Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Solvent and Catalyst Dependent Palladium-Catalyzed Switchable Chemodivergent Cascade Cyclizations of Trimethylenemethanes with *ortho*-Formyl Cinnamates

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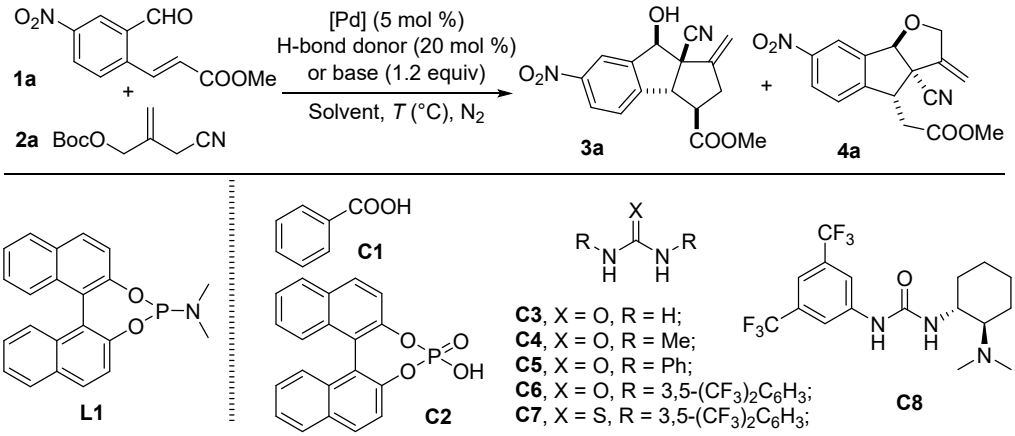
1. General methods

^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz) spectra were recorded on Bruker Avance NEO 600 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet; m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). ESI-HRMS was recorded on a Waters Xevo G2-XS using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. Column chromatography was performed on silica gel (100–200 mesh) eluting with ethyl acetate (EtOAc) and petroleum ether. TLC was performed on glass-backed silica plates. UV light and a solution of potassium permanganate were used to visualize products or starting materials. Petroleum ether and EtOAc were distilled. Dried solvents and liquid reagents were transferred by oven-dried syringes. Electron-deficient styrenes [1], electron-deficient cinnamates [2] and TMM donors [3] were prepared according to the literature procedures.

2. Detailed condition screenings

2.1 Detailed condition screenings for the synthesis of 3a and 4a



Enrty[a]	Solvent	[**1a**] (M)	**2a**/**1a**	*T* (°C)	Base	HB donor	Time (h)	**3a** (%)[b]	**4a** (%)[b]
1	benzene	0.10	1.2	10	-	-	24	19	45
2	DCM	0.10	1.2	10	-	-	24	40	29
3	THF	0.10	1.2	10	-	-	10	82	trace
4	1,4-dioxane	0.10	1.2	10	-	-	10	95	nd
5	1,3-dioxoane	0.10	1.2	10	-	-	10	86	nd
6	DME	0.10	1.2	10	-	-	10	97	nd
7[c]	DME	0.10	1.2	10	-	-	10	27	31
8[d]	DME	0.10	1.2	10	-	-	10	33	trace
9[e]	DME	0.10	1.2	10	-	-	10	trace	trace
10	benzene	0.10	1.2	10	-	-	24	19	45
11	toluene	0.10	1.2	10	-	-	24	13	49
12	*p*-xylene	0.10	1.2	10	-	-	24	18	48
13	mesitylene	0.10	1.2	10	-	-	24	18	51
14	chlorobenzene	0.10	1.2	10	-	-	24	12	32
15	mesitylene	0.03	1.2	10	-	-	24	13	55
16	mesitylene	0.05	1.2	10	-	-	24	15	61
17	mesitylene	0.20	1.2	10	-	-	24	13	40
18	mesitylene	0.05	0.8	10	-	-	48	12	35
19	mesitylene	0.05	1.0	10	-	-	48	16	39
20	mesitylene	0.05	1.4	10	-	-	24	20	63

21	mesitylene	0.05	1.6	10	-	-	24	21	62
22	mesitylene	0.05	1.4	30	-	-	24	19	61
23	mesitylene	0.05	1.4	60	-	-	24	16	28
24	mesitylene	0.05	1.6	10	K_2CO_3	-	24	nd	55
25	mesitylene	0.05	1.6	10	Cs_2CO_3	-	24	9	57
26	mesitylene	0.05	1.6	10	*t*-BuOK	-	24	nd	nd
27	mesitylene	0.05	1.6	10	Et_3N	-	24	12	61
28	mesitylene	0.05	1.6	10	DBU	-	24	10	nd
29	mesitylene	0.05	1.6	10	-	**C1**	24	10	65
30	mesitylene	0.05	1.6	10	-	**C2**	24	nd	nd
31	mesitylene	0.05	1.6	10	-	**C3**	5	nd	78
32	mesitylene	0.05	1.6	10	-	**C4**	5	nd	80
33	mesitylene	0.05	1.6	10	-	**C5**	5	nd	89
34	mesitylene	0.05	1.6	10	-	**C6**	5	nd	92
35	mesitylene	0.05	1.6	10	-	**C7**	5	nd	81
36	mesitylene	0.05	1.6	10	-	**C8**	5	nd	91
37[c]	mesitylene	0.05	1.6	10	-	**C6**	5	trace	76
38[d]	mesitylene	0.05	1.6	10	-	**C6**	5	nd	nd
39[e]	mesitylene	0.05	1.6	10	-	**C6**	5	trace	nd

[a]Unless noted otherwise, reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(PPh_3)_4$ (5 mol %), base (1.2 equiv) and H-bond donor (20 mol %) in solvent (1.0 mL) under N_2 atmosphere at 10 ℃.

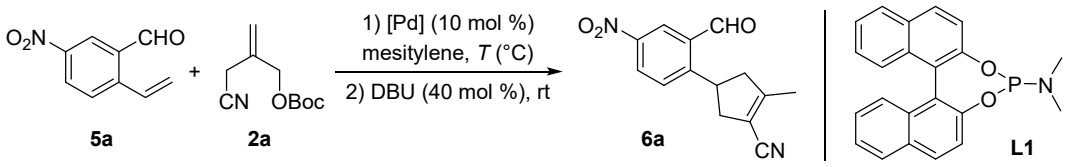
[b]Isolated yield.

[c]with $Pd_2(dba)_3$ (2.5 mol %) and PPh_3 (10 mol %).

[d]with $Pd(OAc)_2$ (5 mol %) and PPh_3 (10 mol %).

[e]with $Pd_2(dba)_3$ (2.5 mol %) and **L1** (10 mol %).

2.2 Detailed condition screenings for the synthesis of 6a



5a **2a** **6a** **L1**

Enrty[a]	*T* (°C)	[**5a**] (M)	**2a**/**5a**	**6a** (%)[b]
1	10	0.05	1.4	66
2	25	0.05	1.4	70
3	40	0.05	1.4	75
4	65	0.05	1.4	70
5	40	0.03	1.4	75
6	40	0.10	1.4	79
7	40	0.20	1.4	76
8	40	0.10	1.6	87
9	40	0.10	1.8	94
10	40	0.10	2.0	95
11[c]	40	0.10	2.0	86
12[d]	40	0.10	2.0	71
13[e]	40	0.10	2.0	trace

[a]Unless noted otherwise, reactions were performed with **5a** (0.1 mmol), **2a** (0.14 mmol) and $Pd(PPh_3)_4$ (10 mol %) in mesitylene (1.0 mL) under N_2 atmosphere for 12 h. After full conversion, the mixture was cooled to room temperature, and 40% DBU were added in situ at room temperature for 10 min.

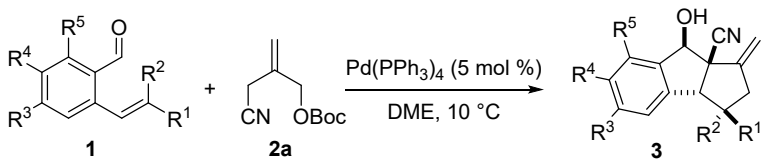
[b]Isolated yield.

[c]with $Pd_2(dba)_3$ (5 mol %) and PPh_3 (20 mol %).

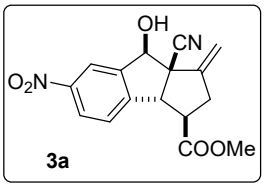
[d]with $Pd(OAc)_2$ (10 mol %) and PPh_3 (20 mol %).

[e]with $Pd_2(dba)_3$ (5 mol %) and **L1** (20 mol %).

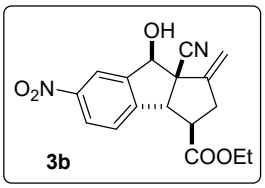
3. General procedure for the synthesis of cycloadducts 3a–m



General procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with *ortho*-formyl-substituted cinnamate **1** (0.10 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol % or 11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.12 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10–48 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3a–m**.

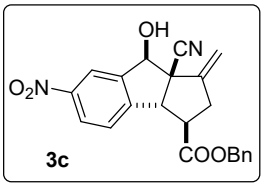


Synthesis of 3a by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with methyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1a** (23.5 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3a**: 30.5 mg, 97% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 1H), 8.26 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 5.59 (s, 1H), 5.38 (s, 1H), 5.27 (s, 1H), 4.57 (d, *J* = 4.8 Hz, 1H), 3.82 (s, 3H), 3.69 (s, 1H), 3.09–3.02 (m, 1H), 2.99–2.91 (m, 1H), 2.55 (dd, *J* = 16.8, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 172.7, 148.8, 148.3, 146.6, 142.9, 125.6, 125.5, 121.2, 119.5, 114.2, 82.2, 59.5, 57.2, 52.7, 48.5, 36.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{16}H_{14}N_2O_5Na^+$ 337.0795, found 337.0799.



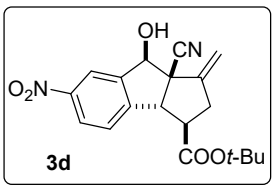
Synthesis of 3b by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with ethyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1b** (25.0 mg, 0.100 mmol, 1.0 equiv) and

$Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3b**: 29.2 mg, 89% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 5.59 (s, 1H), 5.38 (s, 1H), 5.27 (d, *J* = 4.8 Hz, 1H), 4.57 (d, *J* = 4.8 Hz, 1H), 4.33–4.23 (m, 2H), 3.54–3.38 (m, 1H), 3.09–3.00 (m, 1H), 2.99–2.91 (m, 1H), 2.64–2.48 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 172.2, 148.8, 148.4, 146.7, 142.9, 125.6, 125.5, 121.2, 119.5, 114.1, 82.3, 61.9, 59.6, 57.2, 48.7, 36.1, 14.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{16}N_2O_5Na^+$ 351.0951, found 351.0959.



3c

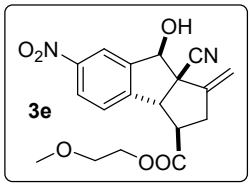
Synthesis of 3c by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with benzyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1c** (31.1 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3c**: 35.6 mg, 91% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.26 (s, 1H), 8.24–8.15 (m, 1H), 7.46–7.30 (m, 6H), 5.58 (s, 1H), 5.37 (s, 1H), 5.29–5.18 (m, 3H), 4.55 (d, *J* = 4.8 Hz, 1H), 3.44 (s, 1H), 3.16–3.01 (m, 1H), 3.01–2.91 (m, 1H), 2.63–2.50 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 172.0, 148.8, 148.1, 146.5, 142.8, 135.2, 128.78, 128.76, 128.7, 125.6, 125.5, 121.1, 119.4, 114.1, 82.2, 67.6, 59.8, 57.2, 48.7, 36.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}N_2O_5Na^+$ 413.1108, found 413.1112.



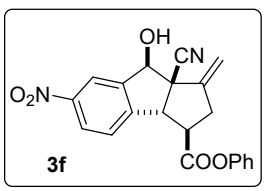
3d

Synthesis of 3d by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with *tert*-butyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1d** (27.7 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL)

and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 20 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3d**: 32.3 mg, 91% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.29–8.24 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 5.57 (s, 1H), 5.37 (s, 1H), 5.25 (d, *J* = 6.0 Hz, 1H), 4.54 (d, *J* = 3.6 Hz, 1H), 3.57 (s, 1H), 2.97–2.88 (m, 2H), 2.54–2.39 (m, 1H), 1.52 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.3, 148.7, 147.1, 142.9, 125.5, 125.5, 121.1, 119.6, 113.8, 82.7, 82.3, 59.4, 57.3, 49.7, 36.0, 28.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{20}N_2O_5Na^+$ 379.1264, found 379.1273.

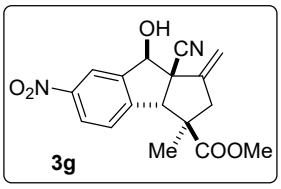


Synthesis of 3e by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-methoxyethyl (*Z*)-3-(2-formyl-4-nitrophenyl)acrylate **1e** (27.9 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3e**: 34.4 mg, 96% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 5.59 (s, 1H), 5.38 (s, 1H), 5.26 (d, *J* = 6.0 Hz, 1H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.46–4.38 (m, 1H), 4.36–4.30 (m, 1H), 3.68–3.63 (m, 2H), 3.42 (s, 1H), 3.41 (s, 3H), 3.10–3.03 (m, 1H), 3.03–2.96 (m, 1H), 2.66–2.55 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 172.1, 148.8, 148.1, 146.6, 142.9, 125.7, 125.6, 121.0, 119.4, 114.1, 82.2, 70.2, 64.5, 59.8, 59.0, 57.2, 48.5, 36.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{18}N_2O_6Na^+$ 381.1057, found 381.1064.



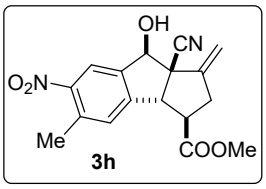
Synthesis of 3f by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-phenyl (*Z*)-3-(2-formyl-4-nitrophenyl)acrylate **1f** (29.7 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was

stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3f**: 34.1 mg, 91% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38–8.23 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.64 (s, 1H), 5.45 (s, 1H), 5.31 (s, 1H), 4.74 (d, *J* = 4.6 Hz, 1H), 3.34–3.27 (m, 1H), 3.21 (s, 1H), 3.17–3.10 (m, 1H), 2.74–2.63 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.9, 150.4, 148.8, 148.0, 146.3, 143.0, 129.7, 126.4, 125.7, 125.6, 121.3, 121.3, 119.5, 114.6, 82.2, 59.4, 57.2, 48.7, 35.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{21}H_{16}N_2O_5Na^+$ 399.0951, found 399.0962.



3g

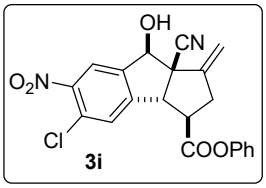
Synthesis of 3g by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with methyl (*E*)-3-(2-formyl-4-nitrophenyl)-2-methylacrylate **1g** (24.9 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3g**: 26.5 mg, 81% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.26 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 5.59 (s, 1H), 5.38 (s, 1H), 5.32 (s, 1H), 4.71 (s, 1H), 3.83 (s, 3H), 3.35 (s, 1H), 3.21 (d, *J* = 15.6 Hz, 1H), 2.47 (d, *J* = 15.6 Hz, 1H), 0.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 175.5, 148.9, 146.9, 145.6, 144.5, 127.4, 124.9, 120.6, 118.9, 113.6, 82.9, 61.4, 60.1, 53.0, 51.4, 45.9, 20.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{16}N_2O_5Na^+$ 351.0951, found 351.0952.



3h

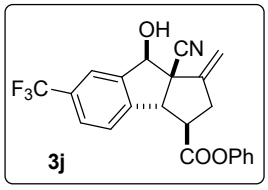
Synthesis of 3h by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with methyl (*E*)-3-(2-formyl-5-methyl-4-nitrophenyl)acrylate **1i** (24.9 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum

ether/EtOAc = 10/1) gave the product **3h**: 31.5 mg, 96% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.01 (s, 1H), 7.29 (s, 1H), 5.57 (s, 1H), 5.37 (s, 1H), 5.21 (s, 1H), 4.52 (d, *J* = 4.2 Hz, 1H), 3.82 (s, 3H), 3.19 (s, 1H), 3.07–3.01 (m, 1H), 2.99–2.87 (m, 1H), 2.61 (s, 3H), 2.57–2.51 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 172.7, 149.9, 146.7, 146.5, 140.3, 136.1, 128.6, 122.1, 119.5, 114.1, 82.2, 59.5, 57.1, 52.7, 48.5, 36.0, 20.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{16}N_2O_5Na^+$ 351.0951, found 351.0952.



3i

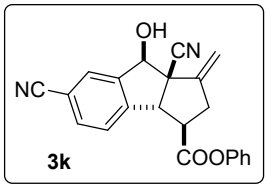
Synthesis of 3i by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with phenyl (*E*)-3-(5-chloro-2-formyl-4-nitrophenyl)acrylate **1i** (33.1 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3i**: 34.4 mg, 84% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.91 (s, 1H), 7.58 (s, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.61 (s, 1H), 5.44 (s, 1H), 5.23 (s, 1H), 4.68 (d, *J* = 4.2 Hz, 1H), 3.73 (s, 1H), 3.31–3.21 (m, 1H), 3.13 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.70 (dd, *J* = 16.8, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.6, 150.3, 148.6, 146.5, 145.9, 141.2, 129.7, 129.0, 128.1, 126.5, 122.9, 121.3, 119.2, 114.8, 81.9, 59.5, 57.0, 48.6, 35.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{16}{}^{35}ClN_2O_5^+$ 411.0743, found 411.0745; Calcd. for $C_{21}H_{16}{}^{37}ClN_2O_5^+$ 413.0713, found 413.0701.



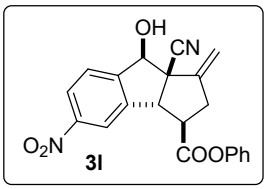
3j

Synthesis of 3j by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with phenyl (*E*)-3-(2-formyl-4-(trifluoromethyl)phenyl)acrylate **1j** (32.0 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3j**: 38.8 mg, 97% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.71 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.46–7.36

(m, 2H), 7.33–7.26 (m, 1H), 7.16 (d, J = 6.6 Hz, 2H), 5.62 (s, 1H), 5.42 (s, 1H), 5.27 (s, 1H), 4.72 (s, 1H), 3.34–3.22 (m, 1H), 3.10 (d, J = 16.8 Hz, 1H), 2.67–2.57 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.0, 150.4, 146.7, 145.0, 141.9, 131.6 (q, J = 32.4 Hz), 129.7, 127.5 (d, J = 3.8 Hz), 126.3, 125.1, 122.9 (d, J = 4.4 Hz), 121.3, 119.7, 114.3, 82.8, 59.1, 57.4, 48.8, 35.7; ^{19}F NMR (565 MHz, CDCl3) δ (ppm) –62.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}F_3NO_3^+$ 400.1155, found 400.1159.

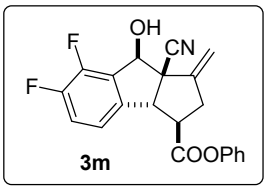


Synthesis of 3k by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with phenyl (*E*)-3-(4-cyano-2-formylphenyl)acrylate **1k** (27.7 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 48 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3k**: 11.6 mg, 33% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.75 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 5.62 (s, 1H), 5.44 (s, 1H), 5.27 (s, 1H), 4.71 (d, J = 4.2 Hz, 1H), 3.29–3.24 (m, 1H), 3.23–3.07 (m, 2H), 2.66 (dd, J = 16.8, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.9, 150.4, 146.4, 146.3, 142.5, 134.0, 129.7, 129.7, 126.4, 125.6, 121.3, 119.6, 118.2, 114.5, 113.0, 82.4, 59.0, 57.6, 48.7, 35.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{16}N_2O_3Na^+$ 379.1053, found 379.1053.



Synthesis of 3l by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with phenyl (*E*)-3-(2-formyl-5-nitrophenyl)acrylate **1l** (29.7 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3l**: 36.4 mg, 97% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.29–8.23 (m, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.8

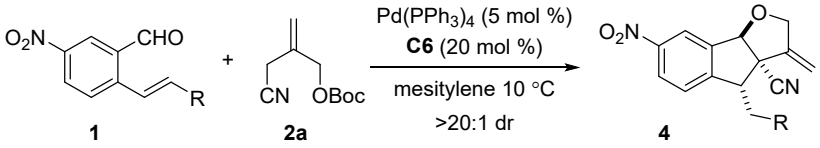
Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.63 (s, 1H), 5.45 (s, 1H), 5.29 (s, 1H), 4.74 (d, *J* = 4.4 Hz, 1H), 3.36–3.31 (m, 1H), 3.29 (s, 1H), 3.14 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.68 (dd, *J* = 16.8, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.7, 150.4, 149.7, 147.6, 146.3, 142.8, 129.7, 126.7, 126.4, 124.6, 121.3, 120.1, 119.3, 114.6, 82.3, 59.5, 57.1, 48.7, 35.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{17}N_2O_5^+$ 377.1132, found 377.1130.



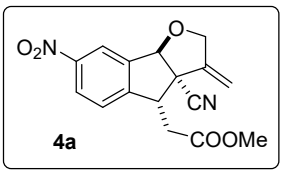
3m

Synthesis of 3m by general procedure A: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with phenyl phenyl (*E*)-3-(3,4-difluoro-2-formylphenyl)acrylate **1m** (28.8 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (1.0 mL) and TMM donor **2a** (23.6 mg, 0.120 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 50 °C for 48 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3m**: 33.1 mg, 45% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.40 (t, *J* = 7.8 Hz, 2H), 7.29–7.21 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.08 (dd, *J* = 8.4, 3.6 Hz, 1H), 5.61 (s, 1H), 5.43 (s, 1H), 5.42 (s, 1H), 4.75 (s, 1H), 3.36 (s, 1H), 3.33 (dt, *J* = 7.8, 3.0 Hz, 1H), 3.05 (d, *J* = 16.8 Hz, 1H), 2.51–2.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.1, 150.5, 150.3 (dd, *J* = 248.1, 11.6 Hz), 147.4 (dd, *J* = 253.6, 13.7 Hz), 129.6, 126.3, 121.4, 120.2 (d, *J* = 18.6 Hz), 119.8 (dd, *J* = 7.1, 3.5 Hz), 119.7, 115.0, 79.9, 58.5, 57.3, 48.8, 34.7; ^{19}F NMR (565 MHz, CDCl3) δ (ppm) –138.0, –141.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{21}H_{15}F_2NO_3Na^+$ 390.0912, found 390.0916.

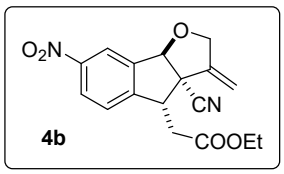
4. General procedure for the synthesis of cycloadducts 4a–f



General procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with *ortho*-formyl-substituted cinnamate **1** (0.10 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol % or 11.6 mg, 0.0100 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.14 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 5–24 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4a–f**.

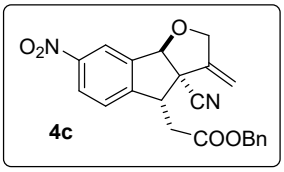


Synthesis of 4a by general procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with methyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1a** (23.5 mg, 0.100 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.140 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 5 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4a**: 29.0 mg, 92% yield, >20:1 dr, as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.29 (s, 1H), 8.23 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H), 5.66 (d, *J* = 1.8 Hz, 1H), 5.35 (d, *J* = 1.8 Hz, 1H), 4.65 (dt, *J* = 13.8, 1.8 Hz, 1H), 4.13 (dt, *J* = 13.8, 1.8 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 3.08 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.81 (dd, *J* = 17.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.0, 149.2, 148.9, 147.9, 140.4, 125.7, 125.5, 121.1, 118.9, 111.4, 90.4, 70.5, 54.4, 52.3, 49.6, 38.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{16}H_{14}N_2O_5Na^+$ 337.0795, found 337.0803.

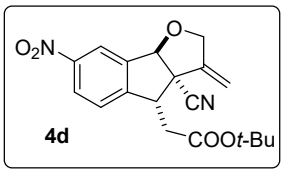


Synthesis of 4b by general procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with ethyl (*E*)-

3-(2-formyl-4-nitrophenyl)acrylate **1b** (25.0 mg, 0.100 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.140 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 5 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4b**: 30.9 mg, 94% yield, >20:1 dr, as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.29 (s, 1H), 8.23 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H), 5.66 (s, 1H), 5.35 (s, 1H), 4.65 (d, *J* = 13.8 Hz, 1H), 4.26–4.18 (m, 2H), 4.13 (d, *J* = 13.2 Hz, 1H), 4.07 (t, *J* = 7.2 Hz, 1H), 3.07 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.79 (dd, *J* = 17.4, 6.6 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.6, 149.3, 148.9, 147.9, 140.4, 125.7, 125.5, 121.1, 119.0, 111.4, 90.5, 70.5, 61.5, 54.4, 49.6, 38.7, 14.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{16}N_2O_5Na^+$ 351.0951, found 351.0954.

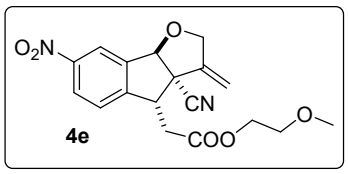


Synthesis of 4c by general procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with benzyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1c** (31.1 mg, 0.100 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.140 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 5 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4c**: 36.6 mg, 94% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.24 (s, 1H), 8.14 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.37–7.32 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.97 (s, 1H), 5.61 (s, 1H), 5.32 (s, 1H), 5.17 (dd, *J* = 32.4, 12.0 Hz, 2H), 4.63 (d, *J* = 13.2 Hz, 1H), 4.10 (d, *J* = 13.8 Hz, 1H), 4.05 (t, *J* = 6.6 Hz, 1H), 3.12 (dd, *J* = 16.8, 6.6 Hz, 1H), 2.84 (dd, *J* = 17.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.3, 149.0, 148.8, 147.9, 140.3, 135.1, 128.7, 128.7, 125.7, 125.5, 121.1, 119.0, 111.4, 90.4, 70.5, 67.3, 54.4, 49.6, 38.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}N_2O_5Na^+$ 413.1108, found 413.1116.

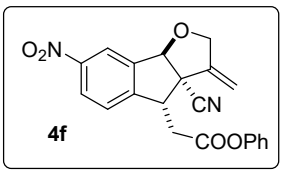


Synthesis of 4d by general procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with *tert*-butyl (*E*)-3-(2-formyl-4-nitrophenyl)acrylate **1d** (27.7 mg, 0.100 mmol, 1.0

equiv), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.140 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 5 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4d**: 29.2 mg, 82% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 1H), 8.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 5.98 (s, 1H), 5.67 (s, 1H), 5.33 (s, 1H), 4.64 (dt, *J* = 13.2, 2.4 Hz, 1H), 4.13 (dt, *J* = 13.8, 2.4 Hz, 1H), 4.04 (t, *J* = 6.9 Hz, 1H), 2.99 (dd, *J* = 16.8, 6.6 Hz, 1H), 2.69 (dd, *J* = 17.4, 7.2 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.8, 149.7, 148.8, 148.0, 140.3, 125.7, 125.4, 121.0, 119.1, 111.4, 90.5, 82.2, 70.5, 54.4, 49.7, 39.9, 28.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{20}N_2O_5Na^+$ 379.1264, found 379.1270.



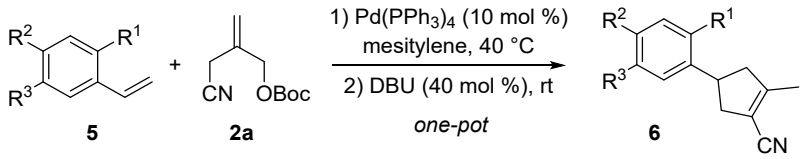
Synthesis of 4e by general procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-methoxyethyl (*Z*)-3-(2-formyl-4-nitrophenyl)acrylate **1e** (27.9 mg, 0.100 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.140 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 5 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4e**: 31.9 mg, 89% yield, >20:1 dr, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.21 (d, *J* = 2.4 Hz, 1H), 8.15 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 5.95 (s, 1H), 5.68–5.50 (m, 1H), 5.34–5.21 (m, 1H), 4.57 (dt, *J* = 13.8, 2.4 Hz, 1H), 4.27–4.19 (m, 2H), 4.05 (dt, *J* = 13.8, 2.4 Hz, 1H), 4.00 (t, *J* = 6.6 Hz, 1H), 3.59–3.45 (m, 2H), 3.31 (s, 3H), 3.05 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.79 (dd, *J* = 17.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.5, 149.1, 148.9, 147.9, 140.4, 125.8, 125.5, 121.1, 119.0, 111.4, 90.4, 70.5, 70.2, 64.3, 59.0, 54.4, 49.6, 38.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{18}N_2O_6Na^+$ 381.1057, found 381.1065.



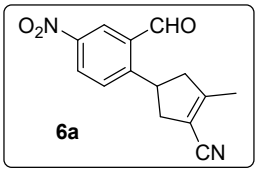
Synthesis of 4f by general procedure B: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-phenyl (*Z*)-3-(2-formyl-4-nitrophenyl)acrylate **1f** (29.7 mg, 0.100 mmol, 1.0 equiv),

$Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol %) and **C6** (9.6 mg, 0.020 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (2.0 mL) and TMM donor **2a** (27.6 mg, 0.140 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 24 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4f**: 27.0 mg, 72% yield, >20:1 dr**,** as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 8.26 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.29–7.24 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.08 (s, 1H), 5.70 (d, *J* = 1.8 Hz, 1H), 5.35 (d, *J* = 1.8 Hz, 1H), 4.65 (dt, *J* = 13.8, 1.8 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 1H), 4.12 (dt, *J* = 13.8, 2.4 Hz, 1H), 3.31 (dd, *J* = 17.4, 7.2 Hz, 1H), 3.11 (dd, *J* = 17.4, 6.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.5, 150.3, 149.0, 148.8, 147.9, 140.6, 129.7, 126.4, 125.7, 125.6, 121.4, 121.2, 119.2, 111.7, 90.6, 70.4, 54.2, 49.9, 38.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{21}H_{16}N_2O_5Na^+$ 399.0951, found 399.0954.

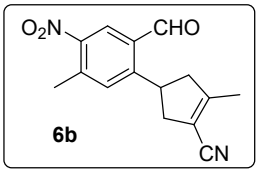
5. General procedure for synthesis of cycloadducts 6a–f



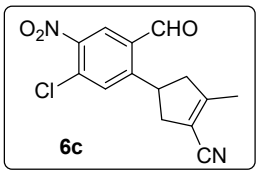
General procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with substituted styrene **5** (0.10 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.20 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6a–f**.



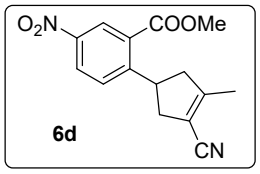
Synthesis of 6a by general procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 5-nitro-2-vinylbenzaldehyde **5a** (17.7 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.200 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After full conversion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6a**: 24.3 mg, 95% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.27 (s, 1H), 8.66 (d, J = 2.4 Hz, 1H), 8.41 (dd, J = 8.4, 2.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 4.78–4.56 (m, 1H), 3.25–3.14 (m, 1H), 3.10 (dd, J = 18.6, 9.6 Hz, 1H), 2.80–2.66 (m, 1H), 2.62–2.48 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 190.6, 159.2, 153.7, 146.9, 134.2, 128.6, 128.5, 128.3, 116.0, 107.4, 46.0, 41.7, 36.9, 16.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{14}H_{12}O_2N_3Na^+$ 279.0740, found 279.0750.



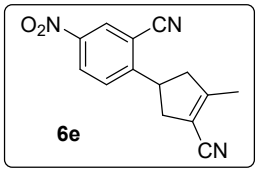
Synthesis of 6b by general procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 4-methyl-5-nitro-2-vinylbenzaldehyde **5b** (19.1 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.200 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After full conversion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6b**: 18.6 mg, 69% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.17 (s, 1H), 8.45 (s, 1H), 7.33 (s, 1H), 4.75–4.60 (m, 1H), 3.21–3.11 (m, 1H), 3.06 (dd, *J* = 18.6, 9.0 Hz, 1H), 2.77–2.72 (m, 1H), 2.71 (s, 3H), 2.57–2.47 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 190.4, 159.3, 151.5, 147.6, 140.2, 132.3, 132.1, 130.6, 116.1, 107.4, 45.9, 41.5, 36.7, 21.3, 16.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{14}O_2N_3Na^+$ 293.0897, found 293.0910.



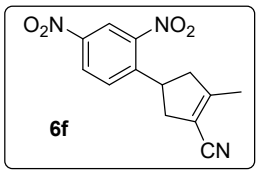
Synthesis of 6c by general procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 4-chloro-5-nitro-2-vinylbenzaldehyde **5c** (21.1 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.200 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After full conversion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6c**: 24.5 mg, 84% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.18 (s, 1H), 8.38 (s, 1H), 7.54 (s, 1H), 4.71–4.60 (m, 1H), 3.21–3.14 (m, 1H), 3.08 (dd, *J* = 18.6, 9.6 Hz, 1H), 2.76–2.68 (m, 1H), 2.60–2.50 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 189.3, 159.1, 152.1, 133.3, 132.5, 131.3, 130.8, 115.8, 107.4, 78.9, 45.7, 41.5, 36.6, 16.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{14}H_{11}{}^{35}ClO_2N_3Na^+$ 313.0351, found 313.0359; Calcd. for $C_{14}H_{11}{}^{37}ClO_2N_3Na^+$ 315.0321, found 315.0342.



Synthesis of 6d by general procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with methyl 5-nitro-2-vinylbenzoate **5d** (20.7 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.200 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After full conversion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6d**: 24.3 mg, 85% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.69 (d, *J* = 2.4 Hz, 1H), 8.32 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 4.68–4.48 (m, 1H), 3.97 (s, 3H), 3.26–3.11 (m, 1H), 3.07 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.77–2.67 (m, 1H), 2.63–2.48 (m, 1H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.1, 159.4, 153.6, 146.1, 130.9, 128.2, 126.8, 125.7, 116.1, 107.5, 52.9, 46.5, 42.3, 38.1, 16.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{14}N_2O_4Na^+$ 309.0846, found 309.0852.

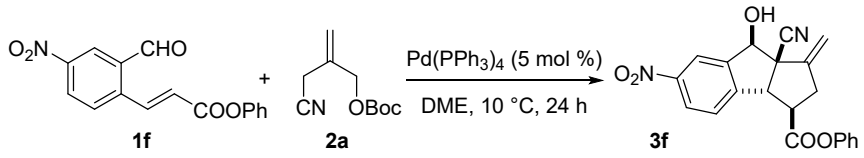


Synthesis of 6e by general procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 5-nitro-2-vinylbenzonitrile **5e** (17.4 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.200 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After full conversion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6c**: 24.7 mg, 98% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 2.4 Hz, 1H), 8.43 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 4.19–4.09 (m, 1H), 3.30–3.19 (m, 1H), 3.19–3.10 (m, 1H), 2.84–2.69 (m, 1H), 2.65–2.55 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 158.9, 155.3, 146.6, 128.2, 128.1, 128.0, 115.7, 115.6, 113.6, 107.4, 45.6, 41.5, 40.4, 16.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{14}H_{11}N_3O_2Na^+$ 276.0743, found 276.0744.



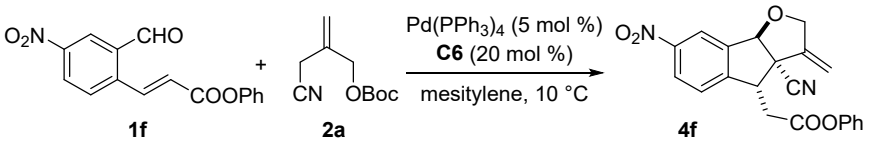
Synthesis of 6f by general procedure C: An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2,4-dinitro-1-vinylbenzene **5f** (19.4 mg, 0.100 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (1.0 mL) and TMM donor **2a** (39.4 mg, 0.200 mmol, 2.0 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 40 °C for 10 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After full conversion, the mixture was cooled to room temperature, and DBU (6.0 μL, 0.039 mmol, 40 mol %) was directly added and stirred for 10 min, monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **6f**: 26.2 mg, 96% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.67 (d, J = 2.4 Hz, 1H), 8.43 (dd, J = 9.0, 2.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 4.19–4.04 (m, 1H), 3.26–3.19 (m, 1H), 3.14 (dd, J = 18.6, 9.6 Hz, 1H), 2.89–2.69 (m, 1H), 2.69–2.54 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 159.0, 149.5, 146.5, 146.2, 129.4, 127.4, 119.9, 115.7, 107.4, 46.2, 42.0, 37.0, 16.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{13}H_{12}N_3O_4^+$ 274.0822, found 274.0828.

6. Synthesis of cycloadducts 3f on a 1.0 mmol scale



An oven-dried 50 mL sealed tube equipped with a septum and a magnetic stir bar was charged with 2-phenyl (*Z*)-3-(2-formyl-4-nitrophenyl)acrylate **1f** (297.0 mg, 1.000 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (58.0 mg, 0.0500 mmol, 5 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous DME (10.0 mL) and TMM donor **2a** (236.0 mg, 1.200 mmol, 1.2 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 24 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **3f**: 308.4 mg, 82% yield, >20:1 dr, as a colorless oil.

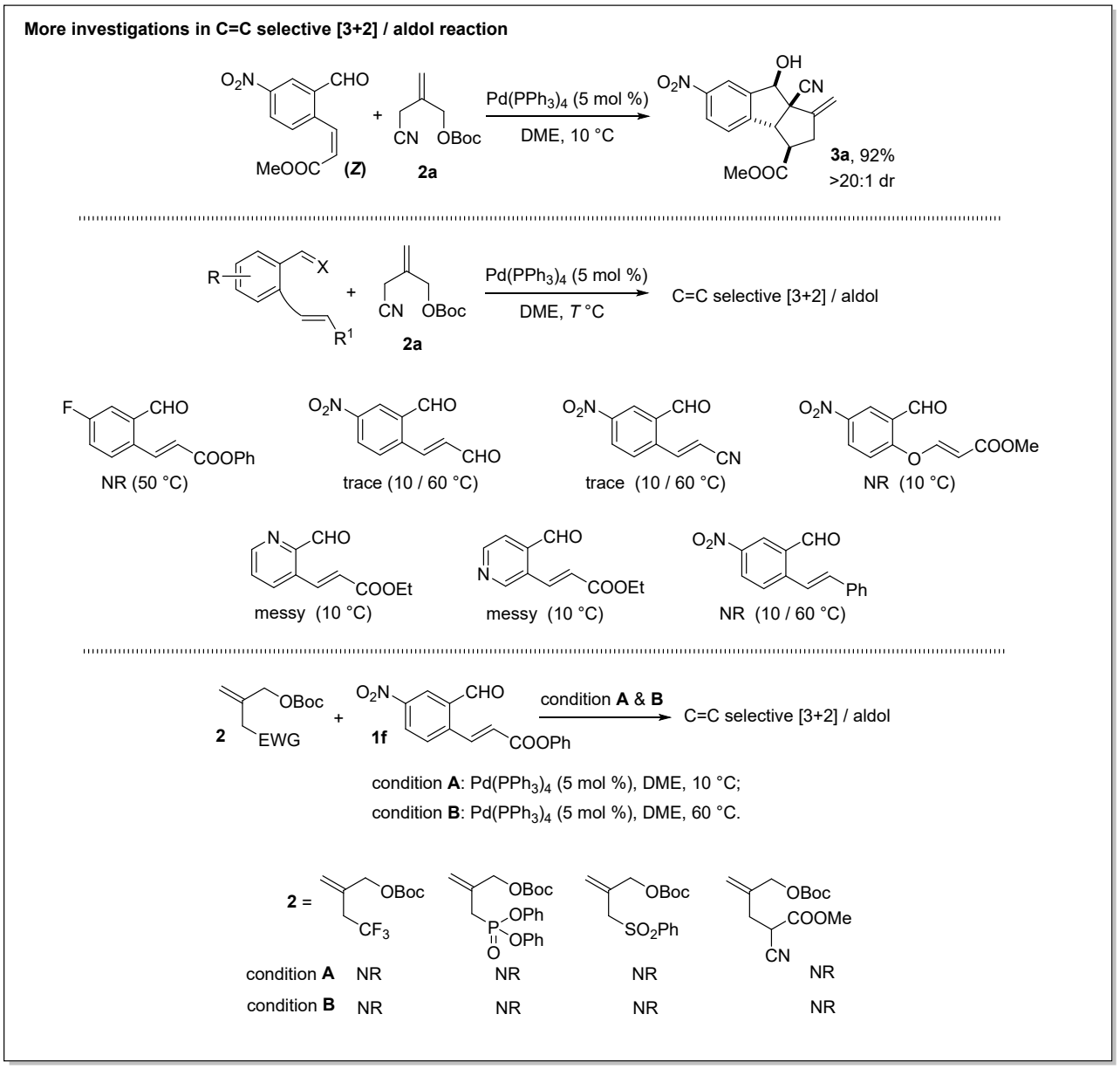
7. Synthesis of cycloadducts 4f on a 1.0 mmol scale



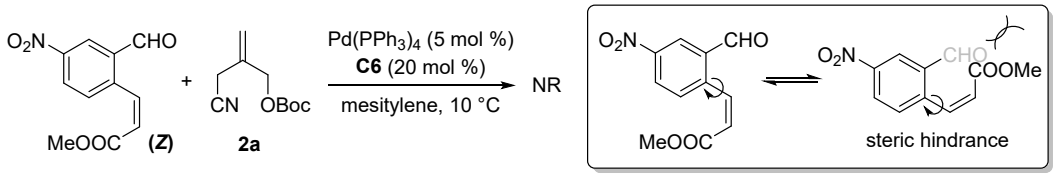
An oven-dried 50 mL sealed tube equipped with a septum and a magnetic stir bar was charged with 2-phenyl (*Z*)-3-(2-formyl-4-nitrophenyl)acrylate **1f** (297.0 mg, 1.000 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (58.0 mg, 0.0500 mmol, 5 mol %) and **C6** (96.0 mg, 0.200 mmol, 20 mol %). The tube was capped, evacuated and back-filled with nitrogen for three times. Then degassed anhydrous mesitylene (20.0 mL) and TMM donor **2a** (276.0 mg, 1.400 mmol, 1.4 equiv) were added via syringe in sequence, and the tube was evacuated and back-filled with nitrogen for three times again. The resulting mixture was stirred at 10 °C for 48 h, and monitored by TLC (petroleum ether/EtOAc = 6/1). After completion, the solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product **4f**: 270.7 mg, 64% yield, >20:1 d**r,** as a yellow oil.

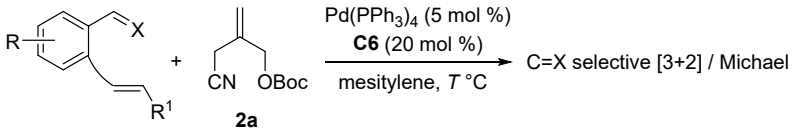
8. More substrate attempts

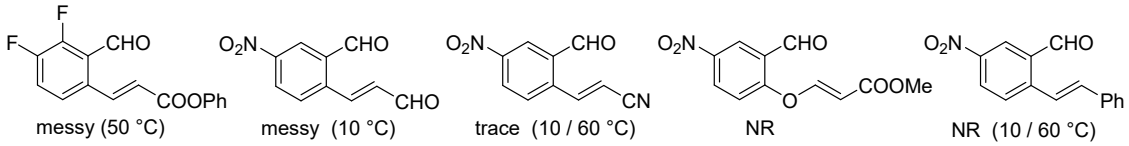
In order to further expand the substrate scope, (*Z*)-formyl cinnamate, more dielectrophiles, TMM donors and aryl ethylenes were investigated under the standard or optimal conditions.

