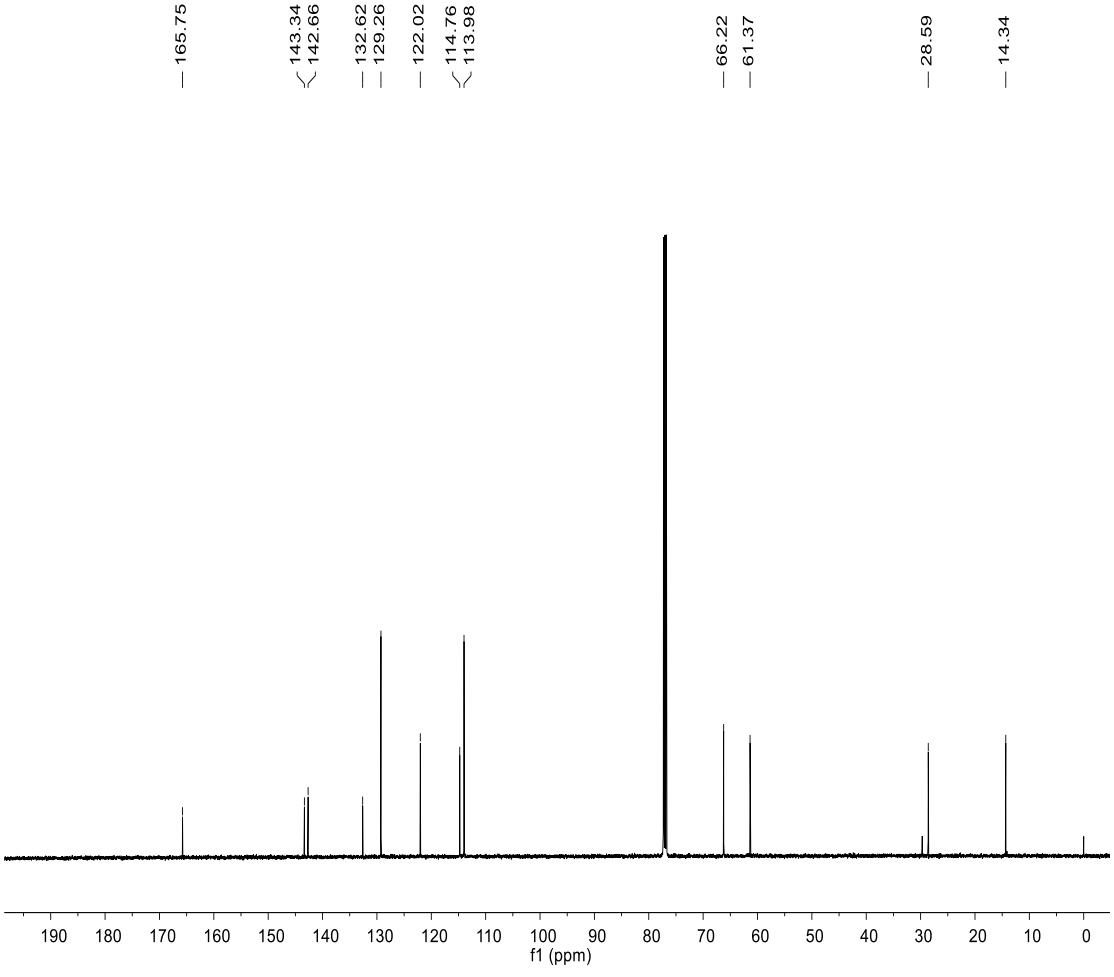
7.30
7.28
7.27
7.19
7.17
6.97
6.96
6.94
5.14
5.08
4.35
4.33
4.32
4.30
4.14
4.13
3.48
2.35
2.34
2.33
1.40
1.39
1.38
OH
NHPh
N
CO2Et
8
1.00
2.00
2.00
0.99
1.00
1.00
2.00
2.00
2.00
1.00
3.00
f1 (ppm)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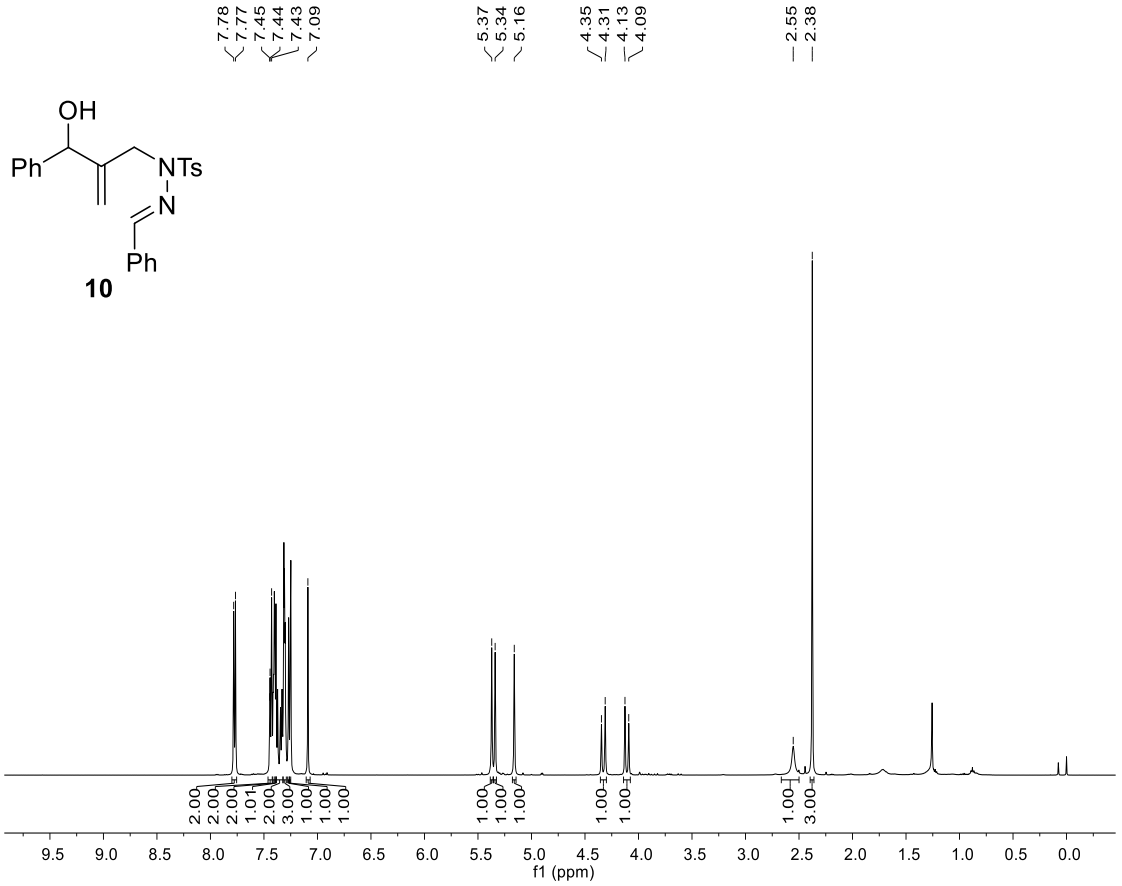
129.26
122.02
