Electronic Supplementary Information for

Ruthenium porphyrin catalysed intermolecular amino-oxyarylation of alkenes to give primary amines via a ruthenium nitrido intermediate

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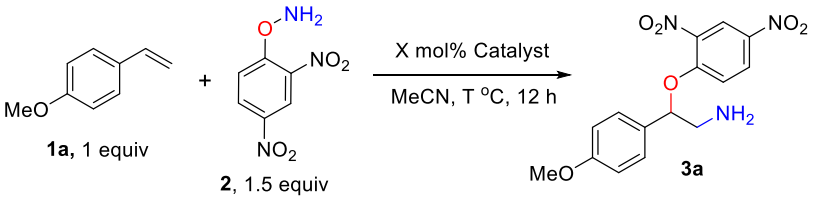
General information

All solvents were purified by standard method. ^{1}H, ^{19}F NMR and ^{13}C NMR spectra were recorded on 500 MHz, 400 MHz, 376 MHz and 126 MHz spectrometer, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{1}H NMR. Flash column chromatograph was carried out using 300–400 mesh silica-gel under medium pressure. [Ru(TPP)(CO)],[1] [Ru(TDCPP)Cl_2],[1] [Ru(TDCPP)(CO)],[1] [Ru(F_{20}TPP)(CO)],[2] [Ru(^{t}Bu-Salen)(PPh_3)$_2$],[3] and [Ru^{VI}(por)(N)(OH)] [4] were prepared by literature methods.

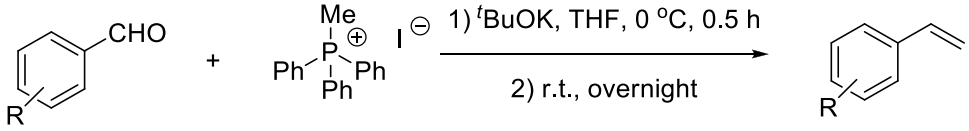
Table S1. Optimisation studies for the catalytic amino-oxyarylation of 4-methoxystyrene



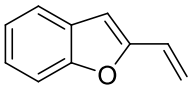
Entry	Catalyst	T (°C)	X mol%	Solvent	Yield (%)[a]
1	[Ru(TPP)(CO)]	40	10	MeCN	33
2	[Ru(TDCPP)(CO)]	40	10	MeCN	35
3	[Ru(F_{20}TPP)(CO)]	30	5	MeCN	78[b]
4	[Ru(F_{20}TPP)(CO)]	40	5	MeCN	70[b]
5	[Ru(F_{20}TPP)(CO)]	50	5	MeCN	59[b]
6	[Ru(F_{20}TPP)(CO)]	70	5	MeCN	51[b]
7	[Ru(F_{20}TPP)(CO)]	30	5	TFE[c]	30
8	[Ru(F_{20}TPP)(CO)]	30	10	PhMe	NR
9	[Ru(F_{20}TPP)(CO)]	40	10	DMF	NR
10	[Ru(F_{20}TPP)(CO)]	40	10	DMSO	NR
11	[Ru(F_{20}TPP)(CO)]	30	5	MeCN/MeOH(9:1)	20
12	[Ru(F_{20}TPP)(CO)]	40	10	MeOH	NR
13[d]	**[Ru(F_{20}TPP)(CO)]**	**30**	**5**	**MeCN**	**86**
14[e]	[Ru(F_{20}TPP)(CO)]	30	5	MeCN	75
15[df]	[Ru(F_{20}TPP)(CO)]	30	5	MeCN	80
16	------	30	5	MeCN	0
17	[Ru(TPP)Cl_2]	30	5	MeCN	43
18	[Ru(TDCPP)Cl_2]	30	5	MeCN	37
19	[Ru(TMP)(CO)]	30	5	MeCN	0
20	[Ru(^{t}Bu-Salen)(PPh_3)$_2$]	40	10	MeCN	28
21	[Ru(*p*-cymene)Cl_2]$_2$	30	10	MeCN	10
22	Ru(PPh_3)$_3Cl_2$	40	10	MeCN	25
23[g]	[Ru(F_{20}TPP)(CO)]	30	5	MeCN	85
24[h]	[Ru(F_{20}TPP)(CO)]	30	5	MeCN	87

[a]Yields determinded by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [b]Isolated yield. [c]TFE is the 2,2,2-trifluoroethanol. [d]Expose to air. [e]Expose to air and MeCN (AR) used as received. [f]DPH was added in two batches of 1.0 equiv and 0.5 equiv., respectively. [g]3 equiv DPH was used. [h]5 equiv DPH was used. NR: no reaction.

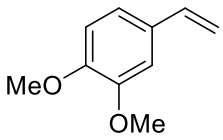
General procedure for the preparation of styrenes



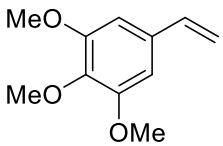
Slurry of methyltriphenylphosphonium iodide (6.54 g, 16 mmol) in THF (50 mL) was cooled to 0 °C. To this was added potassium tertiary-butoxide (2.27 g, 20 mmol). The solution became yellow. The reaction mixture was stirred for 30 min at room temperature and 2-methoxybenzaldehyde (1.83 g, 13 mmol) was added as a solution in THF (10 mL). The reaction mixture was further stirred at room temperature overnight. A saturated solution of NH_4Cl (20 mL) was added to the reaction mixture and then extracted with Et_2O (3×100 mL). The combined organic phase was washed with brine (100 mL), dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (eluent: Petroleum ether :EtOAc = 100:1) to give the desired product as colorless liquid (0.90 g, 50%).



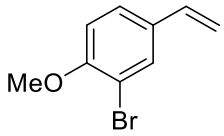
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 6.69 (ddd, *J* = 17.6, 11.3, 1.5 Hz, 1 H), 6.64 (s, 1 H), 6.03 (d, *J* = 17.5 Hz, 1 H), 5.44 (d, *J* = 11.2 Hz, 1 H) ppm.



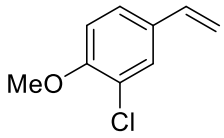
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 1.8 Hz, 1 H), 6.96 (dd, *J* = 8.2, 1.9 Hz, 1 H), 6.84 (d, *J* = 8.2 Hz, 1 H), 6.73 – 6.58 (m, 1 H), 5.63 (dd, *J* = 17.5, 0.6 Hz, 1 H), 5.17 (dd, *J* = 10.9, 0.5 Hz, 1 H), 3.92 (s, 3 H), 3.90 (s, 3 H) ppm.



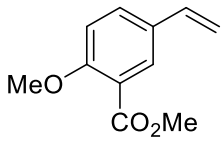
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (dd, *J* = 17.4, 10.9 Hz, 1 H), 6.66 (s, 2 H), 5.68 (d, *J* = 17.5 Hz, 1 H), 5.24 (d, *J* = 10.8 Hz, 1 H), 3.90 (s, 6 H), 3.87 (s,3 H) ppm.



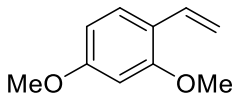
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.0 Hz, 1 H), 7.31 (dd, *J* = 8.5, 2.0 Hz, 1 H), 6.87 (d, *J* = 8.5 Hz, 1 H), 6.62 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.65 (d, *J* = 17.5 Hz, 1 H), 5.20 (d, *J* = 10.9 Hz, 1 H), 3.91 (s, 3 H) ppm.



^{1}H NMR (500 MHz, CD_3CN) δ 7.51 (d, *J* = 2.1 Hz, 1 H), 7.35 (dd, *J* = 8.5, 2.1 Hz, 1 H), 7.02 (d, *J* = 8.5 Hz, 1 H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.71 (d, *J* = 17.6 Hz, 1 H), 5.20 (d, *J* = 10.9 Hz, 1 H), 3.89 (s, 3 H) ppm.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.2 Hz, 1 H), 7.57 – 7.43 (m, 1 H), 6.93 (d, *J* = 8.5 Hz, 1 H), 6.65 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.66 (d, *J* = 17.6 Hz, 1 H), 5.19 (d, *J* = 10.9 Hz, 1 H), 3.91 (s, 3 H), 3.90 (s, 3 H) ppm.

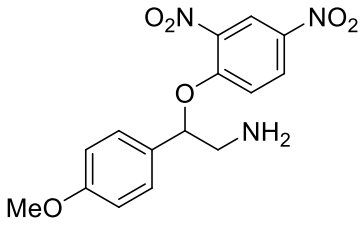


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 1 H), 6.99 (dd, *J* = 17.7, 11.2 Hz, 1 H), 6.51 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.47 (d, *J* = 2.4 Hz, 1 H), 5.66 (dd, *J* = 17.7, 1.6 Hz, 1 H), 5.18 (dd, *J* = 11.2, 1.6 Hz, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H) ppm.

General procedure for ruthenium porphyrin catalyzed intermolecular amino-oxyarylation of styrenes

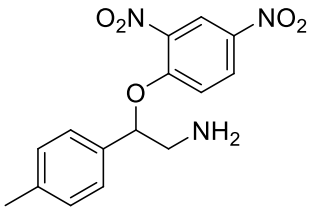
In a 25 mL Schlenk tube charged with [Ru(F_{20}TPP)(CO)] (0.027 g, 0.0025 mmol), DPH (0.15 g, 0.75 mmol), MeCN (4 mL) was added. Then, the alkene substrate (0.5 mmol) was added and the mixture was stirred at 30 °C for 12 h. TLC indicated that DPH decomposed completely. The solvent was evaporated. The residue was purified by silica gel column chromatography (eluent: Petroleum Ether : EtOAc = 3:1).

2-(2,4-Dinitrophenoxy)-2-(4-methoxyphenyl)ethanamine (3a)[5]: yellow solid (80%)



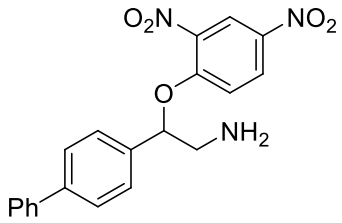
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.93 (t, *J* = 5.5 Hz, 1 H), 8.82 (d, *J* = 2.8 Hz, 1 H), 8.19 (dd, *J* = 9.7, 2.8 Hz, 1 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 9.7 Hz, 1 H), 7.02 – 6.81 (m, 2 H), 5.86 (s, 1 H), 4.86 (dd, *J* = 8.7, 3.9 Hz, 1 H), 3.74 (d, *J* = 1.3 Hz, 3 H), 3.67 (ddd, *J* = 13.2, 5.9, 3.9 Hz, 1 H), 3.51 (ddd, *J* = 13.3, 8.4, 5.0 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.12, 148.77, 135.27, 135.05, 130.22, 129.93, 127.64, 123.92, 116.33, 114.03, 70.49, 55.51, 50.84 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}N_3O_6$: 332.0888; Found: 332.0891.

2-(2,4-Dinitrophenoxy)-2-p-tolylethanamine (3b): yellow solid (61%)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.6 Hz, 1 H), 8.91 (s, 1 H), 8.23 (dd, *J* = 9.5, 2.6 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 7.9 Hz, 2 H), 6.92 (d, *J* = 9.6 Hz, 1 H), 5.07 (dd, *J* = 7.5, 4.4 Hz, 1 H), 3.74 – 3.55 (m, 2 H), 2.63 (br, 1 H), 2.38 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.40, 138.73, 137.70, 136.05, 130.47, 130.24, 129.68, 125.74, 124.30, 114.17, 72.24, 50.43, 21.18 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}N_3O_5$: 316.0939; Found: 316.0941.

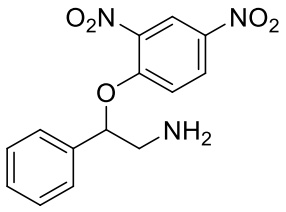
2-([1,1'-Biphenyl]-4-yl)-2-(2,4-dinitrophenoxy)ethanamine (3c): yellow solid (78%)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 2.6 Hz, 1 H), 8.92 (t, *J* = 4.9 Hz, 1 H), 8.16 (dd, *J* = 9.5, 2.5 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 2 H), 7.57 (d, *J* = 7.4 Hz, 2 H), 7.51 (d, *J* = 8.1 Hz, 2 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.37 (t, *J* = 7.3 Hz, 1 H), 6.89 (d, *J* = 9.6 Hz, 1 H), 5.13 (dd, *J* = 7.7, 4.0 Hz, 1 H), 3.77 – 3.50

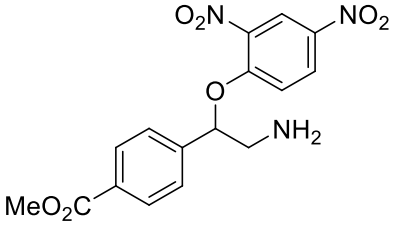
(m, 2 H), 3.20 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.38, 141.51, 140.18, 139.77, 136.00, 130.42, 130.24, 128.92, 127.68, 127.55, 126.99, 126.31, 124.26, 114.23, 72.03, 50.42 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{20}H_{16}N_3O_5$: 378.1095; Found: 378.1097.

2-(2,4-Dinitrophenoxy)-2-phenylethanamine (3d)[5b]: yellow solid (74%)



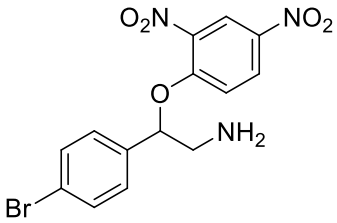
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.6 Hz, 1 H), 8.91 (s, 1 H), 8.22 (dd, *J* = 9.5, 2.6 Hz, 1 H), 7.50 – 7.32 (m, 5 H), 6.93 (d, *J* = 9.5 Hz, 1 H), 5.11 (dd, *J* = 7.7, 4.2 Hz, 1 H), 3.84 – 3.44 (m, 2 H), 2.73 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.39, 140.70, 136.12, 130.54, 130.25, 129.05, 128.85, 125.81, 124.33, 114.14, 72.44, 50.43 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{14}H_{12}N_3O_5$: 302.0782; Found: 302.0785.

Methyl 4-(2-amino-1-(2,4-dinitrophenoxy)ethyl)benzoate (3e): yellow solid (30%)



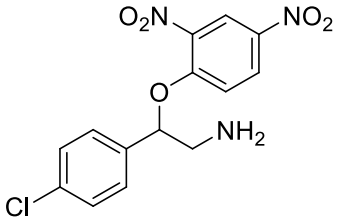
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.93 (d, *J* = 2.7 Hz, 1 H), 8.79 (s, 1 H), 8.18 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 8.2 Hz, 2 H), 7.10 (d, *J* = 9.6 Hz, 1 H), 5.07 (dt, *J* = 7.9, 4.0 Hz, 1 H), 4.10 (d, *J* = 4.3 Hz, 1 H), 3.86 (s, 3 H), 3.73 (ddd, *J* = 13.6, 5.9, 4.1 Hz, 1 H), 3.60 (ddd, *J* = 13.4, 7.8, 5.4 Hz, 1 H); ^{13}C NMR (126 MHz, CD_3CN) δ 167.01, 149.23, 147.71, 136.34, 130.88, 130.38, 130.27, 129.95, 126.74, 124.25, 115.75, 71.41, 52.28, 50.48 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{14}N_3O_7$: 360.0837, Found: 360.0842.

2-(4-Bromophenyl)-2-(2,4-dinitrophenoxy)ethanamine (3f): yellow solid (40%)



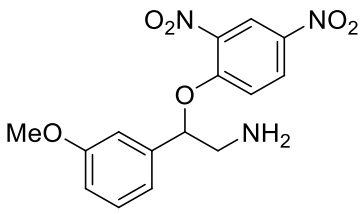
^{1}H NMR (400 MHz, CD_3CN) δ 8.93 (d, *J* = 2.7 Hz, 1 H), 8.77 (s, 1 H), 8.18 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 9.6 Hz, 1 H), 5.02 – 4.94 (m, 1 H), 4.01 (d, *J* = 3.8 Hz, 1 H), 3.69 (ddd, *J* = 13.6, 5.9, 4.1 Hz, 1 H), 3.56 (ddd, *J* = 13.4, 7.8, 5.3 Hz, 1 H); ^{13}C NMR (126 MHz, CD_3CN) δ 149.20, 141.90, 136.31, 131.94, 130.84, 130.38, 128.62, 124.24, 121.62, 115.73, 71.14, 50.49 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{14}H_{11}BrN_3O_5$: 379.9888; Found: 379.9893.

2-(4-Chlorophenyl)-2-(2,4-dinitrophenoxy)ethanamine (3g): yellow solid (26%)



^{1}H NMR (400 MHz, Acetone-d_6) δ 9.07 (d, *J* = 2.7 Hz, 1 H), 8.92 (s, 1 H), 8.32 (dt, *J* = 13.7, 6.9 Hz, 1 H), 7.58 (d, *J* = 8.5 Hz, 2 H), 7.52 (d, *J* = 8.6 Hz, 2 H), 7.23 (d, *J* = 9.6 Hz, 1 H), 5.13 (dt, *J* = 7.8, 3.9 Hz, 1 H), 4.15 (d, *J* = 4.1 Hz, 1 H), 3.83 (ddd, *J* = 13.5, 5.9, 4.1 Hz, 1 H), 3.70 (ddd, *J* = 16.4, 10.8, 6.9 Hz, 1 H); ^{13}C NMR (126 MHz, CD_3CN) δ 148.68, 140.90, 135.78, 132.96, 130.31, 129.85, 128.43, 127.76, 123.72, 115.21, 70.57, 50.02 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{14}H_{11}ClN_3O_5$: 336.0393; Found: 336.0397.

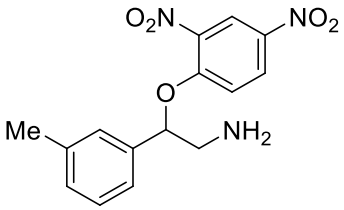
2-(2,4-Dinitrophenoxy)-2-(3-methoxyphenyl)ethanamine (3h): yellow solid (53%)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.6 Hz, 1 H), 8.92 (s, 1 H), 8.25 (dd, *J* = 9.5, 2.6 Hz, 1 H), 7.35 (t, *J* = 8.1 Hz, 1 H), 7.02 (d, *J* = 6.6 Hz, 2 H), 6.97 – 6.85 (m, 3 H), 5.08 (dd, *J* = 7.5, 4.3 Hz, 1 H),

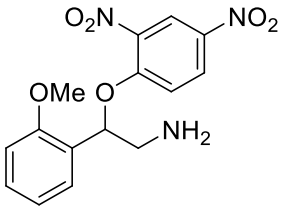
3.85 (s, 3 H), 3.75 – 3.55 (m, 2 H); ^{13}C NMR (126 MHz, CD_3CN) δ 160.81, 149.66, 144.68, 136.70, 131.23, 130.81, 130.57, 124.70, 119.09, 116.19, 114.16, 112.44, 72.08, 55.85, 51.17 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}N_3O_6$: 332.0888, Found: 332.0889.

2-(2,4-Dinitrophenoxy)-2-m-tolylethanamine (3i): yellow solid (55%)



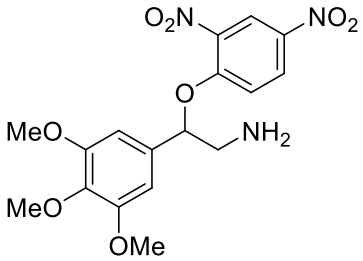
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, *J* = 2.4 Hz, 1 H), 8.90 (s, 1 H), 8.21 (dd, *J* = 9.5, 2.3 Hz, 1 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.27 – 7.21 (m, 2 H), 7.16 (d, *J* = 7.3 Hz, 1 H), 6.92 (d, *J* = 9.6 Hz, 1 H), 5.05 (dd, *J* = 7.8, 4.0 Hz, 1 H), 3.72 – 3.52 (m, 2 H), 2.88 (s, 1 H), 2.38 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.41, 140.75, 138.79, 135.96, 130.39, 130.22, 129.44, 128.88, 126.45, 124.27, 122.83, 114.24, 72.23, 50.48, 21.47 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}N_3O_5$: 316.0939; Found: 316.0941.

2-(2,4-Dinitrophenoxy)-2-(2-methoxyphenyl)ethanamine (3j): yellow solid (50%)



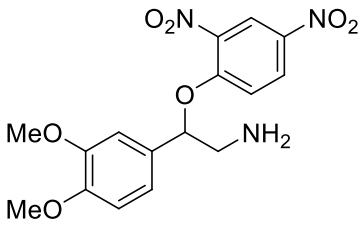
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 2.6 Hz, 1 H), 8.95 (s, 1 H), 8.26 (dd, *J* = 9.5, 2.7 Hz, 1 H), 7.49 (d, *J* = 6.8 Hz, 1 H), 7.36 (t, *J* = 7.8 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 7.03 (d, *J* = 9.7 Hz, 1 H), 6.96 (d, *J* = 8.3 Hz, 1 H), 5.33 (dt, *J* = 8.3, 4.5 Hz, 1 H), 3.94 (s, 3 H), 3.77 (ddd, *J* = 13.3, 6.1, 4.2 Hz, 1 H), 3.65 (ddd, *J* = 13.1, 7.8, 4.9 Hz, 1 H), 2.71 (d, *J* = 5.2 Hz, 1 H); ^{13}C NMR (126 MHz, CD_3CN) δ 156.59, 149.28, 136.19, 130.78, 130.38, 130.15, 129.39, 126.89, 124.27, 121.16, 115.58, 110.97, 66.67, 55.69, 49.52 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}N_3O_6$: 332.0888, Found: 332.0889.

2-(2,4-Dinitrophenoxy)-2-(3,4,5-trimethoxyphenyl)ethanamine (3k): yellow solid (72%)



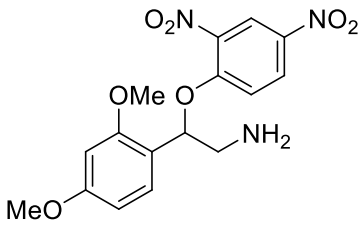
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (t, J = 5.4 Hz, 1 H), 8.86 (d, J = 2.7 Hz, 1 H), 8.22 (dd, J = 9.6, 2.7 Hz, 1 H), 7.29 (d, J = 9.7 Hz, 1 H), 6.77 (s, 2 H), 5.94 (d, J = 3.9 Hz, 1 H), 4.91 – 4.81 (m, 1 H), 3.78 (s, 6 H), 3.74 (ddd, J = 13.2, 5.7, 4.3 Hz, 1 H), 3.63 (s, 3 H), 3.58 (ddd, J = 13.2, 7.7, 5.4 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.22, 148.89, 138.79, 137.03, 135.30, 130.19, 130.02, 123.98, 116.45, 103.57, 71.06, 60.43, 56.24, 50.81 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{17}H_{18}N_3O_8$: 392.1099, Found: 392.1103.

2-(3,4-Dimethoxyphenyl)-2-(2,4-dinitrophenoxy)ethanamine (3l): yellow solid (61%)



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (t, J = 5.3 Hz, 1 H), 8.85 (d, J = 2.7 Hz, 1 H), 8.21 (dd, J = 9.6, 2.6 Hz, 1 H), 7.28 (d, J = 9.7 Hz, 1 H), 7.06 (d, J = 1.5 Hz, 1 H), 6.98-6.92 (m, 2 H), 5.86 (d, J = 4.4 Hz, 1 H), 4.86 (dt, J = 8.0, 4.1 Hz, 1 H), 3.76 (s, 3 H), 3.73 (s, 3 H), 3.70-3.67 (m, 1 H), 3.55 (ddd, J = 13.2, 7.9, 5.2 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.05, 148.84, 148.59, 135.54, 135.30, 130.27, 129.98, 124.00, 118.49, 116.41, 111.98, 110.18, 70.70, 56.01, 55.85, 50.88 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{16}N_3O_7$: 362.0994, Found: 362.0999.

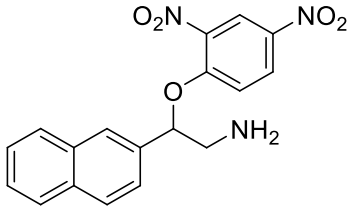
2-(2,4-Dimethoxyphenyl)-2-(2,4-dinitrophenoxy)ethanamine (3m): yellow solid (52%)



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (t, J = 5.4 Hz, 1 H), 8.87 (d, J = 2.7 Hz, 1 H), 8.31 (dd, J = 9.6,

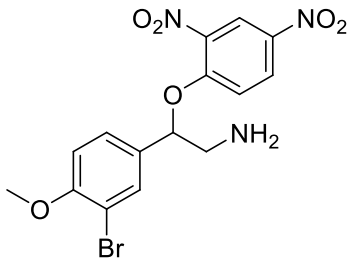
2.6 Hz, 1 H), 7.46 – 7.19 (m, 2 H), 6.58-6.56 (m, 2 H), 5.68 (d, *J* = 4.5 Hz, 1 H), 5.09 (dt, *J* = 7.9, 3.9 Hz, 1 H), 3.84 (s, 3 H), 3.76 (s, 3 H), 3.66 (ddd, *J* = 13.2, 6.0, 3.7 Hz, 1 H), 3.43 (ddd, *J* = 13.2, 7.8, 5.1 Hz, 1 H) ppm; ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 160.40, 157.02, 148.82, 135.34, 130.47, 130.13, 127.48, 124.06, 122.97, 115.96, 105.16, 98.47, 65.06, 55.96, 55.67, 49.83 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{16}N_3O_7$: 362.0994, Found: 362.0992.

2-(2,4-Dinitrophenoxy)-2-(naphthalen-2-yl)ethanamine (3n): yellow solid (75%)



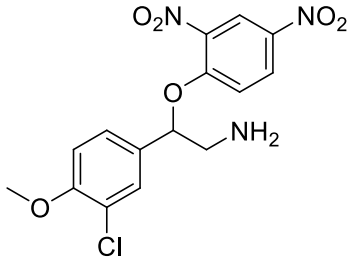
^{1}H NMR (500 MHz, CD_3CN) δ 8.94 (d, *J* = 2.6 Hz, 1 H), 8.84 (s, 1 H), 8.19 (dd, *J* = 9.6, 2.6 Hz, 1 H), 7.95 (s, 1 H), 7.90 (t, *J* = 8.0 Hz, 3 H), 7.59 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.56 – 7.45 (m, 2 H), 7.14 (d, *J* = 9.6 Hz, 1 H), 5.18 (dt, *J* = 7.9, 4.1 Hz, 1 H), 4.04 (d, *J* = 4.1 Hz, 1 H), 3.85 – 3.76 (m, 1 H), 3.75 – 3.66 (m, 1 H); ^{13}C NMR (126 MHz, CD_3CN) δ 148.75, 139.51, 135.75, 133.22, 133.05, 130.33, 129.84, 128.14, 127.87, 127.63, 126.37, 126.12, 124.86, 124.14, 123.74, 115.24, 71.32, 50.11 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{18}H_{14}N_3O_5$: 352.0939; Found: 352.0942.

2-(3-Bromo-4-methoxyphenyl)-2-(2,4-dinitrophenoxy)ethanamine (3o): yellow solid (59%)



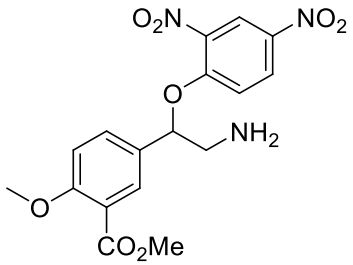
^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.93 (s, 1 H), 8.85 (s, 1 H), 8.21 (d, *J* = 9.1 Hz, 1 H), 7.66 (s, 1 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.32 (d, *J* = 9.2 Hz, 1 H), 7.10 (d, *J* = 8.1 Hz, 1 H), 5.95 (s, 1 H), 4.96 – 4.74 (m, 1 H), 3.84 (s, 3 H), 3.73-3.68 (m, 1 H), 3.60-3.51 (m, 1 H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 155.12, 148.86, 136.83, 135.35, 130.96, 130.22, 130.03, 127.06, 123.98, 116.50, 112.83, 110.85, 69.93, 56.71, 50.61 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}BrN_3O_6$: 411.9973, Found: 411.9969.

2-(3-Chloro-4-methoxyphenyl)-2-(2,4-dinitrophenoxy)ethanamine (3p): yellow solid (60%)



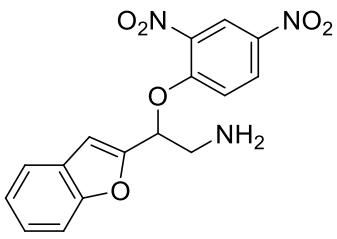
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (t, J = 5.5 Hz, 1 H), 8.86 (d, J = 2.7 Hz, 1 H), 8.23 (dd, J = 9.6, 2.7 Hz, 1 H), 7.52 (d, J = 2.0 Hz, 1 H), 7.39 (dd, J = 8.5, 2.0 Hz, 1 H), 7.33 (d, J = 9.7 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 1 H), 5.96 (br, 1 H), 4.88 (dd, J = 7.8, 3.2 Hz, 1 H), 3.85 (s, 3 H), 3.72 (ddd, J = 13.4, 5.8, 4.0 Hz, 1 H), 3.56 (ddd, J = 13.5, 8.2, 5.3 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.23, 148.86, 136.36, 135.36, 130.25, 130.06, 127.94, 126.36, 124.00, 121.22, 116.51, 112.98, 69.99, 56.58, 50.58 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{13}ClN_3O_6$: 366.0498, Found: 366.0501.

Methyl 5-(2-amino-1-(2,4-dinitrophenoxy)ethyl)-2-methoxybenzoate (3q): yellow solid (72%)



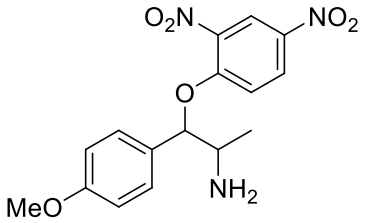
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.94 (d, J = 4.6 Hz, 1 H), 8.85 (s, 1 H), 8.21 (d, J = 9.5 Hz, 1 H), 7.73 (s, 1 H), 7.60 (d, J = 8.5 Hz, 1 H), 7.31 (d, J = 9.6 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 1 H), 5.95 (s, 1 H), 4.90 (s, 1 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.74 – 3.66 (m, 1 H), 3.61 – 3.49 (m, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.65, 158.00, 148.90, 135.32, 134.75, 131.56, 130.21), 130.04, 128.83, 123.98, 120.09, 116.51, 112.85, 70.18, 56.38, 52.35, 50.6 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{17}H_{16}N_3O_8$: 390.0943; Found: 314.0948.

2-(Benzofuran-2-yl)-2-(2,4-dinitrophenoxy)ethanamine (3r): yellow solid (73%)



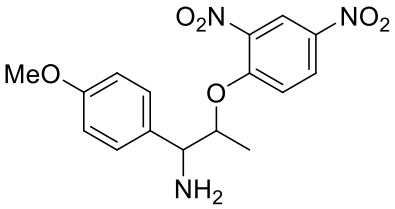
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (dd, *J* = 11.6, 2.6 Hz, 1 H), 8.98 (s, 1 H), 8.27 (dd, *J* = 9.5, 2.6 Hz, 1 H), 7.59 (d, *J* = 7.7 Hz, 1 H), 7.50 (t, *J* = 6.5 Hz, 1 H), 7.35 (t, *J* = 7.7 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 2 H), 7.03 (d, *J* = 9.5 Hz, 1 H), 6.83 (s, 1 H), 5.25 (dt, *J* = 26.3, 13.2 Hz, 1 H), 4.02 – 3.83 (m, 2 H); ^{13}C NMR (126 MHz, CD_3CN) δ 157.80, 155.25, 149.20, 136.36, 130.95, 130.38, 128.57, 125.01, 124.18, 123.55, 121.78, 115.59, 111.54, 104.32, 66.26, 47.84 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{12}N_3O_6$: 342.0732; Found: 342.0733.

