Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Iodine-catalyzed synthesis of N,N'-diaryl-*o*-phenylenediamines from cyclohexanones and anilines using DMSO and O_2 as oxidant

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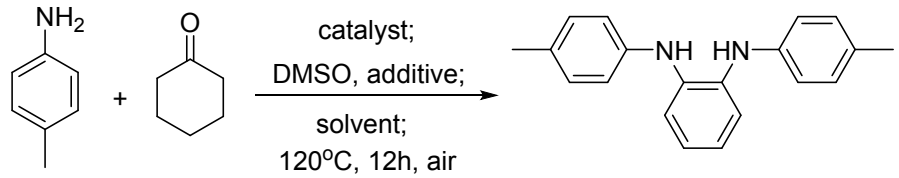
Content

1. Experimental section

1.1. General information

All solvents and chemicals used in the experiments were obtained from common commercial suppliers and used without further purification. Unless otherwise noted, all reactions were carried out in the oven-dried Schlenk tube under air condition. Flash column chromatography was performed on 300-400 mesh silica gel. All NMR spectra were recorded Bruker Ascend-400 spectrometry at 400MHz in $CDCl_3$ for ^1H NMR and ^{13}C NMR, respectively. For ^1H NMR, tetramethylsilane (TMS) served as internal standard (δ = 0.0 ppm) and data are recorded as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. For ^{13}C NMR, $CDCl_3$ worked as internal standard (δ = 77.160 ppm) and spectra were obtained with complete proton decoupling. Melting points were measured with SGW X-4 apparatus. Accurate mass measurements were performed on IT-TOF (Shimadzu, Japan) equipped with an ESI source in positive ion mode.

1.2. Optimization of Reaction Conditions



1a **2a** **3a**

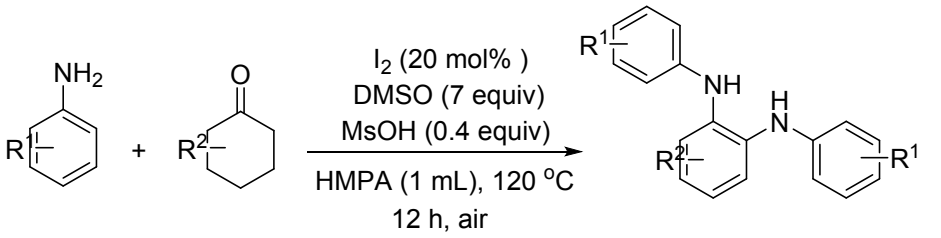
Entry	Catalyst (equiv.)	Oxidant/additive (equiv.)	Solvent	Yeild[b]/ %
1	I_2 (0.2)	-	DMSO	19
2	I_2 (0.2)	DMSO (5)	CH_3OH	24
3	I_2 (0.2)	DMSO (5)	DMA	12
4	I_2 (0.2)	DMSO (5)	1,4-dioxane	10
5	I_2 (0.2)	DMSO (5)	CH_3CN	13
6	I_2 (0.2)	DMSO (5)	THF	8
7	I_2 (0.2)	DMSO (5)	HMPA	37
8	I_2 (0.2)	DMSO (5)	*t*-Amyl-OH	28
9	I_2 (0.2)	DMSO (5)	TBME	trace

10	I_2 (0.2)	DMSO (5)	DCE	trace
11	I_2 (0.2)	DMSO (5)	$CHCl_3$	N.D.
12	I_2 (0.2)	DMSO (5)	AcOH	trace
13	I_2 (0.2)	DMSO (5)	EA	8
14	I_2 (0.2)	DMSO (5)	$PhCH_3$	5
15	I_2 (0.2)	DMSO (5) / Oxone (3)	HMPA	22
16	I_2 (0.2)	DMSO (5) / BzOOBu-*t* (3)	HMPA	trace
17	I_2 (0.2)	DMSO (5)/ $K_2S_2O_4$ (3)	HMPA	11
18	I_2 (0.2)	DMSO (5) / BzOOBz(3)	HMPA	trace
19	I_2 (0.2)	DMSO (5) / *t*-BuOOH (3)	HMPA	19
20	I_2 (0.2)	DMSO (5) / H2O2 (3)	HMPA	16
21	I_2 (0.2)	DMSO (5) / *t*-BzOOBu-*t* (3)	HMPA	14
22[c]	I_2 (0.2)	DMSO (5) / 3Å MS	HMPA	29
23[c]	I_2 (0.2)	DMSO (5) / 4Å MS	HMPA	30
24	I_2 (0.2)	DMSO (5) / $MgSO_4$ (3)	HMPA	23
25	I_2 (0.2)	DMSO (5) / Na_2SO_4 (3)	HMPA	27
26	I_2 (0.2)	DMSO (5) / TsOH (1)	HMPA	43
27	I_2 (0.2)	DMSO (5) / TfOH (1)	HMPA	42
28	I_2 (0.2)	DMSO (5) / AcOH (1)	HMPA	29
29	I_2 (0.2)	DMSO (5) / HCl (1)	HMPA	51
30	I_2 (0.2)	DMSO (5) / MsOH (1)	HMPA	54
31	I_2 (0.2)	DMSO (5) / $BF_3{\cdot}Et_2O$ (1)	HMPA	48
32	I_2 (0.2)	DMSO (5) / $AlCl_3$ (1)	HMPA	40
33	I_2 (0.2)	DMSO (5) / $FeBr_3$ (1)	HMPA	trace
34	I_2 (0.2)	DMSO (5) / CF_3COOH (1)	HMPA	47
35	KI (0.2)	DMSO (5) / MsOH (1)	HMPA	46
36	LiI (0.2)	DMSO (5) / MsOH (1)	HMPA	48
37	HI (0.2)	DMSO (5) / MsOH (1)	HMPA	39
38	*n*-Bu_4NI (0.2)	DMSO (5) / MsOH (1)	HMPA	40
39	NIS (0.2)	DMSO (5) / MsOH (1)	HMPA	49
40	$(CH_3)_4NI$ (0.2)	DMSO (5) / MsOH (1)	HMPA	52
41	I_2 (0.2)	DMSO (4) / MsOH (1)	HMPA	45
42	I_2 (0.2)	DMSO (7) / MsOH (1)	HMPA	63
43	I_2 (0.2)	DMSO (9) / MsOH (1)	HMPA	59
44	I_2 (0.2)	DMSO (7) / MsOH (0.3)	HMPA	70
45	**I_2 (0.2)**	**DMSO (7) / MsOH (0.4)**	**HMPA**	**73**
46	I_2 (0.2)	DMSO (7) / MsOH (0.6)	HMPA	70

47	I_2 (0.2)	DMSO (7) / MsOH (0.8)	HMPA	66
48	I_2 (0.1)	DMSO (7) / MsOH (0.4)	HMPA	61
49	I_2 (0.3)	DMSO (7) / MsOH (0.4)	HMPA	66
50	I_2 (0.5)	DMSO (7) / MsOH (0.4)	HMPA	57
51	I_2 (1.0)	DMSO (7) / MsOH (0.4)	HMPA	48
52[d]	I_2 (0.2)	DMSO (7) / MsOH (0.4)	HMPA	51
53[e]	I_2 (0.2)	DMSO (7) / MsOH (0.4)	HMPA	60
54[f]	I_2 (0.2)	DMSO (7) / MsOH (0.4)	HMPA	74
55[g]	I_2 (0.2)	DMSO (7) / MsOH (0.4)	HMPA	71
56[h]	I_2 (0.2)	DMSO (7) / MsOH (0.4)	HMPA	23
57[i]	I_2 (0.2)	DMSO (7)/MsOH (0.4)	HMPA	11
58	I_2 (0.2)	MsOH (0.4)	HMPA	trace
59	-	DMSO (7) / MsOH (0.4)	HMPA	N.D.

[a]Reaction conditions: **1a** (4equiv.), **2a** (0.25 mmol), catalyst (20 mol%), DMSO, additive, solvent (1 mL), stirred at 120 ℃ under air for 12 h. [b]Determined by ^{1}H NMR analysis using benzyl ether as an internal standard. [c]100 mg molecular sieve. [d]100 ℃. [e]110 ℃. [f]130 ℃. [g]24 h. [h]Under nitrogen atmosphere. [i]Under oxygen atmosphere.

1.3 General Procedure for the Synthesis of 3

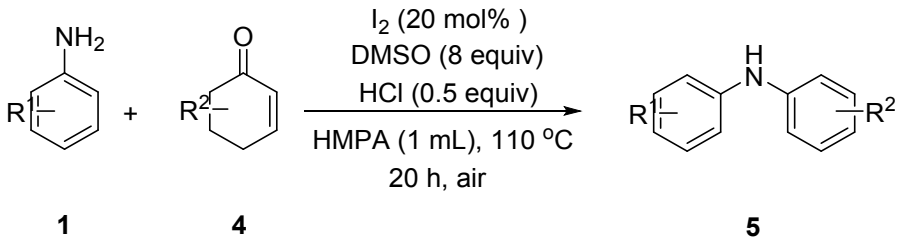


1 **2** **3**

To an oven-dried Schlenk tube with a magnetic bar were added sequentially I_2 (0.05 mmol, 13 mg, 20 mol%), aniline derivatives **1** (1 mmol, 4 equiv.), cyclohexanone derivatives **2** (0.25 mmol), HMPA (1mL), DMSO (1.75 mmol, 126 μL, 7 equiv.) and MsOH (0.1 mmol, 6.4 μL, 0.4 equiv.) under air condition. The Schlenk tube was capped with a cap and heated to 120 ℃ for 12 h. Upon cooling to room temperature, the reaction mixture was added to water (30 mL), extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the residue, which was purified by flash column chromatography on a silica gel using a mixture of petroleum

ether and ethyl acetate to give the products **3**.

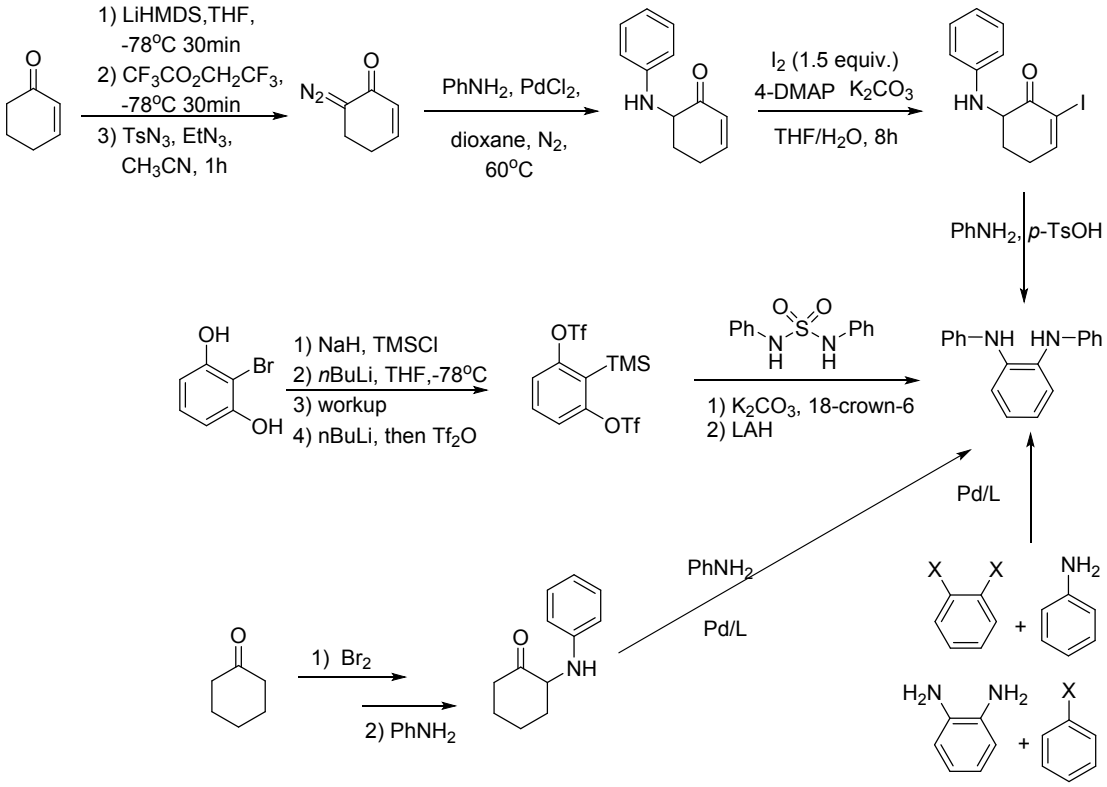
1.4 General Procedure for the Synthesis of 5



1 **4** **5**

To an oven-dried Schlenk tube with a magnetic bar were added sequentially I_2 (0.05 mmol, 13 mg, 20 mol%), aniline derivatives **2** (0.25 mmol), cyclohexenone derivatives **4** (0.75 mmol, 3 equiv.), HMPA (1mL), DMSO (2 mmol, 142 μL, 8 equiv.) and 12M HCl (0.125 mmol, 12 μL, 0.5 equiv.) under air condition. The Schlenk tube was capped with a cap and heated to 110 ℃ for 20 h. Upon cooling to room temperature, the reaction mixture was added to water (30 mL), extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the residue, which was purified by flash column chromatography on a silica gel using a mixture of petroleum ether and ethyl acetate to give the products **5**.

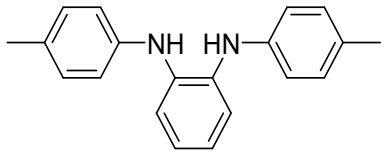
1.5 The detailed comparison of several methods to synthesize N,N'-diaryl-o-phenylenediamines



2. Characterization Data for Products

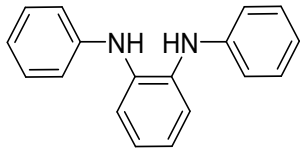
Attention: Maybe due to high asymmetry and electrical quadrupole moment, the signal response of some N,N'-diaryl-*o*-phenylenediamines is weak, so it's very hard to eliminate the impure peaks of NMR spectra, especially 3p-3s, because of experimental condition (40-60 mg sample, dissolved in 0.5 mL CD_3Cl, was scanned under NMR equipment for 2-3h). And the best NMR spectra were chose and presented here after many repeated experimented.

N, N'-bis(4-methylphenyl)-1,2-benzenediamine (3a)[1]:



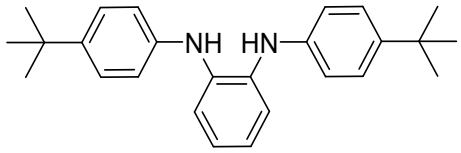
Yellow oil (51.3 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 4H), 6.94 – 6.89 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 4H), 5.51 (br, 2H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.47, 135.38, 130.32, 129.98, 122.64, 119.61, 118.01, 20.76. HRMS (ESI): m/z calcd. for $C_{20}H_{21}N_2$ $[M+H]^+$: 289.1699, found: 289.1711.

N, N'-diphenyl-1,2-benzenediamine (3b)[1]:



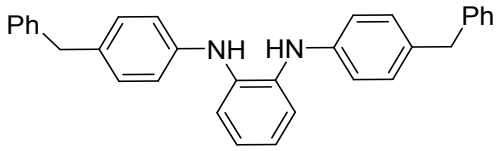
Off-white solid (32.5 mg, 50%). Mp=102-104 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 2H), 7.17 - 7.12 (m, 4H), 6.90 – 6.87 (m, 2H), 6.85 - 6.79 (m, 6H), 5.52 (br, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 144.02, 135.01, 129.46, 123.11, 120.70, 120.33, 117.33; HRMS (ESI): m/z calcd. for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.1386, found: 261.1375.

N, N'-bis(4-*tert*-butylphenyl)-1,2-benzenediamine (3c)[2]:



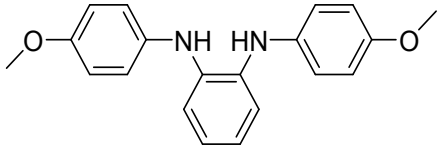
Yellow oil (54.8 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 6H), 6.86 – 6.82 (m, 2H), 6.81 – 6.78 (m, 4H), 5.46 (br, 2H), 1.21 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65, 141.46, 135.29, 126.24, 122.67, 119.80, 117.40, 34.23, 31.62. HRMS (ESI): m/z calcd. for $C_{26}H_{33}N_2$ $[M+H]^+$: 373.2638, found: 373.2614.

N, N'-bis(4-benzylphenyl)-1,2-benzenediamine (3d):



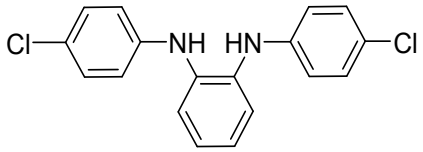
Yellow oil (58.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.08 (m, 12H), 6.95 (d, J = 8.3 Hz, 4H), 6.86 – 6.81 (m, 2H), 6.75 (d, J = 8.3 Hz, 4H), 5.42 (br, 2H), 3.81 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.10, 141.67, 135.15, 133.53, 129.88, 128.95, 128.54, 126.08, 122.82, 119.91, 117.75, 41.28. HRMS (ESI): m/z calcd. for $C_{32}H_{29}N_2$ $[M+H]^+$: 441.2325, found: 441.2318.

N, N'-bis(4-methoxyphenyl)-1,2-benzenediamine (3e)[2]:



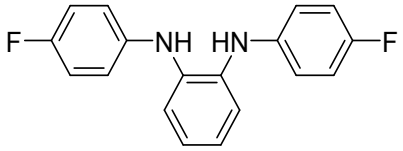
Yellow oil (43.7 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.07 (m, 2H), 6.94 – 6.90 (m, 4H), 6.89 – 6.87 (m, 2H), 6.86 – 6.82 (m, 4H), 5.43 (br, 2H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.71, 137.22, 135.85, 122.21, 120.40, 118.67, 114.86, 55.77. HRMS (ESI): m/z calcd. for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598, found: 321.1584.

N, N'-bis(4-chlorophenyl)-1,2-benzenediamine (3f):



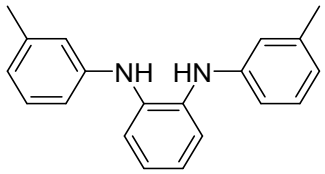
Yellow oil (58.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.18 (d, J = 8.8 Hz, 4H), 7.01 – 6.97 (m, 2H), 6.83 (d, J = 8.8 Hz, 4H), 5.58 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.57, 134.70, 129.43, 125.51, 123.67, 120.63, 118.45. HRMS (ESI): m/z calcd. for $C_{18}H_{15}Cl_2N_2$ $[M+H]^+$: 329.0607, found: 329.0588.

N, N'-bis(4-fluorophenyl)-1,2-benzenediamine (3g)[1]:



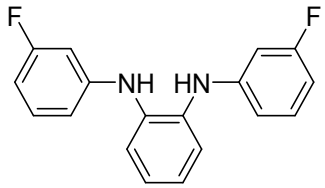
Yellow solid (33.6 mg, 43%). Mp=88-90 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 2H), 7.00 – 6.91 (m, 6H), 6.91 – 6.83 (m, 4H), 5.52 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.85 (d, J_{C-F} =238.1 Hz), 139.99, 135.31, 123.05, 119.68, 119.41 (d, J_{C-F} =5.4 Hz), 116.05 (d, J_{C-F} =22.4 Hz). HRMS (ESI): m/z calcd. for $C_{18}H_{15}F_2N_2$ $[M+H]^+$: 297.1198, found: 297.1179.

N, N'-bis(3-methylphenyl)-1,2-benzenediamine (3h):



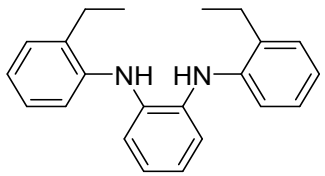
Yellow oil (45.5 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 7.07 – 7.03 (m, 2H), 6.91 – 6.87 (m, 2H), 6.67 – 6.65 (m, 5H), 6.63 (s, 1H), 5.48 (br, 2H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.04, 139.35, 135.11, 129.30, 123.01, 121.57, 120.45, 118.02, 114.42, 77.48, 77.16, 76.84, 21.63. HRMS (ESI): m/z calcd. for $C_{20}H_{21}N_2$ $[M+H]^+$: 289.1699, found: 289.1702.

N,N'-bis(3-fluorophenyl)-1,2-benzenediamine (3i):



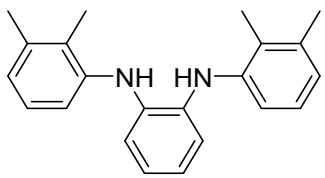
Yellow oil (33.2 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.21 – 7.11 (m, 2H), 7.08 – 7.00 (m, 2H), 6.68 – 6.62 (m, 3H), 6.61 – 6.53 (m, 3H), 5.67 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.93 (d, J = 244.3 Hz), 145.95 (d, J = 10.5 Hz), 134.46, 130.64 (d, J = 9.9 Hz), 124.07, 121.43, 112.48 (d, J = 2.5 Hz), 107.22 (d, J = 21.5 Hz), 103.66 (d, J = 25.1 Hz). HRMS (ESI): m/z calcd. for $C_{18}H_{15}F_2N_2$ $[M+H]^+$: 297.1198, found: 297.1197.

N, N'-bis(2-ethylphenyl)-1,2-benzenediamine (3j):



Yellow oil (37.9 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.2 Hz, 2H), 7.13 – 7.06 (m, 4H), 6.98 – 6.87 (m, 6H), 5.49 (br, 2H), 2.54 (q, J = 7.5 Hz, 4H), 1.17 (t, J = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.47, 135.31, 132.91, 128.96, 126.90, 122.81, 121.56, 120.35, 117.88, 24.44, 13.81. HRMS (ESI): m/z calcd. for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, found: 317.2000.

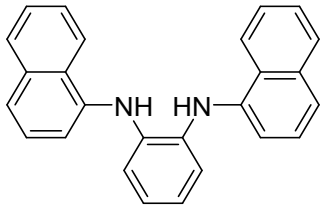
N, N'-bis(2,3-dimethylphenyl)-1,2-benzenediamine (3k):



Yellow oil (23.6 mg, 30%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, J = 7.7 Hz, 2H), 6.96 – 6.85 (m, 4H), 6.81 (t, J = 5.4 Hz, 4H), 5.41 (br, 2H), 2.29 (s, 6H), 2.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

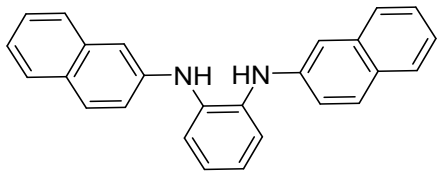
141.95, 137.68, 135.51, 126.65, 126.14, 123.72, 122.36, 119.79, 116.81, 20.77, 13.52. HRMS (ESI): m/z calcd. for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, found: 317.2005.

N, N'-di-1-naphthalenyl-1,2-benzenediamine (3l)[1]:



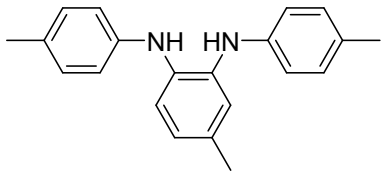
Dark red oil (23.4 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.32 (m, 8H), 7.15 – 7.08 (m, 4H), 7.02 – 6.89 (m,2H), 6.14 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.49, 135.41, 134.72, 128.71, 126.70, 126.26, 126.17, 125.71, 123.10, 122.19, 121.50, 120.65, 113.94. HRMS (ESI): m/z calcd. for $C_{26}H_{21}N_2$ $[M+H]^+$: 361.1699, found: 361.1692.

N, N'-di-2-naphthalenyl -1,2-benzenediamine (3m)[1]:



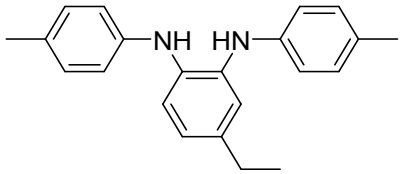
Yellow solid (30.6 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.4, 3.9 Hz, 4H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.30 – 7.20 (m, 4H), 7.13 (dd, *J* = 8.8, 2.3 Hz, 2H), 7.08 – 7.00 (m, 2H), 5.80 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.66, 135.05, 134.76, 129.35, 129.14, 127.78, 126.60, 126.54, 123.52, 120.85, 119.76, 111.21. HRMS (ESI): m/z calcd. for $C_{26}H_{21}N_2$ $[M+H]^+$: 361.1699, found: 361.1683.

N, N'-bis(4-methylphenyl)-4-methyl-1,2-benzenediamine (3n):



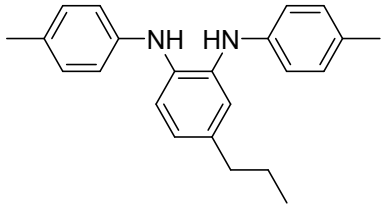
Yellow oil (62.7 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 6.98 (m, 6H), 6.94 – 6.85 (m, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.64 (br, 1H), 5.25 (br, 1H), 2.28 (s, 3H), 2.25 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.57, 141.04, 137.04, 133.51, 131.10, 130.56, 129.95, 129.92, 122.35, 121.86, 118.70, 118.57, 117.99, 116.75, 21.24, 20.78, 20.67. HRMS (ESI): m/z calcd. for $C_{21}H_{23}N_2$ $[M+H]^+$: 303.1856, found: 303.1856.

N, N'-bis(4-methylphenyl)-4-ethyl-1,2-benzenediamine (3o):



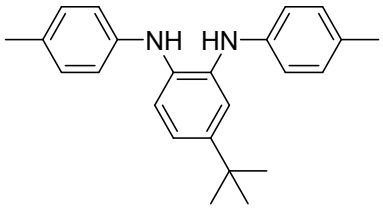
Yellow oil (48.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.0 Hz, 1H), 7.09 – 6.99 (m, 5H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.81 – 6.70 (m, 3H), 5.63 (br, 1H), 5.30 (br, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.43, 141.22, 139.82, 136.60, 131.68, 130.38, 129.96, 129.93, 129.54, 121.45, 121.32, 118.37, 117.87, 116.96, 28.64, 20.77, 20.69, 15.88. HRMS (ESI): m/z calcd. for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, found: 317.2014.

N, N'-bis(4-methylphenyl)-4-propyl-1,2-benzenediamine (3p): (40.2 mg, 2 h for ^{13}C NMR)



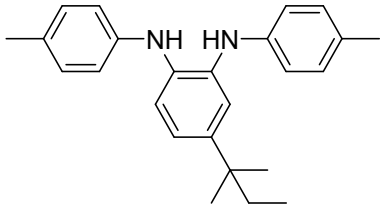
Yellow oil (58.8 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 1H), 7.08 – 6.99 (m, 5H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.71 (dd, 1H), 5.62 (br, 1H), 5.30 (br, 1H), 2.48 (t, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.64 – 1.54 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.41, 141.28, 138.22, 136.41, 131.77, 130.32, 129.96, 129.93, 129.55, 122.02, 121.26, 118.53, 118.30, 116.99, 37.85, 24.83, 20.77, 20.69, 14.01. HRMS (ESI): m/z calcd. for $C_{23}H_{27}N_2$ $[M+H]^+$: 331.2169, found: 331.2170.

