Supporting Information for

$AgNO_3$ as Nitrogen Source for Rhodium(Ⅲ)-Catalyzed Synthesis of 2-Aryl-2*H*-Benzotriazoles from Azobenzenes

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1 General experimental information

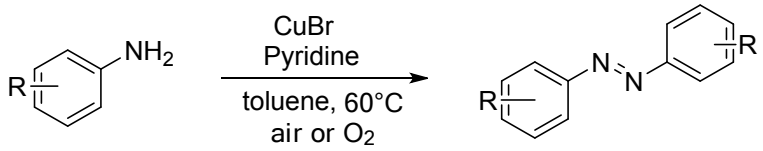
Experimental: All reactions were set up under inert atmosphere (argon or N_2) utilizing glassware that was flame-dried and cooled under vacuum. All non-aqueous manipulations were using standard Schlenk techniques. Reactions were monitored using thin-layer chromatography (TLC) on Silica Gel plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Silica Gel Flash Column Chromatography was performed on SYNTHWARE 40-63μm silica gel.

Materials: Unless otherwise indicated, starting catalysts and materials were obtained from Sigma Aldrich, TCI, Alfa Aesar, or Acros Co. Ltd. Moreover, commercially available reagents were used without additional purification.

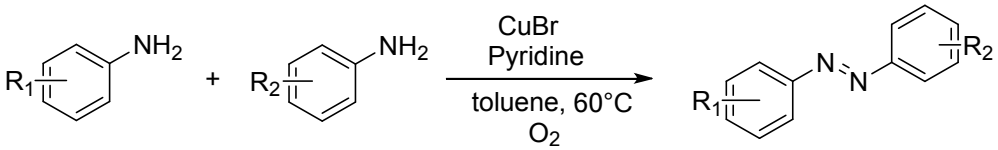
Instrumentation: All NMR spectra were run at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR) or 377 MHz (^{19}F NMR) in $CDCl_3$ or d_6-DMSO solution. ^{1}H NMR spectra were internally referenced to TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet, br = broad), coupling constants (*J*) were reported in Hz. High resolution mass spectra (HRMS) were recorded on Bruker MicrOTOF-Q II mass instrument (ESI).

2 General procedures for preparation of azobenzenes 1

A mixture of CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), and aromatic amine (93 mg, 1 mmol) added in toluene (4 mL) under air (1 atm). The reaction mixture was vigorously stirred at 60 °C for 24 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography with petroleum ether to provide the azo derivative.[1]

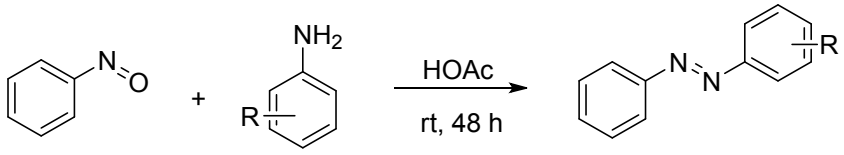


The mixture of CuBr (2.9 mg, 0.02 mmol), pyridine (4.8 mg, 0.06 mmol), aniline (93 mg, 1 mmol) and 4-methoxybenzenamine (0.2 mmol) in toluene (4 mL) was vigorously stirred at 60 °C under O_2 (1 atm) for 24 h. Then cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 200:1) to afford the azo derivatives.[1]



To a round bottom flask equipped with a stir bar was combined the indicated aniline (12.0 mmol, 1.2 equiv) and nitrosobenzene (1.07 g, 10.0 mmol, 1.0 equiv) in glacial acetic acid (100 mL) as solvent. The flask was covered with aluminum foil, and the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was extracted with hexanes and was transferred to a separatory funnel with water. The organic layer was collected and washed with water, then dried with $MgSO_4$, and

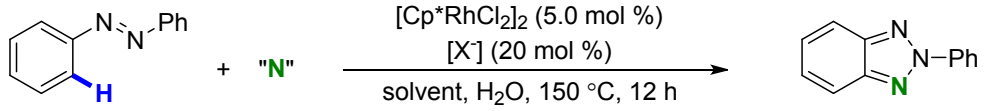
concentrated. Purification by chromatography with hexanes/ethyl acetate afforded the azobenzenes.[2]



3 Details of optimization for the reaction conditions

The reaction mixture was added to a flame-dried Schlenck tube which charged with a magnetic stir bar. The resulting suspension was stirred at specific temperature under N_2 for 12 h. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (petroleum and ethyl acetate=100:1) to yield products.

Table 1: optimization of the reaction conditions

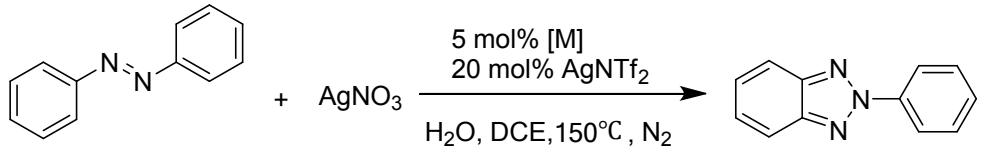


1a **2a**

entry	"N" source	[X⁻]	solvent	yield (%)[b]
1	$AgNO_3$	$AgNTf_2$	CH_2Cl_2	52(42)
2	$AgNO_3$	$AgNTf_2$	DCE	88(73)
3	$AgNO_3$	$AgNTf_2$	Toluene	n.r [c]
4	$AgNO_3$	$AgNTf_2$	THF	n.r
5	$AgNO_3$	$AgNTf_2$	DMF	n.r
6	$AgNO_3$	$AgNTf_2$	$PhNO_3$	25
7	$AgNO_3$	$AgNTf_2$	CH_3NO_2	47
8	KNO_3	$AgNTf_2$	DCE	(39)
9	$Mg(NO_3)_2$	$AgNTf_2$	DCE	45
10	$Zn(NO_3)_2$	$AgNTf_2$	DCE	72(58)
11	$Co(NO_3)_2$	$AgNTf_2$	DCE	70
12	$Ni(NO_3)_2$	$AgNTf_2$	DCE	35
13	$Cu(NO_3)_2$	$AgNTf_2$	DCE	20
14	CH_3NO_2	$AgNTf_2$	DCE	48
15	$AgNO_3$	AgOTf	DCE	68
16	$AgNO_3$	$AgSbF_6$	DCE	35
17	$AgNO_3$	$AgBF_4$	DCE	50
18	$AgNO_3$	Ag_2CO_3	DCE	n.r
19	$AgNO_3$	NaOTf	DCE	30
20	$AgNO_3$	NaBARF	DCE	50
21[d]	$AgNO_3$	$AgNTf_2$	DCE	(67)
22[e]	$AgNO_3$	$AgNTf_2$	DCE	(45)

[a]Unless otherwise noted, the reaction was performed with **1a** (0.1 mmol), "**N**" source (0.2 mmol), $[Cp^*RhCl_2]_2$ (5.0 mol %), counteranion additive $[X^-]$ (20 mol %), and H_2O (0.1 mmol) in 0.5 mL of solvent under 150 °C for 12 hours. [b] Yield was determined by GC-Mass using a standard, yield of isolated product is given in parentheses. [c] n.r means no reaction upon **1a**. [d] 1.0 eq of $AgNO_3$ used. [e] Reaction carried out at 140 °C.

Table 2: The effect of different catalysts

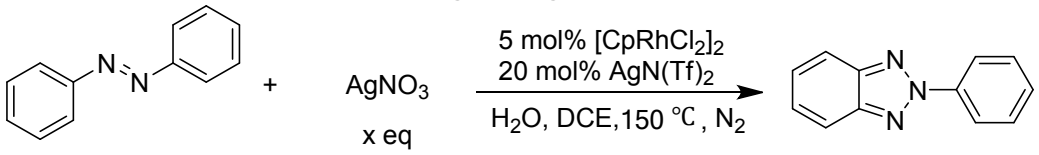


1a **2a**

Entry[a]	[M]	yield[b]
1	$[Cp^*IrCl_2]_2$	NR[c]
2	$Cp^*Ru(PPh_3)_2Cl_2$	NR[c]
3	$Pd(OAc)_2$	NR[c]
4	$[Ir(cod)Cl]_2$	NR[c]
5	$[Cp^*RhCl_2]_2$	73%

[a]Reaction conditions: **1a** (0.1 mmol), $AgNO_3$(0.2 mmol), [M] (5 mol %), $AgNTf_2$ (20 mol%), DCE (1 mL), 150 °C, 12 h. [b] isolated yield. [c] N.R. means no reaction.

Table 2: The effect of the loading of $AgNO_3$

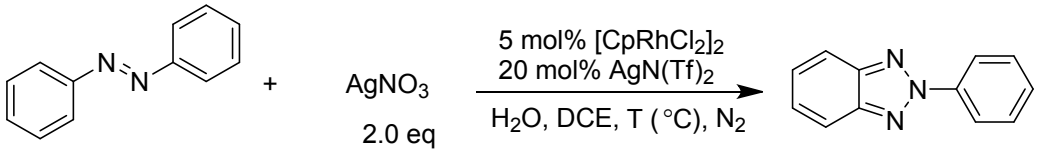


1a **2a**

Entry[a]	x	yield(%)[b]
1	1	67
2	1.5	62
3	2	73
4	2.2	69

[a]Reaction conditions: **1a** (0.1 mmol), $AgNO_3$ (x mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgN(Tf)_2$(20 mol %), 1 eq H_2O, DCE(1mL), N_2, 150 °C, 12 h. [b] isolated yield.

Table 3: The effect of the reaction temperature



1a **2a**

Entry[a]	T(°C)	yield(%)[b]
1	160	70
2	150	73
3	140	trace

[a]Reaction conditions: **1a** (0.1 mmol), $AgNO_3$ (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgN(Tf)_2$ (20 mol %) ,1 eq H_2O, DCE (1 mL), N_2, T °C, 12 h. [b] isolated yield .

4 Experimental characterization data for azobenzenes

(*E*)-1,2-Diphenyldiazene (**1a**).[1]

^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.93-7.91 (m, 4H), 7.52-7.44 (m, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ= 152.7, 131.0, 129.1, 122.8.

(*E*)-1, 2-Di-p-tolyldiazene (**1b**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8 Hz, 4H), 7.30 (d, J = 8 Hz, 4H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.88, 141.2, 129.7, 122.7, 21.5.

(*E*)-Bis(4-ethylphenyl)diazene (**1c**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9(d, J =8 Hz, 4H), 7.37(d, J =8 Hz, 4H), 2.79-2.73(q, J =7.6 Hz, 4H), 1.32(t, J =7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.5, 128.5, 122.8, 28.8, 15.5.

(*E*)-Bis(4-n-butylphenyl)diazene (**1d**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 2.72 (t, 4H),1.72-1.65 (m, 4H), 1.47-1.38 (m, 4H), 0.99 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 146.2, 129.1, 122.8, 35.6, 33.5, 22.4, 14.0.

(*E*)-Bis(4-isopropylphenyl)diazene (**1e**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93(d, *J* = 8.0 Hz, 4H), 7.42(d, *J* = 8.0 Hz, 4H), 3.06-3.03 (m, 2H), 1.36(d, *J* = 8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 151.2, 127.1, 122.8, 34.1, 23.9.

(*E*)-Bis(4-t-butyllphenyl)diazene (**1f**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93(d, *J* =8.0 Hz, 4H), 7.59 (d, *J* =8.0 Hz,

4H), 1.44(s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.2, 150.8, 126.0, 122.5, 35.0, 31.3.

(*E*)-Bis(4-chlorophenyl)diazene (**1g**)[2]:

^{1}H NMR ($CDCl_3$,400 MHz):δ= 7.68 (d, *J* = 8 Hz, 4H), 7.21 (d, *J* = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$,100 MHz):δ= 151.1, 137.4, 129.6, 124.5.

(*E*)-Bis(4-bromophenyl)diazene (**1h**)[2]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79(d, *J* = 8.0 Hz, 4H), 7.63 (d, *J* =8.0 Hz, 4H); ^{13}C NMR (100 MHz, CDCl3) δ = 150.8, 141.2, 129.7, 122.7.

(*E*)-diethyl4,4'-(diazene-1,2-diyl)dibenzoate (**1i**)[2]:

^{1}H NMR ($CDCl_3$,400 MHz):δ= 8.20 (d, *J* = 8 Hz, 4H), 7.97 (d, *J* = 8 Hz, 4H), 4.42(q , 6 H), 1.43(t , 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.88, 154.8, 132.7, 130.6, 122.8, 61.3, 14.3.

(*E*)-1,2-Di-o-tolyldiazene (**1j**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70(d, J = 8.0 Hz ,4H), 7.38-7.41 (m, 4H), 7.30-7.34 (m, 2H), 2.81(s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ = 151.1, 138.1, 131.3, 130.7, 126.4, 115.9, 17.7.

(*E*)-Bis(3,4-dimethylphenyl)diazene (**1k**)[1]:

^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.74 – 7.70 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.39 (d, *J* = 12.0 Hz, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ= 151.3, 139.85, 137.4, 130.3, 123.4, 120.7, 19.9, 19.8.

(*E*)-1-phenyl-2-(p-tolyl)diazene (**1l**)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2H), 7.86 (d, *J* = 8 Hz, 2H), 7.56

–7.49 (m, 3H), 7.35(d, *J* = 8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 150.9, 141.6, 130.7, 129.8, 129.1, 122.9, 122.8, 21.5.

(*E*)-1-(4-chlorophenyl)-2-phenyldiazene (**1m**)[2]:
^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.97– 7.90 (m, 4H), 7.58-7.50 (m, 5H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ= 152.4, 150.9, 136.9, 131.3, 129.3, 129.1, 124.1, 122.9.

(*E*)-4-(phenyldiazenyl)benzonitrile (**1n**)[2]:
^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.99 (d, *J* = 8 Hz, 2H), 7.97-7.94 (m, 2H), 7.81 (d, *J* = 8 Hz, 2H), 7.57-7.53 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 154.5, 152.3, 133.2, 132.2, 129.3, 123.33, 123.29, 118.5, 113.9.

(*E*)-1-(3,5-dimethylphenyl)-2-phenyldiazene(**1o**)[2]:
^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.06-8.04 (m , 2H), 7.74 (d, *J* = 8.0Hz, 1H), 7.62-7.53 (m, 3H), 7.23(s ,1H), 7.17 (d, *J* = 8.0Hz, 1H), 2.83(s, 3H), 2.47(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 166.6, 153.2, 148.8, 141.4, 138.4, 131.9, 130.6, 129.1, 127.3, 122.9, 115.4, 21.5, 17.6.

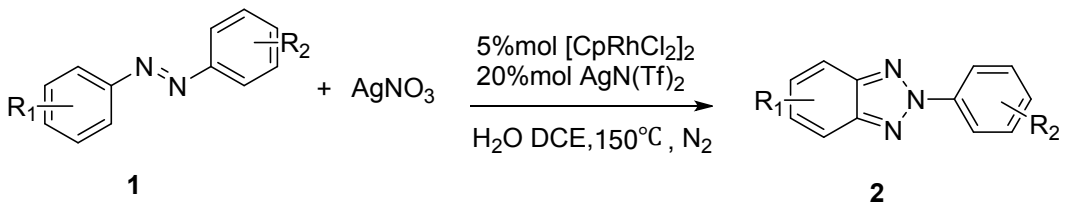
(*E*)-1,2-Di-m-tolyldiazene (**1p**)[1]:
^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.81– 7.79 (m, 4H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.51 (s, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ= 152.8, 139.0, 131.7, 128.9, 122.9, 120.5, 21.4.
(*E*)-1,2-bis(3-isopropylphenyl)diazene(**1q**)[1]:
^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.97 (s, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz ,6H), 3.12-3.17(q, 2H), 1.46 (d, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ= 153.0, 150.0, 129.3, 129.1,

121.1, 121.1, 121.1, 120.3, 34.2, 24.1.

(*E*)-1-(2-nitrophenyl)-2-phenyldiazene(**1r**)[3]:

^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.97-7.91(m, 3H), 7.71-7.68 (m, 2H), 7.62-7.56 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 152.5, 147.5, 145.5, 133.1, 132.3, 130.4, 129.3, 124.1, 123.6, 118.5.

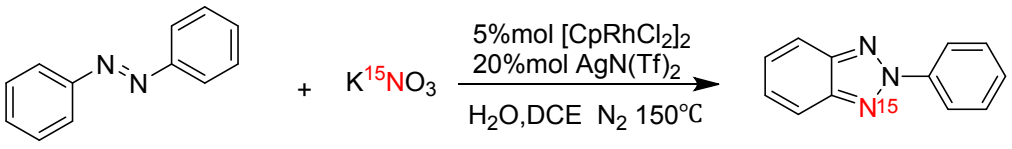
5 General procedures for the synthesis of products 2



1 **2**

azobenzenes **1** (0.3 mmol), $AgNO_3$ (0. 6 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgN(Tf)_2$ (20 mol %) and 1 eq H_2O was added to a flame-dried Schlenck tube which charged with a magnetic stir bar in1.5 mL DCE. The resulting suspension was stirred at 150℃ under N_2 for 12 h. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (petroleum and ethyl acetate = 100:1) to yield products **2**.