1-(2,4-Dinitrophenoxy)-1-(4-methoxyphenyl)propan-2-amine (3s): yellow solid (59%)



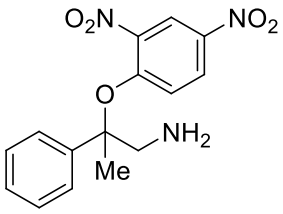
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 2.7 Hz, 1 H), 8.84 (d, *J* = 8.4 Hz, 1 H), 8.22 (dd, *J* = 9.6, 2.6 Hz, 1 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 7.00 (d, *J* = 9.6 Hz, 1 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 4.95 (d, *J* = 3.8 Hz, 1 H), 4.19 – 4.01 (m, 1 H), 3.83 (s, 3 H), 2.40 (br, 1 H), 1.26 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.71, 147.86, 135.73, 131.67, 130.30, 130.13, 127.47, 124.55, 114.47, 114.13, 75.74, 55.3, 54.12, 15.05 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{16}N_3O_6$: 346.1045; Found: 346.1046.

2-(2,4-Dinitrophenoxy)-1-(4-methoxyphenyl)propan-1-amine (3s′): yellow solid (25%)



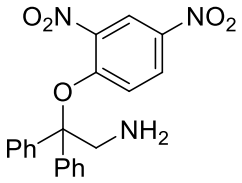
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (d, *J* = 2.7 Hz, 1 H), 8.87 (d, *J* = 8.0 Hz, 1 H), 8.09 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.23 (d, *J* = 8.3 Hz, 2 H), 7.19 (s, 1 H), 6.80 (t, *J* = 9.0 Hz, 3 H), 4.73 (d, *J* = 4.7 Hz, 1 H), 3.91 (q, *J* = 6.6 Hz, 1 H), 3.72 (s, 3 H), 1.28 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.78, 148.18, 135.73, 132.71, 130.32, 130.05, 127.36, 124.53, 114.36, 114.18, 55.33, 54.89, 29.71, 17.68 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{16}N_3O_6$: 346.1045; Found: 346.1048.

2-(2,4-Dinitrophenoxy)-2-phenylpropan-1-amine (3t)[5b]: yellow solid (22%)



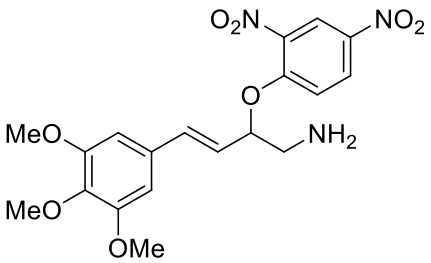
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.7 Hz, 1 H), 8.82 (s, 1 H), 8.19 (dd, *J* = 9.5, 2.7 Hz, 1 H), 7.52 (d, *J* = 7.9 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.3 Hz, 1 H), 6.87 (d, *J* = 9.5 Hz, 1 H), 3.65 (dd, *J* = 5.5, 3.2 Hz, 2 H), 2.13 (s, 1 H), 1.77 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.52, 144.17, 136.03, 130.50, 130.15, 128.91, 128.06, 124.75, 124.30, 114.12, 74.10, 54.71, 27.84 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{15}H_{14}N_3O_5$: 316.0939; Found: 316.0941.

2-(2,4-Dinitrophenoxy)-2,2-diphenylethanamine (3u): yellow solid (42%)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (d, *J* = 4.2 Hz, 1 H), 8.80 (d, *J* = 2.4 Hz, 1 H), 8.24 (dd, *J* = 9.6, 2.1 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 4 H), 7.47 (d, *J* = 9.7 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 4 H), 7.23 (t, *J* = 7.3 Hz, 2 H), 6.47 (s, 1 H), 4.34 (d, *J* = 4.7 Hz, 2 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.75, 145.80, 135.47, 130.48, 129.86, 128.61, 127.48, 126.29, 124.00, 116.48, 76.51, 52.94 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{20}H_{16}N_3O_5$: 378.1095; Found: 378.1100.

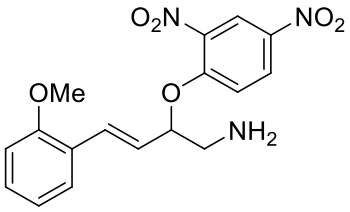
(*E*)-2-(2,4-Dinitrophenoxy)-4-(3,4,5-trimethoxyphenyl)but-3-en-1-amine (5a): yellow solid (67% (from *trans-diene*) and 69% (from *cis-diene*))



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.92 (t, *J* = 5.5 Hz, 1 H), 8.85 (d, *J* = 2.7 Hz, 1 H), 8.26 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.31 (d, *J* = 9.7 Hz, 1 H), 6.74 (s, 2 H), 6.61 (t, *J* = 13.3 Hz, 1 H), 6.35 (dd, *J* = 15.8, 5.6 Hz, 1 H), 5.65 (d, *J* = 4.1 Hz, 1 H), 4.50 (s, 1 H), 3.77 (d, *J* = 15.7 Hz, 6 H), 3.73 – 3.66 (m, 1 H), 3.66

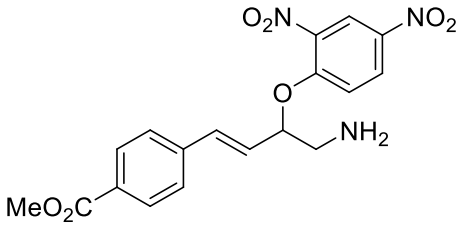
(s, 3 H), 3.51 (ddd, *J* = 13.0, 7.3, 5.4 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 153.44, 148.92, 137.57, 135.29, 132.68, 130.66, 130.47, 130.30, 130.11, 124.04, 116.36, 104.10, 69.63, 60.49, 56.27, 49.12 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{19}H_{21}N_3O_8$: 418.1256, Found:418.1261.

(*E*)-2-(2,4-Dinitrophenoxy)-4-(2-methoxyphenyl)but-3-en-1-amine (5b): yellow solid (66%)



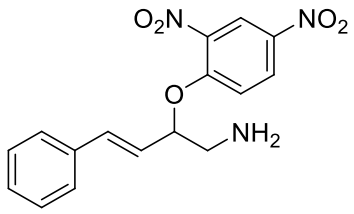
^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.92 (t, *J* = 5.5 Hz, 1 H), 8.86 (d, *J* = 2.7 Hz, 1 H), 8.25 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.32 (d, *J* = 9.7 Hz, 1 H), 7.27 – 7.20 (m, 1 H), 7.00 (d, *J* = 8.0 Hz, 1 H), 6.97 – 6.87 (m, 2 H), 6.34 (dd, *J* = 16.1, 5.6 Hz, 1 H), 5.63 (s, 1 H), 4.51 (dd, *J* = 10.5, 5.5 Hz, 1 H), 3.80 (s, 3 H), 3.68 (ddd, *J* = 13.3, 5.6, 4.8 Hz, 1 H), 3.50 (ddd, *J* = 27.2, 16.3, 12.7 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 156.72, 148.95, 135.27, 131.35, 130.30, 130.08), 129.30, 126.94, 125.34, 125.19, 124.04, 120.97, 116.42, 111.76, 69.97, 55.81, 49.14 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{17}H_{16}N_3O_6$: 358.1045; Found: 358.1049.

(*E*)-Methyl 4-(4-amino-3-(2,4-dinitrophenoxy)but-1-enyl)benzoate (5c): yellow solid (53%)



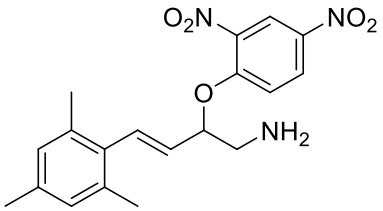
^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.91 (t, *J* = 5.5 Hz, 1 H), 8.85 (d, *J* = 2.7 Hz, 1 H), 8.25 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.92 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 9.7 Hz, 1 H), 6.78 (d, *J* = 16.0 Hz, 1 H), 6.58 (dd, *J* = 16.0, 5.2 Hz, 1 H), 5.74 (s, 1 H), 4.55 (s, 1 H), 3.84 (s, 3 H), 3.72 (dt, *J* = 13.0, 5.1 Hz, 1 H), 3.59 – 3.46 (m, 1 H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 166.42, 148.92, 141.68, 135.33, 134.39, 130.31, 130.15, 130.04, 130.00, 129.38, 128.81, 127.01, 124.02, 116.34, 69.45, 52.55, 48.89 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{18}H_{16}N_3O_7$: 386.0994; Found: 386.0998.

(*E*)-2-(2,4-Dinitrophenoxy)-4-phenylbut-3-en-1-amine (5d): yellow solid (57%)



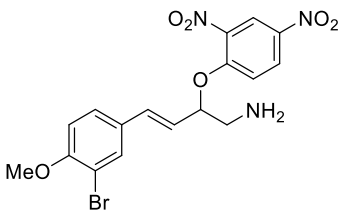
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (t, J = 5.3 Hz, 1 H), 8.86 (d, J = 2.7 Hz, 1 H), 8.26 (dd, J = 9.6, 2.6 Hz, 1 H), 7.44 (d, J = 7.4 Hz, 2 H), 7.35 (d, J = 7.8 Hz, 2 H), 7.32 (d, J = 2.8 Hz, 1 H), 7.25 (t, J = 7.3 Hz, 1 H), 6.70 (d, J = 16.0 Hz, 1 H), 6.39 (dd, J = 16.0, 5.5 Hz, 1 H), 5.66 (d, J = 4.4 Hz, 1 H), 4.52 (br, 1 H), 3.81 – 3.61 (m, 1 H), 3.59 – 3.43 (m, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.93, 136.90, 135.31, 131.10, 130.51, 130.34, 130.13, 129.11, 128.06, 126.80, 124.05, 116.37, 69.57, 49.06 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{16}H_{14}N_3O_5$: 328.0939; Found: 328.0944.

(*E*)-2-(2,4-Dinitrophenoxy)-4-mesitylbut-3-en-1-amine (5e): yellow solid (64%)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.90 (t, J = 5.5 Hz, 1 H), 8.84 (d, J = 2.7 Hz, 1 H), 8.24 (dd, J = 9.6, 2.7 Hz, 1 H), 7.31 (d, J = 9.7 Hz, 1 H), 6.80 (s, 2 H), 6.60 (d, J = 16.2 Hz, 1 H), 5.75 (dd, J = 16.3, 5.5 Hz, 1 H), 5.63 (s, 1 H), 4.53 (q, J = 5.0 Hz, 1 H), 3.68 (dt, J = 13.3, 5.2 Hz, 1 H), 3.55 (ddd, J = 12.8, 6.7, 5.3 Hz, 1 H), 2.18 (s, 9 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.62, 140.54, 140.36, 140.20, 140.06, 138.22, 135.13, 134.75, 133.61, 132.91, 128.84, 128.67, 121.06, 74.48, 53.83, 25.76 ppm; HRMS (ESI) m/z calcd for [M-H]: $C_{19}H_{20}N_3O_5$: 370.1408, Found: 370.1411.

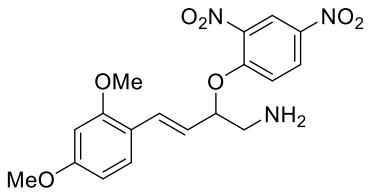
(*E*)-4-(3-Bromo-4-methoxyphenyl)-2-(2,4-dinitrophenoxy)but-3-en-1-amine (5f): yellow solid (56%)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.90 (t, J = 5.6 Hz, 1 H), 8.85 (s, 1 H), 8.25 (d, J = 9.3 Hz, 1 H), 7.67 (s, 1 H), 7.41 (d, J = 8.1 Hz, 1 H), 7.30 (d, J = 9.6 Hz, 1 H), 7.07 (d, J = 8.4 Hz, 1 H), 6.61 (d, J = 15.9

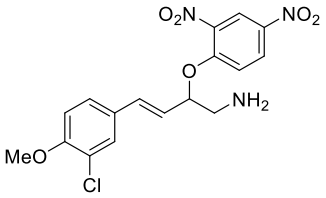
Hz, 1 H), 6.31 (dd, *J* = 15.9, 5.2 Hz, 1 H), 4.49 (s, 1 H), 3.84 (s, 3 H), 3.67 (dt, *J* = 13.6, 5.3 Hz, 1 H), 3.51 (dd, *J* = 13.1, 6.5 Hz, 1 H), 3.38 (s, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.22, 148.91, 135.28, 131.18, 130.84, 130.34, 130.30, 130.10, 128.71, 127.60, 124.02, 116.32, 113.12, 111.42, 69.57, 56.70, 49.07 ppm; HRMS (ESI) m/z calcd for [M+H]: $C_{17}H_{17}BrN_3O_6$: 438.0301, Found: 438.0300.

(*E*)-4-(2,4-Dimethoxyphenyl)-2-(2,4-dinitrophenoxy)but-3-en-1-amine (5g): brown solid (37%)



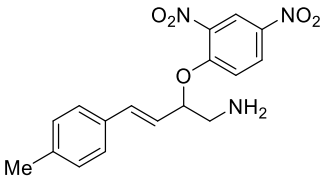
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, *J* = 2.7 Hz, 1 H), 8.89 (t, *J* = 5.3 Hz, 1 H), 8.25 (dd, *J* = 9.6, 2.7 Hz, 1 H), 7.32 (d, *J* = 8.5 Hz, 1 H), 7.05 – 6.86 (m, 2 H), 6.47 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.44 (d, *J* = 2.4 Hz, 1 H), 6.20 (dd, *J* = 16.0, 7.1 Hz, 1 H), 4.65 (td, *J* = 7.2, 4.3 Hz, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.64 (dt, *J* = 13.1, 5.0 Hz, 1 H), 3.55 (ddd, *J* = 12.7, 7.2, 4.9 Hz, 1 H), 2.17 (b, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.10, 158.15, 148.48, 136.01, 130.51, 130.22, 128.35, 128.16, 125.99, 124.33, 117.52, 114.26, 104.94, 98.41, 71.80, 55.46, 55.44, 48.84 ppm; HRMS (ESI) m/z calcd for [M+H]: $C_{18}H_{20}N_3O_7$: 390.1301, Found: 390.1300.

(*E*)-4-(3-Chloro-4-methoxyphenyl)-2-(2,4-dinitrophenoxy)but-3-en-1-amine (5h): yellow solid (88%)



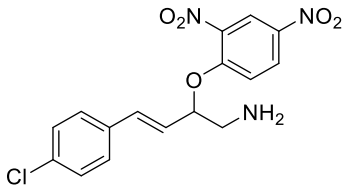
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.90 (t, *J* = 5.6 Hz, 1 H), 8.86 (d, *J* = 2.7 Hz, 1 H), 8.26 (dd, *J* = 9.6, 2.8 Hz, 1 H), 7.53 (d, *J* = 2.1 Hz, 1 H), 7.37 (dd, *J* = 8.5, 2.1 Hz, 1 H), 7.31 (d, *J* = 9.6 Hz, 1 H), 7.11 (d, *J* = 8.6 Hz, 1 H), 6.61 (dd, *J* = 16.0, 1.4 Hz, 1 H), 6.32 (dd, *J* = 15.9, 5.5 Hz, 1 H), 4.49 (d, *J* = 5.5 Hz, 2 H), 3.85 (s, 3 H), 3.67 (ddd, *J* = 13.3, 5.9, 4.4 Hz, 1 H), 3.51 (ddd, *J* = 13.1, 7.3, 5.3 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.34, 148.92, 135.29, 130.69, 130.36, 130.31, 130.12, 128.84, 127.80, 126.95, 124.04, 121.77, 116.34, 113.29, 69.57, 56.58, 49.06 ppm; HRMS (ESI) m/z calcd for [M]: $C_{17}H_{16}ClN_3O_6$: 393.0728, Found: 393.0758.

(*E*)-2-(2,4-Dinitrophenoxy)-4-(p-tolyl)but-3-en-1-amine (5i): brown solid (60%)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.91 (t, *J* = 5.6 Hz, 1 H), 8.85 (d, *J* = 2.6 Hz, 1 H), 8.25 (dd, *J* = 9.6, 2.8 Hz, 1 H), 7.32 (dd, *J* = 8.8, 6.0 Hz, 3 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 6.65 (d, *J* = 15.9 Hz, 1 H), 6.32 (dd, *J* = 16.0, 5.6 Hz, 1 H), 4.50 (q, *J* = 5.6 Hz, 1 H), 3.68 (dt, *J* = 13.3, 5.0 Hz, 1 H), 3.51 (ddd, *J* = 13.0, 7.4, 5.2 Hz, 1 H), 2.29 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.91, 137.38, 135.29, 134.11, 130.48, 130.32, 130.10, 129.96, 129.69, 126.73, 124.04, 116.36, 69.64, 49.11, 21.24 ppm; HRMS (ESI) m/z calcd for [M+H]: $C_{17}H_{17}N_3O_5$: 344.1246, Found: 344.1242.

(*E*)-4-(4-Chlorophenyl)-2-(2,4-dinitrophenoxy)but-3-en-1-amine (5j): yellow solid (30%)

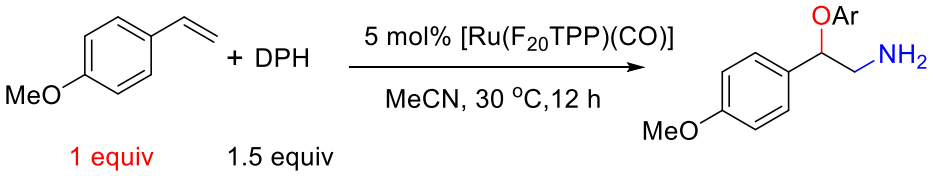


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.90 (t, *J* = 5.5 Hz, 1 H), 8.85 (d, *J* = 2.7 Hz, 1 H), 8.25 (dd, *J* = 9.6, 2.8 Hz, 1 H), 7.47 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 9.6 Hz, 1 H), 6.69 (d, *J* = 15.8 Hz, 1 H), 6.43 (dd, *J* = 16.0, 5.4 Hz, 1 H), 4.52 (q, *J* = 5.2 Hz, 1 H), 3.69 (dt, *J* = 13.4, 5.2 Hz, 1 H), 3.51 (ddd, *J* = 13.1, 7.4, 5.3 Hz, 1 H); ^{13}C NMR (126 MHz,) δ 148.93, 135.89, 135.33, 132.41, 132.16, 130.33, 130.14, 129.21, 129.10, 128.52, 124.04, 116.35, 69.50, 48.98 ppm; HRMS (ESI) m/z calcd for [M+H]: $C_{16}H_{15}ClN_3O_5$: 364.0700, Found: 364.0962.

Conditions for mass spectrometry

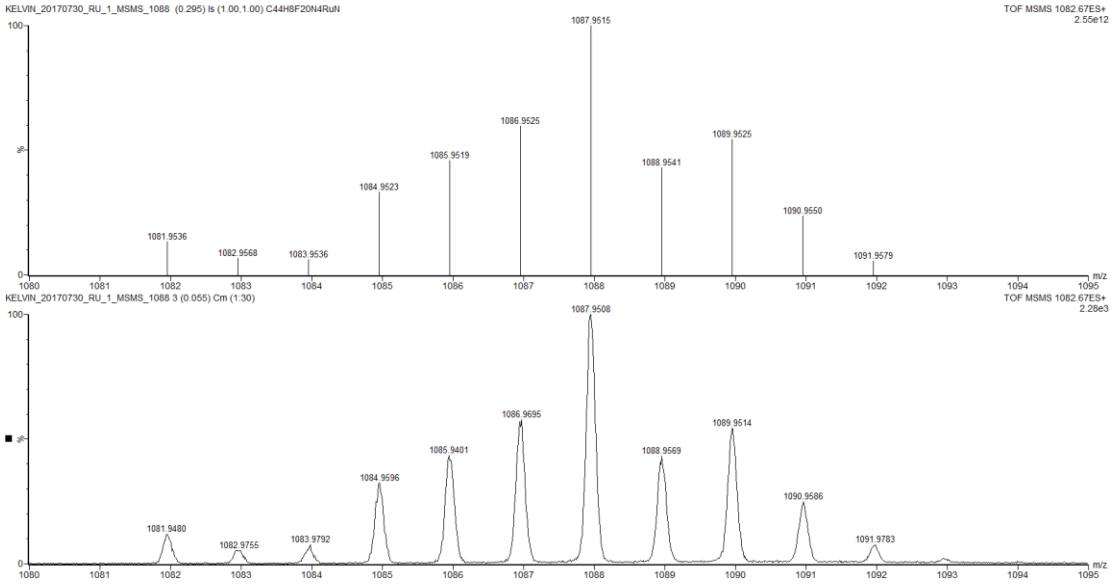
All the ESI-MS spectra were recorded in the positive ion mode using a Finnigan TSQTM Quantum AccessTM triple-quadrupole mass spectrometer (Thermo Electron Corp., San Jose, CA, USA). N_2 was used as collision gas and the collision energy ranged from 0 to 25 eV, depending on the dissociation ability of the precursor ions. Data acquisition and analysis were done with the Xcalibur (Version 2.0, Thermoquest Finnigan) software package. The standard conditions of ESI-TSQ MS were: vacuum, 2.6 $\times 10^{-6}$ torr; spray voltage, 5 kV; capillary temperature, 270 °C; sheath gas flow-rate 25 arb. (arbitrary units for LCQ valve settings), auxiliary gas flow-rate 5 arb; the sample was transferred into the ESI source by a syringe pump at a flow rate of 500 μL·h^{-1}.

General procedure for the mechanism study by ESI-HRMS



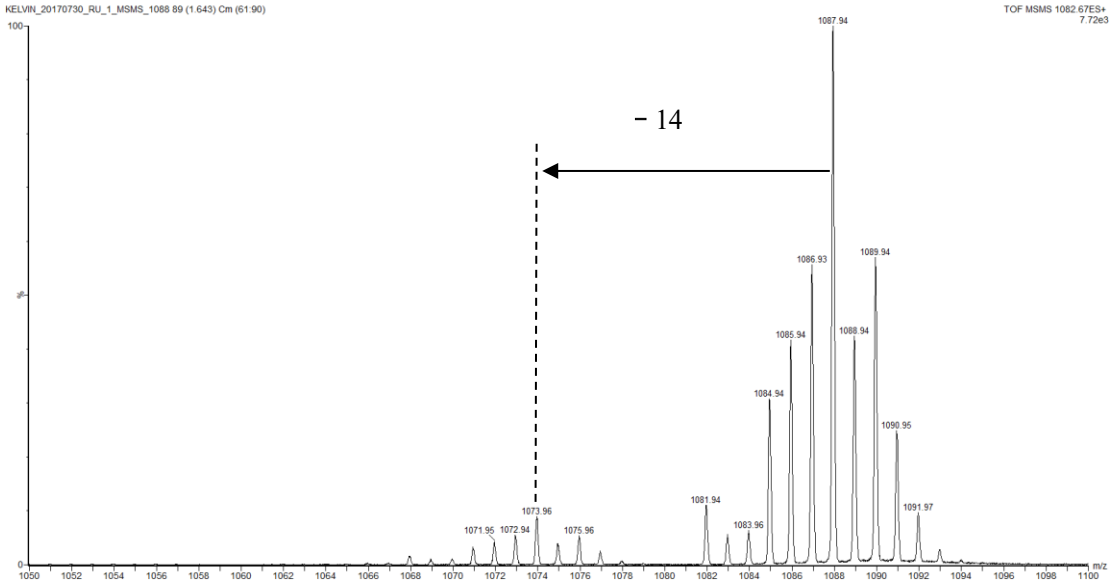
To a solution of [Ru(F_{20}TPP)(CO)] (5 mg) in MeCN (1 mL), DPH (30 mg) was added, then, the reaction mixture (20 μL) was diluted with MeCN to 1 mL and analysed by ESI-HRMS. In parallel, to a solution of [Ru(F_{20}TPP)(CO)] (5 mg) and DPH (30 mg) in MeCN (1 mL), 4-methoxystyrene (13.8 mg) was added. After 1min, detected samples (20 μL) taken from the reaction solution were typically diluted to 1 mL with CH_3CN. Afterwards, the samples taken from the reaction solution at different time intervals were monitored by ESI-MS.

Figure S1. ESI-HRMS spectrum of $[Ru^{VI}(F_{20}TPP)(N)]^+$ with the corresponding simulated pattern



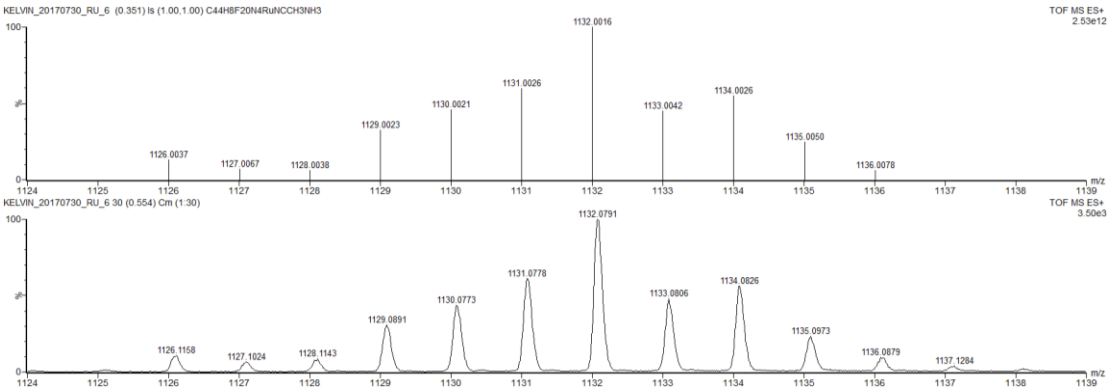
The *m/z* 1088 ion is attributed to $[Ru^{VI}(F_{20}TPP)(N)]^+$ (upper for simulated pattern; lower figure for experimental signal).

Figure S2. The collision induced dissociation experiment of $[Ru^{VI}(F_{20}TPP)(N)]^+$



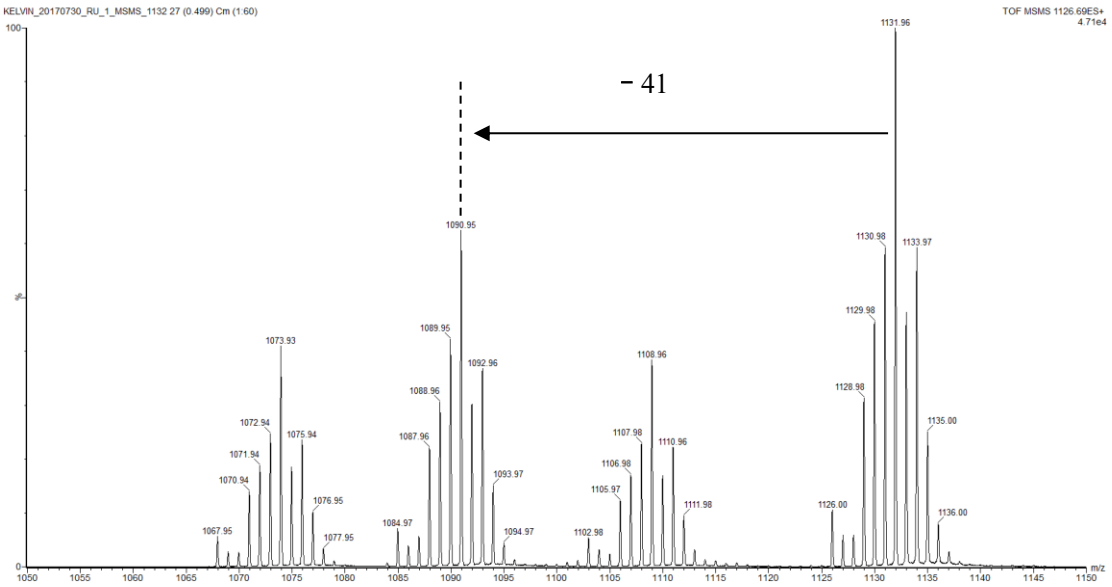
Collision induced dissociation at 50 eV led to loss of N atom.

Figure S3. ESI-HRMS spectrum of $[Ru^{VI}(F_{20}TPP)(N)(MeCN)]^+$ with the corresponding simulated pattern.



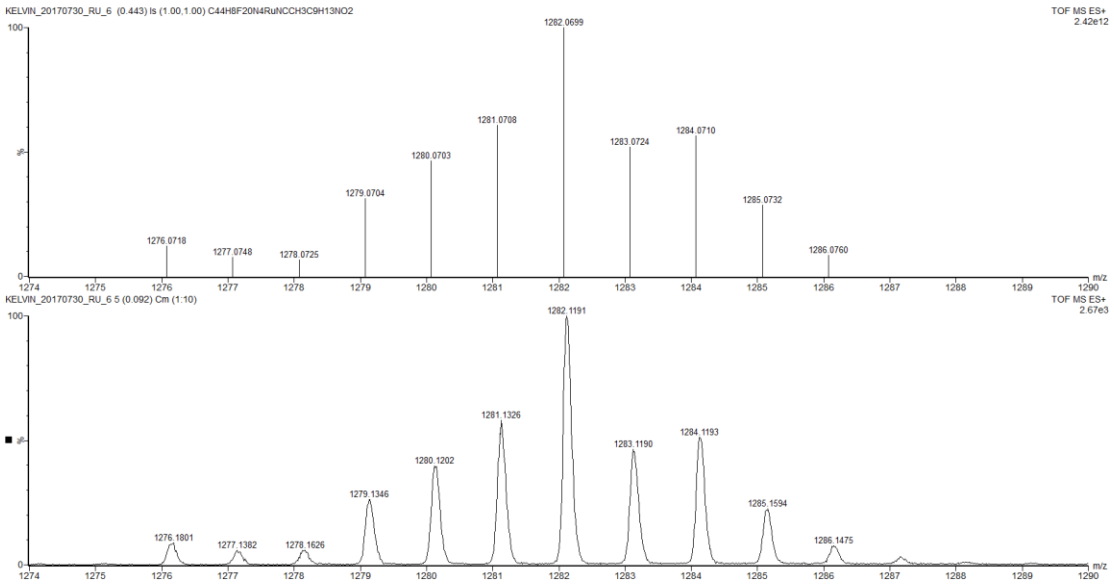
The *m/z* 1132 ion can be attributed to $[Ru^{VI}(F_{20}TPP)(N)(MeCN)]^+$ (upper figure for simulated pattern; lower figure for experimental signal).

Figure S4. The collision induced dissociation experiment of $[Ru^{VI}(F_{20}TPP)(N)(MeCN)]^+$



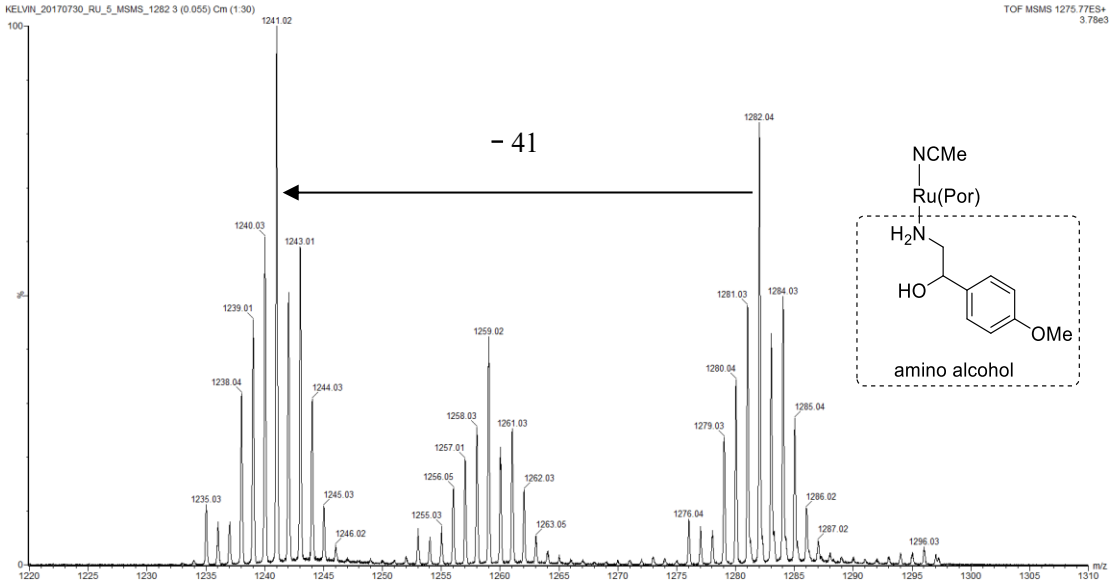
Collision induced dissociation at 16 eV led to loss of MeCN molecule.

