Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Remote Methylene C(sp^3)-H Functionalization Enabled by An Organophosphine Catalyzed Alkyne Isomerization

De Wang, Zefeng Song, Jianyu Zhang, Tao Xu*

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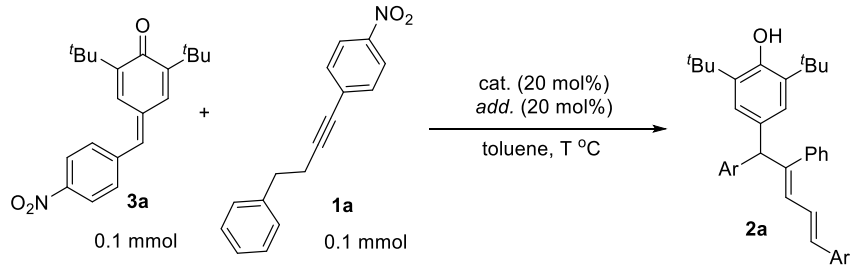
1. General Informations

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 400 and 100 MHz by JEOL, respectively. High-resolution mass spectra were recorded by ESI method. The used organic solvents were dried by standard methods if it was necessary. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Chiral HPLC was performed on an Agilent 1290 Infinity II LC System with chiral columns [Chiralpak IA-H columns 4.6*250 mm, (Daicel Chemical Ind., Ltd.)]. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica-gel-coated plates. Flash column chromatography was carried out by using silica gel or aluminium oxide at increased pressure. IR were tested on Thermo Nicolet Avatar 330 FT-IR (sample preparation: all samples dissolved in DCM and applied evenly to the detector, after evaporation of solvent to form a film-like membrane)

2. The condition optimizations

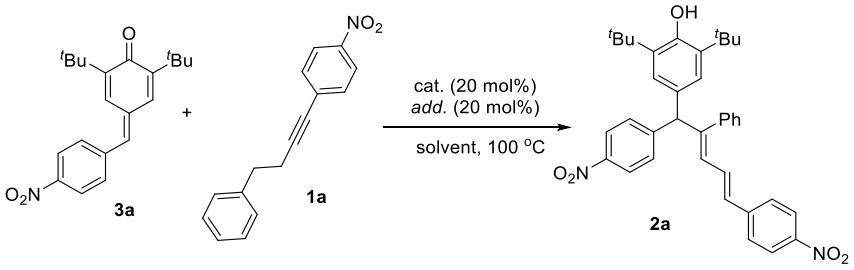
Table S1 Full conditions optimization Part I



entry	cat.	add.	T (°C)	yield (**2a**)	ratio (*Z/E*)[a]
1	P^nBu_3	*o*-NO_2BzOH	80	5	-
2	P^nBu_3	*o*-NO_2BzOH	100	12	-
3	P^nBu_3	*o*-NO_2BzOH	25	NR	-
4	PPh_3	*o*-NO_2BzOH	100	NR	-
5	P^nBu_3	PhOH	100	34	-
6	P^nBu_3	-	100	10	-
7	P^nBu_3	PPh_3AuCl	100	18	-
8	P^nBu_3	$IPrAuNTf_2$	100	6	-
9	P^nBu_3	$AgNTf_2$	100	trace	-
10	PMe_3	PhOH	100	trace	-
11	PMe_2Ph	PhOH	100	52	>20:1
12	$PMePh_2$	PhOH	100	22	-
13	PMe_2Ph	*p*-BrC_6H_4OH	100	24	>20:1
14	PMe_2Ph	2,4-$(NO_2)_2C_6H_3OH$	100	trace	-
15	PMe_2Ph	naphthol	100	36	-
16	PMe_2Ph	HFIP	100	8	-
17	PMe_2Ph	4-FC_6H_4OH	100	44	-
18	PMe_2Ph	4-MeC_6H_4OH	100	18	-
19	-	$PPh_3AuCl/AgBF_4$	100	NR	-
20	PMe_2Ph	$PPh_3AuCl/AgBF_4$	100	4 (NMR)	>20:1
21	PMe_2Ph	Cs_2CO_3	100	trace	-
22[b]	PMe_2Ph	PhOH	100	49	>20:1
23	PMe_2Ph	PhOH	60	13	>20:1
24	PMe_2Ph	PhOH	70	33	>20:1
25	PMe_2Ph	(*R*)-BINOL	100	42	>20:1
26	PMe_2Ph		100	trace	-

[a] The ratio of ompound **2a** was determined by ^1H NMR analysis; [b] Adding 4A MS (50 mg)

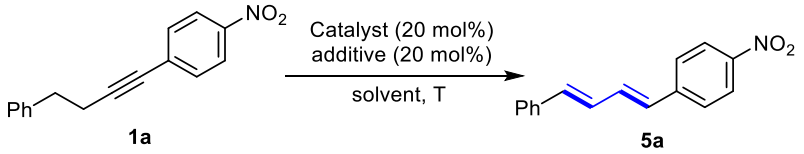
Table S2 Full conditions optimization Part II



entry	cat.	add.	**solvent**	yield (**2a**)	ratio (*Z/E*)
1	PMe_2Ph	PhOH	fluorobenzene	63	>20:1
2	PMe_2Ph	PhOH	chloorobenzene	54	>20:1
3	PMe_2Ph	PhOH	benzene	62	>20:1
4	PMe_2Ph	PhOH	*o*-xylene	56	>20:1
5	PMe_2Ph	PhOH	THF	19	>20:1
6	PMe_2Ph	PhOH	1,4-dioxane	13	>20:1
7	PMe_2Ph	PhOH	DCE	30	>20:1
8	PMe_2Ph	PhOH	CH_3CN	NR	>20:1
9	PMe_2Ph	PhOH	$PhCF_3$	48	>20:1
10[a]	PMe_2Ph	PhOH	PhF	12	>20:1
11[b]	PMe_2Ph	PhOH	PhF	45	>20:1
12[c]	PMe_2Ph	PhOH	PhF	71	>20:1
13[c,d]	PMe_2Ph	PhOH	PhF	85	>20:1
14[d,e]	**PMe_2Ph**	**PhOH**	**PhF**	**85**	**>20:1**
15[d,e,f]	PMe_2Ph	PhOH	PhF	76	>20:1

[a] The reaction run at 120 °C. [b] Mole ratios of **1/2** = 1:2, isolated 18 mg diene from **2**; [c] Mole ratios of **1/2** = 2:1, clean system; [d] Diluted in 4 mL fluorobenzene, 0.025 M concerntration. [e] Mole ratios of **1/2** = 1.5:1; [f] Catalyst loading 10 mol%.

Table S3 Intramolecular isomerization optimizations

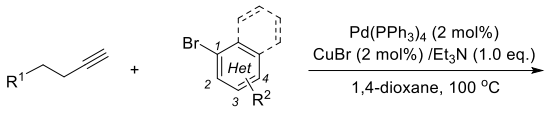


entry[a]	catalyst	additive	solvent	T (°C)	yield (%)[b]	*Z/E*[c]
1	P^nBu_3	-	toluene	80/100	8	>20:1
2	PPh_3	-	toluene	80/120	n.r.	-
3	PPh_2Me	-	toluene	80	trace	-
4	$PPhMe_2$	-	toluene	80	15	>20:1
5	DABCO	-	toluene	80	n.r.	-
6	none	-	toluene	80	n.r.	-
7	$PPhMe_2$	PhOH	toluene	80	96	>20:1
8	$PPhMe_2$	$PhCO_2H$	toluene	80	72	>20:1
9	$PPhMe_2$	PhOH	THF	80	64	>20:1
10	$PPhMe_2$	PhOH	DCE	80	70	>20:1
11	$PPhMe_2$	PhOH	dioxane	80	35	>20:1
12	$PPhMe_2$	PhOH	toluene	60	34	>20:1
13[d]	$PPhMe_2$	PhOH	toluene	80	97	>20:1
14[e]	$PPhMe_2$	PhOH	toluene	80	83	>20:1

[a] All reaction carried out with **1a** (0.1 mmol), phosphine (20 mol%), additive (20 mol%) in solvent (1.0 mL); [b] Isolated yield; [c] Determined by crude ^1H NMR analysis; [d] Decreased the catalyst and additive loading to 10 mol%; [e] Decreased the catalyst and additive loading to 5 mol%

3. Experimental procedure and characterization data

General procedure (I) for preparation alkyne 1a-1u



S-1a, R^1 = Ph;
S-1b, R^1 = 4-FC_6H_4;
S-1c, R^1 = 4-$OMeC_6H_4$;
S-1d, R^1 = Me;
S-1e, R^1 = Et;
S-1f, R^1 = CO_2Me
S-1g, R^1 = 2-methyl propenyl
S-1h, R^1 = CH_2CO_2Me
S-1i, R^1 = 3-indolyl

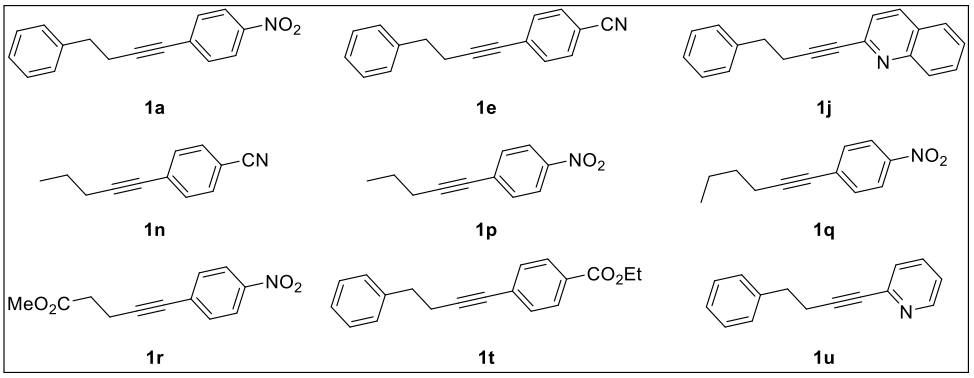
S-2a, R^2 = 4-NO_2;
S-2b, R^2 = 3-Me-4-NO_2;
S-2c, R^2 = 3-F-4-NO_2;
S-2d, R^2 = 2-Cl-4-NO_2;
S-2e, R^2 = 4-CN;
S-2f, R^2 = 4-CO_2Et;

S-2g, R^2 = 2-pyridyl;
S-2h, R^2 = 4-pyridyl;
S-2i, R^2 = 2,5-pyrazinyl;
S-2j, R^2 = 2,6-pyrimidyl;
S-2k, R^2 = 4-quinolinyl;
S-2l, R^2 = 2-quinolinyl.

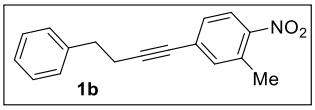
1a, R^1 = Ph, R^2 = 4-NO_2;
1b, R^1 = Ph, R^2 = 3-Me-4-NO_2;
1c, R^1 = Ph, R^2 = 3-F-4-NO_2;
1d, R^1 = Ph, R^2 = 2-Cl-4-NO_2;
1e, R^1 = Ph, R^2 = 4-CN;
1f, R^1 = Ph, R^2 = 4-pyridyl;
1g, R^1 = Ph, R^2 = 2,5-pyrazinyl;
1h, R^1 = Ph, R^2 = 2,6-pyrimidyl;
1i, R^1 = Ph, R^2 = 4-quinolinyl;

1j, R^1 = Ph, R^2 = 2-quinolinyl;
1k, R^1 = 4-FC_6H_4, R^2 = 4-NO_2;
1l, R^1 = 4-$MeOC_6H_4$, R^2 = 4-NO_2;
1m, R^1 = 3-indolyl, R^2 = 4-NO_2
1n, R^1 = Me, R^2 = 4-CN;
1o, R^1 = 2-methyl propenyl, R^2 = 4-CN;
1p, R^1 = Me, R^2 = 4-NO_2;
1q, R^1 = Et, R^2 = 4-NO_2;
1r, R^1 = CO_2Me, R^2 = 4-NO_2;
1s, R^1 = CH_2CO_2Me, R^2 = 4-NO_2;
1t, R^1 = Ph, R^2 = 4-CO_2Et;
1u, R^1 = Ph, R^2 = 2-pyridyl;

To a dry Schlenk tube was added CuBr (0.04 equiv.) and $Pd(PPh_3)_4$ (0.05 equiv.) and dissolved in 1,4-dioxane (10 mL) at room temperature under N_2 protection. After stirring for 10 mins, **S-2** (1.0 equiv.) dissolved in 1,4-dioxane and injected to the above solution followed by addition of TEA (1.0 equiv.). Then alkyne **S-1** (1.0 equiv.) was added to the solution and heated at 100 °C for 10 hours. Cool to room temperature and filter through the celite to collect the solution. The crude product was purified by column chromatography to collect a yellowish product **1**.



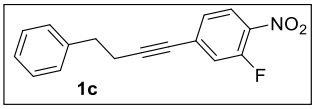
Compounds **1a**, **1e**, **1j**, **1n**, **1p-r, 1t-u** are known compounds and prepared according to the reported procedures.[1a-g]



2-methyl-1-nitro-4-(4-phenylbut-1-yn-1-yl)benzene (1b)

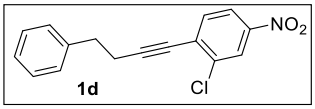
Compound **1b** (87% yield) was obtained as a yellowish solid following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2b** (3 mmol, 645 mg) stirred

for 12 hours. R_f = 0.6 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.37-7.25 (m, 7H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 147.7, 140.2, 135.6, 133.9, 129.7, 129.2, 128.5, 128.4, 126.4, 124.8, 94.4, 79.9, 34.7, 21.7, 20.5; **IR** (neat) ν 2931, 2858, 2229, 1602, 1579, 1513, 1340, 1076, 887, 833, 754, 698 cm^{-1}; **MP**: 56-58 °C; **HRMS** calcd. for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1181. Found: 266.1176.



2-fluoro-1-nitro-4-(4-phenylbut-1-yn-1-yl)benzene (1c)

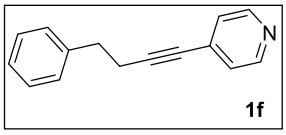
Compound **1c** (86% yield) was obtained as a yellowish solid following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2c** (0.3 mmol, 655 mg) stirred for 12 hours. R_f = 0.4 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.4 Hz, 1H), 7.37-7.20 (m, 7H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.3 (d, *J* = 264.0 Hz), 140.0, 136.2 (d, *J* = 7.0 Hz), 132.0 (d, *J* = 10.0 Hz), 128.4 (d, *J* = 3.8 Hz), 127.5 (d, *J* = 3.8 Hz), 126.5, 126.1 (d, *J* = 2.0 Hz), 121.0 (d, *J* = 22.0 Hz), 96.7, 79.0 (d, *J* = 2.3 Hz), 34.5, 21.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.25 to -117.29 (m); **IR** (neat) ν 2929, 2855, 2228, 1604, 1590, 1519, 1341, 1093, 836, 748, 694 cm^{-1}; **MP**: 65-67 °C; **HRMS** calcd. for $C_{16}H_{11}FNO_2$ $[M-H]^-$: 268.0774. Found: 268.0779.



2-chloro-4-nitro-1-(4-phenylbut-1-yn-1-yl)benzene (1d)

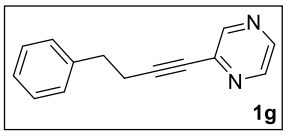
Compound **1d** (42% yield) was obtained as a yellow solid following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2d** (3.0 mmol, 702 mg) stirred for 12 hours. R_f = 0.3 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.4 Hz, 1H), 8.04 (dd, J_1 = 8.8 Hz, J_2 = 2.4Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.36-7.24 (m, 5H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 146.7, 140.0, 136.7, 133.6, 130.4, 128.51, 128.47, 126.5, 124.3, 121.4,

101.4, 77.4, 34.5, 22.0; **IR** (neat) ν 2929, 2861, 2229, 1585, 1519, 1346, 1133, 1118, 887, 835, 742, 700 cm^{-1}; **MP**: 58-60 °C; **HRMS** calcd. for $C_{16}H_{11}NO_2Cl$ $[M-H]^-$: 284.0478. Found: 284.0484.



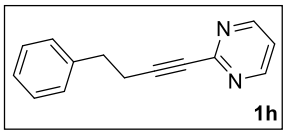
4-(4-phenylbut-1-yn-1-yl)pyridine (1f)

Compound **1f** (56% yield) was obtained as a brown oil following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2h** (3.0 mmol, 470 mg) stirred for 12 hours. R_f = 0.1 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.0 Hz, 2H), 7.35-7.20 (m, 7H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 149.6, 140.2, 132.0, 128.5, 128.4, 126.5, 125.7, 94.9, 79.1, 34.7, 21.7; **IR** (neat) ν 3025, 2927, 2859, 2227, 1592, 1536, 1488, 1454, 1403, 1340, 1213, 989, 821, 760, 698 cm^{-1}; **HRMS** calcd. for $C_{15}H_{14}N$ $[M+H]^+$: 208.1126. Found: 208.1126.



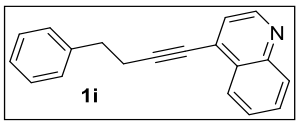
2-(4-phenylbut-1-yn-1-yl)pyrazine (1g)

Compound **1g** (47% yield) was obtained as a yellow oil following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2i** (3.0 mmol, 475 mg) stirred for 12 hours. R_f = 0.2 (PE/EA = 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.6 Hz, 1H), 8.49 (dd, *J* = 2.4, 1.6 Hz, 1H), 8.43 (d, *J* = 2.4 Hz, 1H), 7.35 – 7.21 (m, 5H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 147.6, 144.2, 142.4, 140.6, 140.0, 128.5, 128.4, 126.5, 94.5, 78.3, 34.4, 21.6; **IR** (neat) ν 2958, 2852, 2219, 1558, 1542, 1432, 1251, 878, 754, 698 cm^{-1}; **HRMS** calcd. for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1079. Found: 209.1073.



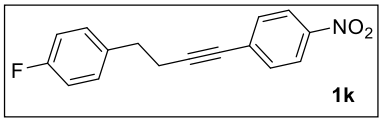
2-(4-phenylbut-1-yn-1-yl)pyrimidine (1h)

Compound **1h** (42% yield) was obtained as a brown oil following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2j** (3.0 mmol, 475 mg) stirred for 12 hours. $\boldsymbol{R_f}$ = 0.2 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.8 Hz, 2H), 7.34-7.16 (m, 6H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 157.2, 153.2, 140.2, 128.5, 128.3, 126.4, 119.5, 89.6, 80.3, 34.4, 21.4; **IR** (neat) ν 3030, 2926, 2234, 1562, 1552, 1413, 1251, 805, 745, 700 cm^{-1}; **HRMS** calcd. for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1079. Found: 209.1073.



4-(4-phenylbut-1-yn-1-yl)quinoline (1i)

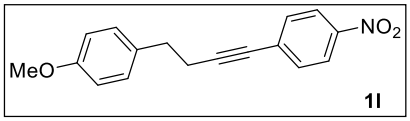
Compound **1i** (64% yield) was obtained as a brown oil following the *general procedure I* from **S-1a** (3.0 mmol, 390 mg, 420 μL) and **S-2k** (3.0 mmol, 618 mg) stirred for 12 hours. $\boldsymbol{R_f}$ = 0.3 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.4 Hz, 1H), 8.14-8.01 (m, 2H), 7.74-7.68 (m, 1H), 7.56-7.50 (m, 1H), 7.43-7.24 (m, 6H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 149.7, 148.0, 140.1, 130.4, 129.7, 129.6, 128.54, 128.48, 128.0, 126.8, 126.5, 126.1, 123.5, 99.6, 77.5, 34.7, 21.8; **IR** (neat) ν 3027, 2927, 2858, 2231, 1577, 1502, 1454, 1390, 846, 763, 698 cm^{-1}; **HRMS** calcd. for $C_{19}H_{16}N$ $[M+H]^+$: 258.1283. Found: 258.1277.



1-Fluoro-4-(4-(4-nitrophenyl)but-3-yn-1-yl)benzene (1k)

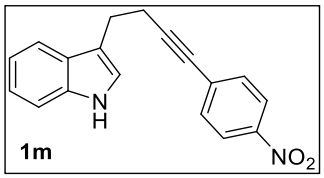
Compound **1k** (61% yield) was obtained as a yellowish solid following the *general procedure I* from **S-1b** (3.0 mmol, 444 mg) and **S-2a** (3.0 mmol, 606 mg) stirred for 12 hours. $\boldsymbol{R_f}$ = 0.4 (PE/EA = 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.2 Hz, 2H),

7.47 (d, *J* = 8.8 Hz, 2H), 7.25-7.19 (m, 2H), 7.05-6.97 (m, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 161.6 (d, *J* = 243.2 Hz), 146.7, 135.8 (d, *J* = 3.1 Hz), 132.2, 130.7, 129.9 (d, *J* = 7.8 Hz) 123.5, 115.2 (d, *J* = 21.1 Hz), 95.2, 80.2, 33.8, 21.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.44 to -116.52 (m); **IR** (neat) ν 2930, 2857, 2211, 1635, 1590, 1340, 1216, 852, 750, 688 cm^{-1}; **MP**: 72-73 ^{o}C; **HRMS** calcd. for $C_{16}H_{11}FNO_2$ $[M-H]^-$: 268.0774. Found: 268.0778.



1-methoxy-4-(4-(4-nitrophenyl)but-3-yn-1-yl)benzene (1l)

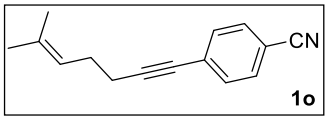
Compound **1l** (57% yield) was obtained as a pale yellow solid following the *general procedure I* from **S-1c** (3.0 mmol, 480 mg) and **S-2a** (3.0 mmol, 606 mg) stirred for 12 hours. R_f = 0.3 (PE/EA = 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 175.2, 158.3, 146.6, 132.2, 130.9, 129.4, 123.5, 113.8, 95.8, 80.0, 53.4, 33.8, 22.0; **IR** (neat) ν 2937, 2852, 2213, 1590, 1508, 1338, 1245, 1180, 1026, 853, 748 cm^{-1}; **MP**: 83-84 ^{o}C; **HRMS** calcd. for $C_{17}H_{14}NO_3$ $[M-H]^-$: 280.0974. Found: 280.0981.



3-(4-(4-nitrophenyl)but-3-yn-1-yl)-1H-indole (1m)

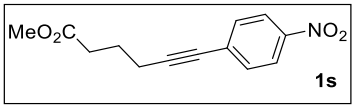
Compound **1m** (92% yield) was obtained as a yellow solid following the *general procedure I* from **S-1i** (3.0 mmol, 507 mg) and **S-2a** (3.0 mmol, 606 mg) stirred for 12 hours. R_f = 0.3 (PE/EA = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 8.02 (brs, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.16-7.12 (m, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (100M Hz, $CDCl_3$) δ 146.6, 136.2, 132.2, 131.0, 127.2, 123.5, 122.1, 121.6, 119.4, 118.7, 114.9, 111.2, 96.5, 79.8, 24.5, 21.1; **IR** (neat)

ν 3442, 3059, 2892, 2850, 1929, 1590, 1508, 1448, 1336, 1108, 1008, 854, 750 cm^{-1}; **MP**: 105-107 °C; **HRMS** calcd. for $C_{18}H_{15}N_2O_2$ $[M+H]^+$: 291.1128. Found: 291.1123.



4-(6-methylhept-5-en-1-yn-1-yl)benzonitrile (1o)

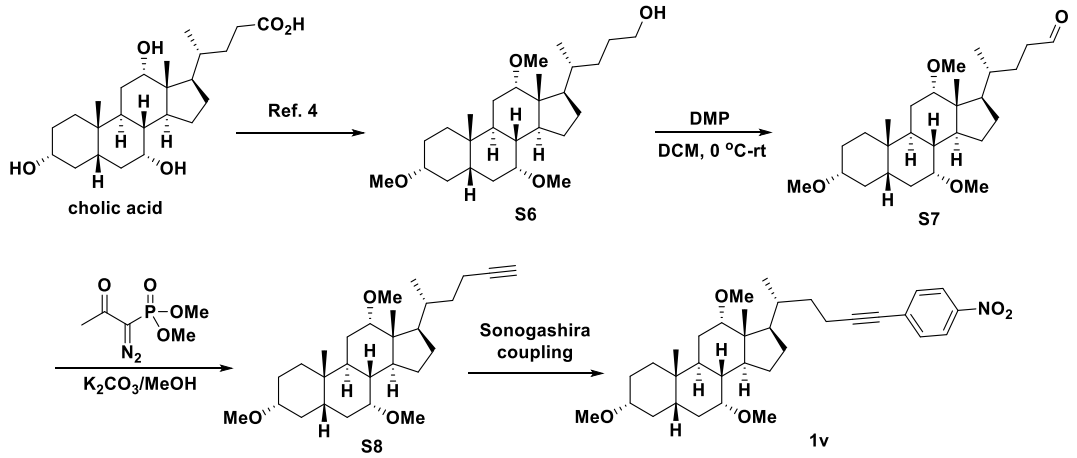
Compound **1o** (32% yield) was obtained as a pale yellow oil following the *general procedure I* from **S-1g** (1.0 mmol, 108 mg) and **S-2e** (1.0 mmol, 182 mg) stirred for 12 hours. $\boldsymbol{R_f}$ = 0.6 (PE/EA = 20/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 5.22-5.18 (m, 1H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.29 (q, *J* = 7.2 Hz, 2H), 1.72 (s, 3H), 1.65 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 133.4, 132.0, 131.8, 129.0, 122.3, 118.6, 110.7, 95.4, 79.3, 27.1, 25.6, 19.9, 17.7; **IR** (neat) ν 3017, 2931, 2859, 2237, 2225, 1602, 1579, 1513, 1340, 1076, 887, 833, 748 cm^{-1}; **HRMS** calcd. for $C_{15}H_{16}N$ $[M+H]^+$: 210.1283. Found: 210.1278.



methyl 6-(4-nitrophenyl)hex-5-ynoate (1s)

Compound **1s** (79% yield) was obtained as a pale yellow solid following the *general procedure I* from **S-1h** (3.0 mmol, 378 mg) and **S-2a** (3.0 mmol, 606 mg) stirred for 12 hours. $\boldsymbol{R_f}$ = 0.5 (PE/EA = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 3H), 2.55-2.49 (m, 4H), 1.96 (p, *J* = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 173.4, 146.7, 132.3, 130.7, 123.5, 95.0, 80.0, 51.7, 32.8, 23.5, 19.0; **IR** (neat) ν 2950, 2844, 2229, 1743, 1594, 1521, 1436, 1344, 1220, 1108, 1012, 854, 750, 688 cm^{-1}; **HRMS** calcd. for $C_{13}H_{13}NO_4$ $[M]^+$: 247.0845. Found: 247.0846.

Preparation of compounds 1v

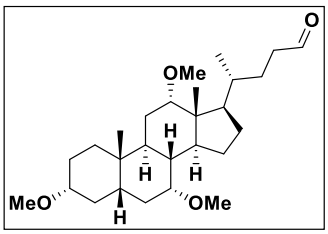


Compound **S6** was prepared according to the reported procedures.[4]

To a solution of DMP (2.7 g, 6.3 mmol, 1.2 equiv) in DCM (20 mL) at 0 ℃, cholic alcohol **S6** (2.28 g, 5.23 mmol, 1.0 equiv) dissolved in DCM (20 mL) was added. The reaction mixture was allowed to stir at room temperature overnight, following aqueous $NaHCO_3$ (15 mL) was added to the reaction mixture. The mixture was extracted with DCM (100 mL) and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuum. The residue crude product was purified by flash column chromatography (PE/EA = 6/1~4/1) to afforded compound **S7** as a viscous solid (1.2 g, 53% yield).

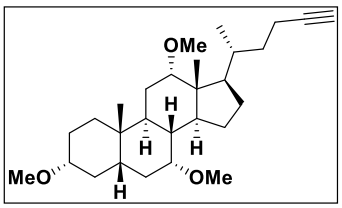
Compound **S7** (434 mg, 1.0 mmol), K_2CO_3 (690 mg, 5.0 mmol) were dissolved in MeOH under N_2 protection and cooled to 0 °C. Bestmann reagent (288 mg, 1.5 mmol) was added to the above mixture slowly. After addition, the reaction mixture was allowed warm to room temperature and keep stirring for 3 hours. TLC monitor the reaction, evacuated the MeOH and water was added to dissolve the potassium carbonate, ethyl ester extracted for twice. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuum. The residue crude product was purified by flash column chromatography (PE/EA = 6/1~4/1) to afforded compound **S8** as a white solid (213 mg, 49% yield).

Compounds **1v** was followed the general procedure *I*.



(R)-4-((3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanal (S7)

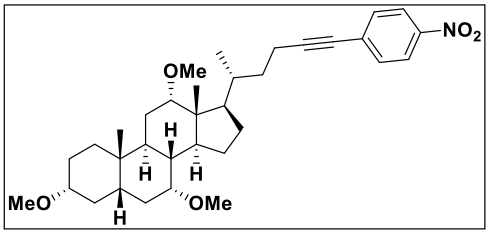
Compound **S7** (1.2 g, 53% yield) was obtained as a white solid following the *general procedure as above* from **S-6** (5.23 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 3.36 (br, 1H), 3.33 (s, 3H), 3.26 (t, *J* = 2.8 Hz, 3H), 3.21 (s, 3H), 3.14 (q, *J* = 3.2 Hz, 1H), 3.03-2.97 (m, 1H), 2.50-2.32 (m, 1H), 2.23-2.02 (m, 2H), 1.98-1.67 (m, 8H), 1.59-1.46 (m, 2H), 1.42-1.18 (m, 7H), 1.07-0.85 (m, 10H), 0.65 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.5, 81.9, 80.7, 55.8, 55.7, 55.4, 53.4, 46.2, 46.1, 42.7, 41.9, 40.8, 39.6, 35.2, 35.0, 34.9, 34.4, 27.93, 27.88, 27.7, 27.4, 26.7, 23.1, 22.8, 21.9, 17.4, 12.4; **IR** (neat) ν 2929, 2867, 2818, 1723, 1457, 1369, 1177, 1098 cm^{-1}; **MP**: 117-119 °C; **HRMS** Calcd. for $C_{27}H_{45}O_4$ $[M-H]^-$: 433.3318, found: 433.3323.



(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((R)-hex-5-yn-2-yl)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (S8)

Compound **S8** (213 mg, 49% yield) was obtained as a white solid following the *general procedure as above* from **S-7** (1.0 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.37 (t, *J* = 2.8 Hz, 1H), 3.32 (s, 3H), 3.25 (s, 3H), 3.21 (s, 3H), 3.14 (q, *J* = 2.8 Hz, 1H), 3.03-2.95 (m, 1H), 2.28-2.01 (m, 5H), 1.95-1.68 (m, 9H), 1.62-1.43 (m, 4H), 1.35-1.15 (m, 5H), 1.06-0.89 (m, 8H), 0.66 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 85.3, 82.0, 80.7, 67.8, 55.8, 55.7, 55.4, 46.4, 46.1, 42.6, 41.9, 39.6, 35.2, 34.9, 34.7, 34.4, 28.0, 27.7, 27.4, 26.7, 23.1, 22.8, 21.9, 17.2, 15.4, 12.4; **IR** (neat) ν 3309, 2933, 2869, 2817, 2115, 1731, 1454, 1371, 1182, 1103, 960, 736, 626 cm^{-1}; **MP**: 115-116 °C; **HRMS** Calcd. for

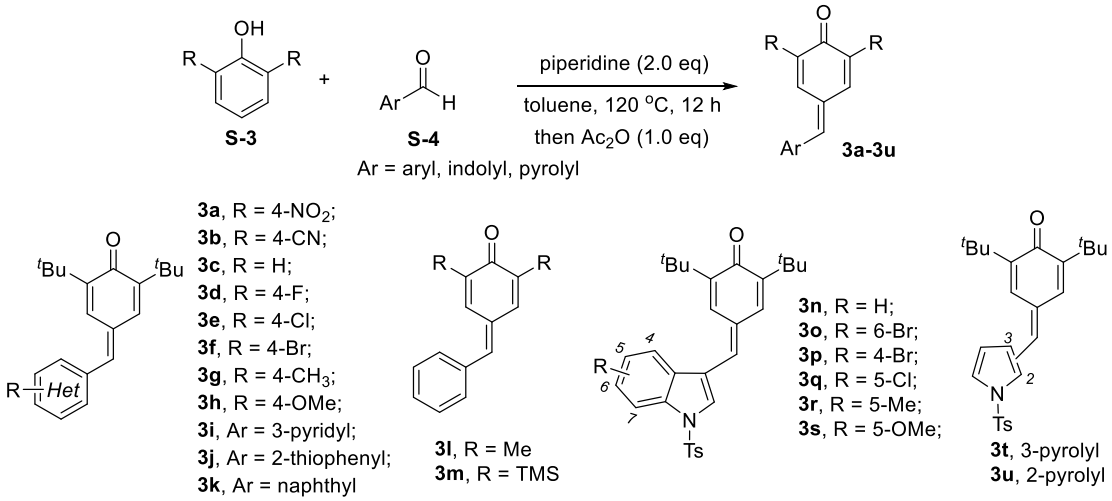
$C_{28}H_{47}O_3$ $[M+H]^+$: 431.3525, found: 431.3522.



(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-3,7,12-trimethoxy-10,13-dimethyl-17-((R)-6-(4-nitrophenyl)hex-5-yn-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (1v)

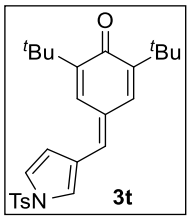
Compound **1v** (152 mg, 79% yield) was obtained as a white solid following the *general procedure I* from **S-8** (0.35 mmol) and **S-2a** (0.35 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 3.38 (s, 1H), 3.33 (s, 3H), 3.26 (s, 3H), 3.21 (s, 3H), 3.15 (d, *J* = 2.8 Hz, 1H), 3.03-2.96 (m, 1H), 2.53-2.46 (m, 1H), 2.40-2.31 (m, 1H), 2.29-2.14 (m, 1H), 2.12-1.94 (m, 3H), 1.89-1.70 (m, 6H), 1.63-1.47 (m, 4H), 1.45-1.16 (m, 6H), 1.07-0.90 (m, 8H), 0.67 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 146.5, 132.2, 131.3, 123.5, 97.5, 82.0, 80.7, 79.1, 55.8, 55.7, 55.4, 46.3, 46.1, 42.7, 41.9, 39.6, 35.2, 35.1, 34.9, 34.6, 34.4, 27.9, 27.7, 27.5, 26.7, 23.1, 22.8, 21.9, 17.3, 16.5, 12.4; **IR** (neat) ν 2929, 2867, 2821, 2228, 1590, 1516, 1454, 1342, 1101, 853, 748 cm $^{-1}$; **MP**: 62-63 °C; **HRMS** Calcd. for $C_{34}H_{50}NO_5$ $[M+H]^+$: 552.3689, found: 552.3688.

General procedure (Ⅱ) for the synthesis of *p*-QMs (3a-3u)



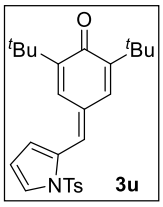
To a solution of 2,6-di-*tert*-butylphenol **S-3** (10 mmol) in toluene (30 mL) was added different aldehyde **S-4** (10 mmol). The reaction mixture was heated in a dry Schlenk tube to reflux. Piperidine (20 mmol) was added drop wise slowly (approx. 0.5 h), and the reaction mixture continued to reflux for 12 h. After the mixture had cooled just below the boiling point of toluene, acetic anhydride (20 mmol) was added, and then the solution was stirred for one hour. The residue was extracted three times with dichloromethane. The combined organic layers were washed with water and brine sequentially, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (pure PE to PE/EA = 200:1, R_f = 0.9-0.6) to afford the corresponding product yellow to red solid **3**

Compounds **3a-s** are known products, their preparation followed the reported procedure.[2]



2,6-Di-tert-butyl-4-((1-tosyl-1H-pyrrol-3-yl)methylene)cyclohexa-2,5-dien-1-one (3t)

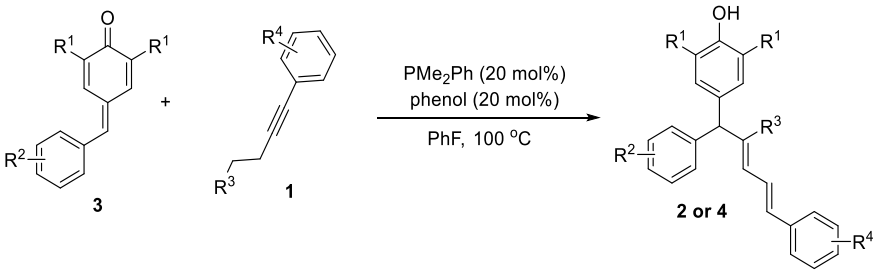
Compound **3t** (2.93 g, 67% yield) was obtained as a red solid following the *general procedure II* from **S-3** (10 mmol) and **S-4** (1-tosyl-1*H*-pyrrole-3-carbaldehyde, 10 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.79 (m, 2H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.39-7.38 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, J_1 = 3.2 Hz, J_2 = 2.4 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.84 (s, 1H), 6.56 (dd, J_1 = 3.2 Hz, J_2 = 2.0 Hz, 1H), 2.43 (s, 3H), 1.31 (s, 9H), 1.30 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.2, 148.7, 147.2, 145.8, 135.3, 135.1, 133.9, 130.7, 130.3, 127.1, 127.0, 125.1, 123.1, 122.4, 114.2, 35.4, 34.9, 30.2, 29.5, 29.4, 21.7; **IR** (neat) ν 2960, 1610, 1567, 1474, 1375, 1358, 1288, 1256, 1240, 1186, 1175, 1104, 1064, 1022, 799, 672 cm^{-1}; **MP**: 93-95 ^oC; **HRMS** Calcd. for $C_{26}H_{32}NO_3S$ $[M+H]^+$: 438.2103, found: 438.2094.



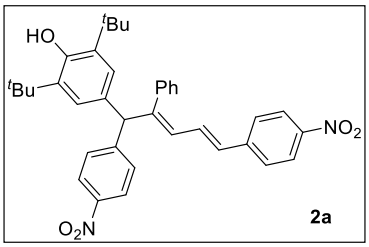
2,6-Di-tert-butyl-4-((1-tosyl-1H-pyrrol-2-yl)methylene)cyclohexa-2,5-dien-1-one (3u)

Compound **3u** (2.44 g, 56% yield) was obtained as a red solid following the *general procedure II* from **S-3** (10 mmol) and **S-4** (1-tosyl-1*H*-pyrrole-2-carbaldehyde, 10 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.50 (dd, J_1 = 3.6 Hz, J_2 = 2.0 Hz, 1H), 7.43 (s, 1H), 7.30-7.26 (m, 3H), 6.99 (d, J = 2.4 Hz, 1H), 6.55 (dt, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 6.41 (t, J = 3.2 Hz, 1H), 2.39 (s, 3H), 1.33 (s, 9H), 1.25 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.7, 149.2, 147.6, 145.5, 135.4, 134.5, 131.5, 131.0, 130.1, 128.6, 127.2, 126.9, 126.1, 121.0, 113.7, 35.3, 35.0, 29.5, 21.7; **IR** (neat) ν 2954, 1607, 1556, 1440, 1358, 1259, 1175, 1146, 1129, 1087, 1016 cm^{-1}; **MP**: 86-88 ^{o}C; **HRMS** Calcd. for $C_{26}H_{30}NO_3S$ [M-H]$^-$: 436.1946, found: 436.1951.

General procedure (III) for the synthesis of compound 2 and 4:

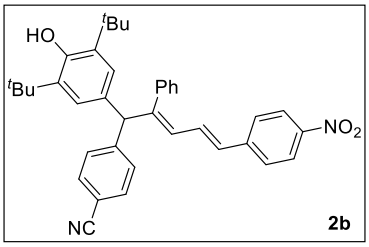


Compounds *p*-quinone methides **3** (1.5 equiv.), alkyne **1** (1.0 equiv.), phenol (0.2 equiv.) and anhydrous fluorobenzene were added to an oven dried vial under N_2 protection, then PMe_2Ph (0.2 equiv.) was added to the above mixture at room temperature. The resulting mixture was stirred at 100 ℃ for 12 hours. The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA = 20/1) to afford the corresponding product **2** and/or **4**.



4-((2Z,4E)-1,5-Bis(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)-2,6-di-tert-butylphenol (2a)

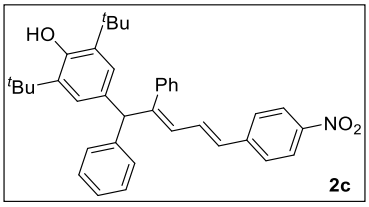
Compound **2a** (50 mg, 85% yield) was obtained as a yellowish solid following the *general procedure III* from **3a** (0.15 mmol, 51 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.40-7.30 (m, 7H), 7.22-7.20 (m, 2H), 6.98-6.91 (m, 3H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.01 (d, *J* = 10.8 Hz, 1H), 5.31 (s, 1H), 5.18 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.8, 150.5, 148.9, 146.5, 143.8, 140.1, 135.9, 130.9, 130.5, 130.31, 130.27, 129.0, 128.4, 127.8, 126.7, 126.0, 124.0, 123.6, 59.3, 34.4, 30.3; **IR** (neat) ν 3626, 2957, 1649, 1590, 1525, 1434, 1344, 1234, 1152, 1107, 1011, 855, 740, 703 cm^{-1}; **MP**: 176-178 ºC; **HRMS** Calcd. for $C_{37}H_{37}N_2O_5$ $[M-H]^-$: 589.2702, found: 589.2711.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)benzonitrile (2b)

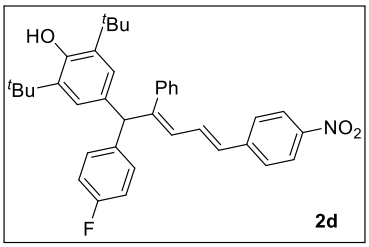
Compound **2b** (57 mg, >99% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.35-7.30 (m, 7H), 7.21-7.19 (m, 2H), 6.97-6.91 (m, 3H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.00 (d, *J* = 11.2 Hz, 1H), 5.26 (s, 1H), 5.17 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 149.1, 148.4, 146.4, 143.8, 140.1, 135.9, 132.1, 130.7, 130.6, 130.4, 130.2, 128.9, 128.3, 127.7, 126.7, 126.0, 124.0, 119.0, 110.2, 59.5, 34.4,

30.2; **IR** (neat) ν 3632, 2960, 2917, 2855, 2227, 1590, 1514, 1432, 1340, 1234, 1107, 971, 827, 745, 700 cm^{-1}; **MP**: 212-213 ^oC; **HRMS** Calcd. for $C_{38}H_{37}N_2O_3$ $[M-H]^-$: 569.2804, found: 569.2807.



2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-1,2-diphenylpenta-2,4-dien-1-yl)phenol (2c)

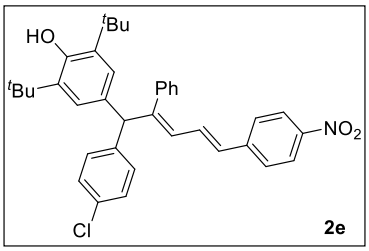
Compound **2c** (47.3 mg, 87% yield) was obtained as a yellow solid following the *general procedure III* from **3c** (0.15 mmol, 44 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.37-7.28 (m, 7H), 7.24-7.19 (m, 5H), 6.99-6.92 (m, 3H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.05 (d, *J* = 11.2 Hz, 1H), 5.20 (s, 1H), 5.10 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.3, 150.9, 146.3, 144.2, 142.5, 140.9, 135.4, 131.8, 131.2, 129.9, 129.8, 129.5, 129.0, 128.2, 128.1, 127.4, 126.5, 126.4, 126.1, 124.0, 59.6, 34.3, 30.3; **IR** (neat) ν 3629, 2957, 2920, 2869, 1587, 1513, 1434, 1338, 1231, 1107, 971, 864, 742, 703 cm^{-1}; **MP**: 66-68 ^oC; **HRMS** Calcd. for $C_{37}H_{38}NO_3$ $[M-H]^-$: 544.2852, found: 544.2853.



2,6-Di-tert-butyl-4-((2Z,4E)-1-(4-fluorophenyl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)phenol (2d)

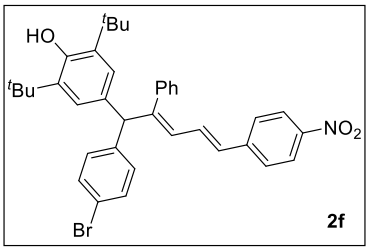
Compound **2d** (45.5 mg, 81% yield) was obtained as a yellowish solid following the *general procedure III* from **3d** (0.15 mmol, 47 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.35-7.28 (m, 5H), 7.20-7.16 (m, 4H), 7.01-6.97 (m, 2H), 6.95-6.91 (m, 3H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.02 (d, *J* = 11.0 Hz, 1H), 5.18 (s, 1H), 5.12 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR**

(100 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.4 Hz), 152.4, 150.6, 146.3, 144.1, 140.7, 138.2, 135.6, 131.7, 131.0, 130.9 (d, *J* = 7.7 Hz), 130.1, 129.8, 129.0, 128.1, 127.5, 126.6, 126.0, 124.0, 115.1 (d, *J* = 20.9 Hz), 58.8, 34.3, 30.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.53 to -116.61 (m); **IR** (neat) ν 3632, 2960, 2912, 1587, 1505, 1432, 1340, 1228, 1158, 1110, 974, 830, 742, 703 cm^{-1}; **MP:** 74-75 ºC; **HRMS** Calcd. for $C_{37}H_{37}FNO_3$ $[M-H]^-$: 562.2757, found: 562.2762.



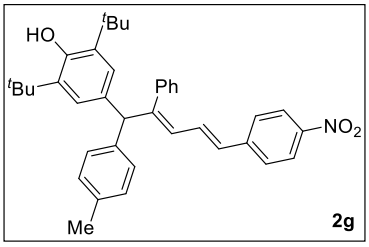
2,6-Di-tert-butyl-4-((2Z,4E)-1-(4-chlorophenyl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)phenol (2e)

Compound **2e** (45.0 mg, 78% yield) was obtained as a yellowish solid following the *general procedure III* from **3e** (0.15 mmol, 49 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.35-7.28 (m, 7H), 7.20-7.14 (m, 4H), 6.97-6.90 (m, 3H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.02 (d, *J* = 10.8 Hz, 1H), 5.17 (s, 1H), 5.12 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.4, 150.2, 146.4, 144.1, 141.2, 140.6, 135.7, 132.1, 131.3, 131.0, 130.8, 130.2, 129.9, 129.0, 128.4, 128.2, 127.5, 126.6, 126.0, 124.0, 58.9, 34.3, 30.3; **IR** (neat) ν 3626, 2957, 2915, 2867, 1587, 1514, 1432, 1338, 1107, 1014, 971, 827, 748, 700 cm^{-1}; **MP:** 184-185 ºC; **HRMS** Calcd. for $C_{37}H_{37}NO_3Cl$ $[M-H]^-$: 578.2462, found: 578.2455.



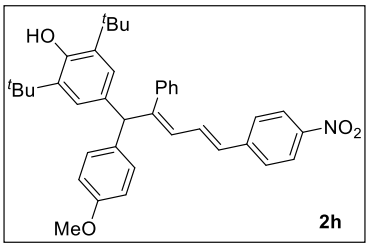
4-((2Z,4E)-1-(4-bromophenyl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)-2,6-di-tert-butylphenol (2f)

Compound **2f** (52.2 mg, 84% yield) was obtained as a yellowish solid following the *general procedure III* from **3f** (0.15 mmol, 56 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.2 Hz, 2H), 7.43-7.41 (m, 2H), 7.35-7.28 (m, 5H), 7.20-7.17 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.97-6.90 (m, 3H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.02 (d, *J* = 11.2 Hz, 1H), 5.15 (s, 1H), 5.12 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.4, 150.1, 146.4, 144.1, 141.7, 140.6, 135.7, 131.3, 131.2, 130.9, 130.3, 130.0, 129.0, 128.2, 127.5, 126.6, 126.0, 124.0, 120.2, 59.0, 34.3, 30.3; **IR** (neat) ν 3626, 2960, 2864, 1593, 1516, 1482, 1434, 1338, 1011, 974, 830, 745, 703 cm^{-1}; **MP:** 181-183 °C; **HRMS** Calcd. for $C_{37}H_{37}NO_3Br$ [M-H]$^-$: 622.1957, found: 622.1948.



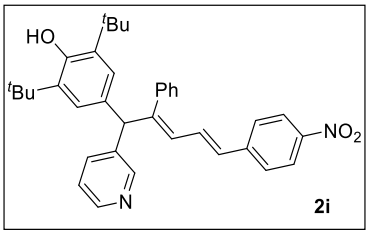
2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-2-phenyl-1-(p-tolyl)penta-2,4-dien-1-yl)phenol (2g)

Compound **2g** (34.6 mg, 62% yield) was obtained as a yellowish solid following the *general procedure III* from **3g** (0.15 mmol, 46 mg) and **1a** (0.1 mmol, 25 mg) stirred at 120 °C in $PhCF_3$ for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.34-7.27 (m, 5H), 7.20-7.18 (m, 2H), 7.14-7.08 (m, 4H), 6.98-6.91 (m, 3H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.05 (d, *J* = 11.2 Hz, 1H), 5.15 (s, 1H), 5.08 (s, 1H), 2.33 (s, 3H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.2, 151.2, 146.2, 144.3, 141.0, 139.5, 135.8, 135.4, 132.0, 131.3, 129.8, 129.6, 129.3, 129.0, 129.0, 128.1, 127.3, 126.5, 126.1, 124.0, 59.2, 34.3, 30.3, 21.1; **IR** (neat) ν 3629, 2960, 2917, 1590, 1514, 1432, 1338, 1231, 1107, 971, 824, 745, 703 cm^{-1}; **MP**: 72-75 °C; **HRMS** Calcd. for $C_{38}H_{40}NO_3$ [M-H]$^-$: 558.3014, found: 558.3019.



2,6-Di-tert-butyl-4-((2Z,4E)-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)phenol (2h)

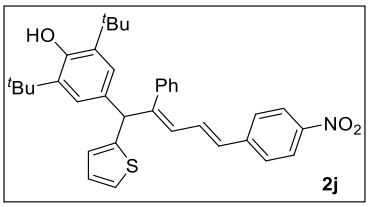
Compound **2h** (24.7 mg, 43% yield) was obtained as a yellowish solid following the *general procedure III* from **3h** (0.15 mmol, 49 mg) and **1a** (0.1 mmol, 25 mg) stirred at 120 ^{o}C in $PhCF_3$ for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.33-7.27 (m, 5H), 7.19-7.17 (m, 2H), 7.13-7.10 (m, 2H), 6.97-6.91 (m, 3H), 6.86-6.83 (m, 2H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.04 (d, *J* = 10.8 Hz, 1H), 5.14 (s, 1H), 5.08 (s, 1H), 3.80 (s, 3H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 158.0, 152.2, 151.3, 146.3, 144.3, 141.0, 135.4, 134.6, 132.2, 131.3, 130.4, 129.8, 129.5, 129.0, 128.1, 127.3, 126.5, 126.0, 124.0, 113.6, 58.8, 55.2, 34.3, 30.3; **IR**(neat) ν 3632, 2963, 2872, 1587, 1508, 1432, 1340, 1248, 1177, 1104, 1033, 974, 833, 742, 706 cm^{-1}; **MP**: 86-87 ^{o}C; **HRMS** Calcd. for $C_{38}H_{40}NO_4$ $[M-H]^-$: 574.2963, found: 574.2967.



2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-2-phenyl-1-(pyridin-3-yl)penta-2,4-dien-1-yl)phenol (2i)

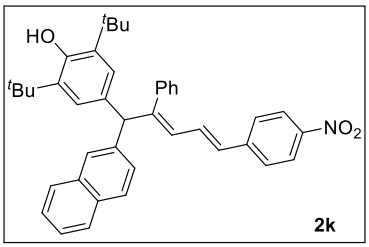
Compound **2i** (45.2 mg, 83% yield) was obtained as a yellowish solid following the *general procedure III* from **3i** (0.15 mmol, 44 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49-8.46 (m, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.36-7.29 (m, 5H), 7.25-7.20 (m, 3H), 6.97-6.91 (m, 3H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.03 (d, *J* = 11.2 Hz, 1H), 5.22 (s, 1H), 5.18 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 150.9, 149.4, 147.7, 146.4, 143.9, 140.2, 138.2, 136.8, 135.8, 130.7, 130.5, 130.2, 129.0, 128.3, 127.6, 126.6, 125.9, 124.0, 123.2,

57.1, 34.3, 30.3; **IR** (neat) ν 3629, 1956, 1869, 1589, 1513, 1434, 1340, 1234, 1107, 1028, 971, 867, 827, 738, 703 cm^{-1}; **MP**: 84-86 ^{o}C; **HRMS** Calcd. for $C_{36}H_{37}N_2O_3$ [M-H]$^-$: 545.2810, found: 545.2819.



2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-2-phenyl-1-(thiophen-2-yl)penta-2,4-dien-1-yl)phenol (2j)

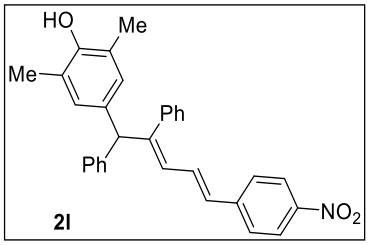
Compound **2j** (38 mg, 69% yield, *Z/E* = 8/1) was obtained as a yellowish solid following the *general procedure III* from **3j** (0.15 mmol, 45 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.39-7.29 (m, 6H), 7.22 (dd, J_1 = 4.2 Hz, J_2 = 1.2 Hz, 1H), 7.16-7.14 (m, 2H), 7.02 (s, 2H), 6.97-6.95 (m, 1H), 6.80-6.79 (m, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 11.2 Hz, 1H), 5.33 (s, 1H), 5.12 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 150.5, 147.0, 146.3, 144.1, 140.1, 135.5, 131.7, 131.0, 130.3, 129.2, 128.9, 128.1, 127.5, 126.7, 126.63, 126.60, 126.4, 125.6, 124.5, 124.0, 54.7, 34.3, 30.3; **IR** (neat) ν 3632, 2957, 2920, 2872, 1589, 1513, 1432, 1338, 1234, 1152, 1107, 971, 830, 740, 703 cm^{-1}; **MP**: 58-60 ^{o}C; **HRMS** Calcd. for $C_{35}H_{36}NO_3S$ [M-H]$^-$: 550.2421, found: 550.2431.



2,6-Di-tert-butyl-4-((2Z,4E)-1-(naphthalen-2-yl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)phenol (2k)

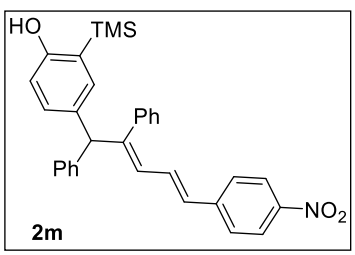
Compound **2k** (33.9 mg, 57% yield) was obtained as a yellowish solid following the *general procedure III* from **3k** (0.15 mmol, 51.6 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.84-7.76 (m,

3H), 7.59 (s, 1H), 7.48-7.42 (m, 3H), 7.34-7.24 (m, 7H), 7.03 (s, 2H), 6.98 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.10 (d, J = 11.2 Hz, 1H), 5.37 (s, 1H), 5.12 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.4, 150.7, 146.3, 144.2, 140.9, 140.3, 135.6, 133.4, 132.2, 131.7, 131.2, 130.1, 129.0, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 126.5, 126.2, 125.9, 125.6, 124.0, 59.7, 34.3, 30.3; **IR** (neat) ν 3632, 2963, 2867, 1587, 1514, 1434, 1338, 1262, 1107, 1025, 974, 742, 703 cm $^{-1}$; **MP**: 84-86 ^{o}C; **HRMS** Calcd. for $C_{41}H_{40}NO_3$ [M-H]$^-$: 594.3008, found: 594.3010.



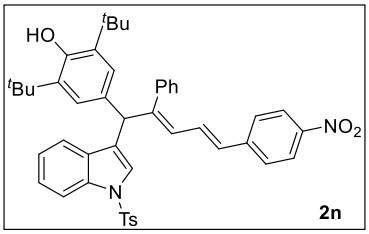
2,6-Dimethyl-4-((2Z,4E)-5-(4-nitrophenyl)-1,2-diphenylpenta-2,4-dien-1-yl)phenol (2l)

Compound **2l** (42.4 mg, 92% yield) was obtained as a white solid following the *general procedure III* from **3l** (0.15 mmol, 31.5 mg) and **1a** (0.1 mmol, 25 mg) stirred at room temperature for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.36-7.33 (m, 3H), 7.31-7.28 (m, 4H), 7.25-7.24 (m, 2H), 7.22-7.20 (m, 3H), 6.96 (dd, J_1 = 15.6 Hz, J_2 =10.8 Hz, 1H), 6.81 (s, 2H), 6.49 (d, J = 15.6 Hz, 1H), 6.03 (d, J = 10.8 Hz, 1H), 5.17 (s, 1H), 4.55 (brs, 1H), 2.21 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 150.8, 150.5, 146.4, 144.2, 142.3, 141.0, 133.1, 131.1, 130.2, 129.9, 129.7, 129.5, 128.9, 128.3, 128.2, 127.5, 126.54, 126.46, 124.0, 122.9, 58.9, 16.0; **IR** (neat) ν 3643, 2923, 2850, 1587, 1488, 1336, 1197, 971, 745, 700 cm^{-1}; **MP:** 78-80 ^{o}C; **HRMS** Calcd. for $C_{31}H_{26}NO_3$ [M-H]$^-$: 460.1913, found: 460.1923.



4-((2Z,4E)-5-(4-nitrophenyl)-1,2-diphenylpenta-2,4-dien-1-yl)-2-(trimethylsilyl)phenol (2m)

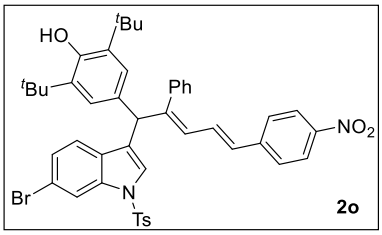
Compound **2m** (23.2 mg, 46% yield, 6.7:1 *E/Z*) was obtained as a yellowish solid following the *general procedure III* from **3m** (0.15 mmol, 49 mg) and **1a** (0.1 mmol, 25 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.35-7.28 (m, 8H), 7.24-7.20 (m, 4H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.95 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.03 (d, *J* = 11.2 Hz, 1H), 5.23 (s, 1H), 4.81 (s, 1H), 0.26 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.0, 150.5, 146.3, 144.1, 142.2, 140.8, 136.4, 133.2, 131.6, 131.0, 130.2, 130.0, 129.5, 128.9, 128.3, 128.2, 127.5, 126.6, 126.5, 125.2, 124.0, 114.4, 58.9, -1.0; **IR** (neat) ν 3494, 2951, 2920, 1587, 1511, 1398, 1338, 1073, 971, 838, 700 cm^{-1}; **MP:** 70-72 °C; **HRMS** Calcd. for $C_{32}H_{30}NO_3Si$ $[M-H]^-$: 504.1995, found: 504.1988.



2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-2-phenyl-1-(1-tosyl-1H-indol-3-yl)penta-2,4-dien-1-yl)phenol (2n)

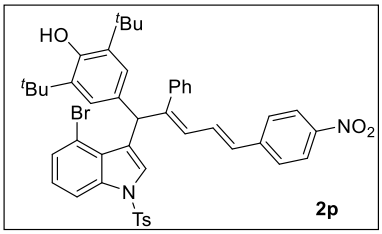
Compound **2n** (35.0 mg, 95% yield) was obtained as a yellowish solid following the *general procedure III* from **3n** (0.075 mmol, 37 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.64-7.61 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.36-7.28 (m, 6H), 7.24-7.16 (m, 5H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.99-6.92 (m, 3H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.08 (d, *J* = 11.2 Hz, 1H), 5.17 (s, 1H), 5.14 (s, 1H), 2.35 (s, 3H), 1.37 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 147.5, 146.3, 144.7, 144.0, 140.5, 135.7, 135.1, 130.8, 130.5, 130.4, 130.2, 129.8, 129.3, 129.0, 128.2, 127.6, 126.7, 126.6, 126.2, 126.0, 125.5, 124.8, 124.0, 123.3, 120.3, 113.8, 50.7, 34.3, 30.3, 21.6; **IR** (neat) ν 3629, 2957, 1590, 1511, 1434, 1369, 1340, 1172, 1118, 977, 745, 703, 660, 570 cm^{-1}; **MP:** 104-106 °C; **HRMS**

Calcd. for $C_{46}H_{45}N_2O_5S$ [M-H]$^-$: 737.3054, found: 737.3049.



4-((2Z,4E)-1-(6-bromo-1-tosyl-1H-indol-3-yl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)-2,6-di-tert-butylphenol (2o)

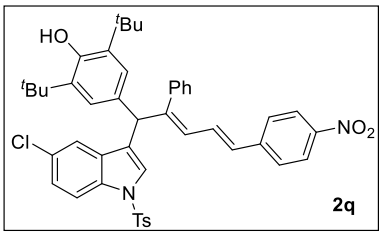
Compound **2o** (37.9 mg, 93% yield) was obtained as a yellowish solid following the *general procedure III* from **3o** (0.075 mmol, 42 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.6 Hz, 1H), 8.10-8.08 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.34-7.29 (m, 6H), 7.27 (s, 1H), 7.25-7.19 (m, 4H), 6.99-6.92 (m, 4H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.05 (d, *J* = 11.2 Hz, 1H), 5.17 (s, 1H), 5.15 (s, 1H), 2.39 (s, 3H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 147.2, 146.4, 145.1, 143.9, 140.2, 136.3, 135.8, 134.8, 130.7, 130.6, 130.0, 129.9, 129.4, 129.3, 128.9, 128.3, 127.7, 126.7, 126.6, 126.3, 125.9, 125.4, 124.0, 121.5, 118.5, 116.9, 115.2, 50.6, 34.3, 30.3, 21.6; **IR** (neat) ν 3632, 2957, 2923, 1590, 1516, 1432, 1372, 1340, 1172, 1129, 980, 810, 742, 703, 669, 576 cm^{-1}; **MP:** 102-104 ^{o}C; **HRMS** Calcd. for $C_{46}H_{44}N_2O_5SBr$ [M-H]$^-$: 815.2160, found: 815.2175.



4-((2Z,4E)-1-(4-bromo-1-tosyl-1H-indol-3-yl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)-2,6-di-tert-butylphenol (2p)

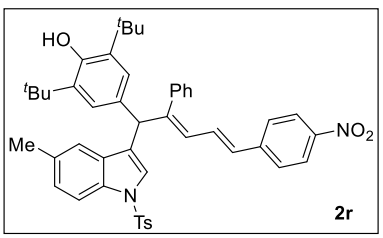
Compound **2p** (30.2 mg, 74% yield, 9.6:1 *E/Z*) was obtained as a yellowish solid following the *general procedure III* from **3p** (0.075 mmol, 42 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.38-7.28 (m, 8H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15-7.08 (m, 2H), 7.05-7.02 (m, 3H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.92 (d, *J* =

11.2 Hz, 1H), 5.90 (s, 1H), 5.15 (s, 1H), 2.37 (s, 3H), 1.40 (s, 18H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 152.5, 148.6, 146.3, 145.1, 144.2, 140.2, 136.9, 135.7, 134.6, 131.1, 131.0, 130.4, 129.9, 129.4, 129.2, 128.4, 128.3, 128.1, 127.5, 126.7, 126.6, 126.2, 125.9, 125.5, 124.0, 115.2, 114.7, 113.0, 50.0, 34.4, 30.4, 21.6; **IR** (neat) ν 3632, 2960, 1590, 1516, 1432, 1375, 1338, 1169, 982, 742, 700, 666, 570 cm^{-1}; **MP**: 108-110 ºC; **HRMS** Calcd. for $C_{46}H_{44}N_2O_5SBr$ $[M-H]^-$: 815.2160, found: 815.2174.



2,6-Di-tert-butyl-4-((2Z,4E)-1-(5-chloro-1-tosyl-1H-indol-3-yl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)phenol (**2q**)

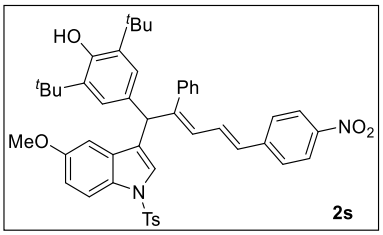
Compound **2q** (35.1 mg, 91% yield) was obtained as a yellowish solid following the *general procedure III* from **3q** (0.075 mmol, 39 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.35-7.33 (m, 6H), 7.27-7.19 (m, 5H), 7.06 (s, 1H), 7.00-6.93 (m, 3H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.06 (d, *J* = 11.2 Hz, 1H), 5.18 (s, 1H), 5.15 (s, 1H), 2.37 (s, 3H), 1.39 (s, 18H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 152.8, 147.2, 146.4, 145.0, 143.9, 140.2, 135.8, 134.7, 134.0, 131.7, 130.7, 130.6, 129.9, 129.4, 129.1, 129.0, 128.3, 127.7, 127.2, 126.7, 126.6, 125.5, 125.4, 125.1, 124.0, 120.0, 115.2, 114.9, 50.5, 34.3, 30.3, 21.6; **IR** (neat) ν 3632, 2957, 2920, 1590, 1514, 1440, 1372, 1340, 1172, 1121, 974, 813, 700, 672, 584, 536 cm^{-1}; **MP:** 239-241 ºC; **HRMS** Calcd. for $C_{46}H_{44}N_2O_5SCl$ $[M-H]^-$: 771.2659, found: 771.2665.



2,6-Di-tert-butyl-4-((2Z,4E)-1-(5-methyl-1-tosyl-1H-indol-3-yl)-5-(4-nitrophenyl)-

2-phenylpenta-2,4-dien-1-yl)phenol (2r)

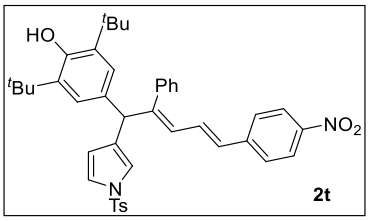
Compound **2r** (32.7 mg, 87% yield) was obtained as a yellowish solid following the *general procedure III* from **3r** (0.075 mmol, 37 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.37-7.31 (m, 5H), 7.25-7.23 (m, 2H), 7.19-7.17 (m, 3H), 7.13-7.10 (m, 1H), 7.01-6.94 (m, 4H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.09 (d, *J* = 11.2 Hz, 1H), 5.16 (s, 1H), 5.15 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 147.6, 146.4, 144.6, 144.1, 140.5, 135.7, 135.1, 134.0, 132.9, 130.9, 130.8, 130.4, 130.3, 129.7, 129.2, 129.0, 128.2, 127.6, 126.64, 126.60, 126.2, 126.1, 125.5, 124.0, 120.1, 113.5, 50.7, 34.4, 30.4, 21.6, 21.4; **IR** (neat) ν 3632, 2954, 2867, 1590, 1514, 1434, 1369, 1338, 1172, 1118, 977, 807, 675 cm^{-1}; **MP:** 233-235 °C; **HRMS** Calcd. for $C_{47}H_{47}N_2O_5S$ $[M-H]^-$: 751.3206, found: 751.3197.



2,6-Di-tert-butyl-4-((2Z,4E)-1-(5-methoxy-1-tosyl-1H-indol-3-yl)-5-(4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)phenol (2s)

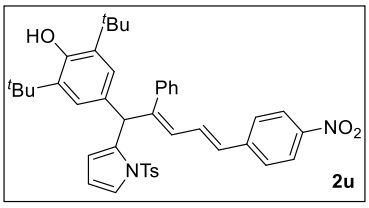
Compound **2s** (32.6 mg, 85% yield) was obtained as a yellowish solid following the *general procedure III* from **3s** (0.075 mmol, 39 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.35-7.32 (m, 5H), 7.24-7.21 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.00-6.97 (m, 4H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.10 (d, *J* = 11.2 Hz, 1H), 5.16 (s, 1H), 5.12 (s, 1H), 3.72 (s, 3H), 2.36 (s, 3H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.3, 152.7, 147.3, 146.4, 144.6, 144.0, 140.5, 135.8, 135.0, 131.6, 130.8, 130.5, 130.4, 130.2, 129.7, 129.4, 128.9, 128.3, 127.6, 126.7, 126.6, 126.4, 125.5, 124.0, 114.8, 113.3, 103.1, 55.5, 50.8, 34.3, 30.4, 21.6; **IR** (neat) ν 3617, 2960, 2920, 2856, 1590, 1514, 1432, 1339, 1170, 1029, 978, 798 cm^{-1}; **MP:** 114-116 °C; **HRMS** Calcd. for $C_{47}H_{47}N_2O_6S$

[M-H]$^-$: 767.3155, found: 767.3146.



2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-2-phenyl-1-(1-tosyl-1H-pyrrol-3-yl)penta-2,4-dien-1-yl)phenol (2t)

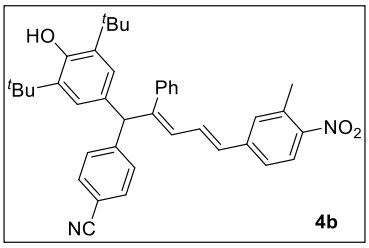
Compound **2t** (28.2 mg, 82% yield) was obtained as a yellowish solid following the *general procedure III* from **3t** (0.075 mmol, 33 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.28-7.26 (m, 5H), 7.12 (dd, J_1 = 3.2 Hz, J_2 = 2.4 Hz, 1H), 7.07-7.05 (m, 2H), 6.91-6.84 (m, 3H), 6.77 (brs, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.20 (dd, J_1 = 3.2 Hz, J_2 = 1.6 Hz, 1H), 6.13 (d, *J* = 10.8 Hz, 1H), 5.10 (s, 1H), 4.90 (s, 1H), 2.42 (s, 3H), 1.34 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.4, 149.9, 146.3, 144.7, 144.1, 140.3, 136.1, 135.4, 131.4, 131.3, 131.1, 130.0, 129.9, 129.1, 128.7, 128.0, 127.4, 126.64, 126.56, 125.5, 124.0, 121.2, 119.7, 115.4, 52.2, 34.3, 30.3, 21.6; **IR** (neat) ν 3629, 2957, 1590, 1514, 1432, 1369, 1341, 1172, 1098, 1059, 978, 703, 675, 587 cm^{-1}; **MP**: 85-87 ^{o}C; **HRMS** Calcd. for $C_{42}H_{43}N_2O_5S$ [M-H]$^-$: 687.2893, found: 687.2895.



2,6-Di-tert-butyl-4-((2Z,4E)-5-(4-nitrophenyl)-2-phenyl-1-(1-tosyl-1H-pyrrol-2-yl)penta-2,4-dien-1-yl)phenol (2u)

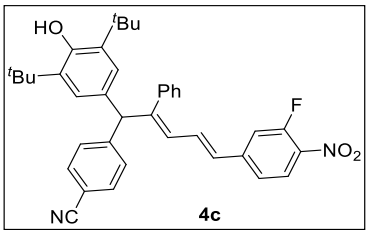
Compound **2u** (23.0 mg, 67% yield) was obtained as a yellowish solid following the *general procedure III* from **3u** (0.075 mmol, 33 mg) and **1a** (0.05 mmol, 13 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, J_1 = 3.2 Hz, J_2 = 1.6 Hz, 1H), 7.34-7.29 (m, 7H), 7.08 (d, *J* = 8.0 Hz,

2H), 6.83 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.75 (s, 2H), 6.32 (d, J = 15.6 Hz, 1H), 6.24 (t, J = 3.2 Hz, 1H), 5.85-5.84 (m, 1H), 5.75 (d, J = 11.2 Hz, 1H), 5.65 (s, 1H), 5.03 (s, 1H), 2.18 (s, 3H), 1.32 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.4, 148.8, 146.3, 144.4, 144.2, 140.1, 136.6, 136.3, 135.4, 130.9, 130.4, 129.9, 129.7, 129.3, 128.8, 128.1, 127.4, 126.7, 126.5, 125.7, 124.0, 123.3, 116.5, 111.3, 51.0, 34.2, 30.3, 21.4; **IR** (neat) ν 3632, 2957, 2923, 2872, 1590, 1514, 1432, 1338, 1172, 974, 810, 672, 587, 545 cm^{-1}; **MP:** 81-83 ^{o}C; **HRMS** (ESI) Calcd. for $C_{42}H_{43}N_2O_5S$ [M-H]$^-$: 687.2893, found: 687.2885.



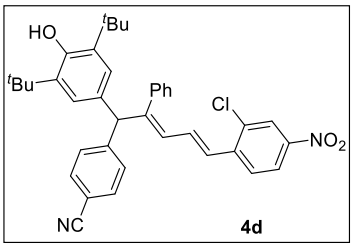
4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-(3-methyl-4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)benzonitrile (**4b**)

Compound **4b** (43.2 mg, 74% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1b** (0.1 mmol, 27 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.36-7.28 (m, 5H), 7.24-7.14 (m, 4H), 6.94-6.85 (m, 3H), 6.45 (d, J = 15.6 Hz, 1H), 5.98 (d, J = 11.2 Hz, 1H), 5.26 (s, 1H), 5.17 (s, 1H), 2.55 (s, 3H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 148.5, 147.3, 142.3, 140.2, 135.9, 134.4, 132.1, 130.8, 130.53, 130.47, 130.2, 130.0, 129.6, 129.0, 128.3, 127.7, 126.0, 125.4, 124.1, 120.6, 119.0, 115.2, 110.1, 59.5, 34.3, 30.2, 21.0; **IR** (neat) ν 3626, 2958, 2228, 1604, 1577, 1513, 1434, 1338, 1234, 1152, 1118, 971, 840, 738, 703 cm^{-1}; **MP:** 179-181 ^{o}C; **HRMS** Calcd. for $C_{39}H_{39}N_2O_3$ [M-H]$^-$: 583.2961, found: 583.2964.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-(3-fluoro-4-nitrophenyl)-2-phenylpenta-2,4-dien-1-yl)benzonitrile (4c)

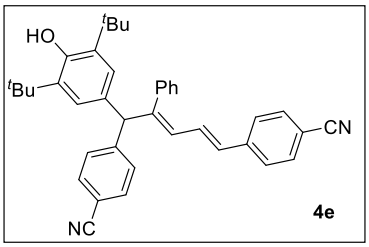
Compound **4c** (38.8 mg, 66% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1c** (0.1 mmol, 27 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.93 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.37-7.31 (m, 5H), 7.19-7.16 (m, 2H), 7.10- 7.05 (m, 2H), 6.94-6.87 (m, 3H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.99 (d, *J* = 10.8 Hz, 1H), 5.25 (s, 1H), 5.16 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.0 (d, *J* = 263.1 Hz), 152.7, 150.3, 148.2, 145.6 (d, *J* = 8.5 Hz), 140.0, 136.0, 132.2, 131.8, 130.3, 130.2, 130.0, 129.6, 128.9, 128.4, 127.9, 126.5, 126.0, 122.0 (d, *J* = 3.3 Hz), 118.9, 115.0 (d, *J* = 21.3 Hz), 110.3, 59.6, 34.4, 30.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –116.82 to -116.88 (m). **IR** (neat) ν 3629, 2957, 2917, 2869, 2225, 1598, 1516, 1432, 1338, 1234, 968, 841, 734, 703 cm^{-1}; **MP:** 89-91 ºC; **HRMS** Calcd. for $C_{38}H_{36}FN_2O_3$ [M-H]$^-$: 587.2710, found: 587.2707.



4d

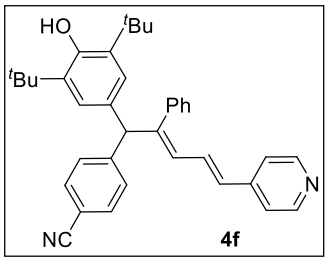
4-((2Z,4E)-5-(2-chloro-4-nitrophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylpenta-2,4-dien-1-yl)benzonitrile (4d)

Compound **4d** (45.2 mg, 75% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1d** (0.1 mmol, 29 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.4 Hz, 1H), 7.95 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.35-7.30 (m, 5H), 7.19-7.16 (m, 2H), 6.97-6.84 (m, 4H), 6.08 (dd, J_1 = 10.2 Hz, J_2 = 1.2 Hz, 1H), 5.26 (s, 1H), 5.17 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 150.3, 148.2, 146.4, 141.7, 140.0, 135.9, 133.2, 132.8, 132.2, 130.4, 130.2, 128.9, 128.3, 127.8, 126.7, 126.4, 126.0, 125.2, 121.7, 119.0, 110.3, 59.6, 34.4, 30.3; **IR** (neat) ν 3626, 2954, 2867, 2225, 1576, 1518, 1432, 1342, 1231, 1118, 974, 895, 734, 700 cm^{-1}; **MP:** 182-184 ºC; **HRMS** Calcd. for $C_{38}H_{36}N_2O_3Cl$ [M-H]$^-$: 603.2414, found: 603.2409.