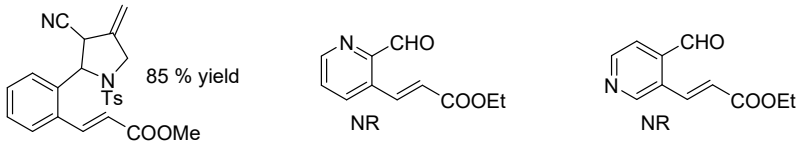


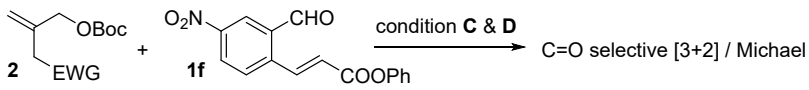
More investigations in C=O selective [3+2] / Michael reaction



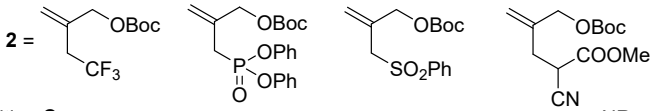






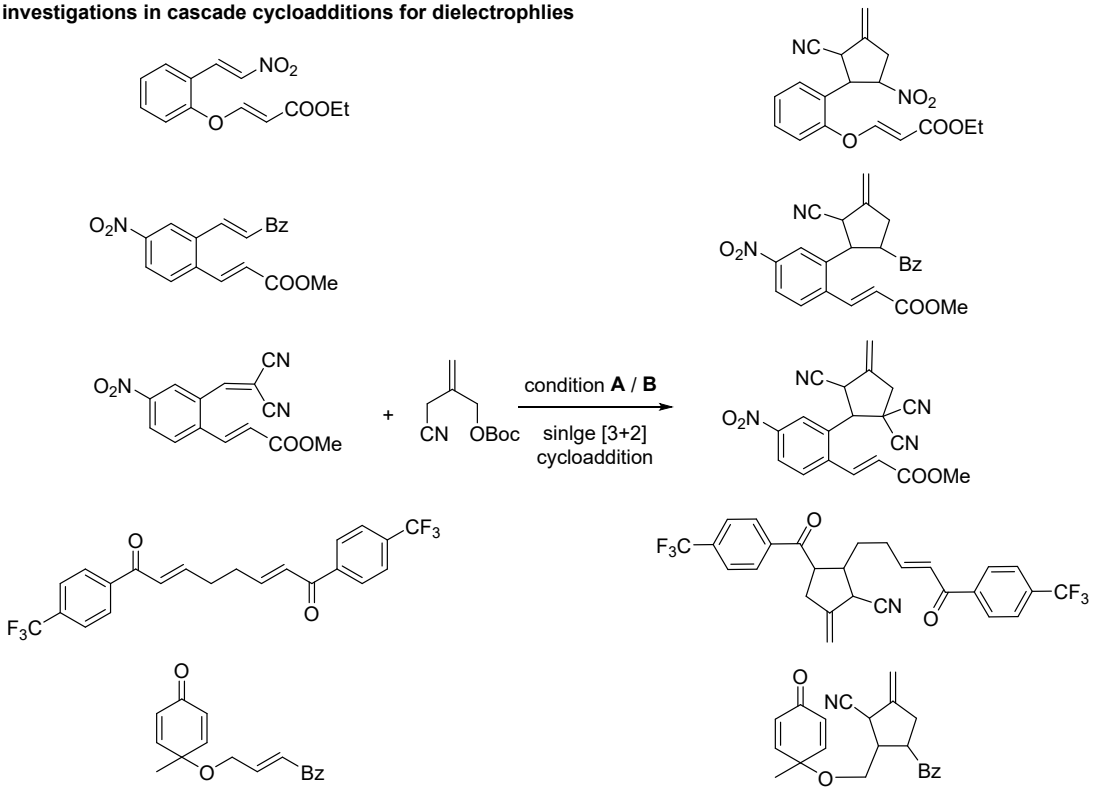


condition **C**: $Pd(PPh_3)_4$ (5 mol %), **C6** (20 mol %), mesitylene, 10 °C;
condition **D**: $Pd(PPh_3)_4$ (5 mol %), **C6** (20 mol %), mesitylene, 60 °C.



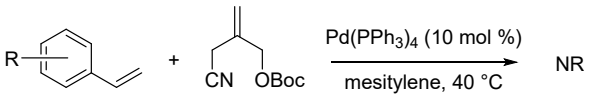
condition **C**	NR	NR	NR	NR
condition **D**	NR	NR	NR	NR

More investigations in cascade cycloadditions for dielectrophlies



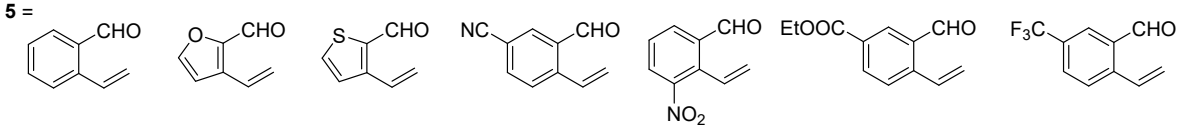
condition **A**: $Pd(PPh_3)_4$ (5 mol %), toluene, rt; condition **B**: $Pd(PPh_3)_4$ (5 mol %), toluene, 60 °C.

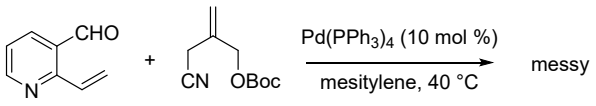
More investigations in Pd-TMM cycloadditions for aryl-substituted alkenes



5 **2a**

5 =

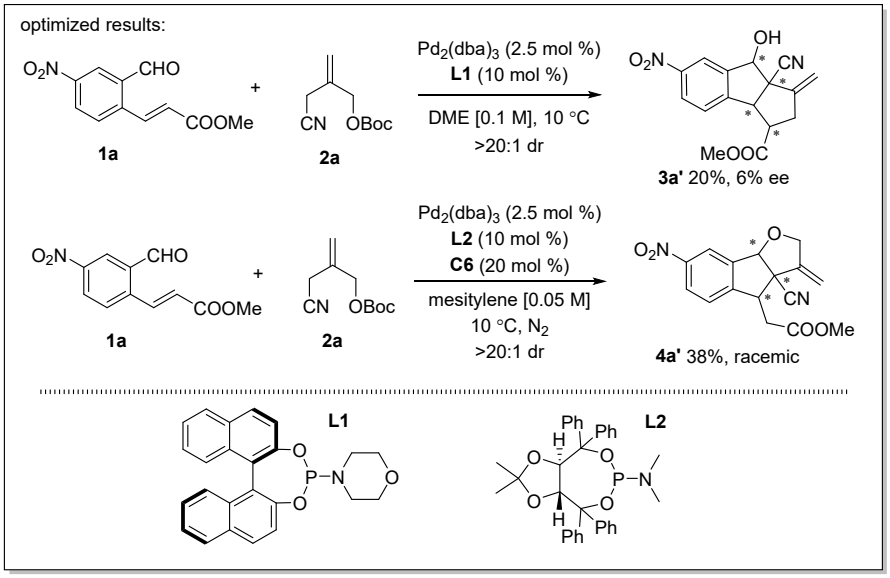




2a

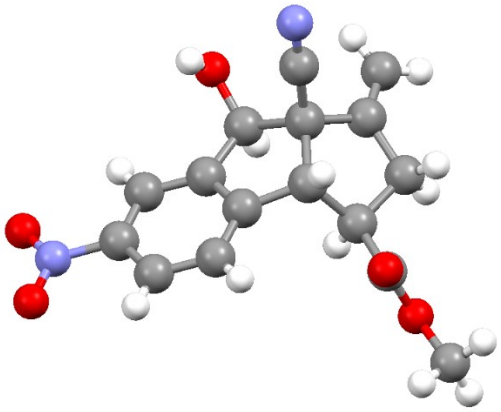
9. Asymmetric explorations

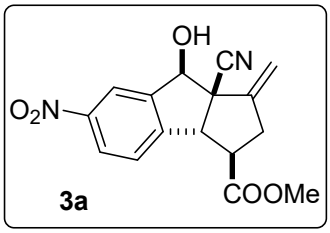
Great efforts have been devoted to investigating the asymmetric version of the cascade reactions. Unfortunately, there was barely enantiocontrol afforded employing commonly used chiral phosphines.



10. Crystal data and structural refinement

Procedure for the recrystallization of **3a**: To a 10 mL tube containing **3a** (20 mg) was added $CHCl_3$ (3.0 mL), which was kept aside overnight at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the configuration of **3a** (CCDC 2283650)





Identification code	**3a**	
Empirical formula	$C_{16}H_{14}N_2O_5$	
Formula weight	314.29	
Temperature	273 K	
Wavelength	1.54178	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.2559(10)	a= 90.558(7)
	b = 8.4217(11)	b= 110.791(7)
	c = 11.5815(15)	g = 98.454(7)
Volume	742.96(17)	
Z	2	
Density (calculated)	1.405 g/cm^3	
Absorption coefficient	0.892 mm^{-1}	
F(000)	328	
Crystal size	0.220 x 0.200 x 0.180 mm^3	
Theta range for data collection	5.322 to 67.136	
Index ranges	-9<=h<=9, -10<=k<=10, -13<=l<=13	
Reflections collected	7925	
Independent reflections	2548 [R(int) = 0.0458]	
Completeness to theta = 67.136	96.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	

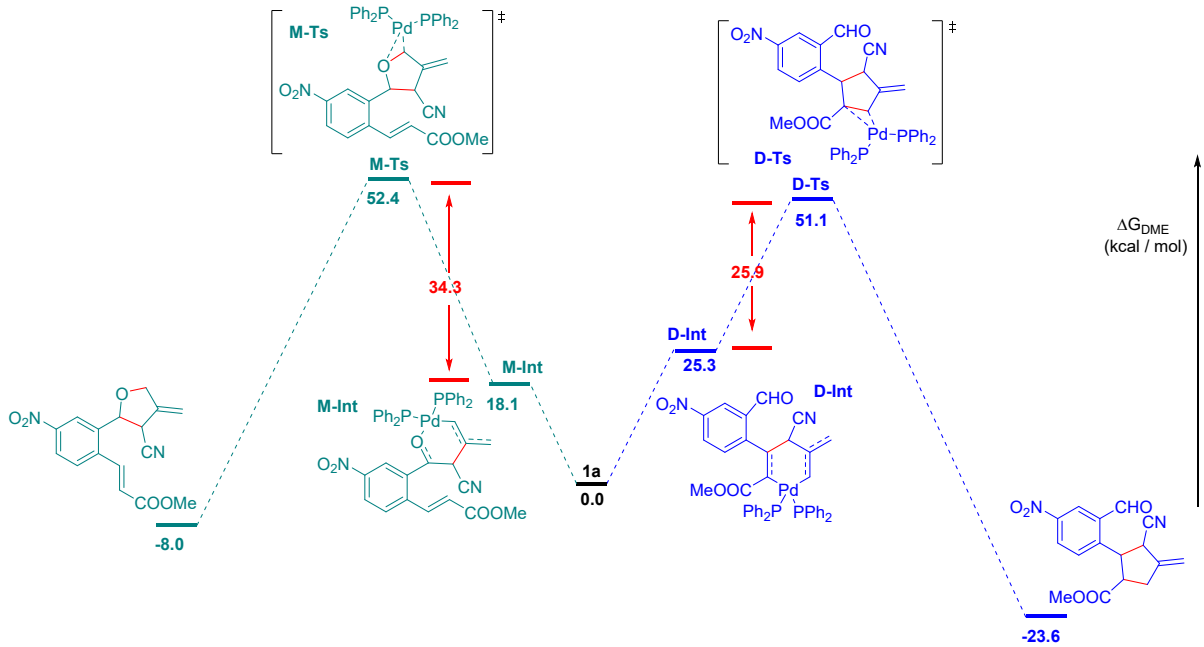
Data / restraints / parameters	2548/0/210
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	$R_1 = 0.0766$, $wR_2 = 0.2154$
R indices (all data)	$R_1 = 0.0952$, $wR_2 = 0.2378$
Extinction coefficient	n/a
Largest diff. peak and hole	0.448 and -0.396

11. Mechanism study

All structures were fully optimized using B3LYP functional in Gaussian16 [4]. Standard 6-31g(d) basis sets (The C=O-selective [3+2] cycloadditions in DME have been investigated at 6-311G(d,p)) were applied for the atoms except phosphorus (P) and palladium (Pd), which was described by relativistic effective core potential (ECP). Phosphorus and palladium were modified by Lanl2dz basis set, in which the secondary outer p functions of the standard Lanl2dz basis set were replaced with optimized ones and an *f* polarization function was added [5]. Normal coordinate analysis of each stationary point was performed to confirm whether the optimized geometry was a minima or a transition state, and to calculate zero-point energy and Gibbs free energy. Natural bond orbital (NBO) [6,7] calculations were performed to analyze how the charge distributes in the bonding and how it transfers in the reaction. In each elementary step, intrinsic reaction coordinate (IRC) [8] calculation was used to verify whether each TS connects the reactant and the product. The effect of solvent (DME) environment on catalytic process was evaluated using the solvation model based on density (SMD) [9] with its dielectric constant of 38.3. The free energy of each species in solution was deemed as the sum of the gas-phase free energy and the free energy of solvation.

11.1 C=O- and C=C-selectivity [3+2] cycloaddition in DME

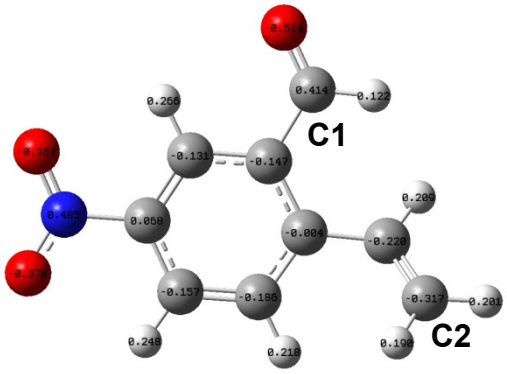
To elucidate high C=O selectivity for the [3+2] cycloaddition in DME, density functional theory (DFT) calculations were conducted. As depicted in the Scheme below, two pathways were proposed and calculated, including C=O selective addition (green line) and C=C selective addition (blue line).

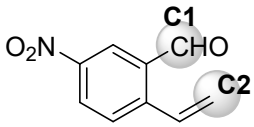


The energy barrier for the C=O-selective [3+2] process from **1a** to **M-Ts** is 52.4 kcal mol^{-1}, in

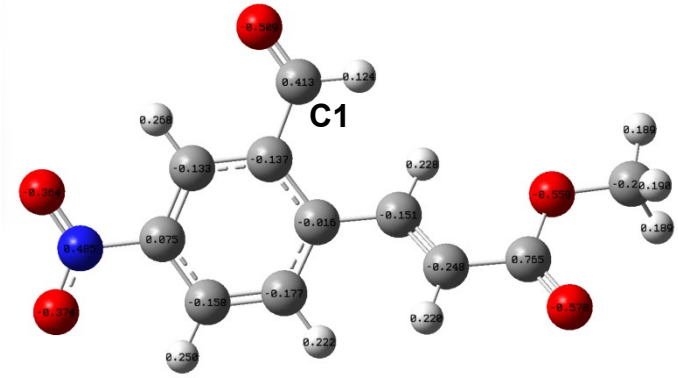
C=C-selective process, from **1a** to **D-Ts** is 51.1 kcal mol^{-1}. In addition, a lower free energy (25.9 kcal mol^{-1} vs 34.3 kcal mol^{-1}) was observed via **D-Int** to form **D-Ts**. These results demonstrate that the C=O [3+2] process is more favorable in the solvent.

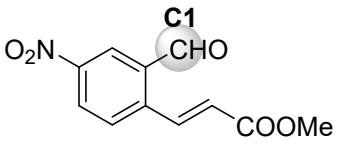
11.2 NBO charge analysis of the substrates and intermediates



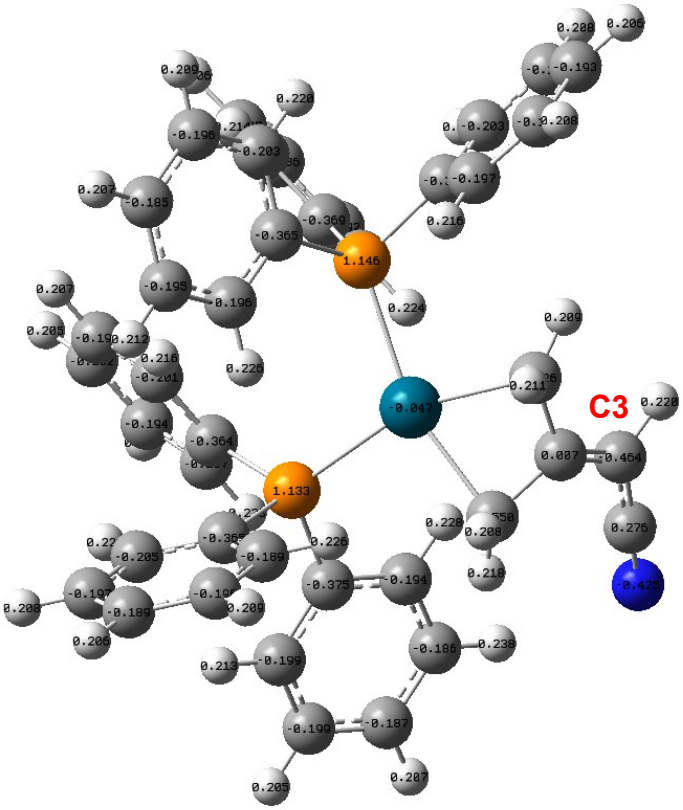


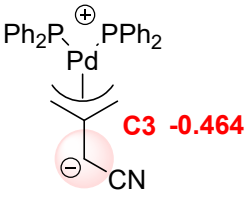
5a



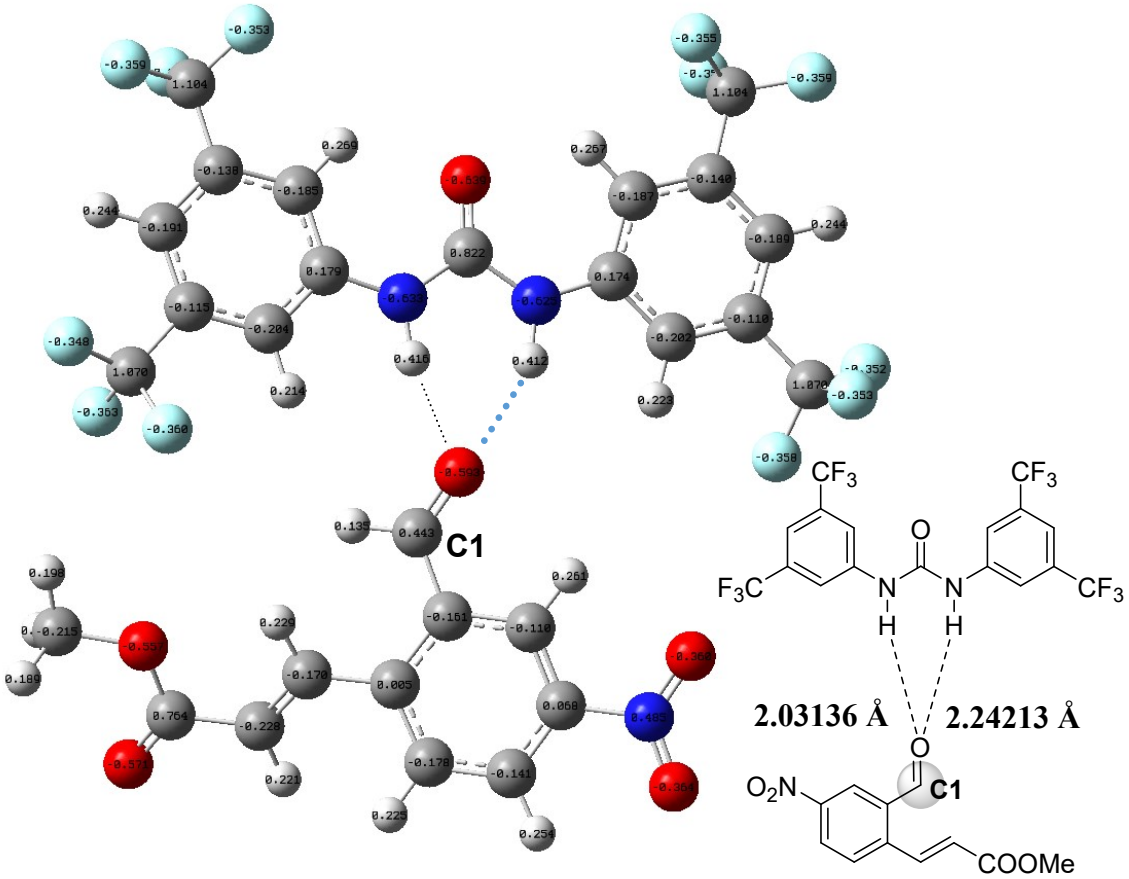


1a



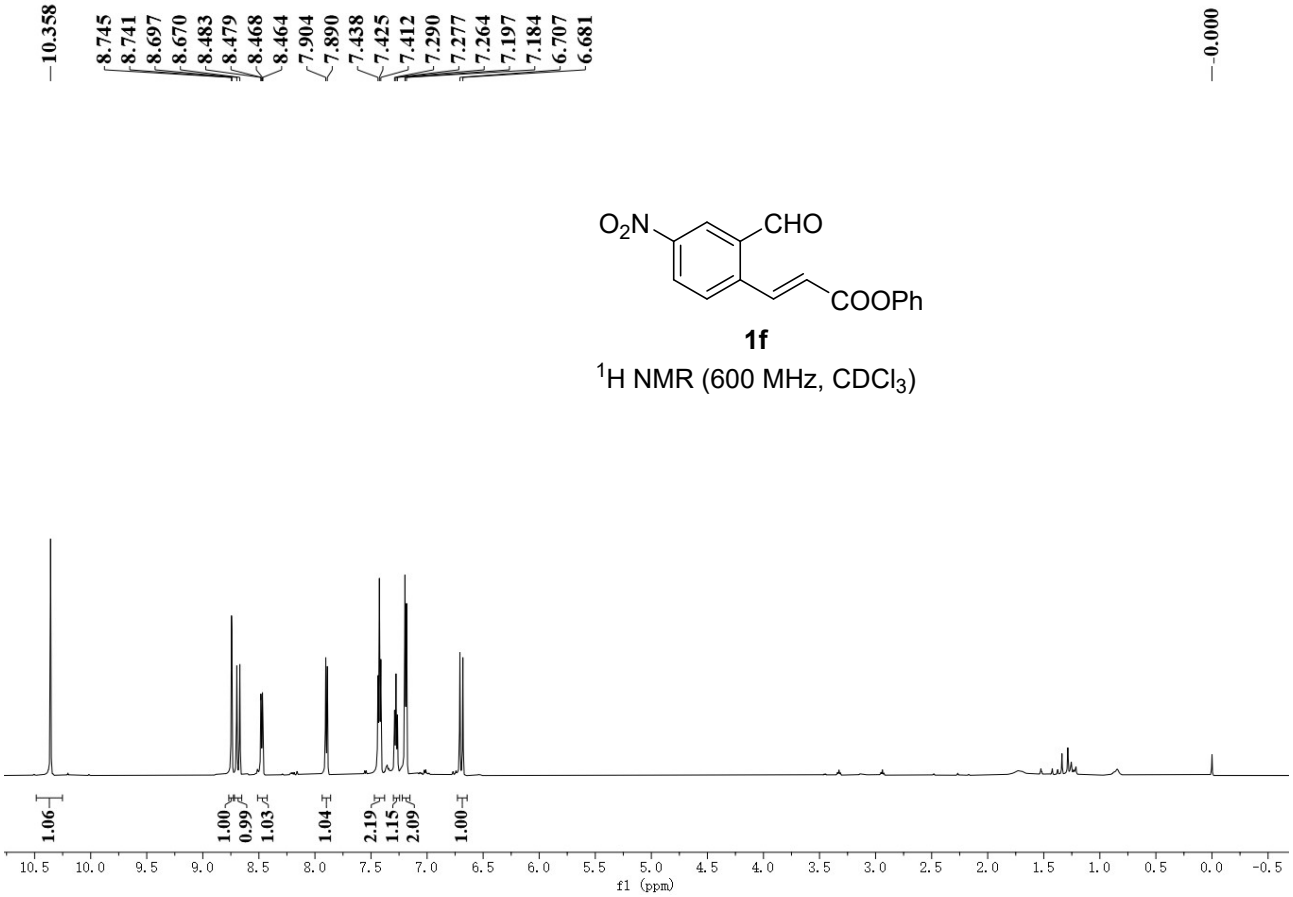


Pd-TMM dipole



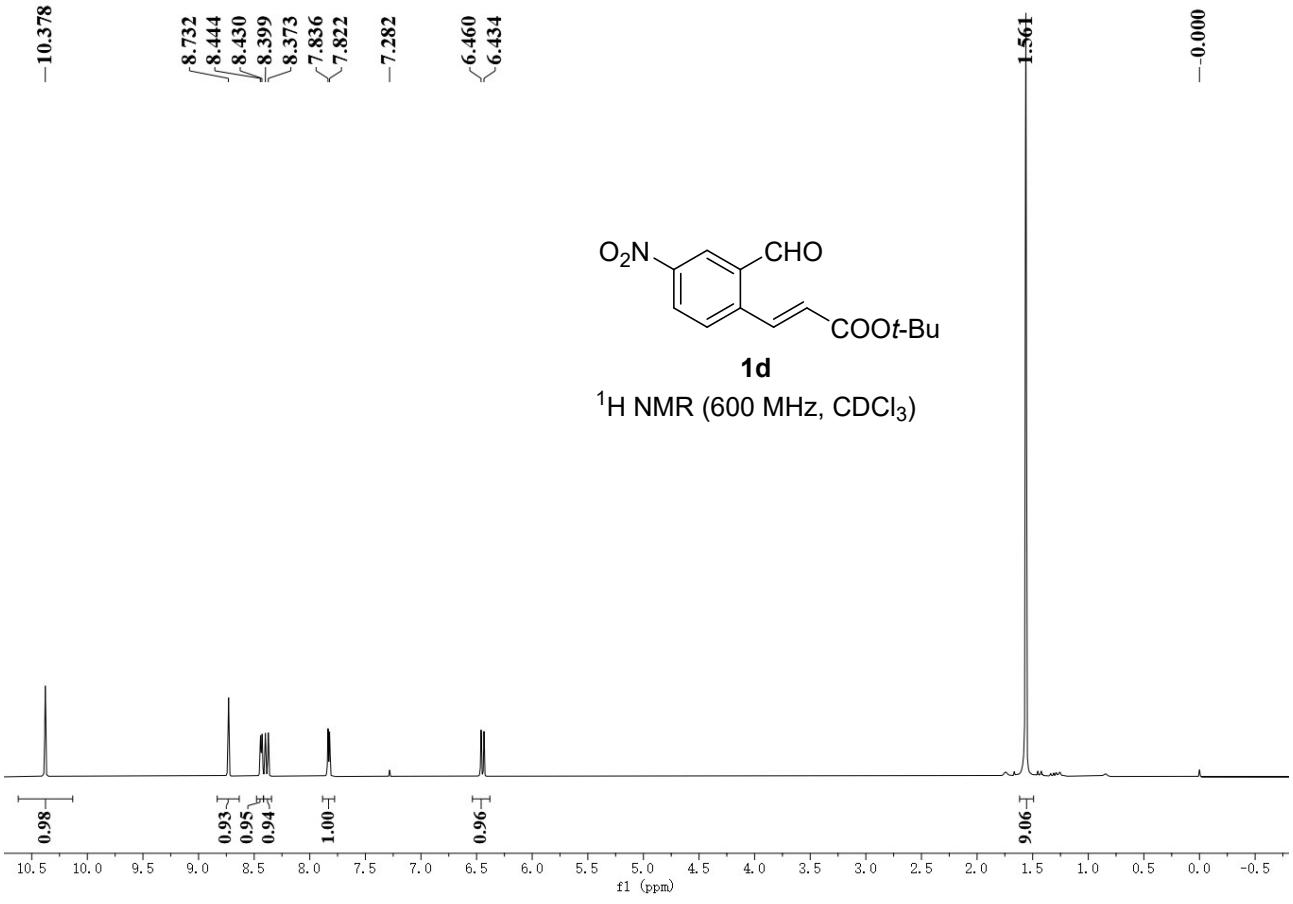
NBO charge analysis revealed that the soft carbon nucleophile **C3** preferentially attacks at the soft electrophile **C2**. Moreover, *ortho*-formyl cinnamate **1a** combined with urea **C8** via O···H–N hydrogen bond, which could drive the charge transferred from **C1** to oxygen atom, and thus enhanced the C=O-selectivity.

11.3 ^{1}H NMR mechanistic experiments



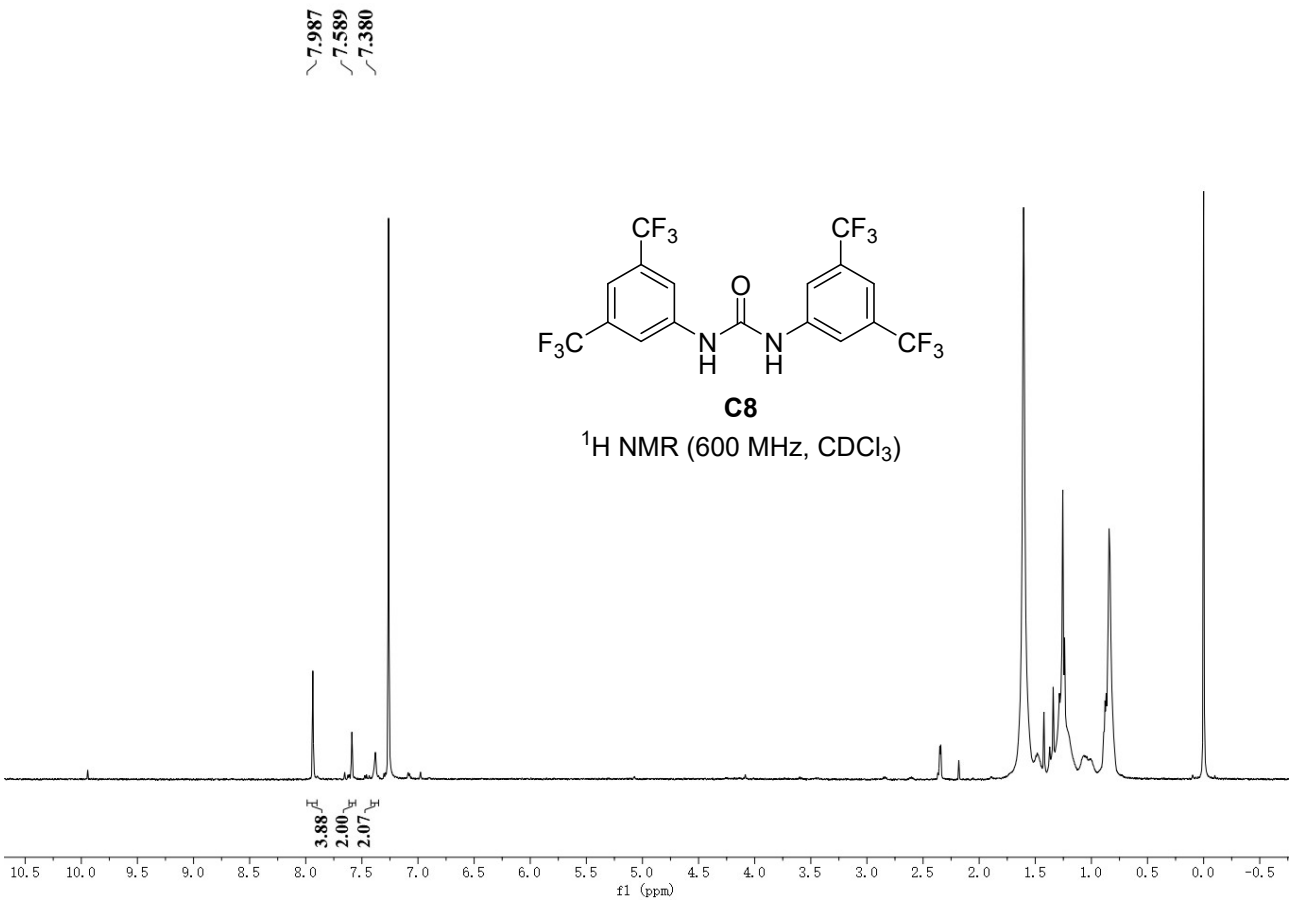
1f

^{1}H NMR (600 MHz, $CDCl_3$)



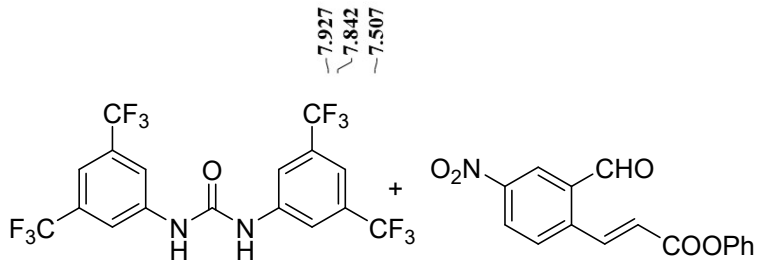
1d

^{1}H NMR (600 MHz, $CDCl_3$)



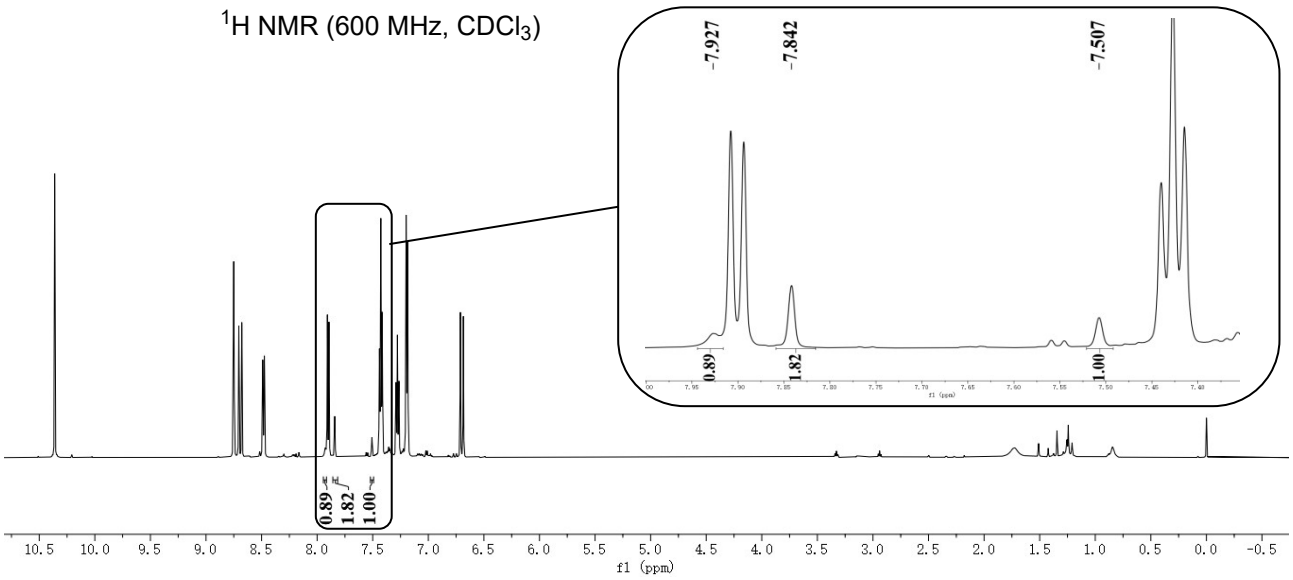
C8

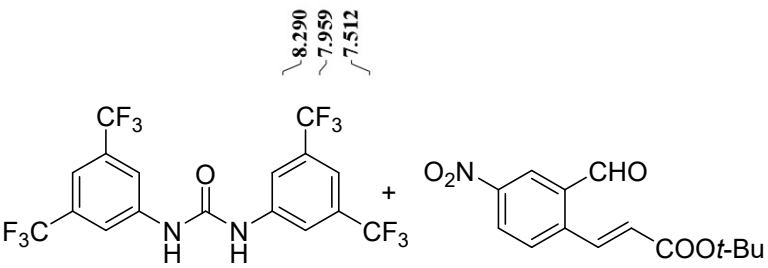
^{1}H NMR (600 MHz, $CDCl_3$)



C8 (20 mol %) **1f** (1.0 equiv)

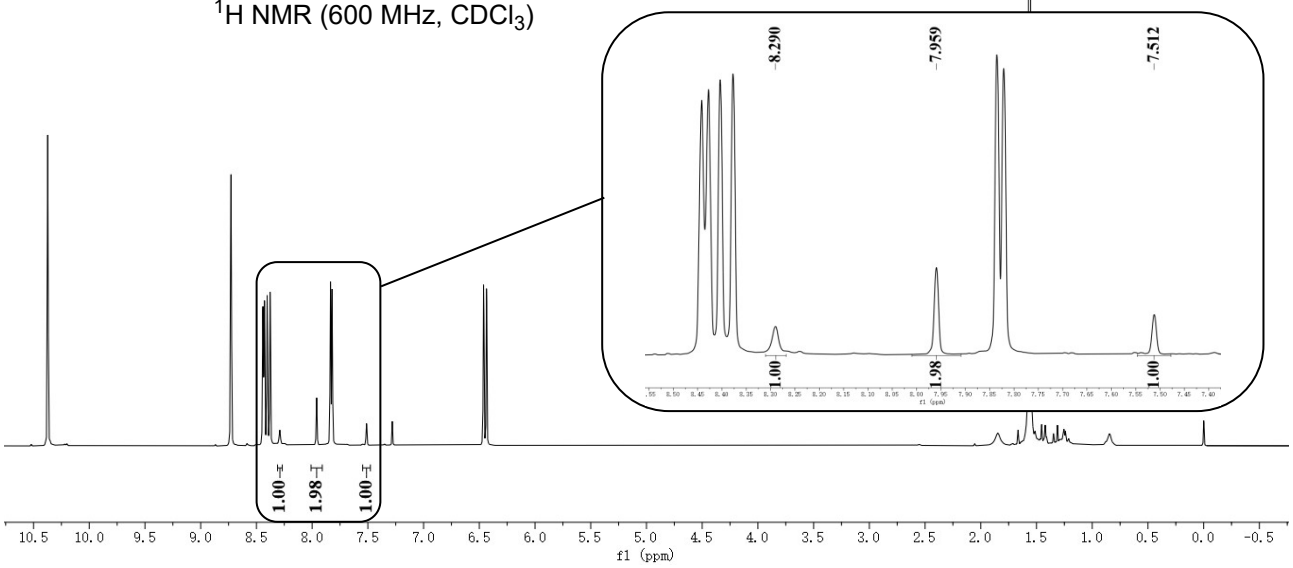
^{1}H NMR (600 MHz, $CDCl_3$)





C8 (20 mol %) **1d** (1.0 equiv)

^{1}H NMR (600 MHz, $CDCl_3$)



12. References

[1] (a) S.Y. Liang, B. Jiang, B.X. Xiao. et al., ChemCatChem 12 (2020) 5374-5377. (b) B. Jiang, B.X. Xiao, Q. Ouyang. et al., Org. Lett. 21 (2019) 3310-3313.

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[4] M.J. Frish, G.W. Trucks, H.B. Schlegel, et al., Gaussian 16, Revision C.01, Gaussian. Inc., Wallingford CT, 2016.

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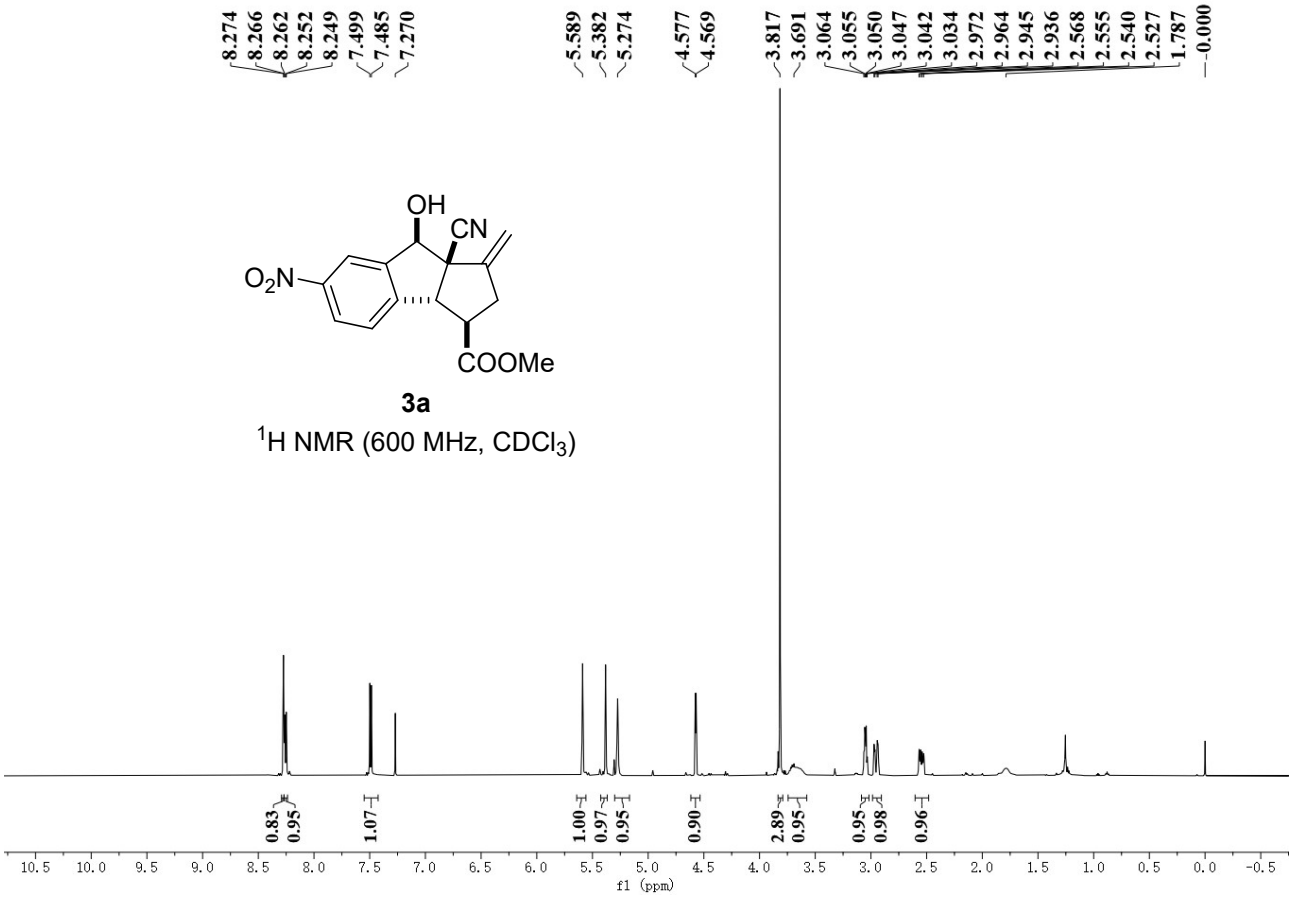
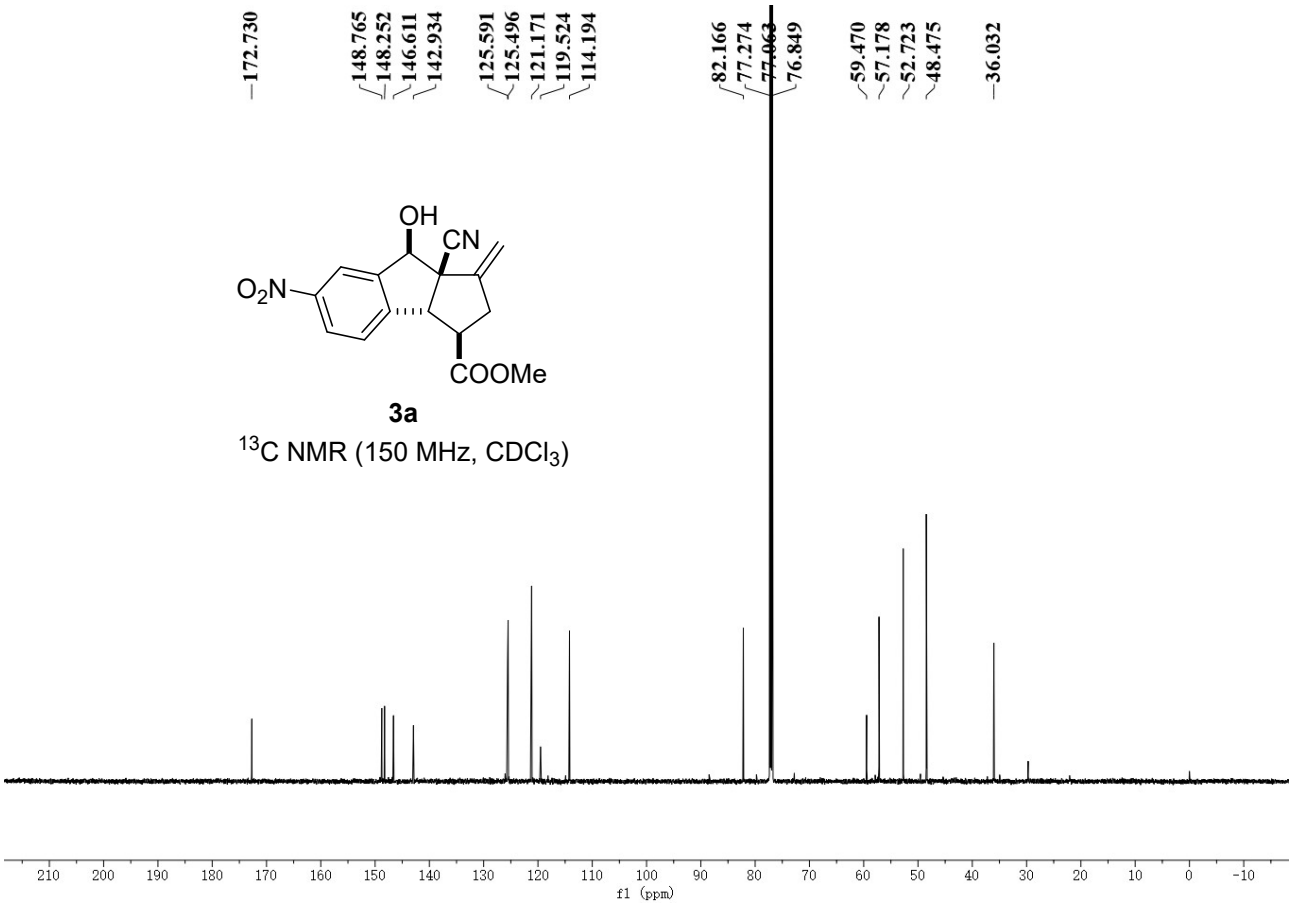
[9] A.V. Marenich, C.J. Cramer, D.G. Truhla, J. Phys. Chem. B 113 (2009) 6378-6396.