N,N'-bis(4-methylphenyl)-4-*tert*-butyl-1,2-benzenediamine (3q): (45.8 mg, 2.5 h for ^{13}C NMR)



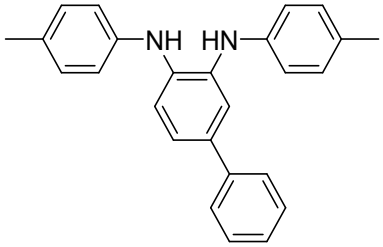
Red oil (68.1 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 2.2 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.95 (t, *J* = 8.3 Hz, 4H), 6.90 – 6.81 (m, 1H), 6.80 – 6.66 (m, 4H), 5.47 (br, 1H), 5.30 (br, 1H), 2.19 (s, 3H), 2.18 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.08, 142.00, 141.70, 134.87, 132.56, 129.96, 129.91, 126.18, 119.90, 119.46, 118.25, 117.38, 117.21, 117.03, 31.57, 20.72. HRMS (ESI): m/z caled for $C_{24}H_{29}N_2$ $[M+H]^+$: 345.2325, found: 345.2336.

N, N'-bis(4-methylphenyl)-4-tert-amyl-1,2-benzenediamine (3r): (50.6 mg, 2.5 h for ^{13}C NMR)



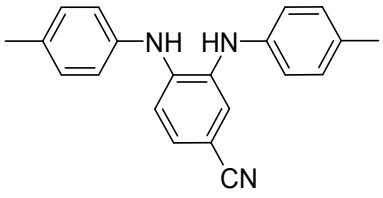
Red oil (57.4 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.11 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 4H), 6.98 – 6.92 (m, 1H), 6.89 – 6.78 (m, 4H), 5.52 (s, 1H), 5.39 (s, 1H), 2.27 (d, *J* = 3.0 Hz, 6H), 1.61 – 1.54 (m, 2H), 1.22 (s, 6H), 0.70 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.34, 141.99, 141.83, 134.61, 132.65, 129.95, 129.90, 126.85, 120.38, 119.70, 118.23, 117.97, 117.44, 117.17, 37.72, 28.62, 20.72, 9.32. HRMS (ESI): m/z calcd. for $C_{25}H_{31}N_2$ $[M+H]^+$: 359.2482, found: 359.2478.

N, N'-bis(4-methylphenyl)-4-phenyl-1,2-benzenediamine (3s):



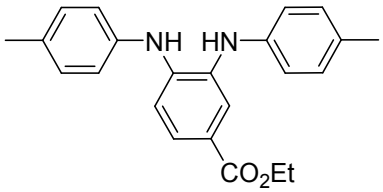
Yellow oil (72.3 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.38 (s, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.03 (m, 1H), 6.98 (dd, *J* = 7.7, 3.3 Hz, 4H), 6.85 – 6.75 (m, 4H), 5.45 (br, 2H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.45, 141.12, 140.94, 135.26, 135.08, 130.43, 130.21, 130.01, 129.97, 128.74, 126.77, 126.68, 121.44, 119.26, 118.50, 118.21, 117.81, 20.74, 20.71. HRMS (ESI): m/z calcd. for $C_{26}H_{25}N_2$ $[M+H]^+$: 365.2012, found: 365.2006.

3,4-bis(*p*-tolylamino)benzonitrile (3t)：



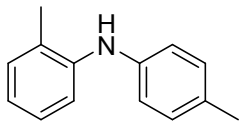
Off-white solid (45.5 mg, 58%). Mp=96-98 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.8 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.05 (t, *J* = 9.0 Hz, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.14 (br, 1H), 5.13 (br, 1H), 2.25 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.49, 135.41, 134.72, 128.71, 126.70, 126.26, 126.17, 125.71, 123.10, 122.19, 121.50, 120.65, 113.94. HRMS (ESI): m/z calcd. for $C_{21}H_{20}N_3$ $[M+H]^+$: 314.1652, found: 314.1644.

Ethyl 3, 4-bis(*p*-tolylamino)benzoate (3u):



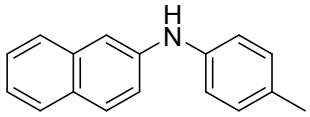
Yellow oil (63.6 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.71 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 8.4 Hz, 4H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.32 (br, 1H), 5.20 (br, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 144.10, 142.49, 138.41, 132.91, 130.08, 130.04, 129.70, 127.37, 125.67, 121.34, 116.19, 113.00, 60.58, 20.91, 20.64, 14.51. HRMS (ESI): m/z calcd. for $C_{23}H_{25}N_2O_2$ $[M+H]^+$: 361.1911, found: 361.1906.

Ethyl 2, 3-bis(*p*-tolylamino)benzoate (3v)[3]:



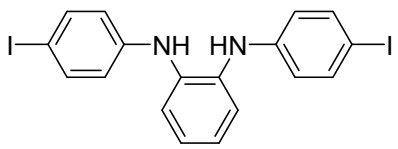
Yellow oil (9.9 mg, 20%). ^{1}H NMR (400 MHz, CDCl3) δ 7.17 (d, J = 8.0 Hz, 2H), 7.14 – 7.10 (m, 1H), 7.08 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.88 (td, J = 7.3, 1.2 Hz, 1H), 2.30 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.12, 141.07, 130.97, 130.65, 129.97, 127.13, 126.87, 121.22, 118.81, 117.34, 20.80, 18.01. HRMS (ESI): m/z calcd. for $C_{14}H_{16}N$ $[M+H]^+$: 198.1277, found: 198.1283.

N-(*p*-tolyl)naphthalen-2-amine (3w):



Yellow solid (39.6 mg, 68%). Mp=95-97 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.29 – 7.23 (m, 1H), 7.17 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.11 (q, *J* = 8.4 Hz, 4H), 5.77 (br, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82, 140.20, 134.83, 131.51, 130.08, 129.26, 128.98, 127.75, 126.53, 126.48, 123.29, 119.70, 119.47, 110.36, 20.89. HRMS (ESI): m/z calcd. for $C_{17}H_{14}N$ $[M-H]^-$: 232.1132, found: 232.1137.

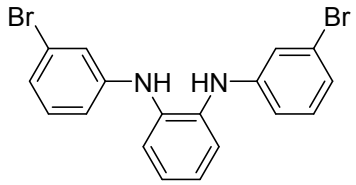
N, N'-bis(4-iodophenyl)-1,2-benzenediamine (3x):



Rufous solid (26.8 mg, 21%). Mp=175-177 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 4H), 7.27 – 7.21 (m, 2H), 7.05 – 6.96 (m, 2H), 6.68 (d, *J* = 8.8 Hz, 4H), 5.59 (br, 2H). ^{13}C NMR

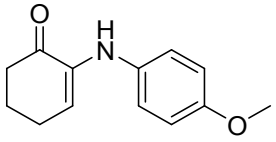
(101 MHz, $CDCl_3$) δ 143.76, 138.24, 134.48, 123.88, 120.93, 119.14, 82.28. HRMS (ESI): m/z calcd. for $C_{18}H_{12}I_2N_2$ [M-H]$^-$: 510.9174, found: 510.9188.

N,N'-bis(3-bromophenyl)-1,2-benzenediamine (3y):



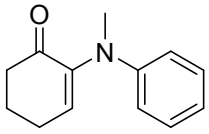
Yellow oil (40.6 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.10 – 6.97 (m, 8H), 6.83 – 6.77 (m, 2H), 5.60 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.49, 134.36, 130.80, 124.15, 123.56, 123.30, 121.39, 119.59, 115.49. HRMS (ESI): m/z calcd. for $C_{18}H_{12}Br_2N_2$ [M-H]$^-$: 414.9451, found: 414.9475.

2-(4-Methoxyphenylamino)cyclohex-2-en-1-one (C1)[4]:



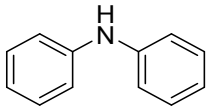
Yellow solid (8.14 mg, 15%). Mp=49-51 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.96 (m, 2H), 6.87 – 6.81 (m, 2H), 6.14 (t, *J* = 4.8 Hz, 1H), 6.09 (br, 1H), 3.78 (s, 3H), 2.61 – 2.49 (m, 2H), 2.40 (q, *J* = 11.1, 2H), 2.05 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.84, 155.06, 137.90, 135.04, 122.36, 114.67, 114.24, 55.68, 37.93, 24.60, 23.27. HRMS (ESI): m/z calcd. for $C_{20}H_{21}N_2O_2$ [M+H]$^+$: 218.1176, found: 218.1170.

2-((4-Methoxyphenyl)(methyl)amino)cyclohex-2-enone (C2)[4]:



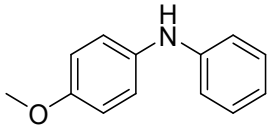
Yellow oil (6.13 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.6, 7.4 Hz, 2H), 6.81 – 6.73 (m, 2H), 6.71 (d, *J* = 7.9 Hz, 2H), 3.07 (s, 3H), 2.59 – 2.49 (m, 4H), 2.14 – 2.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.62, 149.14, 144.82, 143.20, 129.01, 118.59, 114.94, 77.48, 77.16, 76.84, 39.62, 39.51, 26.13, 23.07. HRMS (ESI): m/z calcd. for $C_{13}H_{15}NNaO$ [M+Na]$^+$: 224.1046, found: 224.1035.

Diphenylamine (5a)[5]:



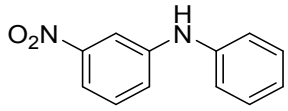
White solid (32.3 mg, 76%). Mp=47-49 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.2, 7.6 Hz, 4H), 7.07 (d, *J* = 7.6 Hz, 4H), 6.93 (t, *J* = 7.3 Hz, 2H), 5.74 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.22, 129.49, 121.14, 117.94. HRMS (ESI): m/z calcd. for $C_{12}H_{12}N$ [M+H]$^+$: 170.0964, found: 170.0970.

4-methoxy-N-phenylaniline (5b)[6]:



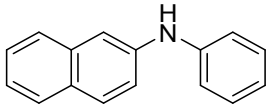
White solid (27.5 mg, 55%). Mp=100-102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.88 – 6.79 (m, 3H), 5.48 (br, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.39, 145.24, 135.80, 129.43, 122.33, 119.71, 115.77, 114.78, 55.70. HRMS (ESI): m/z calcd. for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found: 200.1071.

3-nitro-N-phenylaniline (5c)[7]:



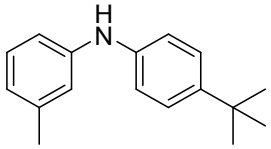
Orange solid (33.2 mg, 62%). Mp=84-86 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J* = 2.2 Hz, 1H), 7.69 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.28 (ddd, *J* = 8.2, 2.2, 0.8 Hz, 1H), 7.15 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.94 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.49, 145.20, 141.08, 130.15, 129.85, 123.36, 121.97, 120.01, 114.84, 110.40. HRMS (ESI): m/z calcd. for $C_{12}H_9N_2O_2$ $[M-H]^-$: 213.0670, found: 213.0683.

N-phenylnaphthalen-2-amine (5d)[8]:



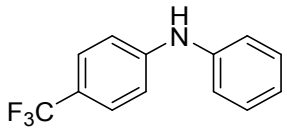
White solid (38.0 mg, 69%). Mp=105-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.34 – 7.27 (m, 3H), 7.22 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.16 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 5.83 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.03, 140.97, 134.74, 129.57, 129.31, 127.78, 126.61, 126.58, 123.62, 121.54, 120.17, 118.39, 111.68. HRMS (ESI): m/z calcd. for $C_{16}H_{14}N$ $[M+H]^+$: 220.1121, found: 220.1112.

N-(4-(*tert*-butyl)phenyl)-3-methylaniline (5e**)[9]:**



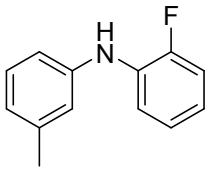
Yellow oil (50 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 7.3 Hz, 1H), 5.58 (br, 1H), 2.29 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.11, 143.75, 140.53, 139.25, 129.25, 126.21, 121.39, 118.20, 117.89, 114.34, 34.28, 31.60, 21.67. HRMS (ESI): m/z calcd. for $C_{17}H_{22}N$ [M+H]+: 240.1747, found: 240.1730.

N-phenyl-4-(trifluoromethyl)aniline (5f)[10]:



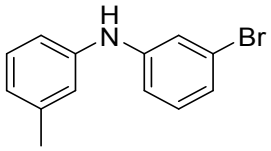
Yellow oil (23.6 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.08 – 6.99 (m, 3H), 5.91 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.89, 141.27, 129.68, 126.83 (q, *J* = 3.8 Hz), 124.75 (q, *J* = 271.8 Hz), 121.75 (q, *J* = 32.8 Hz), 123.06, 120.15, 115.45. HRMS (ESI): m/z calcd. for $C_{13}H_{11}F_3N$ $[M+H]^+$: 238.0838, found: 238.0827.

2-fluoro-N-(*m*-tolyl)aniline (5g):



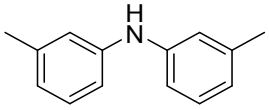
Yellow oil (40.3 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 8.4, 1.5 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.07 (ddd, *J* = 11.4, 8.1, 1.4 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.95 – 6.90 (m, 2H), 6.86 – 6.77 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ153.07 (d, J = 241.7 Hz), 142.05, 139.45, 131.97 (d, J = 11.0 Hz), 129.34, 124.38 (d, J = 3.6), 122.83, 120.43 (d, J = 7.4 Hz), 119.52, 117.28 (d, J = 2.1 Hz), 115.86, 115.53 (d, J = 19.3 Hz), 21.64. HRMS (ESI): m/z calcd. for $C_{13}H_{13}FN$ $[M+H]^+$: 202.1027, found: 202.1025.

3-bromo-N-(*m*-tolyl)aniline (5h):



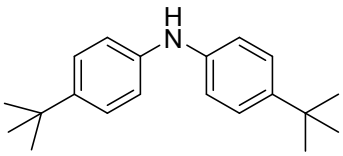
Yellow oil (54.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.92 – 6.84 (m, 3H), 6.80 (d, *J* = 7.5 Hz, 1H), 5.59 (br, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.17, 141.91, 139.50, 130.68, 129.39, 123.30, 123.19, 123.11, 119.83, 119.64, 116.15, 115.58, 21.61. HRMS (ESI): m/z calcd. for $C_{13}H_{13}BrN$ $[M+H]^+$: 262.0226, found: 262.0220.

di-*m*-tolylamine (5i)[11]:



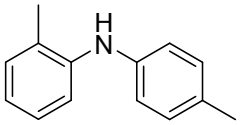
Yellow oil (43.4 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.1 Hz, 2H), 6.90 – 6.85 (m, 4H), 6.74 (d, *J* = 7.7 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.29, 139.31, 129.26, 121.87, 118.66, 115.03, 21.65. HRMS (ESI): m/z calcd. for $C_{14}H_{16}N$ $[M+H]^+$: 198.1277, found: 198.1279.

bis(4-(*tert*-butyl)phenyl)amine (5j)[12]:



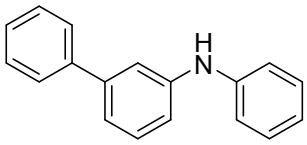
Red solid (18.0 mg, 64%). Mp=106-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 4H), 7.00 (d, *J* = 8.7 Hz, 4H), 5.58 (br, 1H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.69, 141.06, 126.21, 117.52, 34.26, 31.63. HRMS (ESI): m/z calcd. for $C_{20}H_{28}N$ $[M+H]^+$: 282.2216, found: 282.2212.

N-(*p*-tolyl)-[1,1'-biphenyl]-4-amine (5k)[13]:



White solid (33.5 mg, 52%). Mp=129-131 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.12 – 6.98 (m, 6H), 5.63 (br, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.42, 141.00, 140.05, 133.16, 131.31, 130.03, 128.83, 128.05, 126.58, 119.27, 117.00, 77.48, 77.16, 76.84, 20.84. HRMS (ESI): m/z calcd. for $C_{19}H_{18}N$ $[M+H]^+$: 260.1434, found: 260.1439.

N-phenyl-[1,1'-biphenyl]-3-amine (5l)[14]:



Off-white solid (49.6 mg, 81%). Mp=89-91 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.24 (m, 5H), 7.18 – 7.10 (m, 3H), 7.06 (ddd, *J* = 8.0, 2.2, 0.8 Hz, 1H), 6.95 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65, 143.07, 142.67, 141.27, 129.87, 129.55, 128.85, 127.50, 127.27, 121.35, 120.12, 118.19, 116.74, 116.58. HRMS (ESI): m/z calcd. for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277, found: 246.1268.

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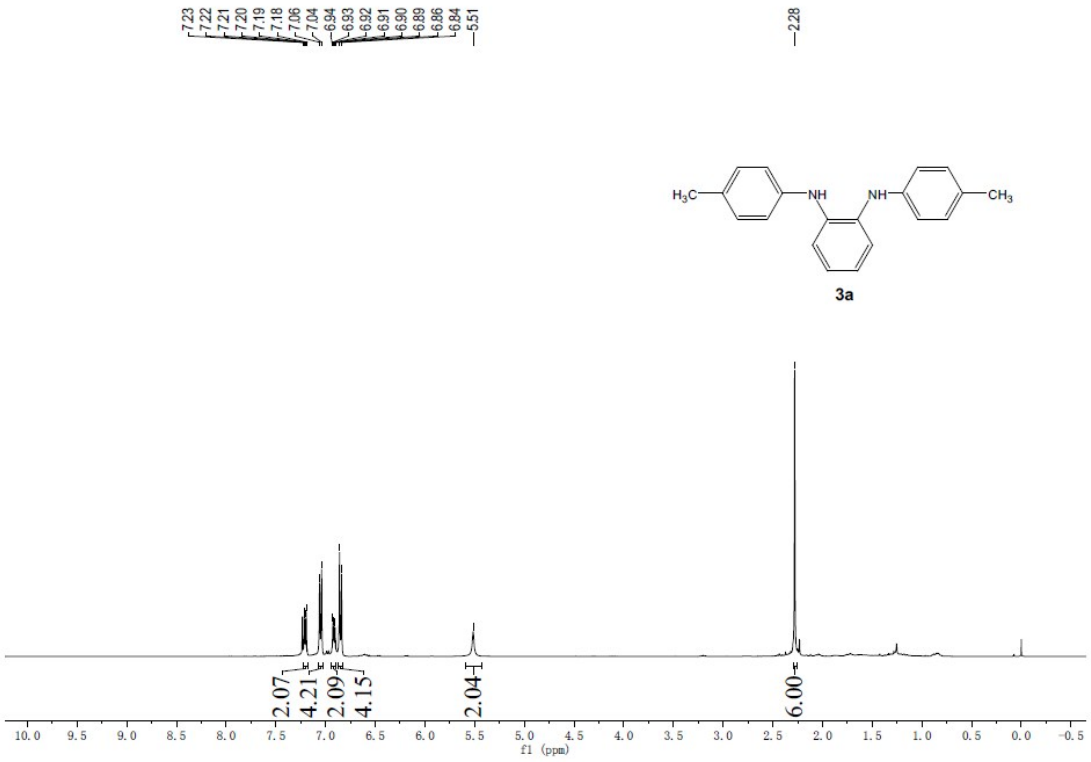
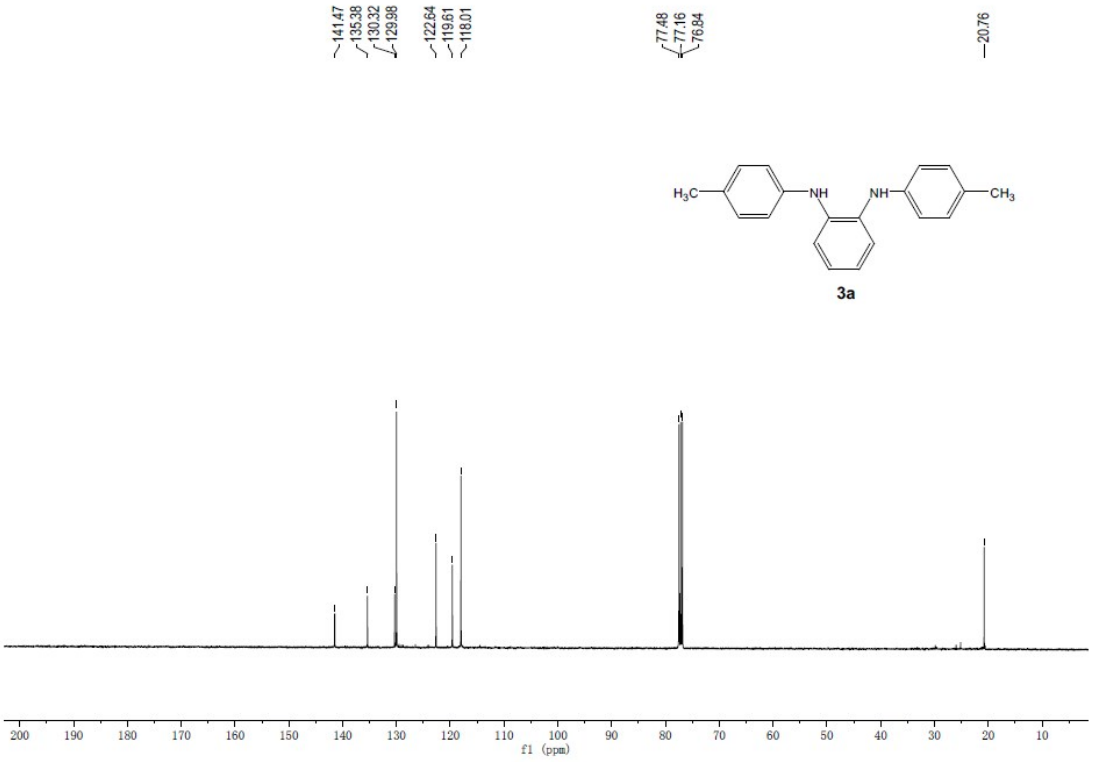
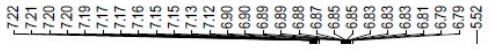
3. ^{1}H NMR and ^{13}C NMR spectra



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7.21
7.20
7.20
7.19
7.17
7.17
7.16
7.15
7.15
7.13
7.12
6.90
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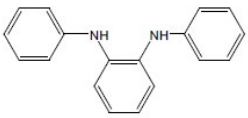
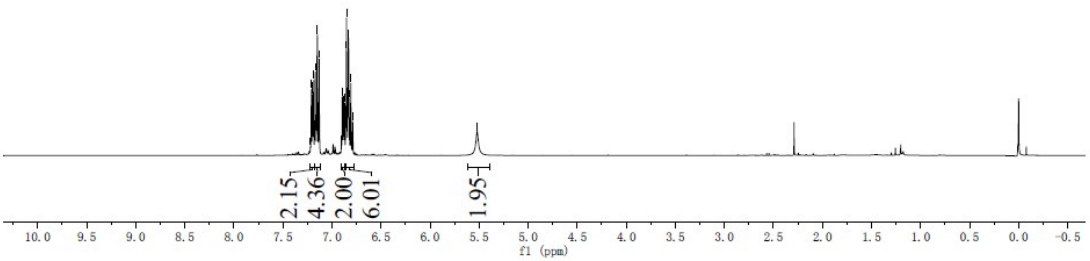
6.83
6.83
6.81
6.79
6.79
5.52


NH
NH

3b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4.36
2.00
6.01
1.95
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f1 (ppm)


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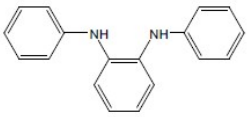
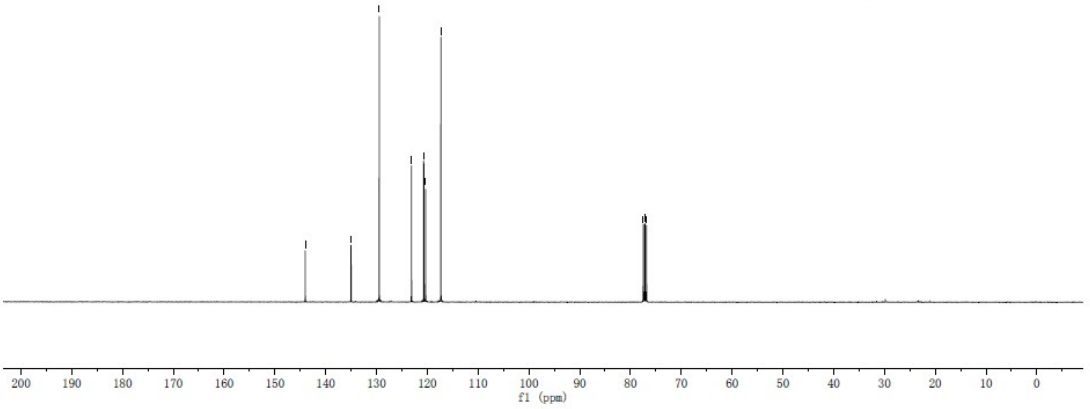
135.01
129.46
123.11
120.70
120.33
117.33
77.48
77.16
76.84