4,4'-((1E,3Z)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylpenta-1,3-diene-1,5-diyl)dibenzonitrile (4e)

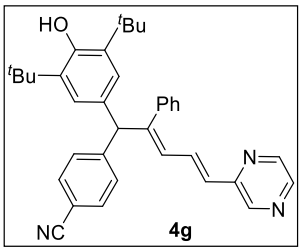
Compound **4e** (37.3 mg, 68% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1e** (0.1 mmol, 23 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.34-7.28 (m, 7H), 7.20-7.18 (m, 2H), 6.92-6.85 (m, 3H), 6.46 (d, *J* = 15.6 Hz, 1H), 5.98 (d, *J* = 10.8 Hz, 1H), 5.25 (s, 1H), 5.16 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 148.44, 148.40, 141.8, 140.2, 135.8, 132.3, 132.1, 131.1, 130.4, 130.2, 129.6, 128.9, 128.3, 127.6, 126.6, 126.0, 119.0, 110.19, 110.16, 59.4, 34.3, 30.2; **IR** (neat) ν 3629, 2956, 2225, 1598, 1497, 1434, 1234, 1152, 1118, 971, 813, 734, 700, 550 cm^{-1}; **MP:** 199-201 °C; **HRMS** Calcd. for $C_{39}H_{37}N_2O$ $[M-H]^-$: 549.2906, found: 549.2910.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-5-(pyridin-4-yl)penta-2,4-dien-1-yl)benzonitrile (4f)

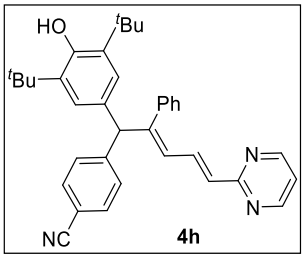
Compound **4f** (33.1 mg, 63% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1f** (0.1 mmol, 21 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.60-7.58 (m, 2H), 7.35-7.28 (m, 5H), 7.19-7.17 (m, 2H), 7.08 (d, *J* = 5.6 Hz, 2H), 6.97 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.91 (s, 2H), 6.39 (d, *J* = 15.6 Hz, 1H), 5.98 (d, *J* = 11.2 Hz, 1H), 5.25 (s, 1H), 5.19 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 149.9, 148.8,

148.4, 144.5, 140.1, 135.9, 132.1, 130.4, 130.32, 130.25, 130.2, 128.9, 128.3, 127.7, 126.0, 120.6, 119.0, 110.2, 59.5, 34.3, 30.2; **IR** (neat) ν 3629, 2957, 2869, 2225, 1590, 1434, 1234, 1118, 971, 737, 703 cm^{-1}; **MP:** 94-96 ºC; **HRMS** Calcd. for $C_{37}H_{37}N_2O$ $[M-H]^-$: 525.2906, found: 525.2899.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-5-(pyrazin-2-yl)penta-2,4-dien-1-yl)benzonitrile (4g)

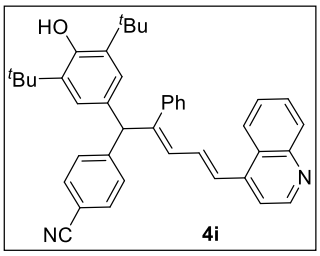
Compound **4g** (35.2 mg, 67% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1g** (0.1 mmol, 21 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42-8.39 (m, 2H), 8.28 (d, *J* = 2.4 Hz, 1H), 7.60-7.58 (m, 2H), 7.39-7.27 (m, 6H), 7.20-7.17 (m, 2H), 6.92 (s, 2H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.05 (d, *J* = 11.2 Hz, 1H), 5.26 (s, 1H), 5.16 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 151.4, 149.8, 148.4, 144.2, 143.4, 142.2, 140.1, 135.9, 132.4, 132.1, 130.5, 130.3, 130.2, 128.93, 128.87, 128.3, 127.7, 126.0, 119.0, 110.2, 59.6, 34.4, 30.3; **IR** (neat) ν 3632, 2960, 2869, 2231, 1627, 1604, 1471, 1434, 1398, 1231, 1118, 1016, 980, 737, 700 cm^{-1}; **MP:** 92-94 ºC; **HRMS** Calcd. for $C_{36}H_{36}N_3O$ $[M-H]^-$: 526.2858, found: 526.2850.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-5-(pyrimidin-2-yl)penta-2,4-dien-1-yl)benzonitrile (4h)

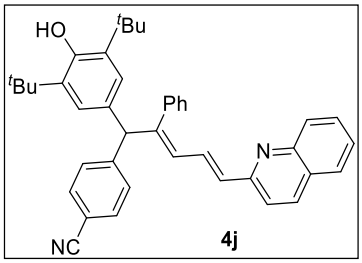
Compound **4h** (42.6 mg, 81% yield) was obtained as a yellowish solid following the

general procedure III from **3b** (0.15 mmol, 48 mg) and **1h** (0.1 mmol, 21 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.9 Hz, 2H), 7.63-7.56 (m, 3H), 7.35-7.28 (m, 5H), 7.20-7.18 (m, 2H), 7.00-6.96 (m, 1H), 6.92 (s, 2H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.10 (d, *J* = 11.2 Hz, 1H), 5.26 (s, 1H), 5.16 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 164.8, 156.9, 152.7, 150.2, 148.4, 140.2, 135.9, 135.3, 132.2, 132.1, 130.6, 130.4, 130.2, 129.0, 128.3, 127.6, 126.0, 119.0, 118.2, 110.2, 59.7, 34.4, 30.3; **IR** (neat) ν 3638, 2957, 2920, 2872, 2231, 1607, 1564, 1550, 1432, 1412, 1234, 1152, 1118, 985, 737, 703 cm^{-1}; **MP:** 82-84 °C; **HRMS** Calcd. for $C_{36}H_{36}N_3O$ $[M-H]^-$: 526.2858, found: 526.2851.



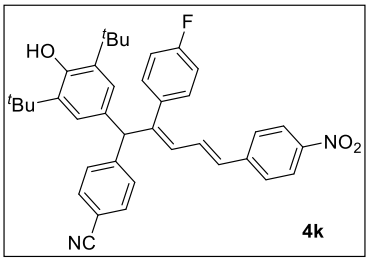
4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-5-(quinolin-4-yl)penta-2,4-dien-1-yl)benzonitrile (4i)

Compound **4i** (43.9 mg, 76% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1i** (0.1 mmol, 26 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.8 Hz, 1H), 8.09-8.06 (m, 2H), 7.71-7.66 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.55-7.51 (m, 1H), 7.39-7.37 (m, 2H), 7.34-7.27 (m, 4H), 7.23-7.18 (m, 3H), 7.05 (dd, J_1 = 15.2 Hz, J_2 = 10.8 Hz, 1H), 6.96 (s, 2H), 6.14 (d, *J* = 10.8 Hz, 1H), 5.29 (s, 1H), 5.19 (s, 1H), 1.40 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 149.9, 149.0, 148.6, 148.5, 142.5, 140.2, 136.0, 132.2, 132.1, 130.6, 130.4, 130.3, 130.0, 129.2, 129.0, 128.3, 127.7, 126.7, 126.4, 126.01, 125.96, 123.2, 119.0, 116.6, 110.3, 59.5, 34.4, 30.3; **IR** (neat) ν 3632, 2954, 2869, 2225, 1604, 1573, 1502, 1434, 1234, 971, 762, 737, 703 cm^{-1}; **MP:** 93-95 °C; **HRMS** Calcd. for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3213, found: 577.3205.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-5-(quinolin-2-yl)penta-2,4-dien-1-yl)benzonitrile (4j)

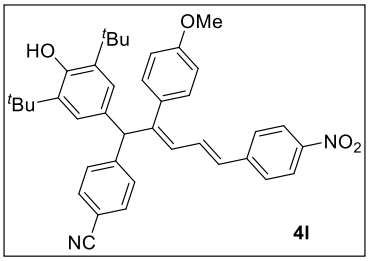
Compound **4j** (41.6 mg, 72% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1j** (0.1 mmol, 26 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.47-7.40 (m, 2H), 7.37-7.33 (m, 4H), 7.31-7.27 (m, 2H), 7.25-7.23 (m, 2H), 6.93 (s, 2H), 6.82-6.76 (m, 1H), 6.10 (d, *J* = 11.2 Hz, 1H), 5.27 (s, 1H), 5.16 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 148.4, 140.3, 135.9, 135.6, 132.2, 132.1, 131.0, 130.7, 130.3, 129.0, 128.3, 127.6, 127.4, 127.1, 126.0, 125.1, 119.0, 118.7, 110.2, 59.6, 34.4, 30.3; **IR** (neat) ν 3629, 2956, 2867, 2225, 1601, 1502, 1434, 1234, 1019, 974, 819, 738, 703 cm^{-1}; **MP:** 97-99 °C; **HRMS** Calcd. for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3213, found: 577.3202.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)-5-(4-nitrophenyl)penta-2,4-dien-1-yl)benzonitrile (4k)

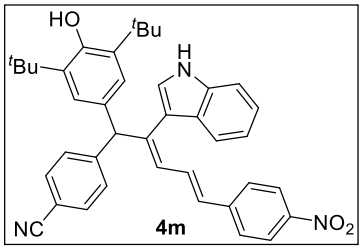
Compound **4k** (51.1 mg, 87% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1k** (0.1 mmol, 27 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.36-7.32 (m, 4H), 7.17-7.13 (m, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.91-6.84 (m, 3H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.01 (d, *J* = 11.2 Hz, 1H), 5.20 (s, 1H), 5.18 (s, 1H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 246.4 Hz), 152.8, 148.0

(d, *J* = 23.6 Hz), 146.6, 143.7, 136.0, 132.2, 131.1, 130.64, 130.56, 130.2, 130.1, 126.7, 125.9, 124.0, 118.9, 115.4 (d, *J* = 21.2 Hz), 110.4, 59.7, 34.4, 30.3; **^{19}F NMR** (376 MHz, $CDCl_3$) -113.53 to -113.61 (m); **IR** (neat) ν 3629, 2957, 2872, 2228, 1587, 1511, 1435, 1336, 1231, 1155, 1107, 974, 850, 745 cm^{-1}; **MP:** 102-104 ^oC; **HRMS** Calcd. for $C_{38}H_{36}FN_2O_3$ $[M-H]^-$: 587.2710, found: 587.2718.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-5-(4-nitrophenyl)penta-2,4-dien-1-yl)benzonitrile (4l)

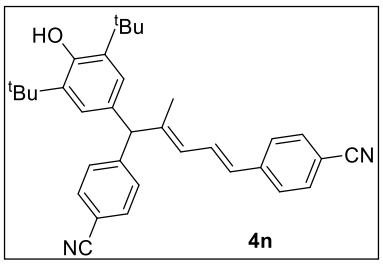
Compound **4l** (49.1 mg, 82% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1l** (0.1 mmol, 28 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.36-7.31 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.98 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.91 (s, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 15.6 Hz, 1H), 5.97 (d, *J* = 10.8 Hz, 1H), 5.24 (s, 1H), 5.16 (s, 1H), 3.82 (s, 3H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.1, 152.7, 148.8, 148.6, 146.4, 144.0, 135.9, 132.4, 132.1, 130.9, 130.6, 130.3, 130.22, 130.18, 130.1, 126.6, 126.0, 124.0, 119.0, 113.7, 110.2, 59.6, 55.2, 34.4, 30.3; **IR** (neat) ν 3626, 2956, 2867, 2228, 1604, 1589, 1511, 1434, 1338, 1247, 1178, 1107, 1028, 971, 844, 830, 736 cm^{-1}; **MP**: 112-114 ^oC; **HRMS** Calcd. for $C_{39}H_{39}N_2O_4$ $[M-H]^-$: 599.2910, found: 599.2914.



4-((2Z,4E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1H-indol-3-yl)-5-(4-

nitrophenyl)penta-2,4-dien-1-yl)benzonitrile (4m)

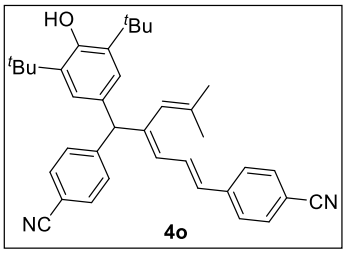
Compound **4m** (52.4 mg, 86% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1m** (0.1 mmol, 29 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.28-7.09 (m, 6H), 6.97-6.92 (m, 5H), 6.75 (s, 1H), 6.61 (d, *J* = 15.2 Hz, 1H), 5.38 (s, 1H), 1.38 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.2, 145.9, 145.6, 144.6, 137.4, 136.5, 135.2, 132.5, 129.5, 128.0, 127.8, 127.5, 127.0, 126.5, 126.1, 125.1, 124.1, 122.9, 121.2, 120.6, 118.5, 114.4, 111.6, 110.6, 63.8, 34.4, 30.1; **IR** (neat) ν 3632, 2960, 2223, 2231, 1584, 1508, 1336, 1234, 1107, 985, 742 cm^{-1}; **MP:** 106-108 °C; **HRMS** Calcd. for $C_{40}H_{38}N_3O_3$ [M-H]$^{-}$: 608.2913, found: 608.2907.



4n

4,4'-((1E,3E)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-methylpenta-1,3-diene-1,5-diyl)dibenzonitrile (4n)

Compound **4n** (28 mg, 58% yield) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1n** (0.1 mmol, 17 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 4H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.28-7.26 (m, 2H), 7.16 (dd, J_1 = 15.2 Hz, J_2 = 11.2 Hz, 1H), 6.87 (s, 2H), 6.39 (d, *J* = 15.2 Hz, 1H), 5.78 (d, *J* = 11.2 Hz, 1H), 5.17 (s, 1H), 4.80 (s, 1H), 1.91 (s, 3H), 1.40 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.7, 148.5, 143.9, 142.1, 136.0, 132.4, 132.1, 130.7, 130.1, 130.0, 128.4, 128.2, 126.5, 125.7, 119.1, 119.0, 110.2, 60.3, 34.4, 30.3, 18.0; **IR** (neat) ν 3629, 2956, 2917, 2867, 2225, 1598, 1499, 1434, 1361, 1234, 1152, 1118, 966, 813, 738, 553 cm^{-1}; **MP:** 102-104 °C; **HRMS** Calcd. for $C_{34}H_{35}N_2O$ [M-H]$^{-}$: 487.2749, found: 487.2756.

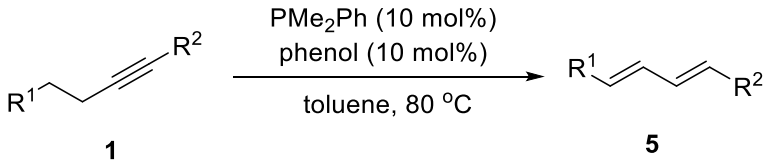


4o

4,4'-(5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(2-methylprop-1-en-1-yl)penta-1,3-diene-1,5-diyl)dibenzonitrile (4o)

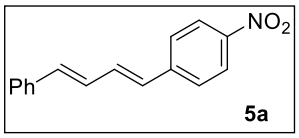
Compound **4o** (22.8 mg, 44% yield, 5.6:1 *E/Z*) was obtained as a yellowish solid following the *general procedure III* from **3b** (0.15 mmol, 48 mg) and **1o** (0.1 mmol, 23 mg) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$, major product) δ 7.63-7.51 (m, 5H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.29-7.22 (m, 2H), 6.93-6.89 (m, 2H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.93 (d, *J* = 10.8 Hz, 1H), 5.62 (s, 1H), 5.15 (s, 1H), 4.82 (s, 1H), 1.80 (d, *J* = 1.2 Hz, 3H), 1.49 (d, *J* = 0.8 Hz, 3H), 1.39 (s, 18H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 148.7, 145.7, 142.3, 138.1, 135.8, 132.4, 132.0, 130.8, 130.1, 130.0, 129.0, 126.4, 125.7, 123.3, 119.1, 110.1, 110.0, 59.1, 34.4 (minor), 34.3, 30.3, 25.9, 20.3; **IR** (neat) ν 3635, 2957, 2225, 1601, 1499, 1434, 1361, 1234, 1152, 1118, 1016, 977, 816, 737, 550 cm^{-1}; **MP:** 189-193 °C; **HRMS** Calcd. for $C_{37}H_{39}N_2O$ $[M-H]^-$: 527.3062, found: 527.3058.

General procedure (IV) for preparing compounds 5a-v



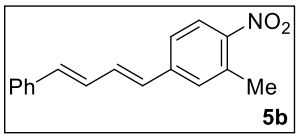
1 **5**

Compounds alkynes **1** (1.0 equiv.) phenol (0.1 equiv.) and anhydrous toluene were added to a oven dried vial under N_2 protection, then PMe_2Ph (0.1 equiv.) was added to the above mixture at room temperature. The resulting mixture was stirred at 80 °C for 4 hours. The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (Al_2O_3, PE/EA = 20/1) to afford the corresponding product **5**.



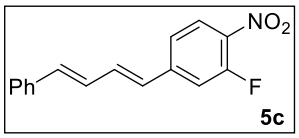
1-nitro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (5a)

This is a known compound.[3a] Compound **5a** (24.2 mg, 97% yield) was obtained as a yellow solid following the *general procedure IV* from **1a** (0.1 mmol, 25 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.48-7.46 (m, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31-7.27 (m, 1H), 7.11 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.98 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 6.70 (d, *J* = 15.2 Hz, 1H).



2-Methyl-1-nitro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (5b)

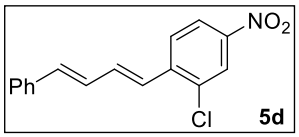
Compound **5b** (26.2 mg, 97% yield) was obtained as a yellow solid following the *general procedure IV* from **1b** (0.1 mmol, 27 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.39-7.34 (m, 4H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.96 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.78 (d, *J* = 15.2 Hz, 1H), 6.64 (d, *J* = 15.2 Hz, 1H), 2.64 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 147.4, 142.3, 136.7, 135.6, 134.6, 133.2, 130.4, 130.1, 128.8, 128.3, 128.2, 126.7, 125.6, 124.2, 21.1; **IR** (neat) ν 3028, 1598, 1576, 1515, 1446, 1338, 1076, 997, 836, 751, 692 cm^{-1}; **MP**: 106-107 °C; **HRMS** Calcd. for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1181, found: 266.1175.



2-Fluoro-1-nitro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (5c)

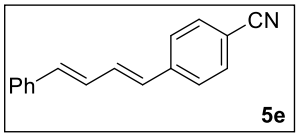
Compound **5c** (23.2 mg, 86% yield) was obtained as a yellow solid following the *general procedure IV* from **1c** (0.1 mmol, 27 mg) stirred for 4 hours. **^{1}H NMR** (400

MHz, $CDCl_3$) δ 8.05 (t, *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 2H), 7.39-7.35 (m, 2H), 7.32-7.27 (m, 3H), 7.09 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.96 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.83 (d, *J* = 15.2 Hz, 1H), 6.62 (d, *J* = 15.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.1 (d, *J* = 263.0 Hz), 145.7 (d, *J* = 8.6 Hz), 137.1, 136.4, 134.9, 128.8, 128.6, 127.8, 126.8, 126.7 (d, *J* = 2.5 Hz), 121.9 (d, *J* = 3.4 Hz), 114.9 (d, *J* = 21.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) -116.71 to -116.76 (m); **IR** (neat) ν 2957, 2923, 1587, 1505, 1336, 1242, 1090, 982, 838, 745, 692 cm^{-1}; **MP**: 111-113 °C; **HRMS** Calcd. for $C_{16}H_{11}FNO_2$ $[M-H]^-$: 268.0774, found: 268.0769.



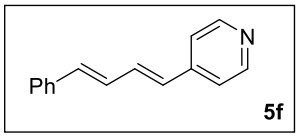
2-chloro-4-nitro-1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (5d)

Compound **5d** (25.8 mg, 89% yield) was obtained as a yellow solid following the *general procedure IV* from **1d** (0.1 mmol, 29 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 1H), 7.15-7.13 (m, 3H), 6.84 (d, *J* = 15.6 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 146.4, 141.7, 137.1, 136.4, 135.8, 133.3, 128.8, 128.6, 128.3, 126.9, 126.11, 126.08, 125.3, 121.9; **HRMS** Calcd. for $C_{16}H_{12}NO_2Cl$ $[M]^+$: 285.0557, found: 285.0551.



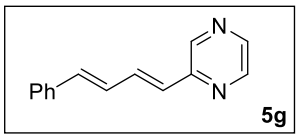
4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzonitrile (5e)

This is a known compound.[3b] Compound **5e** (16.5 mg, 72% yield) was obtained as a white solid following the *general procedure IV* from **1e** (0.1 mmol, 23 mg) stirred at 120 °C for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.53-7.42 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.09-6.93 (m, 2H), 6.77 (d, *J* = 15.2 Hz, 1H), 6.65 (d, *J* = 15.2 Hz, 1H).



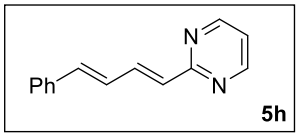
4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)pyridine (5f)

This is a known compound.[3c] Compound **5f** (16.2 mg, 77% yield) was obtained as a yellow solid following the *general procedure IV* from **1f** (0.1 mmol, 21 mg) stirred at 120 ^{o}C for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31-7.28 (m, 3H), 7.15 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.96 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.80 (d, *J* = 15.2 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H).



2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)pyrazine (5g)

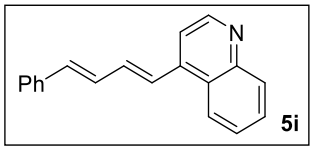
Compound **5g** (19.1 mg, 91% yield) was obtained as a yellow solid following the *general procedure IV* from **1g** (0.1 mmol, 21 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.52 (s, 1H), 8.38 (br, 1H), 7.56 (dd, J_1 = 15.2 Hz, J_2 = 10.8 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.02 (dd, J_1 = 15.2 Hz, J_2 = 10.8 Hz, 1H), 6.85 (d, *J* = 15.2 Hz, 1H), 6.72 (d, *J* = 15.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 151.3, 144.2, 143.6, 142.3, 137.1, 136.6, 135.8, 128.7, 128.4, 127.9, 127.6, 126.8; **IR** (neat) ν 3022, 2923, 2852, 1615, 1449, 1398, 1121, 1056, 1014, 985, 847, 757, 745, 689 cm^{-1}; **MP**: 75-77 ^{o}C; **HRMS** Calcd. for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1079, found: 209.1077.



2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)pyrimidine (5h)

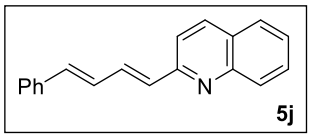
Compound **5h** (19.5 mg, 93% yield) was obtained as a yellow solid following the *general procedure IV* from **1h** (0.1 mmol, 21 mg) stirred for 4 hours. **^{1}H NMR** (400

MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 2H), 7.78 (dd, J_1 = 15.2 Hz, J_2 = 11.2 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.08-7.02 (m, 2H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.79 (d, *J* = 15.6 Hz, 1H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 164.8, 157.0, 138.7, 137.7, 136.7, 130.9, 128.7, 128.4, 127.9, 126.9, 118.3; **IR** (neat) ν 3028, 2923, 2852, 1621, 1564, 1547, 1415, 999, 844, 748, 692 cm^{-1}; **MP**: 93-94 ºC; **HRMS** Calcd. for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1079, found: 209.1077.



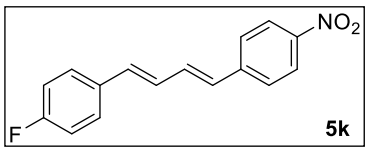
4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)quinoline (5i)

This is a known compound.[3d] Compound **5i** (25.0 mg, 96% yield) was obtained as a yellow solid following the *general procedure IV* from **1i** (0.1 mmol, 26 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.8 Hz, 1H), 8.18 (t, *J* = 9.2 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.63-7.58 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.42-7.36 (m, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.27-7.21 (m, 1H), 7.12 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 6.86 (d, *J* = 15.2 Hz, 1H).



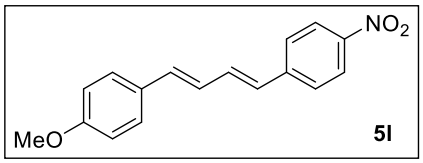
2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)quinoline (5j)

This is a known compound.[3e] Compound **5j** (24.2 mg, 93% yield) was obtained as a yellow solid following the *general procedure IV* from **1j** (0.1 mmol, 26 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.59-7.47 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.07 (dd, J_1 = 15.6 Hz, J_2 = 10.8 Hz, 1H), 6.96 (d, *J* = 15.6 Hz, 1H), 6.87 (d, *J* = 15.6 Hz, 1H).



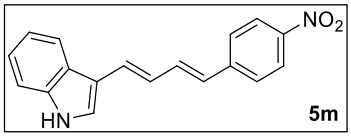
1-fluoro-4-((1E,3E)-4-(4-nitrophenyl)buta-1,3-dien-1-yl)benzene (5k)

Compound **5k** (26.7 mg, 99% yield) was obtained as a yellow solid following the *general procedure IV* from **1k** (0.1 mmol, 27 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 2H), 7.12-7.03 (m, 3H), 6.89 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.76 (d, *J* = 15.6 Hz, 1H), 6.69 (d, *J* = 15.6 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.4 Hz), 146.6, 143.8, 134.7, 133.5, 132.9 (d, *J* = 3.5 Hz), 130.1, 128.3 (d, *J* = 8.0 Hz), 128.0 (d, *J* = 2.7 Hz), 126.6, 124.1, 115.8 (d, *J* = 21.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) -112.55 to -112.63 (m); **IR** (neat) ν 2954, 2923, 2850, 1584, 1505, 1457, 1336, 1155, 1107, 988, 858, 805, 745 cm^{-1}; **HRMS** Calcd. for $C_{16}H_{12}FNO_2$ $[M]^-$: 269.0852, found: 269.0849.



1-Methoxy-4-((1E,3E)-4-(4-nitrophenyl)buta-1,3-dien-1-yl)benzene (5l)

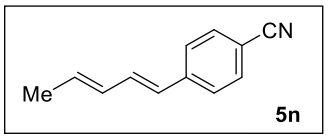
This is a known compound.[3f] Compound **5l** (25.8 mg, 92% yield) was obtained as a yellow solid following the *general procedure IV* from **1l** (0.1 mmol, 28 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.09 (dd, J_1 = 15.6 Hz, J_2 = 10.2 Hz, 1H), 6.91-6.82 (m, 3H), 6.75 (d, *J* = 15.2 Hz, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H).



3-((1E,3E)-4-(4-nitrophenyl)buta-1,3-dien-1-yl)-1H-indole (5m)

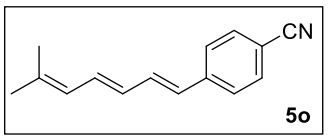
Compound **5m** (27.5 mg, 95% yield) was obtained as a yellow solid following the *general procedure IV* from **1m** (0.1 mmol, 29 mg) stirred for 4 hours. **^{1}H NMR** (400

MHz, Acetone-d_6) δ 10.65 (brs, 1H), 8.19 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 8.8 Hz, 2H), 7.66 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.37 (dd, J_1 = 15.2 Hz, J_2 = 8.4 Hz, 1H), 7.22-7.09 (m, 4H), 6.77 (d, J = 15.6 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, Acetone-d_6) δ 146.7, 146.0, 138.5, 136.9, 131.4, 127.6, 127.2, 127.1, 126.4, 125.4, 124.8, 123.1, 121.1, 120.7, 115.5, 112.8; **IR** (neat) ν 3386, 2917, 2850, 1581, 1505, 1454, 1333, 1107, 980, 742 cm^{-1}; **MP**: 188-189 ºC; **HRMS** Calcd. for $C_{18}H_{13}N_2O_2$ [M-H]$^-$: 289.0977, found: 289.0975.



4-((1E,3E)-penta-1,3-dien-1-yl)benzonitrile (5n)

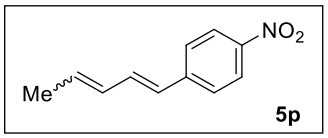
Compound **5n** (10.7 mg, 63% yield, 5:1 *E/Z*) was obtained as a yellow solid following the *general procedure IV* from **1n** (0.1 mmol, 20 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.43 (d, J = 8.0 Hz, 2H), 6.84 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 6.27-6.17 (m, 1H), 6.0-5.91 (m, 1H), 1.85 (d, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, major product) δ 142.2, 133.5, 133.0, 132.4, 131.3, 127.7, 126.4, 119.2, 109.9, 18.5; **IR** (neat) ν 2974, 2926, 2228, 1683, 1604, 1505, 1273, 1175, 974, 833, 734, 550 cm^{-1}; **MP**: 58-60 ºC; **HRMS** Calcd. for $C_{12}H_{12}N$ [M+H]$^+$: 170.0970, found: 170.0965.



4-((1E,3E)-6-methylhepta-1,3,5-trien-1-yl)benzonitrile (5o)

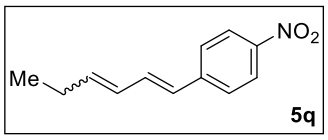
Compound **5o** (5.0 mg, 24% yield, 5:1 *E/Z*) was obtained as a yellow solid following the *general procedure IV* from **1o** (0.1 mmol, 21 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 6.96 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.65 (dd, J_1 = 15.2 Hz, J_2 = 11.2 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.28 (dd, J_1 = 15.2 Hz, J_2 = 10.8 Hz, 1H), 5.96 (d, J = 11.2 Hz, 1H), 1.85 (s, 3H),

1.84 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 142.2, 139.1, 133.4, 132.8, 132.5, 132.4, 129.4, 128.6, 126.9, 126.4, 125.4, 119.2, 109.7, 26.4, 18.6; **IR** (neat) ν 2974, 2920, 2225, 1717, 1604, 1505, 1268, 1107, 994, 838, 737 cm^{-1}; **HRMS** Calcd. for $C_{15}H_{16}N$ $[M+H]^+$: 210.1283, found: 210.1279.



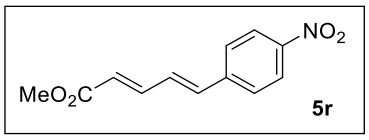
1-nitro-4-((1E,3E)-penta-1,3-dien-1-yl)benzene (5p)

This is a known compound.[3g] Compound **5p** (17.8 mg, 94% yield, 8:1 *E/Z*) was obtained as a yellowish solid following the *general procedure IV* from **1p** (0.1 mmol, 19 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18-8.13 (m, 2H), 7.53-7.46 (m, 2H), 6.89 (dd, J_1 = 15.6 Hz, J_2 = 10.8 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 6.28-6.22 (m, 1H), 6.03-5.94 (m, 1H), 1.87-1.85 (m, 3H).



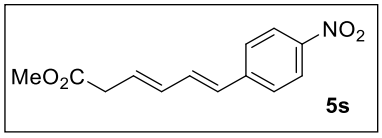
1-((1E,3E)-hexa-1,3-dien-1-yl)-4-nitrobenzene (5q)

Compound **5q** (19.8 mg, 99% yield, 11:1 *E/Z*) was obtained as a yellow solid following the *general procedure IV* from **1q** (0.1 mmol, 20 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18-8.14 (m, 2H), 7.53-7.46 (m, 2H), 6.91 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.24 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.03 (dt, J_1 = 15.6 Hz, J_2 = 6.8 Hz, 1H), 2.24-2.17 (m, 2H), 1.07 (t, J = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 146.3, 144.3, 141.2, 134.1, 129.0, 127.5, 126.4, 124.0, 26.0, 13.3; **IR** (neat) ν 2965, 2926, 2852, 1590, 1508, 1338, 1110, 985, 844, 748, 683 cm^{-1}; **MP:** 63-65 ^{o}C; **HRMS** Calcd. for $C_{12}H_{12}NO_2$ $[M-H]^-$: 202.0868, found: 202.0869.



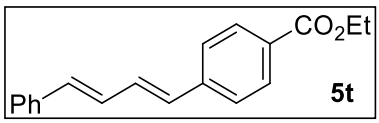
Methyl (2E,4E)-5-(4-nitrophenyl)penta-2,4-dienoate (5r)

This is a known compound.[3h] Compound **5r** (6.7 mg, 30% yield, 10:1 *E/Z*) was obtained as a yellow solid following the *general procedure IV* from **1r** (0.1 mmol, 23 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 7.04-6.91 (m, 2H), 6.11 (d, *J* = 15.2 Hz, 1H), 3.79 (s, 3H).



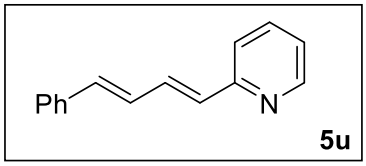
Methyl (3E,5E)-6-(4-nitrophenyl)hexa-3,5-dienoate (5s)

Compound **5s** (23.0 mg, 92% yield) was obtained as a yellow solid following the *general procedure IV* from **1s** (0.1 mmol, 25 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.92 (dd, J_1 = 15.6 Hz, J_2 = 10.8 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.34 (dd, J_1 = 15.6 Hz, J_2 = 10.8 Hz, 1H), 6.08-6.01 (m, 1H), 3.72 (s, 3H), 3.23 (d, *J* = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.5, 146.6, 143.7, 133.2, 132.7, 129.7, 129.0, 126.7, 124.1, 52.0, 37.9; **IR** (neat) ν 2999, 2954, 1728, 1593, 1514, 1437, 1398, 1338, 1169, 988, 878, 847, 745, 692 cm^{-1}; **MP**: 113-115 ºC; **HRMS** Calcd. for $C_{13}H_{12}NO_4$ $[M-H]^-$: 246.0766, found: 246.0763.



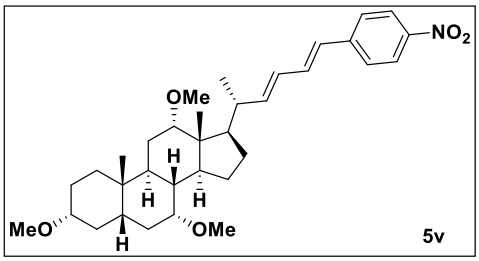
Ethyl 4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzoate (5t)

This is a known compound.[3i] Compound **5t** (19.3 mg, 69% yield) was obtained as a yellow solid following the *general procedure IV* from **1t** (0.1 mmol, 28 mg) stirred at 150 ºC for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.50-7.45 (m, 4H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28-7.24 (m, 1H), 7.09-6.94 (m, 2H), 6.74 (d, *J* = 15.2 Hz, 1H), 6.69 (d, *J* = 14.8 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).



2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)pyridine (5u)

This is a known compound.[3j] Compound **5u** (9.5 mg, 45% yield) was obtained as a yellow solid following the *general procedure IV* from **1g** (0.1 mmol, 21 mg) stirred at 120 ^{o}C for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.48-7.41 (m, 3H), 7.37-7.31 (m, 3H), 7.28-7.24 (m, 1H), 7.13-7.01 (m, 1H), 7.01 (dd, J_1 = 15.6 Hz, J_2 = 10.8 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 1H).

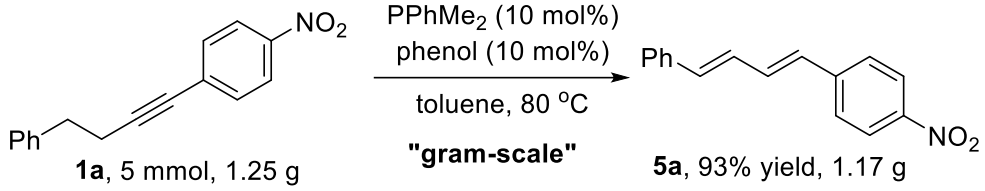


(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-3,7,12-trimethoxy-10,13-dimethyl-17-((R,3E,5E)-6-(4-nitrophenyl)hexa-3,5-dien-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (5v)

Compound **5v** (50 mg, 91% yield, 17/1 *E*/*Z*) was obtained as a white solid following the *general procedure IV* from **1v** (0.1 mmol, 55 mg) stirred for 4 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.88 (dd, J_1 = 15.6 Hz, J_2 = 10.4 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1H), 5.87 (dd, J_1 = 15.2 Hz, J_2 = 8.8 Hz, 1H), 3.37 (s, 1H), 3.33 (s, 3H), 3.29 (s, 3H), 3.20 (s, 3H), 3.13 (d, *J* = 2.4 Hz, 1H), 3.03-2.97 (m, 1H), 2.23-2.04 (m, 5H), 1.86-1.67 (m, 6H), 1.57-1.42 (m, 2H), 1.35-1.14 (m, 7H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 3H), 0.70 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 146.4, 146.2, 144.5, 134.6, 127.4, 127.3, 126.3, 124.0, 81.9, 80.7, 55.84, 55.77, 55.4, 46.24, 46.19, 42.6, 41.9, 40.3, 39.6, 35.2, 34.9, 34.4, 27.9, 27.8, 27.7, 26.7, 23.2, 22.8, 22.0, 19.4, 12.7; **IR** (neat) ν 2927, 2867, 2819, 1590, 1515, 1451, 1367, 1338, 1177, 1101, 985, 855, 737 cm^{-1}; **MP**: 87-88

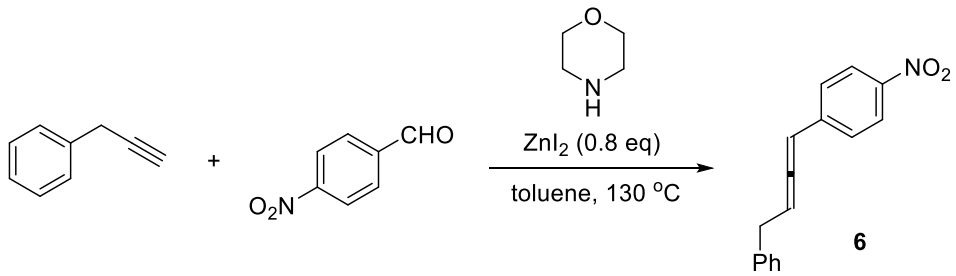
°C; **HRMS** Calcd. for $C_{34}H_{50}NO_5$ $[M+H]^+$: 552.3689, found: 552.3688.

General procedure for the gram-scale reaction



Enlarging the reaction scale up to 5.0 mmol, the compound **5a** was obtained in 93% yield (1.17 g) following the *general procedure IV* from **1a** (5.0 mmol, 1.25 g).

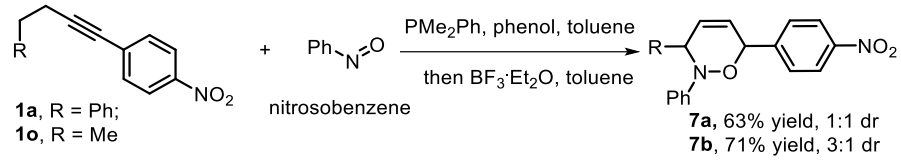
Preparation of allene 6



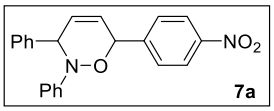
To a dried reaction tube was added ZnI_2 (2.4 mmol). Then the reaction tube was dried under vacuum with a heating gun. Then aldehyde (5.4 mmol), alkyne (3.0 mmol), morpholine (4.2 mmol) and toluene (30 mL) were added sequentially into this dried reaction tube equipped with a reflux condenser under a nitrogen atmosphere and the resulting mixture was stirred at 130 °C overnight. When the reaction was complete as monitored by TLC, the reaction mixture was cooled to room temperature and then filtered. Evaporation and column chromatography on silica gel (PE/Et_2O = 50/1) afforded the corresponding allene as a yellowish syrupy oil (150 mg, 20% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.12 (m, 2H), 7.41-7.25 (m, 7H), 6.26 (dt, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 1H), 5.90 (q, J = 7.2 Hz, 1H), 3.54 (dd, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 207.5, 146.3, 141.9, 139.2, 128.5, 128.3, 126.9, 126.5, 123.8, 95.5, 94.0, 34.9; **IR** (neat) ν 2963, 2926, 2847, 1595, 1514, 1451, 1344 1259, 1104, 1014, 802, 734, 700 cm^{-1}; **HRMS** Calcd. for $C_{16}H_{12}NO_2$ $[M-H]^-$: 250.0868, found: 250.0869.

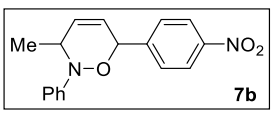
Hetero-D-A preparation of 7-8



To an oven dried vial was charged with **1a** or **1o** (0.1 mmol), phenol (0.01 mmol) and PMe_2Ph (0.01 mmol) in toluene (1.0 mmol). The mixture was heated at 80 ^oC under N_2 protection for 12 hours. TLC detected until all the starting material disappear. Then the reaction mixture cooled to room temperature, nitrosobenzene (0.11 mmol) and $BF_3{\cdot}Et_2O$ (0.02 mmol) added sequentially. The mixture was heated at 80 ^oC under N_2 protection for 2 hours. Cooled the reaction to room temperature and purification by column chromatography (PE/EA = 20/1) to give the cycloaddition product **7a-7b** as a yellowish oil (for **7a**, 22.6 mg, 63% yield, 1:1 dr; for **7b**, 21 mg, 71% yield, 3:1 dr).



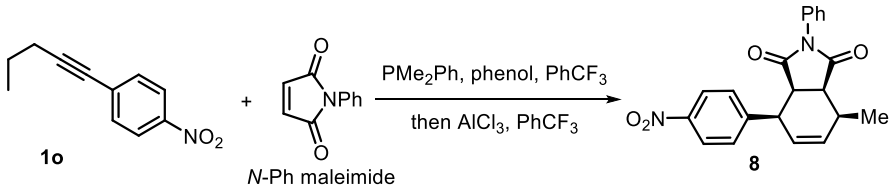
Compound **7a** was obtained as a syrup yellow oil (22.6 mg, 63% yield, 1:1 dr); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48-7.40 (m, 5H), 7.26-7.16 (m, 9H), 6.98-6.87 (m, 6H), 6.27-6.15 (m, 4H), 5.72 (s, 1H), 5.68 (s, 1H), 5.28 (s, 1H), 5.15 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 148.1, 147.8, 147.7, 146.2, 145.8, 137.9, 137.6, 129.62, 129.58, 129.3, 128.83, 128.78, 128.5, 128.3, 128.0, 127.8, 126.6, 126.5, 123.8, 123.3, 123.0, 122.3, 118.1, 116.5, 79.2, 77.9, 64.3, 62.6; **IR** (neat) ν 3059, 3030, 2923, 2852, 1598, 1519, 1491, 1451, 1347, 1110, 1033, 946, 853, 830, 754, 697 cm^{-1}; **HRMS** Calcd. for $C_{22}H_{19}N_2O_3$ $[M+H]^+$: 359.1396, found: 359.1397.



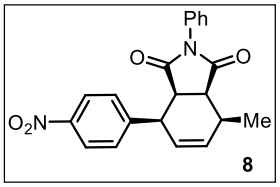
Compound **7b** was obtained as a light yellow oil (21 mg, 71% yield, 3:1 dr); **^{1}H NMR** (400 MHz, $CDCl_3$, major product) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.63-7.60 (m, 2H), 7.33-7.26 (m, 2H), 7.08-7.05 (m, 2H), 7.01-6.98 (m, 1H), 6.20-6.15 (m, 1H), 5.91-5.89 (dd,

J_1 = 10.0 Hz, J_2 = 1.4 Hz, 1H), 5.64 (s, 1H), 4.28-4.22 (m, 1H), 1.22 (d, J = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 148.3, 147.8, 146.0, 131.4, 130.9, 128.9, 128.8, 128.5, 128.4, 126.9, 125.5, 123.8, 123.4, 122.2, 116.6, 78.6, 78.1 (minor), 55.7 (minor), 55.0, 14.9; **IR** (neat) ν 2971, 2926, 2850, 1595, 1516, 1491, 1449, 1344, 1256, 1180, 1064, 1036, 799, 751, 692 cm^{-1}; **HRMS** Calcd. for $C_{17}H_{15}N_2O_3$ [M-H]$^-$: 295.1083, found:295.1085;

General procedure for the Hetero-D-A reaction to prepare 8



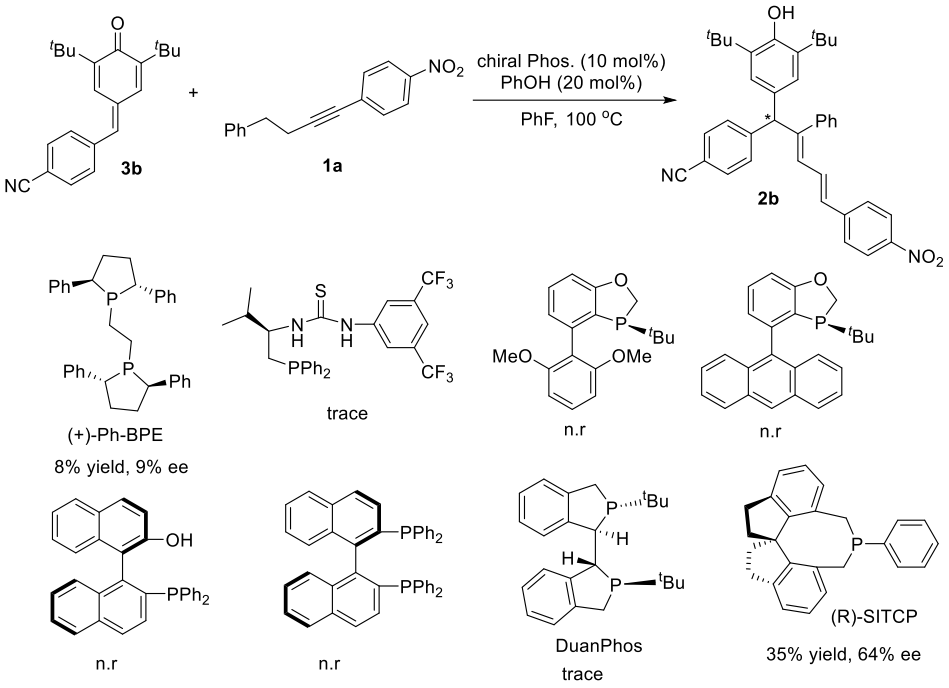
To an oven dried vial was charged with **1o** (0.1 mmol), phenol (0.01 mmol) and PMe_2Ph (0.01 mmol) in benzotrifluoride (1.0 mmol) under N_2 protection. The mixture was heated at 120 ^{o}C under N_2 protection for 12 hours. TLC detected until all the starting material disappear, then cooled the reaction to room temperature and added $AlCl_3$ (0.02 mmol) and *N*-Ph maleimide (0.1 mmol) sequentially, heated the reaction mixture at 150 ^{o}C overnight. Quenched the reaction with water and extracted by ethyl acetate. Dried the organic solution with Na_2SO_4 and purification by column chromatography (PE/EA = 6/1) to give the Diels-Alder annulation product **8** as a yellowish solid (31.3 mg, 87% yield, >20:1 dr).



Compound **8** was obtained as a yellowish solid (31.3 mg, 87% yield, >20:1 dr); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.43-7.32 (m, 3H), 7.13 (d, J = 7.2 Hz, 2H), 6.35 (dt, J_1 = 9.2 Hz, J_2 = 3.6 Hz, 1H), 6.06 (dt, J_1 = 9.2 Hz, J_2 = 3.6 Hz, 1H), 3.81-3.80 (m, 1H), 3.59 (dd, J_1 = 8.4 Hz, J_2 = 6.4 Hz,1H), 3.34 (dd, J_1 = 8.4 Hz, J_2 = 6.8 Hz, 1H), 2.74-2.70 (m, 1H), 1.60 (d, J = 7.2 Hz, 3H);

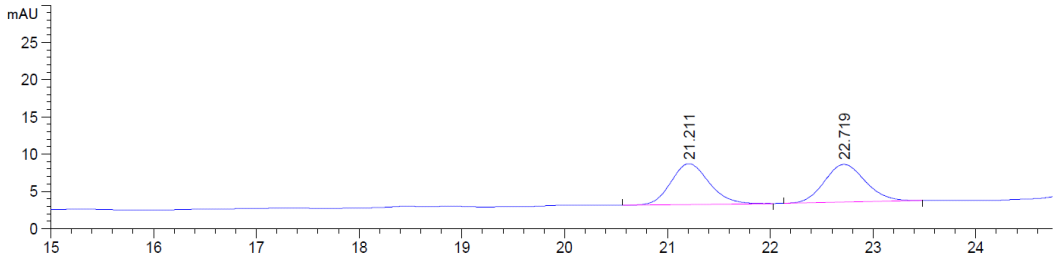
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.6, 175.1, 147.0, 146.9, 136.3, 131.5, 129.7, 129.1, 128.7, 128.6, 126.3, 123.4, 47.1, 44.8, 41.4, 31.7, 16.8; **MP:** 76-77 ^{o}C; **IR** (neat) ν 2920, 2847, 1708, 1652, 1598, 1517, 1498, 1382, 1346, 1186, 833, 752, 692 cm^{-1}; **HRMS** Calcd. for $C_{21}H_{17}N_2O_4$ $[M-H]^-$: 361.1188, found: 361.1192.

4. Asymmetric version



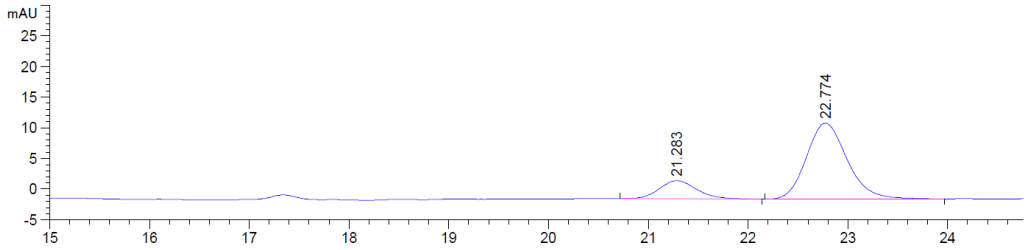
Compound **2b** $[\alpha]^{20}_{D}$ = -6.86 (c 0.23, $CHCl_3$) for 64% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 230 nm, t_{minor} = 21.283 min, t_{major} = 22.774 min.

Racemic Sample of 2b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.211	BB	0.3938	141.97778	5.48839	50.1832
2	22.719	BB	0.4306	140.94115	5.06597	49.8168
Totals :				282.91893	10.55435	

Enantiomeric Sample of 2b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.283	BB	0.3908	77.23494	2.95602	18.0443
2	22.774	BB	0.4348	350.79349	12.37260	81.9557
Totals :				428.02843	15.32862	

5. References

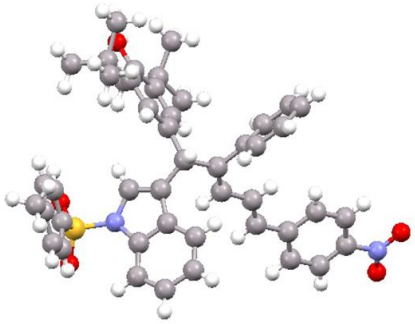
[1] (a) C. Dal Zotto, J. Wehbe, D. Virieux, J.-M. Campagne, *Synlett* **2008**, 2033; (b) A. J. Warner, J. R. Lawson, V. Fasano, M. J. Ingleson, *Angew. Chem., Int. Ed.* **2015**, *54*, 11245; (c) Y. Liu, M. Liu, Z. Song, *J. Am. Chem. Soc.* **2005**, *127*, 3662; (d) E. A. Reddy, D. K. Barange, A. Islam, K. Mukkanti, M. Pal, *Tetrahedron* **2008**, *64*, 7143; (e) G. Hamasaka, Y. Uozumi, *Chem. Commun.* **2014**, *50*, 14516; (f) F. Maesing, H. Nuesse, J. Klingauf, A. Studer, *Org. Lett.* **2017**, *19*, 2658; (g) X. Wang, A. Studer, *Org. Lett.* **2017**, *19*, 2977.

[2] W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F.-X. Wang, X.-Y. Ma, C.-A. Fan, *Angew. Chem., Int. Ed.* **2013**, *52*, 9229.

[3] (a) S. Cicco, C. Martinelli, V. Pinto, F. Naso, G. M. Farinola, *J. Organomet. Chem.* **2013**, *732*, 15; (b) D. Hadrich, F. Berthold, E. Steckhan, H. Bonisch, *J. Med. Chem.* **1999**, *42*, 3101; (c) S. Yamada, Y. Azuma, K. Aya, *Tetrahedron Lett.* **2014**, *55*, 2801; (d) J. L. Gage, H. A. Kirst, D. O'Neil, B. A. David, C. K. Smith, S. A. Naylor, *Bioorg. Med. Chem.* **2003**, *11*, 4083; (e) G. E. M. Crisenza, E. M. Dauncey, J. F. Bower, *Org. Bio. Chem.* **2016**, *14*, 5820; (f) S. Khan, S. Roy, A. Ghatak, A. Pramanik, S. Bhar, *Tetrahedron Lett.* **2014**, *55*, 5019; (g) T. Mitsudo, W. Fischetti, R. F. Heck, *J. Org. Chem.* **1984**, *49*, 1640; (h) R. Lekkala, R. Lekkala, B. Moku, H.-L. Qin, *Org. Chem. Front.* **2019**, *6*, 796; (i) K. Itami, T. Nokami, J.-I. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 5600; (j) Q.-Q. Li, Z. Shah, J.-P. Qu, Y.-B. Kang, *J. Org. Chem.* **2018**, *83*, 296;

[4] H. Behera, N. Madhavan, *J. Am. Chem. Soc.* **2017**, *139*, 12919.

6. X-ray data of compound 2n and 5d



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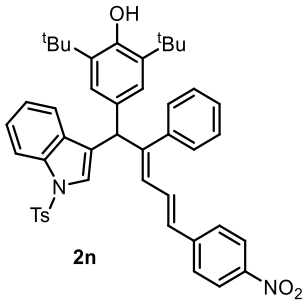
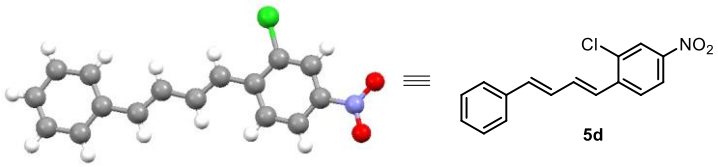


Crystal data and structure refinement for compound 2n.

Identification code	190309b
Empirical formula	$C_{46}H_{46}N_2O_5S$
Formula weight	738.91
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	21.3754(10)
b/Å	15.8343(7)
c/Å	24.1944(9)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	8188.9(6)
Z	8
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	1.075
F(000)	3136.0
Crystal size/mm^3	0.35 × 0.18 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.3 to 132.1
Index ranges	-25 ≤ h ≤ 24, -18 ≤ k ≤ 17, -21 ≤ l ≤ 28
Reflections collected	18738
Independent reflections	7144 [R_{int} = 0.0520, R_{sigma} = N/A]
Data/restraints/parameters	7144/0/495
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0586, wR_2 = 0.1184
Final R indexes [all data]	R_1 = 0.1266, wR_2 = 0.1498
Largest diff. peak/hole / e Å^{-3}	0.21/-0.20

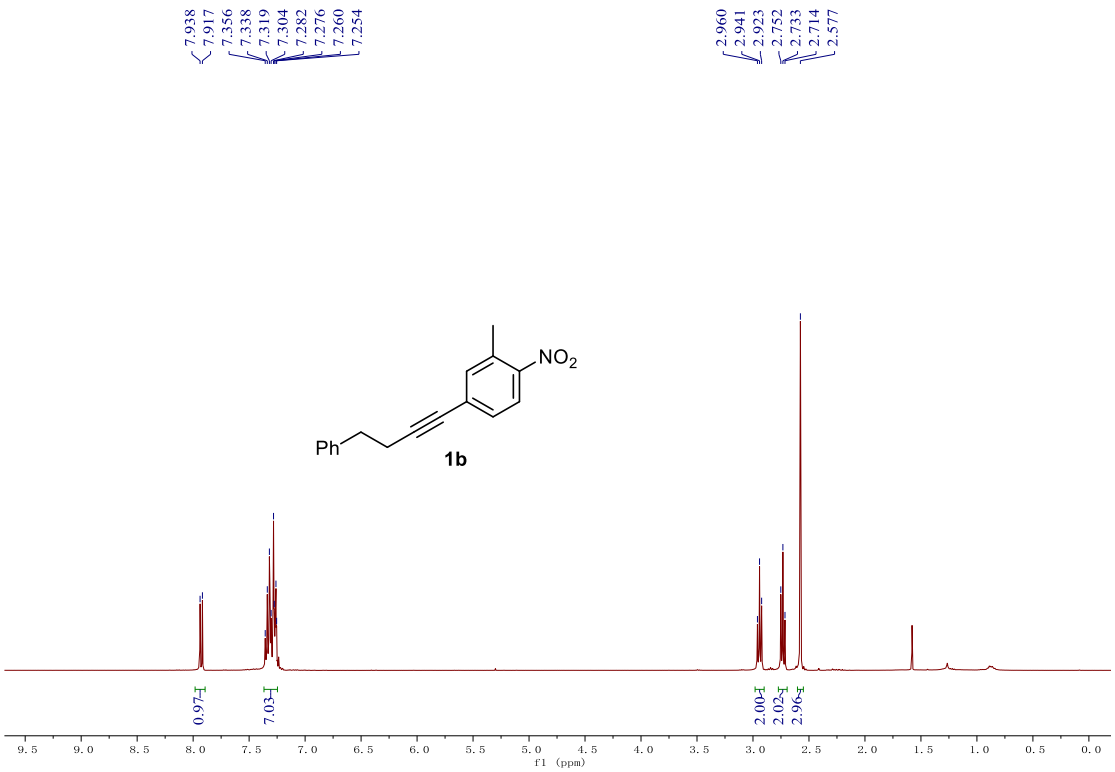


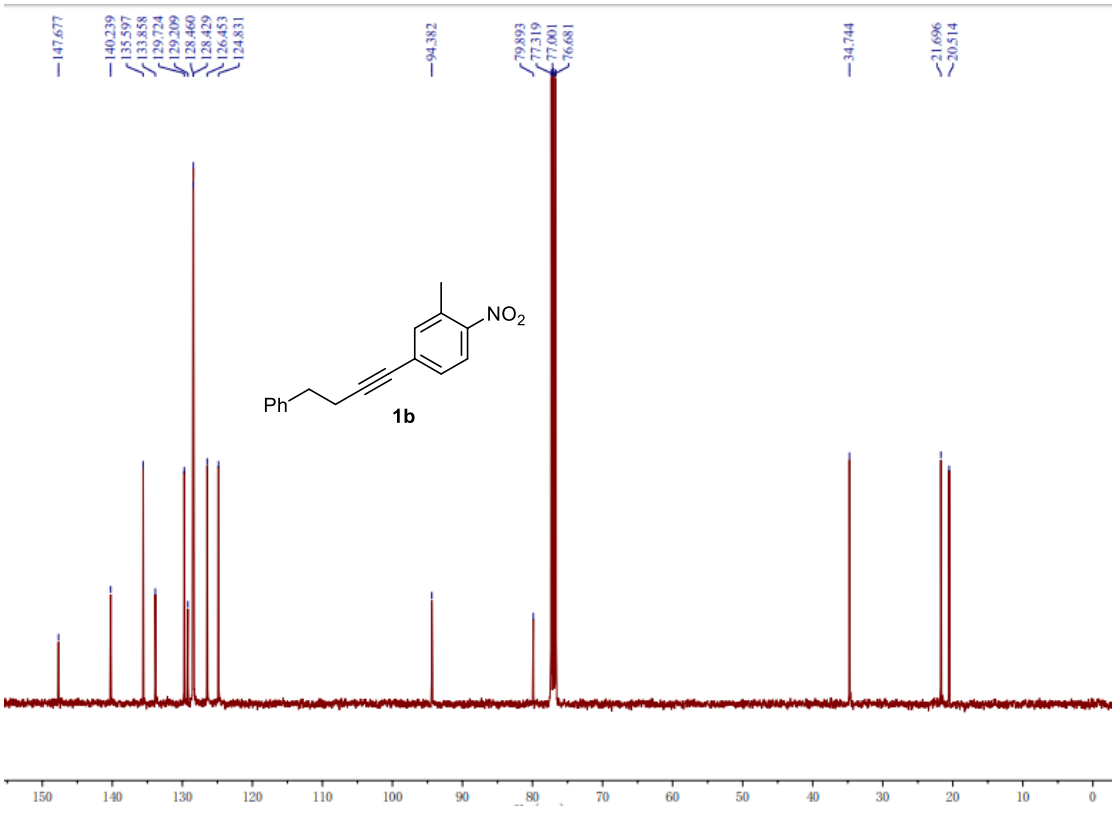
Crystal data and structure refinement for 5d.

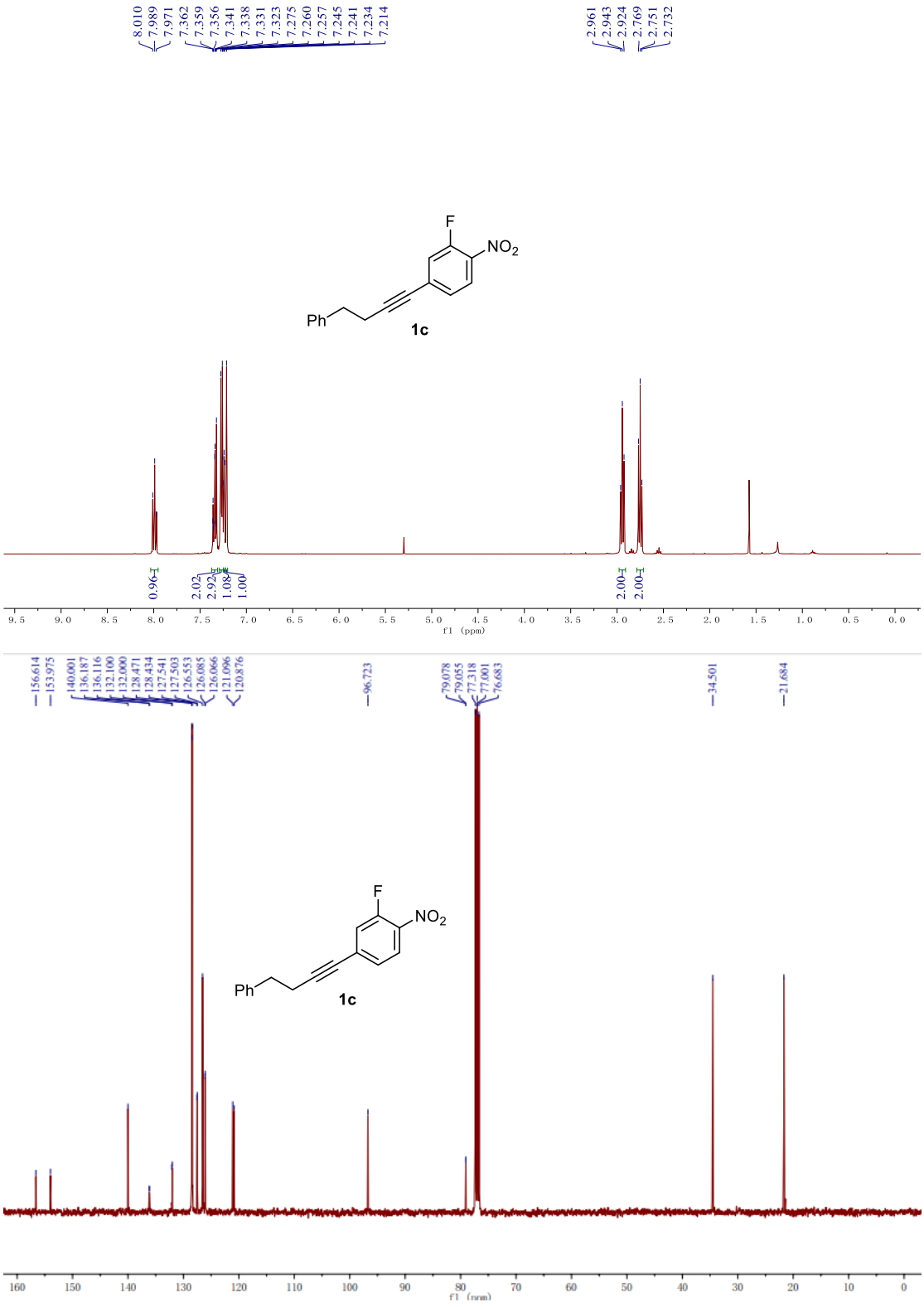
Identification code	200731d
Empirical formula	$C_{16}H_{12}ClNO_2$
Formula weight	285.72
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	24.528(2)
b/Å	32.202(3)
c/Å	7.0287(7)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	5551.6(9)
Z	16
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.275
F(000)	2368.0
Crystal size/mm^3	0.25 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.06 to 50.04
Index ranges	-25 ≤ h ≤ 28, -36 ≤ k ≤ 38, -8 ≤ l ≤ 8
Reflections collected	6890
Independent reflections	2437 [R_{int} = 0.0565, R_{sigma} = 0.1017]
Data/restraints/parameters	2437/1/181
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0644, wR_2 = 0.1674
Final R indexes [all data]	R_1 = 0.1253, wR_2 = 0.1973
Largest diff. peak/hole / e Å^{-3}	0.23/-0.24
Flack parameter	0.6(2)

7. NMR Spectra data

NMR spectra of compound 1



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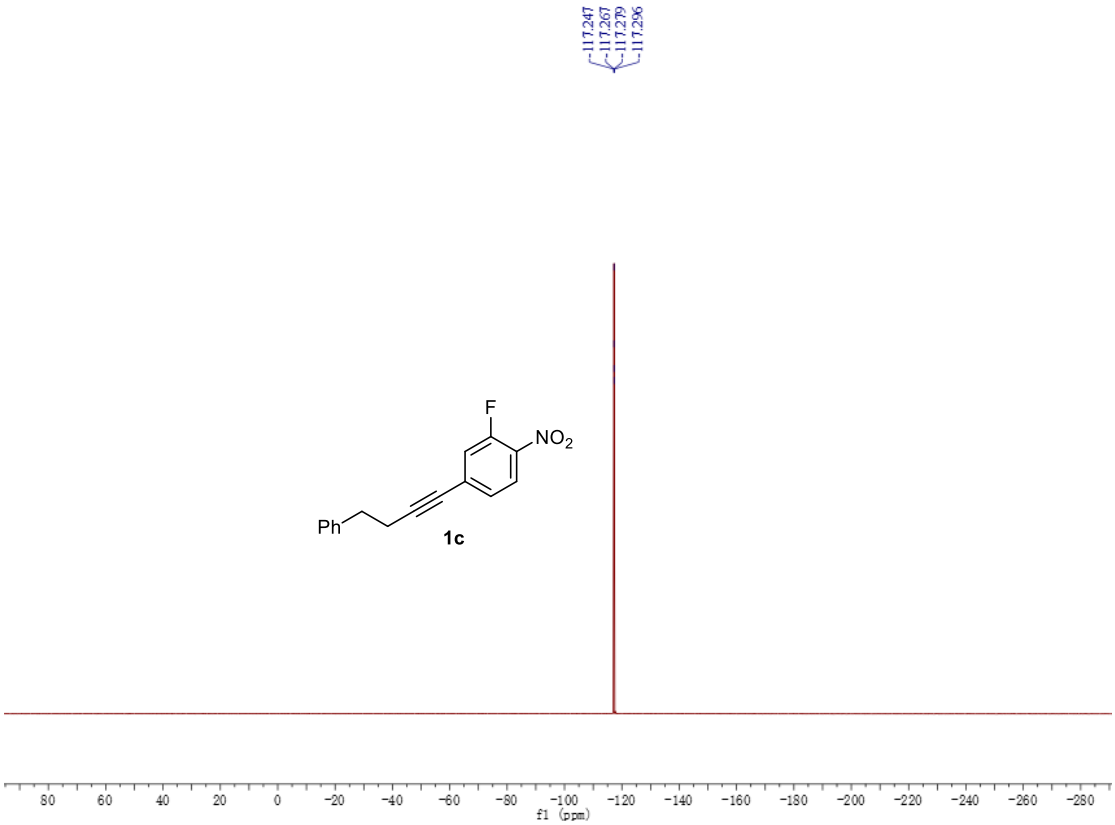
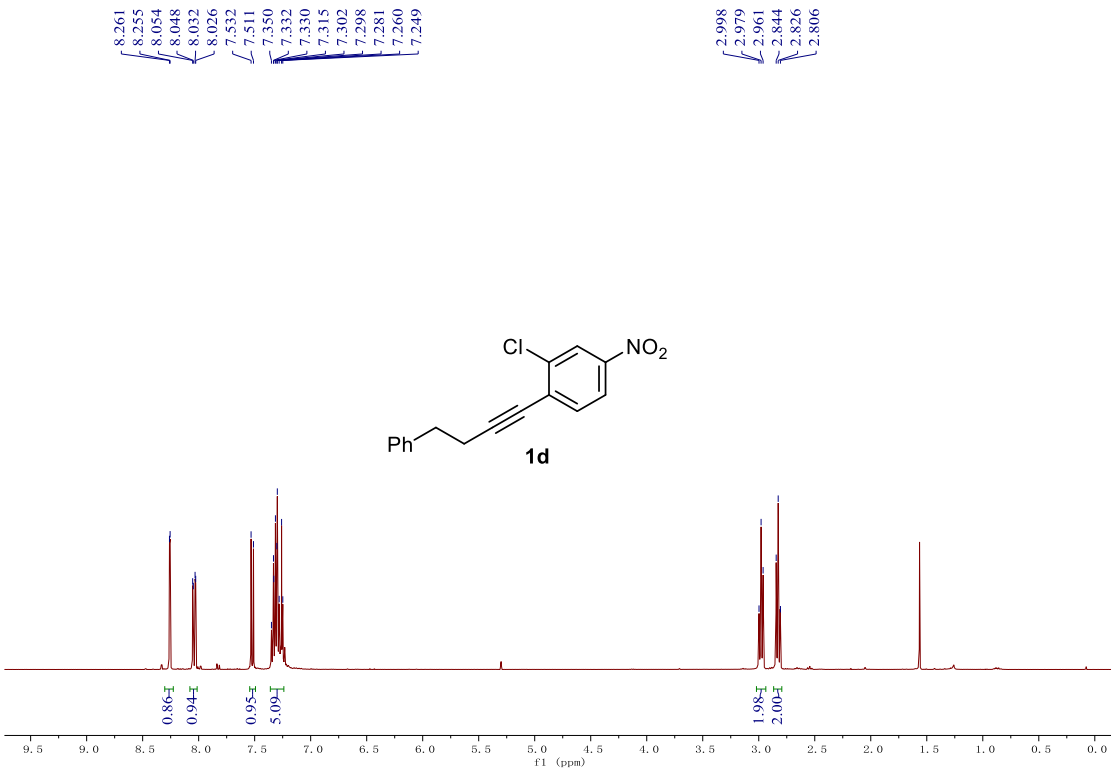
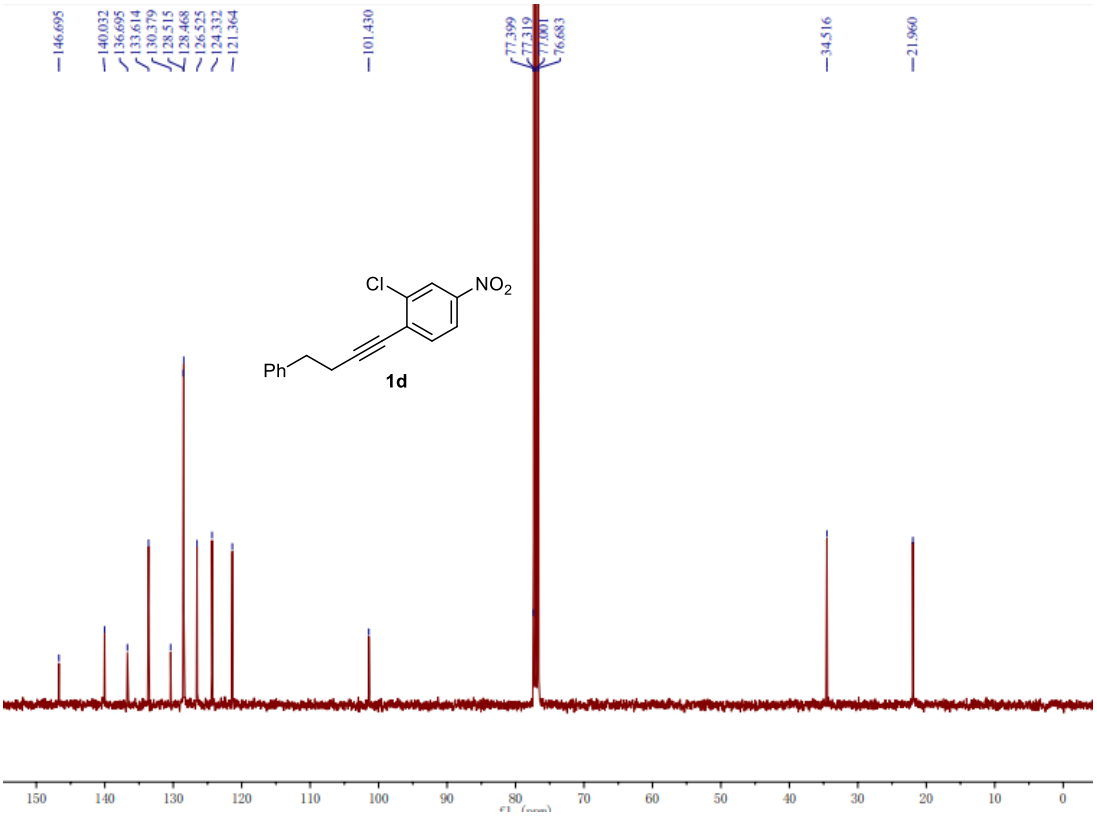
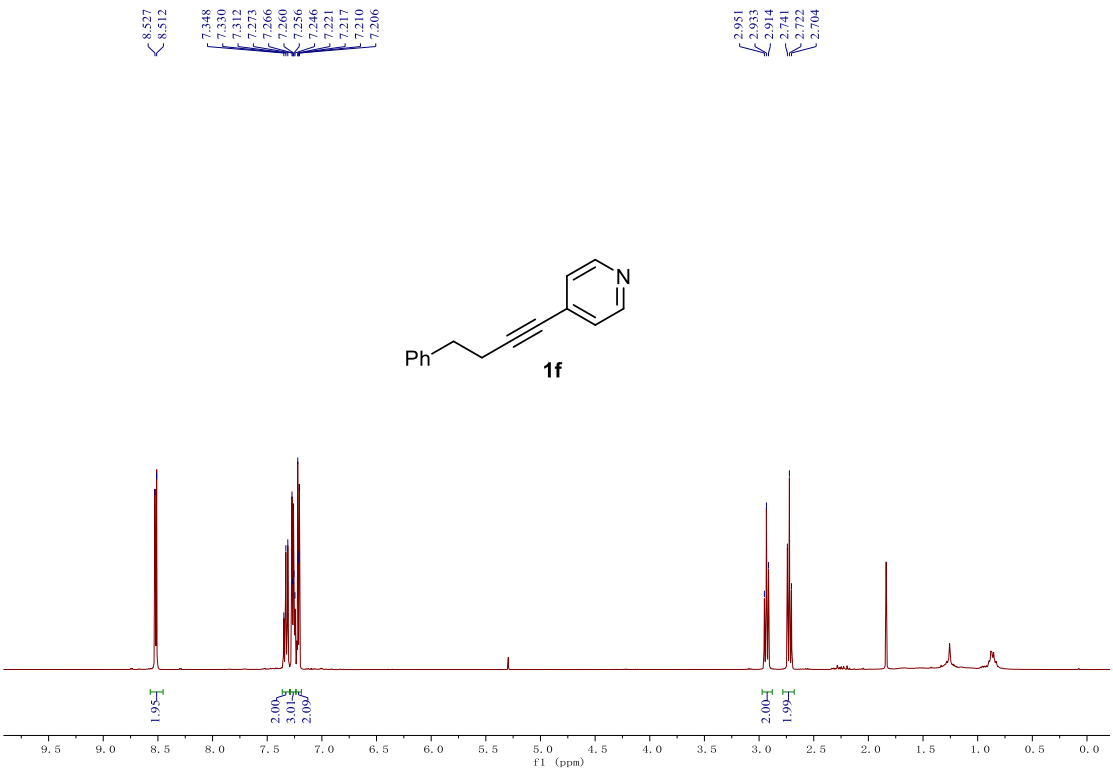
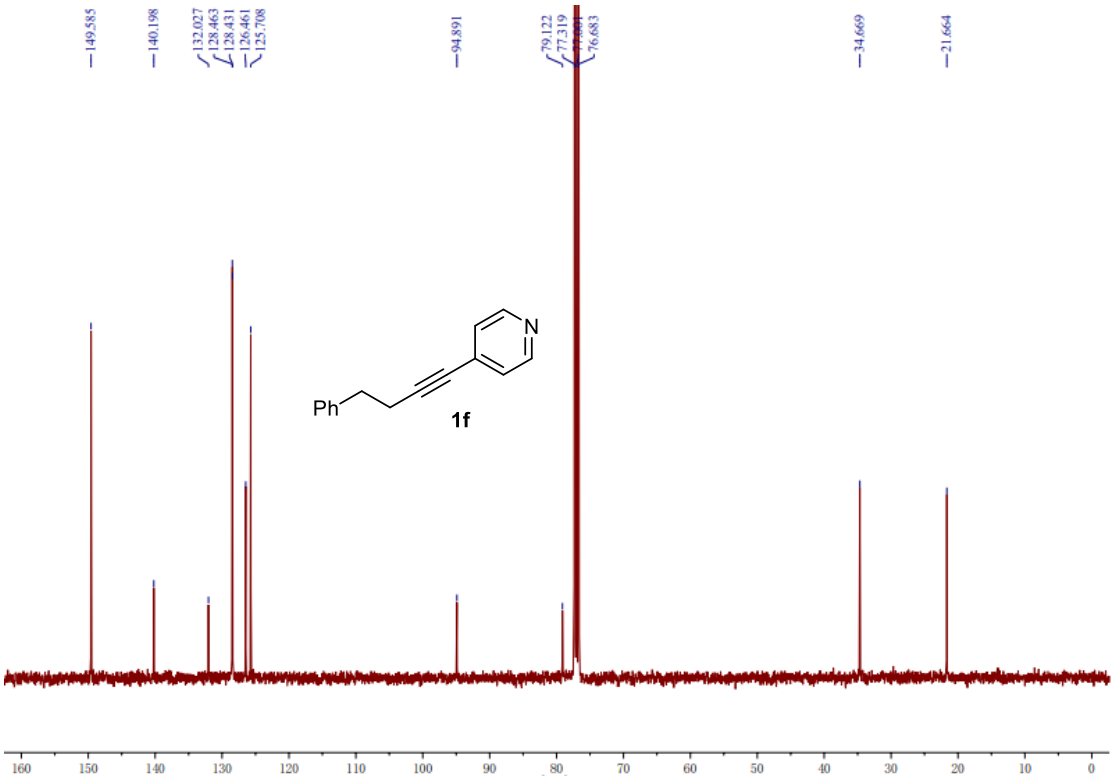
7.989
7.971
7.362
7.359
7.356
7.341
7.338
7.331
7.323
7.275
7.260
7.257
7.245
7.241
7.234
7.214
2.961
2.943
2.924
2.769
2.751
2.732
F
NO2
Ph
1c
0.96
2.02
2.92
1.08
1.00
2.00
2.00
f1 (ppm)
156.614
153.975
140.001
136.187
136.116
132.100
132.000
128.471
128.434
127.541
127.503
126.553
126.085
126.066
121.096
120.876
96.723
79.078
79.055
77.318
77.001
76.683
34.501
21.684
f1 (ppm)