Figure S5. ESI-HRMS spectrum of $[Ru^{III}(F_{20}TPP)(MeCN)(aminoalcohol)]^+$ with the corresponding simulated pattern.



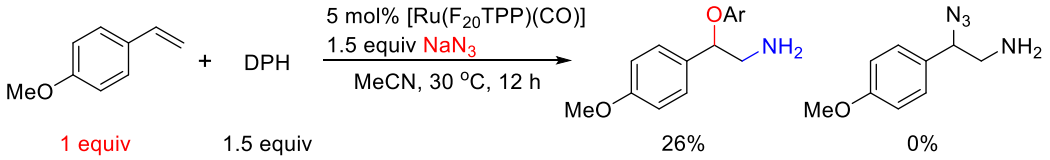
The *m/z* 1282 ion is attributed to $[Ru^{III}(F_{20}TPP)(MeCN)(amino\ alcohol)]^+$ (upper figure for simulated pattern; lower figure for experimental signal).

Figure S6. The collision induced dissociated experiment of $[Ru^{VI}(F_{20}TPP)(MeCN)(amino\ alcohol)]^+$

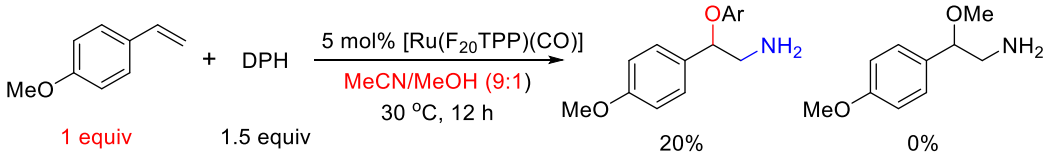


Collision induced dissociation at 15 eV led to loss of MeCN molecule.

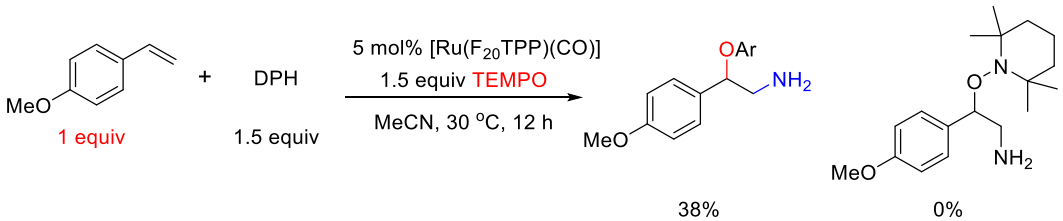
Mechanism study experiments



In a 25 mL Schlenk tube, [Ru(F_{20}TPP)(CO)] (0.027 g, 0.0025 mmol), DPH (0.15 g, 0.75 mmol), NaN_3 (0.006 g, 0.75 mmol) were added into MeCN (2 mL). To the mixture, 4-methoxystyrene (0.5 mmol) was added. Then the mixture was stirred at 30 °C for 12 h. TLC indicated that DPH decomposed completely. The solvent was washed by water, brine. The organic layer was dried by Na_2SO_4, the residue was purified by silica gel column chromatography (eluent: Petroleum ether : EtOAc = 3:1) to give a yellow solid (26%).



In a 25 mL Schlenk tube, [Ru(F_{20}TPP)(CO)] (0.027 g, 0.0025 mmol), DPH (0.15 g, 0.75 mmol) were added into MeCN/MeOH (9:1) (4 mL). To the mixture, 4-methoxystyrene (0.5 mmol) was added. Then the mixture was stirred at 30 °C for 12 h. TLC indicated that DPH decomposed completely. The solvent was washed by water, brine. The organic layer was dried by Na_2SO_4, the residue was purified by silica gel column chromatography (eluent: Petroleum ether : EtOAc = 3:1) to give a yellow solid (20%).



In a 25 mL Schlenk tube,[Ru(F_{20}TPP)(CO)] (0.027 g, 0.0025 mmol), DPH (0.15 g, 0.75 mmol), and TEMPO (0.078 g, 0.75 mmol) were added into MeCN (2 mL). To the mixture, 4-methoxystyrene (0.5 mmol) was added. Then the mixture was stirred at 30 °C for 12 h. TLC indicated that DPH decomposed completely. The solvent was washed by water, brine. The organic layer was dried by Na_2SO_4, the residue was purified by silica gel column chromatography (eluent: Petroleum ether : EtOAc = 3:1) to give a yellow solid (38%).

IR and UV-vis spectra

Figure S7: IR Spectra

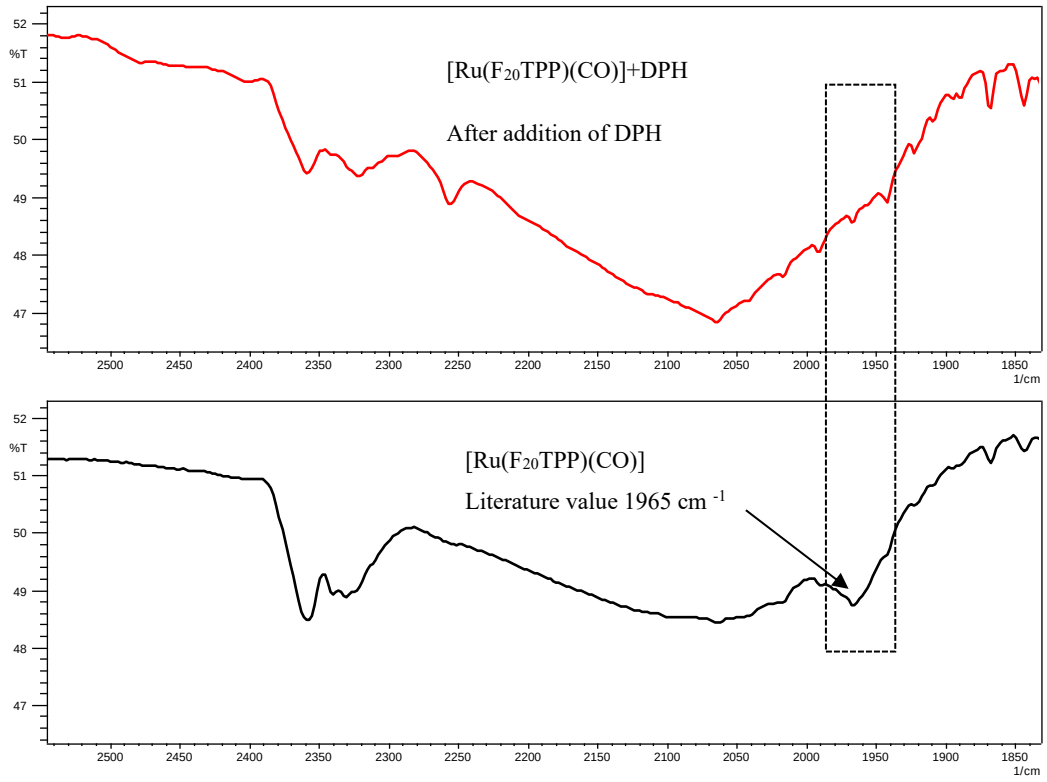
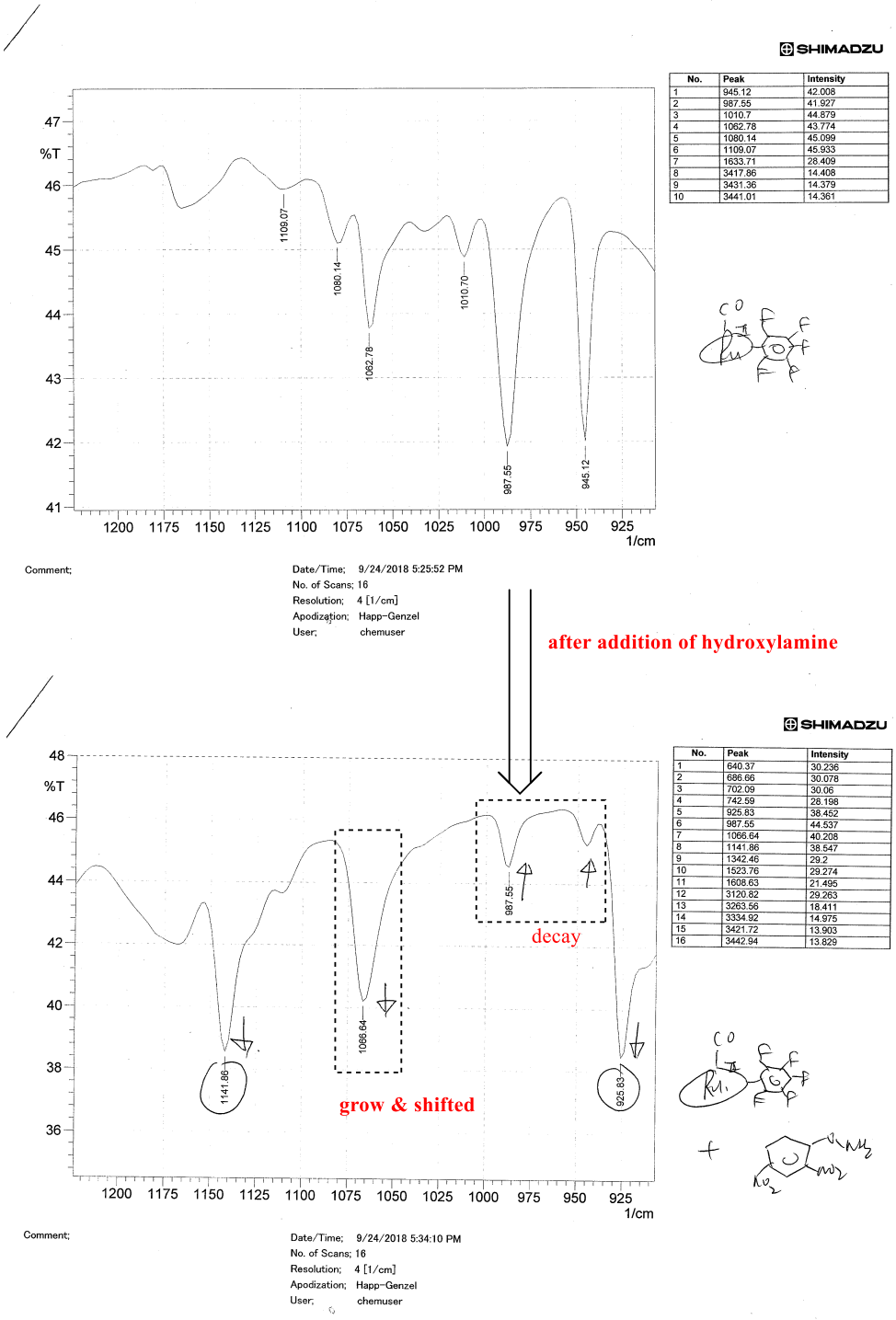


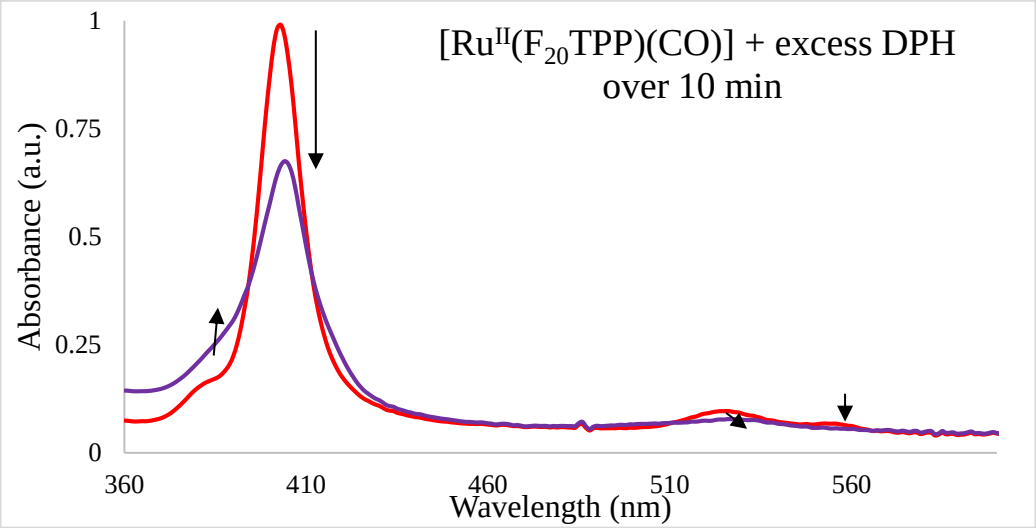
Figure S8: IR spectra



No.	Peak	Intensity
1	945.12	42.008
2	987.55	41.927
3	1010.7	44.879
4	1062.78	43.774
5	1080.14	45.099
6	1109.07	45.933
7	1633.71	28.409
8	3417.86	14.408
9	3431.36	14.379
10	3441.01	14.361

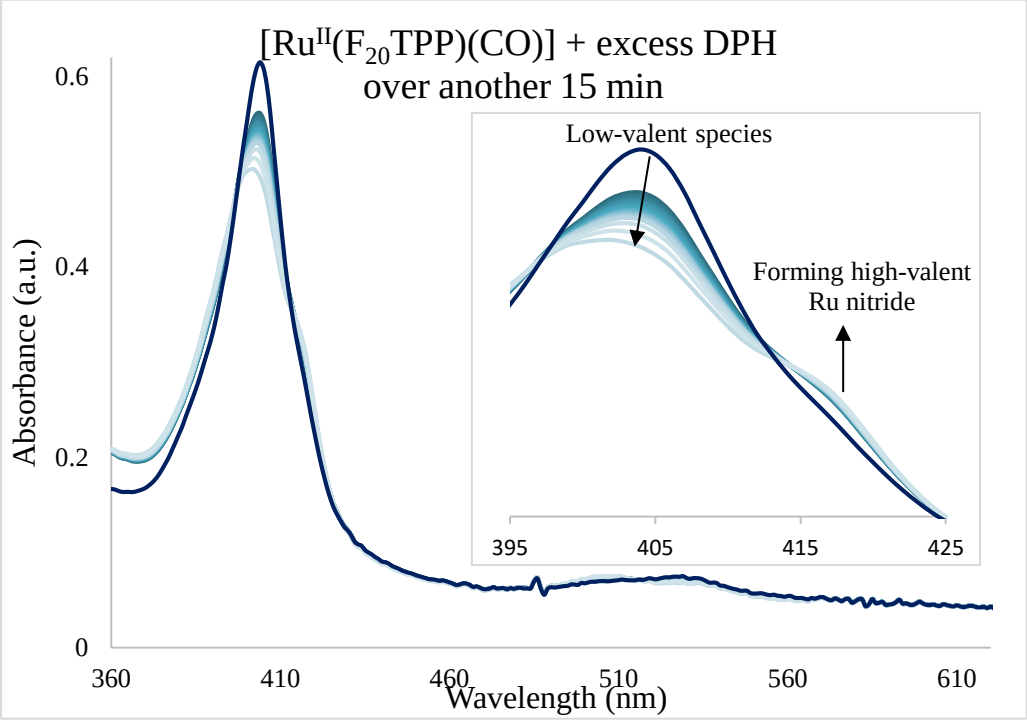
No.	Peak	Intensity
1	640.37	30.236
2	686.66	30.078
3	702.09	30.06
4	742.59	28.198
5	925.83	38.452
6	987.55	44.537
7	1066.64	40.208
8	1141.86	38.547
9	1342.46	29.2
10	1523.76	29.274
11	1608.63	21.495
12	3120.82	29.263
13	3263.56	18.411
14	3334.92	14.975
15	3421.72	13.903
16	3442.94	13.829

Figure S9: UV-vis spectra at 10 min



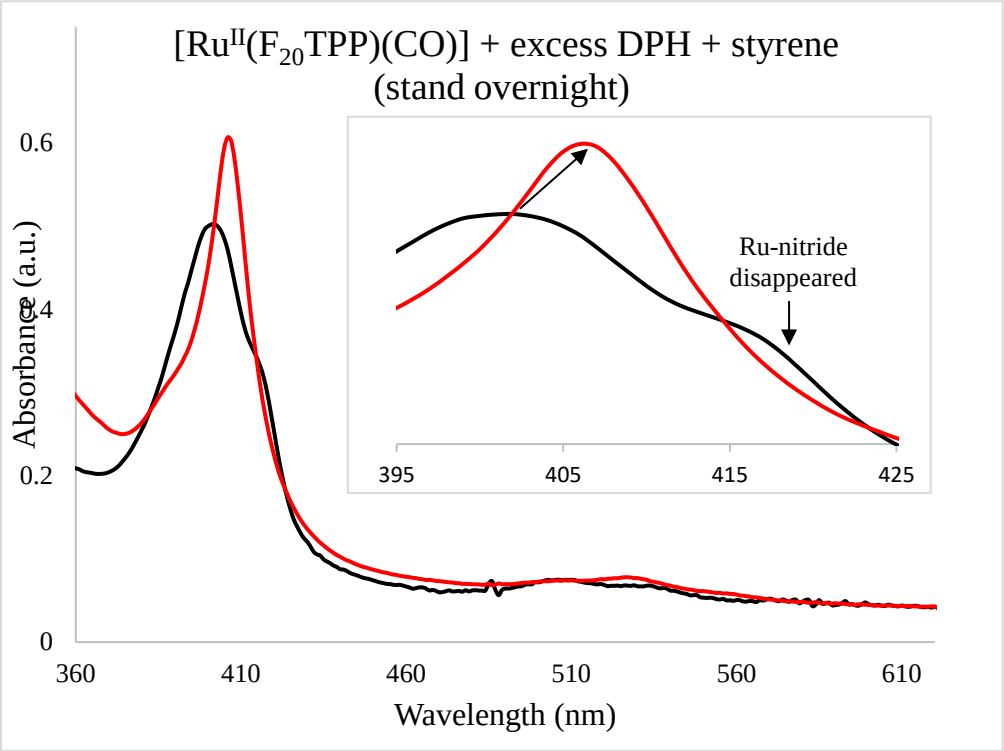
(Arrows pointing the directions of spectral changes as time elapsed)

Figure S10: UV-vis spectra at 25 min



(Arrows pointing the directions of spectral changes as time elapsed)

Figure S11: UV-vis spectra for overnight



(Arrows pointing the directions of spectral changes as time elapsed)

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2 C. Wang, K. V. Shalyaev, M. Bonchio, T. Carofiglio and J. T. Groves, *Inorg. Chem.*, 2006, **45**, 4769.

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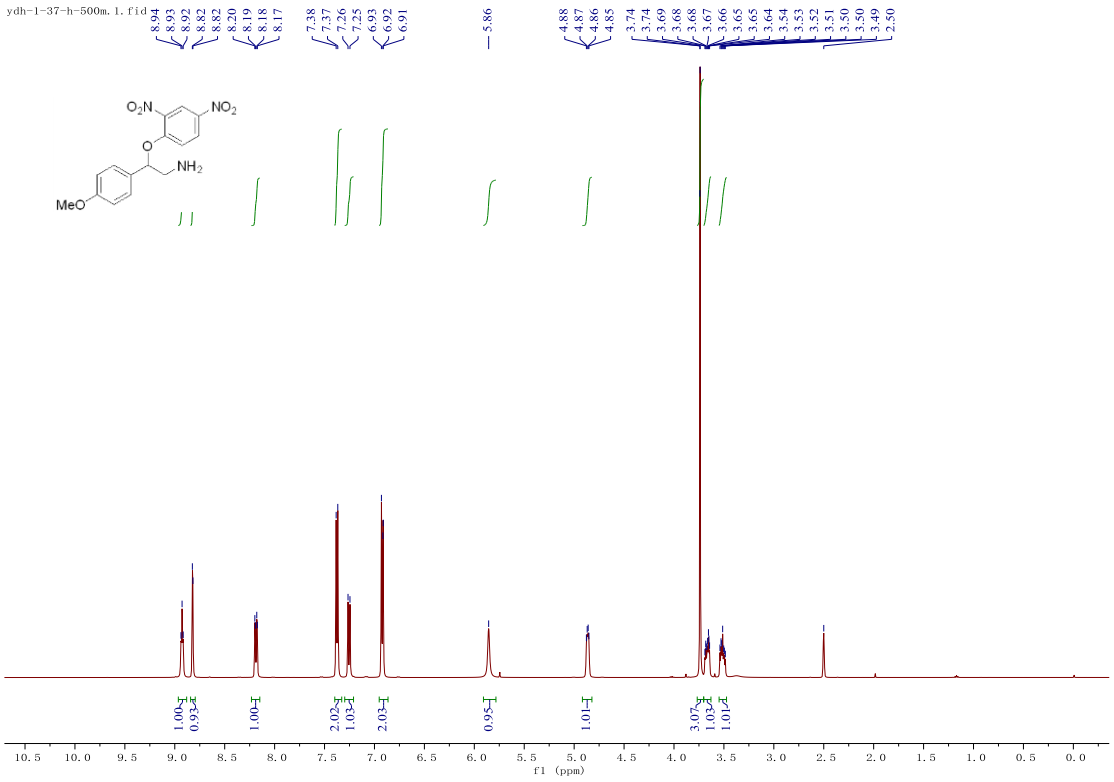
4. S. K.-Y. Leung, J.-S. Huang, J.-L. Liang, C.-M. Che and Z.-Y. Zhou, *Angew. Chem. Int. Ed.*, 2003, **42**, 340

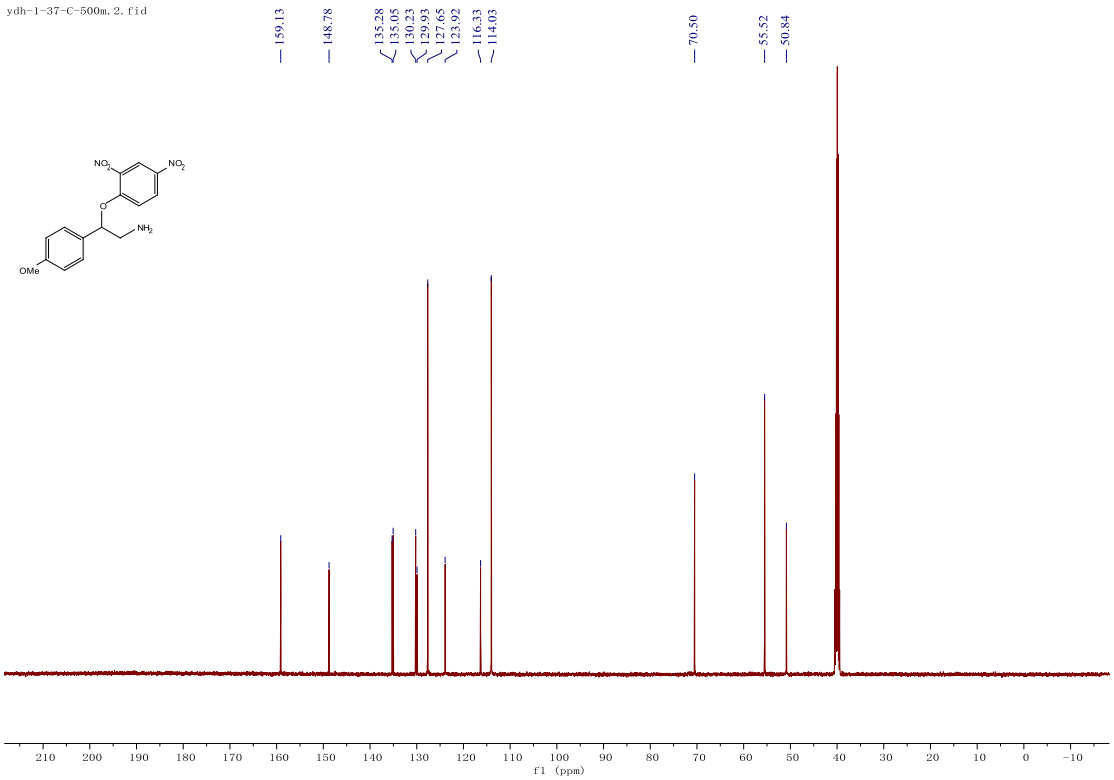
5 *(a)* J. L. Jat, M. P. Paudyal, H. Gao, Q.-L. Xu, M. Yousufuddin, D. Devarajan, D. H. Ess, L. Kürti and J. R. Falck, *Science*, 2014, **343**, 61; *(b) United States Pat.,* US2016340305A1, 2015.