NH
NH

3b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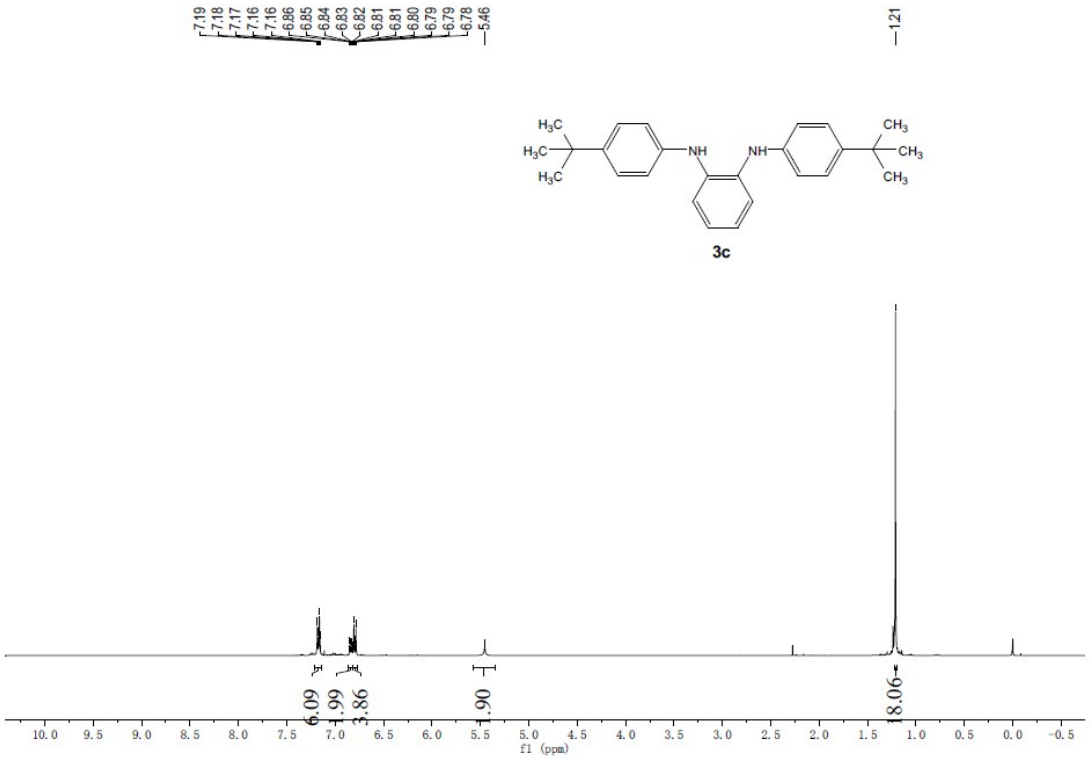
f1 (ppm)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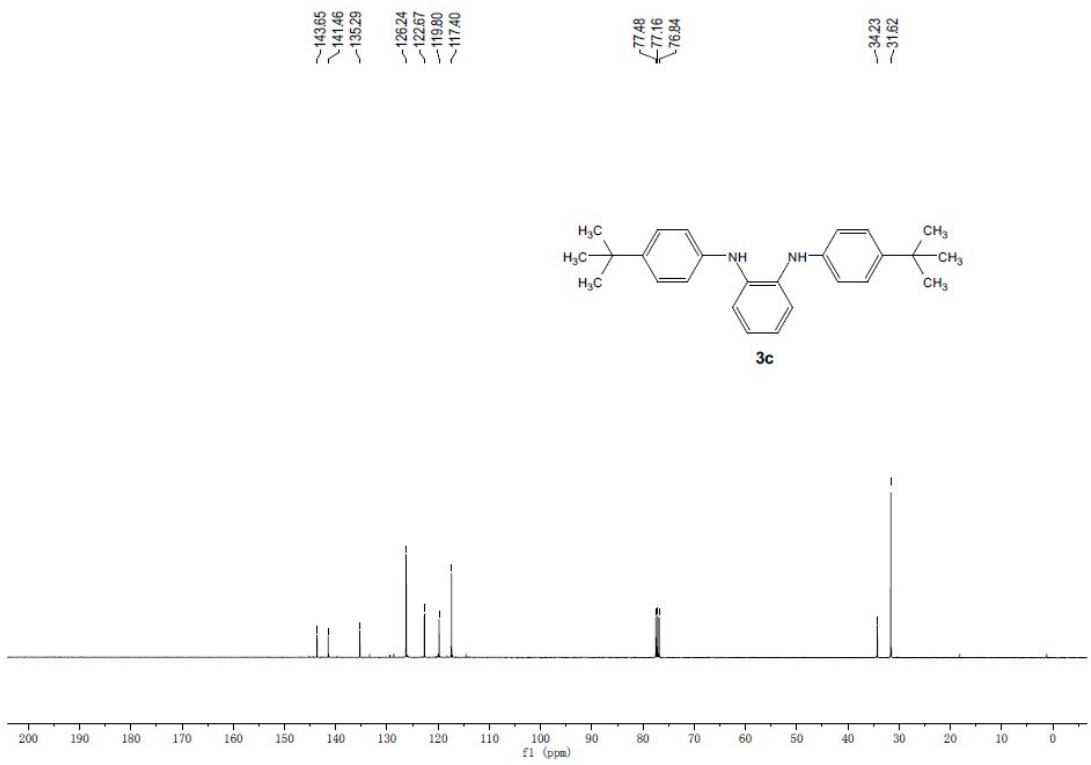
1.99
3.86
1.90
18.06
f1 (ppm)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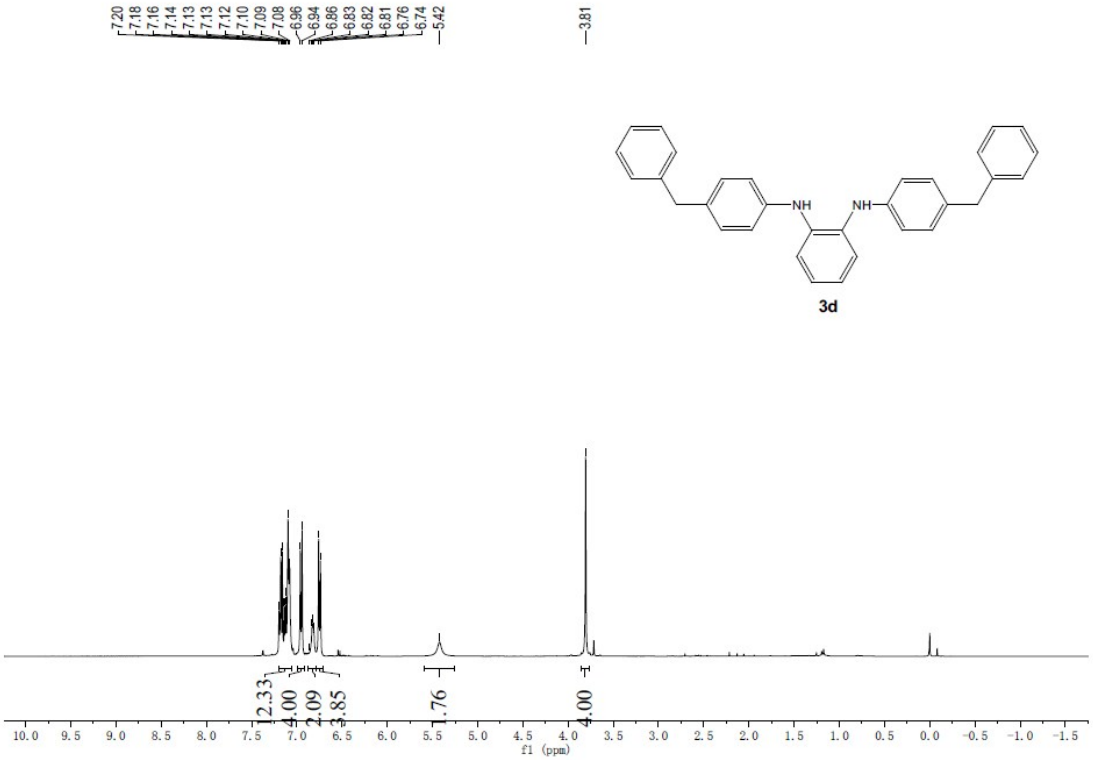
76.84
34.23
31.62
3c
f1 (ppm)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7.08
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6.86
6.83
6.82
6.81
6.76
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NH
NH
3d
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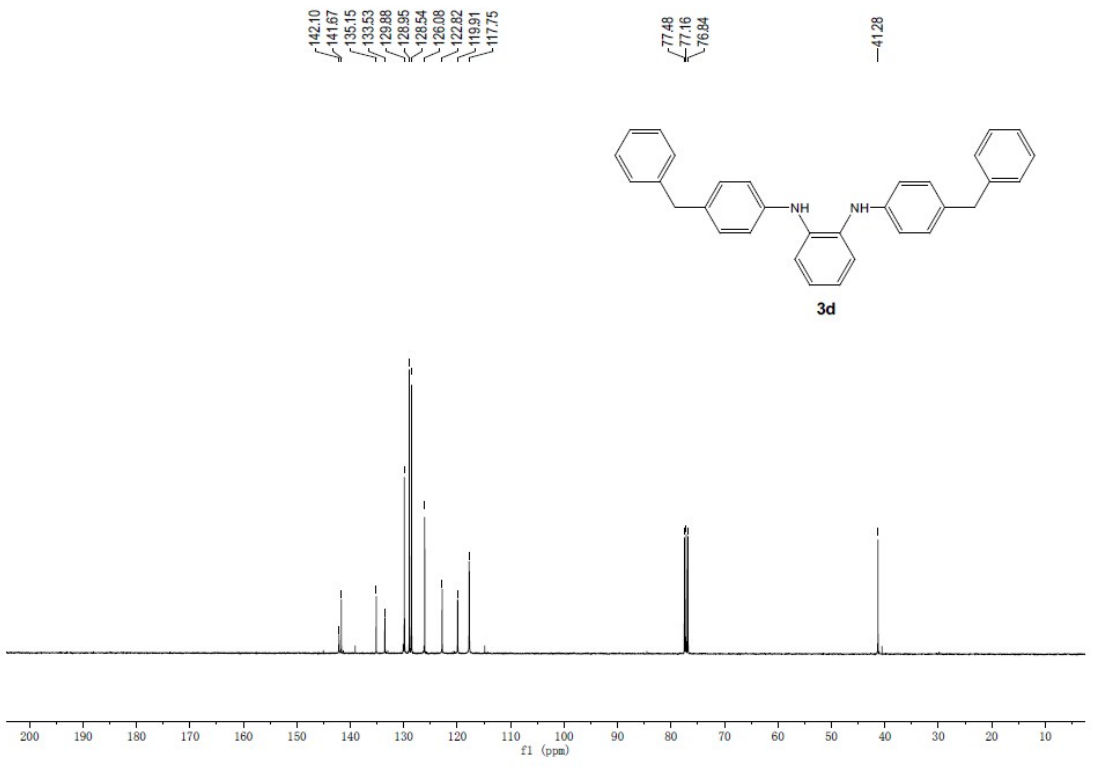
4.00
2.09
3.85
1.76
4.00
f1 (ppm)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119.91
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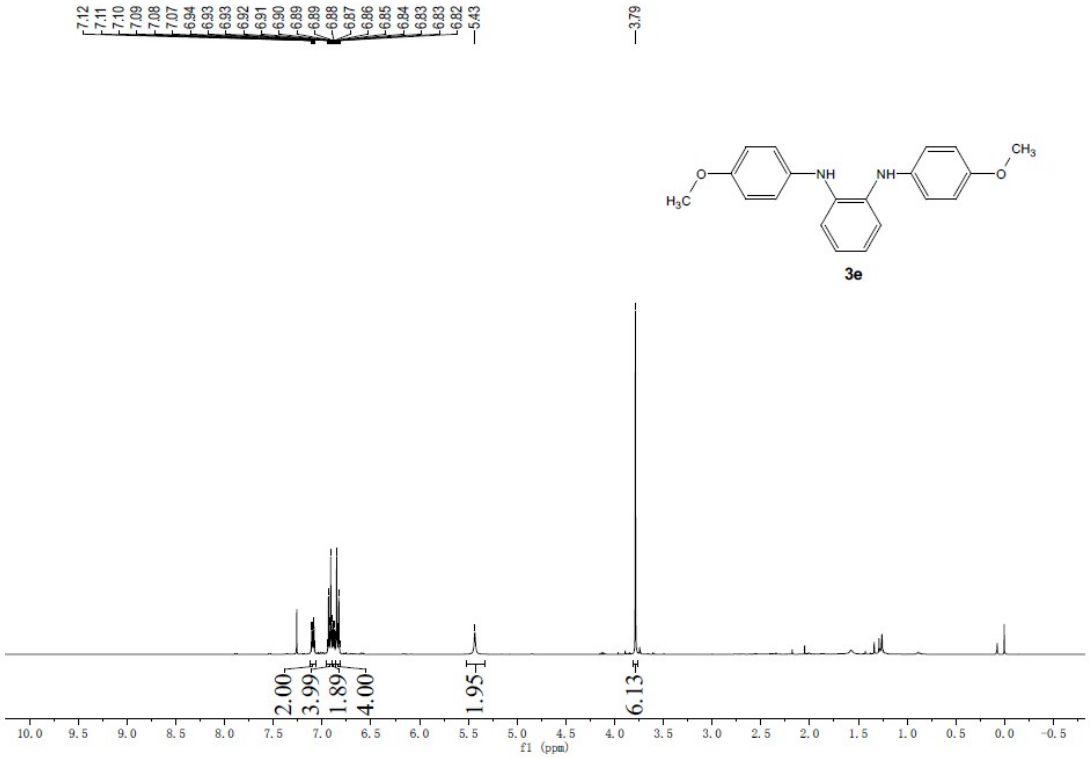
76.84
41.28
NH
NH
3d
f1 (ppm)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6.90
6.89
6.89
6.88
6.87
6.86
6.85
6.84
6.83
6.83
6.82
5.43
3.79
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4.00
1.95
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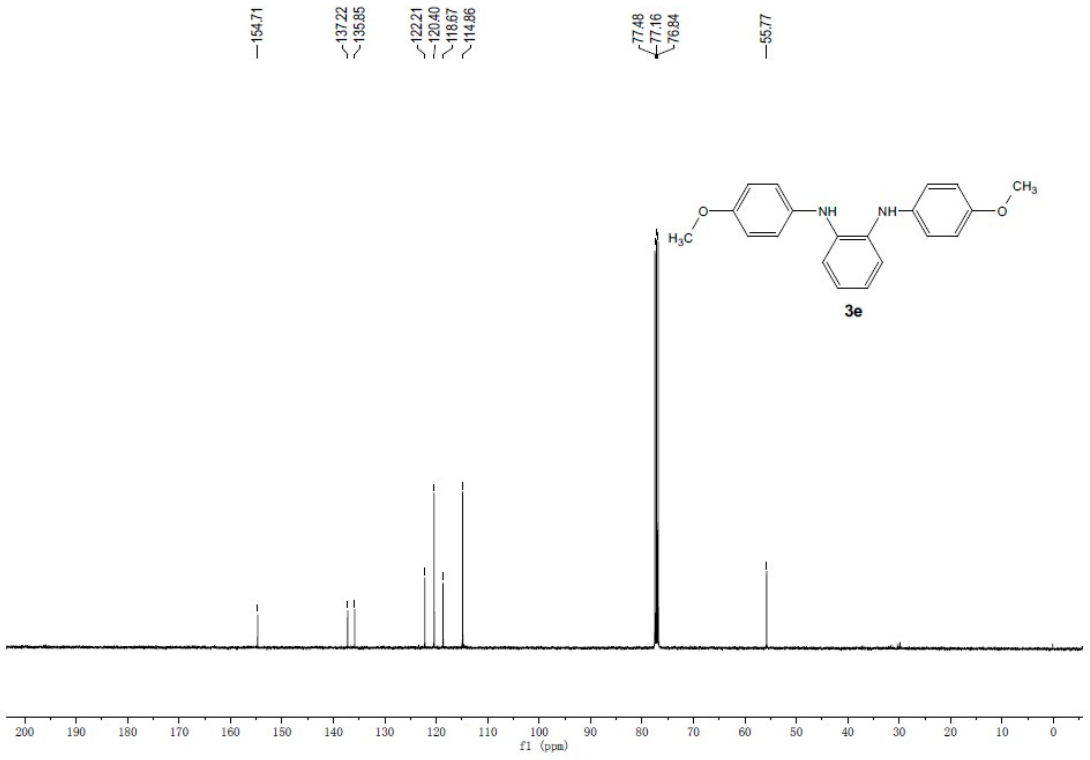
f1 (ppm)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NH
NH
O
H3C
CH3
3e
f1 (ppm)


7.25
7.24
7.23
7.22
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7.17
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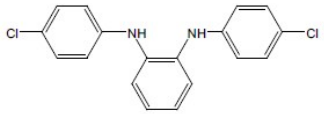
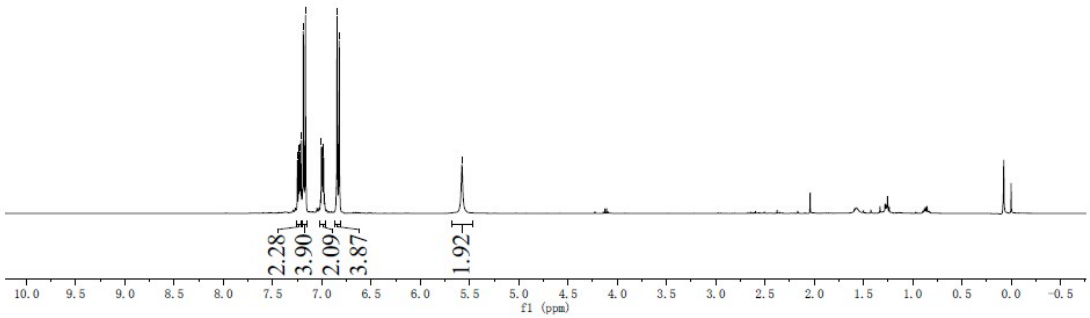
6.85
6.82
5.58


Cl
NH
NH
Cl

3f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3.87
1.92
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f1 (ppm)


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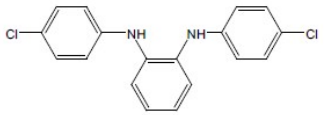
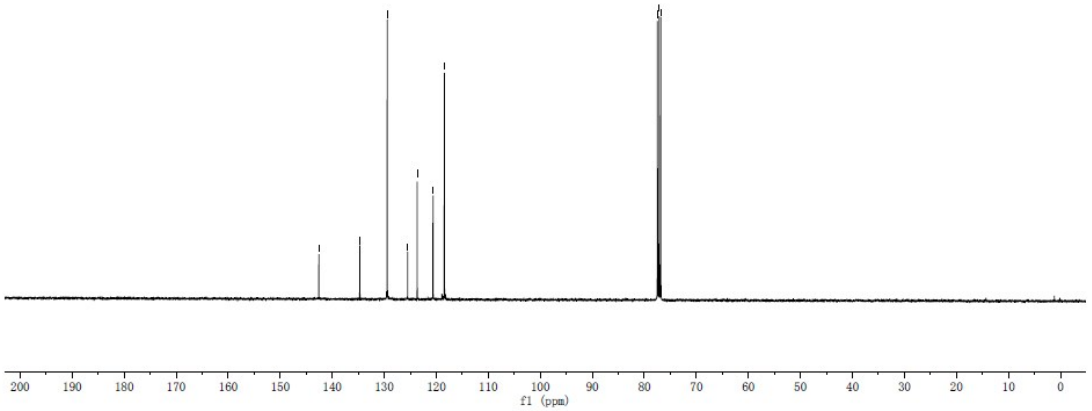

Cl
NH
NH
Cl

3f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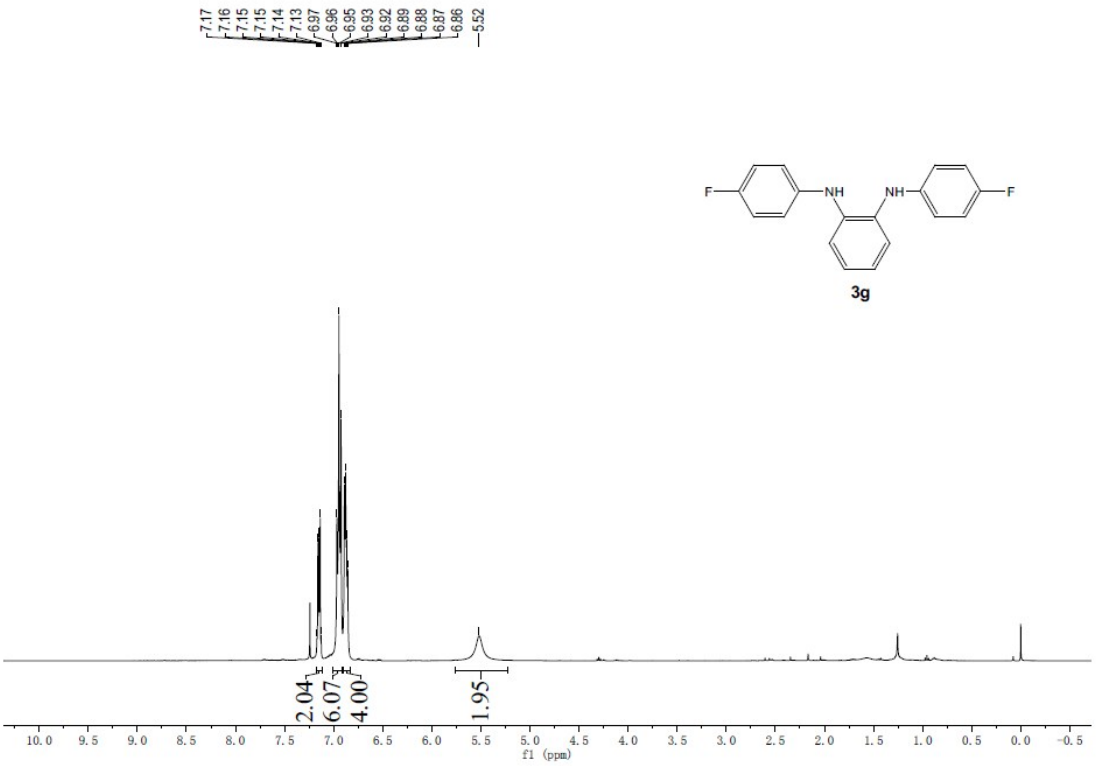
f1 (ppm)


7.17
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7.15
7.15
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7.13
6.97
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6.93
6.92
6.89
6.88
6.87
6.86
5.52
F
NH
NH
F
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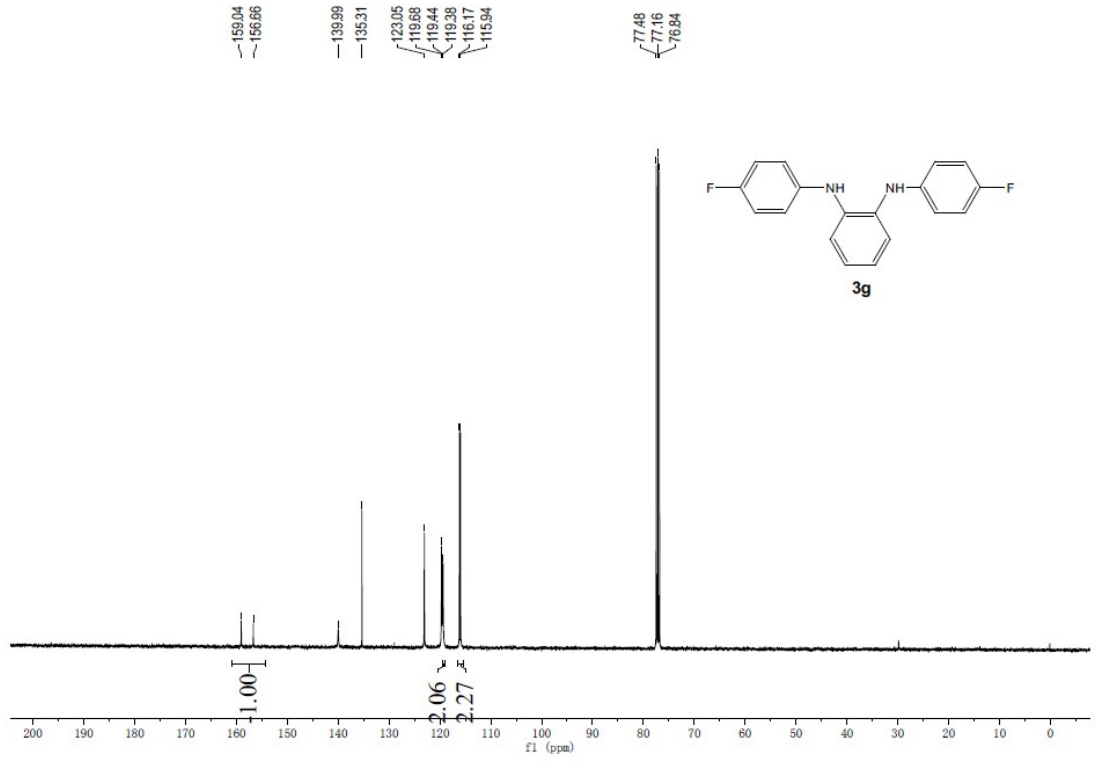
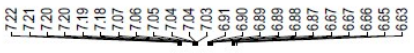
6.07
4.00
1.95
f1 (ppm)


159.04
156.66
139.99
135.31
123.05
119.68
119.44
119.38
116.17
115.94
77.48
77.16
76.84
F
NH
NH
F
3g
1.00
2.06
2.27
f1 (ppm)


7.22
7.21
7.20
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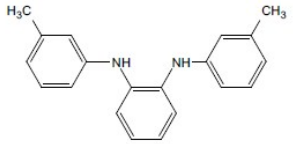
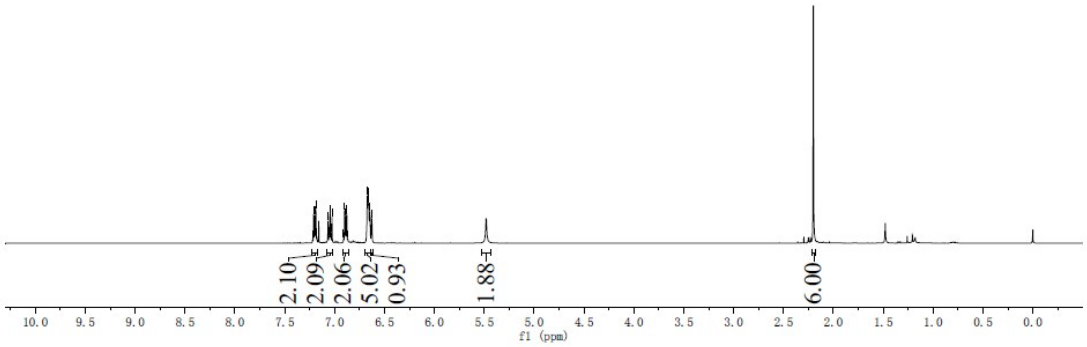
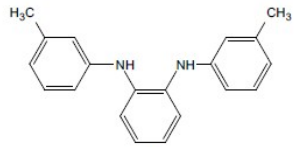
7.19
7.18
7.07
7.06
7.05
7.04
7.04
7.03
6.91
6.90
6.89
6.89
6.88
6.87
6.67
6.67
6.66
6.65
6.63


H3C
CH3
NH
NH

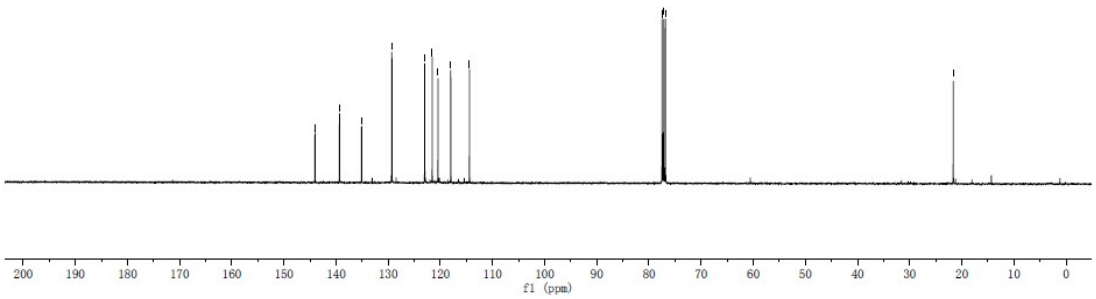
3h

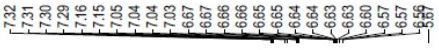

2.10
2.09
2.06
5.02
0.93
1.88
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.04
139.35
135.11
129.30
123.01
121.57
120.45
118.02
114.42
77.48
77.16
76.84
21.63


H3C
CH3
NH
NH

3h


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


7.32
7.31
7.30
7.29
7.16
7.15
7.05
7.04
7.04
7.03
6.67
6.67
6.66
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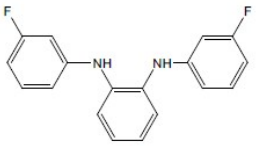
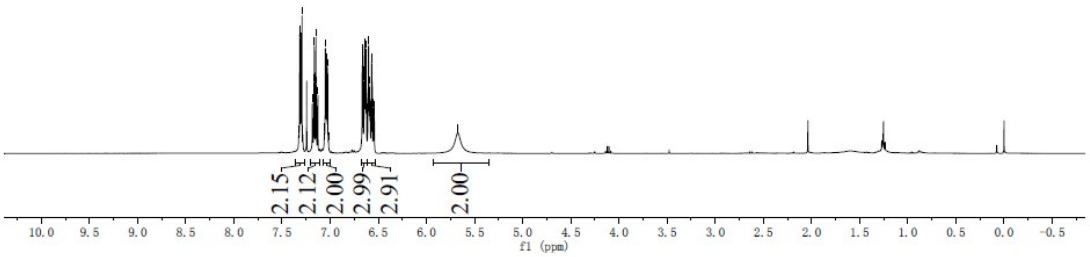
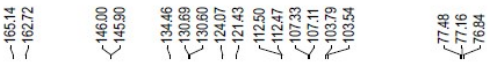
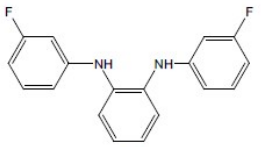
6.63
6.60
6.57
6.57
6.56
6.56