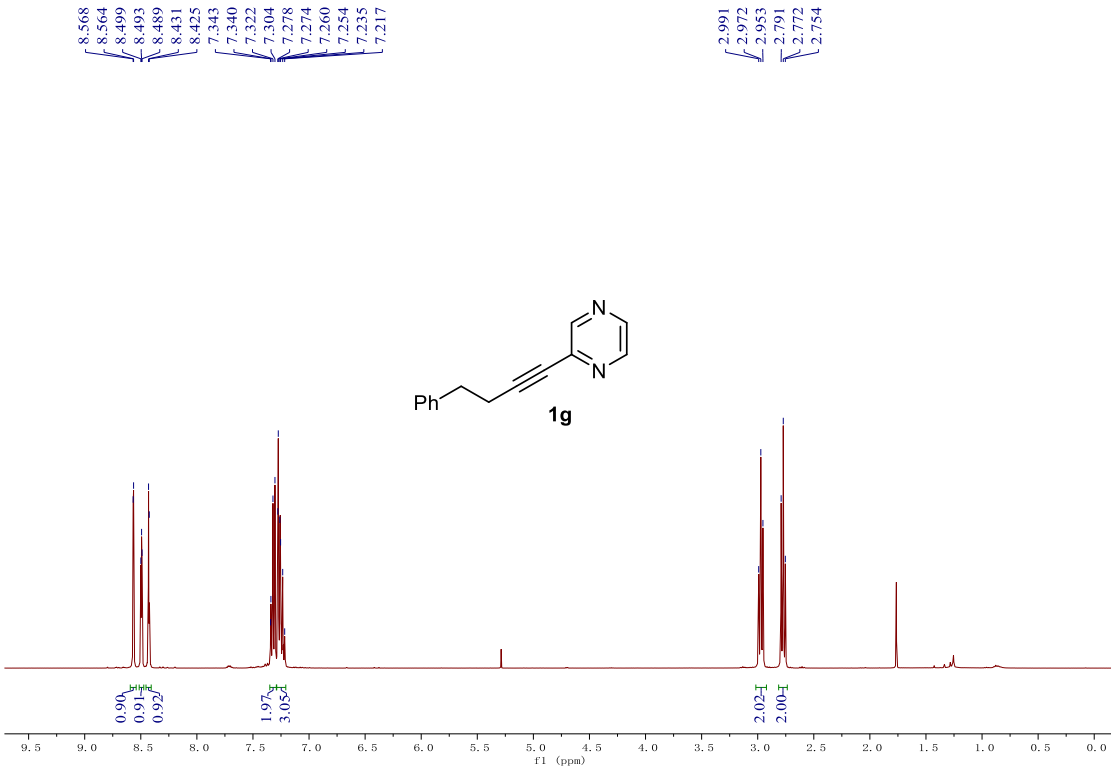

-117.247
-117.267
-117.279
-117.296
F
NO2
Ph
1c
80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


8.261
8.255
8.054
8.048
8.032
8.026
7.532
7.511
7.350
7.332
7.330
7.315
7.302
7.298
7.281
7.260
7.249
2.998
2.979
2.961
2.844
2.826
2.806
Cl
NO2
Ph
1d
0.86
0.94
0.95
5.09
1.98
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.695
140.032
136.695
133.614
130.379
128.515
128.468
126.525
124.332
121.364
101.430
77.399
77.319
77.001
76.683
34.516
21.960
Cl
NO2
Ph
1d


8.527
8.512
7.348
7.330
7.312
7.273
7.266
7.260
7.256
7.246
7.221
7.217
7.210
7.206
2.951
2.933
2.914
2.741
2.722
2.704
N
Ph
1f
1.95
2.00
3.01
2.09
2.00
1.99
f1 (ppm)


149.585
140.198
132.027
128.463
128.431
126.461
125.708
94.891
79.122
77.319
76.683
34.669
21.664
N
Ph
1f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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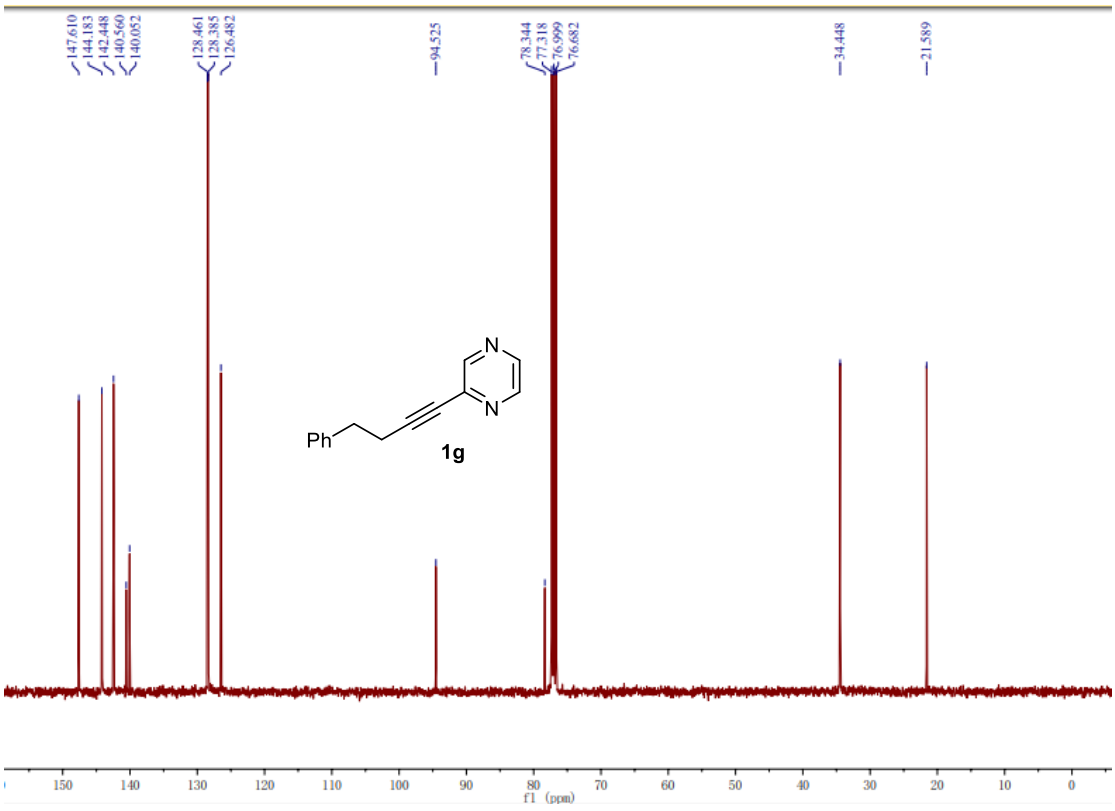
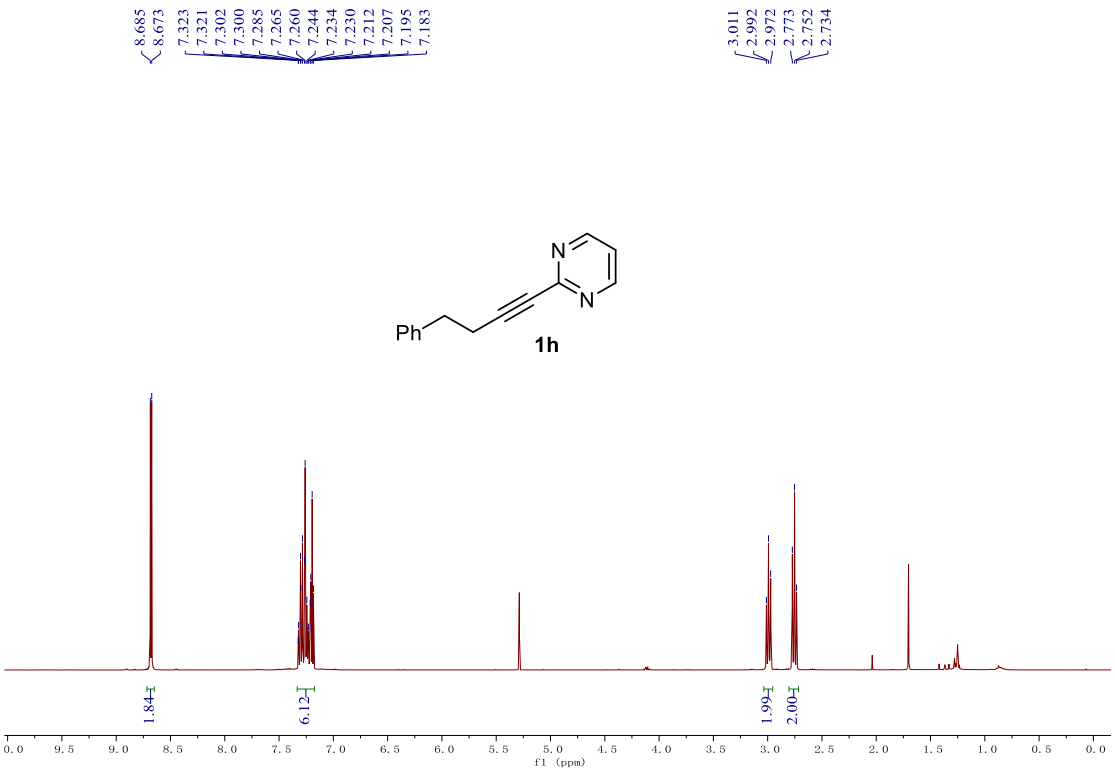
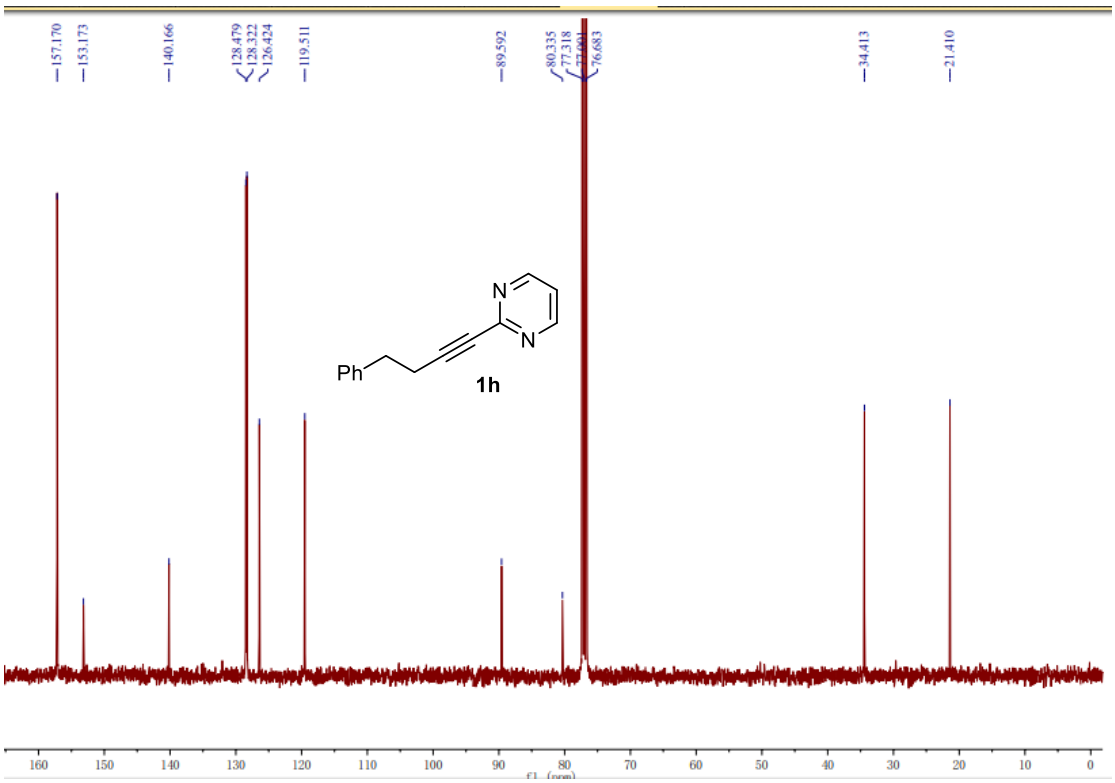
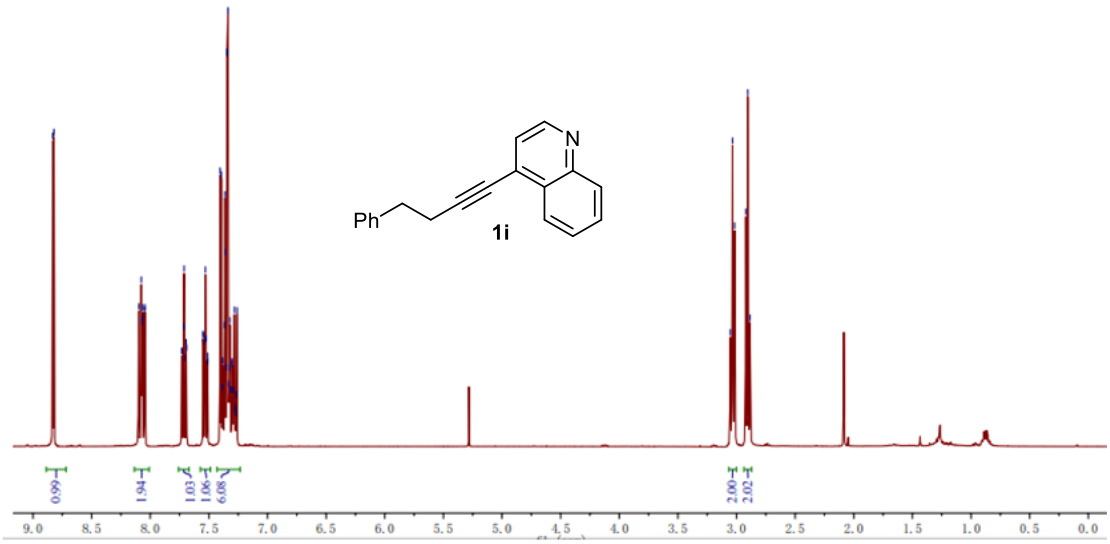
8.564
8.499
8.493
8.489
8.431
8.425
7.343
7.340
7.322
7.304
7.278
7.274
7.260
7.254
7.235
7.217
2.991
2.972
2.953
2.791
2.772
2.754
N
N
Ph
1g
0.90
0.91
0.92
1.97
3.05
2.02
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.610
144.183
142.448
140.560
140.052
128.461
128.385
126.482
94.525
78.344
77.318
76.999
76.682
34.448
21.589
N
N
Ph
1g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.685
8.673
7.323
7.321
7.302
7.300
7.285
7.265
7.260
7.244
7.234
7.230
7.212
7.207
7.195
7.183
3.011
2.992
2.972
2.773
2.752
2.734
N
N
Ph
1h
1.84
6.12
1.99
2.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.170
153.173
140.166
128.479
128.322
126.424
119.511
89.592
80.335
77.318
76.683
34.413
21.410
N
N
Ph
1h


8.832
8.821
8.098
8.077
8.070
8.068
8.066
8.048
8.045
7.732
7.728
7.715
7.711
7.707
7.694
7.690
7.550
7.547
7.533
7.529
7.526
7.512
7.509
7.403
7.392
7.384
7.381
7.366
7.363
7.360
7.352
7.346
7.344
7.336
7.329
7.325
7.320
7.316
7.304
7.300
7.294
7.289
7.283
7.275
7.271
7.266
7.260
3.052
3.034
3.016
2.921
2.904
2.886


N
Ph
1i
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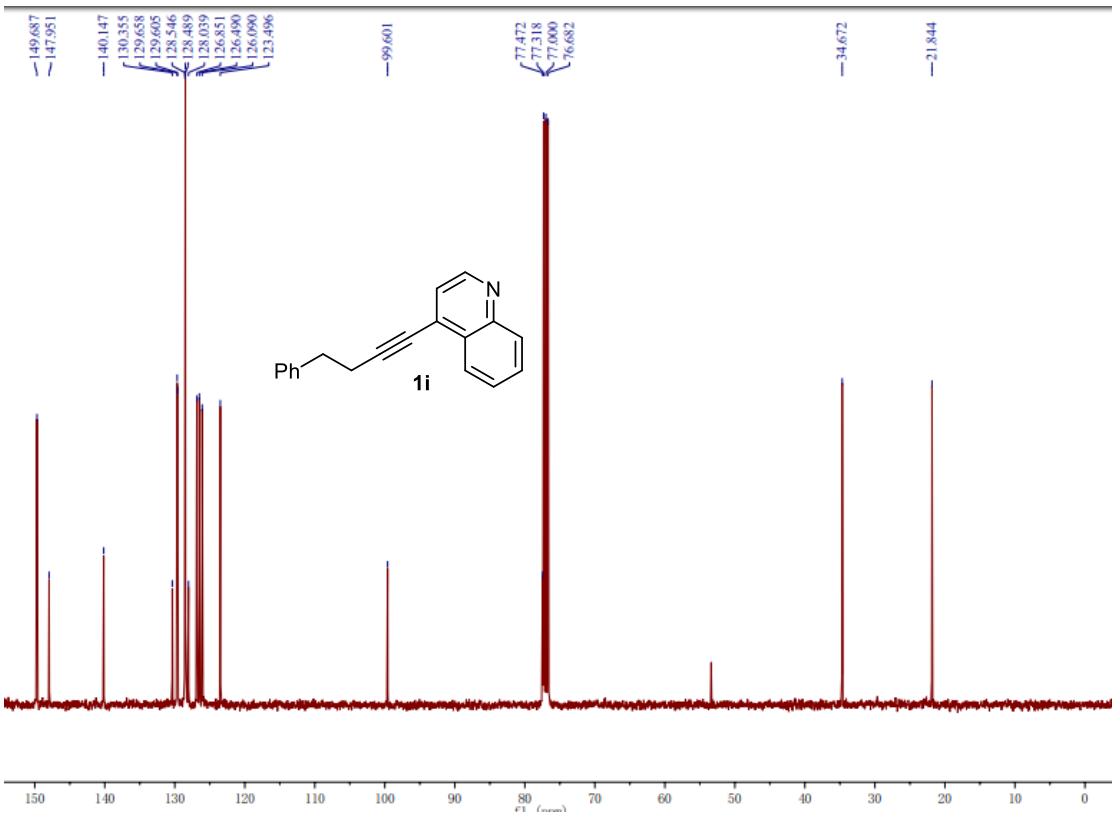
1.94
1.03
1.06
6.08
2.00
2.02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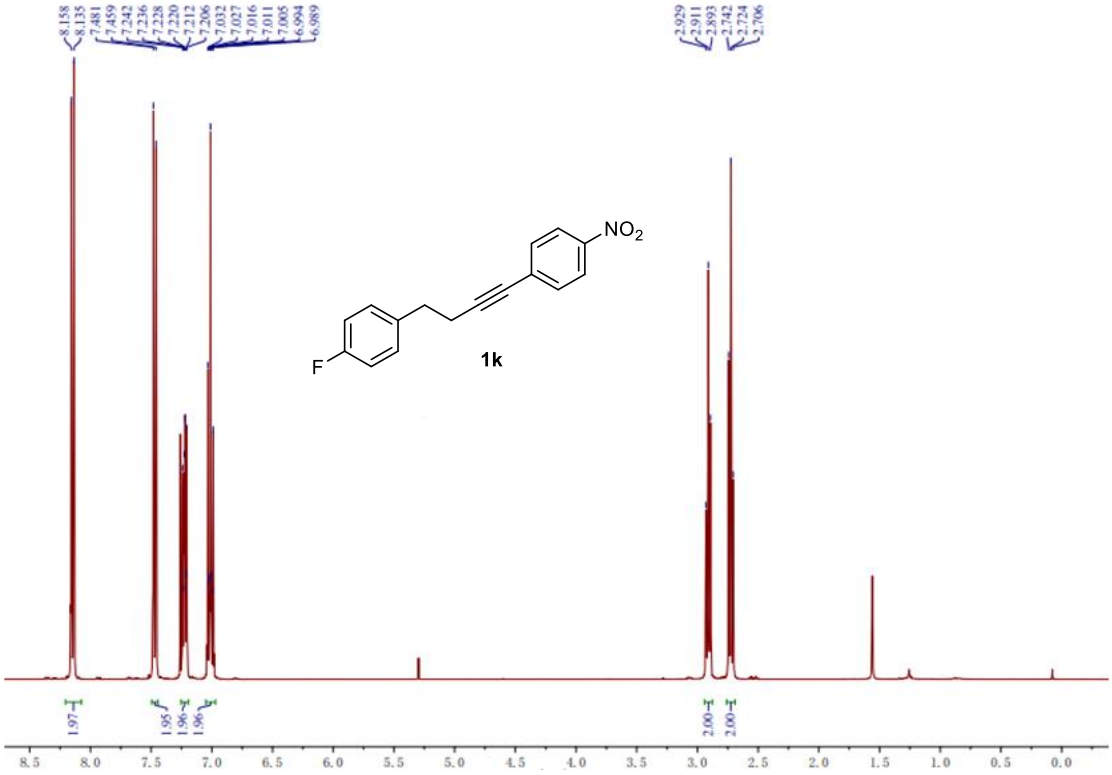
140.147
130.355
129.658
129.605
128.546
128.489
128.039
126.851
126.490
126.090
123.496
99.601
77.472
77.318
77.000
76.682
34.672
21.844
N
Ph
1i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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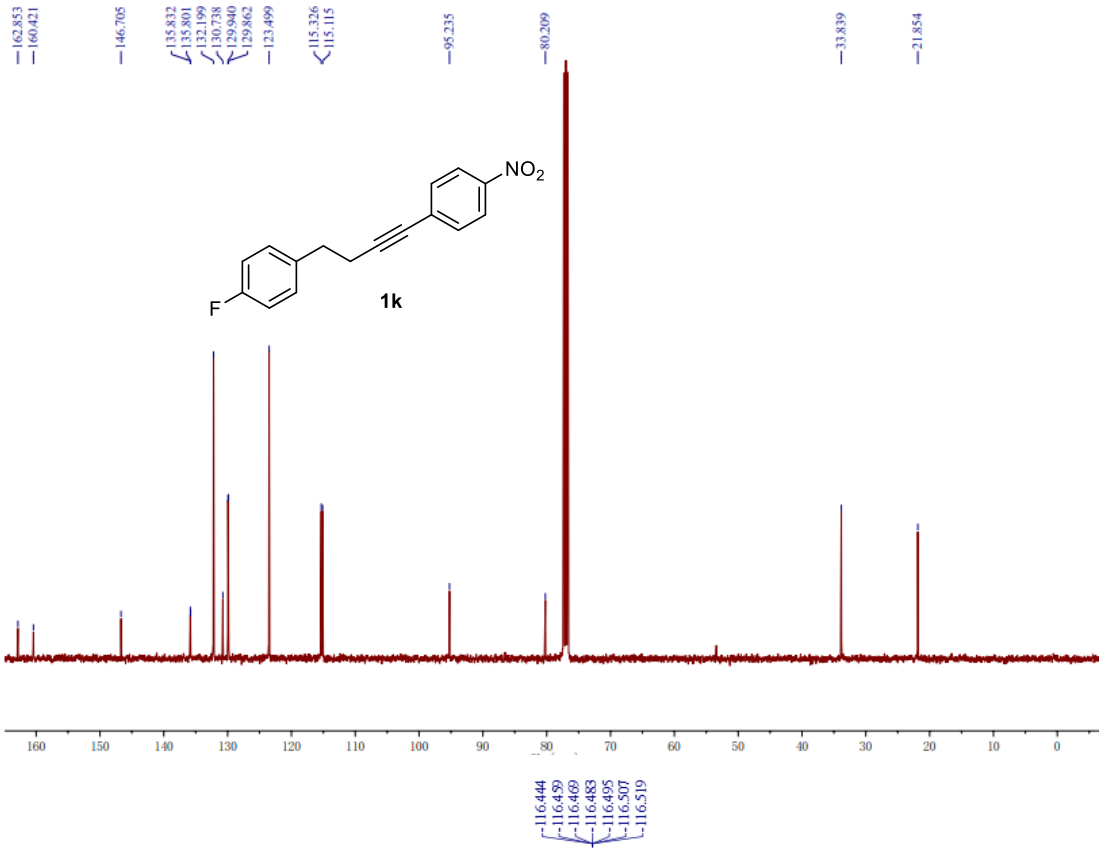
8.135
7.481
7.459
7.242
7.236
7.228
7.220
7.212
7.206
7.032
7.027
7.016
7.011
7.005
6.994
6.989
2.929
2.911
2.893
2.742
2.724
2.706
NO2
F
1k
1.97
1.95
1.96
1.96
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


162.853
160.421
146.705
135.832
135.801
132.199
130.738
129.940
129.862
123.499
115.326
115.115
95.235
80.209
33.839
21.854
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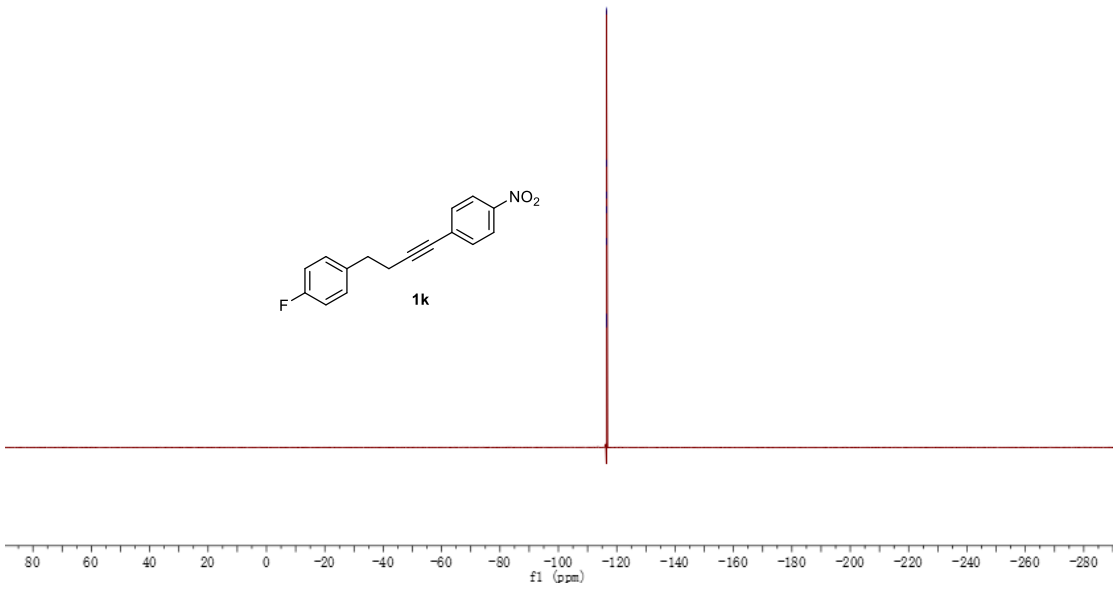
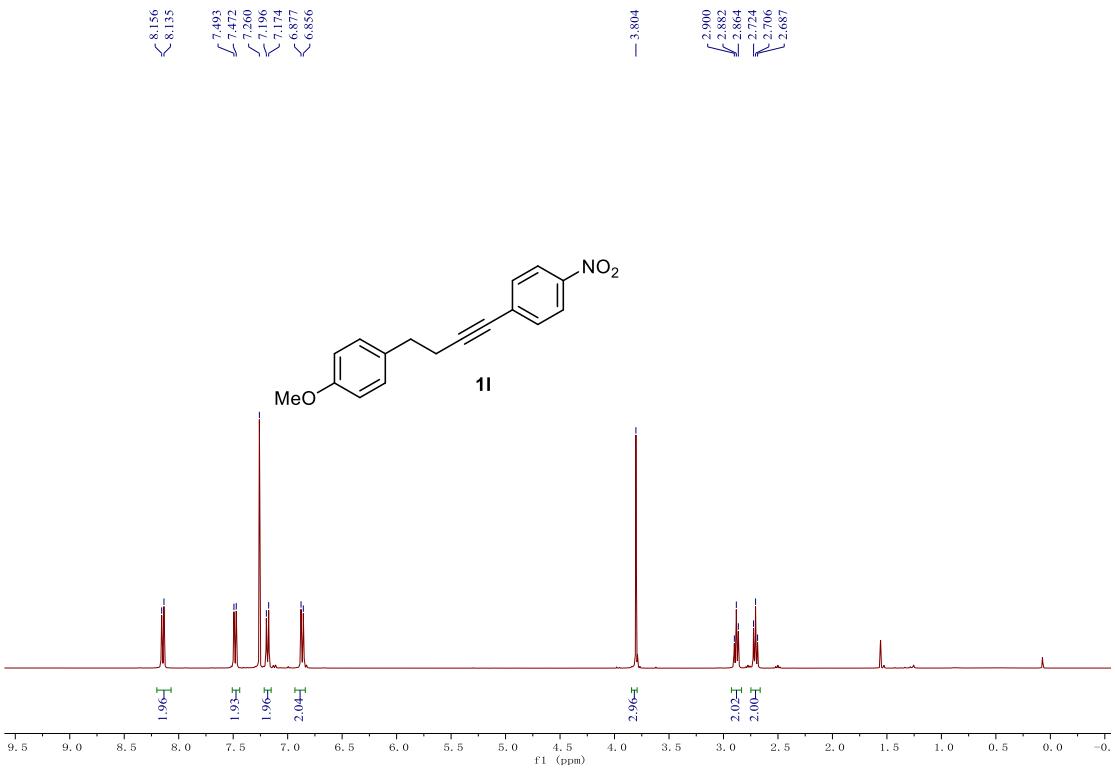
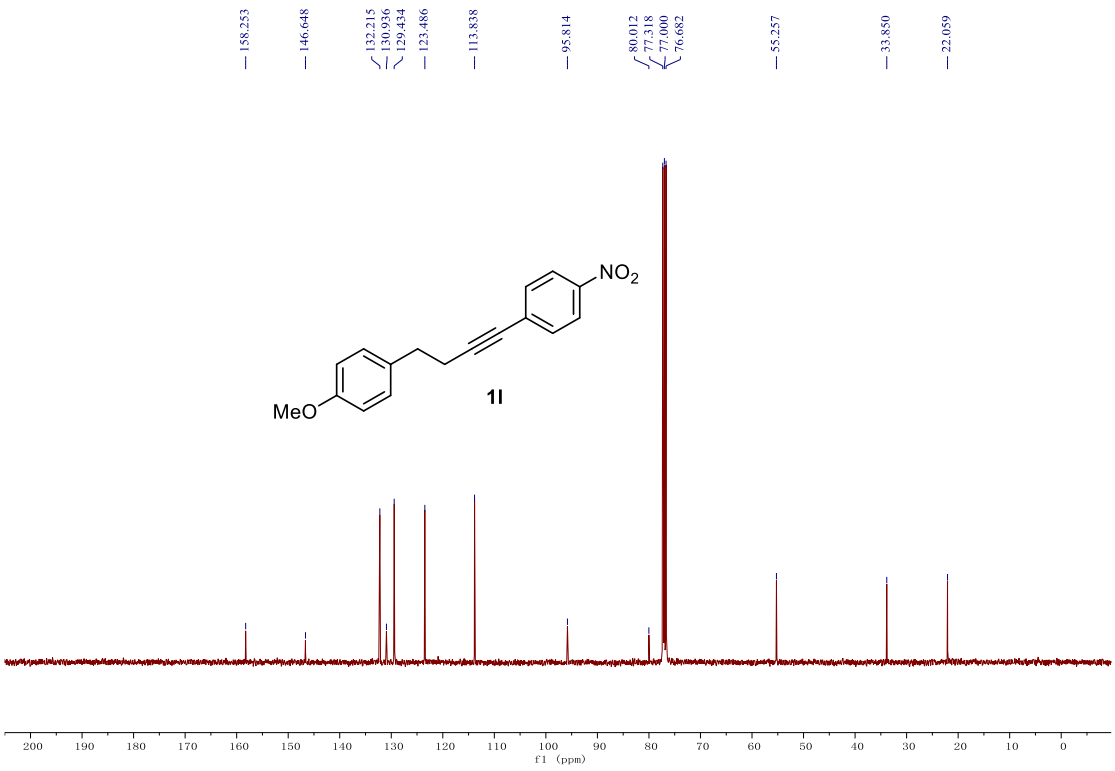
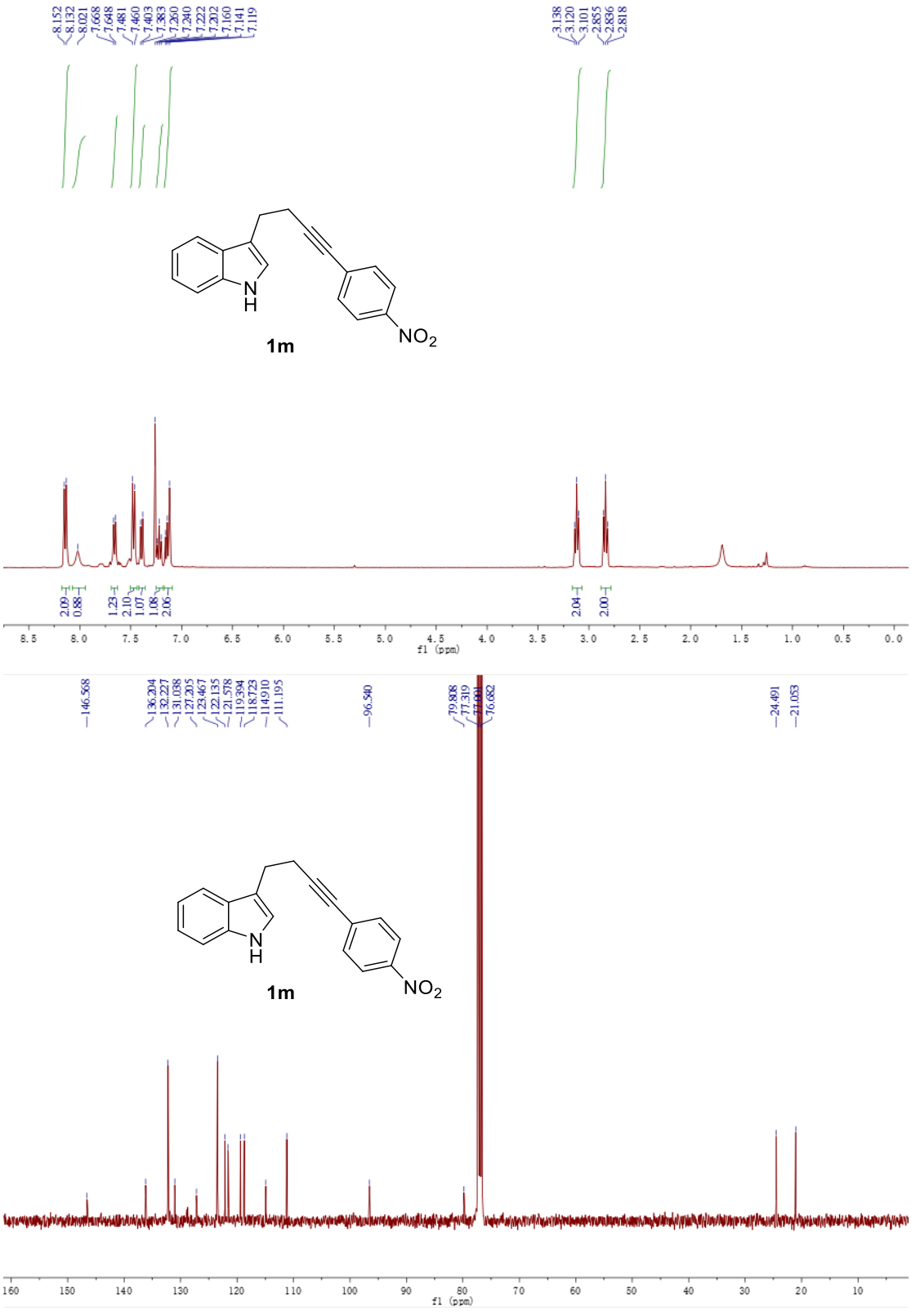
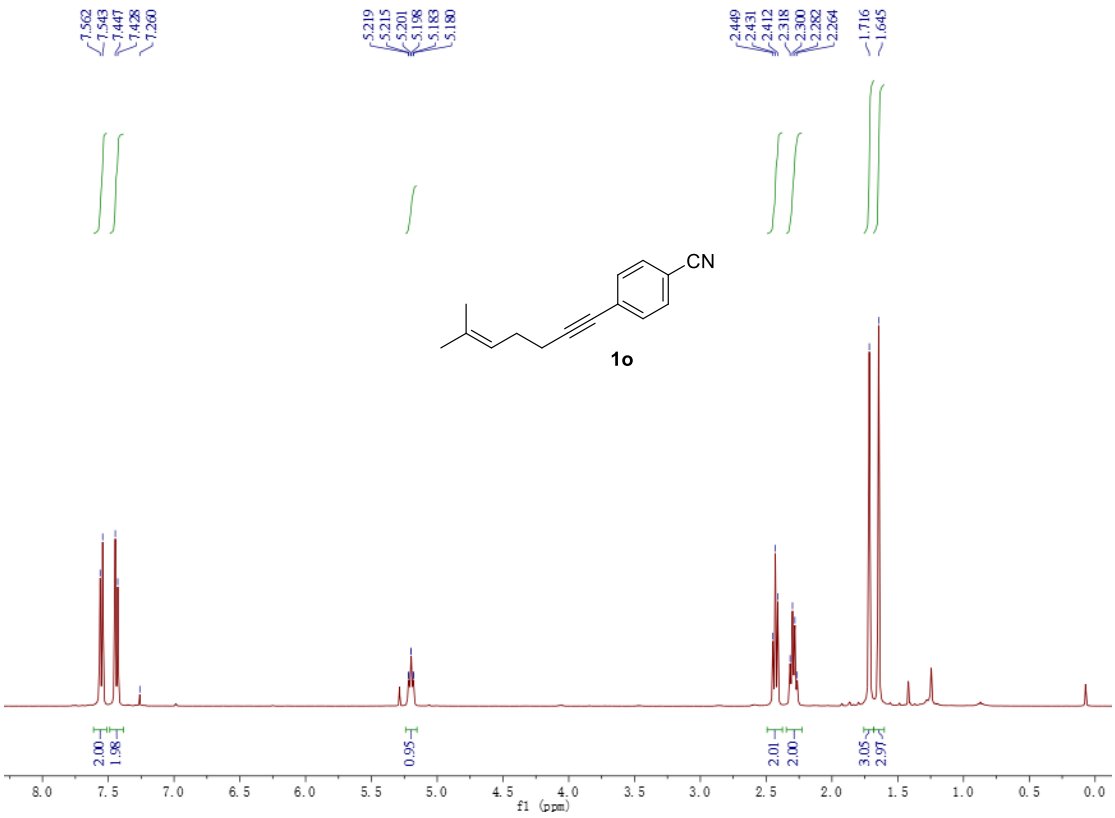
90
80
70
60
50
40
30
20
10
0

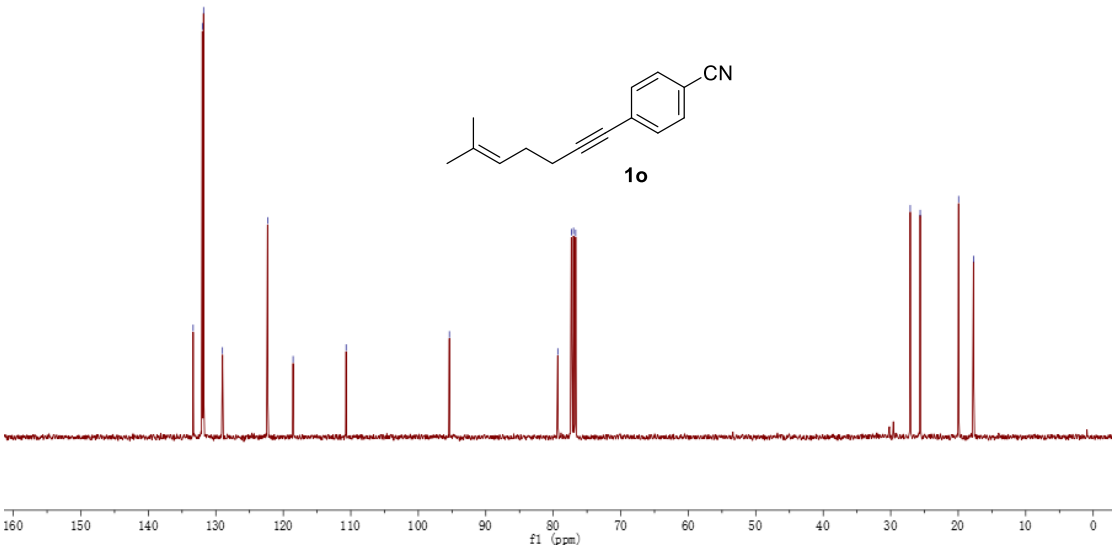

116.444
116.459
116.469
116.483
116.495
116.507
116.519
NO2
F
1k
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)


8.156
8.135
7.493
7.472
7.260
7.196
7.174
6.877
6.856
3.804
2.900
2.882
2.864
2.724
2.706
2.687
NO2
MeO
1l
1.96
1.93
1.96
2.04
2.96
2.02
2.00
f1 (ppm)


158.253
146.648
132.215
130.936
129.434
123.486
113.838
95.814
80.012
77.318
77.000
76.682
55.257
33.850
22.059
NO2
MeO
1l
f1 (ppm)


8.152
8.132
8.021
7.668
7.648
7.481
7.460
7.403
7.383
7.260
7.240
7.222
7.202
7.160
7.141
7.119
3.138
3.120
3.101
2.855
2.836
2.818
1m
2.09
0.88
1.23
2.10
1.07
1.08
2.06
2.04
2.00
f1 (ppm)
146.568
136.204
132.227
131.038
127.205
123.467
122.135
121.578
119.394
118.723
114.910
111.195
96.540
79.808
77.319
76.682
24.491
21.053
1m
f1 (ppm)


7.562
7.543
7.447
7.428
7.260
5.219
5.215
5.201
5.198
5.183
5.180
2.449
2.431
2.412
2.318
2.300
2.282
2.264
1.716
1.645
CN
1o
2.00
1.98
0.95
2.01
2.00
3.05
2.97
f1 (ppm)


133.356
131.997
131.819
129.006
122.332
118.552
110.697
95.393
79.337
77.318
77.000
76.681
27.108
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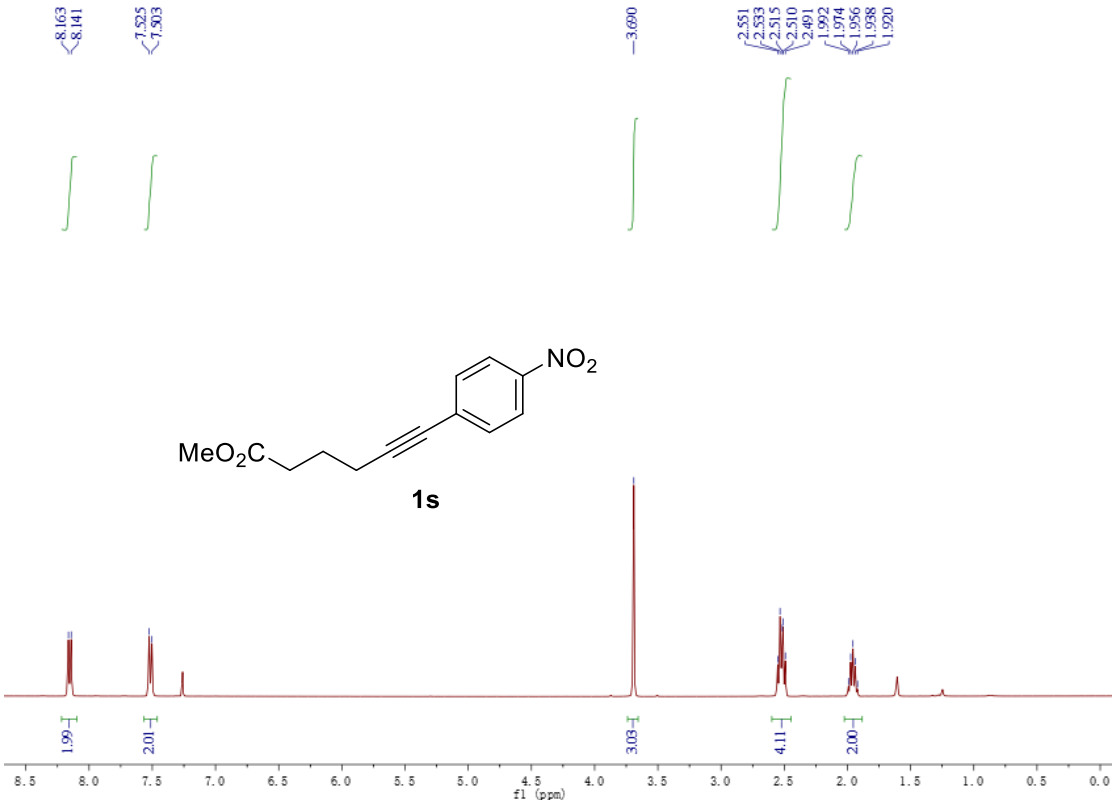
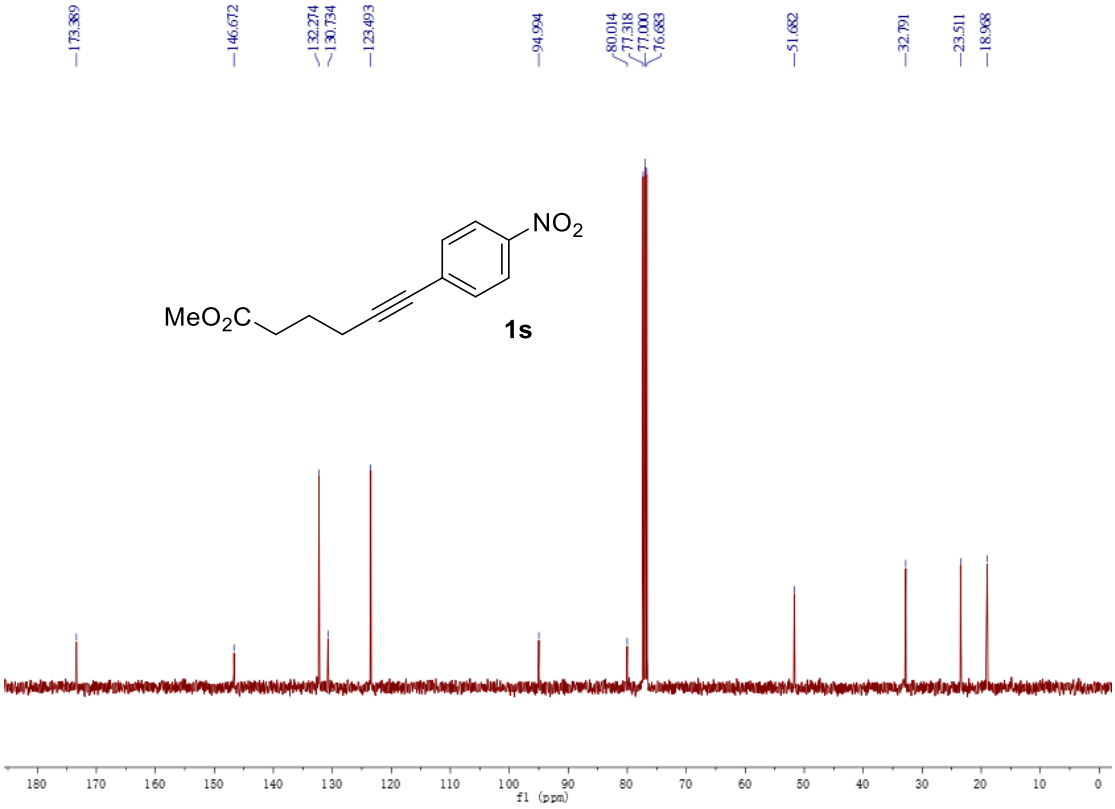
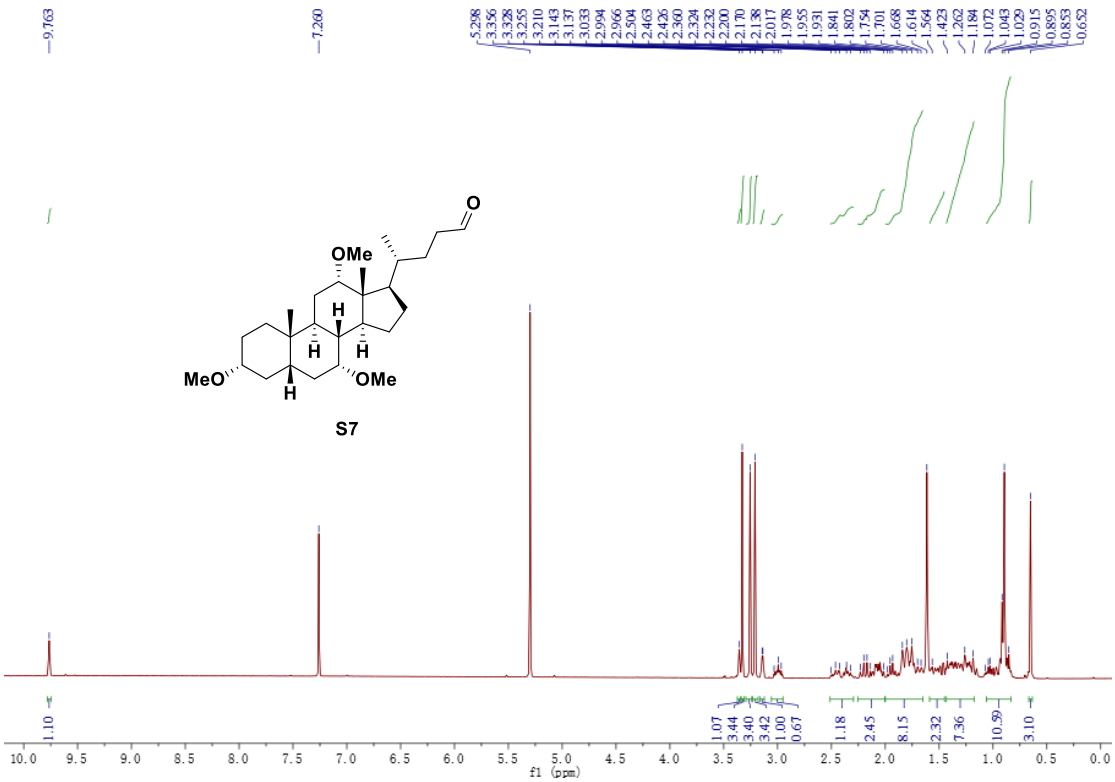
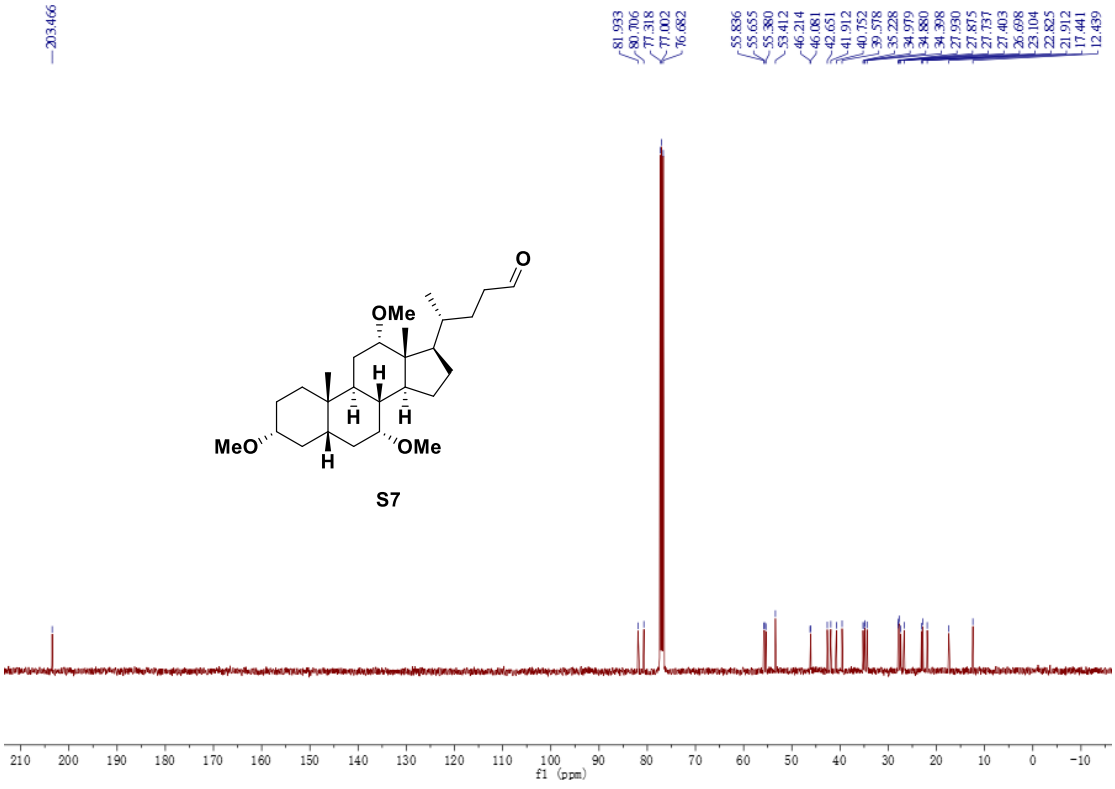
19.947
17.734
CN
1o
f1 (ppm)


8.163
8.141
7.525
7.503
3.690
2.551
2.533
2.515
2.510
2.491
1.992
1.974
1.956
1.938
1.920
NO2
MeO2C
1s
1.99
2.01
3.03
4.11
2.00
f1 (ppm)


173.389
146.672
132.274
130.734
123.493
94.994
80.014
77.318
77.000
76.683
51.682
32.791
23.511
18.968
NO2
MeO2C
1s
f1 (ppm)


9.763
7.260
5.298
3.356
3.328
3.255
3.210
3.143
3.137
3.033
2.994
2.966
2.594
2.463
2.426
2.360
2.324
2.232
2.200
2.170
2.138
2.017
1.978
1.955
1.931
1.841
1.802
1.754
1.701
1.668
1.614
1.564
1.423
1.262
1.184
1.072
1.043
1.029
0.915
0.895
0.853
0.652
O
OMe
H
H
H
MeO
OMe
H
S7
1.10
1.07
3.44
3.40
3.42
1.00
0.67
1.18
2.45
8.15
2.32
7.36
10.99
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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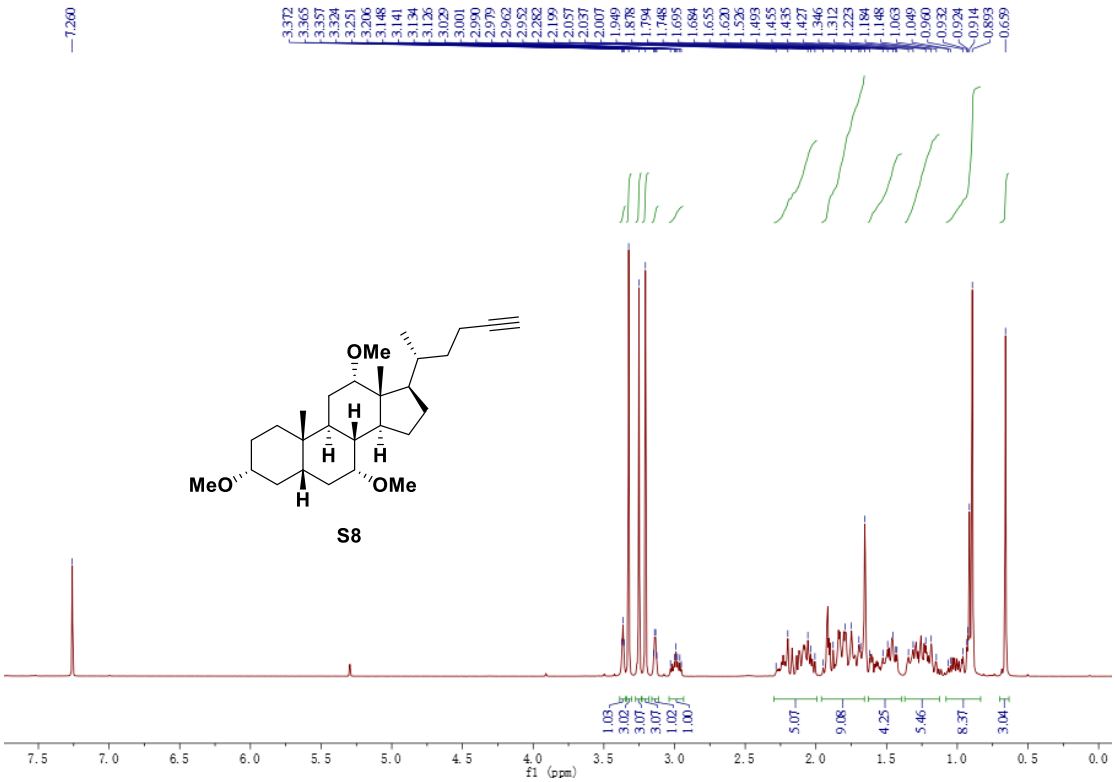
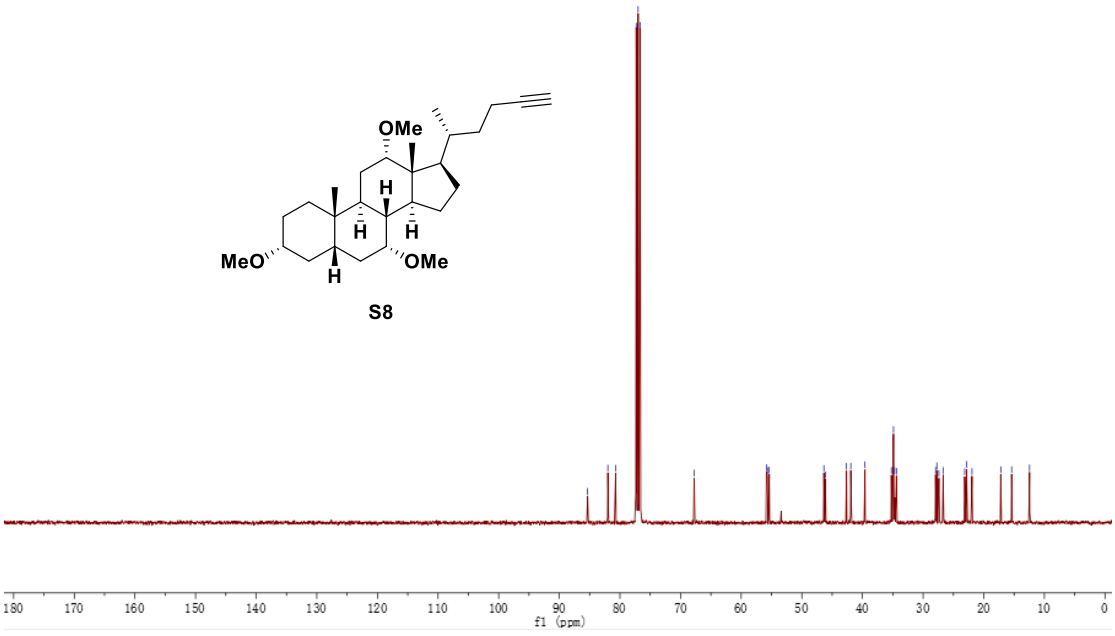
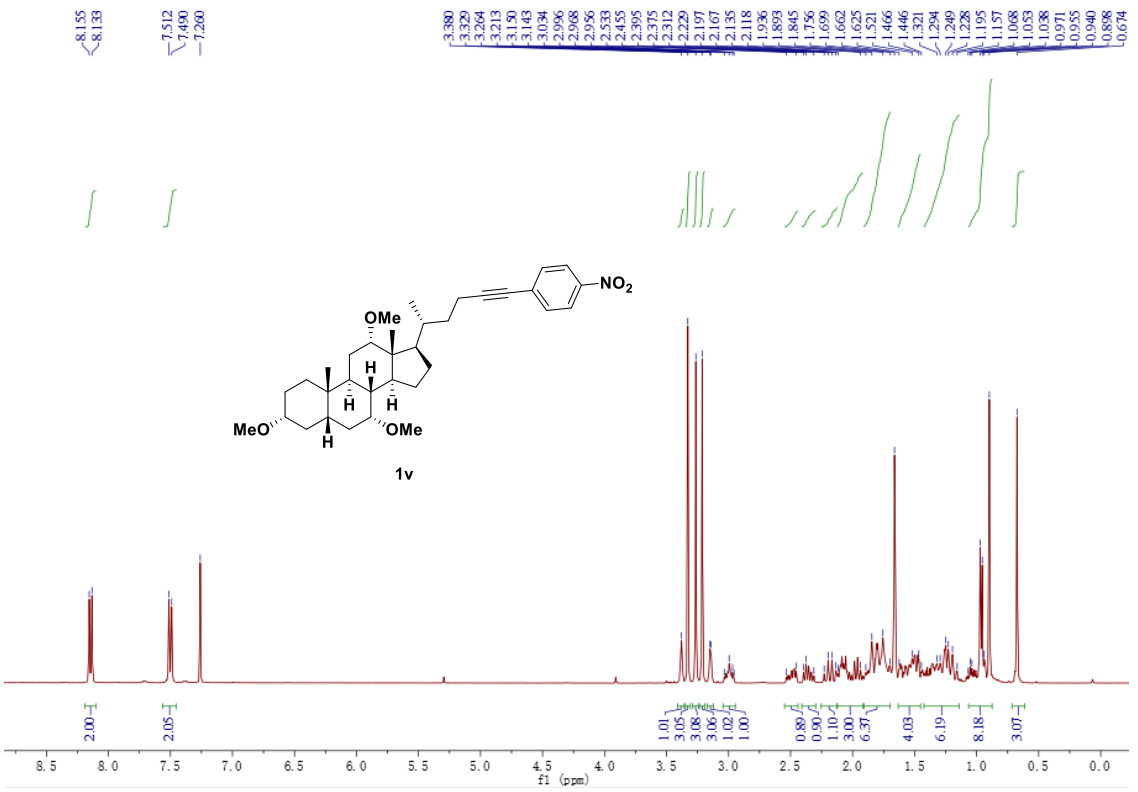
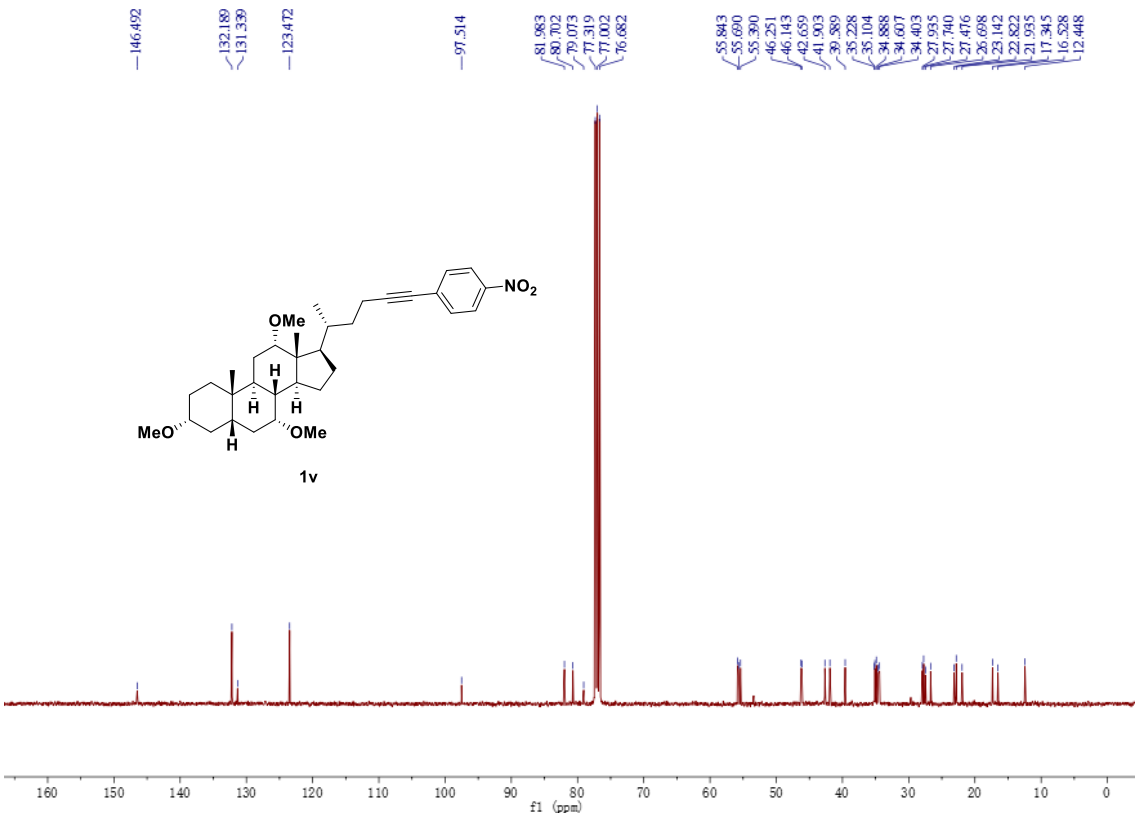
80.706
77.318
77.002
76.682
55.836
55.655
55.380
53.412
46.214
46.081
42.651
41.912
40.752
39.578
35.228
34.979
34.880
34.398
27.930
27.875
27.737
27.403
26.698
23.104
22.825
21.912
17.441
12.439
O
OMe
H
H
H
MeO
OMe
H
S7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

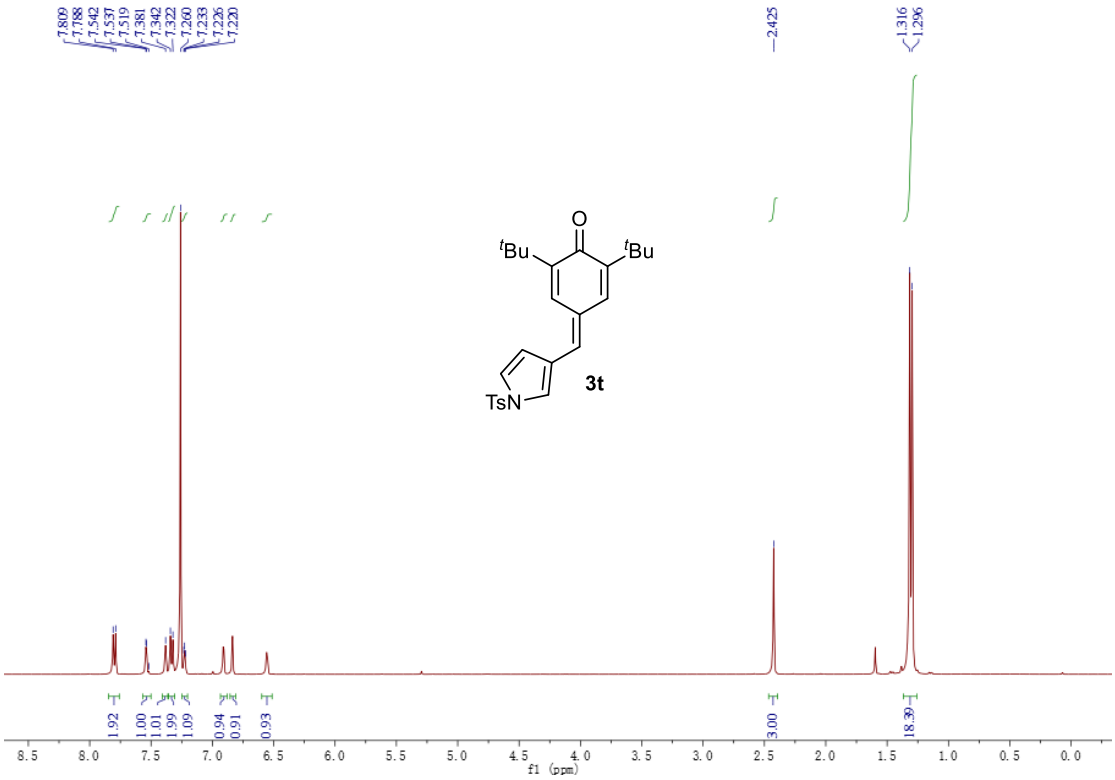

OMe
H
H
H
MeO
H
OMe
S8
f1 (ppm)

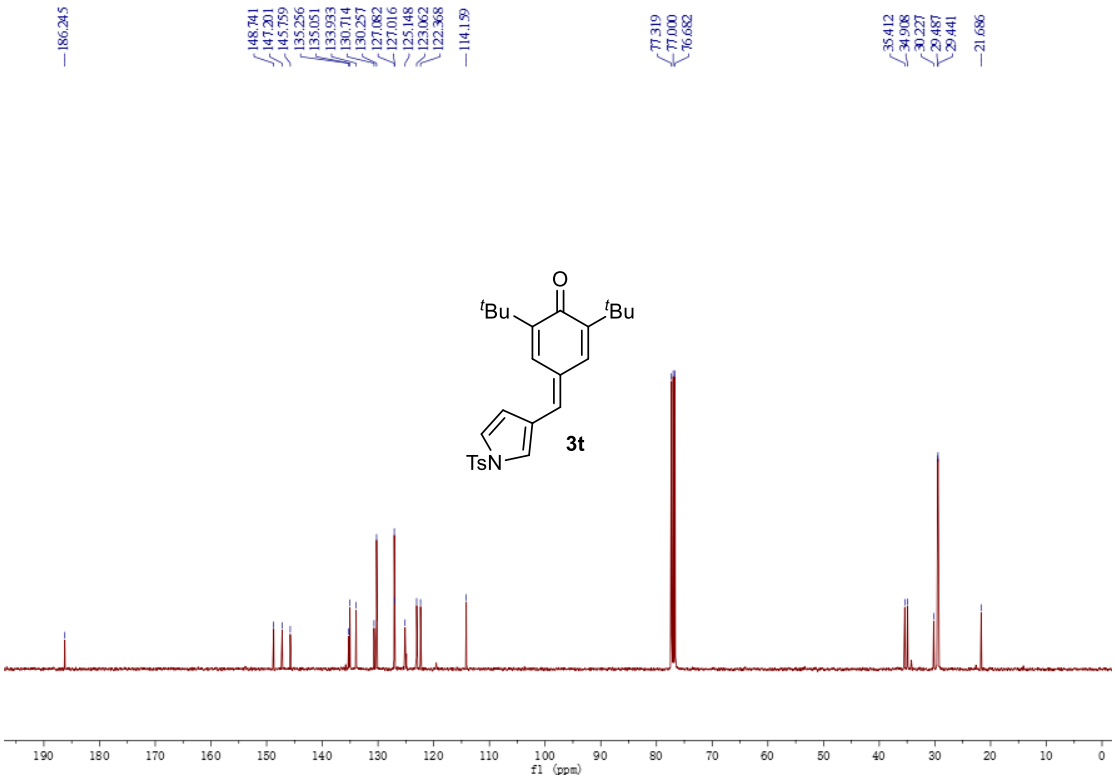

OMe
H
H
H
MeO
H
OMe
S8
f1 (ppm)