114.76
113.98
66.22
61.37
28.59
14.34
f1 (ppm)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7.45
7.44
7.43
7.09
5.37
5.34
5.16
4.35
4.31
4.13
4.09
2.55
2.38
OH
Ph
NTs
N
Ph
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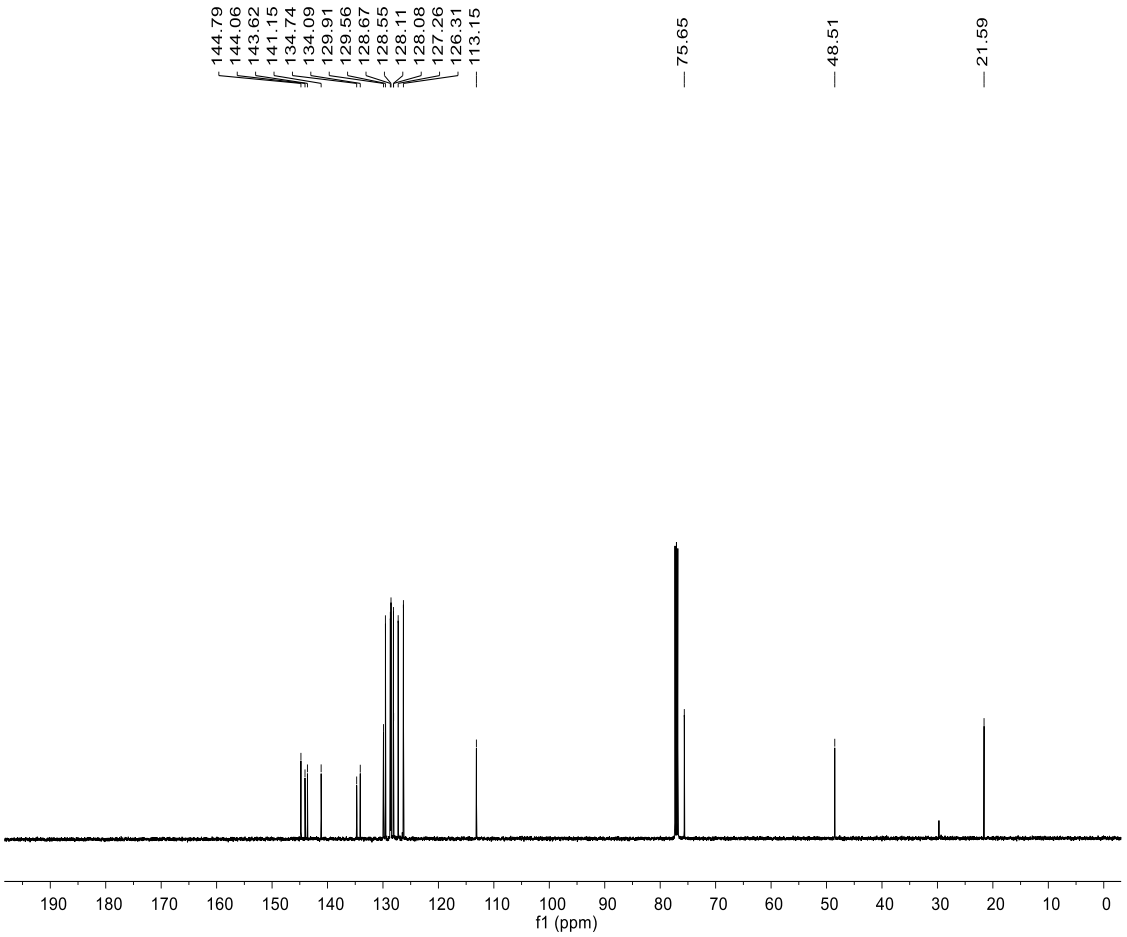
2.00
2.00
2.00
1.01
2.00
3.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.06