^{1}H and ^{13}C NMR spectra of compounds 3a-w and 4a-j

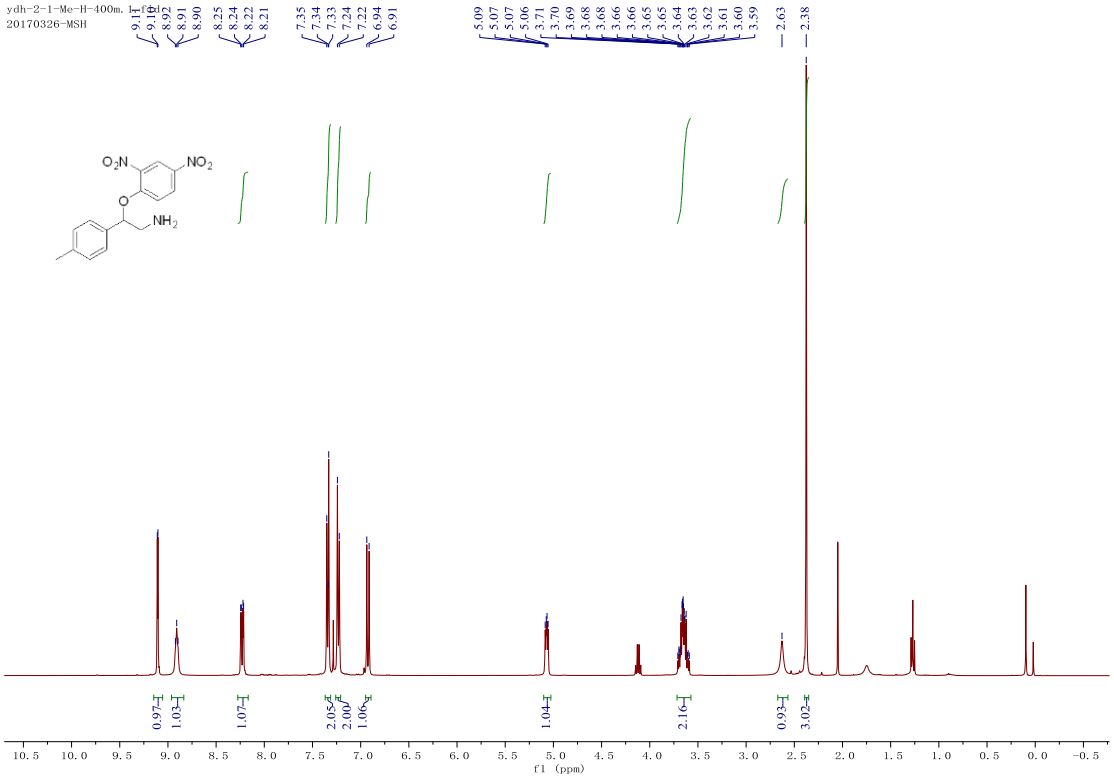
^{1}H NMR Spectrum of 3a



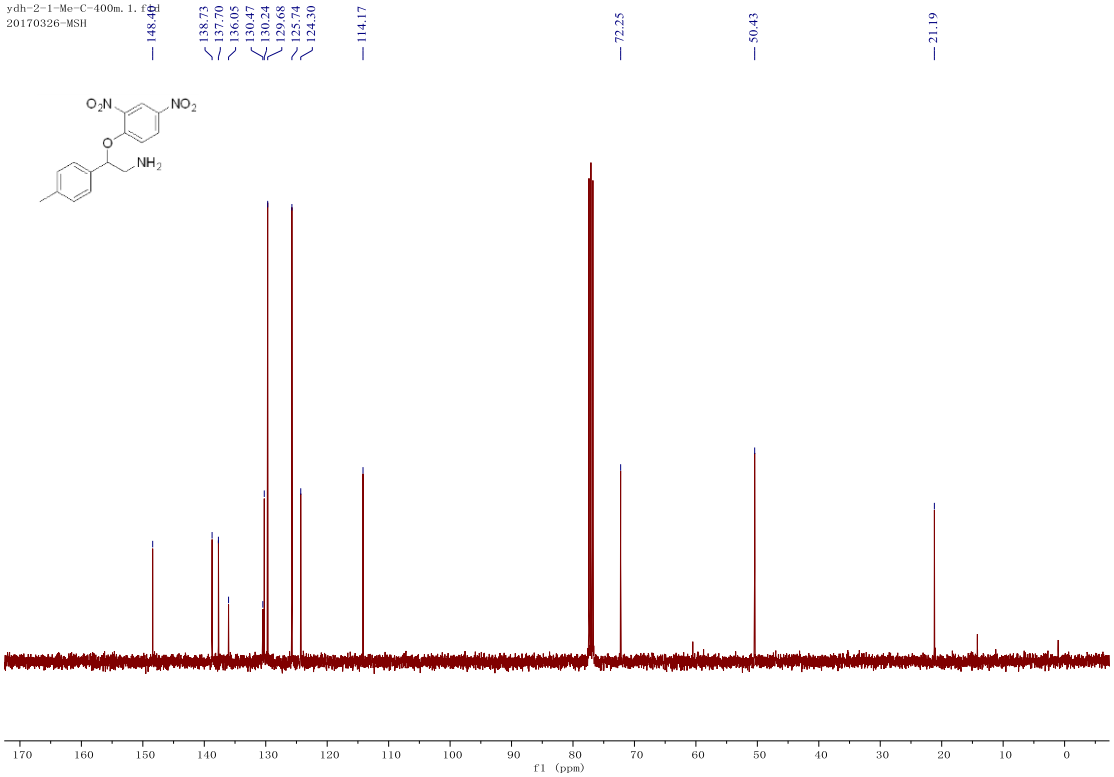
^{13}C NMR Spectrum of 3a



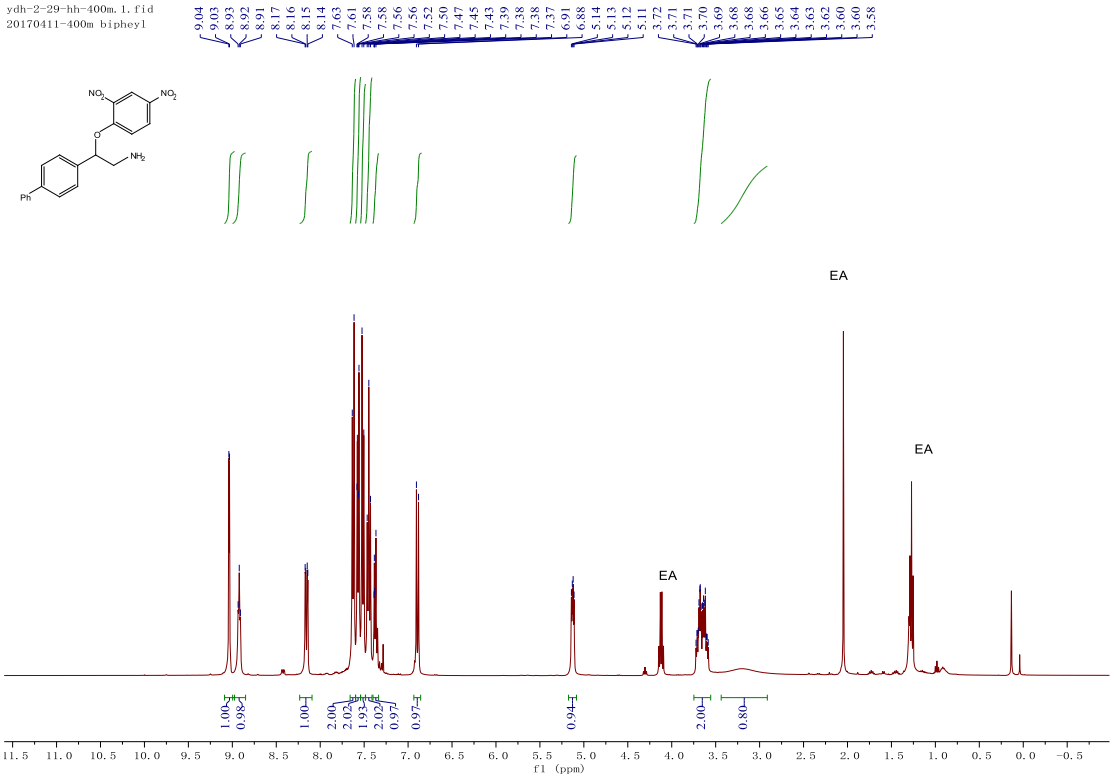
^{1}H NMR Spectrum of 3b



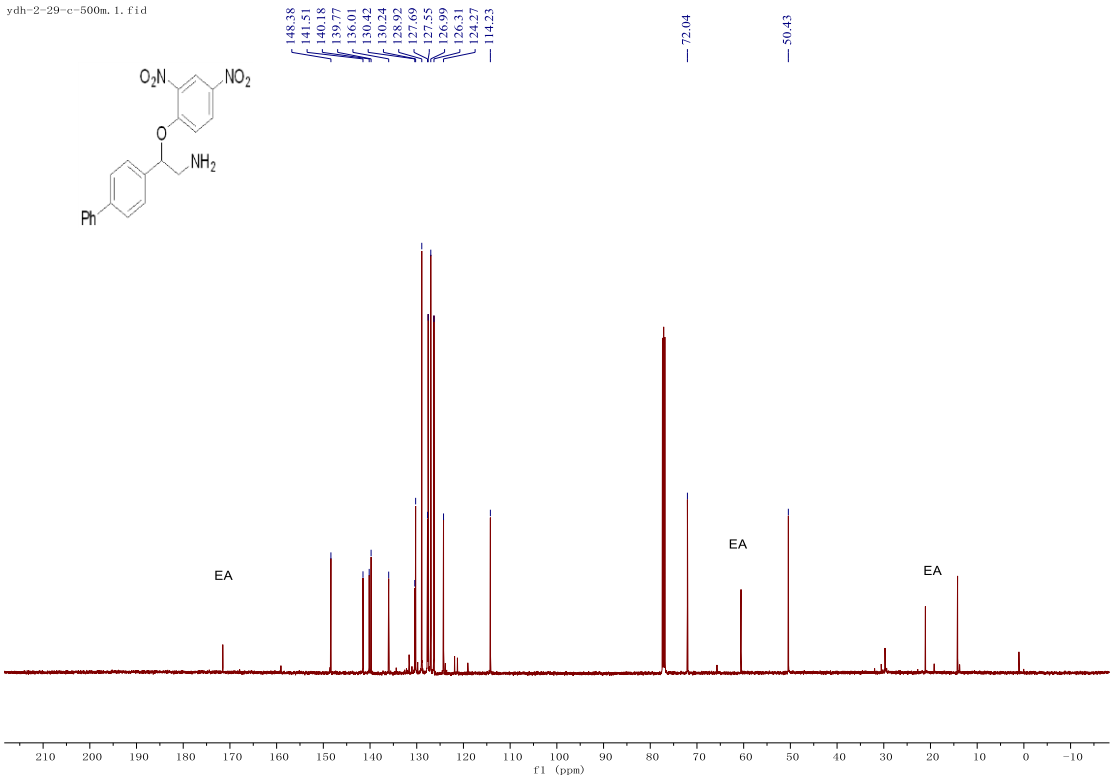
^{13}C NMR Spectrum of 3b



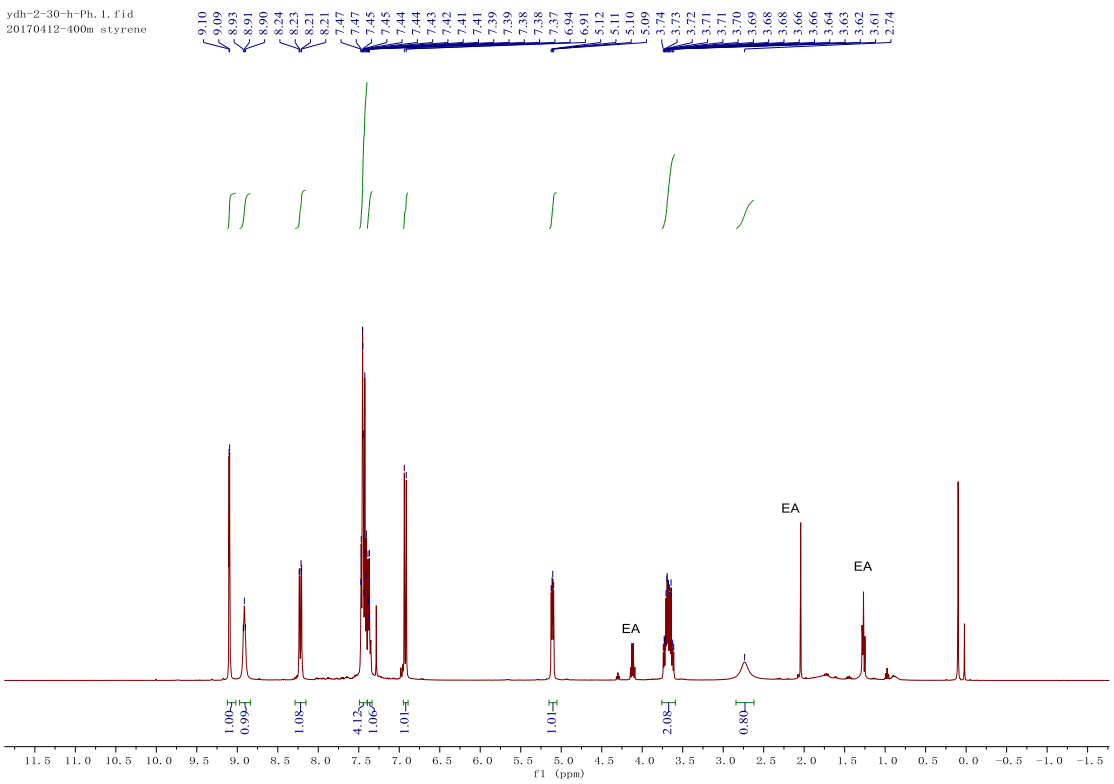
^{1}H NMR Spectrum of 3c



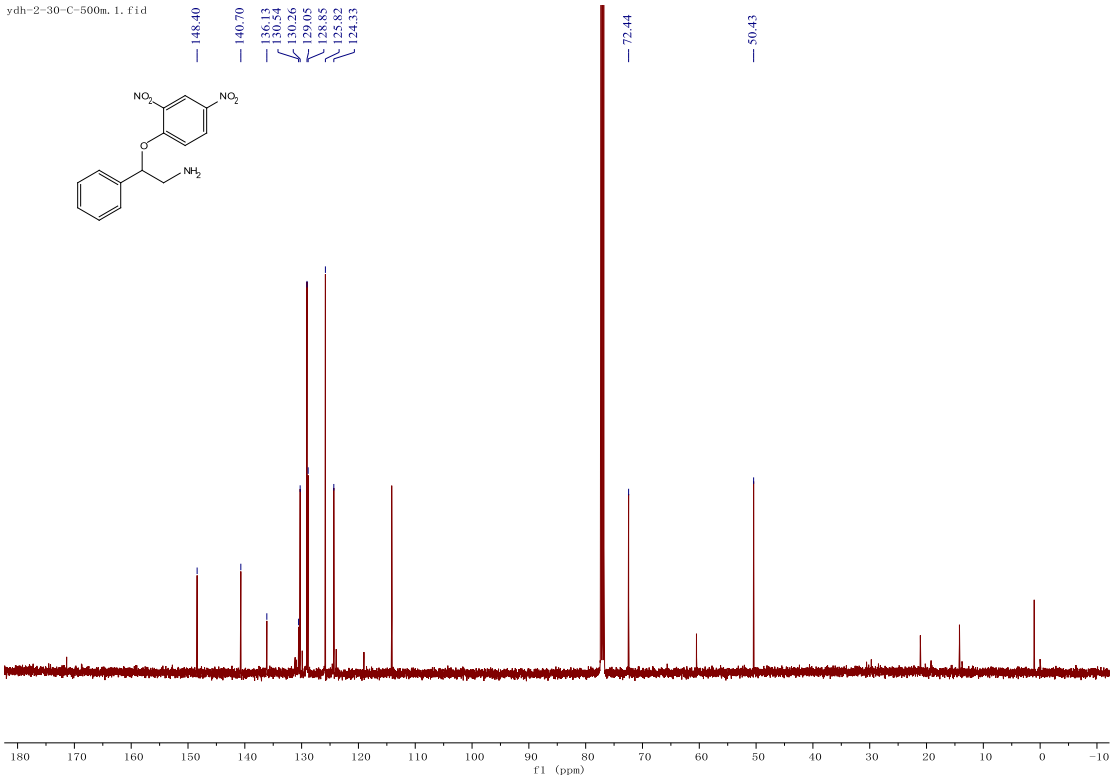
^{13}C NMR Spectrum of 3c



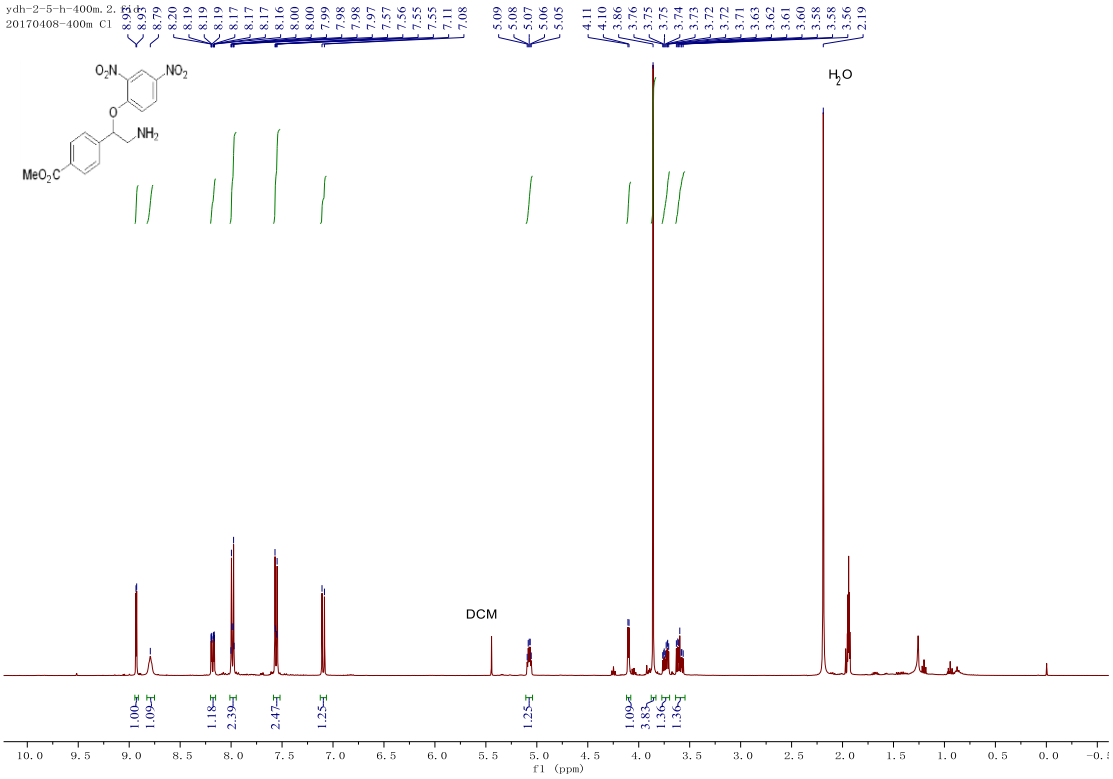
^{1}H NMR Spectrum of 3d



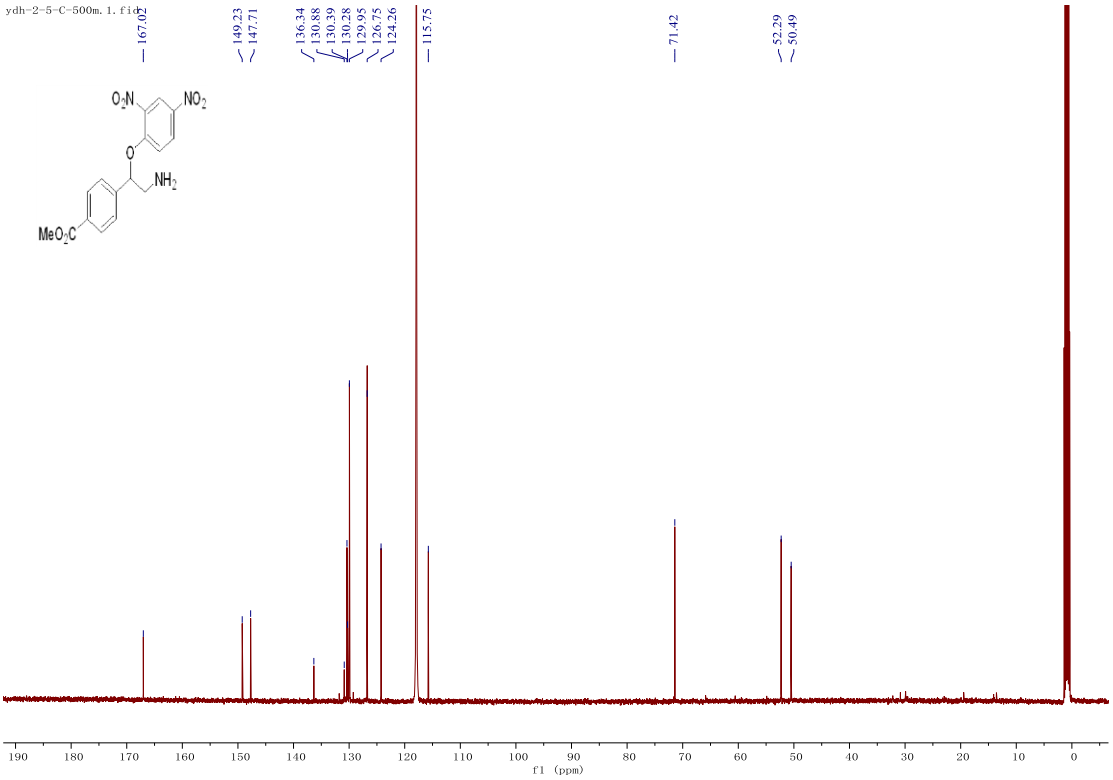
^{13}C NMR Spectrum of 3d



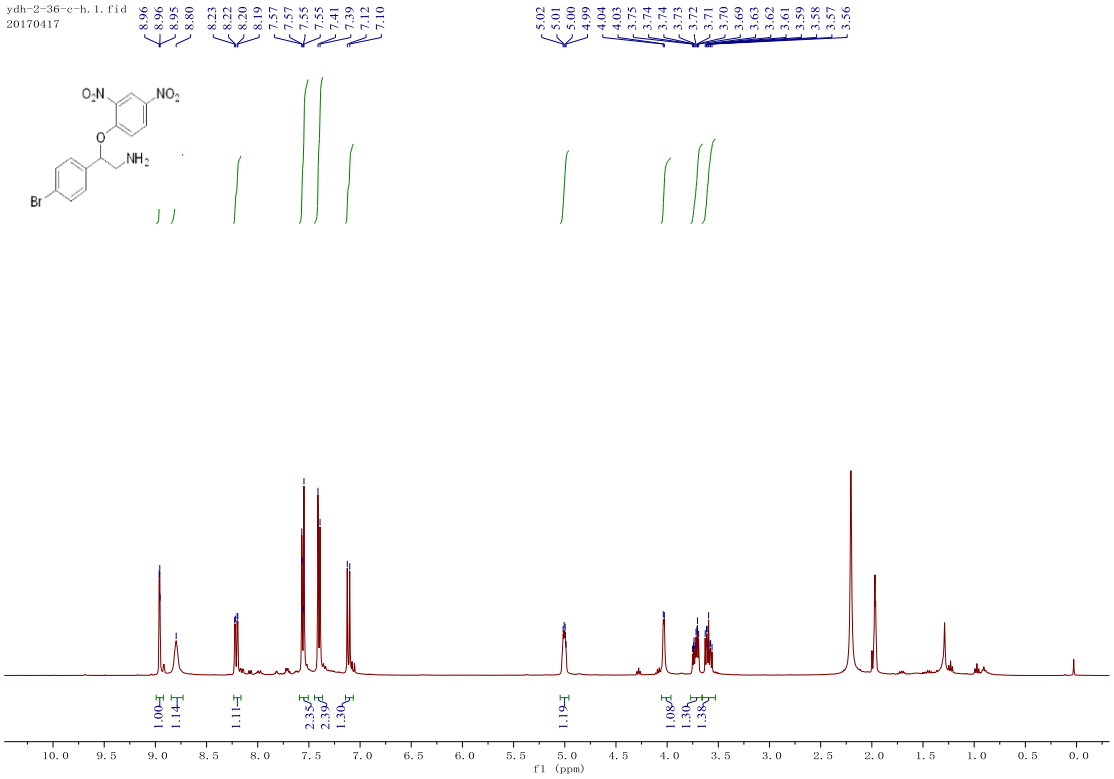
^{1}H NMR Spectrum of 3e



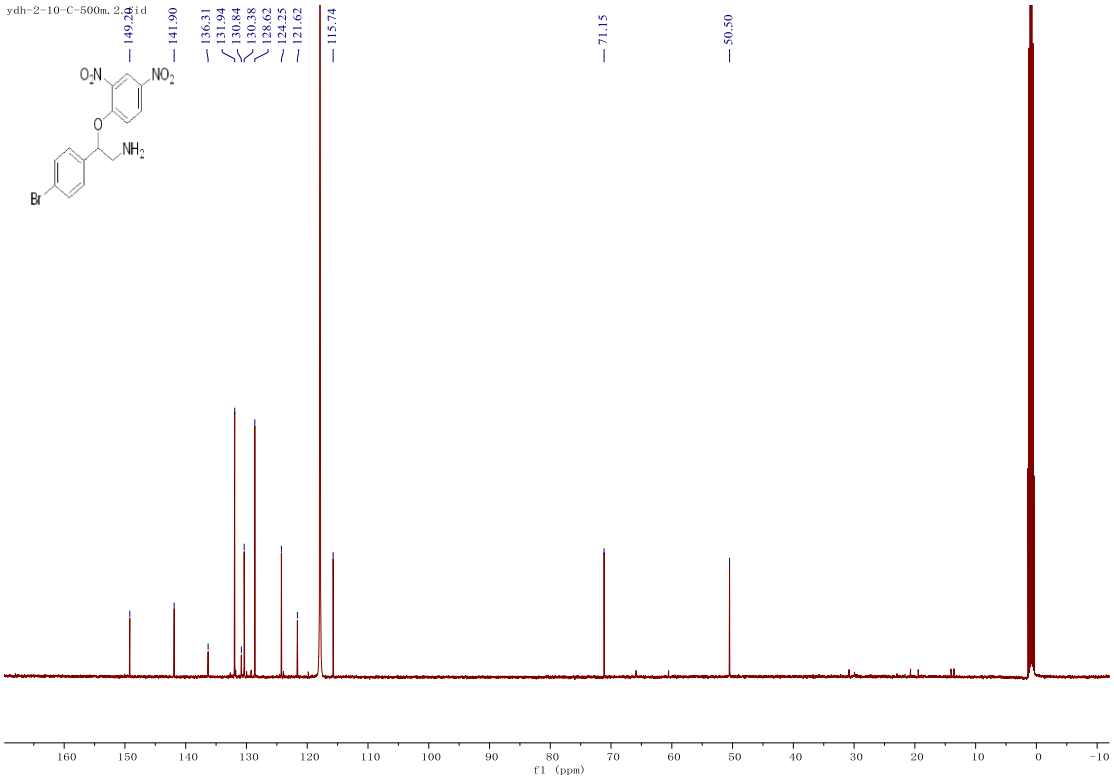
^{13}C NMR Spectrum of 3e



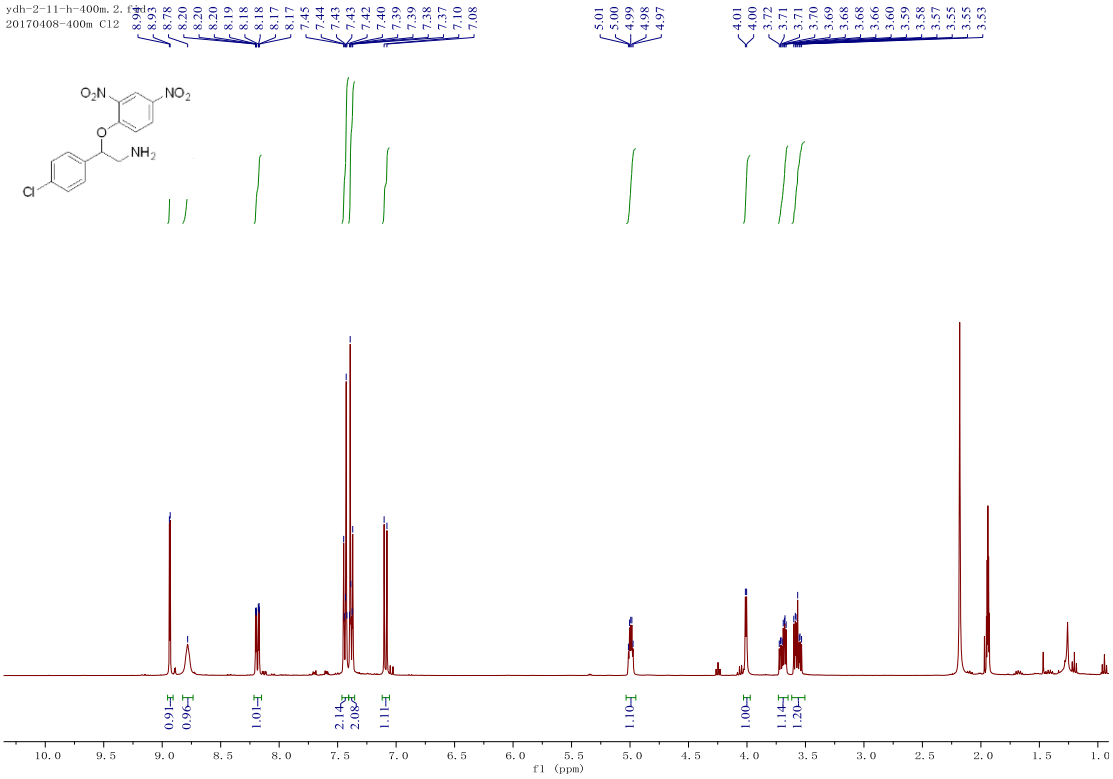
^{1}H NMR Spectrum of 3f



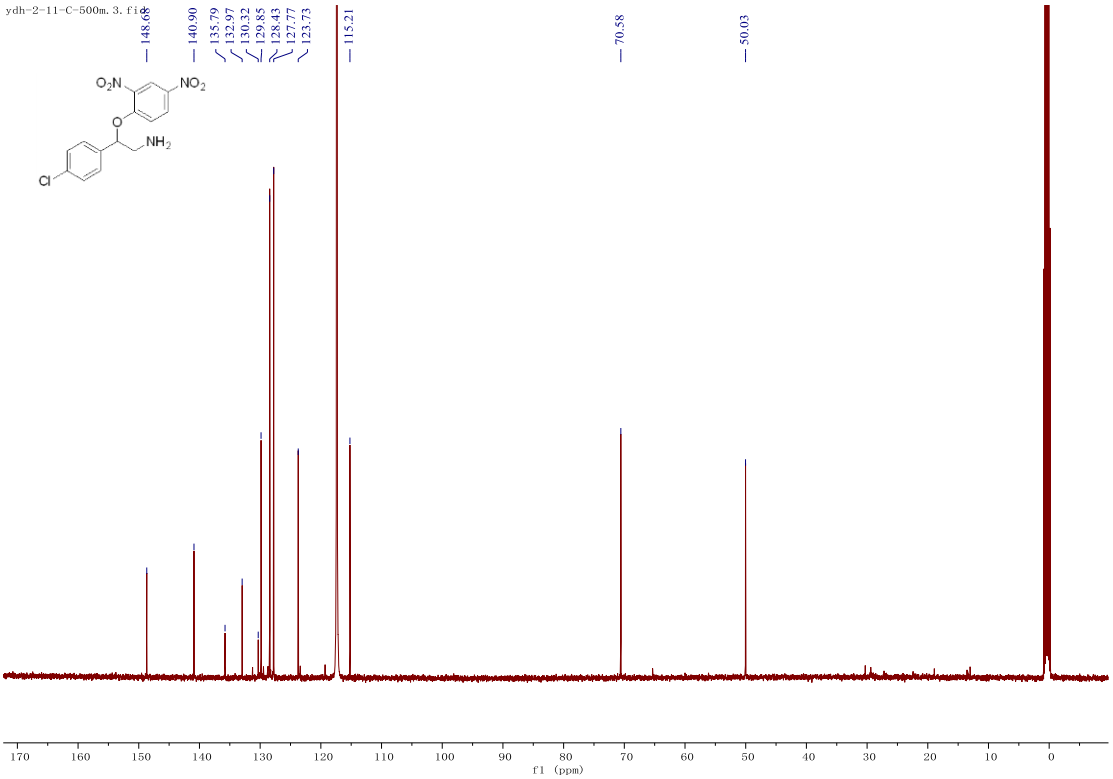