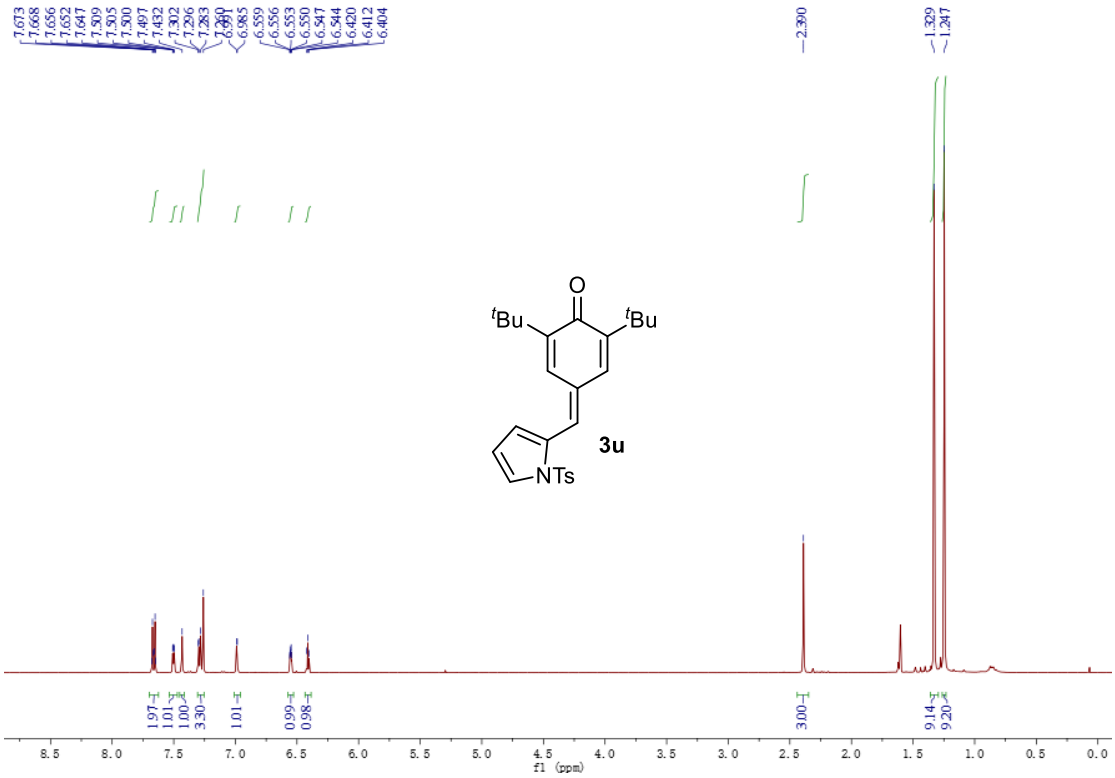


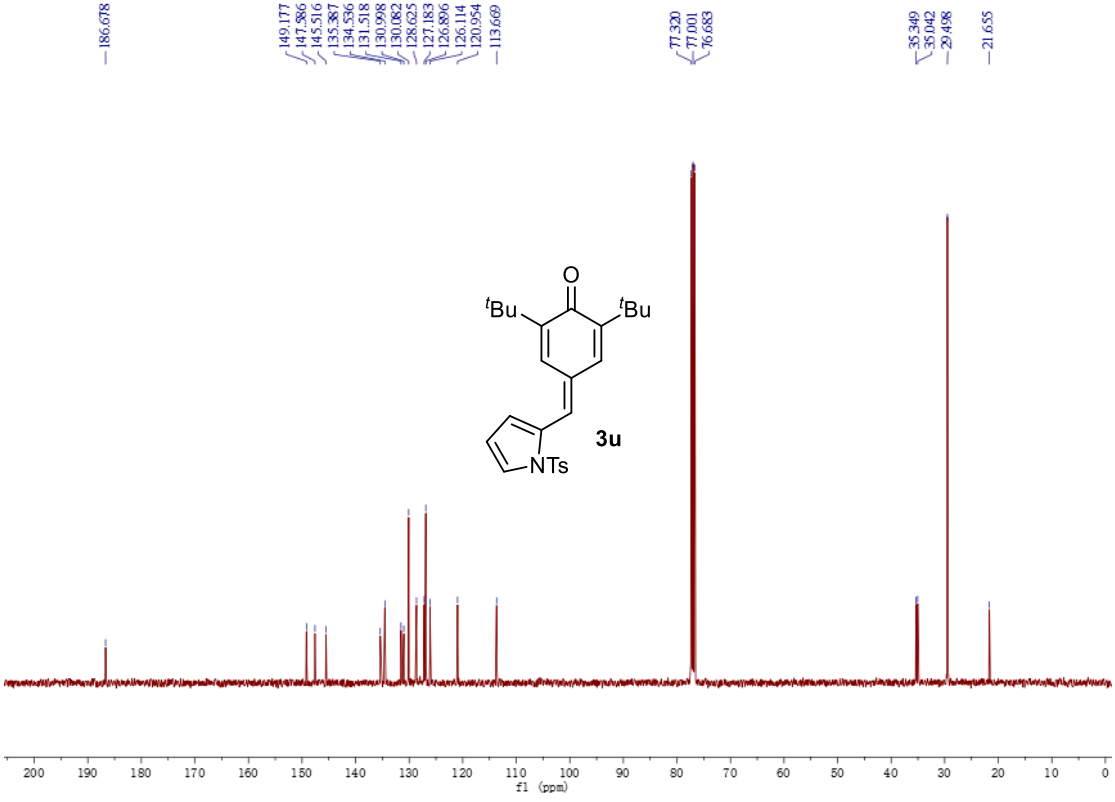


NMR spectra of compound 3

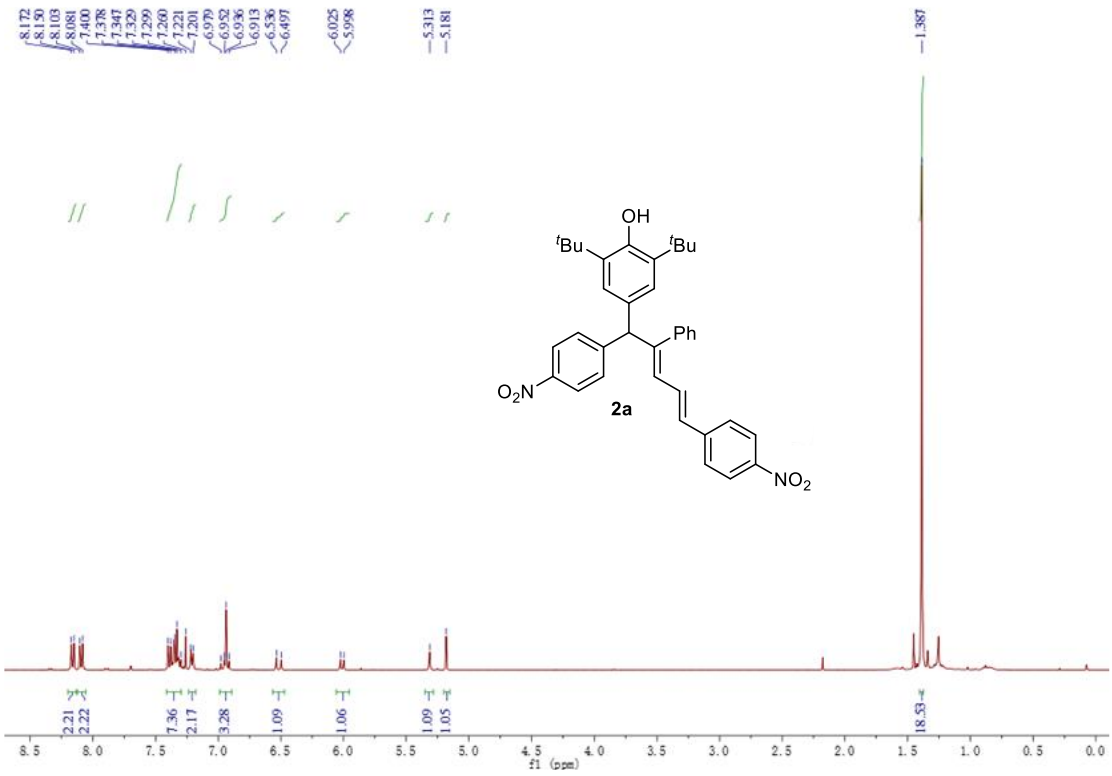

7.809
7.788
7.542
7.537
7.519
7.381
7.342
7.322
7.260
7.233
7.226
7.220
2.425
1.316
1.296
tBu
tBu
O
TsN
3t
1.92
1.00
1.01
1.99
1.09
0.94
0.91
0.93
3.00
18.39
f1 (ppm)

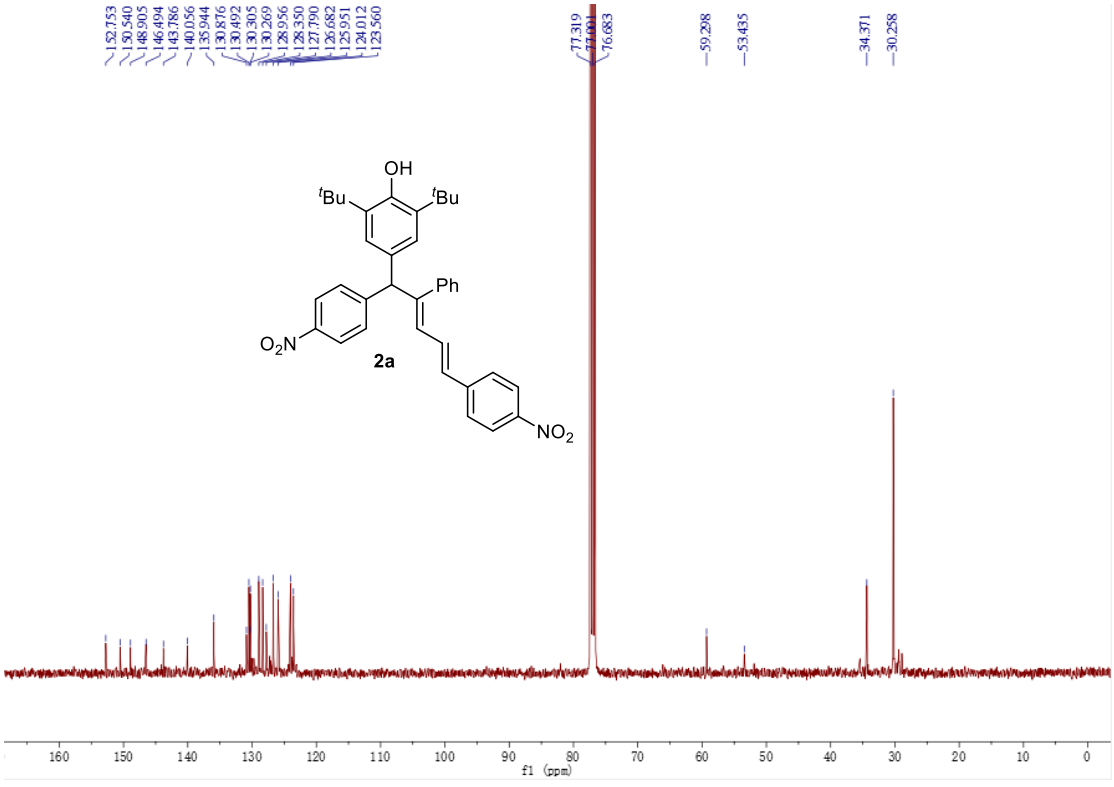

186.245
148.741
147.201
145.759
135.256
135.051
133.933
130.714
130.257
127.082
127.016
125.148
123.062
122.368
114.159
77.319
77.000
76.682
35.412
34.908
30.227
29.487
29.441
21.686
tBu
tBu
O
TsN
3t
f1 (ppm)

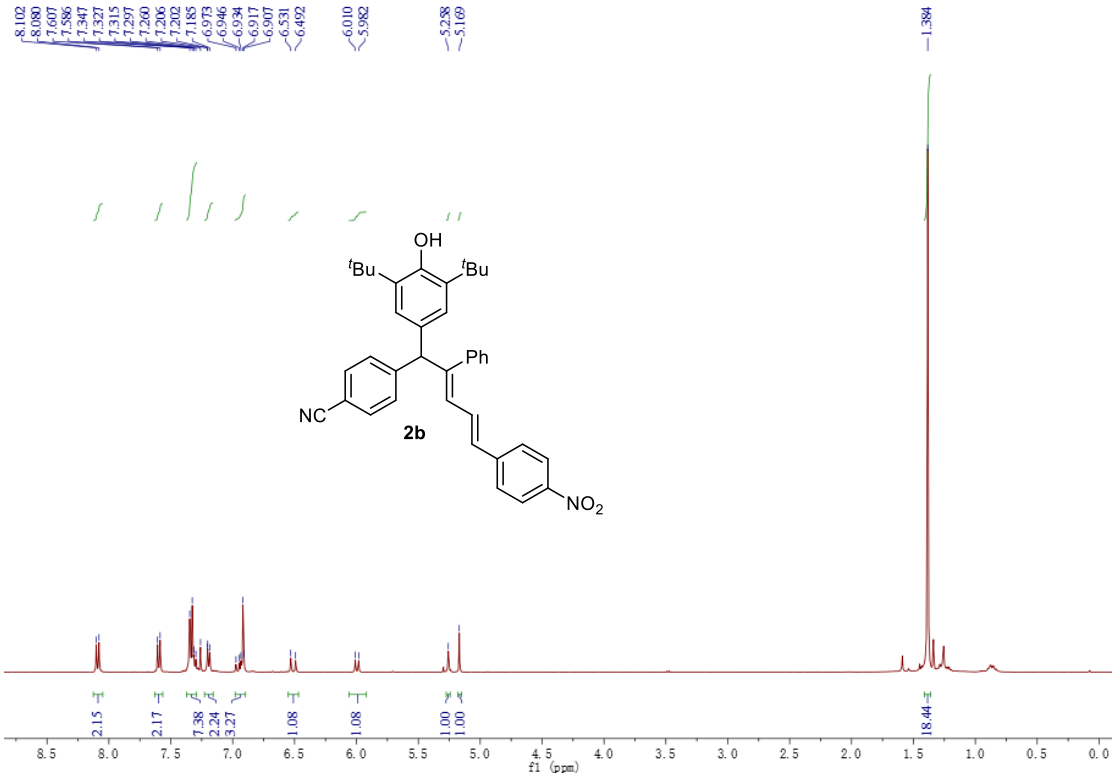


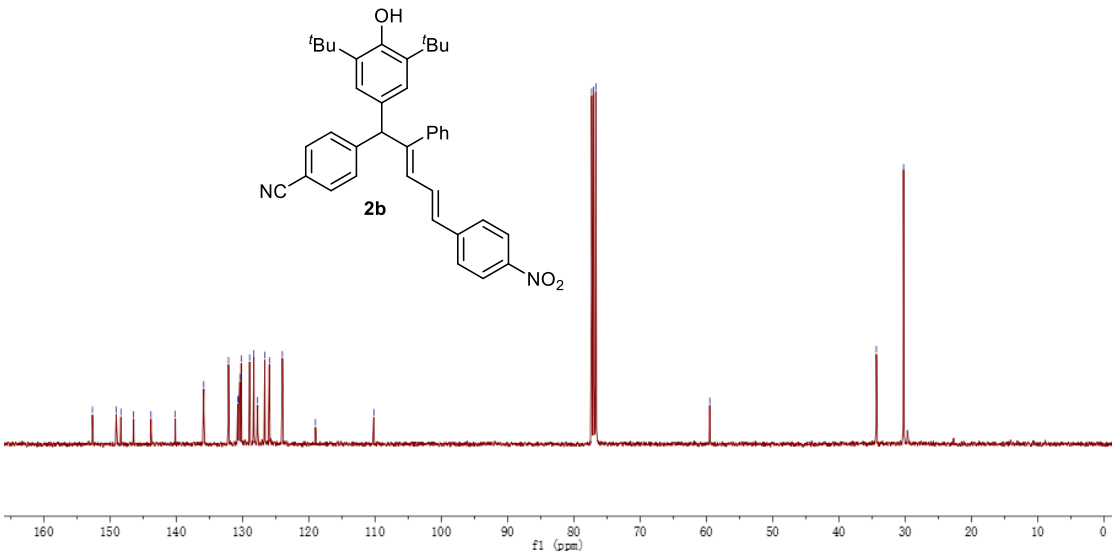


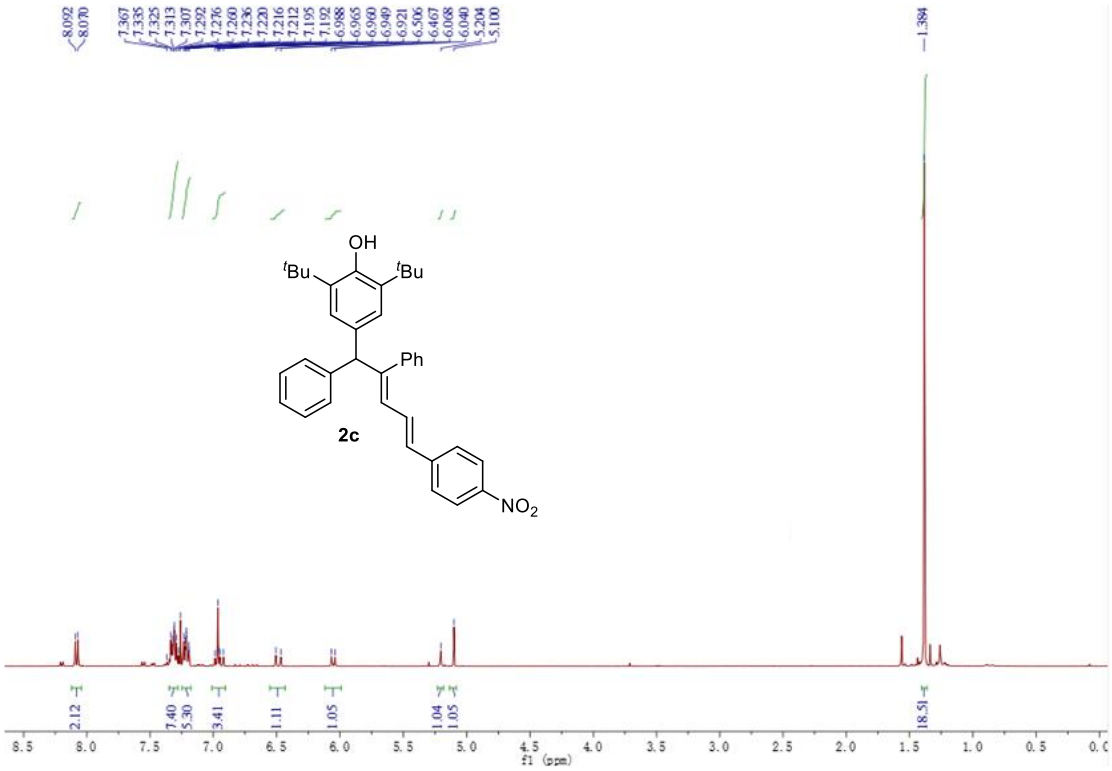
NMR spectra of compound 2 and 4

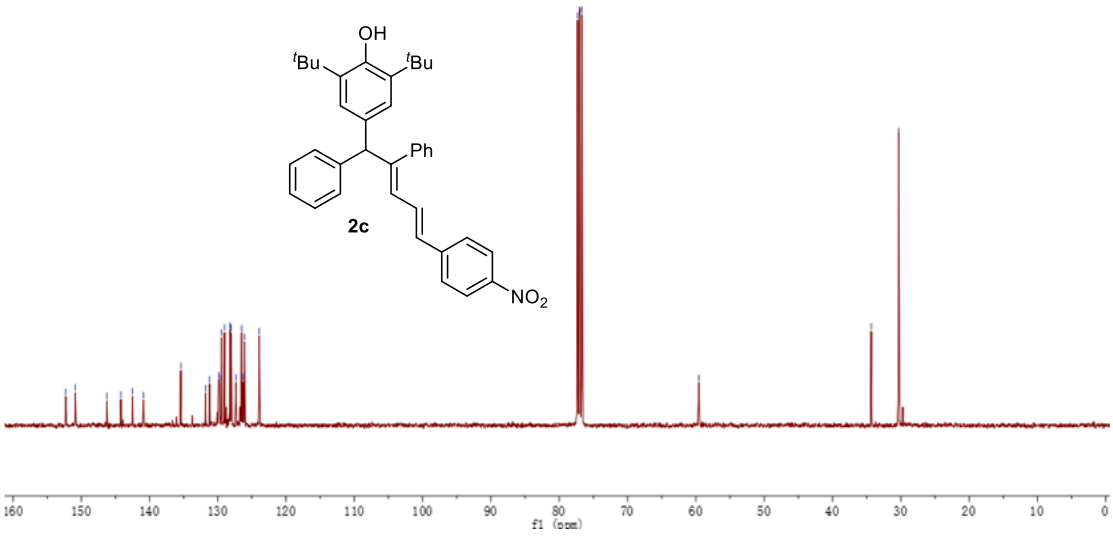

OH
tBu
tBu
Ph
O2N
NO2
2a
f1 (ppm)

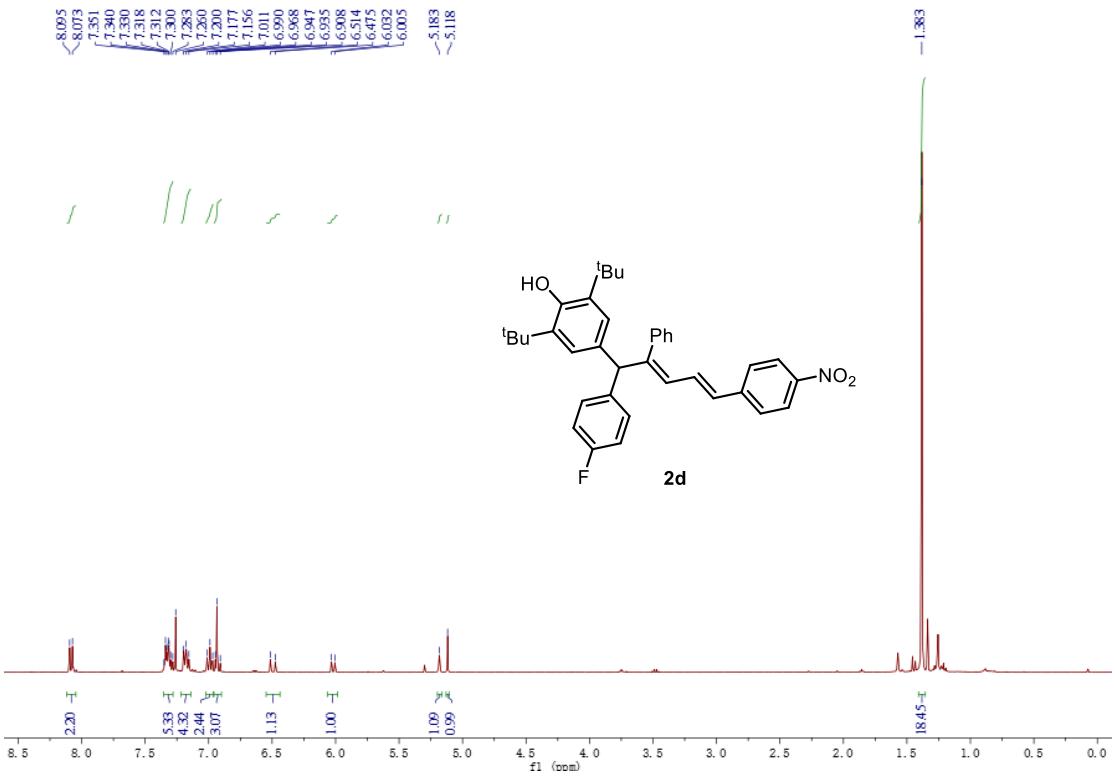

OH
tBu
tBu
Ph
O2N
NO2
2a
f1 (ppm)


OH
tBu
tBu
Ph
NC
NO2
2b


OH
tBu
tBu
Ph
NC
NO2
2b


OH
tBu
tBu
Ph
2c
NO2
f1 (ppm)


OH
tBu
tBu
Ph
2c
NO2
f1 (ppm)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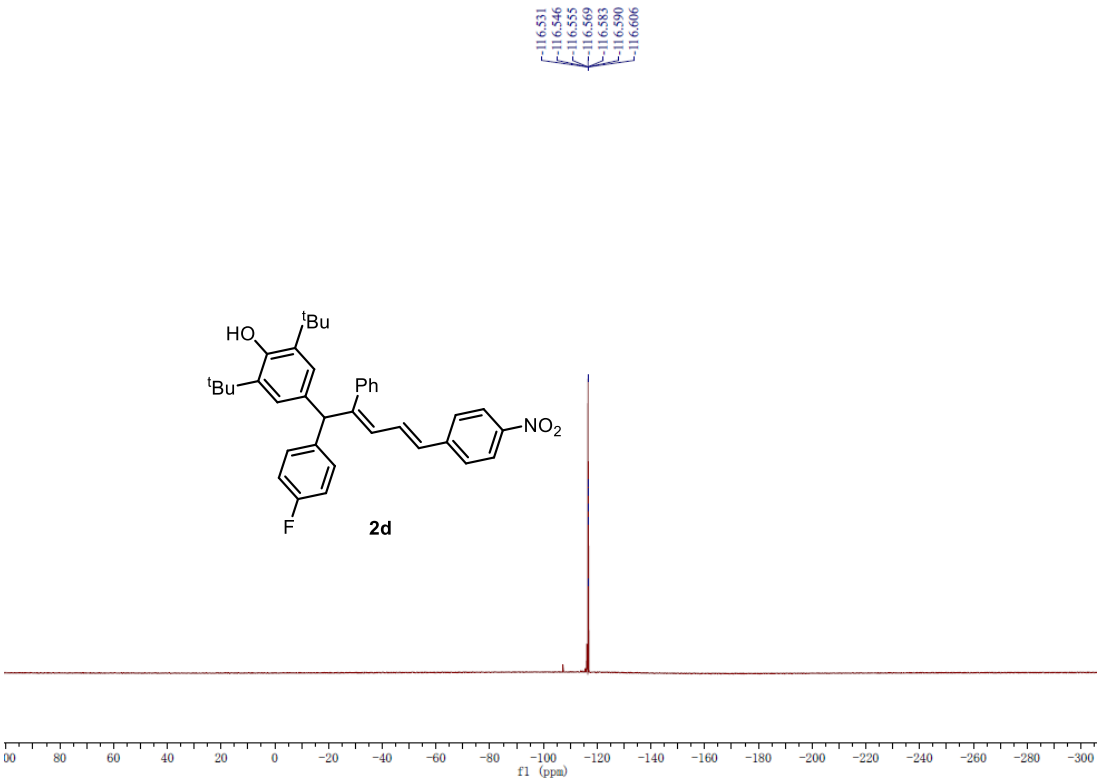
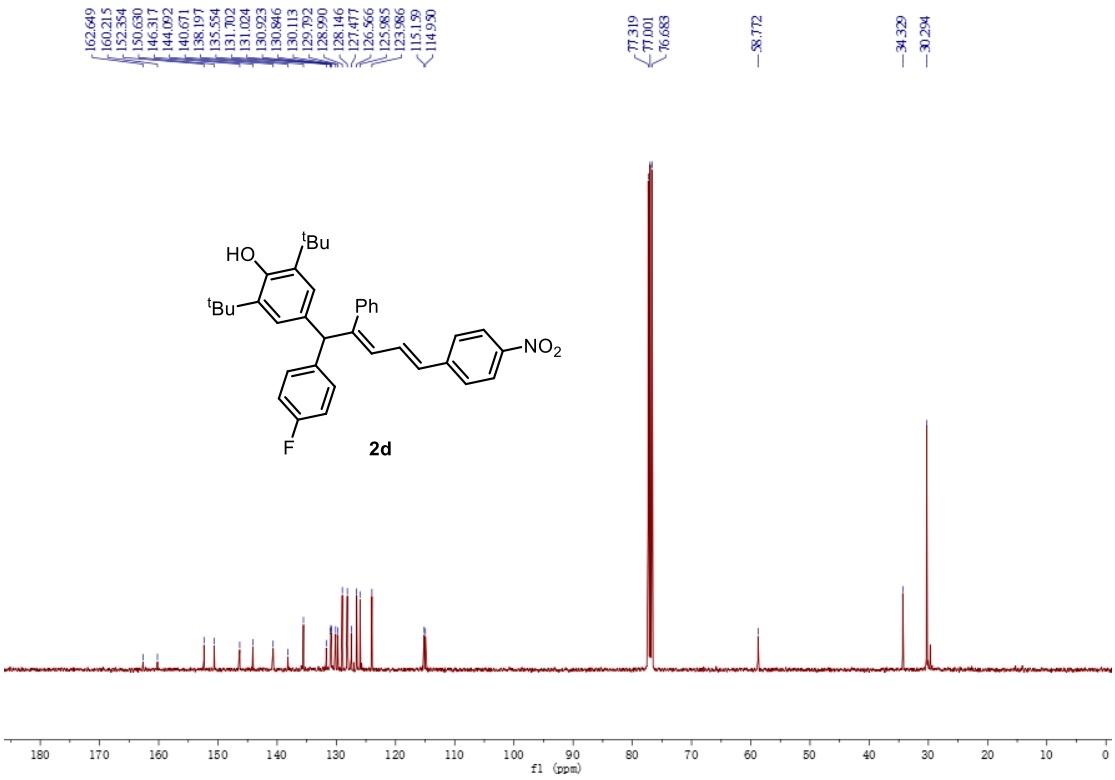
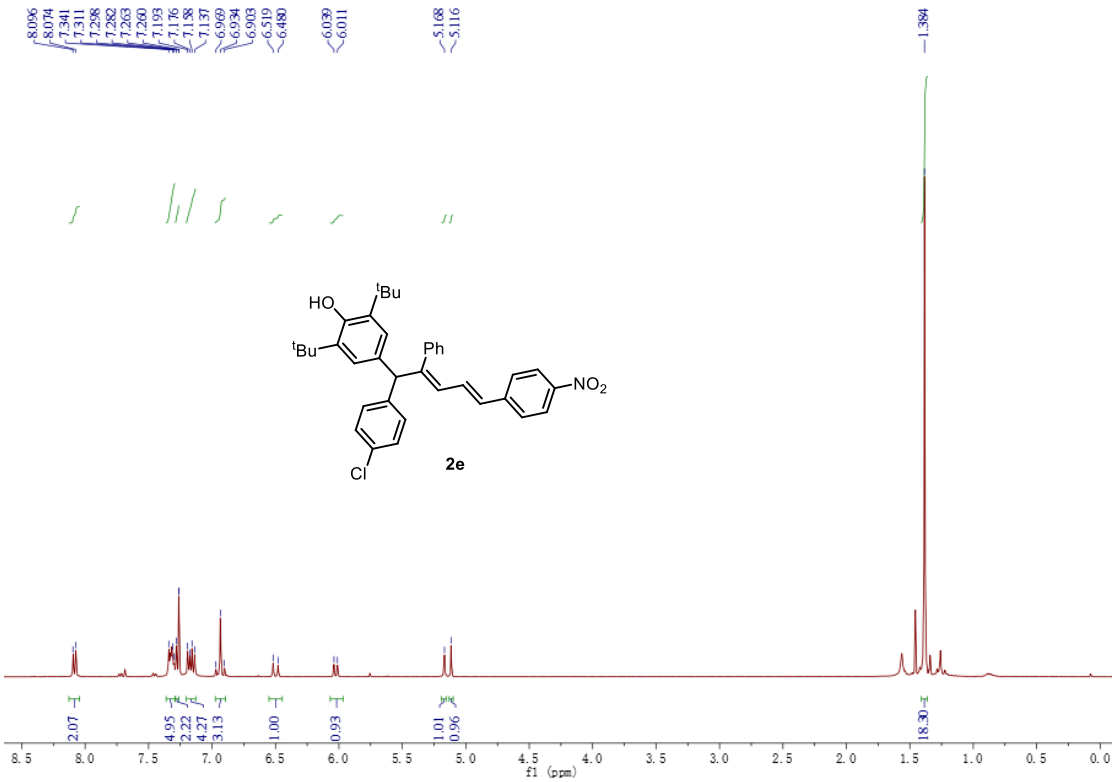
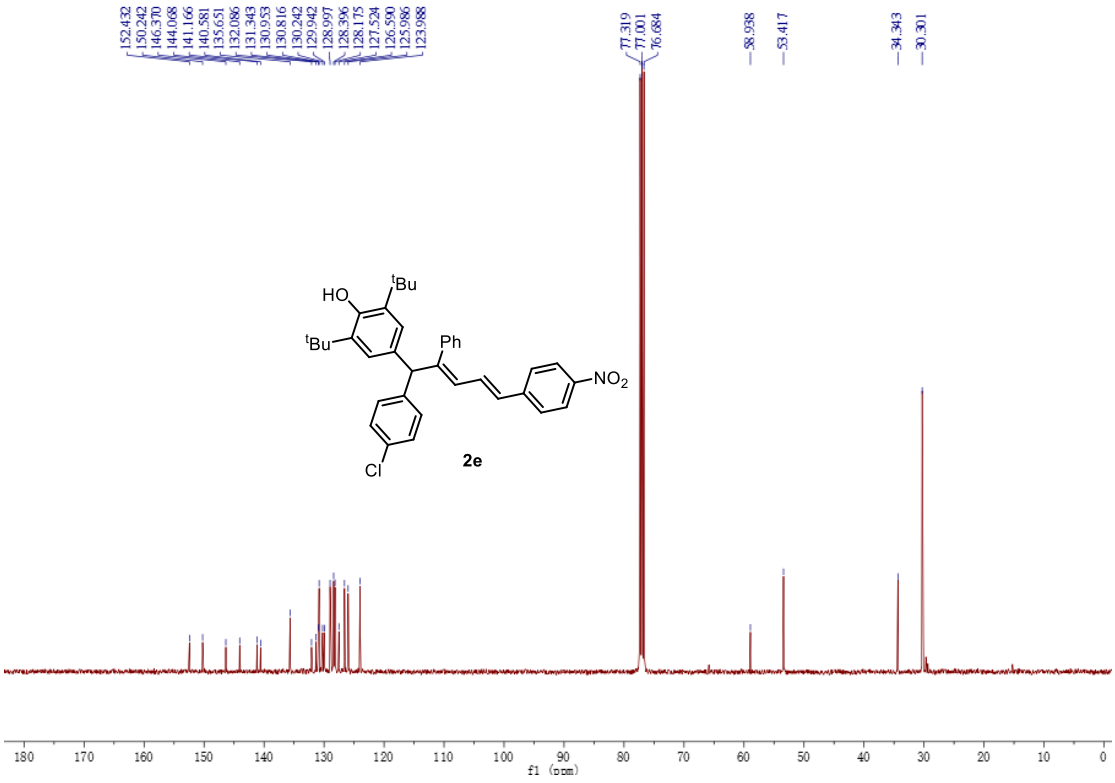
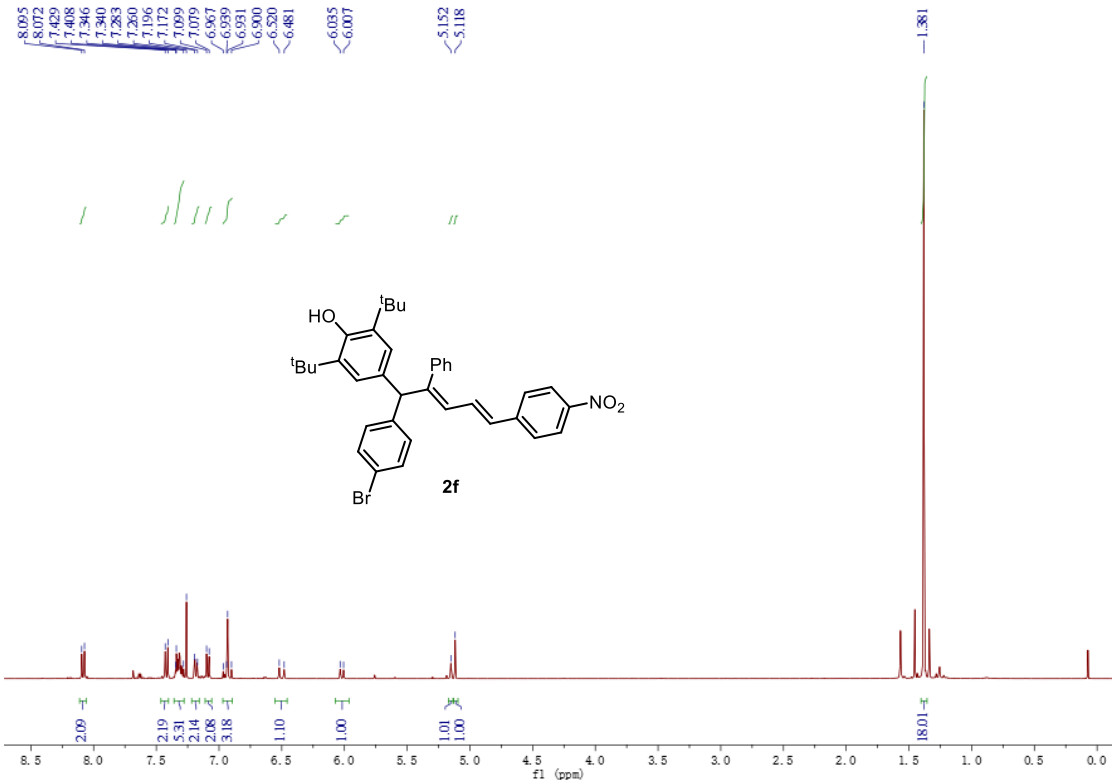
8.073
7.351
7.340
7.330
7.318
7.312
7.300
7.283
7.260
7.200
7.177
7.156
7.011
6.990
6.968
6.947
6.935
6.908
6.514
6.475
6.032
6.005
5.183
5.118
1.383
HO
tBu
tBu
Ph
NO2
F
2d
2.20
5.33
4.32
2.44
3.07
1.13
1.00
1.09
0.99
18.45
f1 (ppm)


-116.531
-116.546
-116.555
-116.569
-116.583
-116.590
-116.606
HO
tBu
tBu
Ph
NO2
F
2d
f1 (ppm)


162.649
160.215
152.354
150.630
146.317
144.092
140.671
138.197
135.554
131.702
131.024
130.923
130.846
130.113
129.792
128.990
128.146
127.477
126.566
125.585
123.586
115.139
114.930
77.319
77.001
76.683
58.772
34.329
30.294
HO
tBu
tBu
Ph
NO2
F
2d
f1 (ppm)


8.096
8.074
7.341
7.311
7.298
7.282
7.263
7.260
7.193
7.176
7.138
7.137
6.969
6.934
6.903
6.519
6.480
6.039
6.011
5.168
5.116
1.384
HO
tBu
tBu
Ph
NO2
Cl
2e
2.07
4.95
2.22
4.27
3.13
1.00
0.93
1.01
0.96
18.30
f1 (ppm)


152.432
150.242
146.370
144.068
141.166
140.581
135.651
132.086
131.343
130.953
130.816
130.242
129.942
128.997
128.396
128.175
127.524
126.590
125.986
123.988
77.319
77.001
76.684
58.938
53.417
34.343
30.301
HO
tBu
tBu
Ph
NO2
Cl
2e
f1 (ppm)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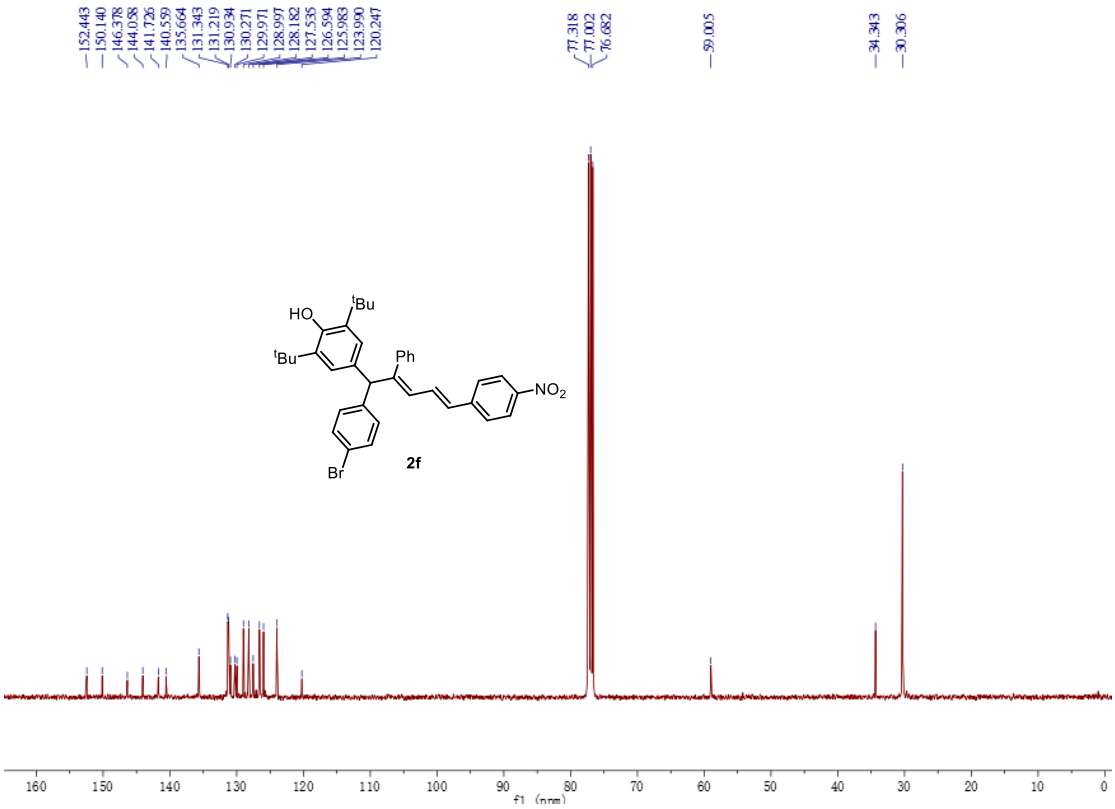
7.429
7.408
7.346
7.340
7.283
7.260
7.196
7.172
7.099
7.079
6.967
6.939
6.931
6.900
6.520
6.481
6.035
6.007
5.152
5.118
1.381
HO
tBu
tBu
Ph
NO2
Br
2f
2.09
2.19
5.31
2.14
2.08
3.18
1.10
1.00
1.01
1.00
18.01
f1 (ppm)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129.971
128.997
128.182
127.535
126.594
125.983
123.990
120.247
77.318
77.002
76.682
59.005
34.343
30.306
HO
tBu
tBu
Ph
NO2
Br
2f
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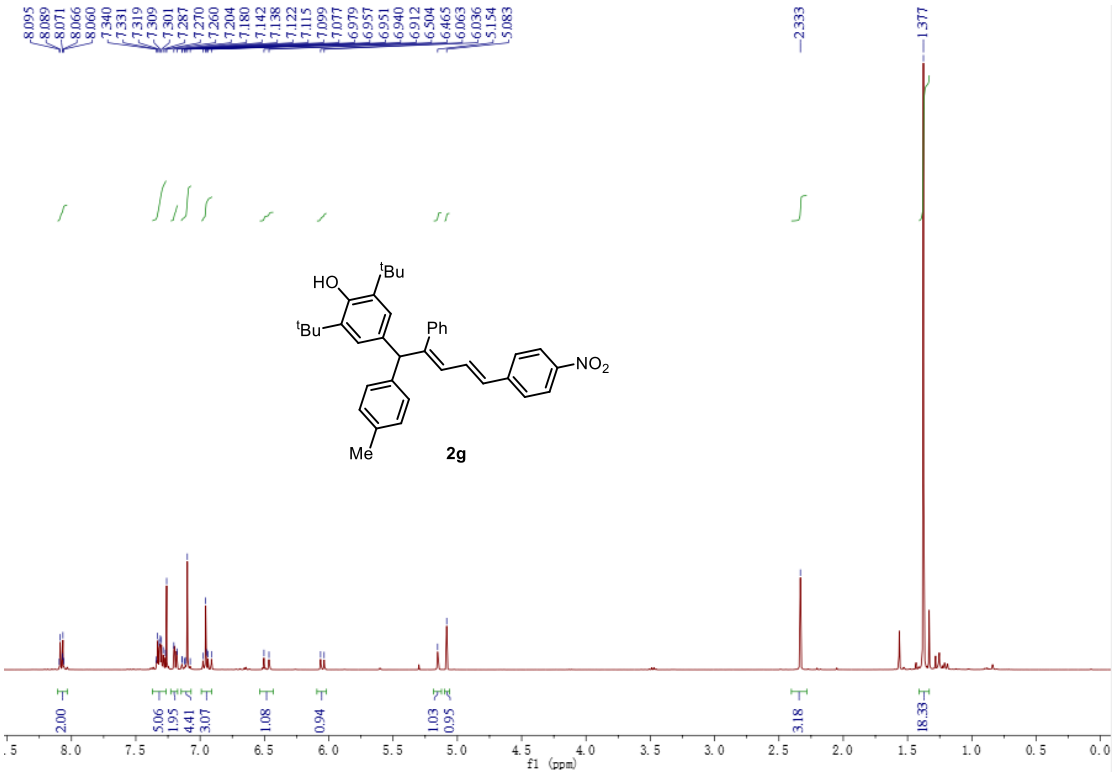
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.071
8.066
8.060
7.340
7.331
7.319
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7.301
7.287
7.270
7.260
7.204
7.180
7.142
7.138
7.122
7.115
7.099
7.077
6.979
6.957
6.951
6.940
6.912
6.504
6.465
6.063
6.036
5.154
5.083
2.333
1.377
HO
tBu
tBu
Ph
NO2
Me
2g
2.00
5.06
1.95
4.41
3.07
1.08
0.94
1.03
0.95
3.18
18.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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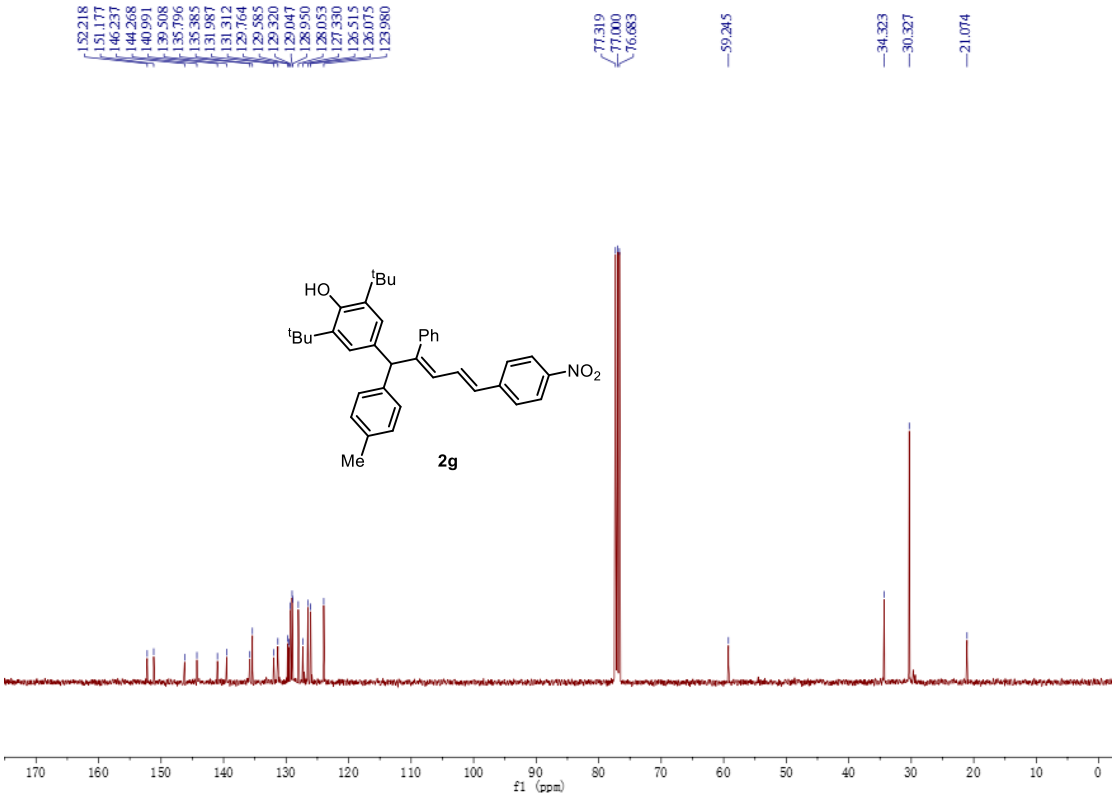
1.0
0.5
0.0
f1 (ppm)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139.508
135.796
135.385
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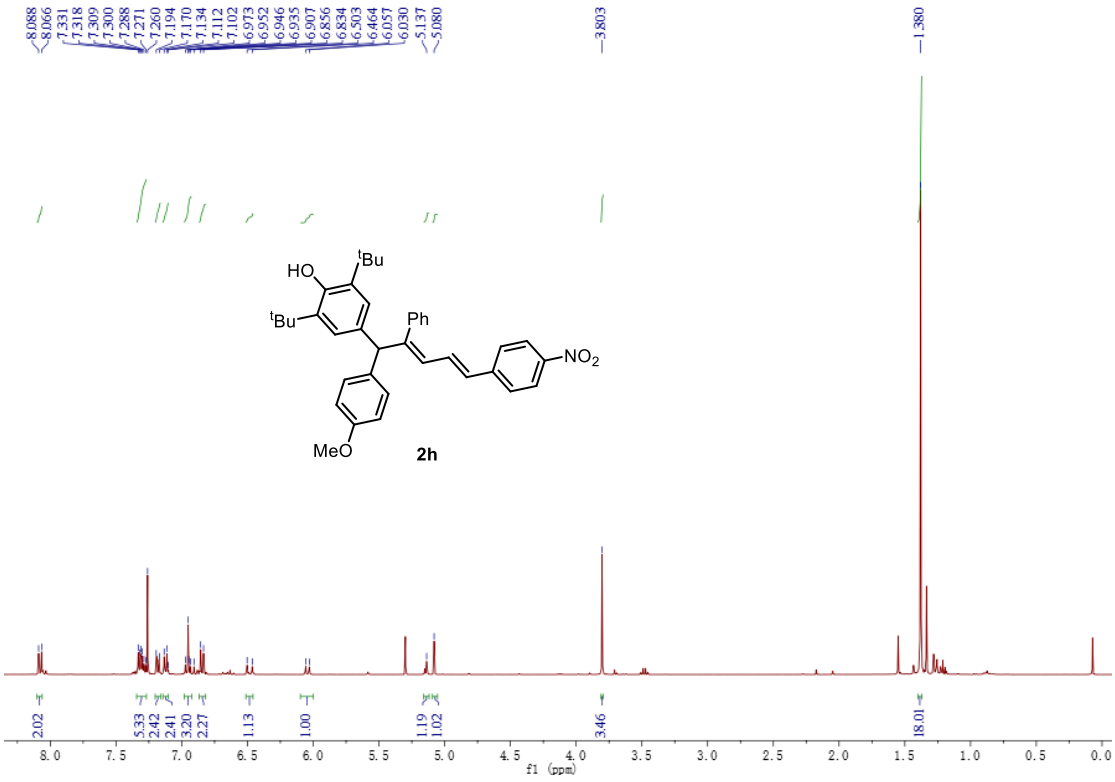
131.312
129.764
129.585
129.320
129.047
128.950
128.053
127.330
126.515
126.075
123.980
77.319
77.000
76.683
59.245
34.323
30.327
21.074
HO
tBu
tBu
Ph
NO2
Me
2g
f1 (ppm)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7.300
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7.194
7.170
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7.102
6.973
6.952
6.946
6.935
6.907
6.856
6.834
6.503
6.464
6.057
6.030
5.137
5.080
3.803
1.380
HO
tBu
tBu
Ph
NO2
MeO
2h
2.02
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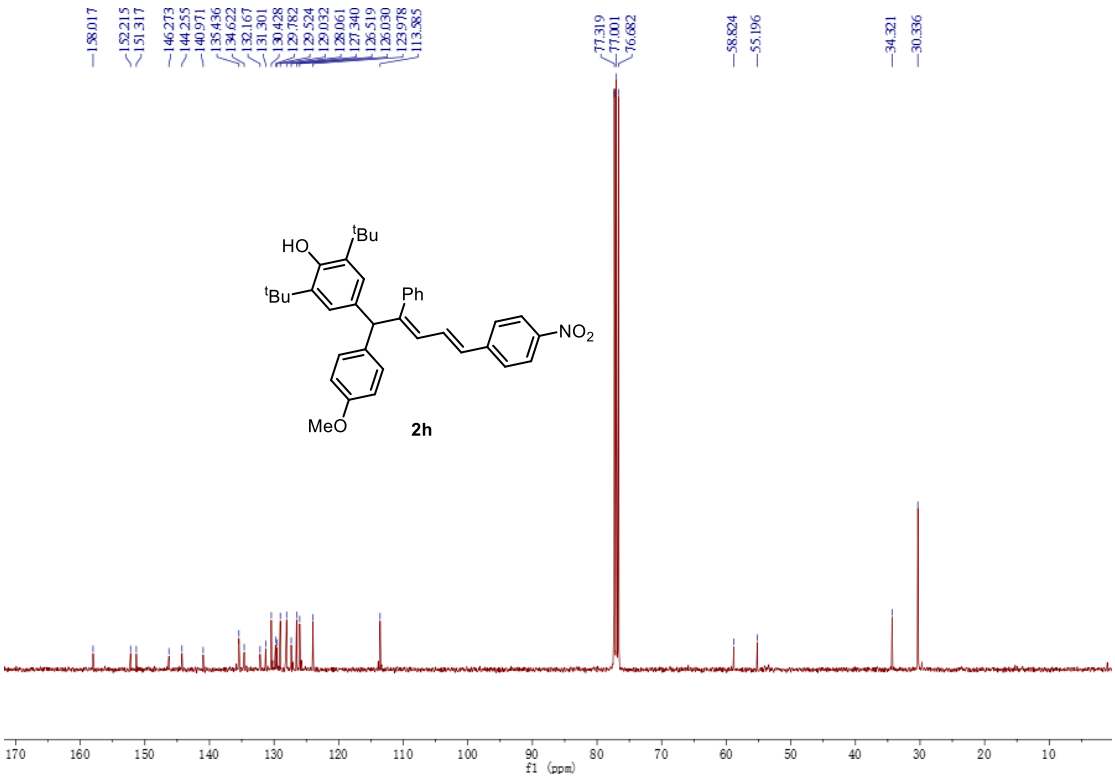
2.42
2.41
3.20
2.27
1.13
1.00
1.19
1.02
3.46
18.01
f1 (ppm)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134.622
132.167
131.301
130.428
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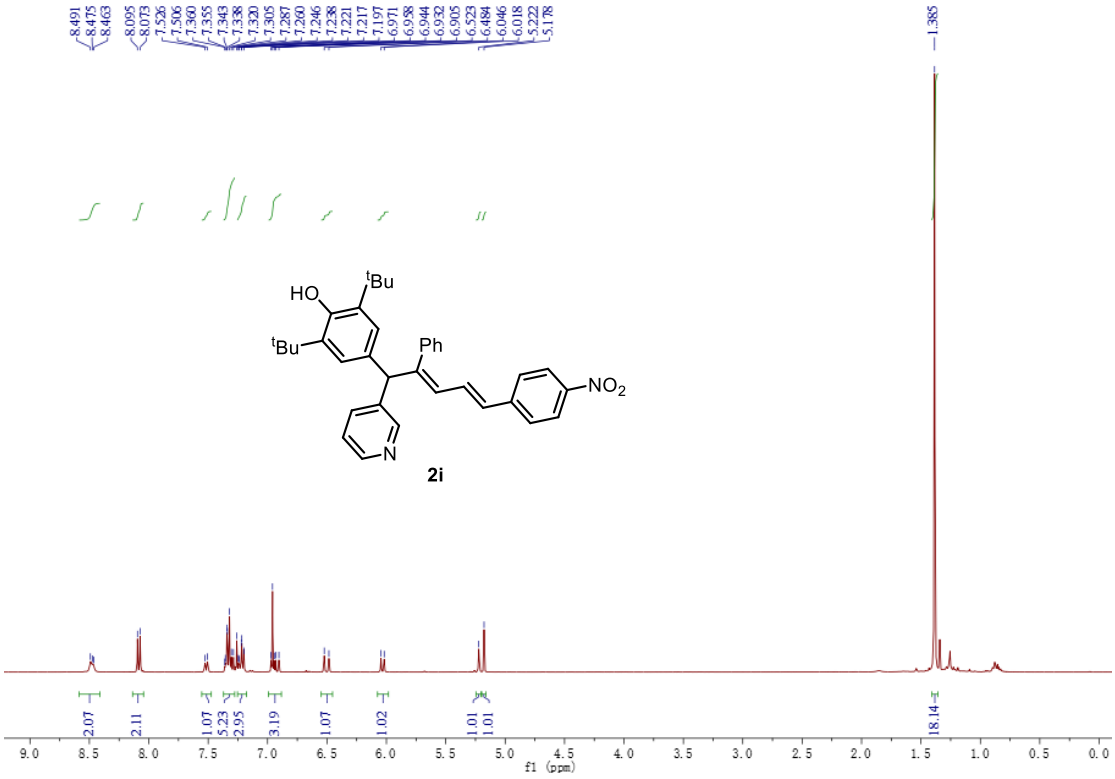
129.524
129.032
128.061
127.340
126.519
126.030
123.978
113.385
77.319
77.001
76.682
58.824
55.196
34.321
30.336
HO
tBu
tBu
Ph
NO2
MeO
2h
f1 (ppm)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7.526
7.506
7.360
7.355
7.343
7.338
7.320
7.305
7.287
7.260
7.246
7.238
7.221
7.217
7.197
6.971
6.958
6.944
6.932
6.905
6.523
6.484
6.046
6.018
5.222
5.178
1.385
HO
tBu
tBu
Ph
NO2
N
2i
2.07
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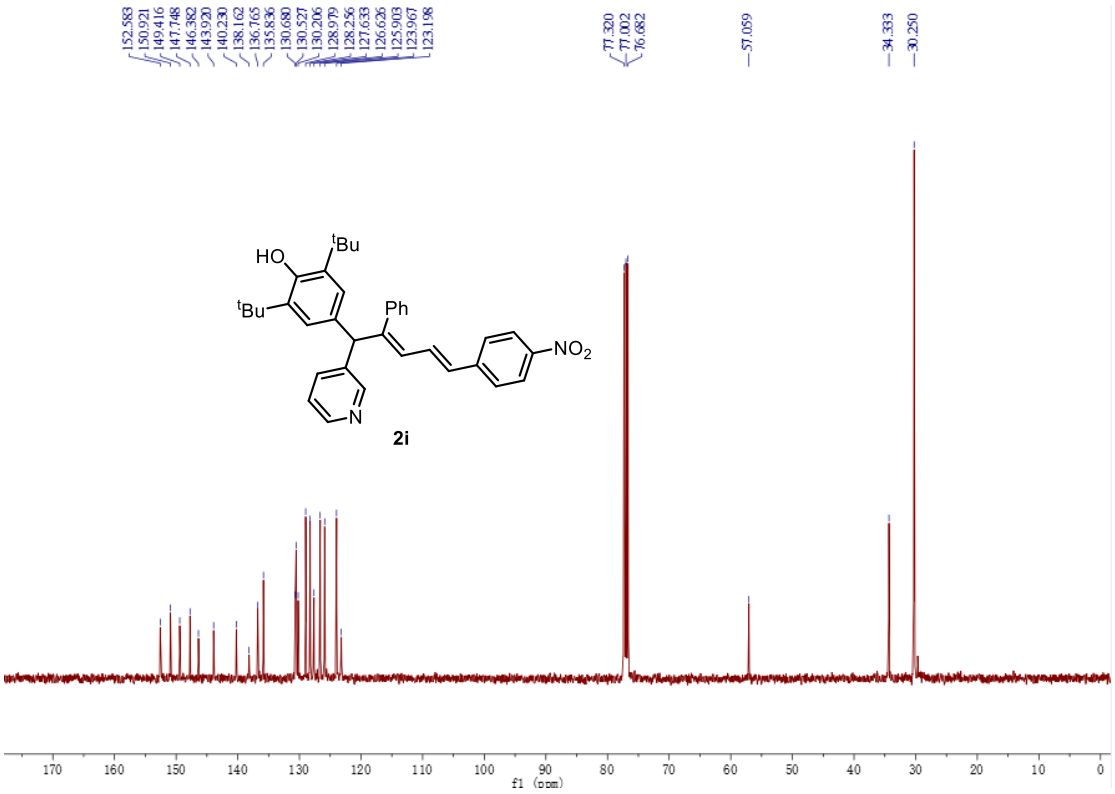
5.23
2.95
3.19
1.07
1.02
1.01
1.01
18.14
f1 (ppm)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140.230
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130.527
130.206
128.979
128.256
127.633
126.626
125.903
123.967
123.198
77.320
77.002
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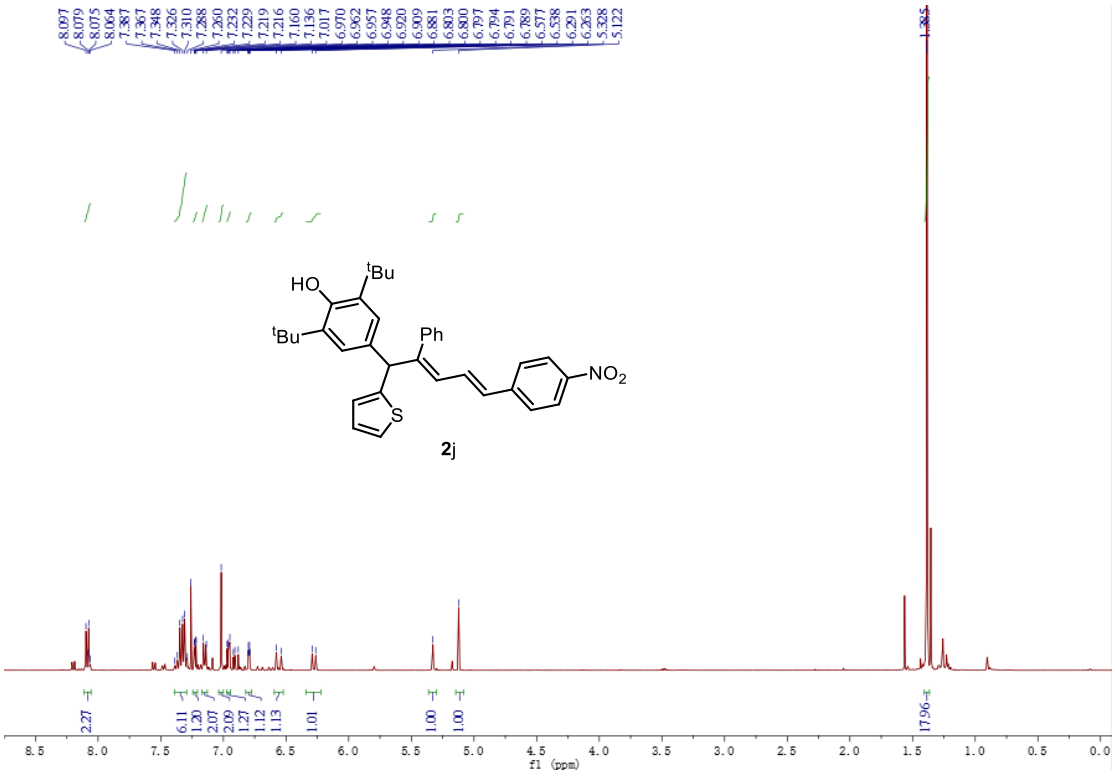
57.059
34.333
30.250
HO
tBu
tBu
Ph
NO2
N
2i
f1 (ppm)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8.075
8.064
7.387
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7.229
7.219
7.216
7.160
7.136
7.017
6.970
6.962
6.957
6.948
6.920
6.909
6.881
6.803
6.800
6.797
6.794
6.791
6.789
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6.291
6.263
5.328
5.122
1.385
HO
tBu
tBu
Ph
NO2
S
2j
2.27
6.11
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2.09
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1.12
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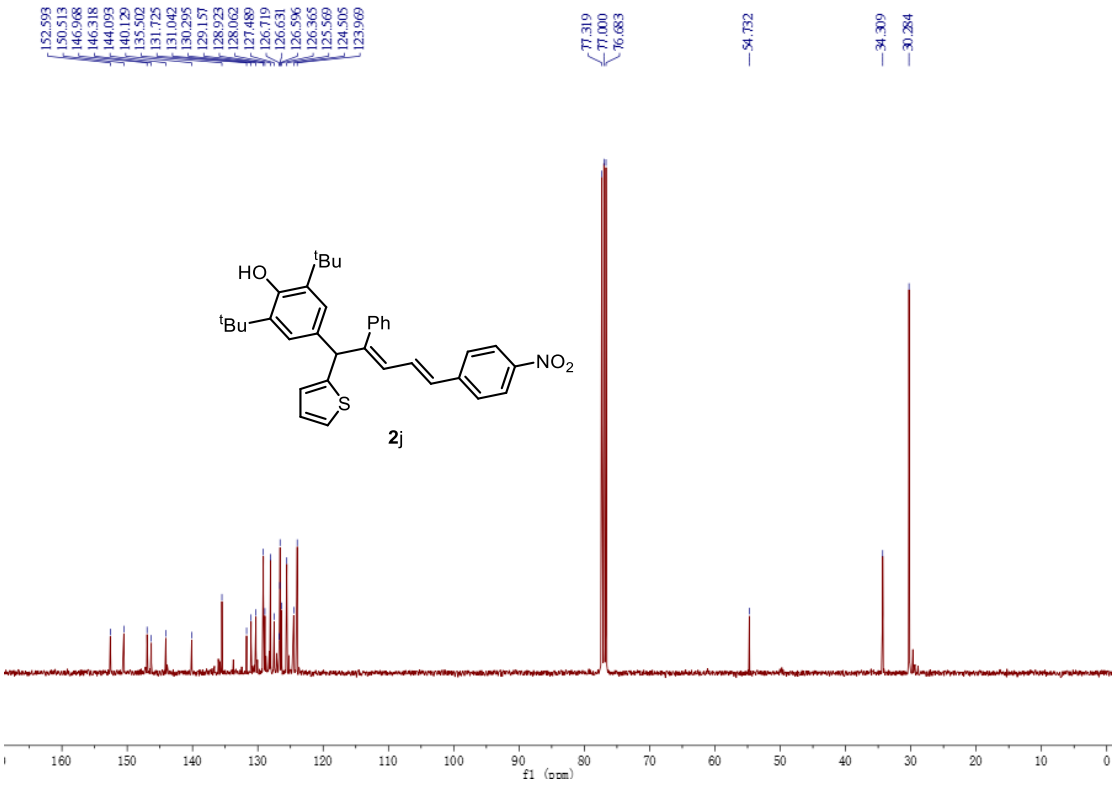
1.00
1.00
17.96
f1 (ppm)


152.593
150.513
146.968
146.318
144.093
140.129
135.502
131.725
131.042
130.295
129.157
128.923
128.062
127.489
126.719
126.631
126.596
126.365
125.569
124.505
123.969
77.319
77.000
76.683
54.732
34.309
30.284
HO
tBu
tBu
Ph
NO2
S
2j
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150
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130
120
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90
80
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50
40
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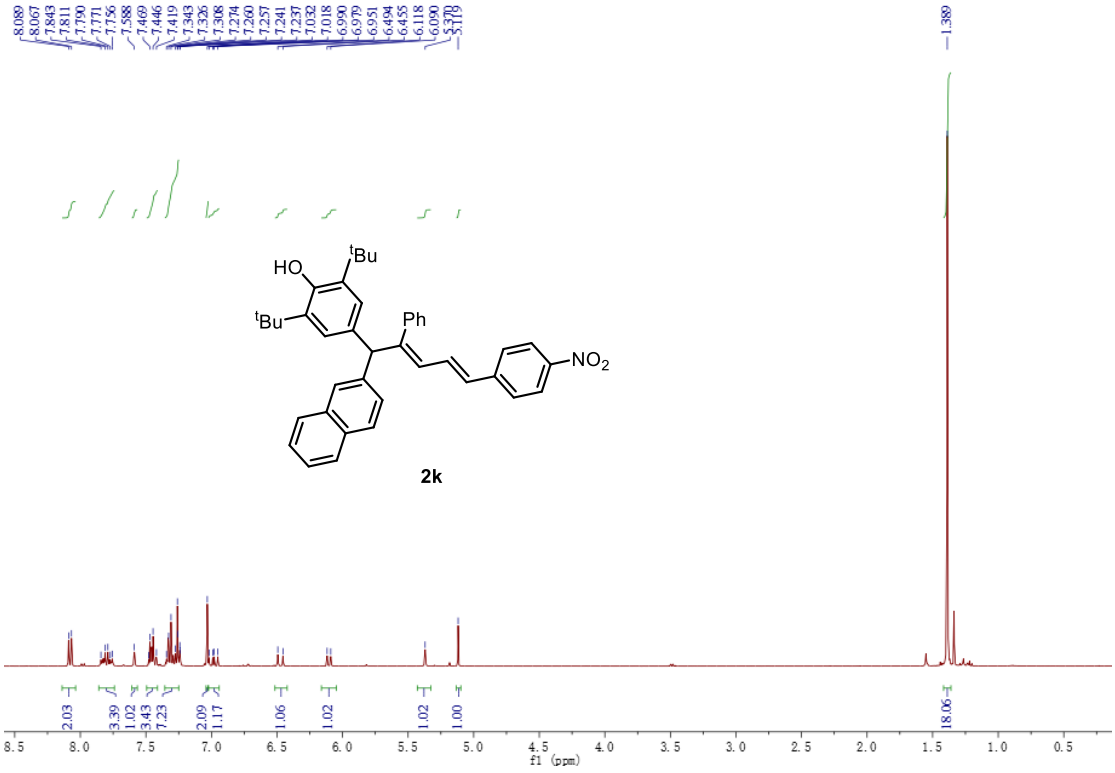
f1 (ppm)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7.308
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7.257
7.241
7.237
7.032
7.018
6.990
6.979
6.951
6.494
6.455
6.118
6.090
5.370
5.179
1.389
HO
tBu
tBu
Ph
NO2
2k
2.03
3.39
1.02
3.43
7.23
2.09
1.17
1.06
1.02
1.02
1.00
18.06
8.5
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6.0
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3.0
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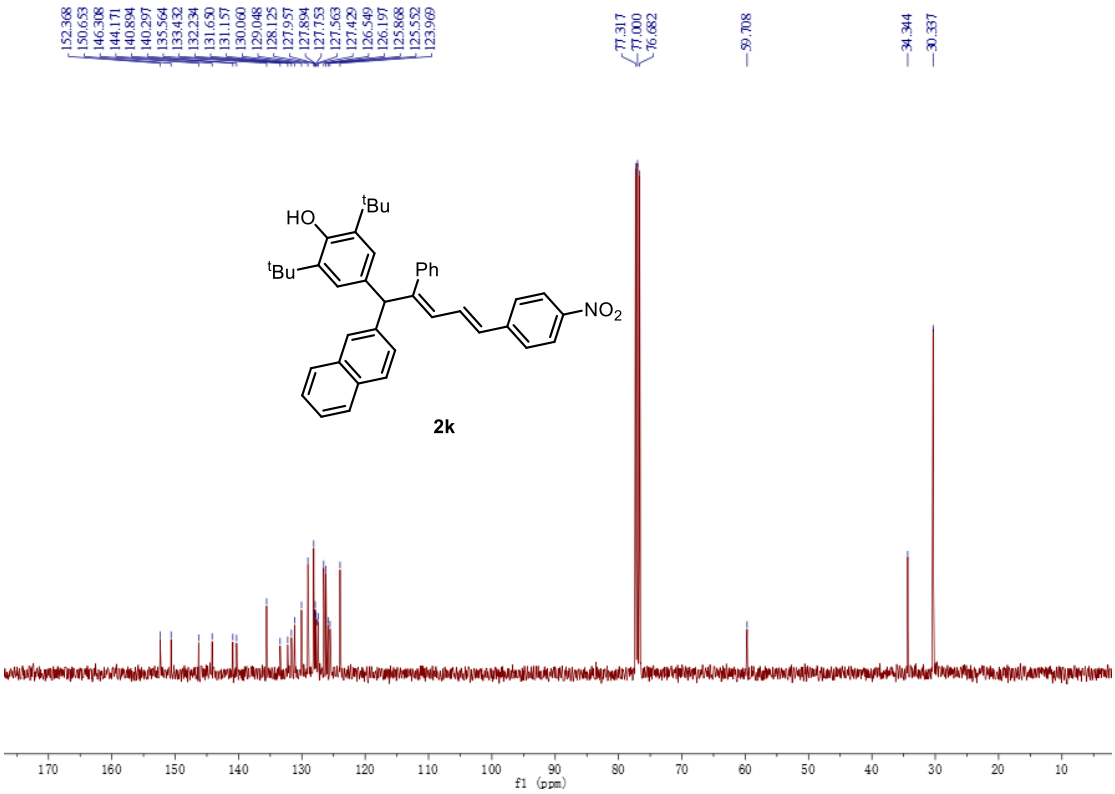
f1 (ppm)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127.957
127.894
127.753
127.563
127.429
126.549
126.197
125.868
125.552
123.969
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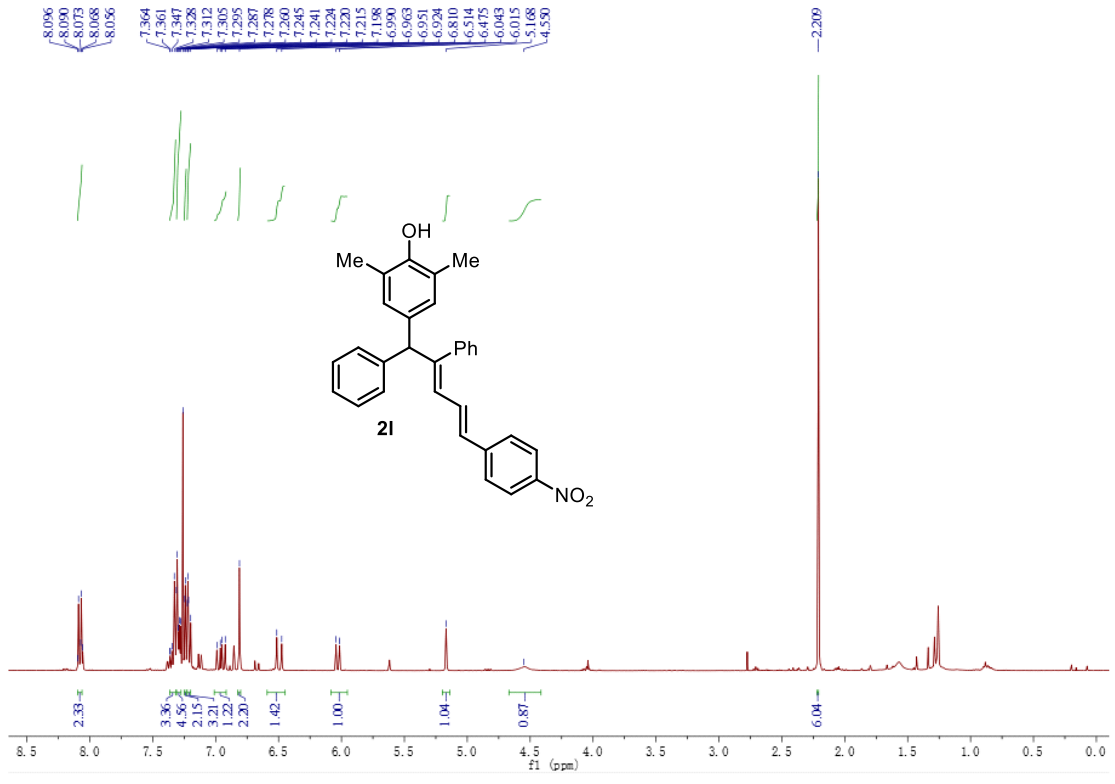
76.682
59.708
34.344
30.337
HO
tBu
tBu
Ph
NO2
2k
f1 (ppm)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7.278
7.260
7.245
7.241
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7.220
7.215
7.198
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6.951
6.924
6.810
6.514
6.475
6.043
6.015
5.168
4.590
2.209
OH
Me
Me
Ph
NO2
2l
2.33
3.36
4.56
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3.21
1.22
2.20
1.42
1.00
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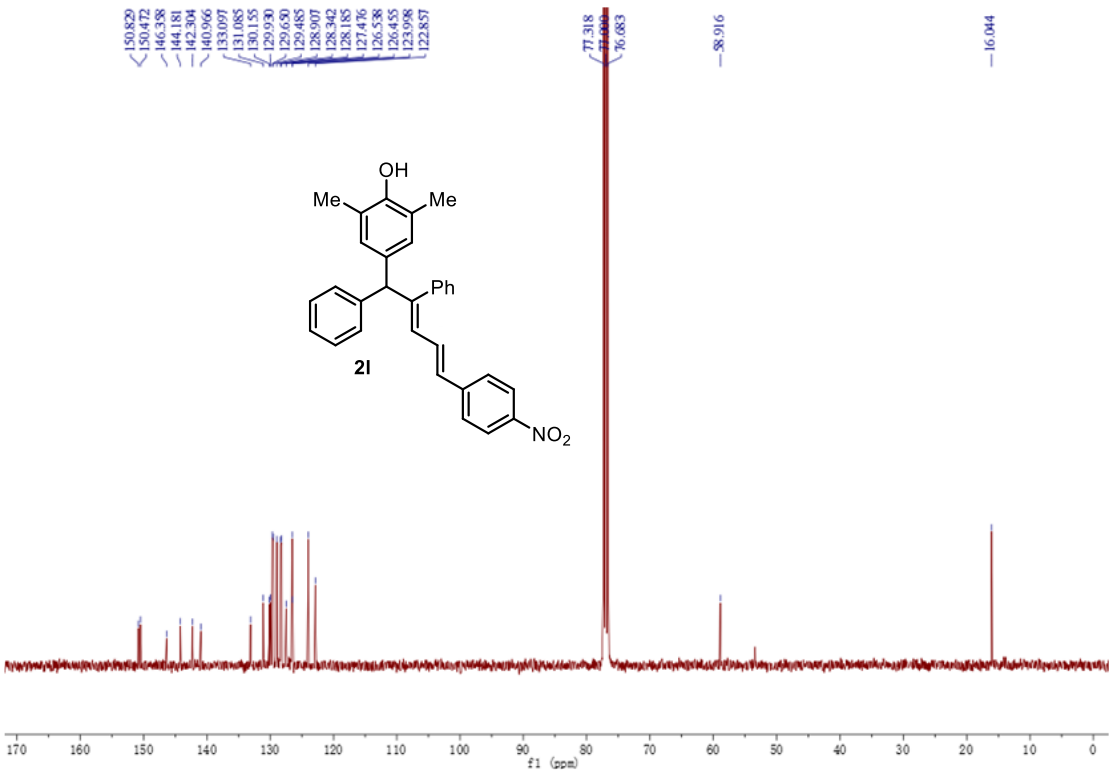
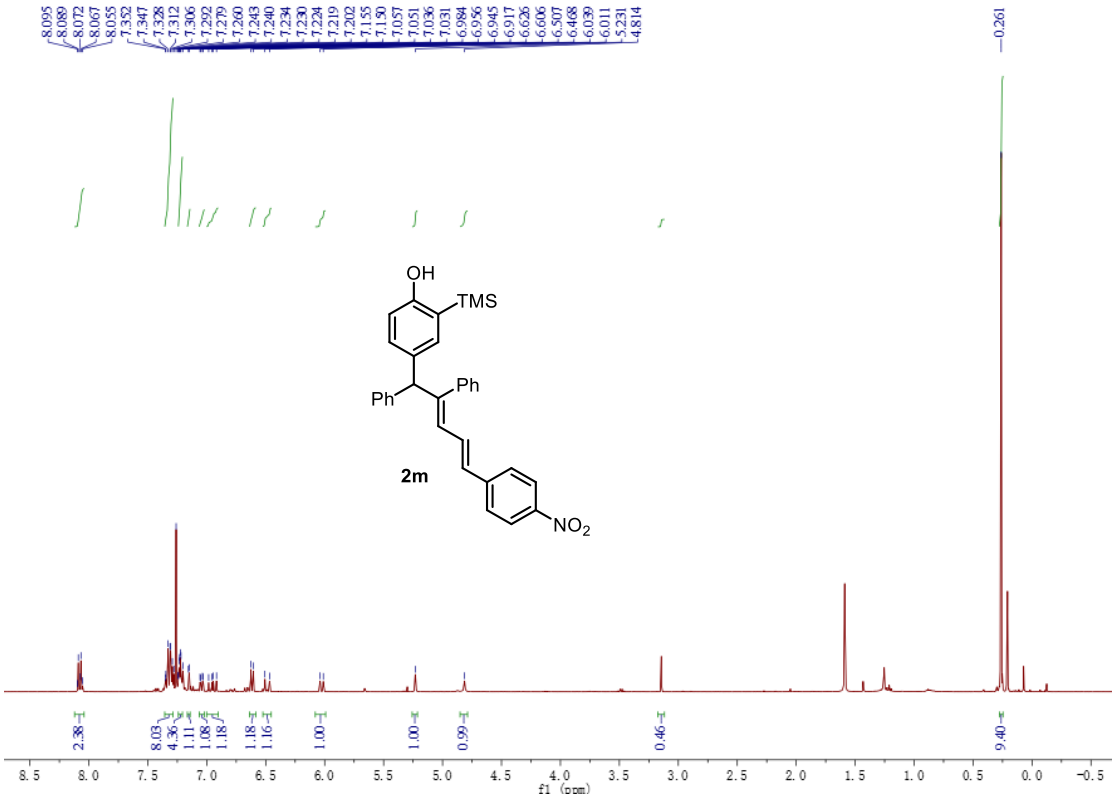
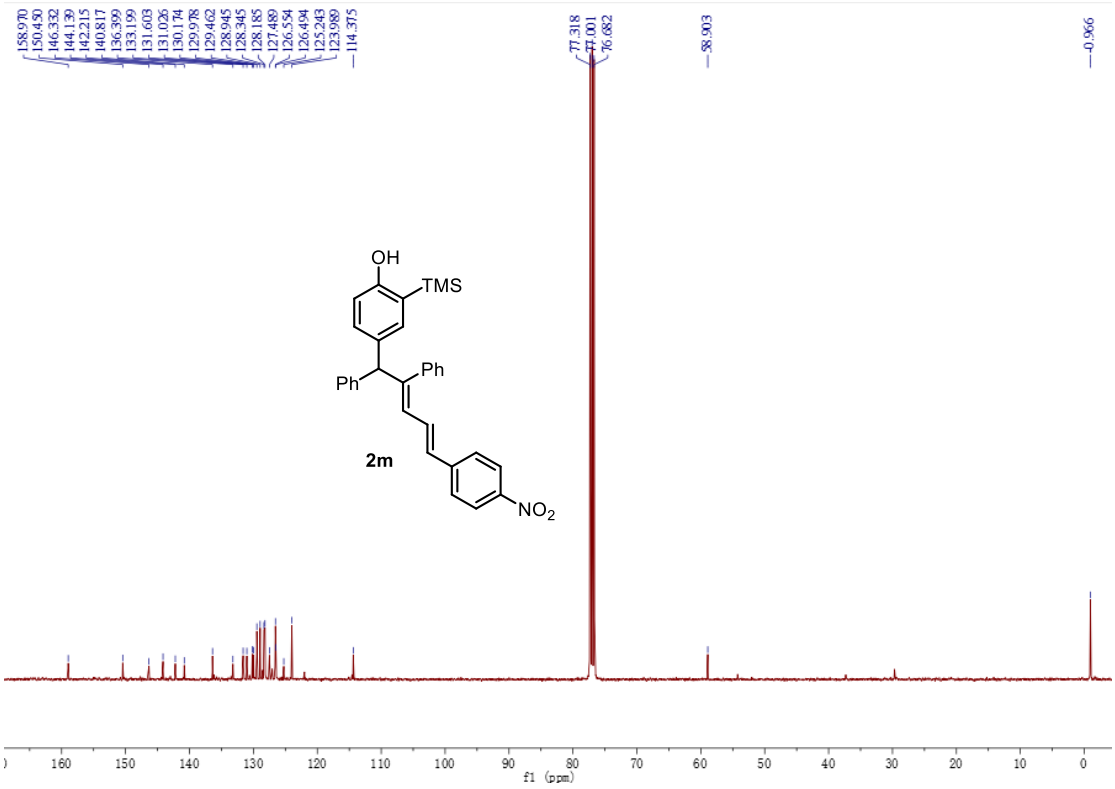
6.04
f1 (ppm)


