Supporting Information

Molybdenum-Catalyzed Deoxygenative Heterocyclization of 2-Nitroazobenzenes: A Novel Strategy for Catalytic Synthesis of 2-Aryl-2*H*-benzo[*d*][1,2,3]triazoles

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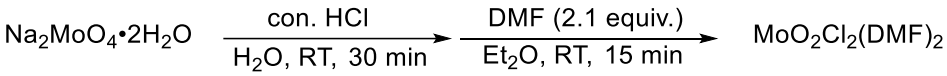
1. General information

All reactions were carried out under an atmosphere of nitrogen in flame-dried sealed tube with magnetic stirring, and monitored by thin layer chromatography (TLC) using silica gel plates. Toluene was freshly distilled from CaH_2. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM) and eluted with petroleum ether/ethyl acetate. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ and ^{19}F NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$. All signals are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). The data are reported as follows: chemical shift (ppm; br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constant (Hz), and integration.

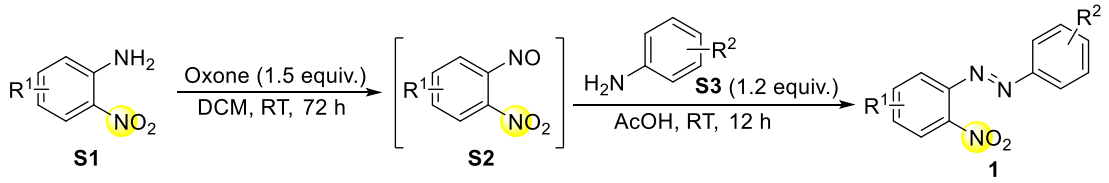
2. Synthesis of the catalyst and starting materials

2.1 Synthesis of $MoO_2Cl_2(DMF)_2$[1]



Concentrated HCl (8.3 mL, ca. 100 mmol) was added to a solution of $Na_2MoO_4{\cdot}2H_2O$ (2.42 g, 10 mmol) in distilled water (5 mL). The mixture was stirred at room temperature for 30 min resulting in a colorless solution with precipited NaCl. Et_2O (15 mL) was added and the mixture vigorously stirred for 5 min. The upper Et_2O layer was separated and dried over $MgSO_4$. The solution was collected by filtration and the $MgSO_4$ solid was washed with Et_2O (3 × 3 mL). The resulting solution was treated with a solution of DMF (1.54 g, 21 mmol) in Et_2O (10 mL) to result a suspension. The mixture was stirred for 5 min and the white solid filtered, washed with Et_2O (3 × 3 mL) and dried under vacuum to give the desired complex $MoO_2Cl_2(DMF)_2$ (3.15 g, 91% yield).

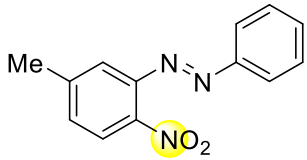
2.2 Synthesis of the starting materials 2-nitroazobenzenes (1)[2]



Oxone (7.5 mmol in 12 mL H_2O) was added dropwise to a solution of 2-nitroaniline (**S1**, 5 mmol) in DCM (35 mL), and the mixture was stirred at room temperature for 72 h. After completion of the reaction (TLC monitoring), the organic layer was separated and washed twice by distilled water to remove the residual inorganic salts. The solvent was evaporated under reduced pressure to give the crude nitroso intermediate **S2** without further purification. The freshly-prepared crude **S2** was all dissolved by AcOH (15 mL) followed by the addition of aniline (**S3**, 6 mmol). The solution was stirred at room temperature for 12 h, and neutralized to pH ≈ 7 by aqueous

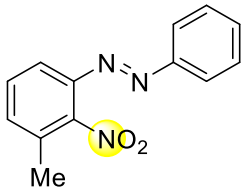
solution of $NaHCO_3$ dropped carefully. After extracted with ethyl acetate, the solvent was removed under reduced pressure. The product was purified by column chromatography to give substituted 2-nitroazobenzene **1** as an orange or red solid.

5-Methyl-2-nitroazobenzene (1b')



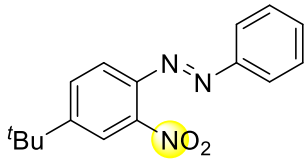
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.92 (m, 2H), 7.89-7.86 (m, 1H), 7.54-7.52 (m, 3H), 7.37-7.33 (m, 2H), 2.47(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 145.9, 144.8, 144.6, 132.1, 130.7, 129.2, 124.3, 123.5, 118.5, 21.5.

3-Methyl-2-nitroazobenzene (1c')



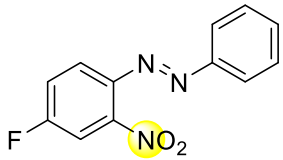
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.52-7.44 (m, 4H), 7.38 (d, J = 7.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 150.6, 142.8, 133.3, 132.2, 130.2 129.1, 123.5, 114.5, 16.7.

4-*tert*-Butyl-2-nitroazobenzene (1e)



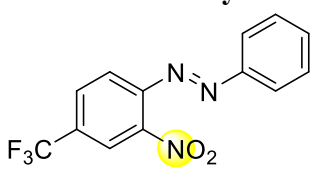
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (m, 3H), 7.69-7.62 (m, 2H), 7.53-7.49 (m, 3H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 152.3, 147.6, 142.9, 132.0, 130.0, 129.1, 123.4, 120.7, 117.9, 35.2, 30.9.

4-Fluoro-2-nitroazobenzene (1h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.78-7.75 (m, 1H), 7.62-7.61 (m, 1H), 7.53-7.52 (m, 3H), 7.39-7.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J = 254.0 Hz), 152.1, 148.3 (d, J = 7.0 Hz), 141.5, 132.4, 129.2, 123.6, 120.2 (d, J = 3.0 Hz), 120.1 (d, J = 12.0 Hz), 111.5 (d, J = 27.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.5.

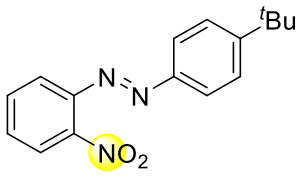
4-Trifluoromethyl-2-nitroazobenzene (1i)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.96-7.92 (m, 3H), 7.76 (d, J = 8.3 Hz, 1H),

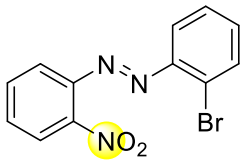
7.59-7.52 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 147.5, 146.8, 133.1, 132.1 (q, J = 34.0 Hz), 129.9 (q, J = 3.0 Hz), 129.3, 123.9, 121.7 (q, J = 4.0 Hz), 119.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7.

4'-*tert*-Butyl-2-nitroazobenzene (1p)



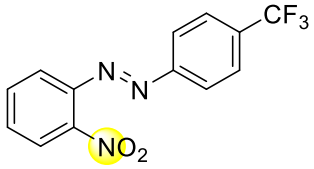
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.86 (m, 3H), 7.67-7.63 (m, 2H), 7.55-7.51 (m, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 150.4, 147.3, 145.6, 133.0, 130.1, 126.2, 124.0, 123.4, 118.4, 35.1, 31.1.

2'-Bromo-2-nitroazobenzene (1r)



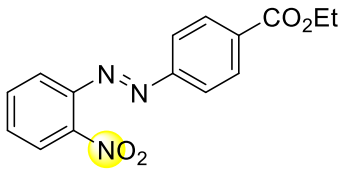
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 1H), 7.80-7.67 (m, 4H), 7.62-7.58 (m, 1H), 7.42-7.35 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 149.4, 145.3, 133.9, 133.3, 133.2, 131.0, 128.2, 126.6, 124.1, 119.0, 118.5.

4'-Trifluoromethyl-2-nitroazobenzene (1v)



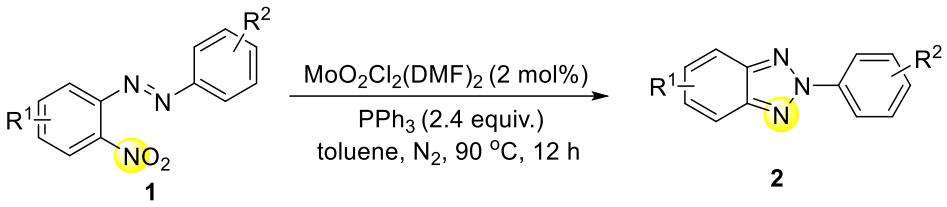
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.71-7.59 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 (d, J = 1.0 Hz), 147.6, 145.0, 133.3 (q, J = 33.0 Hz), 133.2, 131.2, 126.4 (q, J = 4.0 Hz), 124.1, 123.7, 123.6 (q, J = 271.0 Hz), 118.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7.

4'-Ethoxycarbonyl-2-nitroazobenzene (1w)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 2H), 7.95-7.93 (m, 3H), 7.70-7.58 (m, 3H), 4.41 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 154.4, 147.6, 145.0, 133.1, 133.0, 131.0, 130.5, 124.0, 123.2, 118.1, 61.3, 14.2.

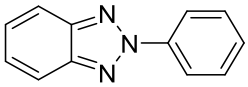
3. General procedure



Under nitrogen atmosphere, a sealed tube was charged with substituted 2-nitroazobenzene **1** (0.2 mmol, 1.0 equiv.), $MoO_2Cl_2(DMF)_2$ (0.004 mmol, 2 mol%), PPh_3 (0.15 mmol, 1.5 equiv.) and 2.0 mL dry toluene were successively added. The reaction mixture was kept stirring at 90 °C for 12 h under nitrogen atmosphere. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the desired product **2**.

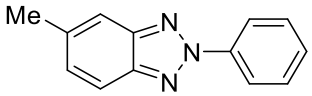
4. Characterization of products

2-Phenyl-2*H*-benzo[*d*][1,2,3]triazole (2a)



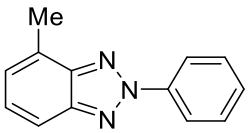
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 100-102 °C. Yield: 95% (37.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 7.8 Hz, 2H), 7.96-7.92 (m, 2H), 7.56 (t, J = 8.1 Hz, 2H), 7.47-7.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.2, 129.4, 128.9, 127.1, 120.5, 118.3.

5-Methyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2b)



Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 93 -95 °C. Yield: 82% (34.2 mg, from **1b**), 80% (33.6 mg, from **1b'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 8.8 Hz, 1H), 7.58 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 143.6, 140.3, 137.3, 130.1, 129.3, 128.6, 120.3, 117.7, 116.4, 22.1.

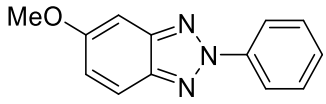
4-Methyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2c)



Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 72-74 °C. Yield: 95% (39.7 mg, from **1c**), 82% (34.3 mg, from **1c'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H),

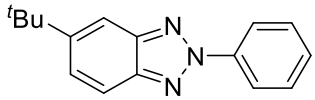
7.43 (t, J = 7.3 Hz, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.13 (d, J = 6.7 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.8, 140.3, 129.2, 129.0, 128.6, 127.3, 126.0, 120.4, 115.4, 17.1. HRMS-ESI$^+$ (m/z): found $[M+H]^+$ 210.1028, calc'd $[C_{13}H_{12}N_3]^+$ requires 210.1026.

5-Methoxyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2d)



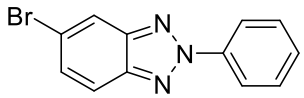
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 100/1. White solid. Mp: 66-67 ºC. Yield: 90% (40.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 7.7 Hz, 2H), 7.77 (d, J = 8.9 Hz, 1H), 7.51 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 7.0 Hz, 1H), 7.09-7.07 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 145.8, 141.1, 140.2, 129.2, 128.3, 122.4, 120.0, 119.0, 94.5, 55.4.

5-*tert*-Butyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2e)



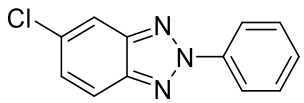
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 73-74 ºC. Yield: 42% (21.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.3 Hz, 3H), 7.43 (t, J = 7.3 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 145.4, 143.5, 140.4, 129.4, 128.6, 127.0, 120.4, 117.6, 112.7, 35.3, 31.0.

5-Bromo-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2f)



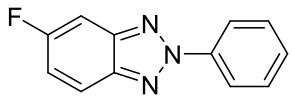
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 118-121 ºC. Yield: 72% (39.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 6.7 Hz, 2H), 8.08 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.52-7.44 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 143.5, 139.9, 130.9, 129.4, 129.2, 120.8, 120.7, 120.5, 119.6.

5-Chrolo-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2g)



Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 110-111 ºC. Yield: 89% (41.2 mg, from **1g**), 54% (24.6 mg, from **1g'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.9 Hz, 2H), 7.90 (s, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 143.4, 140.0, 132.9, 129.4, 129.2, 128.7, 120.5, 119.5, 117.3.

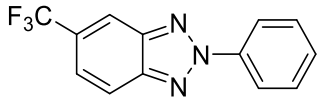
5-Fluoro-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2h)



Eluent for column chromatographic purification: petroleum ether. White solid. Mp:

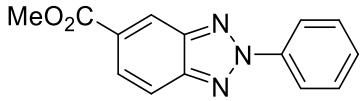
127-129 ºC. Yield: 87% (36.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.9 Hz, 2H), 7.90-7.87 (m, 1H), 7.55-7.49 (m, 3H), 7.44 (t, J = 7.4 Hz, 1H), 7.20 (td, J = 9.2 Hz, J = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, J = 245 Hz), 144.8 (d, J = 14.0 Hz), 142.1, 140.1, 129.4, 129.0, 120.4, 120.1 (d, J = 11.0 Hz), 118.7 (d, J = 29.0 Hz), 101.6 (d, J = 25.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.7.

5-Trifluoromethyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazole (2i)



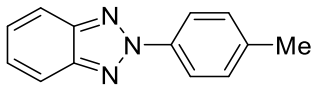
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 91-92 ºC. Yield: 59% (31.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 7.9 Hz, 2H), 8.29 (s, 1H), 8.05 (d, J = 9.0 Hz, 1H), 7.61-7.56 (m, 3H), 7.51 (t, J = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 143.7, 139.9, 129.6, 129.5, 129.2 (q, J = 32.0 Hz), 125.4 (d, J = 271 Hz), 123.1 (d, J = 3.0 Hz), 120.8, 119.6, 117.1 (q, J = 5.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5.

Methyl 2-phenyl-2*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (2j)



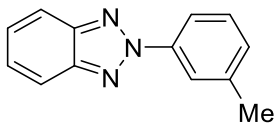
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 100/1. White solid. Mp: 124-126 ºC. Yield: 49% (24.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.36 (d, J = 7.6 Hz, 2H), 8.06-8.03 (m, 1H), 7.95-7.93 (m, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 146.7, 144.4, 140.0, 129.5, 129.5, 128.9, 127.0, 122.0, 120.7, 118.3, 52.4.

2-(*p*-Tolyl)-2*H*-benzo[*d*][1,2,3]triazole (2k)



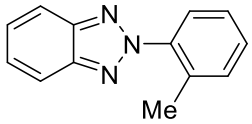
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 106-108 ºC. Yield: 73% (30.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.2 Hz, 2H), 7.94-7.92 (m, 2H), 7.42-7.40 (m, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 139.1, 138.1, 130.0, 127.0, 120.4, 118.2, 21.2.

2-(*m*-Tolyl)-2*H*-benzo[*d*][1,2,3]triazole (2l)



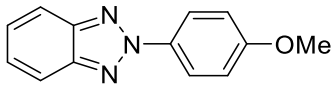
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 96-97 ºC. Yield: 92% (38.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.86-7.84 (m, 2H), 7.37-7.32 (m, 3H), 7.18 (d, J = 7.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 140.1, 139.5, 129.7, 129.1, 127.0, 121.0, 118.2, 117.7, 21.4.

2-(*o*-Tolyl)-2*H*-benzo[*d*][1,2,3]triazole (2m)



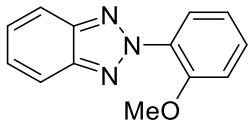
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 93-94 ºC. Yield: 98% (41.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.71 (d, J = 7.5 Hz, 1H), 7.46-7.37 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 140.1, 133.2, 131.6, 129.4, 126.8, 126.5, 125.9, 118.3, 18.8.

2-(4-Methoxyphenyl)-2*H*-benzo[*d*][1,2,3]triazole (2n)



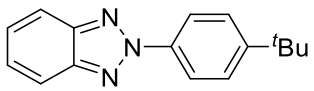
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 120/1. White solid. Mp: 104-106 ºC. Yield: 79% (35.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 9.0 Hz, 2H), 7.93-7.91 (m, 2H), 7.42-7.39 (m, 2H), 7.05 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 144.8, 133.9, 126.8, 121.9, 118.1, 114.4, 55.6.

2-(2-Methoxyphenyl)-2*H*-benzo[*d*][1,2,3]triazole (2o)



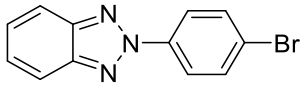
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 150/1. White solid. Mp: 92-94 ºC. Yield: 83% (37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.66 (dd, J = 7.7 Hz, 1.6 Hz, 1H), 7.52-7.47 (m, 1H), 7.44-7.41 (m, 2H), 7.14-7.09 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 144.5, 130.9, 129.9, 127.4, 126.6, 120.4, 118.2, 112.4, 56.0.

2-(4-*tert*-Butylphenyl)-2*H*-benzo[*d*][1,2,3]triazole (2p)



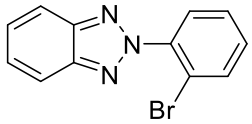
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 109-111 ºC. Yield: 62% (31.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 2H), 7.95-7.93 (m, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.42-7.40 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 144.9, 138.0, 127.0, 126.3, 120.2, 118.3, 34.8, 31.3.

2-(4-Bromophenyl)-2*H*-benzo[*d*][1,2,3]triazole (2q)



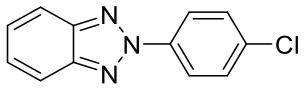
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 165-167 ºC. Yield: 65% (35.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.8 Hz, 2H), 7.92-7.90 (m, 2H), 7.67 (d, J = 8.9 Hz, 2H), 7.44-7.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.2, 132.5, 127.4, 122.8, 121.9, 118.3.

2-(2-Bromophenyl)-2*H*-benzo[*d*][1,2,3]triazole (2r)



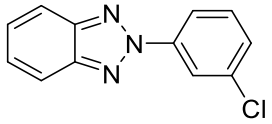
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 100-103 ºC. Yield: 94% (51.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.53-7.40 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.2, 134.0, 131.1, 128.3, 128.0, 127.2, 118.7, 118.4.

2-(4-Chlorophenyl)-2*H*-benzo[*d*][1,2,3]triazole (2s)



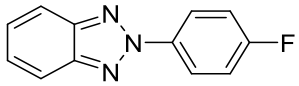
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 159-160 ºC. Yield: 76% (35.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.8 Hz, 2H), 7.92-7.90(m, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.43-7.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 138.7, 134.7, 129.5, 127.4, 121.6, 118.3.

2-(3-Chlorophenyl)-2*H*-benzo[*d*][1,2,3]triazole (2t)



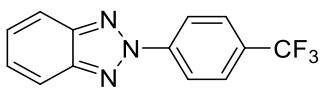
Eluent for column chromatographic purification: petroleum ether. White solid. Mp: 139-140 ºC. Yield: 70% (32.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.93-7.91 (m, 2H), 7.50-7.42 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 141.0, 135.2, 130.4, 128.8, 127.5, 120.7, 118.4, 118.3.

2-(4-Fluorophenyl)-2*H*-benzo[*d*][1,2,3]triazole (2u)



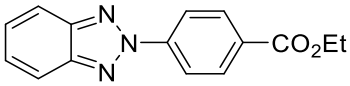
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 120/1. White solid. Mp: 111-113 ºC. Yield: 82% (35.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.24 (m, 2H), 7.85-7.83 (m, 2H), 7.35-7.33 (m, 2H), 7.16 (t, J = 8.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, J = 248 Hz), 144.8, 136.4, 127.1, 122.2 (d, J = 9.0 Hz), 118.2, 116.1 (d, J = 23.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.2.

2-(4-Trifluoromethylphenyl)-2*H*-benzo[*d*][1,2,3]triazole (2v)



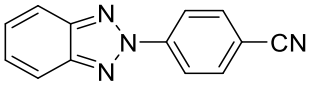
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 150/1. White solid. Mp: 151-154 ºC. Yield: 58% (30.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 2H), 7.94-7.92 (m, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.46-7.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 142.5, 130.6 (d, J = 33.0 Hz), 127.8, 126.7 (q, J = 4.0 Hz), 126.4 (q, J = 271 Hz), 120.6, 118.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.4.

Ethyl 4-(2*H*-benzo[*d*][1,2,3]triazol-2-yl)benzoate (2w)



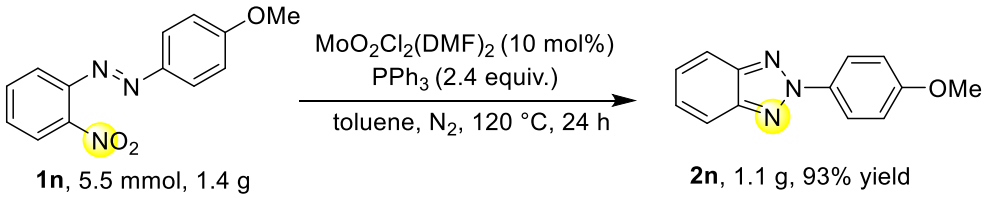
Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 20/1. White solid. Mp: 155-156 °C. Yield: 69% (36.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.8 Hz, 2H), 8.22 (d, J = 8.8 Hz, 2H), 7.94-7.91 (m, 2H), 7.44-7.42 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 145.1, 143.0, 130.8, 130.4, 127.6, 120.0, 118.4, 61.2, 14.2.

2-(4-Cyanphenyl)-2*H*-benzo[*d*][1,2,3]triazole (2x)



Eluent for column chromatographic purification: petroleum ether/ethyl acetate = 20/1. White solid. Mp: 216-218 °C. Yield: 76% (33.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.9 Hz, 2H), 7.93-7.89 (m, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.47-7.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 142.9, 133.5, 128.1, 120.8, 118.5, 118.0, 112.3.

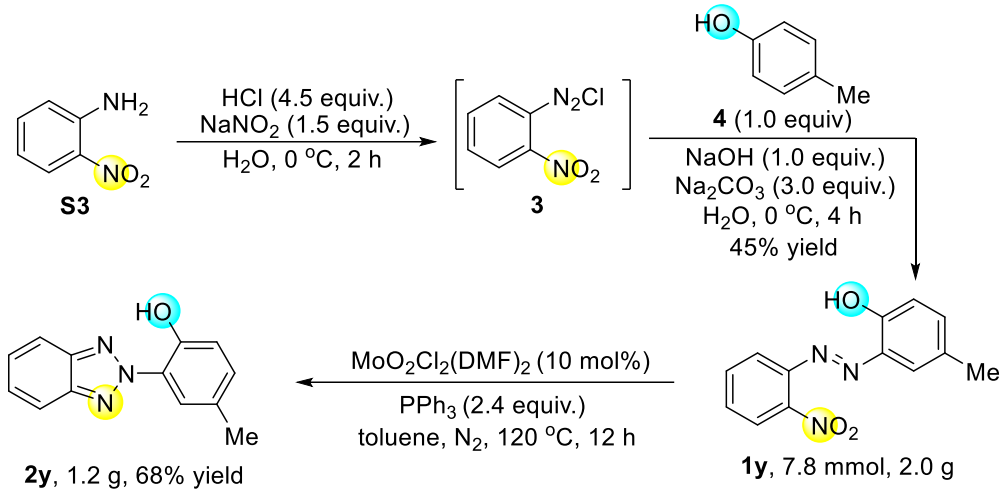
5. Gram-scale synthesis of 2n and 2y



1n, 5.5 mmol, 1.4 g

2n, 1.1 g, 93% yield

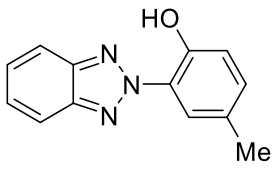
Under nitrogen atmosphere, a sealed tube was charged with substituted 2-nitroazobenzene **1n** (1.4 g, 5.5 mmol, 1.0 equiv.), $MoO_2Cl_2(DMF)_2$ (0.55 mmol, 10 mol%), PPh_3 (13.2 mmol, 2.4 equiv.) and 55 mL dry toluene were successively added. The reaction mixture was kept stirring at 120 °C for 12 h under nitrogen atmosphere. After completion of the reaction (monitored by TLC), the mixture was washed with aq. H_2O_2 to oxidize the residual PPh_3, and concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the desired product **2n** in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 9.0 Hz, 2H), 7.93-7.91 (m, 2H), 7.42-7.39 (m, 2H), 7.05 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 144.8, 133.9, 126.8, 121.9, 118.1, 114.4, 55.6.



2-Nitroaniline (**S3**, 5.5 g, 40 mmol) and concentrated hydrochloric acid (15 mL) was mixed to in a 500 mL beaker and the mixture was stirred and heated at 70 °C to form a suspension. The beaker was cooled to 0 °C for 15 min, and a solution of $NaNO_2$ (4.1 g, 60 mmol) in 8 mL of distilled water was added dropwise to the suspension with vigorous stirring. The reaction was kept at 0 °C for 2 h to give 2-nitrophenyldiazonium chloride (**3**). A small amount of urea was added to eliminate the redundant HNO_2. The mixture was then added slowly to a solution of *p*-cresol (**4**, 4.3 g, 40 mmol), NaOH (1.6 g, 40 mmol) and Na_2CO_3 (12.7 g, 120 mmol) in 120 mL of distilled water, and the solution began to turn red and a red solid precipitated. With stirred for 4 h, the suspension was filtered and the red solid was washed with water and dried. The crude product was recrystallized from ^{i}PrOH and washed with Et_2O twice to afford 4.6 g of pure **1y** in 45% yield.[3]

Under nitrogen atmosphere, a sealed tube was charged with **1y** (7.8 mmol, 1.0 equiv.), $MoO_2Cl_2(DMF)_2$ (0.78 mmol, 10 mol%), PPh_3 (18.7 mmol, 2.4 equiv.) and 78 mL dry toluene were successively added. The reaction mixture was kept stirring at 120 °C for 12 h under nitrogen atmosphere. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-dichloromethane as eluent to give 1.2 g of **2y** in 68% yield.

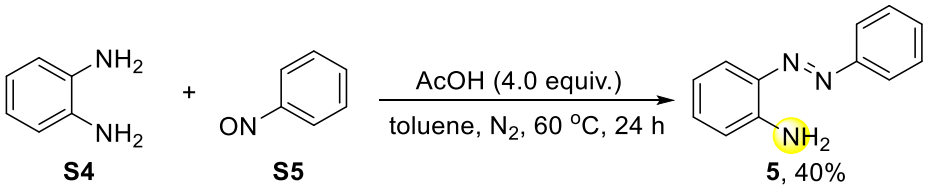
2-(2*H*-Benzo[*d*][1,2,3]triazol-2-yl)-4-methylphenol (Tinuvin-P, 2y)[4]



Eluent for column chromatographic purification: petroleum ether. Yellow solid. Mp: 122-124 °C. Yield: 73% (1.3 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 8.20 (s, 1H), 7.94-7.92 (m, 2H), 7.49-7.46 (m, 2H), 7.16-7.08 (m, 2H), 2.40 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 142.6, 131.1, 129.5, 127.5, 124.6, 120.9, 118.6, 117.5, 20.4.

6. Mechanistic study

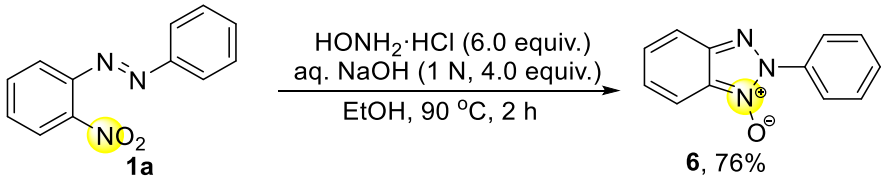
Synthesis of 2-aminoazobenzene (5)[5]



S4 **S5** **5**, 40%

The solution of 1,2-phenylenediamine (**S4**, 1.6 g, 15.0 mmol) in dry toluene (100 mL) was degassed under a stream of N_2 for 15 min. Nitrosobenzene (**S5**, 1.6 g, 15.0 mmol) and acetic acid (3.4 mL, 60 mmol) were added and the mixture was stirred at 60 °C for 24 h. The solvent was evaporated under reduced pressure, and the concentrated solution was diluted with water and CH_2Cl_2. The separated organic phase was dried with $MgSO_4$ and concentrated. The residue purified through column chromatography (petroleum ether/ethyl acetate = 20/1) to give 1.2 g of **5** in 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 3H), 7.53-7.49 (m, 2H), 7.43 (t, J =7.3 Hz, 1H), 7.25-7.21 (m, 1H), 6.86-6.82 (m, 1H), 6.77 (d, J = 8.2 Hz, 1H), 5.91 (br, 2H).