13. NMR and HRMS spectra



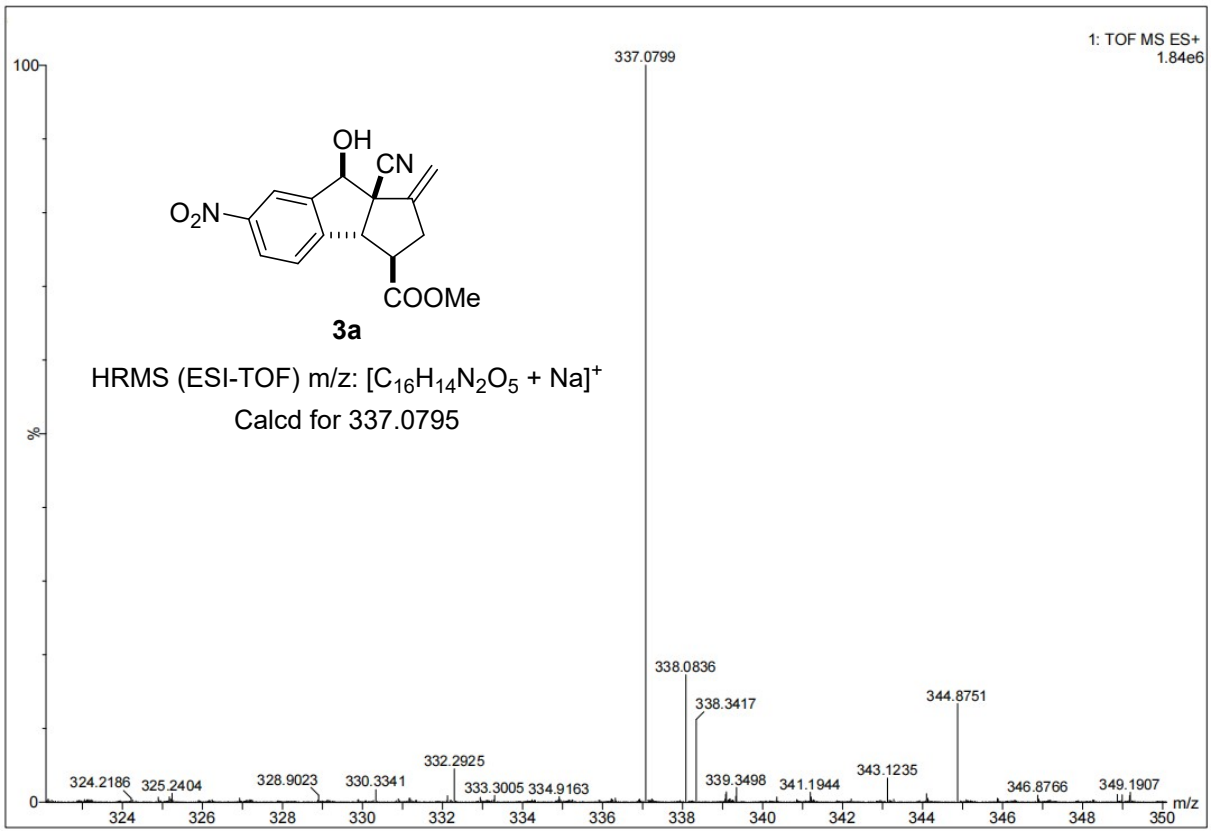
3a

^{1}H NMR (600 MHz, $CDCl_3$)



3a

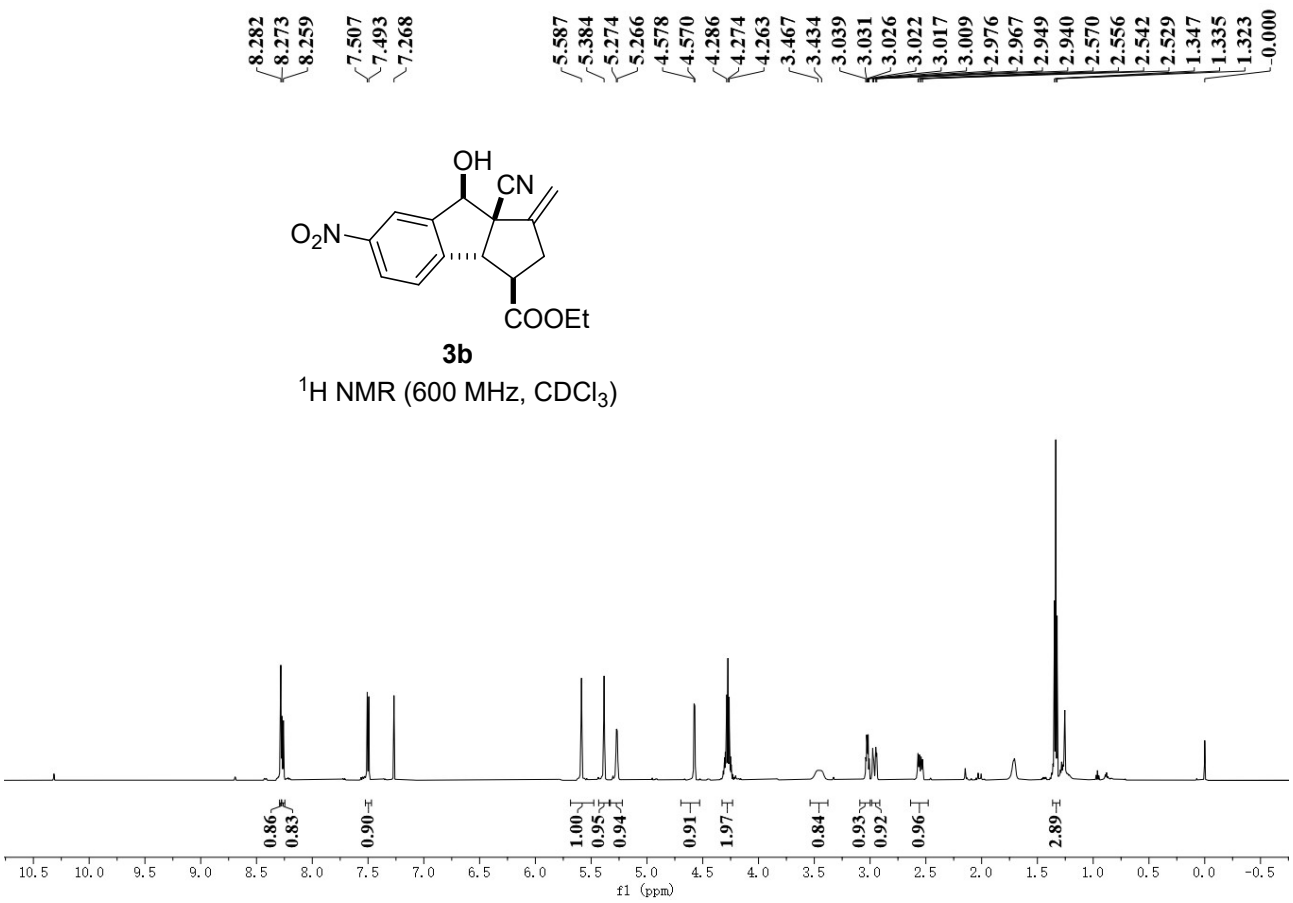
^{13}C NMR (150 MHz, $CDCl_3$)



3a

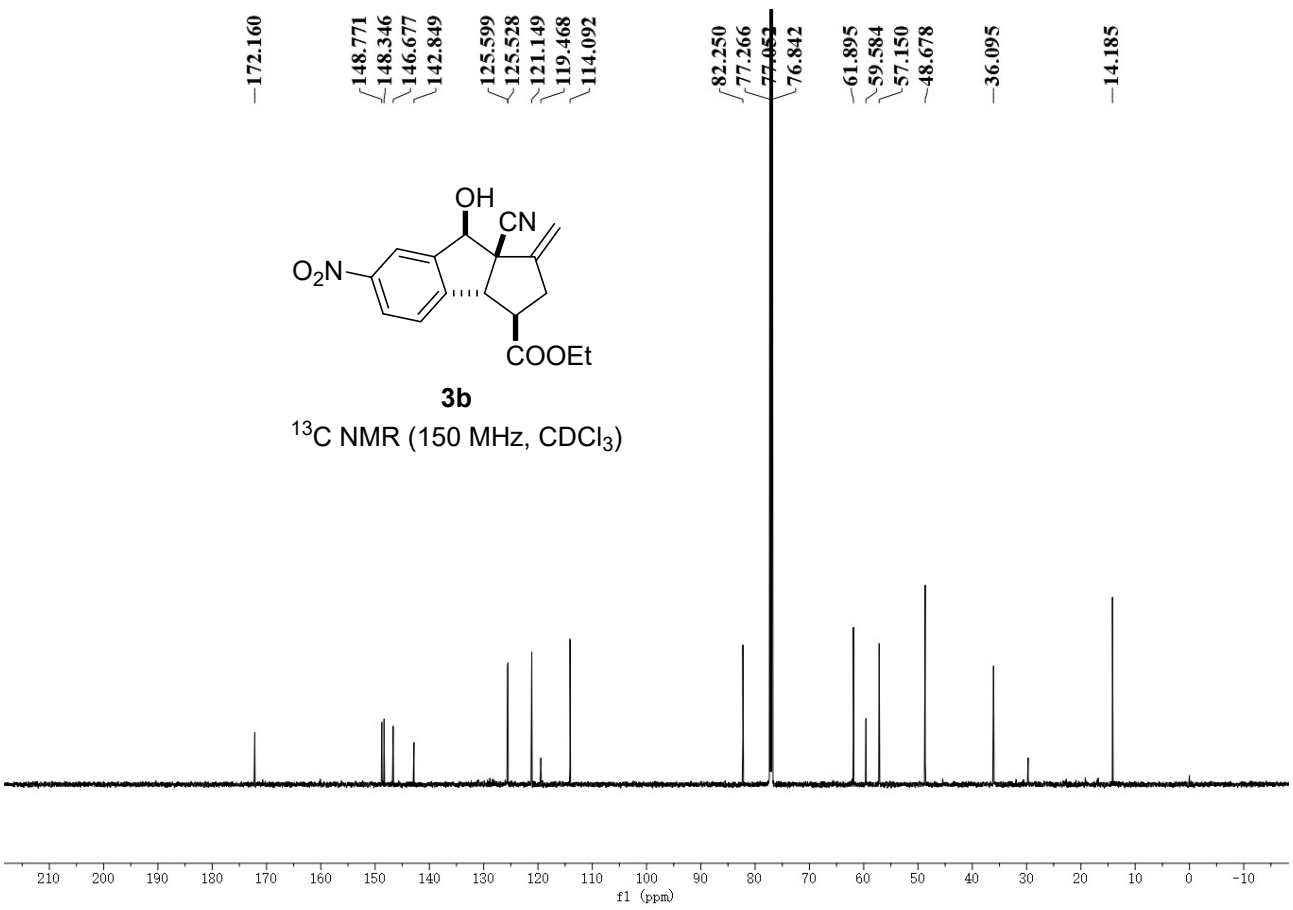
HRMS (ESI-TOF) m/z: $[C_{16}H_{14}N_2O_5 + Na]^+$

Calcd for 337.0795



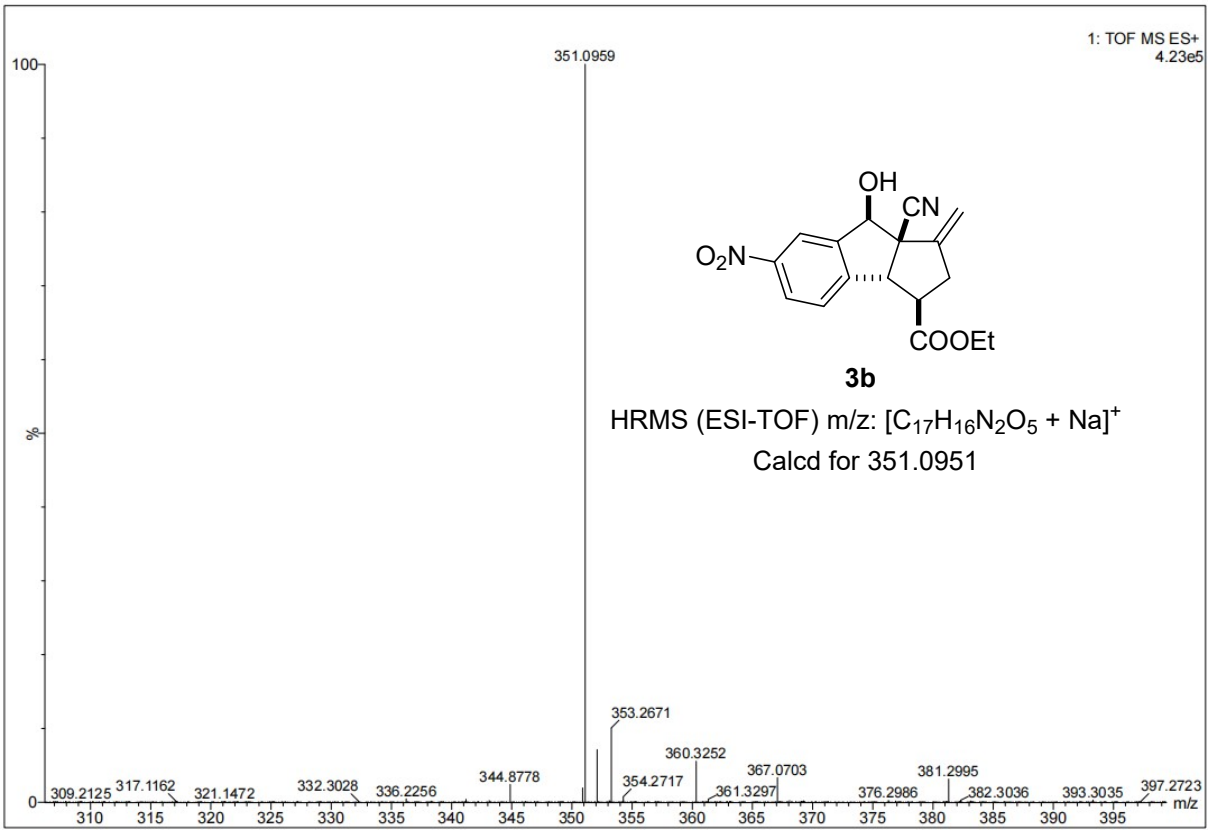
3b

^{1}H NMR (600 MHz, $CDCl_3$)



3b

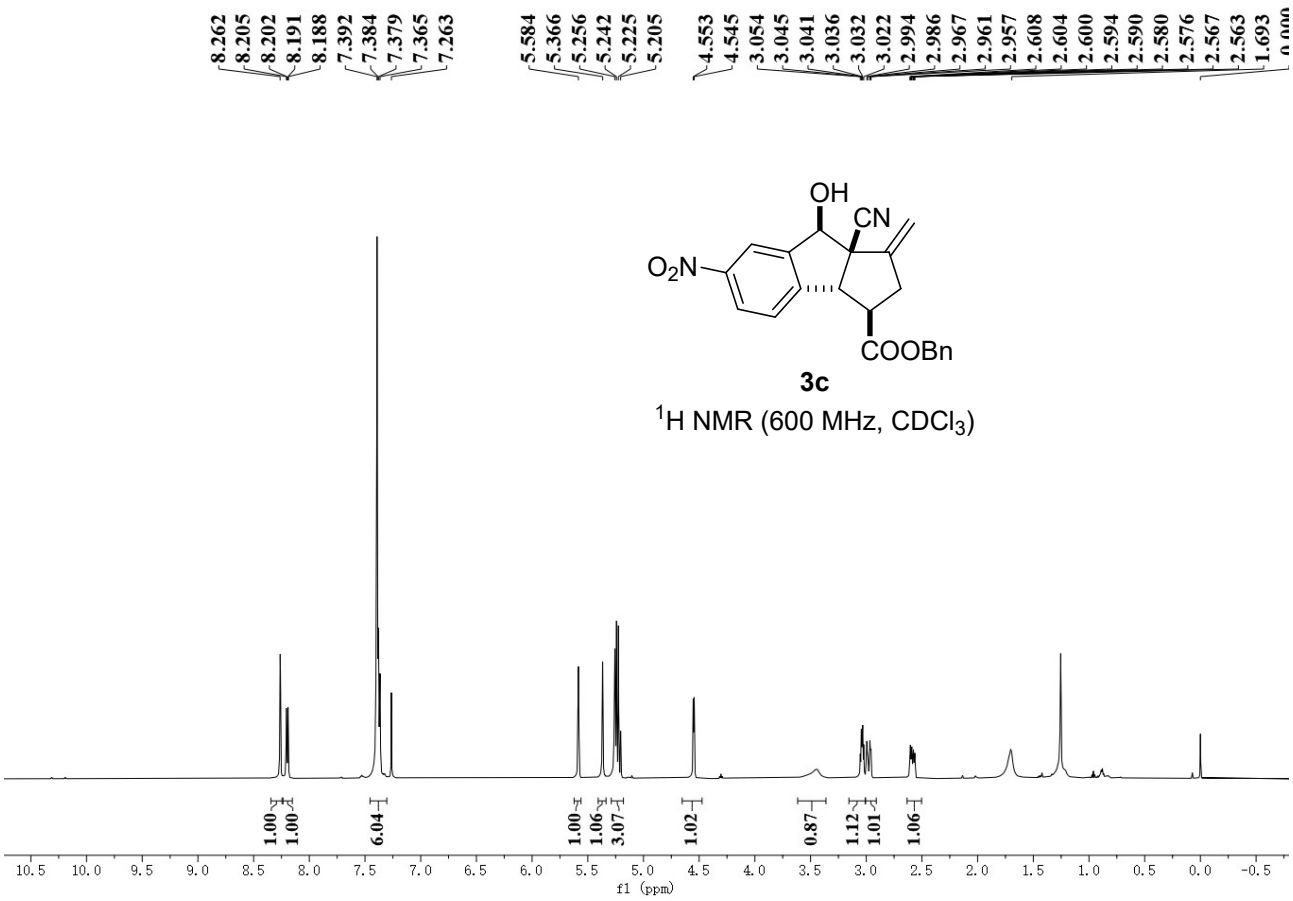
^{13}C NMR (150 MHz, $CDCl_3$)



3b

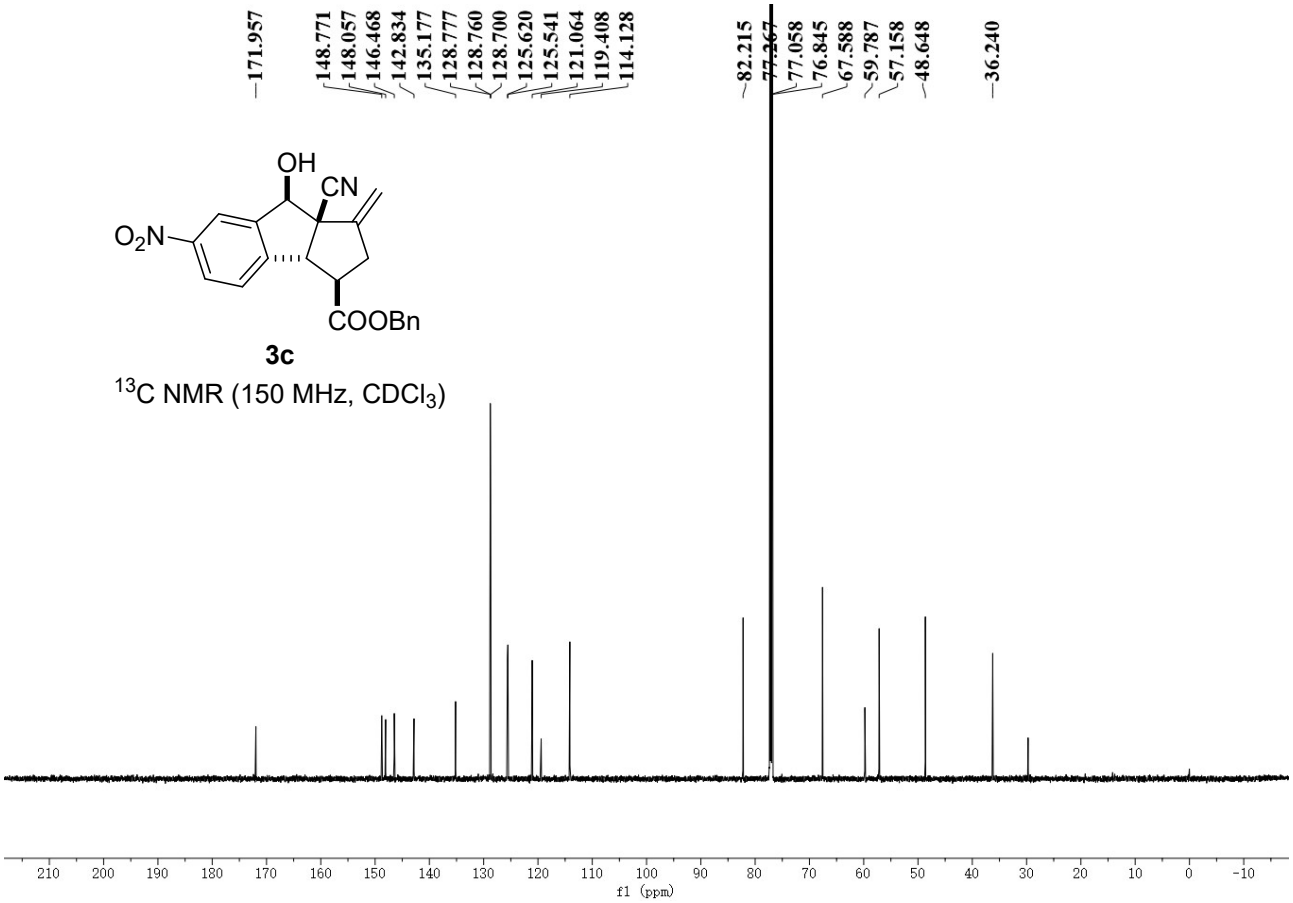
HRMS (ESI-TOF) m/z: $[C_{17}H_{16}N_2O_5 + Na]^+$

Calcd for 351.0951



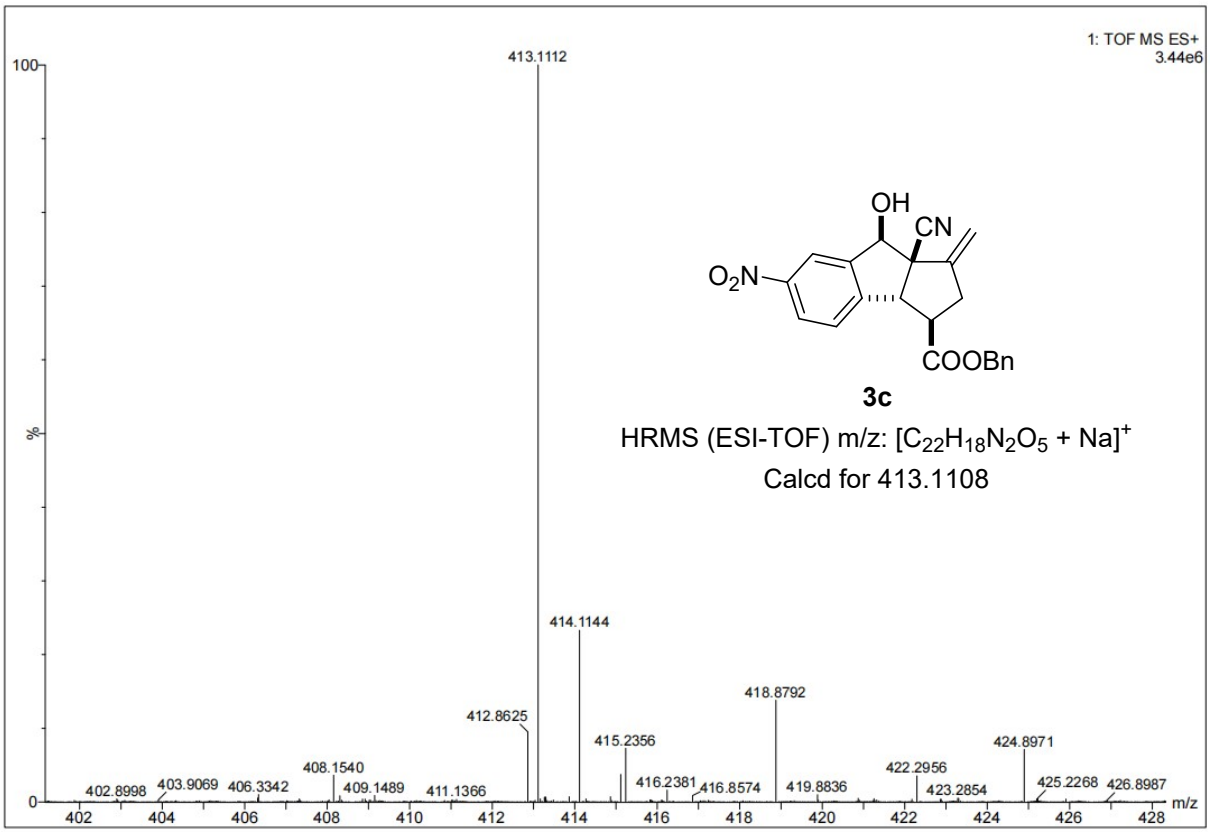
3c

^{1}H NMR (600 MHz, $CDCl_3$)



3c

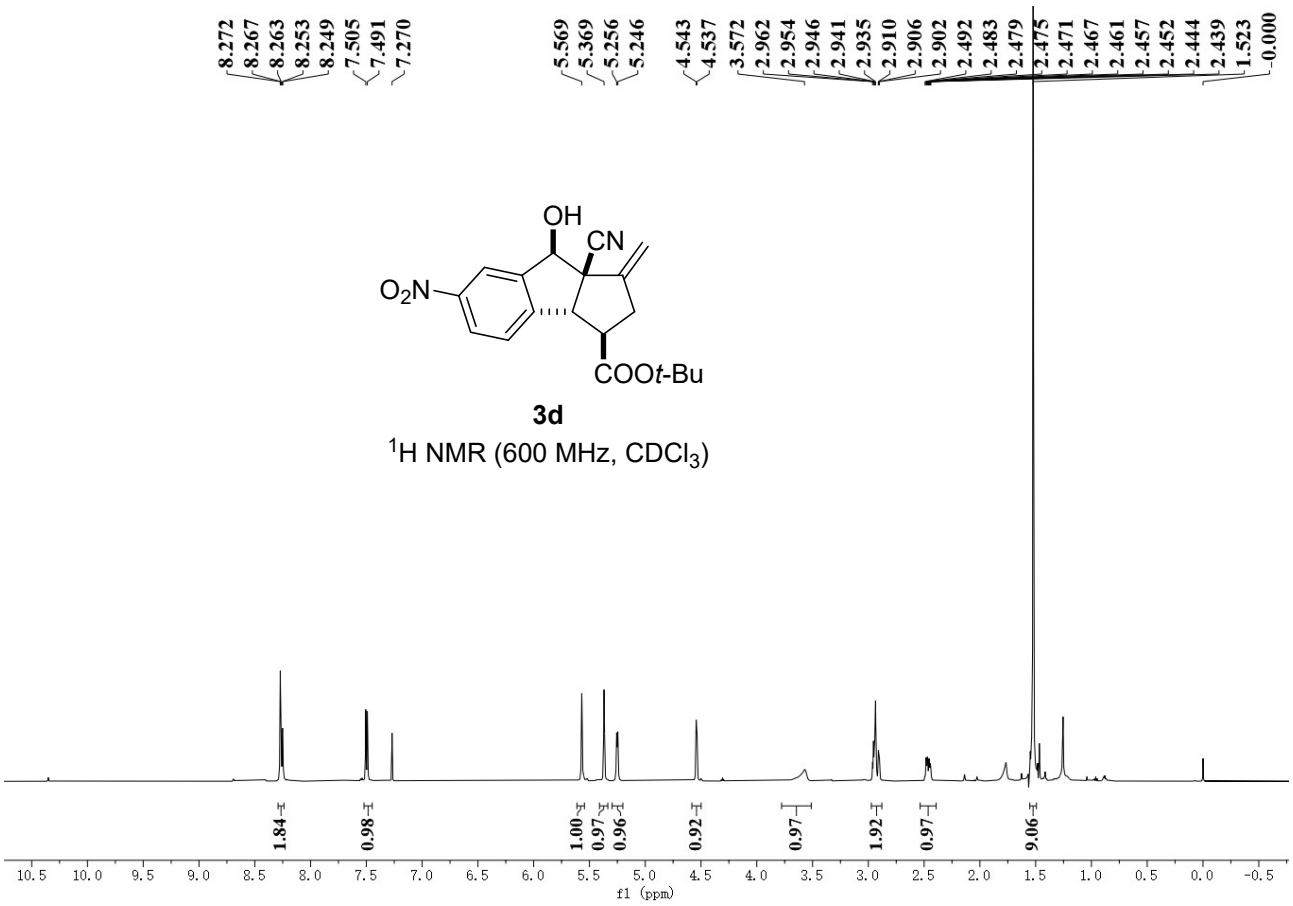
^{13}C NMR (150 MHz, $CDCl_3$)



3c

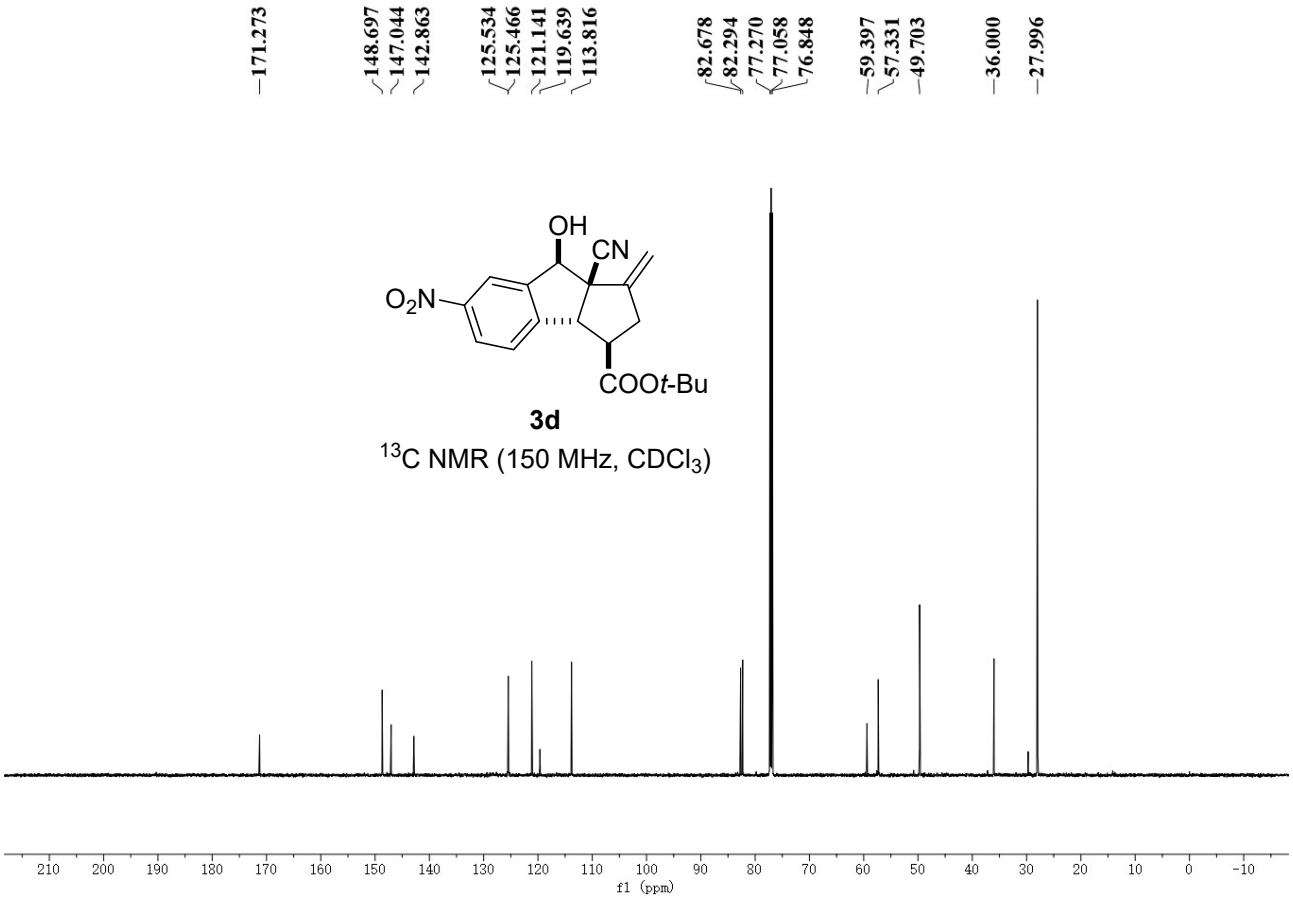
HRMS (ESI-TOF) m/z: $[C_{22}H_{18}N_2O_5 + Na]^+$

Calcd for 413.1108



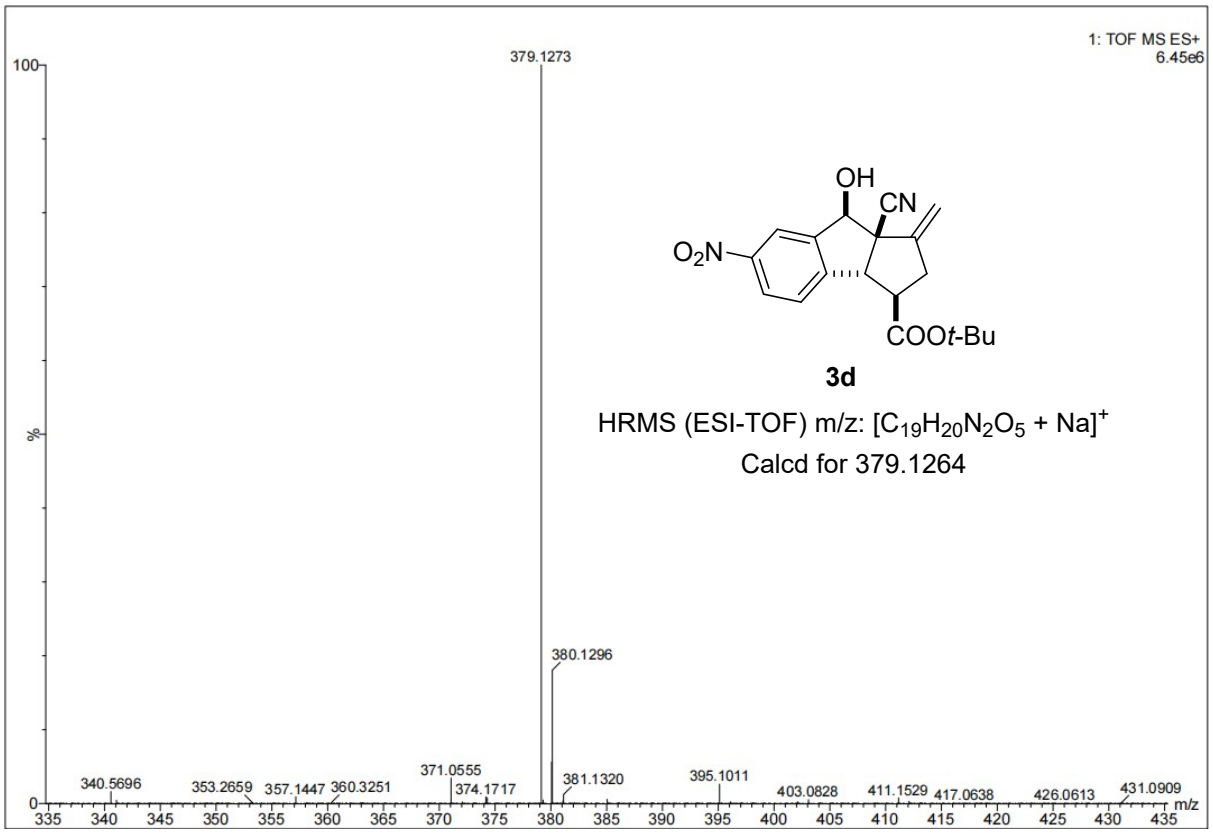
3d

^{1}H NMR (600 MHz, $CDCl_3$)



3d

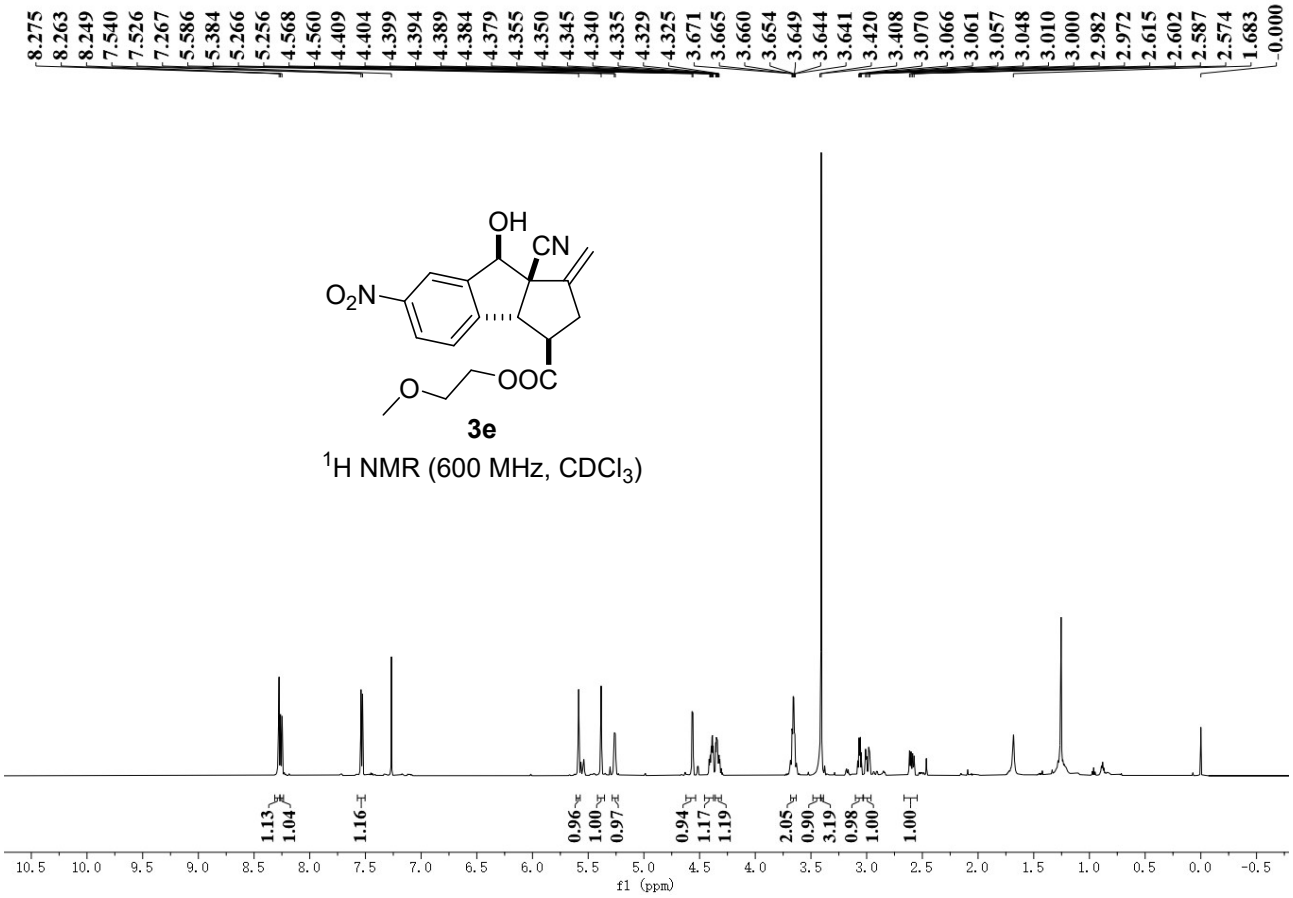
^{13}C NMR (150 MHz, $CDCl_3$)



3d

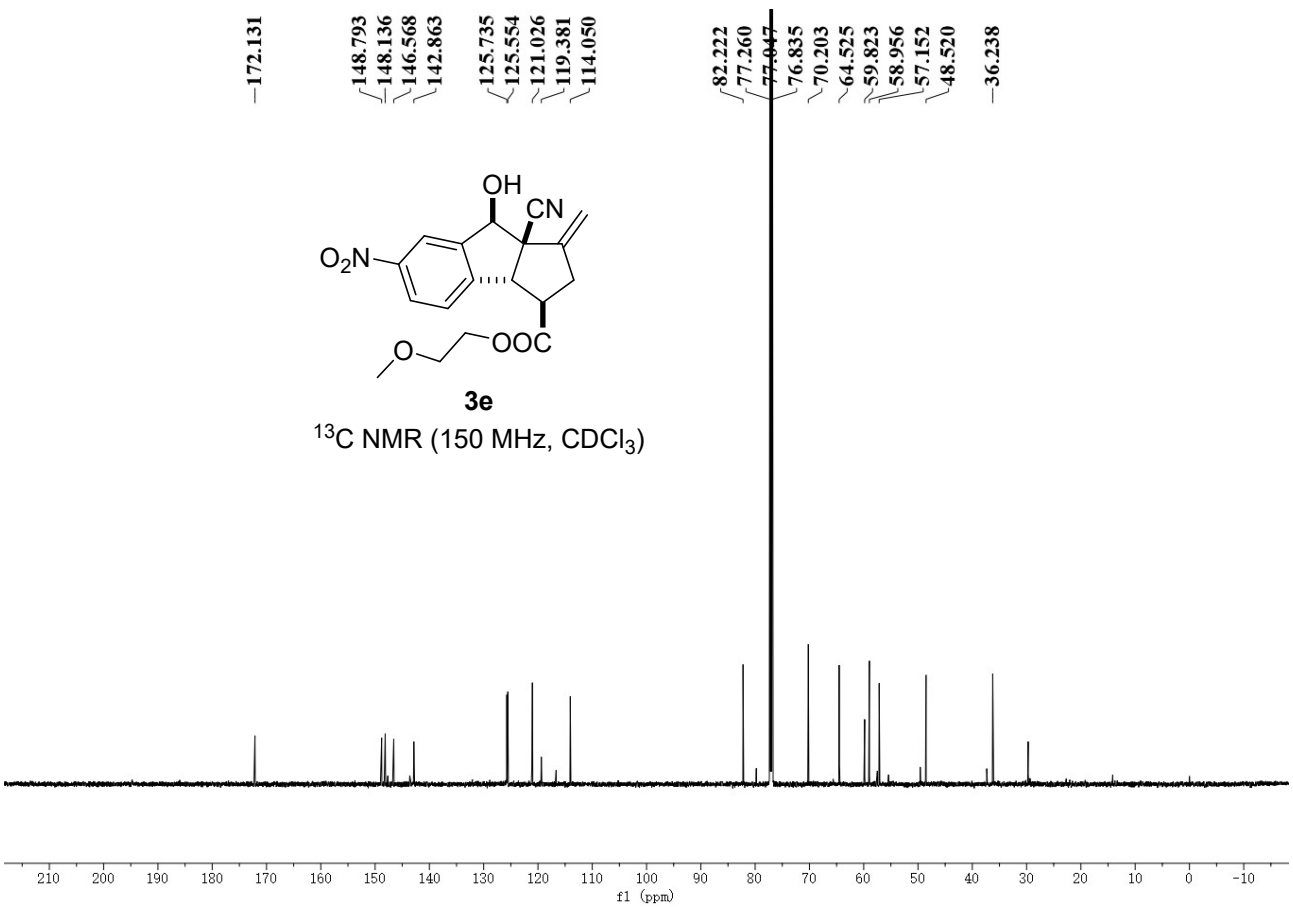
HRMS (ESI-TOF) m/z: $[C_{19}H_{20}N_2O_5 + Na]^+$