^{13}C NMR Spectrum of 3f



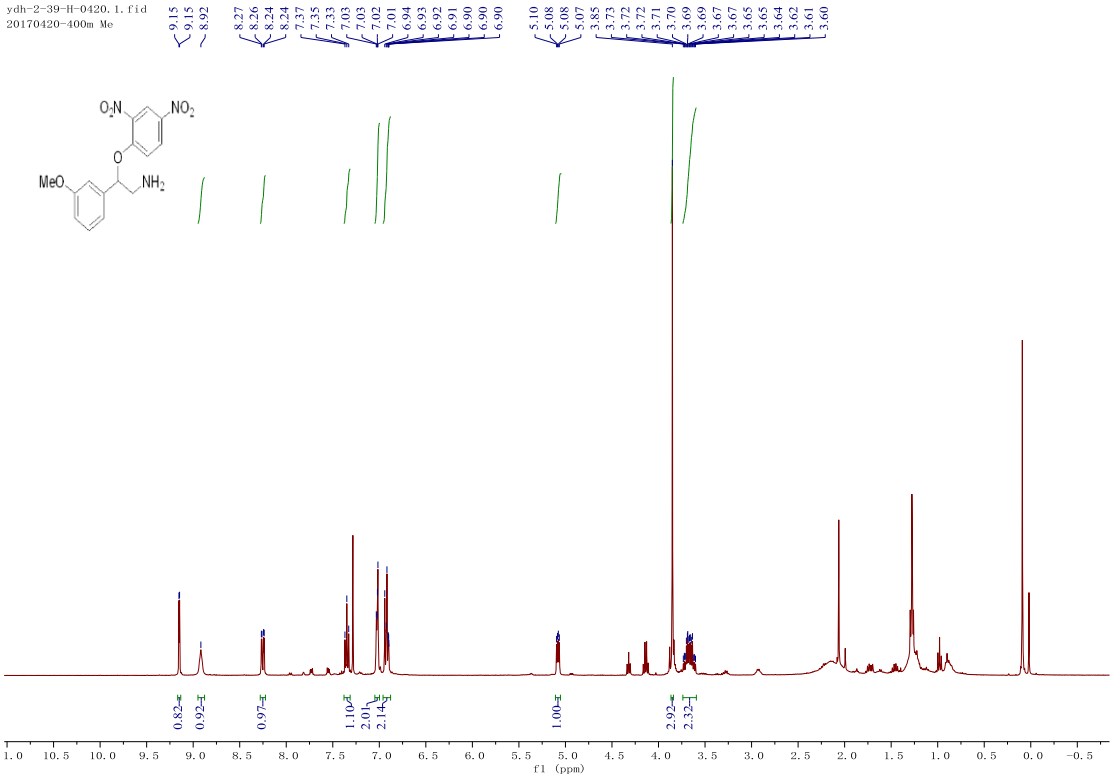
^{1}H NMR Spectrum of 3g



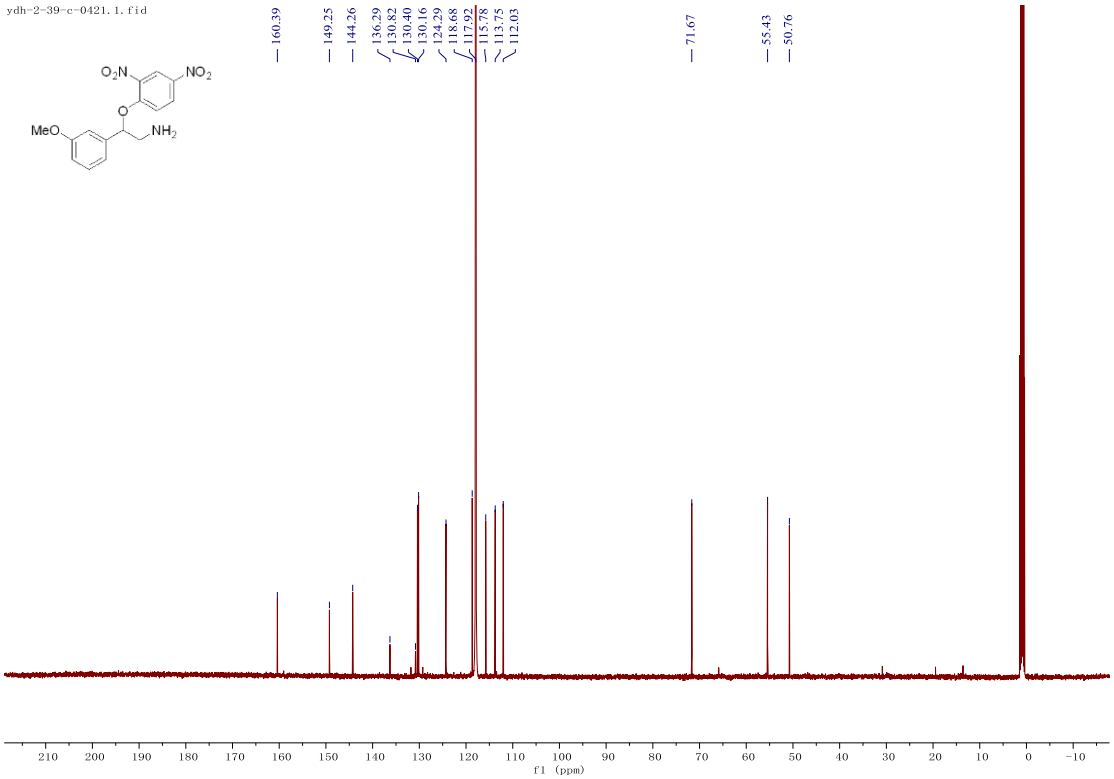
^{13}C NMR Spectrum of 3g



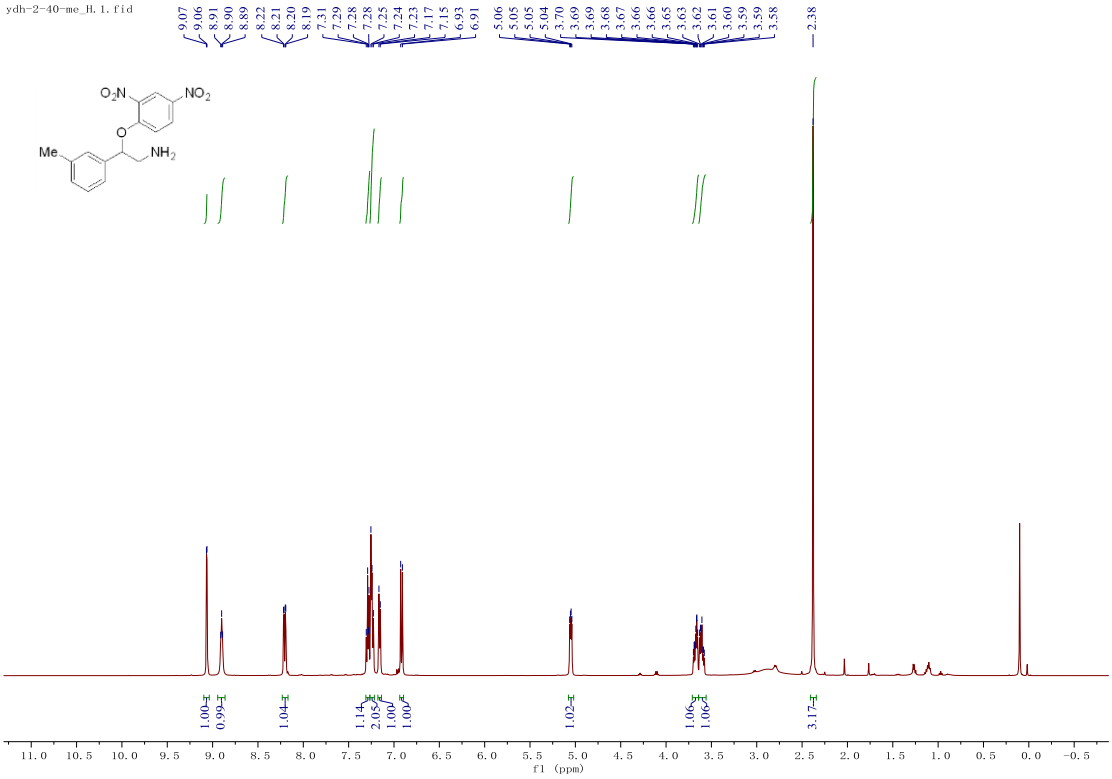
^{1}H NMR Spectrum of 3h



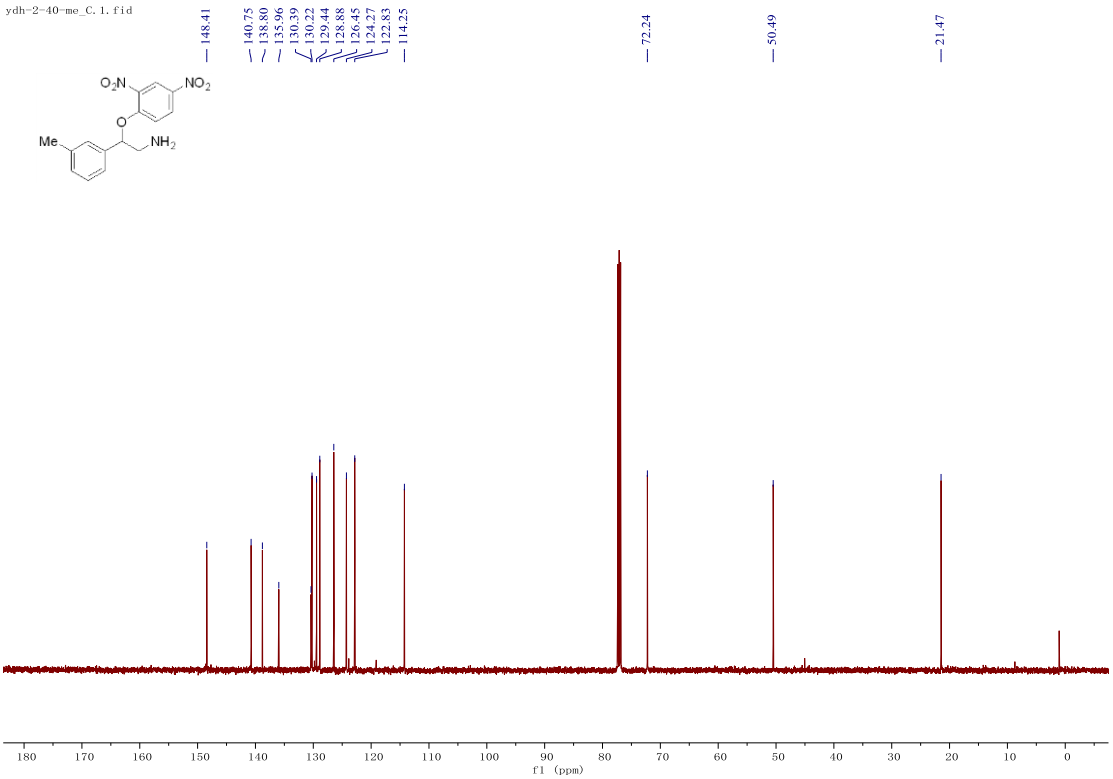
^{13}C NMR Spectrum of 3h



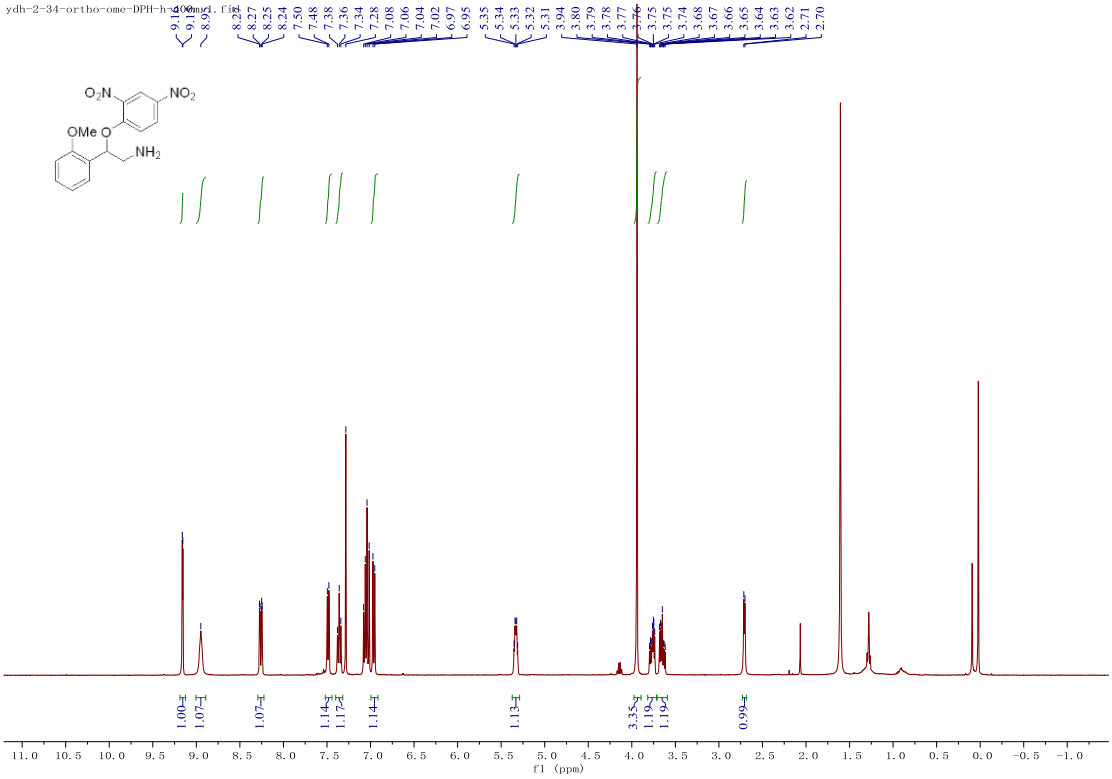
^{1}H NMR Spectrum of 3i



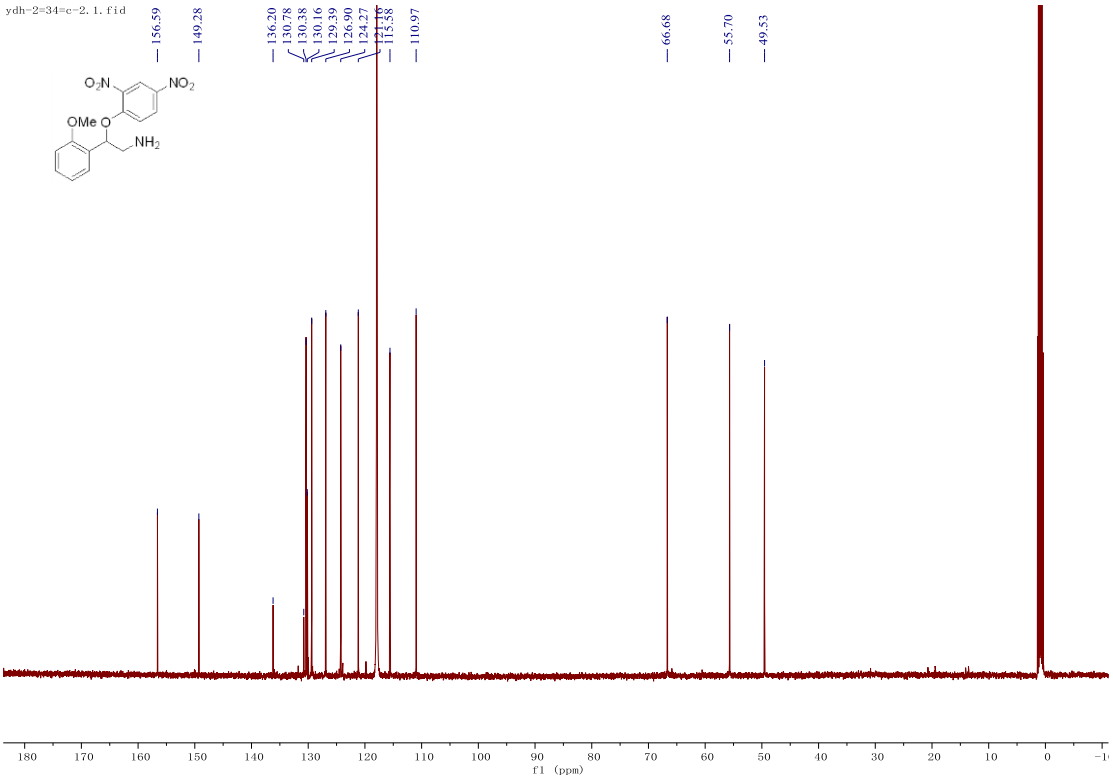
^{13}C NMR Spectrum of 3i



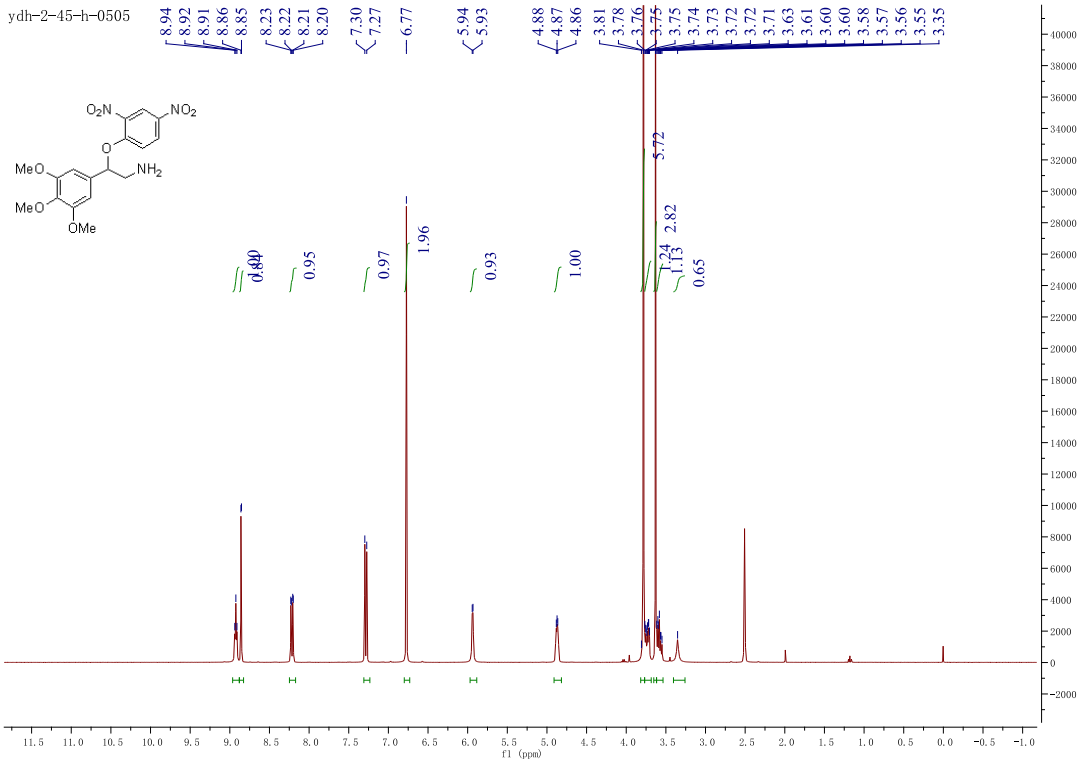
^{1}H NMR Spectrum of 3j



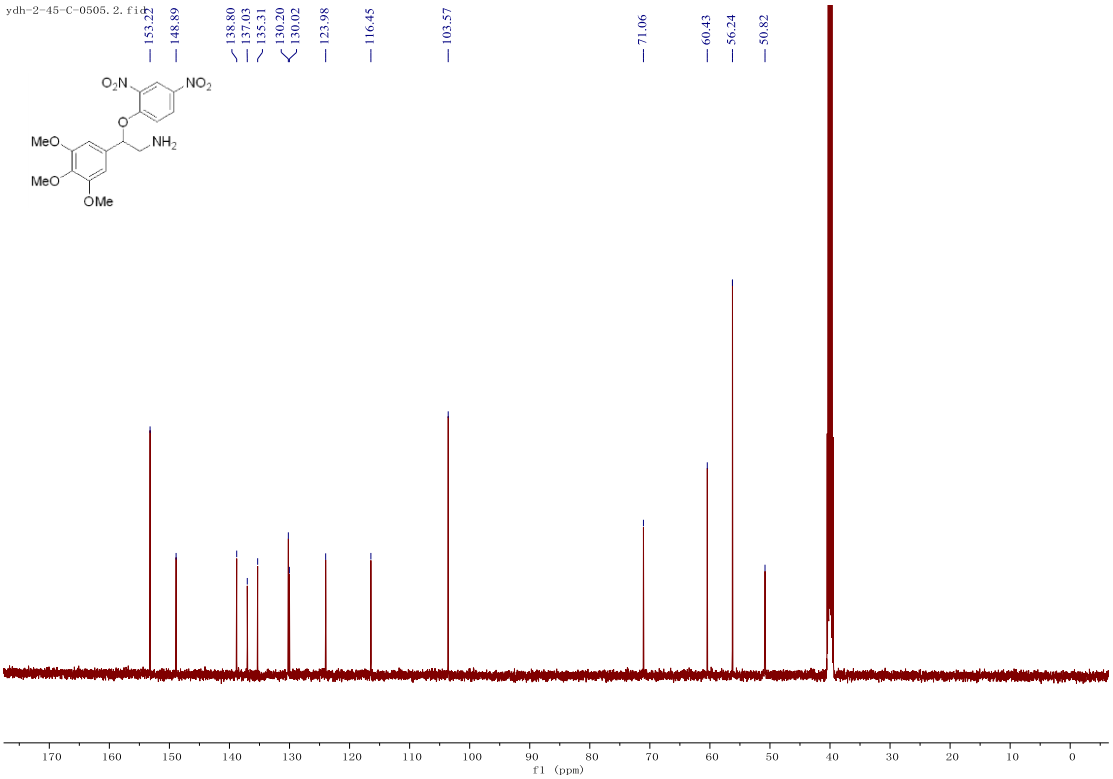
^{13}C NMR Spectrum of 3j



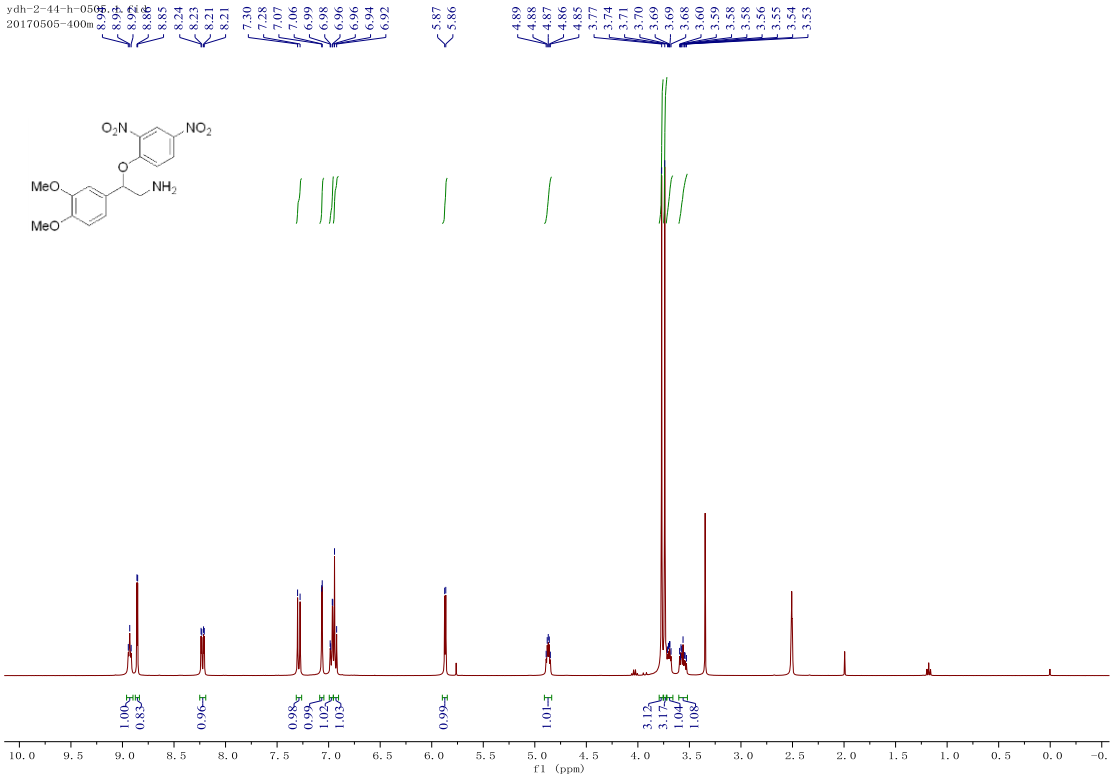
^{1}H NMR Spectrum of 3k



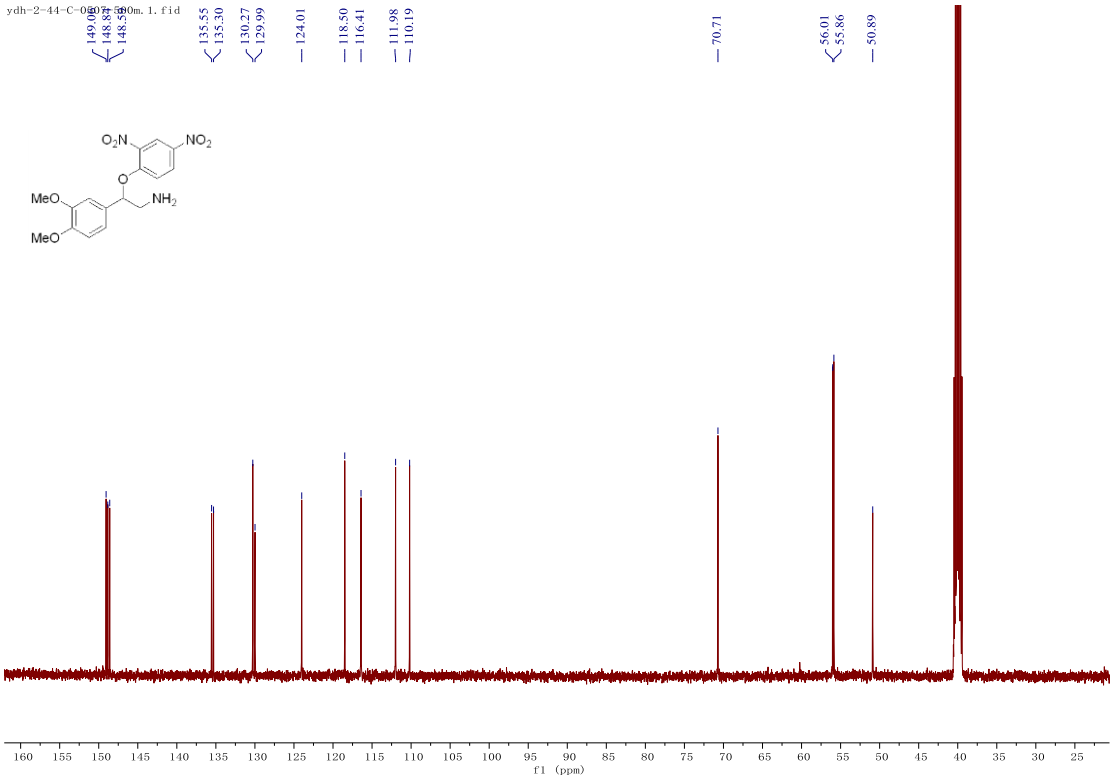
^{13}C NMR Spectrum of 3k



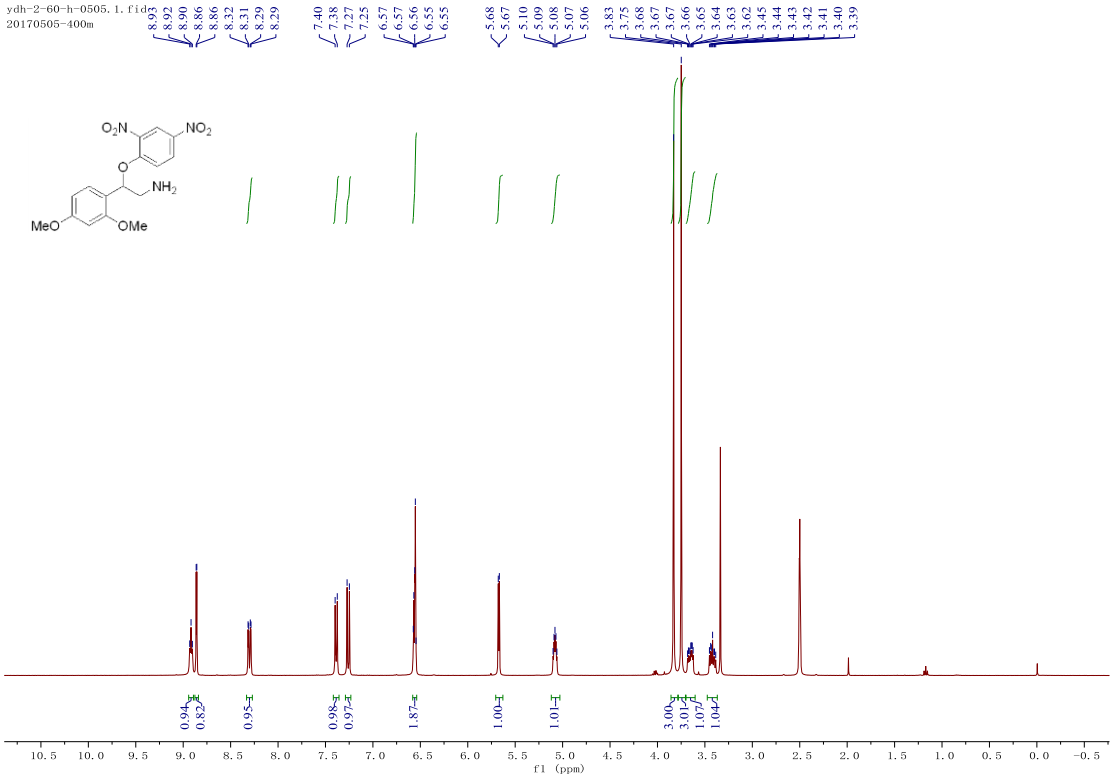
^{1}H NMR Spectrum of 3l



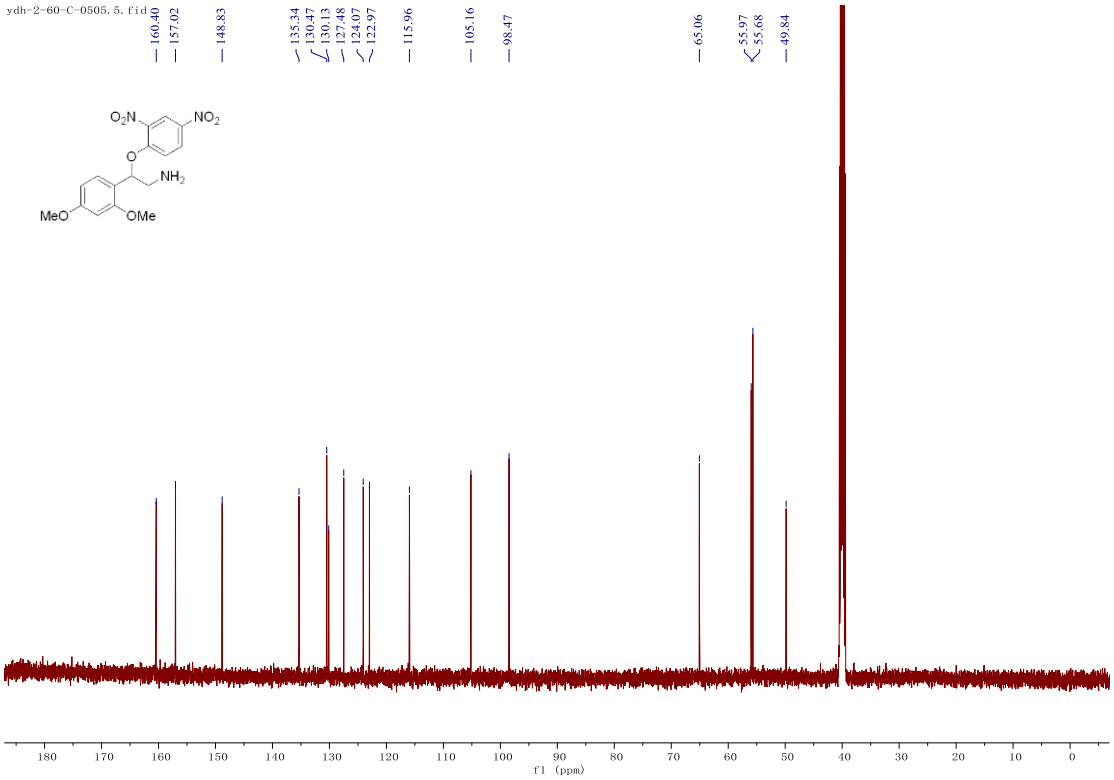
^{13}C NMR Spectrum of 3l



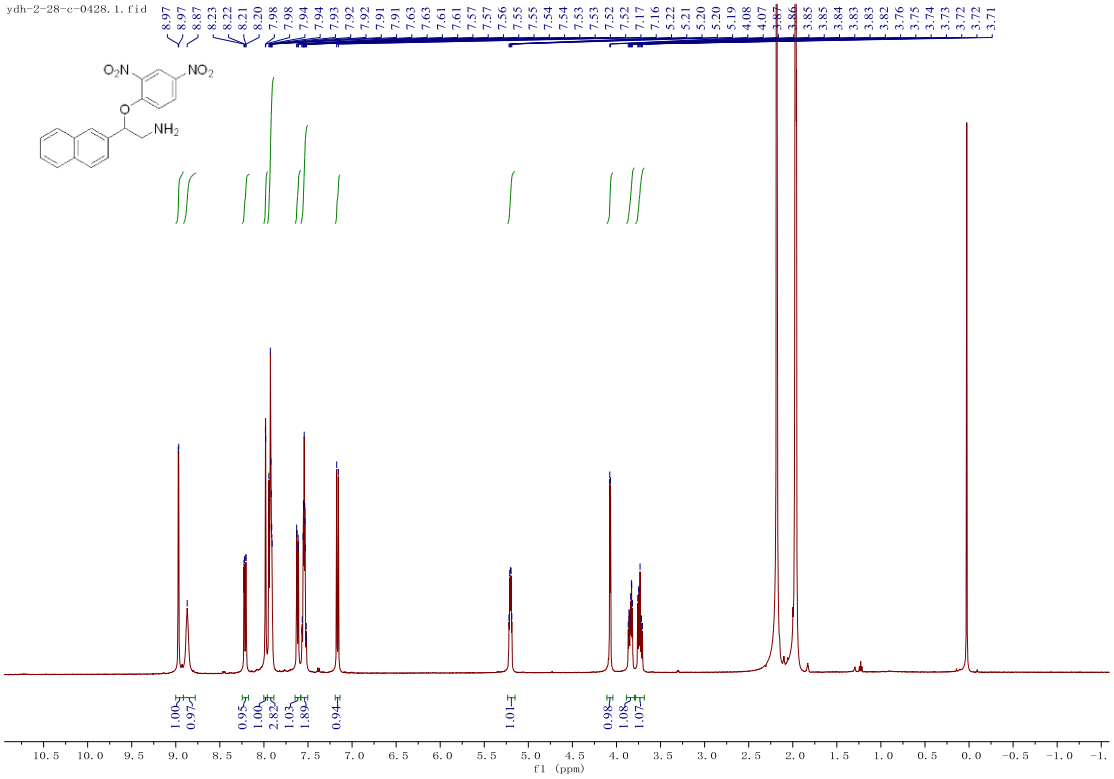