6 Experimental for Isotopic Tracer Experiments

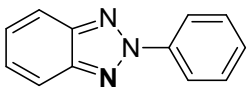


1a **2a'**

azobenzenes **1** (0.3 mmol), $K^{15}NO_3$ (0. 6 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgN(Tf)_2$ (20 mol %) and 1 eq H_2O was added to a flame-dried Schlenck tube which charged with a magnetic stir bar in 1.5 mL DCE. The resulting suspension was stirred at 150℃ under N_2 for 12 h. After celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (petroleum and ethyl acetate = 100:1) to yield products **2a'**.

7 Experimental characterization data for products 2

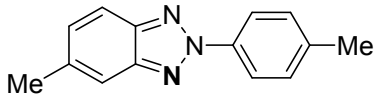
2-Phenyl-2Hbenzo[d][1,2,3]triazole (**2a**):



The title compound was prepared according to the general procedure as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ= 8.38-8.36 (m, 2H), 7.94- 7.92 (m, 2H), 7.54-7.50 (m,

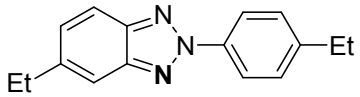
2H), 7.43-7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 145.0, 129.4, 128.9, 127.1, 120.6, 118.4; HRMS (ESI) calcd. for $C_{12}H_9N_3$ [M^+]: 195.0796, found: 195.0816

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



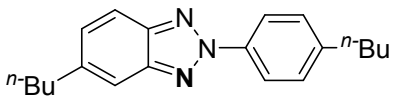
The title compound was prepared according to the general procedure as a white solid. ^{1}HNMR ($CDCl_3$, 400 MHz): δ=8.20 (d, 2H, *J* = 8.4 Hz), 7.90 (d, *J* = 8Hz,1H), 7.66 (s, 1H), 7.33 (d, *J* = 8.4 Hz,2H), 7.26−7.23 (m, 1H), 2.43 (s, 3H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=145.6, 143.8, 139.0, 138.4, 137.3, 130.1, 120.5, 117.8, 116.7, 11.4, 21.3; HRMS (ESI) calcd. for $C_{14}H_{13}N_3$ [M^+]: 223.1109, found: 223.1151.

5-Ethyl-2-(4-ethylphenyl)-2H-benzo[d][1,2,3]triazole (**2c**):



The title compound was prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.26 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31-7.29 (m, 1H), 2.83 (q, *J* = 8.0Hz,2H), 2.76 (q, *J* = 8.0 Hz,2H), 1.37-1.30(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)δ=145.4, 143.6, 138.9, 138.2, 137.2, 130.0, 129.9, 120.3, 117.7, 116.5, 29.2, 28.5,15.5, 15.3; HRMS (ESI) calcd. for $C_{16}H_{17}N_3$ [M^+]: 251.1422, found: 251.1450.

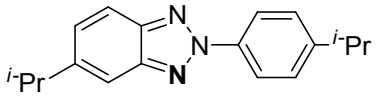
5-Butyl-2-(4-butylphenyl)-2H-benzo[d][1,2,3]triazole (**2d**):



The title compound was prepared according to the general procedure as a reddish liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.23 (d, *J* =8.0 Hz, 2H), 7.83 (d, *J* = 8.0Hz,1H), 7.67 (s, 1H), 7.34 (d, *J* = 8.0 Hz,2H), , 7.25-7.27 (m, 1H) ,

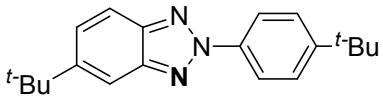
2.77 (t, *J* = 8.0 Hz,2H), 2.68 (t, *J* = 8.0 Hz,2H), 1.73-1.67 (m, 4H) , 1.30-1.44 (m, 4H),0.98-0.94 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 145.4, 143.8, 142.1, 129.3, 129.3, 120.4, 117.8, 115.9, 36.1, 35.27, 33.46, 33.26, 22.33, 22.29, 13.95, 13.9; HRMS (ESI) calcd. for $C_{20}H_{25}N_3$ [M^+]: 307.2048, found: 307.2067.

5-Isopropyl-2-(4-isopropylphenyl)-2H-benzo[d][1,2,3]triazole (**2e**):



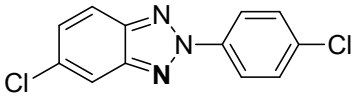
The title compound was prepared according to the general procedure as a light red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.24 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz,1H), 7.72 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33(d, *J* = 8.4 Hz, 1H), 3.07- 2.98 (m, 2H),1.35 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.30 (s,3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 149.9, 148.3, 145.6, 144.1, 138.6, 128.1, 127.5, 120.6, 118.1, 113.8, 34.7, 34.0, 24.1, 23.9; HRMS (ESI) calcd. for $C_{18}H_{21}N_3$ [M^+]: 279.1735, found: 279.1750.

5-Tertbutyl-2-(4-tertbutylphenyl)-2H-benzo[d][1,2,3]triazole (**2f**):



The title compound was prepared according to the general procedure as a yellow solid. ^{1}HNMR ($CDCl_3$, 400 MHz): δ= 8.28-8.24 (m, *J* =8.0 Hz 2H), 7.97 (m, 2H), 7.58-7.52 (m, 3H), 1.42 (s, 9H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 152.0, 150.3, 145.4, 143.5, 126.8, 126.3, 120.1, 117.6, 112.8, 35.3, 34.8, 31.3, 31.1; HRMS (ESI) calcd. for $C_{20}H_{25}N_3$ [M^+]: 307.2048, found: 307.2059.

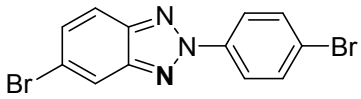
5-Chloro-2-(3-chlorophenyl)-2H-benzo[d][1,2,3]triazole (**2g**):



The title compound was prepared according to the general procedure as a white solid; ^{1}H NMR

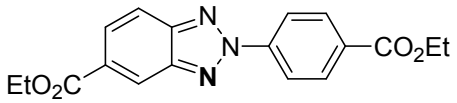
($CDCl_3$,400 MHz): δ= 8.25-8.28 (m, 2H), 7.90 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz 1H), 7.85(dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz 1H), 7.54-7.50 (m, 2H), 7.37 (m 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 145.4, 143.6, 135.2, 133.27, 129.7, 129.1, 121. 8, 119.6, 117.4; HRMS (ESI) calcd. for $C_{12}H_7Cl_2N_3$ [M^+]: 263.0017, found: 263.0026.

5-Bromo-2-(4-bromophenyl)-2H-benzo[d][1,2,3]triazole (**2h**):



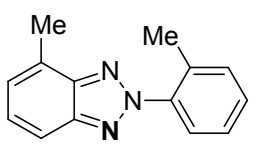
The title compound was prepared according to the general procedure as a brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.22 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 12.0 Hz, 1H),8.10 (s, 1H), 7.69-7.67 (m, 2H), 7.50 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 146.0, 143.7, 134.0, 132.6, 131.4, 123.3, 122.1, 122.0, 121.2, 120.8, 119.8; HRMS (ESI) calcd. for $C_{12}H_7Br_2N_3$ [M^+]: 350.9007, found: 350.9029.

Ethyl2-(4-(ethoxycarbonyl)phenyl)-2H-benzo[d][1,2,3]triazole-5-carboxylate (**2i**):



The title compound was prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.68 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 8.0 Hz, 2H), 8.22-8.19 (m, 2H), 8.04 (dd, J = 8.0 Hz, 1.0 Hz, 1H),7.93-7.91 (m, 1H), 4.44-4.33 (m, 4H), 1.46-1.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ= 166.0, 165.5, 146.9, 144.7, 143.0, 131.2, 131.0, 129.9, 127.6, 122.9,122.1,120.5, 118.4, 61.5, 61.4, 14.3; HRMS (ESI) calcd. for $C_{18}H_{17}N_3O_4$ [M^+]: 339.1219, found: 339.1236.

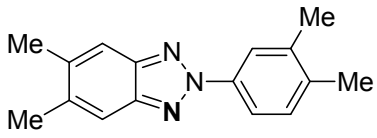
4-Methyl-2-(o-tolyl)-2H-benzo[d][1,2,3]triazole (**2j**):



The title compound was prepared according to the

general procedure as a red liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.79 (d, 1H, *J* = 12.0 Hz) , 7.70 (d, 1H, *J* = 8.0 Hz), 7.33-7.43 (m, 4H), 7.19 (d, 1H, *J* = 6.8 Hz), 2.41 (s, 3H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 145.3, 144.7, 140.4, 133.5, 131.7, 129.5, 129.52, 129.09, 128.1, 127.1, 126.7, 126.1, 125.8, 115.6, 18.7, 17.2; HRMS (ESI) calcd. for $C_{14}H_{13}N_3$ [M^+]: 223.1109, found: 223.1136.

2-(3,4-dimethylphenyl)-5,6-dimethyl-2H-benzo[d][1,2,3]triazole(**2k**):



The title compound was prepared according to the general procedure as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.11 (s, 1H), 8.03 (dd, J_1 = 8 Hz, J_2 = 3.6, 1H), 7.67 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 6H), 2.40 (s, 3H), 2. 53(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.4, 137.5, 130.4, 121.3, 117.7, 116.6, 21.0, 19.9, 19.5; HRMS (ESI) calcd. for $C_{16}H_{17}N_3$ [M^+]: 251.1422, found: 251.1446.

2-(p-tolyl)-2H-benzo[d][1,2,3]triazole(2l)+5-methyl-2-phenyl-2H-benzo[d][1,2,3]triazole(**2l/l'**):

The title mixture was prepared according to the general procedure as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.37(m, 2H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.74-8.773 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H),7.54-7.58 (m, 1H),7.42-7.47 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.26-7.28 (m, 1H), 2.53 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 144.9, 143.8, 139.2, 137.3, 131.2, 130.2, 130.0, 129.7, 129.4, 129.0, 128.7, 127.0, 122.9, 122.7, 120.5, 120.5, 118.3, 117.8, 116.5, 22.2, 21.2; HRMS (ESI) calcd. for $C_{13}H_{11}N_3$ [M^+]: 209.0953, found: 209.0966.

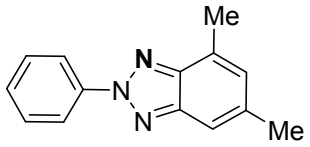
2-(4-chlorophenyl)-2H-benzo[d][1,2,3]triazole(3n)+5-chloro-2-phenyl-2H-benzo[d][1,2,3]triazole(**2m/m'**):

The title compound was prepared according to the general procedure as a whitesolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.29 (t, *J* = 4.0 Hz,1H), 8.30 (t, *J* = 4.0 Hz, 3H), 8.28 (t, *J* = 8.0 Hz, 2H), 7.88-7.937.29 (m, 5H), 7.86 (d, *J* = 4.0 Hz, 0.5H), 7.84 (d, J = 4.0 Hz, 0.5H), 7.51-7.56(m, 1.5H), 7.46-7.53(m, 5H), 7.39-7.44(m, 4H), 7.36 (d, *J* = 4.0 Hz, 0.5H), 7.34 (d, *J* = 4.0 Hz, 0.5H). ^{13}C NMR (100 MHz) δ= 145.3, 145.1, 143.5, 134.8, 132.9, 129.6, 129.5, 129.3, 128.7, 127.4, 121.7, 120.6, 119.6, 118.4, 117.4; HRMS (ESI) calcd. for $C_{12}H_8ClN_3$ [M^+]: 229.0407, found: 229.0452.

4-(2H-benzo[d][1,2,3]triazol-2-yl)benzonitrile(2n)+2-phenyl-2H-benzo[d][1,2,3]triazole-5-carbonitrile(**2n/n'**):

The title compound was prepared according to the general procedure as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.49 (d, *J* = 8.0 Hz, 2H), 8.35-8.37(m, 0.5H), 8.03(d, *J* = 12.0 Hz, 0.25H), 8.88-7.93 (m, 2H), 8.82-7.85(m, 2H), 8.51-7.60(m, 1H), 7.43-7.47(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.5, 133.6, 130.1, 129.7, 128.2, 128.0, 125.6, 121.0, 120.2, 118.6, 118.1, 112.4; HRMS (ESI) calcd. for $C_{13}H_8N_4$ [M^+]: 220.0749, found: 220.0761.

2-(3,5-Dimethylphenyl)-2H-benzo[d][1,2,3]triazole (**2o**):



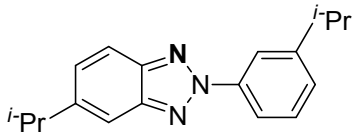
The title compound was prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.33-8.35 (m, 2H), 7.52-7.56 (m,2H), 7.48 (s, 1H), 7.41-7.44 (m, 1H), 2.45 (d, *J* = 0.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 145.6, 144.4, 129.3, 129.1, 128.49, 128.40,

120.5, 113.8, 22.2, 17.1; HRMS (ESI) calcd. for $C_{14}H_{13}N_3$ [M^+]: 223.1109, found: 223.1128.

5-Methyl-2-m-tolyl-2H-benzo[d][1,2,3]triazole (2p)+ 4-methyl-2- (m-tolyl)-2H-benzo[d][1,2,3]triazole(**2p/p'**):

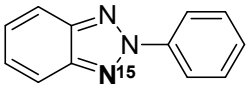
The title compound was prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.15 (s, 1H), 8.11 (d, *J* = 8.0Hz,1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.71-7.72 (m, 0.4H), 7.65 (d, *J* = 4.0 Hz, 1H),7.41(t, *J* = 8.0 Hz, 1H), 7.34-7.37 (m, 0.4H), 7.22-7.25 (m, 2H), 7.13 (s, 0.4H), 2.50 (s, 3H), 2.47 (s, 3H), 2.45 (s, 0.6H), 2.41 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 145.5, 143.7, 141.7, 140.4, 139.5, 139.5, 139.0, 137.3, 131.7, 130.4, 130.3, 130.1, 129.9, 129.2, 129.2, 128.9, 122.9, 121.9, 121.0, 120.5, 118.5, 117.8, 117.7, 116.5,7 22.18, 21.4; HRMS (ESI) calcd. for $C_{14}H_{13}N_3$ [M^+]: 223.1109, found: 223.1121.

5-isopropyl-2-(3-isopropylphenyl)-2H-benzo[d][1,2,3]triazole(**2q**):



The title compound was prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.22 (s, 1H), 8.15 (d, *J* = 8.0 Hz,1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.35(t, *J* = 8.0 Hz,1H), 3.04-3.10 (m, 2H),1.37 (s, 3H), 1.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.6, 148.2, 145.5, 143.9, 129.3, 128.1, 127.0, 118.6, 118.1, 117.9, 113.7, 113.7, 113.7, 34.5, 34.3, 23.9, 23.7, HRMS (ESI) calcd. for $C_{18}H_{21}N_3$ [M^+]: 279.1735, found: 279.1762.