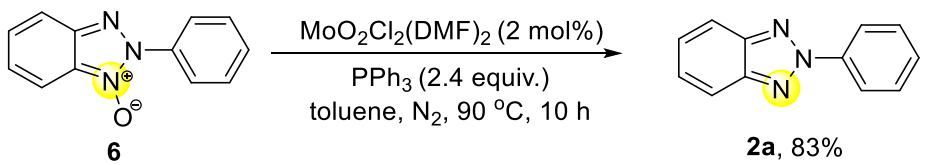
Synthesis of 2-phenyl-2*H*-benzo[*d*][1,2,3]triazole-1-oxide (6)[6]



1a **6**, 76%

A mixture of 2-nitroazobenzene (**1a**, 681 mg, 3 mmol), EtOH (10 mL) and NaOH solution (1 N, 12 mL) heated at 90 °C was treated with powdered $HONH_2$·HCl (625 mg, 9 mmol). After 15 min, another $HONH_2$·HCl (625 mg, 9 mmol) was added, and then the reaction was maintained at 90 °C for 2 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and diluted with DCM and water. The organic phase was separated and concentrated followed by column chromatography to give 477 mg of **6** (76% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 2H), 7.82-7.75 (m, 2H), 7.61-7.57 (m, 2H), 7.54-7.51 (m, 1H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 135.1, 129.8, 129.1, 129.0, 126.4, 126.3, 123.4, 119.0, 113.9.

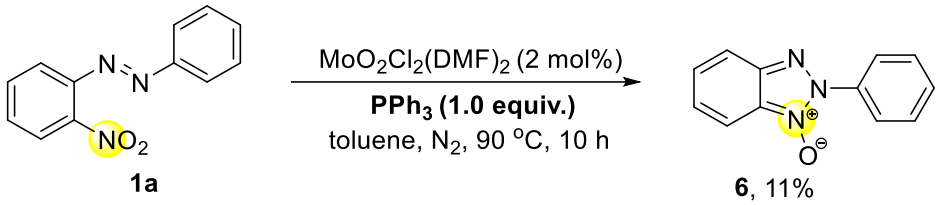
Controlled experiments



6 **2a**, 83%

Under nitrogen atmosphere, a sealed tube was charged with **6** (0.2 mmol, 1.0 equiv.), $MoO_2Cl_2(DMF)_2$ (0.004 mmol, 2 mol%), PPh_3 (0.48 mmol, 2.4 equiv.) and 2 mL dry toluene were successively added. The reaction mixture was kept stirring at 90 °C for 12 h. After completion of the reaction (monitored by TLC), the mixture was washed with aq. H_2O_2 to oxidize the residual PPh_3, and concentrated in vacuum and the

residue was purified by flash column chromatography on silica gel with petroleum ether-dichloromethane as eluent to give the product **2a** in 83% yield.



Under nitrogen atmosphere, a sealed tube was charged with **1a** (0.2 mmol, 1.0 equiv.), $MoO_2Cl_2(DMF)_2$ (0.004 mmol, 2 mol%), PPh_3 (0.2 mmol, 1.0 equiv.) and 2 mL dry toluene were successively added. The reaction mixture was kept stirring at 90 °C for 10 h. A small amount of **6** could be detected by TLC. Then, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give 4.6 mg of **6** in 11% yield.

7. References

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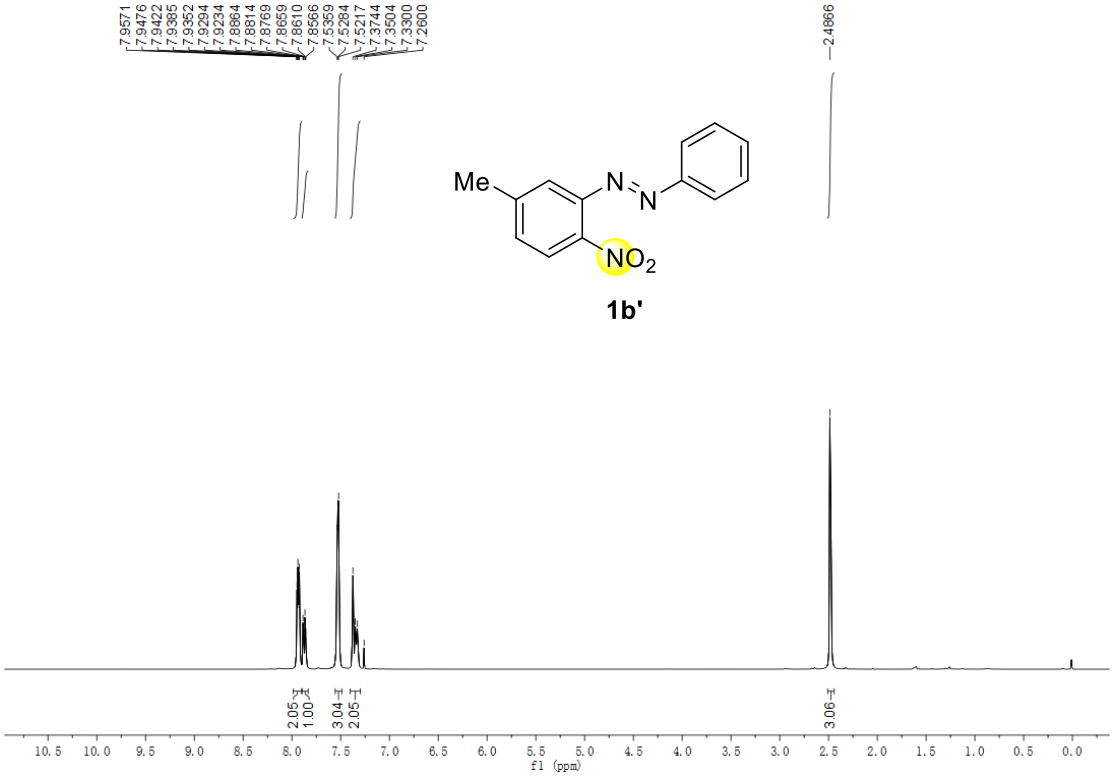
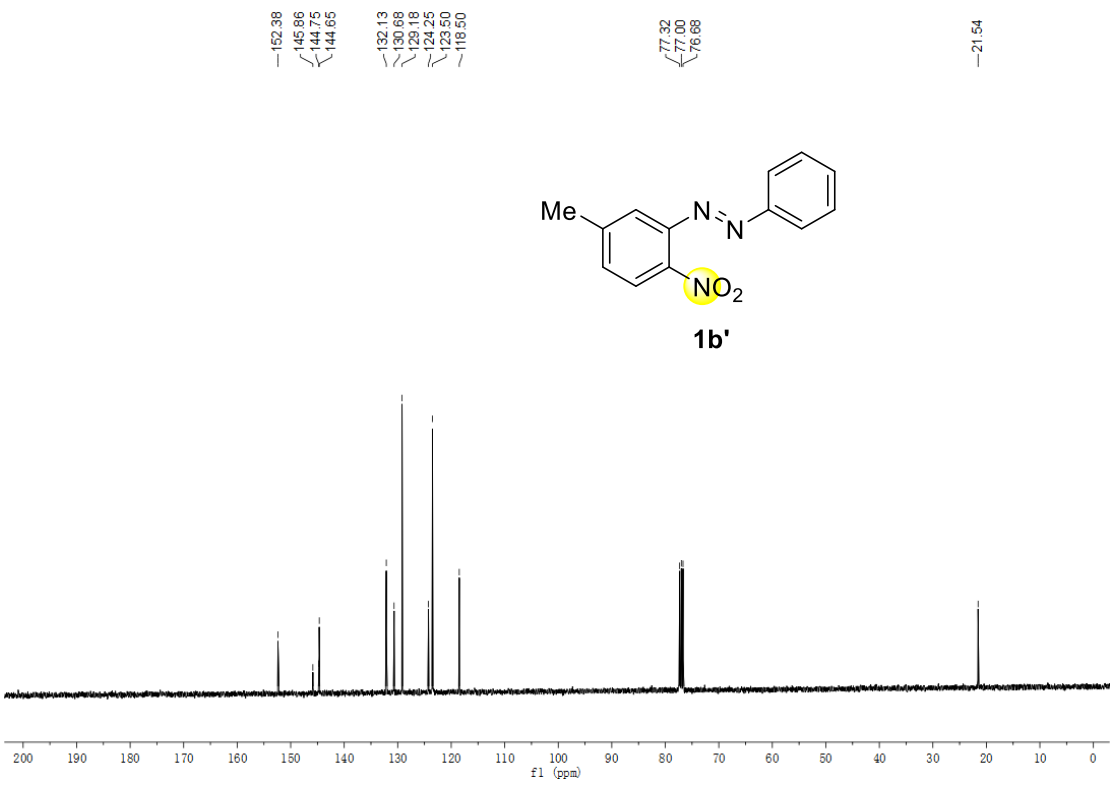
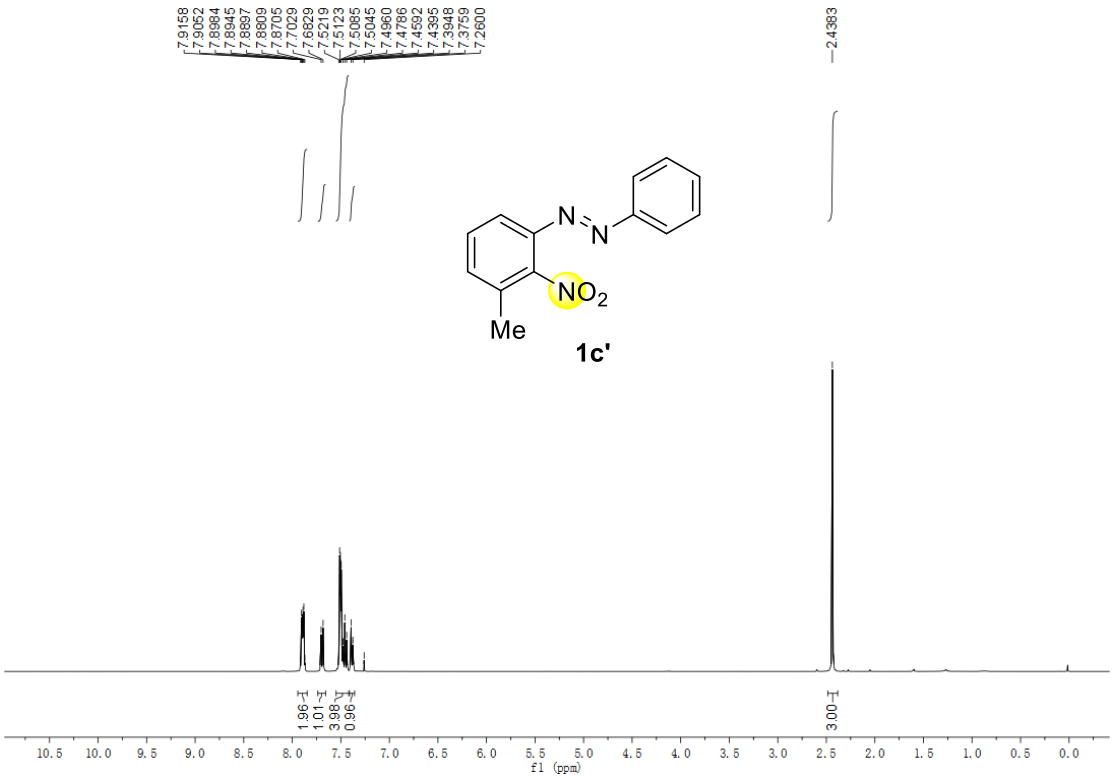
[6] J. F. K. Wilshire, *Aust. J. Chem.*, 1988, **41**, 617.