Calcd for 379.1264



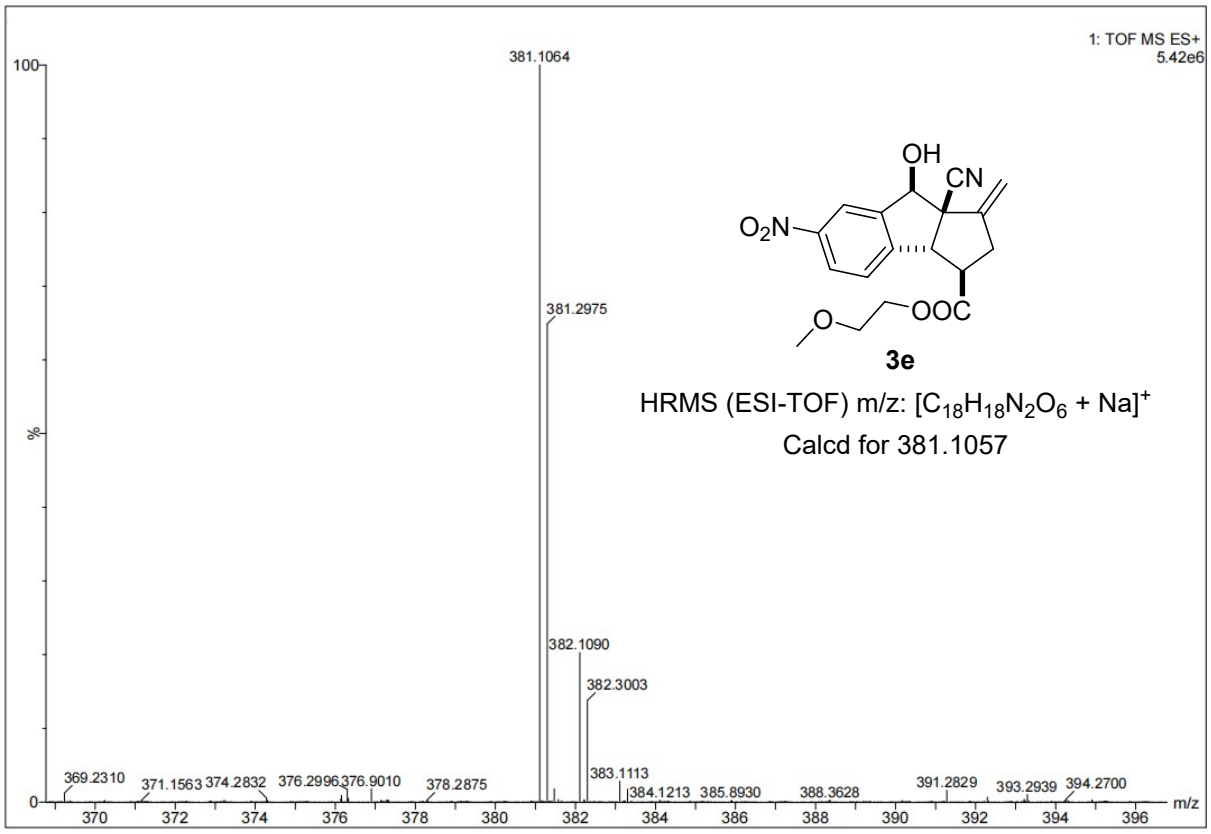
3e

^{1}H NMR (600 MHz, $CDCl_3$)



3e

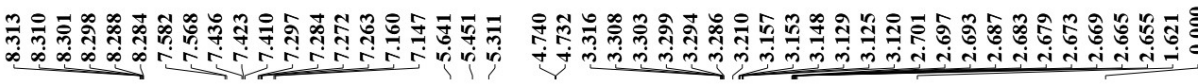
^{13}C NMR (150 MHz, $CDCl_3$)

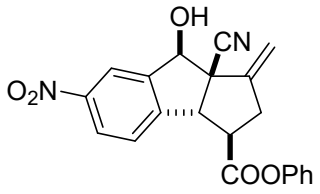


3e

HRMS (ESI-TOF) m/z: $[C_{18}H_{18}N_2O_6 + Na]^+$

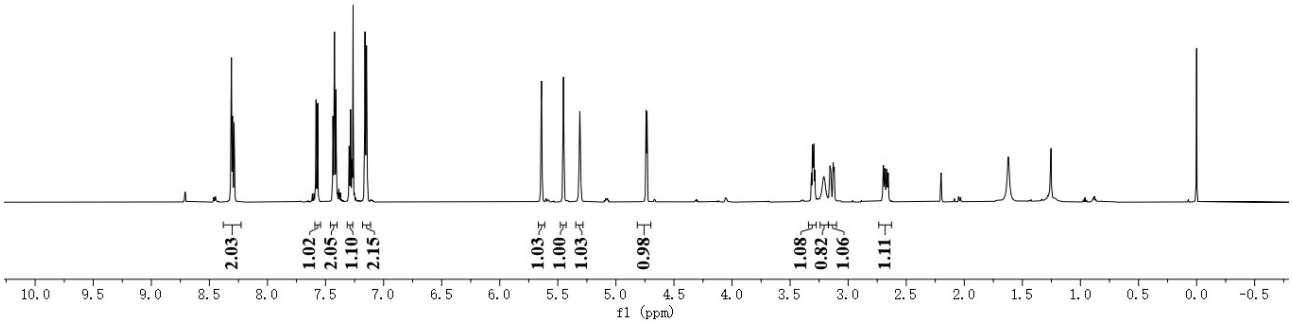
Calcd for 381.1057

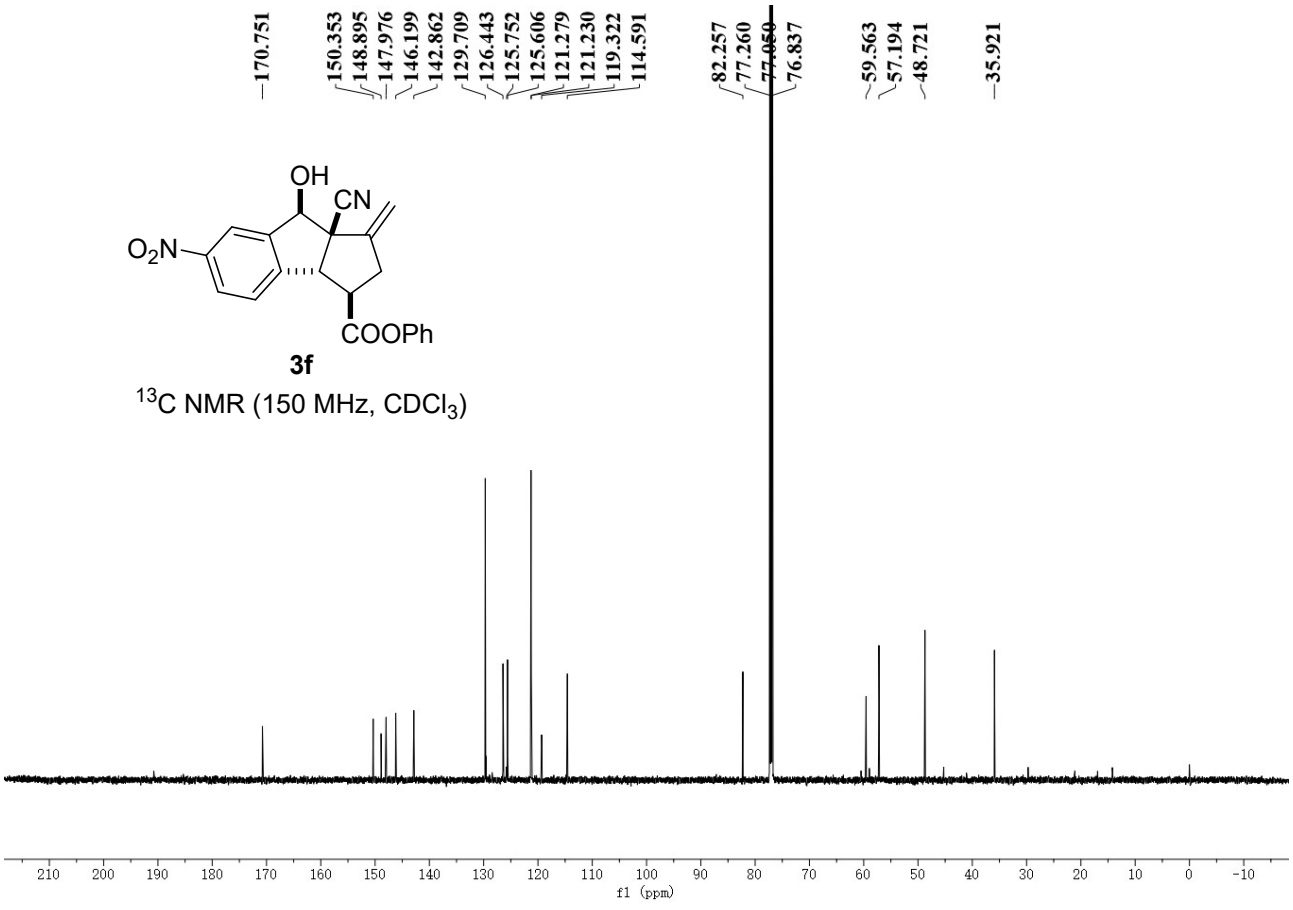




3f

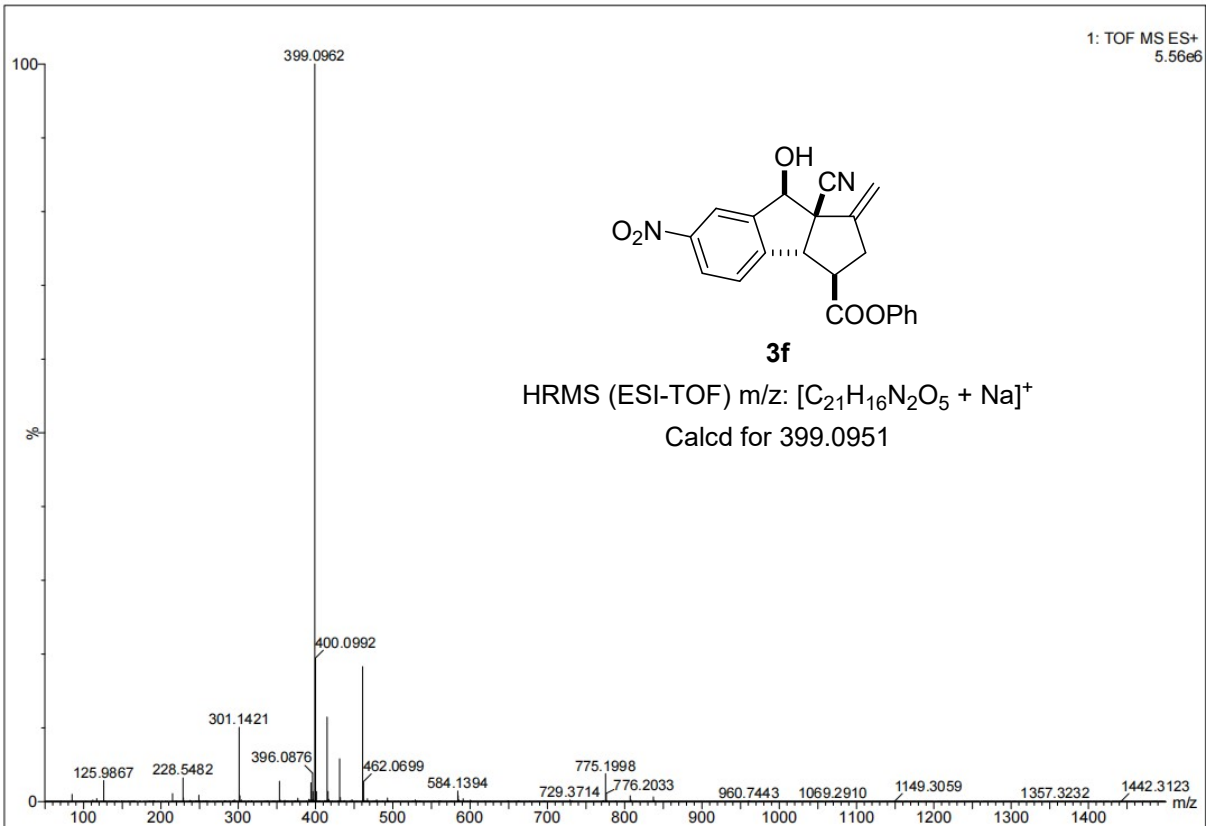
^{1}H NMR (600 MHz, $CDCl_3$)





3f

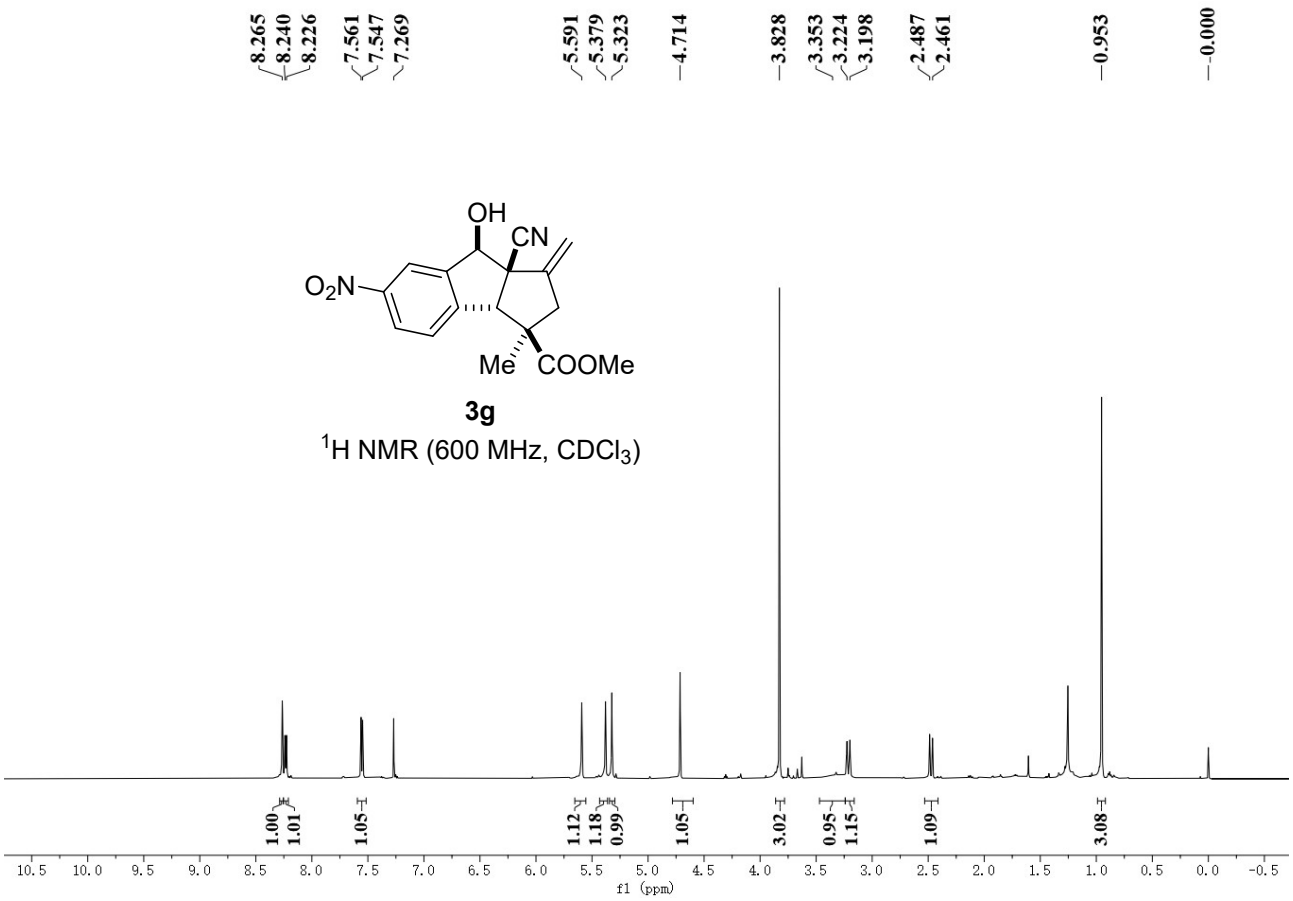
^{13}C NMR (150 MHz, $CDCl_3$)



3f

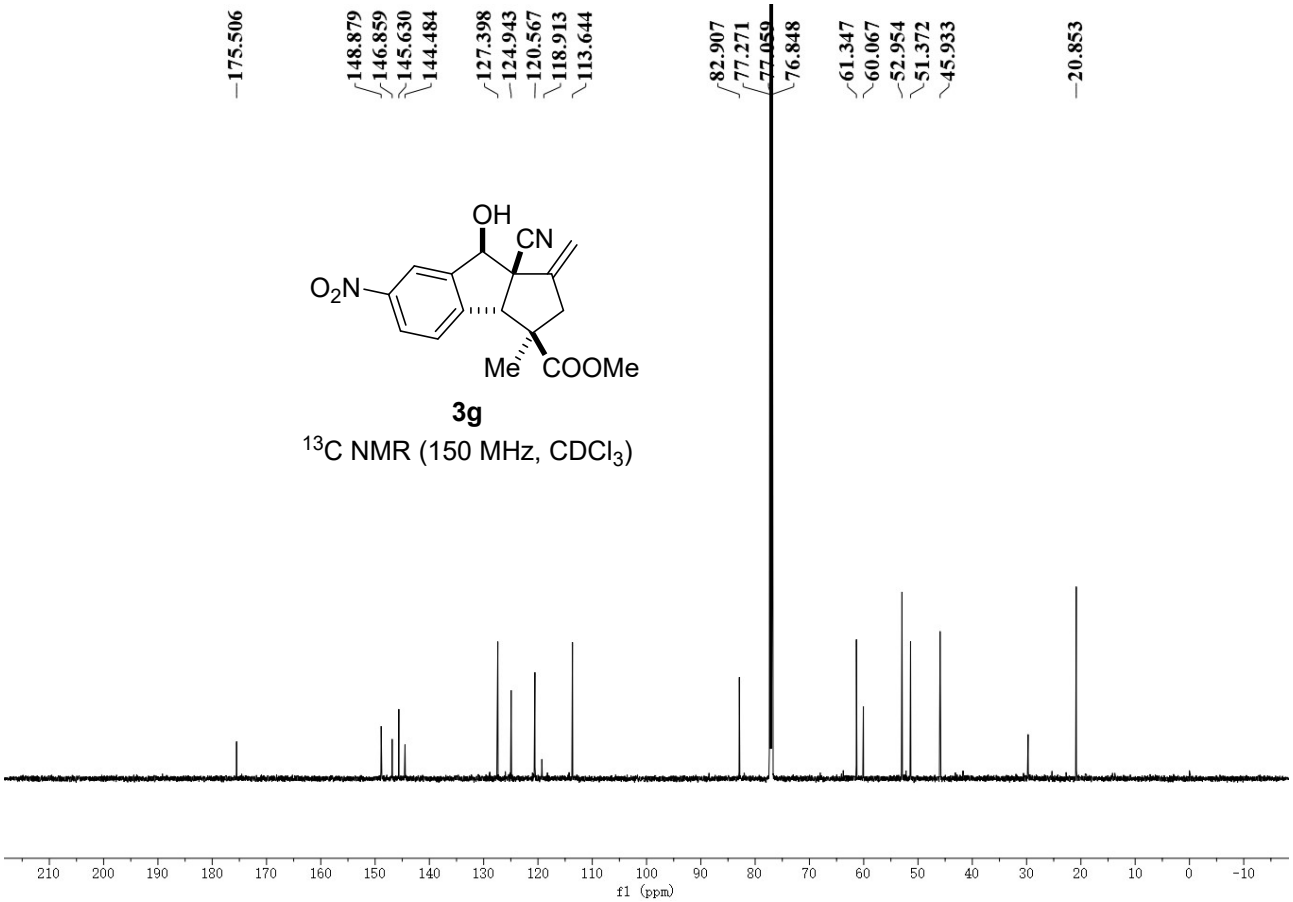
HRMS (ESI-TOF) m/z: $[C_{21}H_{16}N_2O_5 + Na]^+$

Calcd for 399.0951



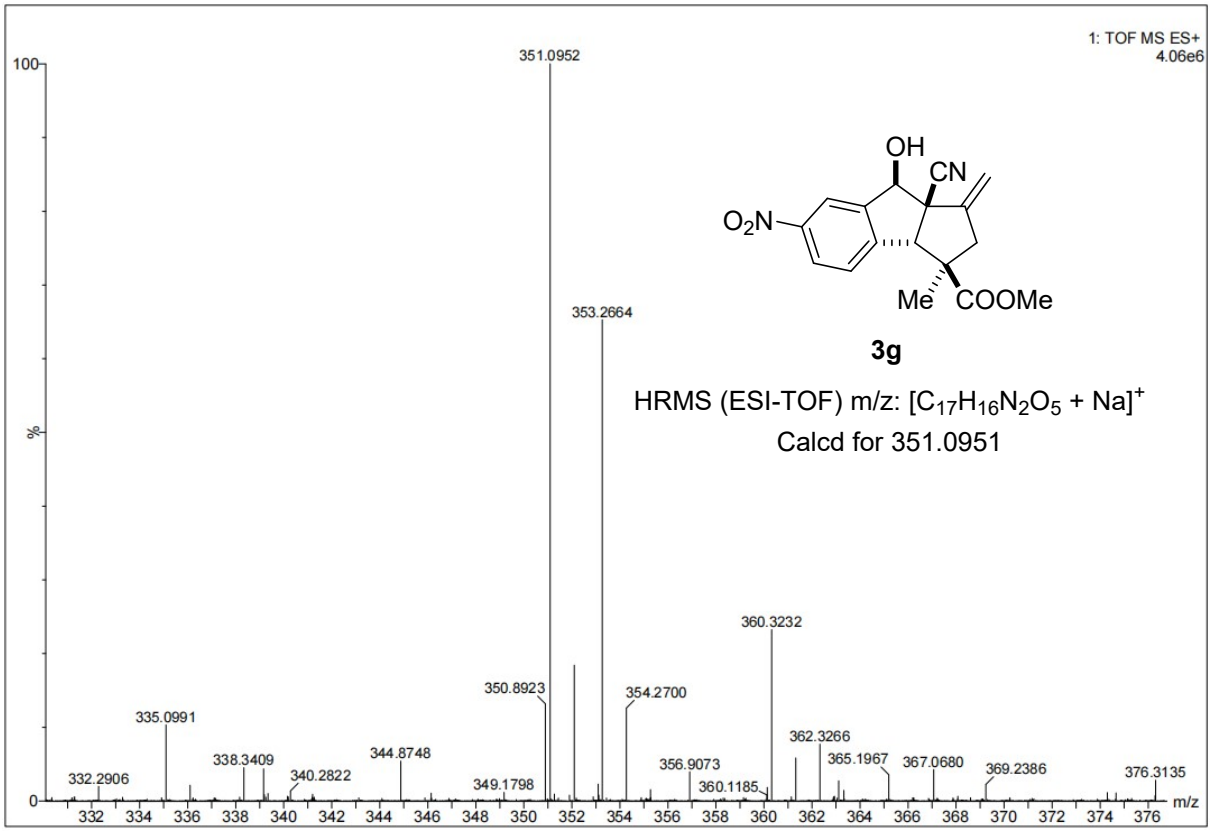
3g

^{1}H NMR (600 MHz, $CDCl_3$)



3g

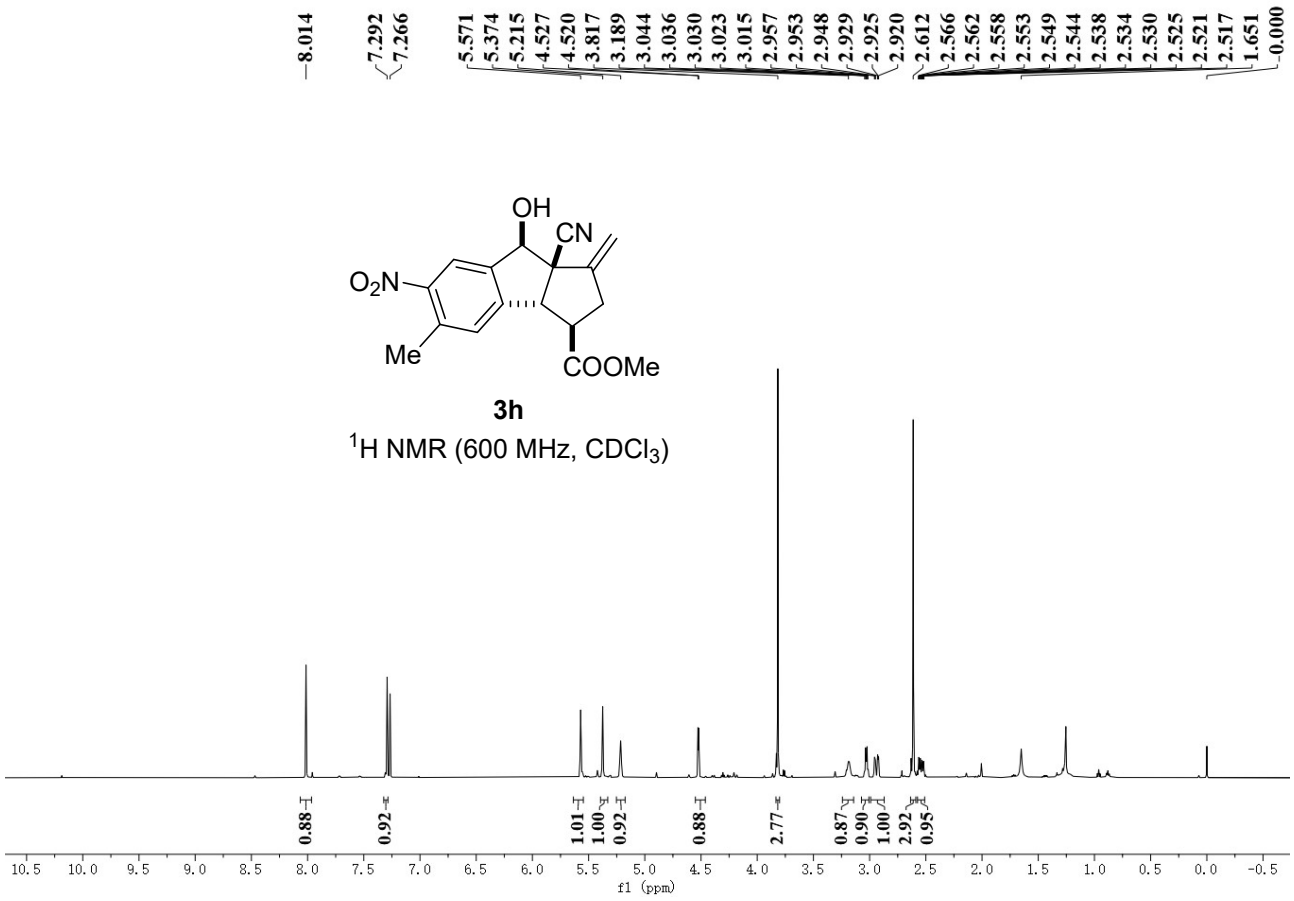
^{13}C NMR (150 MHz, $CDCl_3$)



3g

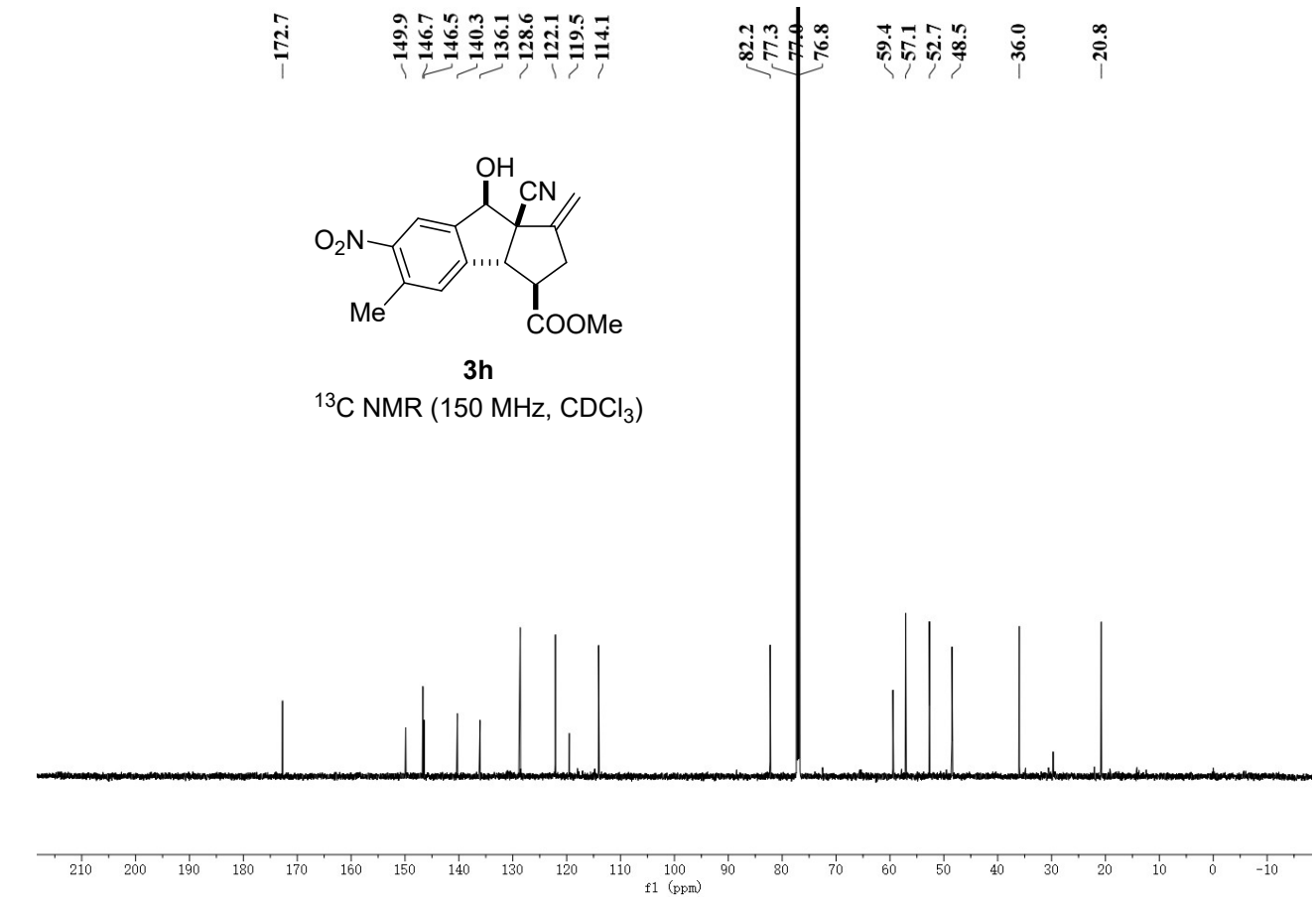
HRMS (ESI-TOF) m/z: $[C_{17}H_{16}N_2O_5 + Na]^+$

Calcd for 351.0951



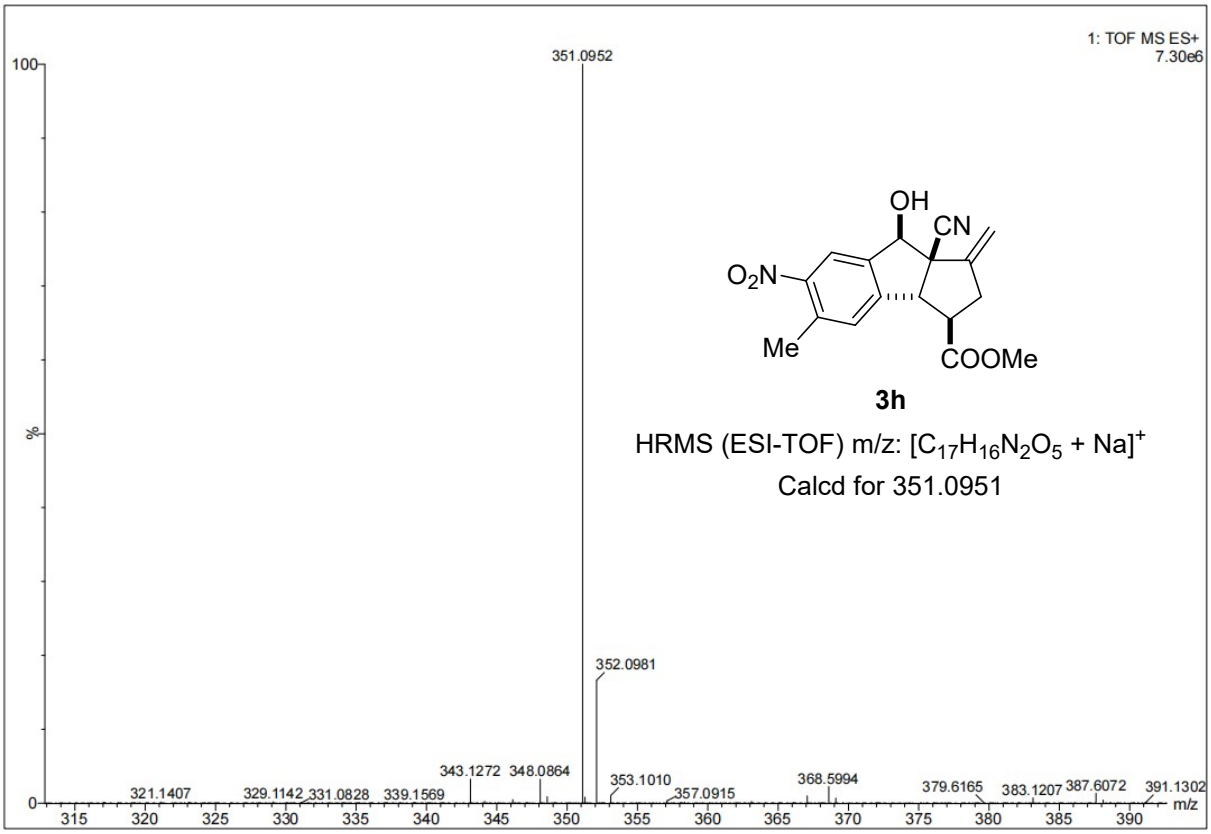
3h

^{1}H NMR (600 MHz, $CDCl_3$)



3h

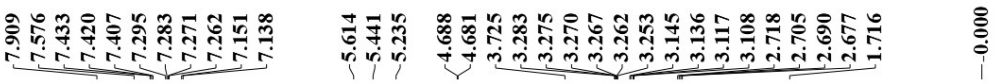
^{13}C NMR (150 MHz, $CDCl_3$)

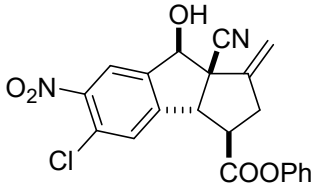


3h

HRMS (ESI-TOF) m/z: $[C_{17}H_{16}N_2O_5 + Na]^+$

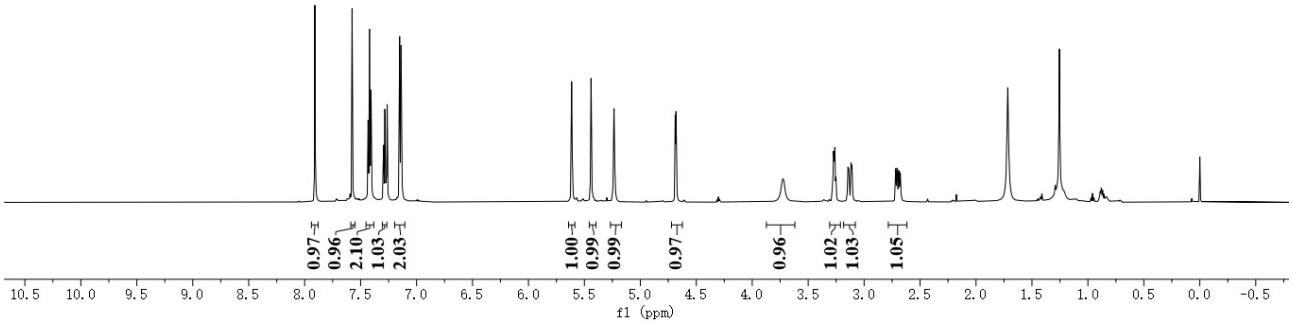
Calcd for 351.0951

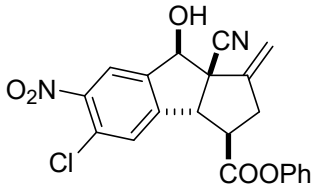




3i

^{1}H NMR (600 MHz, $CDCl_3$)

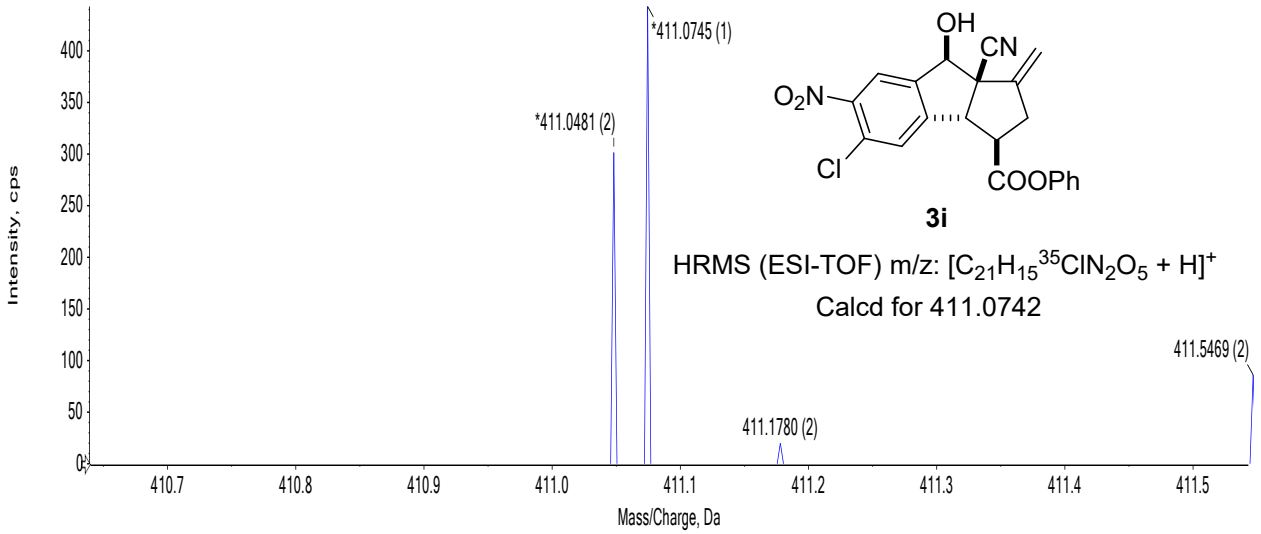




3i

^{13}C NMR (150 MHz, $CDCl_3$)

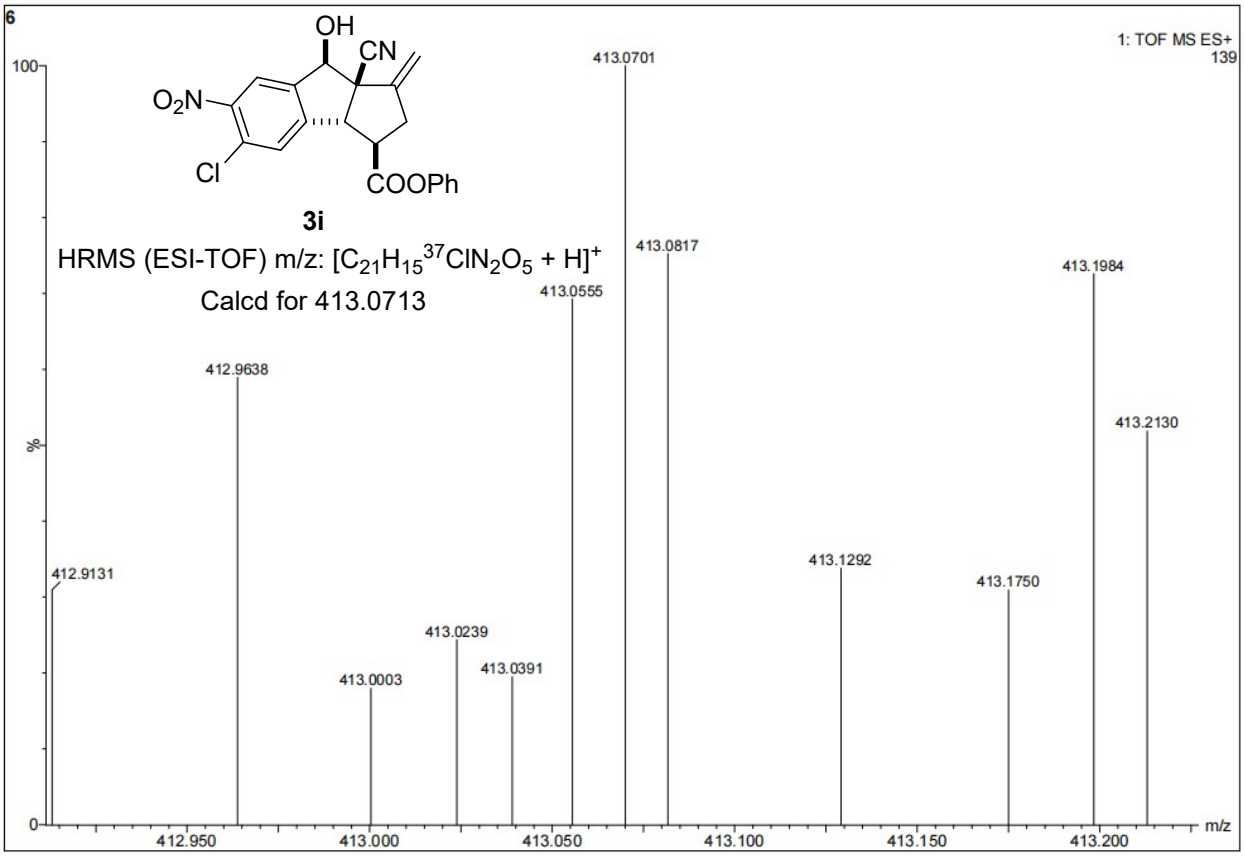
Spectrum from 20230617.wiff2 (sample 76) - 43, +TOF MS (200 - 600) from 0.037 to 0.088 min, noise filtere...4 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points)], Recalibrated, centroided