143.62
141.15
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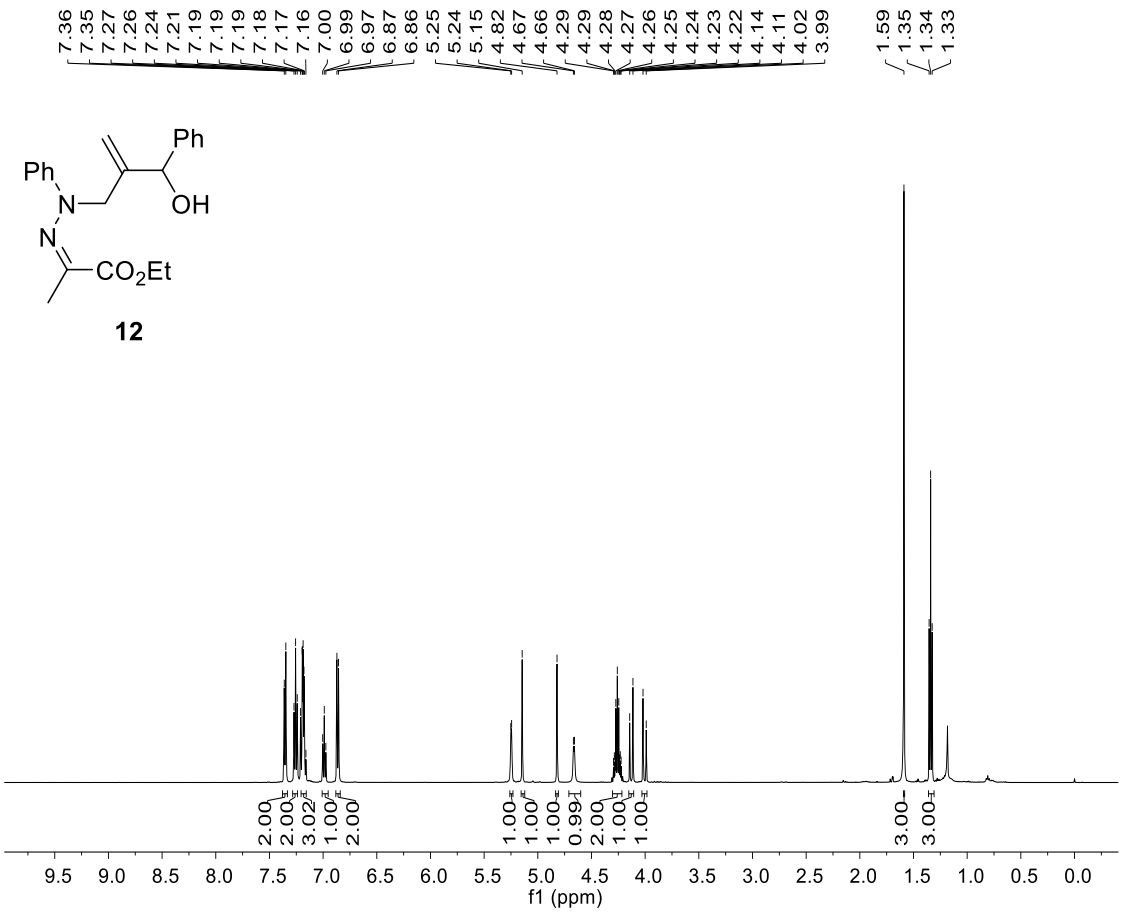
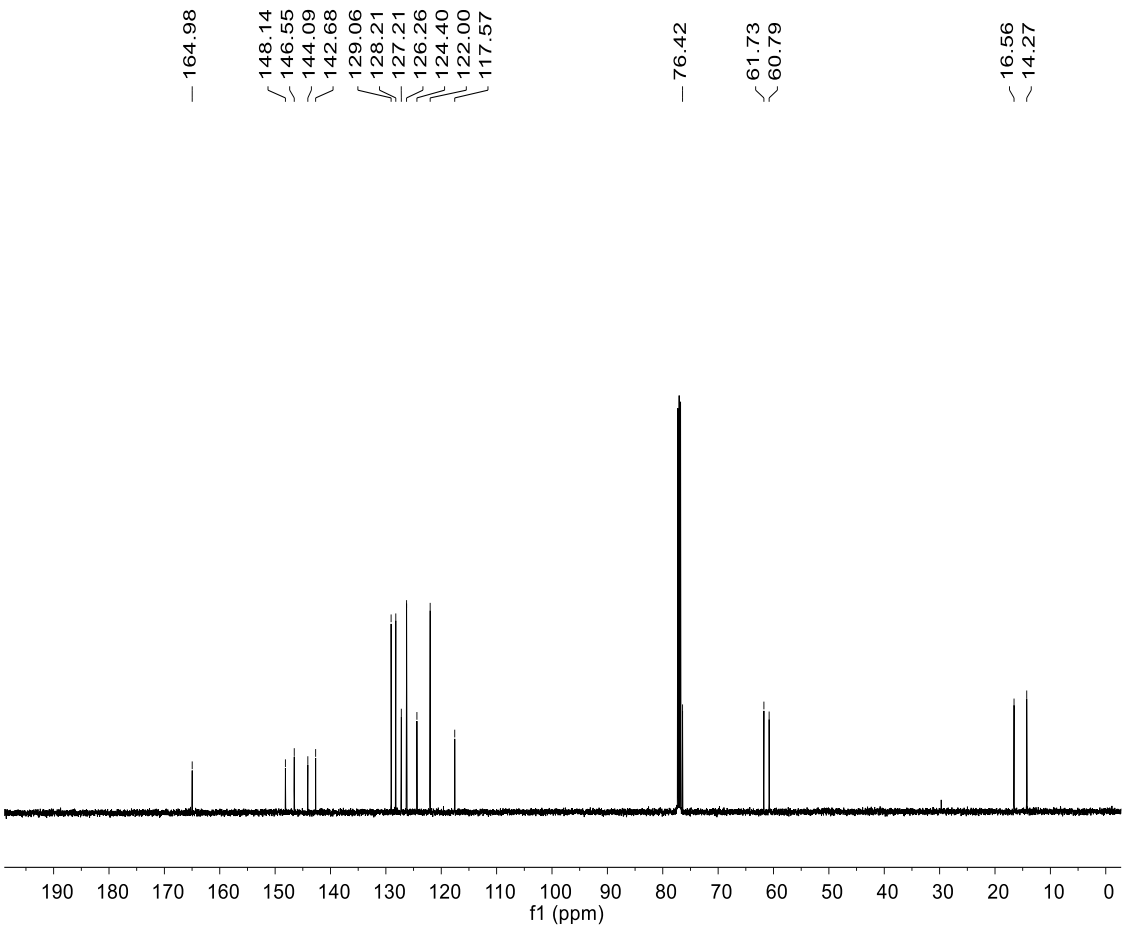
134.09
129.91
129.56
128.67
128.55
128.11
128.08
127.26
126.31
113.15
75.65
48.51
21.59
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.36
7.35
7.27
7.26
7.24
7.21
7.19
7.19
7.19
7.18
7.17
7.16
7.00
6.99
6.97
6.87
6.86
5.25
5.24
5.15
4.82
4.67
4.66
4.29
4.29
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.14
4.11
4.02
3.99
1.59
1.35
1.34
1.33
Ph
Ph
N
N
OH
CO2Et
12
2.00
2.00
3.02
1.00
2.00
1.00
1.00
0.99
2.00
1.00
1.00
3.00
3.00
9.5 9.0 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
f1 (ppm)