F
NH
NH
F

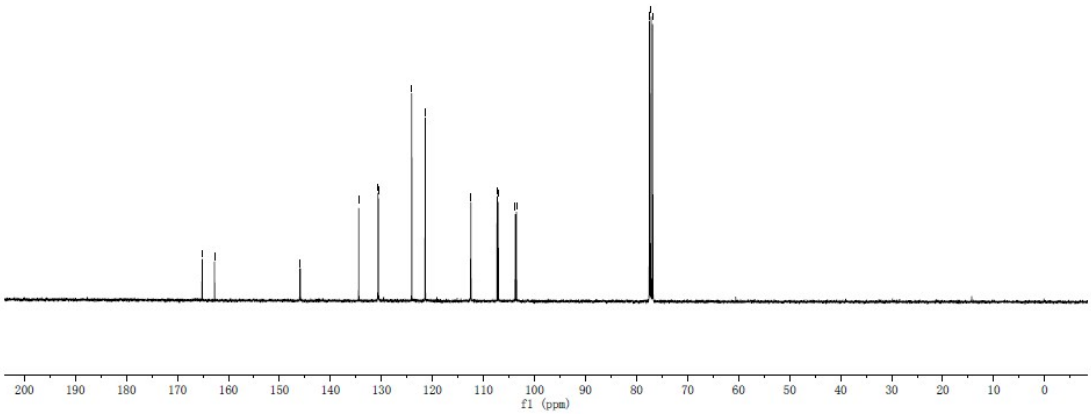
3i

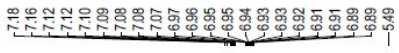

2.15
2.12
2.00
2.99
2.91
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.14
162.72
146.00
145.90
134.46
130.69
130.60
124.07
121.43
112.50
112.47
107.33
107.11
103.79
103.54
77.48
77.16
76.84


F
NH
NH
F

3i


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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7.16
7.12
7.12
7.10
7.09
7.08
7.08
7.07
6.97
6.96
6.95
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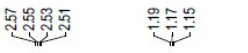
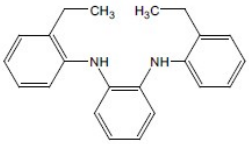
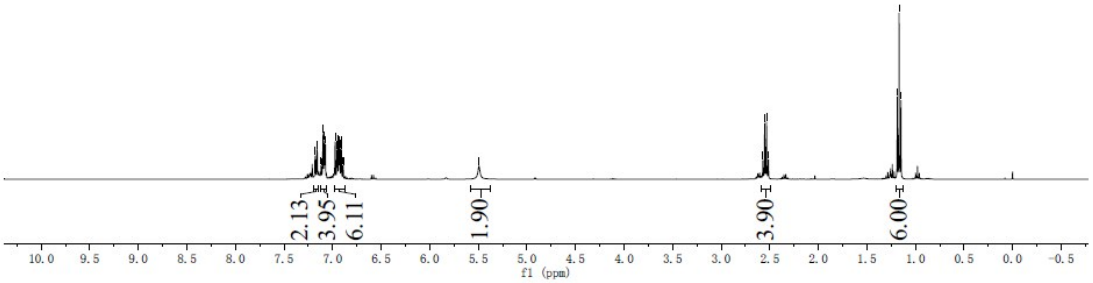
6.92
6.91
6.91
6.89
6.89
5.49


2.57
2.55
2.53
2.51
1.19
1.17
1.15


CH3
H3C
NH
NH

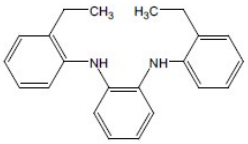
3j


2.13
3.95
6.11
1.90
3.90
6.00
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 -0.5
f1 (ppm)

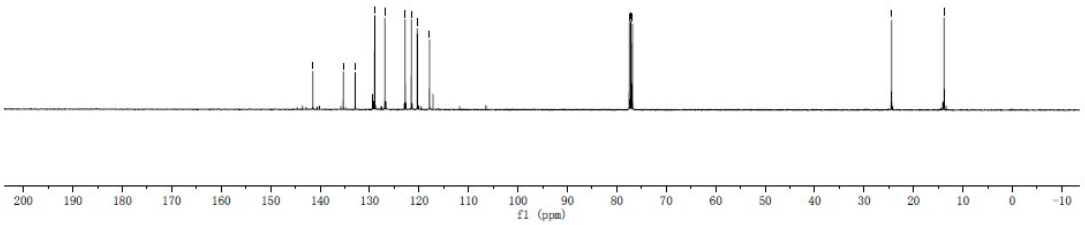

141.47
135.31
132.91
128.96
126.90
122.81
121.56
120.35
117.88

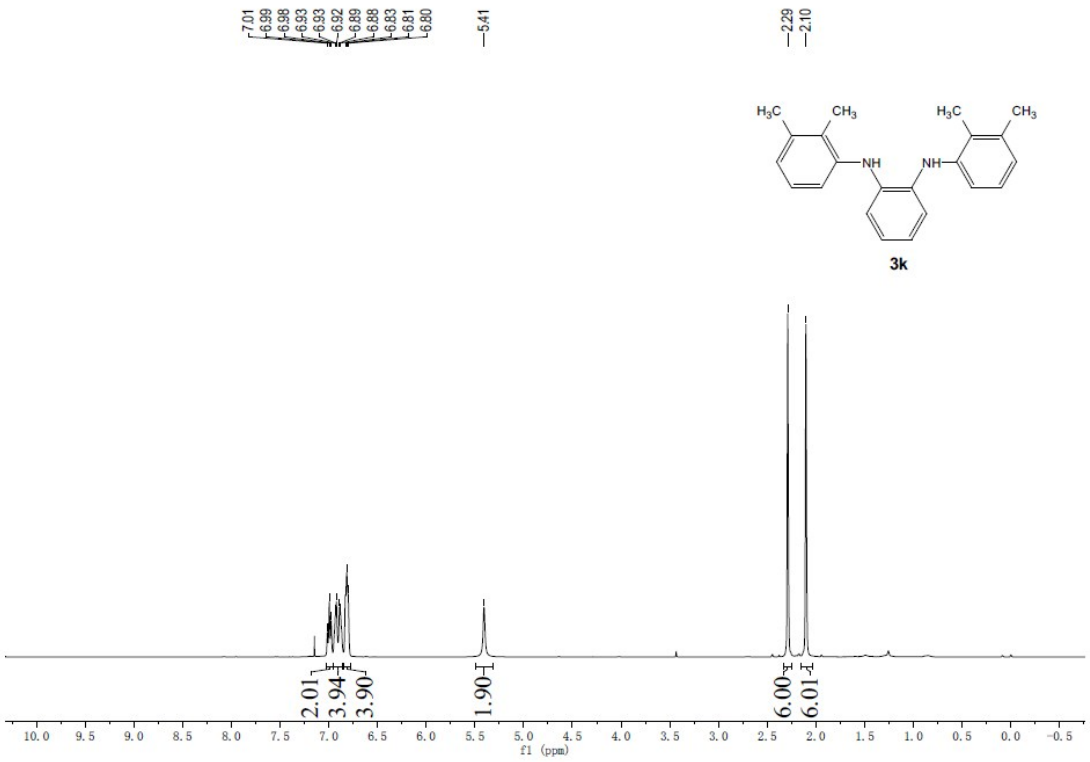
77.48
77.16
76.84

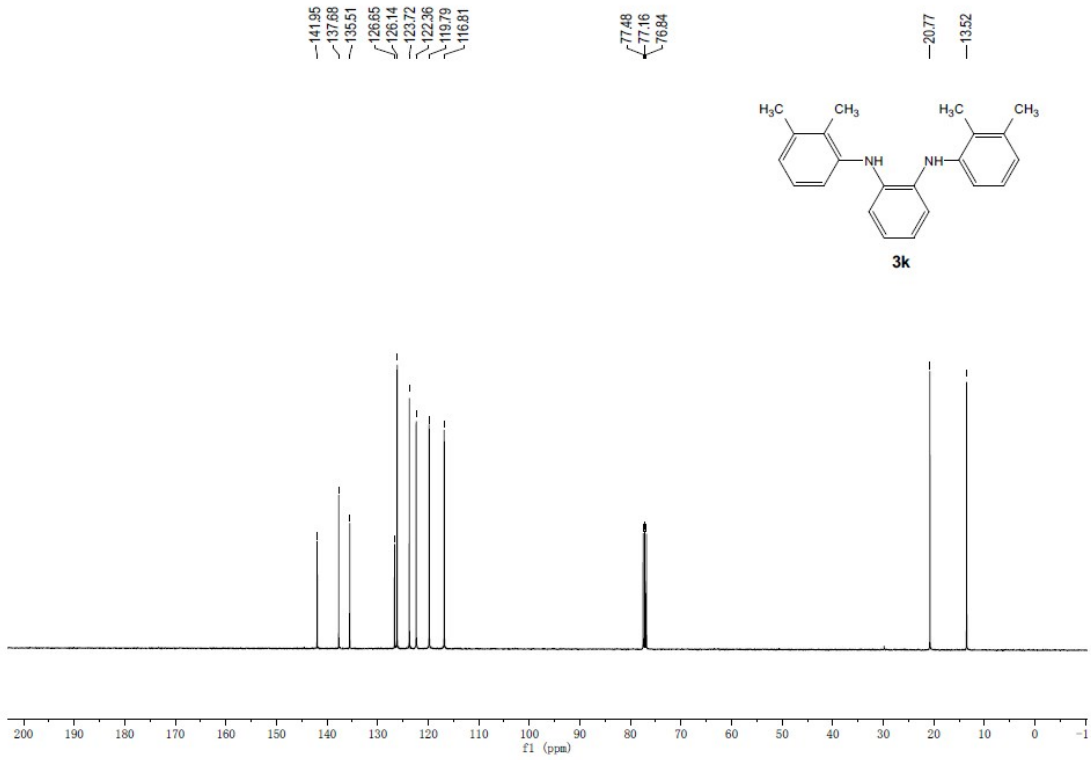

24.44
13.81

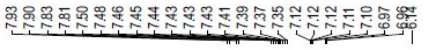

CH3
H3C
NH
NH

3J


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


7.01
6.99
6.98
6.93
6.92
6.89
6.88
6.83
6.81
6.80
5.41
2.29
2.10
H3C
CH3
NH
3k
2.01
3.94
3.90
1.90
6.00
6.01
f1 (ppm)


141.95
137.68
135.51
126.65
126.14
123.72
122.36
119.79
116.81
77.48
77.16
76.84
20.77
13.52
H3C
CH3
NH
3k
f1 (ppm)


7.93
7.90
7.83
7.81
7.50
7.48
7.46
7.45
7.44
7.43
7.43
7.43
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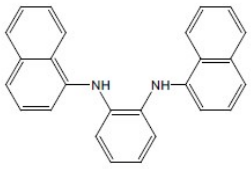
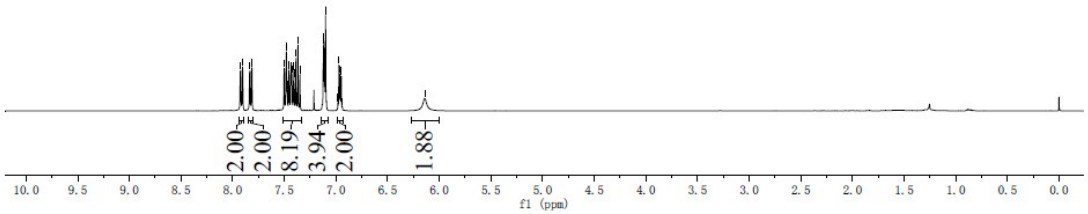
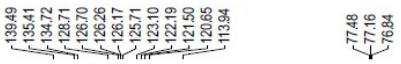
7.12
7.11
7.10
6.97
6.96
6.14


NH
NH

3l


2.00
2.00
8.19
3.94
2.00
1.88
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)


139.49
135.41
134.72
128.71
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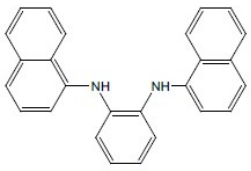
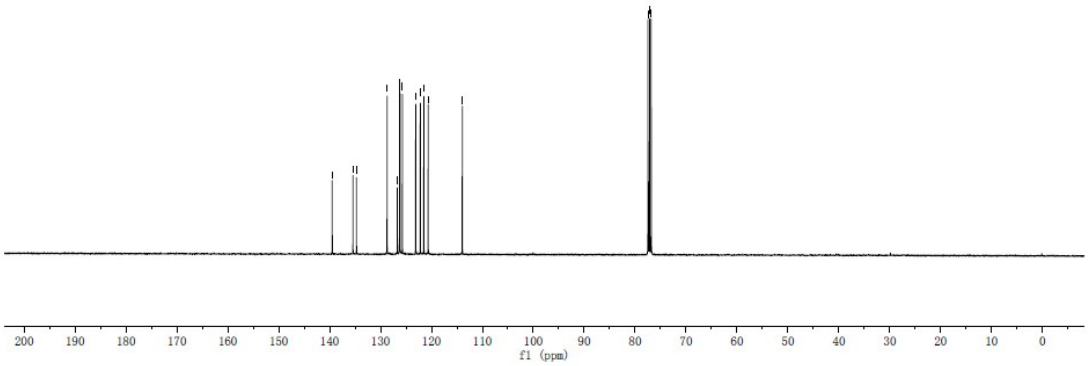
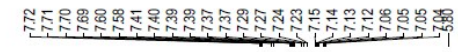
126.26
126.17
125.71
123.10
122.19
121.50
120.65
113.94

77.48
77.16
76.84


NH
NH

3l


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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7.71
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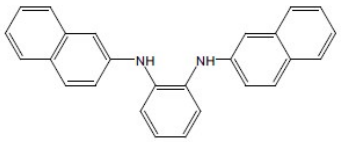
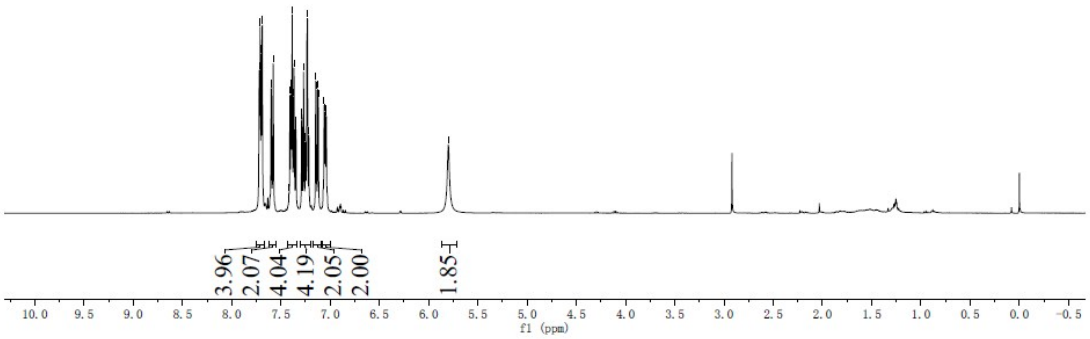
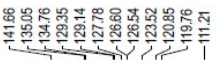
7.69
7.60
7.58
7.41
7.40
7.39
7.39
7.37
7.37
7.29
7.27
7.24
7.23
7.15
7.14
7.13
7.12
7.06
7.05
7.05
5.80


NH
NH

3m


3.96
2.07
4.04
4.19
2.05
2.00
1.85
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 -0.5
f1 (ppm)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126.60
126.54
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120.85
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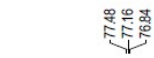
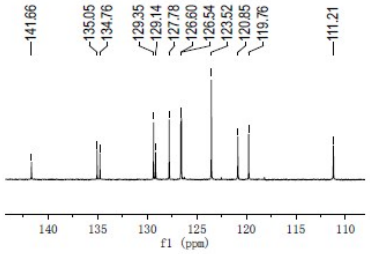
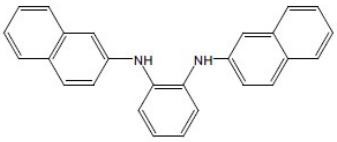
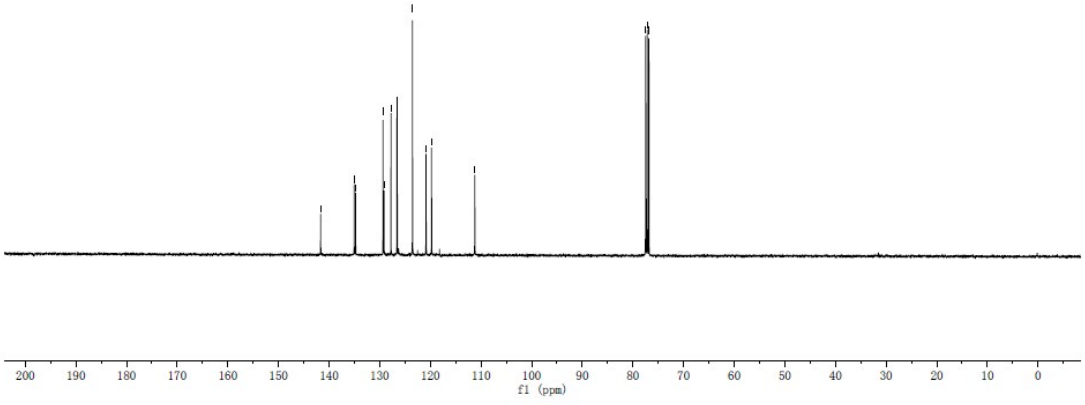
111.21

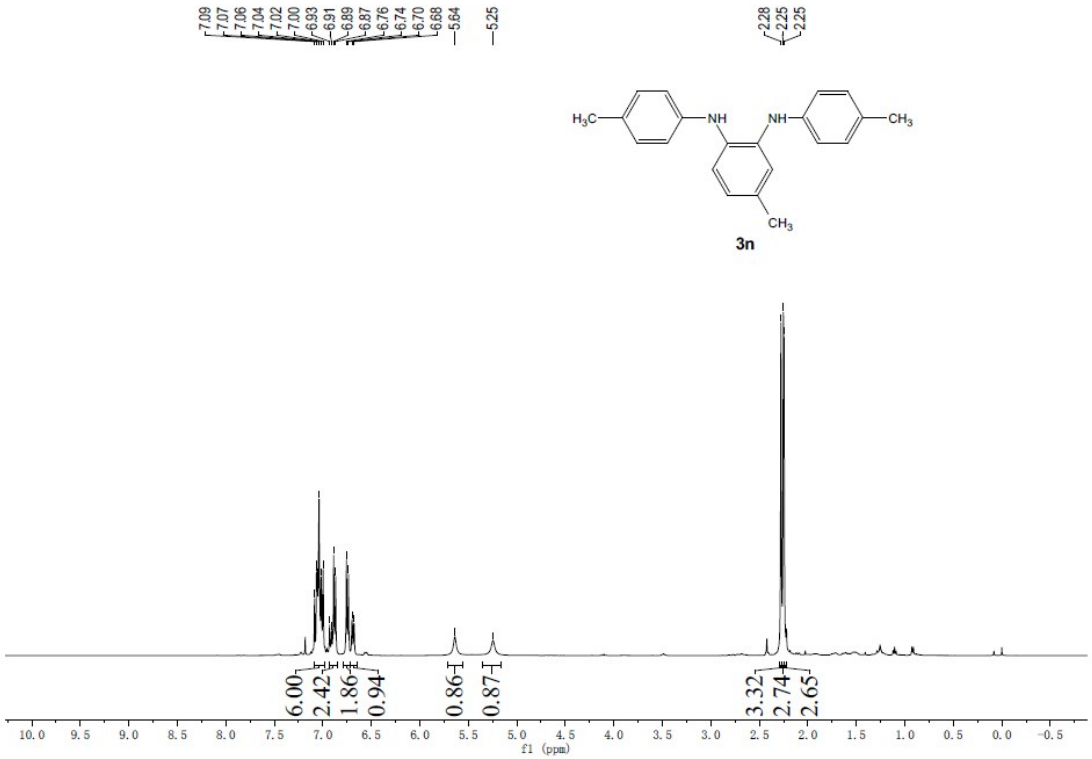

77.48
77.16
76.84


141.66
135.05
134.76
129.35
129.14
127.78
126.60
126.54
123.52
120.85
119.76
111.21
140 135 130 125 120 115 110
f1 (ppm)


NH
NH

3m


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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7.07
7.06
7.04
7.02
7.00
6.93
6.91
6.89
6.87
6.76
6.74
6.70
6.68
5.64
5.25
2.28
2.25
2.25
H3C
NH
NH
CH3
CH3
3n
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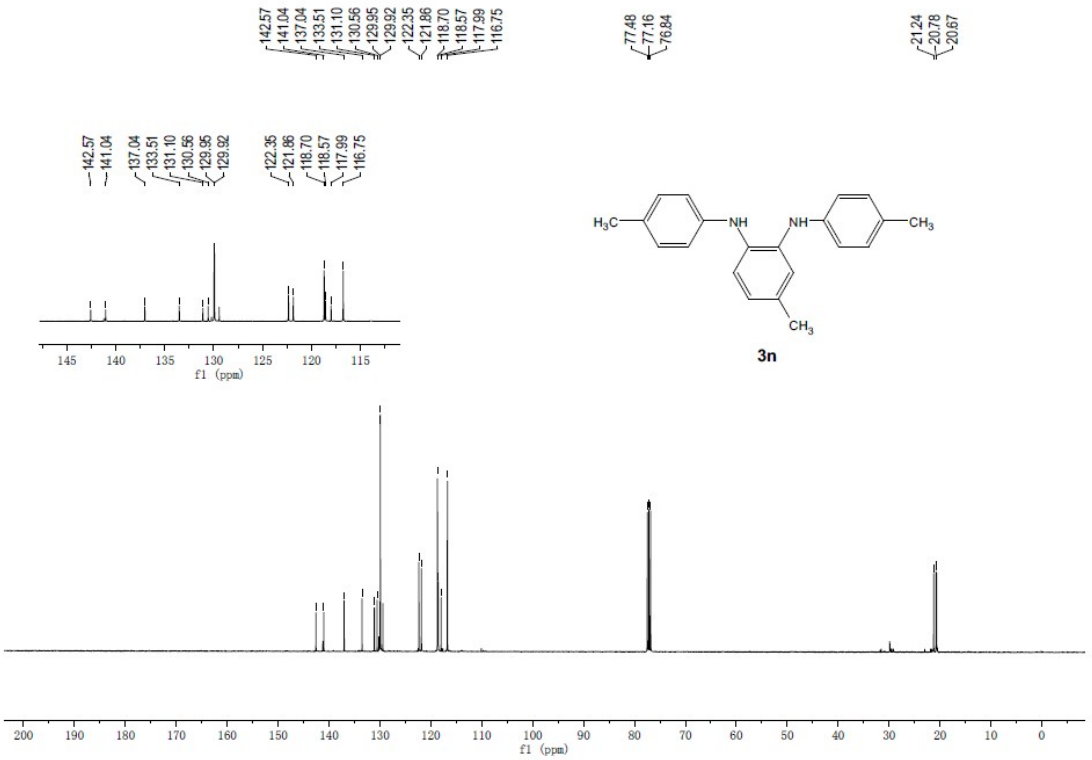
2.42
1.86
0.94
0.86
0.87
3.32
2.74
2.65
f1 (ppm)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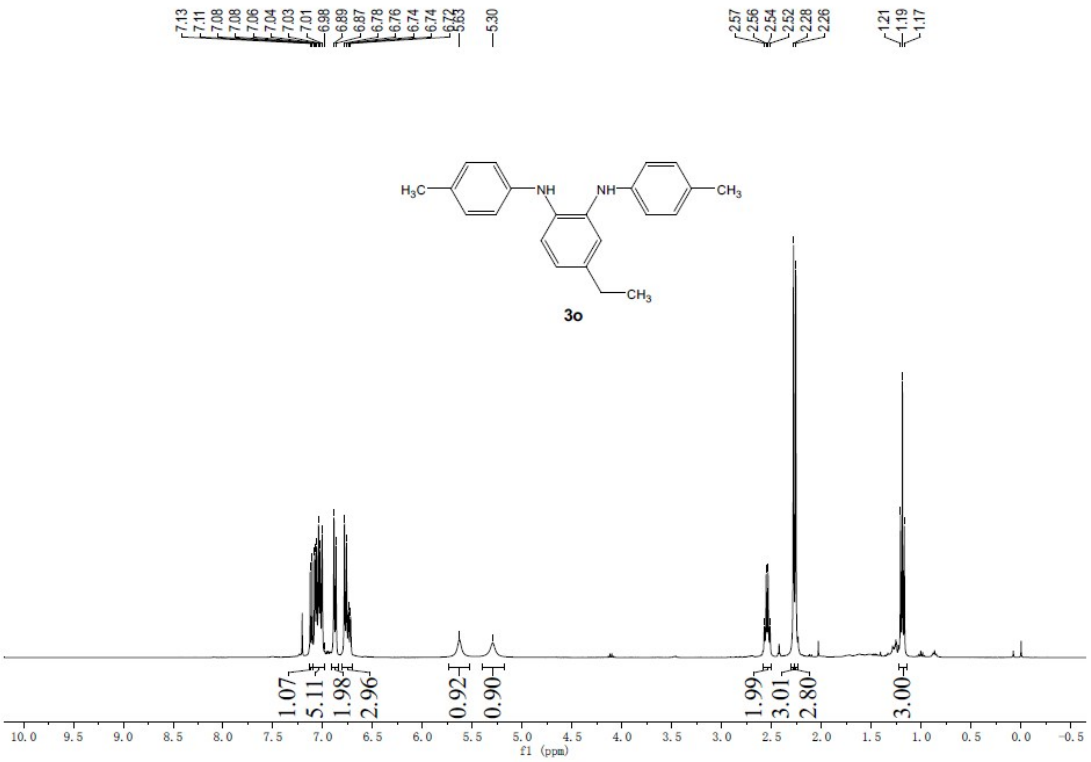
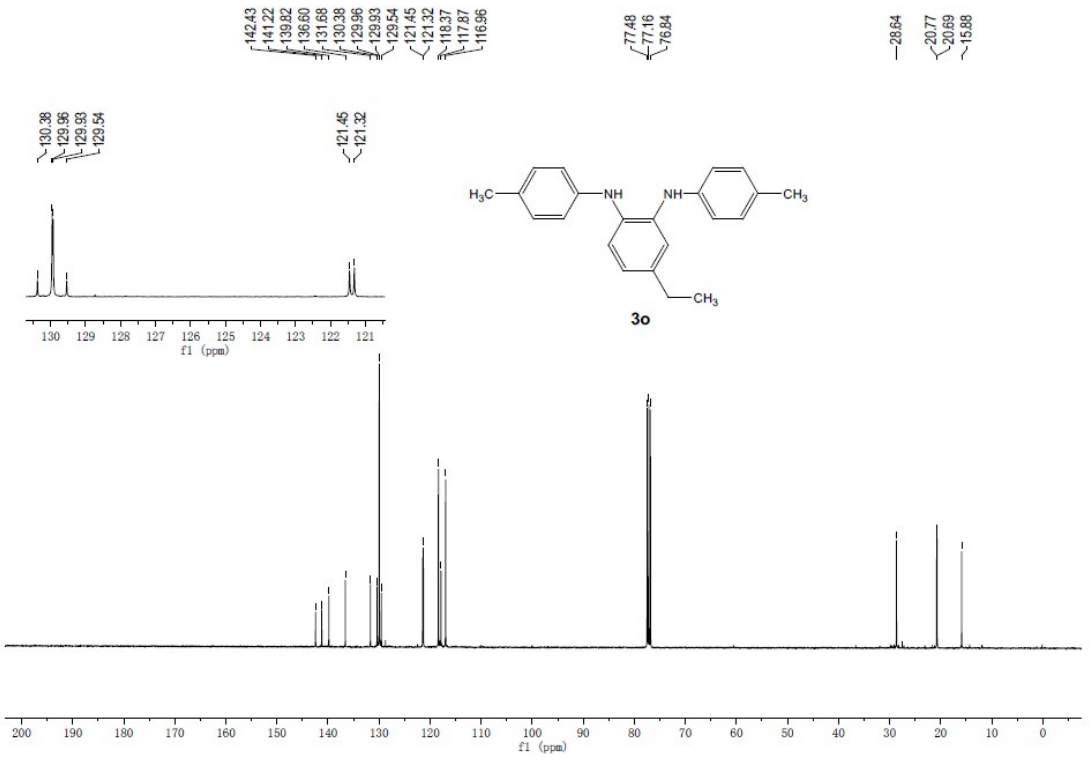
137.04
133.51
131.10
130.56
129.95
129.92
122.35
121.86
118.70
118.57
117.99
116.75
77.48
77.16
76.84
21.24
20.78
20.67
H3C
NH
NH
CH3
CH3
3n
f1 (ppm)