3i

HRMS (ESI-TOF) m/z: $[C_{21}H_{15}{}^{35}ClN_2O_5 + H]^+$

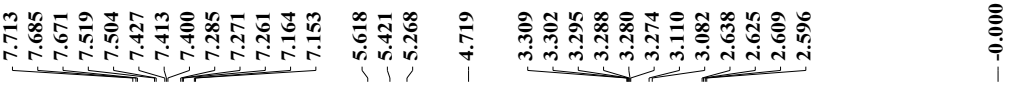
Calcd for 411.0742

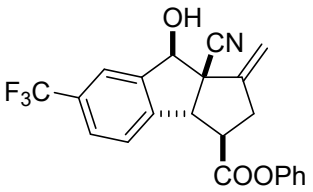


3i

HRMS (ESI-TOF) m/z: $[C_{21}H_{15}{}^{37}ClN_2O_5 + H]^+$

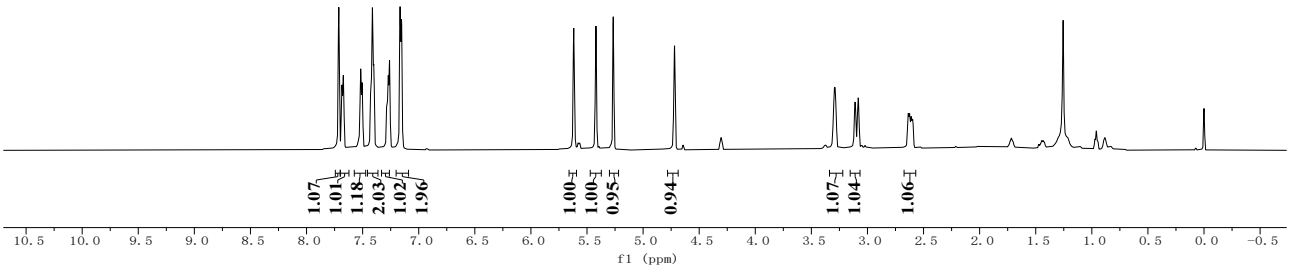
Calcd for 413.0713

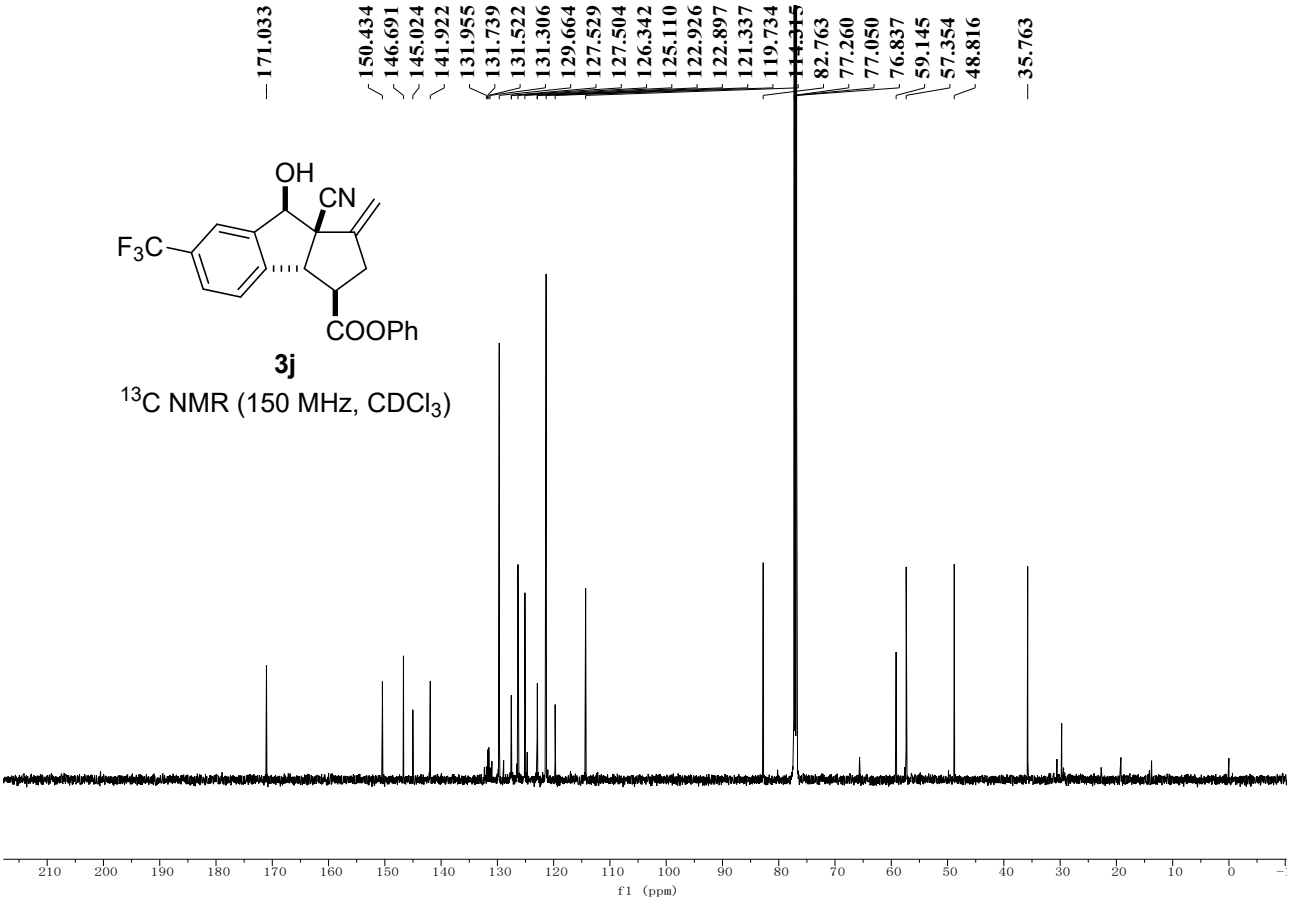




3j

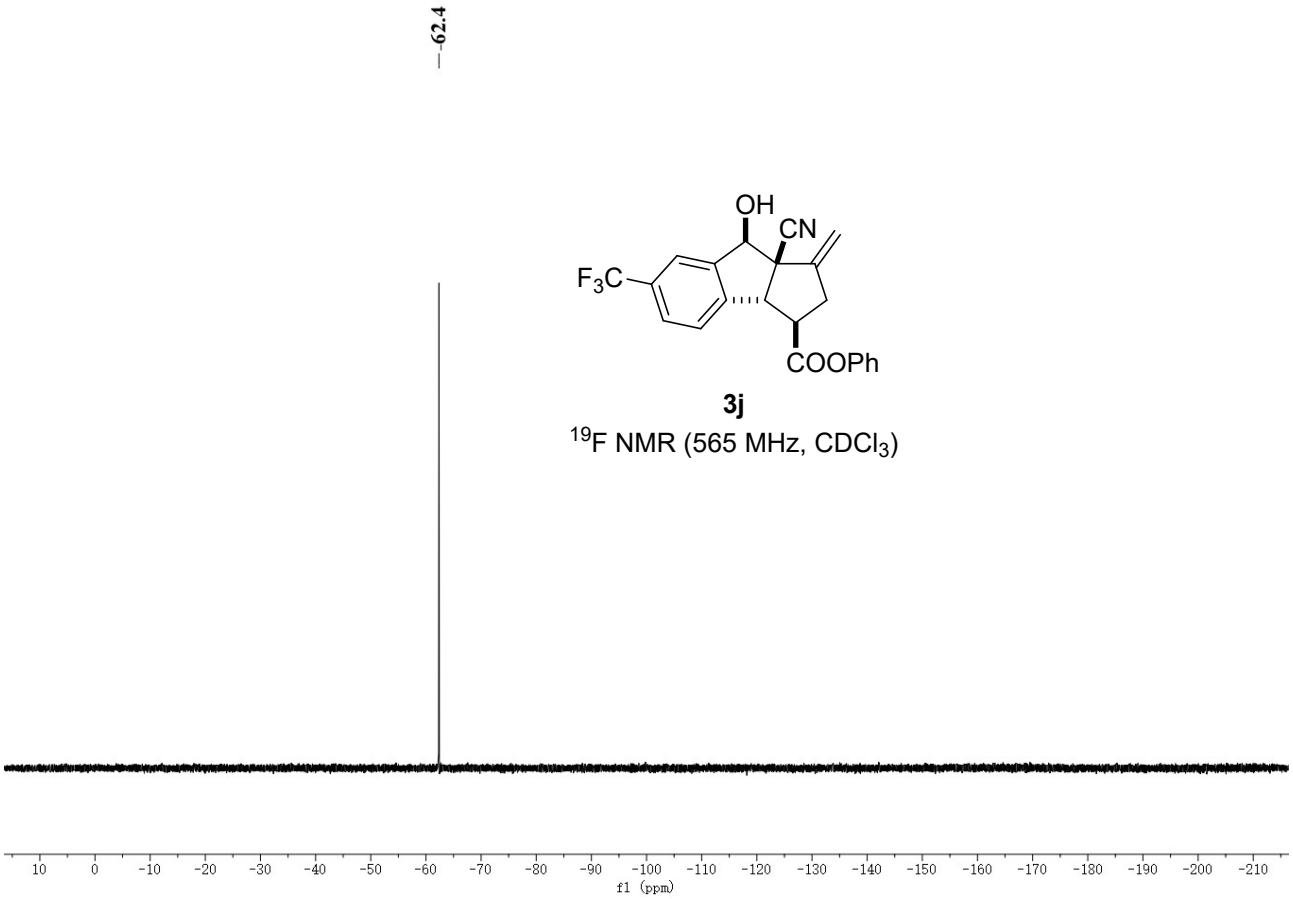
^{1}H NMR (600 MHz, $CDCl_3$)





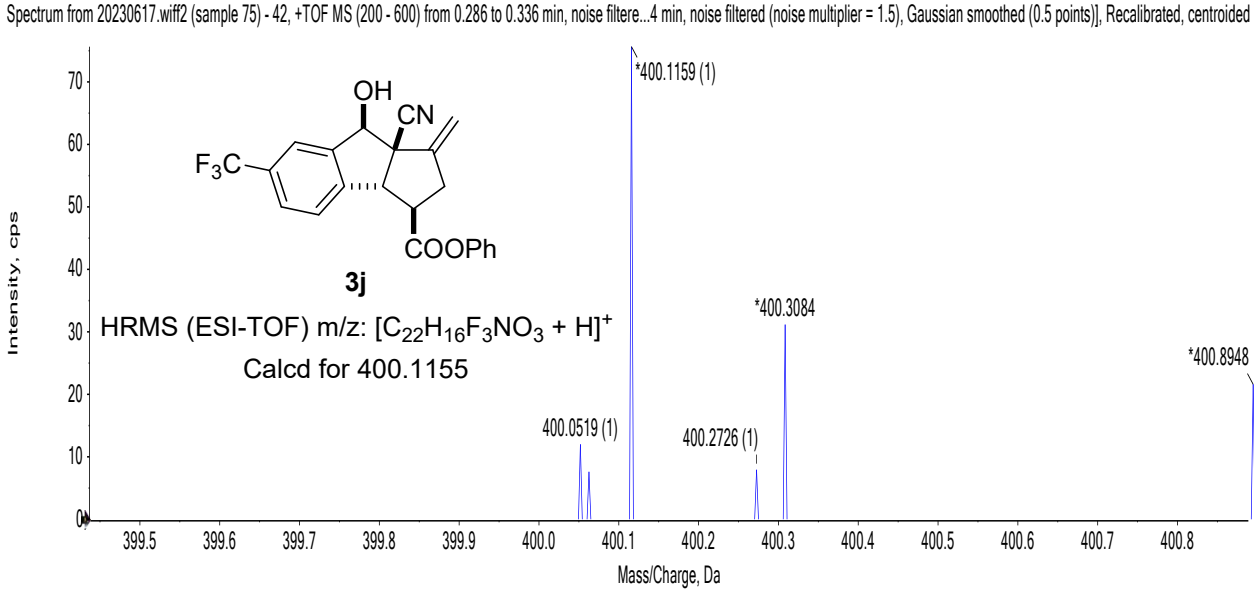
3j

^{13}C NMR (150 MHz, $CDCl_3$)



3j

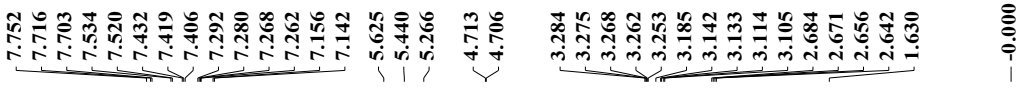
^{19}F NMR (565 MHz, $CDCl_3$)

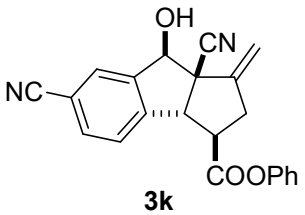


3j

HRMS (ESI-TOF) m/z: $[C_{22}H_{16}F_3NO_3 + H]^+$

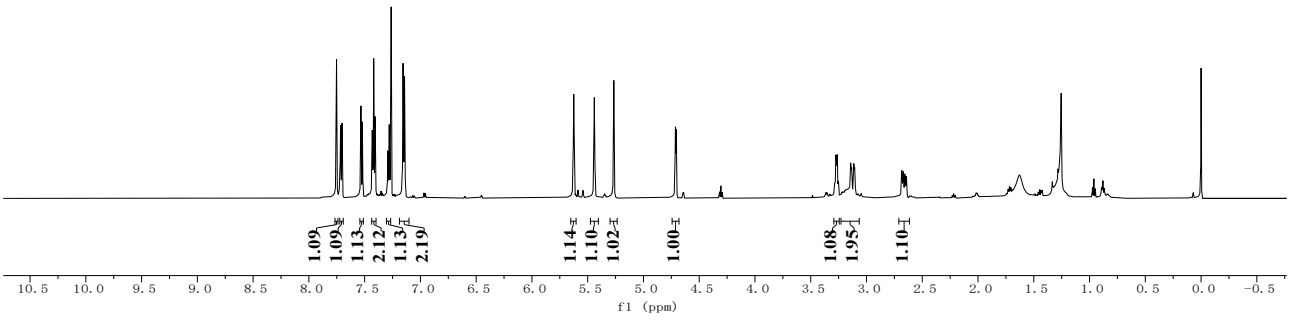
Calcd for 400.1155

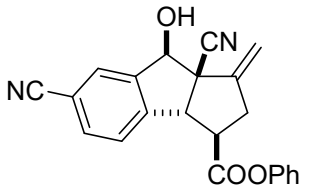




3k

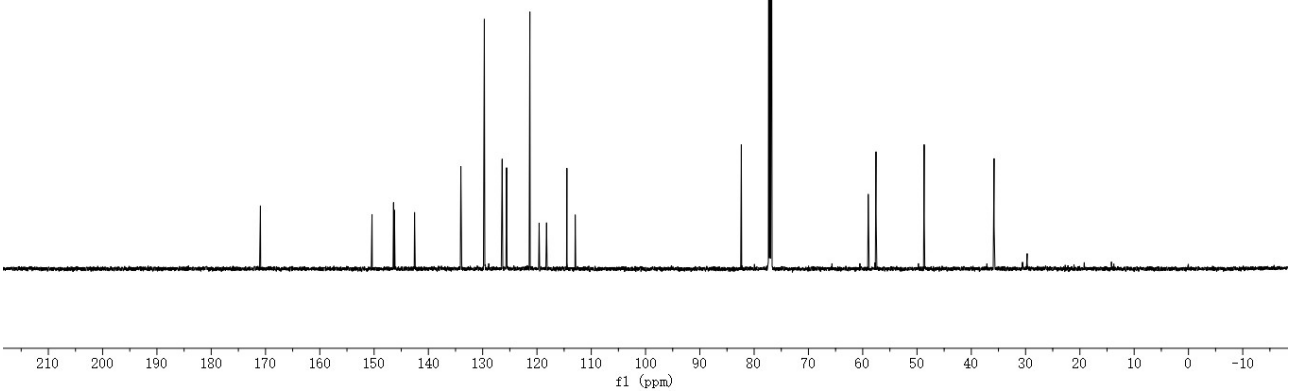
^{1}H NMR (600 MHz, $CDCl_3$)

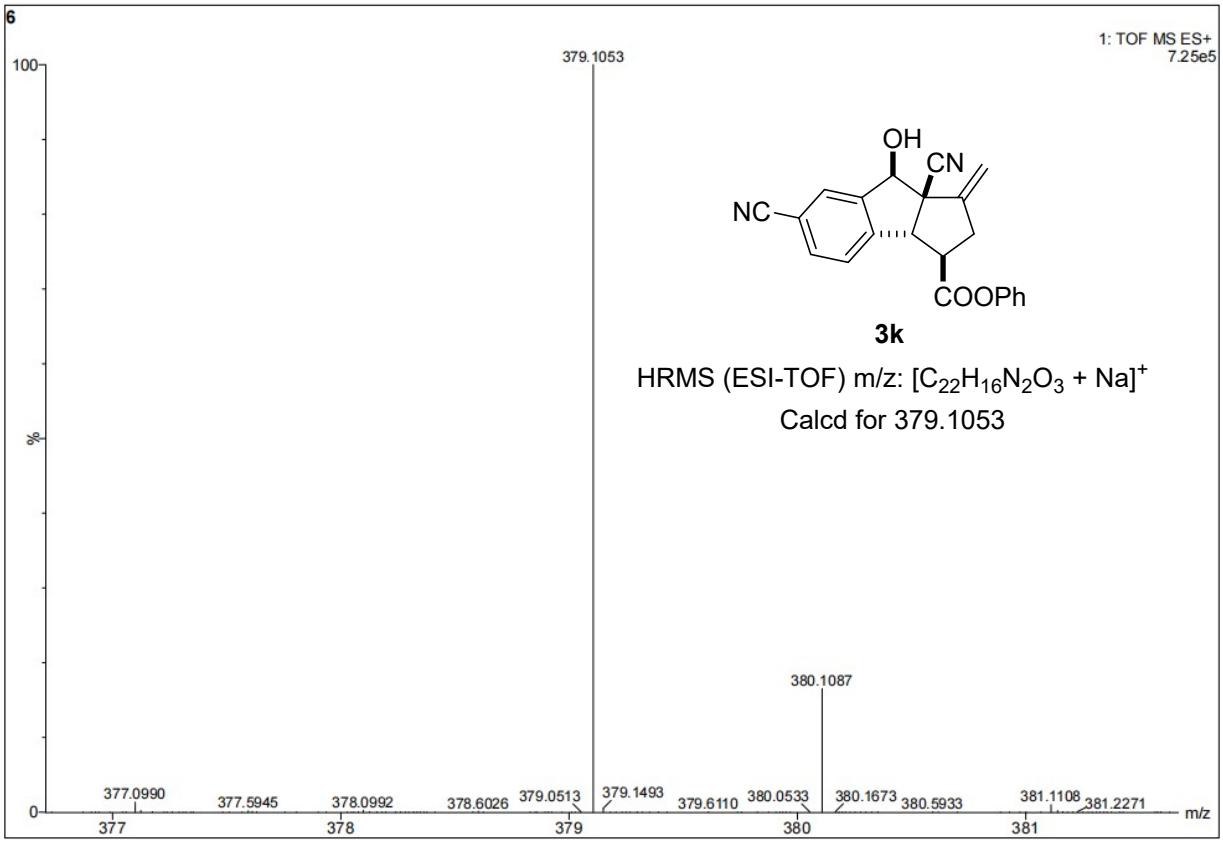




3k

^{13}C NMR (150 MHz, $CDCl_3$)

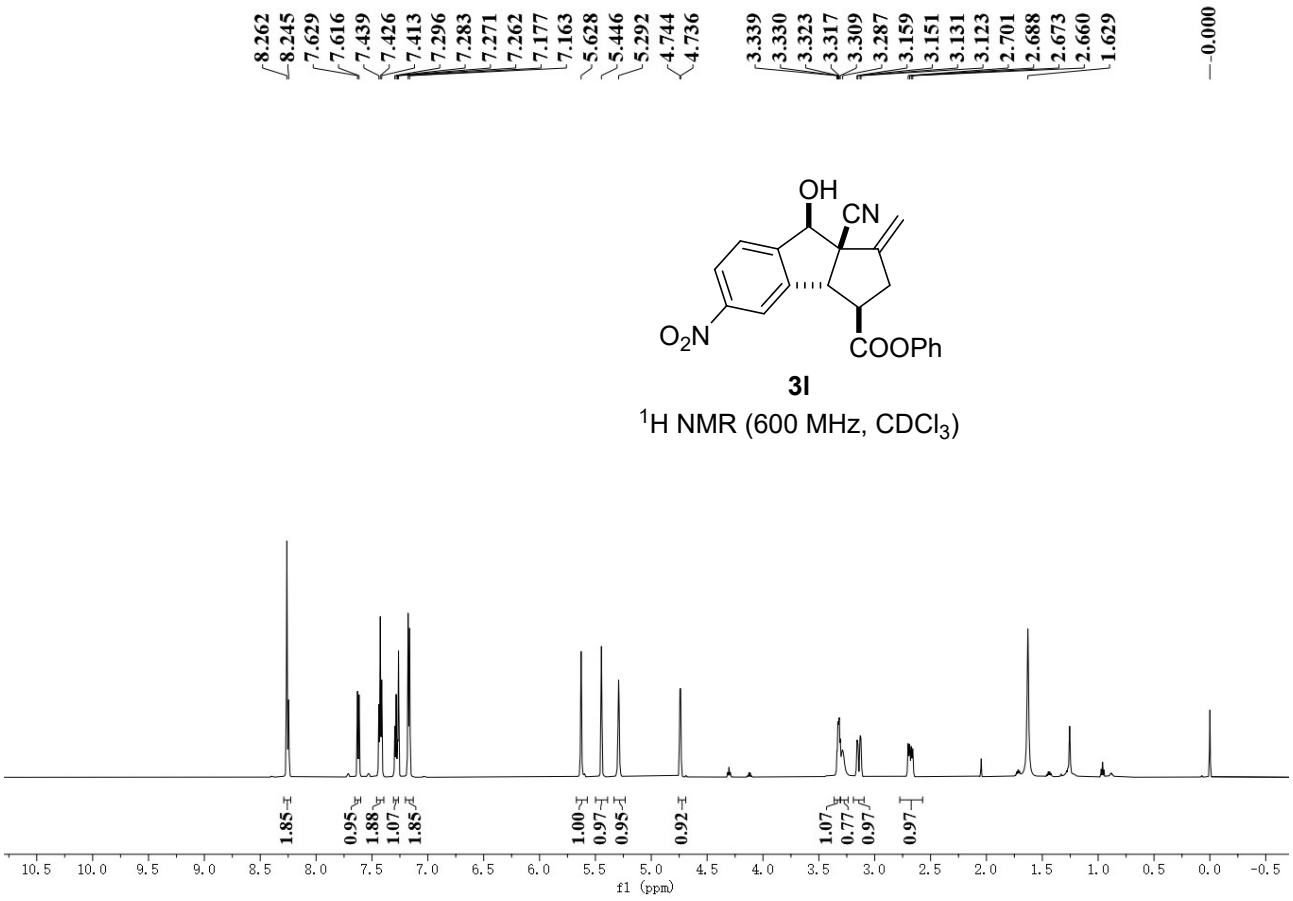




3k

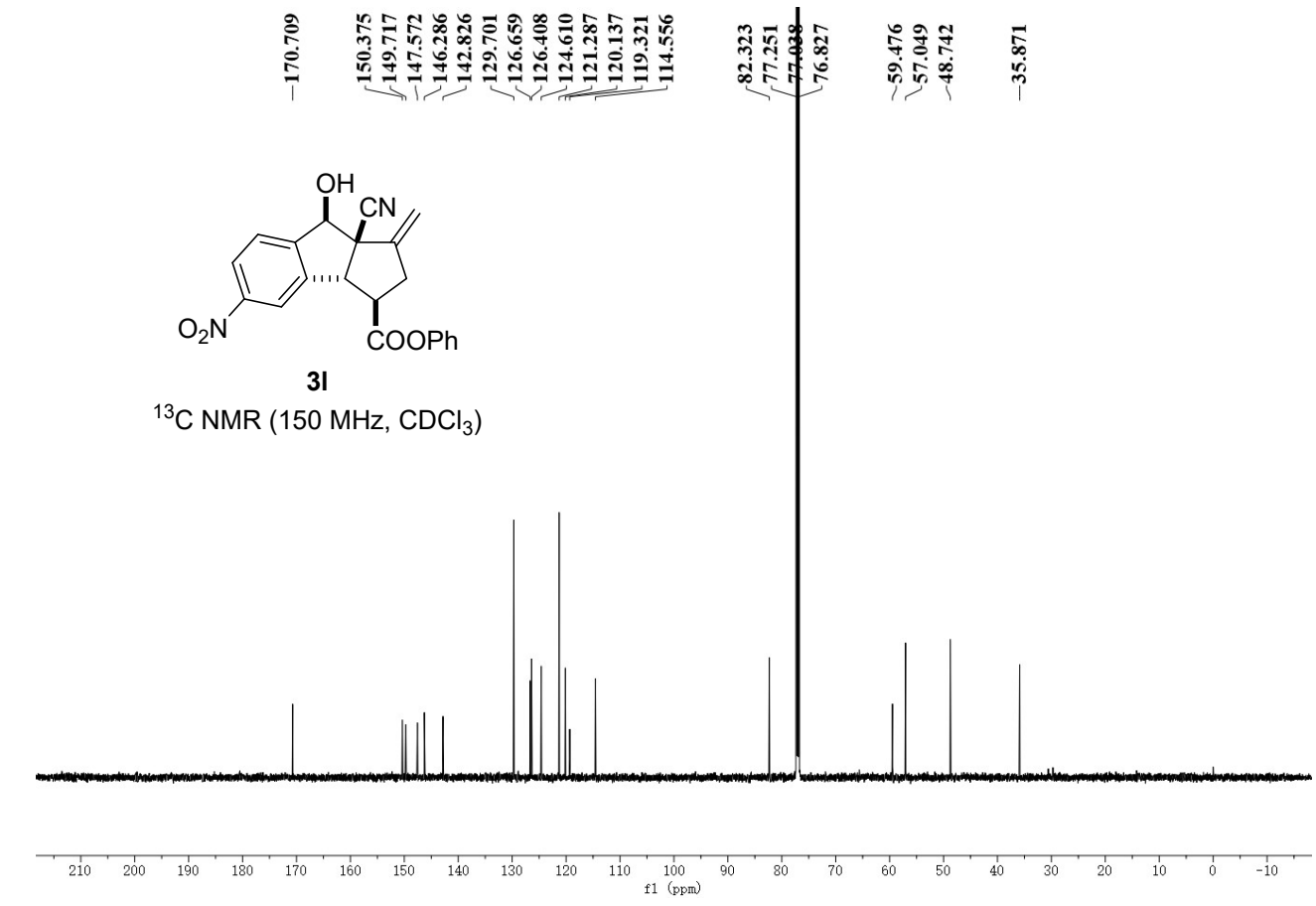
HRMS (ESI-TOF) m/z: $[C_{22}H_{16}N_2O_3 + Na]^+$

Calcd for 379.1053



3l

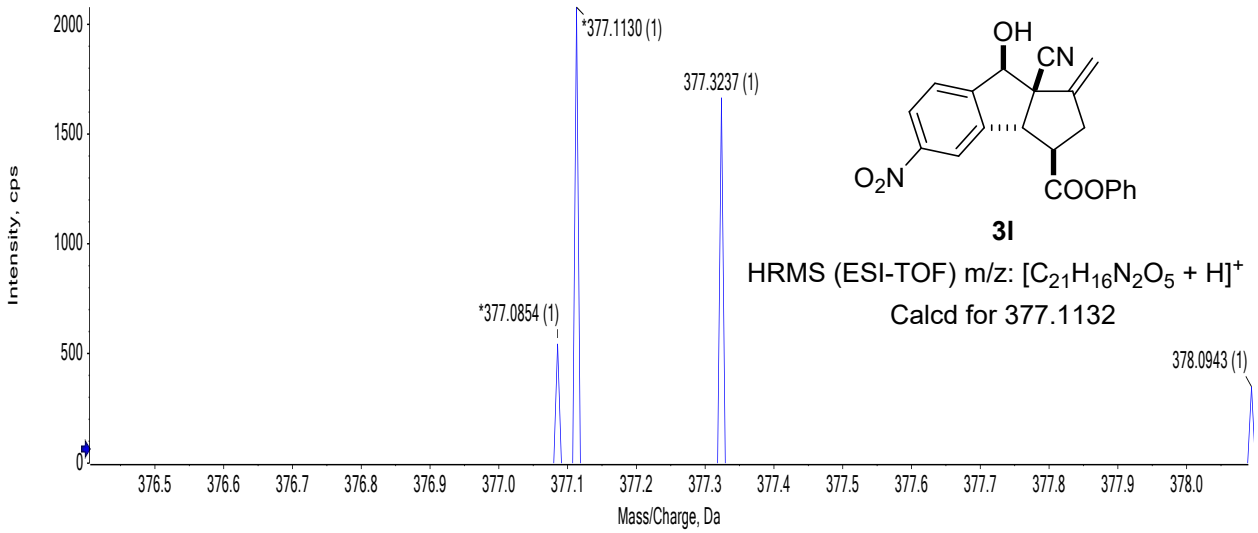
^{1}H NMR (600 MHz, $CDCl_3$)



3l

^{13}C NMR (150 MHz, $CDCl_3$)

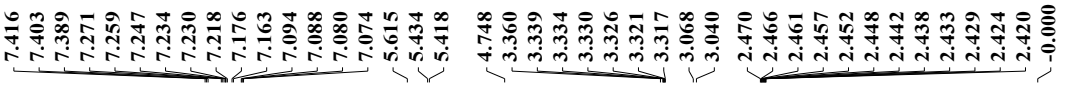
Spectrum from 20230617.wiff2 (sample 77) - 44, +TOF MS (200 - 600) from 0.037 to 0.073 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points), Recalibrated, centroided

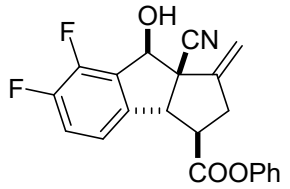


3l

HRMS (ESI-TOF) m/z: $[C_{21}H_{16}N_2O_5 + H]^+$

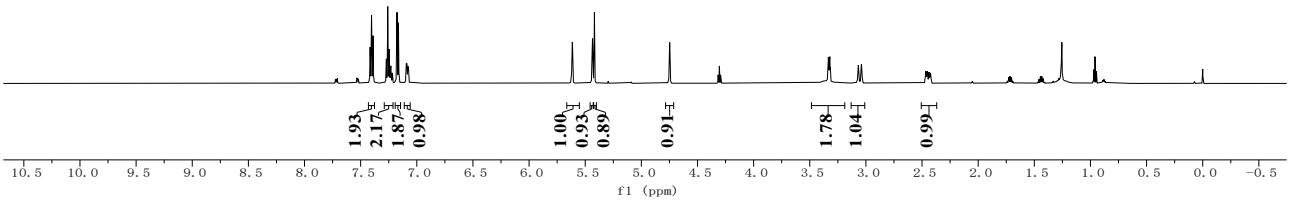
Calcd for 377.1132

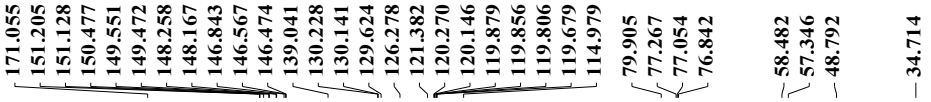


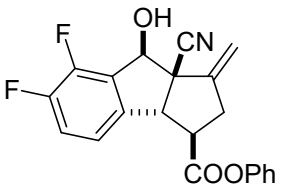


3m

^{1}H NMR (600 MHz, $CDCl_3$)

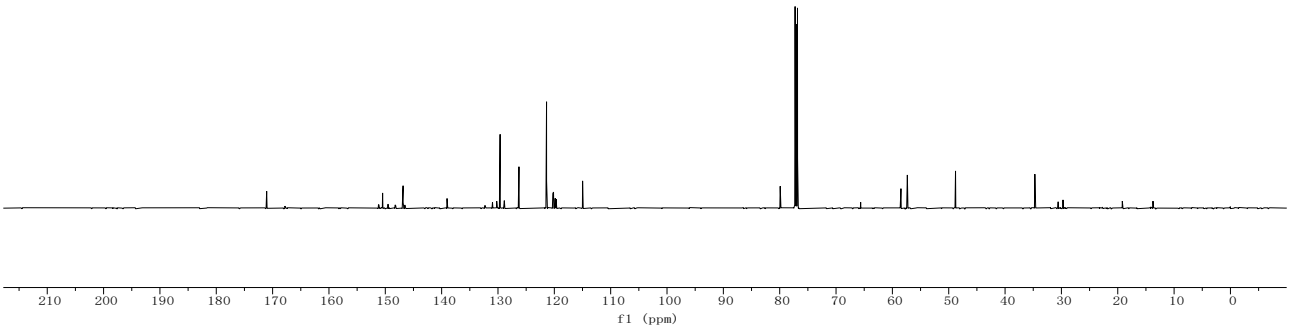


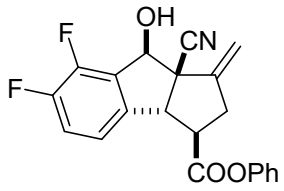




3m

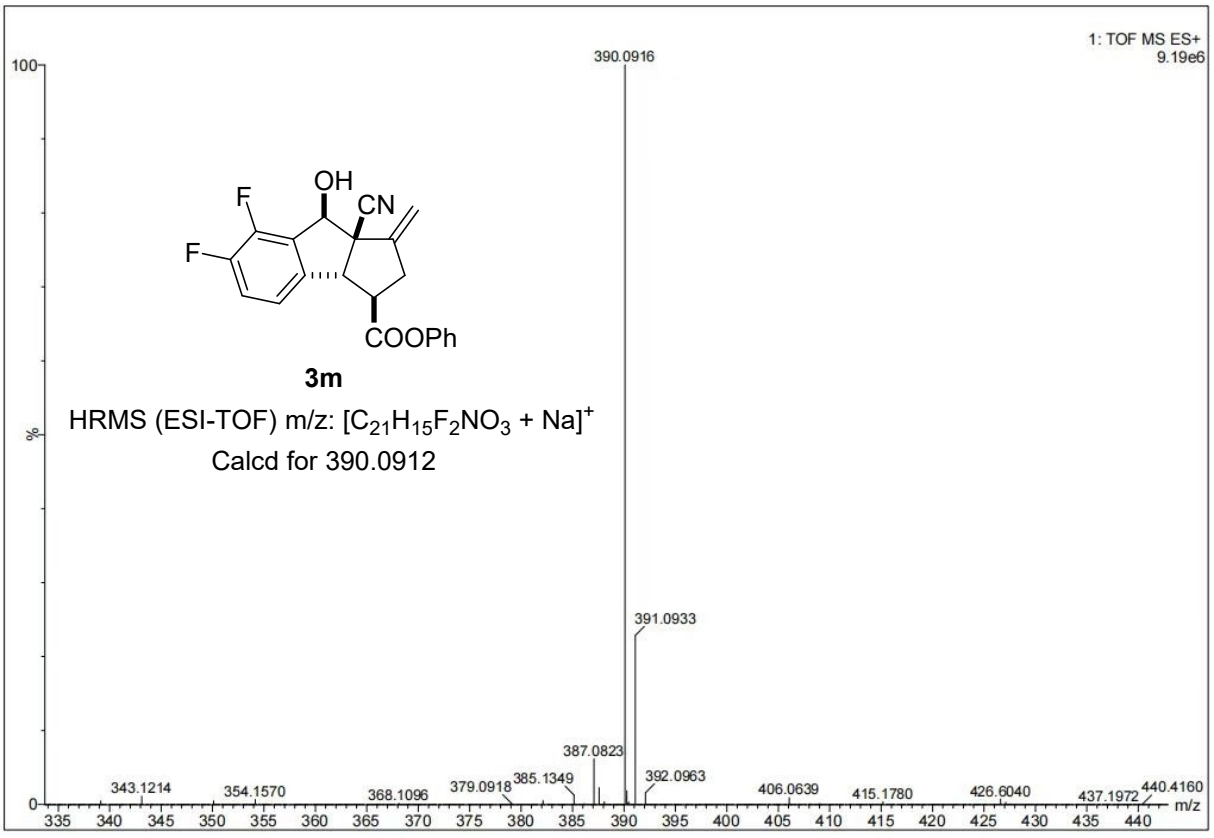
^{13}C NMR (150 MHz, $CDCl_3$)





3m

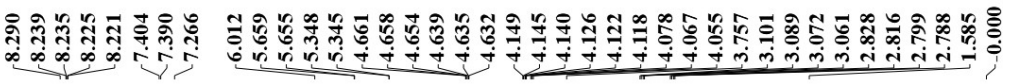
^{19}F NMR (565 MHz, $CDCl_3$)

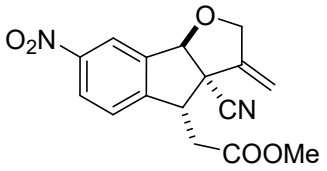


3m

HRMS (ESI-TOF) m/z: $[C_{21}H_{15}F_2NO_3 + Na]^+$

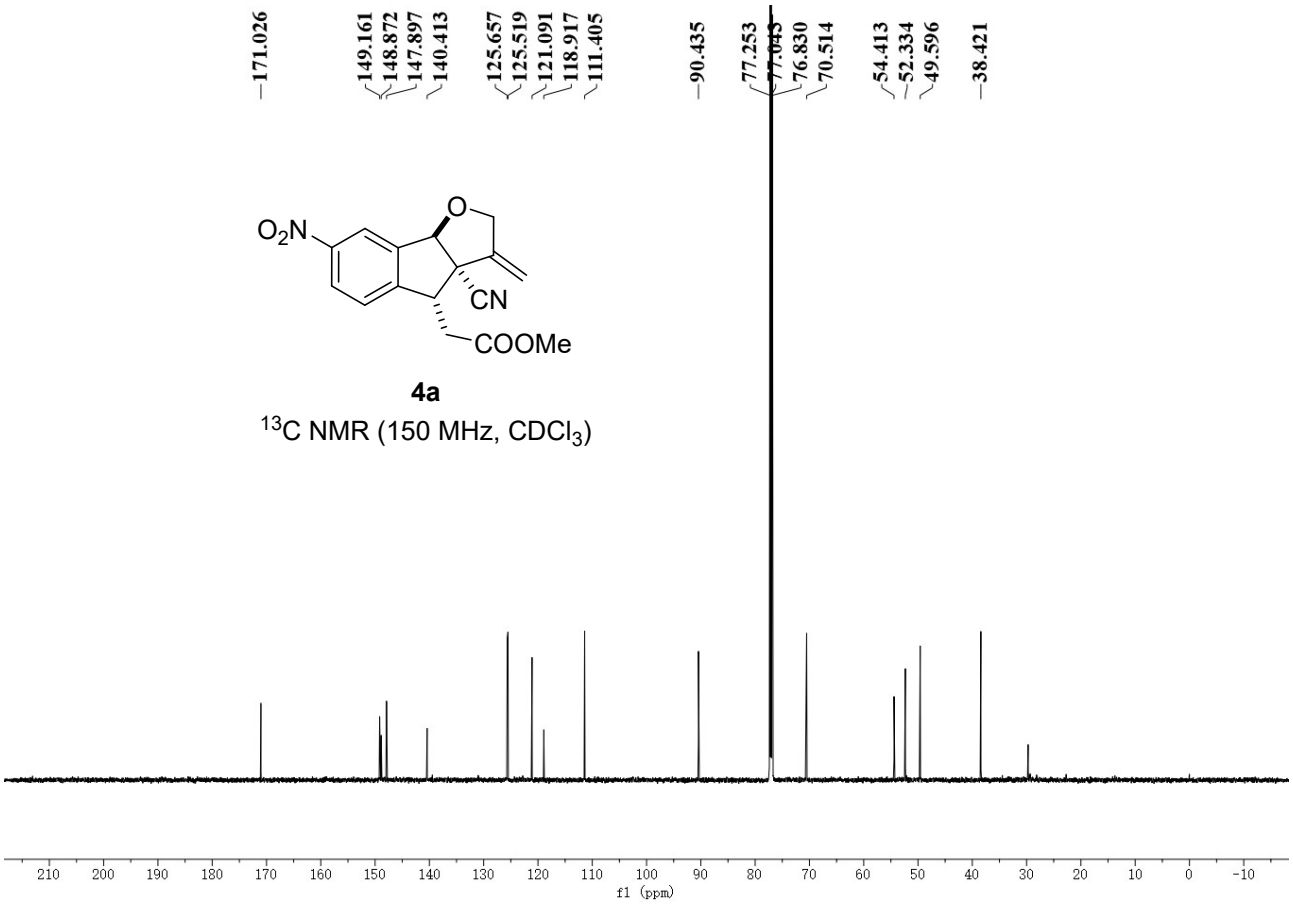
Calcd for 390.0912





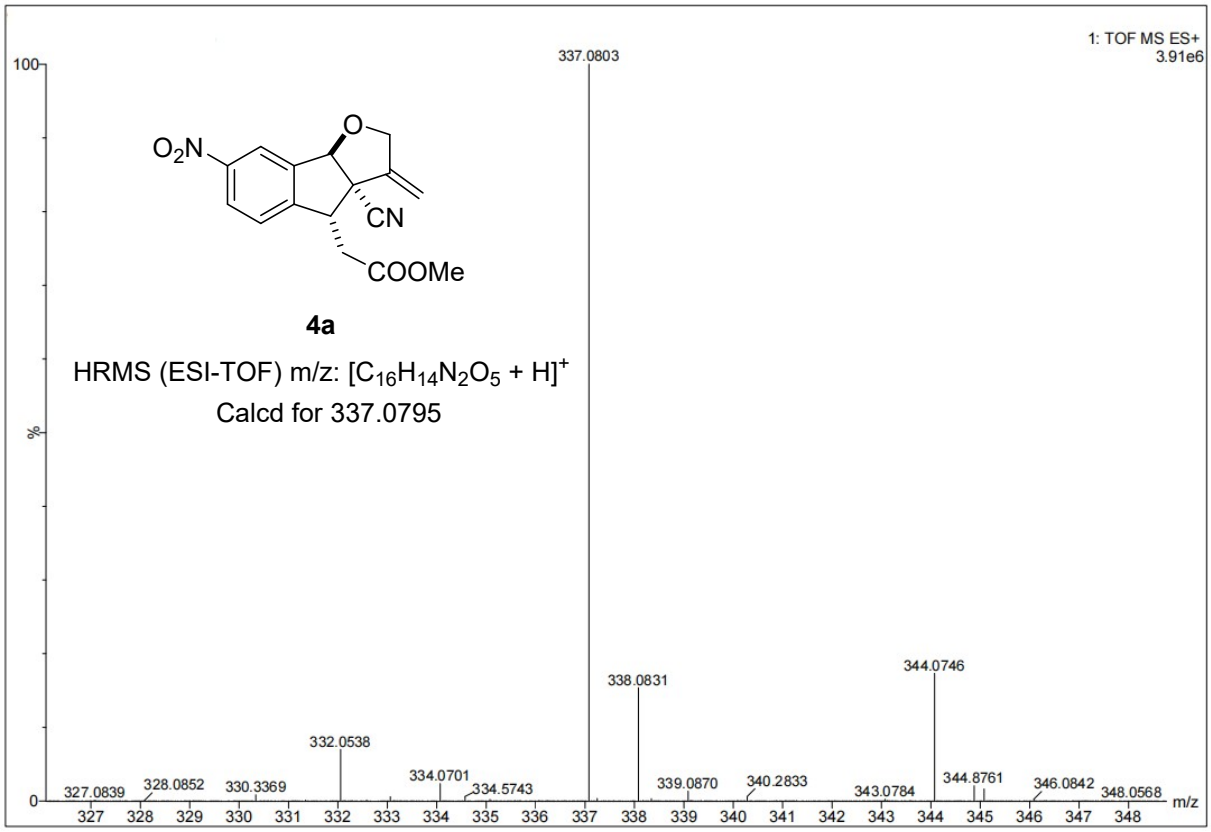
4a

^{1}H NMR (600 MHz, $CDCl_3$)



4a

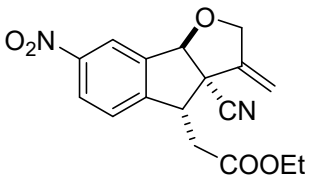
^{13}C NMR (150 MHz, $CDCl_3$)



4a

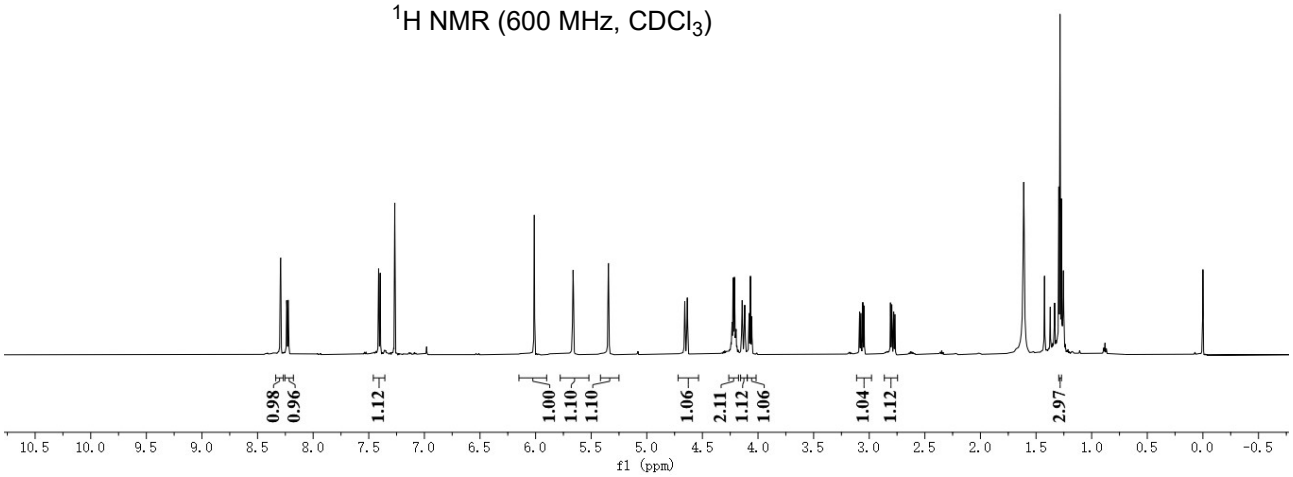
HRMS (ESI-TOF) m/z: $[C_{16}H_{14}N_2O_5 + H]^+$