2-Phenyl-2Hbenzo[d][1,2,3]triazole (**2a'**):



The title compound was prepared according to the general procedure as a yellow solid. ^{1}H NMR (400 MHz,

$CDCl_3$) δ= 8.38-8.35 (m, 2H), 7.96-7.92 (m, 2H), 7.55 (t, J = 8.0 Hz, 2H), 7.48-7.41(m, 3H); HRMS for $C_{12}H_9N_2N^{15}$ [M^+]: 196.1579

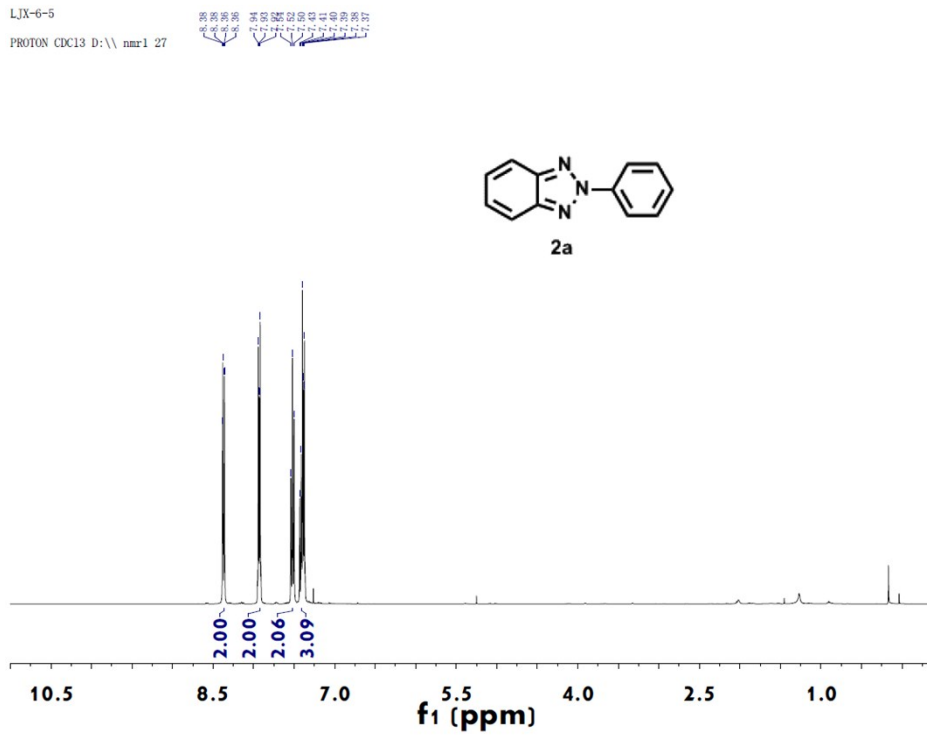
References 1

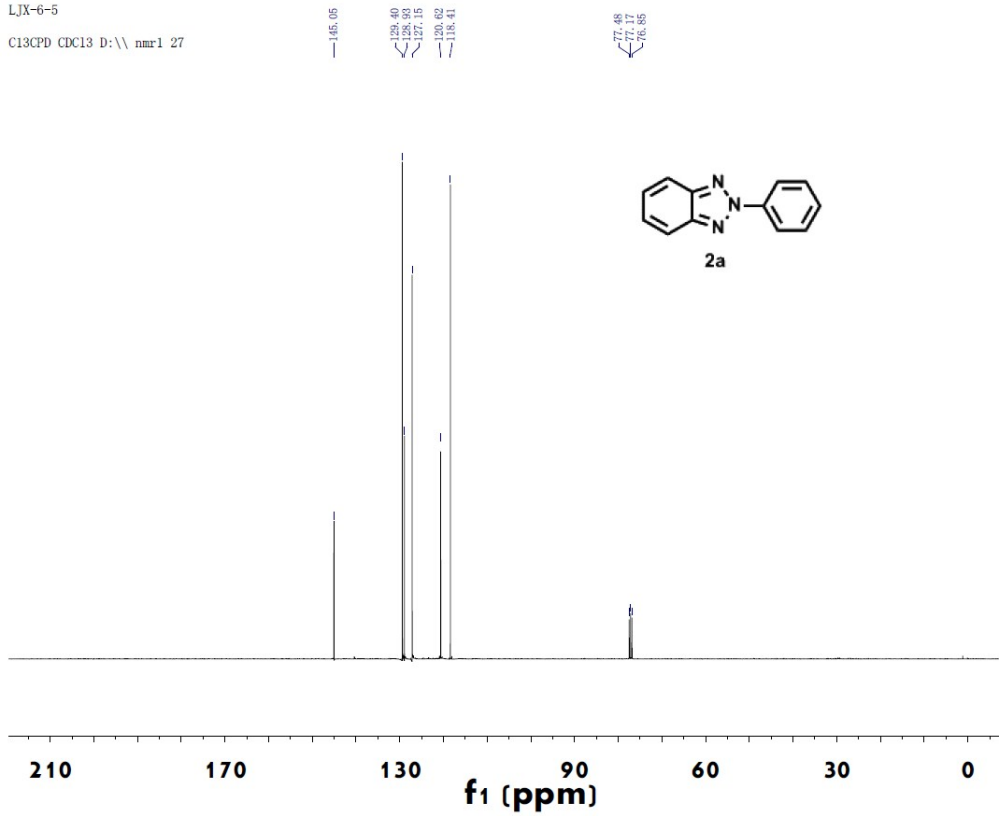
Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed*. 2010, **49,** 6174. 2

Ellman, J. A.; Lavis, L. D.; Bergman, R. G.; Lian. Y. *J. Am. Chem. Soc.* 2013, **135,** 7122.

3 Dong, J. W; Jin, B.; Sun, P. P. *Org. Lett*., 2014, **16,** 4540.

8 ^{1}H and ^{13}C NMR spectra for all compounds

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129.40
128.93
127.15
120.62
118.41
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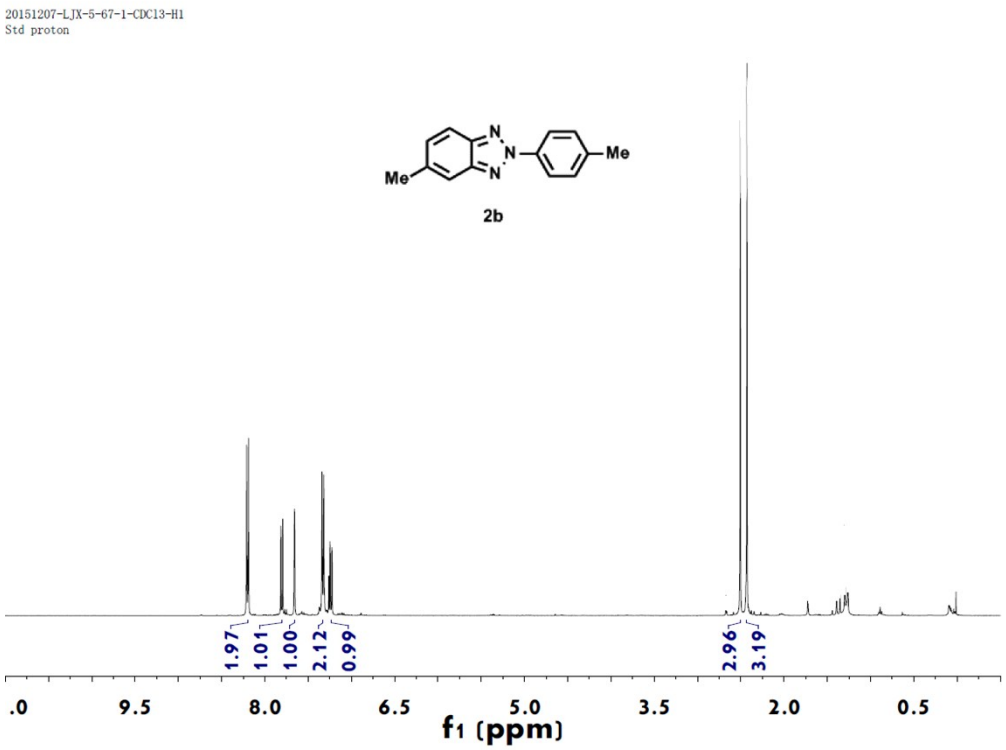
77.17
76.85
2a
210
170
130
90
60
30
0
f1 (ppm)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Std proton
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Me
2b
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1.01
1.00
2.12
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9.5
8.0
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3.5
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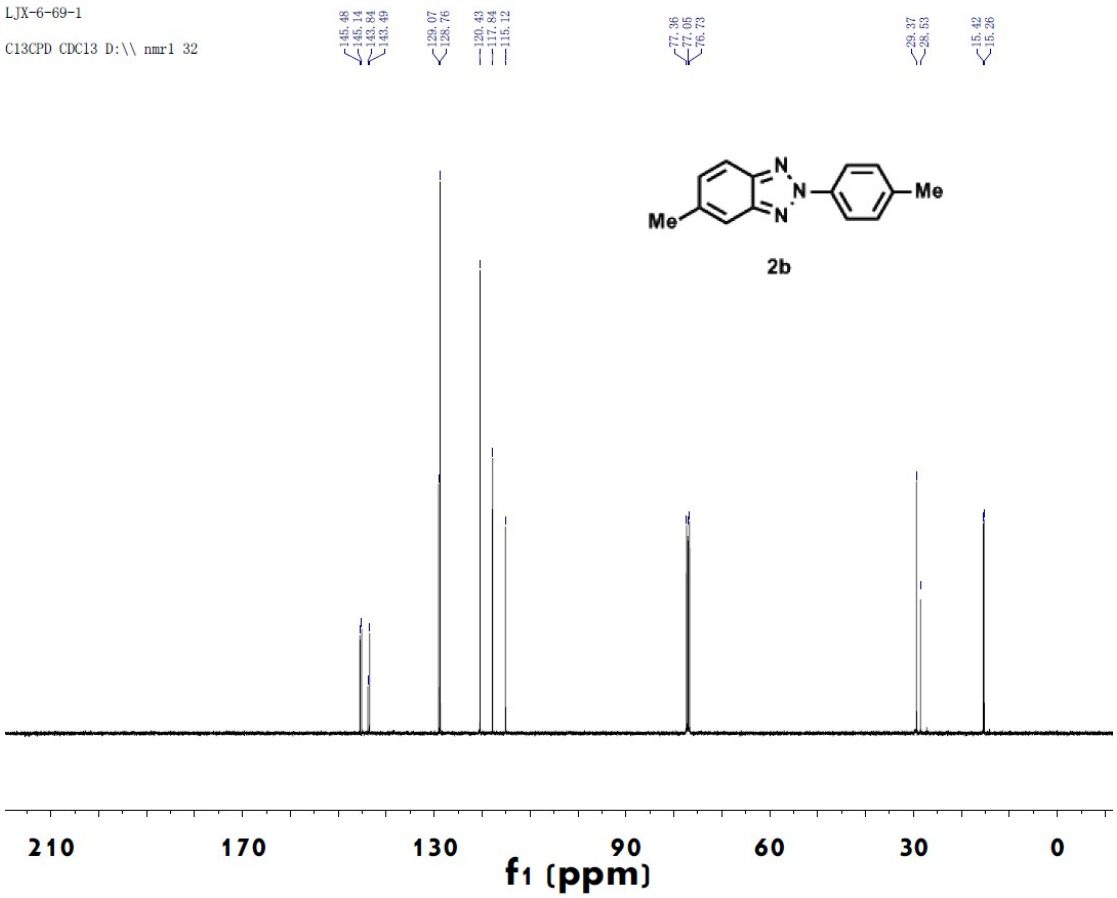
0.5
f1 (ppm)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115.12
77.36
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29.37
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15.42
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Me
Me
2b
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170
130
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30
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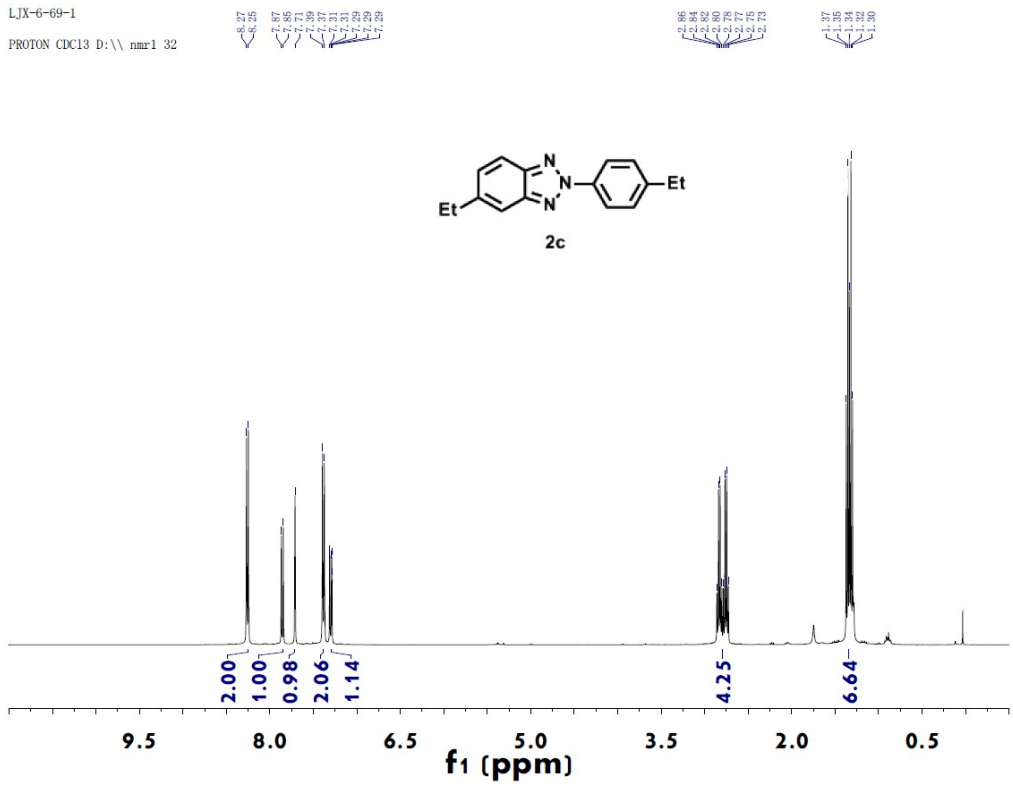
f1 (ppm)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7.29
7.29
7.29
2.86
2.84
2.82
2.80
2.78
2.77
2.75
2.73
1.37
1.35
1.34
1.32
1.30
Et
Et
2c
2.00
1.00
0.98
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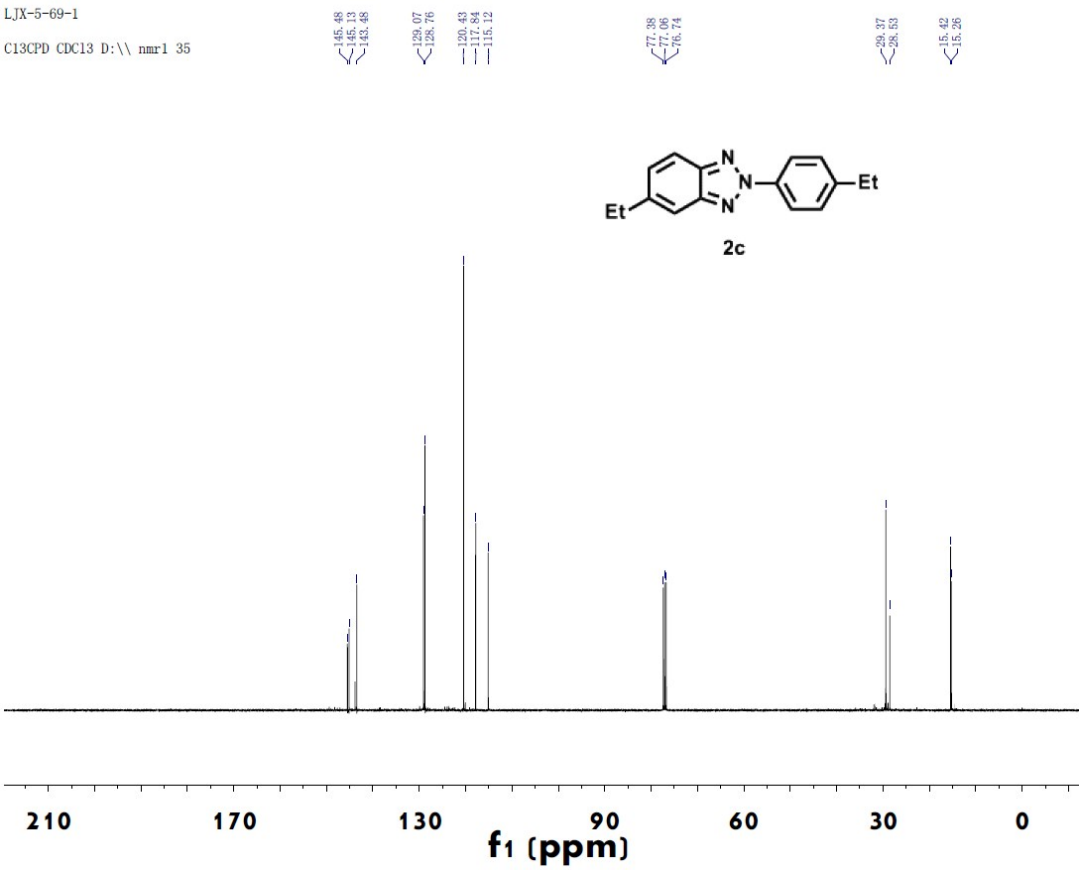
0.5
f1 (ppm)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145.13
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129.07
128.76
120.43
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Et
Et
2c
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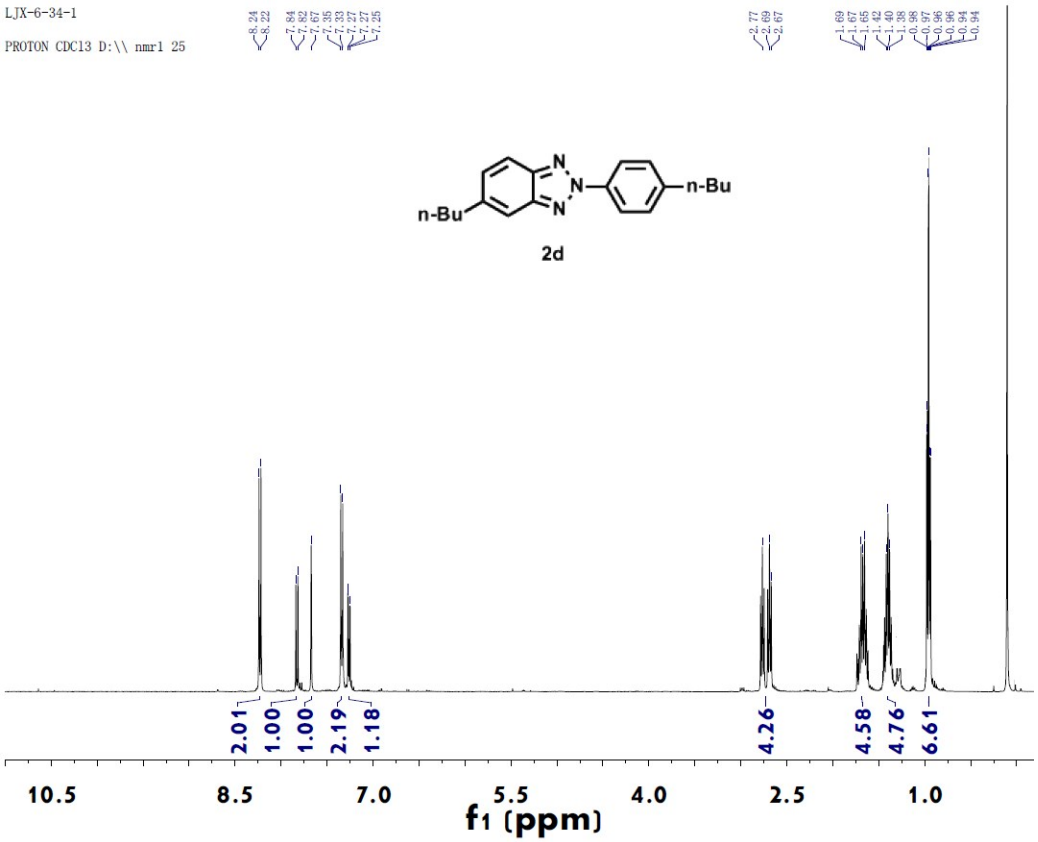
170
130
90
60
30
0
f1 (ppm)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2.69
2.67
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1.67
1.65
1.42
1.40
1.38
0.98
0.97
0.96
0.96
0.94
0.94
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n-Bu
2d
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1.00
1.00
2.19
1.18
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7.0
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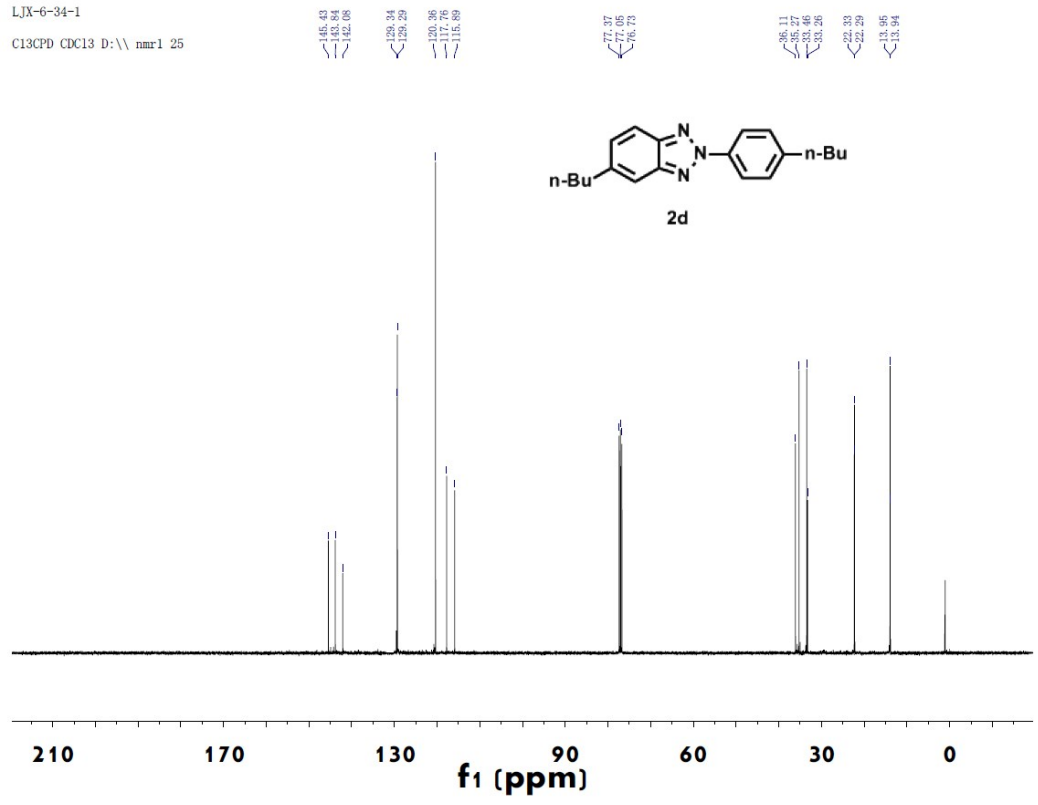
2.5
1.0
f1 (ppm)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33.46
33.26
22.33
22.29
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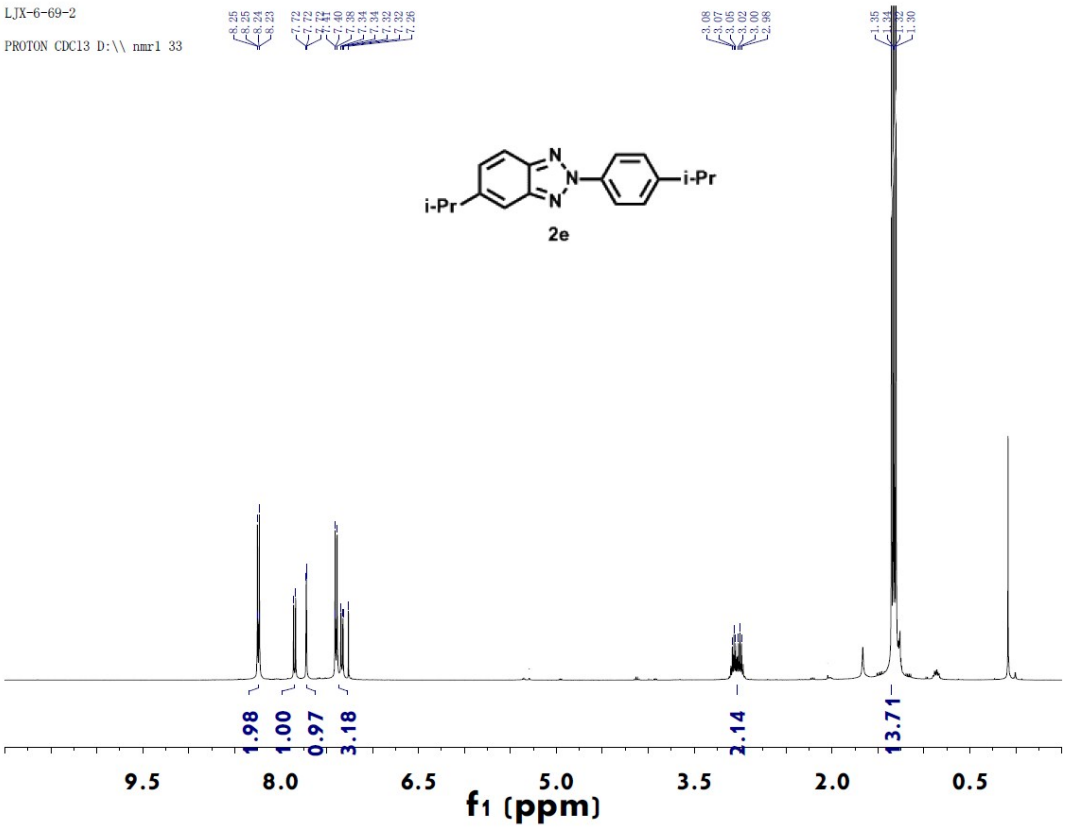
n-Bu
2d
210
170
130
90
60
30
0
f1 (ppm)