OH
Me
Me
Ph
2l
NO2
f1 (ppm)


OH
TMS
Ph
Ph
2m
NO2
f1 (ppm)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128.345
128.185
127.489
126.554
126.494
125.243
123.989
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76.682
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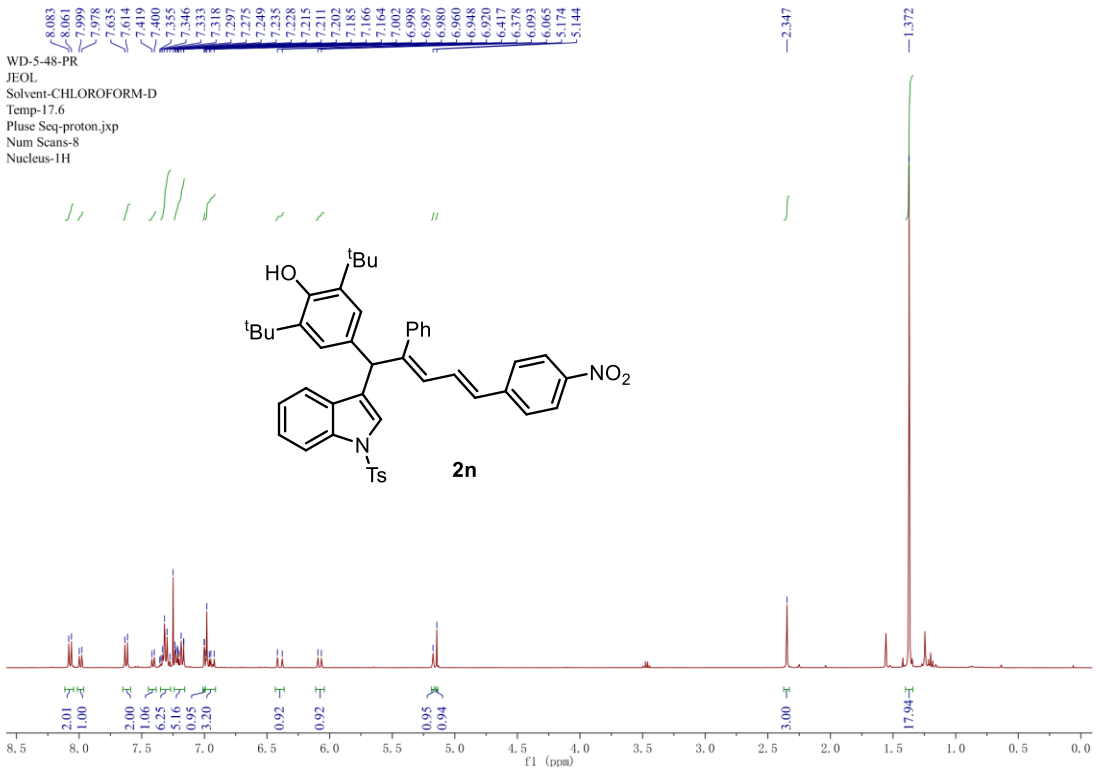
TMS
Ph
Ph
2m
NO2
f1 (ppm)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7.333
7.318
7.297
7.275
7.249
7.235
7.228
7.215
7.211
7.202
7.185
7.166
7.164
7.002
6.998
6.987
6.980
6.960
6.948
6.920
6.417
6.378
6.093
6.065
5.174
5.144
2.347
1.372
WD-5-48-PR
JEOL
Solvent-CHLOROFORM-D
Temp-17.6
Pluse Seq-proton.jxp
Num Scans-8
Nucleus-1H
HO
tBu
tBu
Ph
NO2
N
Ts
2n
2.01
1.00
2.00
1.06
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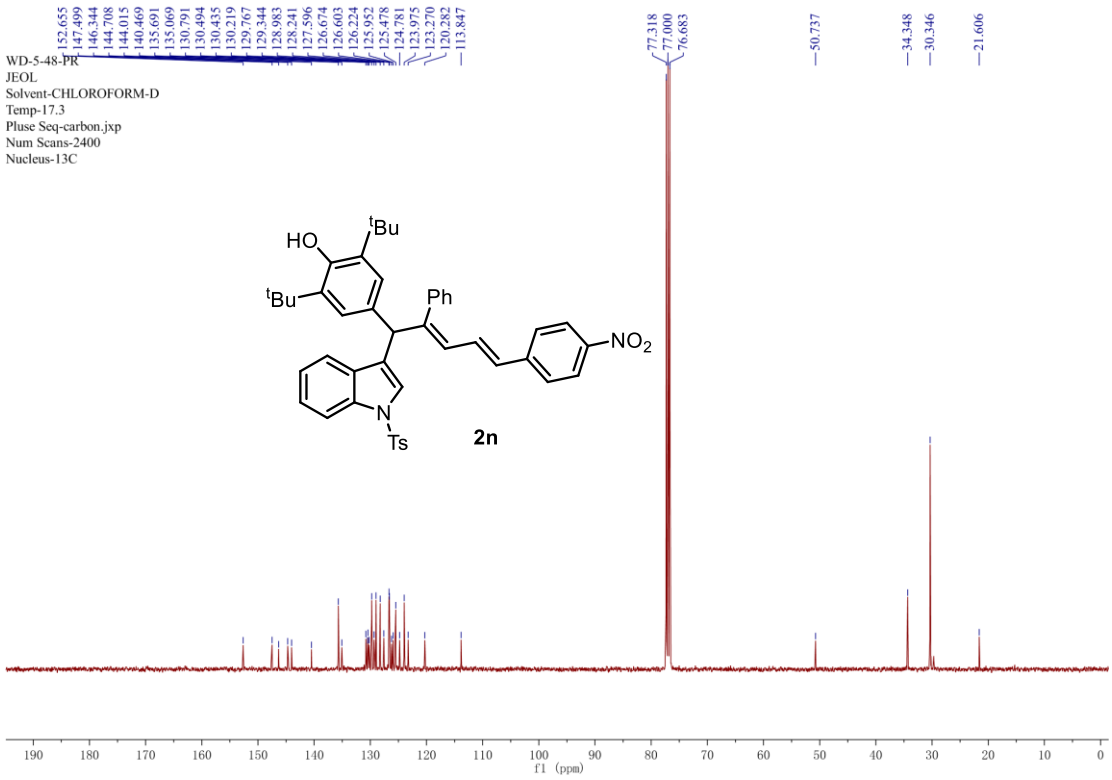
0.95
3.20
0.92
0.92
0.95
0.94
3.00
17.94
f1 (ppm)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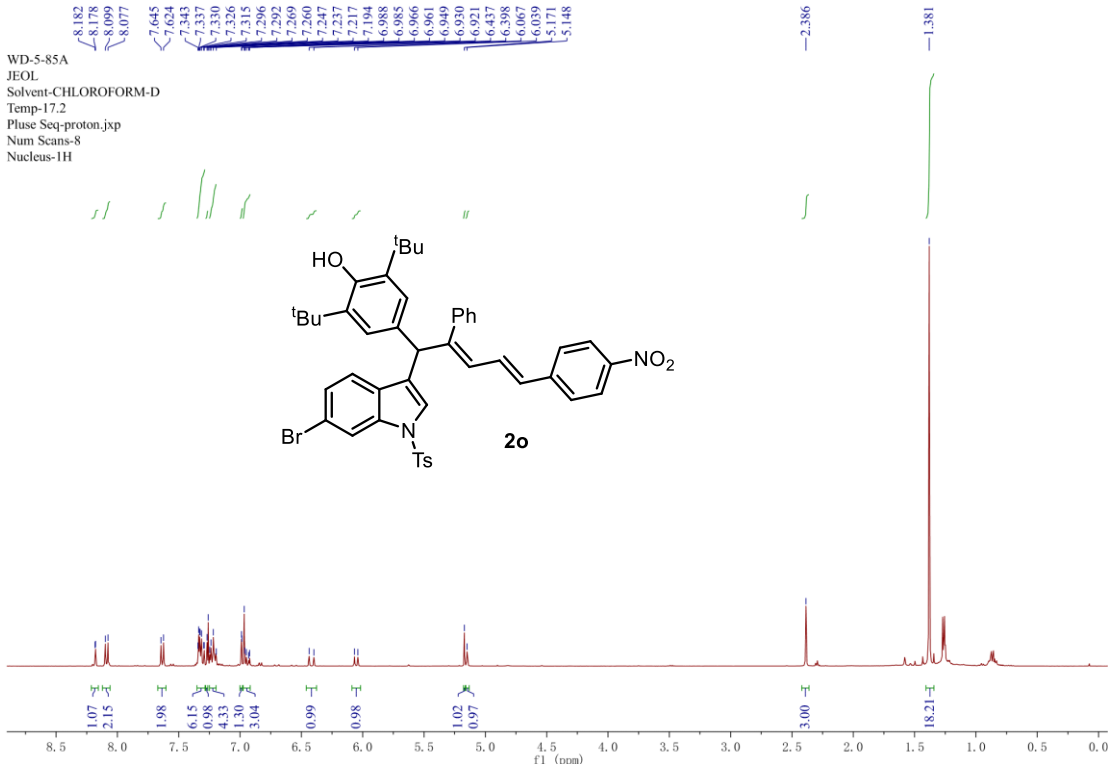
129.344
128.983
128.241
127.596
126.674
126.603
126.224
125.952
125.478
124.781
123.975
123.270
120.282
113.847
77.318
77.000
76.683
50.737
34.348
30.346
21.606
WD-5-48-PR
JEOL
Solvent-CHLOROFORM-D
Temp-17.3
Pluse Seq-carbon.jxp
Num Scans-2400
Nucleus-13C
HO
tBu
tBu
Ph
NO2
N
Ts
2n
f1 (ppm)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8.178
8.099
8.077
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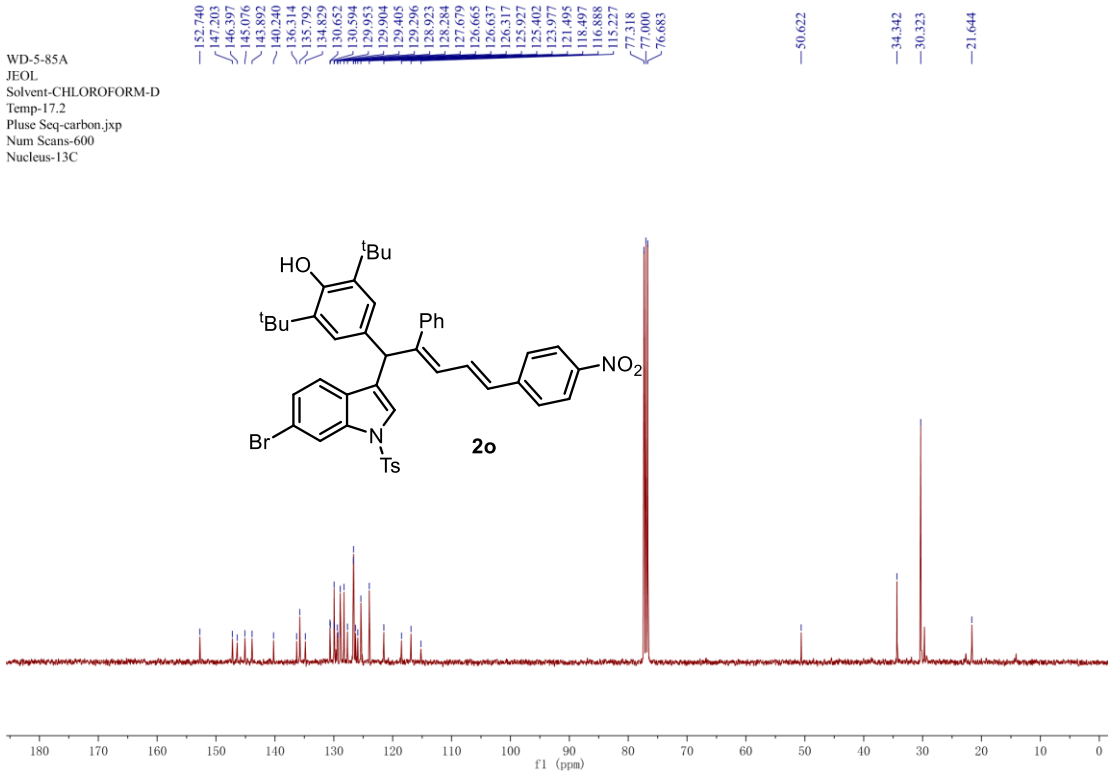
7.624
7.343
7.337
7.330
7.326
7.315
7.296
7.292
7.269
7.260
7.247
7.237
7.217
7.194
6.988
6.985
6.966
6.961
6.949
6.930
6.921
6.437
6.398
6.067
6.039
5.171
5.148
2.386
1.381
WD-5-85A
JEOL
Solvent-CHLOROFORM-D
Temp-17.2
Pluse Seq-proton.jxp
Num Scans-8
Nucleus-1H
HO
tBu
tBu
Ph
NO2
Br
N
Ts
2o
1.07
2.15
1.98
6.15
0.98
4.33
1.30
3.04
0.99
0.98
1.02
0.97
3.00
18.21
f1 (ppm)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JEOL
Solvent-CHLOROFORM-D
Temp-17.2
Pluse Seq-carbon.jxp
Num Scans-600
Nucleus-13C
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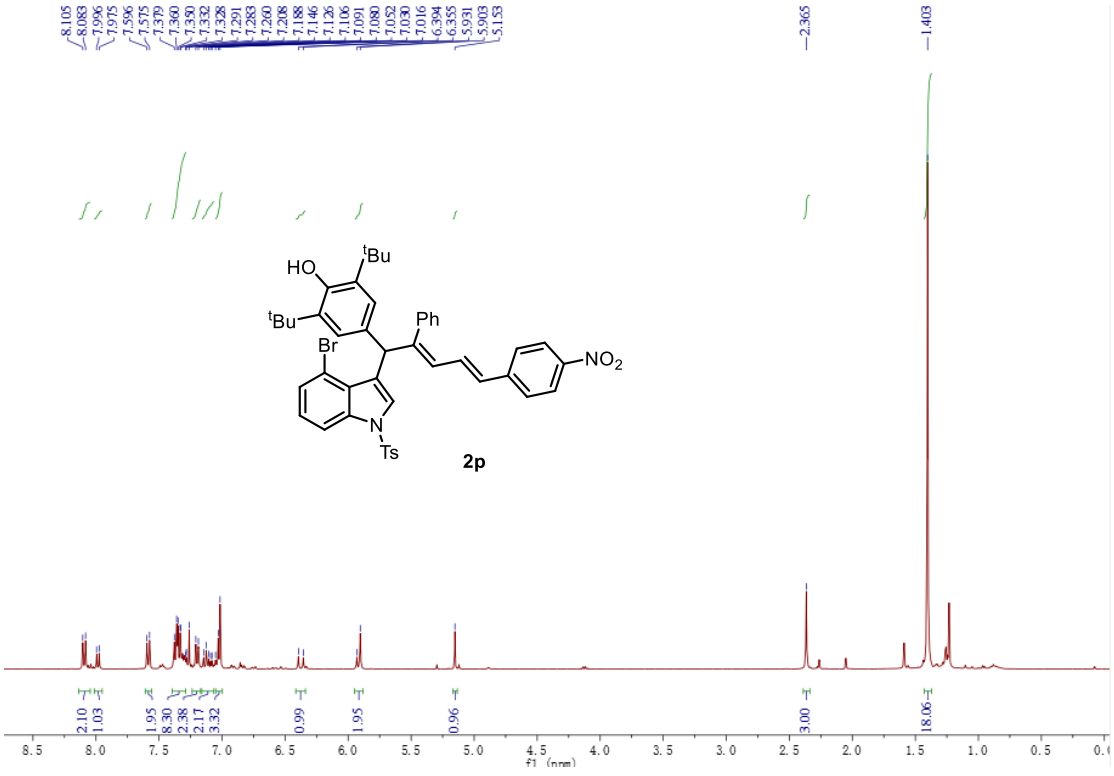
147.203
146.397
145.076
143.892
140.240
136.314
135.792
134.829
130.652
130.594
129.953
129.904
129.405
129.296
128.923
128.284
127.679
126.665
126.637
126.317
125.927
125.402
123.977
121.495
118.497
116.888
115.227
77.318
77.000
76.683
50.622
34.342
30.323
21.644
HO
tBu
tBu
Ph
NO2
Br
N
Ts
2o
f1 (ppm)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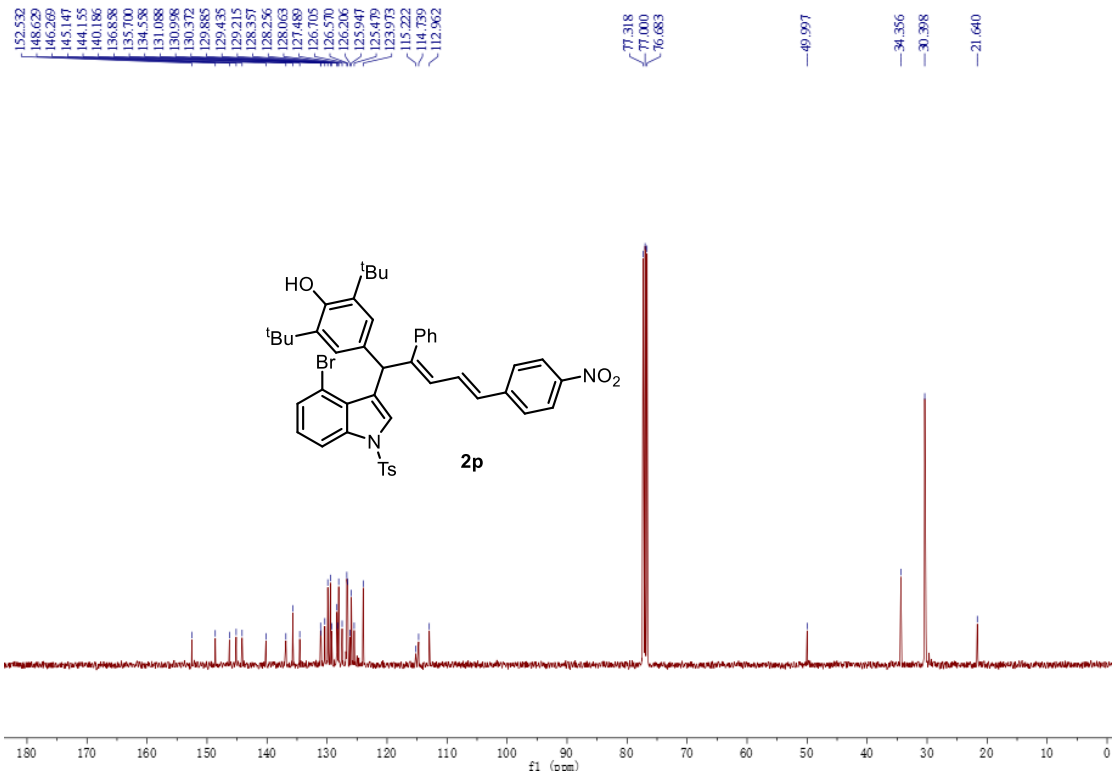
7.328
7.291
7.283
7.260
7.208
7.188
7.146
7.126
7.106
7.091
7.080
7.052
7.030
7.016
6.394
6.355
5.931
5.903
5.153
2.365
1.403
HO
tBu
tBu
Ph
Br
NO2
N
Ts
2p
2.10
1.03
1.95
8.30
2.38
2.17
3.32
0.99
1.95
0.96
3.00
18.06
f1 (ppm)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131.088
130.998
130.372
129.885
129.435
129.215
128.357
128.256
128.063
127.489
126.705
126.570
126.206
125.947
125.479
123.973
115.222
114.739
112.962
77.318
77.000
76.683
49.997
34.356
30.398
21.640
HO
tBu
tBu
Br
Ph
NO2
N
Ts
2p
180
170
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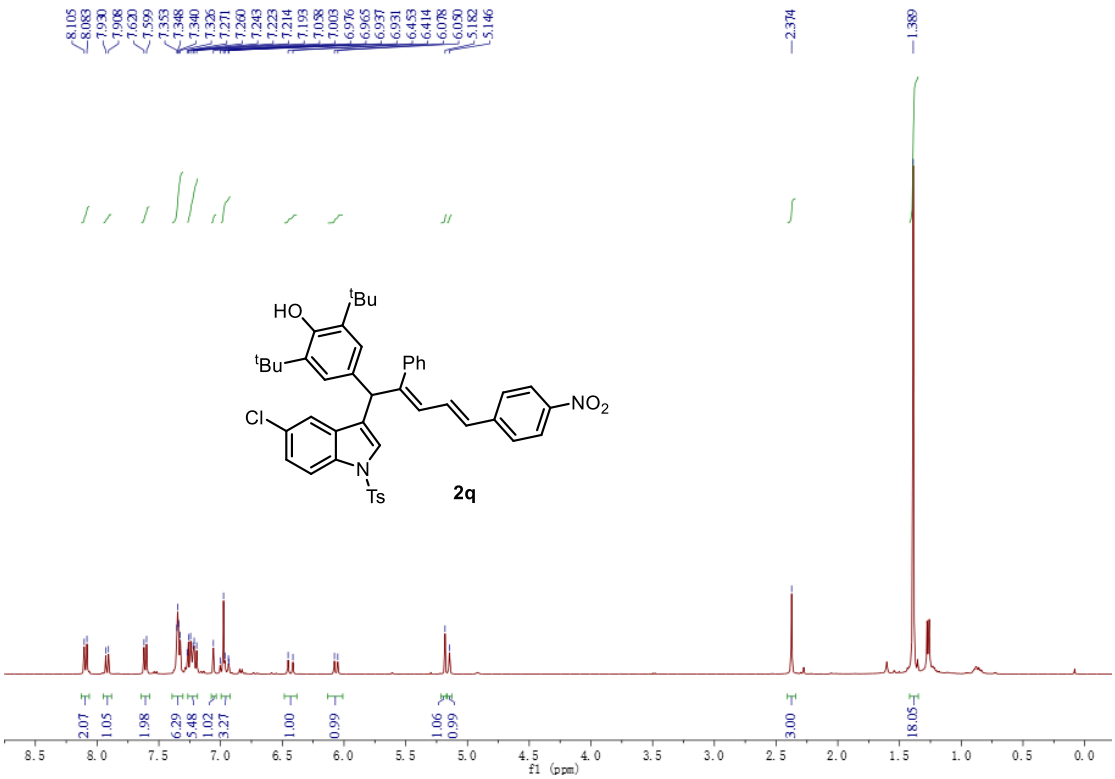
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.340
7.326
7.271
7.260
7.243
7.223
7.214
7.193
7.038
7.003
6.976
6.965
6.937
6.931
6.453
6.414
6.078
6.050
5.182
5.146
2.374
1.389
HO
tBu
tBu
Ph
NO2
Cl
N
Ts
2q
2.07
1.05
1.98
6.29
5.48
1.02
3.27
1.00
0.99
1.06
0.99
3.00
18.05
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8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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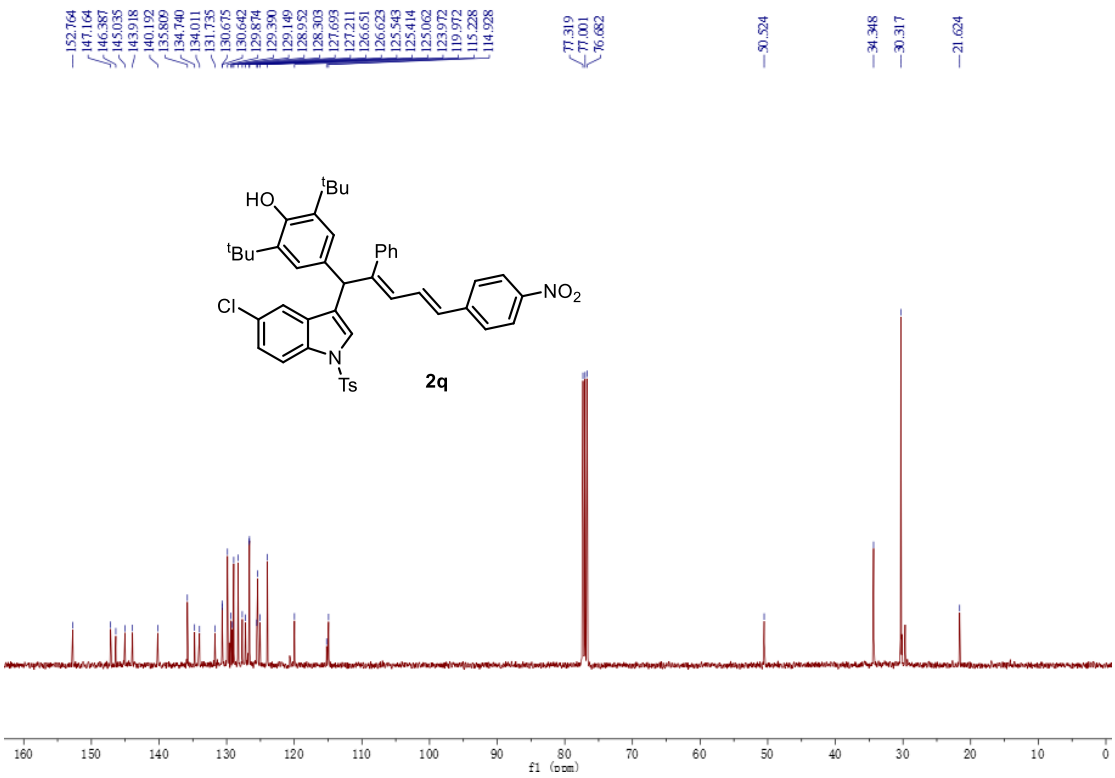
0.0
f1 (ppm)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129.149
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128.303
127.693
127.211
126.651
126.623
125.543
125.414
125.062
123.972
119.972
115.228
114.928
77.319
77.001
76.682
50.524
34.348
30.317
21.624
HO
tBu
tBu
Ph
NO2
Cl
N
Ts
2q
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150
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130
120
110
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90
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70
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50
40
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10
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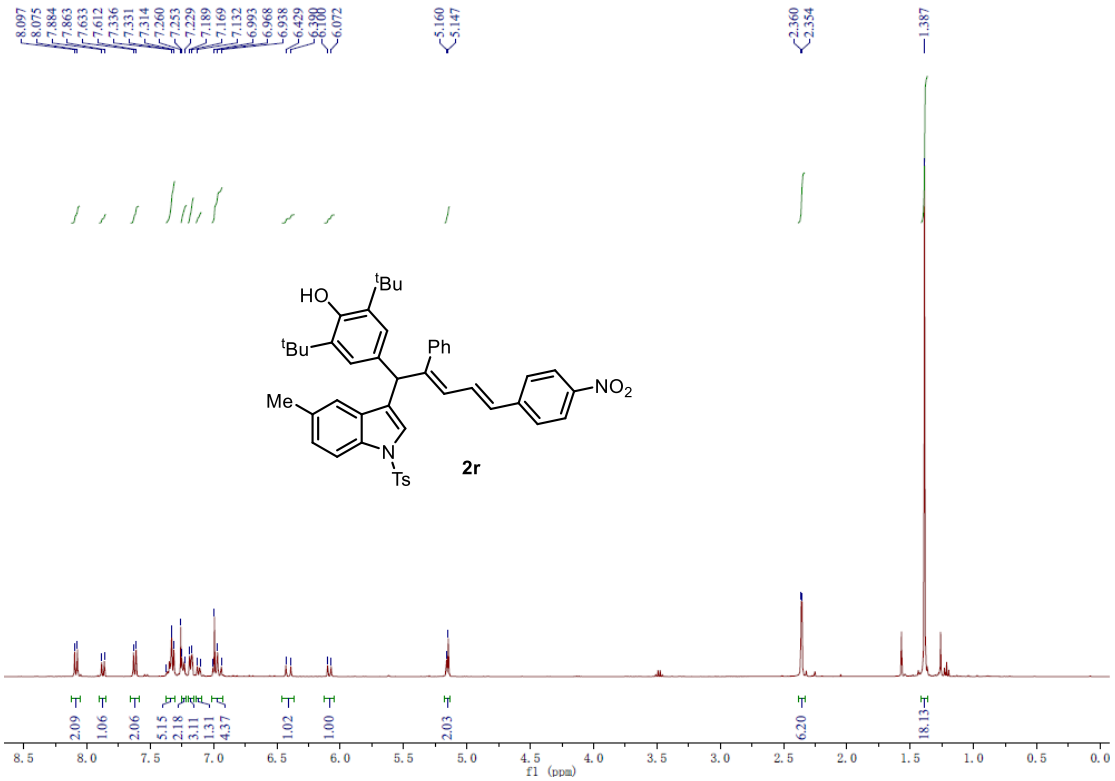
f1 (ppm)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7.132
6.993
6.968
6.938
6.429
6.072
5.160
5.147
2.360
2.354
1.387
HO
tBu
tBu
Ph
NO2
Me
N
Ts
2r
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1.06
2.06
5.15
2.18
3.11
1.31
4.37
1.02
1.00
2.03
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7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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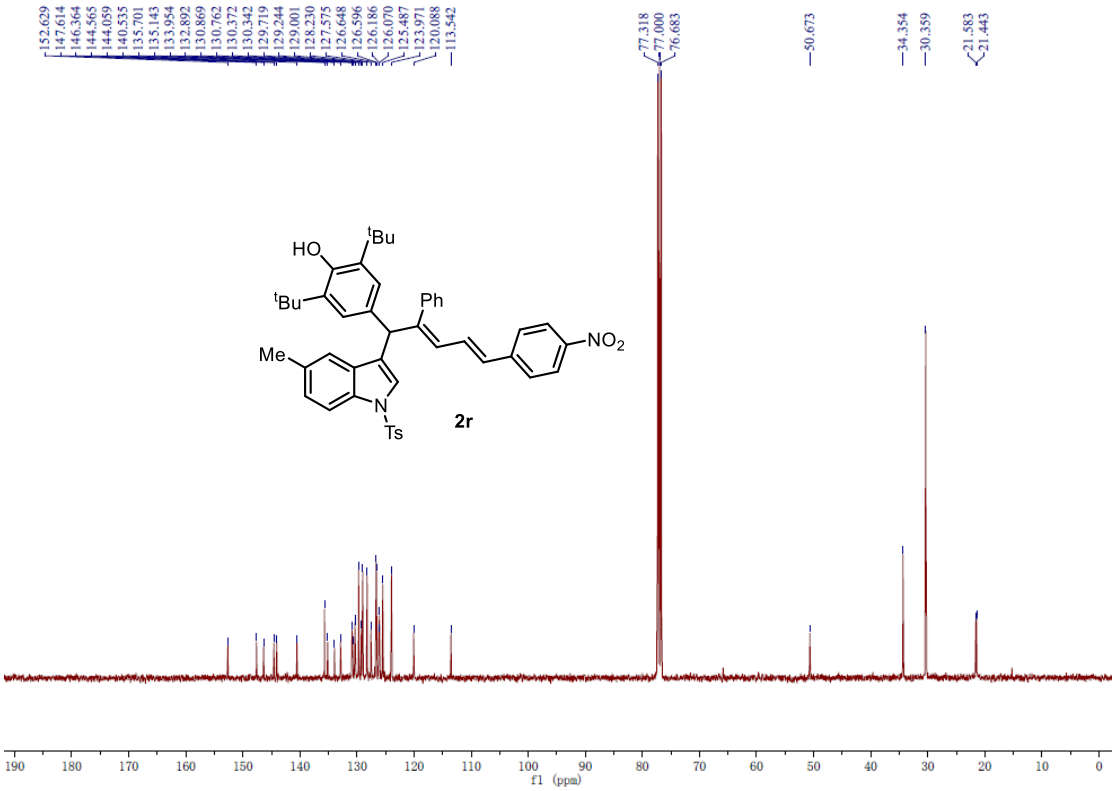
0.0
f1 (ppm)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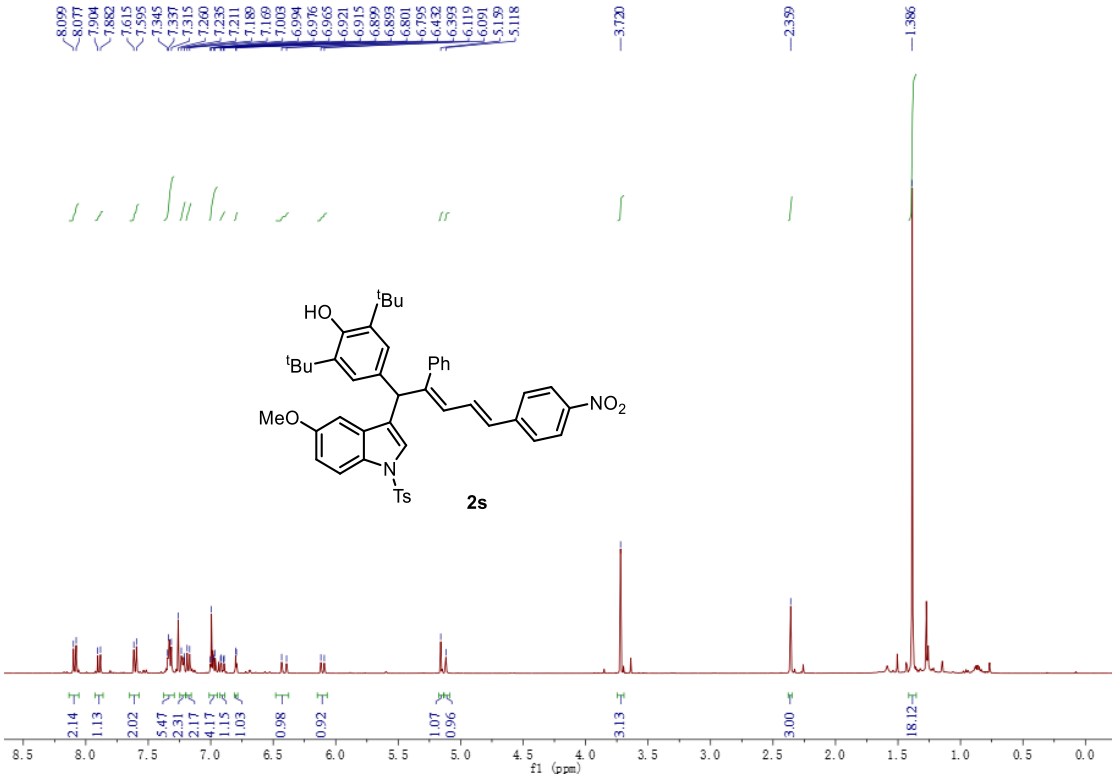
tBu
Ph
NO2
Me
N
Ts
2r
f1 (ppm)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6.893
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6.393
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5.159
5.118
3.720
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1.386
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tBu
tBu
Ph
NO2
MeO
N
Ts
2s
2.14
1.13
2.02
5.47
2.31
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3.13
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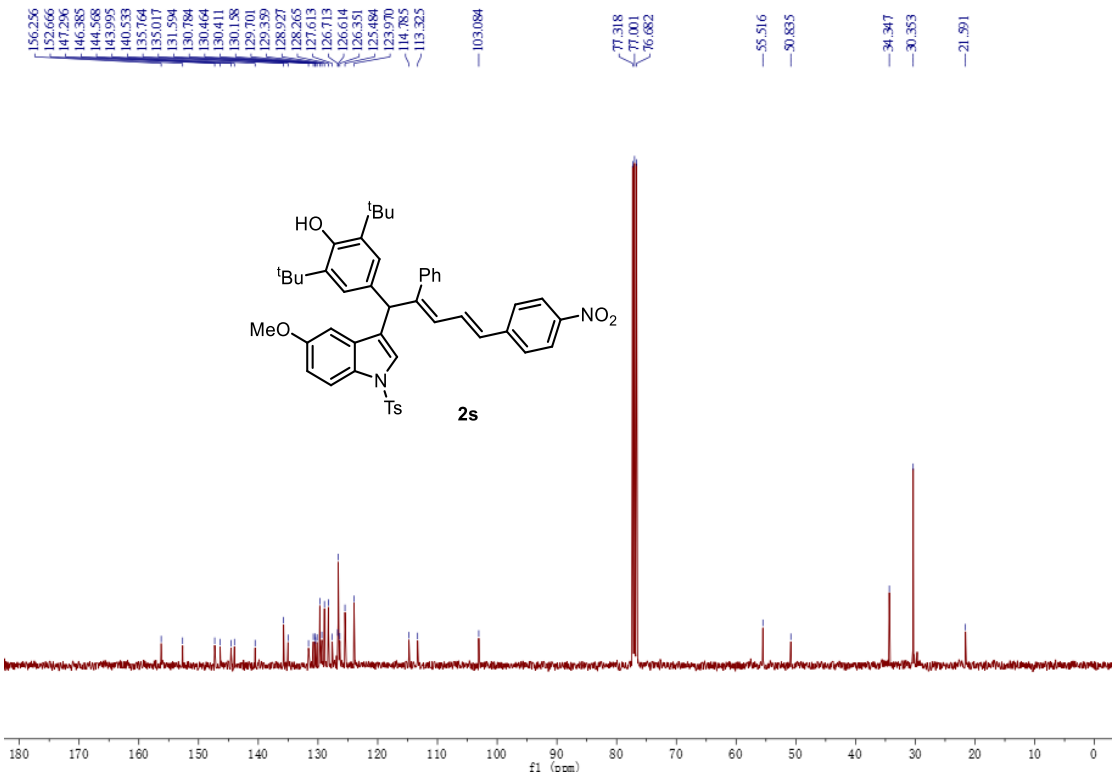
18.12
f1 (ppm)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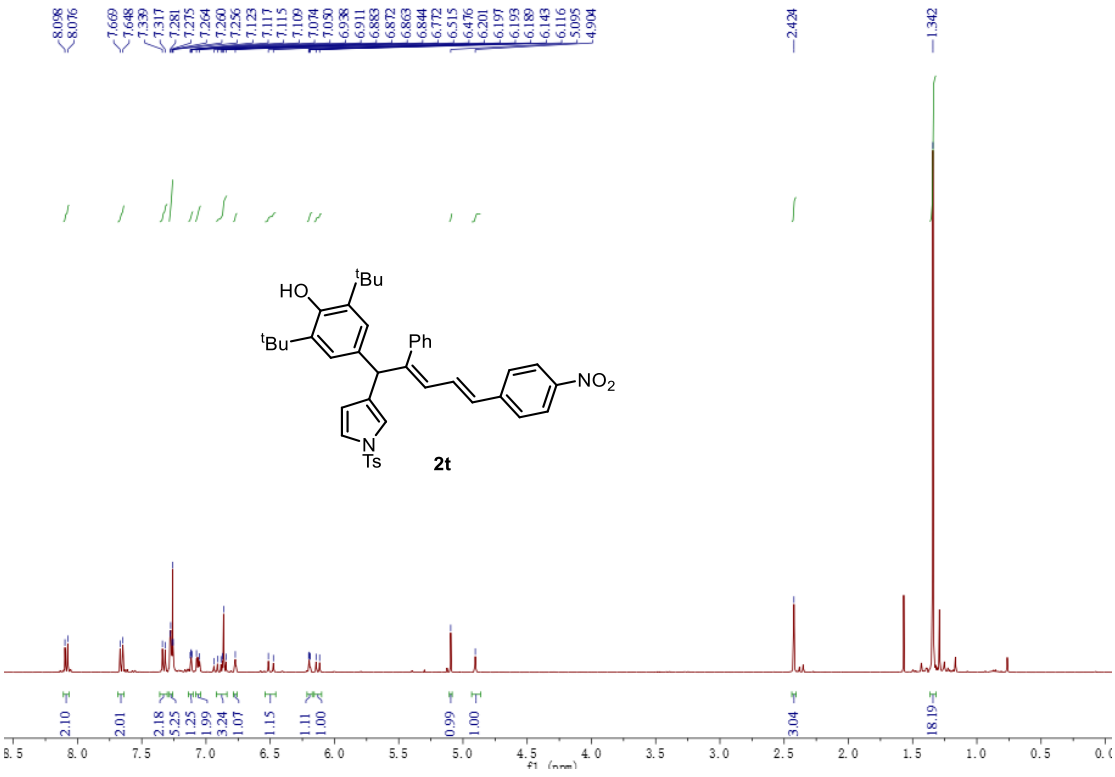
tBu
tBu
Ph
MeO
NO2
N
Ts
2s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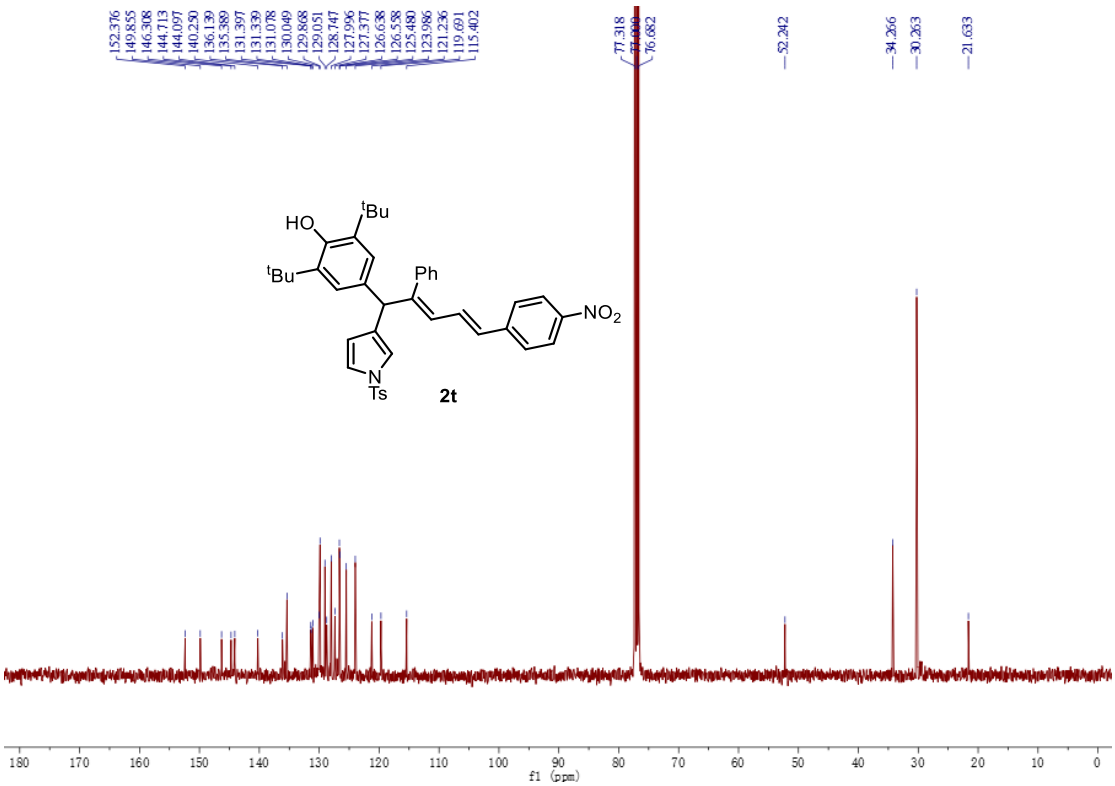
Ph
NO2
N
Ts
2t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126.638
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121.236
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77.318
77.000
76.682
52.242
34.266
30.263
21.633
HO
tBu
tBu
Ph
NO2
N
Ts
2t
180
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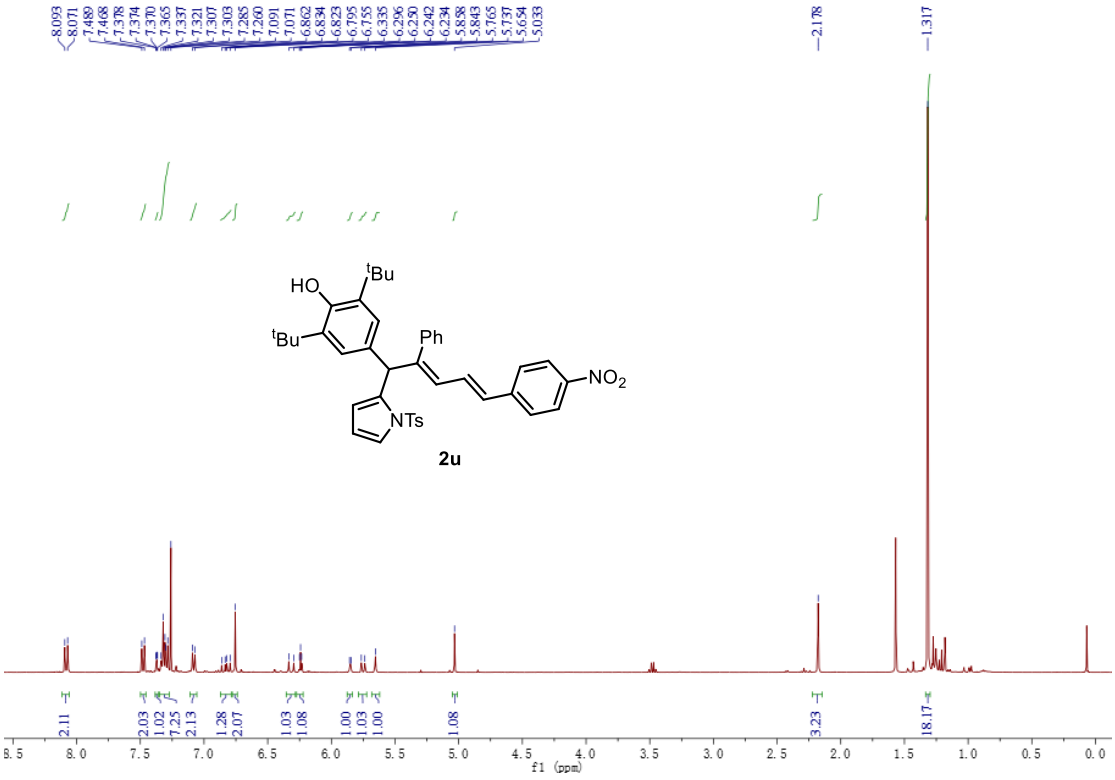
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.250
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5.654
5.033
2.178
1.317
HO
tBu
tBu
Ph
NO2
NTs
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1.02
7.25
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1.28
2.07
1.03
1.08
1.00
1.03
1.00
1.08
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18.17
9.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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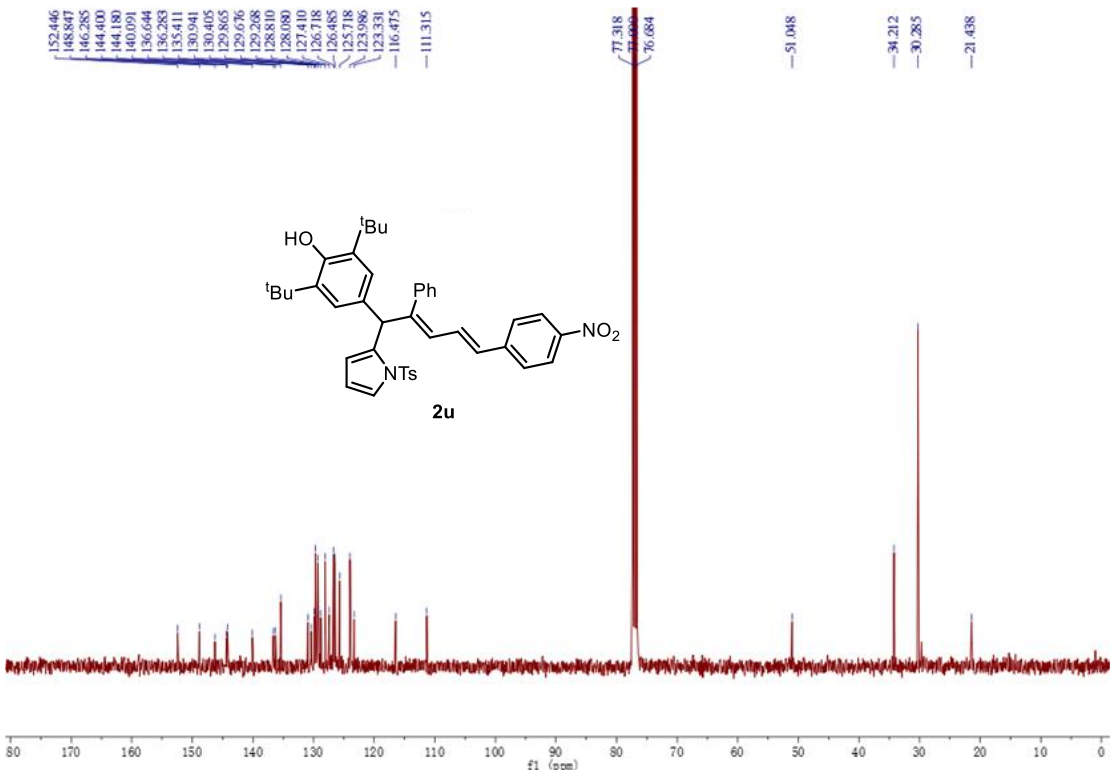
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.676
129.268
128.810
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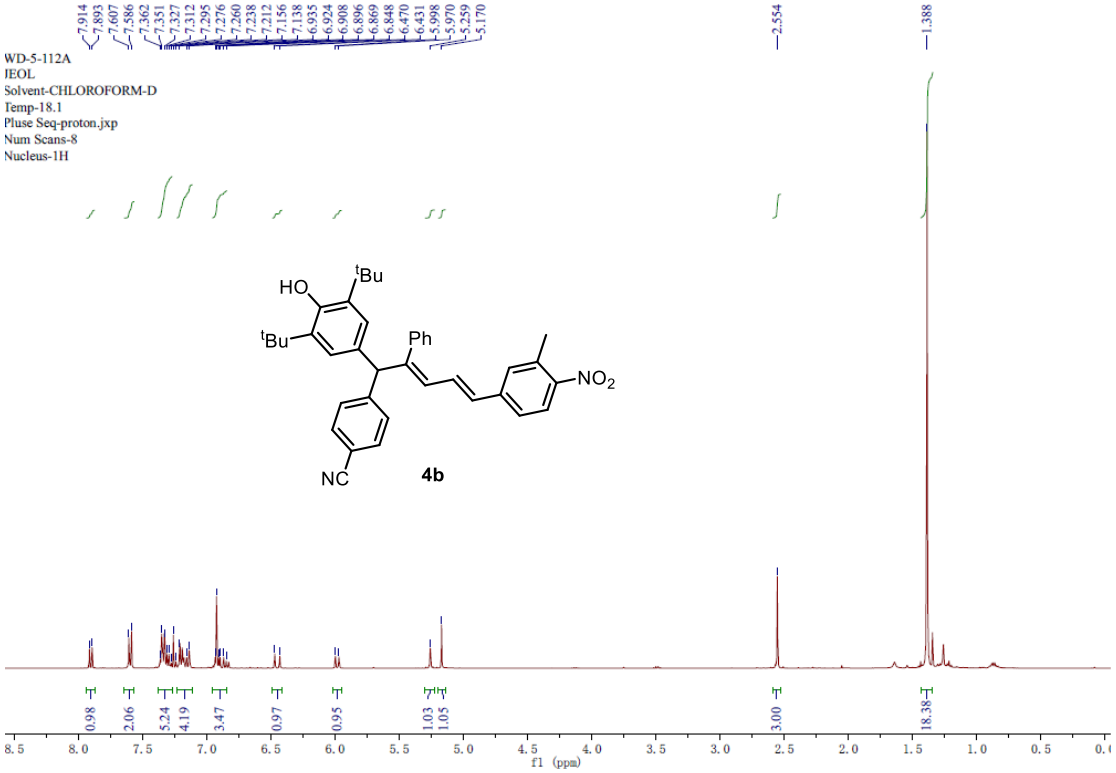
126.718
126.485
125.718
123.986
123.331
116.475
111.315
77.318
76.684
51.048
34.212
30.285
21.438
HO
tBu
tBu
Ph
NO2
NTs
2u
f1 (ppm)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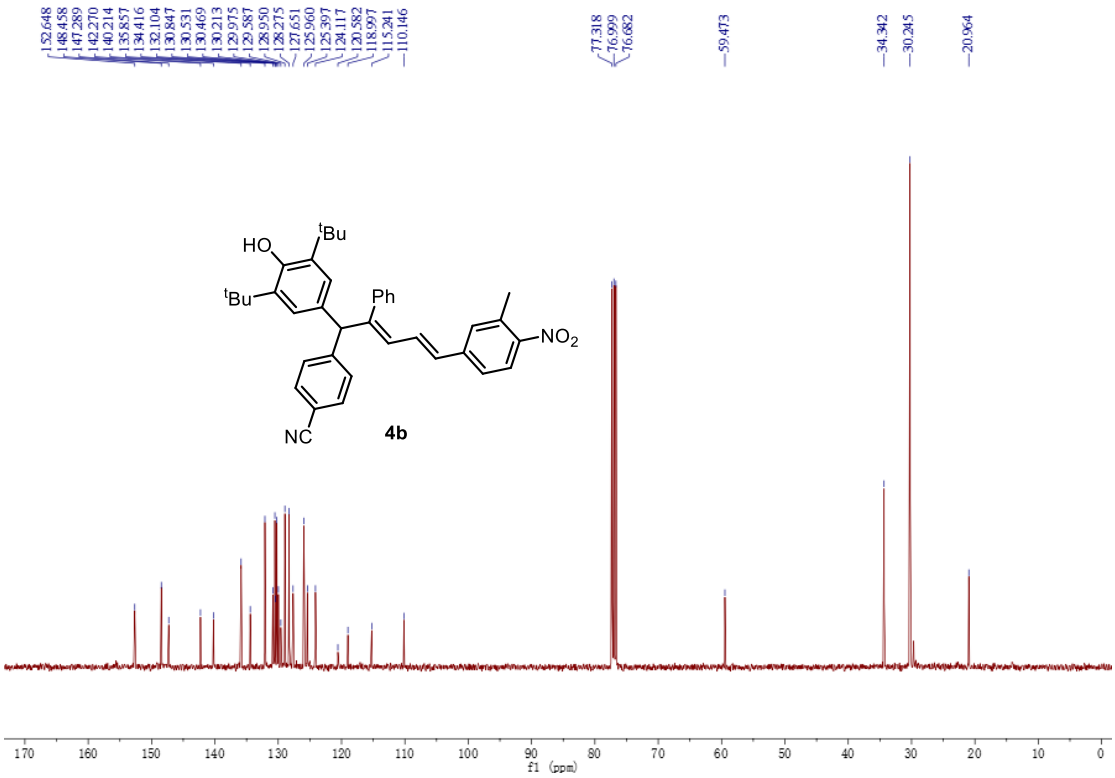
7.607
7.586
7.362
7.351
7.327
7.312
7.295
7.276
7.260
7.238
7.212
7.156
7.138
6.935
6.924
6.908
6.896
6.869
6.848
6.470
6.431
5.998
5.970
5.259
5.170
2.554
1.388
WD-5-112A
JEOL
Solvent-CHLOROFORM-D
Temp-18.1
Pluse Seq-proton.jxp
Num Scans-8
Nucleus-1H
HO
tBu
tBu
Ph
NO2
NC
4b
0.98
2.06
5.24
4.19
3.47
0.97
0.95
1.03
1.05
3.00
18.38
f1 (ppm)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147.289
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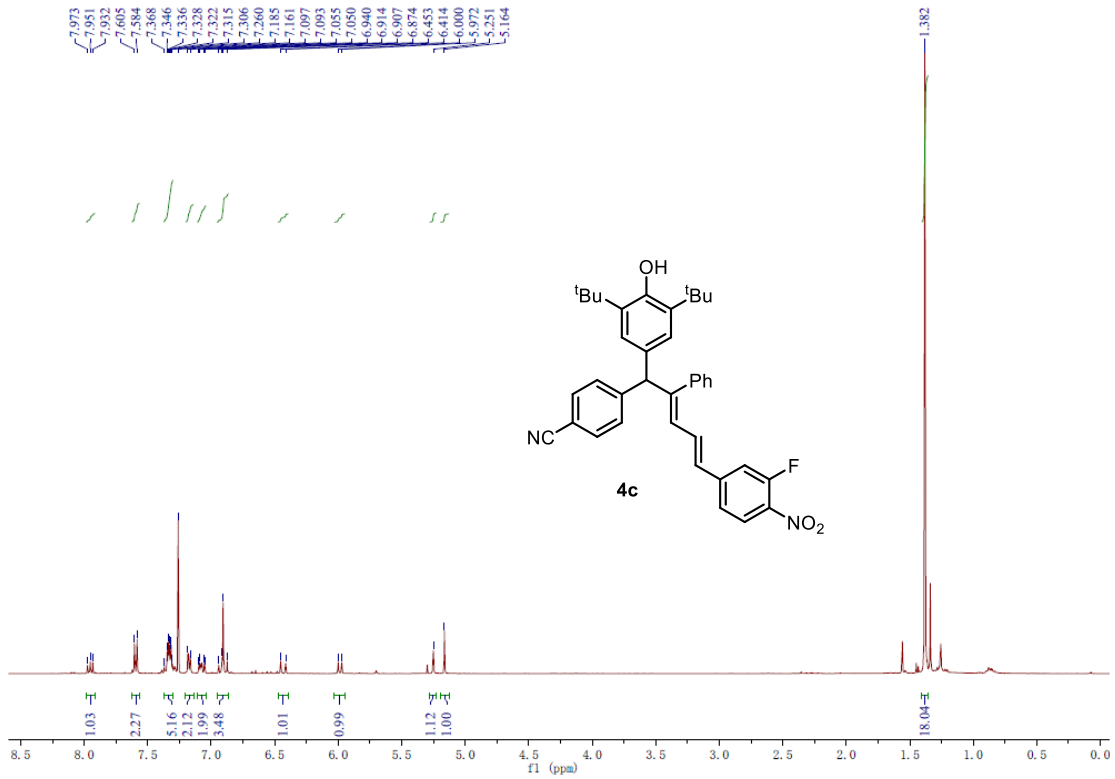
135.857
134.416
132.104
130.847
130.531
130.469
130.213
129.975
129.587
128.950
128.275
127.651
125.960
125.597
124.117
120.582
118.997
115.241
110.146
77.318
76.999
76.682
59.473
34.342
30.245
20.964
HO
tBu
tBu
Ph
NO2
NC
4b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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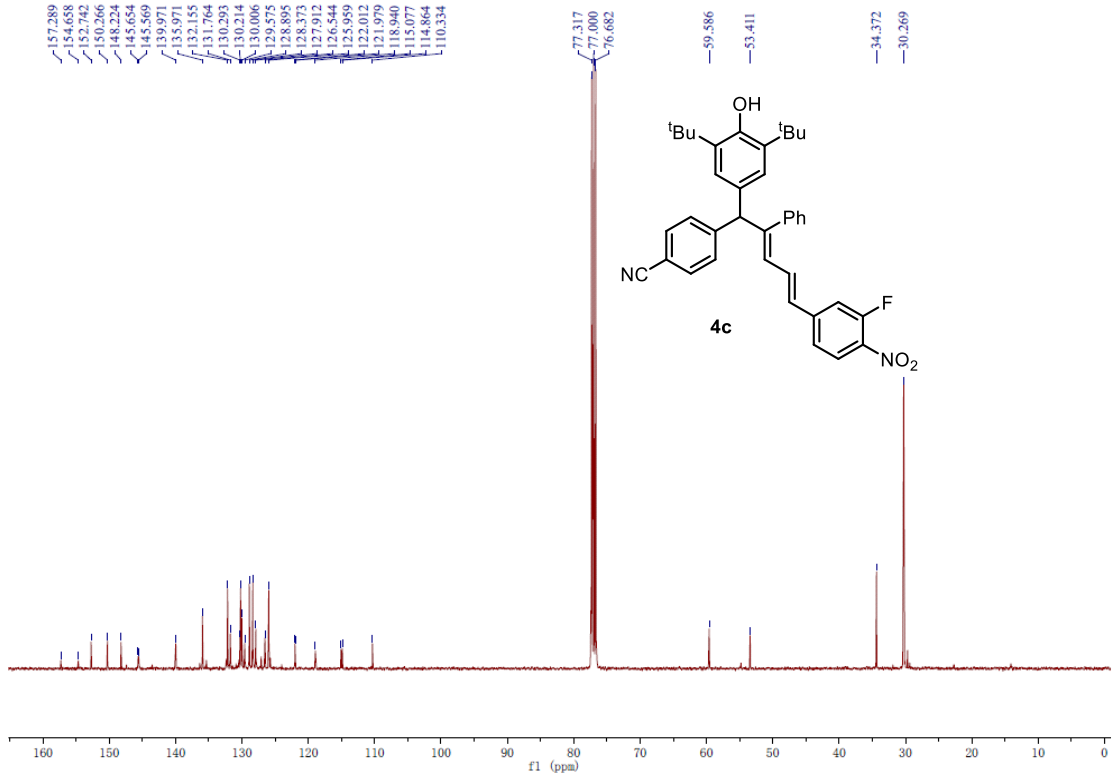
7.328
7.322
7.315
7.306
7.260
7.185
7.161
7.097
7.093
7.055
7.050
6.940
6.914
6.907
6.874
6.453
6.414
6.000
5.972
5.251
5.164
1.382
OH
tBu
tBu
Ph
NC
F
NO2
4c
1.03
2.27
5.16
2.12
1.99
3.48
1.01
0.99
1.12
1.00
18.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


116.823
116.843
116.855
116.875
OH
tBu
tBu
Ph
NC
F
NO2
4c
f1 (ppm)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145.569
139.971
135.971
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131.764
130.293
130.214
130.006
129.575
128.895
128.373
127.912
126.544
125.959
122.012
121.979
118.940
115.077
114.864
110.334
77.317
77.000
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53.411
34.372
30.269
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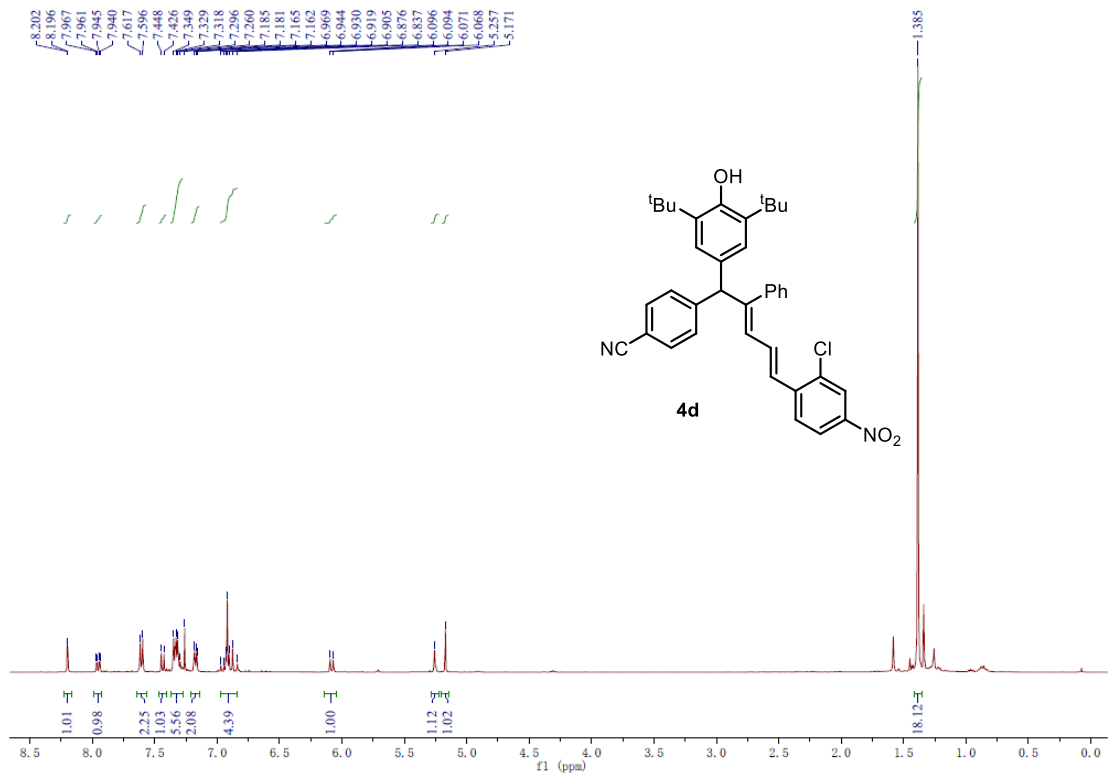
tBu
tBu
Ph
NC
F
NO2
4c
f1 (ppm)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8.196
7.967
7.961
7.945
7.940
7.617
7.596
7.448
7.426
7.349
7.329
7.318
7.296
7.260
7.185
7.181
7.165
7.162
6.969
6.944
6.930
6.919
6.905
6.876
6.837
6.096
6.094
6.071
6.068
5.257
5.171
1.385
OH
tBu
tBu
Ph
NC
Cl
NO2
4d
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0.98
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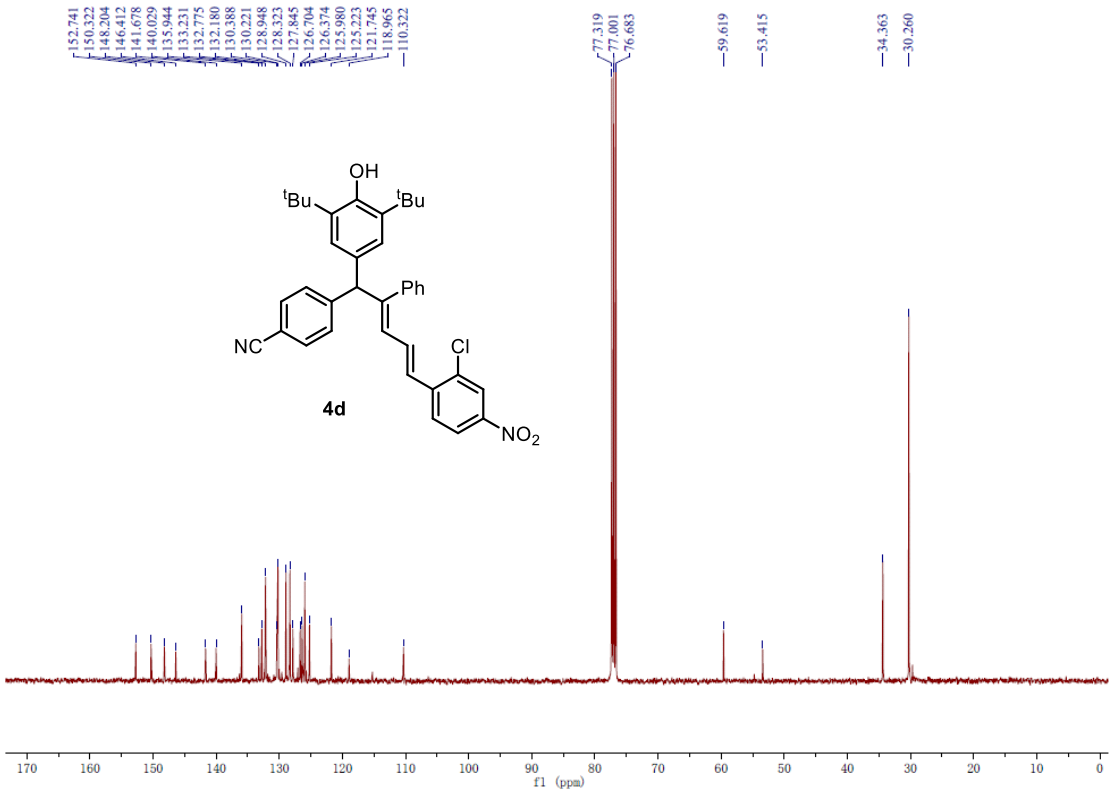
1.03
5.56
2.08
4.39
1.00
1.12
1.02
18.12
f1 (ppm)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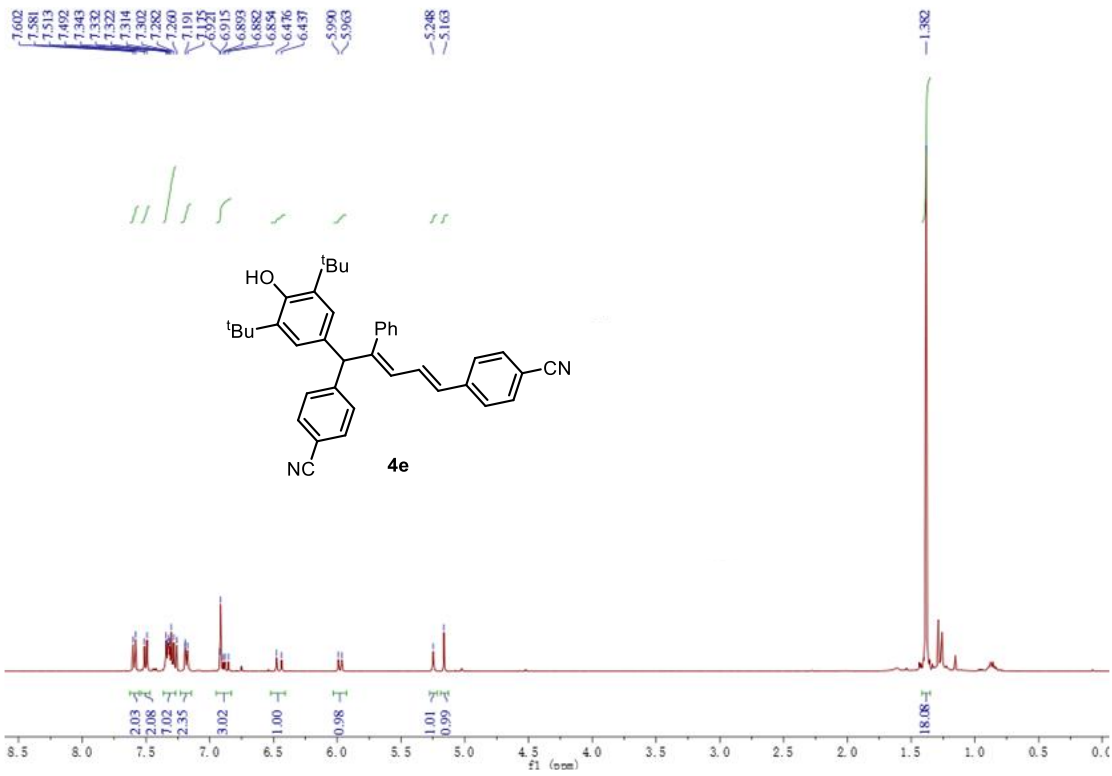
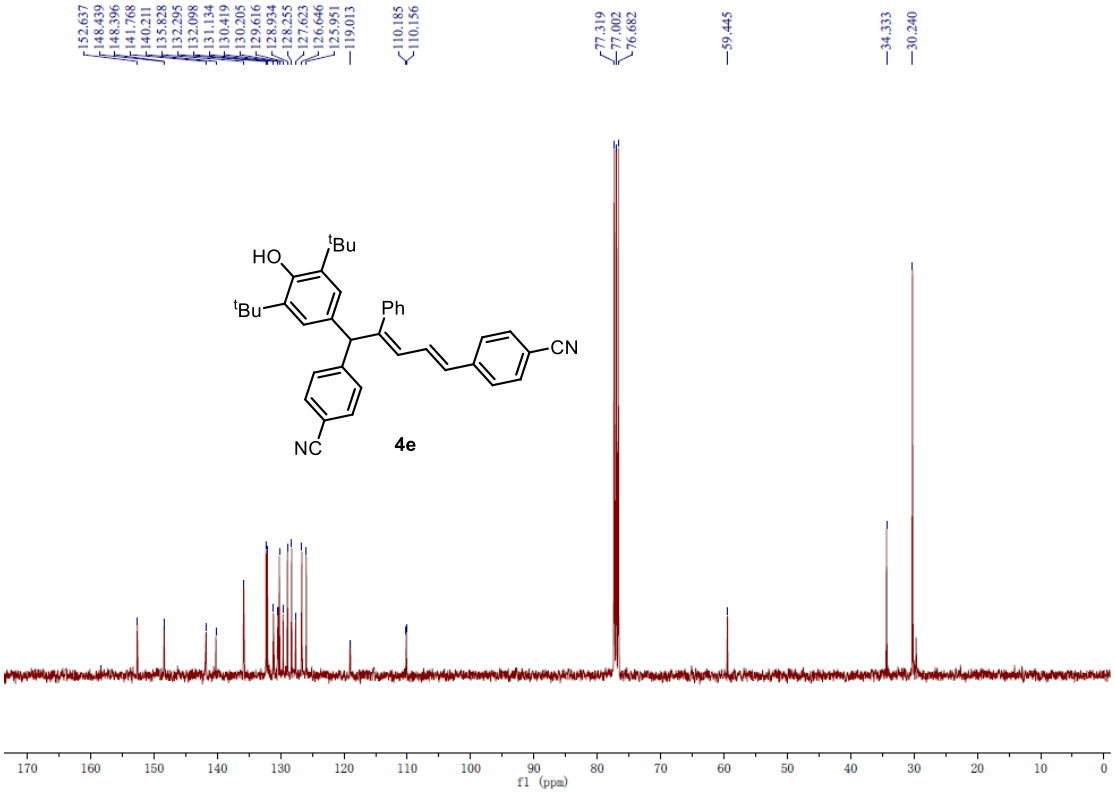
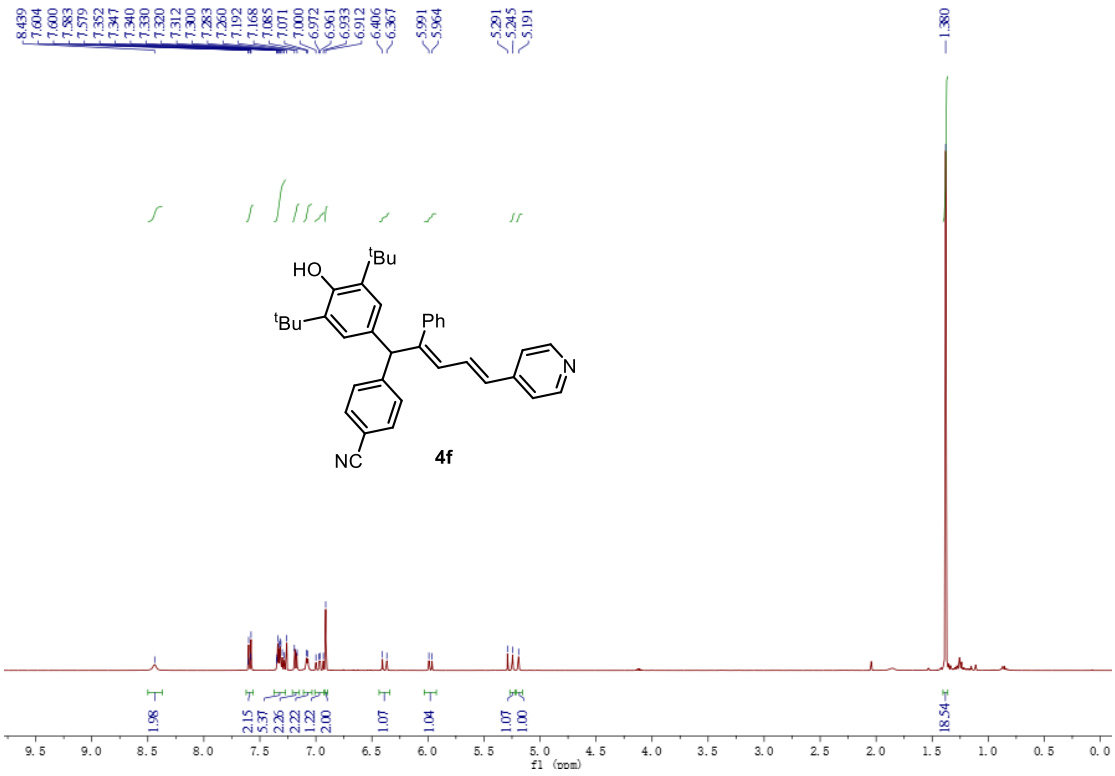
140.029
135.944
133.231
132.775
132.180
130.388
130.221
128.948
128.323
127.845
126.704
126.374
125.980
125.223
121.745
118.965
110.322
77.319
77.001
76.683
59.619
53.415
34.363
30.260
OH
tBu
tBu
Ph
NC
Cl
NO2
4d
f1 (ppm)