8. NMR spectra of products



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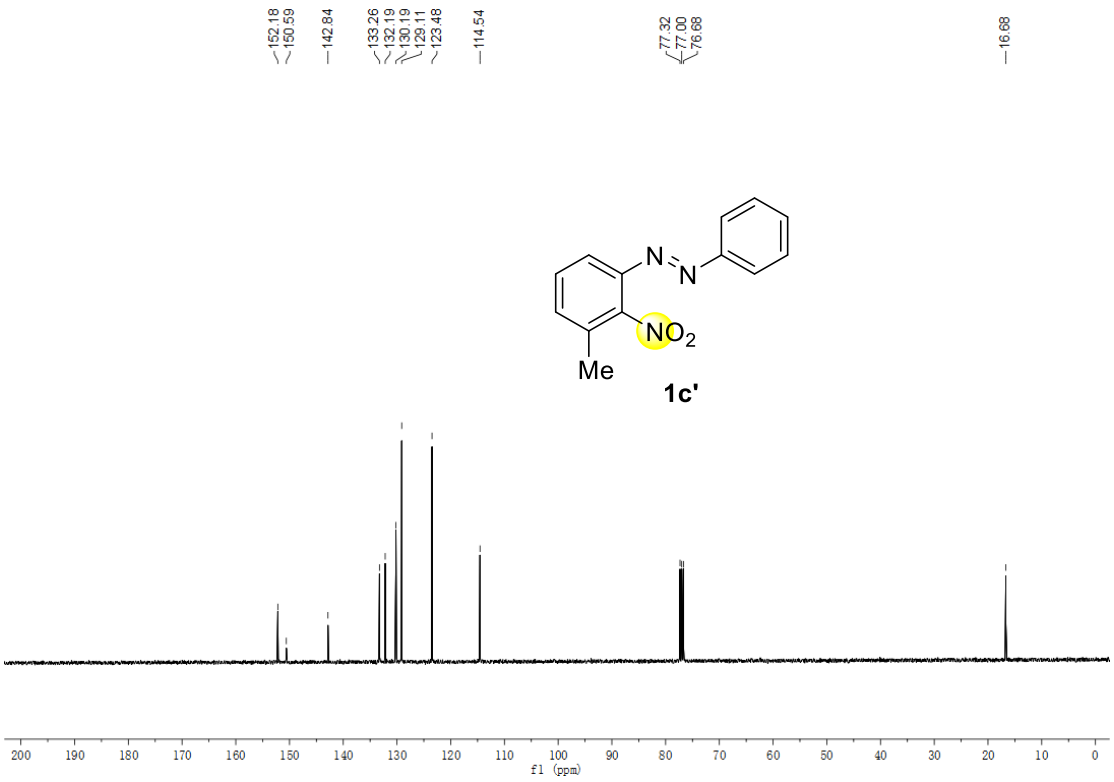
7.5123
7.5085
7.5045
7.4960
7.4786
7.4592
7.4395
7.3948
7.3759
7.2600
2.4383
N
N
NO2
Me
1c'
1.96
1.01
3.98
0.96
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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150.59
142.84
133.26
132.19
130.19
129.11
123.48
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77.32
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16.68
N
N
NO2
Me
1c'
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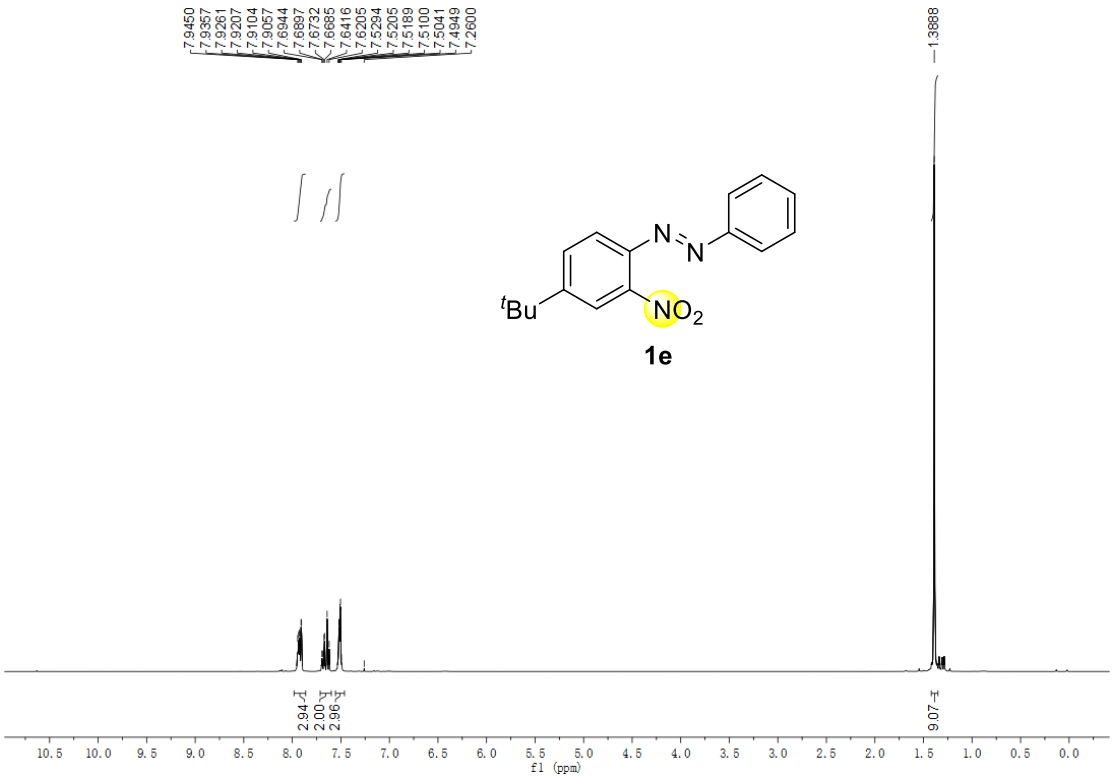
f1 (ppm)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7.9357
7.9261
7.9207
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7.9057
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7.6685
7.6416
7.6205
7.5294
7.5205
7.5189
7.5100
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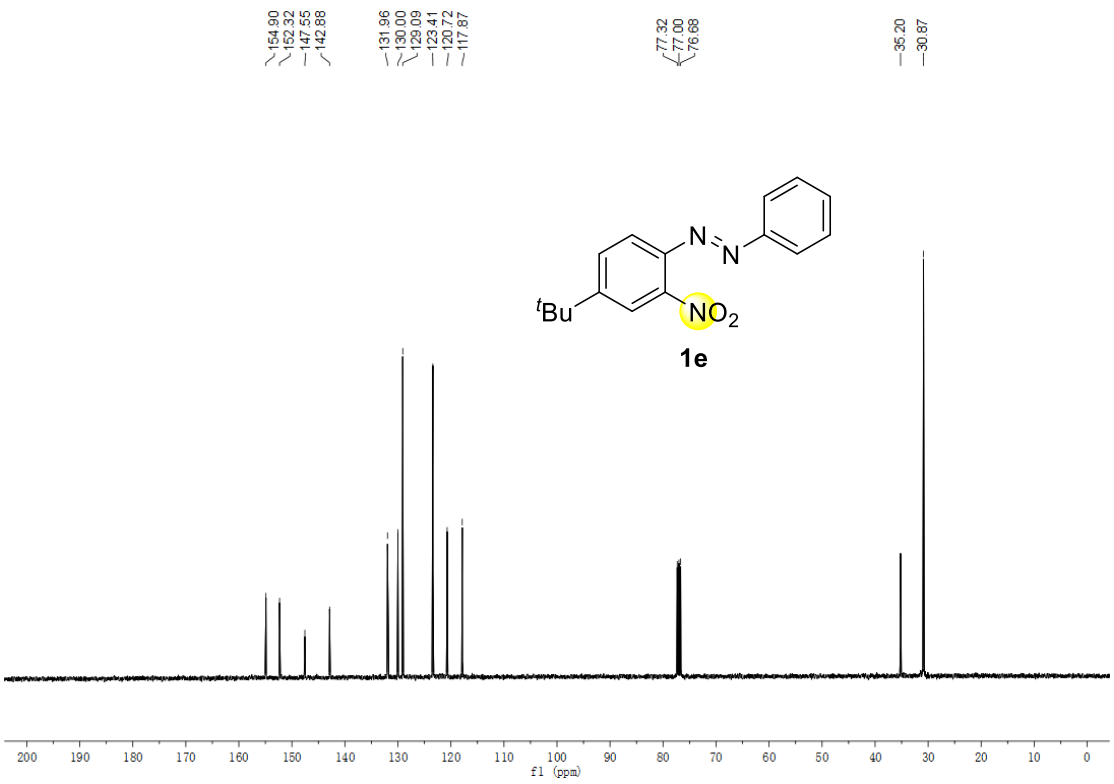
7.2600
1.3888
tBu
NO2
1e
2.94
2.00
2.96
9.07
f1 (ppm)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129.09
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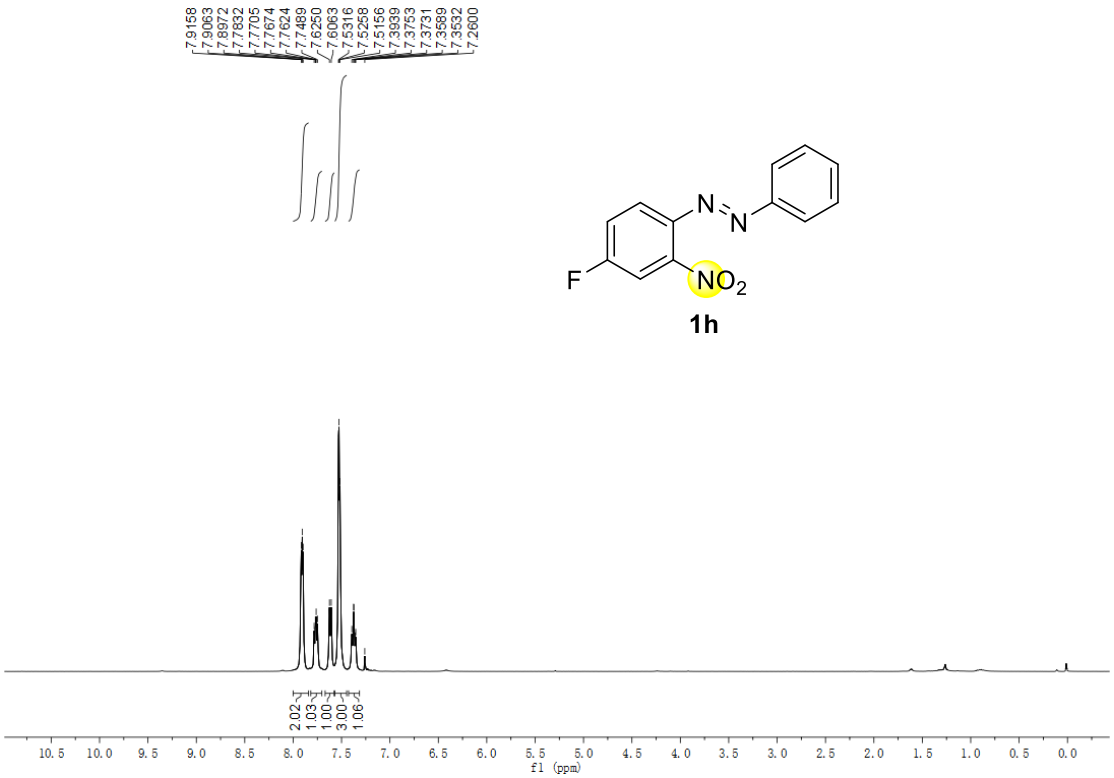
77.00
76.68
35.20
30.87
tBu
NO2
1e
f1 (ppm)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7.8972
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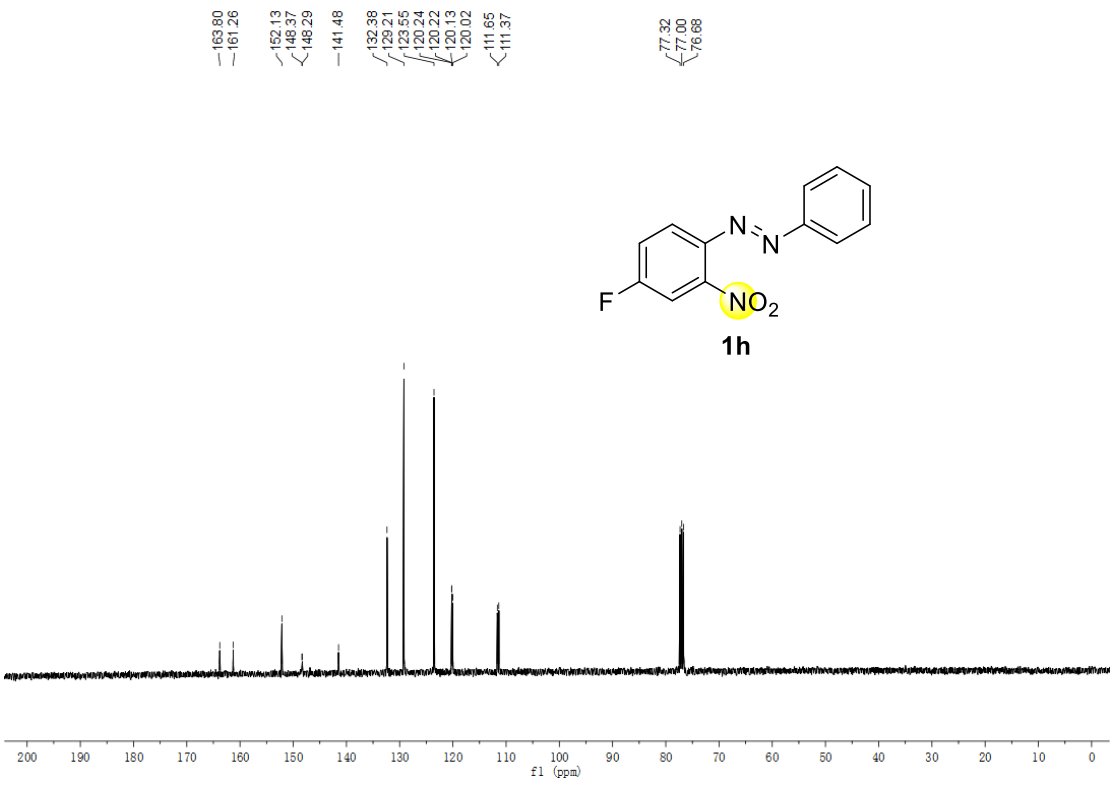
7.5316
7.5258
7.5156
7.3939
7.3753
7.3731
7.3589
7.3532
7.2600
N
N
F
NO2
1h
2.02
1.03
1.00
3.00
1.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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148.37
148.29
141.48
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129.21
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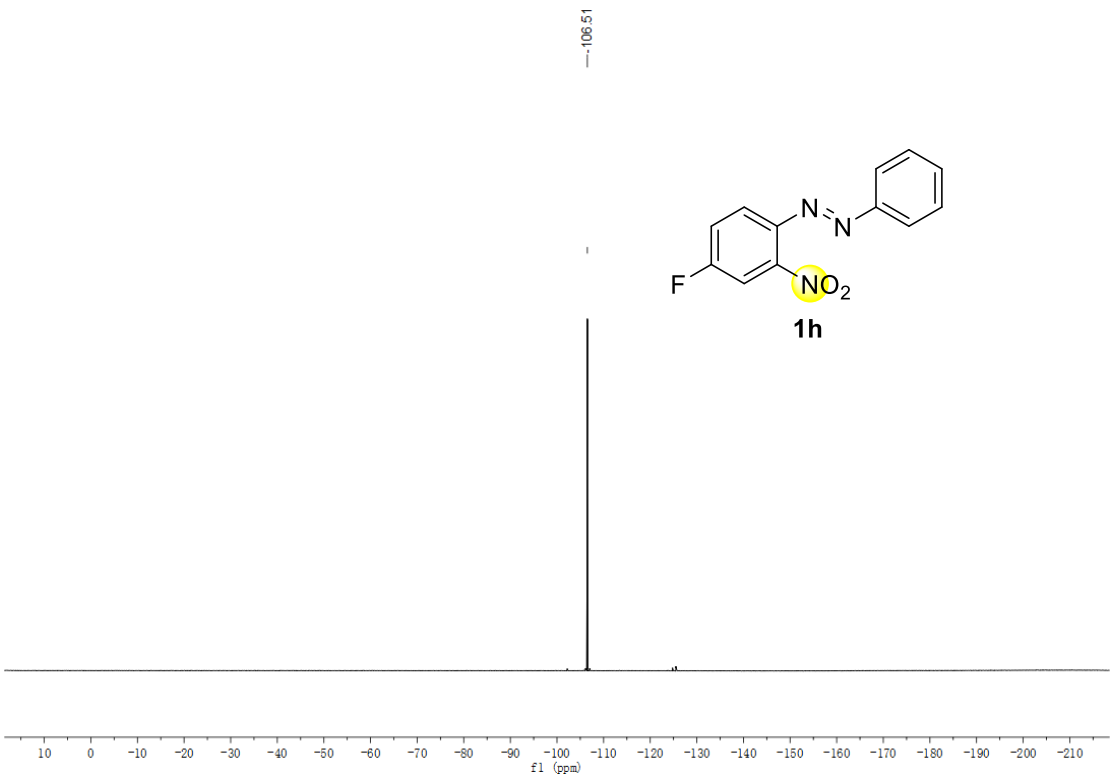
120.24
120.22
120.13
120.02
111.65
111.37
77.32
77.00
76.68
N
N
F
NO2
1h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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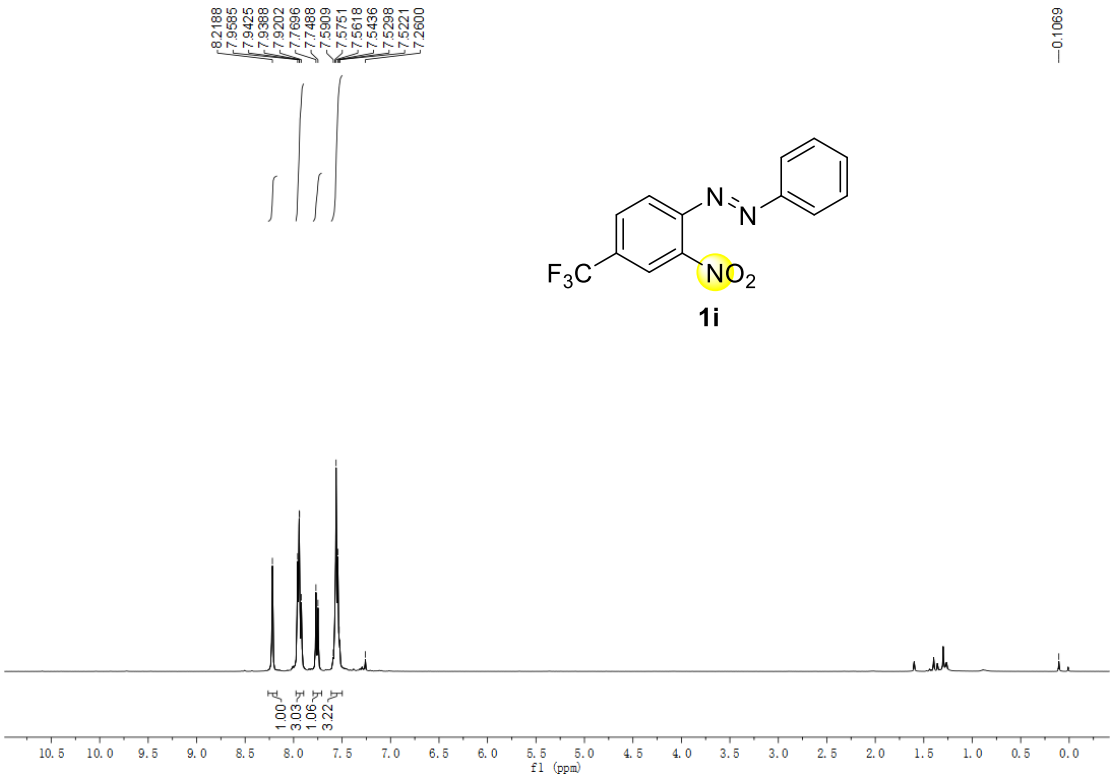
N
F
NO2
1h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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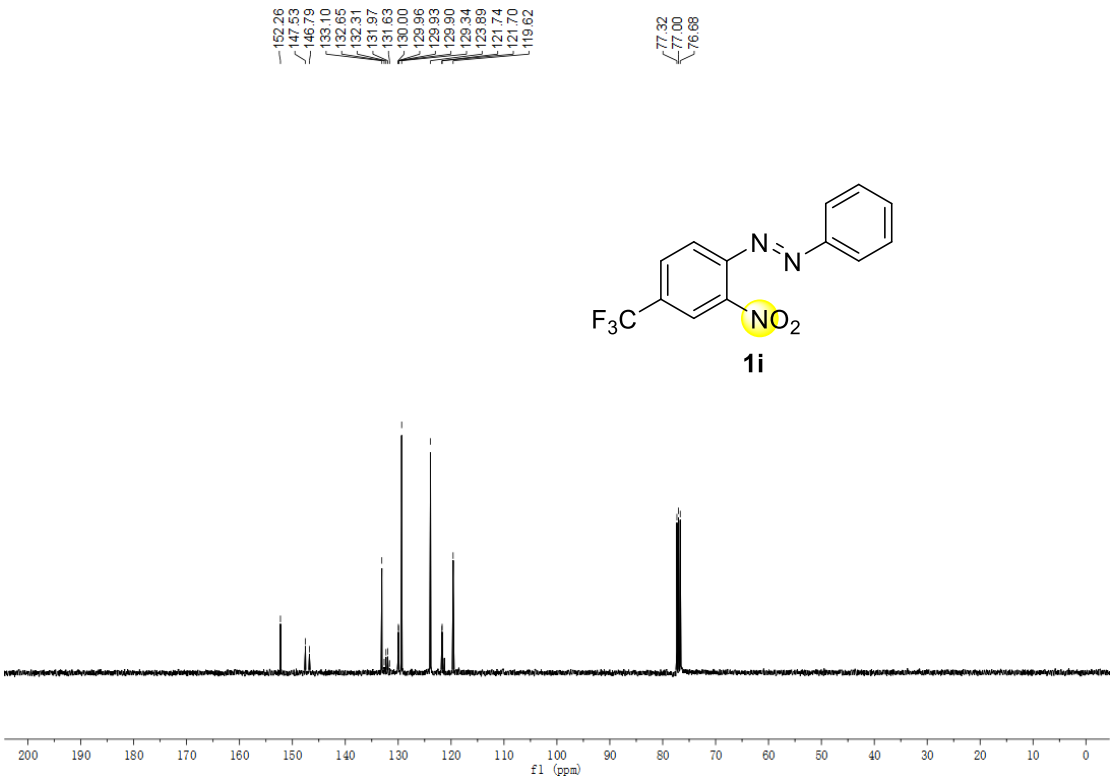
7.9425
7.9388
7.9202
7.7696
7.7488
7.5909
7.5751
7.5618
7.5436
7.5298
7.5221
7.2600
0.1069
N
N
F3C
NO2
1i
1.00
3.03
1.06
3.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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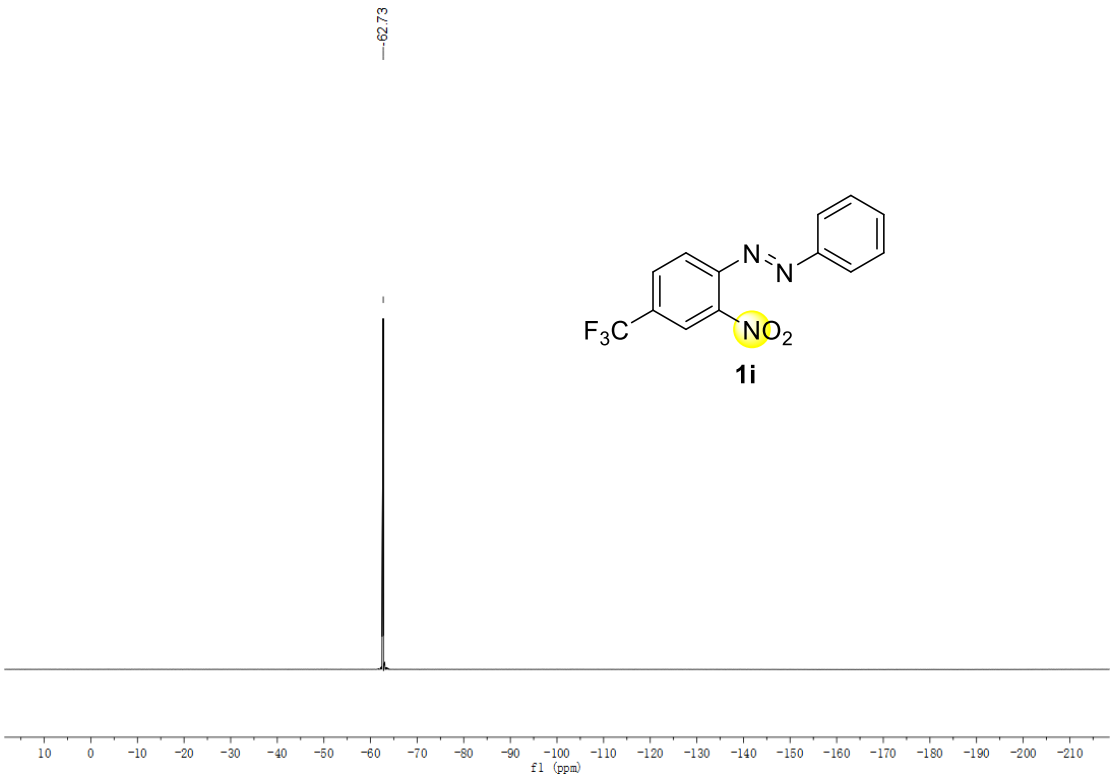
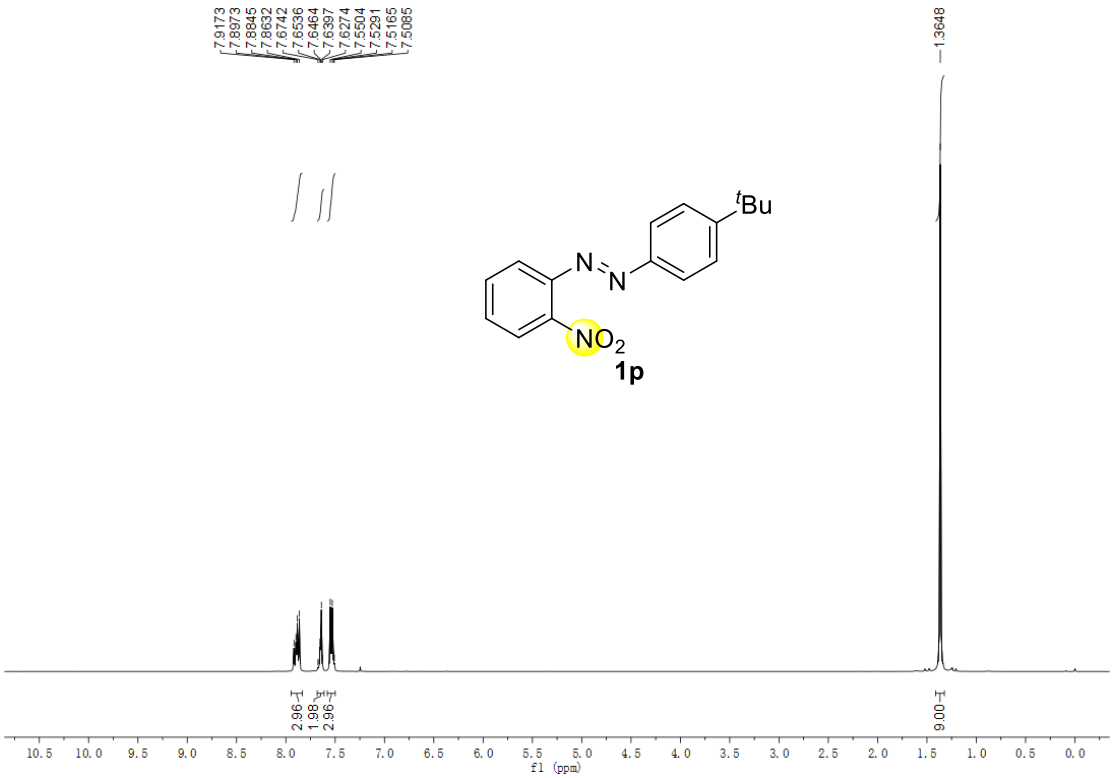
147.53
146.79
133.10
132.65
132.31
131.97
131.63
130.00
129.96
129.93
129.90
129.34
123.89
121.74
121.70
119.62
77.32
77.00
76.68
N
N
F3C
NO2
1i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.73
N
N
F3C
NO2
1i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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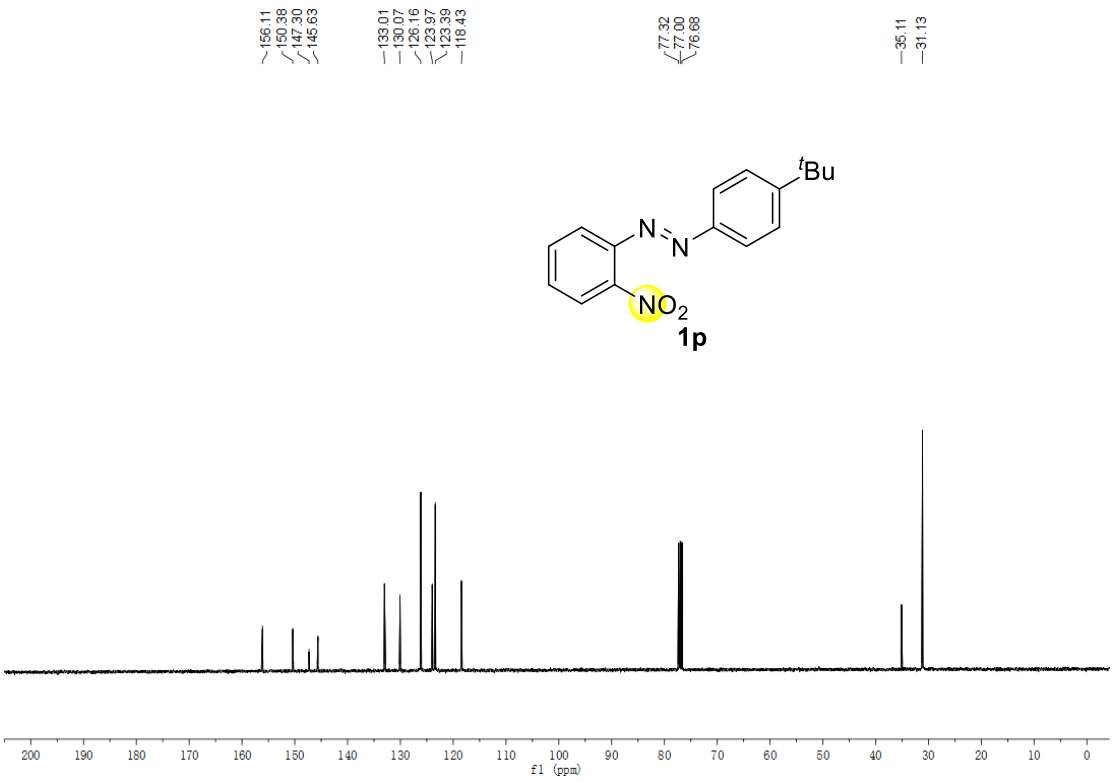
7.8632
7.6742
7.6536
7.6464
7.6397
7.6274
7.5504
7.5291
7.5165
7.5085
1.3648
tBu
N
N
NO2
1p
2.96
1.98
2.96
9.00
f1 (ppm)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150.38
147.30
145.63
133.01
130.07
126.16
123.97
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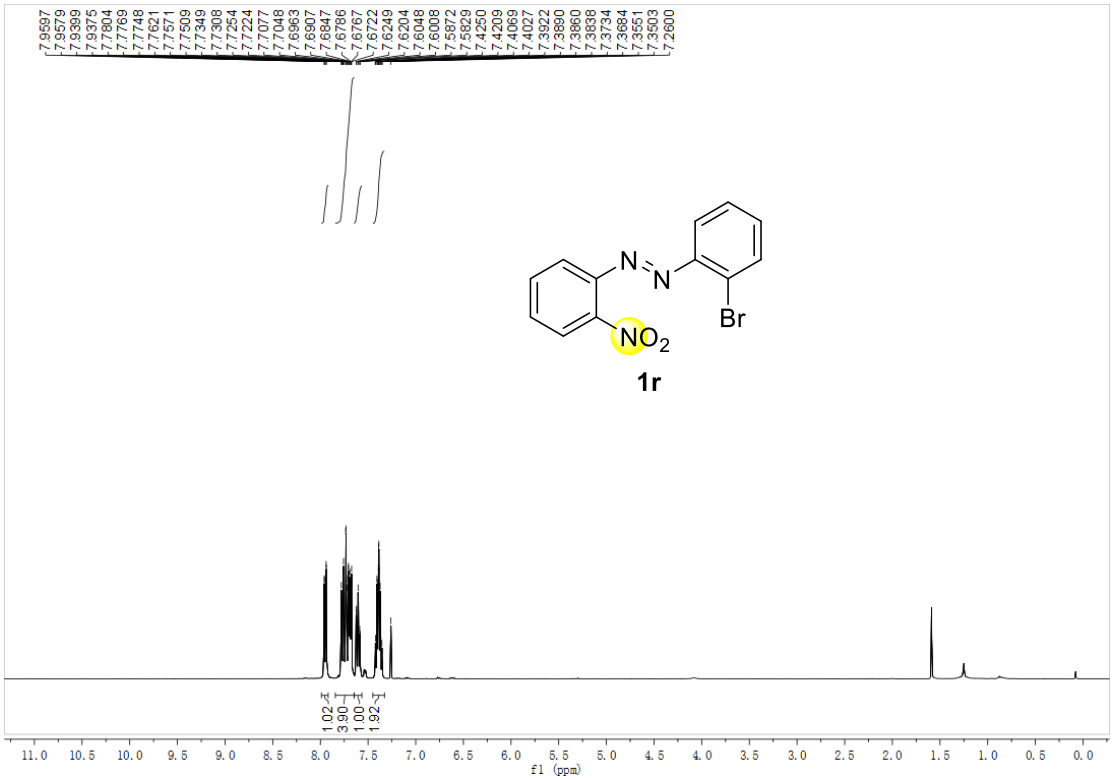
118.43
77.32
77.00
76.68
35.11
31.13
tBu
N
N
NO2
1p
f1 (ppm)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7.7571
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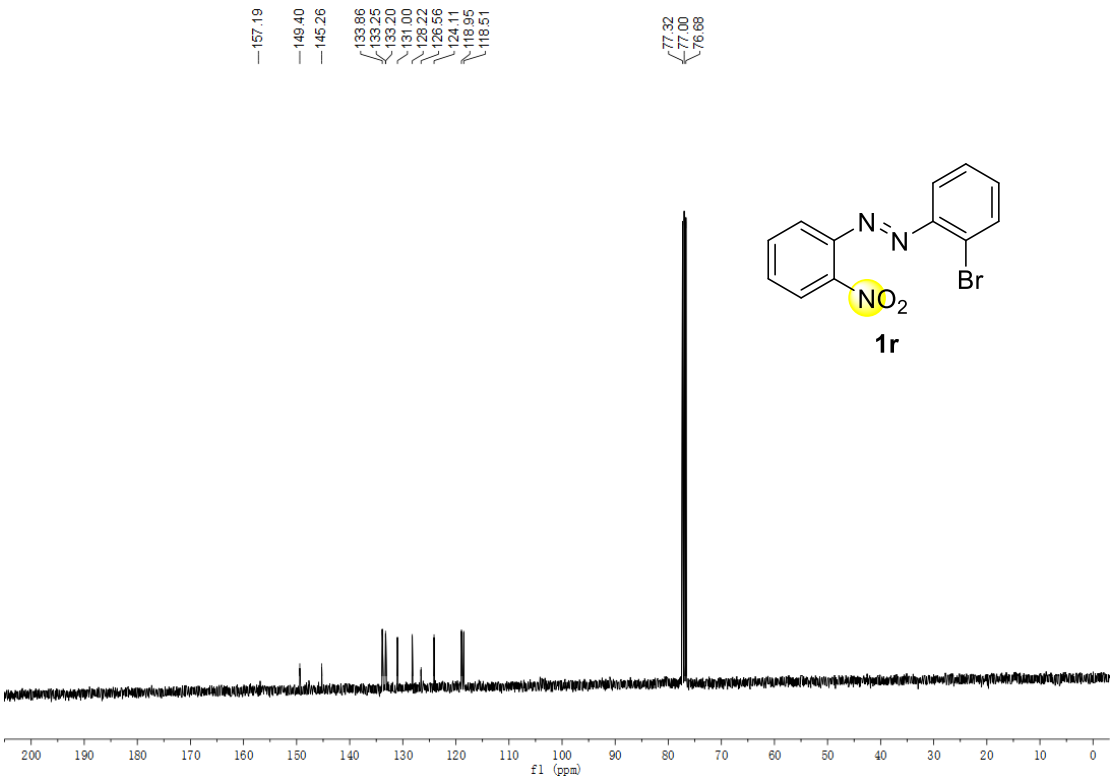
7.7349
7.7308
7.7254
7.7224
7.7077
7.7048
7.6963
7.6907
7.6847
7.6786
7.6767
7.6722
7.6249
7.6204
7.6048
7.6008
7.5872
7.5629
7.4250
7.4209
7.4069
7.4027
7.3922
7.3890
7.3860
7.3838
7.3734
7.3684
7.3551
7.3503
7.2600
N
N
Br
NO2
1r
1.02
3.90
1.00
1.92
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 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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133.20
131.00
128.22
126.56
124.11
118.95
118.51
77.32
77.00
76.68
N
N
Br
NO2
1r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.0058
7.9849
7.9551
7.9352
7.7825
7.7615
7.7115
7.6938
7.6918
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7.6592
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7.6079
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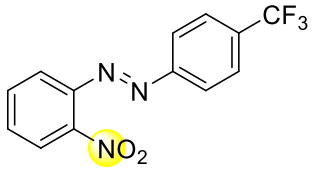
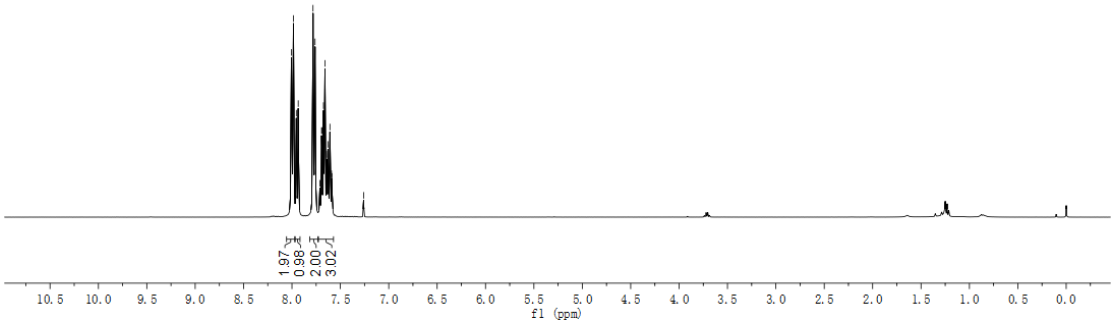
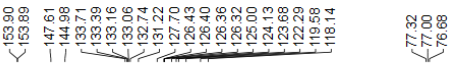
7.5873
7.2600


CF3
N
N
NO2

1v


1.97
0.98
2.00
3.02
10.5 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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119.58
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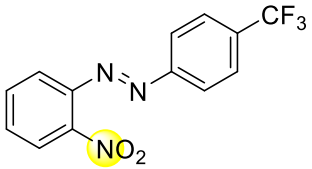
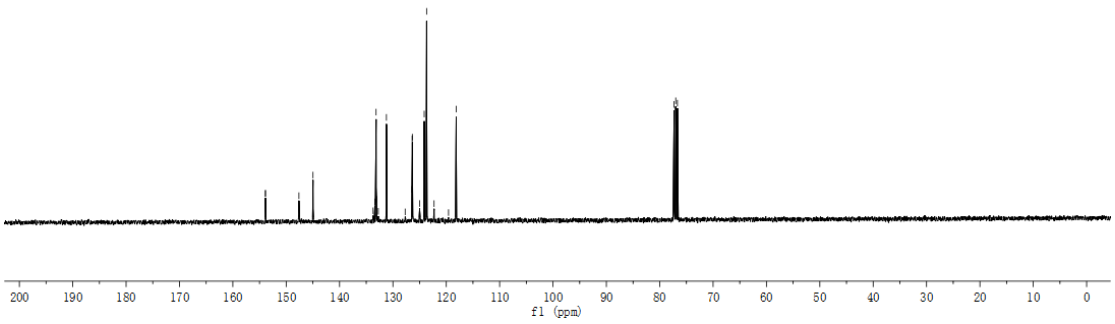
77.32
77.00
76.68


CF3
N
N
NO2

1v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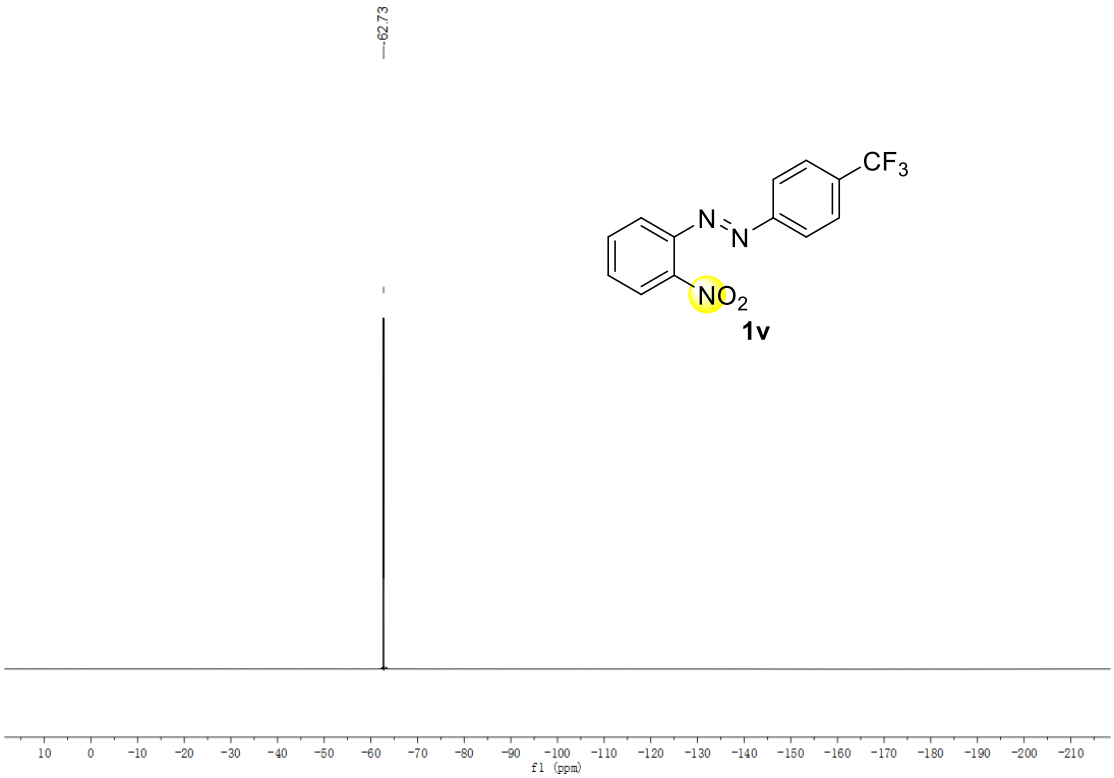
f1 (ppm)