164.98
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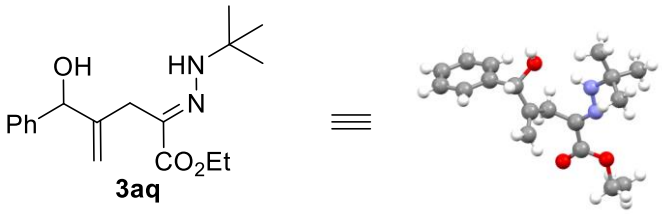
144.09
142.68
129.06
128.21
127.21
126.26
124.40
122.00
117.57
76.42
61.73
60.79
16.56
14.27
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

X-Ray Crystallographic Data of 3aq and 4a

Crystallographic data for **3aq** have been deposited with the Cambridge Crystallographic Data Centre as deposition number 2183433. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of **3aq** were obtained by slow evaporation of a solution containing **3aq** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **3aq** are listed in the Table S1.



3aq

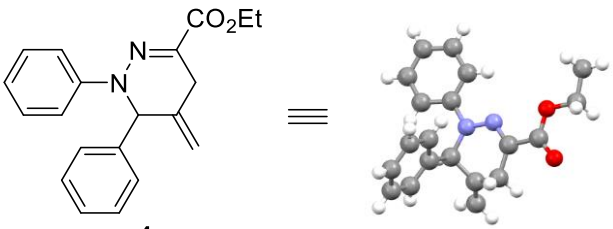
Table S1 Crystal data and structure refinement for 3aq.

Identification code	**3aq**
Empirical formula	$C_{18}H_{26}N_2O_3$
Formula weight	318.41
Temperature/K	298.00
Crystal system	orthorhombic
Space group	P212121
a/Å	6.9618(3)
b/Å	14.6189(6)
c/Å	18.3457(7)
α/°	90
β/°	90
γ/°	90
Volume/Å3	1867.11(13)
Z	4
ρcalcg/cm3	1.133
μ/mm-1	0.077
F(000)	688.0
Crystal size/mm3	0.2 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.562 to 54.948
Index ranges	-8 ⩽ h ⩽ 8, -18 ⩽ k ⩽ 18, -22 ⩽ l ⩽ 23
Reflections collected	17434

Independent reflections	4150 [Rint = 0.0524, Rsigma = 0.0433]
Data/restraints/parameters	4150/156/214
Goodness-of-fit on F2	1.101
Final R indexes [I>=2σ (I)]	R1 = 0.0954, wR2 = 0.2786
Final R indexes [all data]	R1 = 0.1082, wR2 = 0.2936
Largest diff. peak/hole / e Å-3	0.68/-0.60
Flack parameter	-1(4)

Crystallographic data for **4a** have been deposited with the Cambridge Crystallographic Data Centre as deposition number 2183504. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of **4a** were obtained by slow evaporation of a solution containing **4a** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **4a** are listed in the Table S2.



4a

Table S2 Crystal data and structure refinement for 4a.

Identification code	**4a**
Empirical formula	$C_{20}H_{20}N_2O_2$
Formula weight	320.38
Temperature/K	200.00
Crystal system	monoclinic
Space group	P21/n
a/Å	8.1524(2)
b/Å	14.0253(4)
c/Å	15.1337(4)
α/°	90
β/°	102.5470(10)
γ/°	90

Volume/Å3	1689.06(8)
Z	4
ρcalcg/cm3	1.260
μ/mm-1	0.082
F(000)	680.0
Crystal size/mm3	0.2 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.004 to 55
Index ranges	-10 ⩽ h ⩽ 10, -18 ⩽ k ⩽ 18, -15 ⩽ l ⩽ 19
Reflections collected	17254
Independent reflections	3838 [Rint = 0.0358, Rsigma = 0.0293]
Data/restraints/parameters	3838/0/218
Goodness-of-fit on F2	1.027
Final R indexes [I>=2σ (I)]	R1 = 0.0388, wR2 = 0.0976
Final R indexes [all data]	R1 = 0.0486, wR2 = 0.1039
Largest diff. peak/hole / e Å-3	0.19/-0.16