HO
tBu
tBu
Ph
CN
NC
4e
f1 (ppm)


HO
tBu
tBu
Ph
CN
NC
4e
f1 (ppm)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7.600
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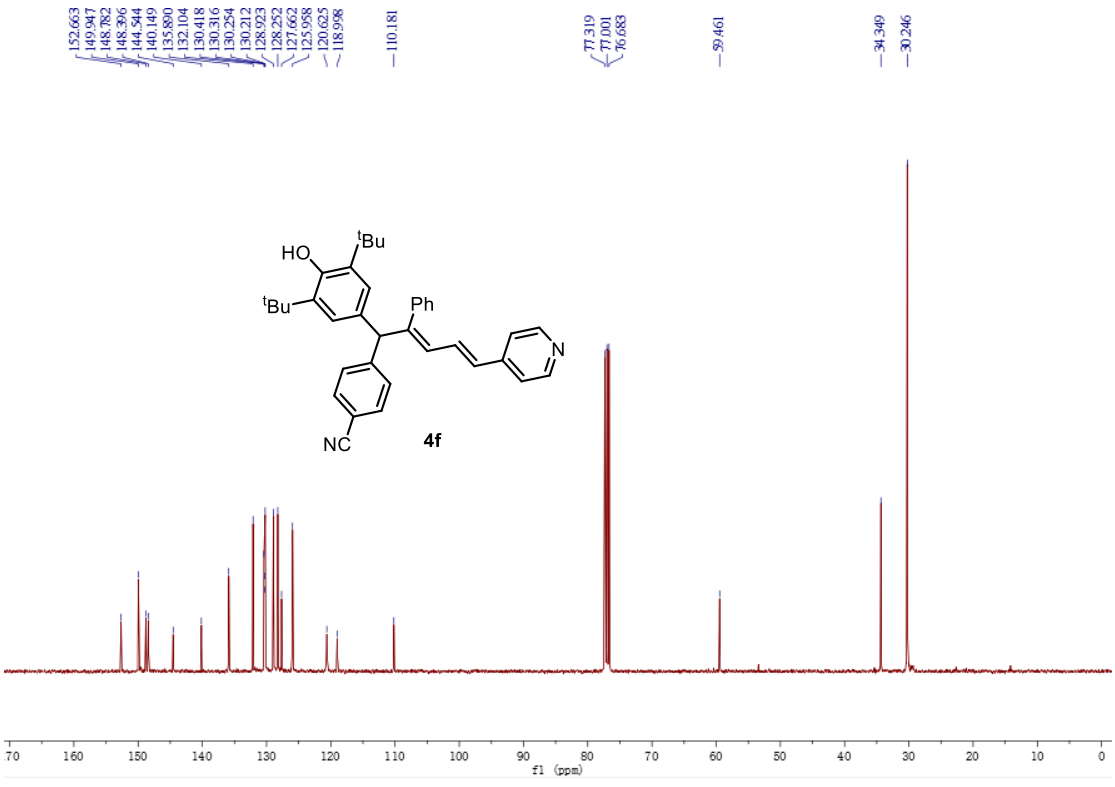
7.579
7.352
7.347
7.340
7.330
7.320
7.312
7.300
7.283
7.260
7.192
7.168
7.085
7.071
7.000
6.972
6.961
6.933
6.912
6.406
6.367
5.991
5.964
5.291
5.245
5.191
1.380
HO
tBu
tBu
Ph
N
NC
4f
1.98
2.15
5.37
2.26
2.22
1.22
2.00
1.07
1.04
1.07
1.00
18.54
f1 (ppm)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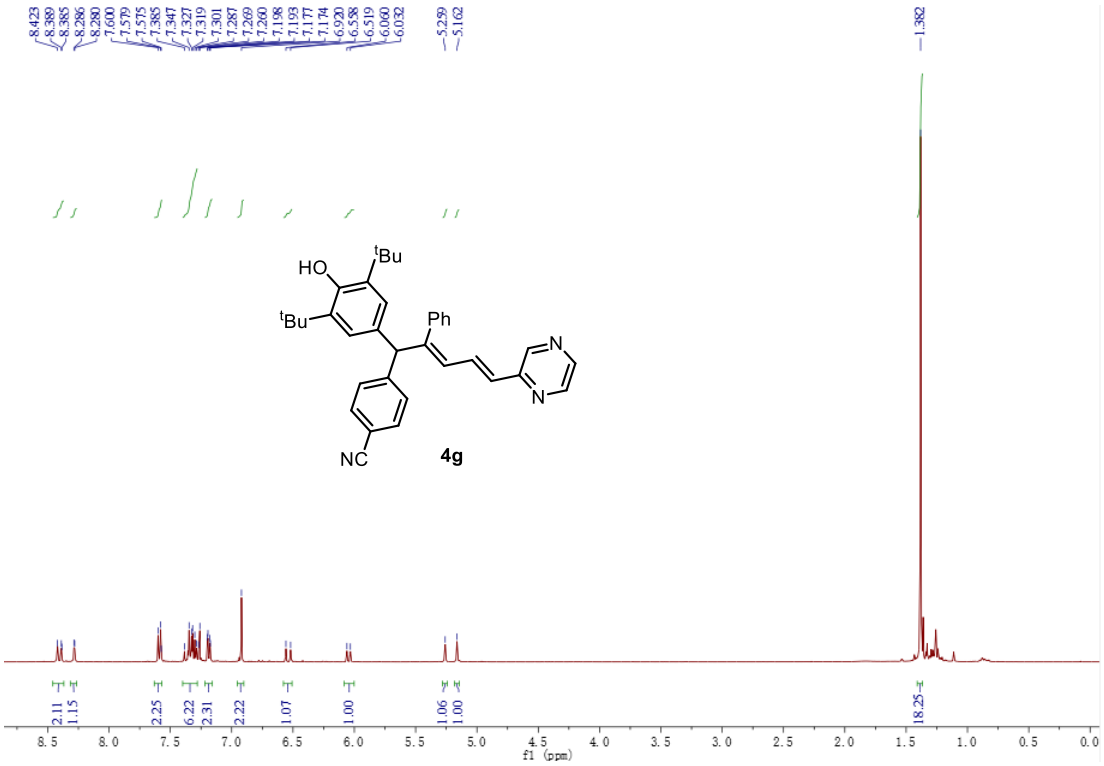
144.584
140.149
135.890
132.104
130.418
130.316
130.254
130.212
128.923
128.252
127.662
125.958
120.625
118.998
110.181
77.319
77.001
76.683
59.461
34.349
30.246
HO
tBu
tBu
Ph
N
NC
4f
f1 (ppm)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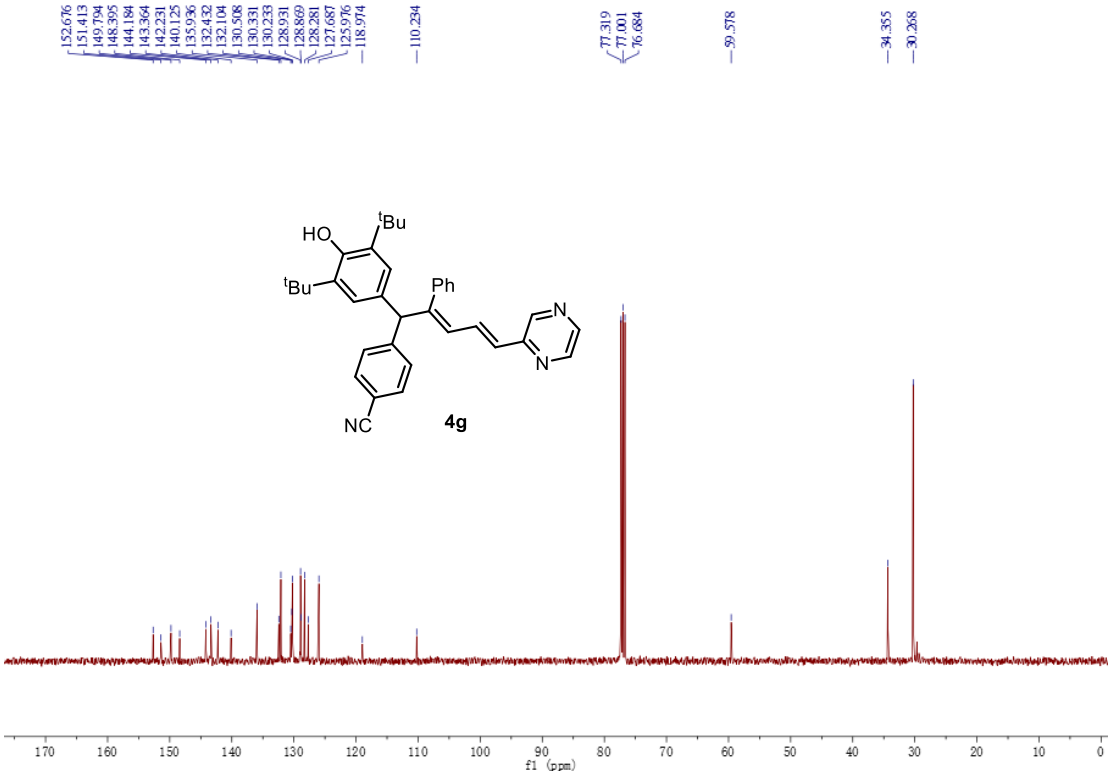
tBu
tBu
Ph
N
N
NC
4g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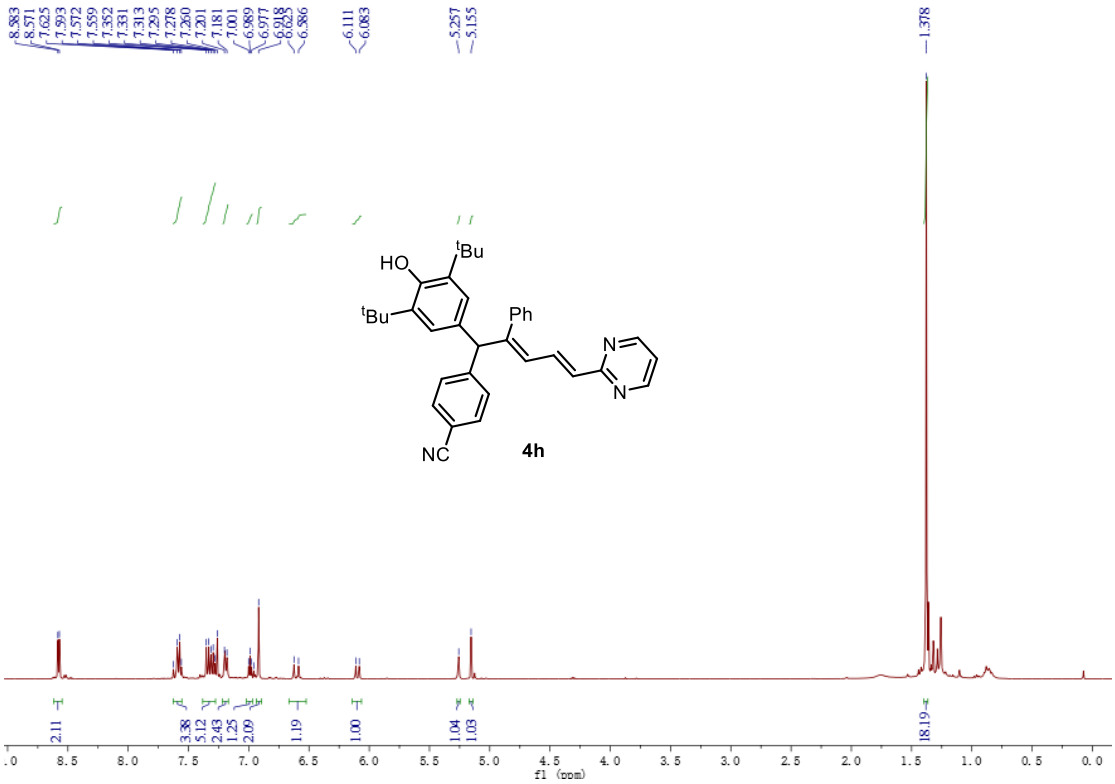
tBu
tBu
Ph
N
N
NC
4g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7.352
7.331
7.313
7.295
7.278
7.260
7.201
7.181
7.001
6.989
6.977
6.918
6.623
6.586
6.111
6.083
5.257
5.155
1.378
HO
tBu
tBu
Ph
N
N
NC
4h
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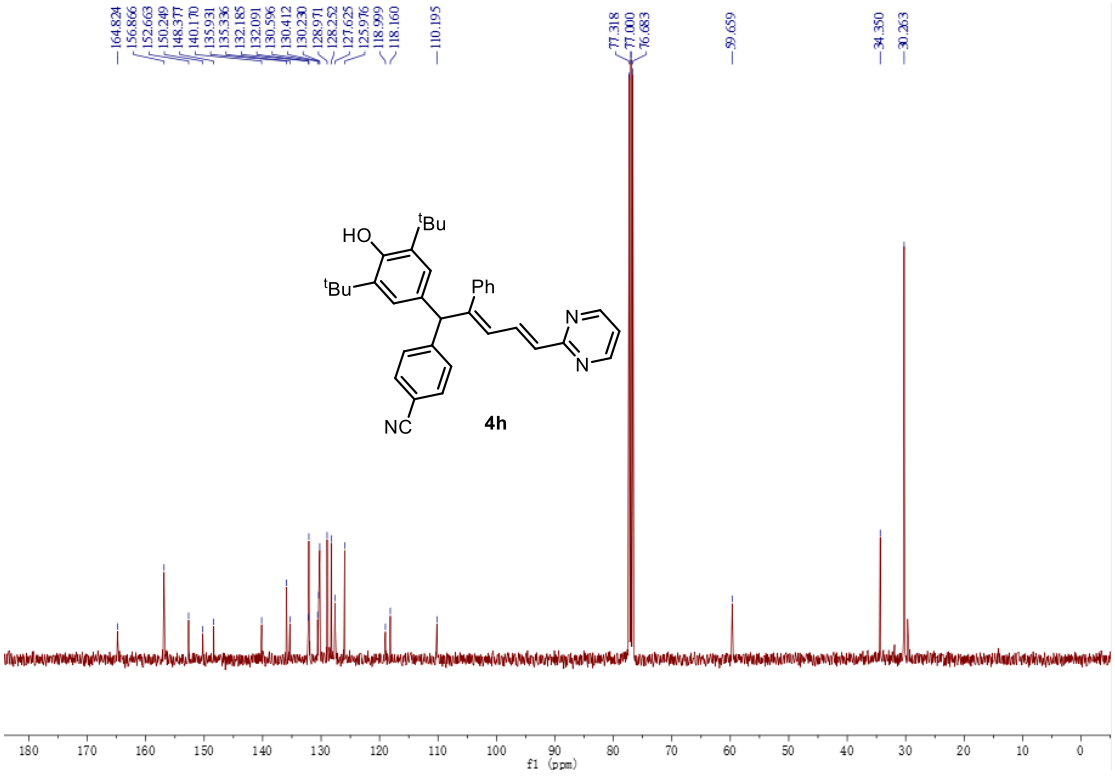
3.38
5.12
2.43
1.25
2.09
1.19
1.00
1.04
1.03
18.19
f1 (ppm)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156.866
152.663
150.249
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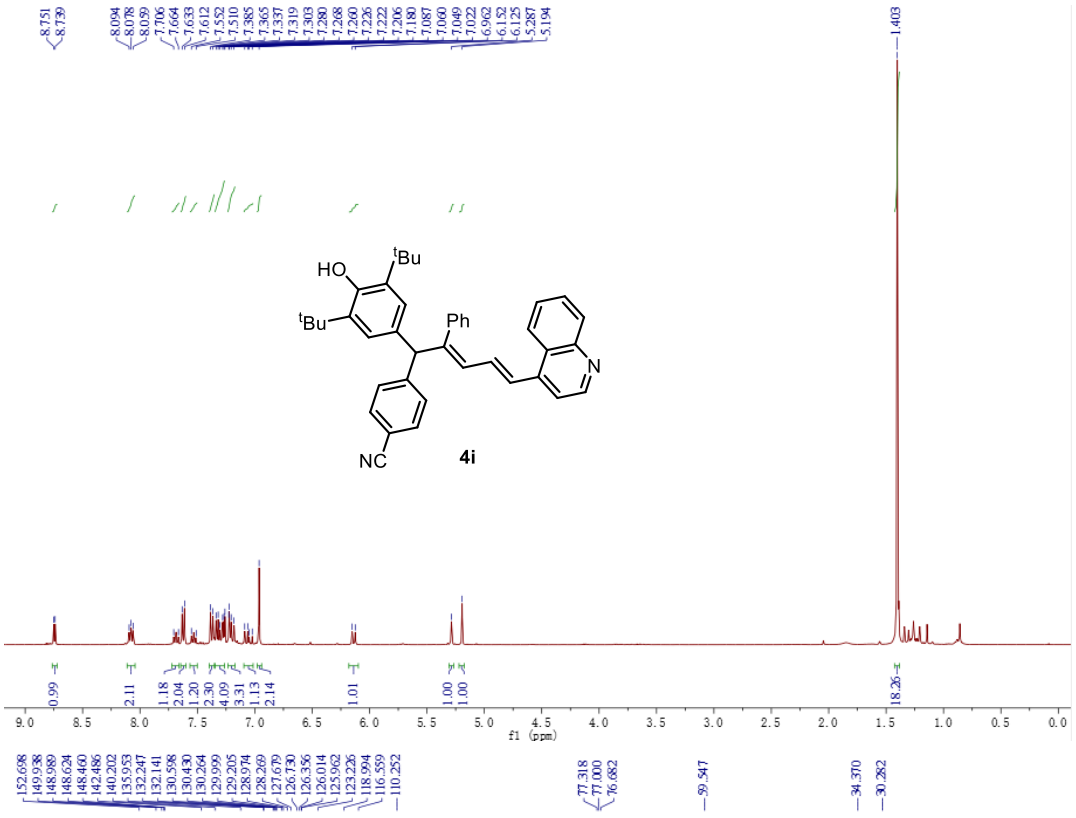
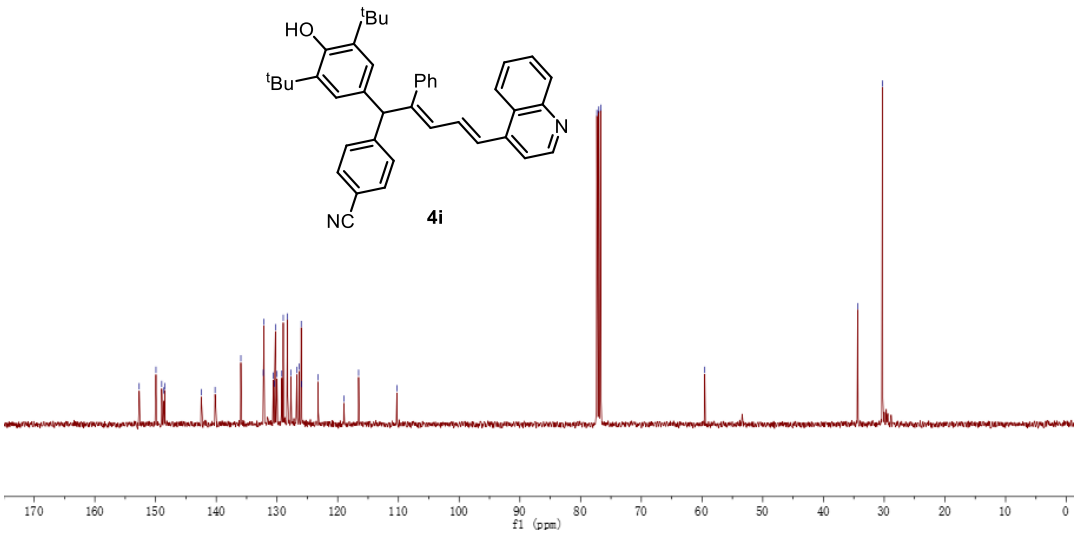
140.170
135.931
135.336
132.185
132.091
130.596
130.412
130.230
128.971
128.252
127.625
125.976
118.999
118.160
110.195
77.318
77.000
76.683
59.659
34.350
30.263
HO
tBu
tBu
Ph
N
N
NC
4h
f1 (ppm)


HO
tBu
tBu
Ph
N
NC
4i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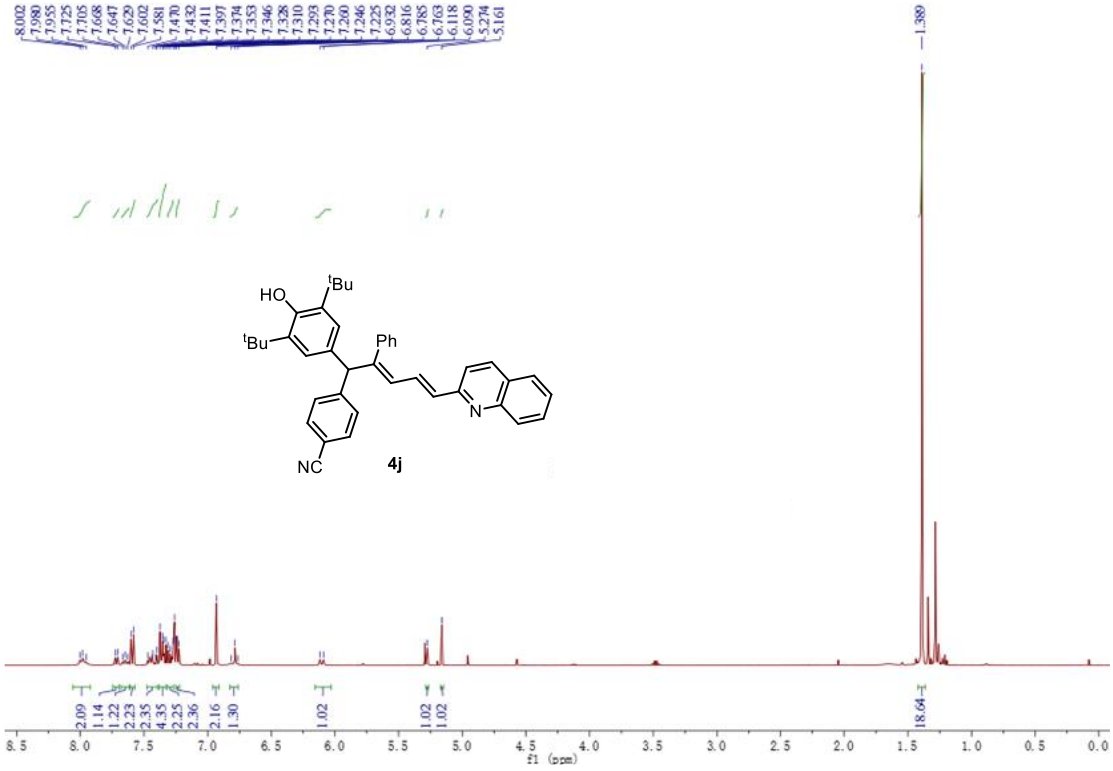
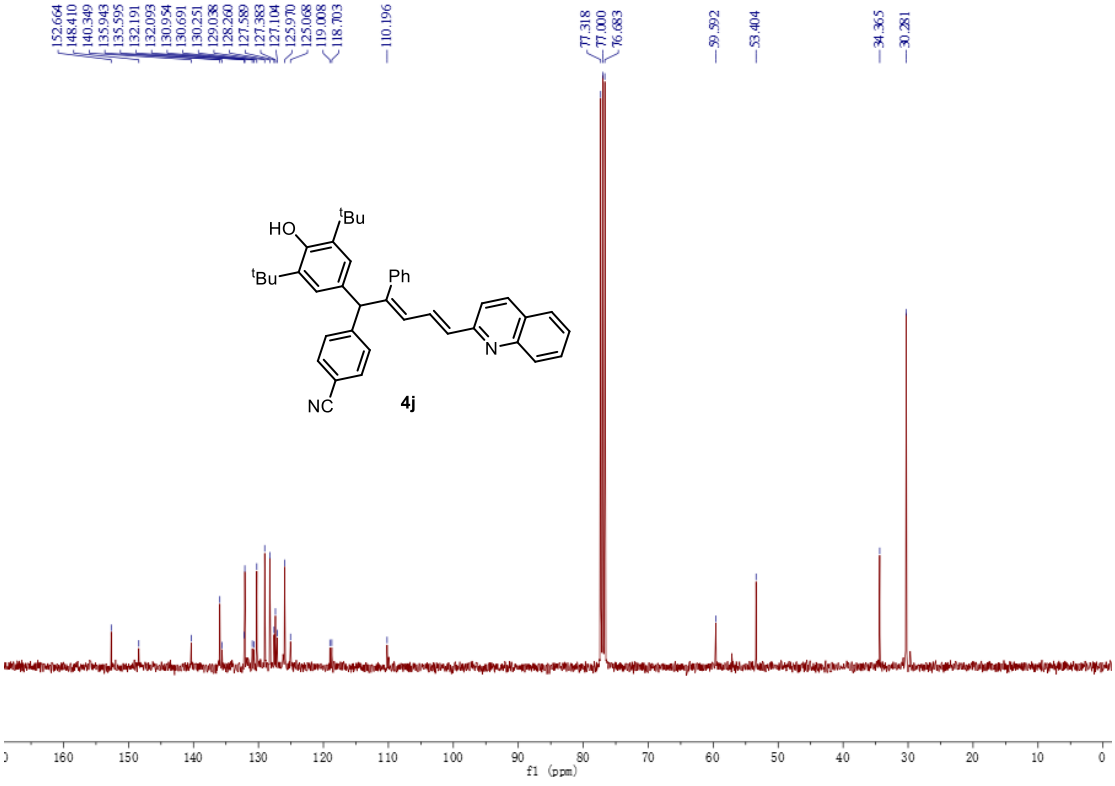
tBu
tBu
Ph
N
NC
4i


HO
tBu
tBu
Ph
N
NC
4j
f1 (ppm)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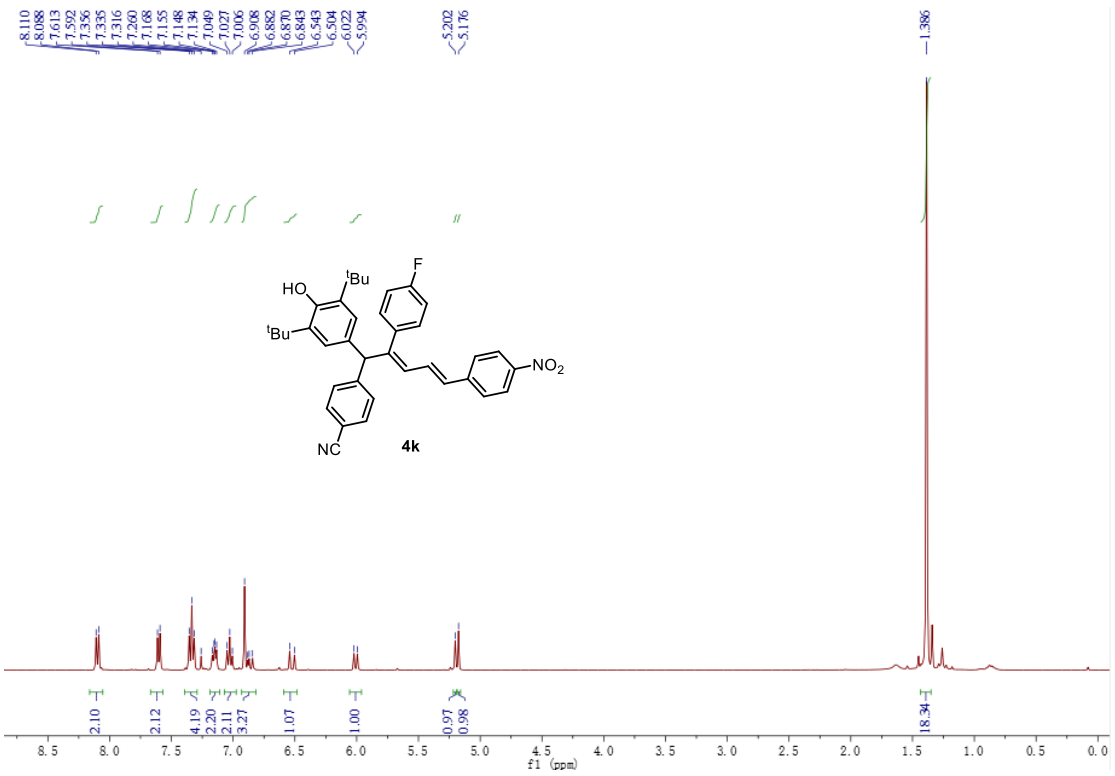
tBu
tBu
Ph
N
NC
4j
f1 (ppm)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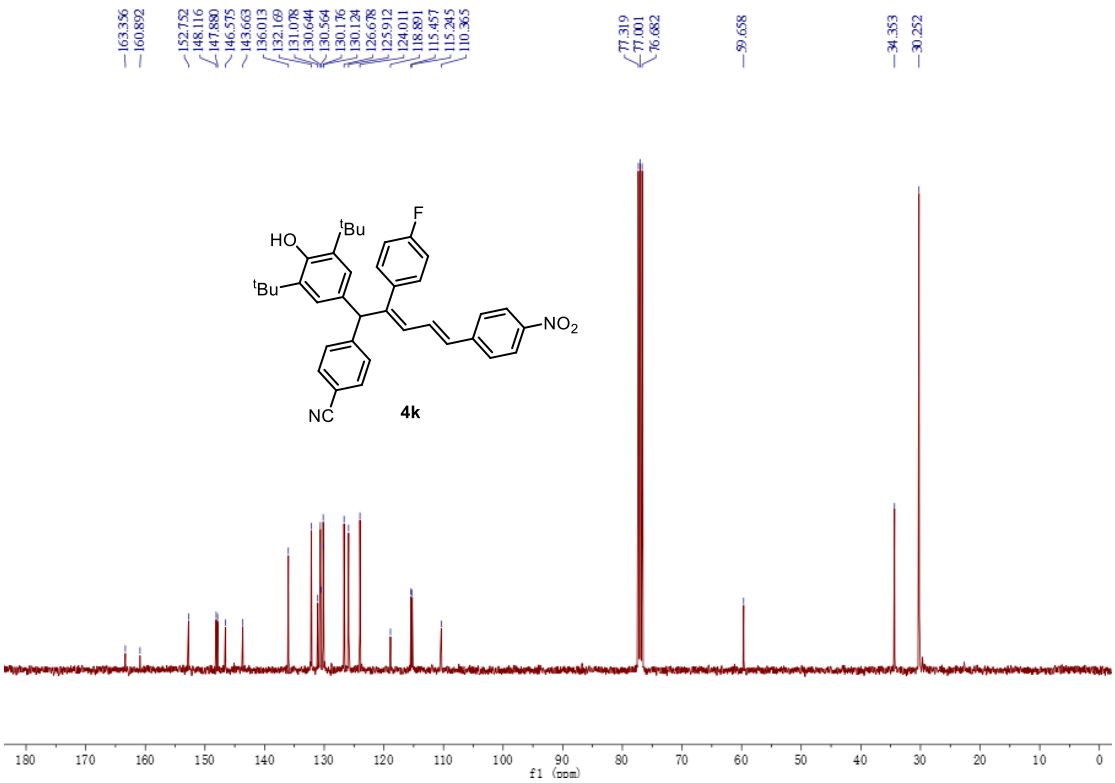
7.592
7.356
7.335
7.316
7.260
7.168
7.155
7.148
7.134
7.049
7.027
7.006
6.908
6.882
6.870
6.843
6.543
6.504
6.022
5.994
5.202
5.176
1.386
HO
tBu
tBu
F
NO2
NC
4k
2.10
2.12
4.19
2.20
2.11
3.27
1.07
1.00
0.97
0.98
18.34
f1 (ppm)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136.013
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131.078
130.644
130.564
130.176
130.124
126.678
125.912
124.011
118.891
115.457
115.245
110.365
77.319
77.001
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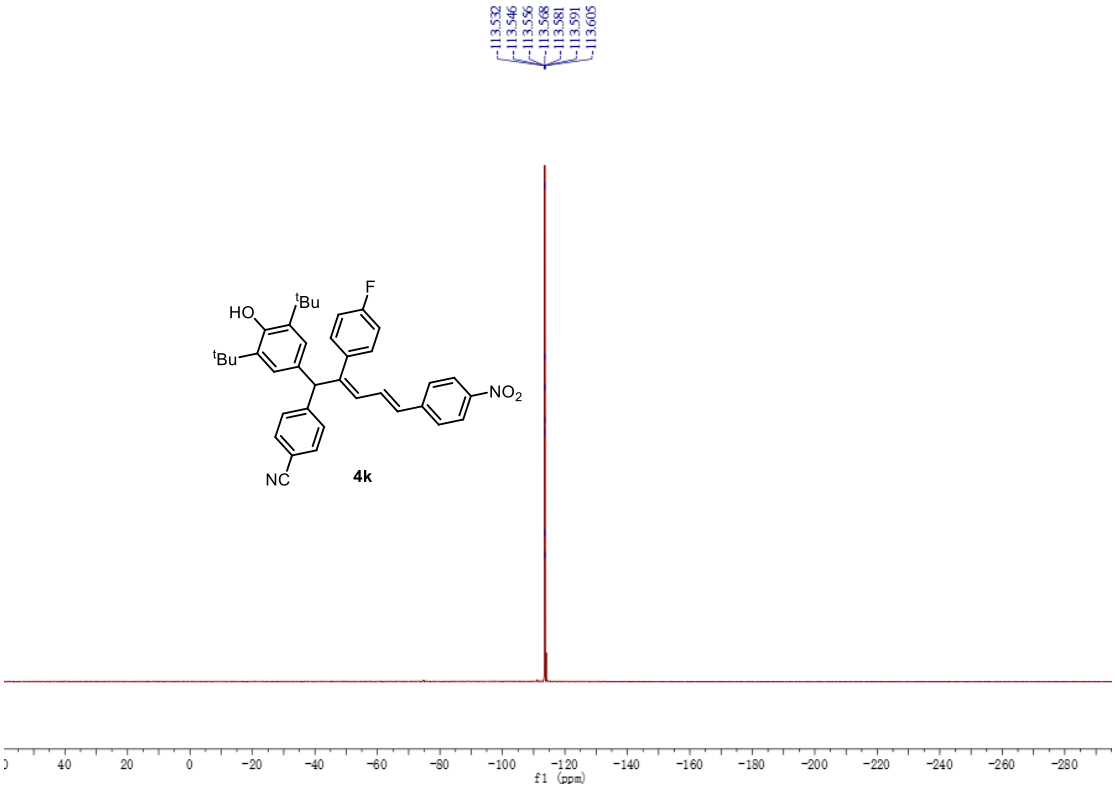
59.658
34.353
30.252
HO
tBu
tBu
F
NO2
NC
4k
f1 (ppm)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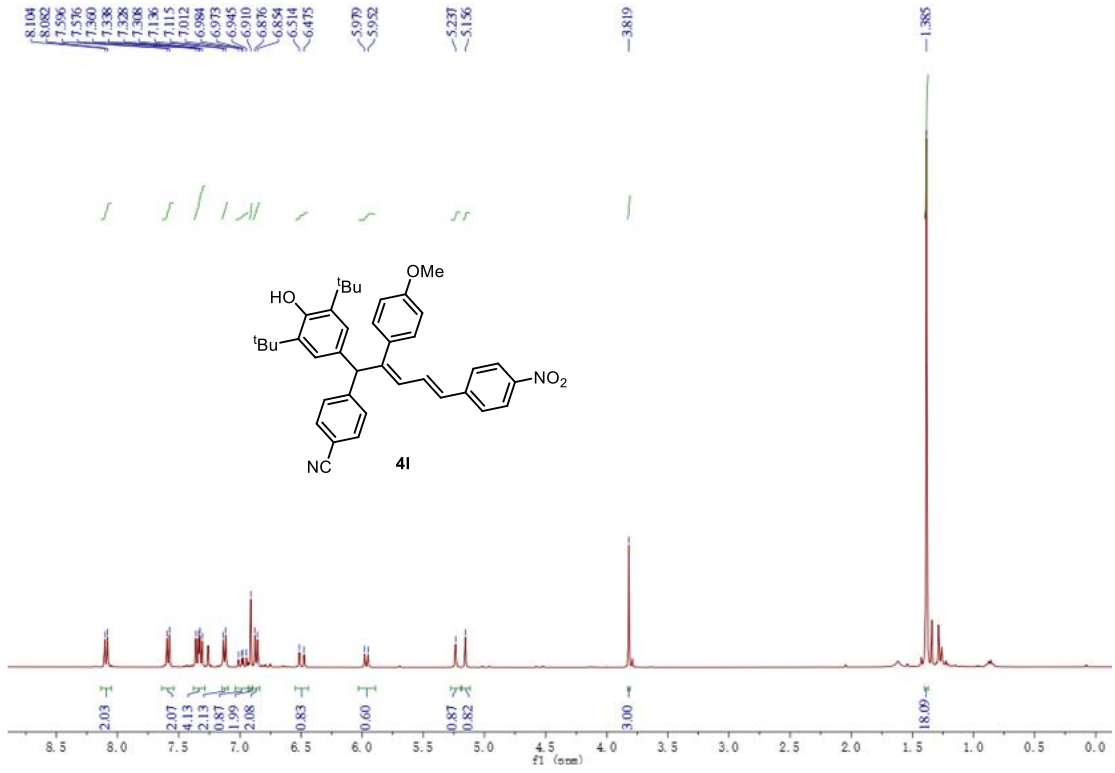
-113.591
-113.605
HO
tBu
tBu
F
NO2
NC
4k
f1 (ppm)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7.308
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7.115
7.012
6.984
6.973
6.945
6.910
6.876
6.854
6.514
6.475
5.979
5.952
5.237
5.156
3.819
1.385
HO
tBu
tBu
OMe
NO2
NC
4l
2.03
2.07
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0.60
0.87
0.82
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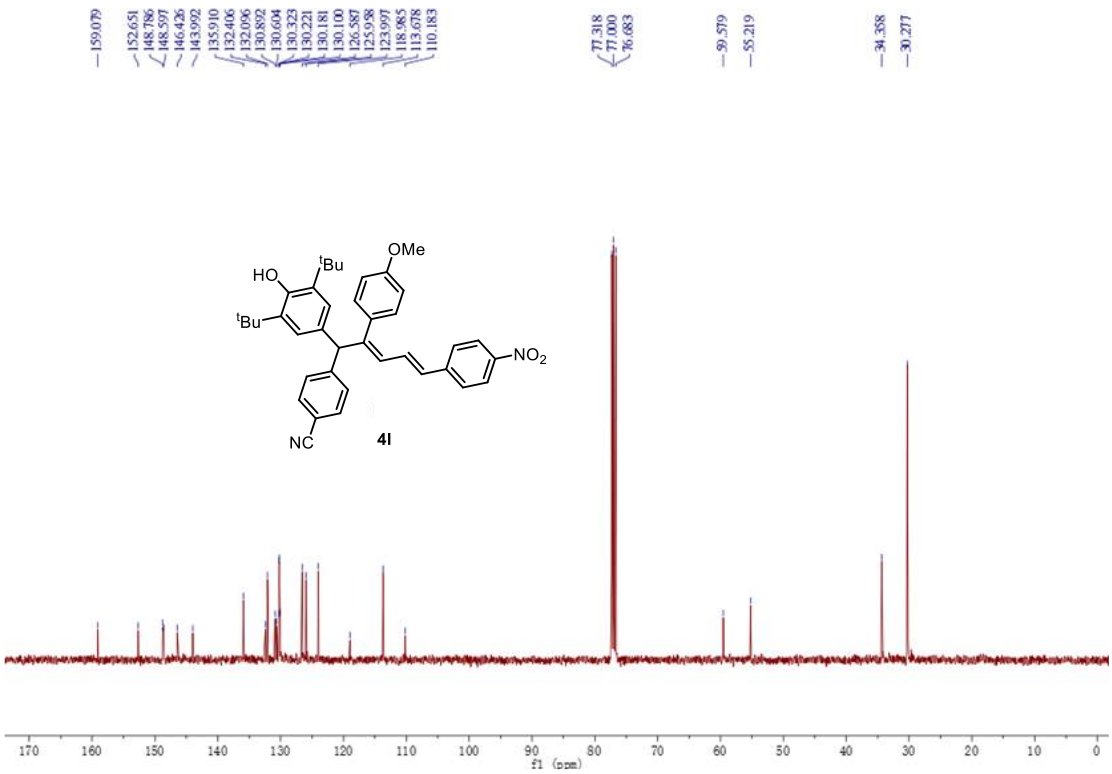
18.09
f1 (ppm)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130.221
130.181
130.100
126.587
125.958
123.997
118.985
113.678
110.183
77.318
77.000
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55.219
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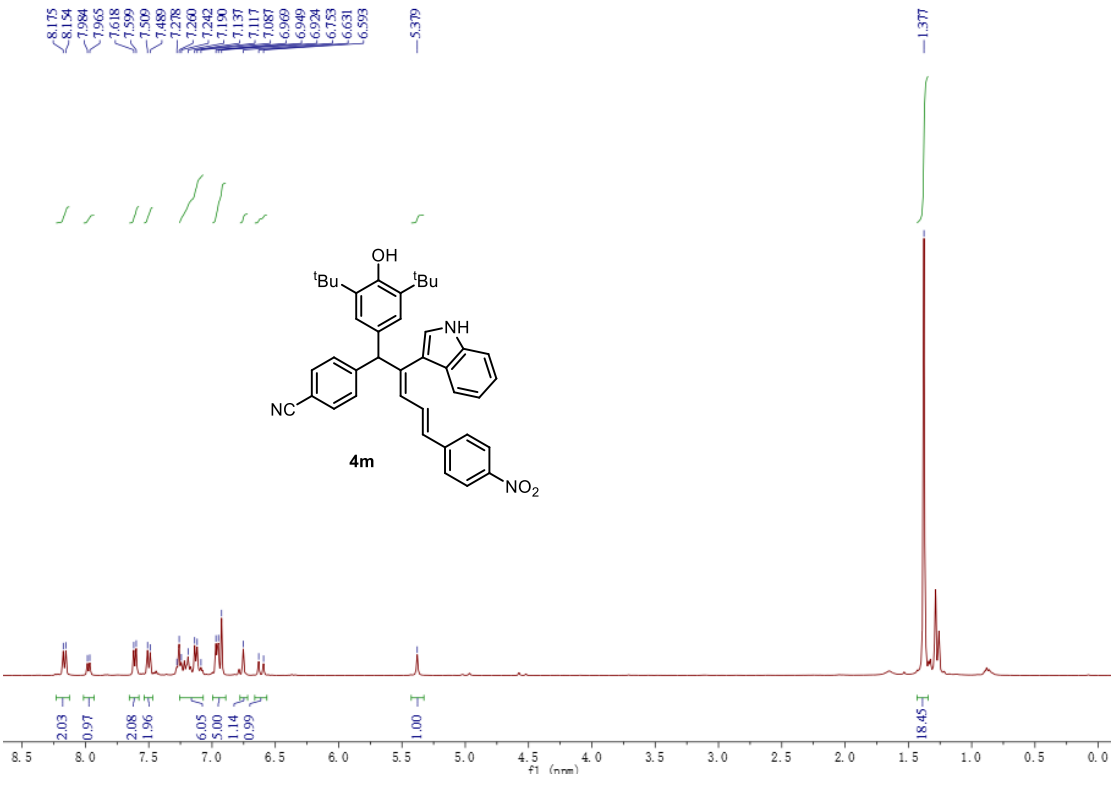
30.277
HO
tBu
tBu
OMe
NO2
NC
4l
f1 (ppm)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7.260
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7.190
7.137
7.117
7.087
6.969
6.949
6.924
6.753
6.631
6.593
5.379
1.377
OH
tBu
tBu
NH
NC
4m
NO2
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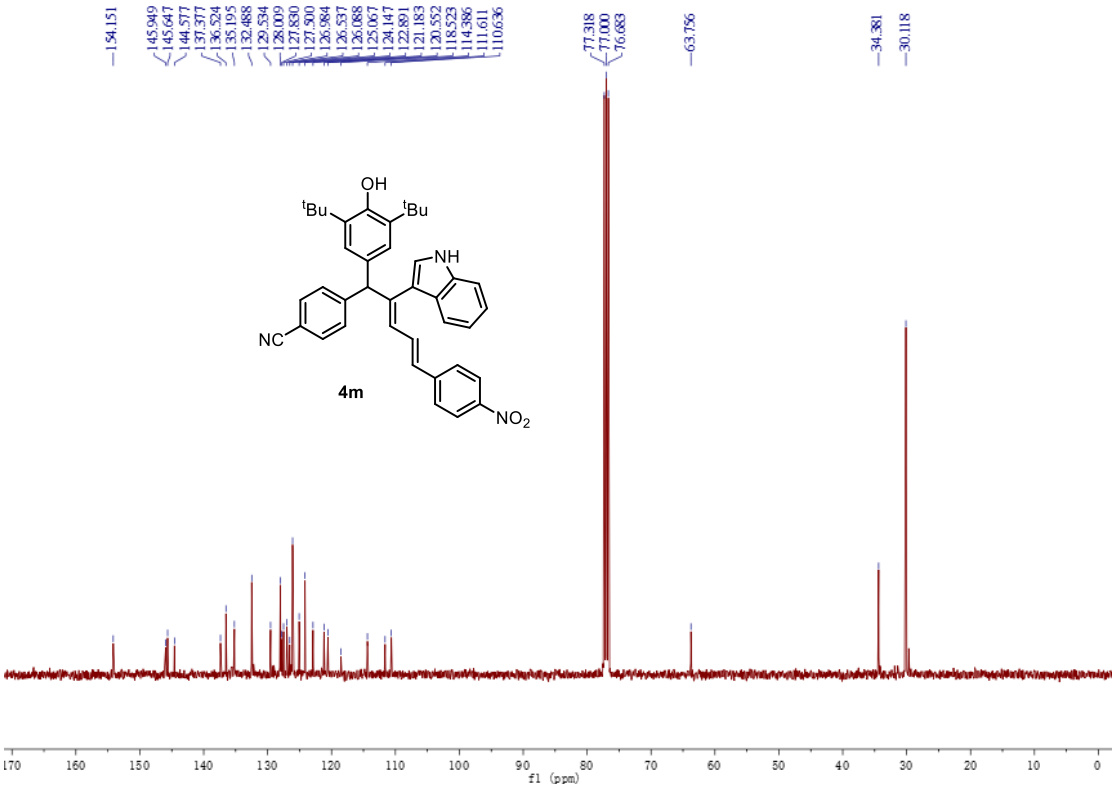
1.00
18.45
f1 (ppm)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127.830
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126.984
126.537
126.088
125.067
124.147
122.891
121.183
120.552
118.523
114.386
111.611
110.636
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77.000
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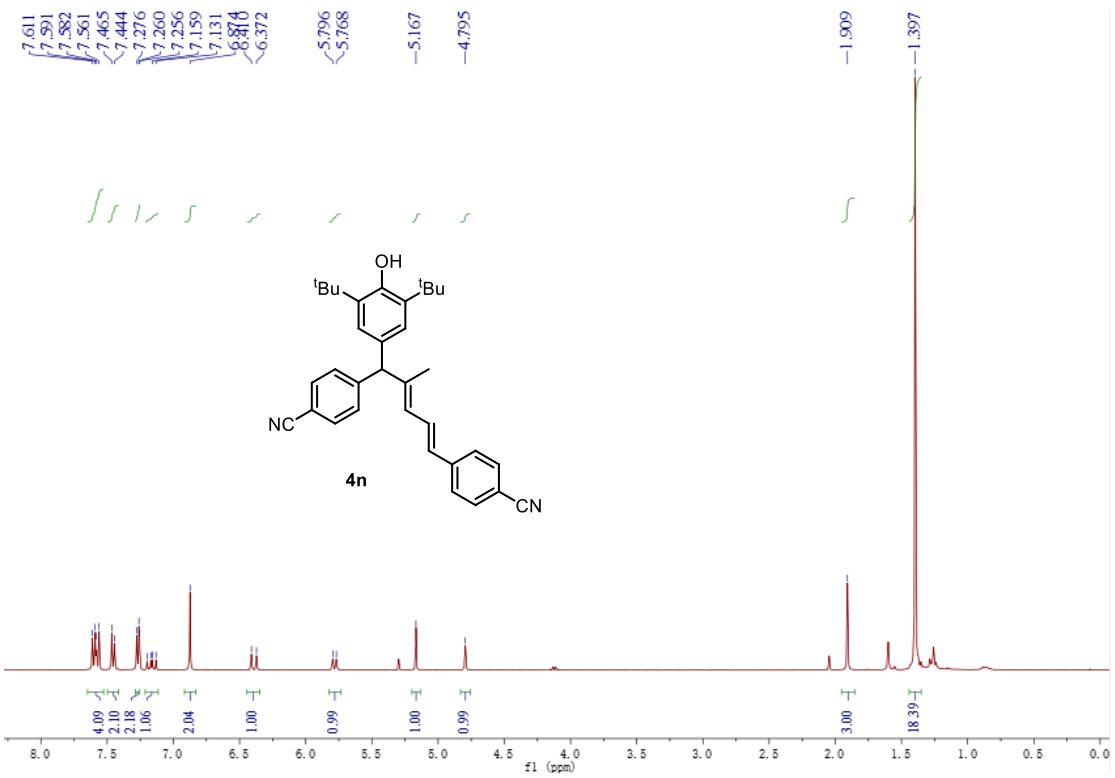
63.756
34.381
30.118
OH
tBu
tBu
NH
NC
NO2
4m
f1 (ppm)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7.444
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7.260
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7.159
7.131
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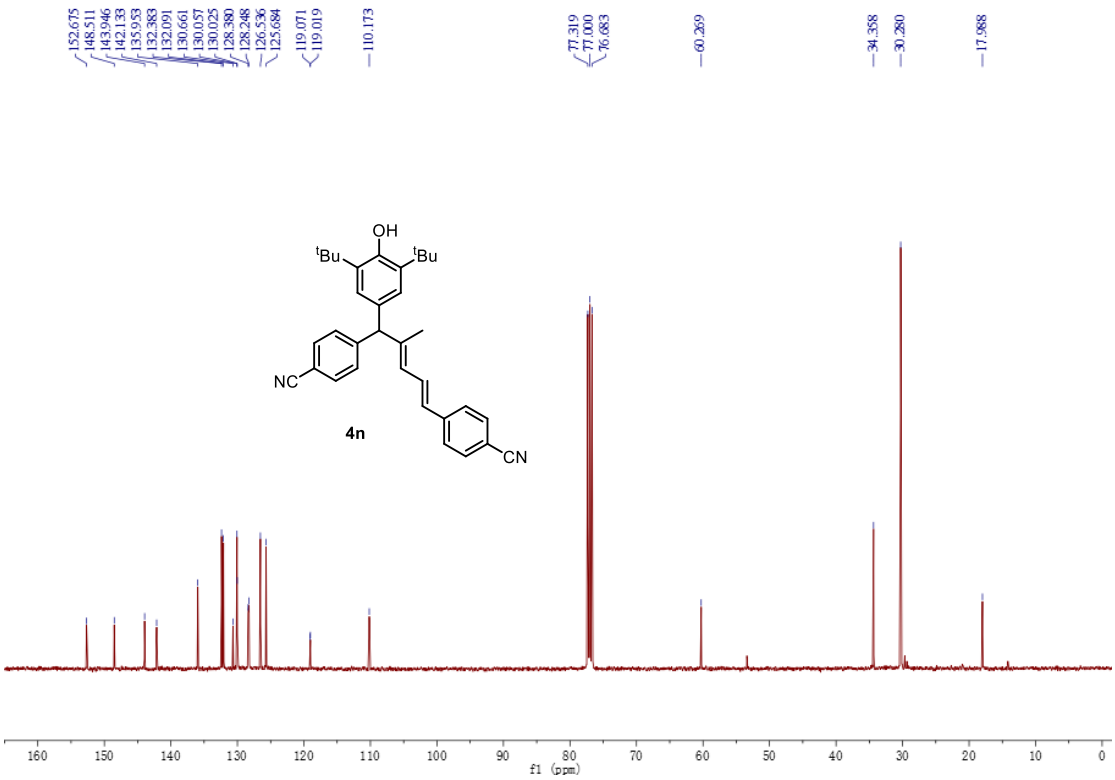
6.372
5.796
5.768
5.167
4.795
1.909
1.397
OH
tBu
tBu
NC
CN
4n
4.09
2.10
2.18
1.06
2.04
1.00
0.99
1.00
0.99
3.00
18.39
f1 (ppm)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143.946
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132.383
132.091
130.661
130.057
130.025
128.380
128.248
126.536
125.684
119.071
119.019
110.173
77.319
77.000
76.683
60.259
34.358
30.280
17.988
OH
tBu
tBu
NC
CN
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110
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90
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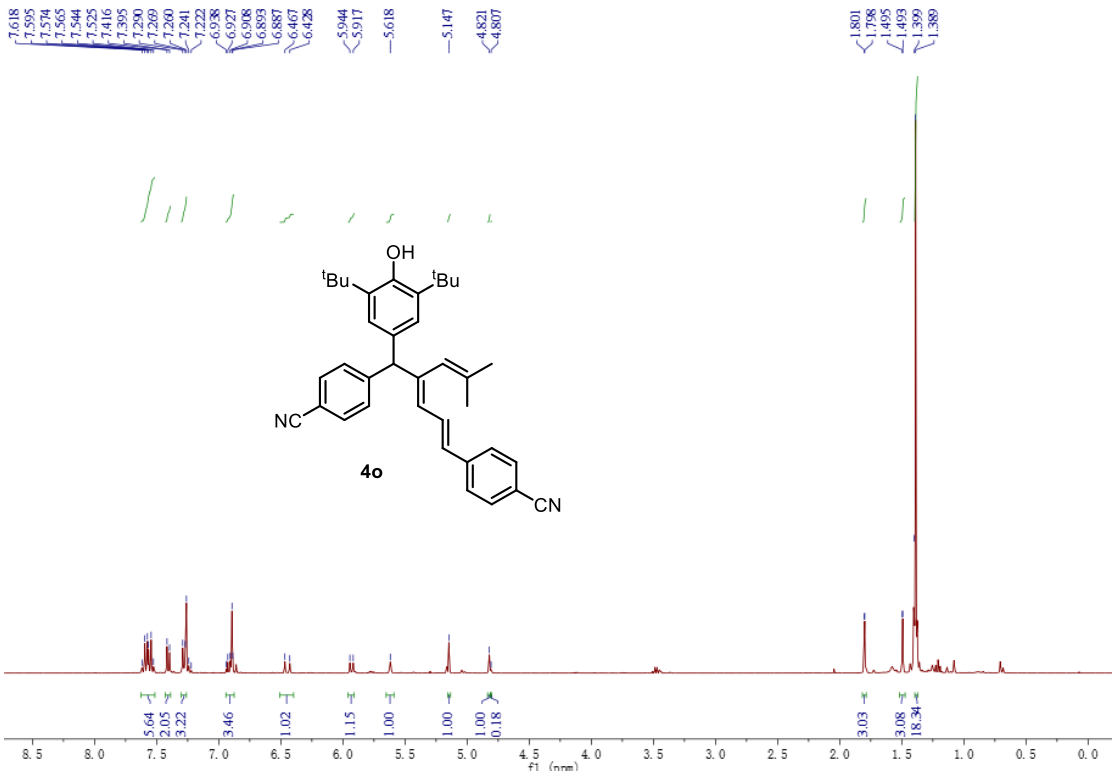
70
60
50
40
30
20
10
0
f1 (ppm)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7.222
6.938
6.927
6.908
6.893
6.887
6.467
6.428
5.944
5.917
5.618
5.147
4.821
4.807
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1.798
1.495
1.493
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1.389
OH
tBu
tBu
NC
CN
4o
5.64
2.05
3.22
3.46
1.02
1.15
1.00
1.00
1.00
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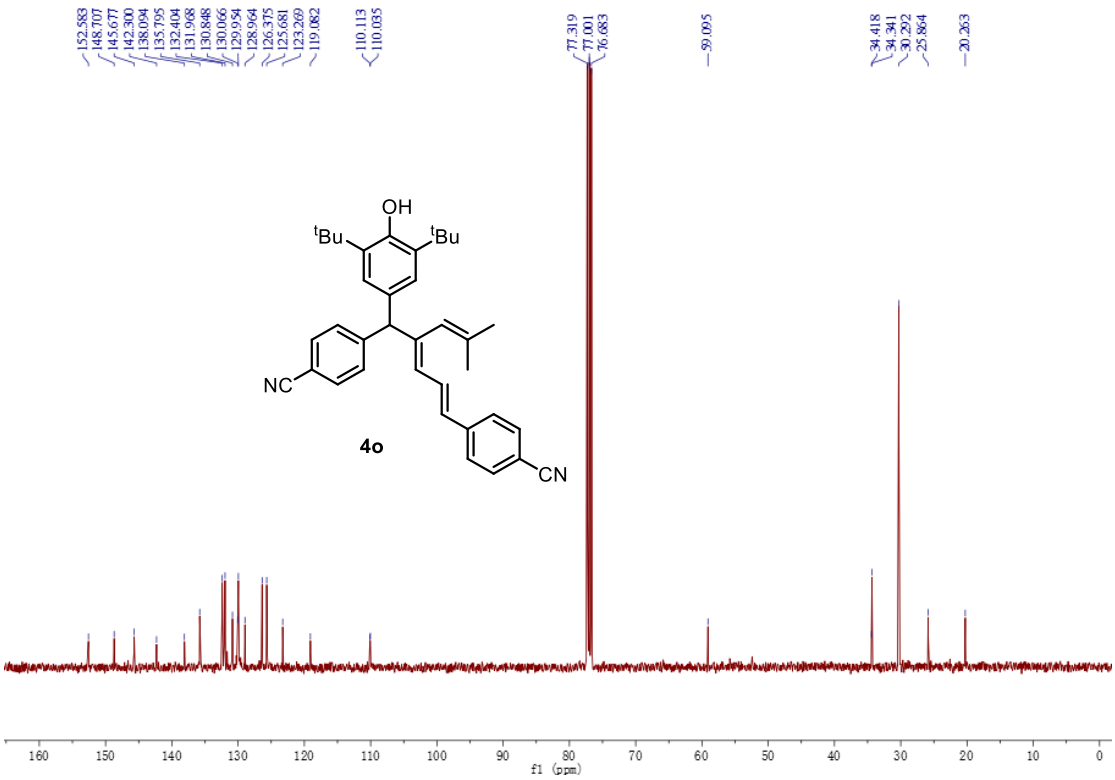
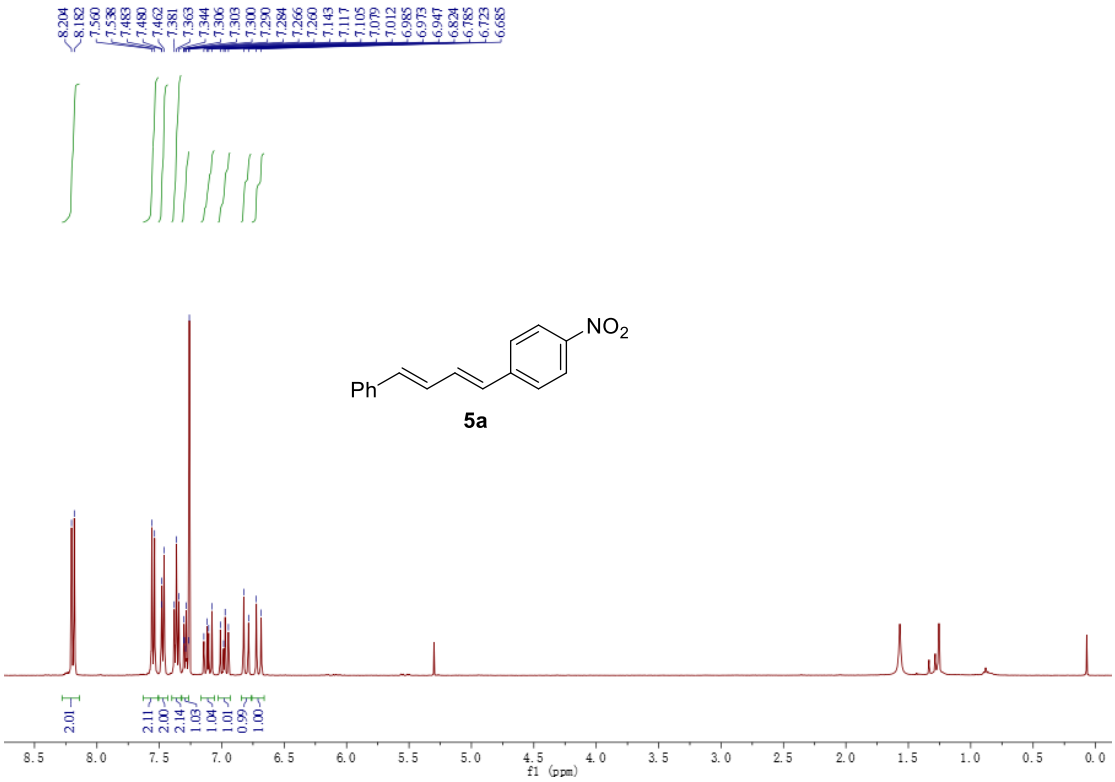
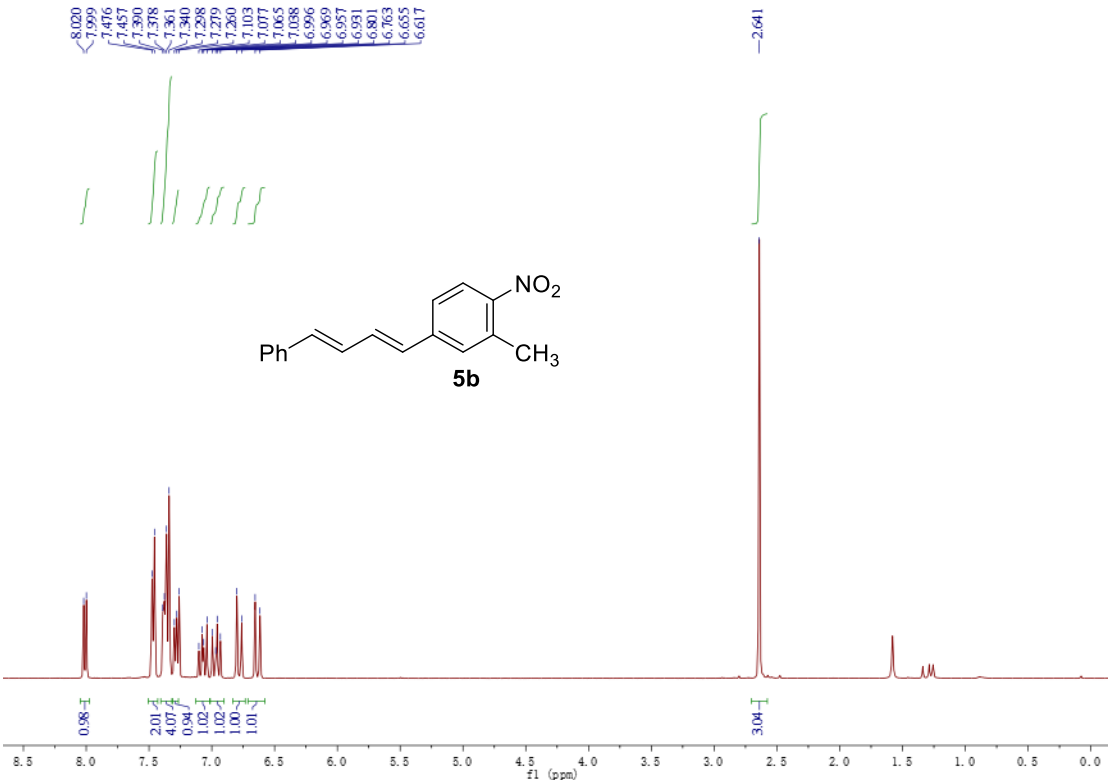
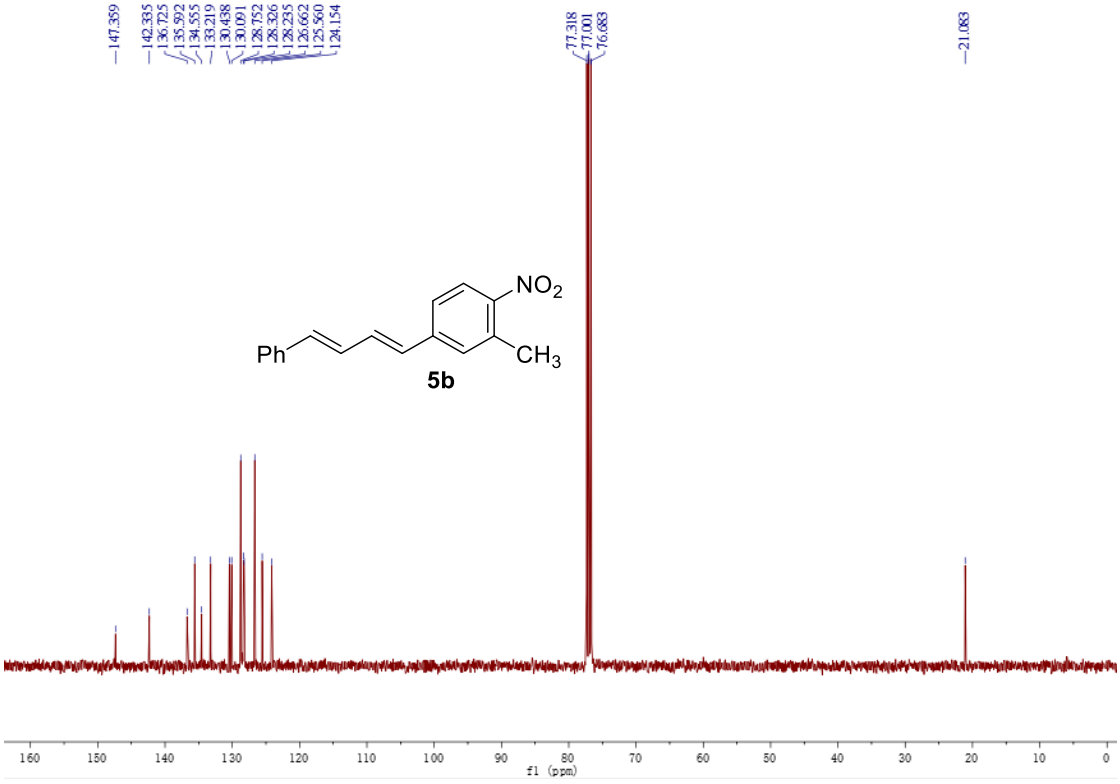
3.03
3.08
18.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

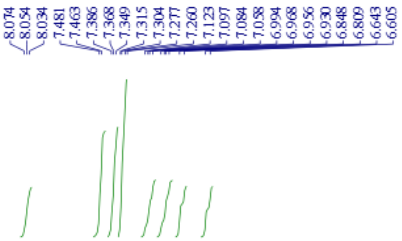


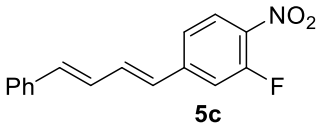
NMR spectra of compound 5



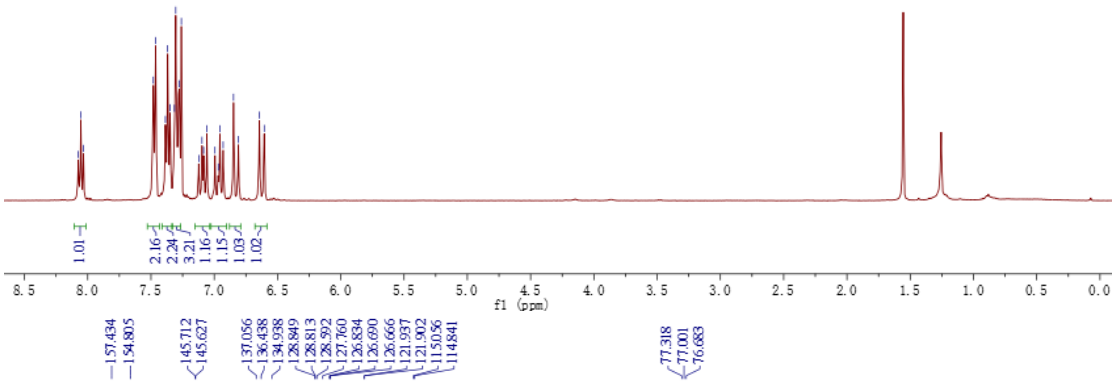

8.020
7.999
7.476
7.457
7.390
7.378
7.361
7.340
7.298
7.279
7.260
7.103
7.077
7.065
7.038
6.996
6.969
6.957
6.931
6.801
6.763
6.655
6.617
2.641
NO2
Ph
CH3
5b
0.98
2.01
4.07
0.94
1.02
1.02
1.00
1.01
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

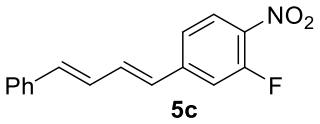

147.359
142.335
136.725
135.592
134.555
133.219
130.438
130.091
128.752
128.326
128.235
126.662
125.560
124.154
77.318
77.001
76.683
21.083
NO2
Ph
CH3
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.074
8.054
8.034
7.481
7.463
7.386
7.368
7.349
7.315
7.304
7.277
7.260
7.123
7.097
7.084
7.038
6.994
6.968
6.956
6.930
6.848
6.809
6.643
6.605