7.13
7.11
7.08
7.08
7.06
7.04
7.03
7.01
6.98
6.89
6.87
6.78
6.76
6.74
6.74
6.72
5.63
5.30
2.57
2.56
2.54
2.52
2.28
2.26
1.21
1.19
1.17
H3C
NH
NH
CH3
CH3
3o
1.07
5.11
1.98
2.96
0.92
0.90
1.99
3.01
2.80
3.00
f1 (ppm)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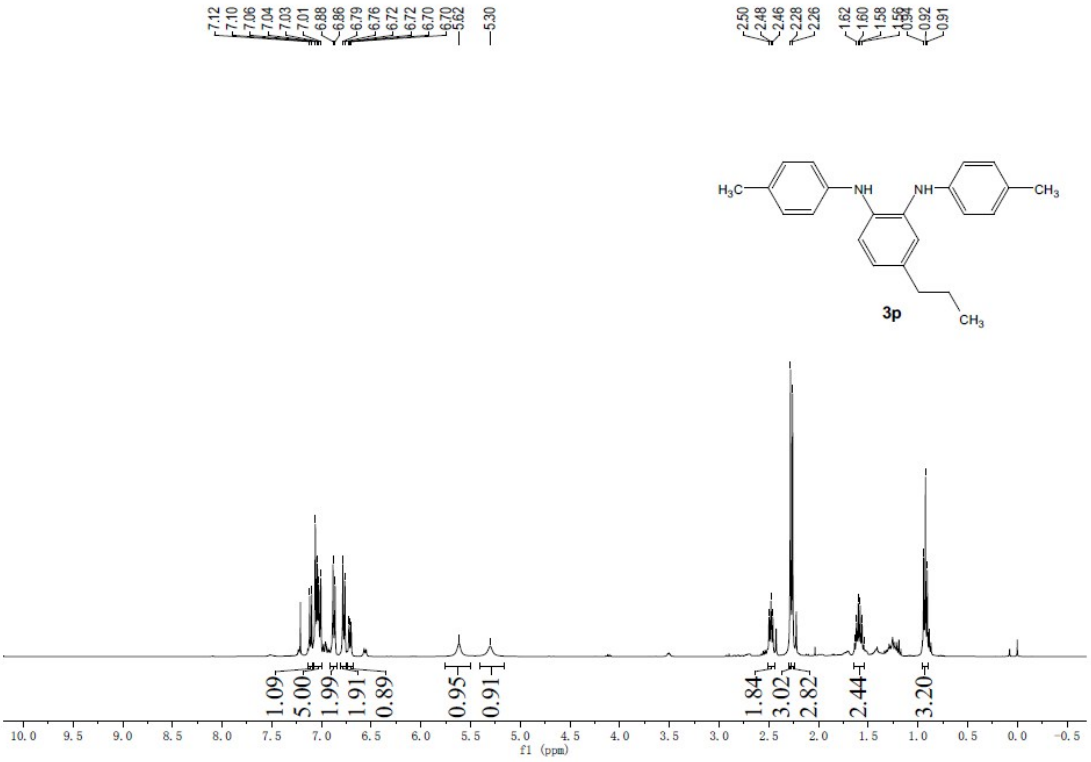
130.38
129.96
129.93
129.54
121.45
121.32
118.37
117.87
116.96
77.48
77.16
76.84
28.64
20.77
20.69
15.88
130.38
129.96
129.93
129.54
121.45
121.32
H3C
NH
NH
CH3
CH3
3o
f1 (ppm)
f1 (ppm)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7.10
7.06
7.04
7.03
7.01
6.88
6.86
6.79
6.76
6.72
6.72
6.70
6.70
5.62
5.30
2.50
2.48
2.46
2.28
2.26
1.62
1.60
1.58
0.92
0.91
H3C
NH
NH
CH3
3p
CH3
1.09
5.00
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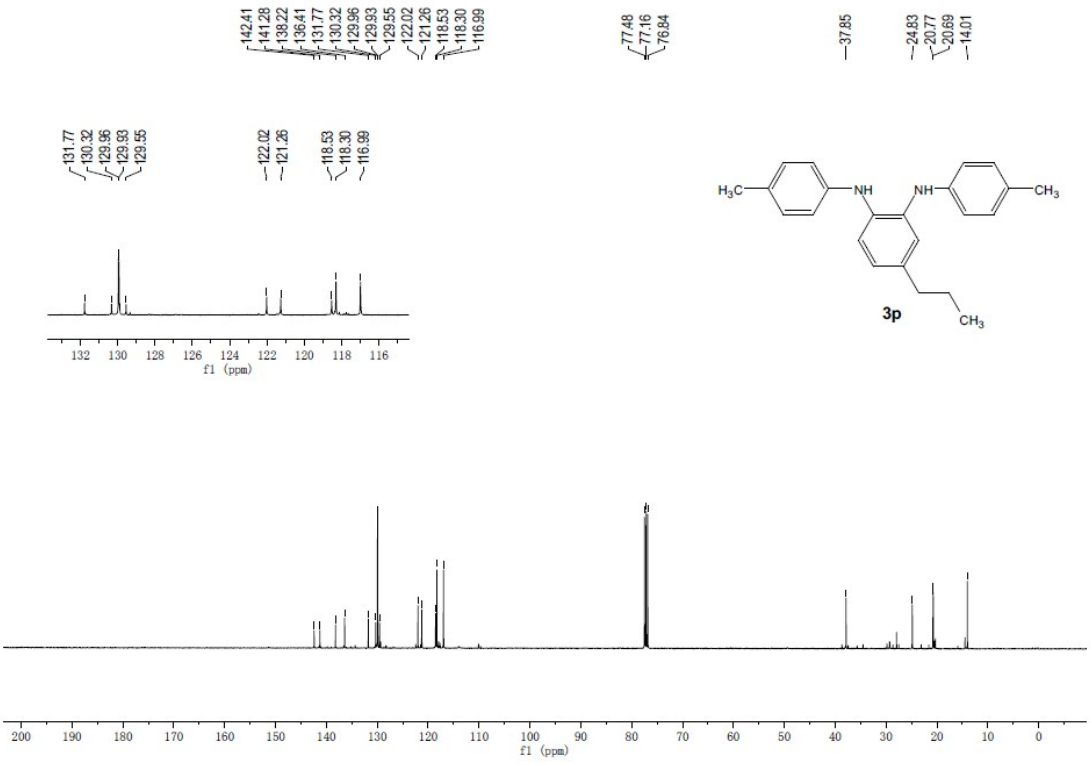
0.89
0.95
0.91
1.84
3.02
2.82
2.44
3.20
f1 (ppm)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130.32
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129.93
129.55
122.02
121.26
118.53
118.30
116.99
77.48
77.16
76.84
37.85
24.83
20.77
20.69
14.01
131.77
130.32
129.96
129.93
129.55
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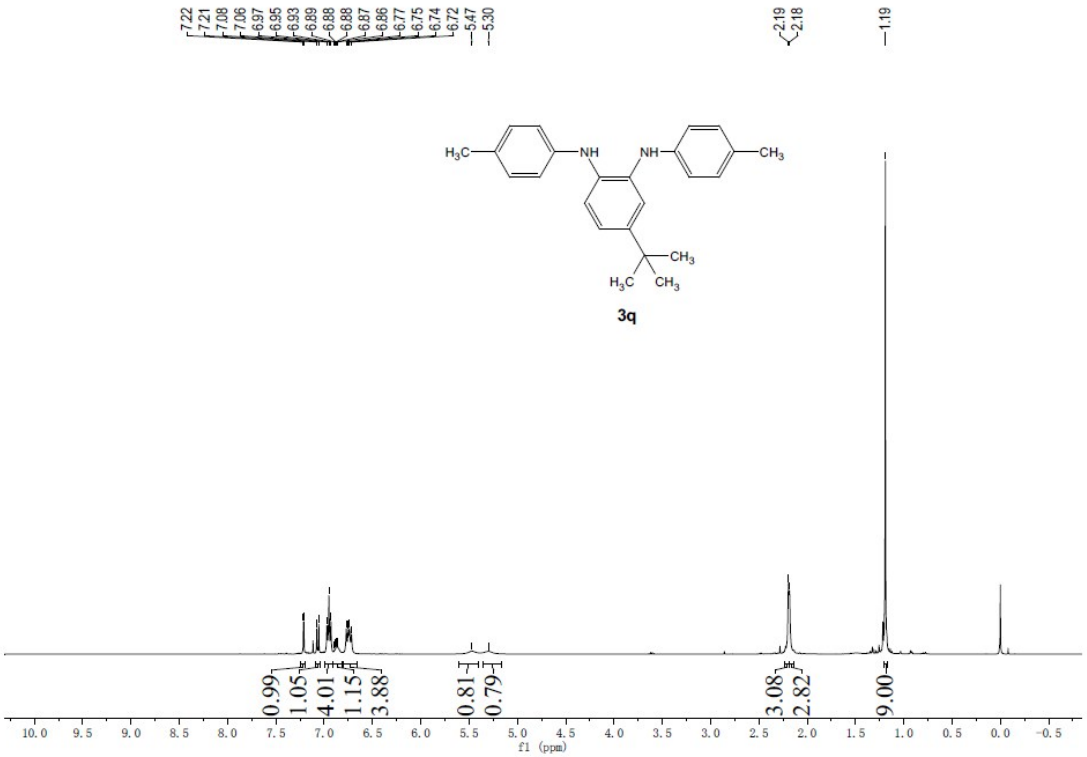
118.30
116.99
H3C
NH
NH
CH3
3p
CH3
f1 (ppm)
f1 (ppm)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6.95
6.93
6.89
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6.88
6.87
6.86
6.77
6.75
6.74
6.72
5.47
5.30
2.19
2.18
1.19
H3C
NH
NH
CH3
CH3
H3C
CH3
3q
0.99
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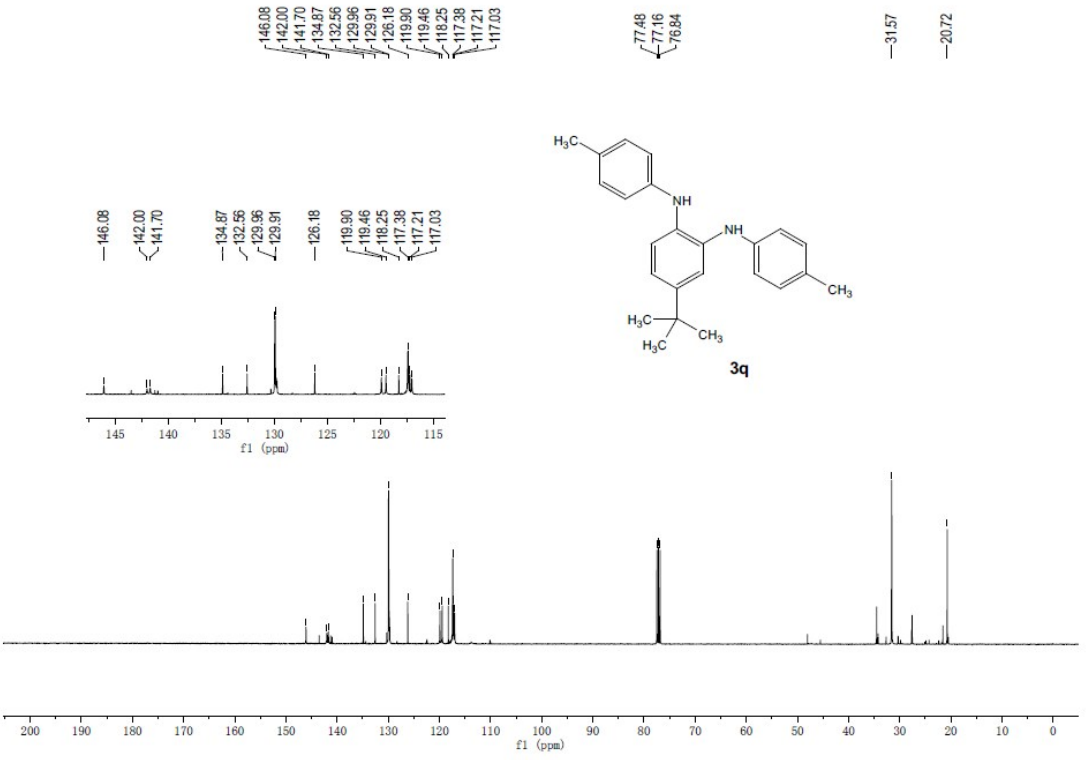
4.01
1.15
3.88
0.81
0.79
3.08
2.82
9.00
f1 (ppm)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129.91
126.18
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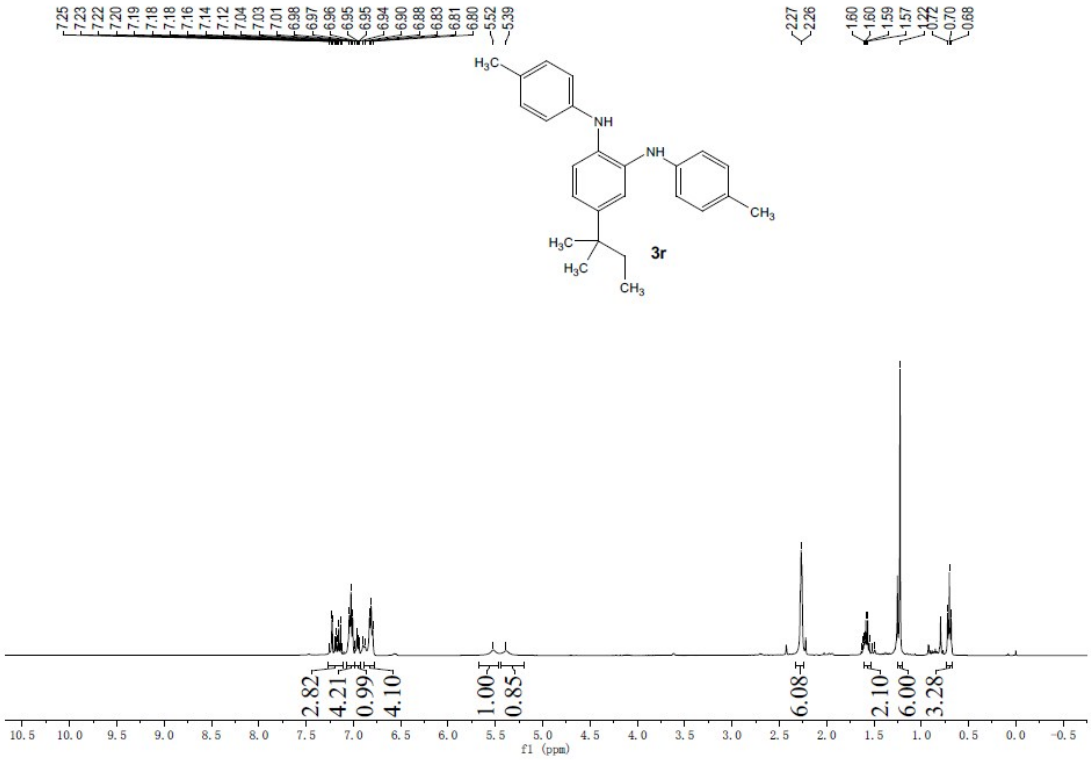
119.46
118.25
117.38
117.21
117.03
77.48
77.16
76.84
31.57
20.72
H3C
NH
NH
CH3
H3C
CH3
H3C
3q
f1 (ppm)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7.23
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7.18
7.16
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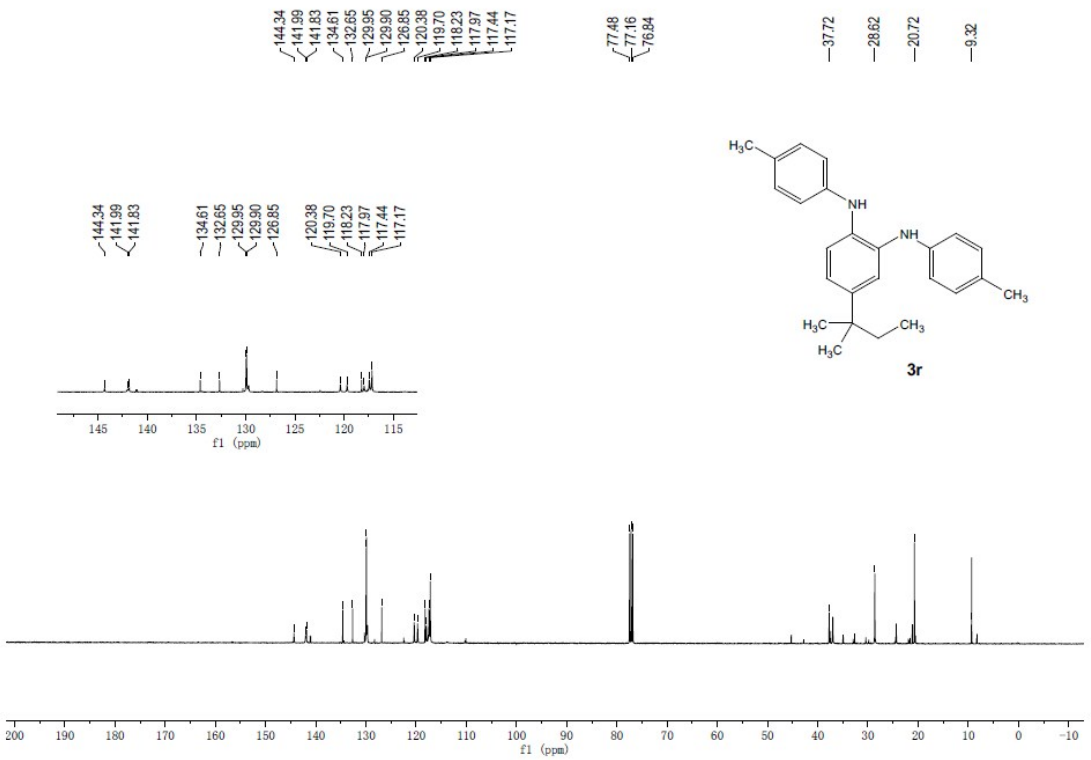
7.12
7.04
7.03
7.01
6.98
6.97
6.96
6.95
6.95
6.94
6.90
6.88
6.83
6.81
6.80
5.52
5.39
2.27
2.26
1.60
1.60
1.59
1.57
1.22
0.72
0.70
0.68
NH
NH
CH3
H3C
H3C
CH3
3r
2.82
4.21
0.99
4.10
1.00
0.85
6.08
2.10
6.00
3.28
f1 (ppm)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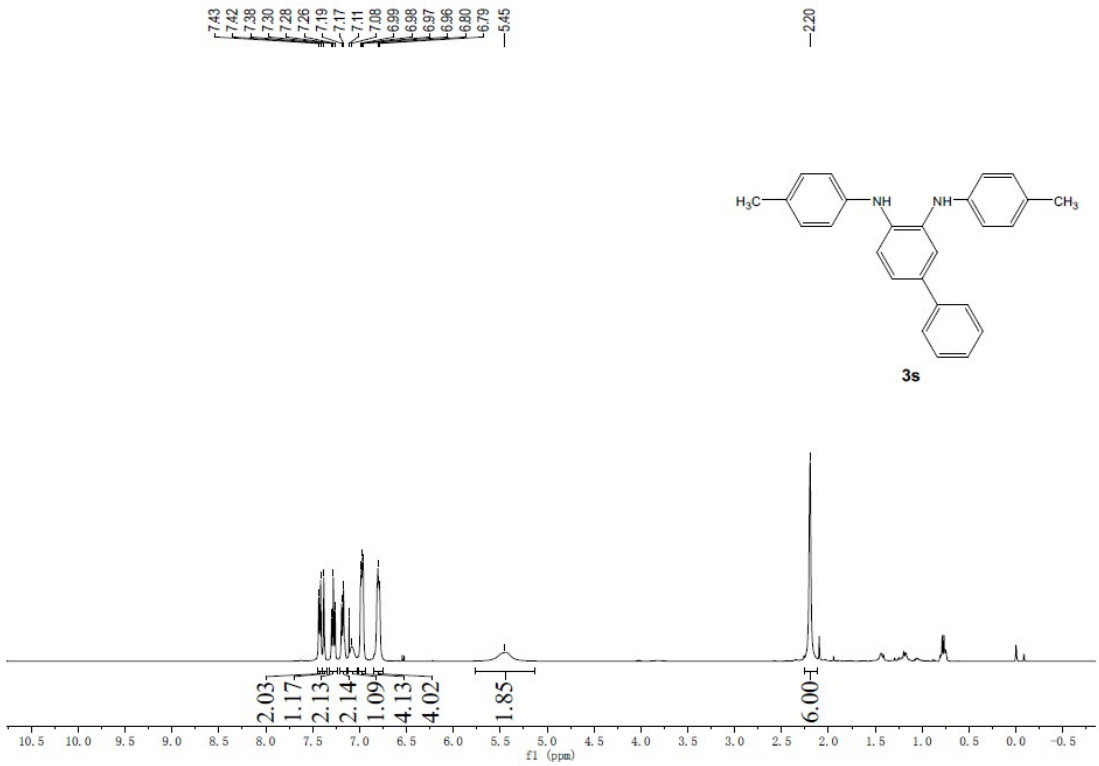
129.95
129.90
126.85
120.38
119.70
118.23
117.97
117.44
117.17
77.48
77.16
76.84
37.72
28.62
20.72
9.32
NH
NH
CH3
H3C
CH3
H3C
3r
f1 (ppm)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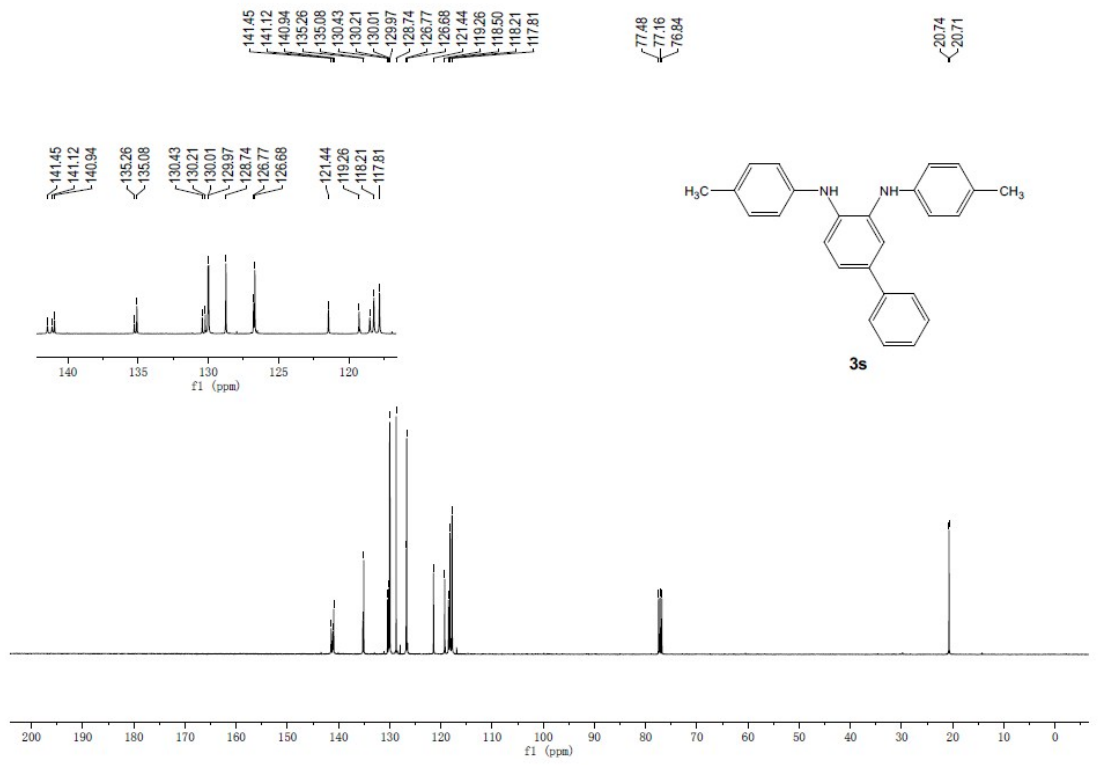
7.28
7.26
7.19
7.17
7.11
7.08
6.99
6.98
6.97
6.96
6.80
6.79
5.45
2.20
H3C
NH
NH
CH3
3s
2.03
1.17
2.13
2.14
1.09
4.13
4.02
1.85
6.00
f1 (ppm)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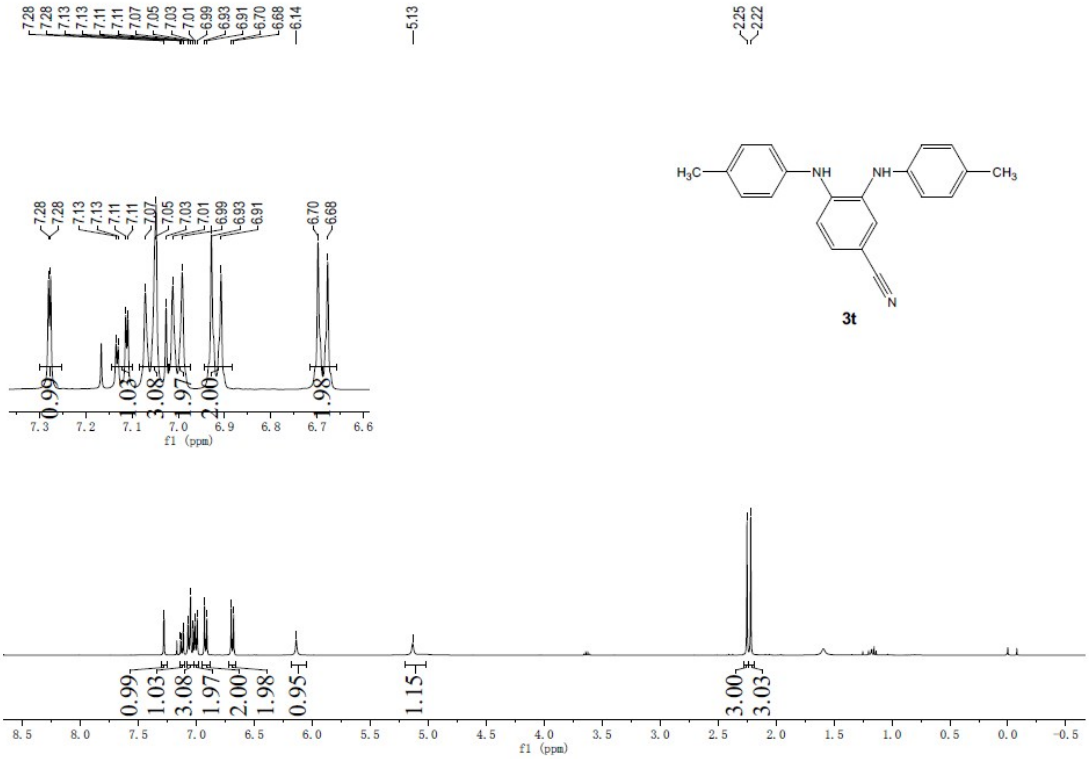
141.12
140.94
135.26
135.08
130.43
130.21
130.01
129.97
128.74
126.77
126.68
121.44
119.26
118.50
118.21
117.81
77.48
77.16
76.84
20.74
20.71
H3C
NH
NH
CH3
3s
f1 (ppm)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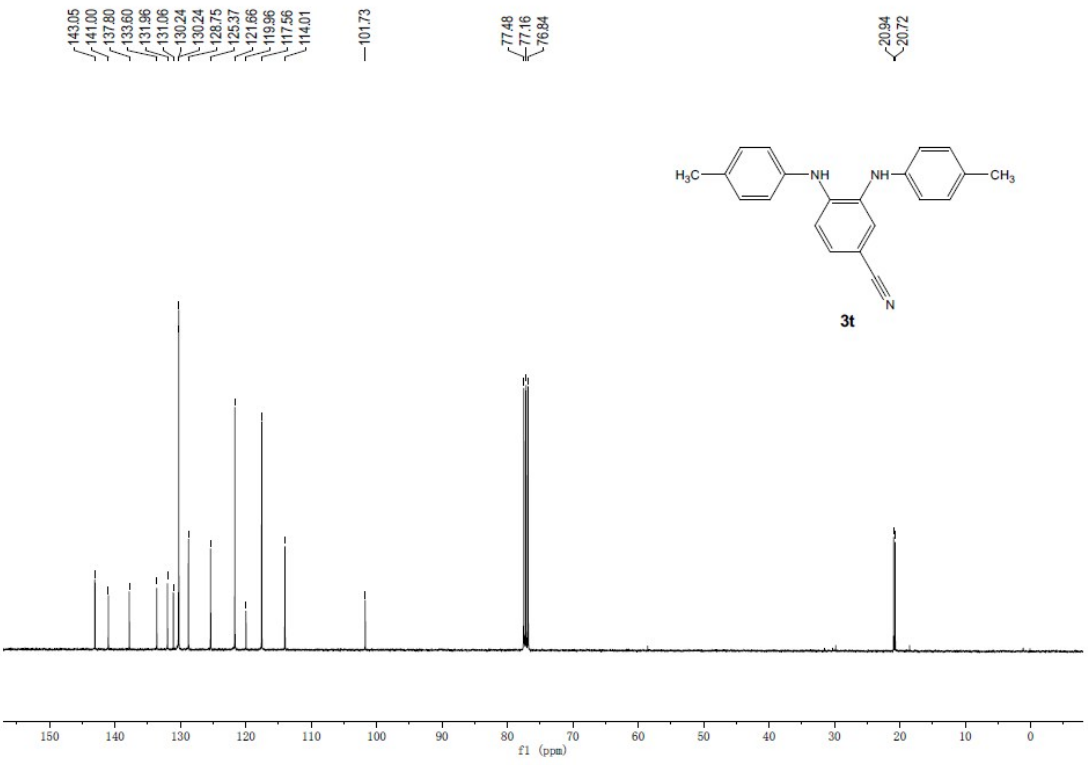
7.28
7.13
7.13
7.11
7.11
7.07
7.05
7.03
7.01
6.99
6.93
6.91
6.70
6.68
6.14
5.13
2.25
2.22
0.99
1.03
3.08
1.97
2.00
1.98
0.95
1.15
3.00
3.03
f1 (ppm)
3t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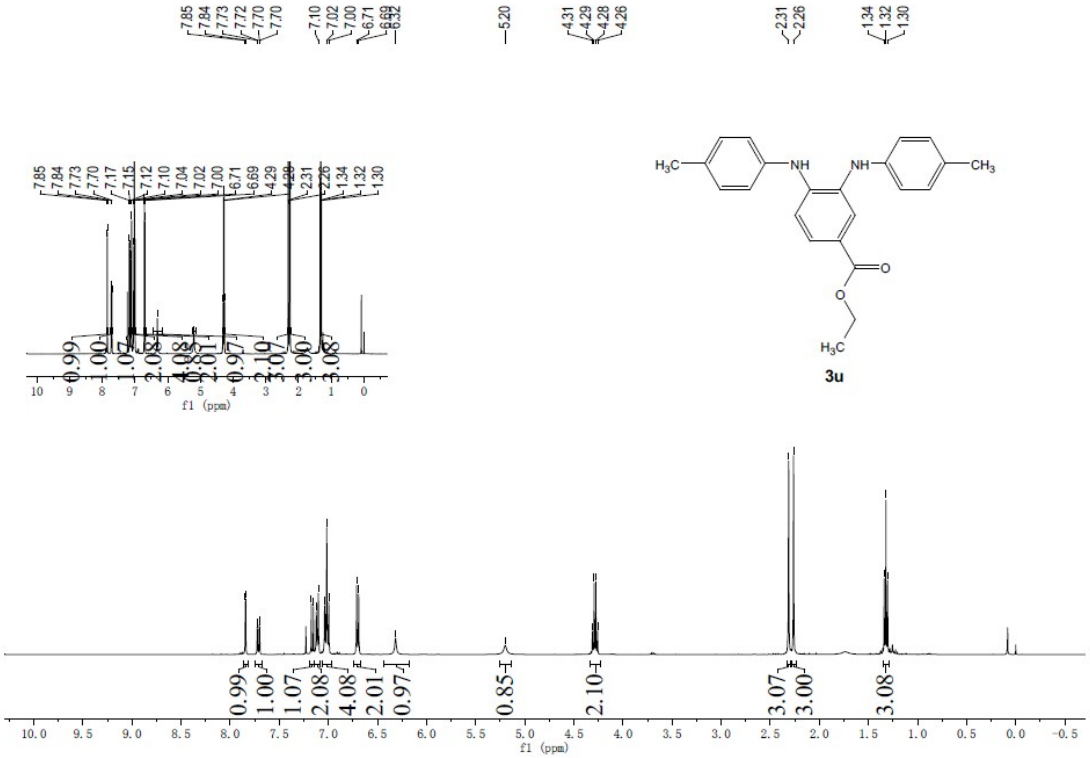
137.80
133.60
131.96
131.06
130.24
130.24
128.75
125.37
121.66
119.96
117.56
114.01
101.73
77.48
77.16
76.84
20.94
20.72
f1 (ppm)
3t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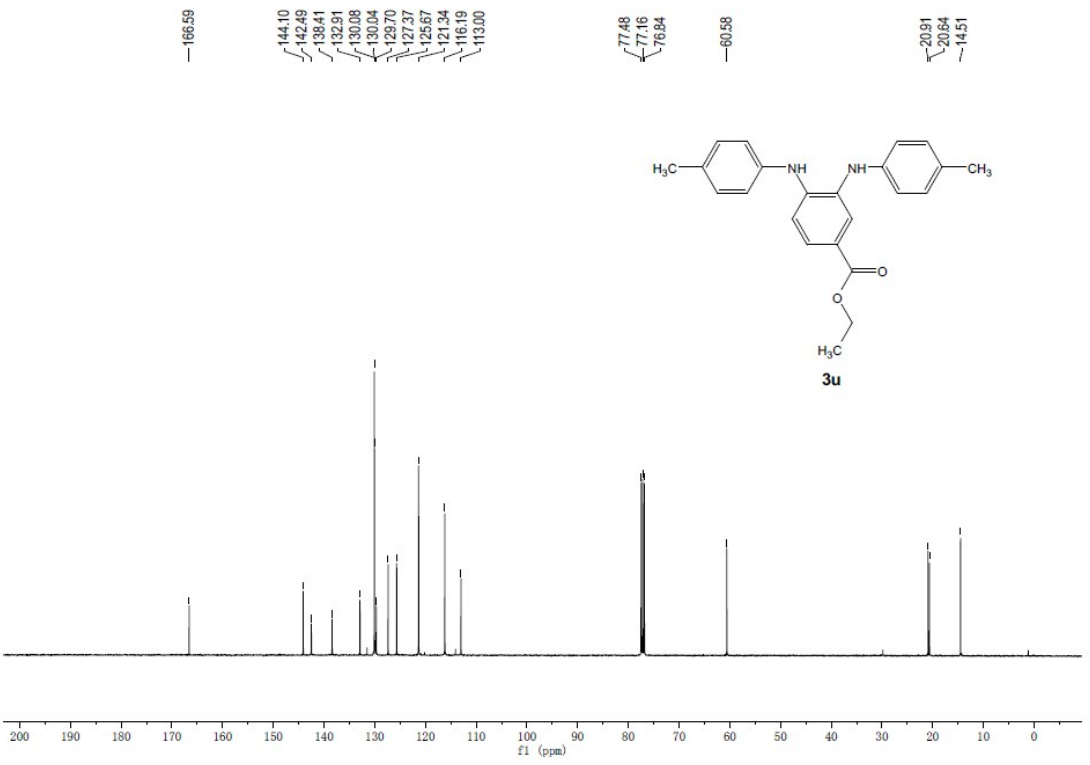
7.84
7.73
7.72
7.70
7.70
7.10
7.02
7.00
6.71
6.69
6.32
5.20
4.31
4.29
4.28
4.26
2.31
2.26
1.34
1.32
1.30
0.99
1.00
1.07
2.08
4.08
2.01
0.97
0.85
2.10
3.07
3.00
3.08
f1 (ppm)
H3C
NH
NH
CH3
O
O
H3C
3u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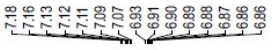
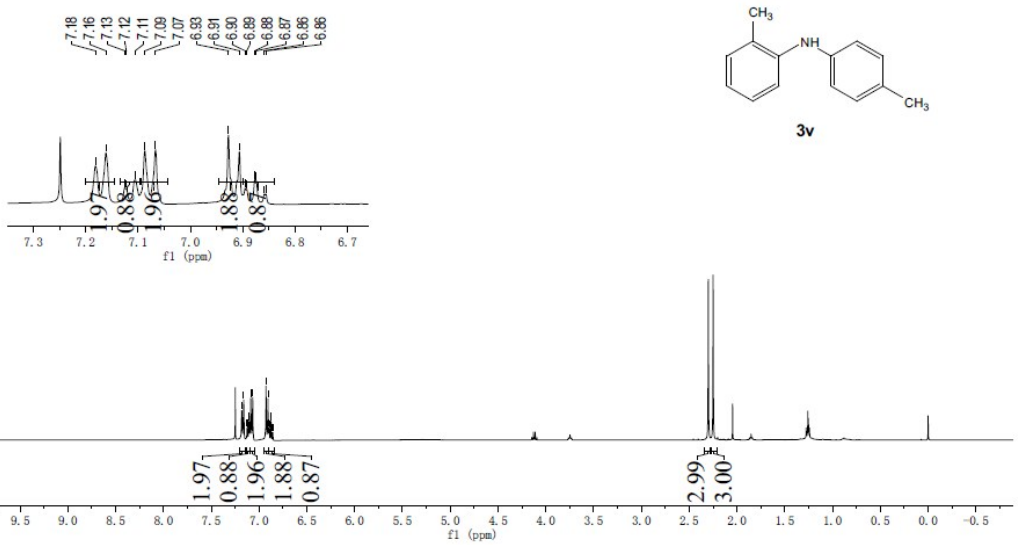
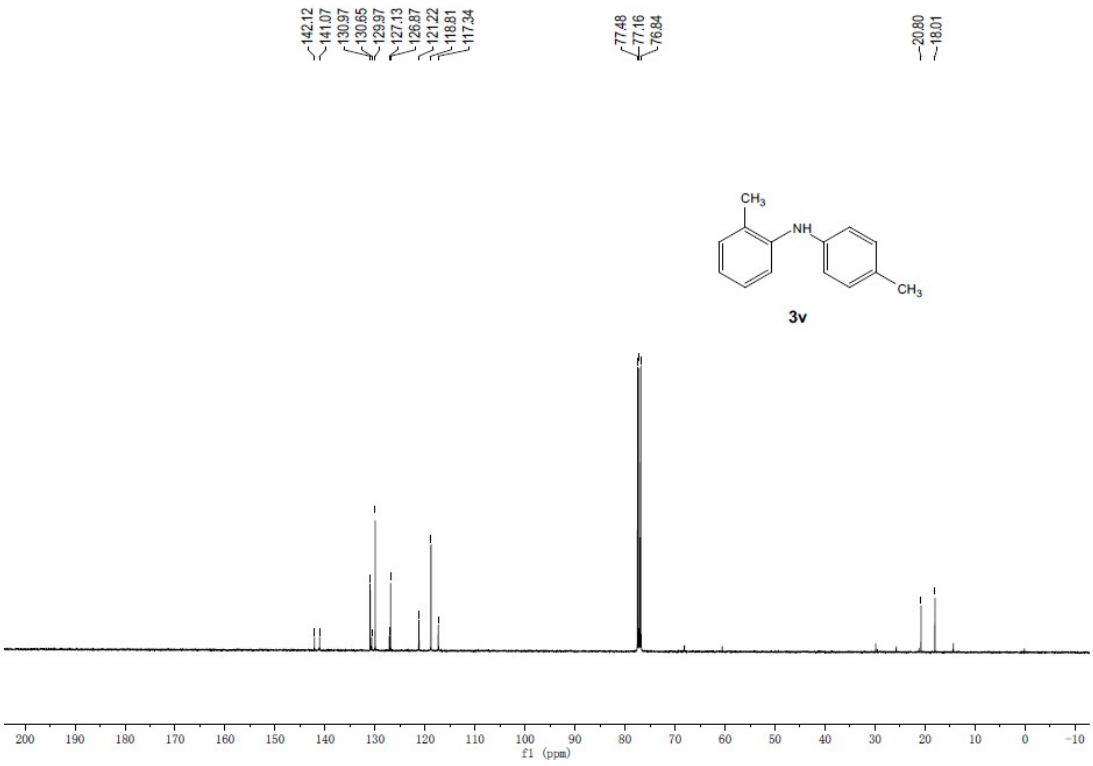
142.49
138.41
132.91
130.08
130.04
129.70
127.37
125.67
121.34
116.19
113.00
77.48
77.16
76.84
60.58
20.91
20.64
14.51
H3C
NH
NH
CH3
O
O
H3C
3u
f1 (ppm)