LJX-6-69-2
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i-Pr
2e
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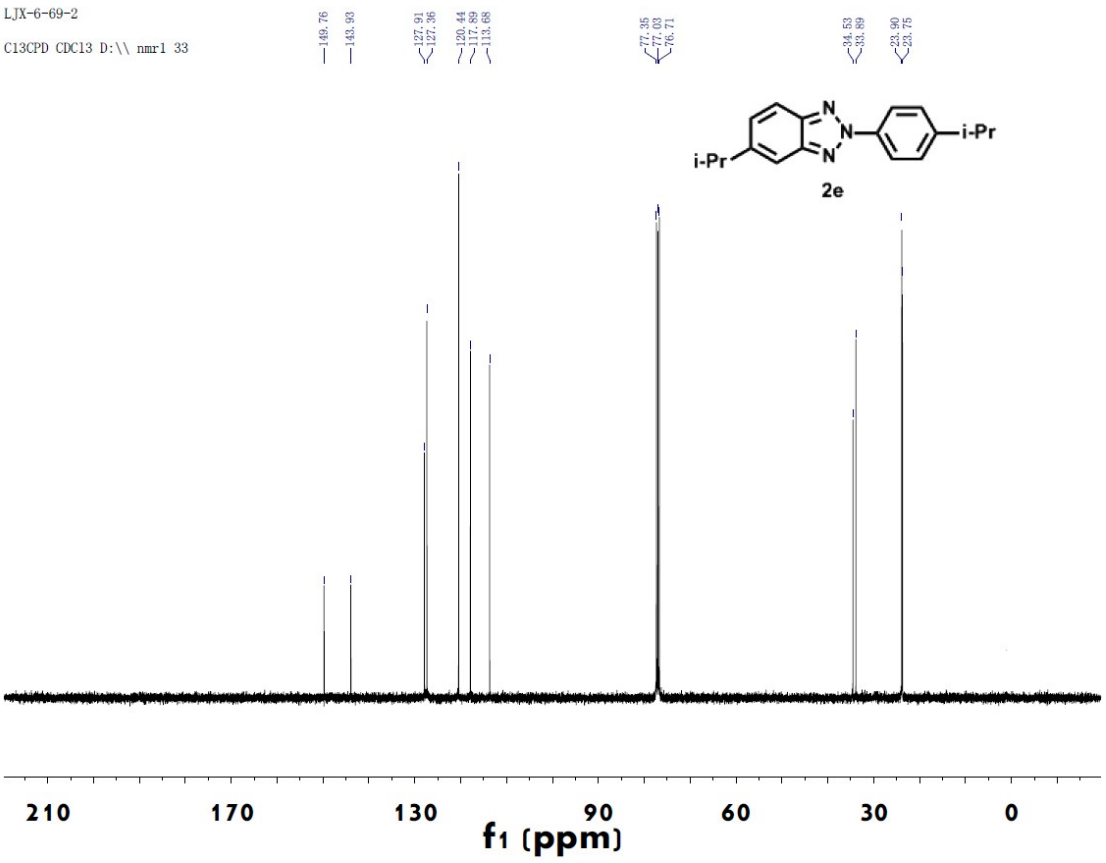
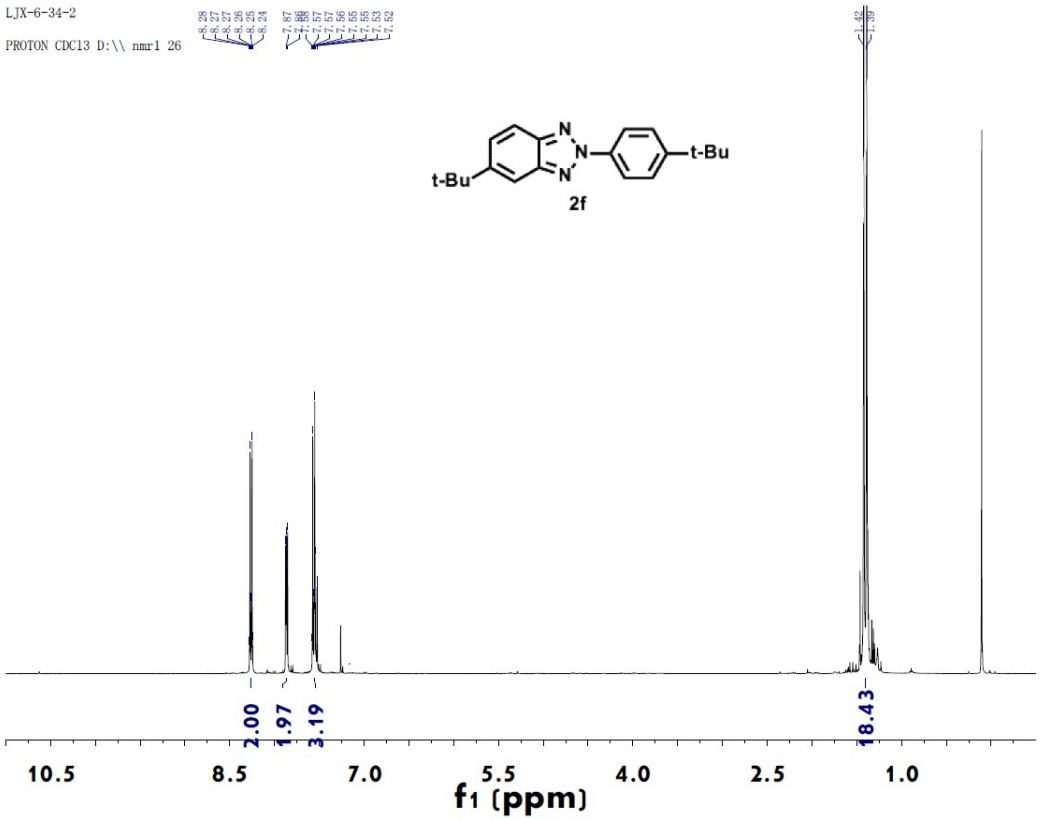
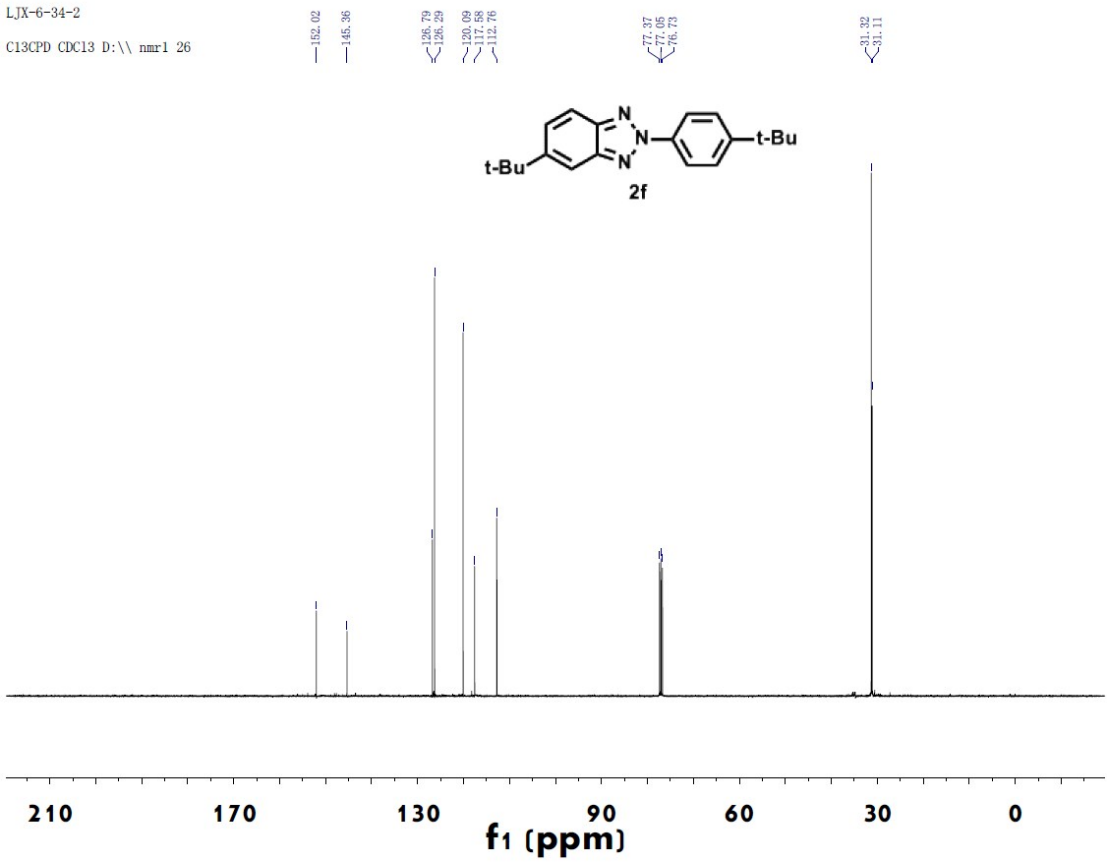
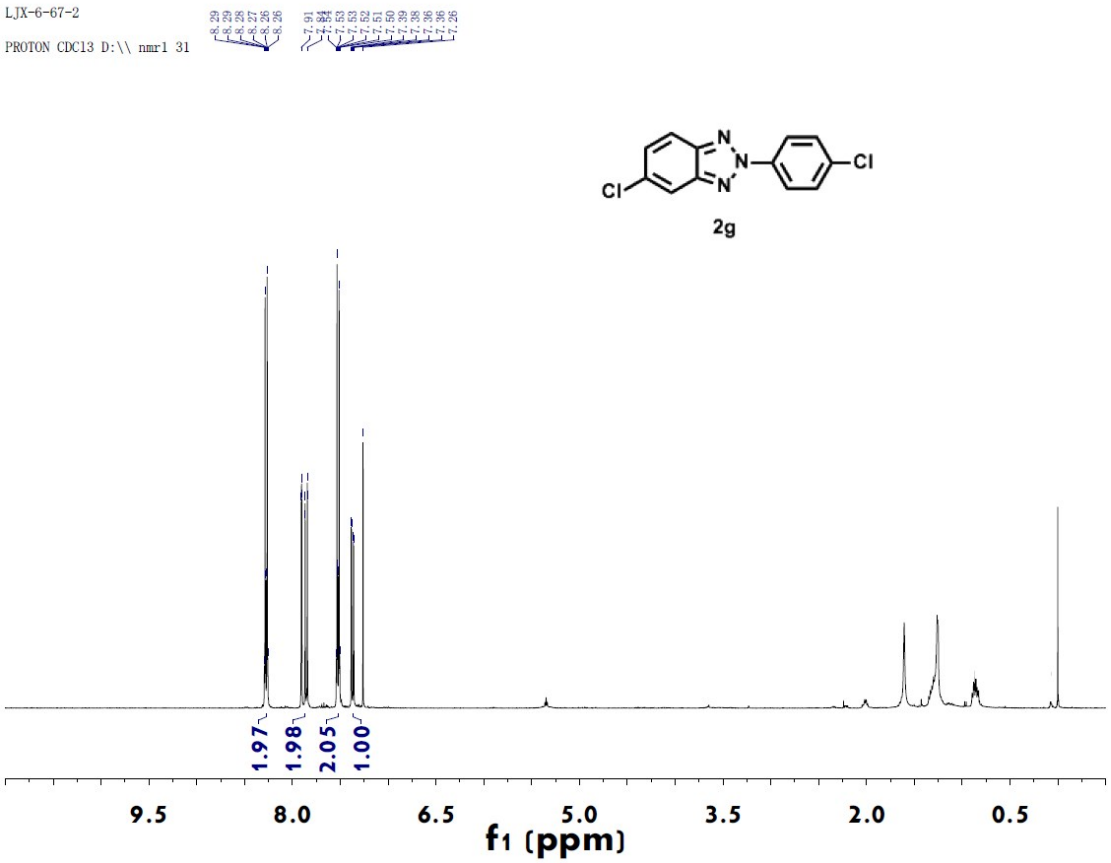
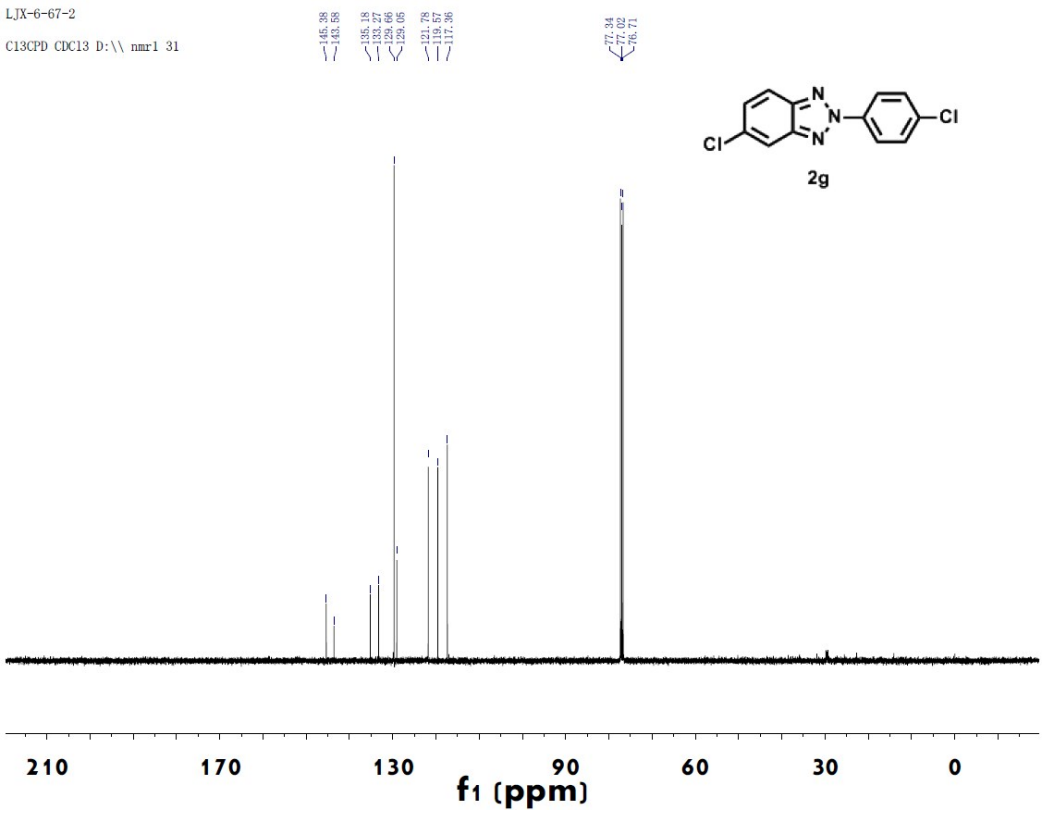
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