NO2
Ph
F

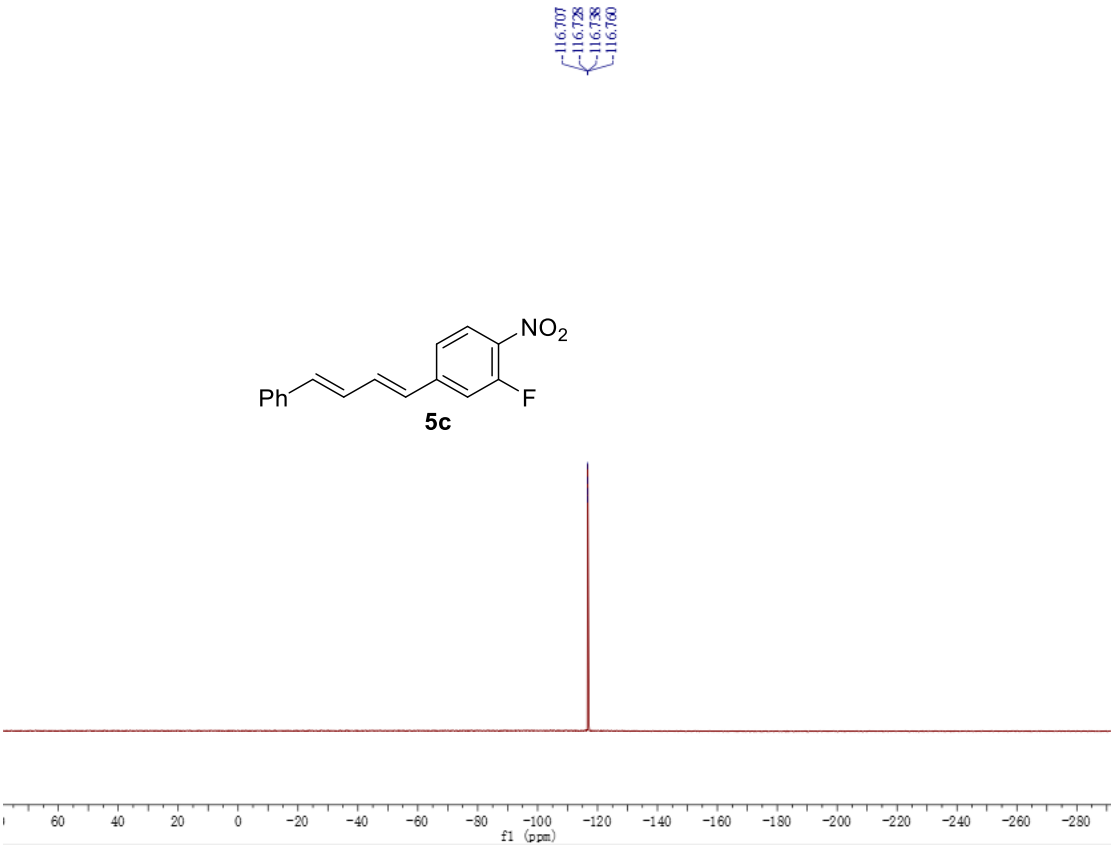
5c

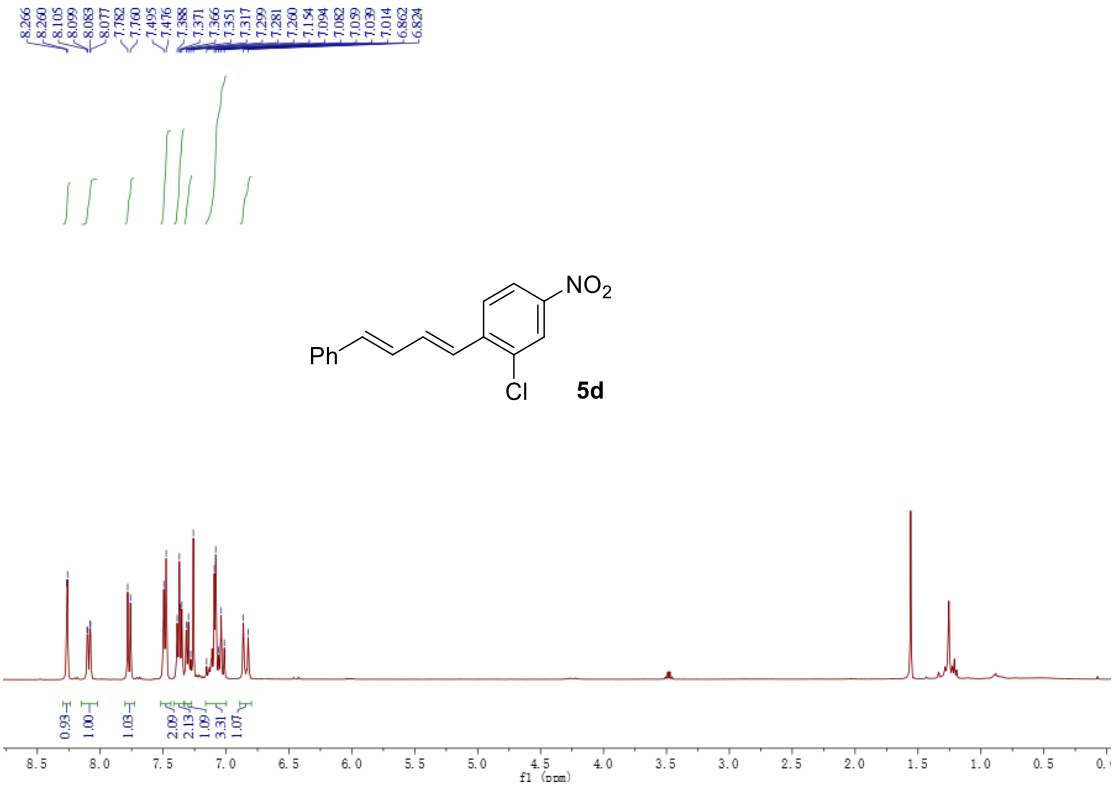

1.01
2.16
2.24
3.21
1.16
1.15
1.03
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
157.434
154.805
145.712
145.627
137.056
136.438
134.938
128.849
128.813
128.592
127.760
126.834
126.690
126.666
121.937
121.902
115.056
114.841
77.318
77.001
76.683

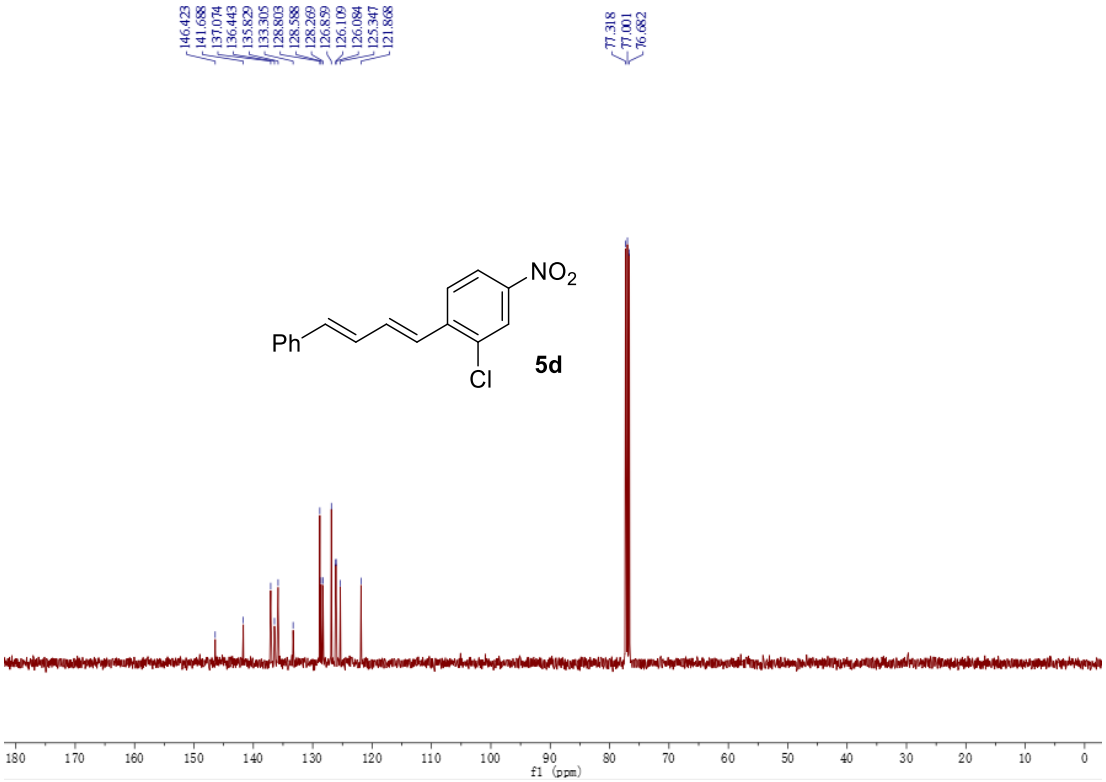

NO2
Ph
F

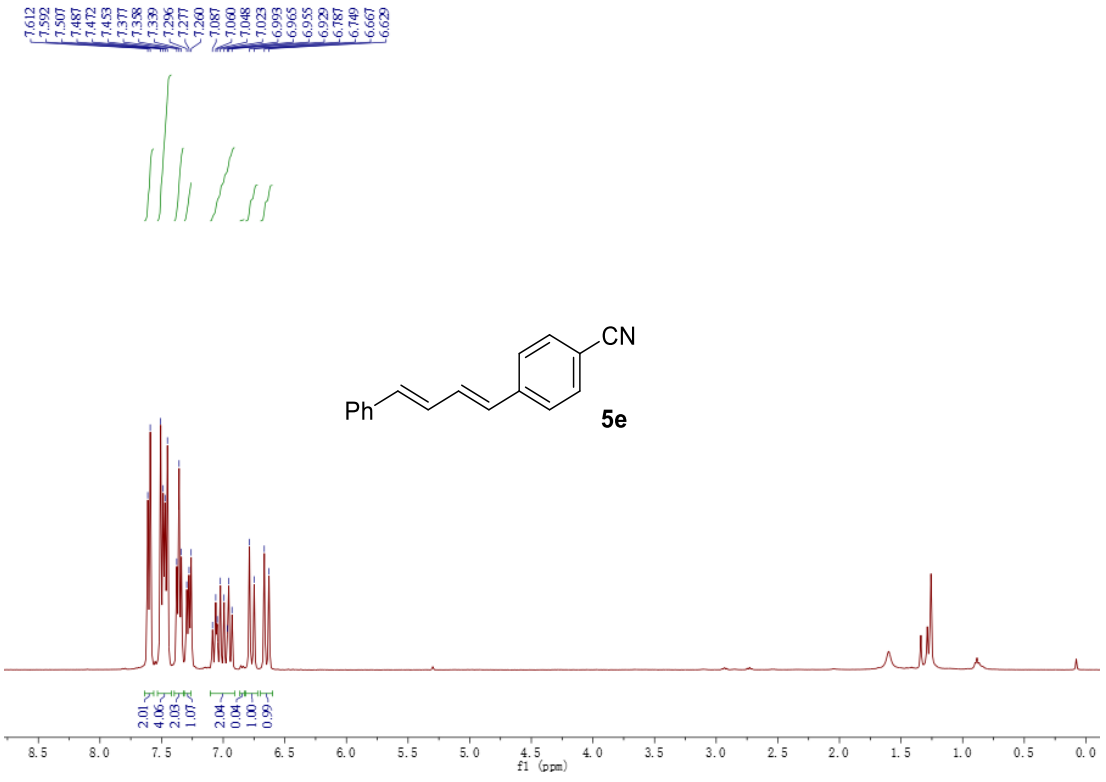
5c

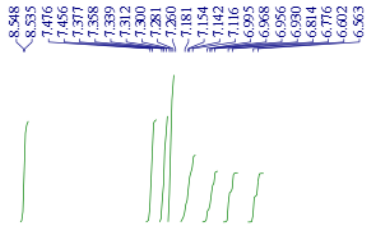
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

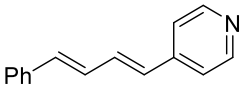

116.707
116.728
116.738
116.760
NO2
Ph
F
5c
f1 (ppm)


8.266
8.260
8.105
8.099
8.083
8.077
7.782
7.760
7.495
7.476
7.388
7.371
7.366
7.351
7.317
7.299
7.281
7.260
7.154
7.094
7.082
7.059
7.039
7.014
6.862
6.824
NO2
Ph
Cl
5d
0.93
1.00
1.03
2.09
2.13
1.09
3.31
1.07
f1 (ppm)

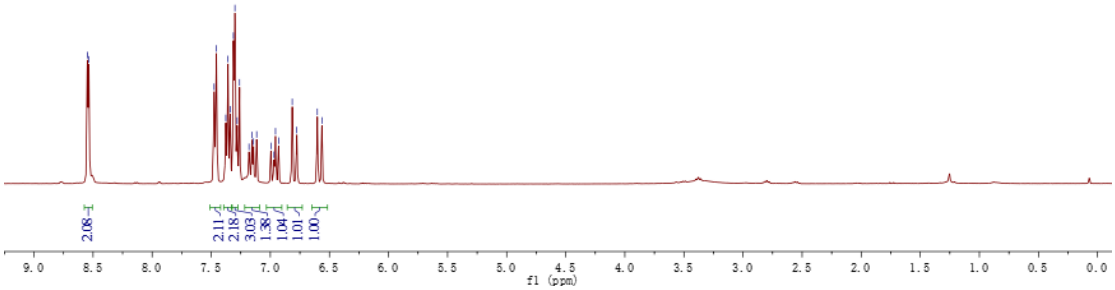

146.423
141.688
137.074
136.443
135.829
133.305
128.803
128.588
128.269
126.859
126.109
126.084
125.347
121.868
77.318
77.001
76.682
NO2
Ph
Cl
5d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

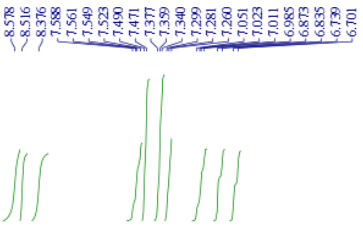

7.612
7.592
7.507
7.487
7.472
7.453
7.377
7.358
7.339
7.296
7.277
7.260
7.087
7.060
7.048
7.023
6.993
6.965
6.955
6.929
6.787
6.749
6.667
6.629
CN
Ph
5e
2.01
4.06
2.03
1.07
2.04
0.04
1.00
0.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

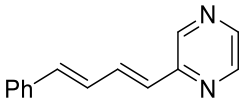

8.548
8.535
7.476
7.456
7.377
7.358
7.339
7.312
7.300
7.281
7.260
7.181
7.154
7.142
7.116
6.995
6.968
6.956
6.930
6.814
6.776
6.602
6.563


Ph
N

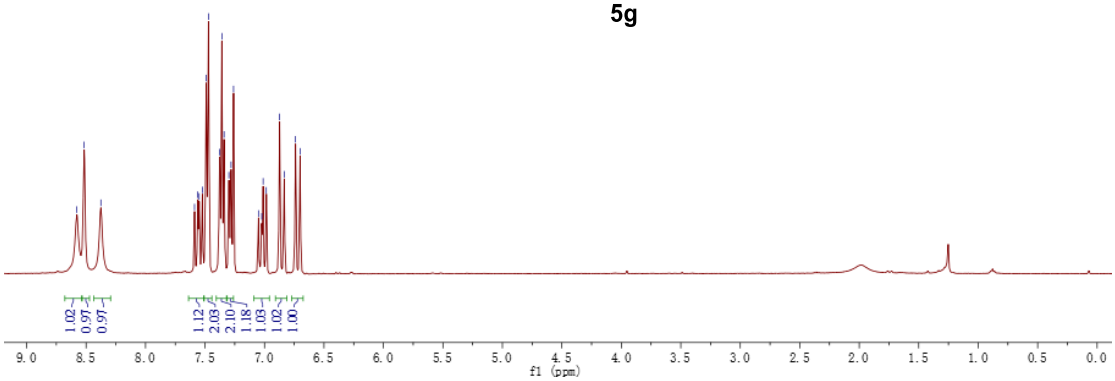
5f

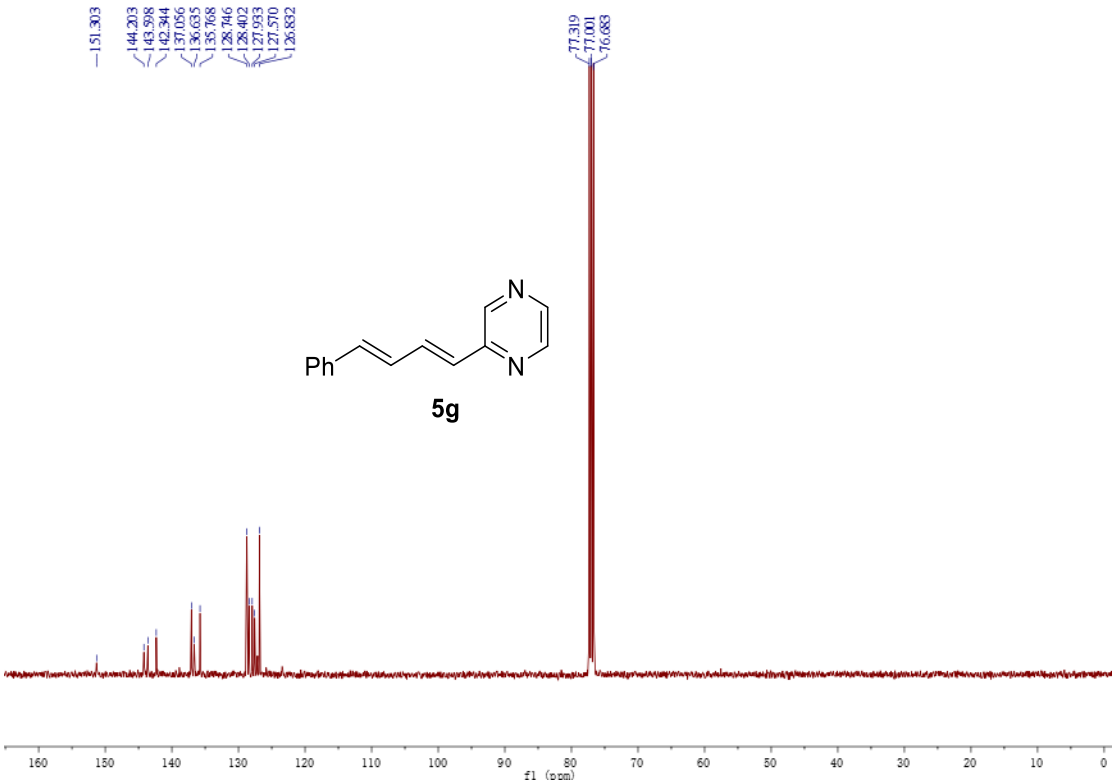

2.08
2.11
2.18
3.03
1.38
1.04
1.01
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

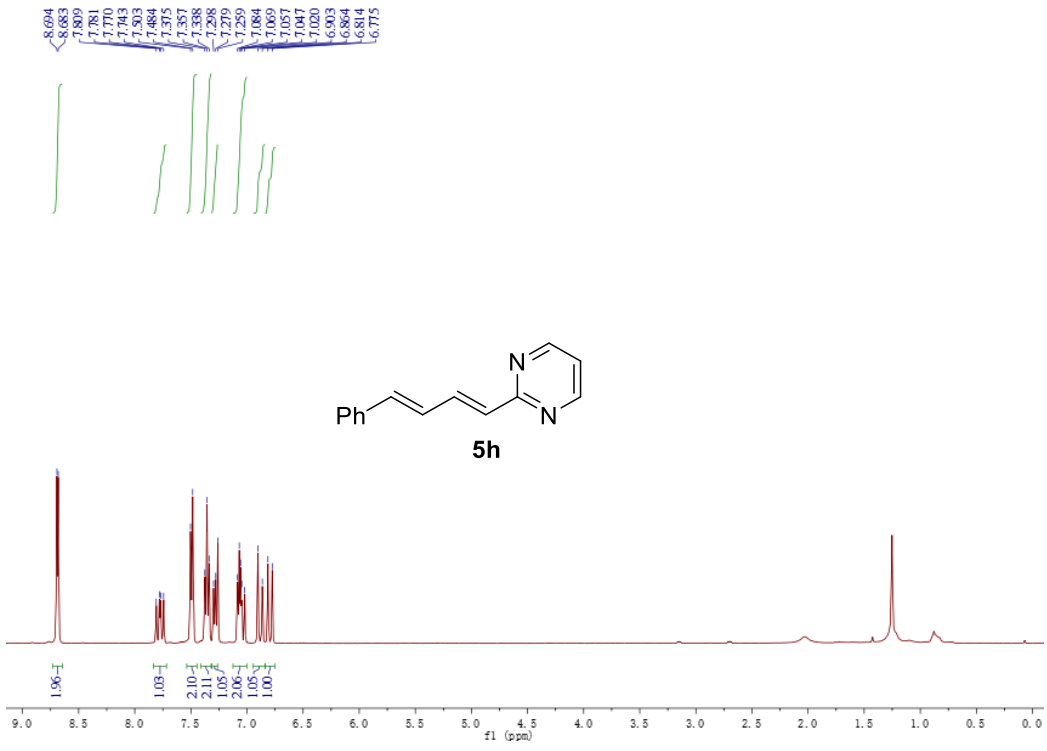

8.578
8.516
8.376
7.588
7.561
7.549
7.523
7.490
7.471
7.377
7.339
7.340
7.299
7.281
7.260
7.051
7.023
7.011
6.985
6.873
6.835
6.739
6.701

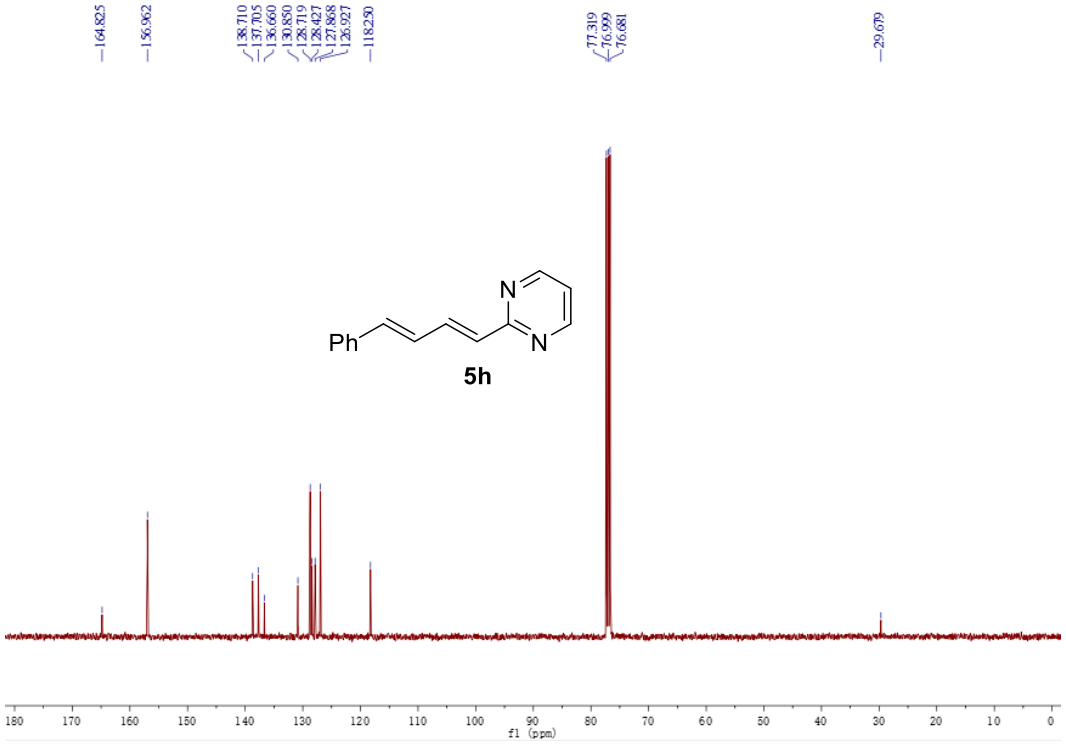

Ph
N
N

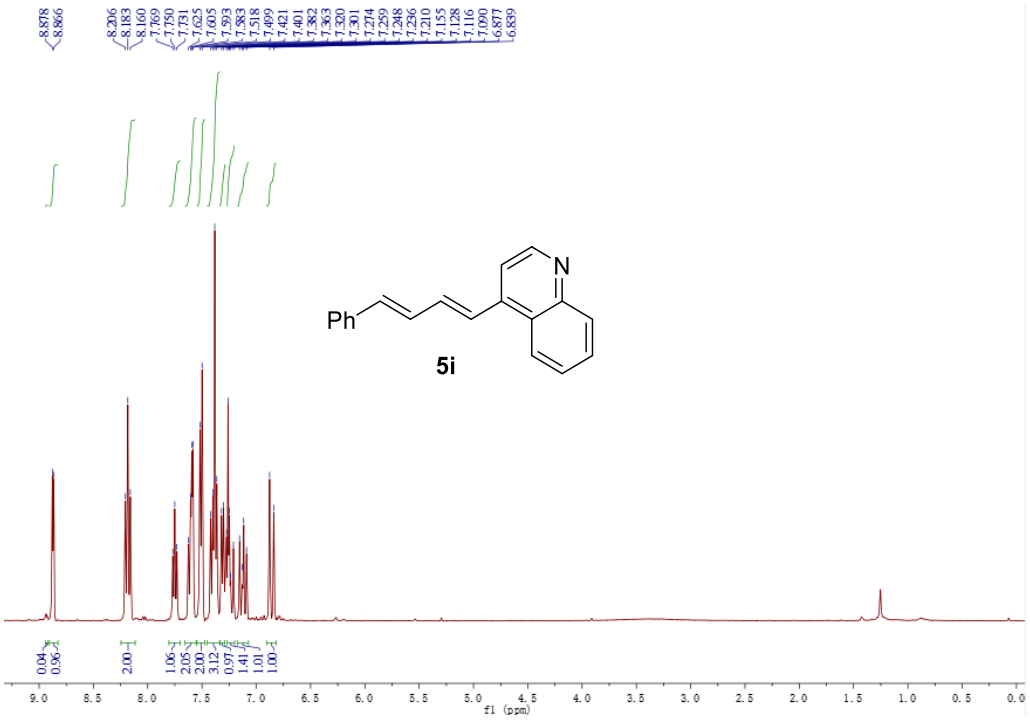
5g

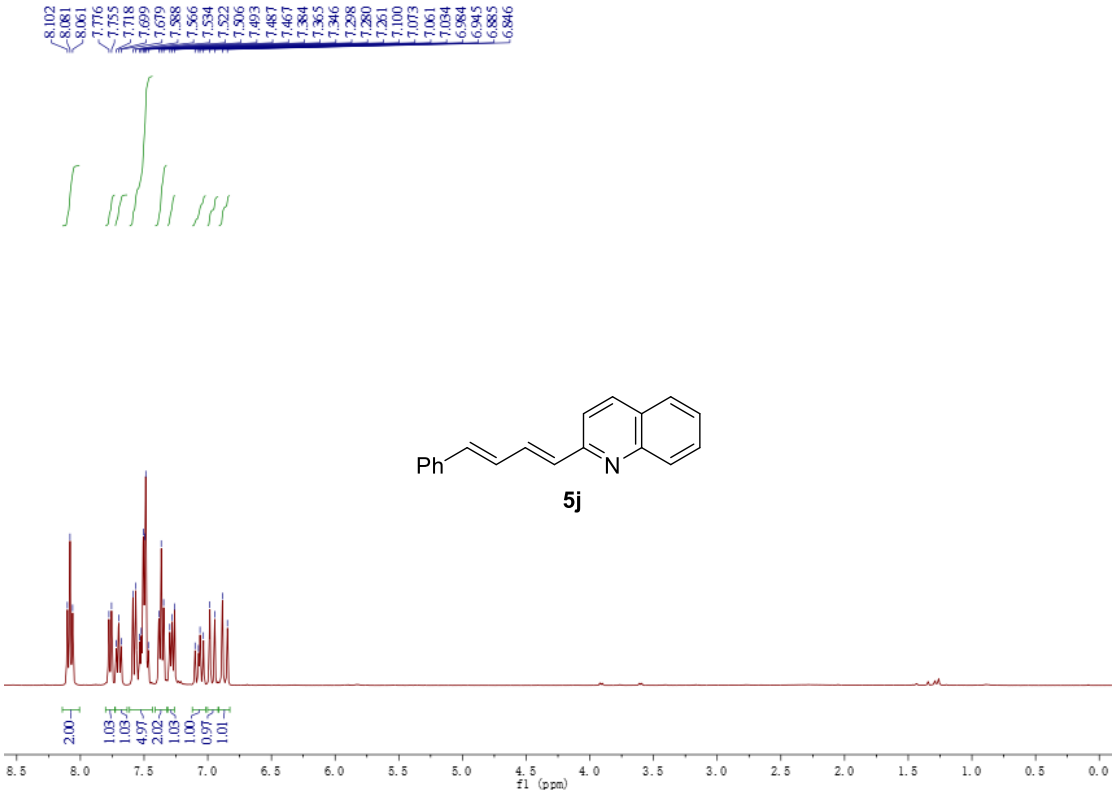

1.02
0.97
0.97
1.12
2.03
2.10
1.18
1.03
1.02
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.303
144.203
143.598
142.344
137.056
136.635
135.768
128.746
128.402
127.933
127.570
126.832
77.319
77.001
76.683
N
N
Ph
5g
f1 (ppm)


8.694
8.683
7.809
7.781
7.770
7.743
7.503
7.484
7.375
7.357
7.338
7.298
7.279
7.259
7.084
7.069
7.057
7.047
7.020
6.903
6.864
6.814
6.775
N
N
Ph
5h
1.96
1.03
2.10
2.11
1.05
2.06
1.05
1.00
f1 (ppm)

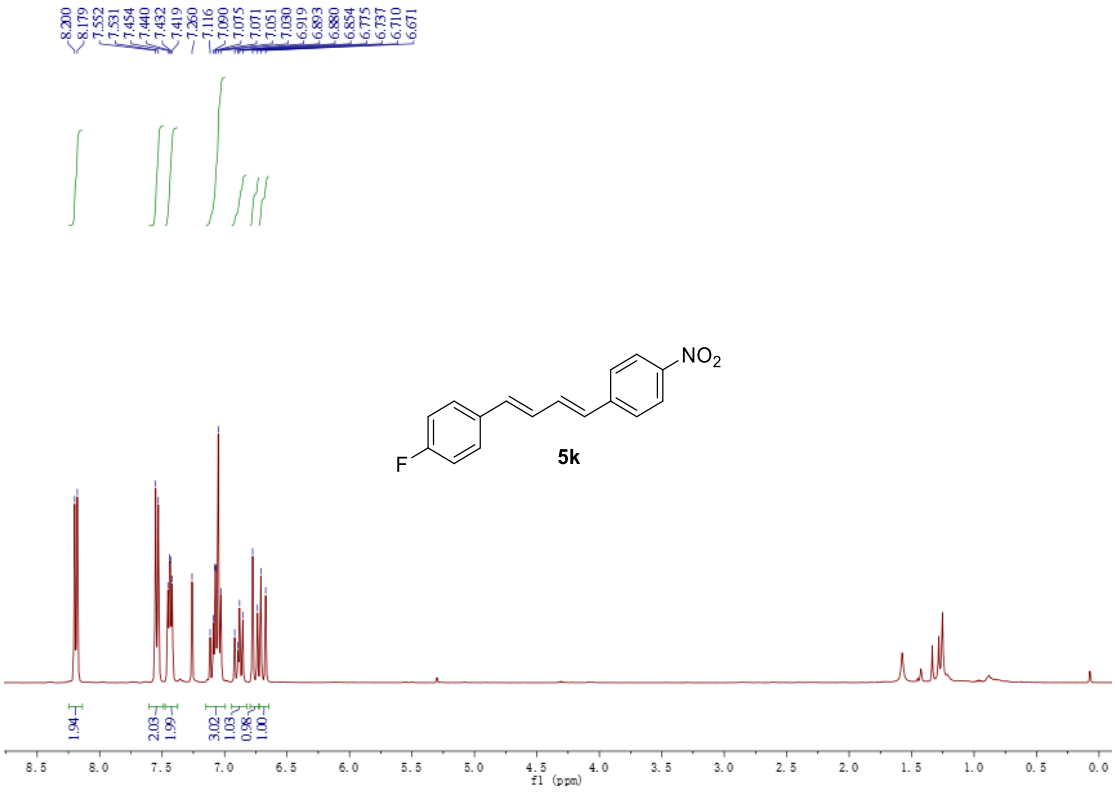

164.825
156.962
138.710
137.705
136.660
130.850
128.719
128.427
127.868
126.927
118.250
77.319
76.999
76.681
29.679
N
N
Ph
5h
f1 (ppm)


8.878
8.866
8.206
8.183
8.160
7.769
7.750
7.731
7.625
7.605
7.593
7.583
7.518
7.499
7.421
7.401
7.382
7.363
7.320
7.301
7.274
7.259
7.248
7.236
7.210
7.155
7.128
7.116
7.090
6.877
6.839
N
Ph
5i
0.04
0.96
2.00
1.06
2.05
2.00
3.12
0.97
1.41
1.01
1.00
f1 (ppm)


8.102
8.081
8.061
7.776
7.755
7.718
7.699
7.679
7.588
7.566
7.534
7.522
7.506
7.493
7.487
7.467
7.384
7.365
7.346
7.298
7.280
7.261
7.100
7.073
7.061
7.034
6.984
6.945
6.885
6.846
2.00
1.03
1.03
4.97
2.02
1.03
1.00
0.97
1.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

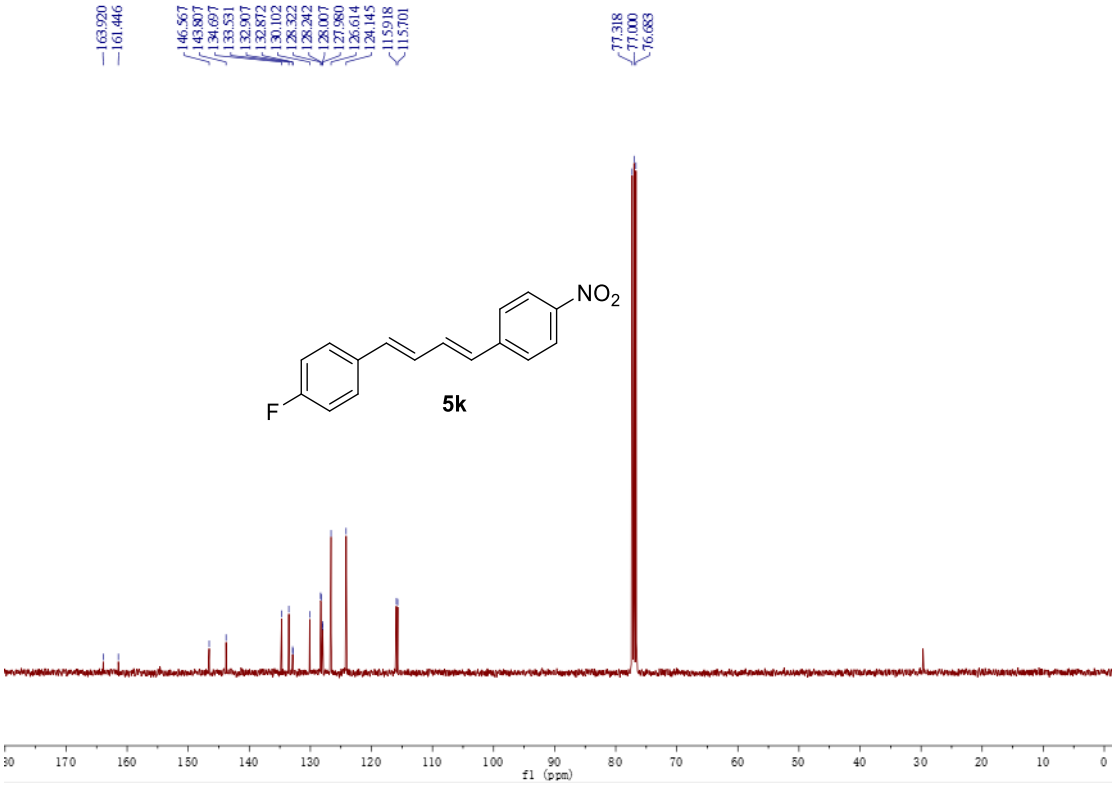
Ph
N

5j

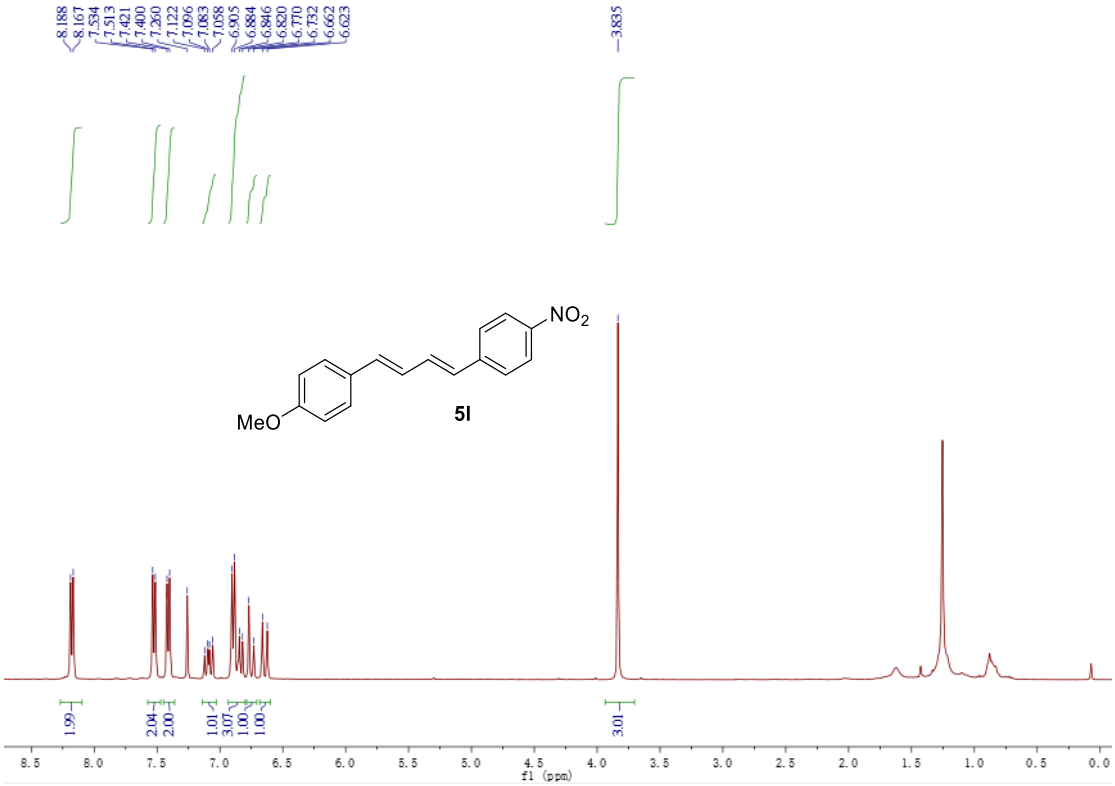

8.200
8.179
7.552
7.531
7.454
7.440
7.432
7.419
7.260
7.116
7.090
7.075
7.071
7.051
7.030
6.919
6.893
6.880
6.854
6.775
6.737
6.710
6.671
1.94
2.03
1.99
3.02
1.03
0.98
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

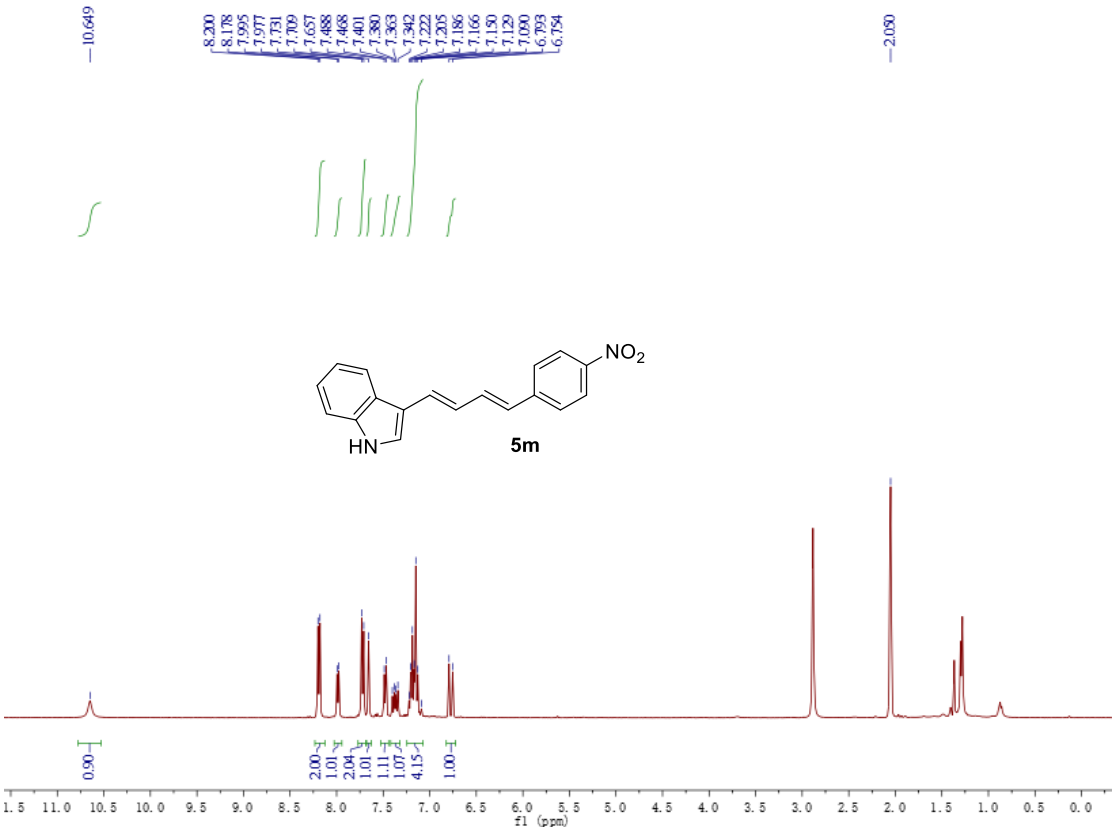
NO2
F

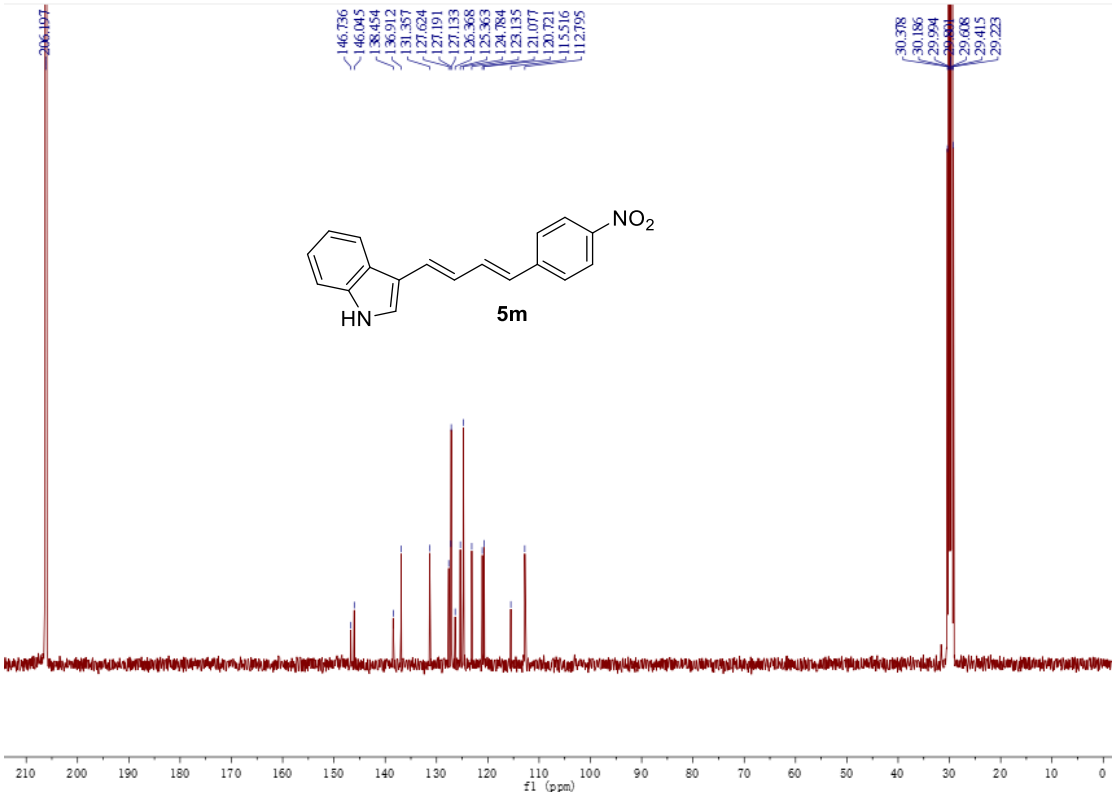
5k

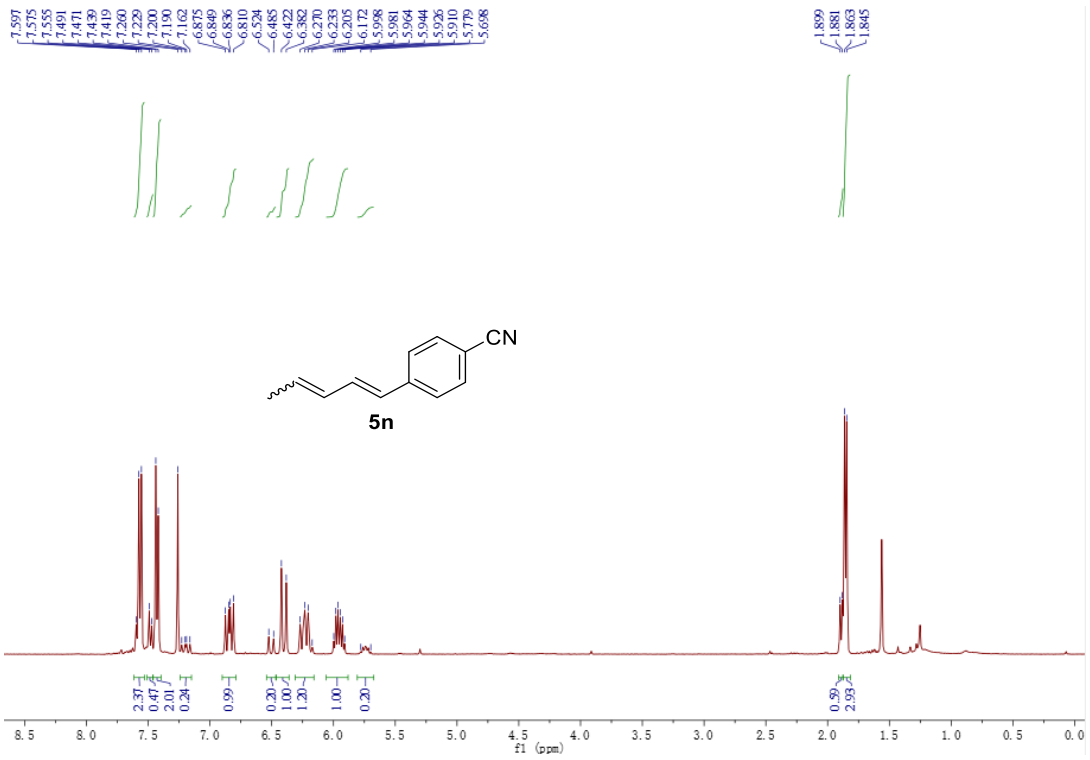

163.920
161.446
146.567
143.807
134.697
133.531
132.907
132.872
130.102
128.322
128.242
128.007
127.980
126.614
124.145
115.918
115.701
77.318
77.000
76.683
NO2
F
5k
f1 (ppm)

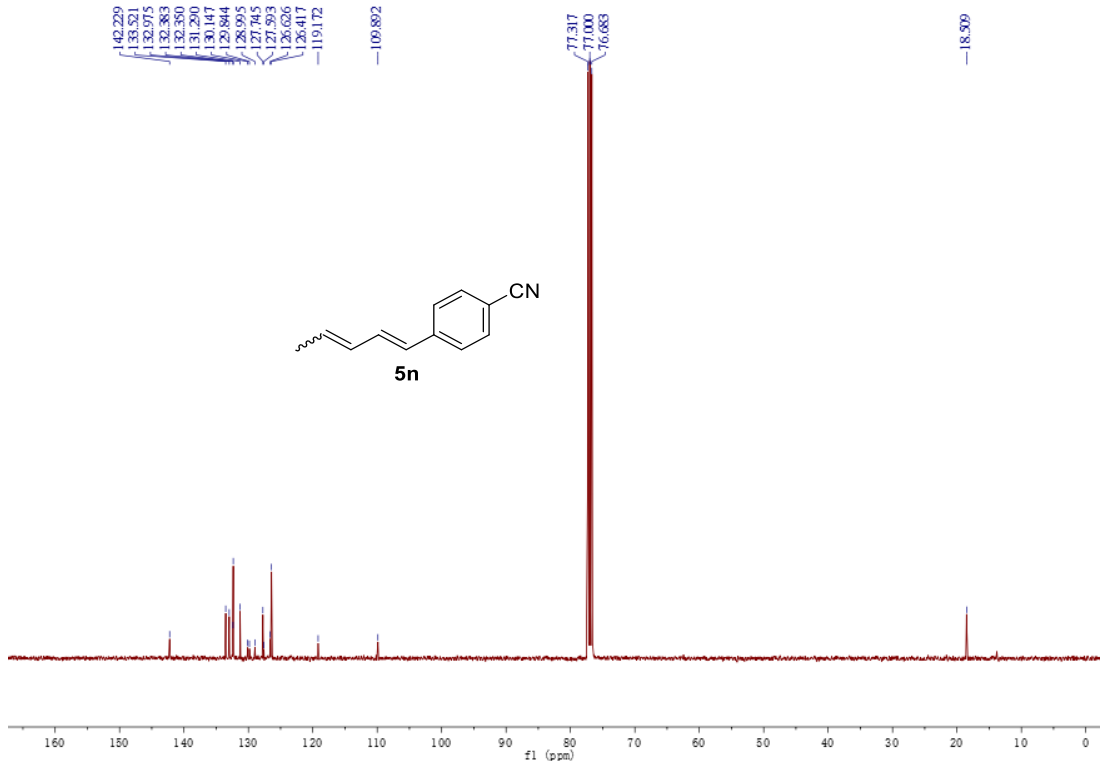

-112.551
-112.566
-112.574
-112.588
-112.601
-112.610
-112.625
NO2
F
5k
f1 (ppm)

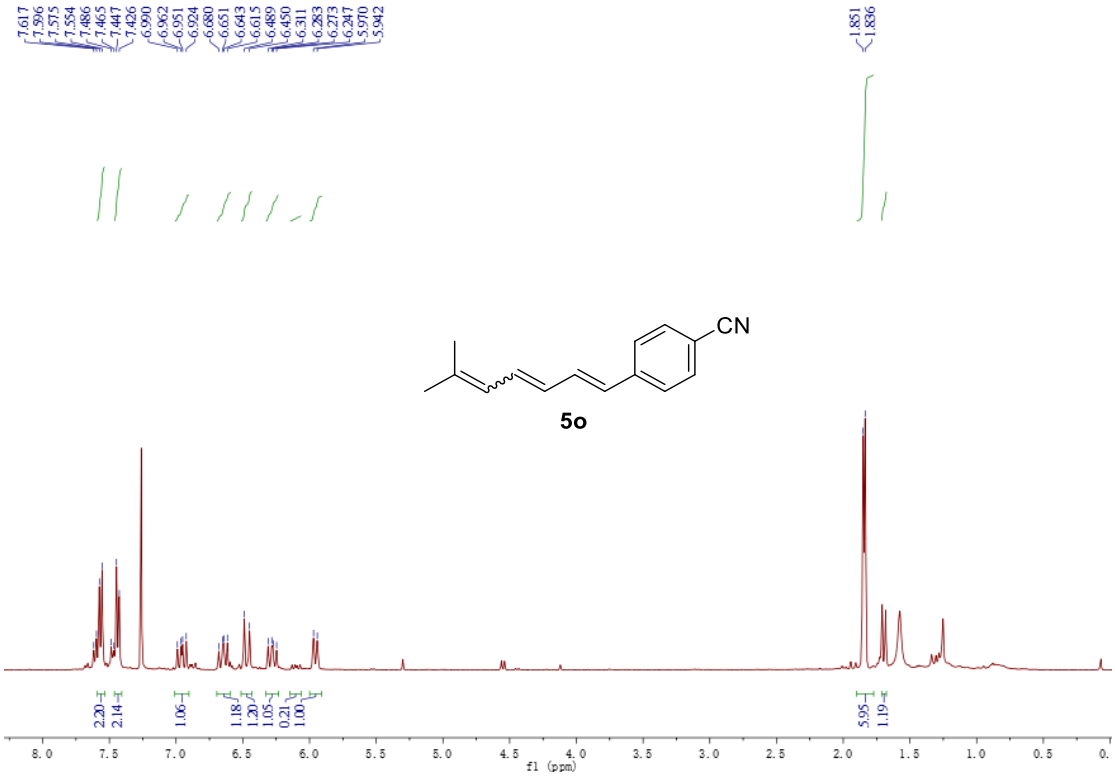

8.188
8.167
7.534
7.513
7.421
7.400
7.260
7.122
7.096
7.083
7.058
6.905
6.884
6.846
6.820
6.770
6.732
6.662
6.623
3.835
NO2
MeO
5l
1.99
2.04
2.00
1.01
3.07
1.00
1.00
3.01
f1 (ppm)


10.649
8.200
8.178
7.995
7.977
7.731
7.709
7.657
7.488
7.468
7.401
7.380
7.363
7.342
7.222
7.205
7.186
7.166
7.150
7.129
7.090
6.793
6.754
2.050
NO2
HN
5m
0.90
2.00
1.01
2.04
1.01
1.11
1.07
4.15
1.00
f1 (ppm)


206.197
146.736
146.045
138.454
136.912
131.357
127.624
127.191
127.133
126.368
125.363
124.784
123.135
121.077
120.721
115.516
112.795
30.378
30.186
29.994
29.801
29.608
29.415
29.223
NO2
HN
5m
f1 (ppm)


7.597
7.575
7.555
7.491
7.471
7.439
7.419
7.260
7.229
7.200
7.190
7.162
6.875
6.849
6.836
6.810
6.524
6.485
6.422
6.382
6.270
6.233
6.205
6.172
5.998
5.981
5.964
5.944
5.926
5.910
5.779
5.698
1.899
1.881
1.863
1.845
CN
5n
2.37
0.47
2.01
0.24
0.99
0.20
1.00
1.20
1.00
0.20
0.59
2.93
f1 (ppm)


142.229
133.521
132.975
132.383
132.350
131.290
130.147
129.844
128.995
127.745
127.593
126.626
126.417
119.172
109.892
77.317
77.000
76.683
18.909
CN
5n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.575
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7.426
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6.962
6.951
6.924
6.680
6.651
6.643
6.615
6.489
6.450
6.311
6.283
6.273
6.247
5.970
5.942
1.851
1.836
CN
5o
2.20
2.14
1.06
1.18
1.20
1.05
0.21
1.00
5.95
1.19
8.0
7.5
7.0
6.5
6.0
5.5
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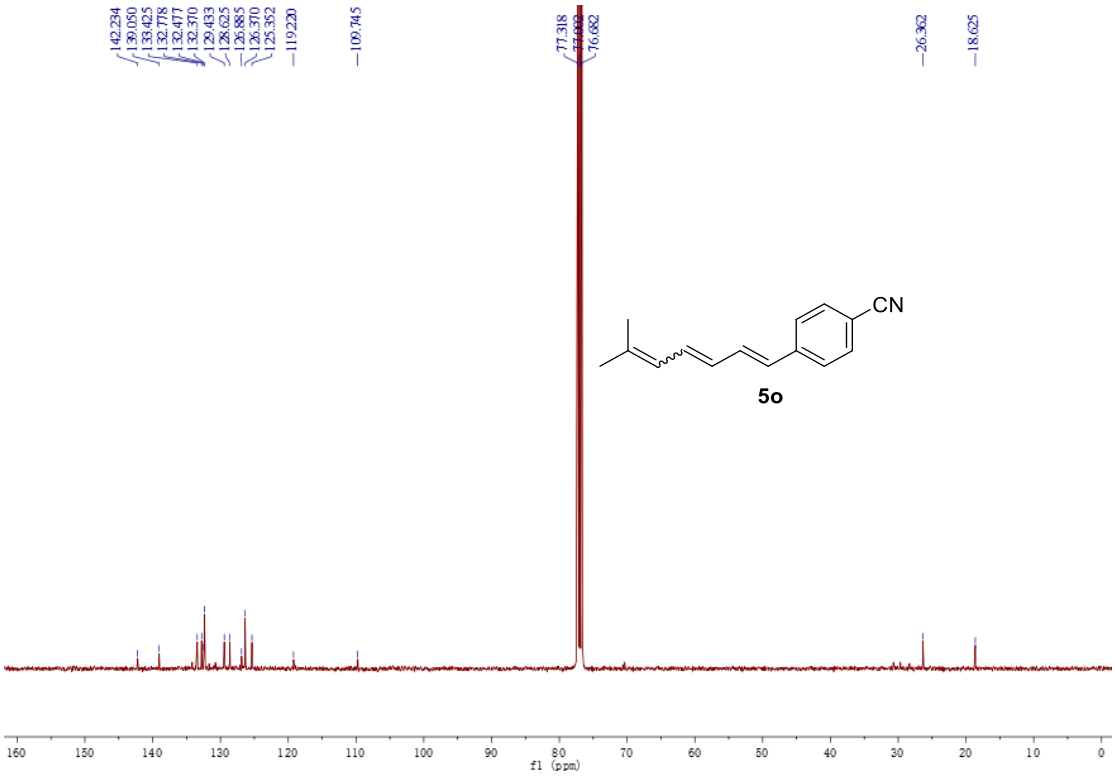
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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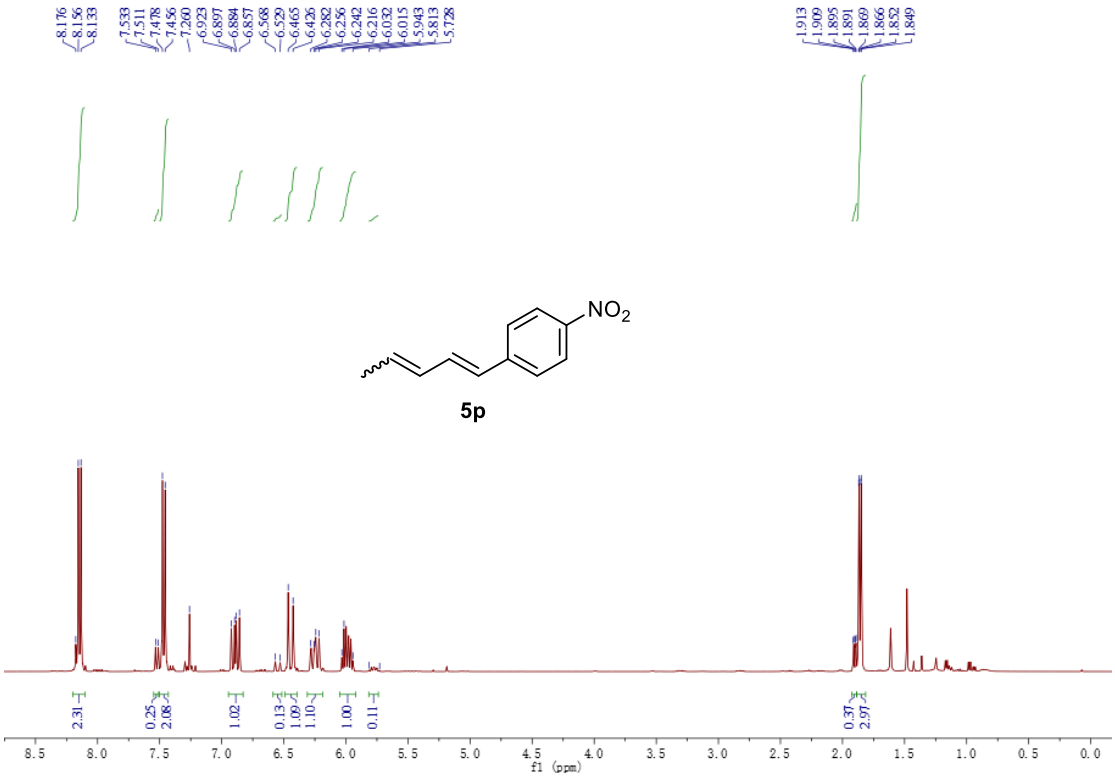
139.050
133.425
132.778
132.477
132.370
129.433
128.625
126.885
126.370
125.352
119.220
109.745
77.318
77.068
76.682
26.362
18.625
CN
5o
f1 (ppm)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8.133
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7.511
7.478
7.456
7.260
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6.897
6.884
6.857
6.568
6.529
6.465
6.426
6.282
6.256
6.242
6.216
6.032
6.015
5.943
5.813
5.728
1.913
1.909
1.895
1.891
1.869
1.866
1.852
1.849
NO2
5p
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1.02
0.13
1.09
1.10
1.00
0.11
0.37
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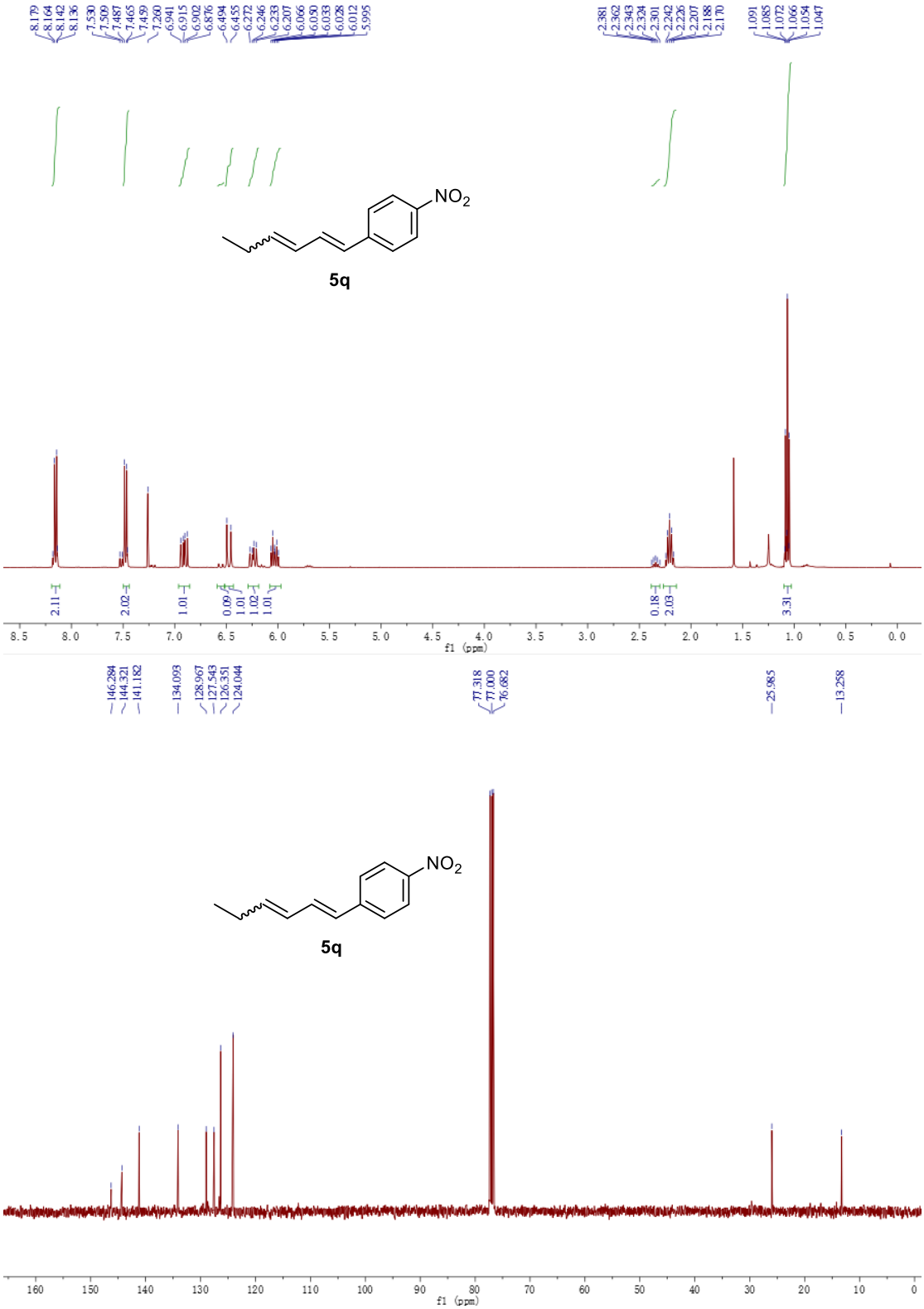
f1 (ppm)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8.142
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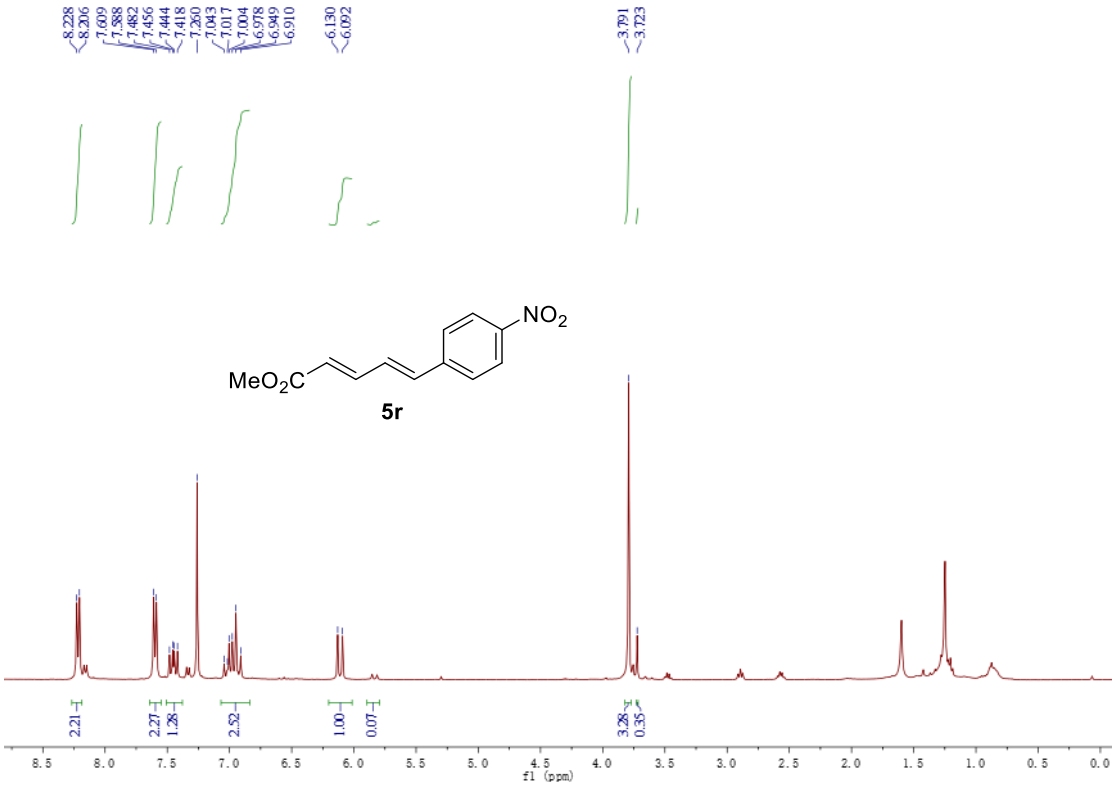
7.509
7.487
7.465
7.459
7.260
6.941
6.915
6.902
6.876
6.494
6.455
6.272
6.246
6.233
6.207
6.066
6.050
6.033
6.028
6.012
5.995
2.381
2.362
2.343
2.324
2.301
2.242
2.226
2.207
2.188
2.170
1.091
1.085
1.072
1.066
1.054
1.047
NO2
5q
2.11
2.02
1.01
0.09
1.01
1.02
1.01
0.18
2.03
3.31
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
146.284
144.321
141.182
134.093
128.967
127.543
126.351
124.044
77.318
77.000
76.682
25.985
13.258
NO2
5q
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.609
7.588
7.482
7.456
7.444
7.418
7.260
7.043
7.017
7.004
6.978
6.949
6.910
6.130
6.092
3.791
3.723
NO2
MeO2C
5r
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2.27
1.28
2.52
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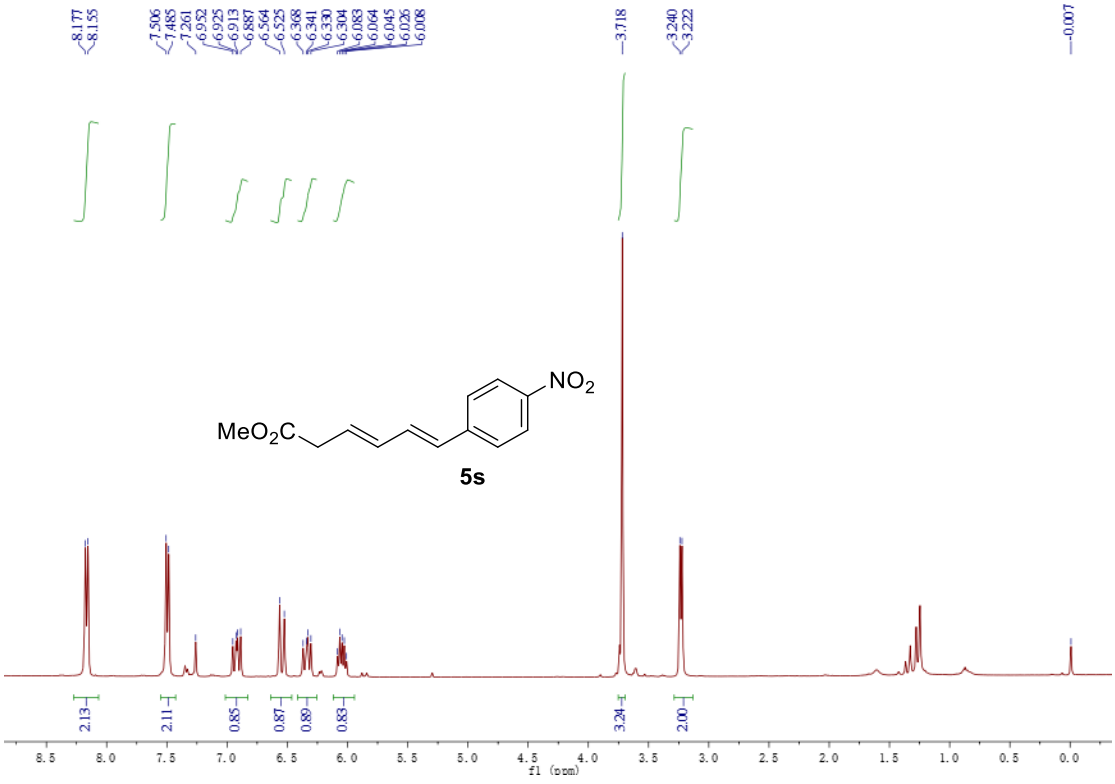
0.07
3.28
0.35
f1 (ppm)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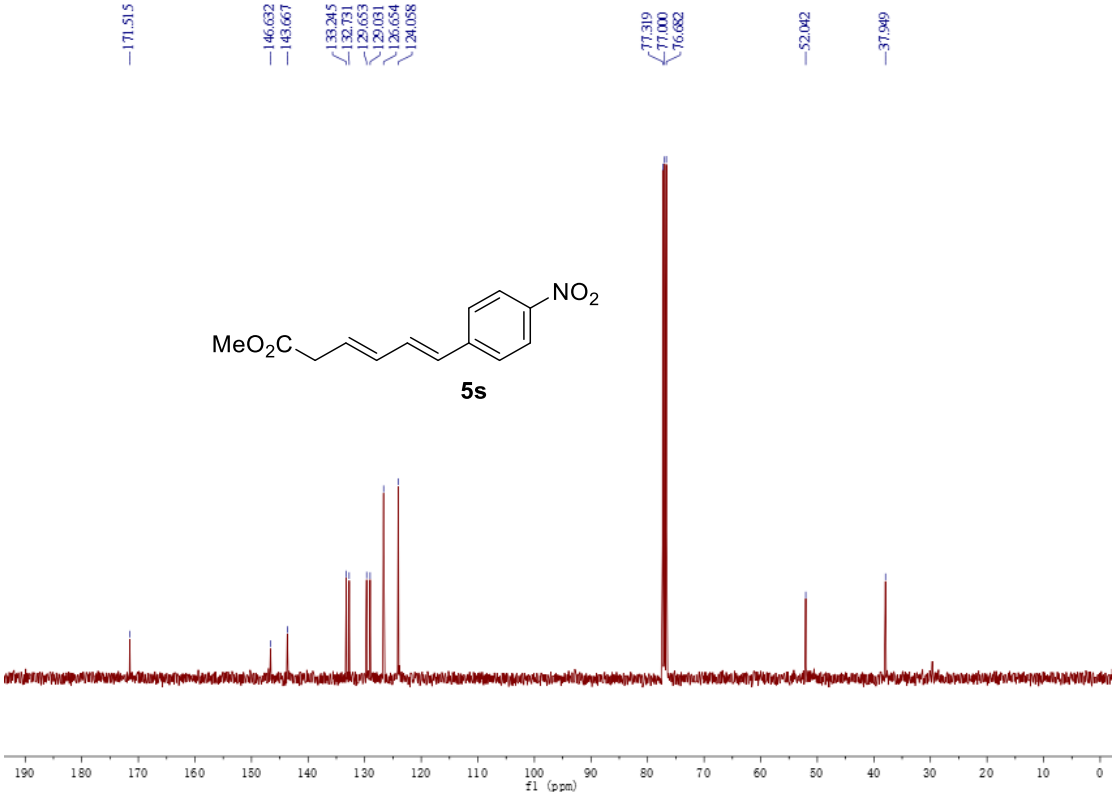
8.155
7.506
7.485
7.261
6.952
6.925
6.913
6.887
6.564
6.525
6.368
6.341
6.330
6.304
6.083
6.064
6.045
6.026
6.008
3.718
3.240
3.222
0.007
NO2
MeO2C
5s
2.13
2.11
0.85
0.87
0.89
0.83
3.24
2.00
f1 (ppm)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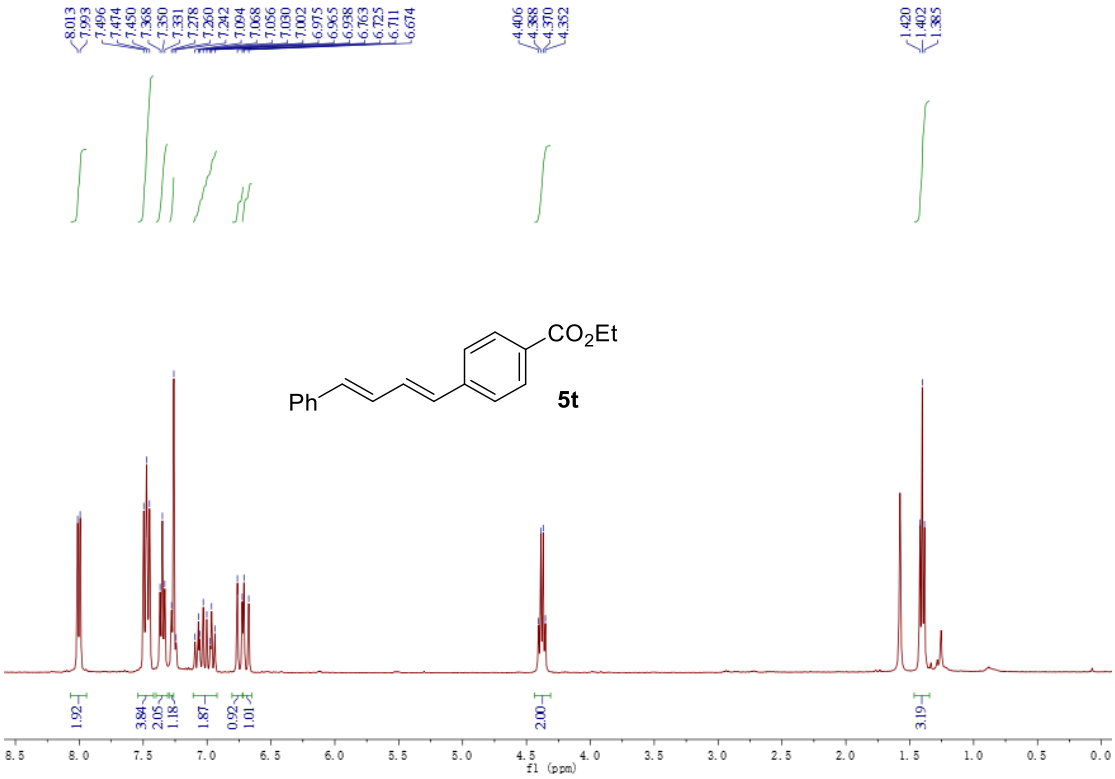
143.667
133.245
132.731
129.653
129.031
126.654
124.058
77.319
77.000
76.682
52.042
37.949
NO_2
MeO_2C
5s
f1 (ppm)