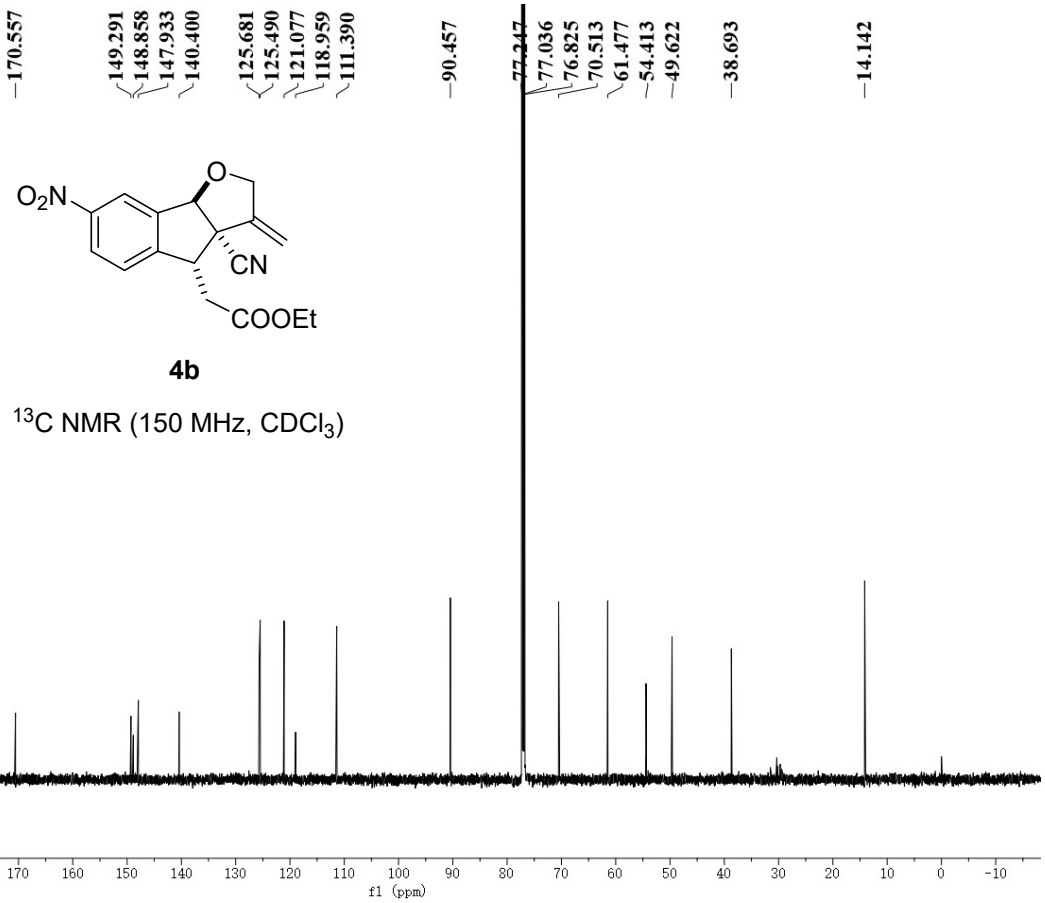
Calcd for 337.0795



4b

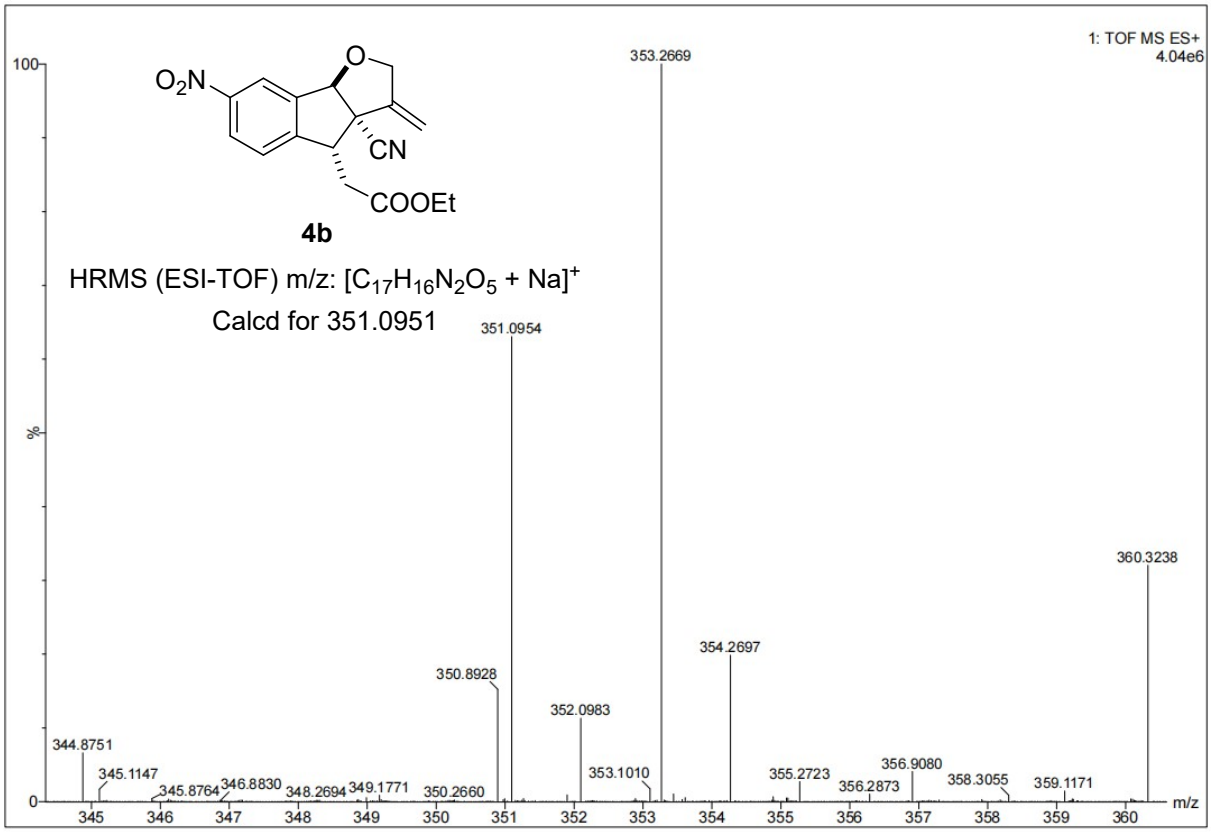
^{1}H NMR (600 MHz, $CDCl_3$)





4b

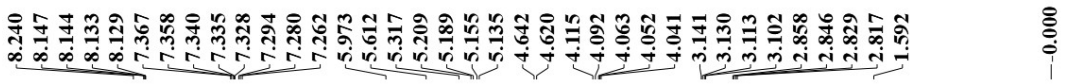
^{13}C NMR (150 MHz, $CDCl_3$)

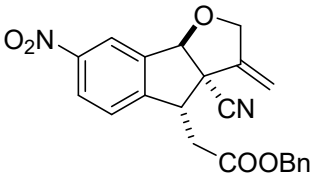


4b

HRMS (ESI-TOF) m/z: $[C_{17}H_{16}N_2O_5 + Na]^+$

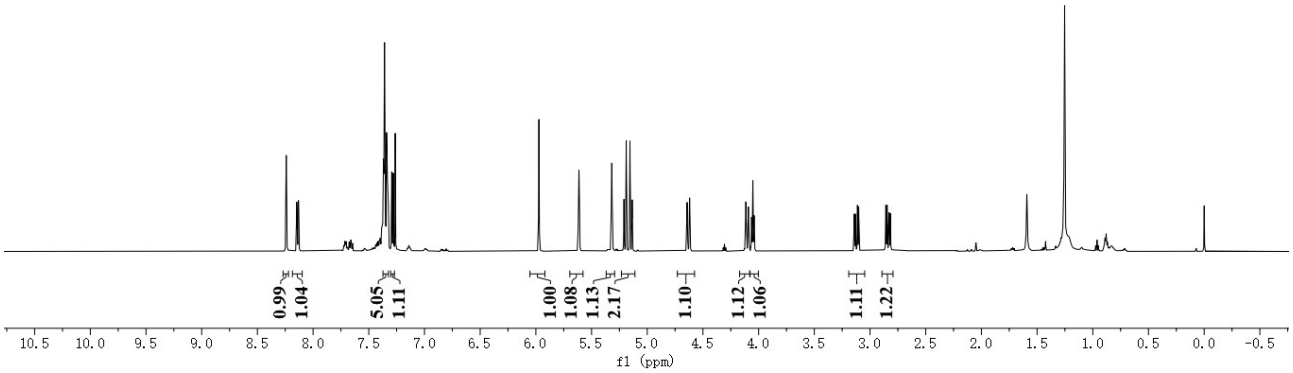
Calcd for 351.0951

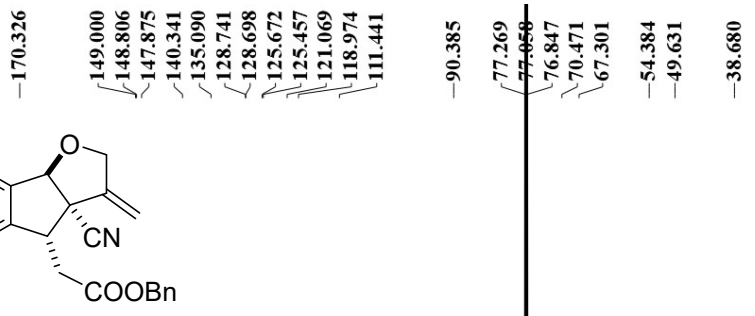




4c

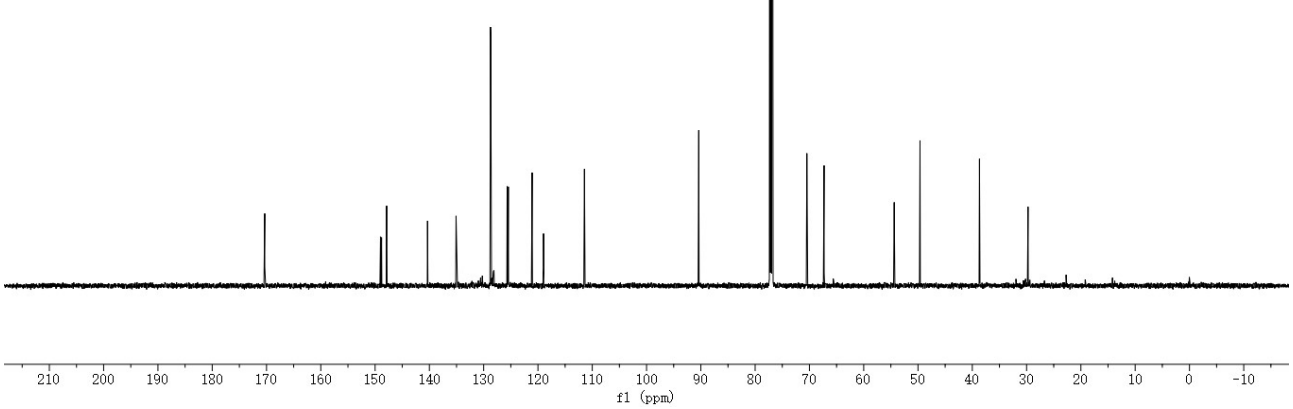
^{1}H NMR (600 MHz, $CDCl_3$)

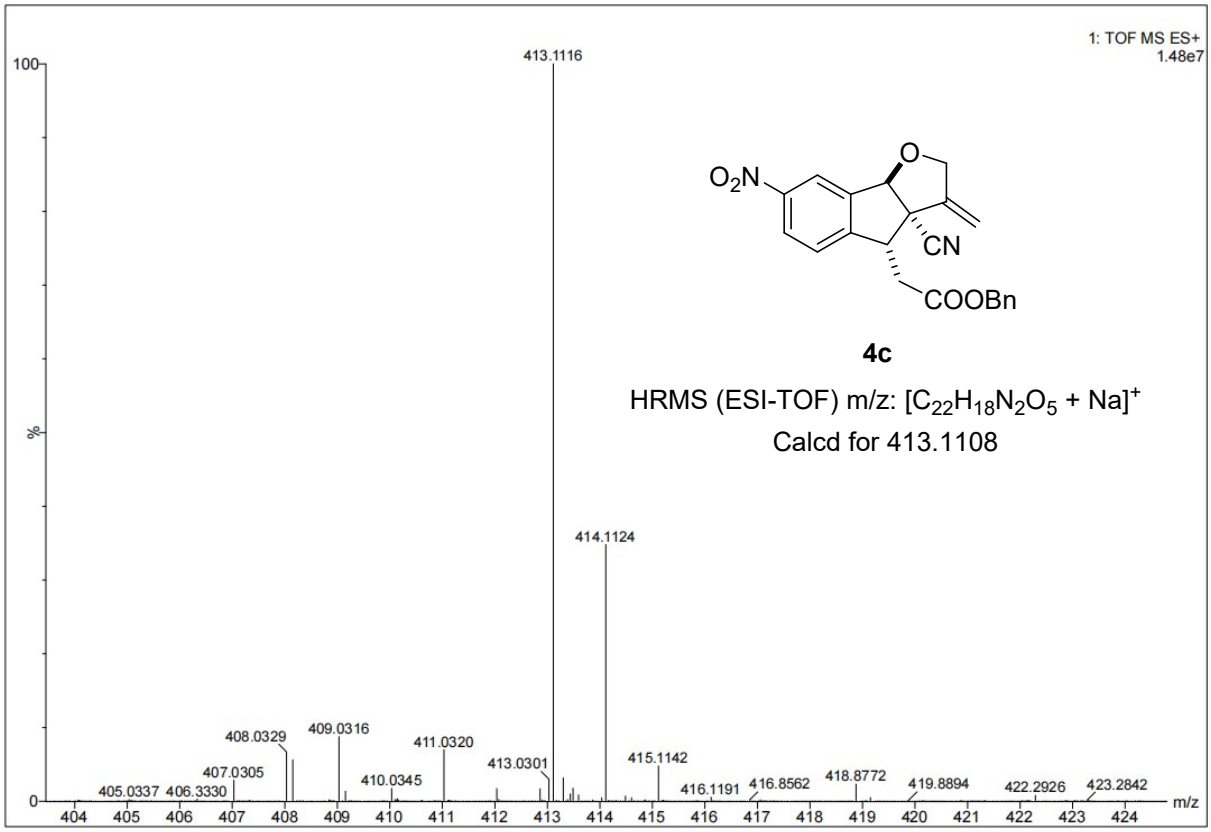




4c

^{13}C NMR (150 MHz, $CDCl_3$)

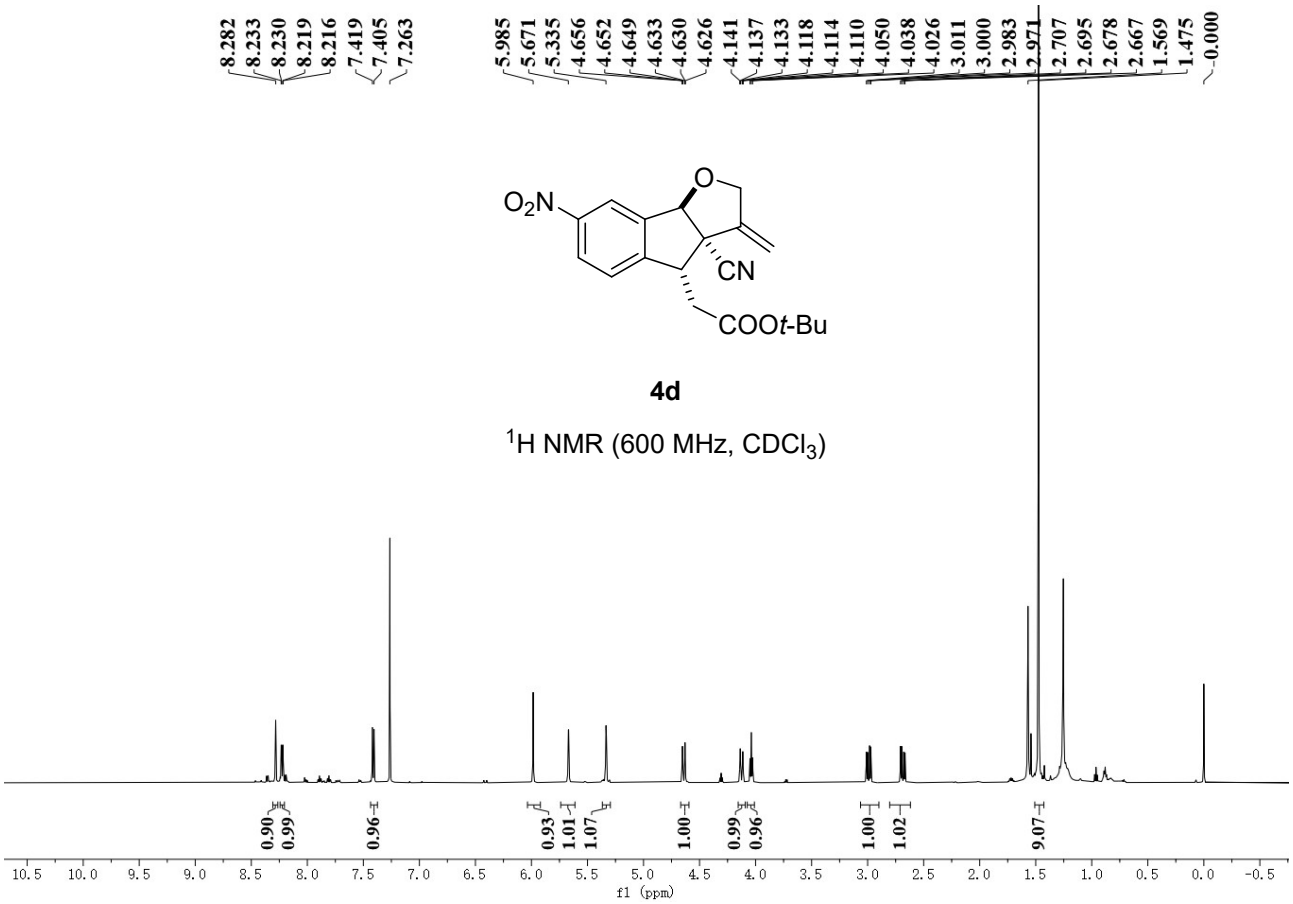




4c

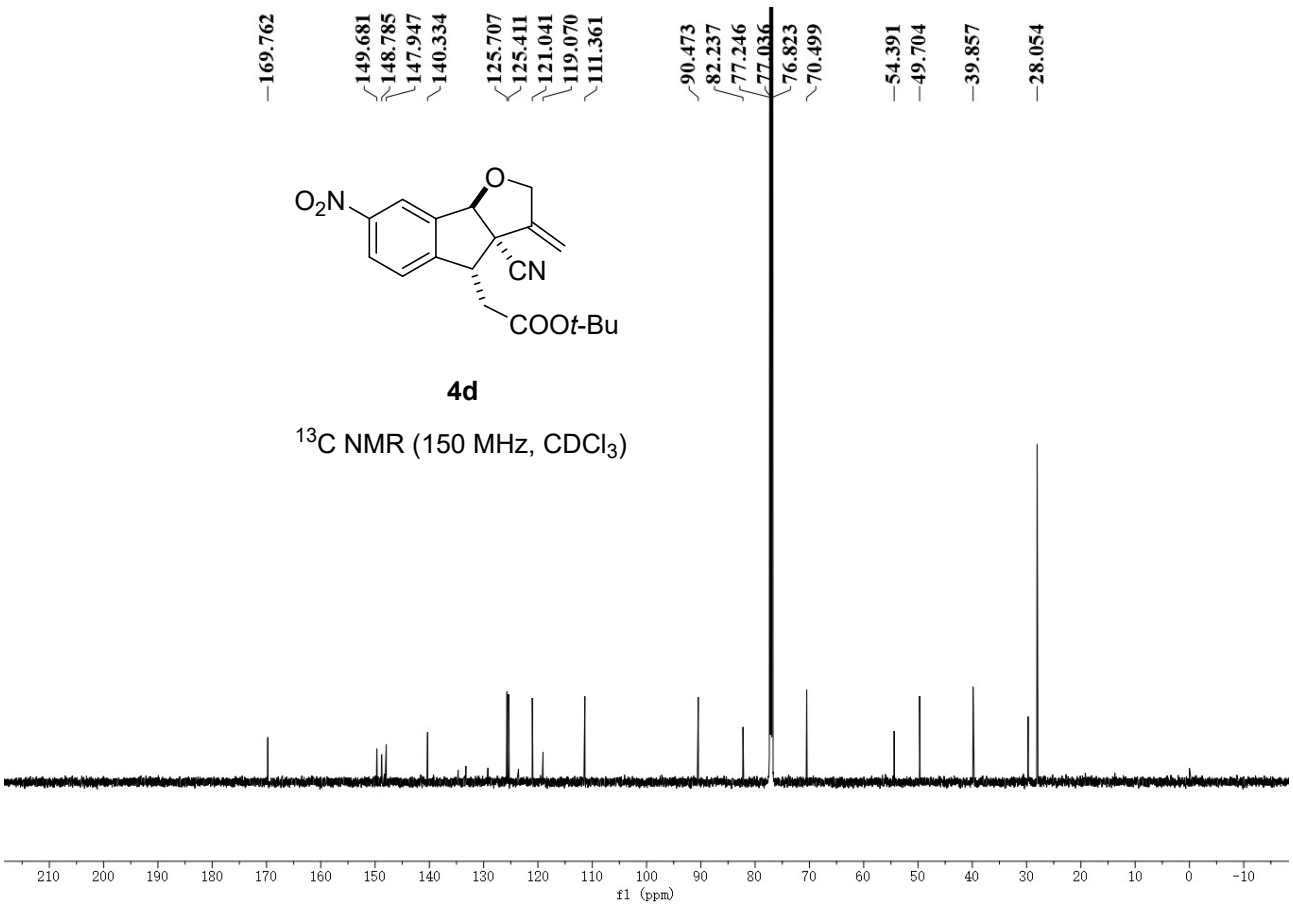
HRMS (ESI-TOF) m/z: $[C_{22}H_{18}N_2O_5 + Na]^+$

Calcd for 413.1108



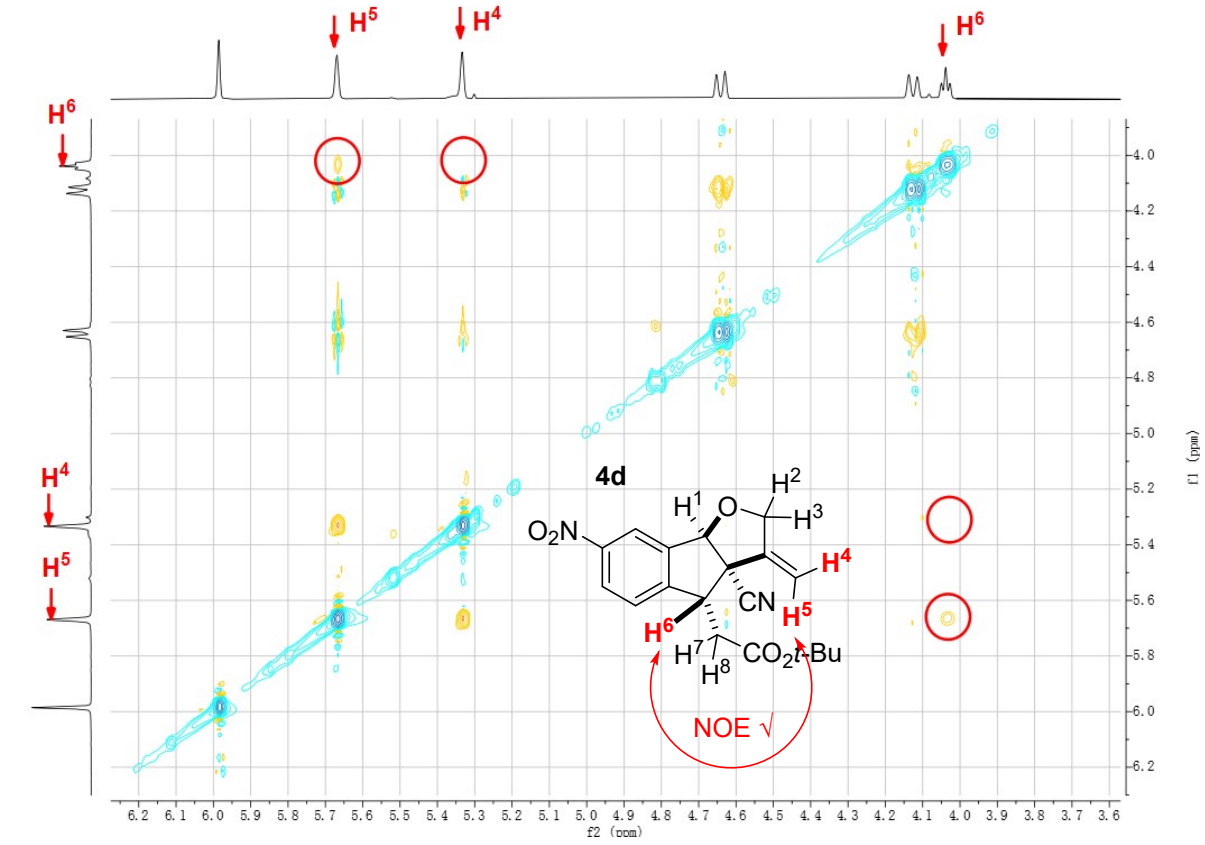
4d

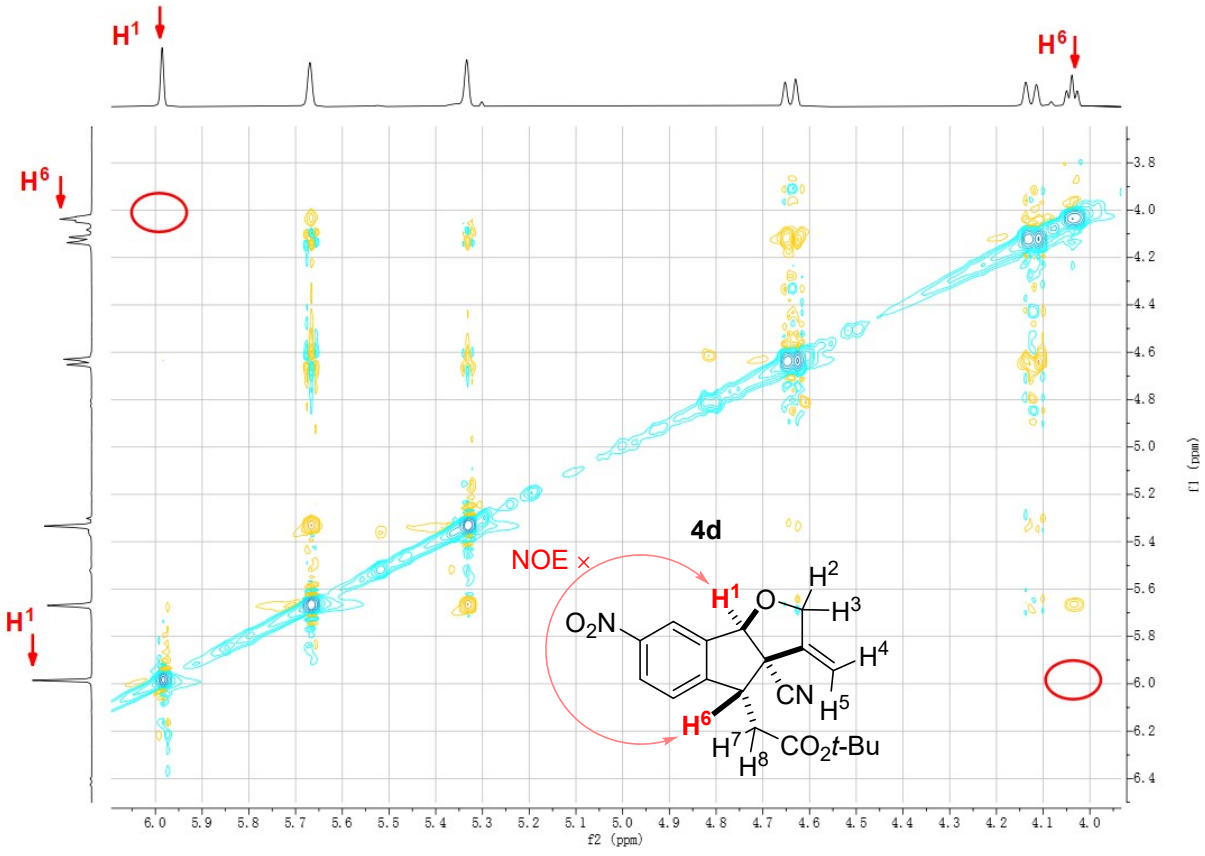
^{1}H NMR (600 MHz, $CDCl_3$)

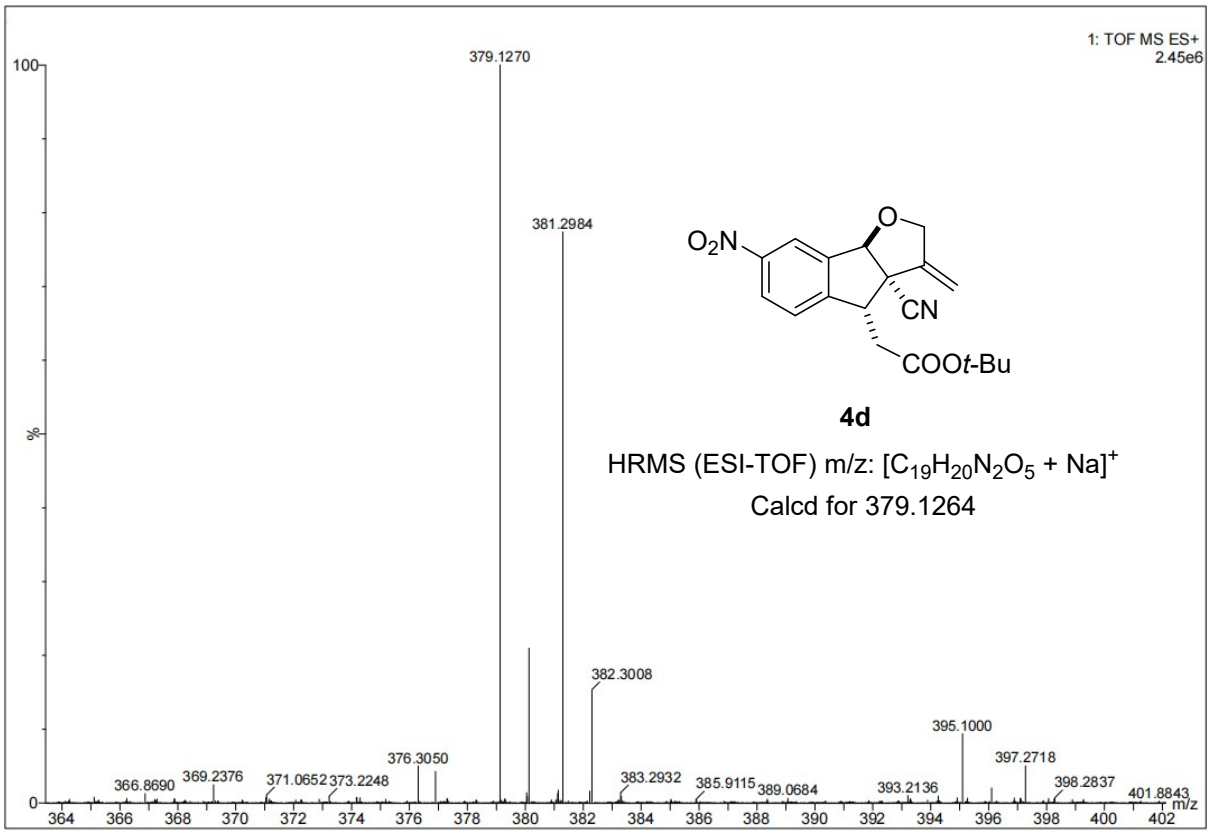


4d

^{13}C NMR (150 MHz, $CDCl_3$)


H5
H4
H6
H6
H4
H5
4d
O2N
H1
O
H2
H3
H4
CN
H5
H6
H7
H8
CO2t-Bu
NOE √
f2 (ppm)
f1 (ppm)

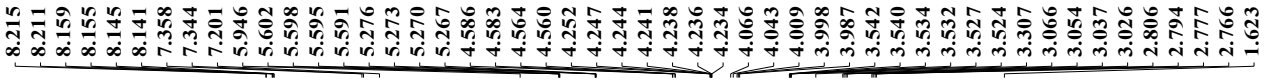

H1
H6
H6
H1
4d
NOE ×
O2N
H1
O
H2
H3
H4
CN
H5
H6
H7
H8
CO2t-Bu
f2 (ppm)
f1 (ppm)

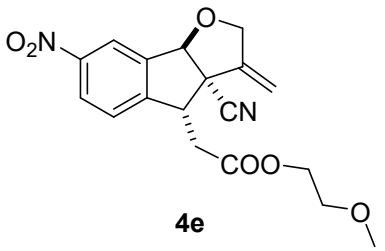


4d

HRMS (ESI-TOF) m/z: $[C_{19}H_{20}N_2O_5 + Na]^+$

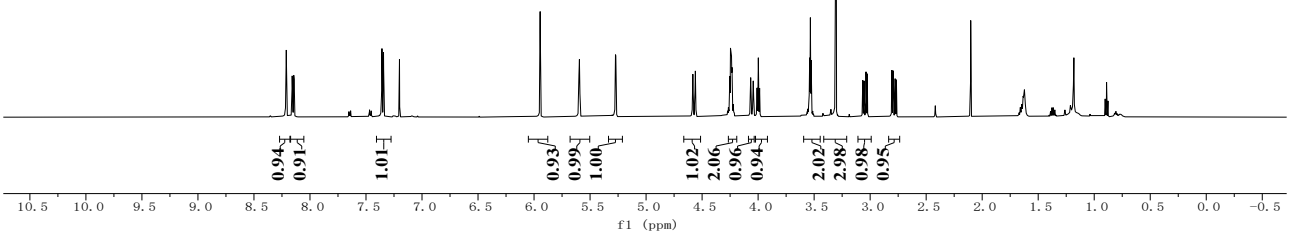
Calcd for 379.1264

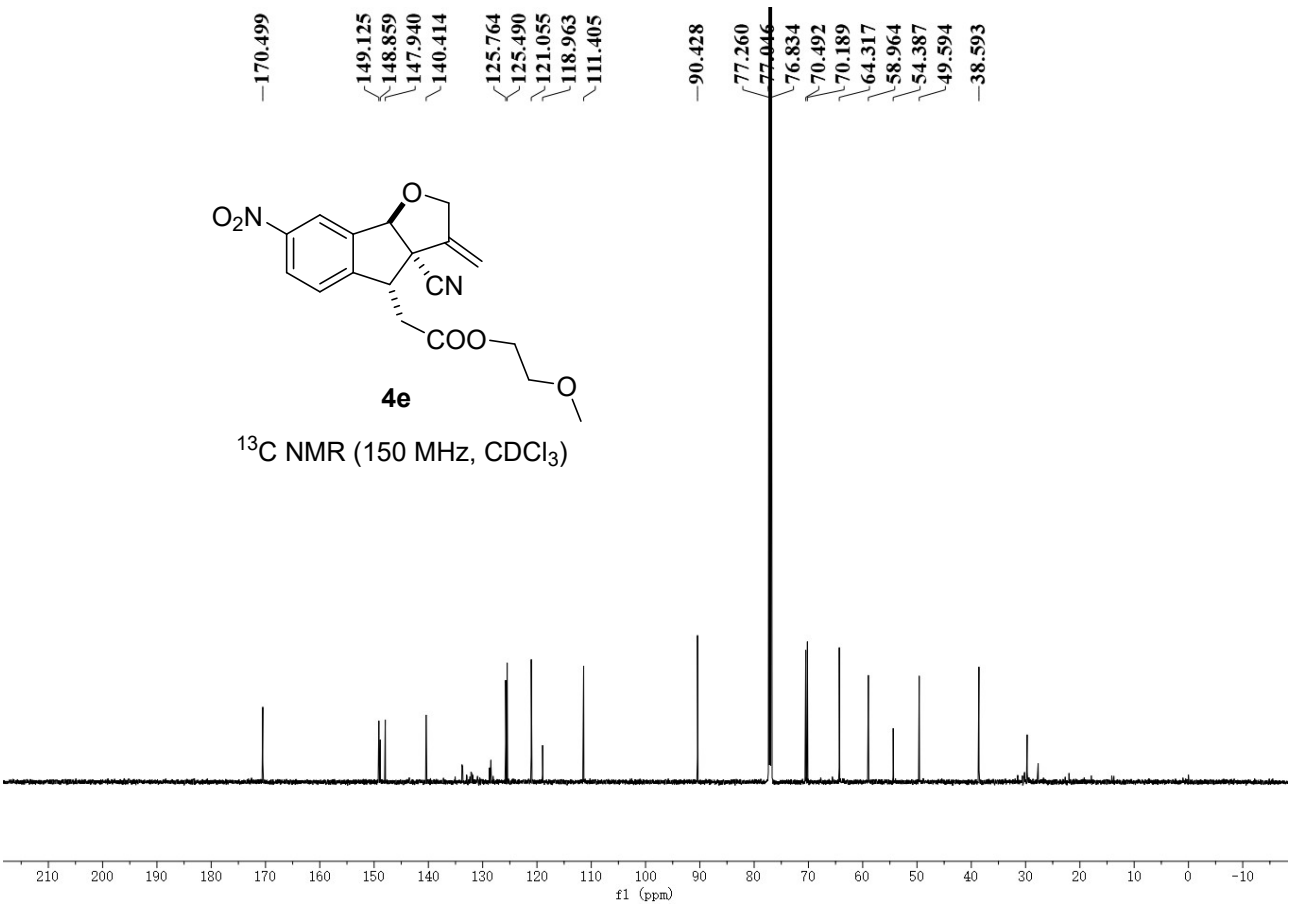




4e

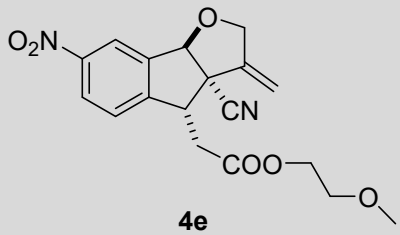
^{1}H NMR (600 MHz, $CDCl_3$)





4e

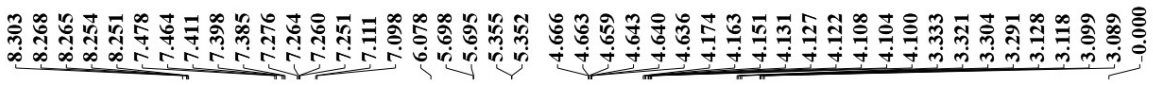
^{13}C NMR (150 MHz, $CDCl_3$)

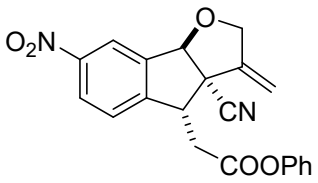


4e

HRMS (ESI-TOF) m/z: $[C_{18}H_{18}N_2O_6 + Na]^+$

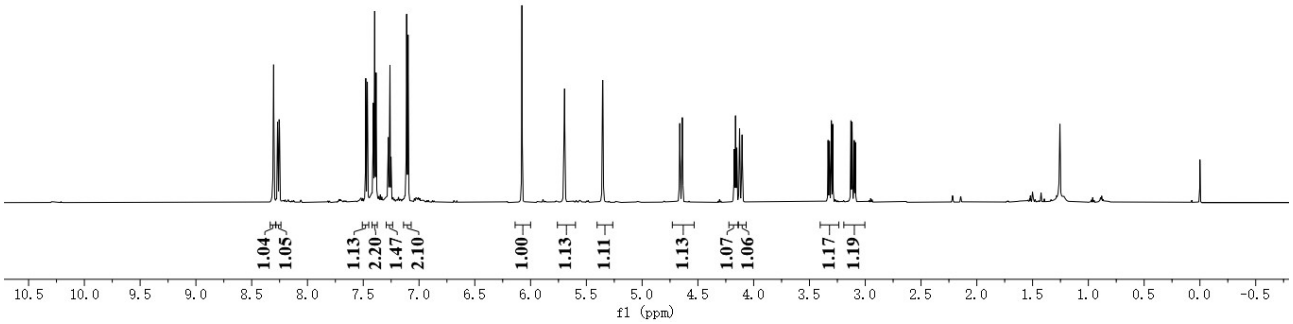
Calcd for 381.1057

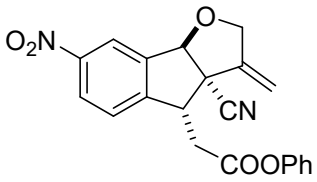




4f

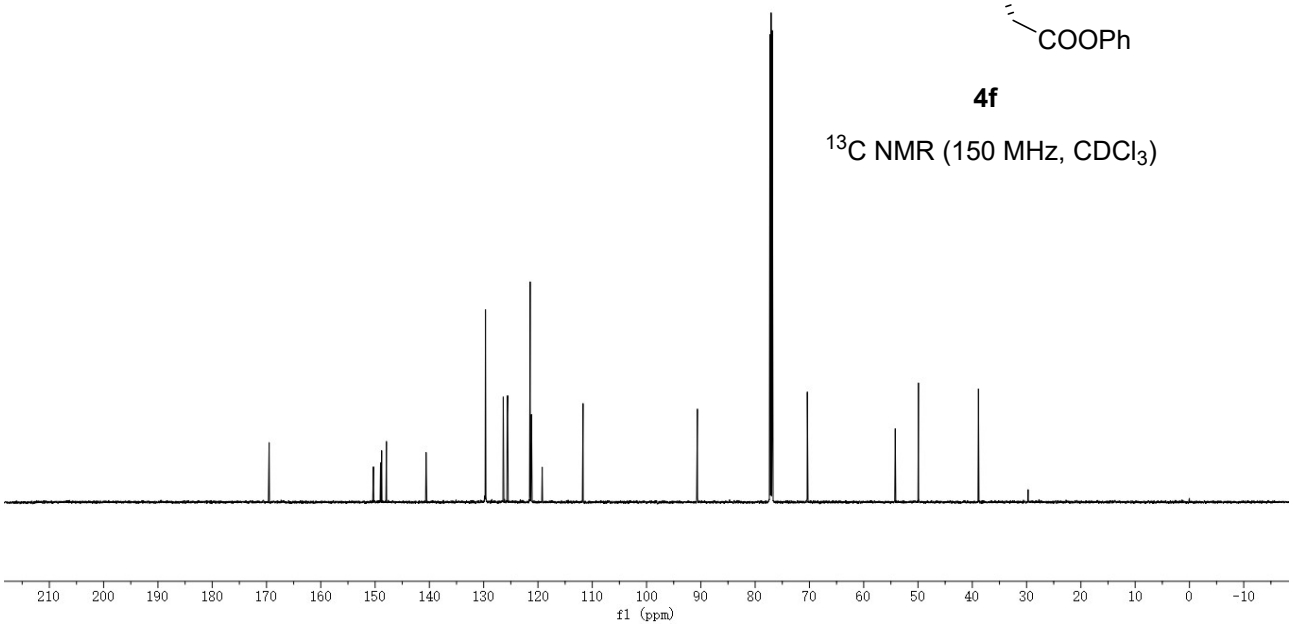
^{1}H NMR (600 MHz, $CDCl_3$)

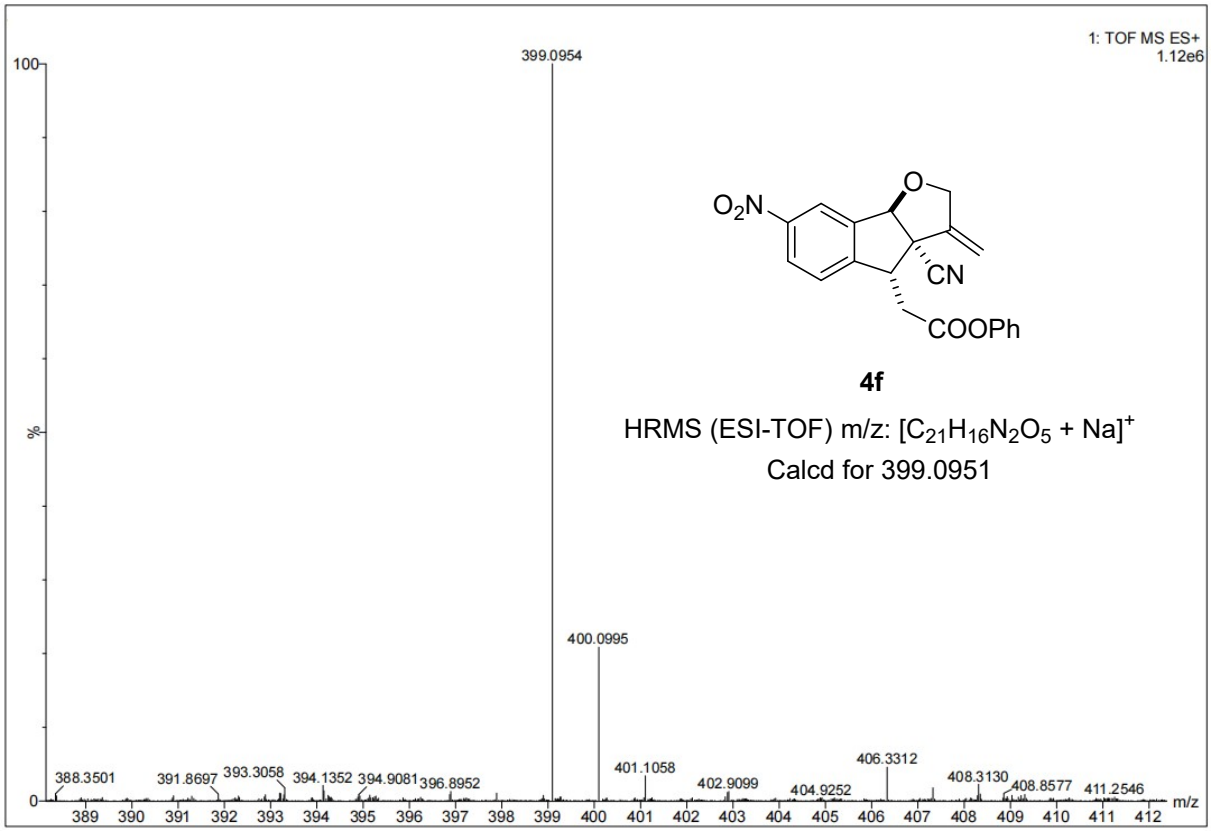




4f

^{13}C NMR (150 MHz, $CDCl_3$)