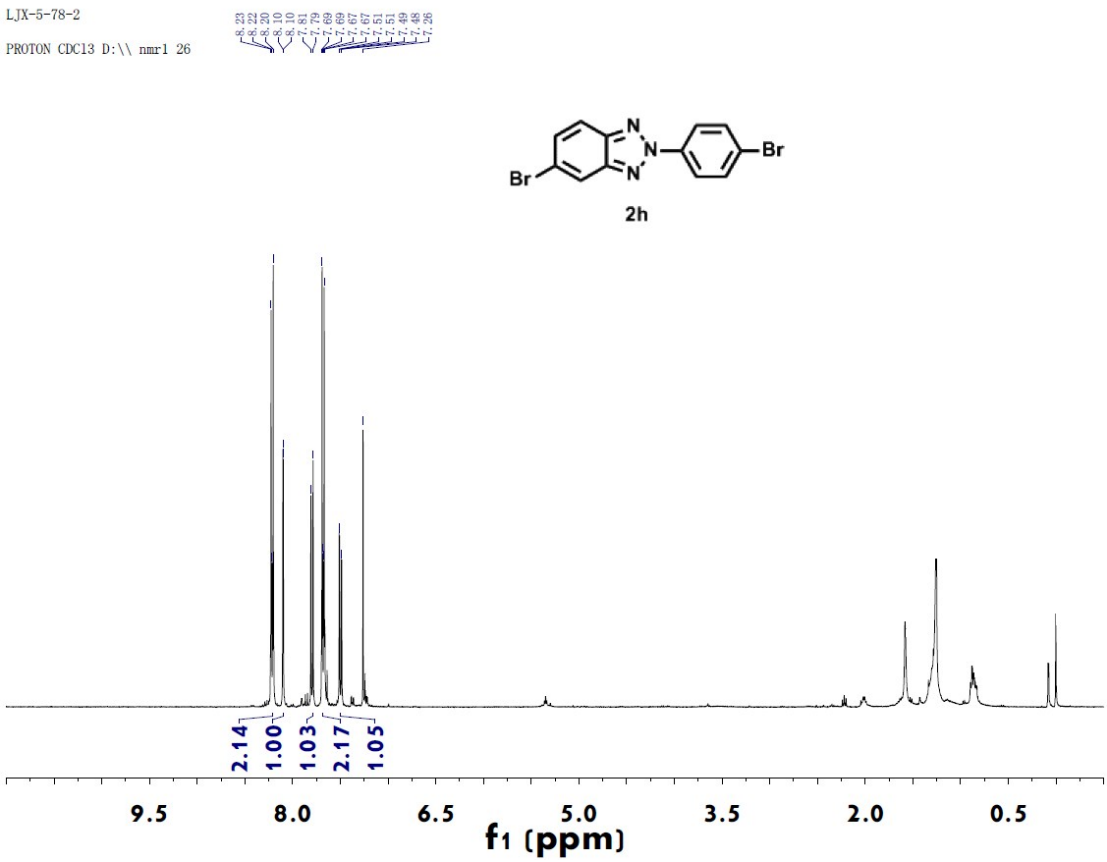

LJX-6-69-2
C13CPD CDCl3 D:\\ nmr1 33
i-Pr
i-Pr
2e
210
170
130
90
60
30
0
f1 (ppm)

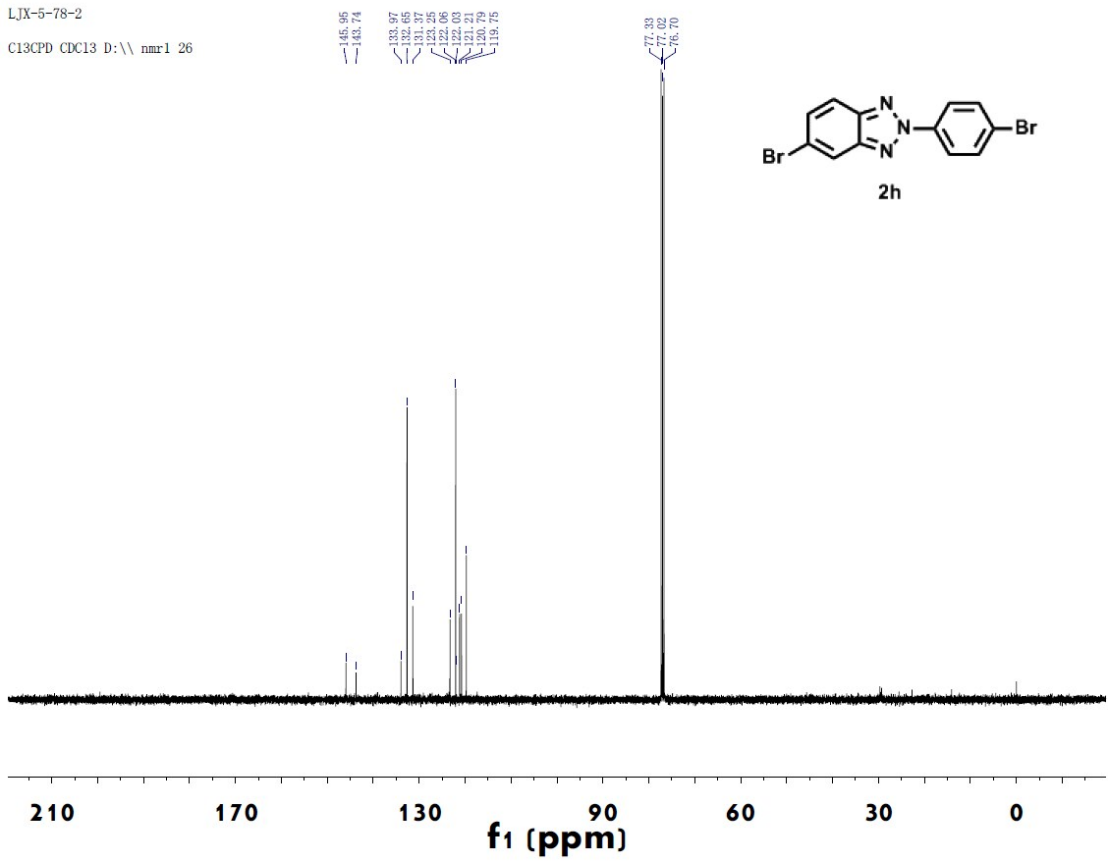

LJX-6-34-2
PROTON CDC13 D:\\ nmr1 26
t-Bu
t-Bu
2f
2.00
1.97
3.19
18.43
10.5
8.5
7.0
5.5
4.0
2.5
1.0
f1 (ppm)

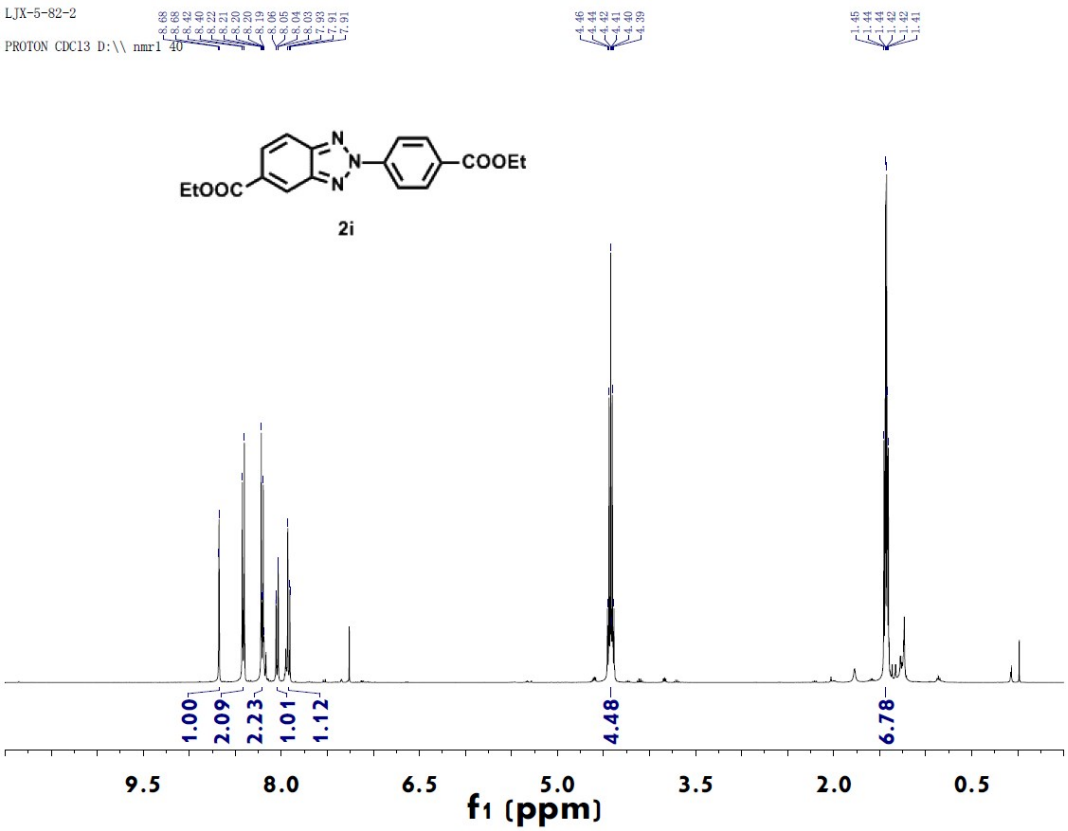

LJX-6-34-2
C13CPD CDC13 D:\\ nmr1 26
152.02
145.36
126.79
126.29
120.09
117.58
112.76
77.37
77.05
76.73
31.32
31.11
t-Bu
t-Bu
2f
210
170
130
90
60
30
0
f1 (ppm)

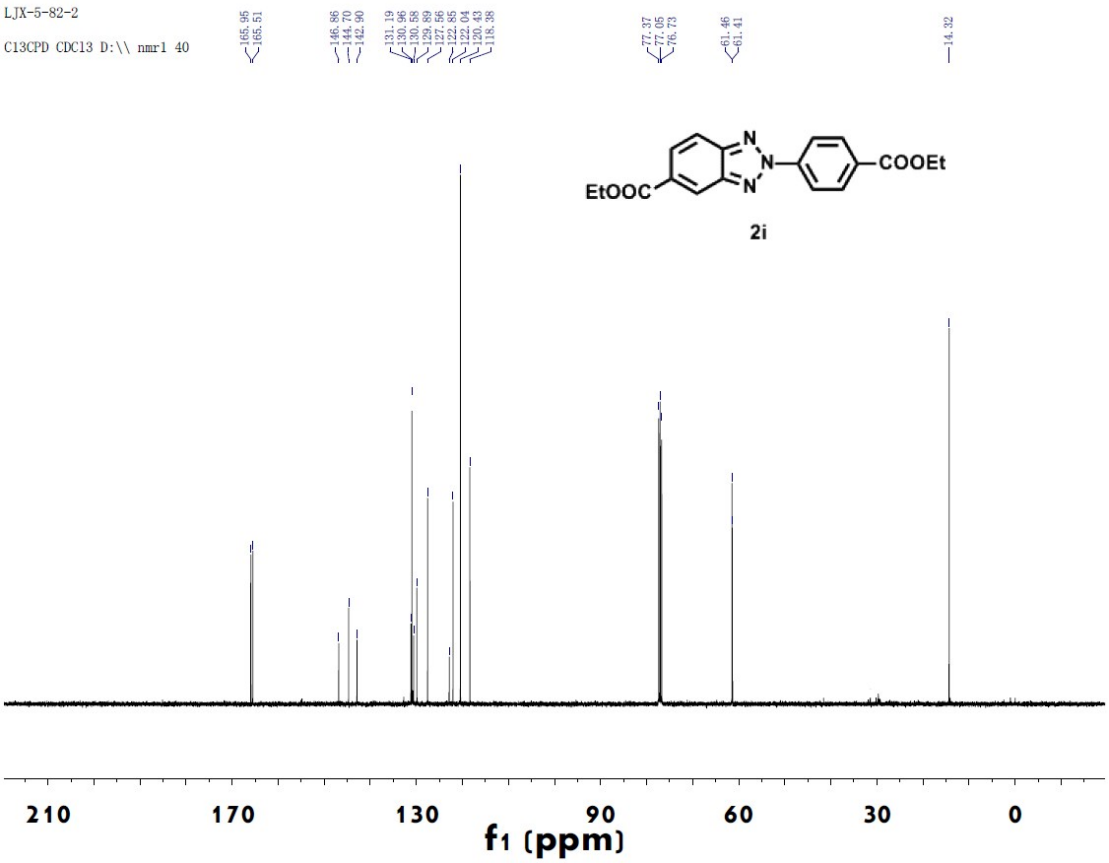

LJX-6-67-2
PROTON CDCl3 D:\\ nmr1 31
8.29
8.28
8.27
8.26
8.26
7.91
7.84
7.53
7.52
7.51
7.50
7.39
7.38
7.36
7.36
7.26
Cl
N
N
N
Cl
2g
1.97
1.98
2.05
1.00
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