8.013
7.993
7.496
7.474
7.450
7.368
7.350
7.331
7.278
7.260
7.242
7.094
7.068
7.056
7.030
7.002
6.975
6.965
6.938
6.763
6.725
6.711
6.674
4.406
4.388
4.370
4.352
1.420
1.402
1.385
CO_2Et
Ph
5t
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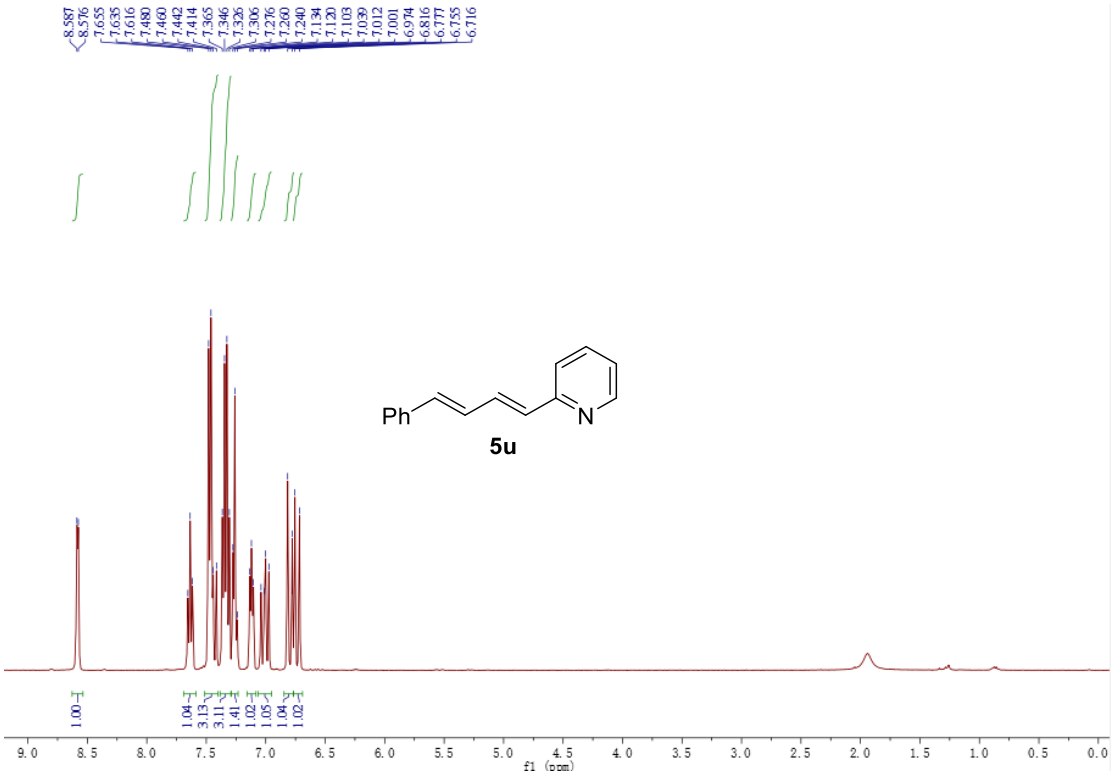
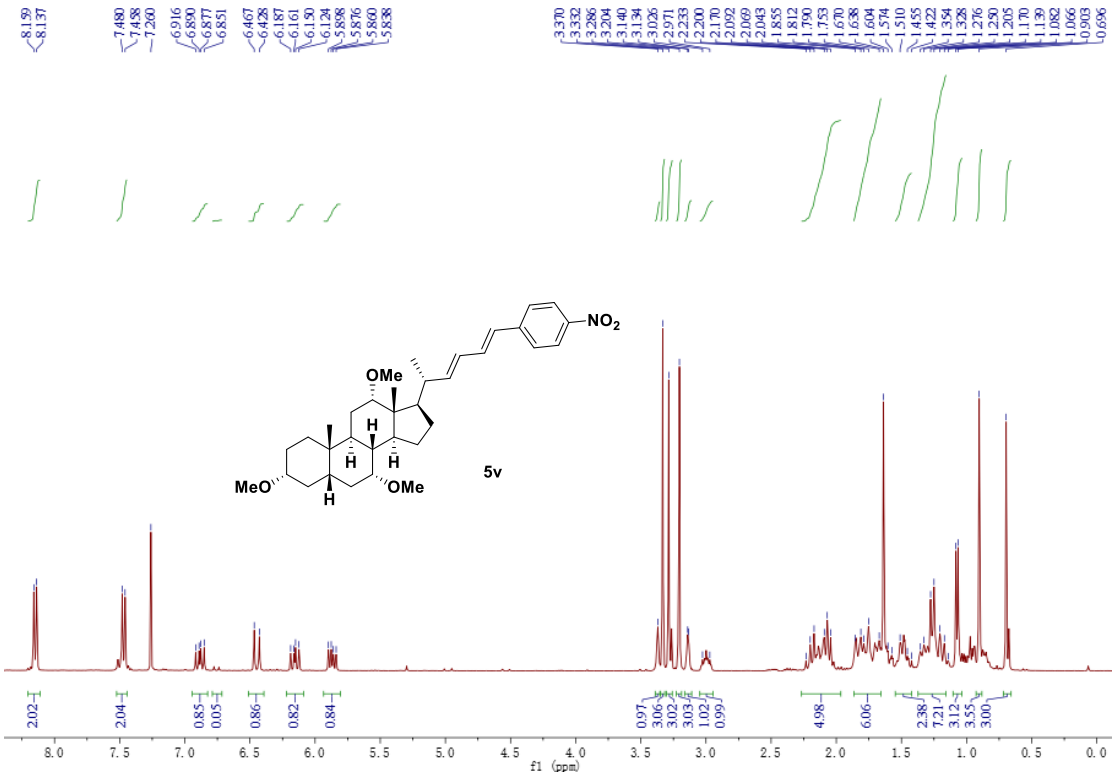
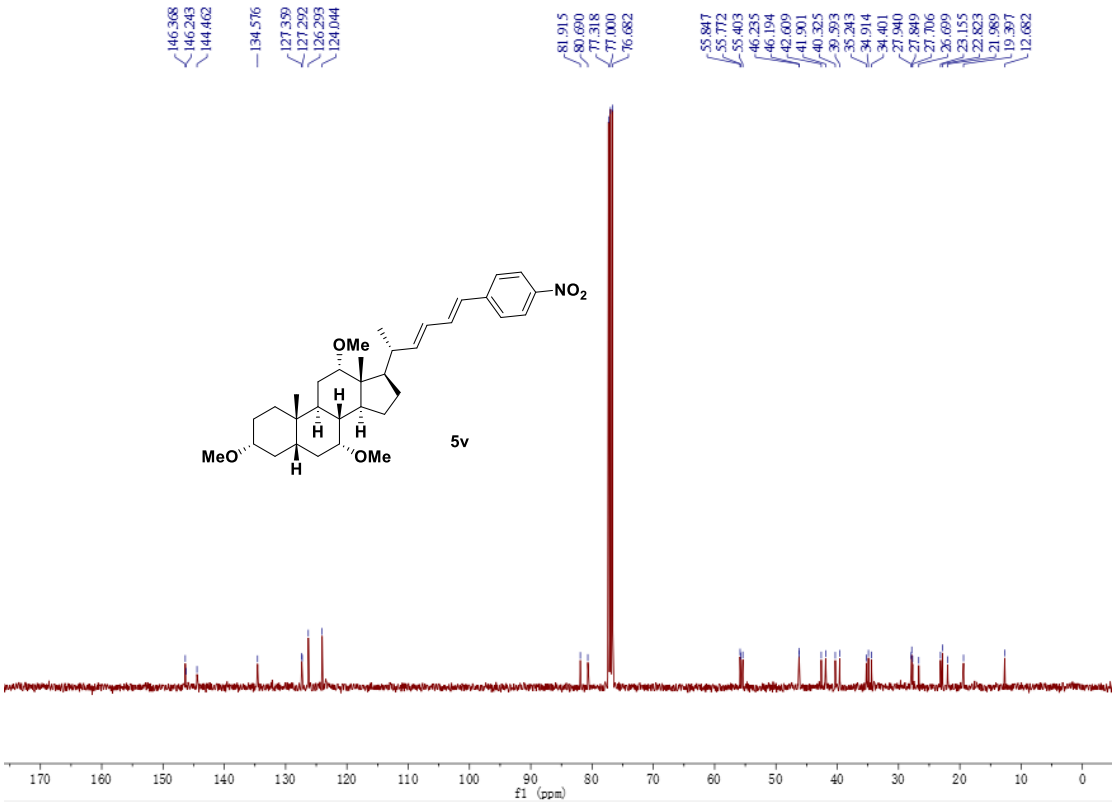
3.84
2.05
1.18
1.87
0.92
1.01
2.00
3.19
f1 (ppm)


Ph
N
5u


NO2
OMe
MeO
OMe
5v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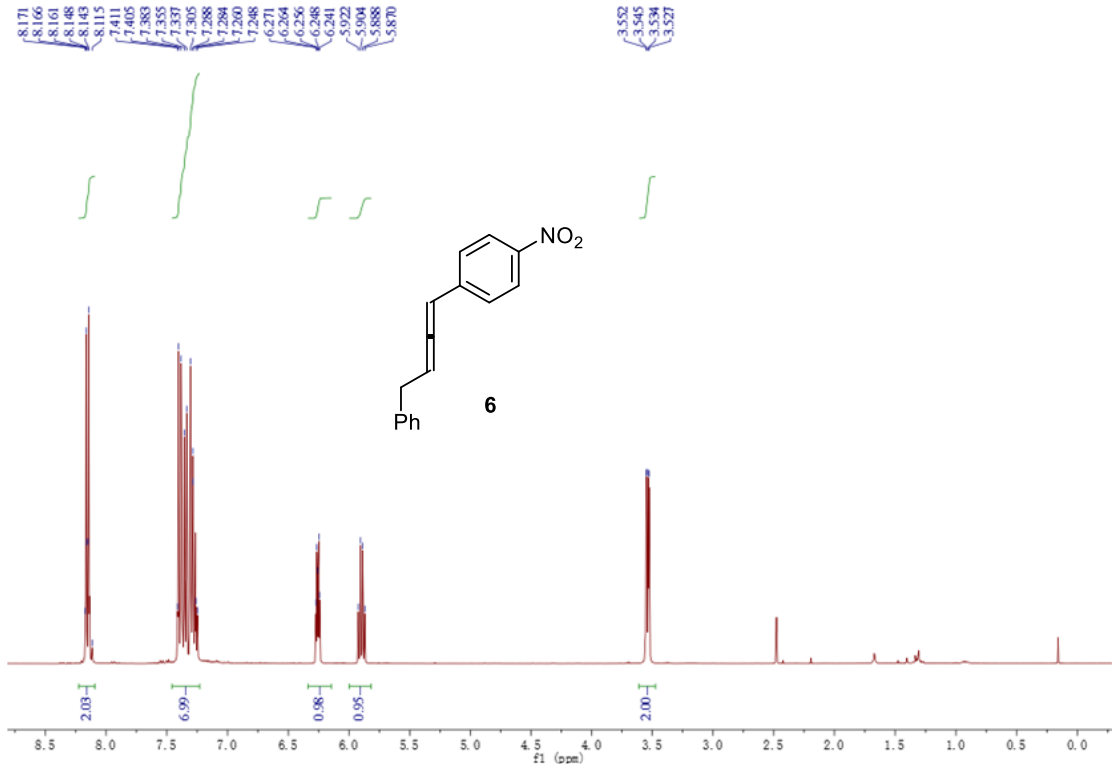
134.576
127.359
127.292
126.293
124.044
81.915
80.690
77.318
77.000
76.682
55.847
55.772
55.403
46.235
46.194
42.609
41.501
40.325
39.593
35.243
34.914
34.401
27.940
27.849
27.706
26.699
23.155
22.823
21.989
19.397
12.682
NO2
OMe
H
H
H
MeO
OMe
H
5v
f1 (ppm)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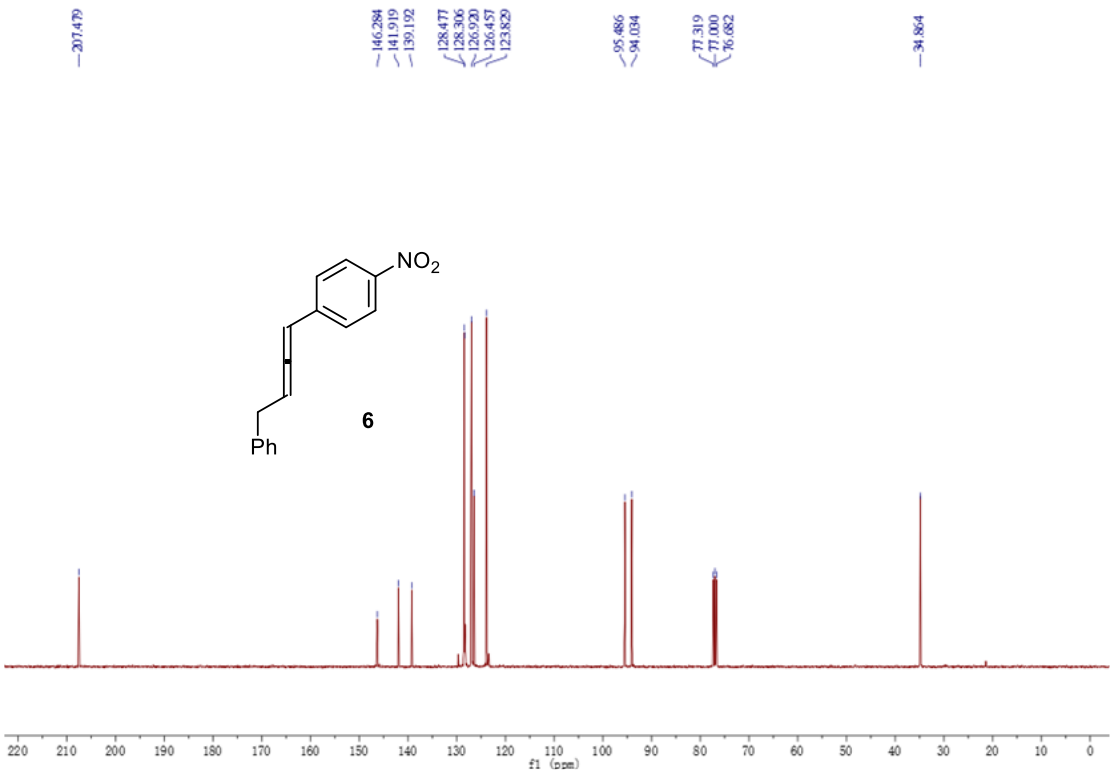
8.166
8.161
8.148
8.143
8.115
7.411
7.405
7.383
7.355
7.337
7.305
7.288
7.284
7.260
7.248
6.271
6.264
6.256
6.248
6.241
5.922
5.904
5.888
5.870
3.552
3.545
3.534
3.527
NO2
Ph
6
2.03
6.99
0.98
0.95
2.00
f1 (ppm)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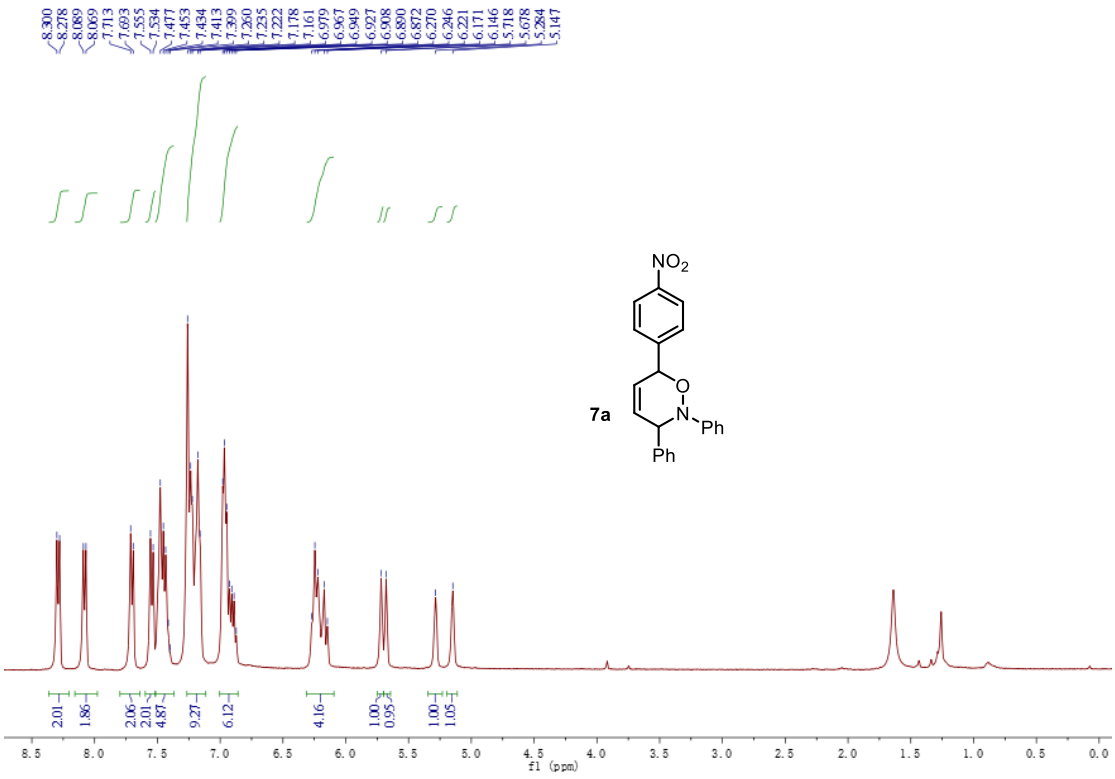
146.284
141.919
139.192
128.477
128.306
126.920
126.457
123.829
95.486
94.034
77.319
77.000
76.682
34.864
NO2
Ph
6
f1 (ppm)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8.278
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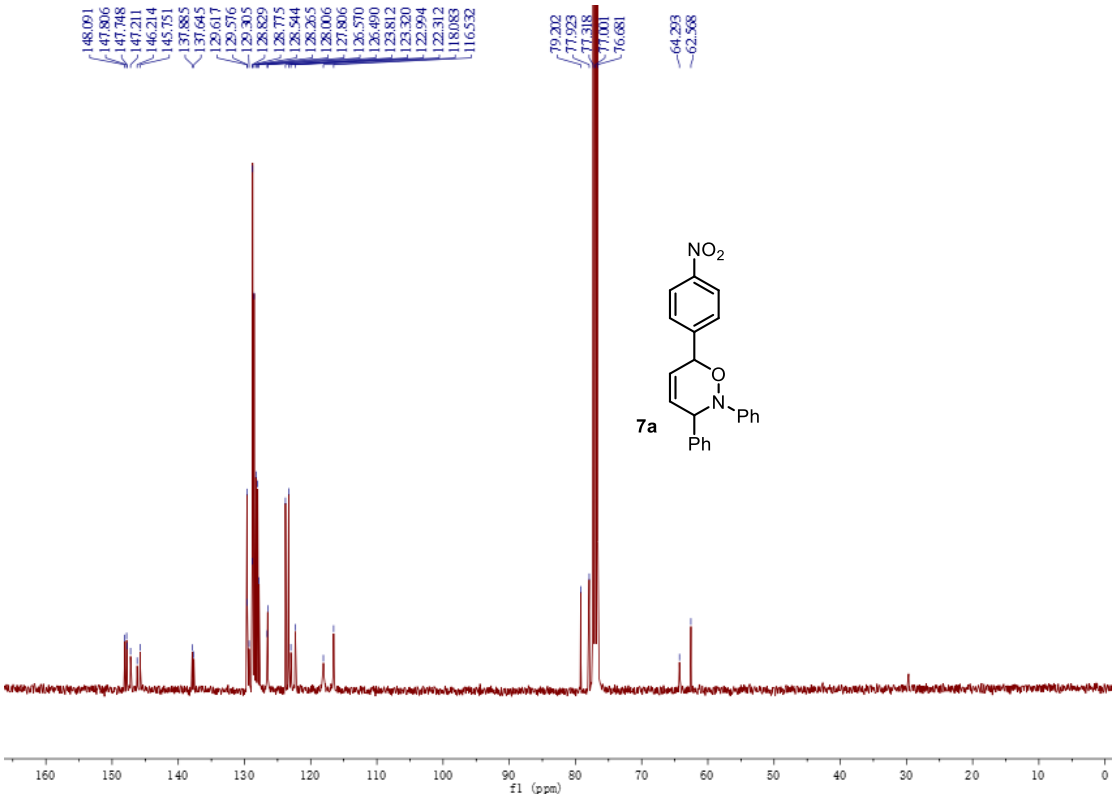
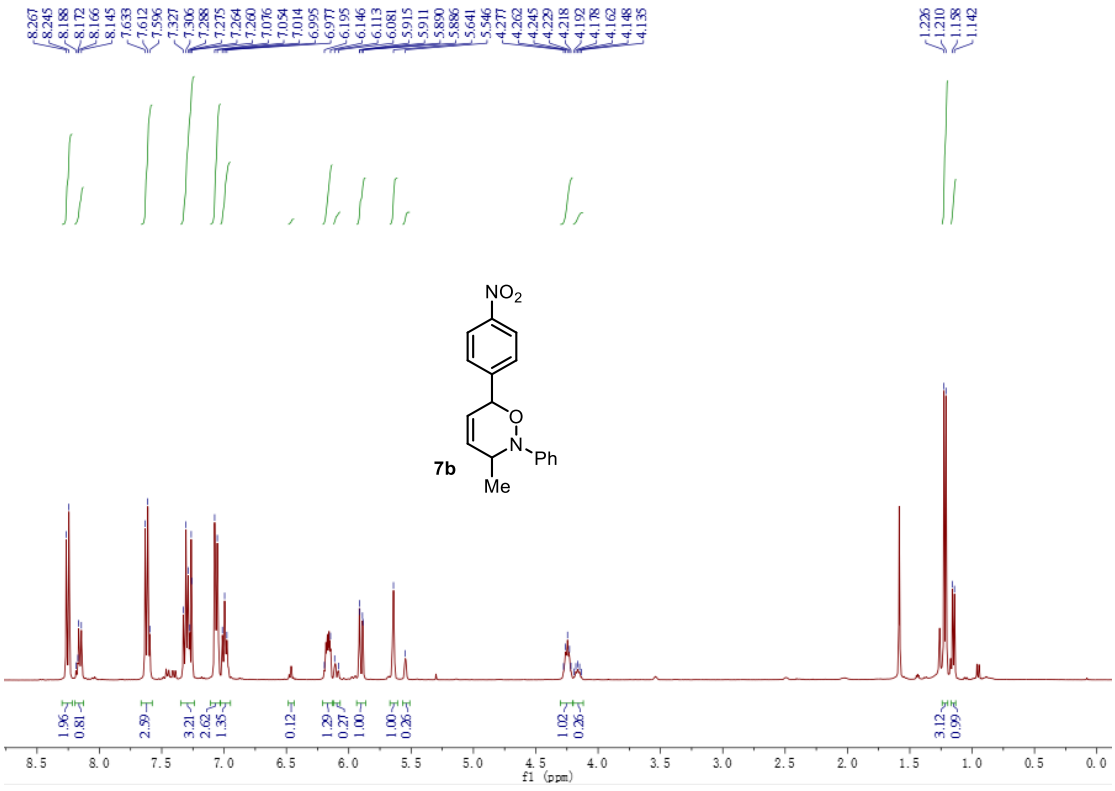
8.069
7.713
7.693
7.555
7.534
7.477
7.453
7.434
7.413
7.399
7.260
7.235
7.222
7.178
7.161
6.979
6.967
6.949
6.927
6.908
6.890
6.872
6.270
6.246
6.221
6.171
6.146
5.718
5.678
5.284
5.147
NO2
O
N
Ph
Ph
7a
2.01
1.86
2.06
2.01
4.87
9.27
6.12
4.16
1.00
0.95
1.00
1.05
f1 (ppm)


148.091
147.806
147.748
147.211
146.214
145.751
137.885
137.645
129.617
129.576
129.305
128.829
128.775
128.544
128.265
128.006
127.806
126.570
126.490
123.812
123.320
122.994
122.312
118.083
116.532
79.202
77.923
77.318
77.001
76.681
64.293
62.568
NO2
O
N
Ph
Ph
7a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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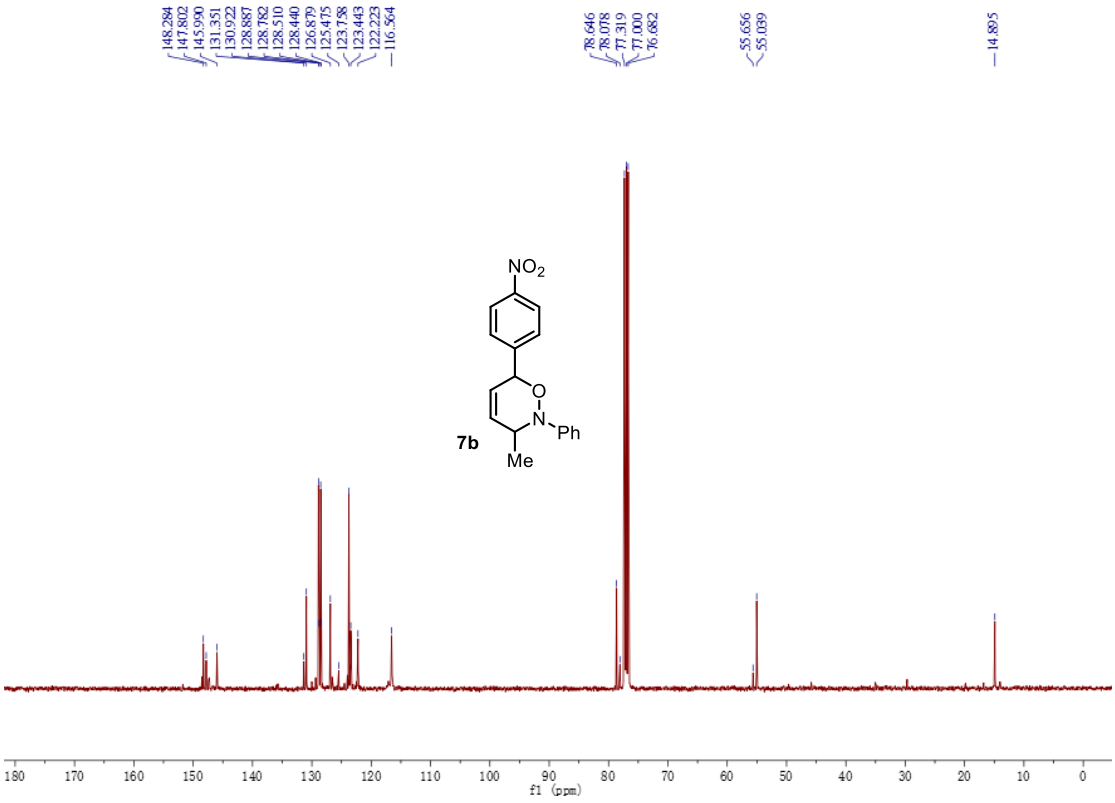
8.188
8.172
8.166
8.145
7.633
7.612
7.596
7.327
7.306
7.288
7.275
7.264
7.260
7.076
7.054
7.014
6.995
6.977
6.195
6.146
6.113
6.081
5.915
5.911
5.890
5.886
5.641
5.546
4.277
4.262
4.245
4.229
4.218
4.192
4.178
4.162
4.148
4.135
1.226
1.210
1.138
1.142
NO2
O
N
Ph
Me
7b
1.96
0.81
2.59
3.21
2.62
1.35
0.12
1.29
0.27
1.00
1.00
0.26
1.02
0.25
3.12
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.284
147.802
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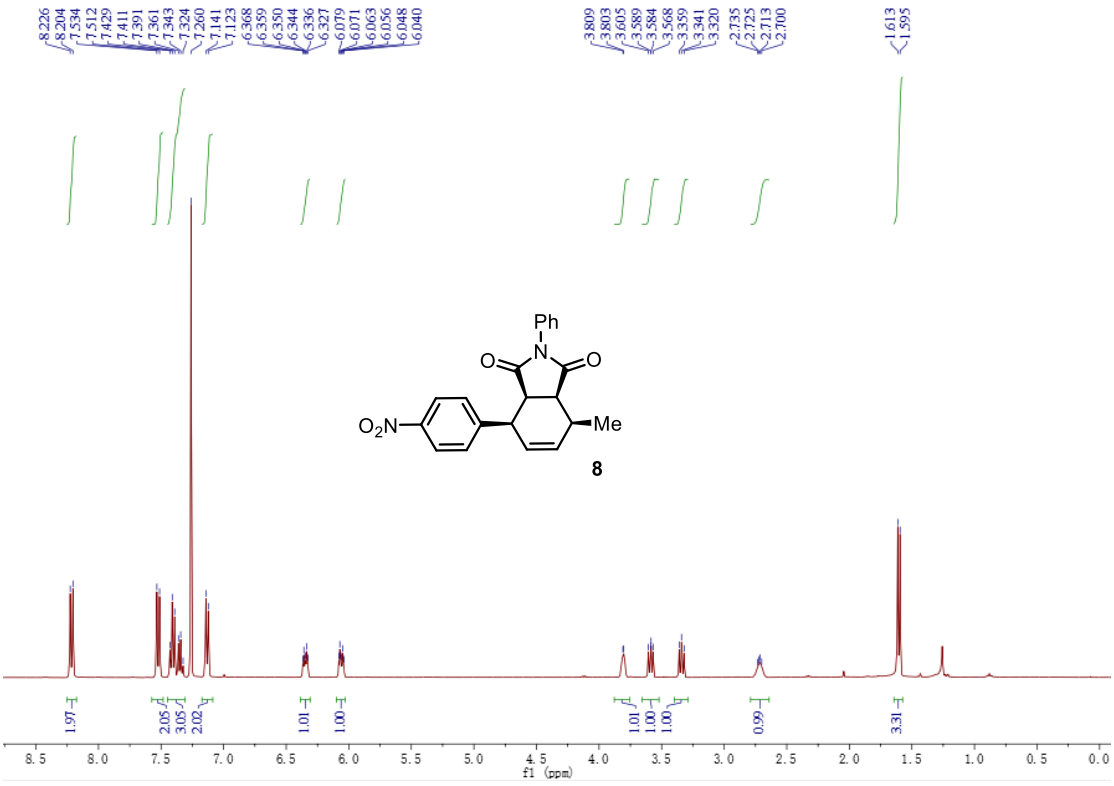
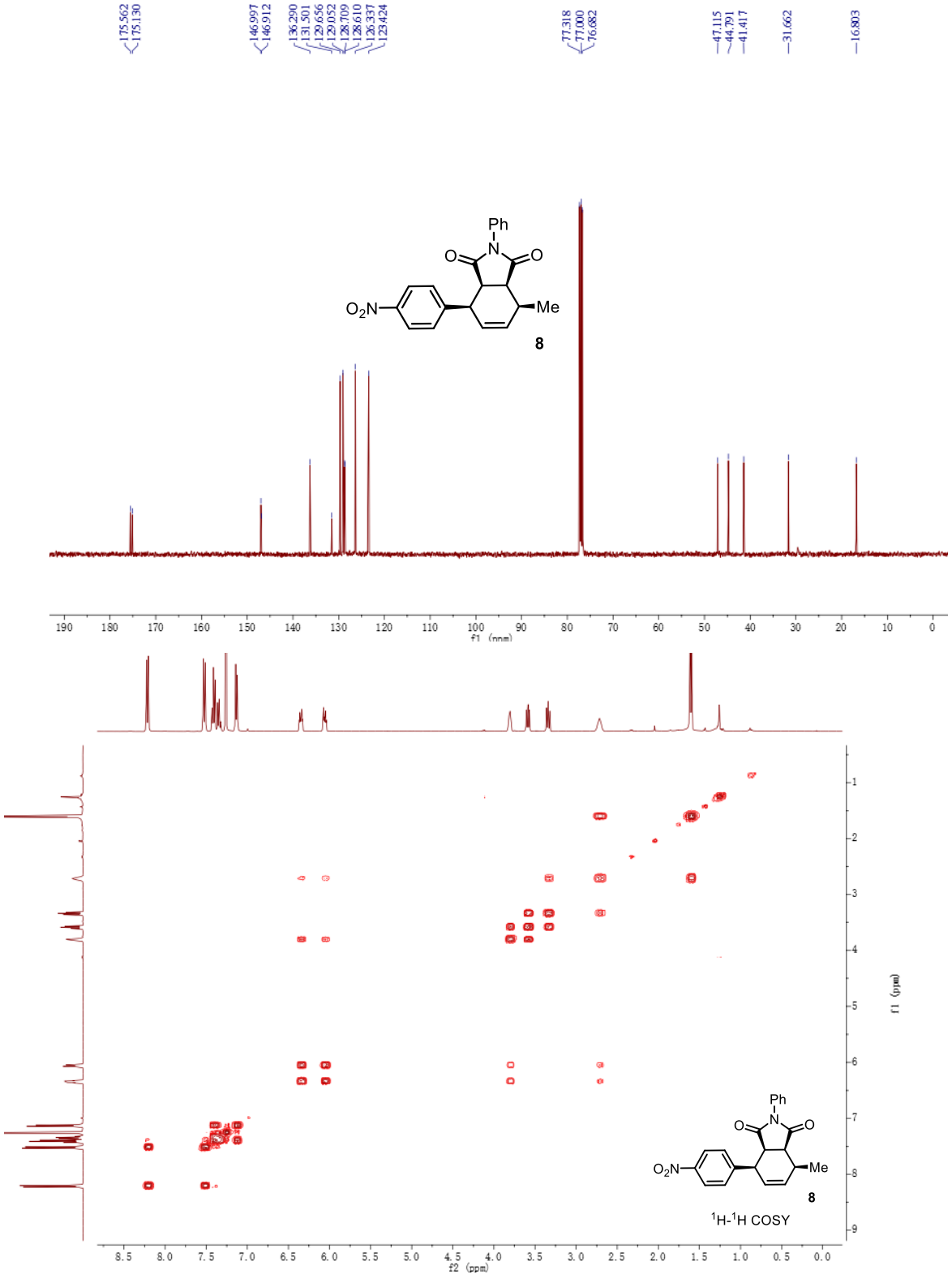
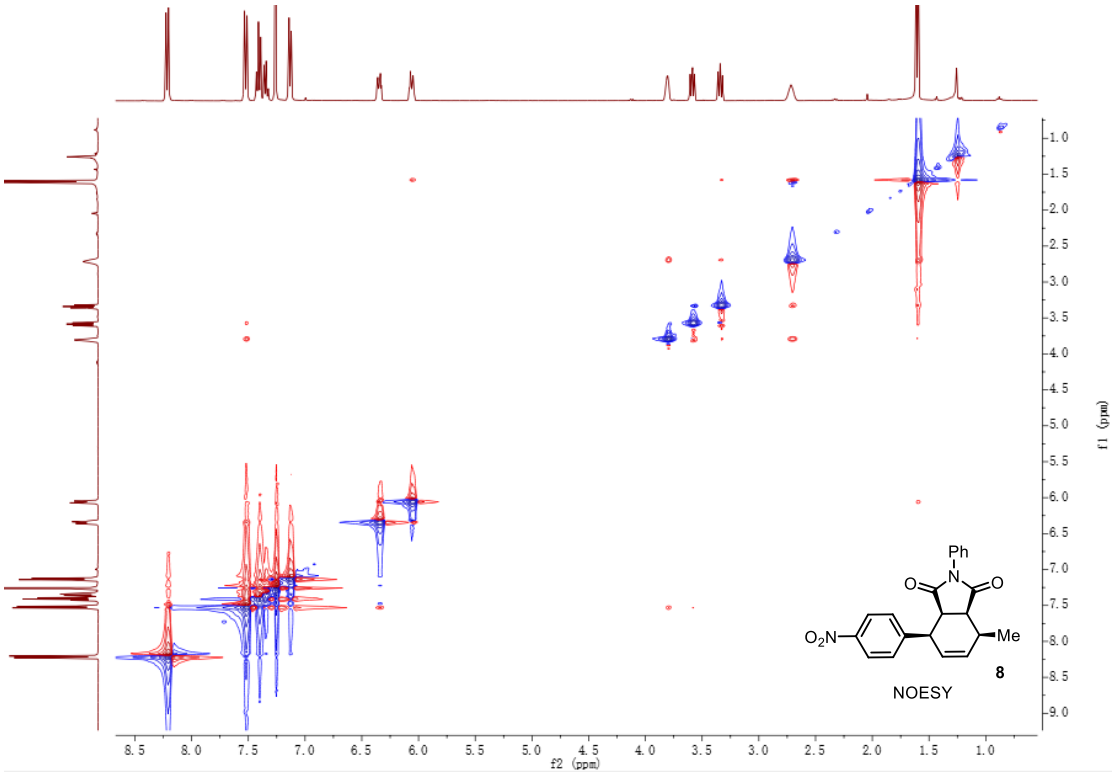
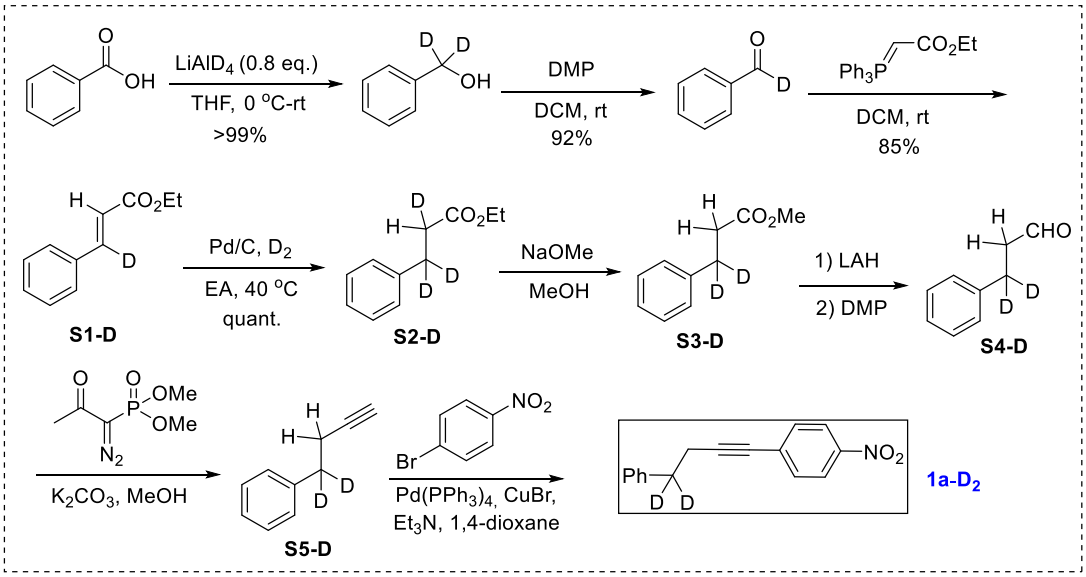
131.351
130.922
128.887
128.782
128.510
128.440
126.879
125.475
123.758
123.443
122.223
116.564
78.646
78.078
77.319
77.000
76.682
55.656
55.039
14.895
NO2
O
N
Ph
Me
7b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.226
8.204
7.534
7.512
7.429
7.411
7.391
7.361
7.343
7.324
7.260
7.141
7.123
6.368
6.359
6.350
6.344
6.336
6.327
6.079
6.071
6.063
6.056
6.048
6.040
3.809
3.803
3.605
3.589
3.584
3.568
3.359
3.341
3.320
2.735
2.725
2.713
2.700
1.613
1.595
Ph
N
O
O
O2N
Me
8
1.97
2.05
3.05
2.02
1.01
1.00
1.01
1.00
1.00
0.99
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.562
175.130
146.997
146.912
136.290
131.501
129.656
129.052
128.709
128.610
126.337
123.424
77.318
77.000
76.682
47.115
44.791
41.417
31.662
16.803
Ph
N
O
O
O2N
Me
8
f1 (ppm)
f2 (ppm)
1H-1H COSY



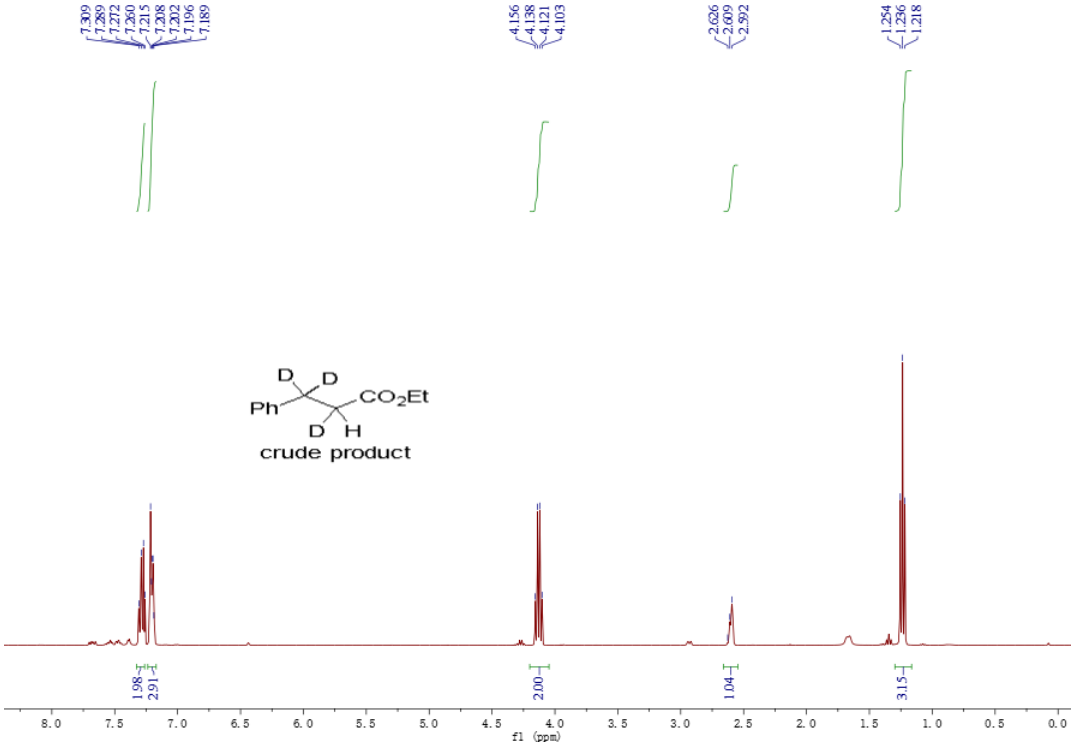
8. Synthesis of deuterated alkynes 1a-D_2



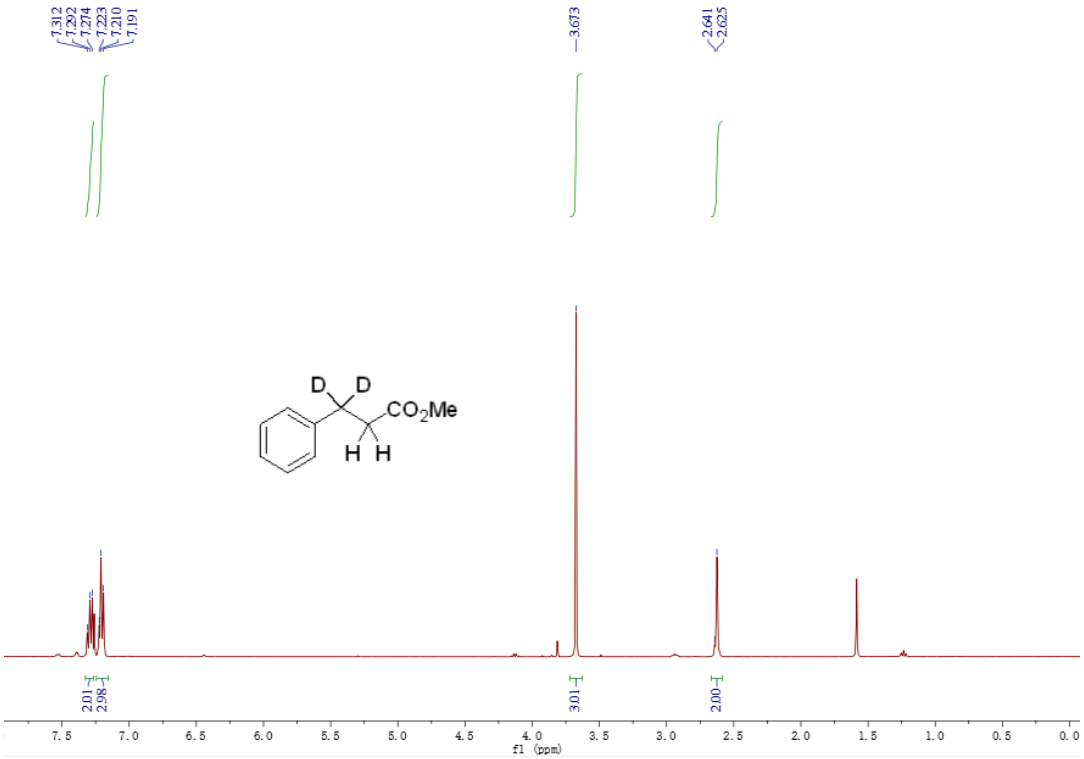
Compounds **S1-D** was known compound and prepared according to the previous literatures (For **S1-D** see: *Chem. Sci.* **2014**, *5*, 2416; *Tetrahedron Lett.* **1983**, *24*, 743; For **S2-D** see: *Adv. Synth. Catal.* **2018**, 360, 2303; For **S3-D** see: *J. Am. Chem. Soc.* **2017**, 139, 13969).

Compounds **S2-D** (crude product). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H),

7.22-7.19 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.63-2.59 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

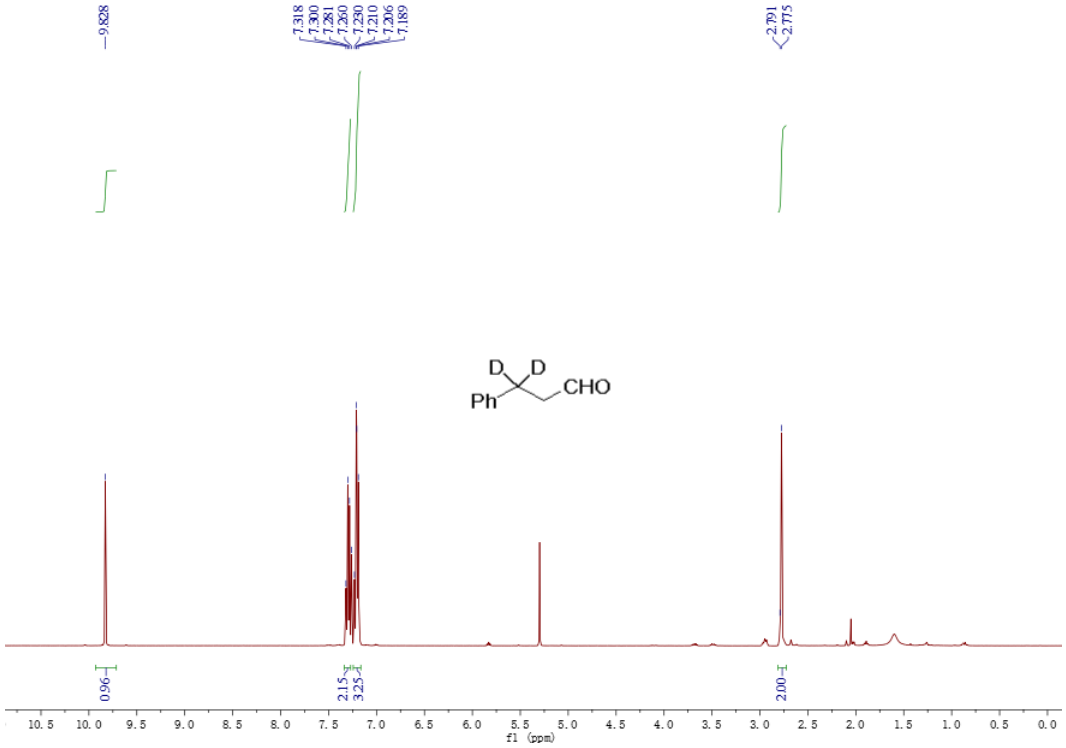


Compounds **S3-D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.22-7.19 (m, 3H), 3.67 (s, 3H), 2.63 (s, 2H).

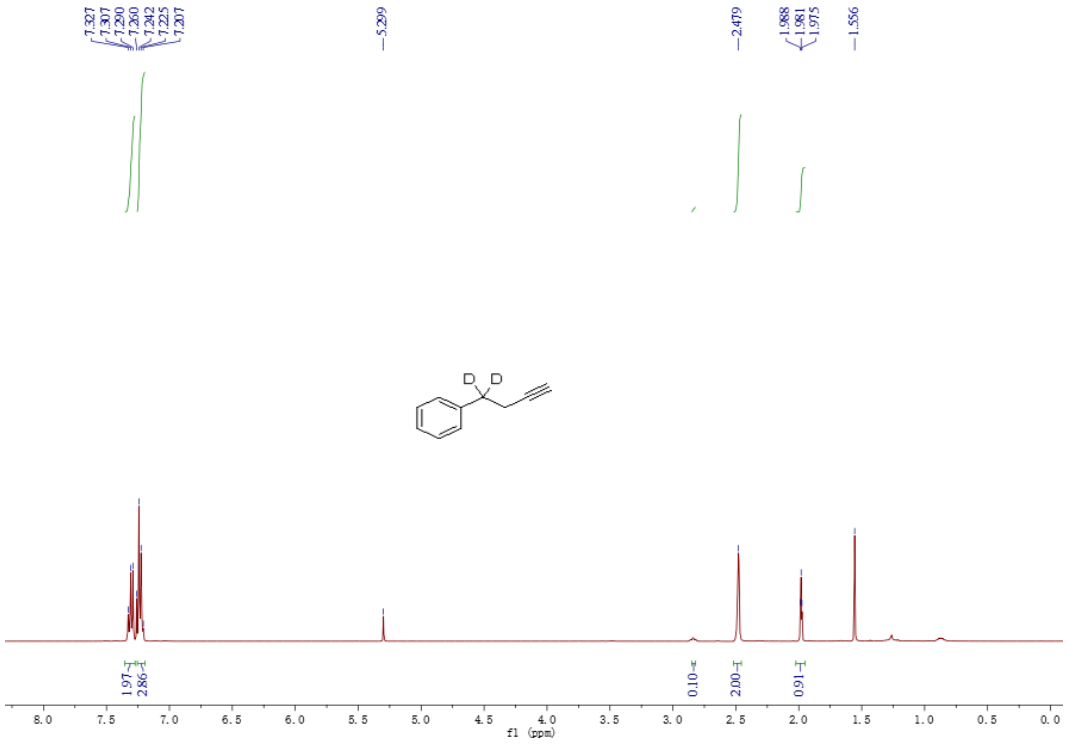


Compounds **S4-D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.32-7.28 (m, 2H), 7.23-

7.19 (m, 3H), 2.77 (s, 2H).

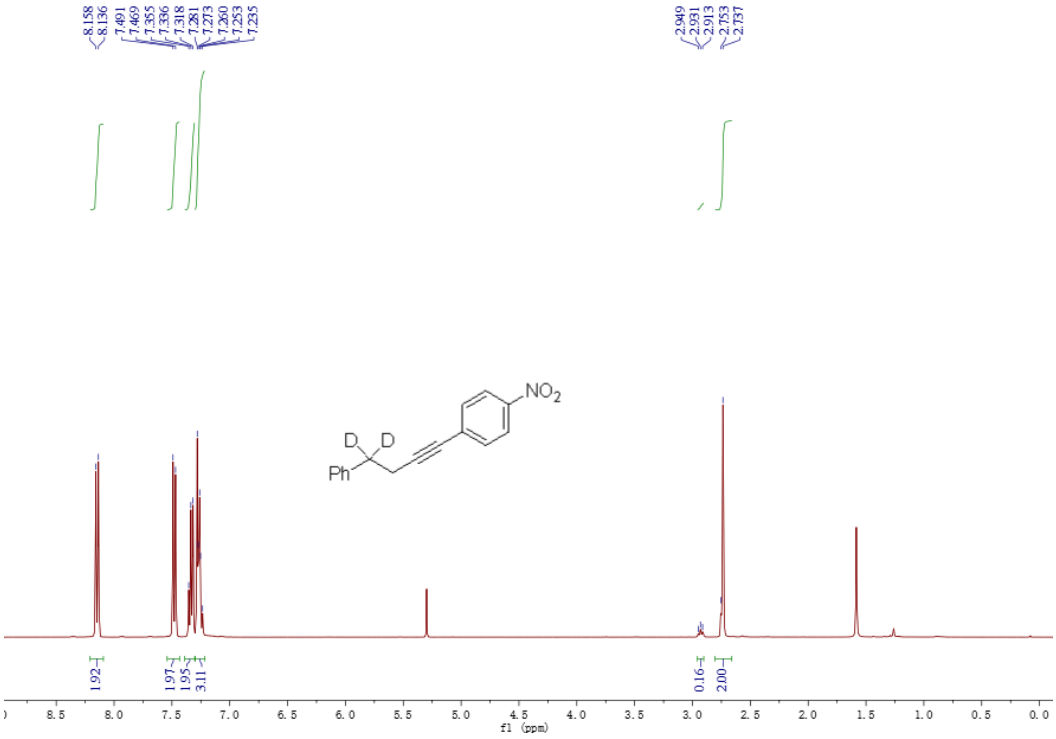


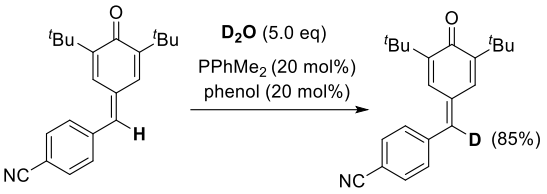
Compounds **S5-D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.24-7.21 (m, 3H), 2.48 (s, 2H), 1.98 (t, *J* = 2.6 Hz, 1H).

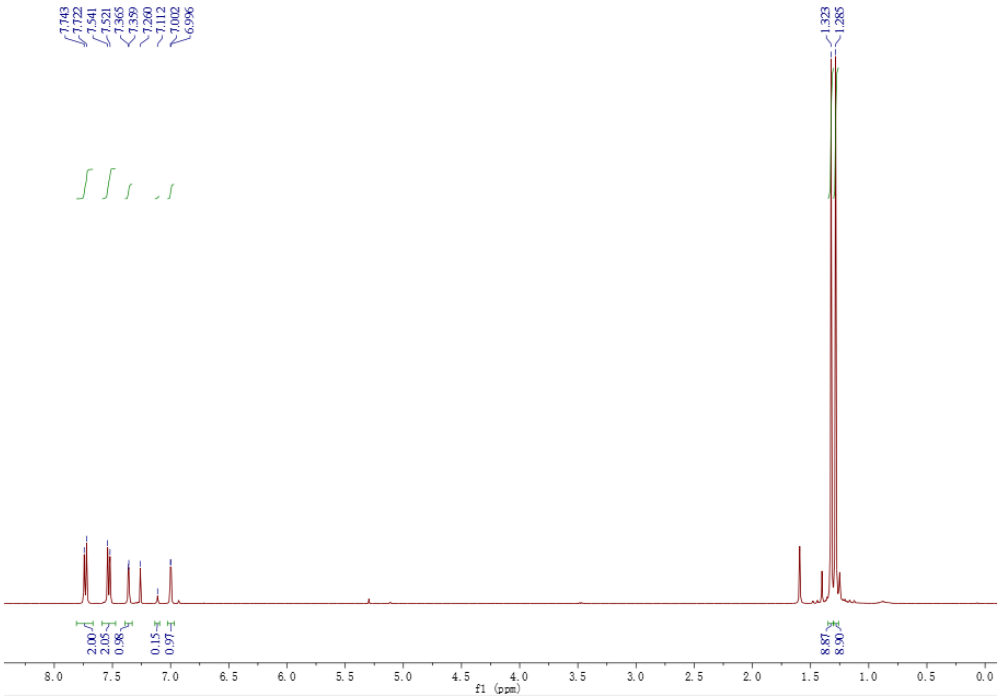


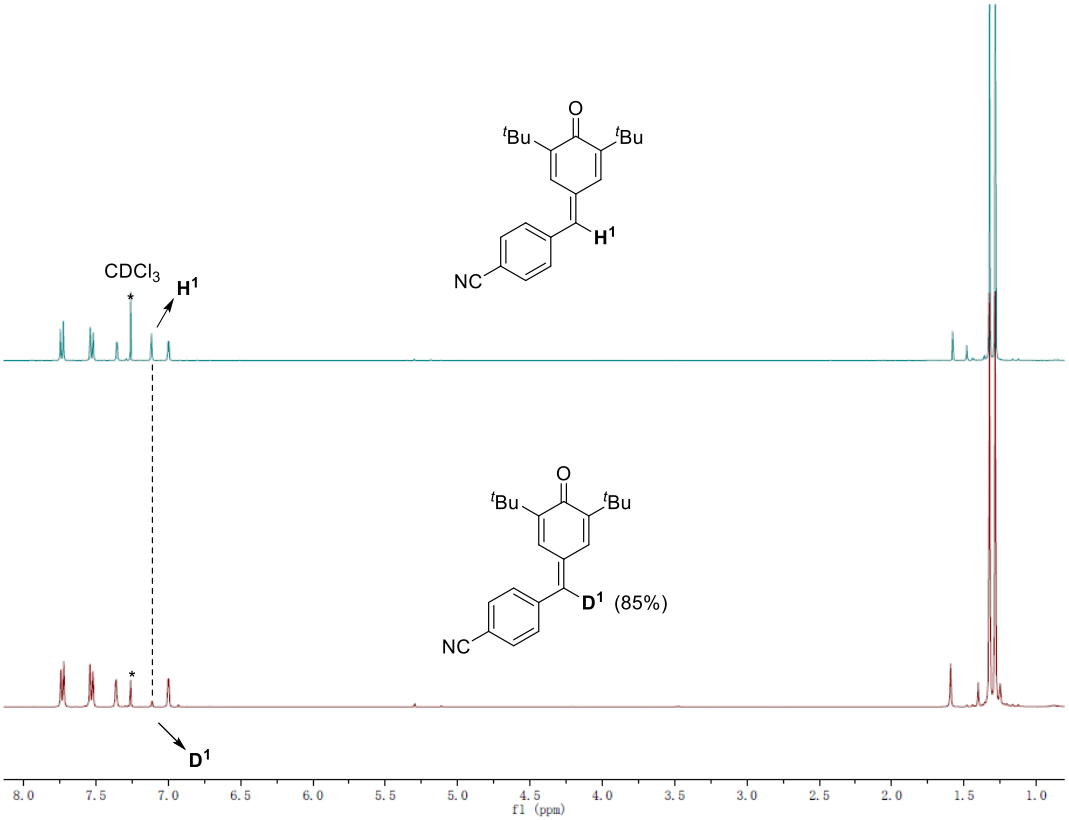
Compound **1a-D$_2$**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.36-7.32 (m, 2H), 7.27-7.24 (m, 3H), 2.93 (t, *J* = 7.2 Hz, 0.16 H, 92% D),

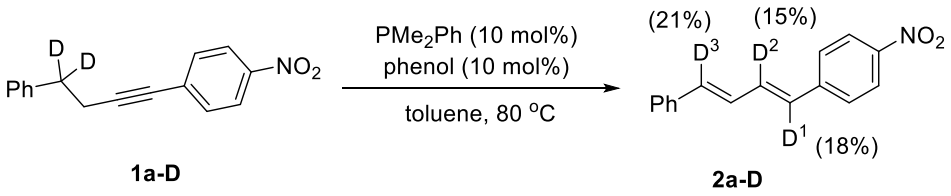
2.75-2.74 (m, 2H).


8.158
8.136
7.491
7.469
7.355
7.336
7.318
7.281
7.273
7.260
7.253
7.235
2.949
2.931
2.913
2.753
2.737
NO2
D
D
Ph
1.92
1.97
1.95
3.11
0.16
2.00
f1 (ppm)


tBu
tBu
O
H
NC
D2O (5.0 eq)
PPhMe2 (20 mol%)
phenol (20 mol%)
tBu
tBu
O
D (85%)
NC

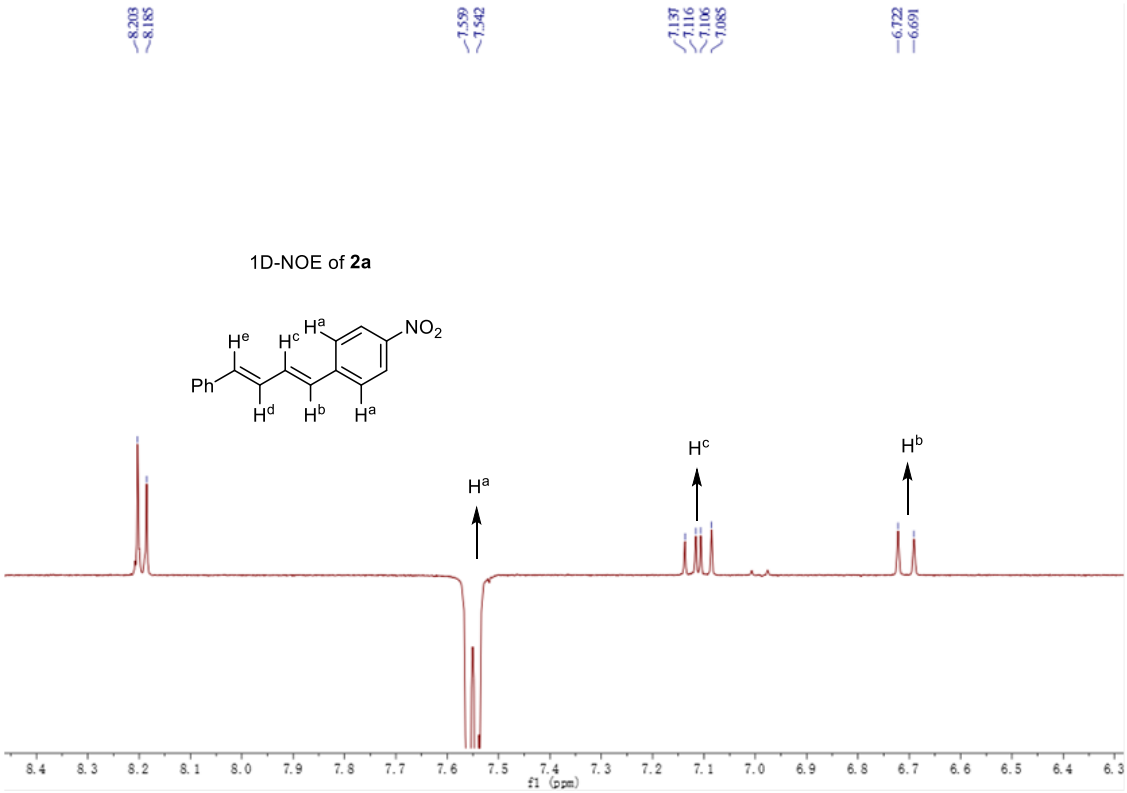

7.743
7.722
7.541
7.521
7.365
7.339
7.200
7.112
7.002
6.996
1.323
1.285
2.00
2.05
0.98
0.15
0.97
8.87
8.90
f1 (ppm)

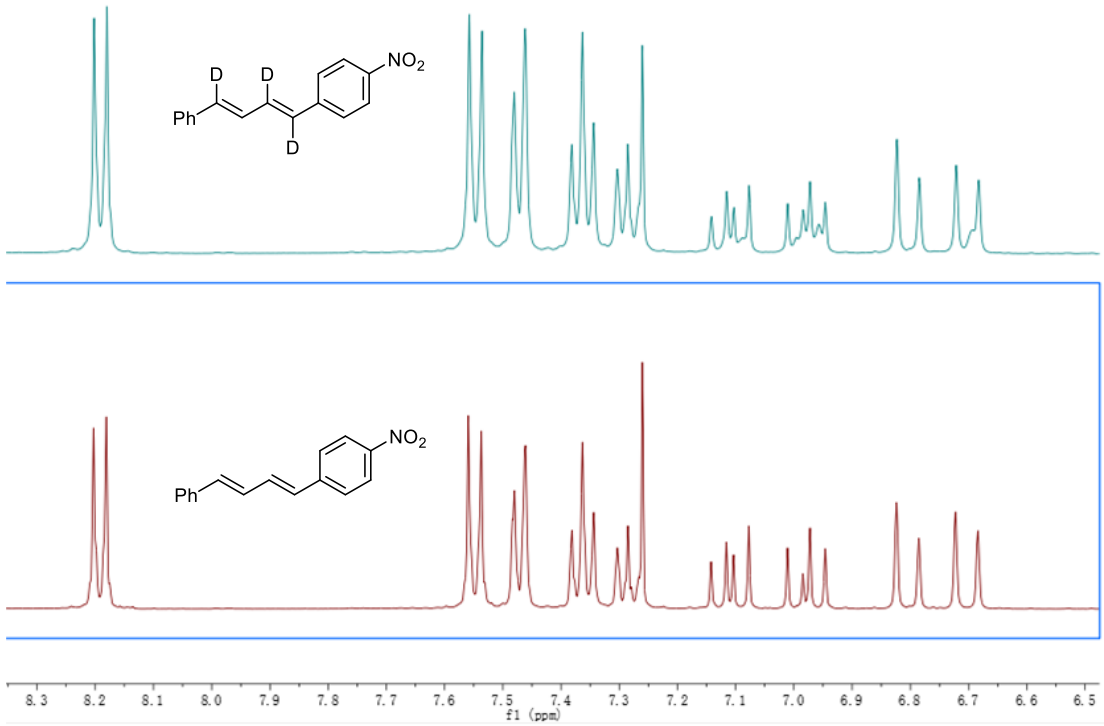


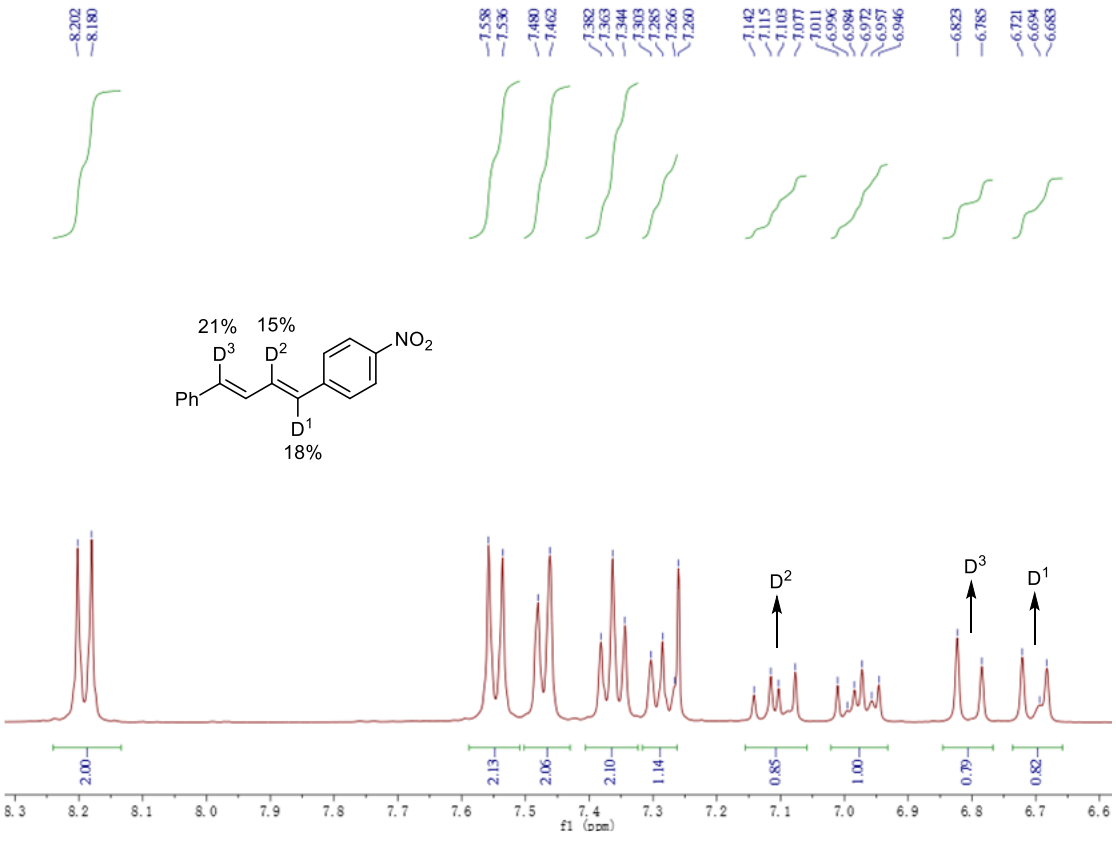


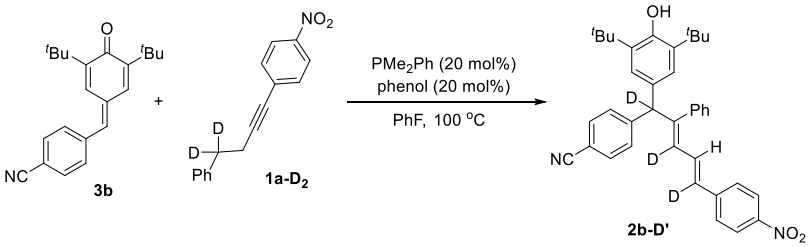
1a-D **2a-D**

Deuterium compound **1a-D** (0.1 mmol), phenol (0.01 mmol) and anhydrous toluene (1.0 mL) were added to a dried vial under N_2 protection, then PMe_2Ph (0.01 mmol) was added to the above mixture at room temperature (operated in glove box). The resulting mixture was stirred at 80 ℃ for 12 hours. The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA = 20/1) to afford the corresponding product **2a-D** in 82% yield.

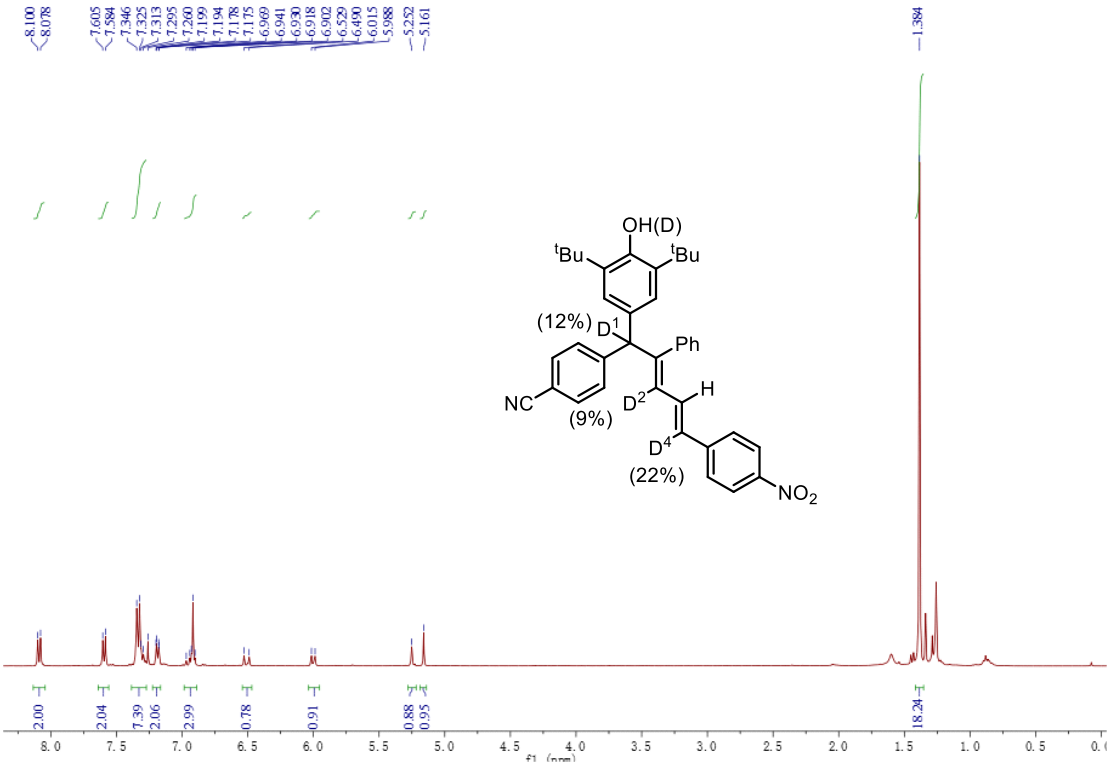

8.203
8.185
7.599
7.542
7.137
7.116
7.106
7.085
6.722
6.691
1D-NOE of 2a
Ph
NO2
Ha
Hb
Hc
Hd
He
f1 (ppm)

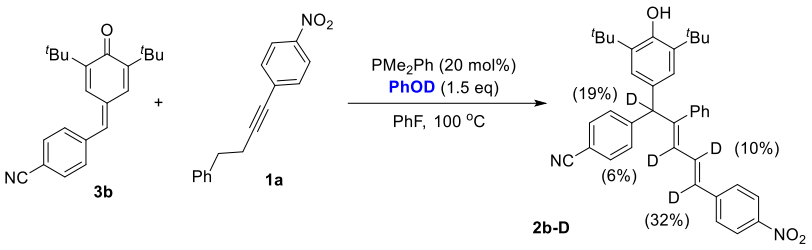

D
Ph
NO2
f1 (ppm)



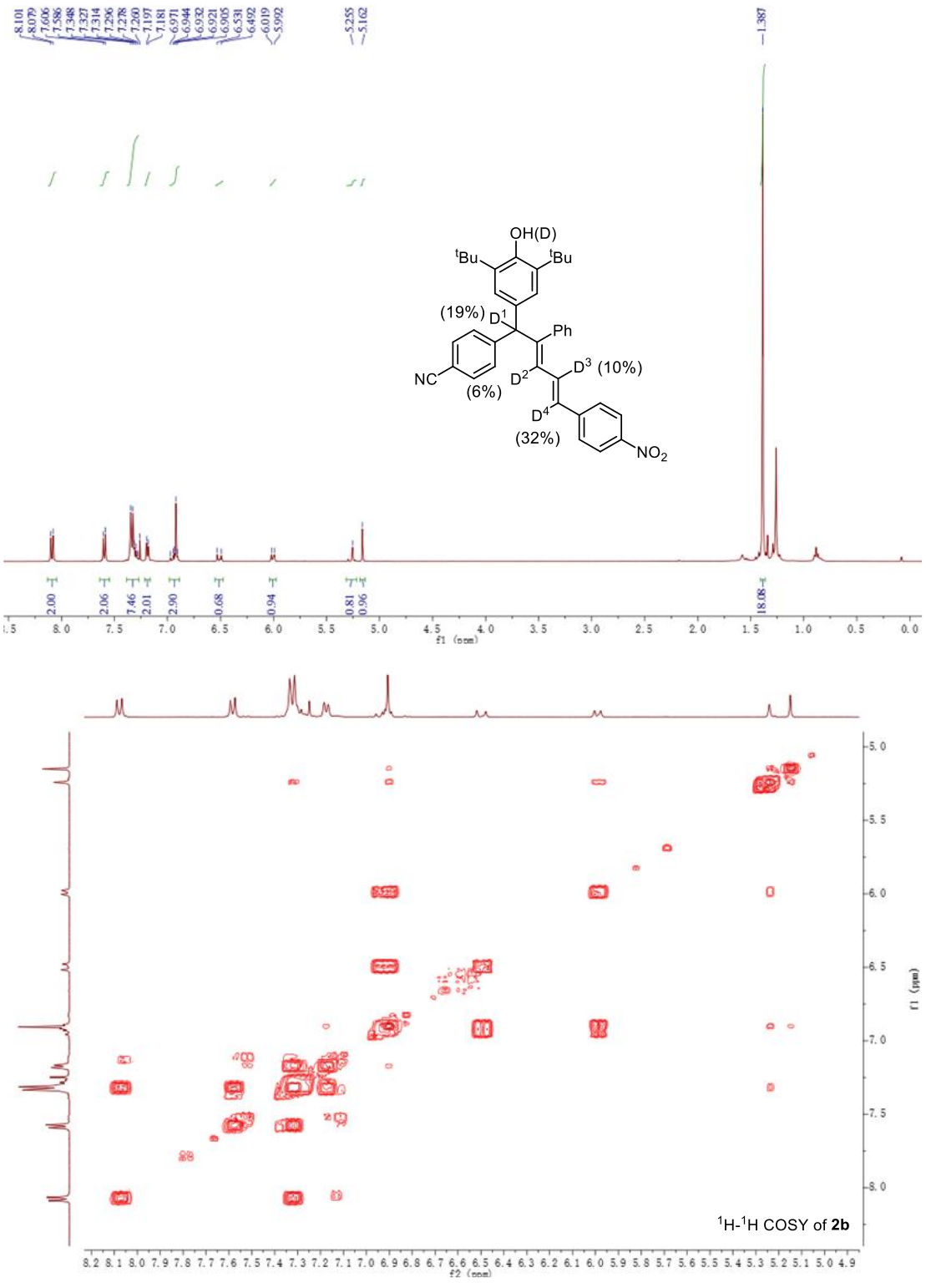


Compound *p*-quinone methide **3b** (0.15 mmol), alkyne **1a-D1** (0.1 mmol), phenol (0.02 mmol) and anhydrous fluorobenzene (4.0 mL) were added to a dried vial under N_2 protection, then PMe_2Ph (0.02 mmol) was added to the above mixture at room temperature (operated in glove box). The resulting mixture was stirred at 100 ℃ for 12 hours. The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA = 20/1) to afford the corresponding product **2b-D'** in 76% yield.





Compound *p*-quinone methide **3b** (0.15 mmol), alkyne **1a** (0.1 mmol), **PhOD** (0.15 mmol) and anhydrous fluorobenzene (4.0 mL) were added to a dried vial under N_2 protection, then PMe_2Ph (0.02 mmol) was added to the above mixture at room temperature (operated in glove box). The resulting mixture was stirred at 100 ℃ for 12 hours. The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA = 20/1) to afford the corresponding product **2b-D** in 68% yield.



^{1}H-^{1}H COSY of **2b**