7.18
7.16
7.13
7.12
7.11
7.09
7.07
6.93
6.91
6.90
6.89
6.88
6.87
6.86
6.86


7.18
7.16
7.13
7.12
7.11
7.09
7.07
6.93
6.91
6.90
6.89
6.88
6.87
6.86
6.86
1.97
0.88
1.96
1.88
0.87
2.99
3.00
f1 (ppm)

CH3
NH
CH3

3v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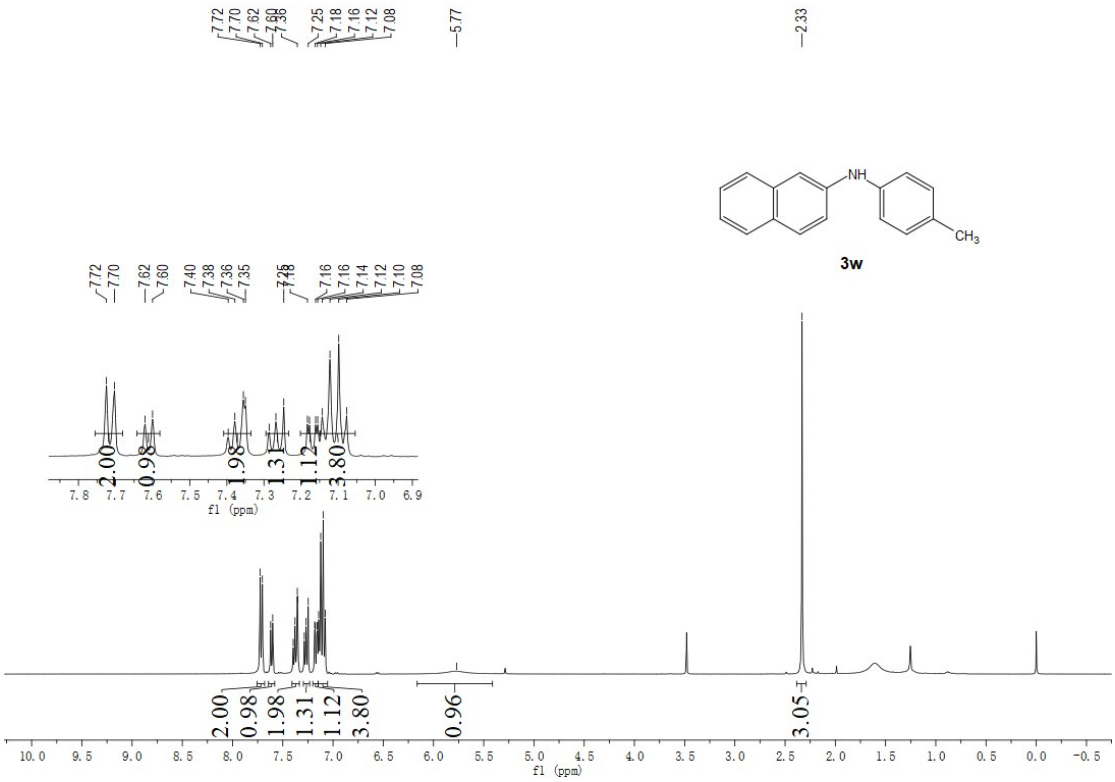
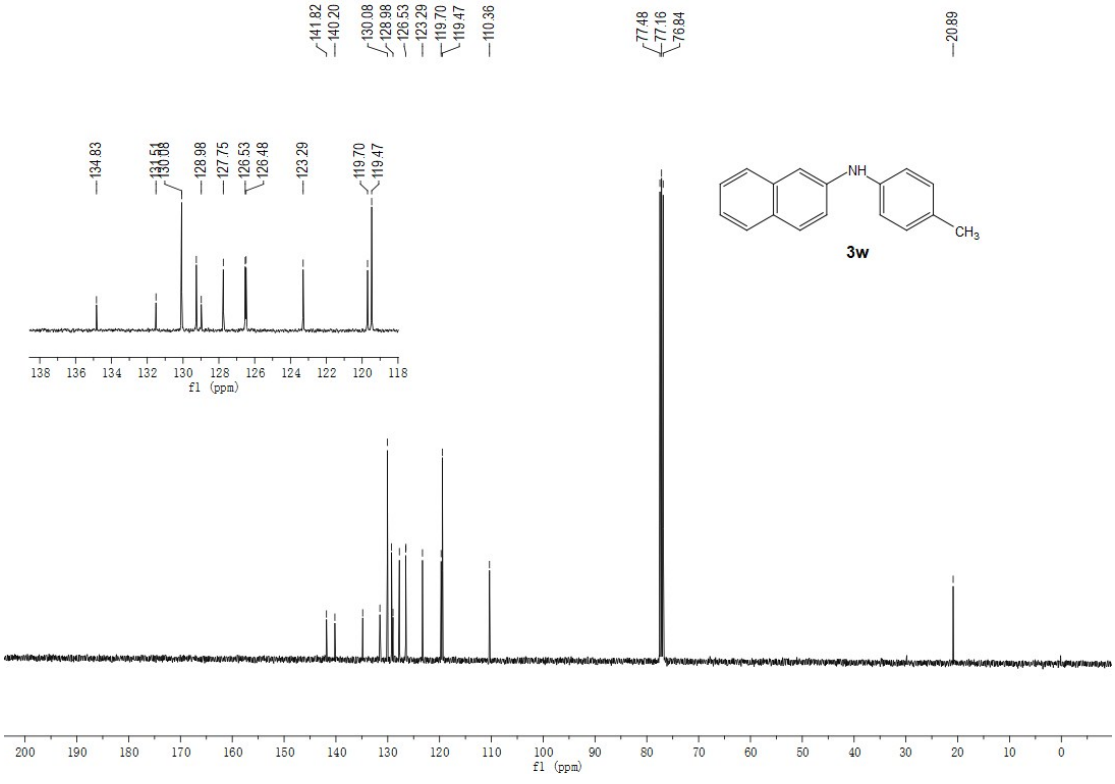
141.07
130.97
130.65
129.97
127.13
126.87
121.22
118.81
117.34
77.48
77.16
76.84
20.80
18.01
f1 (ppm)

CH3
NH
CH3

3v


7.72
7.70
7.62
7.60
7.38
7.36
7.25
7.18
7.16
7.12
7.08
5.77
2.33
NH
CH3
3w
2.00
0.98
1.98
1.31
1.12
3.80
0.96
3.05
f1 (ppm)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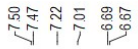
140.20
130.08
128.98
126.53
123.29
119.70
119.47
110.36
77.48
77.16
76.84
20.89
134.83
131.61
130.08
128.98
127.75
126.53
126.48
123.29
119.70
119.47
NH
CH3
3w
f1 (ppm)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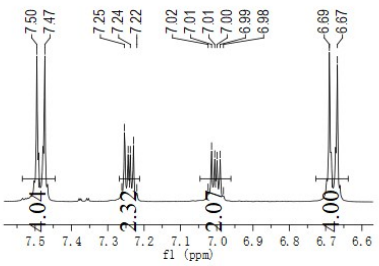
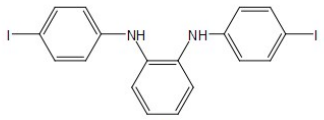
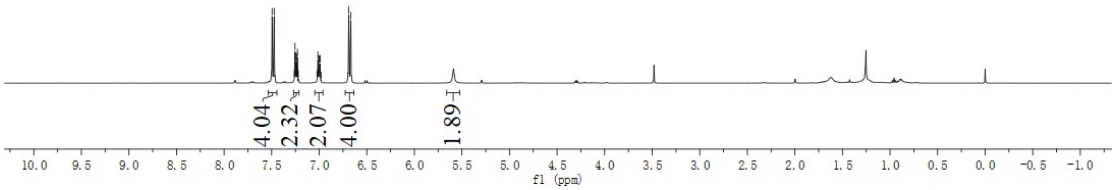
7.47
7.22
7.01
6.69
6.67

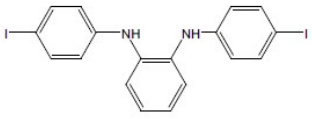

7.50
7.47
7.25
7.24
7.22
7.02
7.01
7.01
7.00
6.99
6.98
6.69
6.67
4.04
2.32
2.07
4.00
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)


I
NH
NH
I

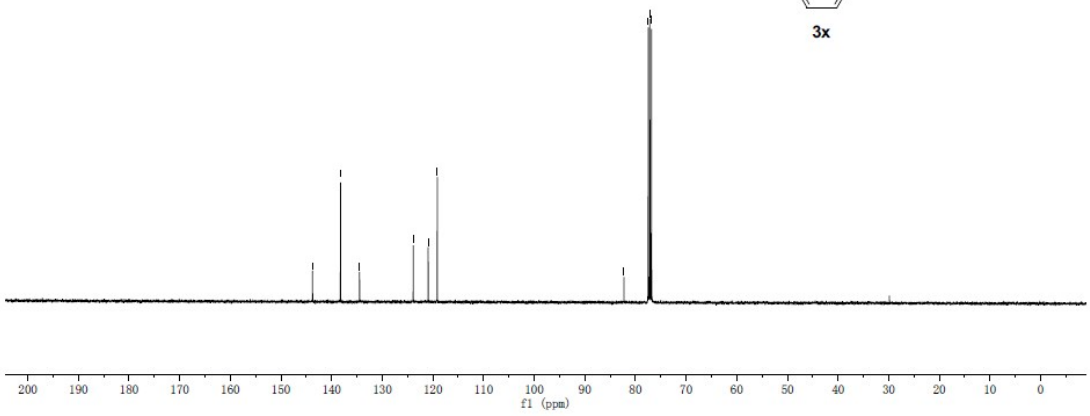
3x


4.04
2.32
2.07
4.00
1.89
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 -0.5 -1.0
f1 (ppm)


143.76
138.24
134.48
123.88
120.93
119.14
82.28
77.48
77.16
76.84


I
NH
NH
I

3x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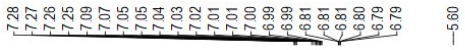
f1 (ppm)


7.28
7.27
7.26
7.25
7.09
7.07
7.05
7.05
7.04
7.03
7.02
7.01
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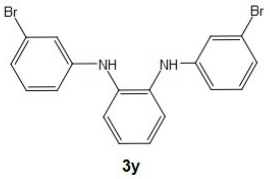
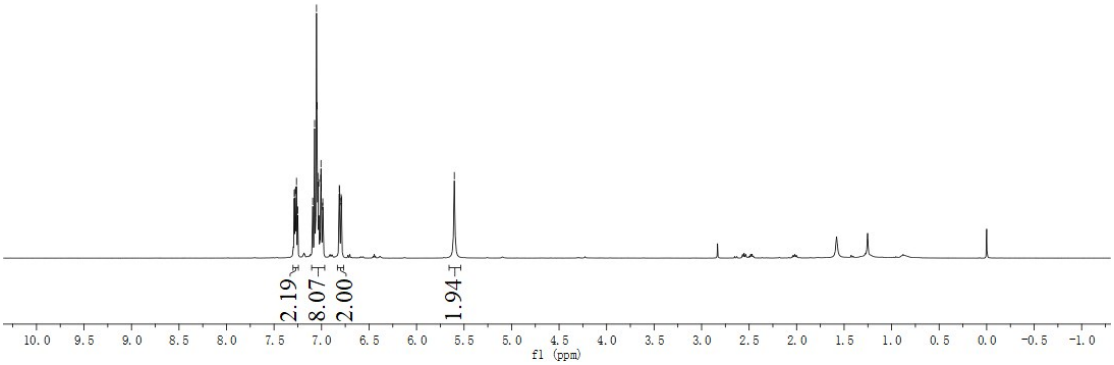
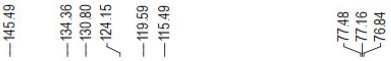
6.81
6.81
6.80
6.79
6.79
5.60