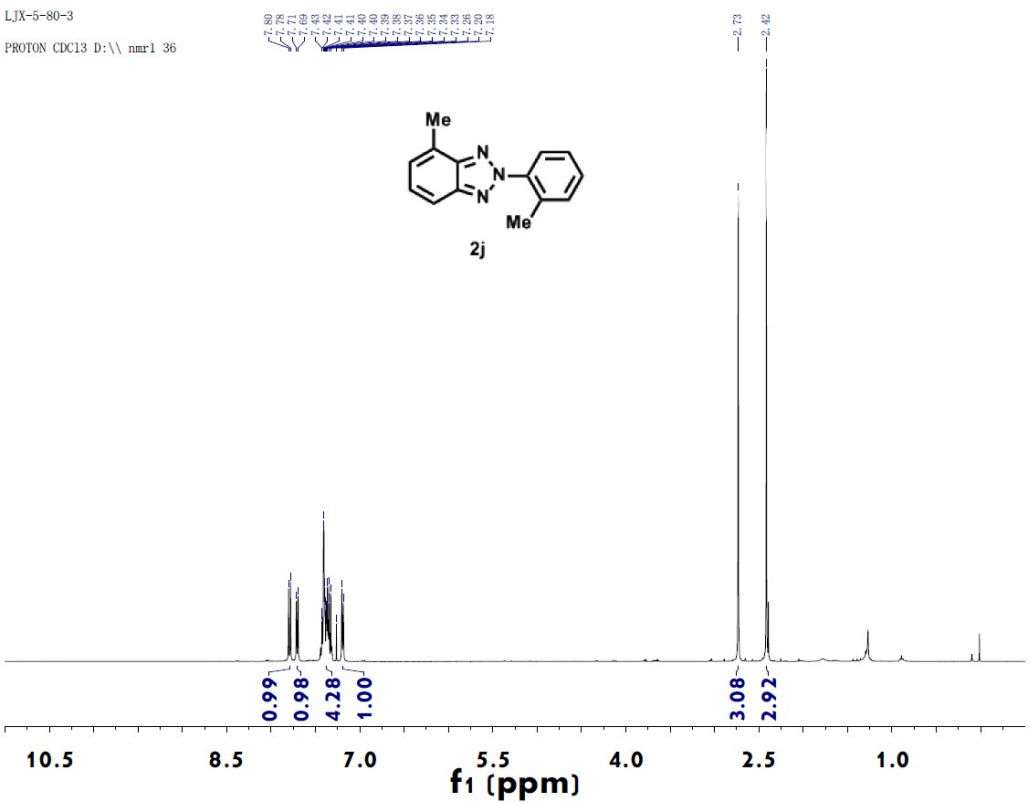

LJX-6-67-2
C13CPD CDCl3 D:\\ nmr1 31
145.38
143.58
135.18
133.27
129.66
129.05
121.78
119.67
117.36
77.34
77.02
76.71
Cl
N
N
N
Cl
2g
210
170
130
90
60
30
0
f1 (ppm)

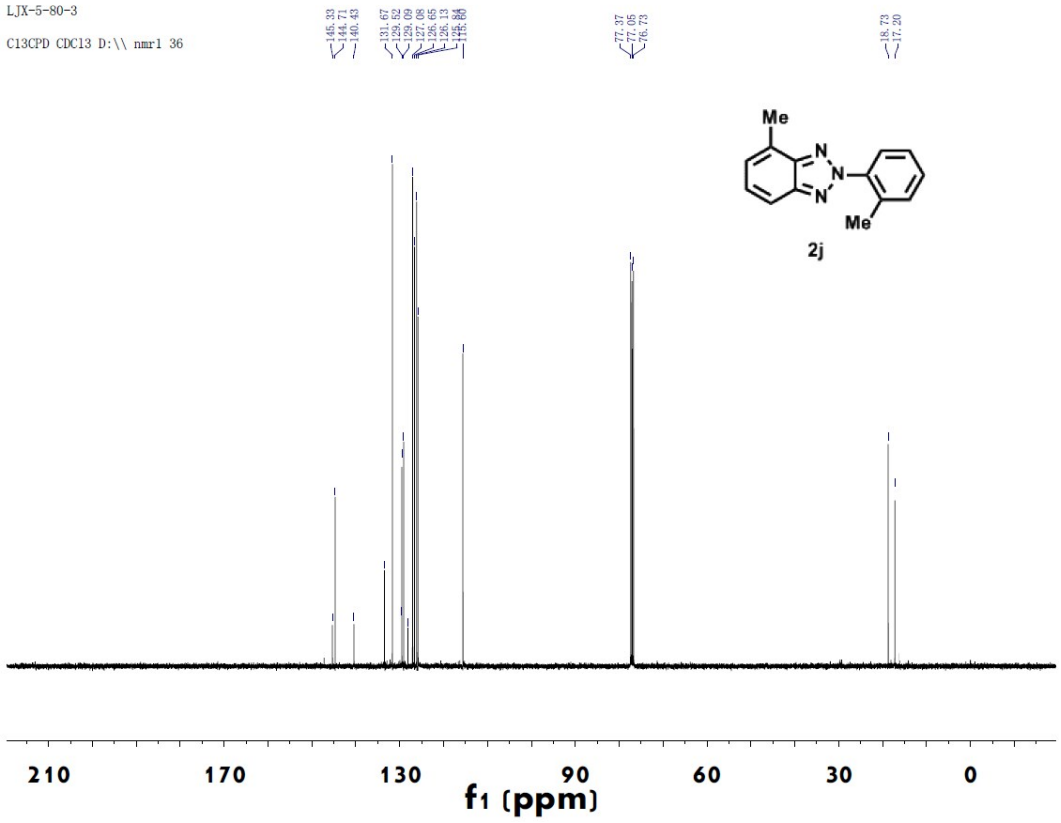

LJX-5-78-2
PROTON CDCl3 D:\\ nmr1 26
8.23
8.22
8.20
8.10
8.10
7.81
7.79
7.69
7.69
7.67
7.67
7.51
7.51
7.49
7.48
7.26
Br
N
N
N
Br
2h
2.14
1.00
1.03
2.17
1.05
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

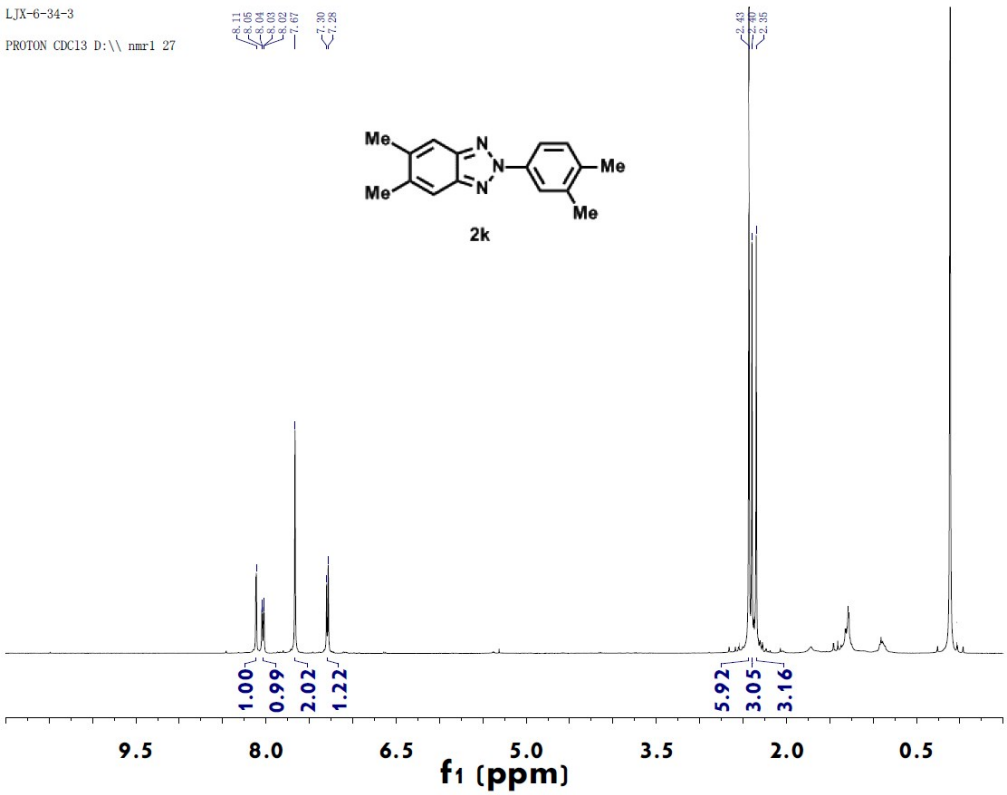

LJX-5-78-2
C13CPD CDCl3 D:\\ nmr1 26
145.95
143.74
133.97
132.65
131.37
123.25
122.06
122.03
121.21
120.79
119.75
77.33
77.02
76.70
Br
N
N
N
Br
2h
210
170
130
90
60
30
0
f1 (ppm)

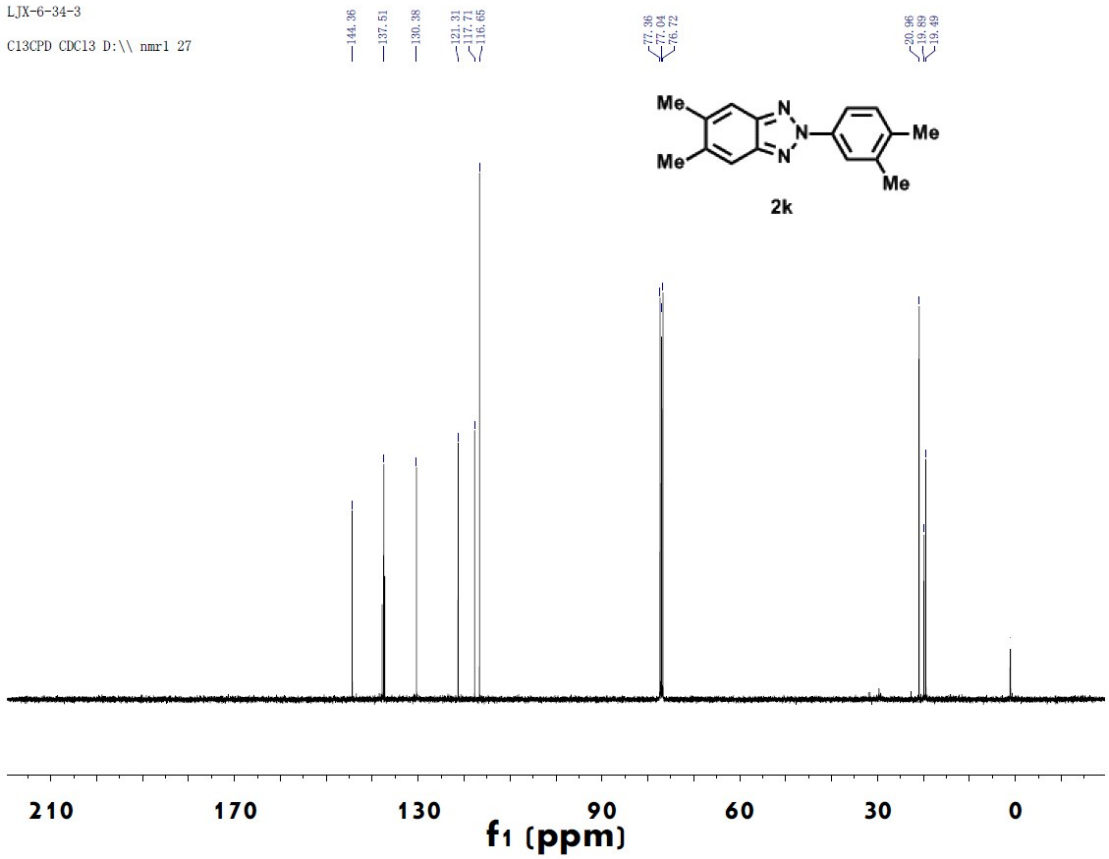

LJX-5-82-2
PROTON CDC13 D:\\ nmr1 40
EtOOC
COOEt
2i
1.00
2.09
2.23
1.01
1.12
4.48
6.78
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

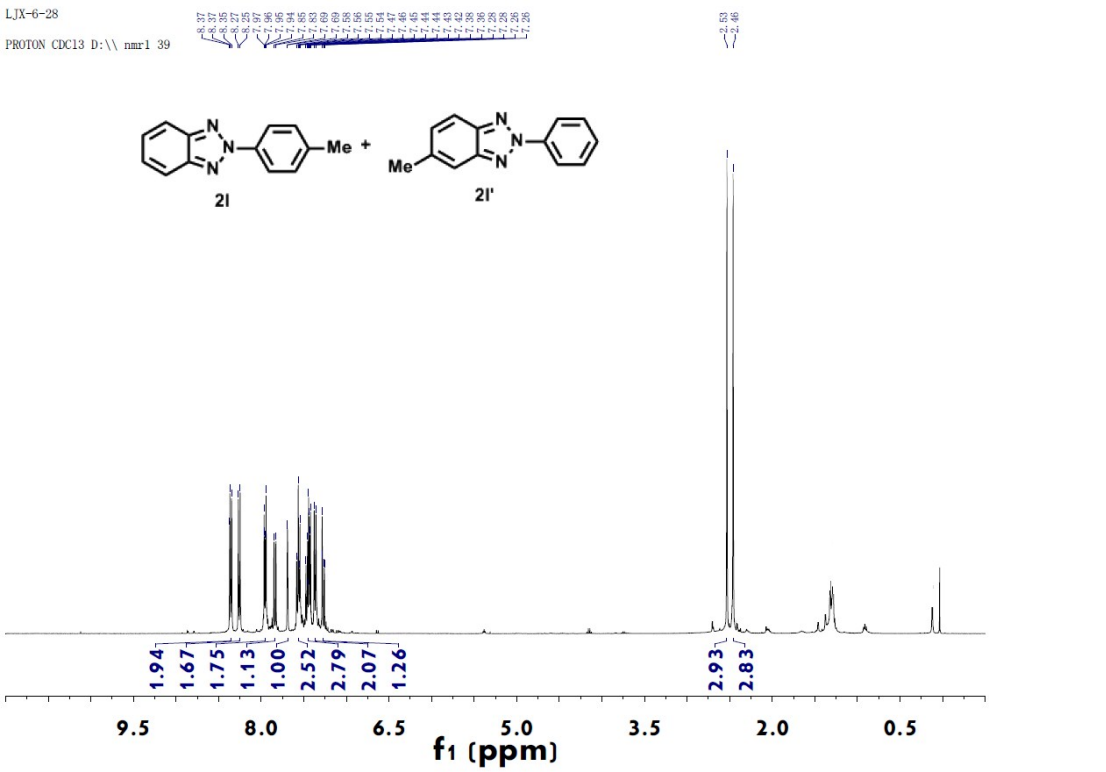

LJX-5-82-2
C13CPD CDC13 D:\\ nmr1 40
EtOOC
COOEt
2i
210
170
130
90
60
30
0
f1 (ppm)