^{1}H NMR Spectrum of 3m



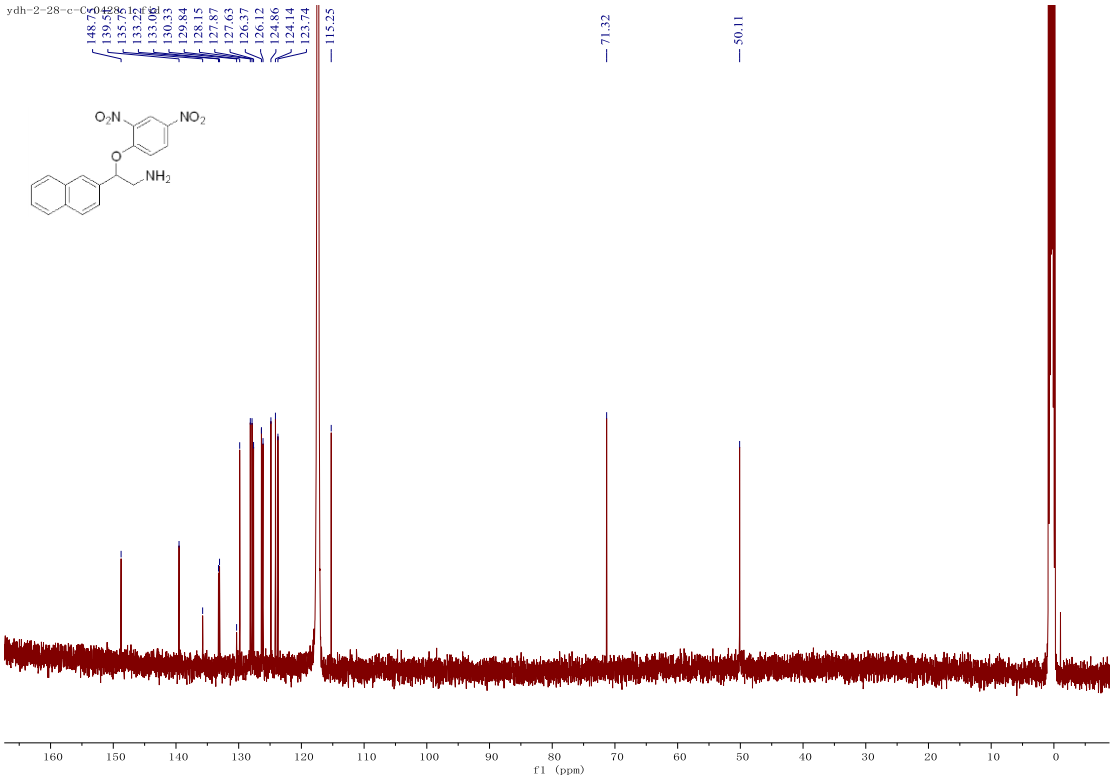
^{13}C NMR Spectrum of 3m



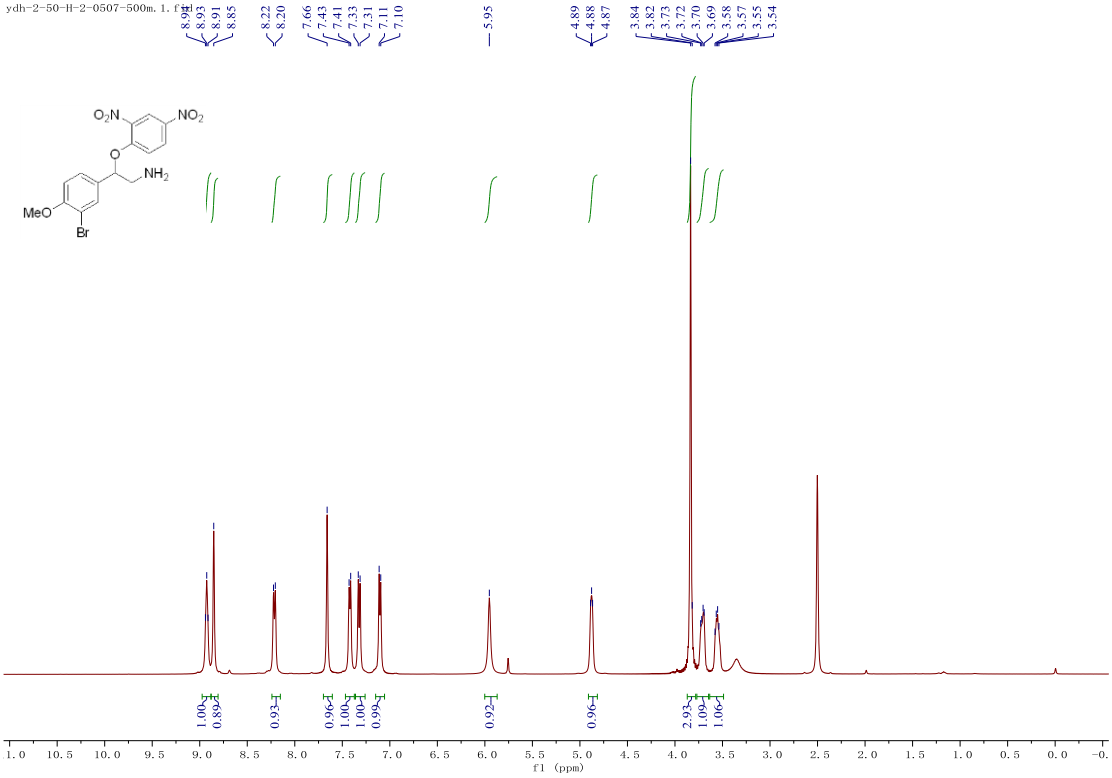
^{1}H NMR Spectrum of 3n



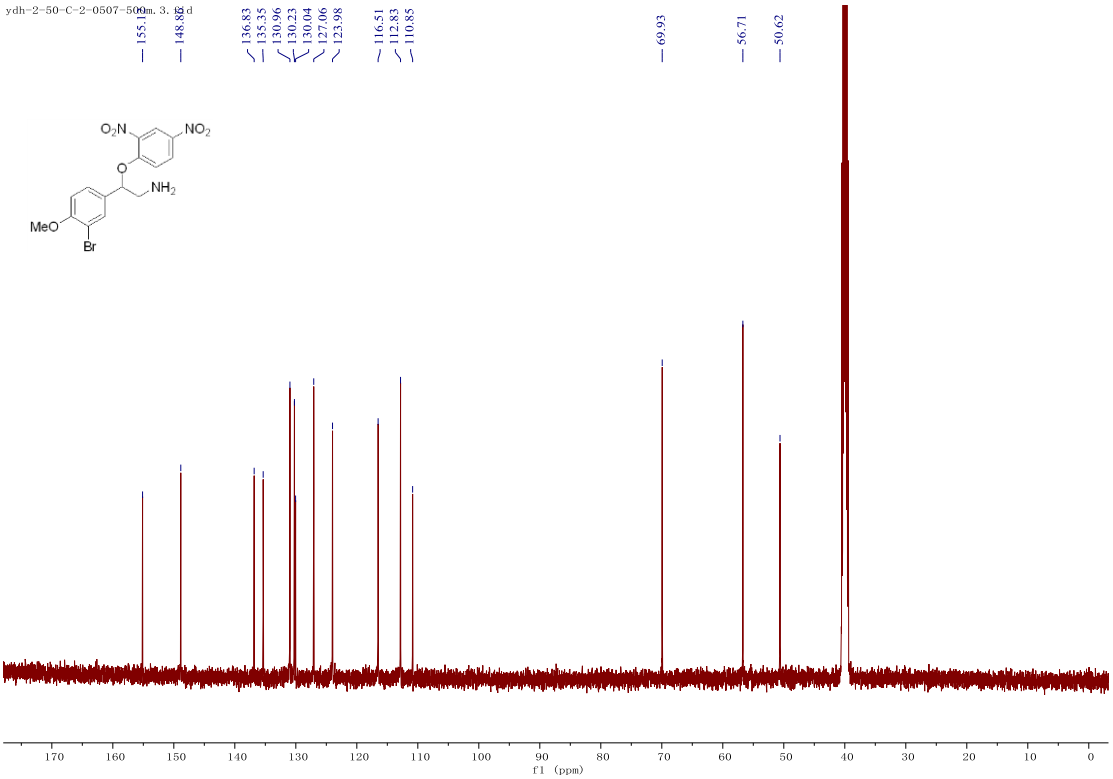
^{13}C NMR Spectrum of 3n



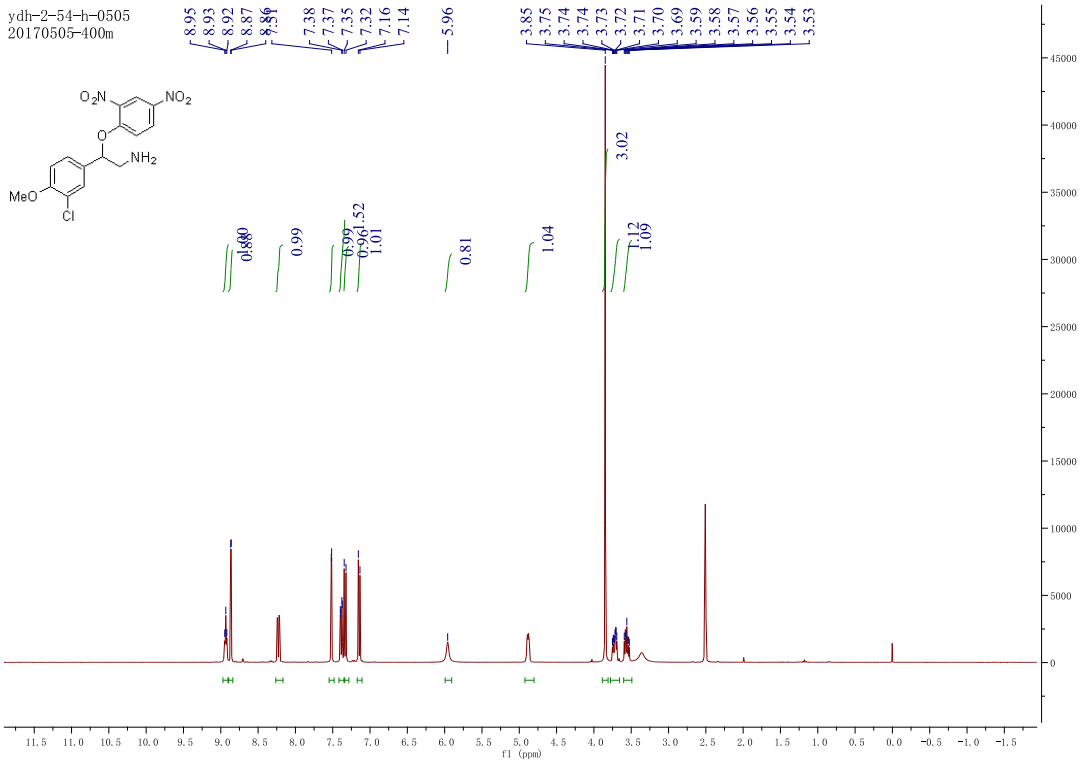
^{1}H NMR Spectrum of 3o



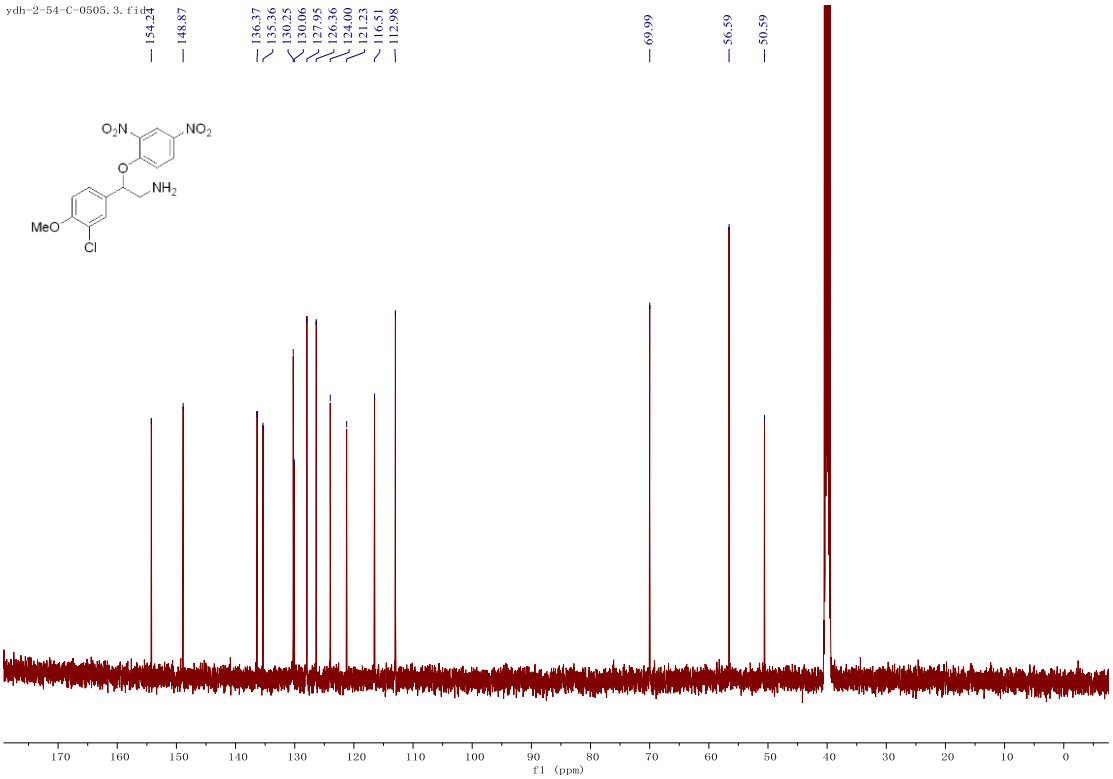
^{13}C NMR Spectrum of 3o



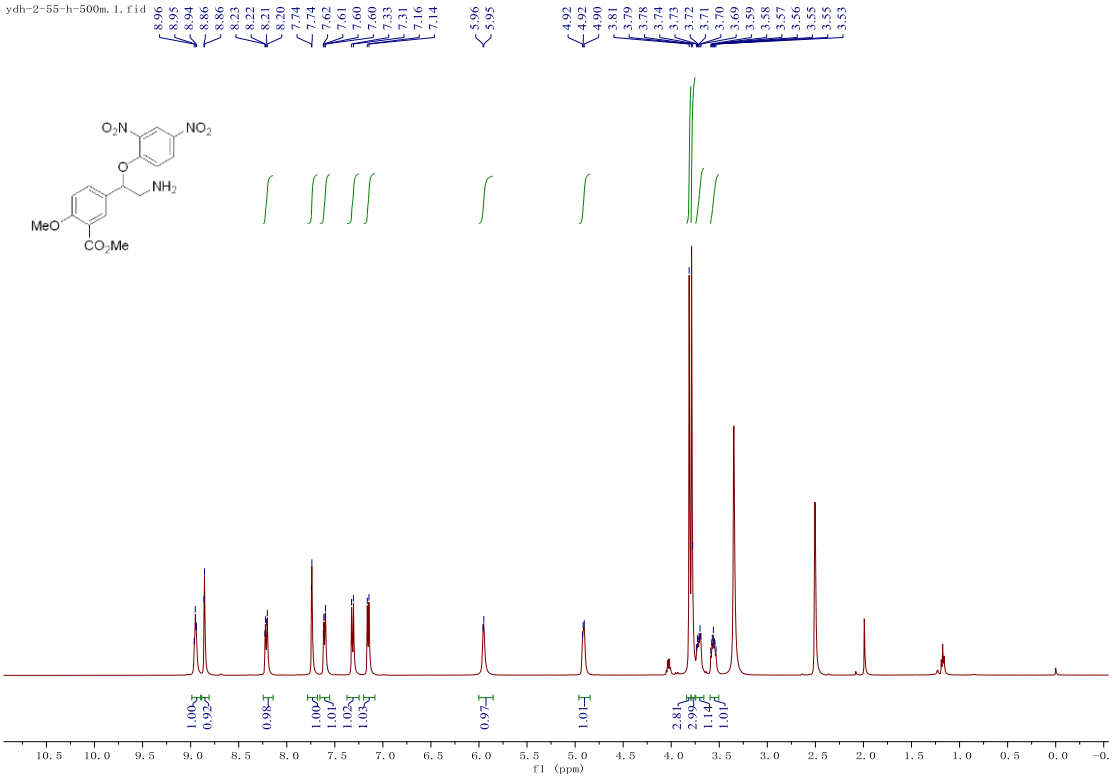
^{1}H NMR Spectrum of 3p



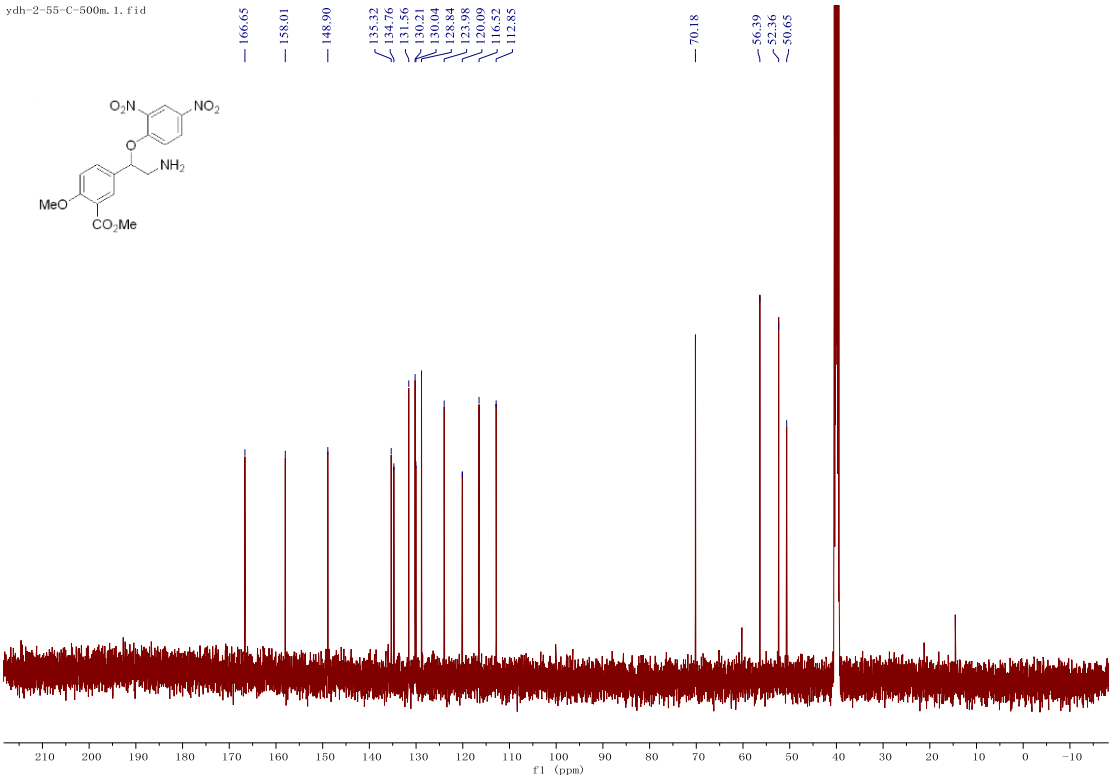
^{13}C NMR Spectrum of 3p



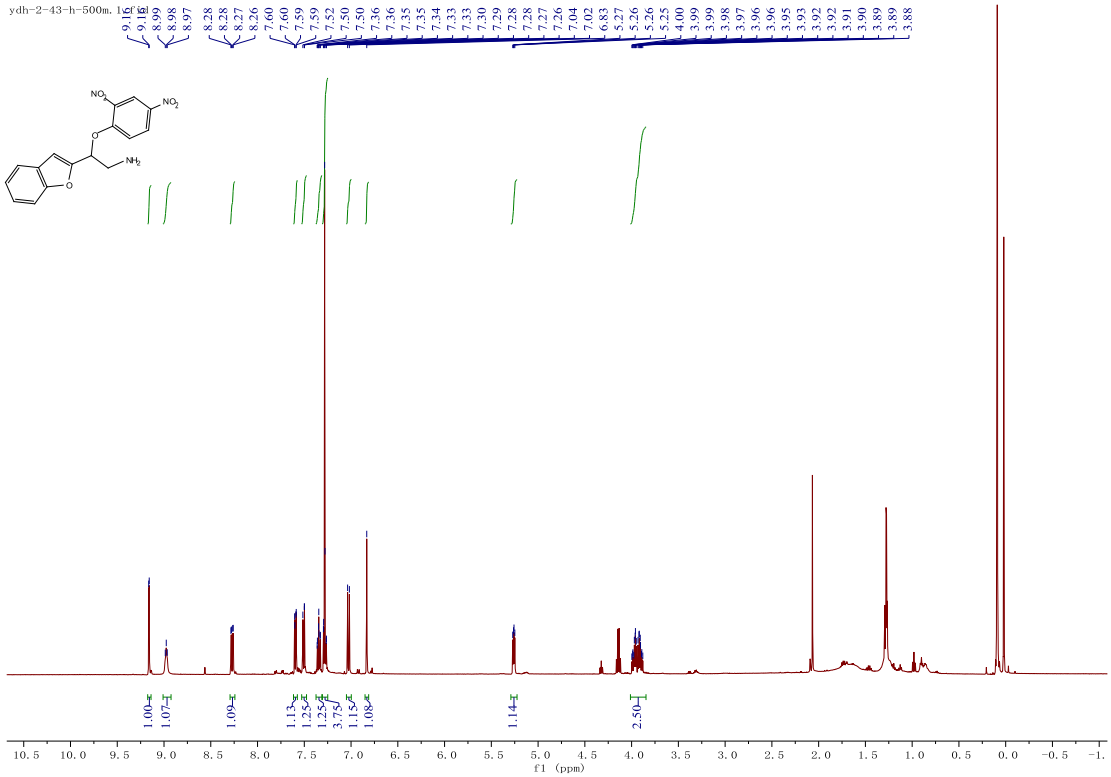
^{1}H NMR Spectrum of 3q



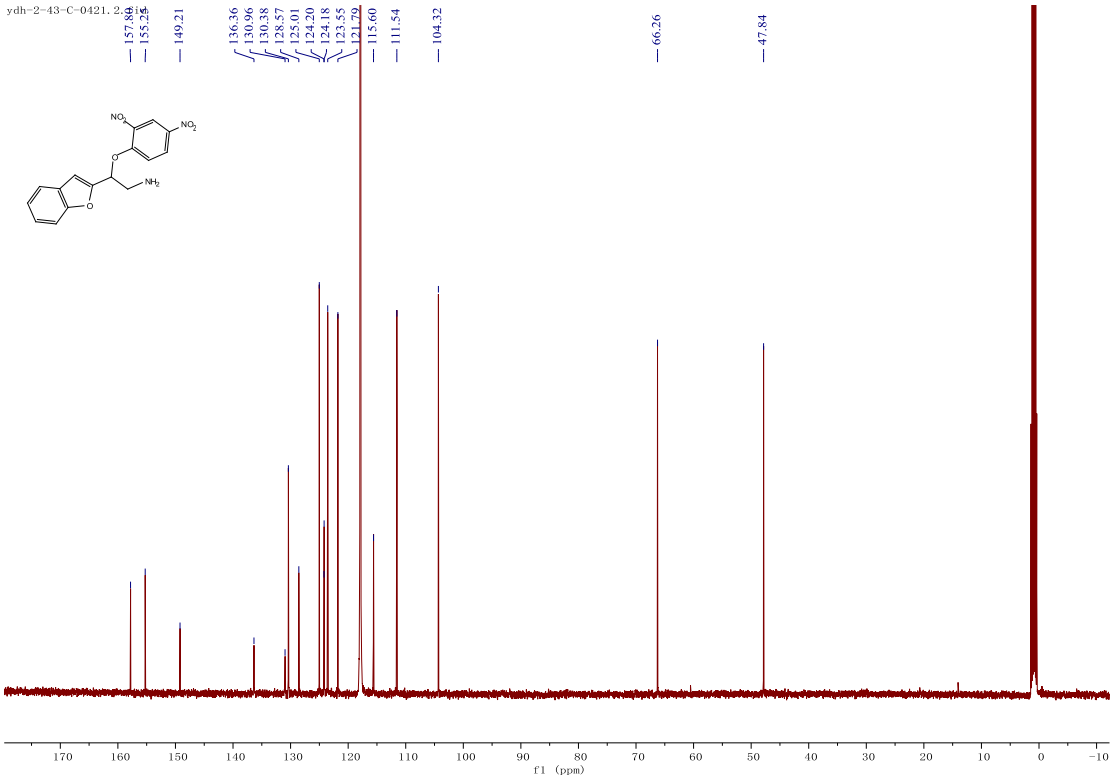
^{13}C NMR Spectrum of 3q



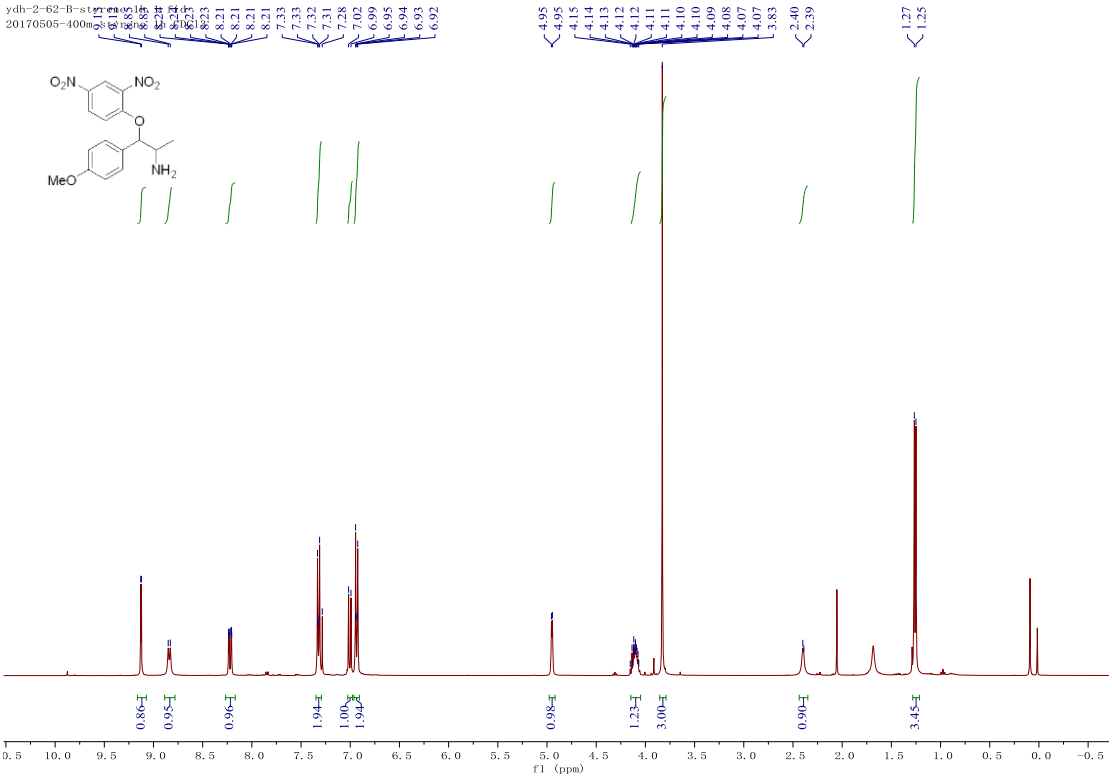
^{1}H NMR Spectrum of 3r



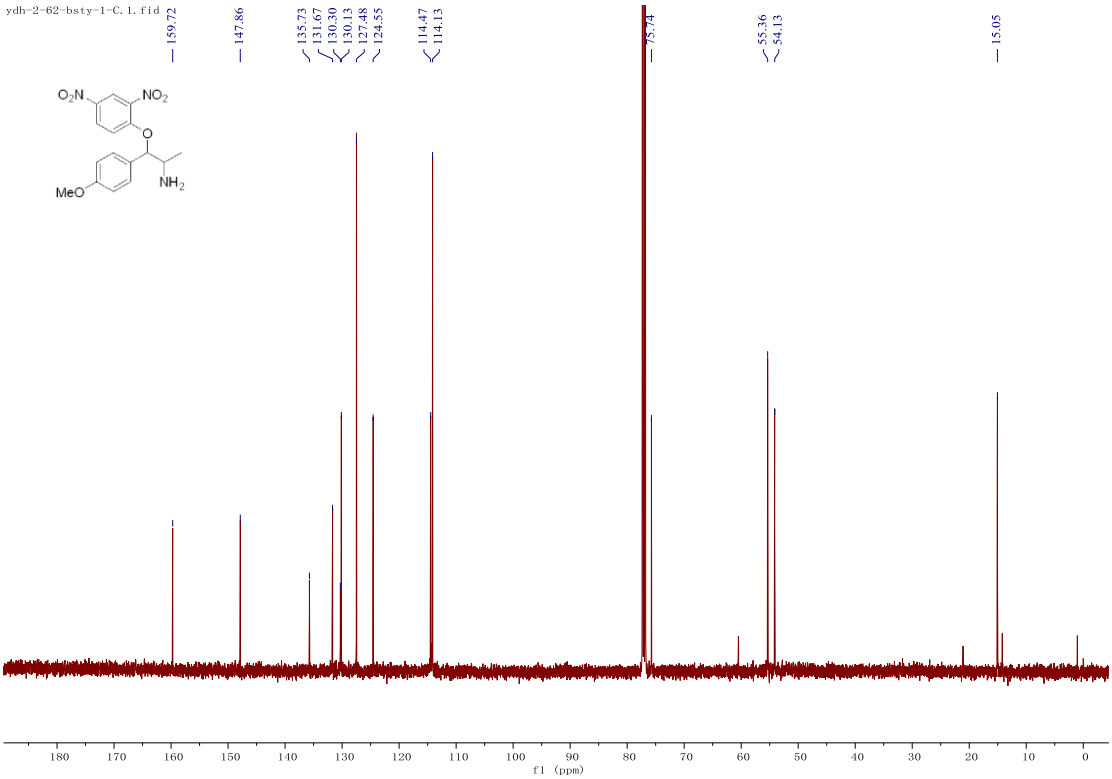
^{13}C NMR Spectrum of 3r



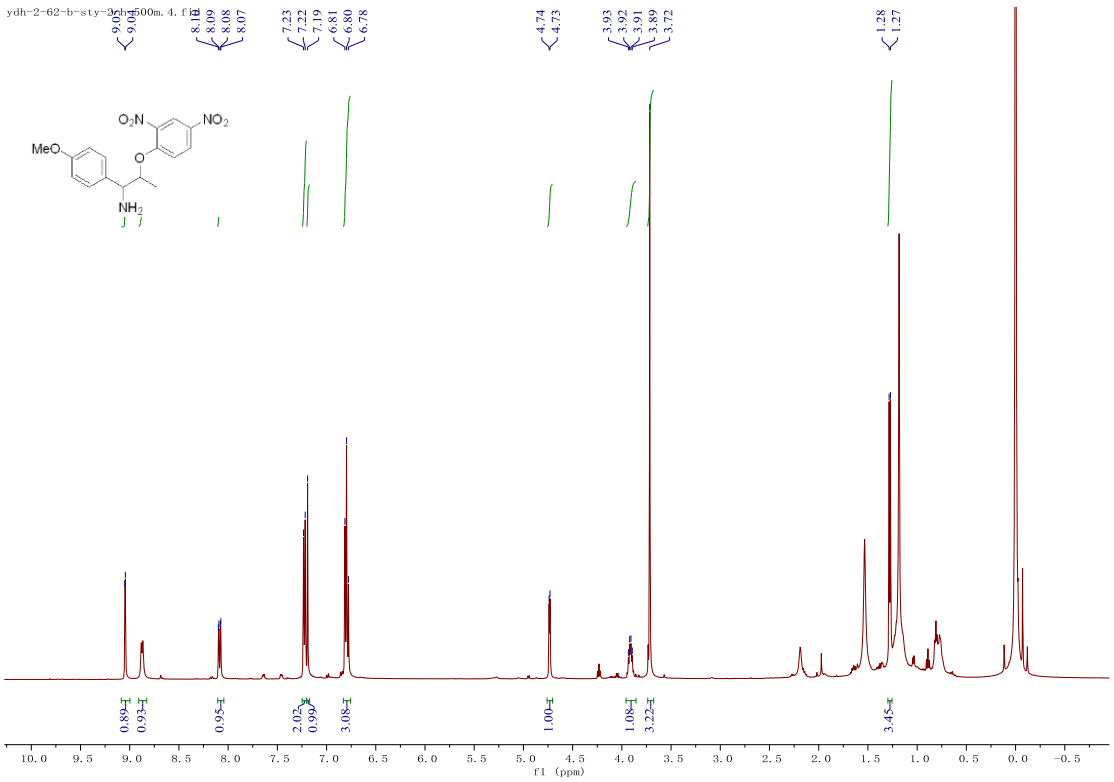
^{1}H NMR Spectrum of 3s