Br
NH
NH
Br

3y


2.19
8.07
2.00
1.94
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 -0.5 -1.0
f1 (ppm)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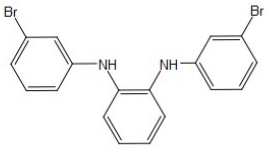
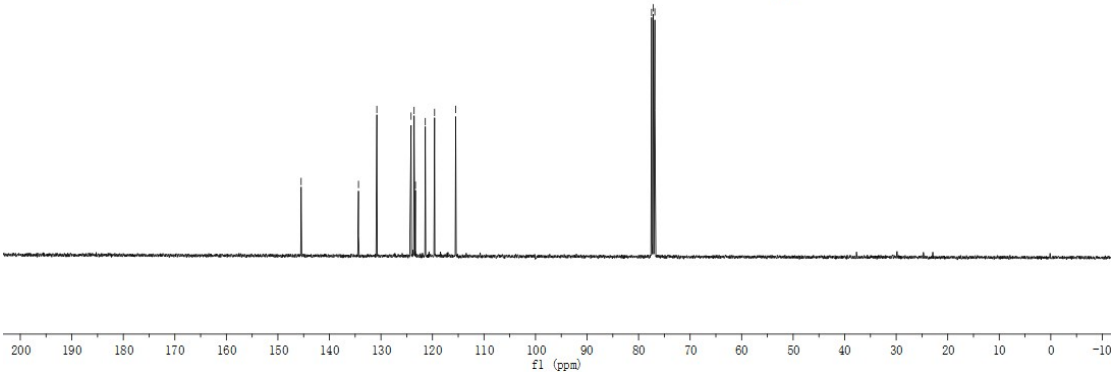
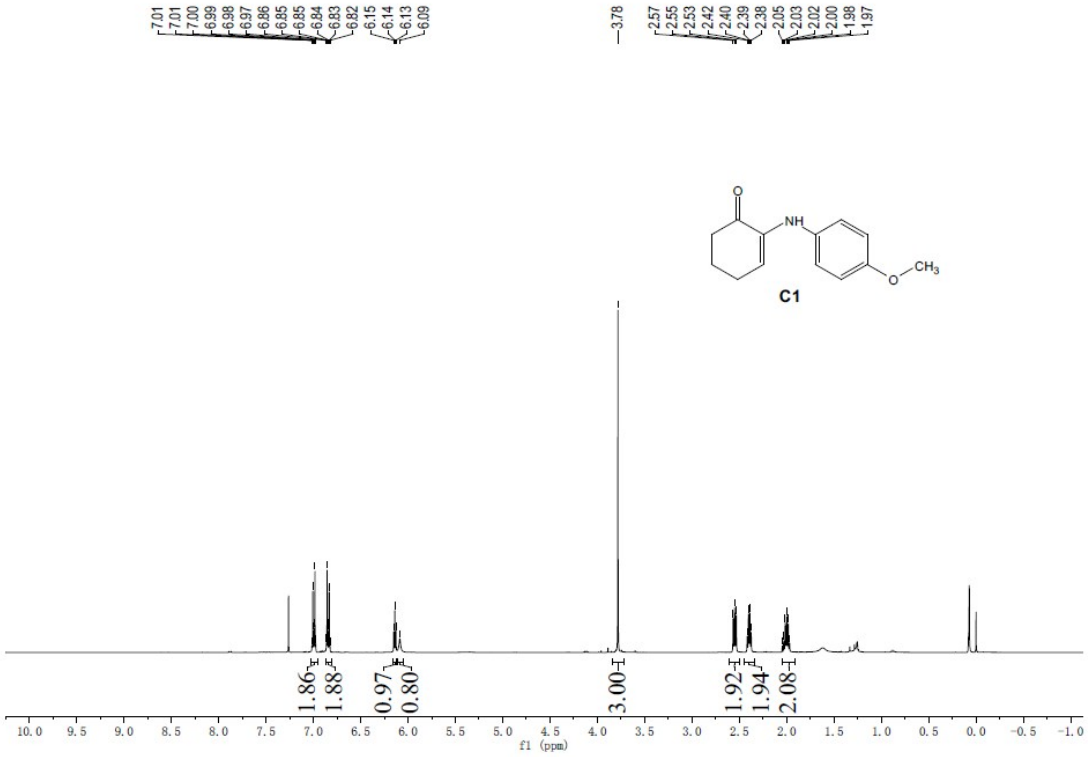
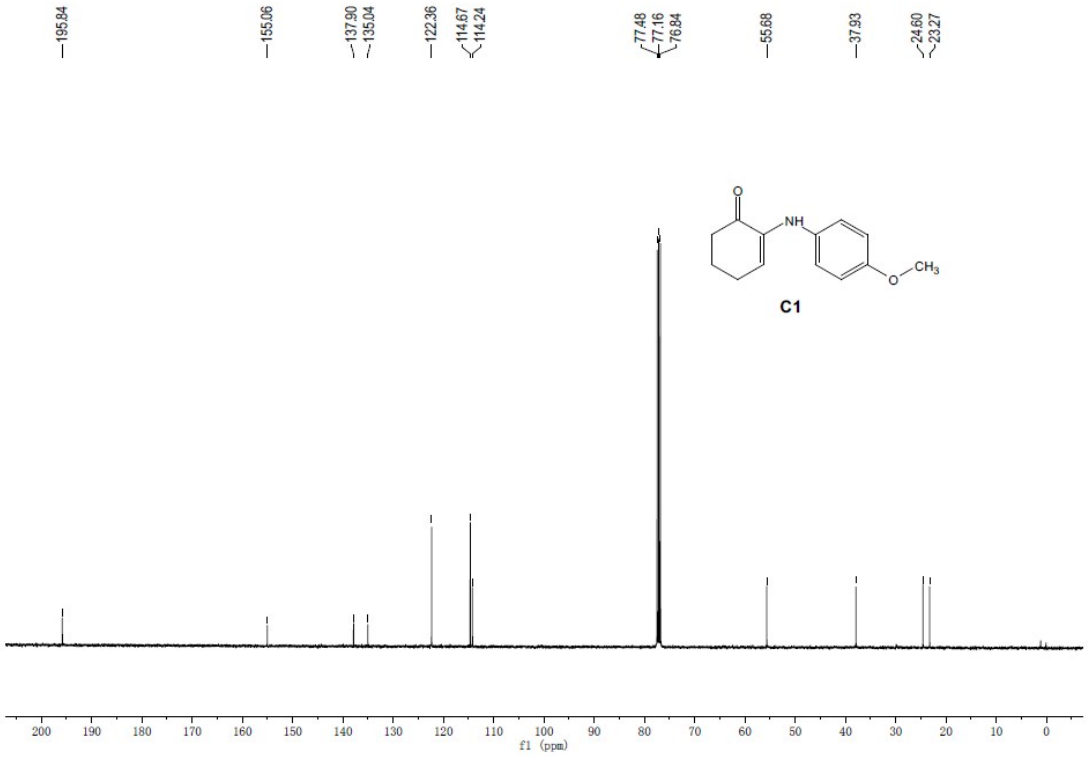
130.80
124.15
119.59
115.49
77.48
77.16
76.84


Br
NH
NH
Br

3y


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


7.01
7.01
7.00
6.99
6.98
6.97
6.86
6.85
6.85
6.84
6.83
6.82
6.15
6.14
6.13
6.09
3.78
2.57
2.55
2.53
2.42
2.40
2.39
2.38
2.05
2.03
2.02
2.00
1.98
1.97
O
NH
O
CH3
C1
1.86
1.88
0.97
0.80
3.00
1.92
1.94
2.08
f1 (ppm)


195.84
155.06
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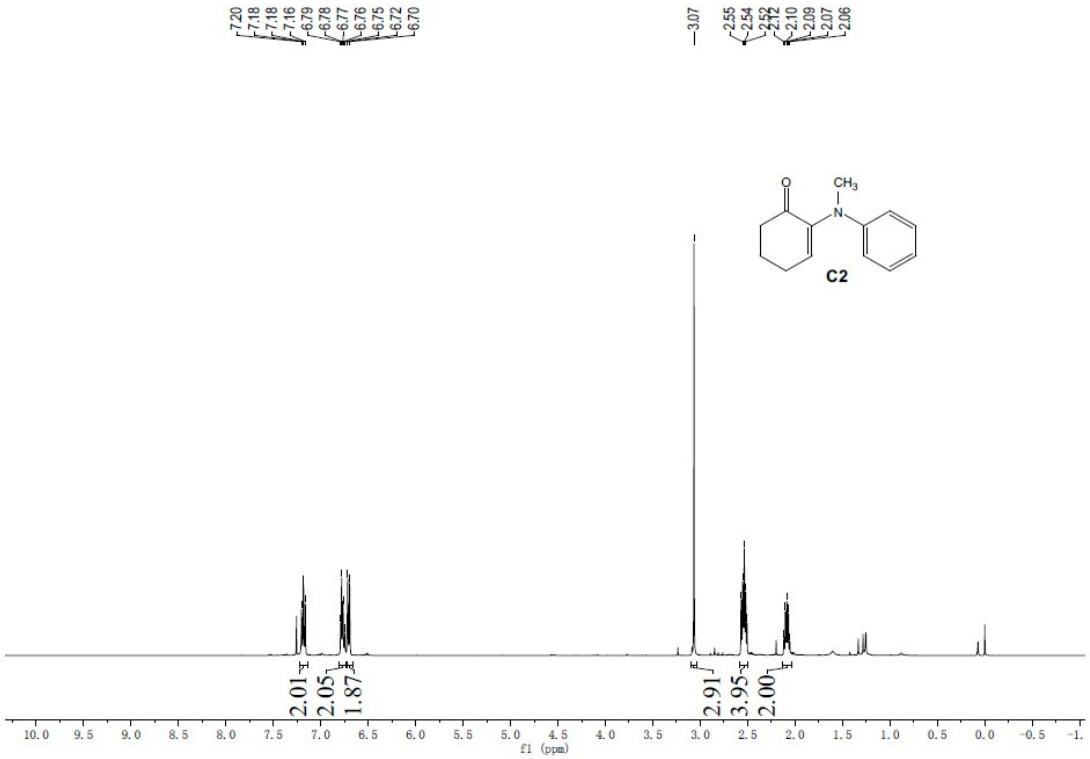
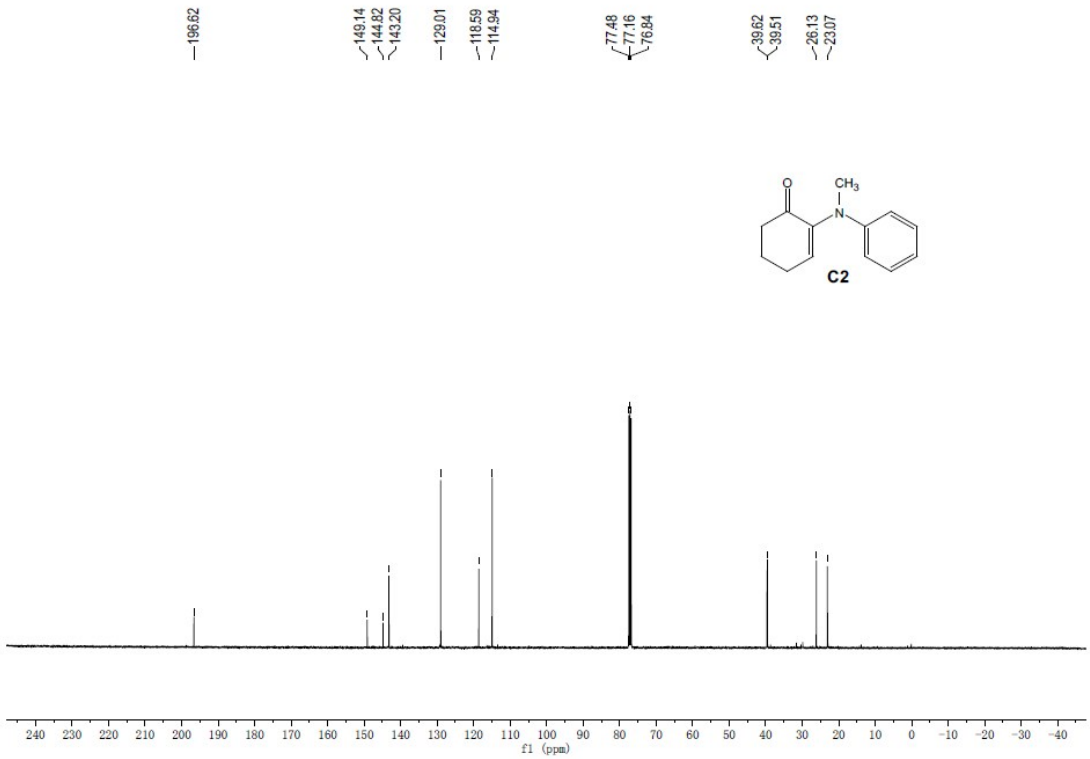
135.04
122.36
114.67
114.24
77.48
77.16
76.84
55.68
37.93
24.60
23.27
O
NH
O
CH3
C1
f1 (ppm)


7.20
7.18
7.18
7.16
6.79
6.78
6.77
6.76
6.75
6.72
6.70
3.07
2.55
2.54
2.52
2.12
2.10
2.09
2.07
2.06
O
CH3
N
C2
2.01
2.05
1.87
2.91
3.95
2.00
f1 (ppm)


196.62
149.14
144.82
143.20
129.01
118.59
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77.48
77.16
76.84
39.62
39.51
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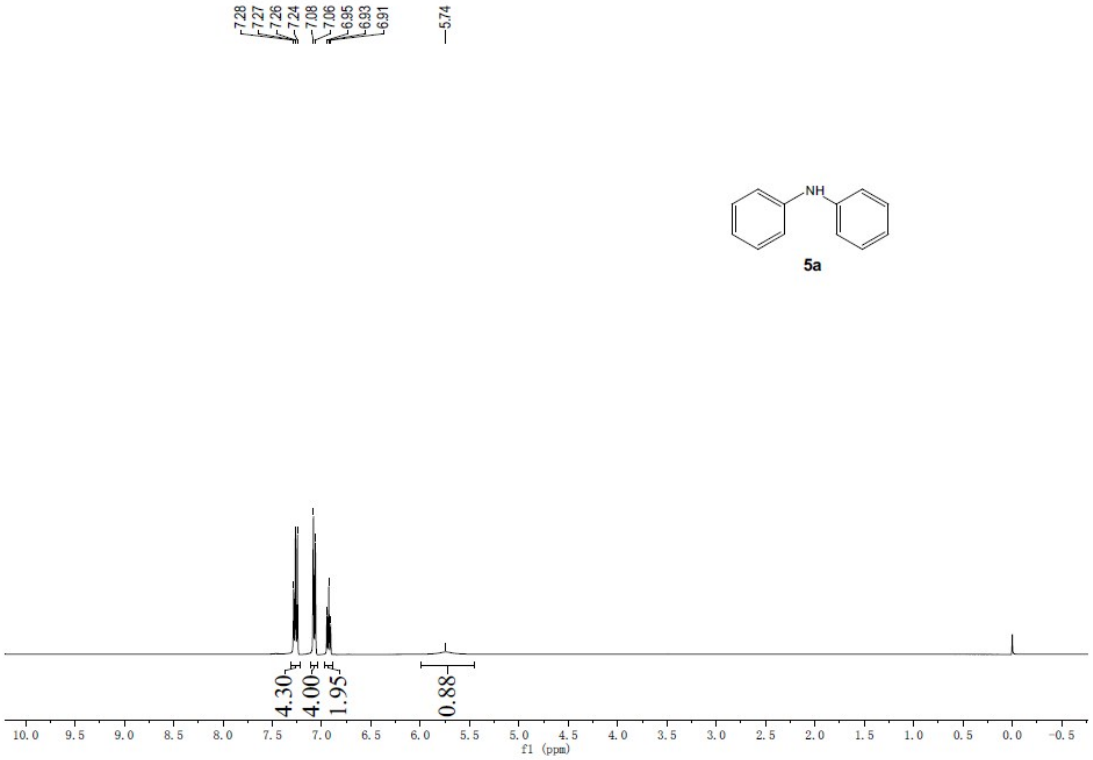
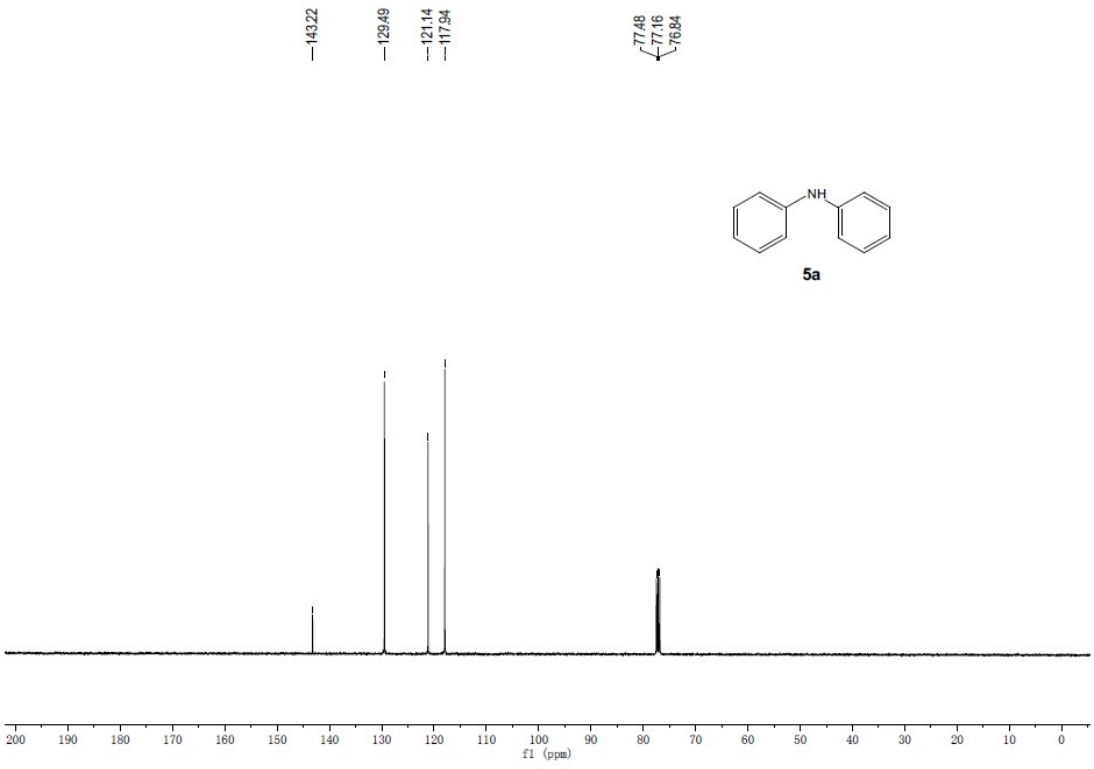
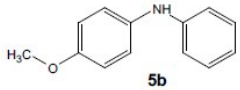
23.07
O
CH3
N
C2
f1 (ppm)


7.28
7.27
7.26
7.24
7.08
7.06
6.95
6.93
6.91
5.74
NH
5a
4.30
4.00
1.95
0.88
f1 (ppm)

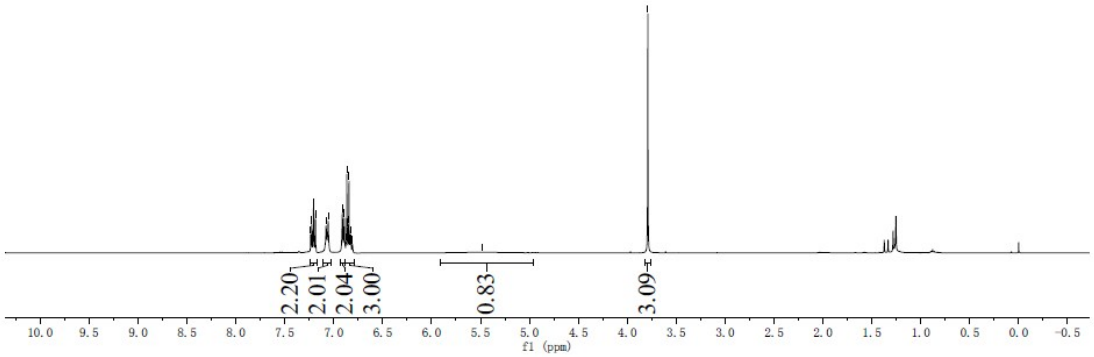

143.22
129.49
121.14
117.94
77.48
77.16
76.84
NH
5a
f1 (ppm)

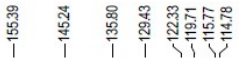

7.24
7.23
7.22
7.21
7.20
7.19
7.08
7.06
6.91
6.89
6.87
6.87
6.86
6.85
6.84
6.83
6.83
6.81
5.48


3.79


NH
H3C
O

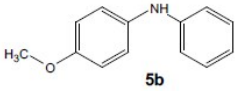
5b


2.20
2.01
2.04
3.00
0.83
3.09
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 -0.5
f1 (ppm)