-62.73
CF3
N
N
NO2
1v
10
0
-10
-20
-30
-40
-50
-60
-70
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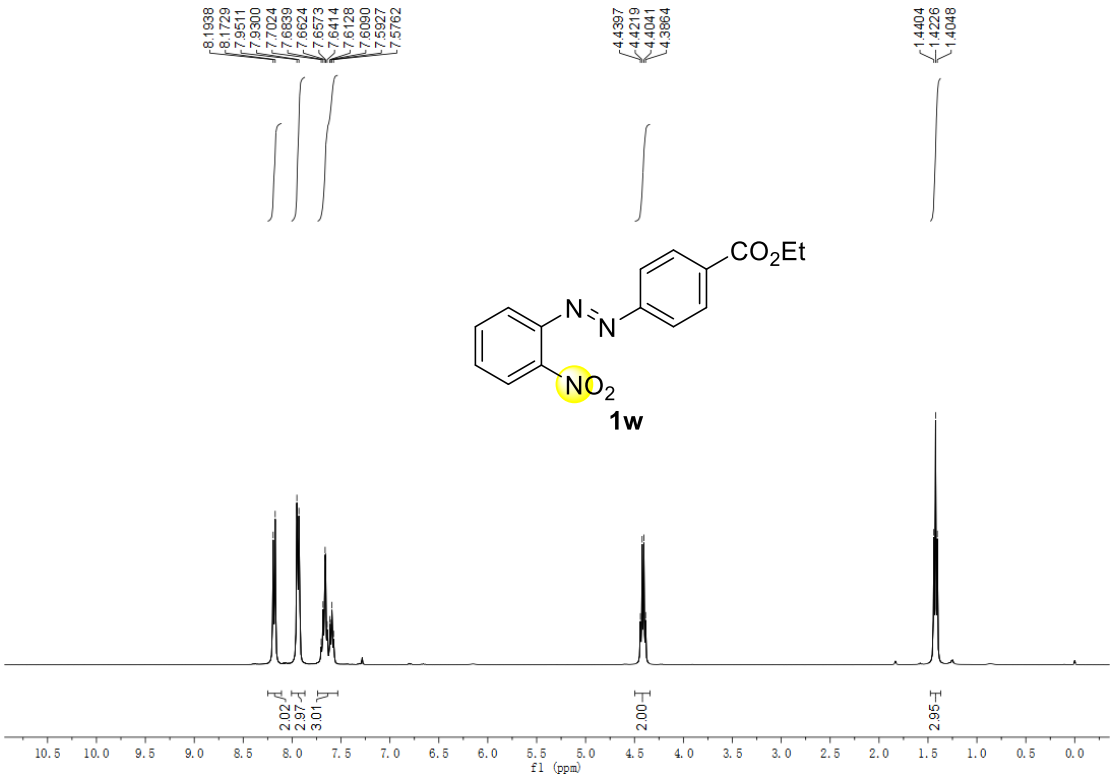
-170
-180
-190
-200
-210
f1 (ppm)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7.6414
7.6128
7.6090
7.5927
7.5762
4.4397
4.4219
4.4041
4.3864
1.4404
1.4226
1.4048
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N
N
NO2
1w
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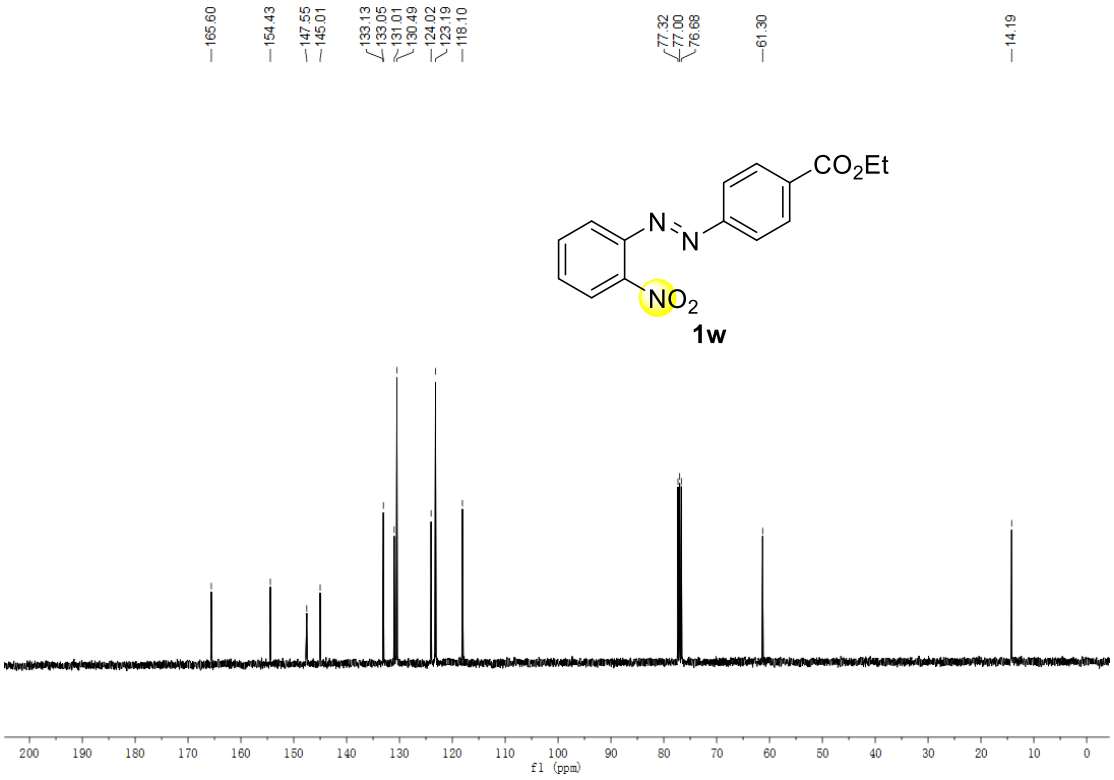
3.01
2.00
2.95
f1 (ppm)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145.01
133.13
133.05
131.01
130.49
124.02
123.19
118.10
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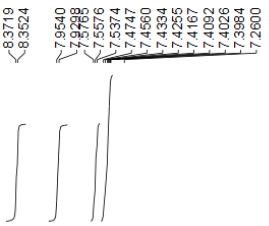
77.00
76.68
61.30
14.19
CO2Et
N
N
NO2
1w
f1 (ppm)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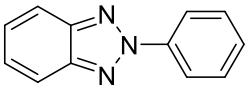
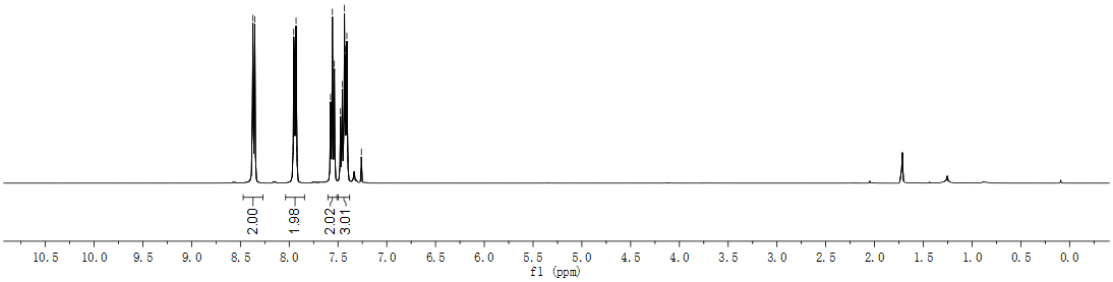
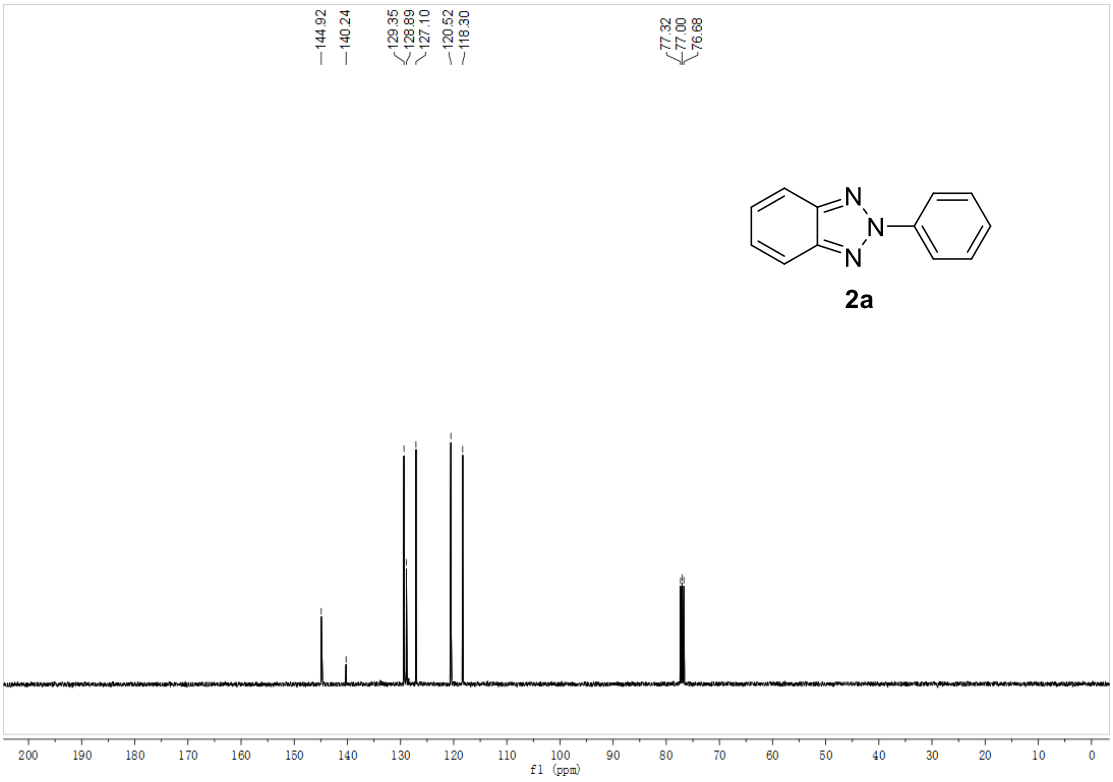
7.4092
7.4026
7.3984
7.2600

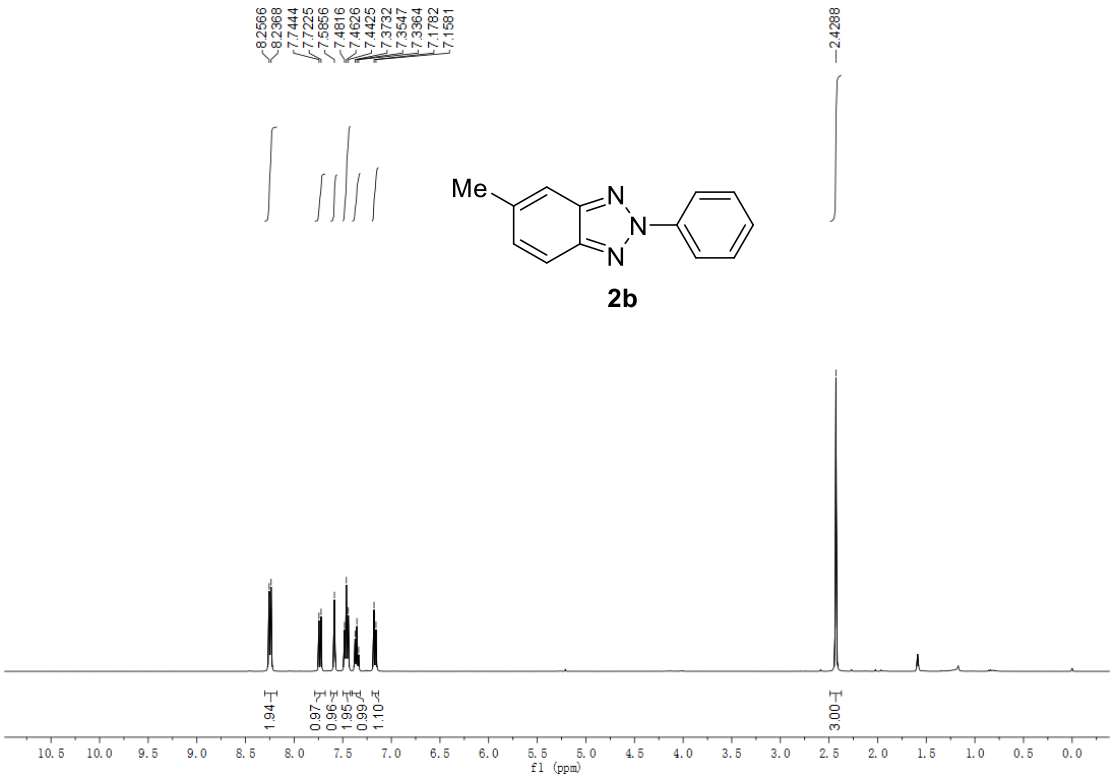


2a


2.00
1.98
2.02
3.01
10.5 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)


144.92
140.24
129.35
128.89
127.10
120.52
118.30
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2a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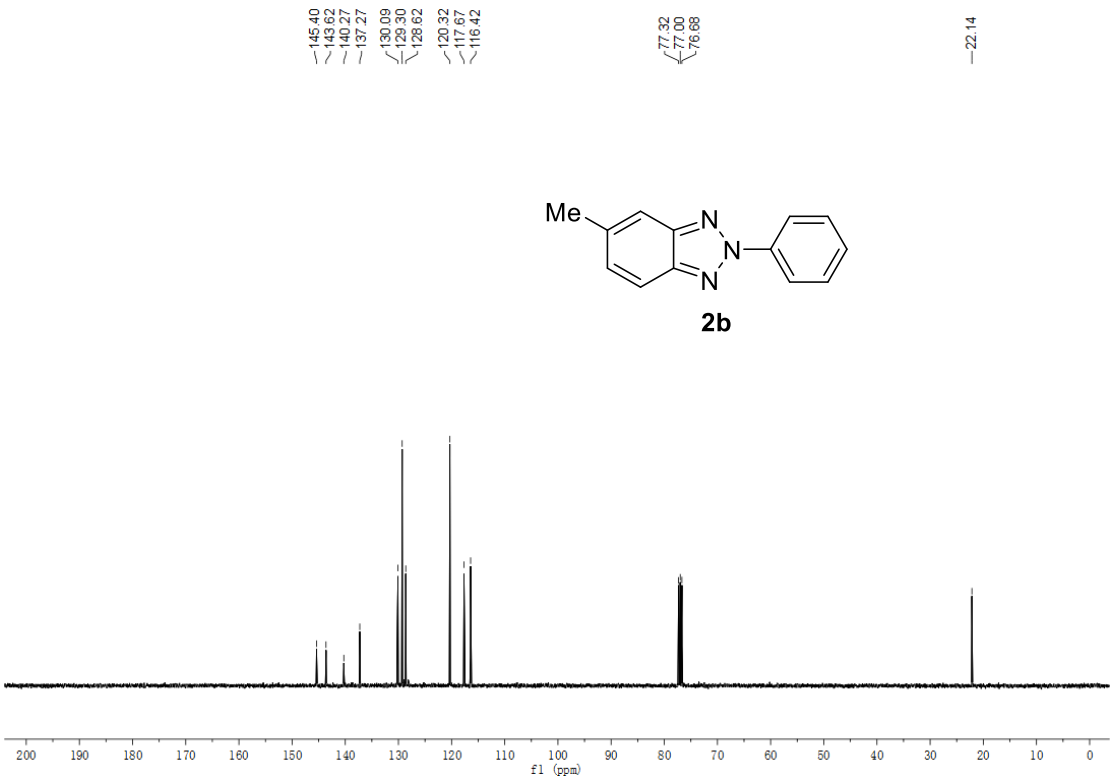
7.5856
7.4816
7.4626
7.4425
7.3732
7.3547
7.3364
7.1782
7.1581
2.4288
Me
N
N
N
1.94
0.97
0.96
1.95
0.99
1.10
3.00
f1 (ppm)

2b


145.40
143.62
140.27
137.27
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129.30
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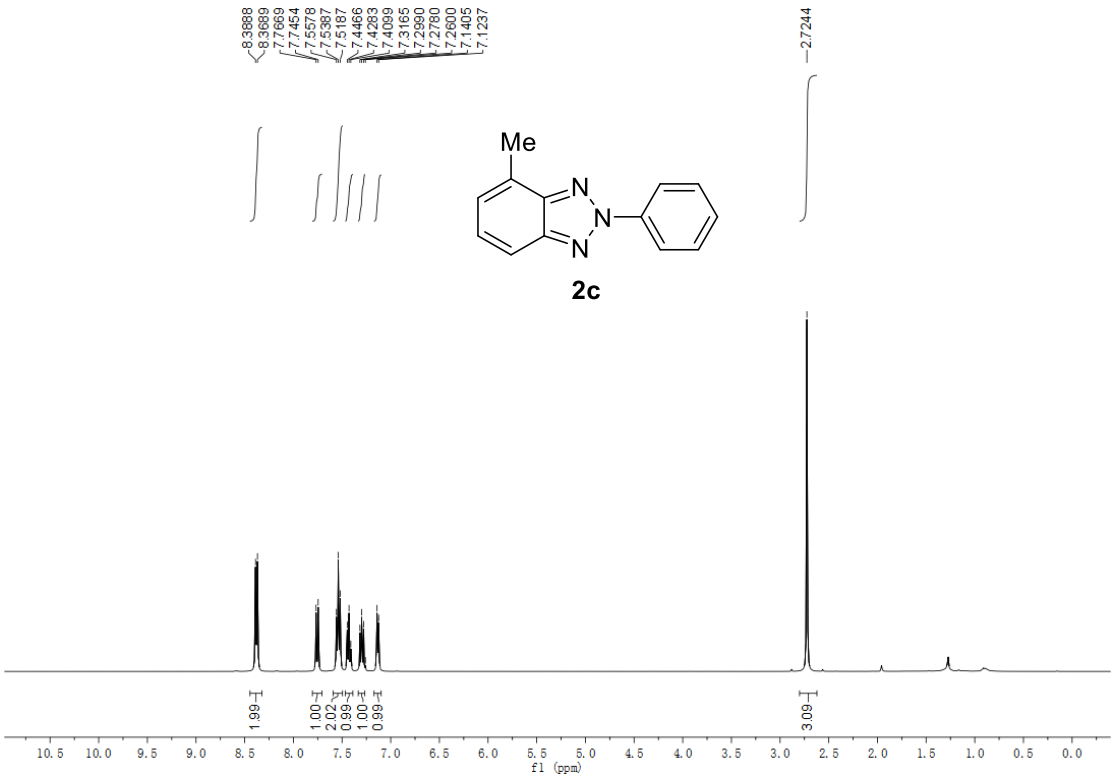
120.32
117.67
116.42
77.32
77.00
76.68
22.14
f1 (ppm)

2b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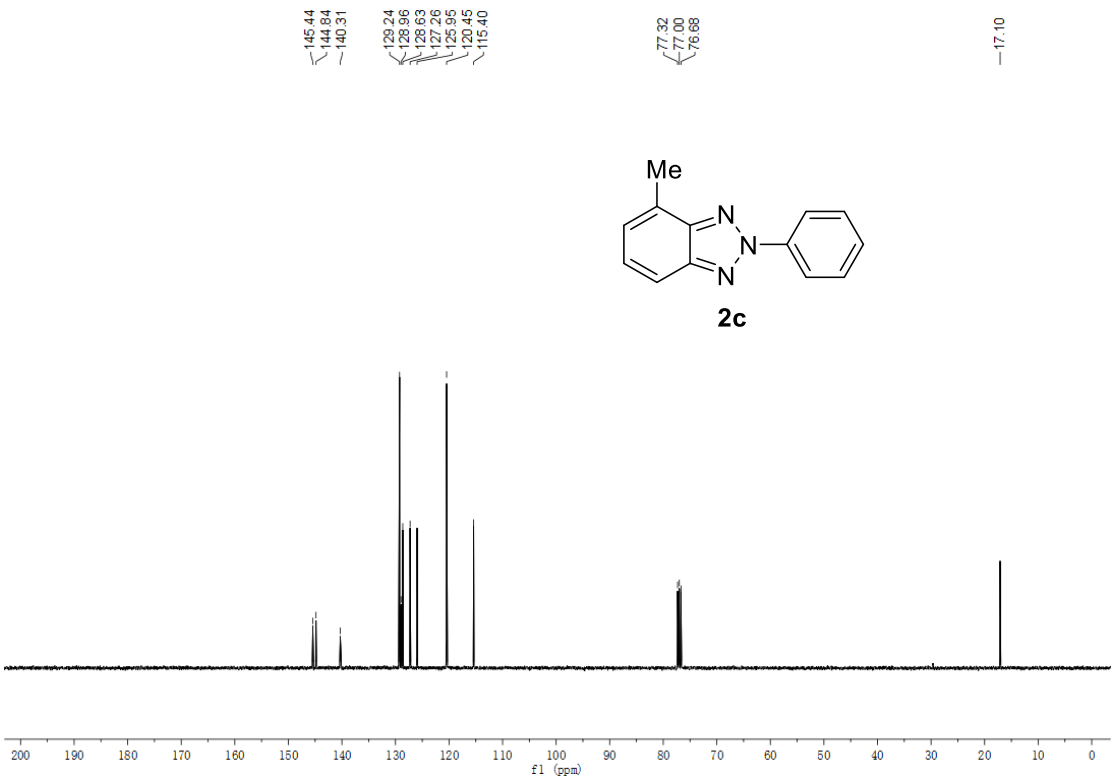
7.7454
7.5578
7.5387
7.5187
7.4466
7.4283
7.4099
7.3165
7.2990
7.2780
7.2600
7.1405
7.1237
2.7244
Me
N
N
N
1.99
1.00
2.02
0.99
1.00
0.99
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2c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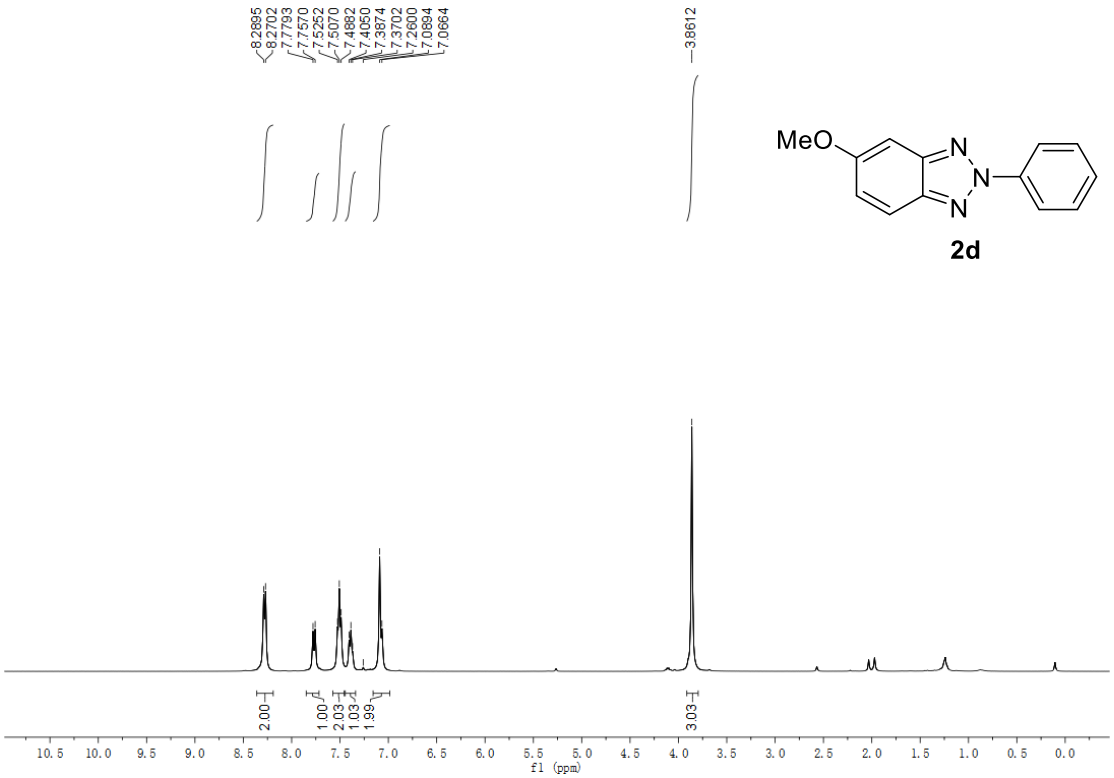
144.84
140.31
129.24
128.96
128.63
127.26
125.95
120.45
115.40
77.32
77.00
76.68
17.10
Me
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2c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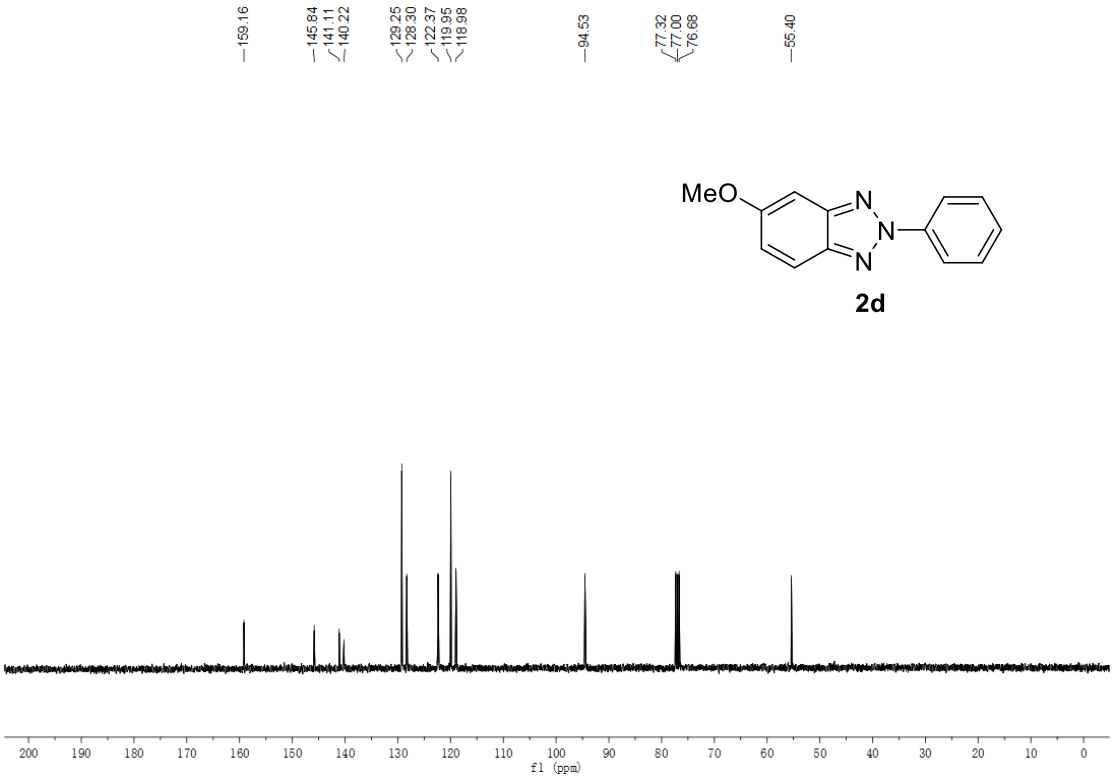
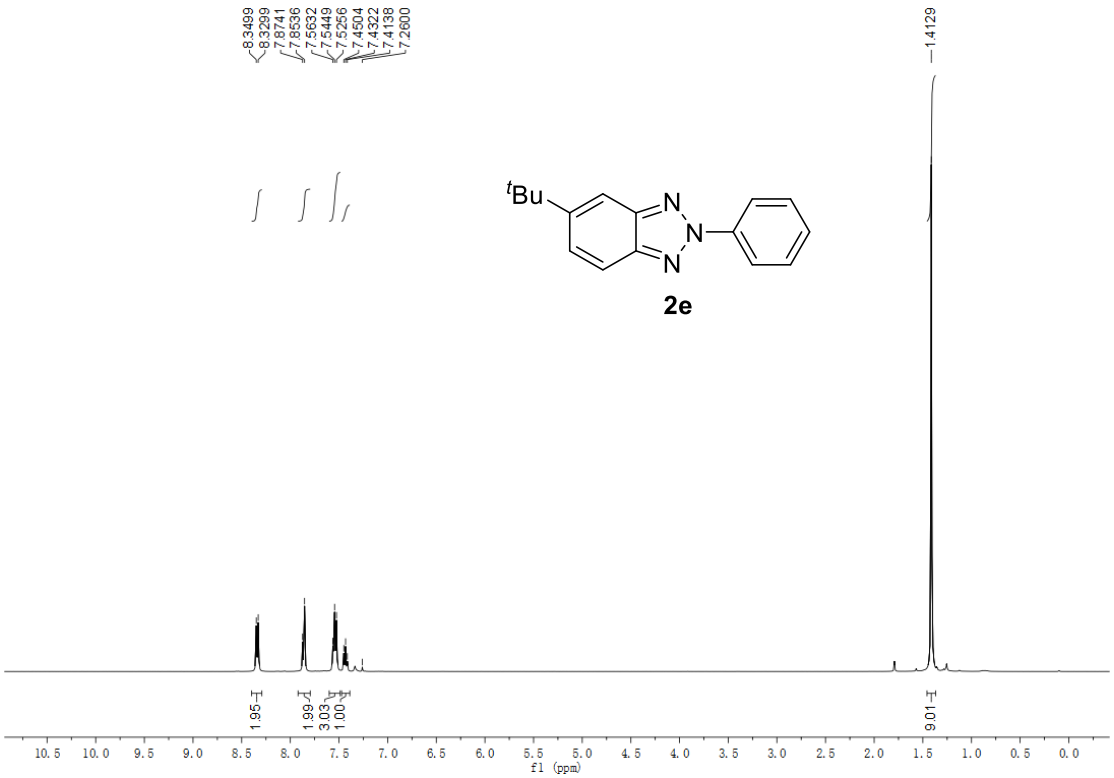
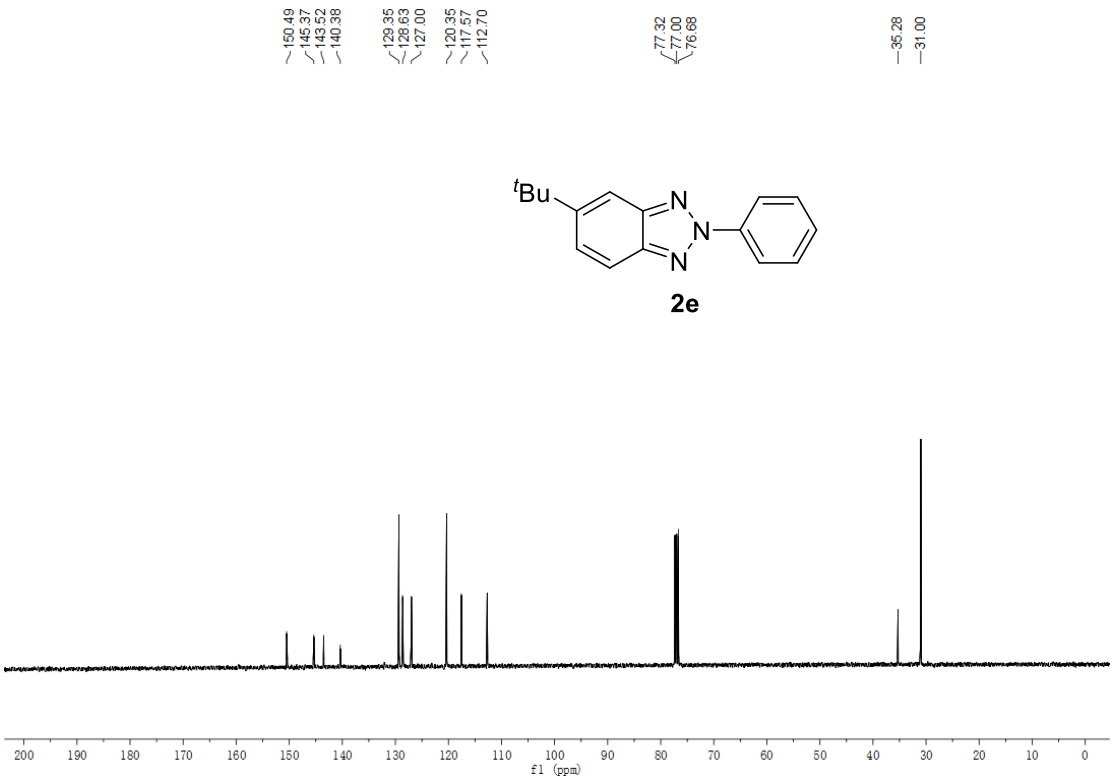
8.2702
7.7793
7.7570
7.5252
7.5070
7.4882
7.4050
7.3874
7.3702
7.2600
7.0894
7.0664
3.8612
MeO
N
N
N
2d
2.00
1.00
2.03
1.03
1.99
3.03
f1 (ppm)