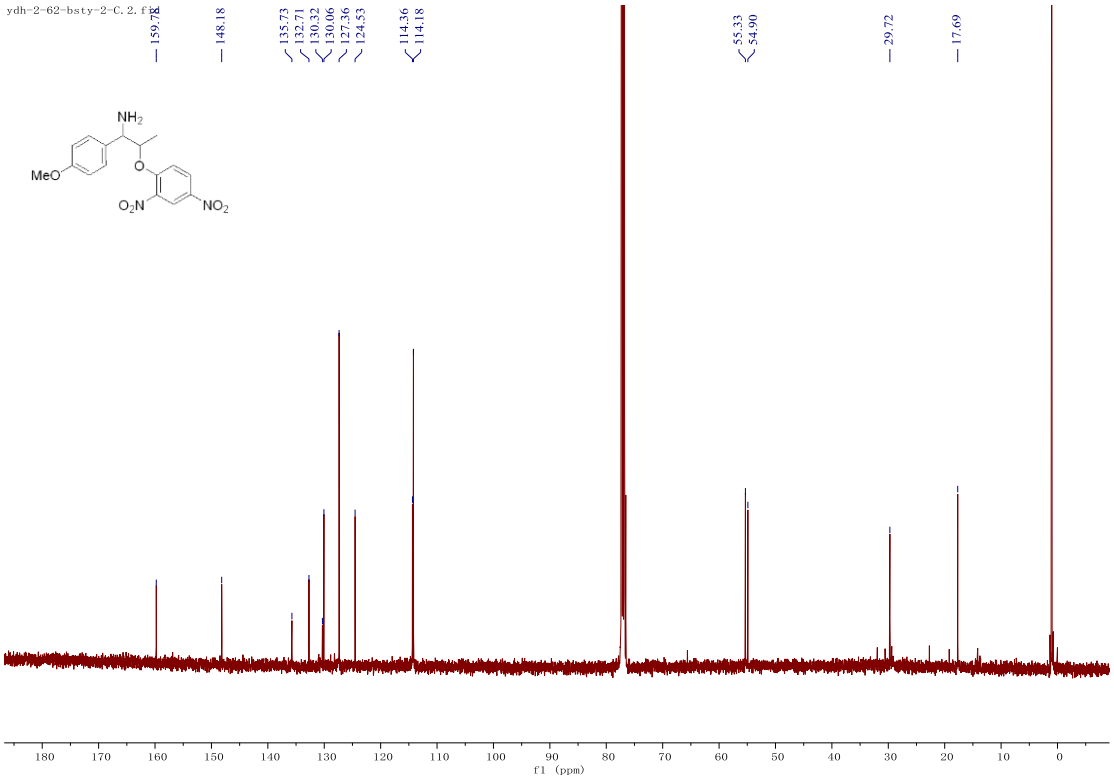
^{13}C NMR Spectrum of 3s



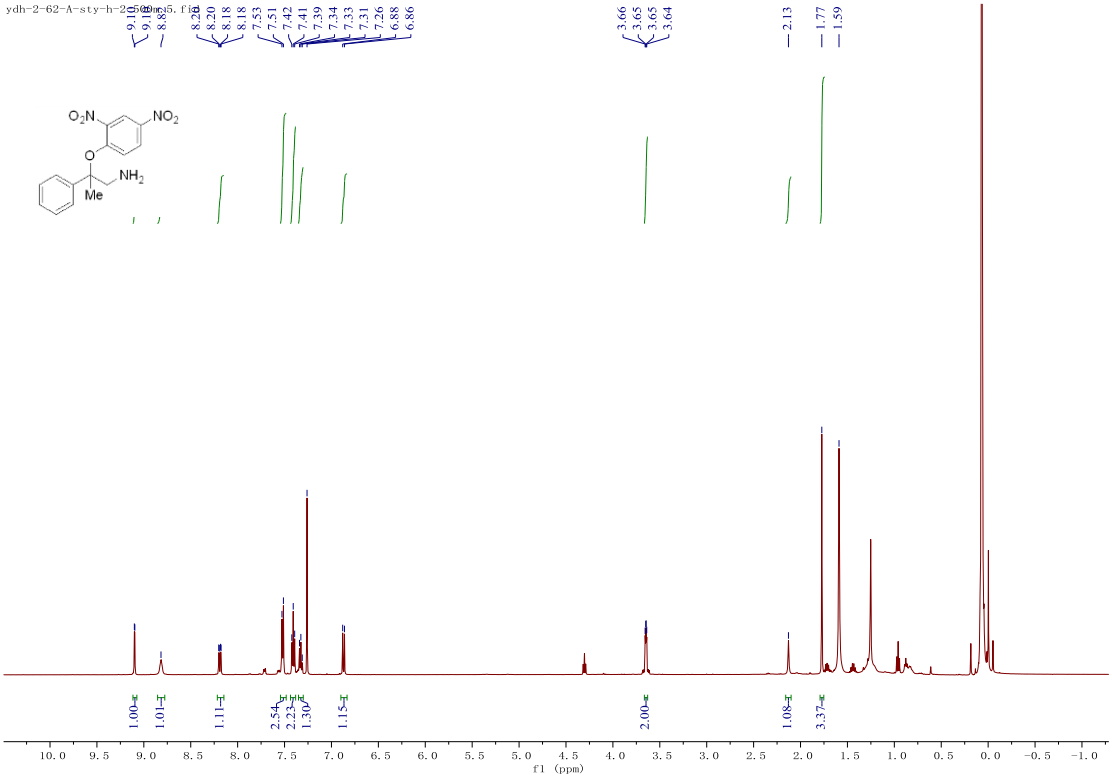
^{1}H NMR Spectrum of 3s′



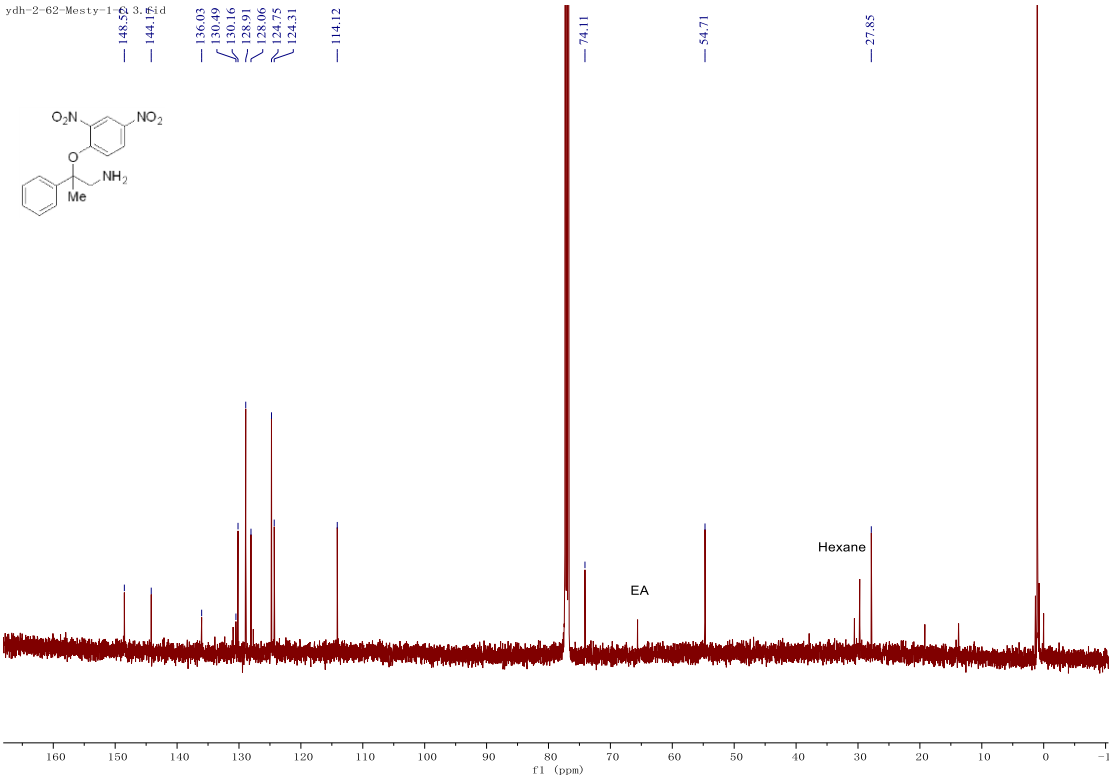
^{13}C NMR Spectrum of 3s′



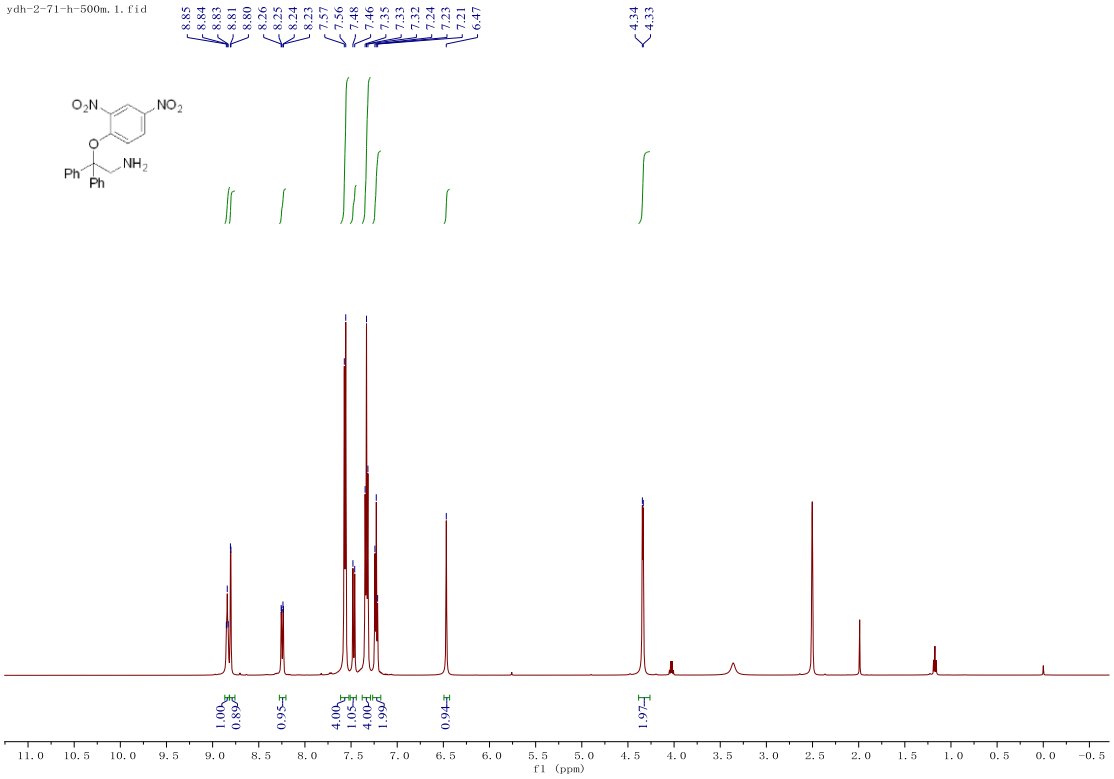
^{1}H NMR Spectrum of 3t



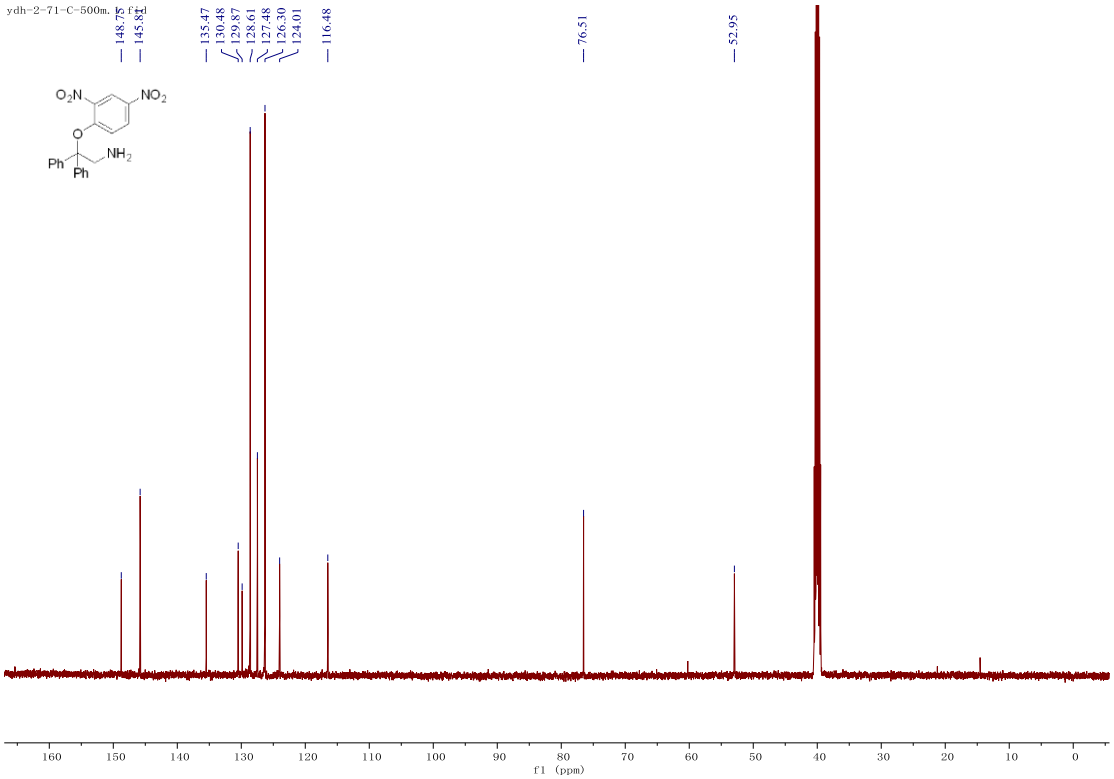
^{13}C NMR Spectrum of 3t



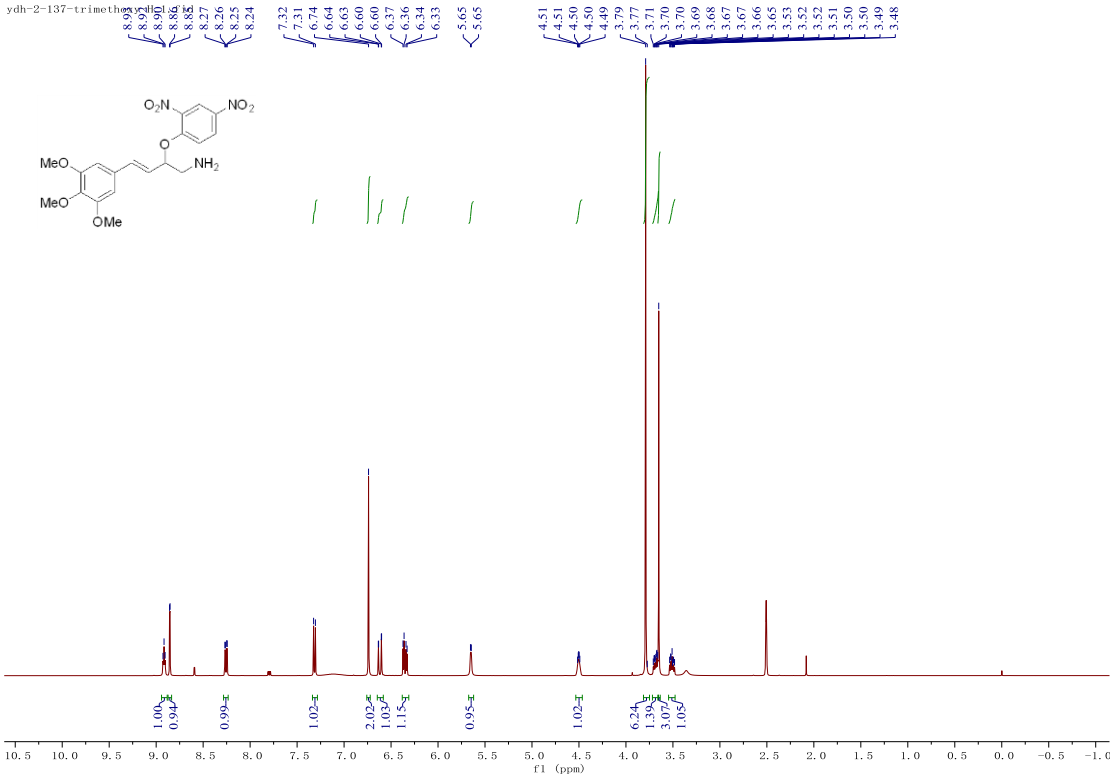
^{1}H NMR Spectrum of 3u



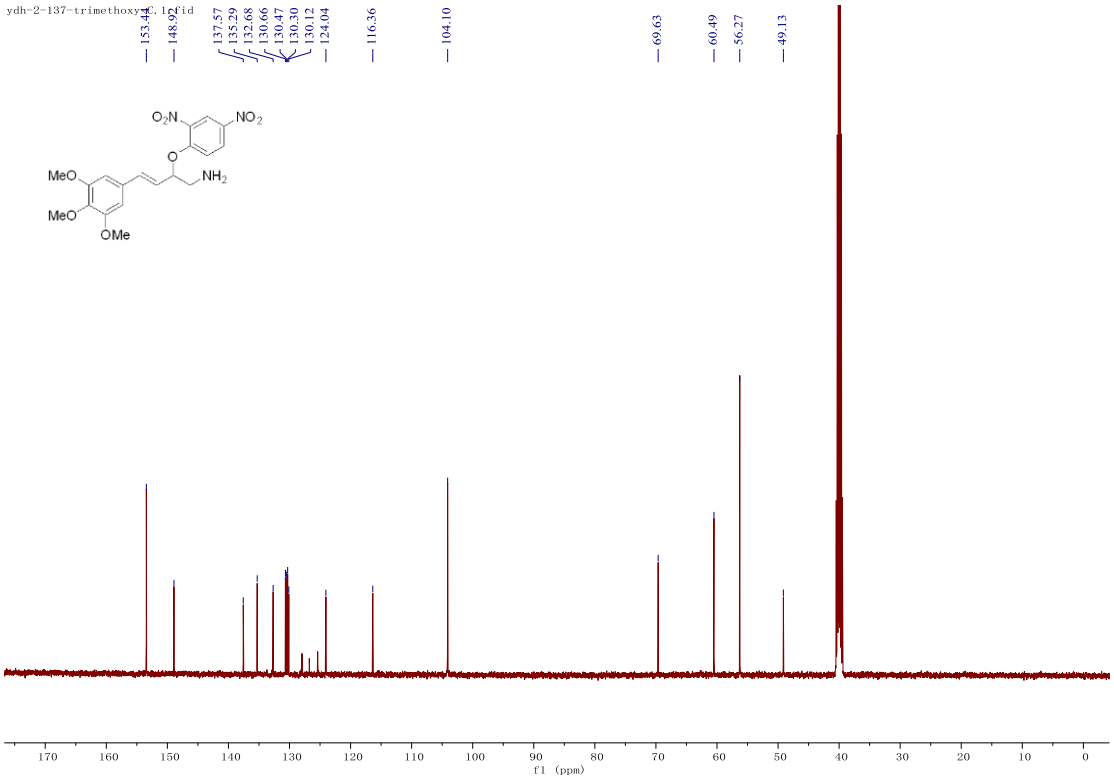
^{13}C NMR Spectrum of 3u



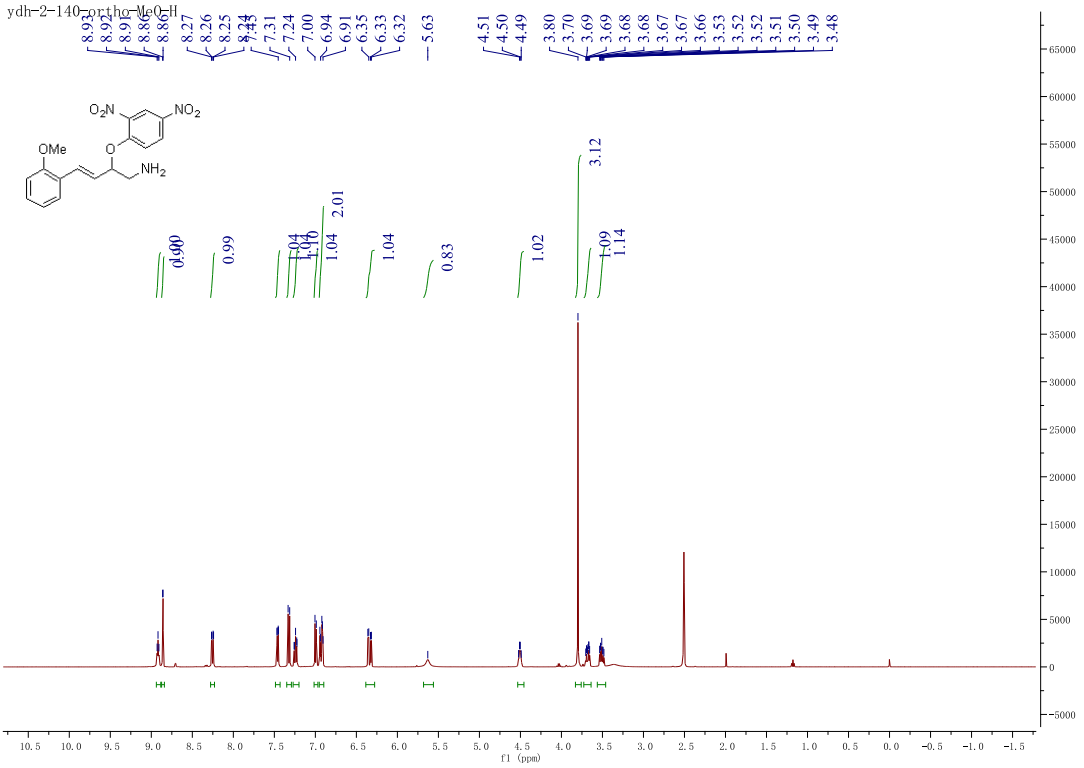
^{1}H NMR Spectrum of 4a



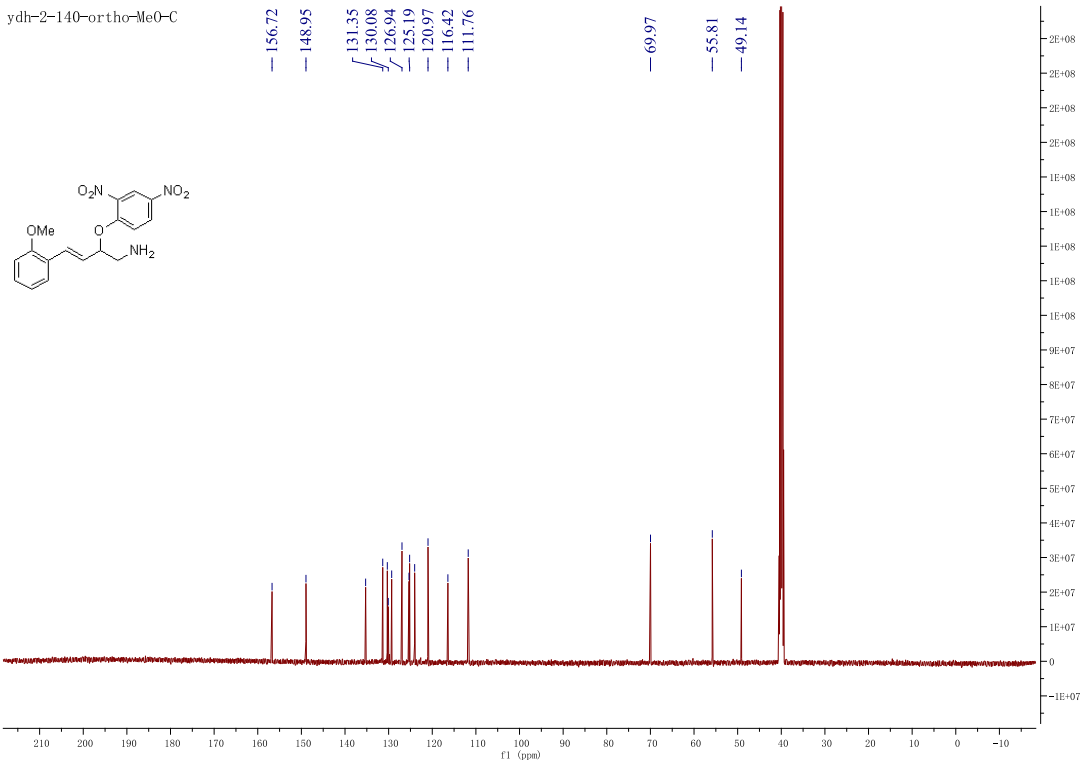
^{13}C NMR Spectrum of 4a



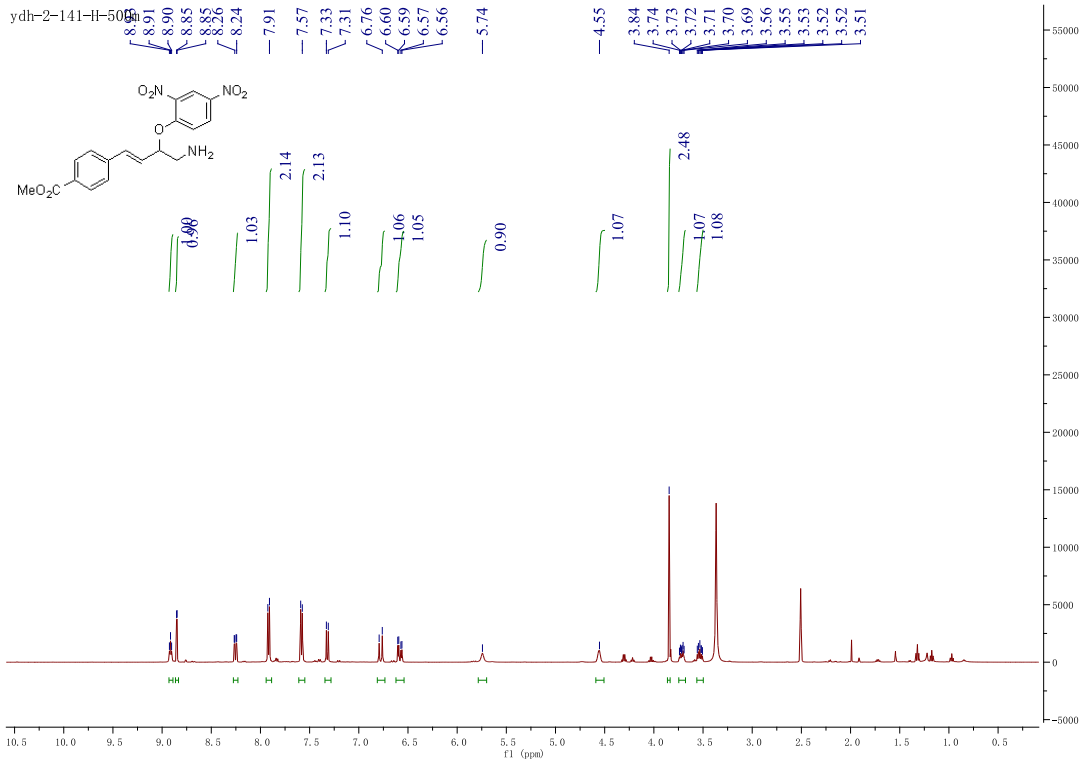
^{1}H NMR Spectrum of 4b



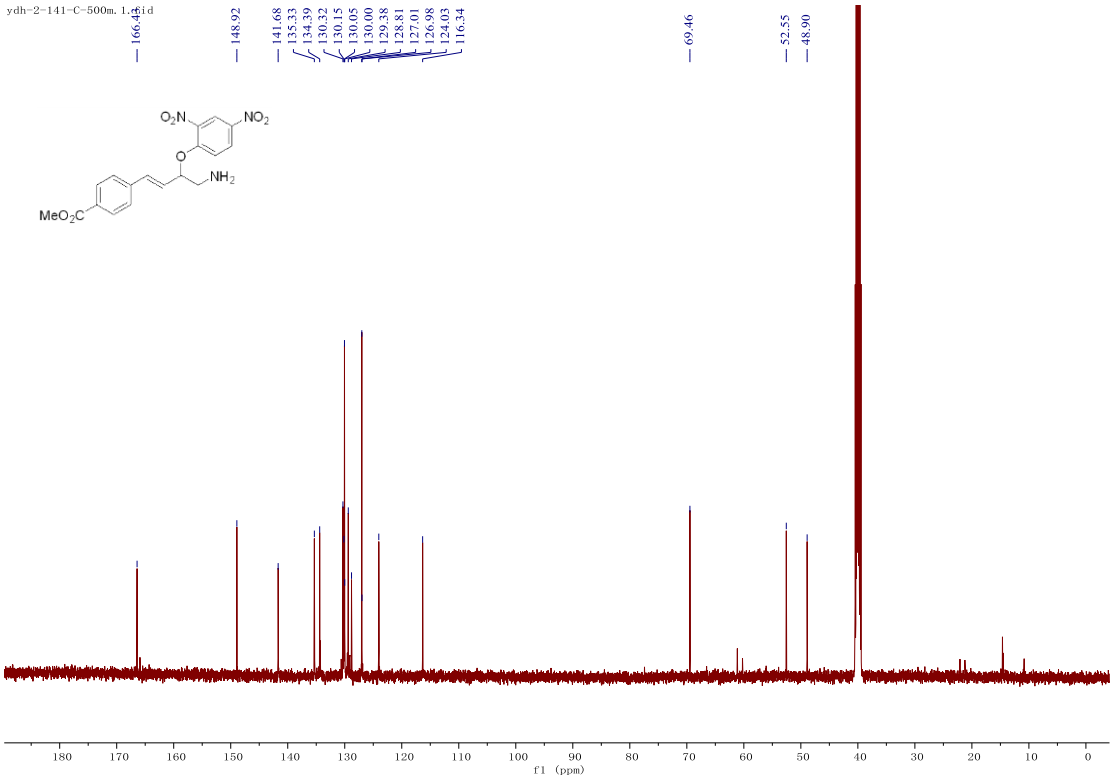
^{13}C NMR Spectrum of 4b



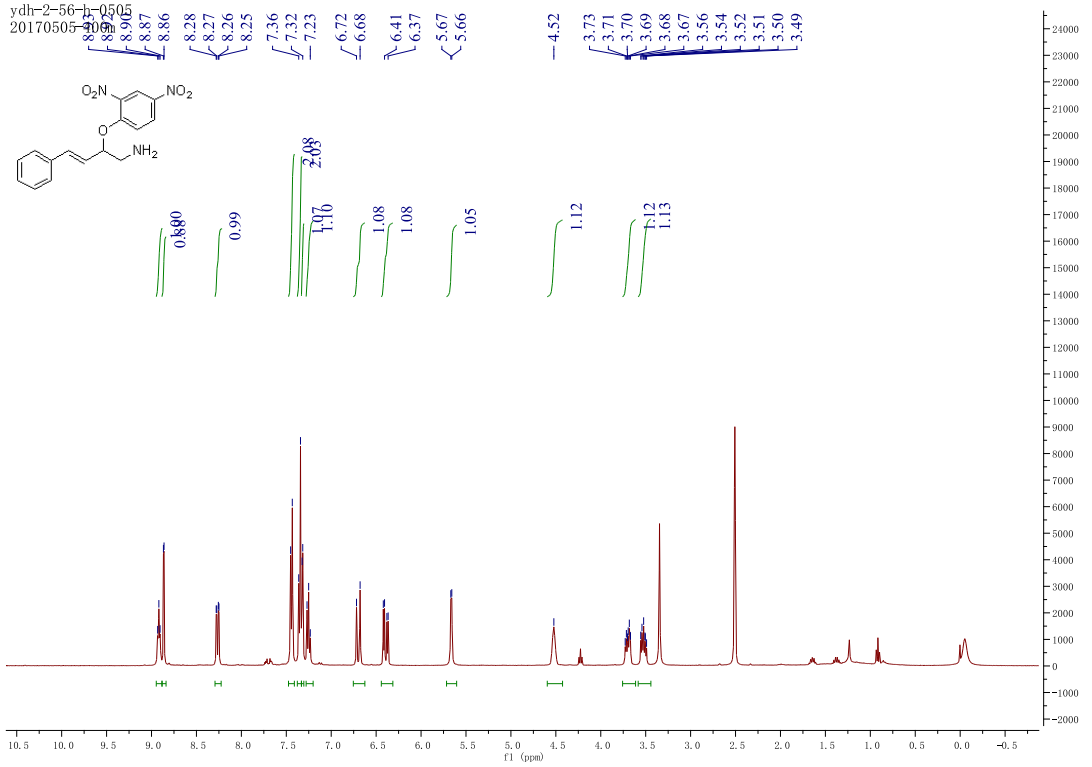
^{1}H NMR Spectrum of 4c



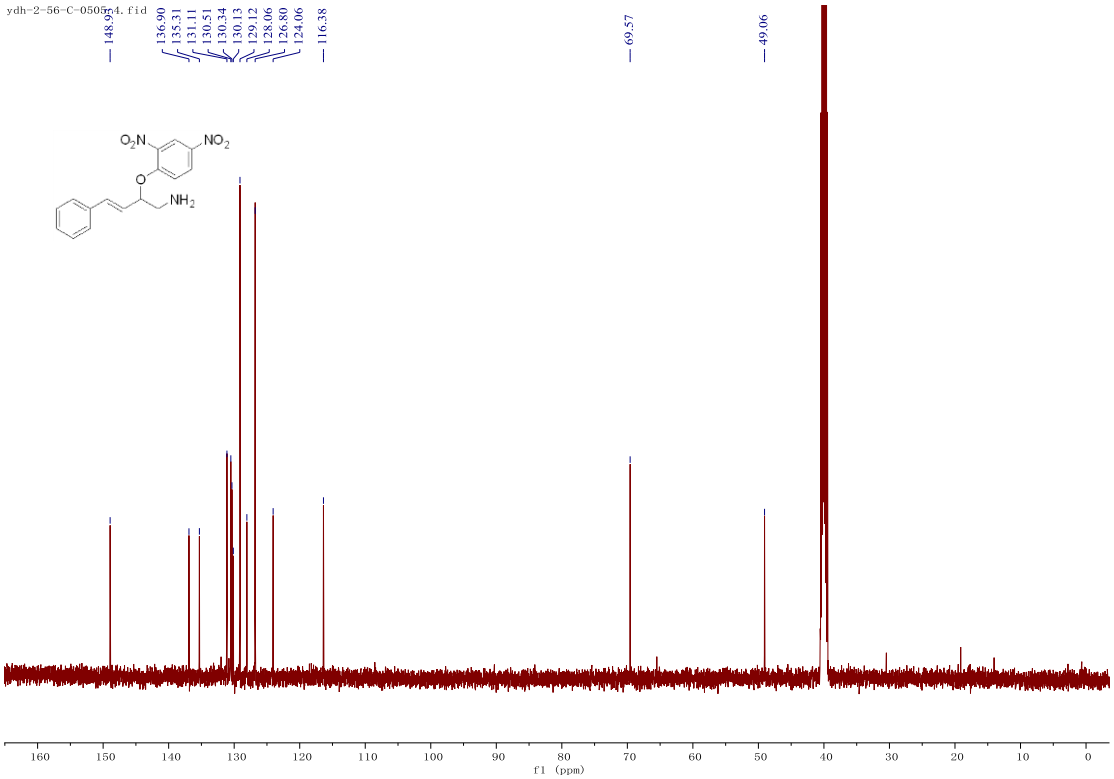