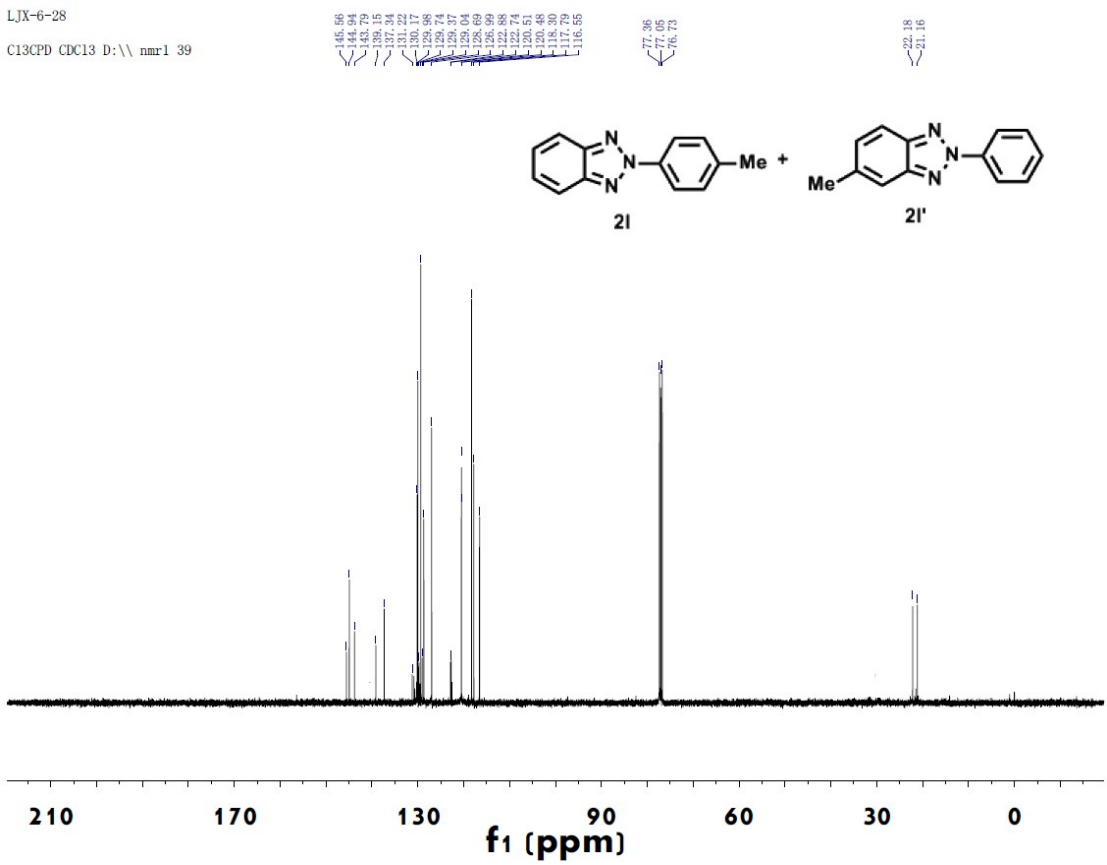

LJX-5-80-3
PROTON CDCl3 D:\\ nmr1 36
Me
Me
2j
0.99
0.98
4.28
1.00
3.08
2.92
10.5
8.5
7.0
5.5
4.0
2.5
1.0
f1 (ppm)

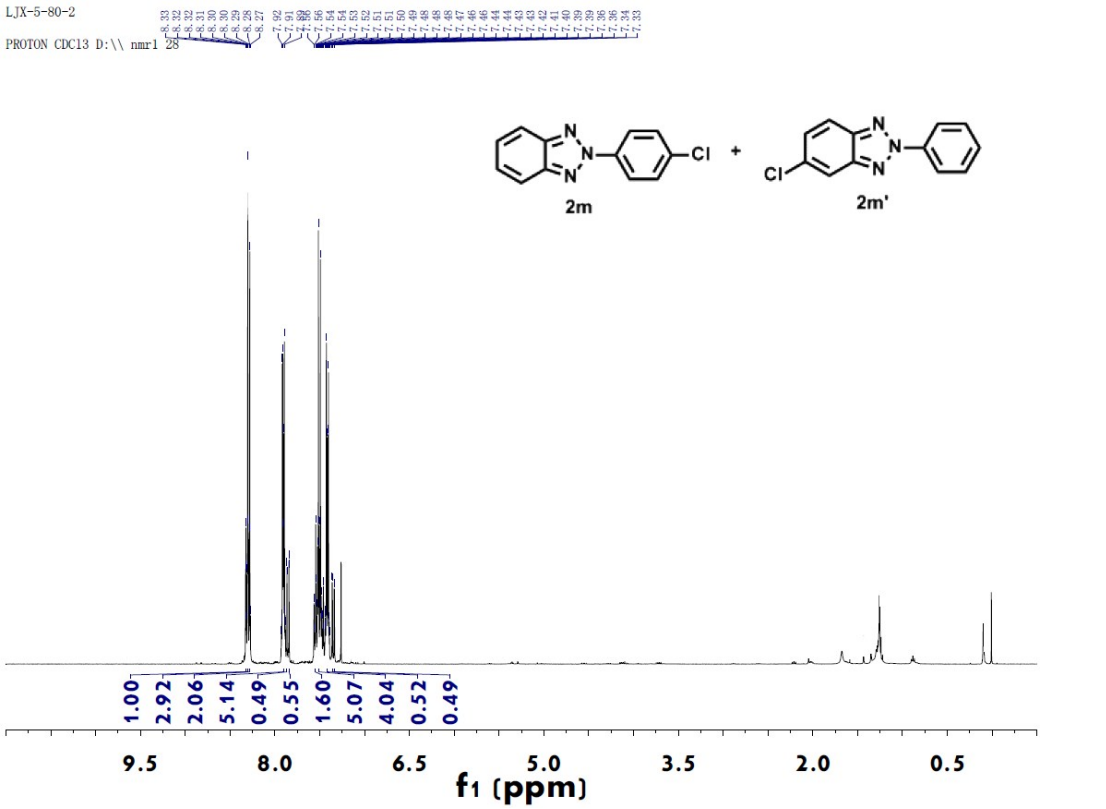

LJX-5-80-3
C13CPD CDCl3 D:\\ nmr1 36
Me
Me
2j
210
170
130
90
60
30
0
f1 (ppm)

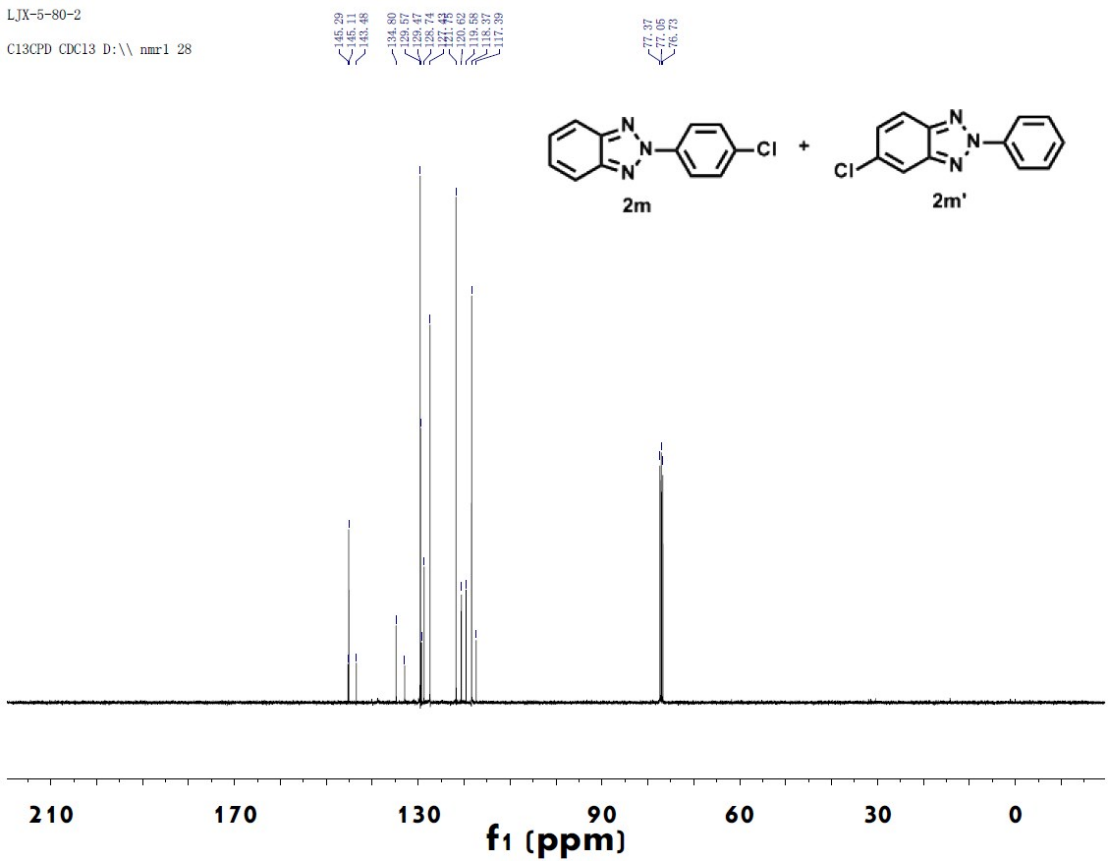

LJX-6-34-3
PROTON CDCl3 D:\\ nmr1 27
8.11
8.05
8.04
8.03
8.02
7.67
7.30
7.28
2.43
2.40
2.35
Me
Me
N
N
N
Me
Me
2k
1.00
0.99
2.02
1.22
5.92
3.05
3.16
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

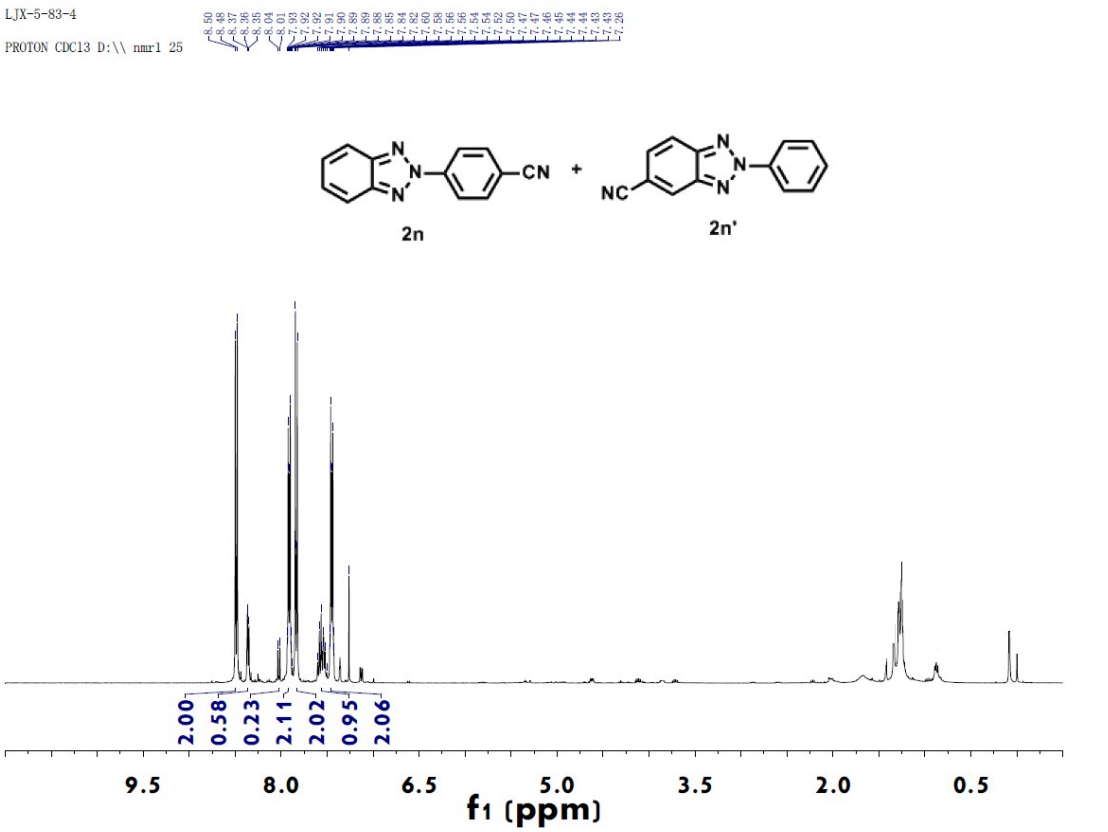

LJX-6-34-3
C13CPD CDCl3 D:\\ nmr1 27
144.36
137.51
130.38
121.31
117.71
116.65
77.36
77.04
76.72
20.96
19.69
19.49
Me
Me
N
N
N
Me
Me
2k
210
170
130
90
60
30
0
f1 (ppm)

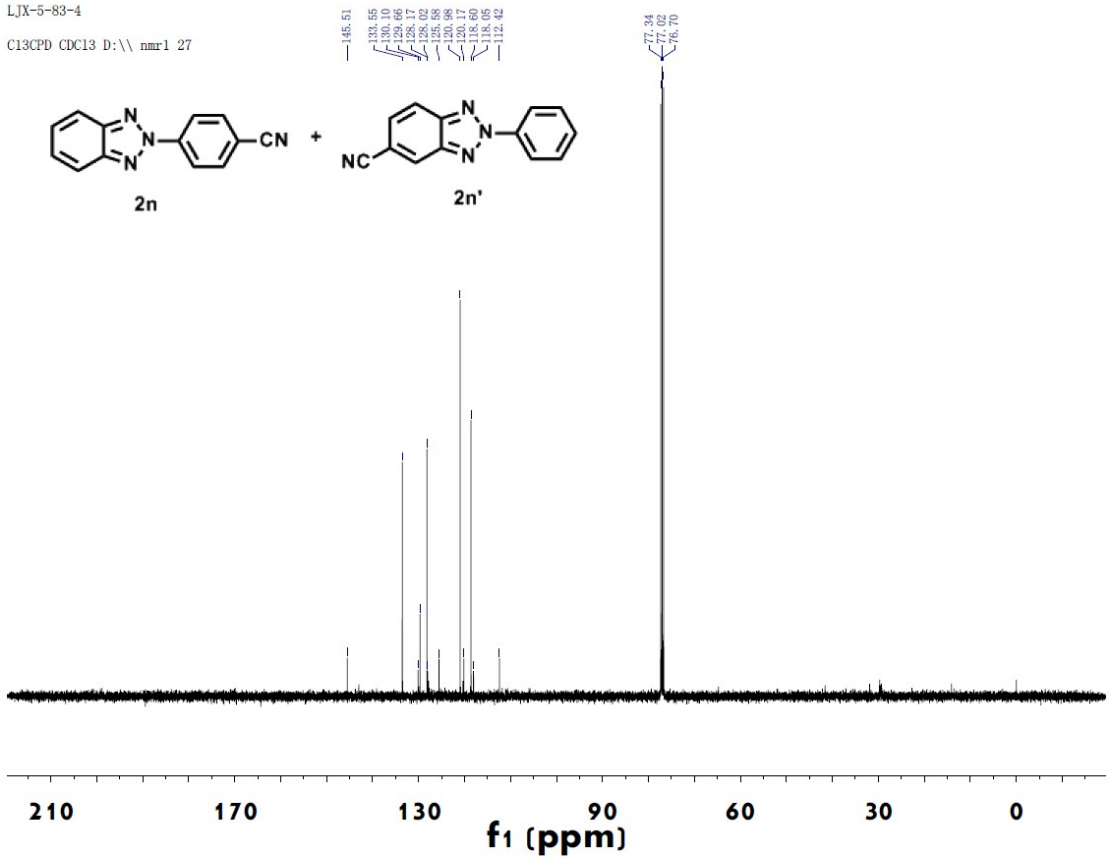

LJX-6-28
PROTON CDCl3 D:\\ nmr1 39
Me +
Me
2l
2l'
1.94
1.67
1.75
1.13
1.00
2.52
2.79
2.07
1.26
2.93
2.83
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

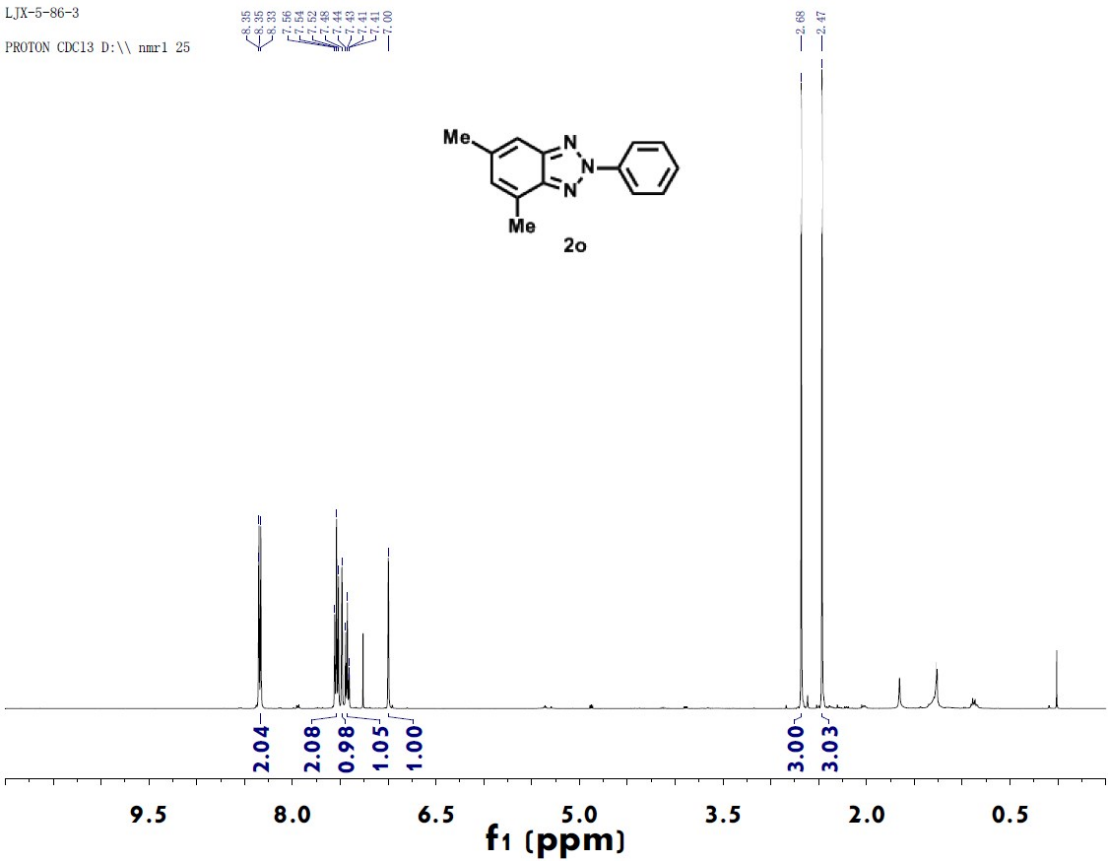

LJX-6-28
C13CPD CDCl3 D:\\ nmr1 39
Me +
Me
2l
2l'
210
170
130
90
60
30
0
f1 (ppm)