159.16
145.84
141.11
140.22
129.25
128.30
122.37
119.95
118.98
94.53
77.32
77.00
76.68
55.40
MeO
N
N
N
2d
f1 (ppm)


8.3499
8.3299
7.8741
7.8536
7.5632
7.5449
7.5256
7.4504
7.4322
7.4138
7.2600
1.4129
1.95
1.99
3.03
1.00
9.01
10.5 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)

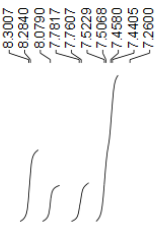
tBu
N
N
N

2e


150.49
145.37
143.52
140.38
129.35
128.63
127.00
120.35
117.57
112.70
77.32
77.00
76.68
35.28
31.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

tBu
N
N
N

2e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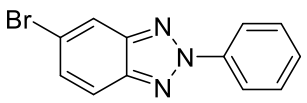
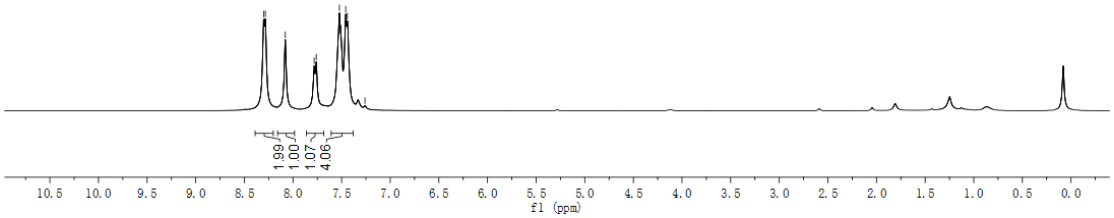
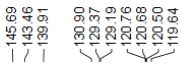
8.0790
7.7817
7.7607
7.5229
7.5068
7.4580
7.4405
7.2600

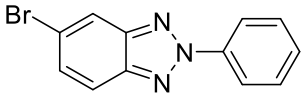

Br
N
N
N

2f

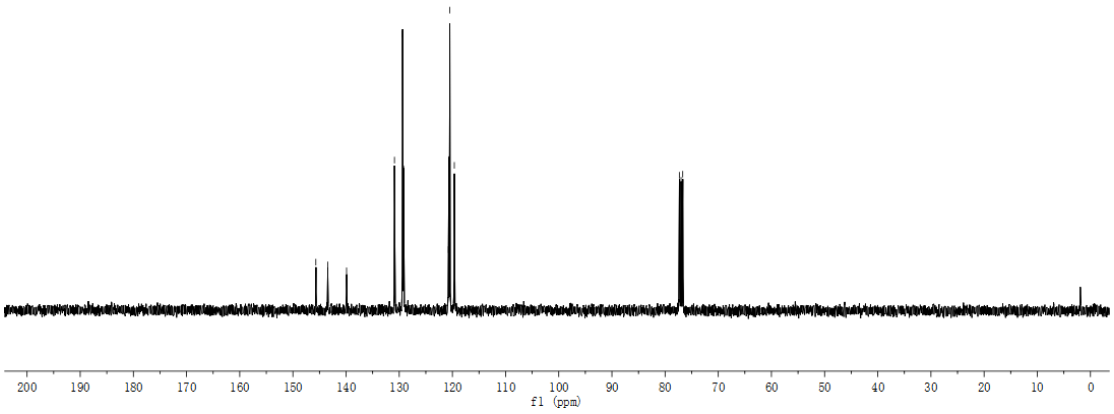

1.99
1.00
1.07
4.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

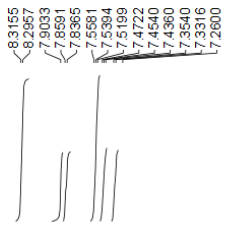

145.69
143.46
139.91
130.90
129.37
129.19
120.76
120.68
120.50
119.64


77.32
77.00
76.68


Br
N
N
N

2f


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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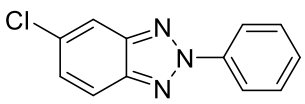
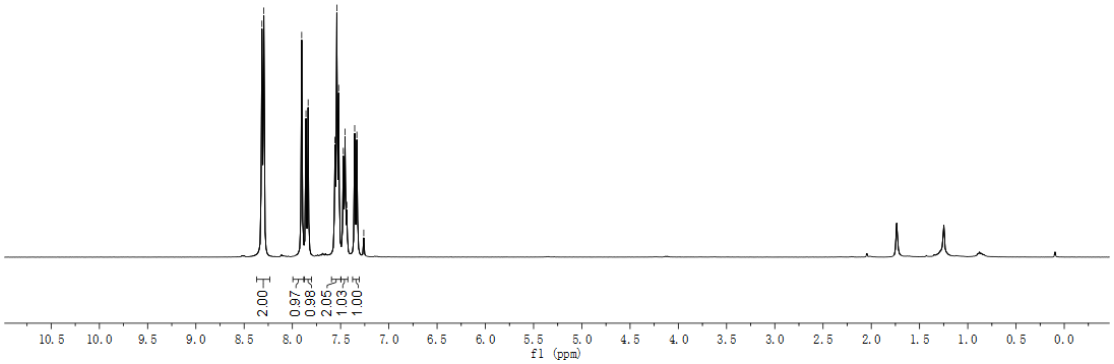
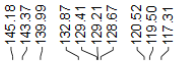
8.2957
7.9033
7.8591
7.8365
7.5581
7.5394
7.5199
7.4722
7.4540
7.4360
7.3540
7.3316
7.2600

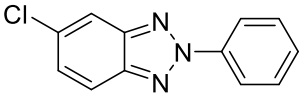

Cl
N
N
N

2g

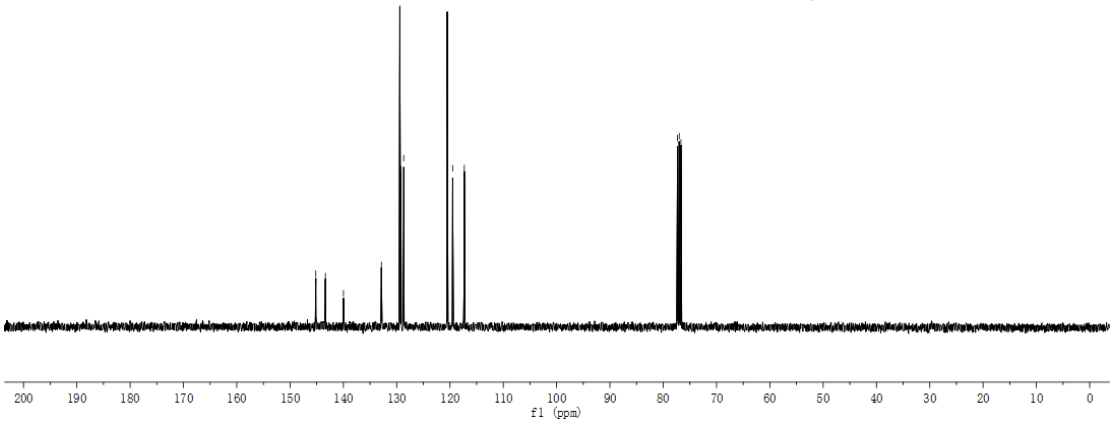

2.00
0.97
0.98
2.05
1.03
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

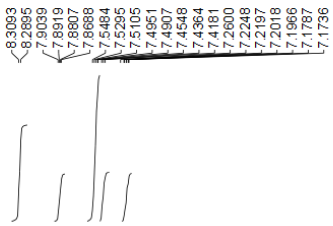

145.18
143.37
139.99
132.87
129.41
129.21
128.67
120.52
119.50
117.31


77.32
77.00
76.68


Cl
N
N
N

2g


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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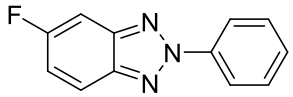
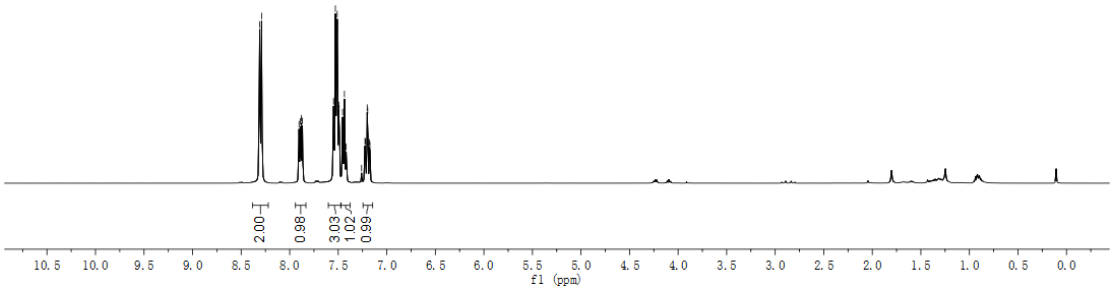
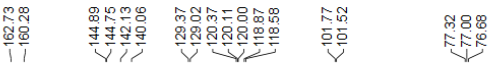
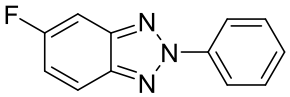
8.2895
7.9039
7.8919
7.8807
7.8688
7.5484
7.5295
7.5105
7.4951
7.4907
7.4548
7.4364
7.4181
7.2600
7.2248
7.2197
7.2018
7.1966
7.1787
7.1736


F
N
N
N

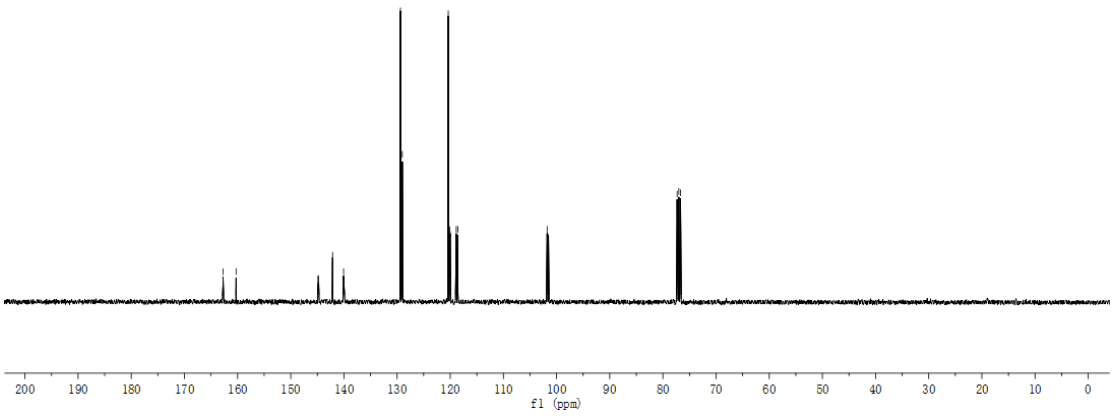
2h

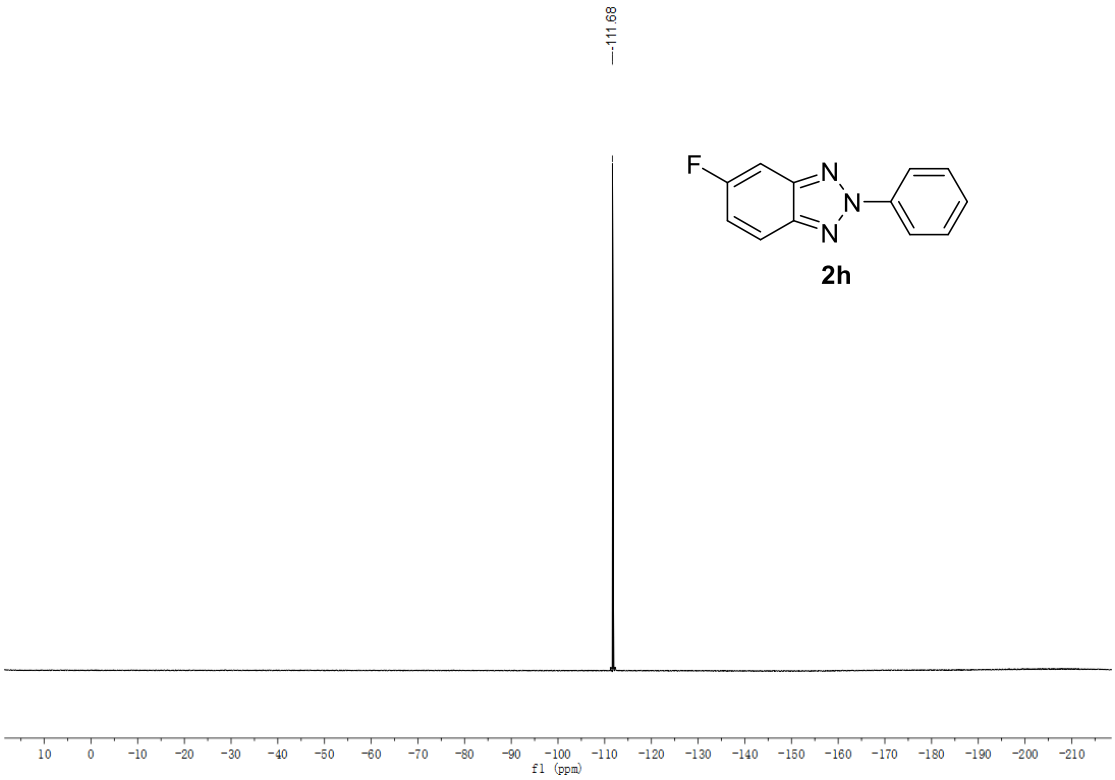

2.00
0.98
3.03
1.02
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

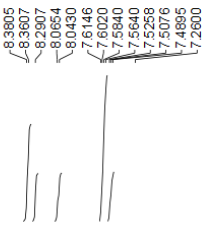

162.73
160.28
144.89
144.75
142.13
140.06
129.37
129.02
120.37
120.11
120.00
118.87
118.58
101.77
101.52
77.32
77.00
76.68

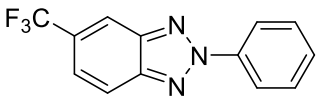

F
N
N
N

2h

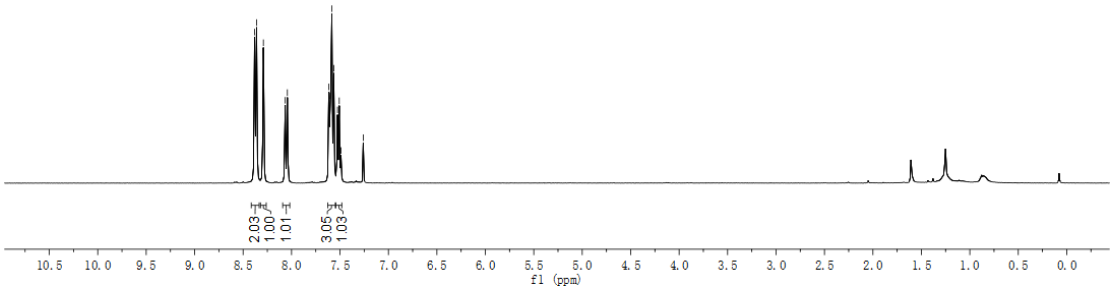

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

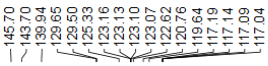

-111.68
F
N
N
N
2h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.3805
8.3607
8.2907
8.0654
8.0430
7.6146
7.6020
7.5840
7.5640
7.5258
7.5076
7.4895
7.2600

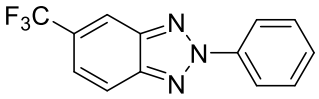

F3C
N
N
N

2i

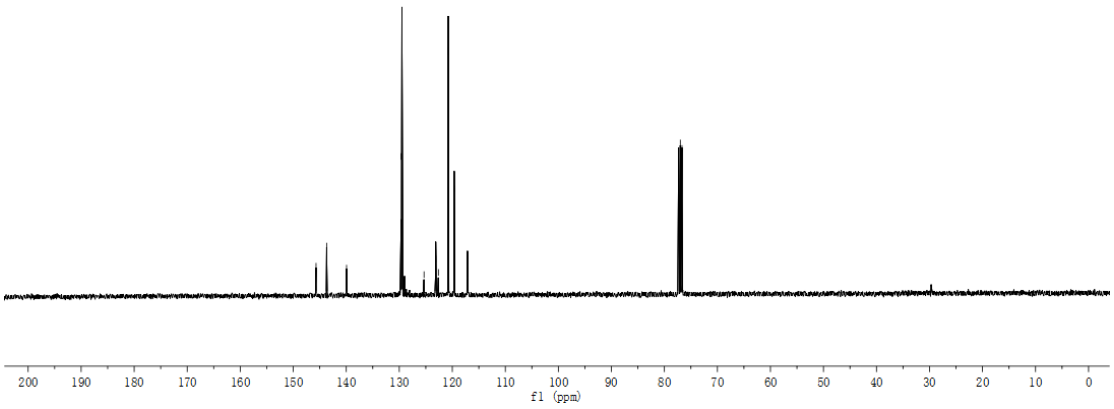

2.03
1.00
1.01
3.05
1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

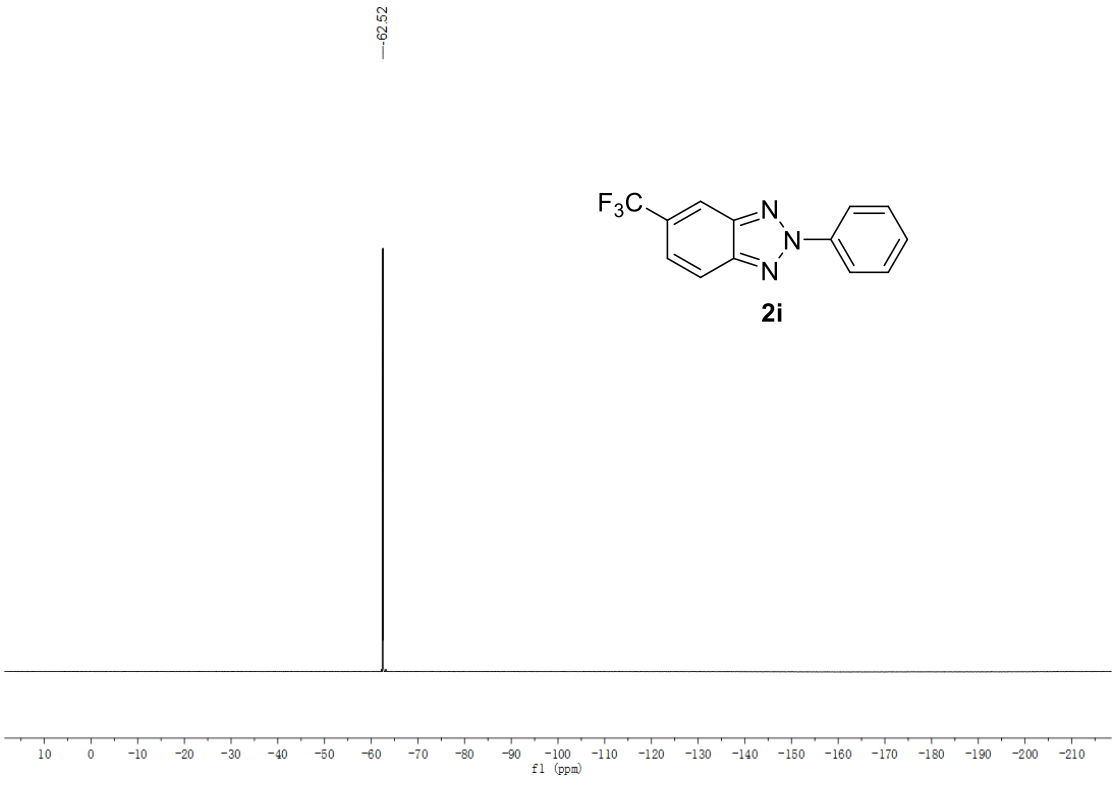

145.70
143.70
139.94
129.65
129.50
125.33
123.16
123.13
123.10
123.07
122.62
120.76
119.64
117.19
117.14
117.09
117.04