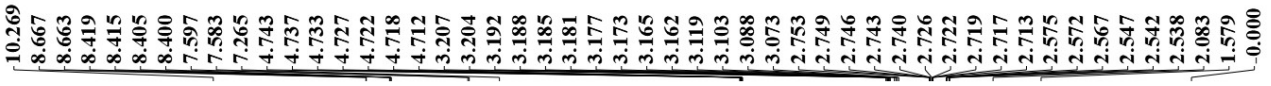


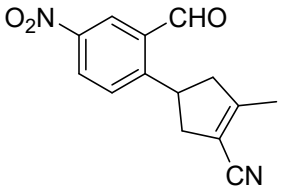


4f

HRMS (ESI-TOF) m/z: $[C_{21}H_{16}N_2O_5 + Na]^+$

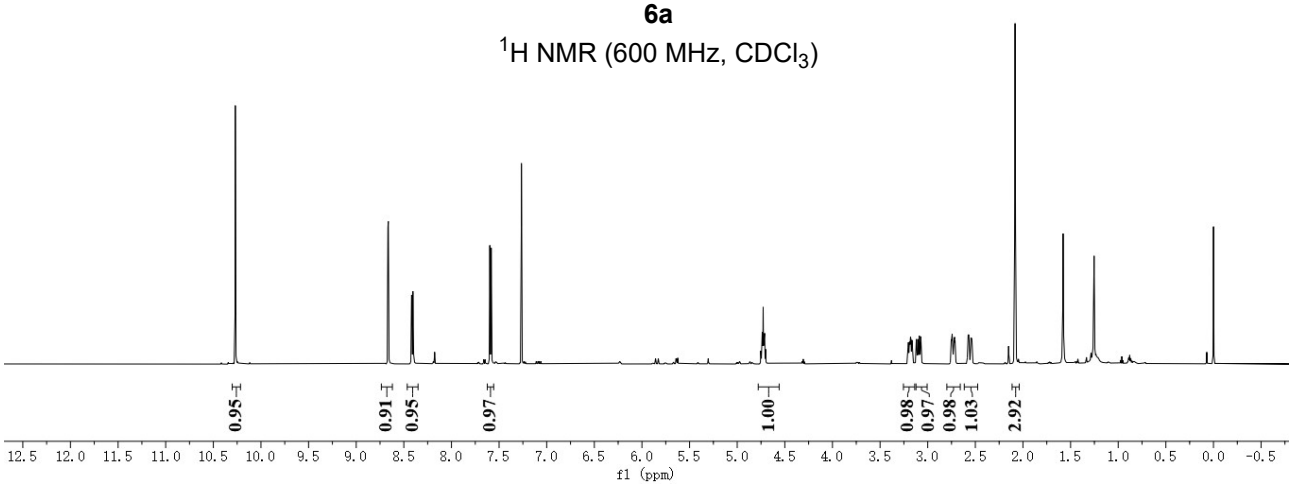
Calcd for 399.0951

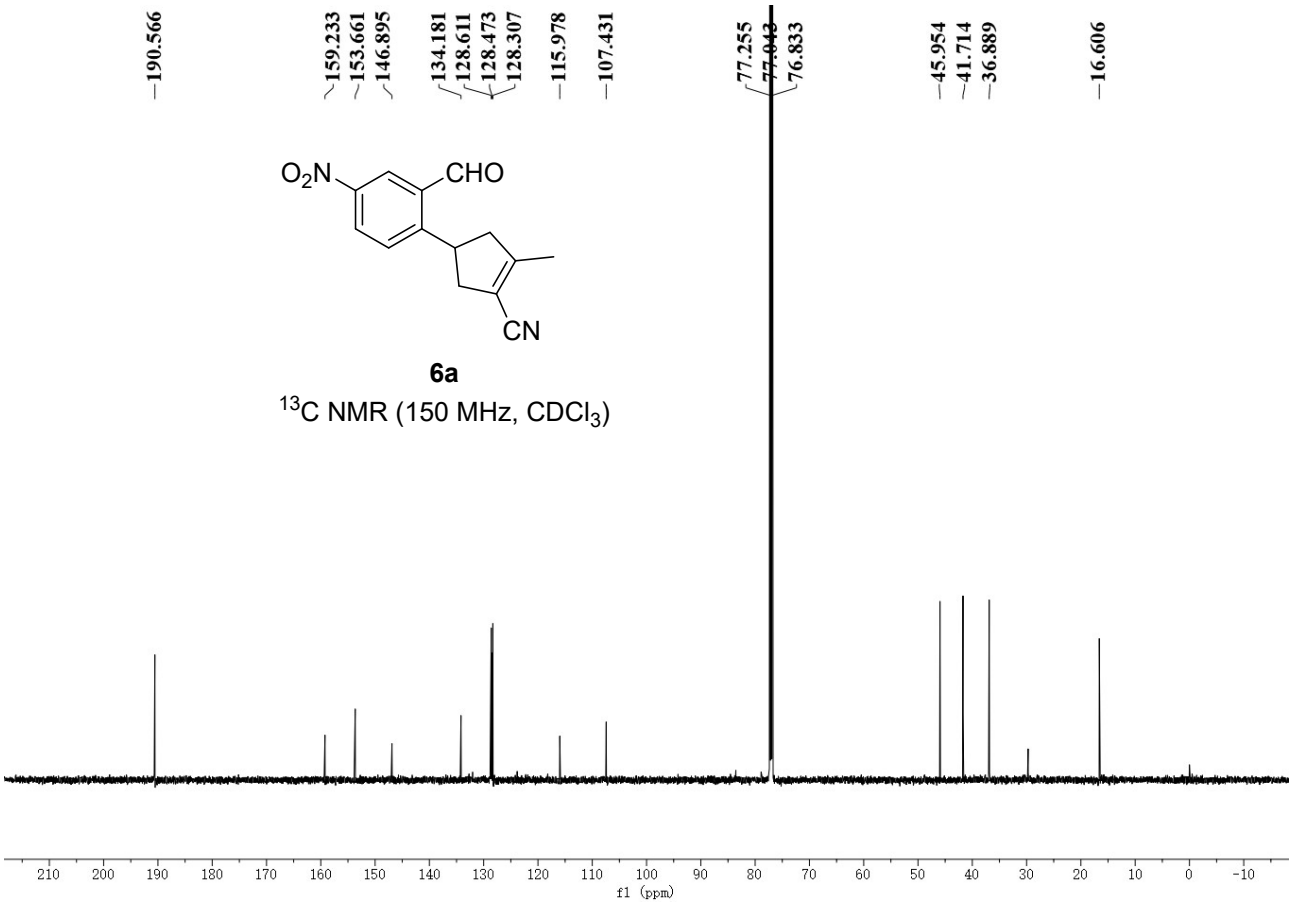




6a

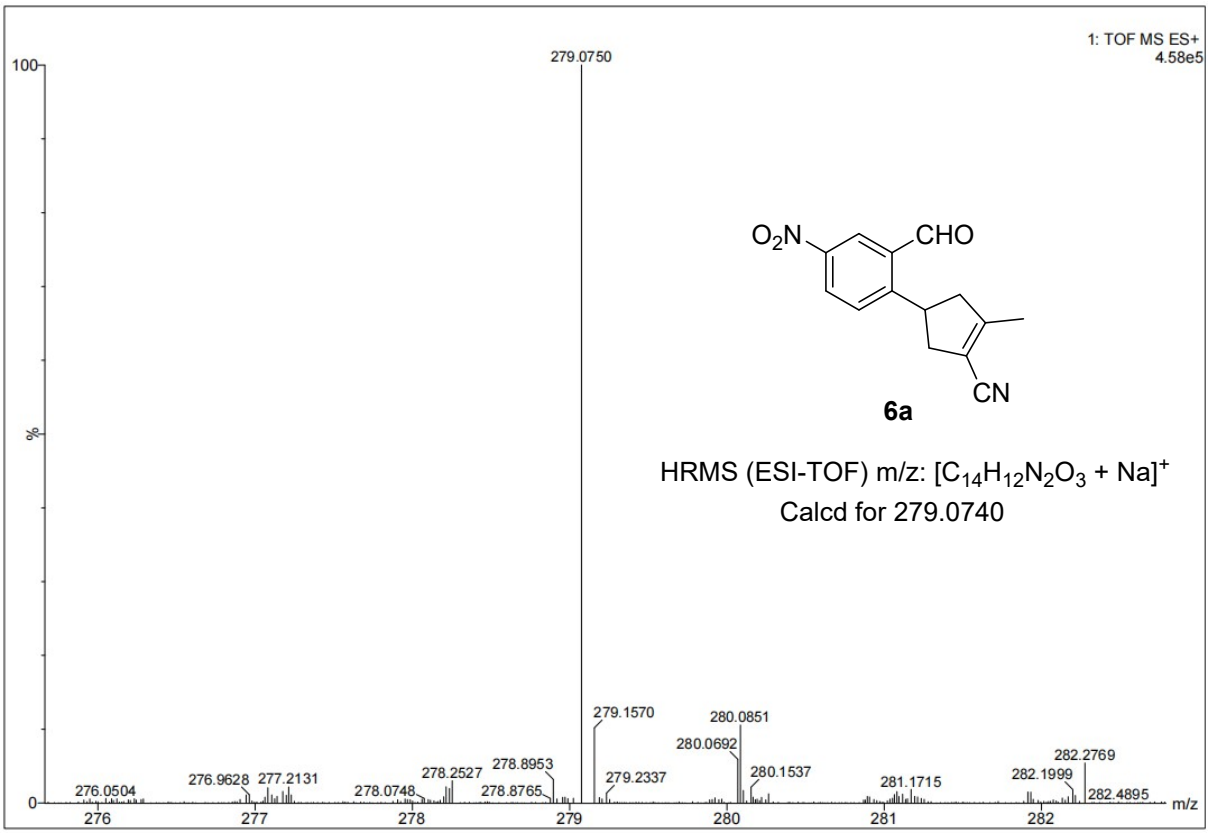
^{1}H NMR (600 MHz, $CDCl_3$)





6a

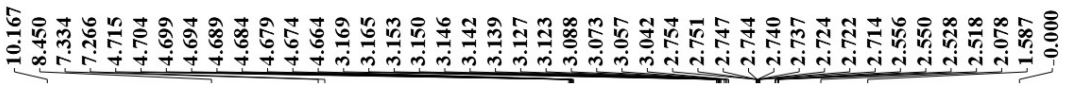
^{13}C NMR (150 MHz, $CDCl_3$)

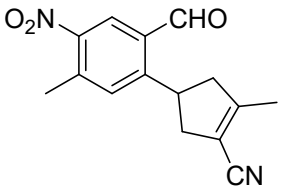


6a

HRMS (ESI-TOF) m/z: $[C_{14}H_{12}N_2O_3 + Na]^+$

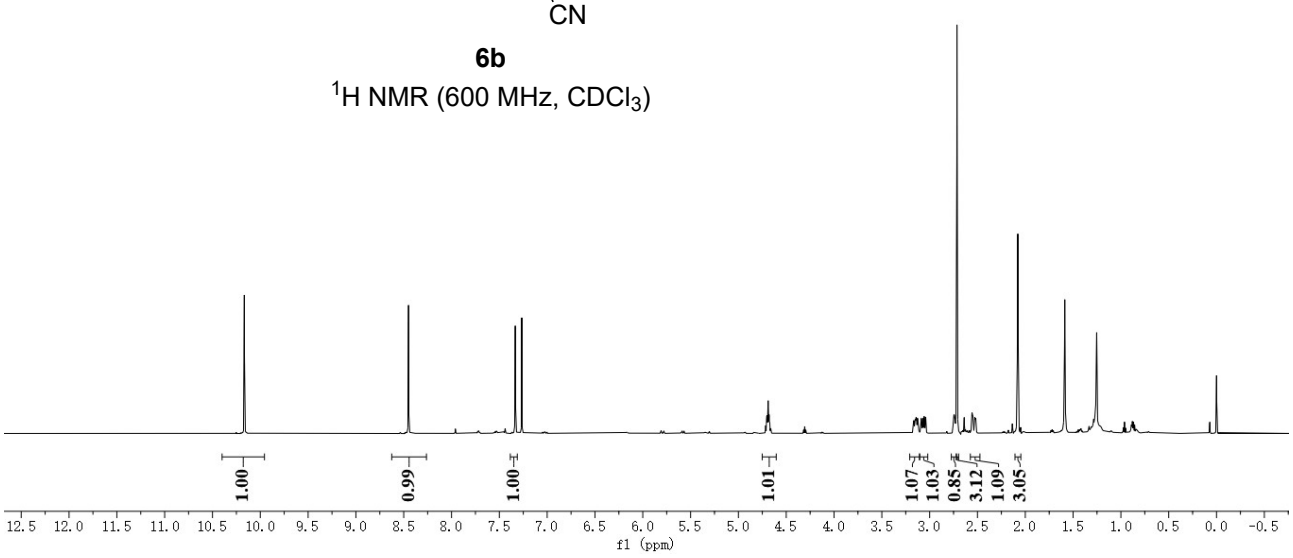
Calcd for 279.0740

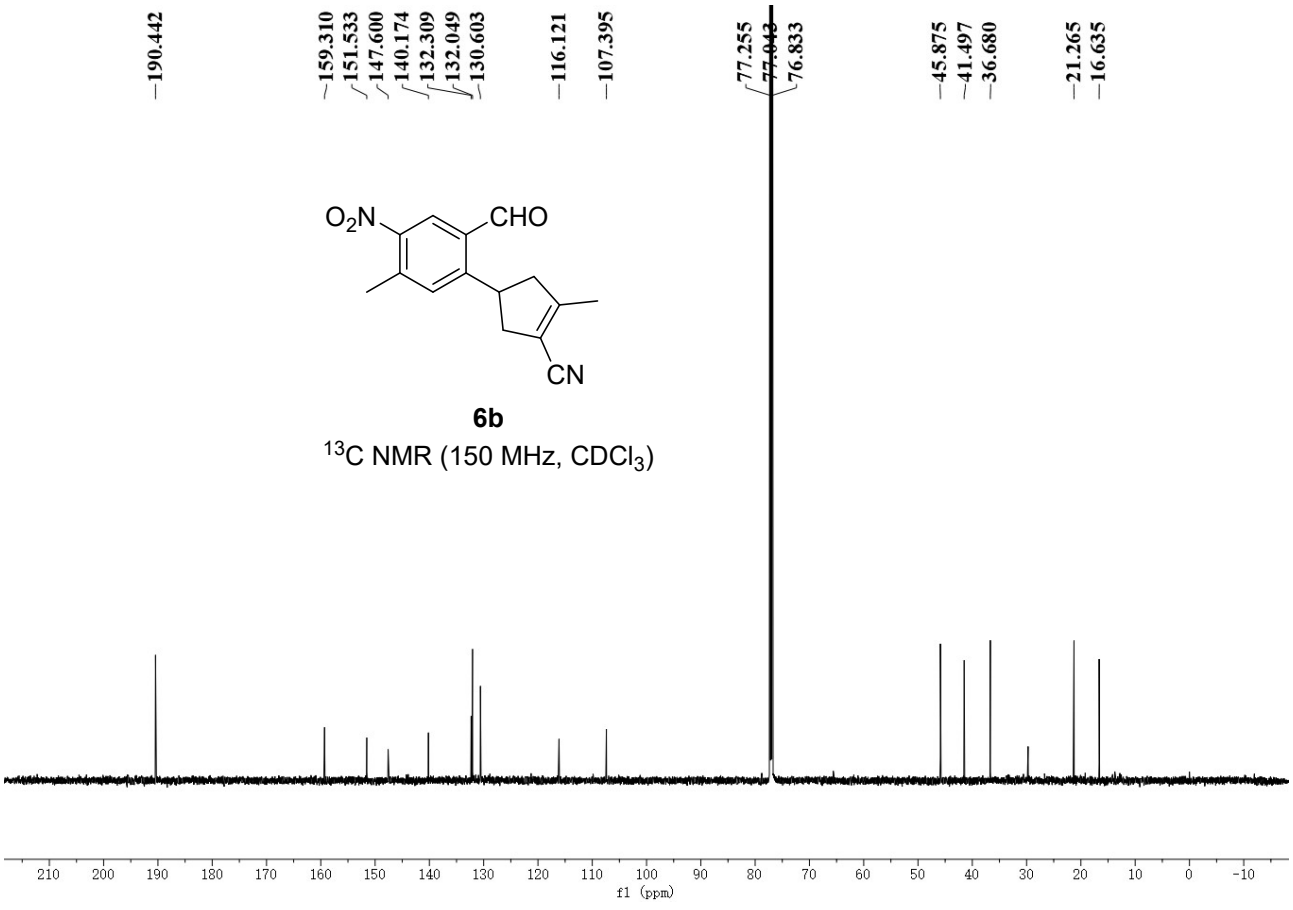




6b

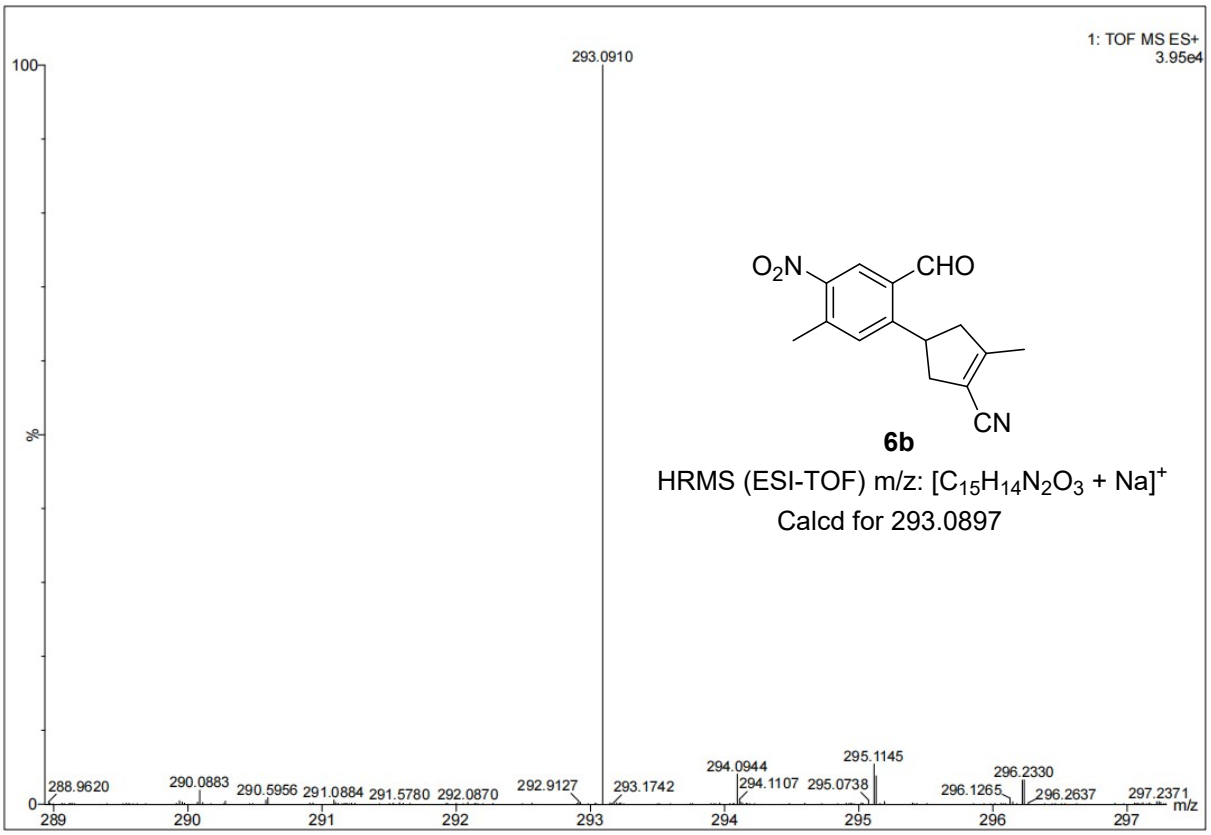
^{1}H NMR (600 MHz, $CDCl_3$)





6b

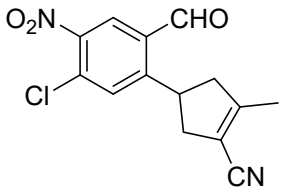
^{13}C NMR (150 MHz, $CDCl_3$)



6b

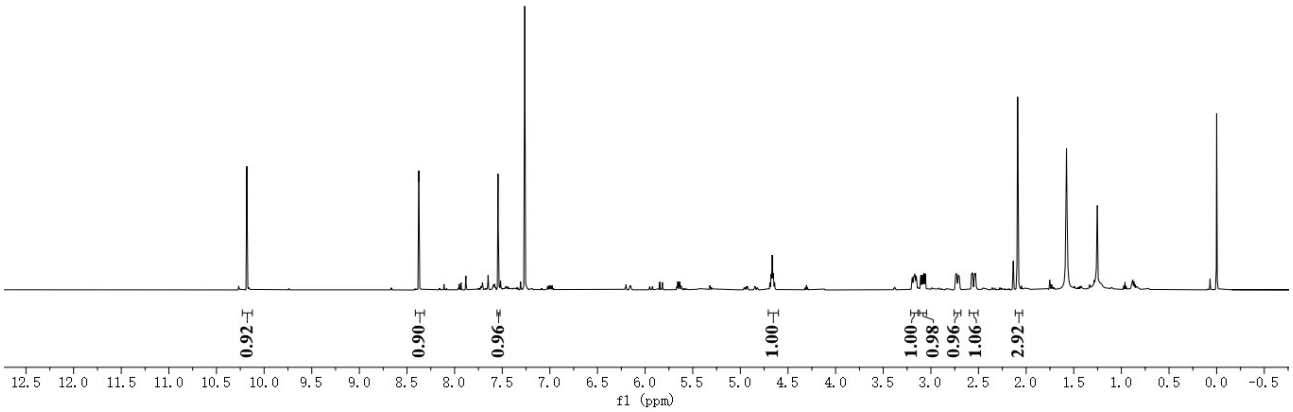
HRMS (ESI-TOF) m/z: $[C_{15}H_{14}N_2O_3 + Na]^+$

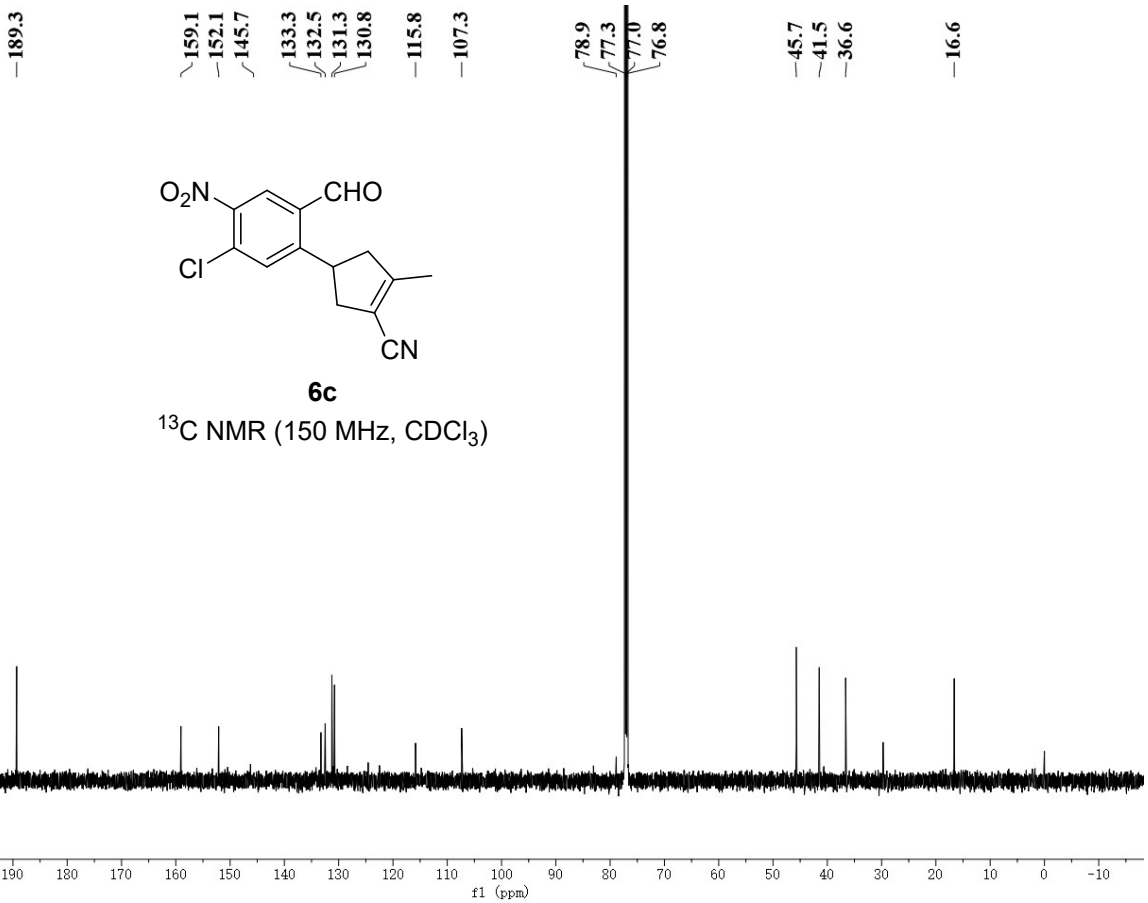
Calcd for 293.0897



6c

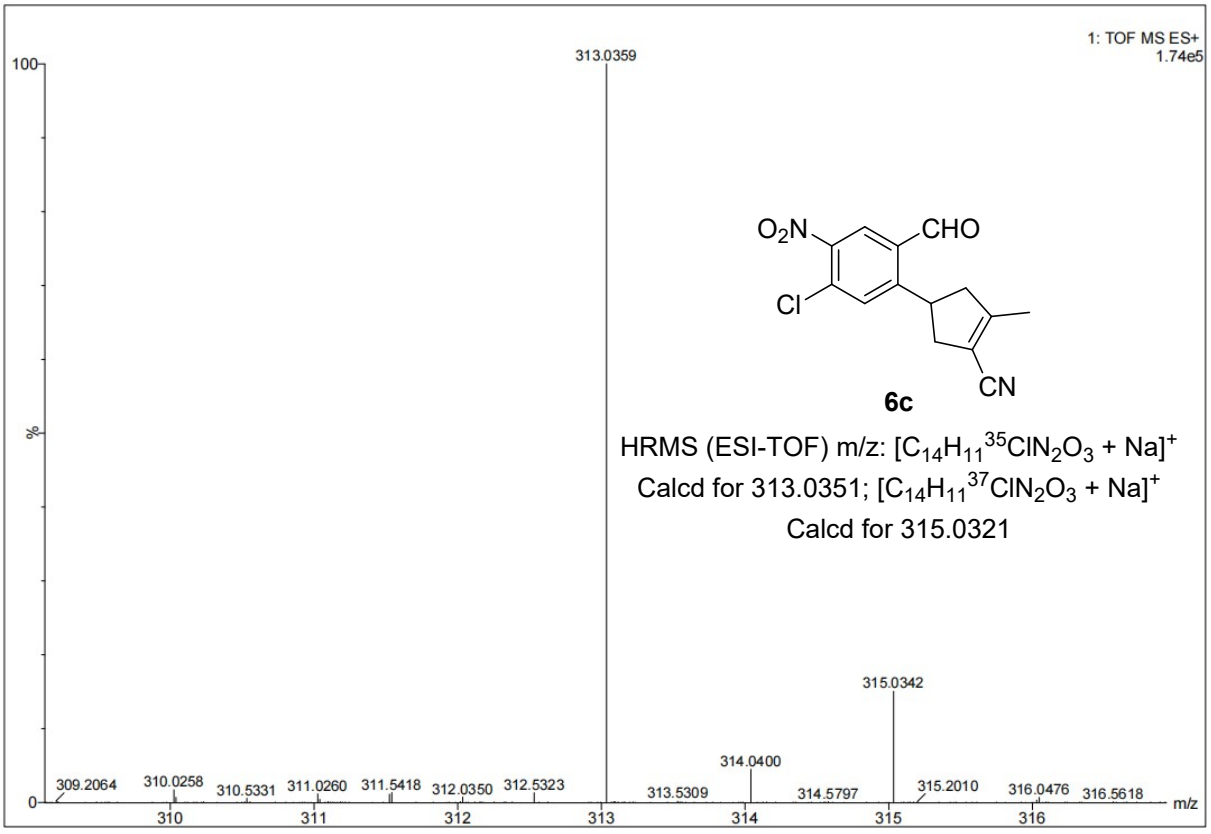
^{1}H NMR (600 MHz, $CDCl_3$)





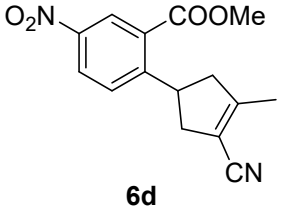
6c

^{13}C NMR (150 MHz, $CDCl_3$)



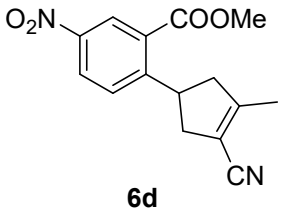
6c

HRMS (ESI-TOF) m/z: $[C_{14}H_{11}{}^{35}ClN_2O_3 + Na]^+$
Calcd for 313.0351; $[C_{14}H_{11}{}^{37}ClN_2O_3 + Na]^+$
Calcd for 315.0321



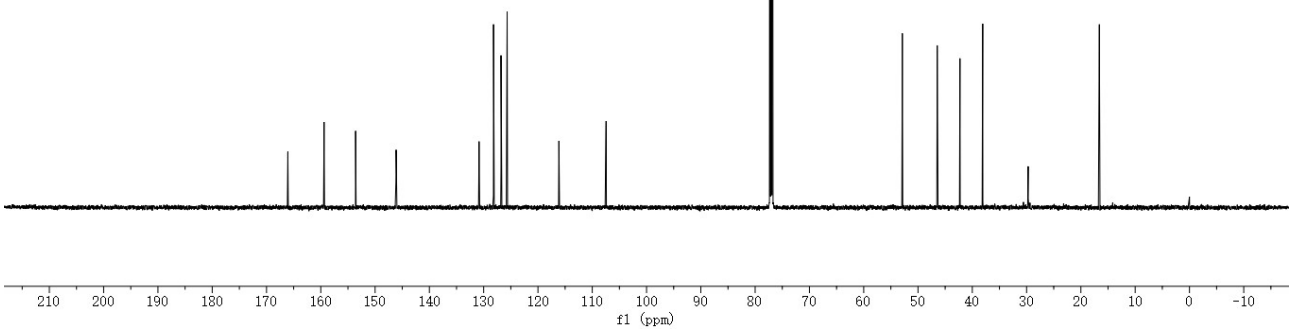
6d

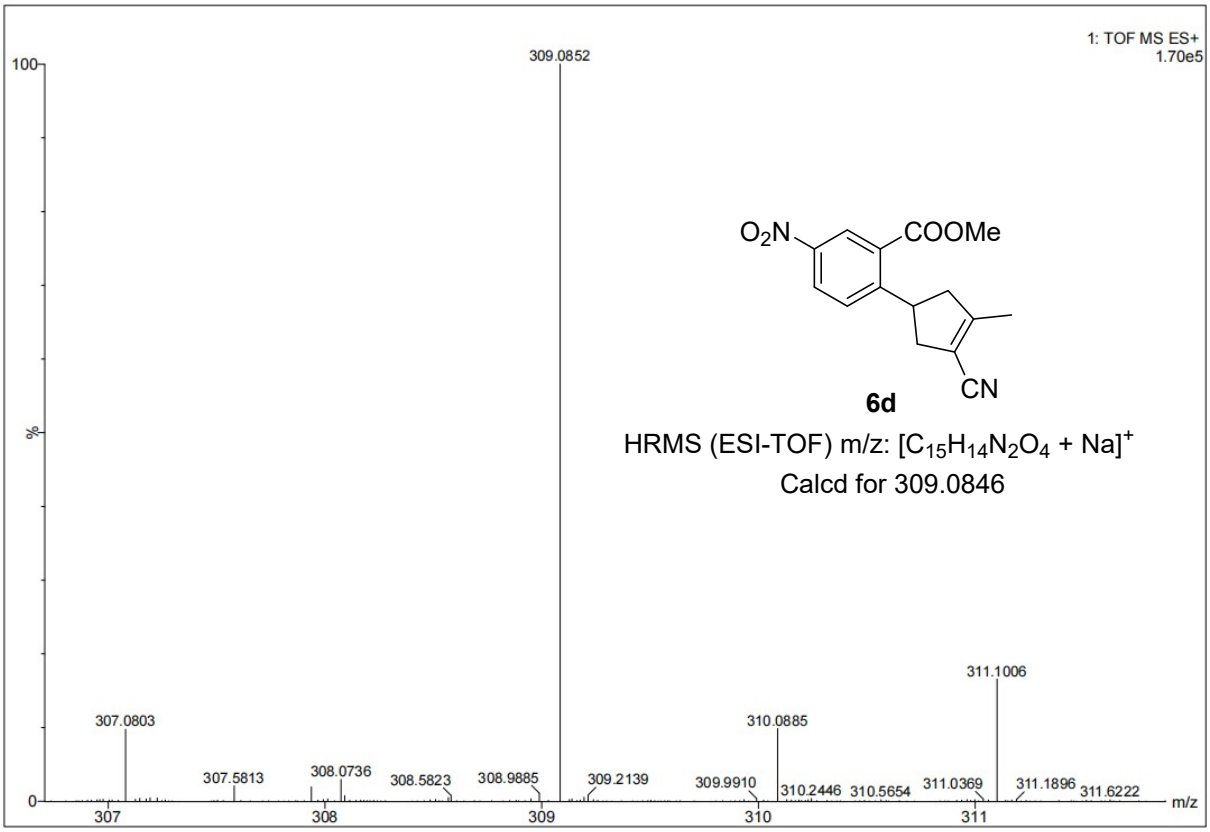
^{1}H NMR (600 MHz, $CDCl_3$)



6d

^{13}C NMR (150 MHz, $CDCl_3$)

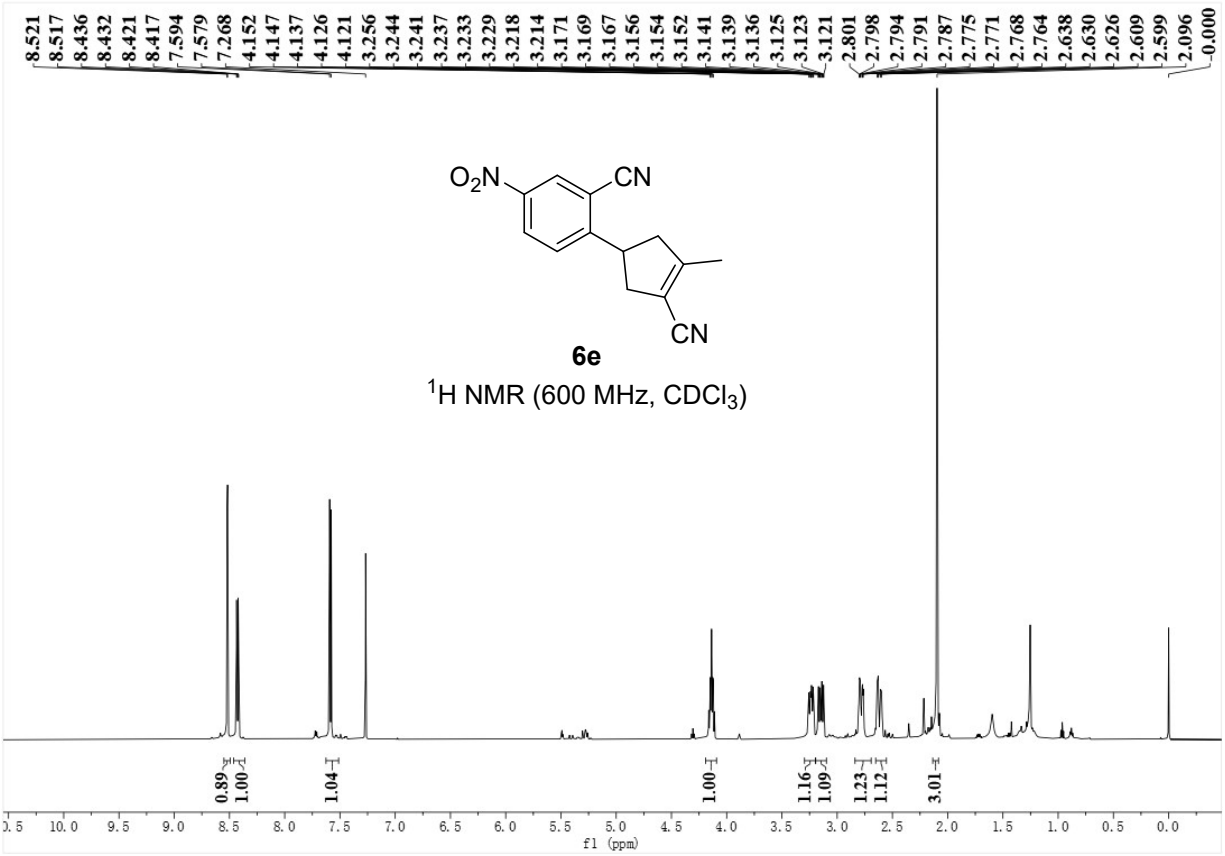




6d

HRMS (ESI-TOF) m/z: $[C_{15}H_{14}N_2O_4 + Na]^+$

Calcd for 309.0846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4.126
4.121
3.256
3.244
3.241
3.237
3.233
3.229
3.218
3.214
3.171
3.169
3.167
3.156
3.154
3.152
3.141
3.139
3.136
3.125
3.123
3.121
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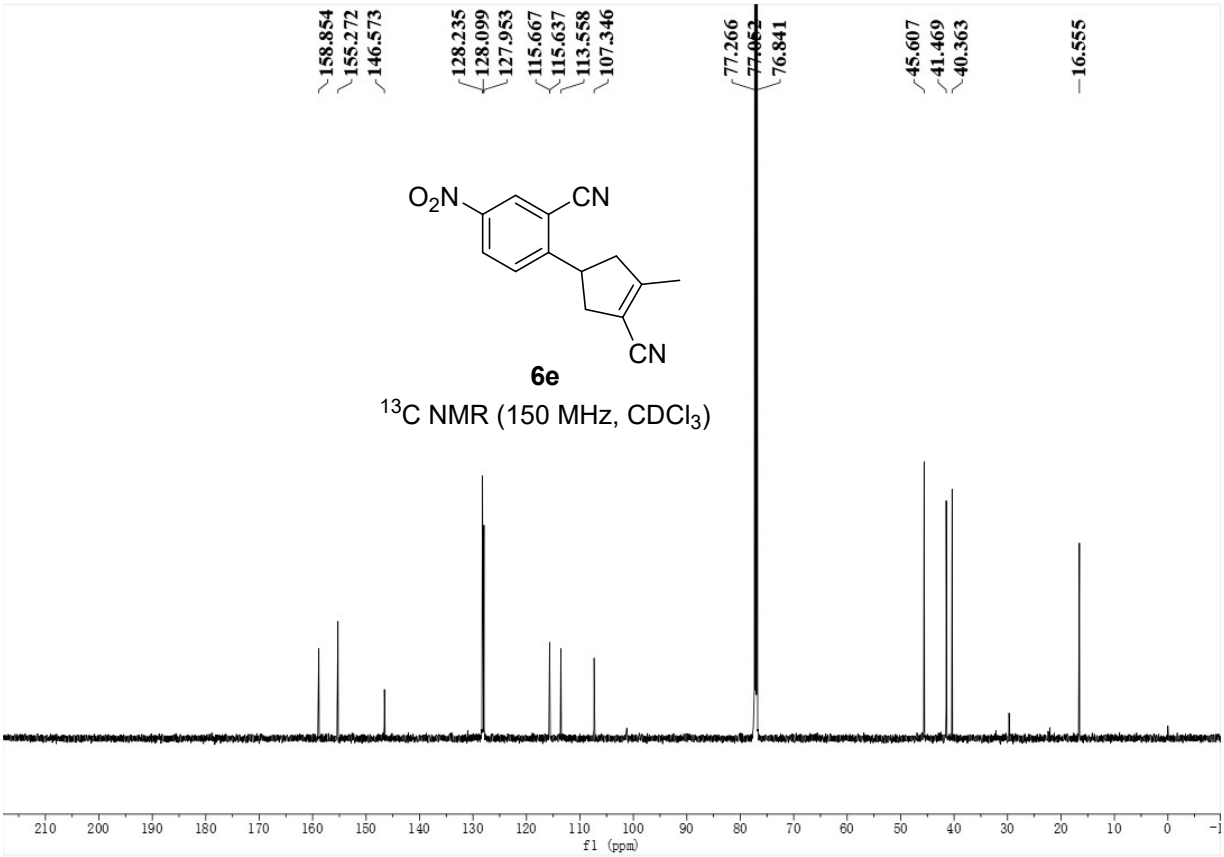
2.794
2.791
2.787
2.775
2.771
2.768
2.764
2.638
2.630
2.626
2.609
2.599
2.096
0.000
O2N
CN
CN
6e
1H NMR (600 MHz, CDCl3)
0.89
1.00
1.04
1.00
1.16
1.09
1.23
1.12
3.01
f1 (ppm)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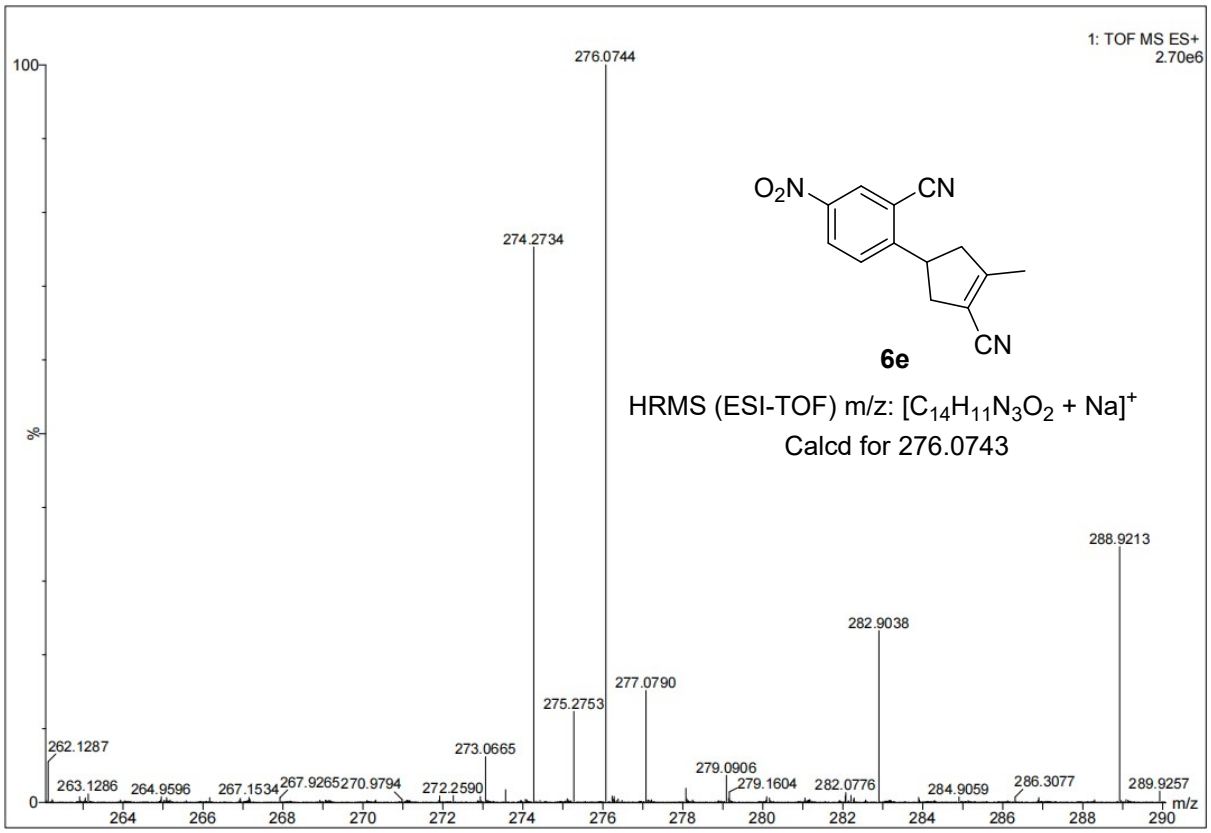
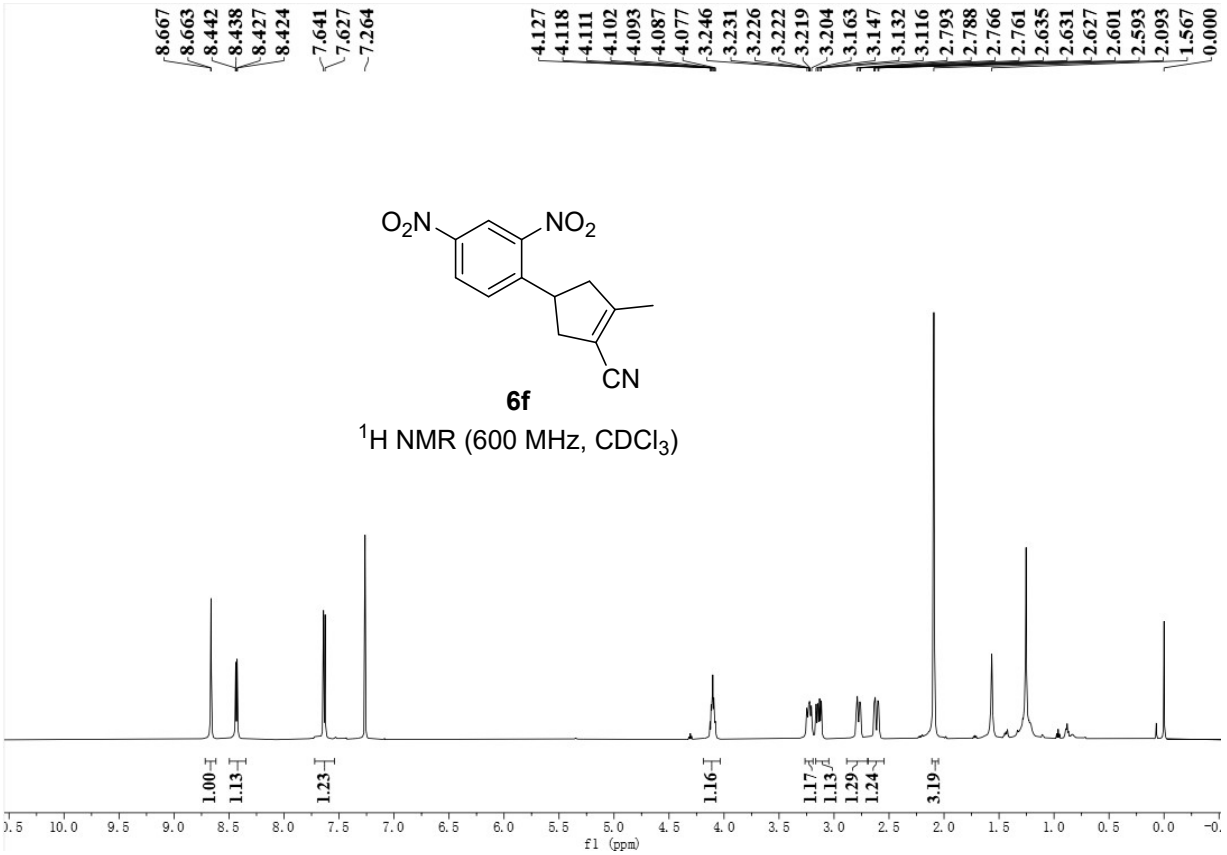
128.235
128.099
127.953
115.667
115.637
113.558
107.346
77.266
77.062
76.841
45.607
41.469
40.363
16.555
O2N
CN
CN
6e
13C NMR (150 MHz, CDCl3)
f1 (ppm)