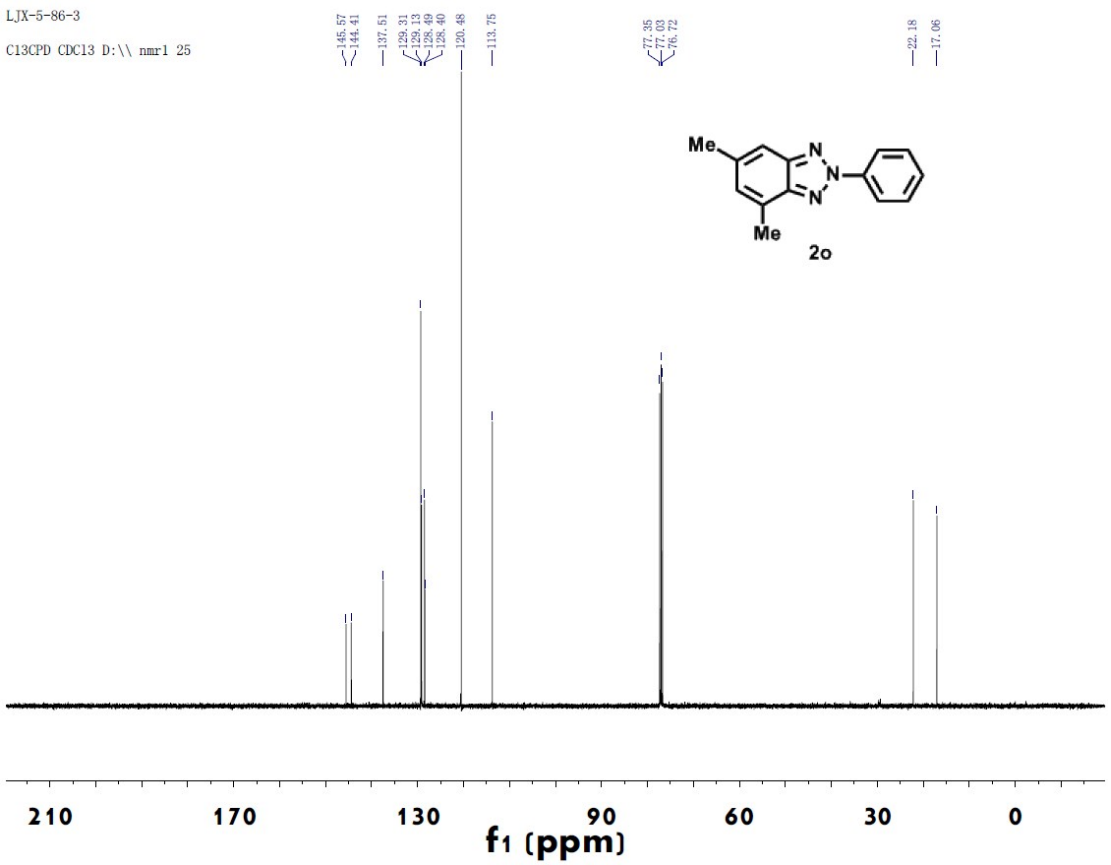

LJX-5-80-2
PROTON CDC13 D:\\ nmr1 28
2m
2m'
1.00
2.92
2.06
5.14
0.49
0.55
1.60
5.07
4.04
0.52
0.49
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)

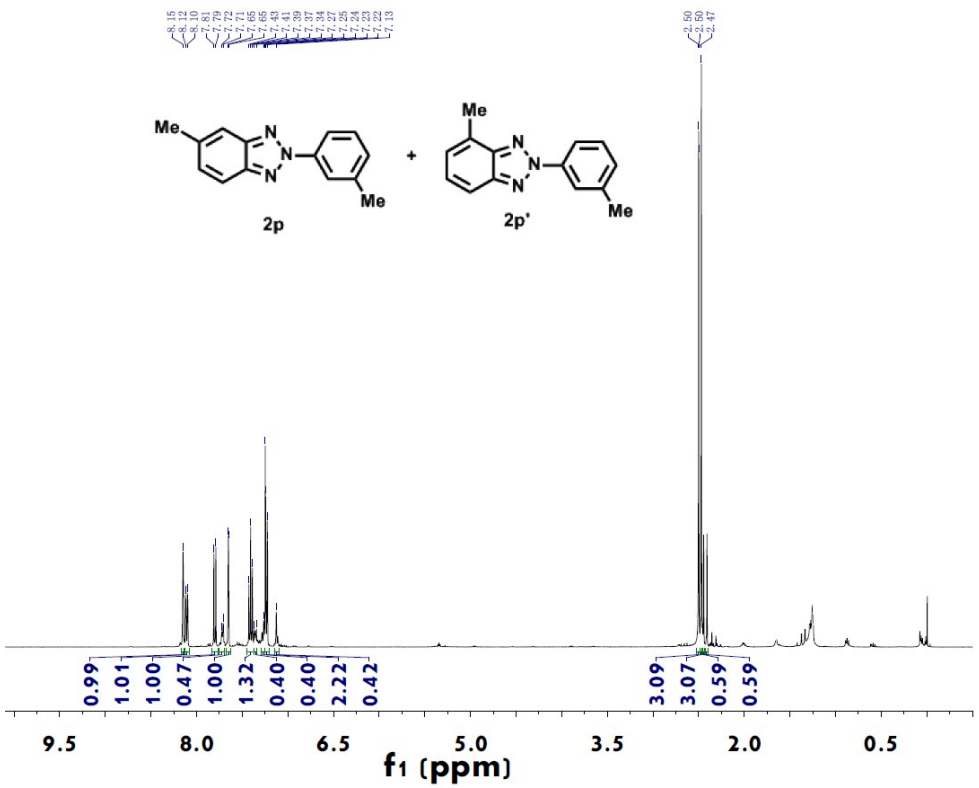

LJX-5-80-2
C13CPD CDC13 D:\\ nmr1 28
2m
2m'
210
170
130
90
60
30
0
f1 (ppm)

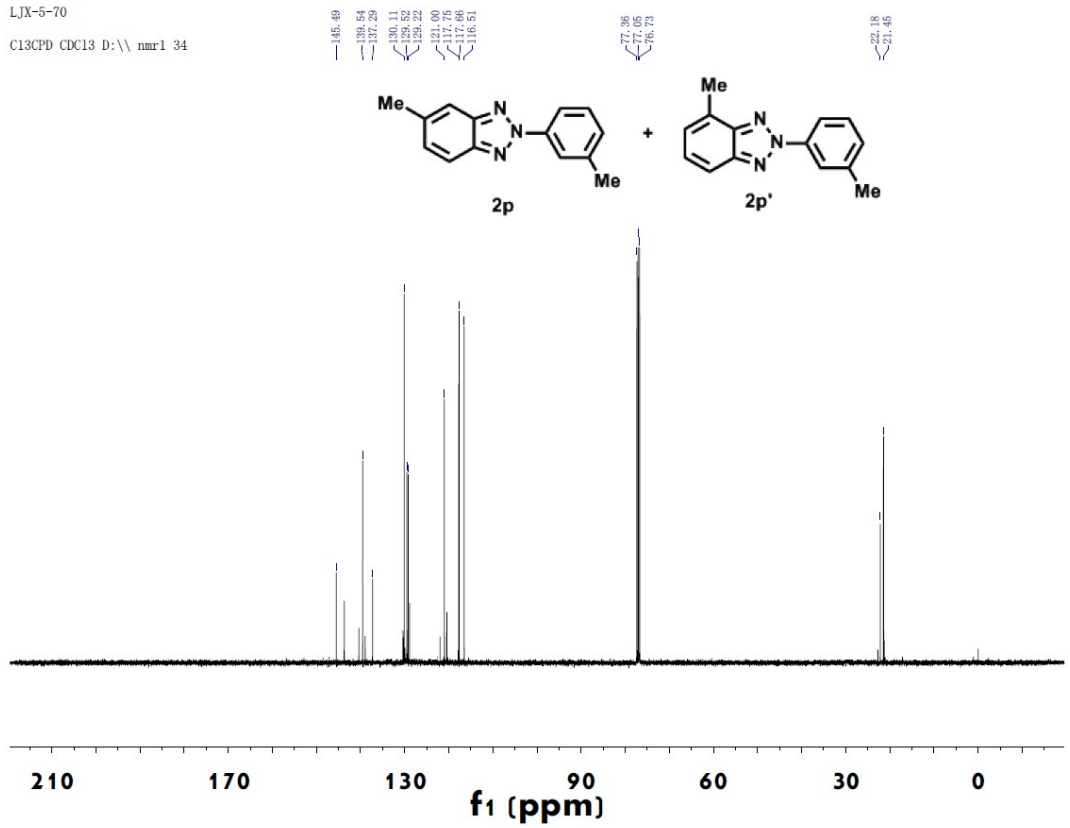

LJX-5-83-4
PROTON CDCl3 D:\\ nmr1 25
2n
2n'
2.00
0.58
0.23
2.11
2.02
0.95
2.06
f1 (ppm)

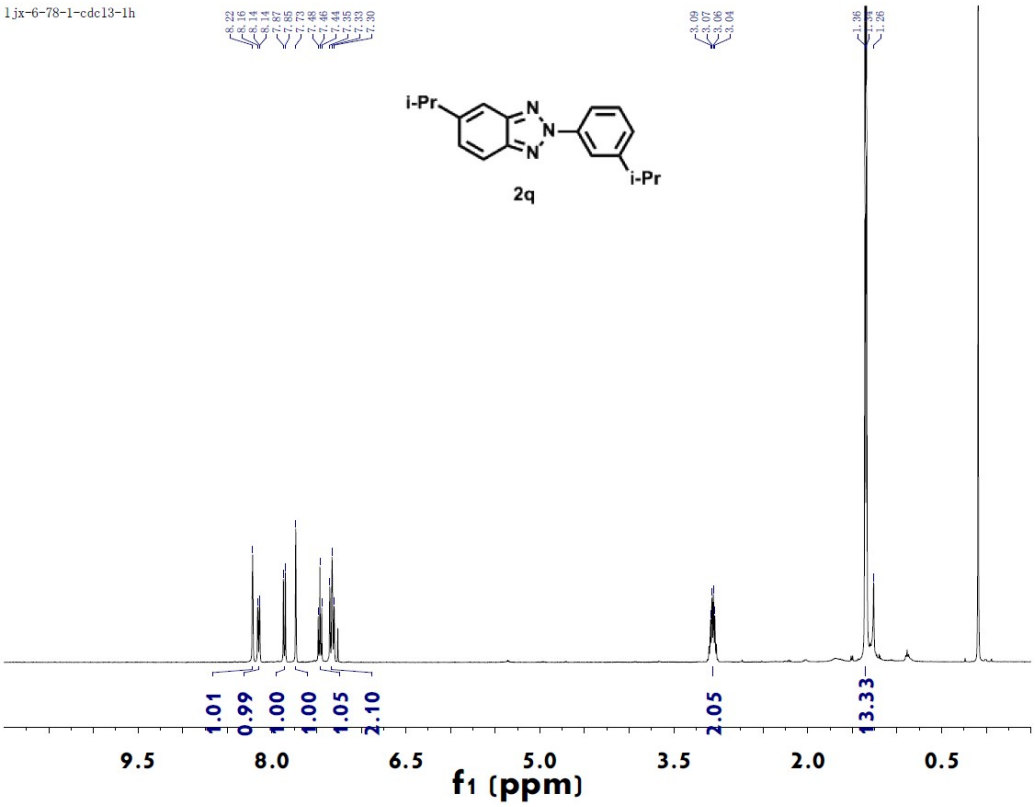

LJX-5-83-4
C13CPD CDCl3 D:\\ nmr1 27
2n
2n'
f1 (ppm)

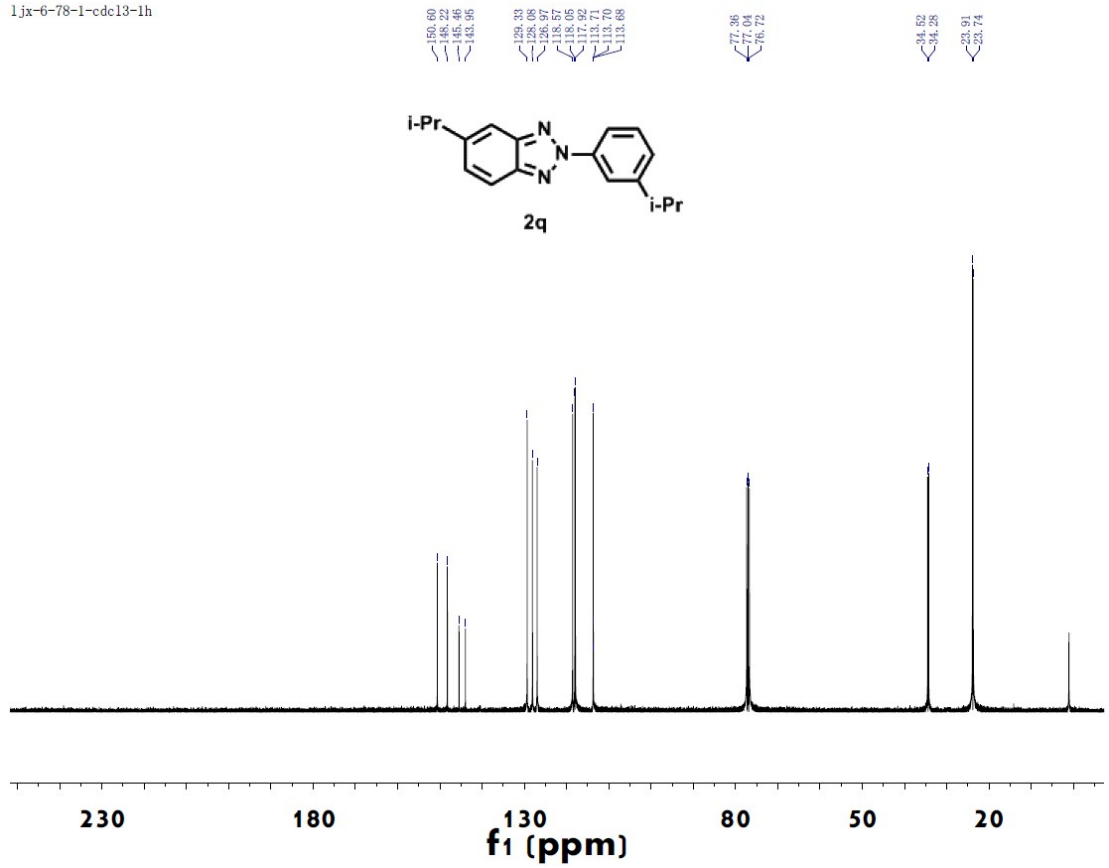

LJX-5-86-3
PROTON CDCl3 D:\\ nmr1 25
8.35
8.35
8.33
7.56
7.54
7.52
7.48
7.44
7.43
7.41
7.41
7.00
2.68
2.47
Me
Me
2o
2.04
2.08
0.98
1.05
1.00
3.00
3.03
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)


LJX-5-86-3
C13CPD CDCl3 D:\\ nmr1 25
145.57
144.41
137.51
129.31
129.13
128.49
128.40
120.48
113.75
77.35
77.03
76.72
22.18
17.06
Me
Me
2o
210
170
130
90
60
30
0
f1 (ppm)


Me
Me
2p
Me
Me
2p'
0.99
1.01
1.00
0.47
1.00
1.32
0.40
0.40
2.22
0.42
3.09
3.07
0.59
0.59
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)


LJX-5-70
C13CPD CDCl3 D:\\ nmr1 34
Me
Me
2p
Me
Me
2p'
210
170
130
90
60
30
0
f1 (ppm)


ljx-6-78-1-cdcl3-1h
i-Pr
i-Pr
2q
1.01
0.99
1.00
1.00
1.05
2.10
2.05
13.33
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)


ljx-6-78-1-cdcl3-1h
i-Pr
i-Pr
2q
230
180
130
80
50
20
f1 (ppm)

GC-Mass of 2a' [-N^{15}]