77.32
77.00
76.68


F3C
N
N
N

2i


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.52
F3C
N
N
N
2i
10
0
-10
-20
-30
-40
-50
-60
-70
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-100
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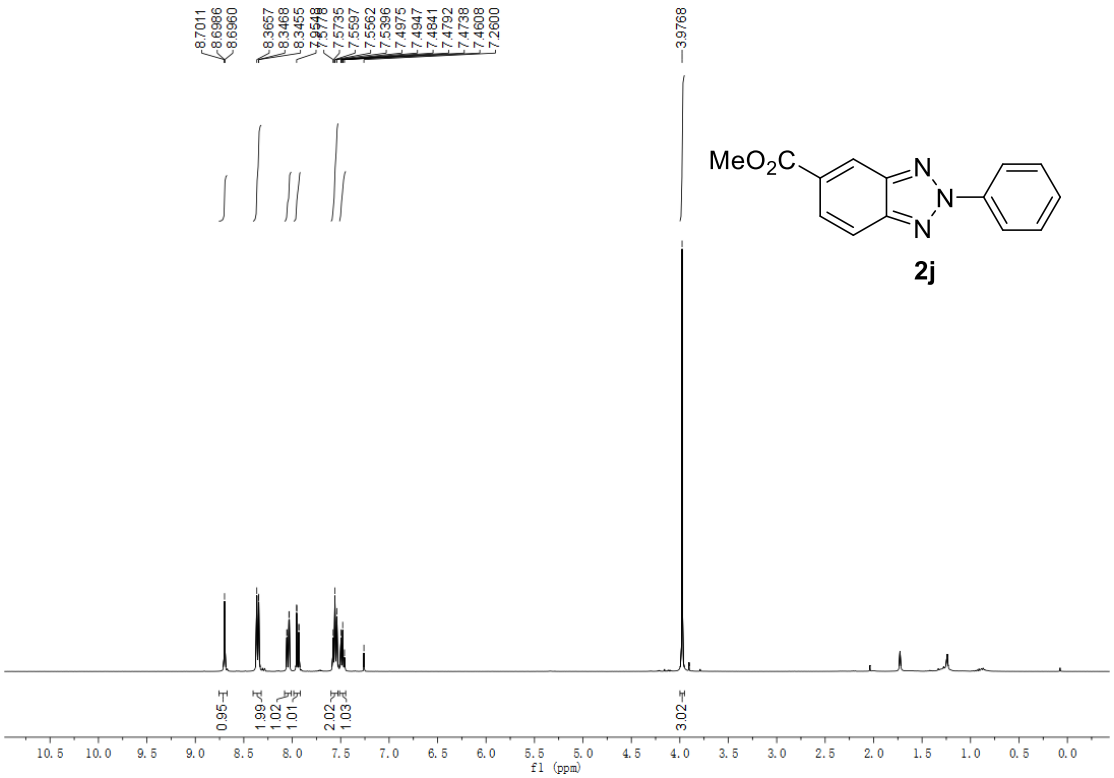
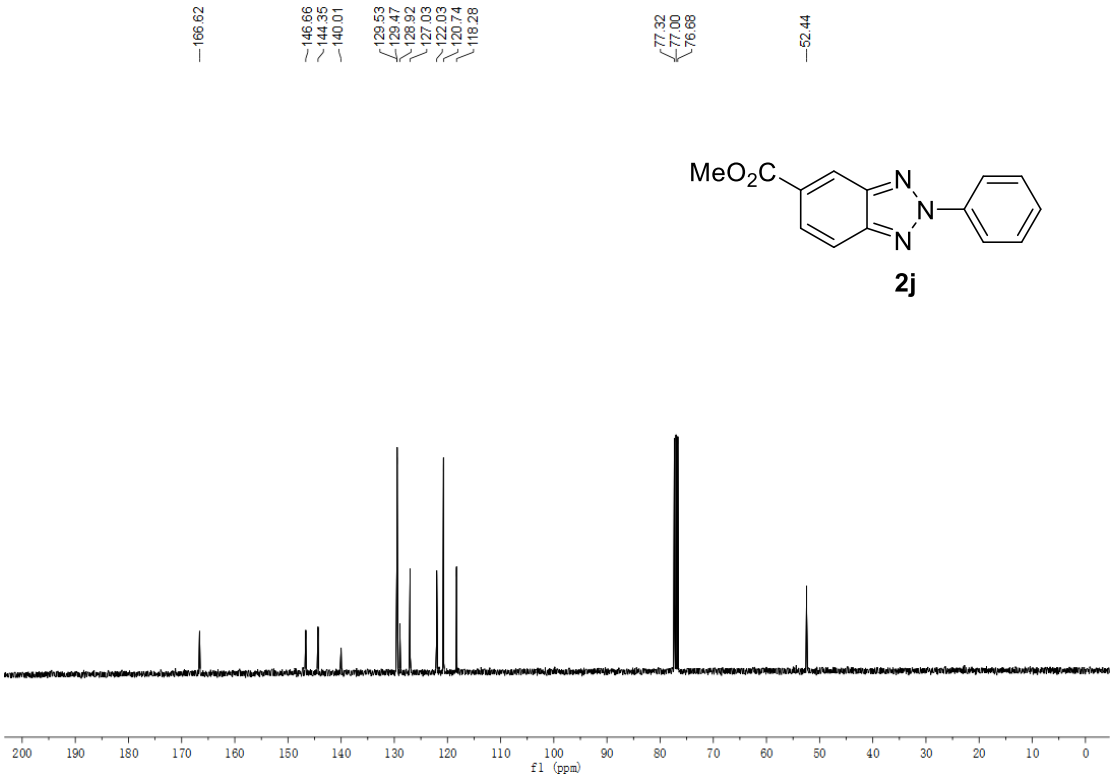
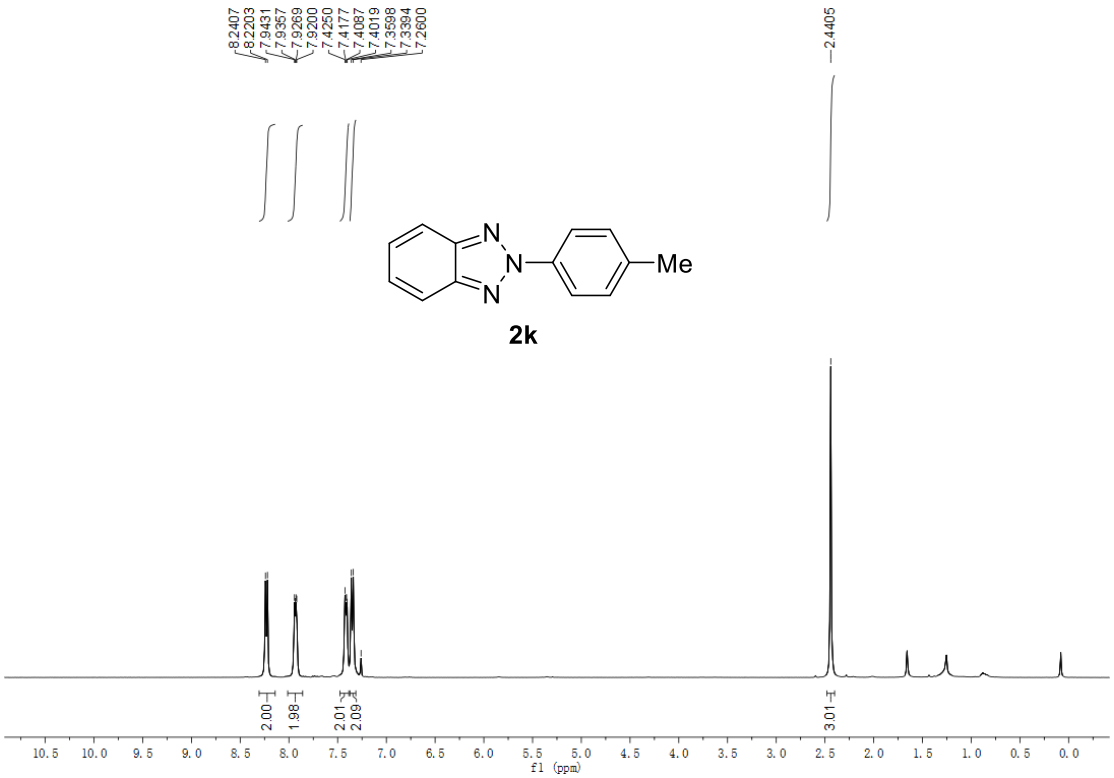
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.7011
8.6986
8.6960
8.3657
8.3468
8.3455
7.5735
7.5597
7.5562
7.5396
7.4975
7.4947
7.4841
7.4792
7.4738
7.4608
7.2600
3.9768
MeO2C
N
N
N
2j
0.95
1.99
1.02
1.01
2.02
1.03
3.02
f1 (ppm)


166.62
146.66
144.35
140.01
129.53
129.47
128.92
127.03
122.03
120.74
118.28
77.32
77.00
76.68
52.44
MeO2C
N
N
N
2j
f1 (ppm)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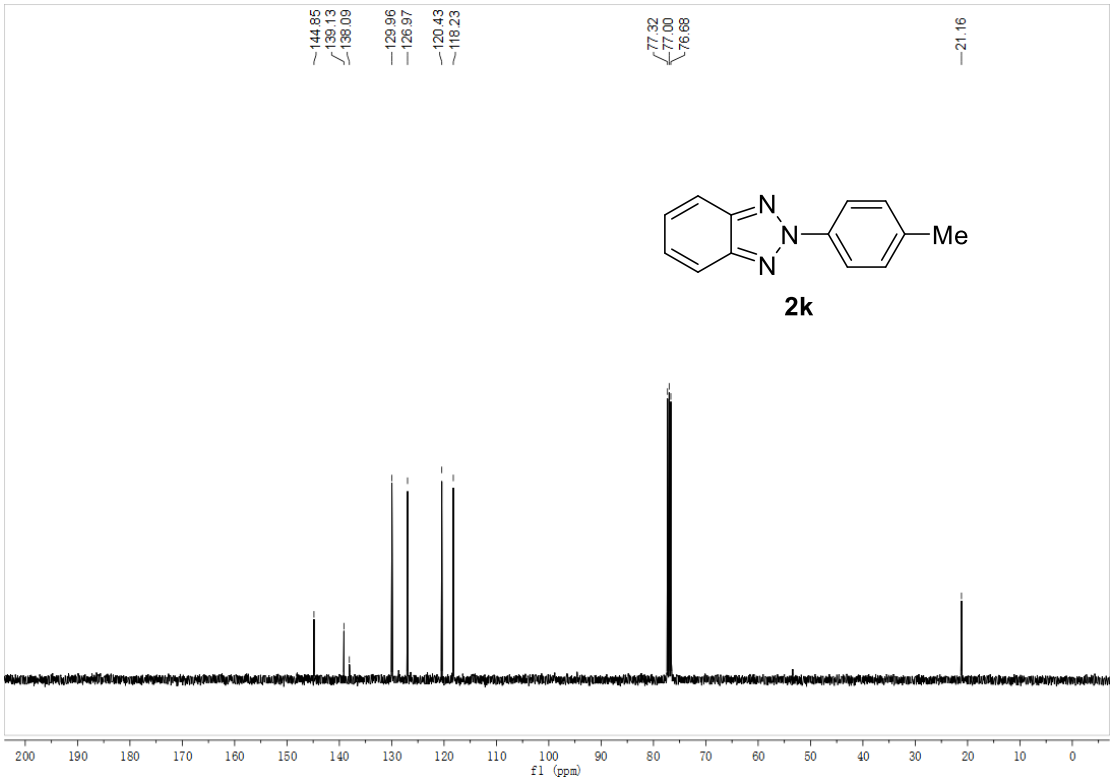
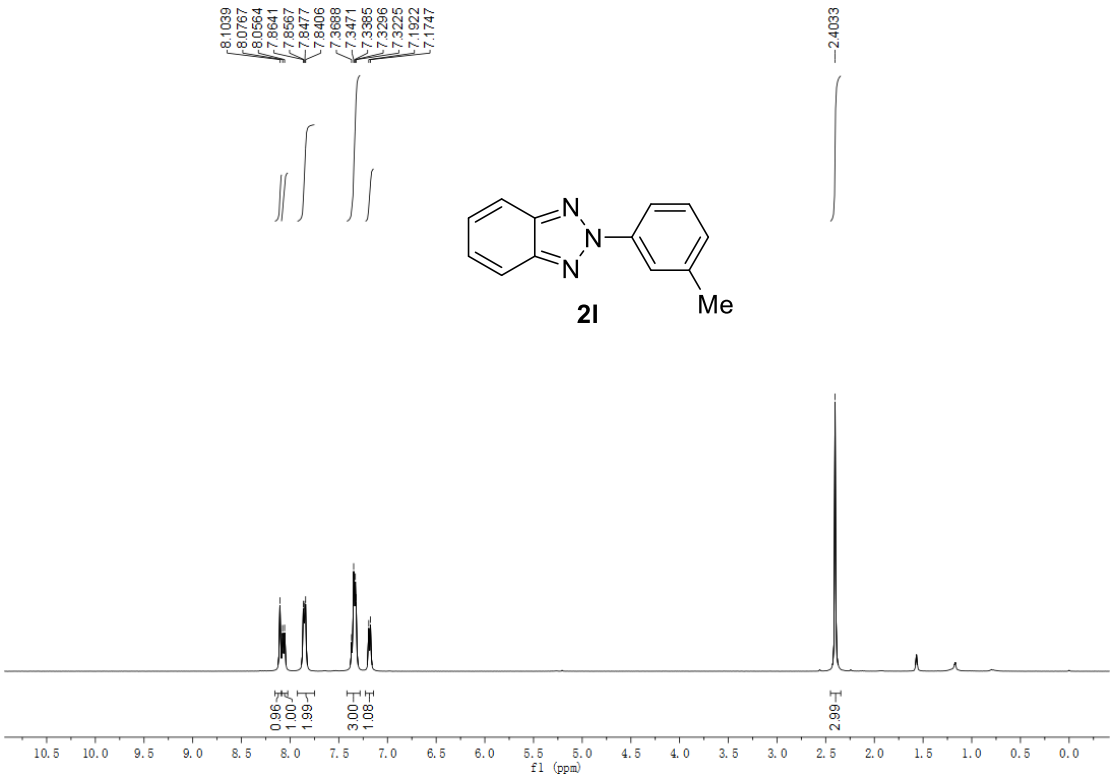
8.2203
7.9431
7.9357
7.9269
7.9200
7.4250
7.4177
7.4087
7.4019
7.3598
7.3394
7.2600
2.4405
N
N
N
Me
2k
2.00
1.98
2.01
2.09
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.85
139.13
138.09
129.96
126.97
120.43
118.23
77.32
77.00
76.68
21.16
N
N
N
Me
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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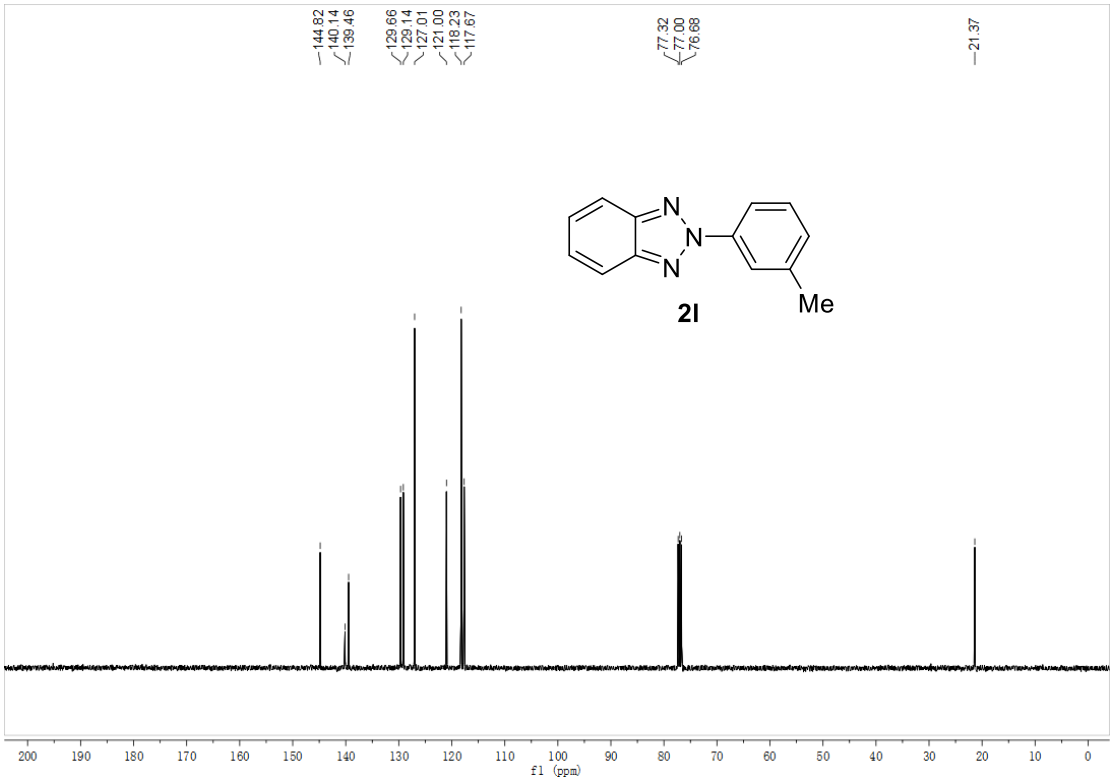
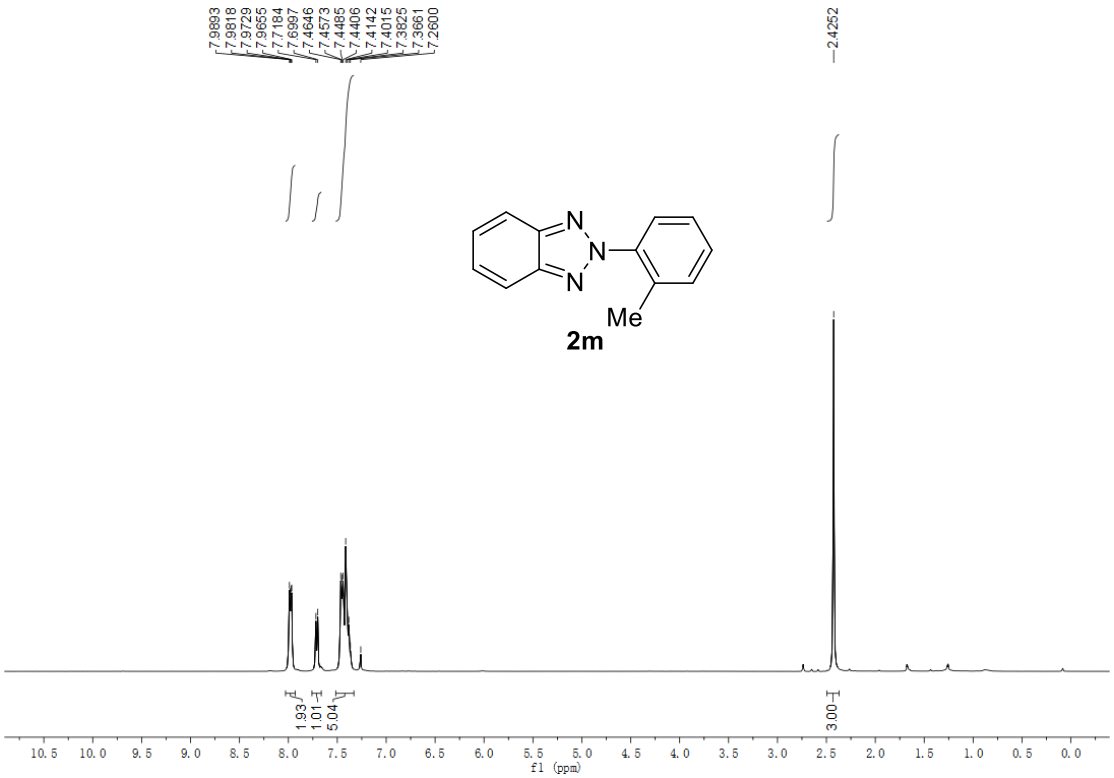
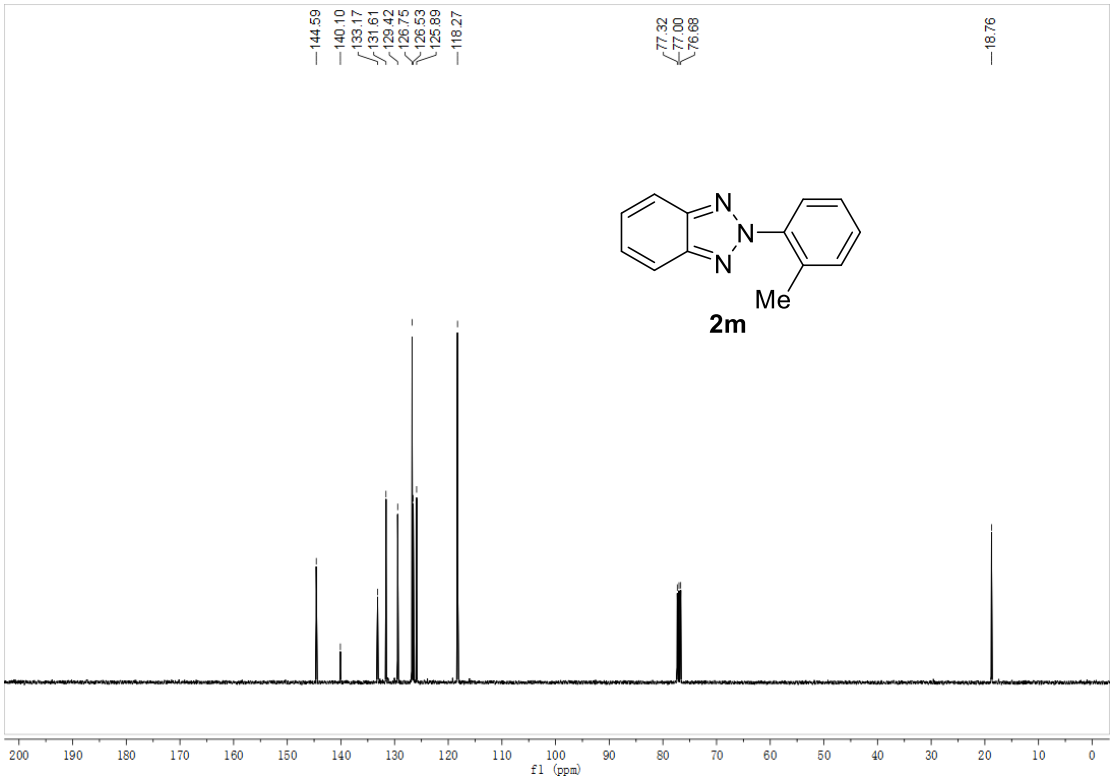
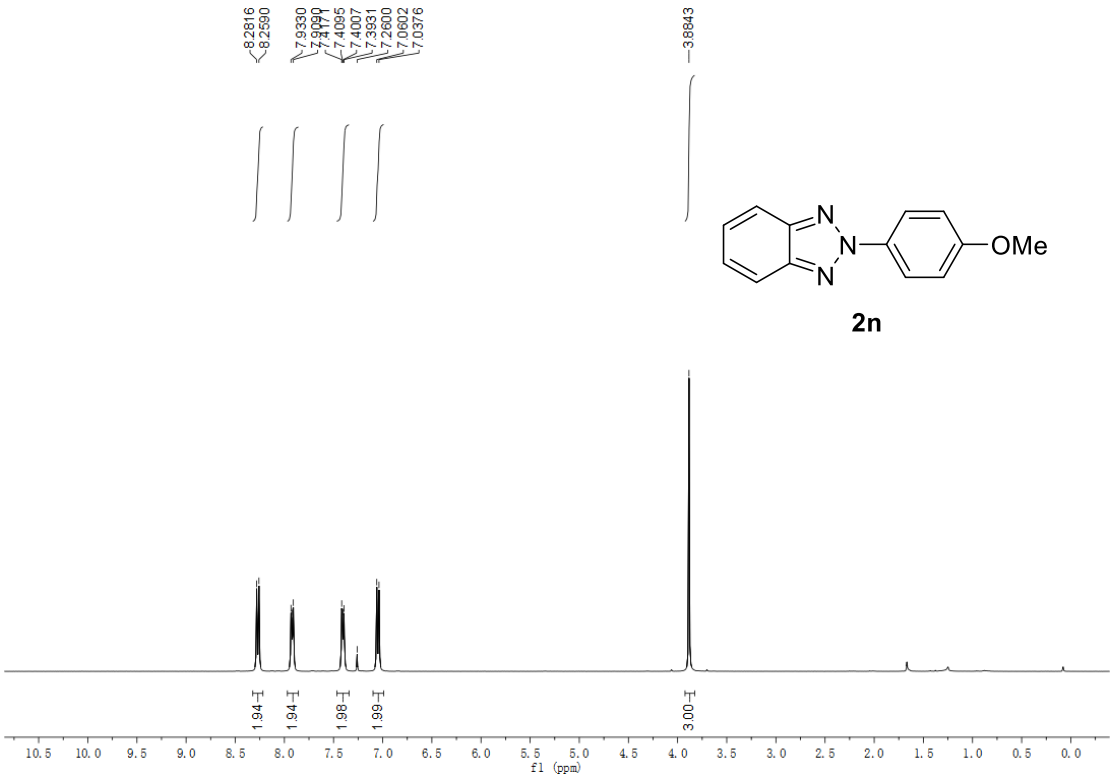
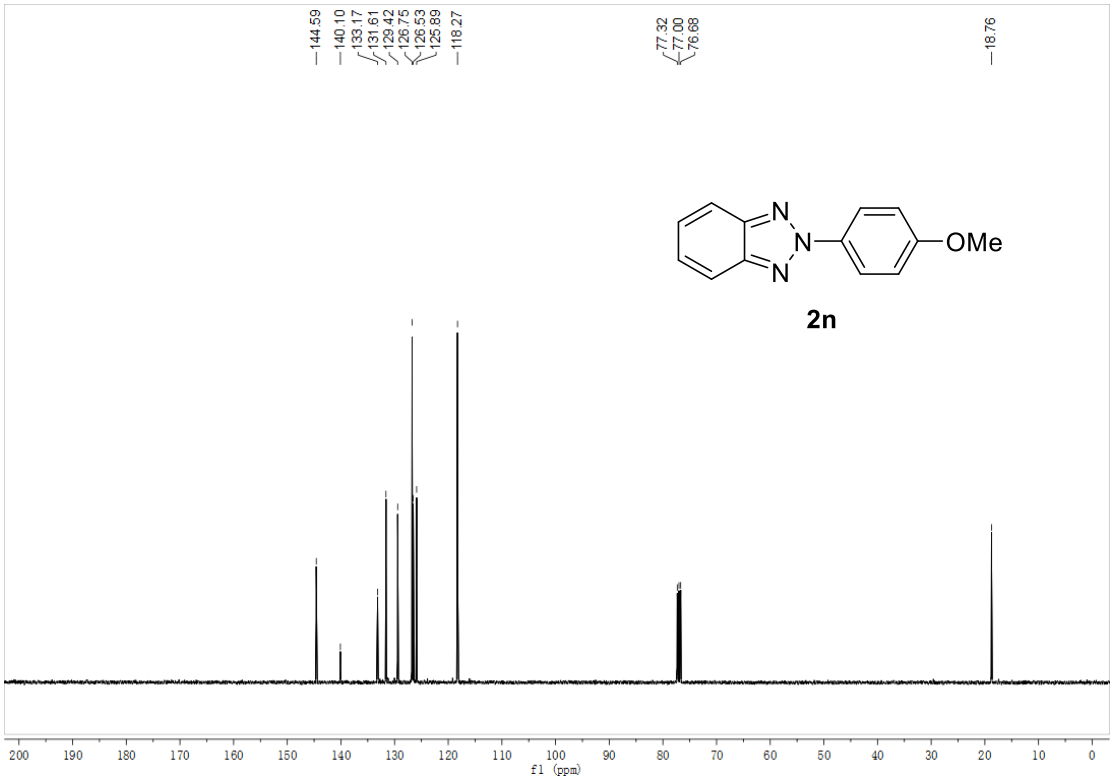
8.0767
8.0564
7.8641
7.8567
7.8477
7.8406
7.3688
7.3471
7.3385
7.3296
7.3225
7.1922
7.1747
2.4033
N
N
N
Me
2l
0.96
1.00
1.99
3.00
1.08
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

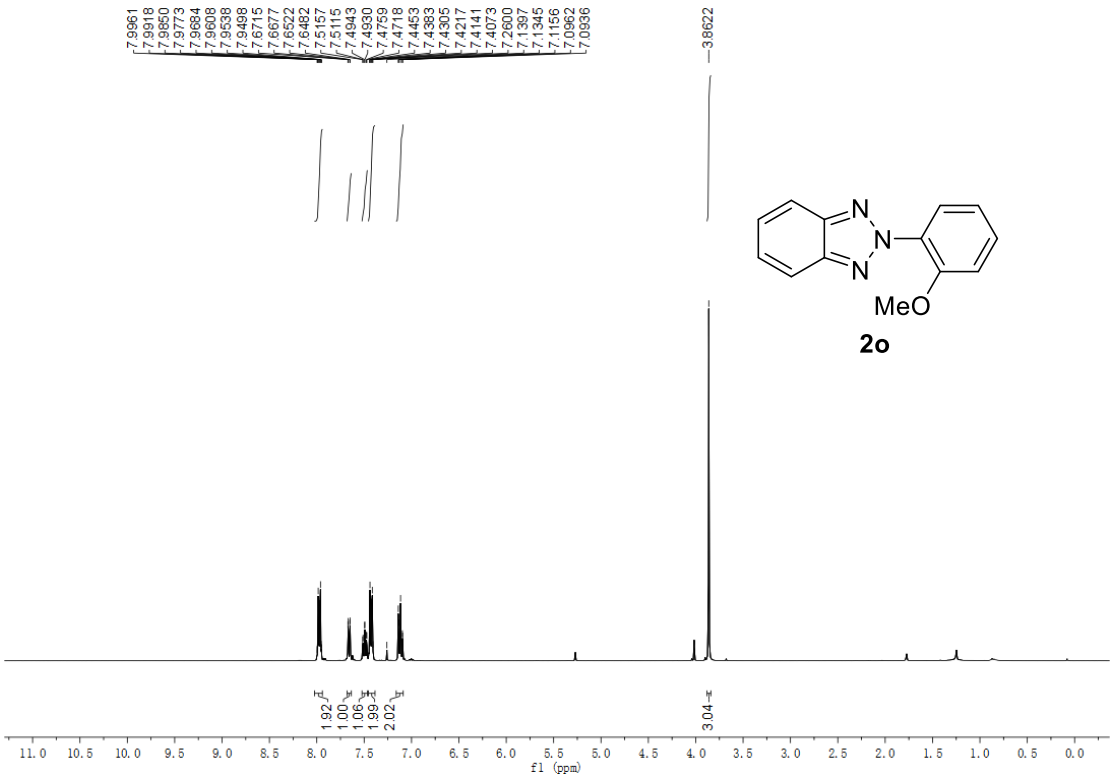

144.82
140.14
139.46
129.66
129.14
127.01
121.00
118.23
117.67
77.32
77.00
76.68
21.37
N
N
N
Me
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