^{13}C NMR Spectrum of 4c



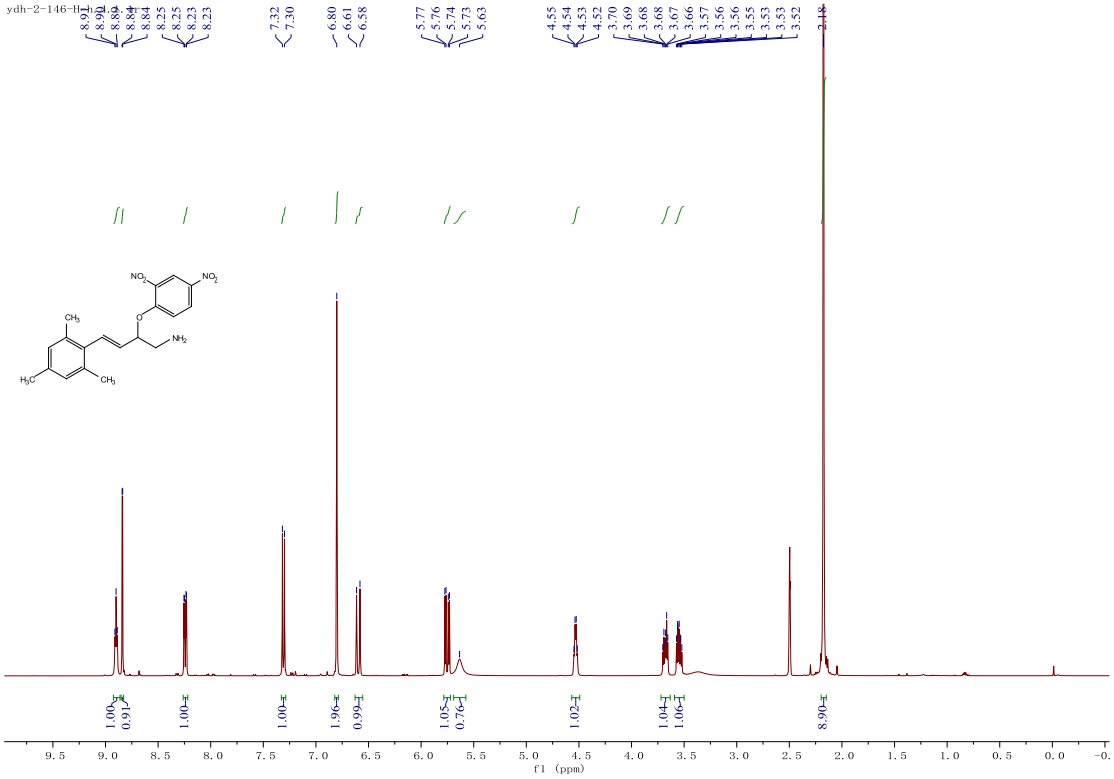
^{1}H NMR Spectrum of 4d



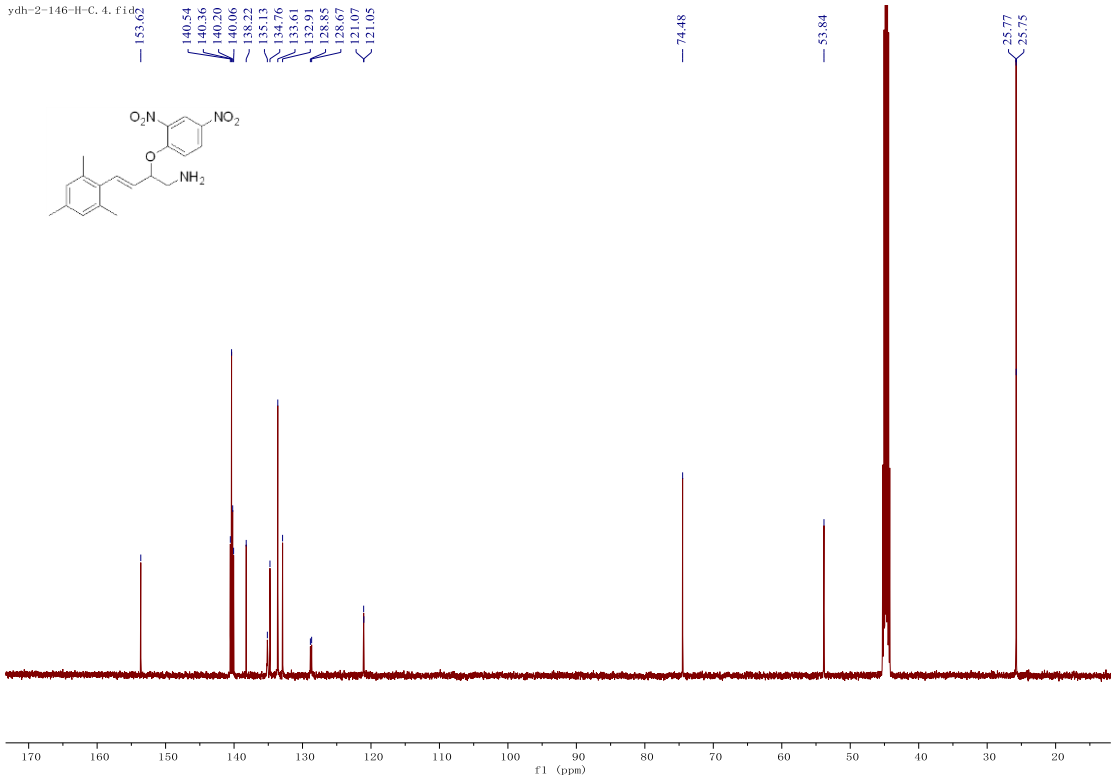
^{13}C NMR Spectrum of 4d



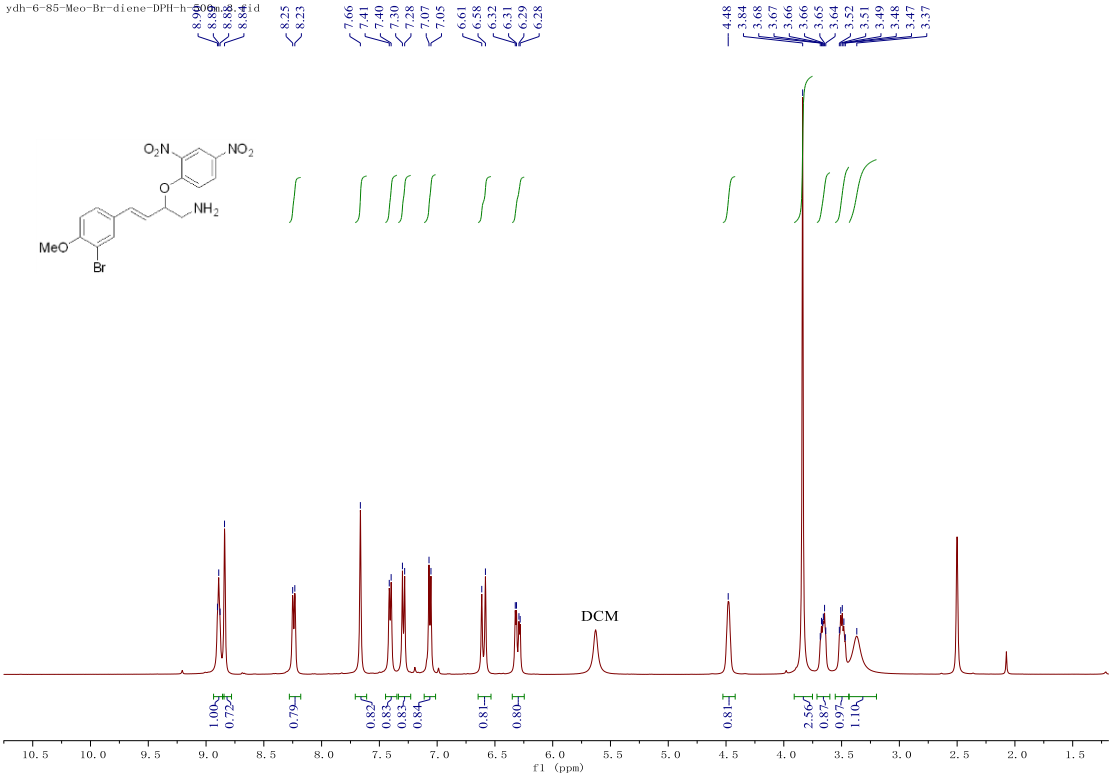
^{1}H NMR Spectrum of 4e



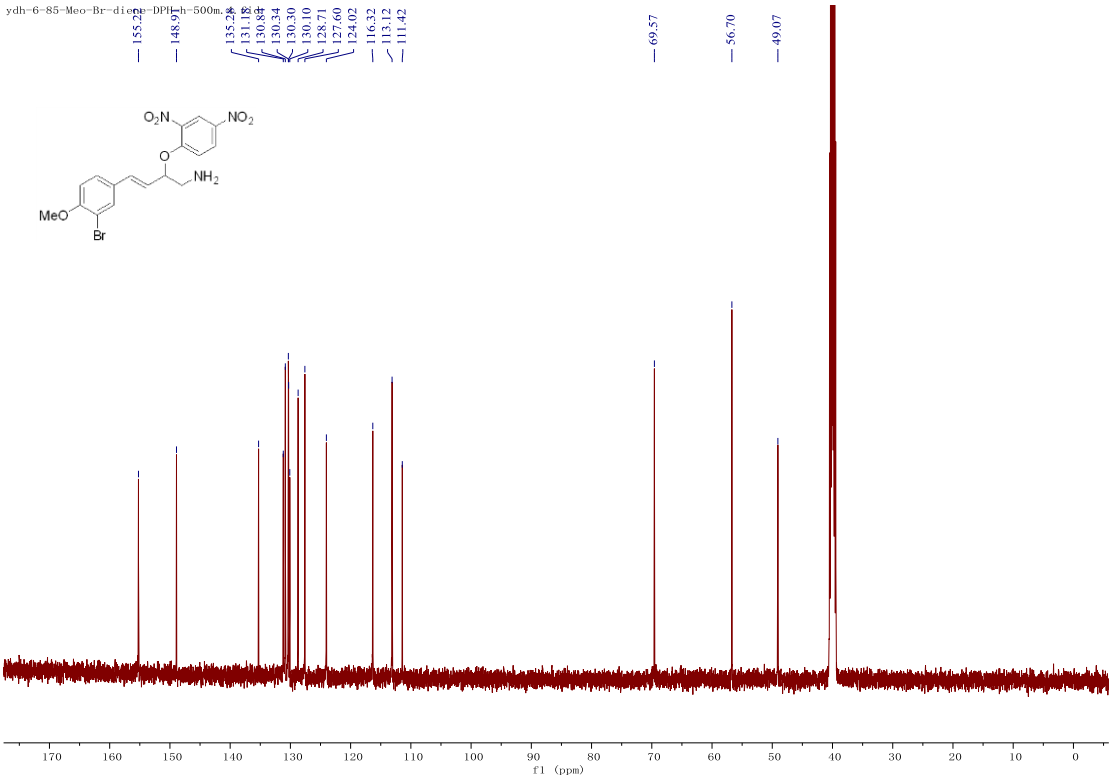
^{13}C NMR Spectrum of 4e



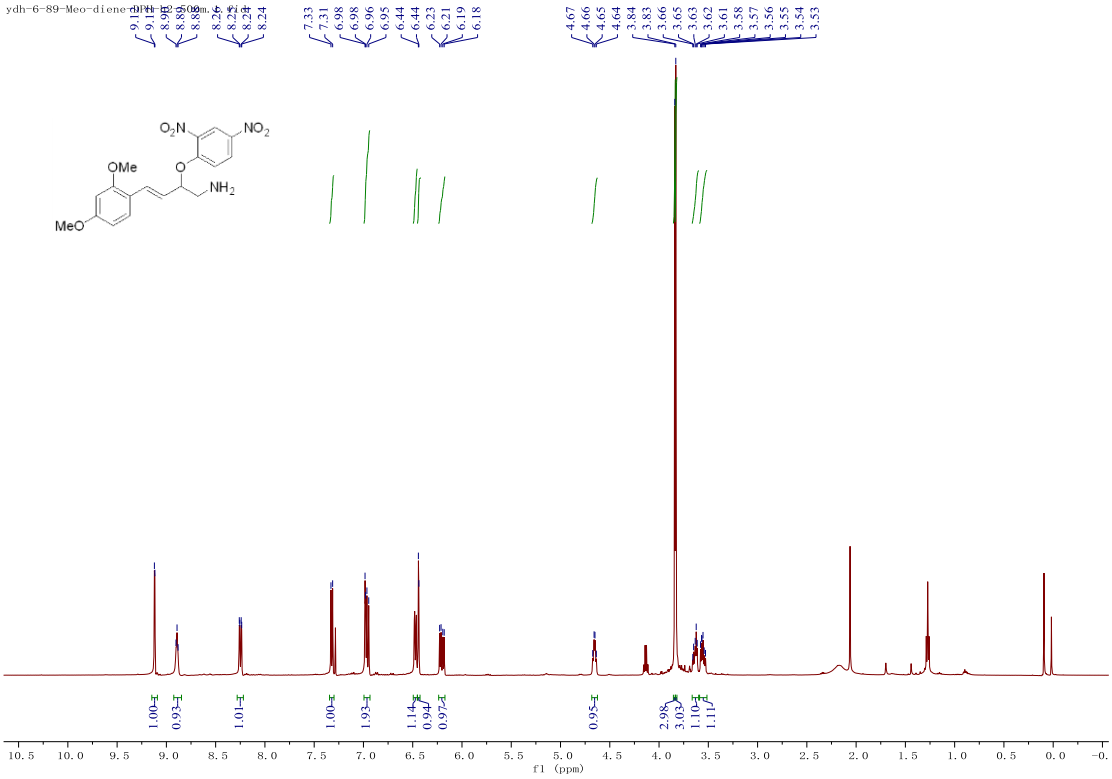
^{1}H NMR Spectrum of 4f



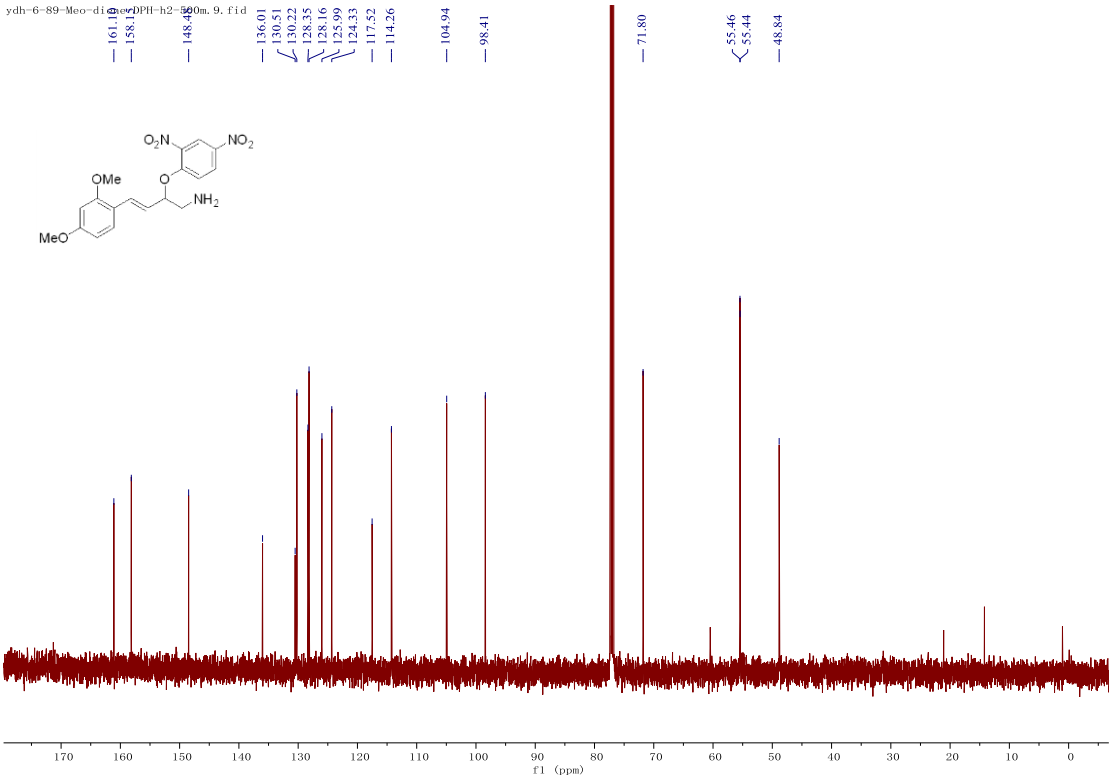
^{13}C NMR Spectrum of 4f



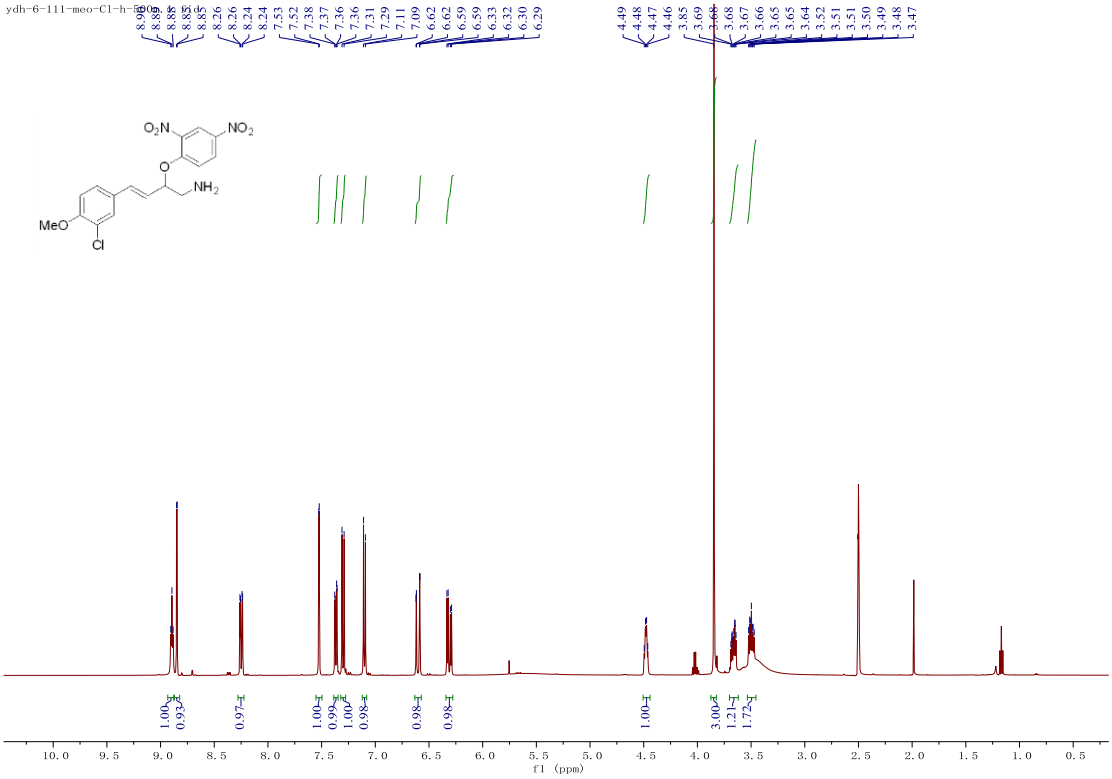
^{1}H NMR Spectrum of 4g



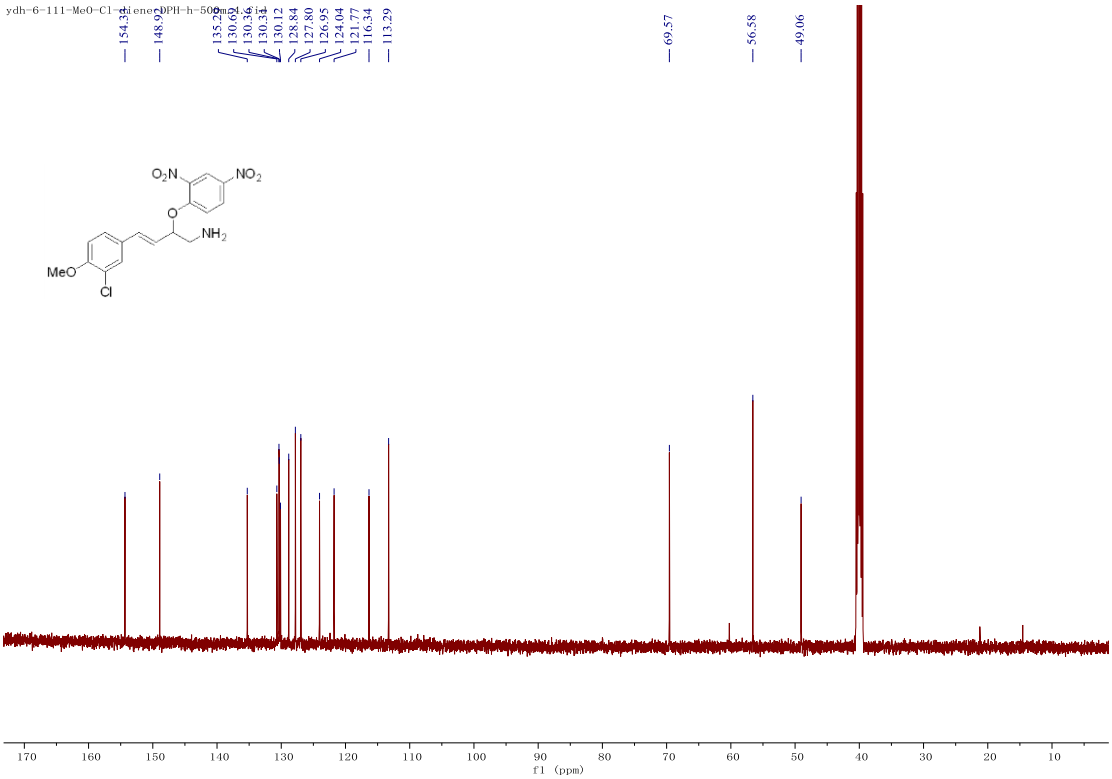
^{13}C NMR Spectrum of 4g



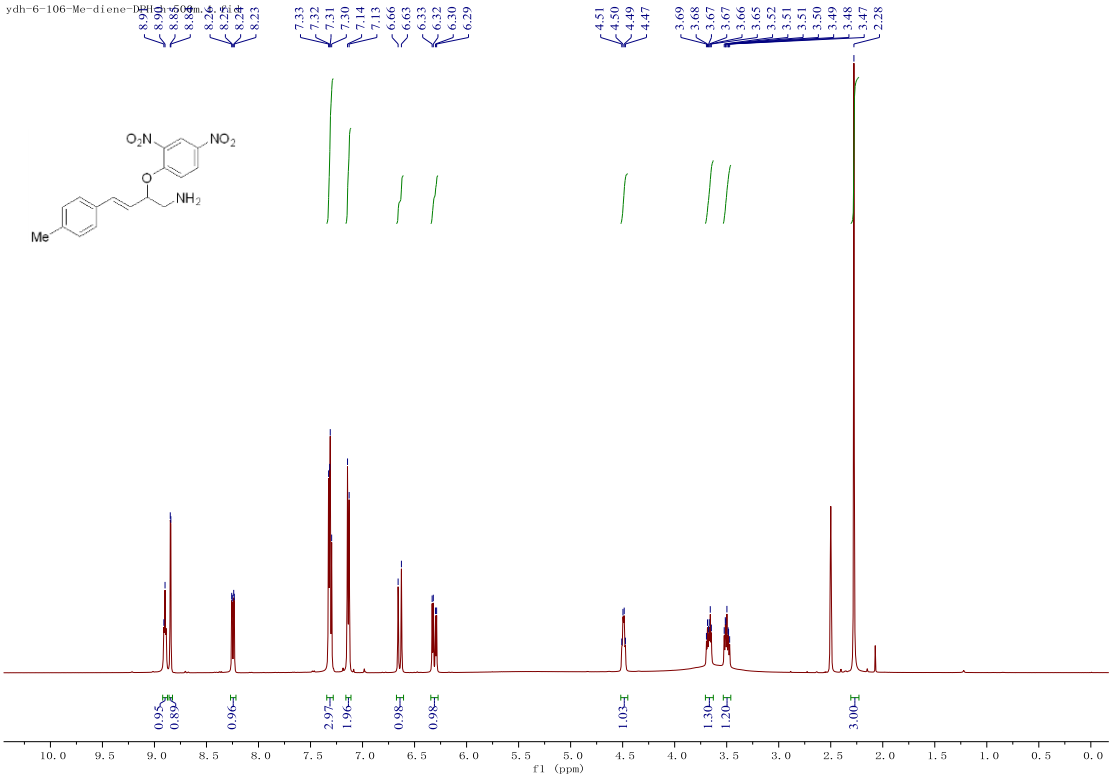
^{1}H NMR Spectrum of 4h



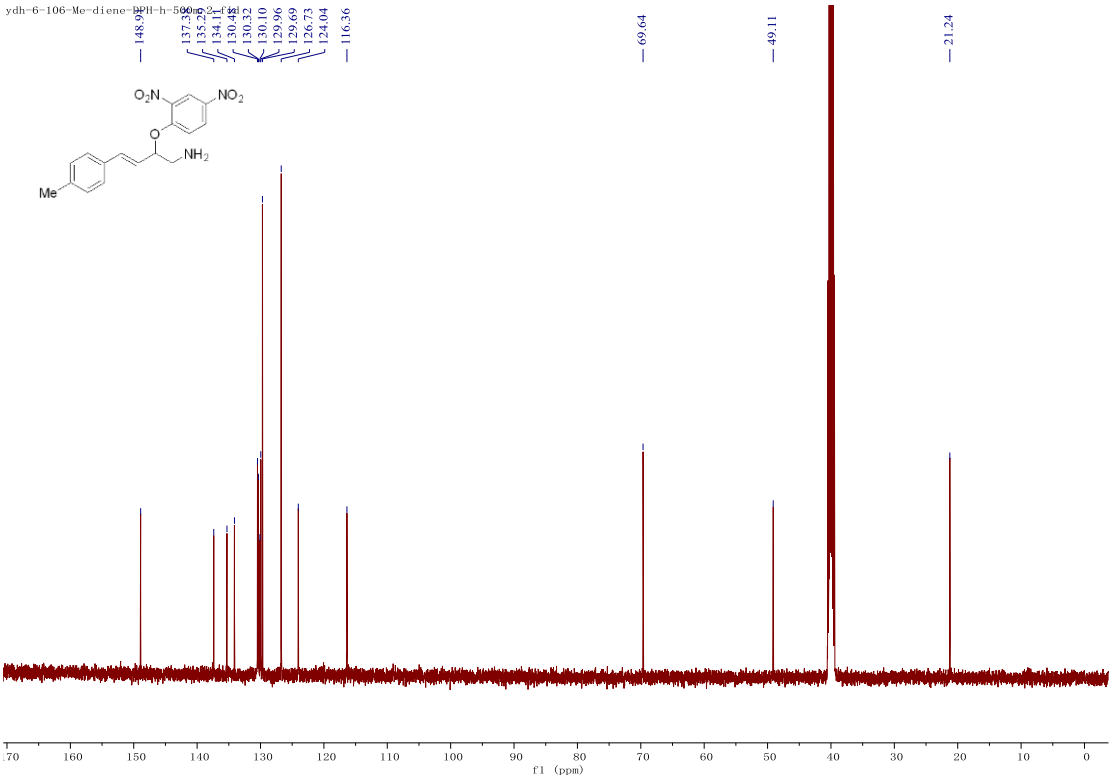
^{13}C NMR Spectrum of 4h



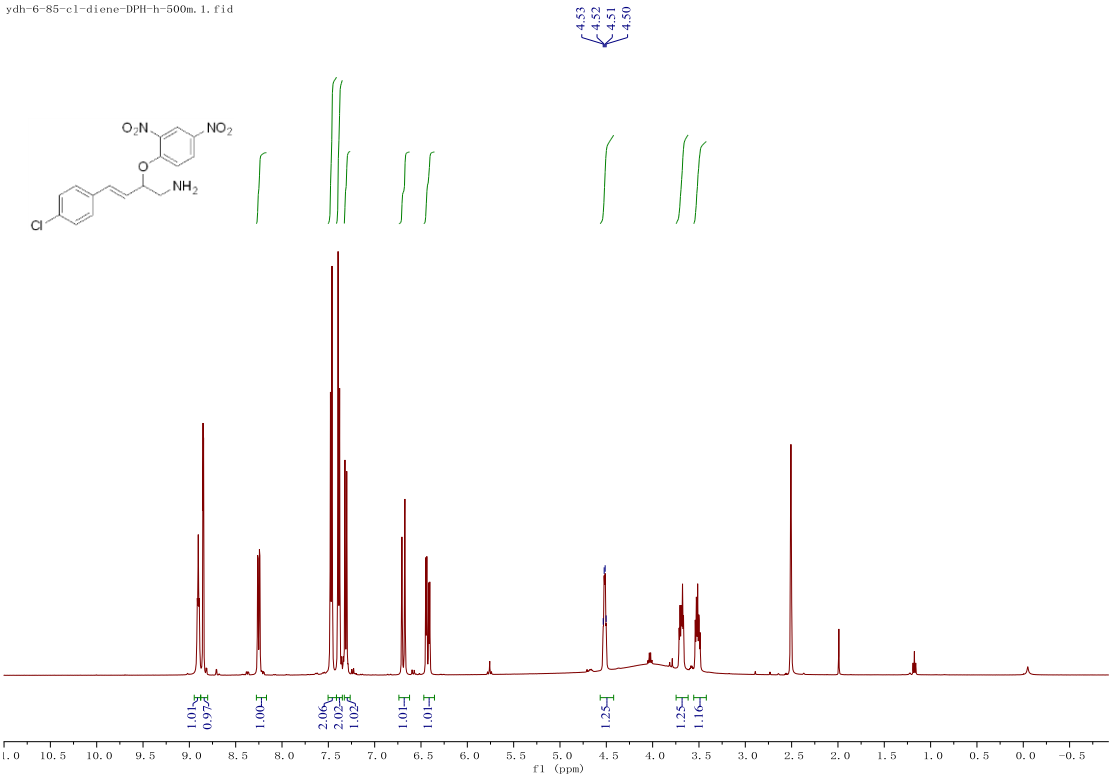
^{1}H NMR Spectrum of 4i



^{13}C NMR Spectrum of 4i



^{1}H NMR Spectrum of 4j



^{13}C NMR Spectrum of 4j