6e

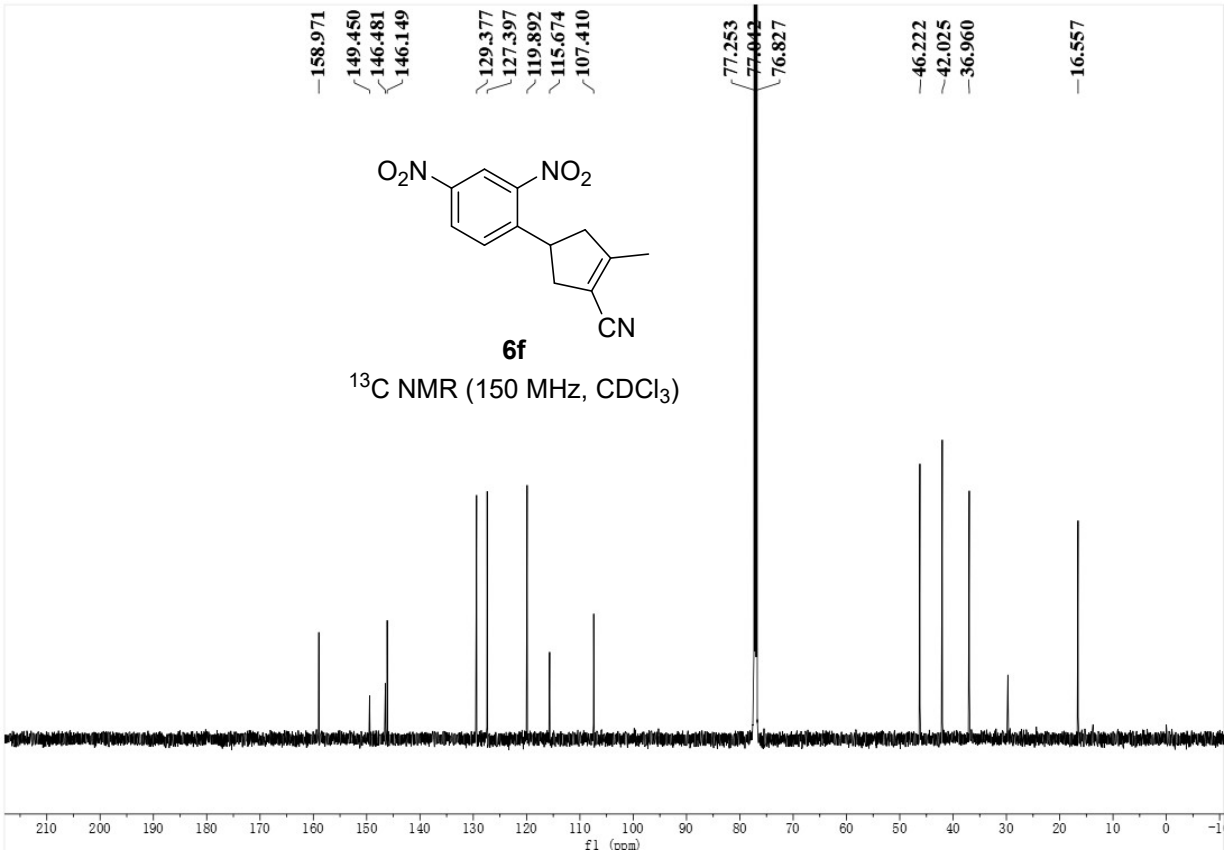
HRMS (ESI-TOF) m/z: $[C_{14}H_{11}N_3O_2 + Na]^+$

Calcd for 276.0743



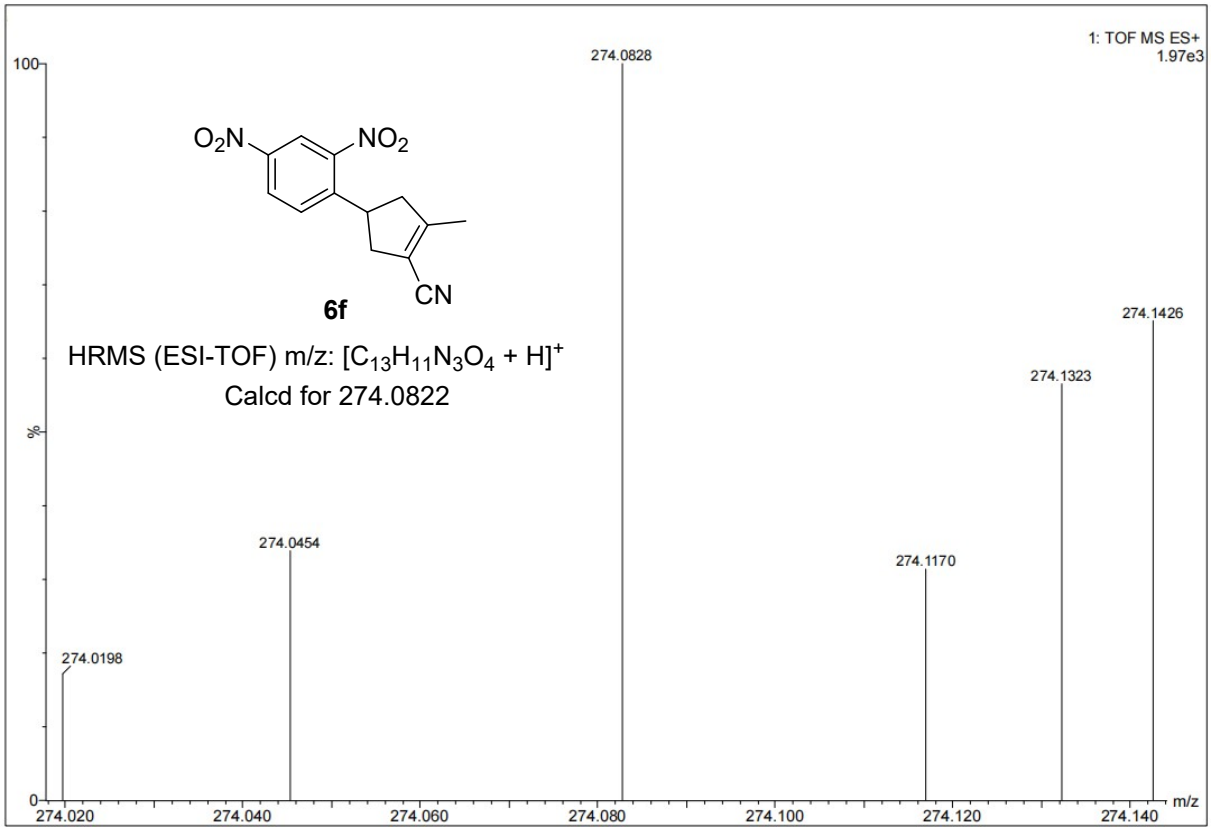
6f

^{1}H NMR (600 MHz, $CDCl_3$)



6f

^{13}C NMR (150 MHz, $CDCl_3$)



6f

HRMS (ESI-TOF) m/z: $[C_{13}H_{11}N_3O_4 + H]^+$

Calcd for 274.0822

14. Computational data

D-Int

zero-point Energies/(ev): -2632.431614

thermal Free Energies/(ev): -2632.431614

G(solv)/(kcal/mol): -26.49

C	0.81328700	2.70918600	0.95318900
C	-0.35838100	3.61528600	1.07887800
C	-0.29784700	4.93460500	0.85559000
Pd	0.55210800	0.79931200	0.11177400
P	2.97524400	0.45639100	0.27323000
C	3.74304900	-0.48915900	1.67479200
C	5.13177400	-0.51964100	1.89693600
C	5.66159100	-1.22819000	2.97528100
C	4.81395400	-1.90297000	3.85847800
C	3.43352000	-1.85894700	3.66287300
C	2.90265800	-1.15310200	2.57957300
C	3.97780900	2.02547000	0.32689300
C	4.44633600	2.64068500	-0.84345500
C	5.12785100	3.85813000	-0.78045900
C	5.34870300	4.48029800	0.44911100
C	4.88178700	3.87856300	1.61946600
C	4.19940500	2.66331600	1.55960200
C	3.55046300	-0.32964400	-1.30683600
C	4.67881300	-1.15643700	-1.40548700
C	5.07950800	-1.65890700	-2.64413400
C	4.36416600	-1.33763400	-3.79925900
C	3.23476200	-0.52299500	-3.70889000
C	2.82100800	-0.02786400	-2.47023500
H	-1.15619000	5.58709900	0.98928400
H	0.62972100	5.40284900	0.53749500
H	5.79944700	0.02830500	1.23910100
H	6.73687700	-1.24495000	3.13165000
H	5.22913700	-2.44899900	4.70126700
H	2.76403900	-2.36539700	4.35268400
H	1.82699400	-1.11251500	2.44222200

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H	5.88065000	5.42659900	0.49583800
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H	5.95234500	-2.30368500	-2.70420700
H	4.68068300	-1.72837700	-4.76274000
H	2.66233200	-0.27636300	-4.59890400
H	1.92333700	0.58414800	-2.41726000
H	-4.69887000	-3.53414500	-1.28108400
H	-2.72446700	-3.22483400	0.15398900
C	-3.86733300	-2.93194300	-1.63735700
C	-2.74610000	-2.75636000	-0.82372800
C	-3.92403000	-2.33588400	-2.89843200
H	-4.80071300	-2.46886900	-3.52617600
C	-1.66503200	-1.97613600	-1.26158900
H	-0.47624000	-4.46352500	0.92778800
C	-2.85631700	-1.55276600	-3.34014900
C	-1.73610400	-1.36556600	-2.52705900
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H	0.06660700	-3.22012400	-2.83110700
H	-0.93999600	-0.70535600	-2.86053900
C	0.86628600	-3.56377100	-2.18428500
C	1.74501500	-4.54354600	-2.65132400
H	1.61770300	-4.93923900	-3.65551500
H	-1.44900200	-1.17128600	4.51450500
H	-1.63816200	-3.60897000	4.97541500
C	-1.24289200	-1.89346600	3.72877800
C	-1.34679100	-3.26096800	3.98813800
C	-0.86845800	-1.44988300	2.45804500
H	-0.77539900	-0.38555300	2.25630800
C	-1.07172700	-4.18100100	2.97321600
H	-1.14973800	-5.24718100	3.16845700
C	-0.59124100	-2.36327200	1.42925500

C	-0.69536200	-3.73758700	1.70441200
P	-0.12756500	-1.69805300	-0.24698300
C	1.00172100	-3.04048400	-0.88986800
H	2.17655200	-3.13617600	0.92675200
C	2.04594800	-3.51862900	-0.08009500
C	2.91677900	-4.50348500	-0.54588600
C	2.77009400	-5.02026700	-1.83444800
H	3.71017300	-4.86594500	0.10261000
H	3.44765700	-5.78859100	-2.19712800
C	-1.65855800	2.92016400	1.46888100
H	-1.39419900	2.08904900	2.13545200
C	-2.58630400	3.79648700	2.19921900
N	-3.32979100	4.48453600	2.76711400
C	-3.80532600	0.86698200	1.67406000
C	-3.59813900	1.52476400	0.45103500
C	-4.58261600	1.35860700	-0.55827700
C	-5.70771500	0.55722500	-0.33417100
C	-5.86288200	-0.07941400	0.88746600
C	-4.92186300	0.06960100	1.90406300
H	-3.08780700	0.97516000	2.47806500
H	-6.44275800	0.44294900	-1.12142500
H	-5.07093600	-0.43463400	2.85089000
C	-4.49256600	1.99811600	-1.90341400
H	-3.63307600	2.66757300	-2.08228400
O	-5.31336400	1.81420400	-2.78376700
C	-2.33234600	2.33886000	0.18190500
H	-2.62002800	3.22378800	-0.39026700
C	-1.34489000	1.50126400	-0.67313900
H	-1.80167300	0.55264200	-0.94140000
N	-7.03538500	-0.93506900	1.11511200
O	-7.13573900	-1.48345300	2.21368400
O	-7.84236900	-1.05775200	0.19488400
C	-0.84918400	2.11214700	-1.93655700
O	-1.07603600	3.44817300	-2.03991900
O	-0.28336900	1.50050300	-2.84090400

C	-0.56029600	4.08132600	-3.21826300
H	0.52770100	3.98107100	-3.26406200
H	-0.99556000	3.63936700	-4.11839800
H	-0.84217900	5.13139700	-3.13149600
H	1.13809700	2.38169000	1.95329000
H	1.64736300	3.21601500	0.46639500

D-Ts

zero-point Energies/(ev): -2632.391237

thermal Free Energies/(ev): -2632.495721

G(solv)/(kcal/mol): -25.75

C	0.38863700	2.28410700	1.52846100
C	-0.62268600	3.04113400	2.32249100
C	-0.38171700	4.21607500	2.91107200
Pd	0.57359100	0.27290300	0.54006200
P	2.97854600	0.55687000	-0.11763100
C	4.26596000	-0.13022700	1.03585600
C	5.64343800	0.08888700	0.85778700
C	6.56748600	-0.42357800	1.76831400
C	6.13015600	-1.15200300	2.87864400
C	4.76516100	-1.36119200	3.07648900
C	3.84042500	-0.85122600	2.16065300
C	3.60393800	2.30770500	-0.29209300
C	3.71215900	2.96741600	-1.52540900
C	4.08745000	4.31200300	-1.58328700
C	4.35408400	5.02482400	-0.41278700
C	4.24475300	4.38078300	0.82167800
C	3.87097900	3.03758200	0.88170300
C	3.33390000	-0.20752100	-1.77155600
C	4.37905900	-1.11046800	-2.01186300
C	4.54854500	-1.67659600	-3.27760500
C	3.68410300	-1.34409200	-4.32080300
C	2.63451300	-0.45234600	-4.08850400
C	2.44803400	0.10178700	-2.82119900
H	-1.13403000	4.72365100	3.50776900

H	0.58796600	4.69768400	2.82068600
H	5.99219500	0.67075600	0.00940100
H	7.62922100	-0.24848100	1.61542900
H	6.85143900	-1.54564200	3.58991900
H	4.41677600	-1.91427800	3.94481600
H	2.77560500	-1.00035700	2.32167600
H	3.51188400	2.43325400	-2.44760300
H	4.17960000	4.79888200	-2.55095300
H	4.64874500	6.06965600	-0.46151500
H	4.45609600	4.92108600	1.74098800
H	3.80700500	2.54811900	1.85018600
H	5.05922600	-1.38559700	-1.21329800
H	5.36084000	-2.37919500	-3.44496800
H	3.82160100	-1.78265500	-5.30568700
H	1.95007200	-0.19312900	-4.89224000
H	1.61579000	0.77869900	-2.64480300
H	-4.60740000	-3.62866600	-1.54067800
H	-2.77459100	-3.58955000	0.10620100
C	-3.74076200	-2.99746700	-1.71758200
C	-2.70415700	-2.96904600	-0.78121700
C	-3.67161400	-2.20931300	-2.86814600
H	-4.47921200	-2.23232800	-3.59478500
C	-1.58732500	-2.14280100	-0.97672900
H	-0.64113200	-4.89847000	0.96982900
C	-2.56309800	-1.38535500	-3.07578600
C	-1.53336000	-1.34468600	-2.13388100
H	-2.50179600	-0.76543000	-3.96631000
H	-0.04466100	-3.73389100	-2.28730400
H	-0.68069300	-0.69042300	-2.29936000
C	0.83699000	-3.93876800	-1.68955900
C	1.77754600	-4.86362800	-2.15245000
H	1.61350900	-5.36171300	-3.10452800
H	-1.77479300	-2.10097800	4.91282700
H	-2.04707300	-4.57180100	5.01841700
C	-1.53890600	-2.71425000	4.04702400

C	-1.68890300	-4.10060500	4.10709600
C	-1.07370000	-2.11377500	2.87480300
H	-0.93098300	-1.03620000	2.83156900
C	-1.36632100	-4.88164900	2.99426400
H	-1.47253400	-5.96239200	3.03827600
C	-0.76041300	-2.88422800	1.74536700
C	-0.90224300	-4.27993100	1.82347500
P	-0.16032200	-2.01129800	0.21203900
C	1.02678100	-3.28195500	-0.46596700
H	2.35212200	-3.07353500	1.22990400
C	2.18024100	-3.57342900	0.28153300
C	3.11198700	-4.50337500	-0.17587300
C	2.91426200	-5.15148200	-1.39806500
H	3.99472700	-4.71756400	0.42106600
H	3.64202500	-5.87385600	-1.75814200
C	-1.96405300	2.34408800	2.30500300
H	-1.82407700	1.30889200	2.64426400
C	-2.99796800	2.96318300	3.13619200
N	-3.81897700	3.46161600	3.78838700
C	-3.80706800	0.29130000	1.05653700
C	-3.56062000	1.51867100	0.42007700
C	-4.46651200	1.93994500	-0.58626800
C	-5.56851000	1.14354500	-0.92532200
C	-5.76199200	-0.06719400	-0.28125300
C	-4.89249300	-0.50661400	0.71537600
H	-3.13452000	-0.06815500	1.82642400
H	-6.24867100	1.48102100	-1.69790100
H	-5.06766200	-1.45870100	1.19979800
C	-4.31647800	3.20708400	-1.36027000
H	-3.42982800	3.82781200	-1.14097100
O	-5.10850100	3.56165600	-2.21377600
C	-2.32850300	2.33774500	0.78518100
H	-2.51246300	3.38483800	0.54841600
C	-1.08275900	1.88717600	-0.00725000
H	-1.26800400	0.93726700	-0.51770900

N	-6.88899100	-0.92451800	-0.67547700
O	-6.97658200	-2.03049600	-0.13900100
O	-7.66831800	-0.49293400	-1.52241300
C	-0.51535100	2.81524000	-1.02427500
O	-0.82009800	4.11799100	-0.80311400
O	0.16848100	2.46018900	-1.97125000
C	-0.25314200	5.05389400	-1.73669300
H	0.83819300	4.99915300	-1.71323300
H	-0.60198800	4.84312400	-2.75089600
H	-0.59783700	6.03483300	-1.40839400
H	0.85142800	1.52917300	2.20285300
H	1.15563500	2.92475300	1.09732000

M-Int

zero-point Energies/(ev): -2632.442496

thermal Free Energies/(ev): -2632.545401

G(solv)/(kcal/mol): -26.03

C	-0.06751900	2.56407400	0.62040500
C	1.34129600	2.78840000	0.24013800
C	1.72068400	3.62377300	-0.74425800
Pd	-0.62538400	0.59875300	0.03361600
P	-2.79946900	1.23817900	0.59953300
C	-4.27614300	0.19015100	0.17658700
C	-5.42416400	0.69924600	-0.44591600
C	-6.52735500	-0.12714800	-0.67745900
C	-6.49753300	-1.46579600	-0.28838300
C	-5.35668800	-1.98069500	0.33287800
C	-4.25403700	-1.16031900	0.56085400
C	-3.29801700	2.92500300	0.00858600
C	-3.72070200	3.95439600	0.85992700
C	-4.05089500	5.20979200	0.34117800
C	-3.96671100	5.45052800	-1.02990100
C	-3.53814300	4.43250700	-1.88640500
C	-3.19703900	3.18342700	-1.36978700
C	-2.95145400	1.27238600	2.45253300

C	-4.20215800	1.46274500	3.06823600
C	-4.31099700	1.47238300	4.45811200
C	-3.17694500	1.28057000	5.25328700
C	-1.93607900	1.07184100	4.65246700
C	-1.82330900	1.06367800	3.25950500
H	2.76650200	3.77155100	-1.00361100
H	0.98870400	4.18452500	-1.31964200
H	-5.46754800	1.74087300	-0.74552500
H	-7.41194900	0.28278800	-1.15794800
H	-7.35703800	-2.10619100	-0.46694200
H	-5.32259000	-3.02328400	0.63600500
H	-3.37308200	-1.57327000	1.04493400
H	-3.78589100	3.78555700	1.92928200
H	-4.37085100	5.99975800	1.01522200
H	-4.22368700	6.42751800	-1.42996800
H	-3.45806200	4.61428300	-2.95477900
H	-2.83617800	2.40660300	-2.03956700
H	-5.09427000	1.59114500	2.46195600
H	-5.28309800	1.62315100	4.92014800
H	-3.26499000	1.28725100	6.33643000
H	-1.04574200	0.91787500	5.25499200
H	-0.85262600	0.88816500	2.80893900
H	0.83784900	-1.18296200	-5.93490900
H	-0.88898300	-1.28771800	-4.19001100
C	1.13313000	-1.33917800	-4.90052500
C	0.15271600	-1.39383400	-3.90703100
C	2.47948500	-1.49482500	-4.57082900
H	3.24098900	-1.45739000	-5.34534300
C	0.50632300	-1.59903900	-2.56501700
H	-2.15811000	-4.25645500	-1.65679400
C	2.84038600	-1.70470800	-3.23799500
C	1.86569600	-1.75210000	-2.24121200
H	3.88562100	-1.83320300	-2.96868600
H	0.38624100	-4.32051900	-1.76013000
H	2.15453900	-1.89894000	-1.20829700

C	0.23819800	-4.22757100	-0.68818400
C	0.58526600	-5.28749200	0.15074700
H	0.98913700	-6.20178000	-0.27613900
H	-4.73918200	-0.74401300	-4.02961600
H	-5.45827200	-3.12322000	-4.16122200
C	-4.17131300	-1.51584900	-3.51731500
C	-4.57648400	-2.85003800	-3.58780300
C	-3.04337500	-1.16774300	-2.77370400
H	-2.74495400	-0.12441000	-2.70842400
C	-3.84802800	-3.82902700	-2.91058500
H	-4.16055700	-4.86917700	-2.95466300
C	-2.29008000	-2.14657800	-2.10519800
C	-2.71197700	-3.48214700	-2.17652500
P	-0.76237800	-1.59433100	-1.19906400
C	-0.27971400	-3.03710200	-0.15108700
H	-0.78496300	-1.99445600	1.66809000
C	-0.42713700	-2.92625400	1.23955900
C	-0.07530100	-3.98614000	2.07715000
C	0.42980200	-5.16816900	1.53382500
H	-0.16925700	-3.87800300	3.15326500
H	0.71861600	-5.98602200	2.18781800
C	2.40450000	1.95445600	0.94008700
H	3.37886500	2.44714500	0.84347500
C	2.12940400	1.78127900	2.37129100
N	1.89332500	1.63545600	3.49955400
C	6.01723100	-0.77879700	1.03768100
C	4.99844600	0.01128500	0.46592300
C	3.64415900	-0.27622200	0.77678800
C	3.35360900	-1.32049500	1.65830000
C	4.38802300	-2.06677200	2.21236300
C	5.72686200	-1.81605400	1.91113000
H	7.05076700	-0.58767800	0.76643400
H	2.32090200	-1.54105400	1.89116800
H	6.50362200	-2.43067200	2.34811500
C	2.47288600	0.54260000	0.21664800

H	2.70678800	0.80776800	-0.83256400
O	1.30291000	-0.15225100	0.31983600
C	5.34518700	1.11052200	-0.44580300
H	4.60794800	1.38032300	-1.19634000
C	6.48772500	1.82274800	-0.41916000
H	7.26533400	1.64846200	0.31818200
N	4.06729500	-3.16449900	3.13747000
O	5.00284900	-3.84716100	3.55952400
O	2.88710600	-3.34090400	3.43823500
C	6.80501600	2.91512500	-1.36239100
O	5.78716600	3.19966100	-2.21440600
O	7.86764000	3.50661800	-1.37475800
C	6.05778200	4.24681800	-3.15692800
H	6.27652200	5.18454000	-2.63874600
H	6.91122200	3.98563100	-3.78876700
H	5.15179600	4.34200000	-3.75641100
H	-0.21974600	2.64175800	1.69909700
H	-0.72779100	3.25911100	0.10076800

M-Ts

zero-point Energies/(ev): -2632.384784

thermal Free Energies/(ev): -2632.491929

G(solv)/(kcal/mol): -26.43

C	0.02451700	0.79503700	-2.03444900
C	1.31195400	0.39159200	-2.61779500
C	1.41694200	-0.59538900	-3.51946400
Pd	-0.91491900	-0.11603500	-0.01934800
P	-2.94383100	1.13165300	-0.25571300
C	-4.39015300	0.68074400	0.82938500
C	-5.63984700	0.27401000	0.34074600
C	-6.67349900	-0.05561800	1.22267200
C	-6.47654000	0.02494100	2.60140100
C	-5.23426500	0.43149500	3.09863800
C	-4.19856100	0.74848400	2.22064400
C	-3.62402600	0.94148300	-1.97729600

C	-4.01099000	2.01932400	-2.78710000
C	-4.45872500	1.80105200	-4.09304600
C	-4.53411900	0.50571300	-4.60598200
C	-4.14938500	-0.57611100	-3.80930800
C	-3.68730600	-0.35948500	-2.51093900
C	-2.87673500	2.97022100	0.01231300
C	-4.03157000	3.75618700	0.17014100
C	-3.92552100	5.13150500	0.37622600
C	-2.66692500	5.73741000	0.43596000
C	-1.51414700	4.96524500	0.28978200
C	-1.61849900	3.58691600	0.08006700
H	2.37021800	-0.85807700	-3.97085400
H	0.54520700	-1.15272300	-3.85027500
H	-5.81298200	0.21639900	-0.72904700
H	-7.63626100	-0.36851000	0.82663200
H	-7.28364600	-0.22482000	3.28500000
H	-5.07025300	0.49961200	4.17091600
H	-3.23292300	1.05323600	2.61732700
H	-3.96106900	3.03275500	-2.40288800
H	-4.74919400	2.64877200	-4.70814300
H	-4.88394000	0.33936100	-5.62136900
H	-4.19855900	-1.58883100	-4.20095100
H	-3.36625900	-1.20307700	-1.90429500
H	-5.01320600	3.29142300	0.14174600
H	-4.82529400	5.72925500	0.49822700
H	-2.58613900	6.80772700	0.60632700
H	-0.53307800	5.42590700	0.35750200
H	-0.71968200	2.98308400	-0.01419000
H	-2.72113500	-6.03907300	-1.89312800
H	-2.36935000	-4.54354000	0.03537000
C	-1.87659200	-5.35471800	-1.89349600
C	-1.67826100	-4.50634500	-0.80056600
C	-0.99428000	-5.33258800	-2.97373700
H	-1.14685400	-5.99685900	-3.82011400
C	-0.59588500	-3.61450800	-0.77560800

H	0.04952800	-4.62763100	2.58697600
C	0.08943700	-4.45000700	-2.95811500
C	0.28177500	-3.59443900	-1.87366300
H	0.78636300	-4.42766800	-3.79239700
H	1.60330900	-4.71094500	0.34682900
H	1.12399500	-2.90777400	-1.87754700
C	2.06996900	-3.92380300	0.93124100
C	3.36238700	-4.11083800	1.42847300
H	3.88455900	-5.04384500	1.23086100
H	-4.43403900	-2.66297000	3.41197200
H	-3.63911400	-4.58639500	4.78703900
C	-3.45703200	-3.10268600	3.23145600
C	-3.00979900	-4.17728800	4.00084400
C	-2.64103500	-2.57244600	2.22914300
H	-2.98377800	-1.72567400	1.64261900
C	-1.74486700	-4.72136300	3.76221500
H	-1.38792900	-5.55485300	4.36184400
C	-1.37409000	-3.11661000	1.97560300
C	-0.93266200	-4.19752600	2.75601000
P	-0.36068600	-2.37599000	0.59619100
C	1.37680800	-2.72807600	1.17666600
H	1.48874400	-0.78826900	2.11390100
C	2.00947100	-1.72549200	1.93052800
C	3.29614100	-1.91782400	2.43719900
C	3.97821300	-3.11038100	2.18296500
H	3.76777000	-1.13309000	3.02280200
H	4.98320000	-3.25727900	2.56898100
C	2.50325500	1.14041500	-2.05993500
H	3.45010200	0.66739100	-2.34184600
C	2.52183300	2.53154300	-2.52757500
N	2.52702300	3.62880300	-2.90779000
C	5.33298200	2.60544400	1.20081600
C	4.53585400	1.67868600	0.49864600
C	3.16327700	1.97090800	0.29239200
C	2.63680100	3.16732400	0.78086400

C	3.45923000	4.05822000	1.46110900
C	4.81028300	3.79696800	1.68234500
H	6.37397100	2.36616800	1.39304800
H	1.59139600	3.39466200	0.63091400
H	5.41678500	4.50906800	2.22751000
C	2.25135300	1.04116100	-0.50342800
H	2.48692900	-0.00345000	-0.24372200
O	0.91606800	1.33309600	-0.29049000
C	5.13142200	0.42568000	0.01051300
H	4.48852200	-0.44936900	-0.02696400
C	6.40984600	0.27645600	-0.38397800
H	7.10902600	1.10667500	-0.41219100
N	2.88681500	5.31388800	1.97081200
O	3.63783400	6.07658500	2.57852100
O	1.69265700	5.52991300	1.76307100
C	6.99680000	-1.00594700	-0.82903100
O	6.10566800	-2.02745800	-0.82638300
O	8.15914600	-1.13392600	-1.16261800
C	6.62827000	-3.29736500	-1.23949300
H	6.97473500	-3.25334500	-2.27600800
H	7.46454300	-3.59643800	-0.60171400
H	5.79907500	-3.99860200	-1.14046400
H	-0.24322800	1.84216300	-2.11888600
H	-0.79490700	0.12375400	-2.31046800

5a

C	0.65064700	-1.65026100	-0.14942000
C	1.47039900	-0.50775600	-0.12343900
C	0.84592400	0.76068500	-0.04854900
C	-0.54842100	0.86131900	0.00128800
C	-1.31341000	-0.29024000	-0.01604300
C	-0.73008500	-1.55437000	-0.08936300
H	1.10821000	-2.62642100	-0.24942200
H	-1.01264000	1.83662500	0.06325800
H	-1.35960300	-2.43332900	-0.11404300

C	1.62490300	2.02796700	0.02970000
O	1.11948600	3.12743600	0.01838800
H	2.72094400	1.92254700	0.11775900
C	2.93705400	-0.65846300	-0.20548800
C	3.62932000	-1.66737500	0.33029300
H	3.48175600	0.10901700	-0.74515300
H	4.70513900	-1.72592900	0.21734900
H	3.15629600	-2.45065400	0.91254100
N	-2.78833300	-0.18249500	0.04039700
O	-3.43059800	-1.22553300	0.01697800
O	-3.27385800	0.93766900	0.10726700

1a

C	1.89082400	-1.90714400	0.36393600
C	0.96558200	-0.91546000	-0.01223500
C	1.46310700	0.34663800	-0.41461100
C	2.83970100	0.58691600	-0.43731600
C	3.71322400	-0.42184500	-0.07161000
C	3.25637700	-1.67526500	0.33117500
H	1.52810400	-2.86340000	0.71919500
H	3.20723100	1.55518700	-0.75005200
H	3.96660900	-2.43673400	0.62279000
C	0.56474700	1.44989600	-0.87245600
O	0.96206900	2.58503300	-1.03424200
H	-0.48561200	1.19286000	-1.07134900
C	-0.48007000	-1.19346300	0.07535000
C	-1.00952300	-2.40592700	-0.14807900
H	-1.13343900	-0.37185300	0.35164100
H	-0.40317100	-3.24510400	-0.46958000
N	5.17067100	-0.16551100	-0.10235500
O	5.91153600	-1.08053000	0.23675500
O	5.54569500	0.94134300	-0.46283200
C	-2.43872300	-2.75640200	-0.00373800
O	-2.87237400	-3.86335500	-0.23695800
O	-3.20893400	-1.73430100	0.42659300

C	-4.59963000	-2.04564000	0.62625200
H	-4.70966900	-2.84839300	1.35644900
H	-5.05247400	-1.12862600	0.99685400
H	-5.06218300	-2.35274600	-0.31298900
C	-2.20874300	2.93259100	0.81824300
H	-1.56083700	3.57710400	0.20882400
H	-2.68986600	3.55459200	1.58816200
C	-3.28900000	2.32057600	-0.04519900
H	-3.85555400	1.57972700	0.53709100
H	-3.98210700	3.11773600	-0.35496800
O	-1.44126300	1.90839900	1.43676000
O	-2.71081700	1.71010400	-1.18676200
C	-3.67317000	1.16270600	-2.06966100
H	-4.35480900	1.93810400	-2.44537400
H	-3.13142100	0.72955500	-2.91063600
H	-4.26317900	0.37682500	-1.58028100
C	-0.49138200	2.42392400	2.35742500
H	-0.98675200	2.97621300	3.16735900
H	0.04055300	1.57292100	2.78329100
H	0.22666900	3.08845200	1.86068500

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C	-2.82520500	-5.50936400	0.05095300
C	-2.77935600	-4.11047700	-0.07496800
C	-1.57481900	-3.44711400	0.27967100
C	-0.47467100	-4.17569300	0.74849300
C	-0.56806100	-5.54925600	0.85279000
C	-1.73270600	-6.23193800	0.50471300
H	-3.74428600	-6.03291200	-0.17898200
H	0.43982400	-3.66614400	1.01923900
H	-1.77135700	-7.30798900	0.60830700
C	-3.96728600	-3.37030000	-0.52821000
H	-4.12759500	-2.37487500	-0.13197600
C	-4.87633500	-3.83591100	-1.39539300
H	-4.79153800	-4.80930200	-1.86460500

N	0.59805500	-6.31713700	1.35276500
O	0.47488800	-7.53110300	1.43207000
O	1.60063900	-5.68610900	1.65150400
C	-6.07828400	-3.07410700	-1.82092700
O	-6.12134900	-1.83269400	-1.30377200
O	-6.91931100	-3.53440900	-2.55749900
C	-7.26299100	-1.02638800	-1.66778600
H	-7.31526500	-0.91626100	-2.75119500
H	-8.18103600	-1.49054400	-1.30609200
H	-7.09896000	-0.06482500	-1.18829300
C	1.29369300	1.85449200	0.16876700
N	-0.06177900	1.63182400	0.37067500
H	-0.35471500	0.66445800	0.46469600
N	2.00682600	0.66335000	0.15736800
H	1.47771900	-0.18992500	0.27955200
O	1.79306100	2.95385500	0.02180900
C	-1.08545200	2.58329600	0.42471800
C	-0.89027900	3.96162300	0.25624000
C	-2.38252800	2.10767700	0.66451200
C	-1.98486600	4.82037700	0.32540500
H	0.10403000	4.34343800	0.08448300
C	-3.45891500	2.98354400	0.72577800
H	-2.54567900	1.04838400	0.82243200
C	-3.27648900	4.35330300	0.55351300
H	-4.11182300	5.03644300	0.61156100
C	3.38436000	0.49154200	-0.04403700
C	4.28911700	1.54964800	-0.19647600
C	3.86094700	-0.82627300	-0.09014300
C	5.64008600	1.26914800	-0.39233100
H	3.93488800	2.56777100	-0.15971500
C	5.21190200	-1.07993700	-0.28775300
H	3.17187900	-1.65506300	0.02364100
C	6.12078300	-0.03528800	-0.44191800
H	7.17177200	-0.23414200	-0.59652700
C	-4.84163700	2.42469900	0.92742100

C	-1.76161600	6.29459300	0.08844300
C	5.70401000	-2.50431600	-0.27640900
C	6.58906300	2.42179200	-0.61194300
F	-2.73170400	7.05085000	0.64760200
F	-1.75479800	6.58546500	-1.23607900
F	-0.58354000	6.71888400	0.58746000
F	-5.68961300	3.32080300	1.46506300
F	-4.83973900	1.33574100	1.73432500
F	-5.39562500	2.01968000	-0.24921000
F	6.80814500	-2.66703500	-1.03463500
F	4.76957400	-3.36768600	-0.73714000
F	6.02485100	-2.91204400	0.97562500
F	6.27986400	3.48832500	0.15463700
F	6.56404700	2.84590200	-1.89983100
F	7.86862300	2.08741400	-0.33719900
C	-1.42263100	-1.98950200	0.12711800
O	-0.42368500	-1.36568500	0.45101200
H	-2.27329600	-1.45152400	-0.32016700

Pd-TMM dipole

C	-0.27589800	3.46452900	-1.32009000
C	-1.30428100	2.51690300	-1.75816800
H	-1.24281300	2.23672000	-2.81283500
H	-2.32459800	2.65298200	-1.40818800
C	0.99435100	2.79012500	-1.60334800
H	1.17039000	2.52388800	-2.64853300
H	1.89086500	3.13579200	-1.09071700
C	-0.42377900	4.54996700	-0.48545400
H	0.45712000	5.06803200	-0.11568300
Pd	-0.01357400	1.08003000	-0.79420700
P	-1.83772500	-0.39397600	-0.08225900
P	2.01851300	0.01815600	-0.01724000
C	2.04748700	-0.38025000	1.79558500
C	3.56523500	1.03142100	-0.22945900
C	2.49669500	-1.54585200	-0.89933200

C	-2.35238100	-1.55113800	-1.44543600
C	-3.39761200	0.52242000	0.33039300
C	-1.65689700	-1.53603000	1.37841200
C	1.29718800	0.45421200	2.63929100
C	1.30837300	0.26194100	4.02183100
C	2.05766700	-0.77684100	4.57646600
C	2.79606100	-1.62049100	3.74381600
C	2.79485700	-1.42308600	2.36231600
C	4.21752100	1.64398200	0.84884400
C	5.34178800	2.44643700	0.63322000
C	5.82915400	2.64401200	-0.65829800
C	5.18345500	2.03855200	-1.73996100
C	4.05848900	1.24337300	-1.52841200
C	1.53456900	-2.20548700	-1.67835300
C	1.85285900	-3.38397400	-2.35842200
C	3.14104500	-3.91311200	-2.27516500
C	4.11393700	-3.25402800	-1.51878800
C	3.79767000	-2.07606600	-0.84146000
C	-2.92946000	-2.80948700	-1.20939300
C	-3.31702000	-3.62278900	-2.27642600
C	-3.13484700	-3.19206100	-3.59208700
C	-2.56037600	-1.94327300	-3.83791600
C	-2.16880100	-1.13011200	-2.77302200
C	-3.29568100	1.81363000	0.86874300
C	-4.44044900	2.54075600	1.20229300
C	-5.70148100	1.97521200	1.00883200
C	-5.81467000	0.68708300	0.47888200
C	-4.67125500	-0.03624700	0.13777200
C	-2.38838900	-1.34547700	2.56000400
C	-2.20593800	-2.19582900	3.65348400
C	-1.29678100	-3.25071500	3.58163400
C	-0.56128000	-3.44764600	2.41038500
C	-0.73377600	-2.59399500	1.32184600
H	-4.77528000	-1.02959000	-0.28742700
H	-6.79550800	0.24663500	0.31887600

H	-6.59515100	2.54224300	1.25565700
H	-4.33020900	3.55812600	1.56420300
H	-2.32077100	2.27332700	0.99961300
H	-3.07079200	-3.15987400	-0.19197600
H	-3.76187500	-4.59421400	-2.07704300
H	-3.43680500	-3.82694200	-4.42081100
H	-2.41267500	-1.60088900	-4.85867700
H	-1.71403100	-0.16323700	-2.96747300
H	-3.10680300	-0.53602500	2.63000600
H	-2.78345100	-2.03271400	4.55967900
H	-1.15969200	-3.91446400	4.43113100
H	0.15291500	-4.26398400	2.34396200
H	-0.14963800	-2.76071800	0.42180400
H	4.57062600	-1.55730000	-0.28242300
H	5.12357000	-3.65229800	-1.46279200
H	3.39132000	-4.82759300	-2.80622700
H	1.09360800	-3.87804600	-2.95838600
H	0.53647100	-1.78786500	-1.76724800
H	3.85428700	1.49754900	1.86066700
H	5.83619300	2.91342700	1.48091400
H	6.70391300	3.26700400	-0.82366500
H	5.55344400	2.18857500	-2.75071400
H	3.56172400	0.78309300	-2.37827000
H	3.36939300	-2.09148600	1.72963000
H	3.37569900	-2.43550200	4.16951000
H	2.06166300	-0.93238300	5.65198400
H	0.72404500	0.91797300	4.66104100
H	0.69886800	1.25325200	2.20833700
C	-1.67646200	4.99980400	-0.01339300
N	-2.70839400	5.37145300	0.39687100