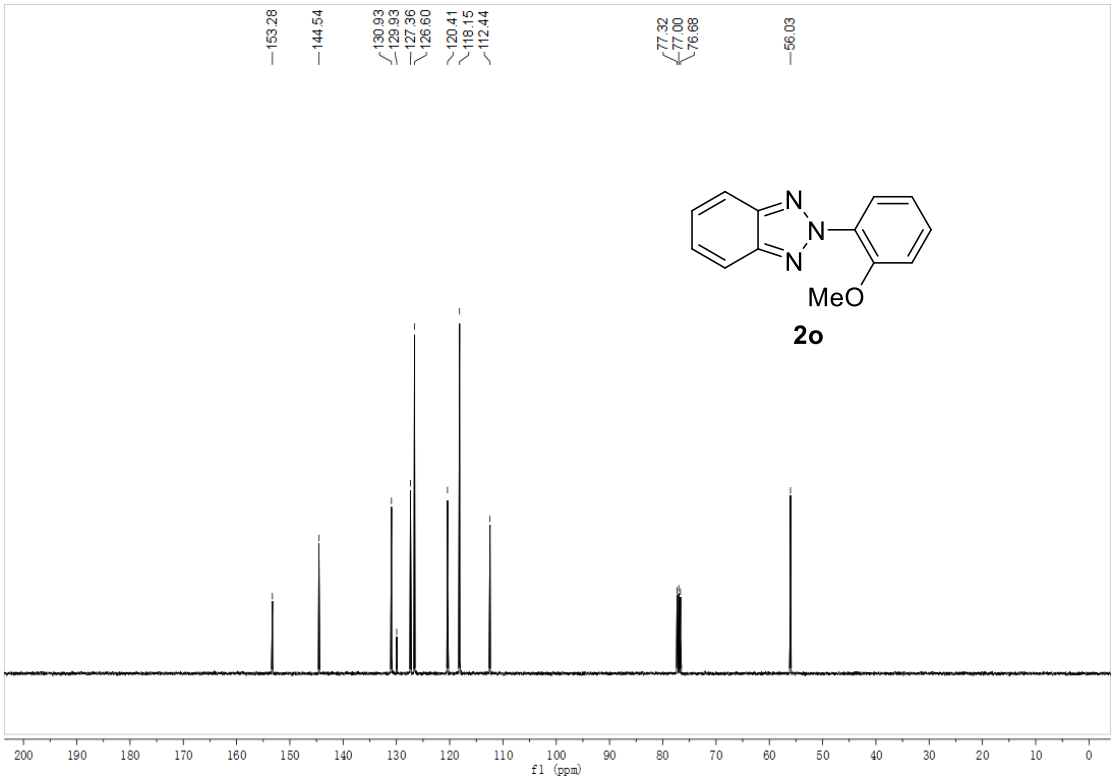

7.9893
7.9818
7.9729
7.9655
7.7184
7.6997
7.4646
7.4573
7.4485
7.4406
7.4142
7.4015
7.3825
7.3661
7.2600
2.4252
N
N
N
Me
2m
1.93
1.01
5.04
3.00
f1 (ppm)

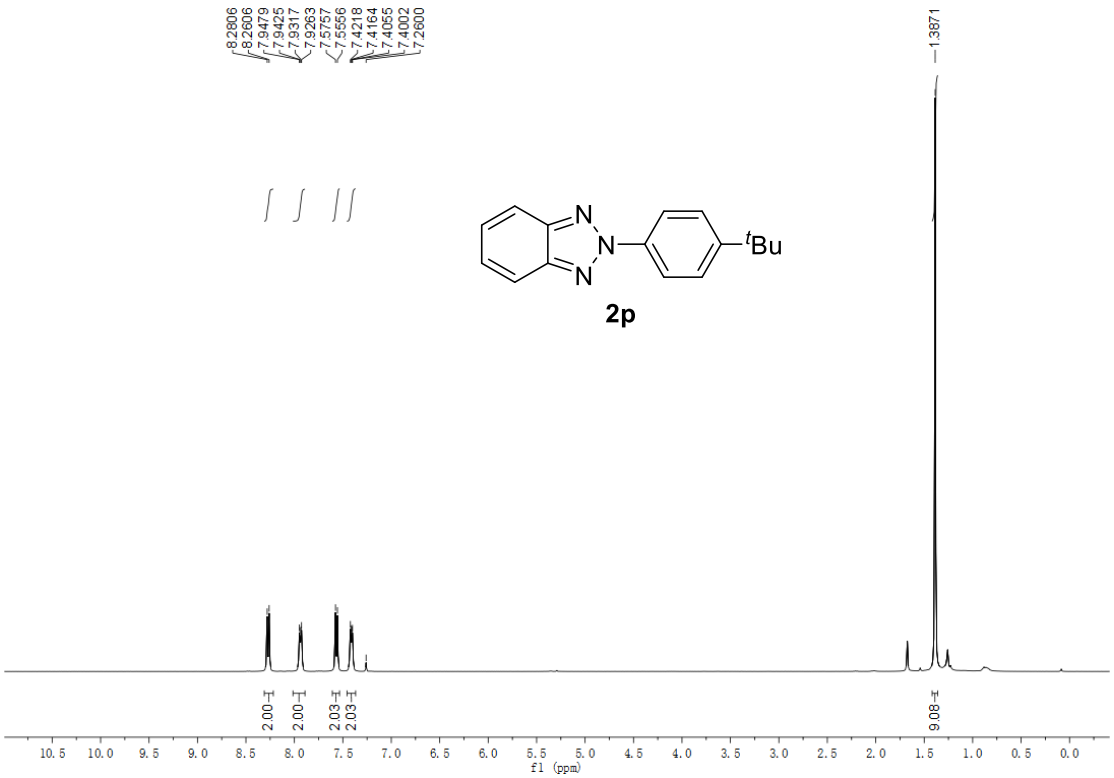

144.59
140.10
133.17
131.61
129.42
126.75
126.53
125.89
118.27
77.32
77.00
76.68
18.76
N
N
N
Me
2m
f1 (ppm)


8.2816
8.2590
7.9330
7.9090
7.4177
7.4095
7.4007
7.3931
7.2600
7.0602
7.0376
3.8843
N
N
N
OMe
2n
1.94
1.94
1.98
1.99
3.00
10.5 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)


144.59
140.10
133.17
131.61
129.42
126.75
126.53
125.89
118.27
77.32
77.00
76.68
18.76
N
N
N
OMe
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

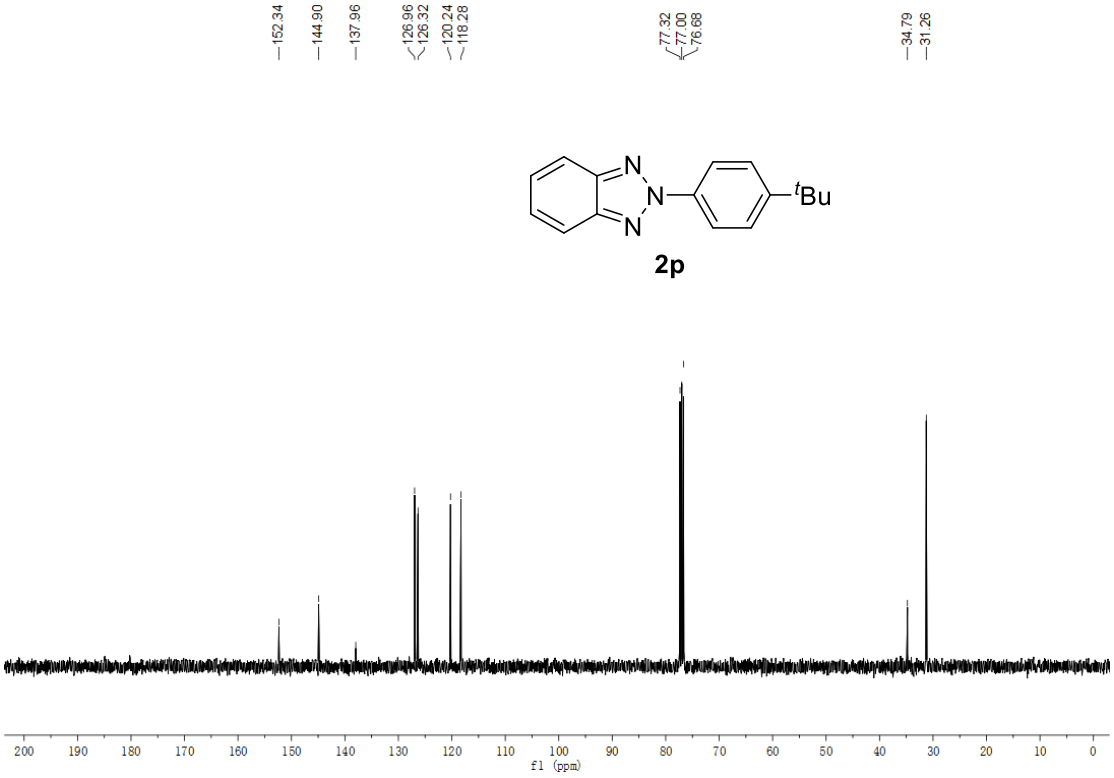

7.9961
7.9918
7.9850
7.9773
7.9684
7.9608
7.9538
7.9498
7.6715
7.6677
7.6522
7.6482
7.5157
7.5115
7.4943
7.4930
7.4759
7.4718
7.4453
7.4383
7.4305
7.4217
7.4141
7.4073
7.2600
7.1397
7.1345
7.1156
7.0962
7.0936
3.8622
N
N
N
MeO
2o
1.92
1.00
1.06
1.99
2.02
3.04
f1 (ppm)


153.28
144.54
130.93
129.93
127.36
126.60
120.41
118.15
112.44
77.32
77.00
76.68
56.03
N
N
N
MeO
2o
f1 (ppm)


8.2806
8.2606
7.9479
7.9425
7.9317
7.9263
7.5757
7.5556
7.4218
7.4164
7.4055
7.4002
7.2600
1.3871
2.00
2.00
2.03
2.03
9.08
f1 (ppm)

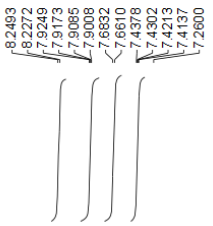
N
N
N
tBu

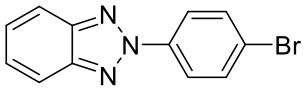
2p


152.34
144.90
137.96
126.96
126.32
120.24
118.28
77.32
77.00
76.68
34.79
31.26
f1 (ppm)

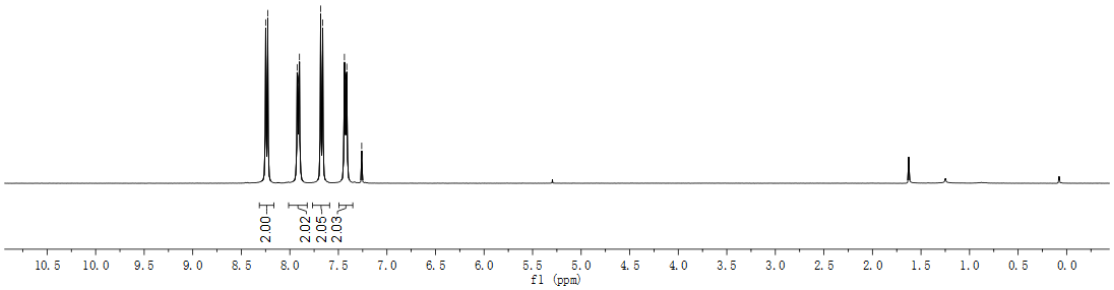
N
N
N
tBu

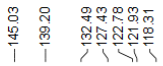
2p

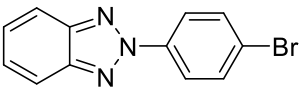

8.2493
8.2272
7.9249
7.9173
7.9085
7.9008
7.6832
7.6610
7.4378
7.4302
7.4213
7.4137
7.2600


N
N
N
Br

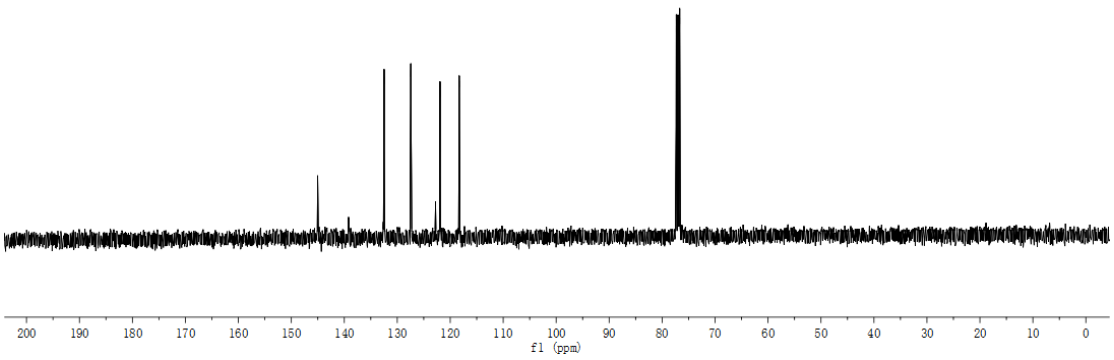
2q

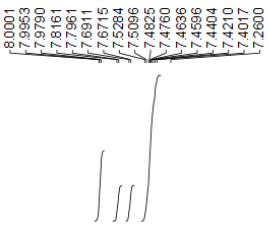

2.00
2.02
2.05
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.03
139.20
132.49
127.43
122.78
121.93
118.31
77.32
77.00
76.68


N
N
N
Br

2q


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.0001
7.9953
7.9790
7.8161
7.7961
7.6911
7.6715
7.5284
7.5096
7.4825
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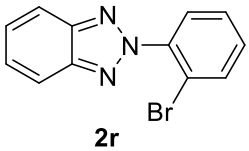
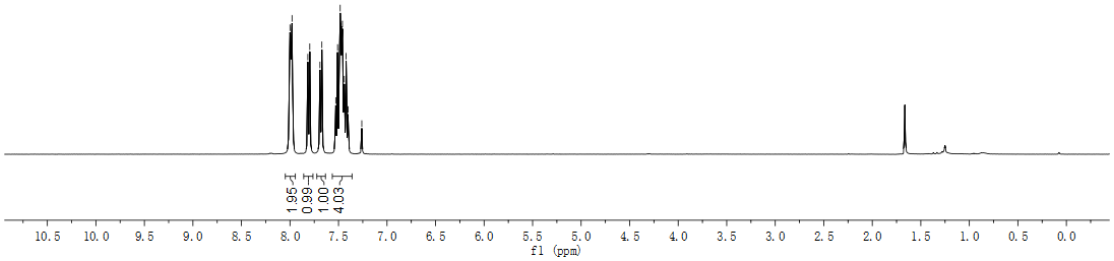
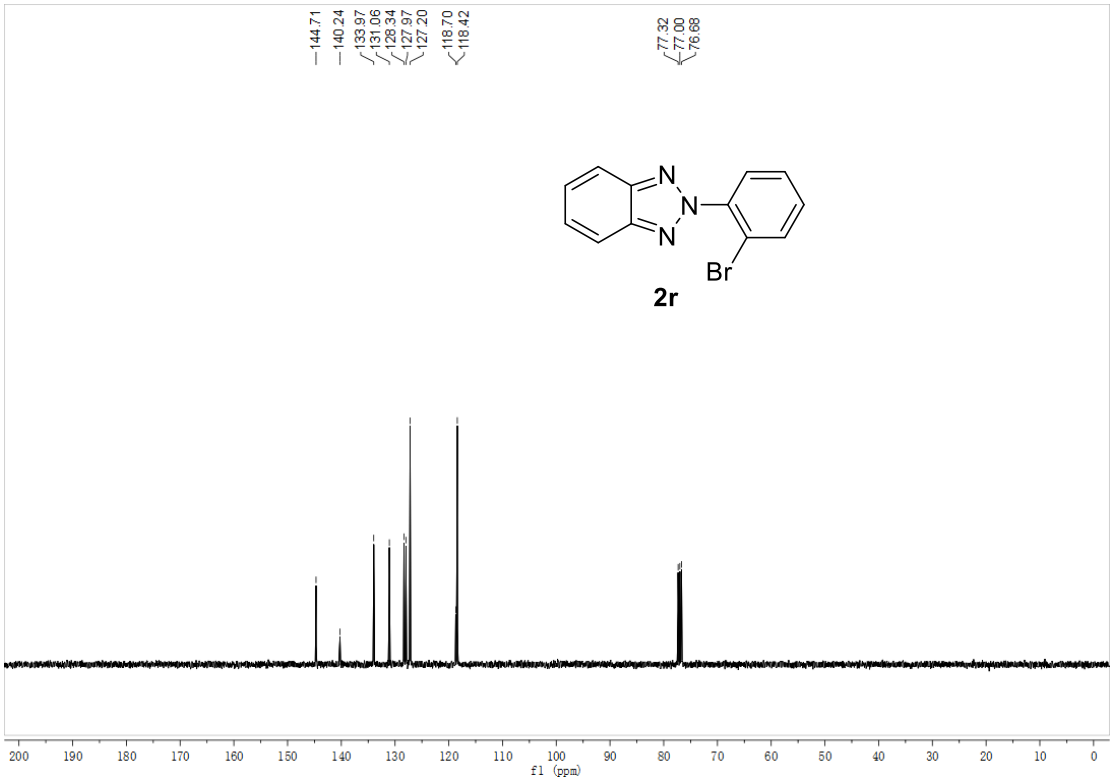
7.4596
7.4404
7.4210
7.4017
7.2600

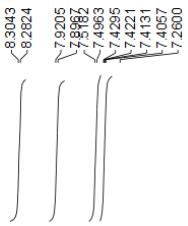

N
N
N
Br

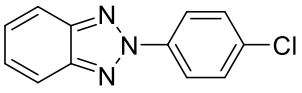
2r


1.95
0.99
1.00
4.03
10.5 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)

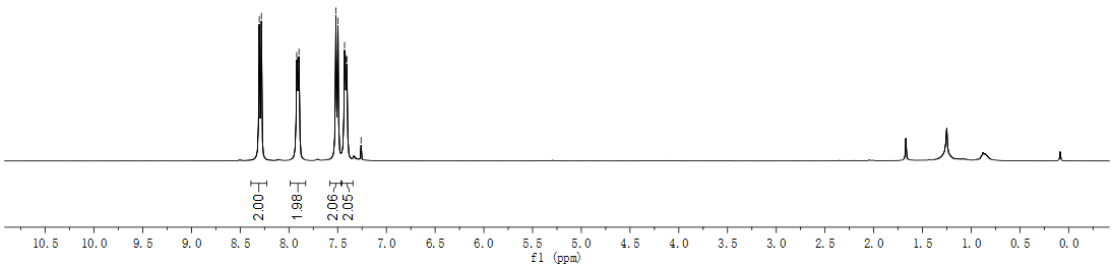

144.71
140.24
133.97
131.06
128.34
127.97
127.20
118.70
118.42
77.32
77.00
76.68
N
N
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

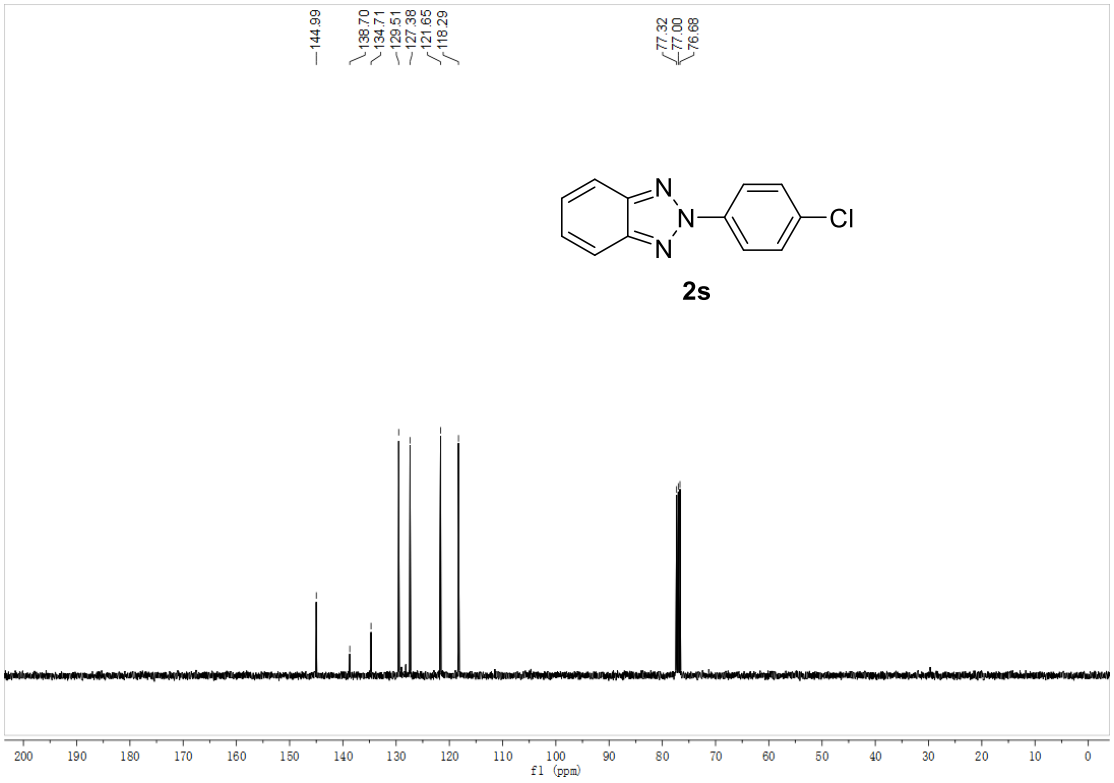
2r

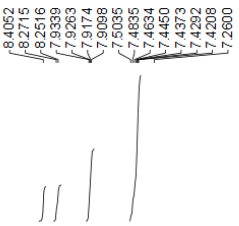

8.3043
8.2824
7.9205
7.8967
7.8782
7.5182
7.4963
7.4295
7.4221
7.4131
7.4057
7.2600

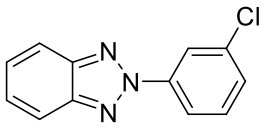

N
N
N
Cl

2s

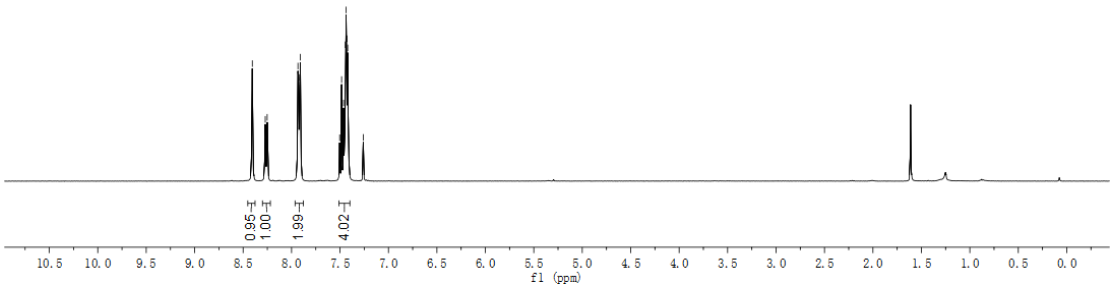

2.00
1.98
2.06
2.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

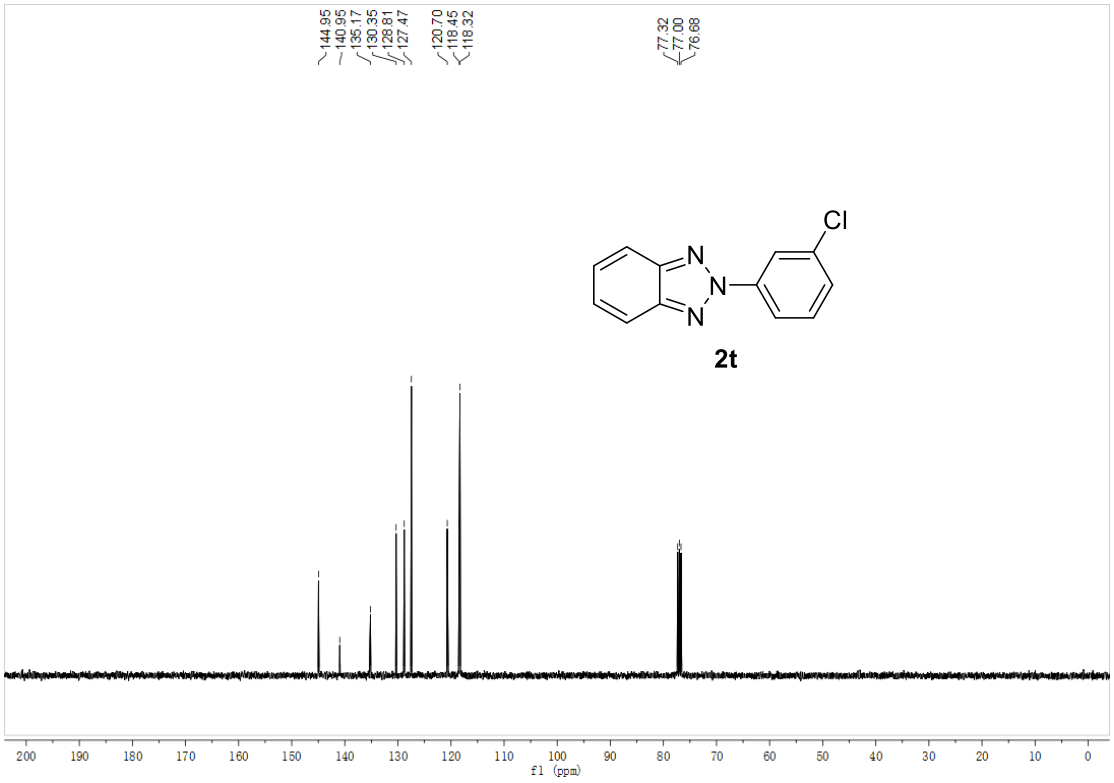

144.99
138.70
134.71
129.51
127.38
121.65
118.29
77.32
77.00
76.68
N
N
N
Cl
2s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

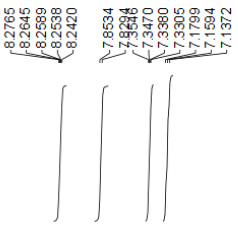

8.4052
8.2715
8.2516
7.9339
7.9263
7.9174
7.9098
7.5035
7.4835
7.4634
7.4450
7.4373
7.4292
7.4208
7.2600

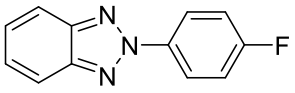

Cl
N
N
N

2t

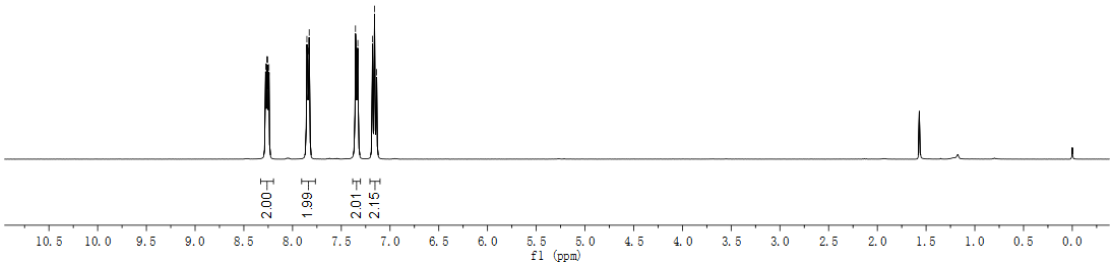

0.95
1.00
1.99
4.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

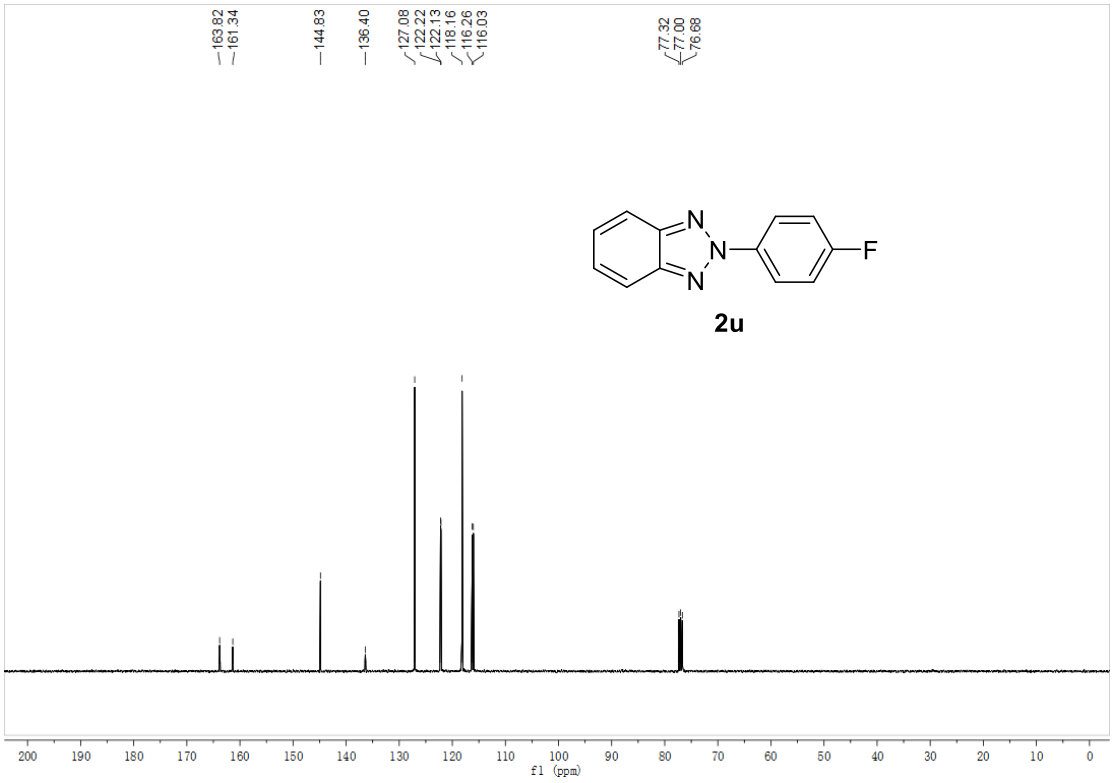

144.95
140.95
135.17
130.35
128.81
127.47
120.70
118.45
118.32
77.32
77.00
76.68
Cl
N
N
N
2t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.2765
8.2645
8.2589
8.2538
8.2420
7.8534
7.3546
7.3470
7.3380
7.3305
7.1799
7.1594
7.1372

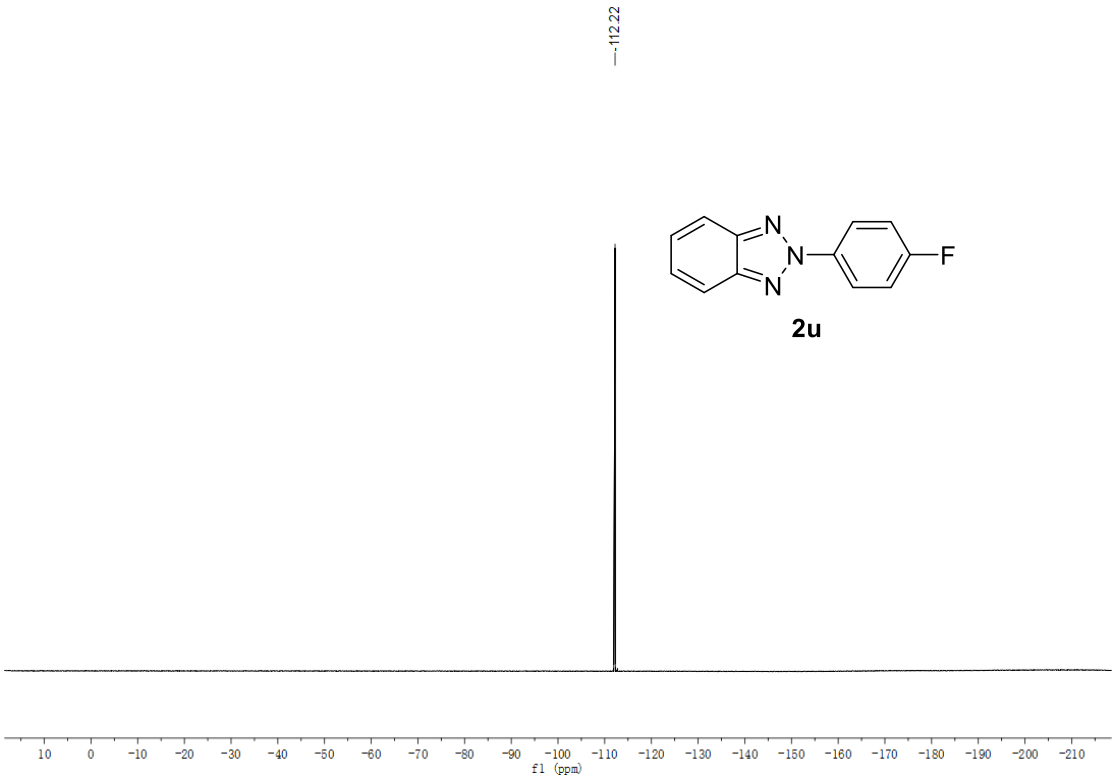


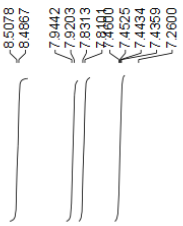
2u

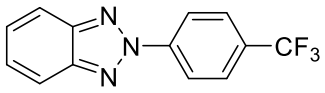

2.00
1.99
2.01
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.82
161.34
144.83
136.40
127.08
122.22
122.13
118.16
116.26
116.03
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

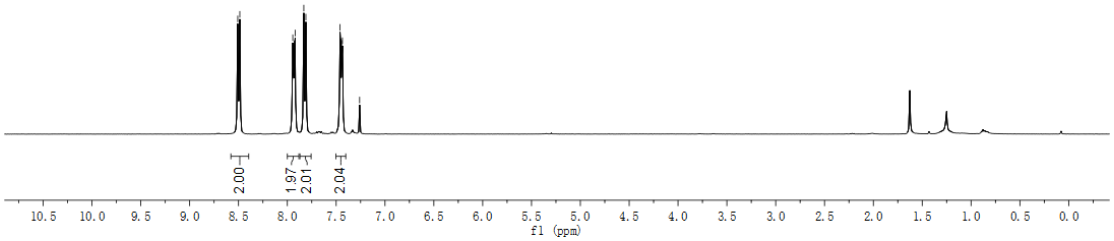
2u

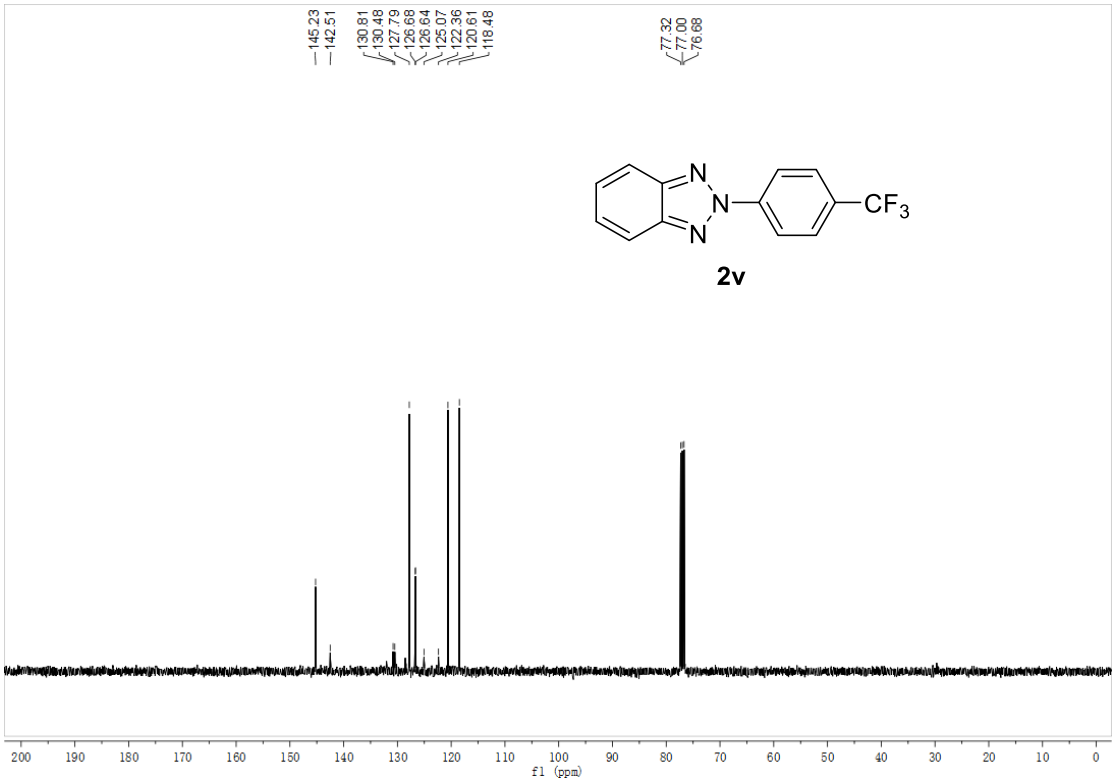

-112.22
N
N
N
F
2u
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.5078
8.4867
7.9442
7.9203
7.8313
7.8101
7.4525
7.4434
7.4359
7.2600

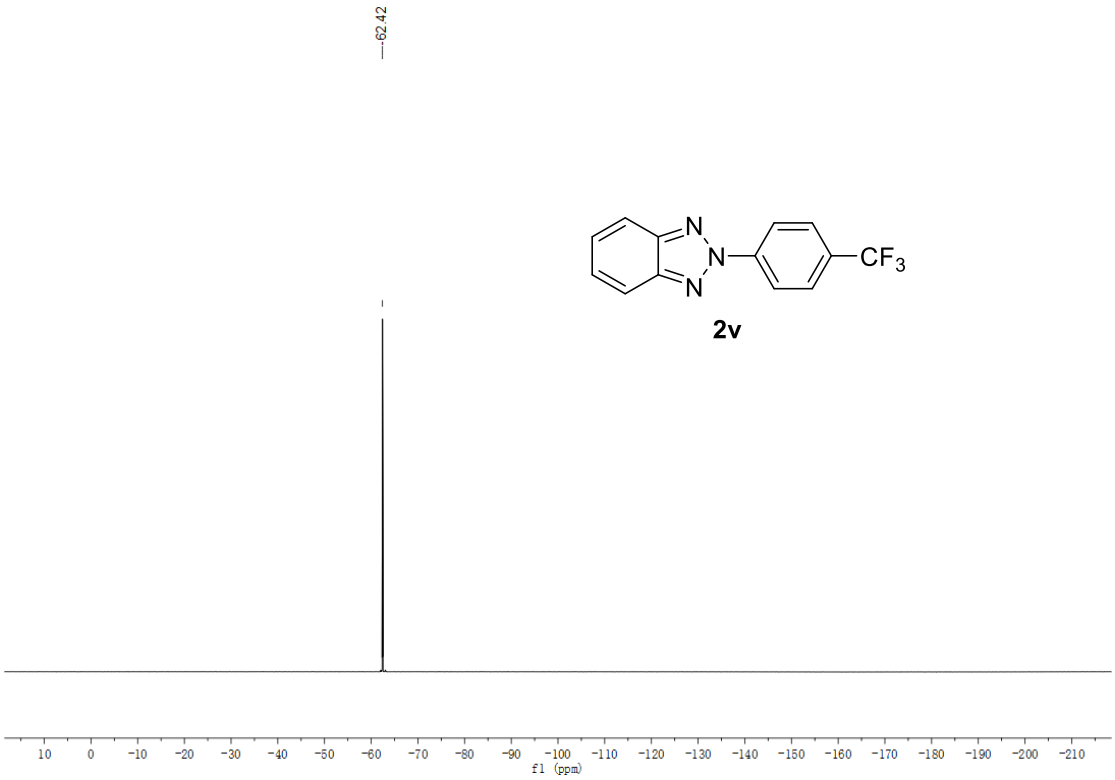


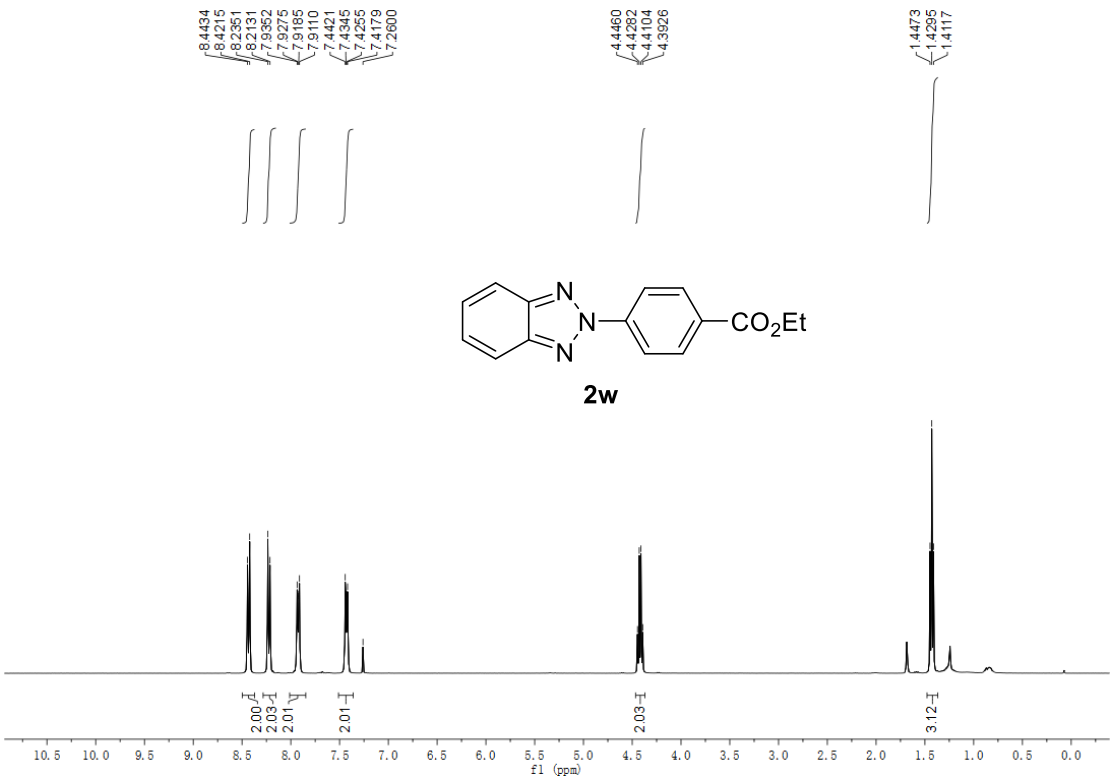
2v

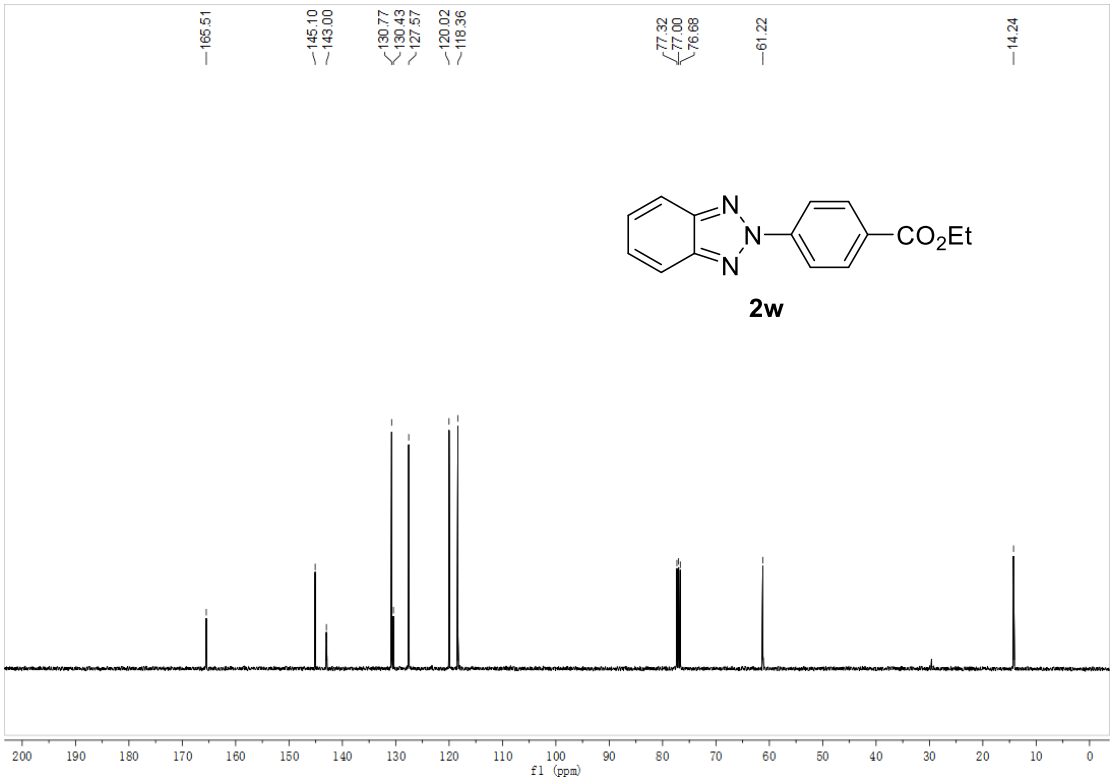

2.00
1.97
2.01
2.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

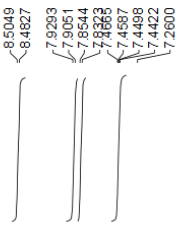

145.23
142.51
130.81
130.48
127.79
126.88
126.64
125.07
122.36
120.61
118.48
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

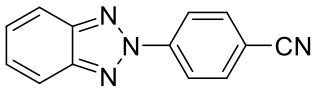
2v


-62.42
N
N
N
CF3
2v
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

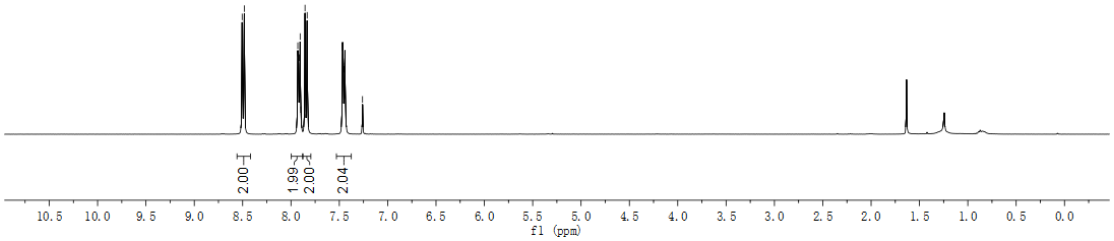

8.4434
8.4215
8.2351
8.2131
7.9352
7.9275
7.9185
7.9110
7.4421
7.4345
7.4255
7.4179
7.2600
4.4460
4.4282
4.4104
4.3926
1.4473
1.4295
1.4117
N
N
N
CO2Et
2w
2.00
2.03
2.01
2.01
2.03
3.12
f1 (ppm)

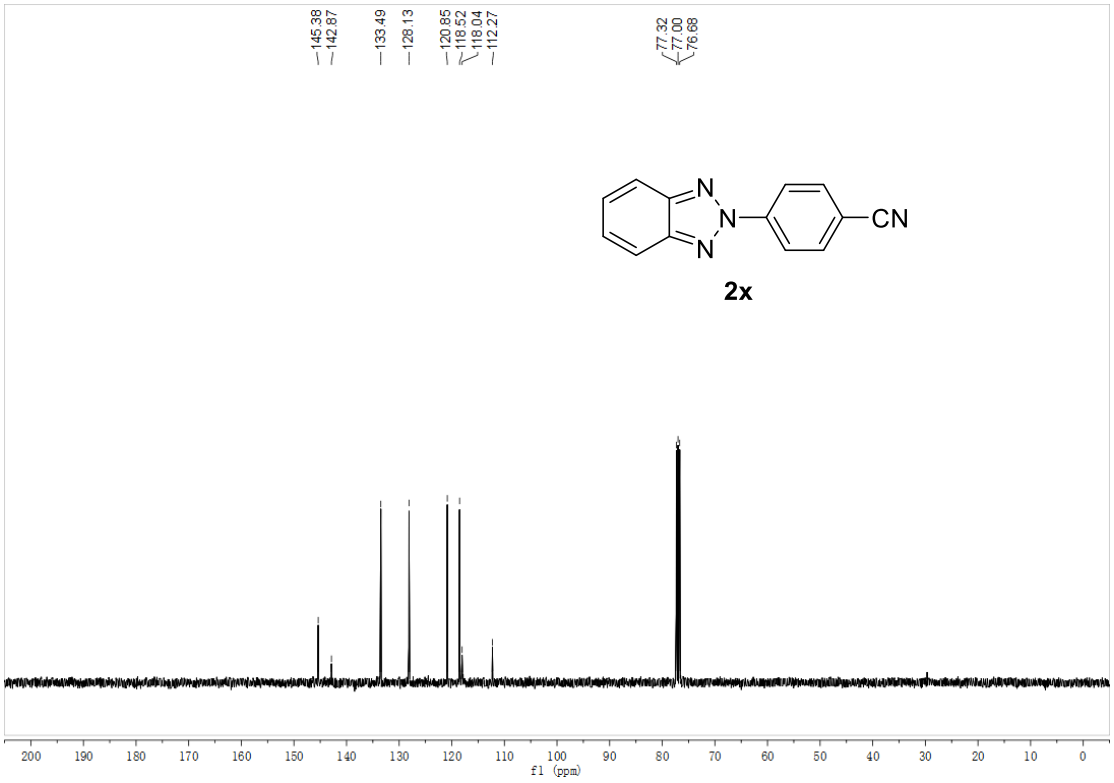

165.51
145.10
143.00
130.77
130.43
127.57
120.02
118.36
77.32
77.00
76.68
61.22
14.24
N
N
N
CO2Et
2w
f1 (ppm)


8.5049
8.4827
7.9293
7.9051
7.8544
7.8323
7.4587
7.4498
7.4422
7.2600

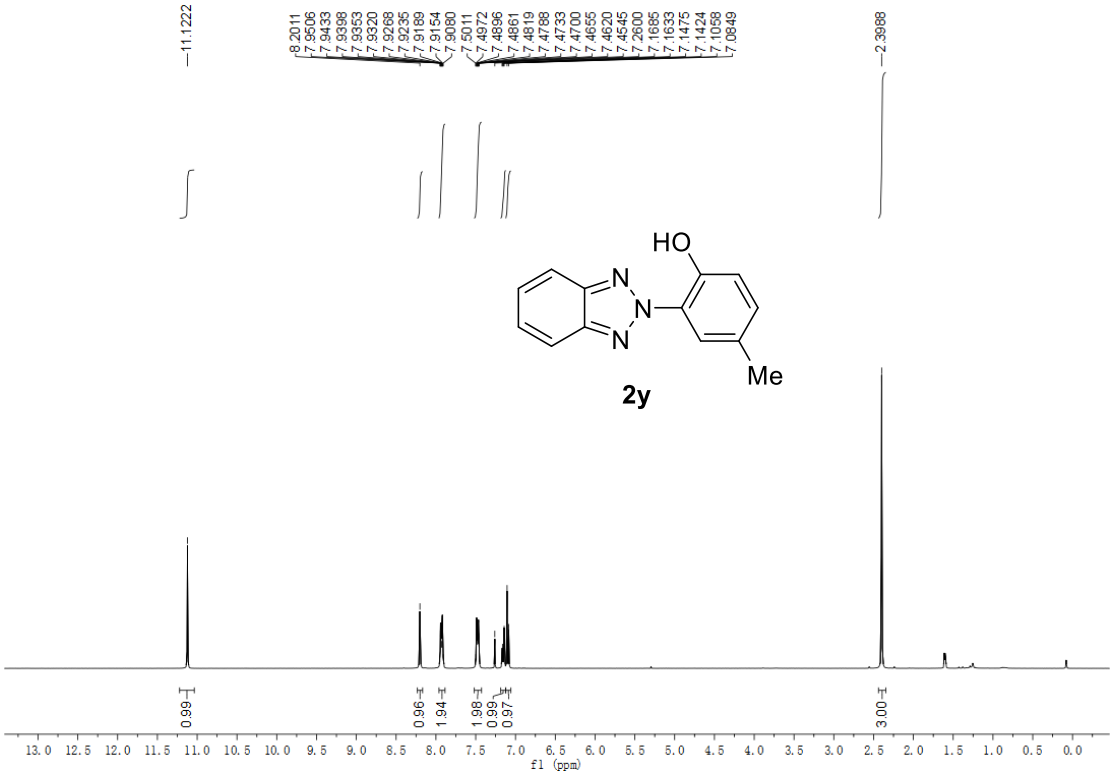

N
N
N
CN

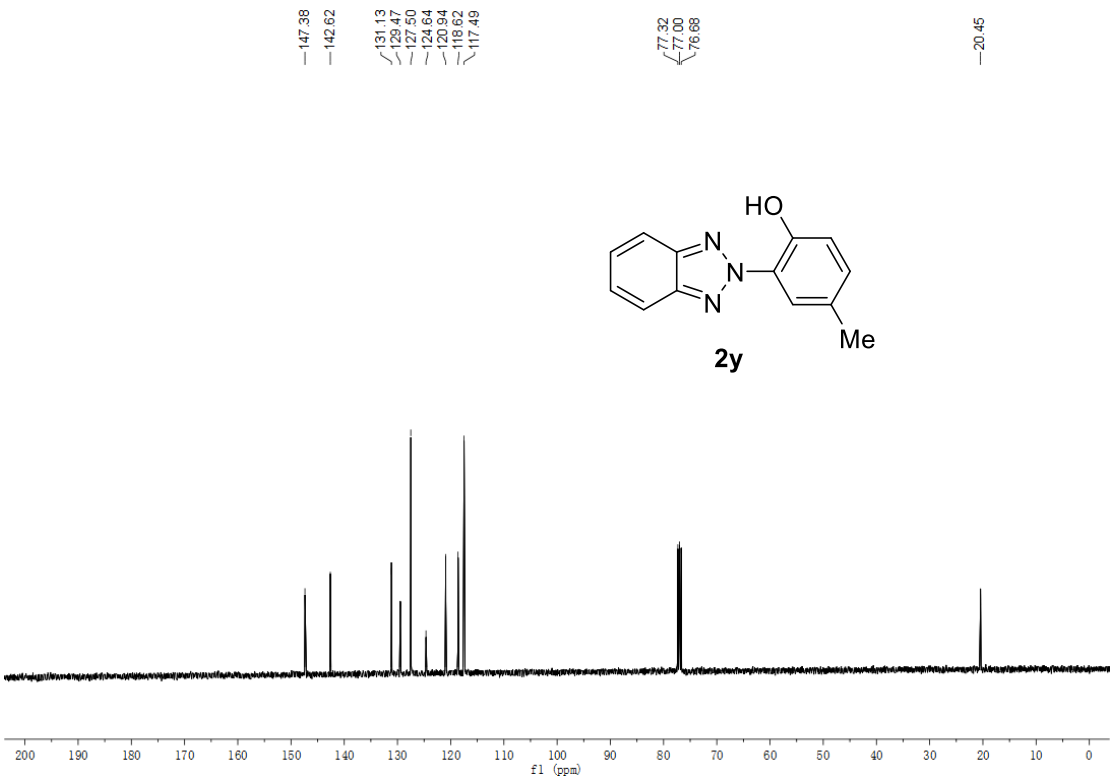
2x


2.00
1.99
2.00
2.04
10.5 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)


145.38
142.87
133.49
128.13
120.85
118.52
118.04
112.27
77.32
77.00
76.68
N
N
N
CN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2x


11.1222
8.2011
7.9506
7.9433
7.9398
7.9353
7.9320
7.9268
7.9235
7.9189
7.9154
7.9080
7.5011
7.4972
7.4896
7.4861
7.4819
7.4788
7.4733
7.4700
7.4655
7.4620
7.4545
7.2600
7.1685
7.1633
7.1475
7.1424
7.1058
7.0849
2.3988
HO
N
N
N
Me
2y
0.99
0.96
1.94
1.98
0.99
0.97
3.00
f1 (ppm)


147.38
142.62
131.13
129.47
127.50
124.64
120.94
118.62
117.49
77.32
77.00
76.68
20.45
HO
N
N
N
Me
2y
f1 (ppm)