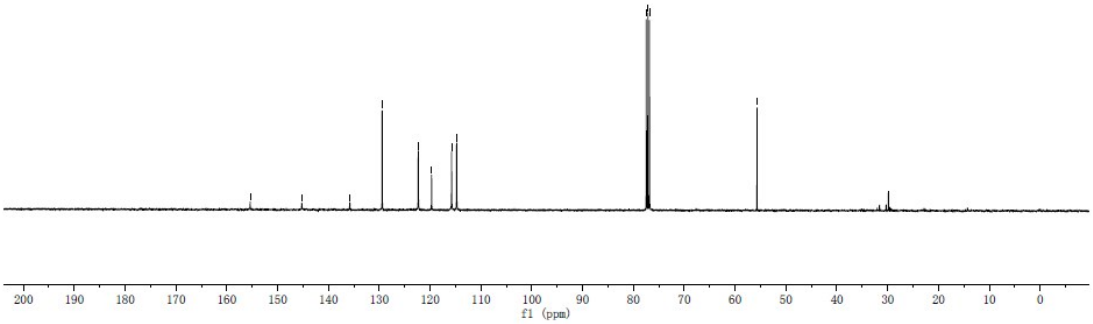

155.39
145.24
135.80
129.43
122.33
119.71
115.77
114.78

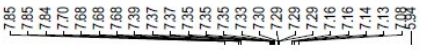

77.48
77.16
76.84

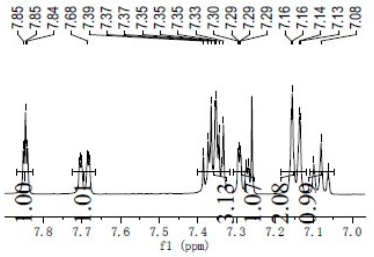
55.70

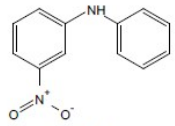

NH
H3C
O

5b

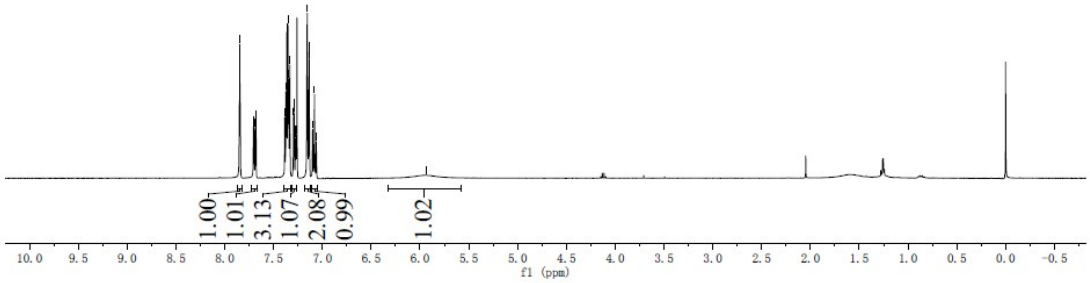

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

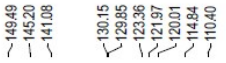


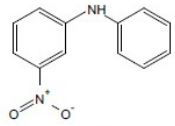




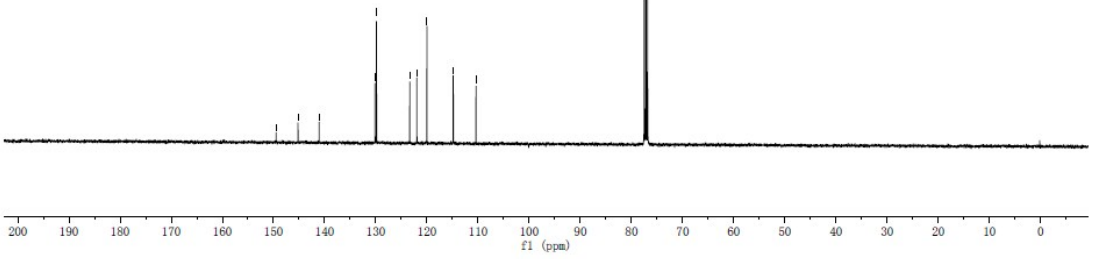
5c

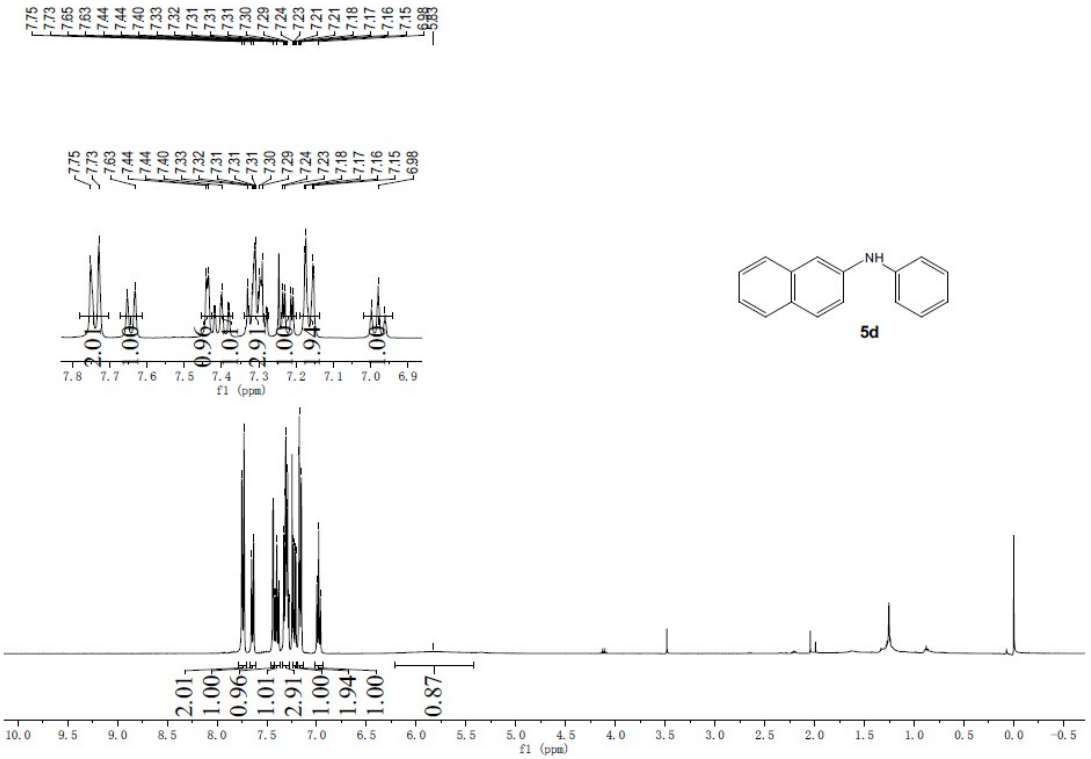


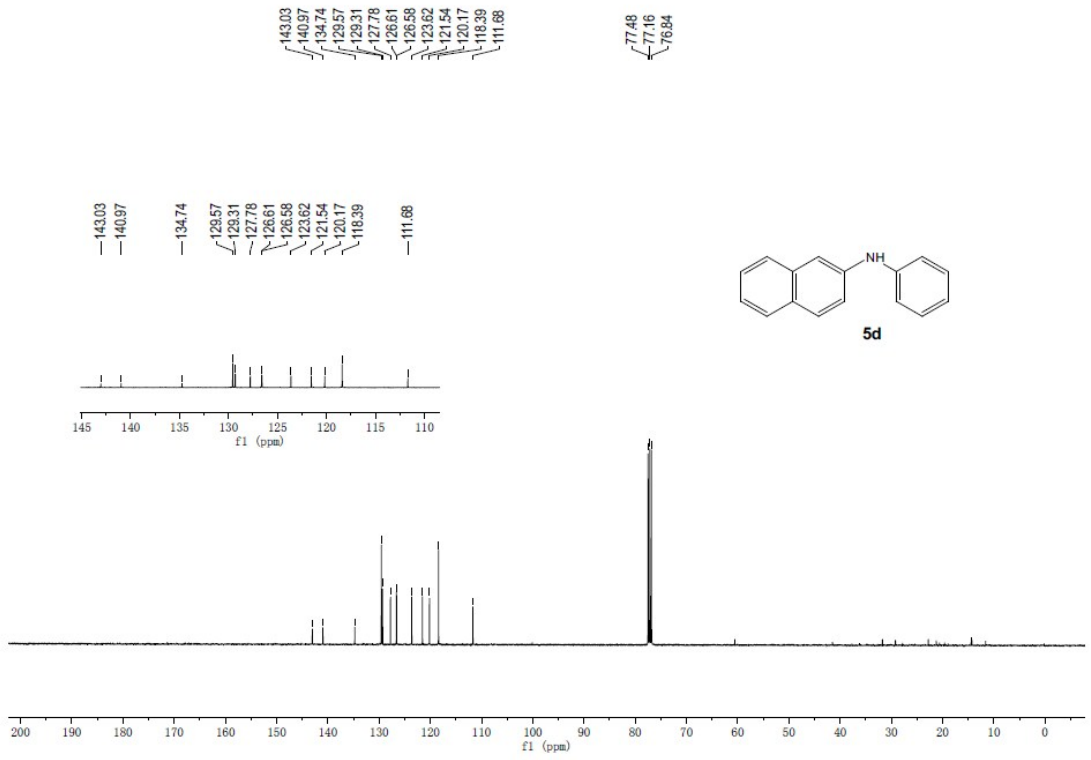


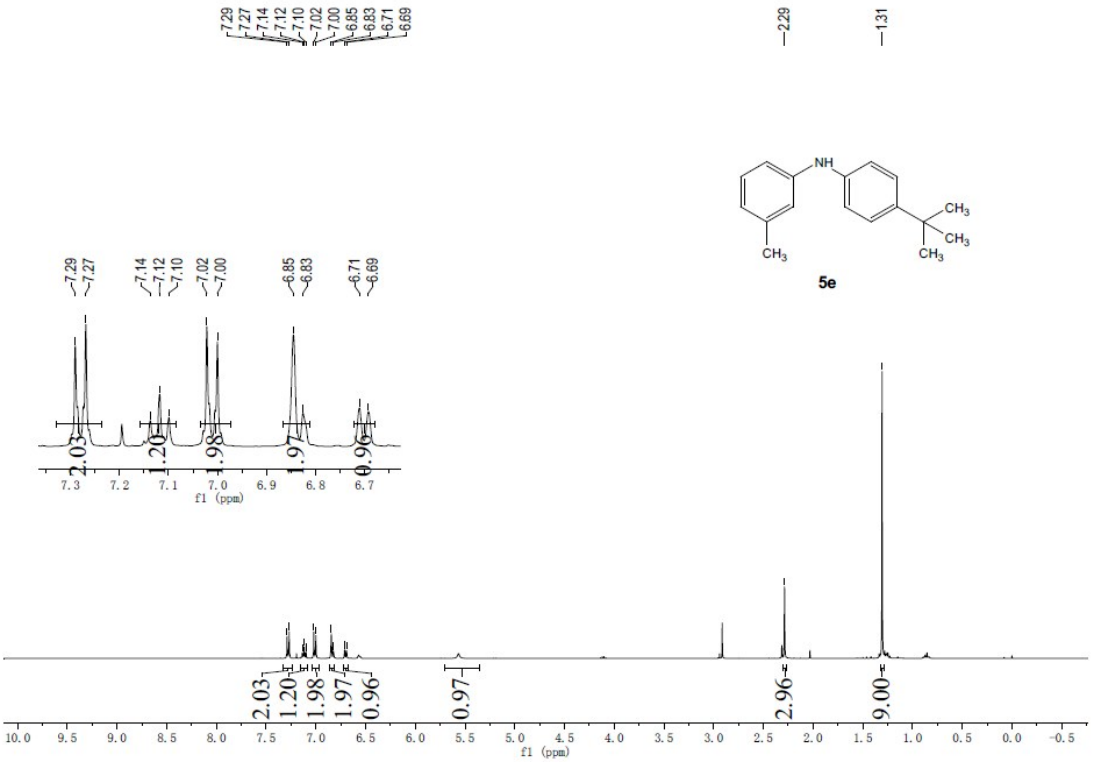


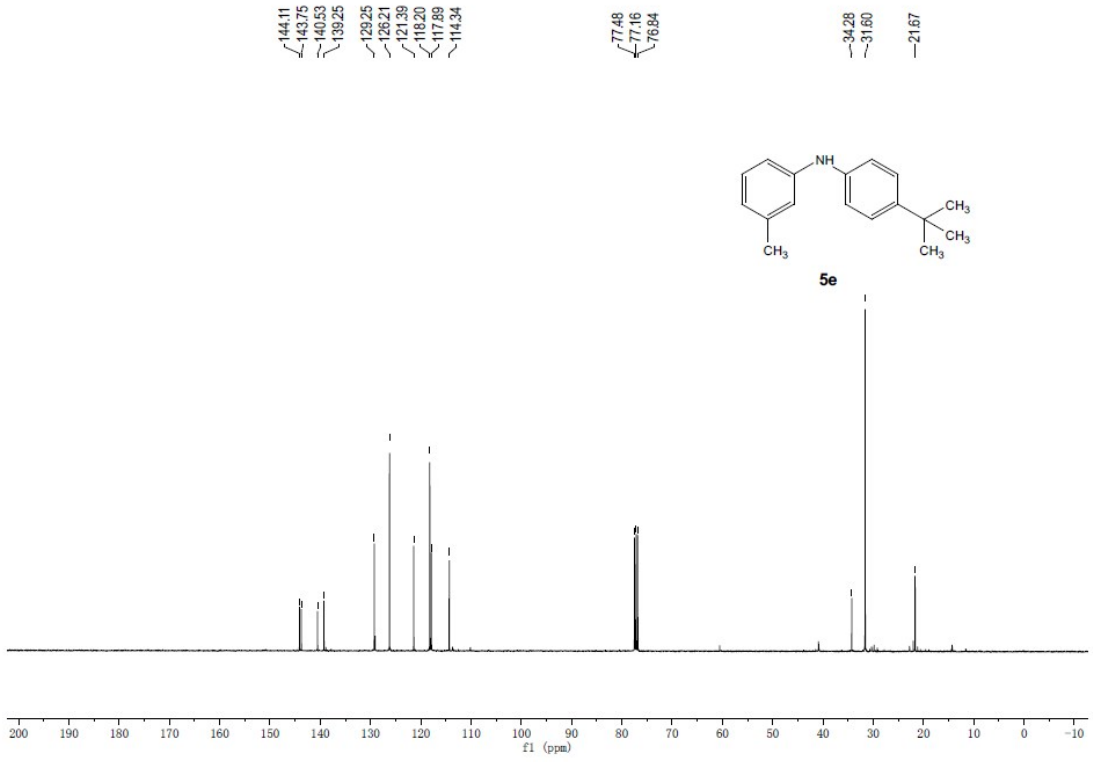
5c




7.75
7.73
7.65
7.63
7.44
7.44
7.40
7.33
7.32
7.31
7.31
7.31
7.30
7.29
7.24
7.23
7.21
7.21
7.18
7.17
7.16
7.15
6.98
2.01
1.00
0.96
1.01
2.91
1.00
1.94
1.00
0.87
f1 (ppm)
NH
5d


143.03
140.97
134.74
129.57
129.31
127.78
126.61
126.58
123.62
121.54
120.17
118.39
111.68
77.48
77.16
76.84
f1 (ppm)
NH
5d


7.29
7.27
7.14
7.12
7.10
7.02
7.00
6.85
6.83
6.71
6.69
2.29
1.31
NH
CH3
CH3
CH3
CH3
5e
2.03
1.20
1.98
1.97
0.96
0.97
2.96
9.00
f1 (ppm)


144.11
143.75
140.53
139.25
129.25
126.21
121.39
118.20
117.89
114.34
77.48
77.16
76.84
34.28
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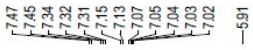
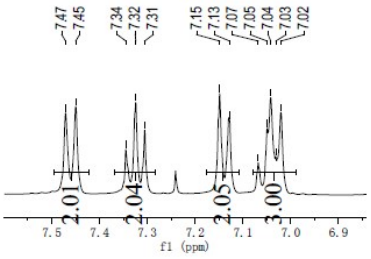
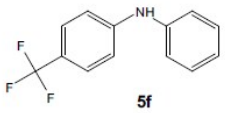
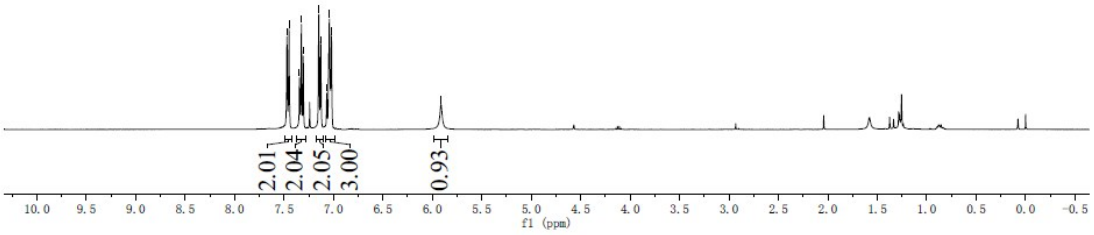
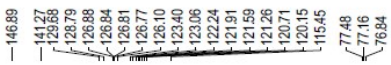
21.67
NH
CH3
CH3
CH3
CH3
5e
f1 (ppm)

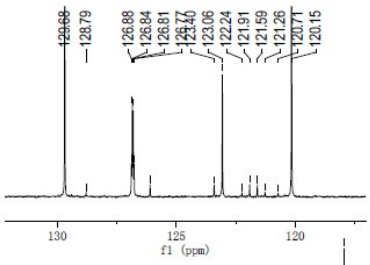

7.47
7.45
7.34
7.32
7.31
7.15
7.13
7.07
7.05
7.04
7.03
7.02
5.91

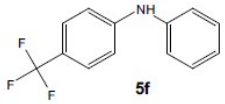

7.47
7.45
7.34
7.32
7.31
7.15
7.13
7.07
7.05
7.04
7.03
7.02
2.01
2.04
2.05
3.00
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)

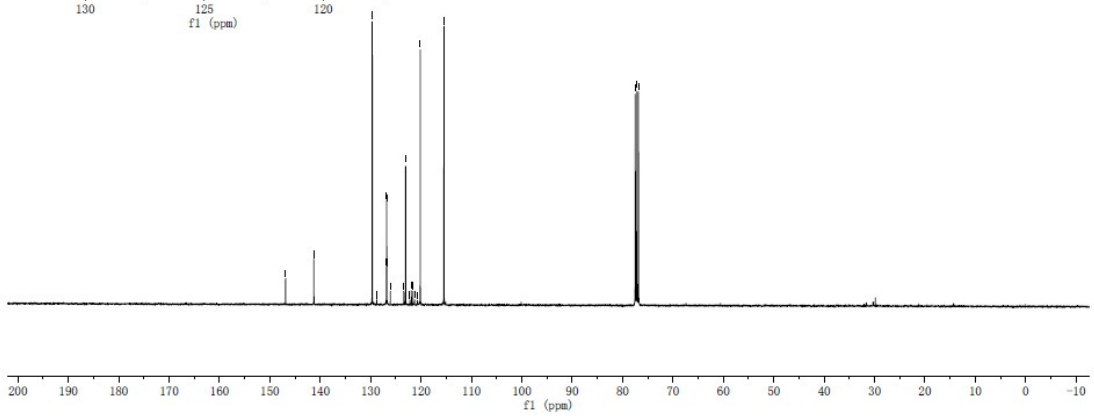

NH
F
F
F
5f

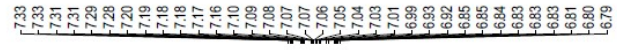

2.01
2.04
2.05
3.00
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

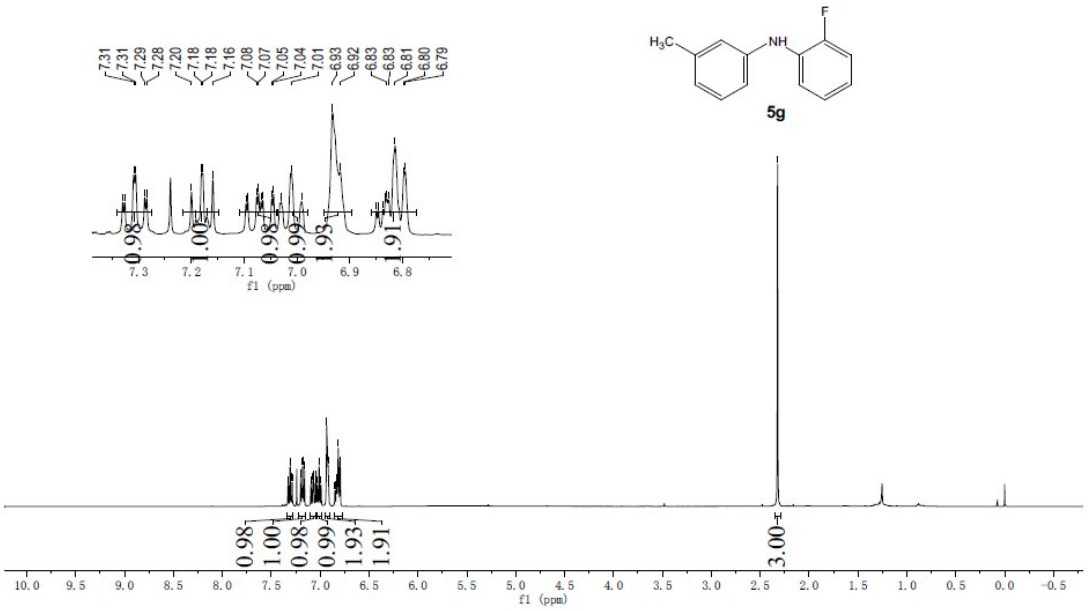

146.89
141.27
129.88
128.79
126.88
126.84
126.81
126.77
126.10
123.40
123.06
122.24
121.91
121.59
121.26
120.71
120.15
115.45
77.48
77.16
76.84

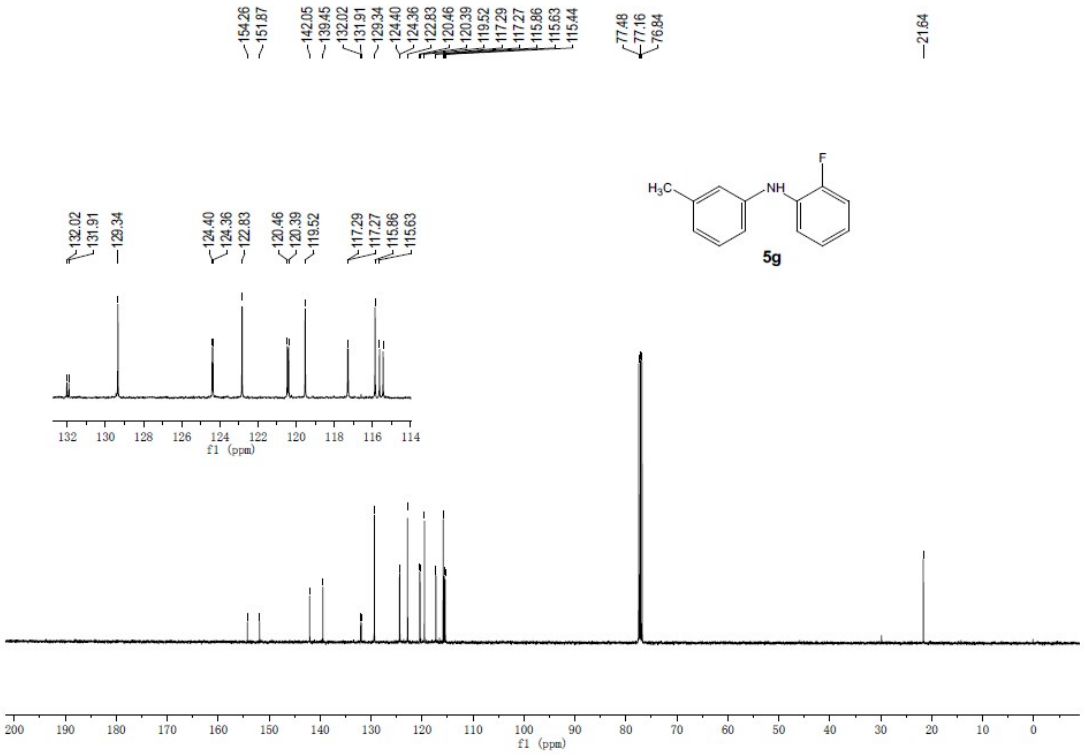

128.88
128.79
126.88
126.84
126.81
126.77
123.40
123.06
122.24
121.91
121.59
121.26
120.71
120.15
130
125
120
f1 (ppm)

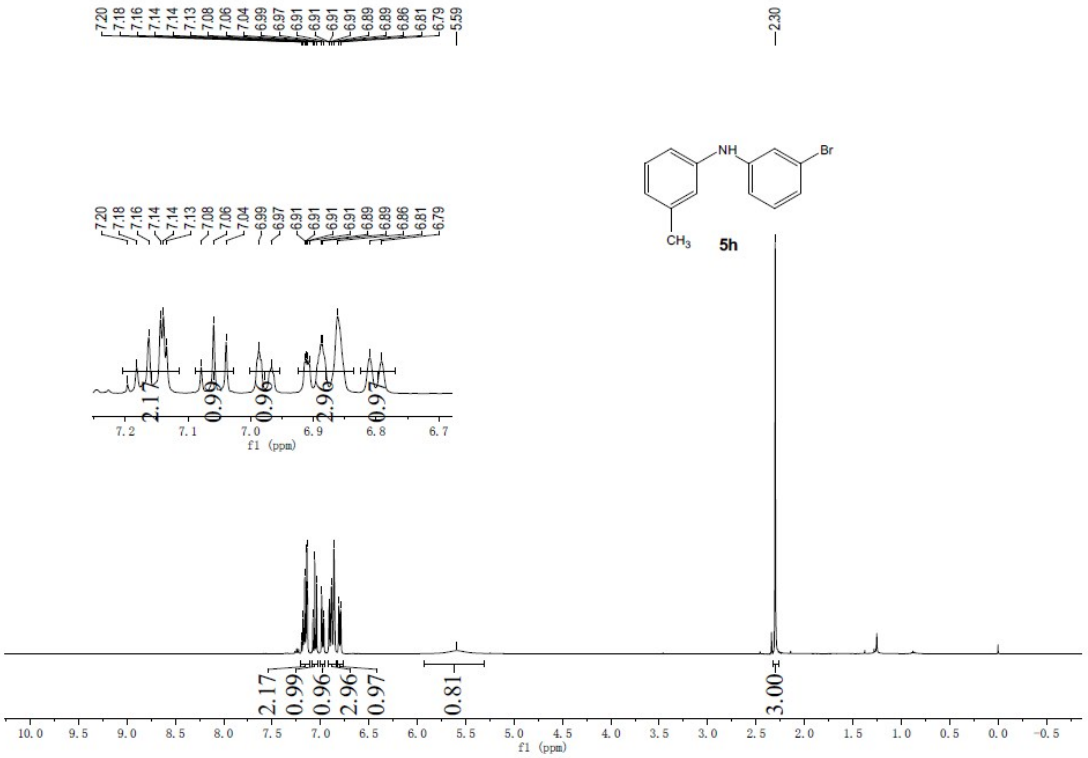

NH
F
F
F
5f


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


7.33
7.33
7.31
7.31
7.29
7.28
7.20
7.19
7.18
7.18
7.17
7.16
7.10
7.09
7.08
7.07
7.07
7.06
7.05
7.04
7.03
7.01
6.99
6.93
6.92
6.85
6.84
6.83
6.83
6.81
6.80
6.79
2.32


7.31
7.31
7.29
7.28
7.20
7.18
7.18
7.16
7.08
7.07
7.05
7.04
7.01
6.93
6.92
6.83
6.83
6.81
6.80
6.79
0.98
1.00
0.98
0.99
1.93
1.91
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
H3C
NH
F
5g
0.98
1.00
0.98
0.99
1.93
1.91
3.00
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
-0.5
f1 (ppm)


154.26
151.87
142.05
139.45
132.02
131.91
129.34
124.40
124.36
122.83
120.46
120.39
119.52
117.29
117.27
115.86
115.63
115.44
77.48
77.16
76.84
21.64
132.02
131.91
129.34
124.40
124.36
122.83
120.46
120.39
119.52
117.29
117.27
115.86
115.63
132
130
128
126
124
122
120
118
116
114
f1 (ppm)
H3C
NH
F
5g
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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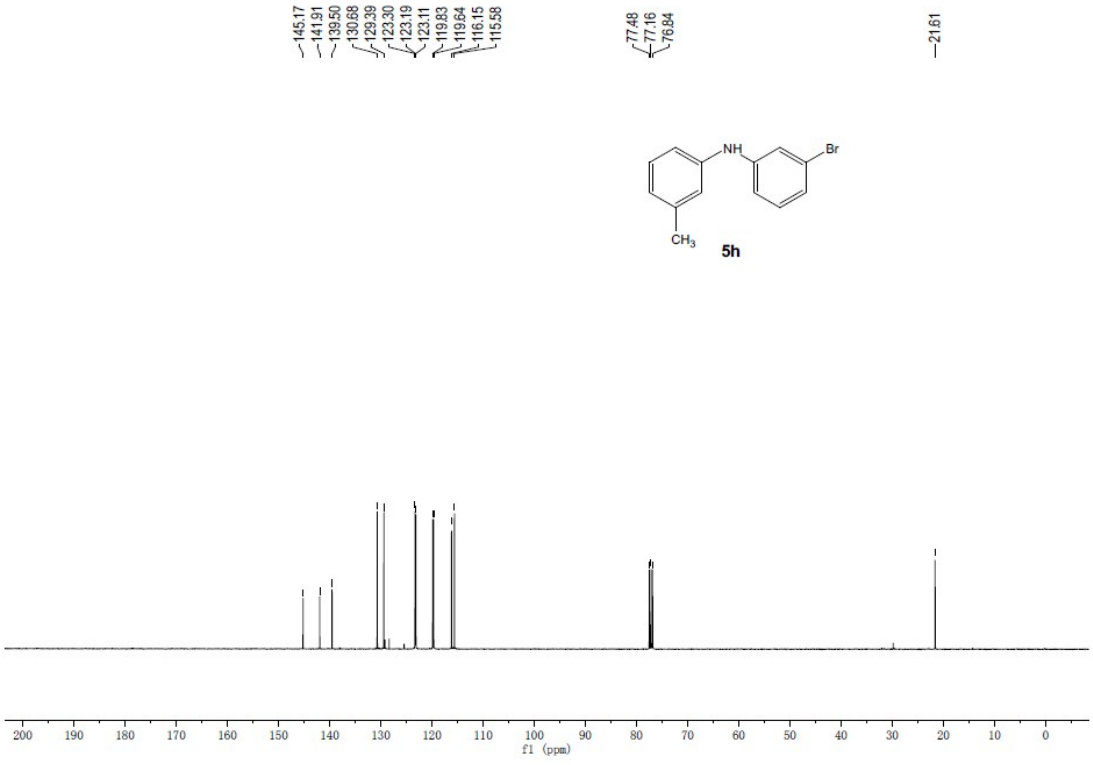
7.18
7.16
7.14
7.14
7.13
7.08
7.06
7.04
6.99
6.97
6.91
6.91
6.91
6.91
6.89
6.89
6.86
6.81
6.79
5.59
2.30
NH
Br
CH3
5h
2.17
0.99
0.96
2.96
0.97
0.81
3.00
f1 (ppm)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141.91
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130.68
129.39
123.30
123.19
123.11
119.83
119.64
116.15
115.58
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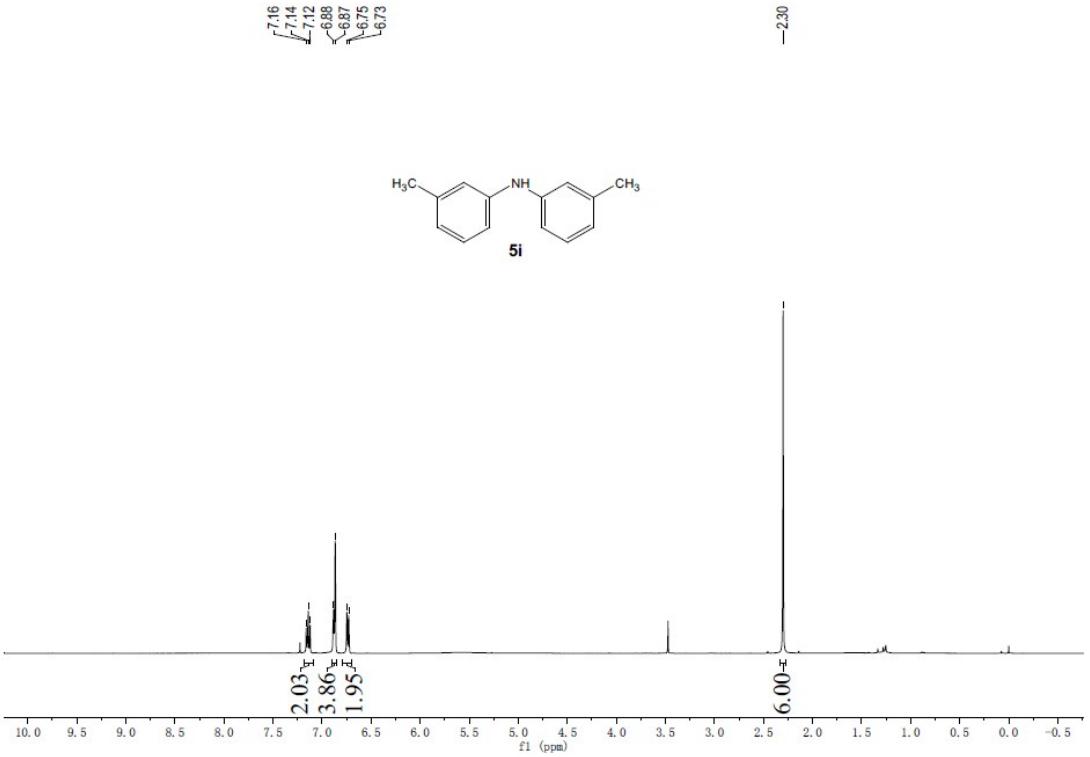
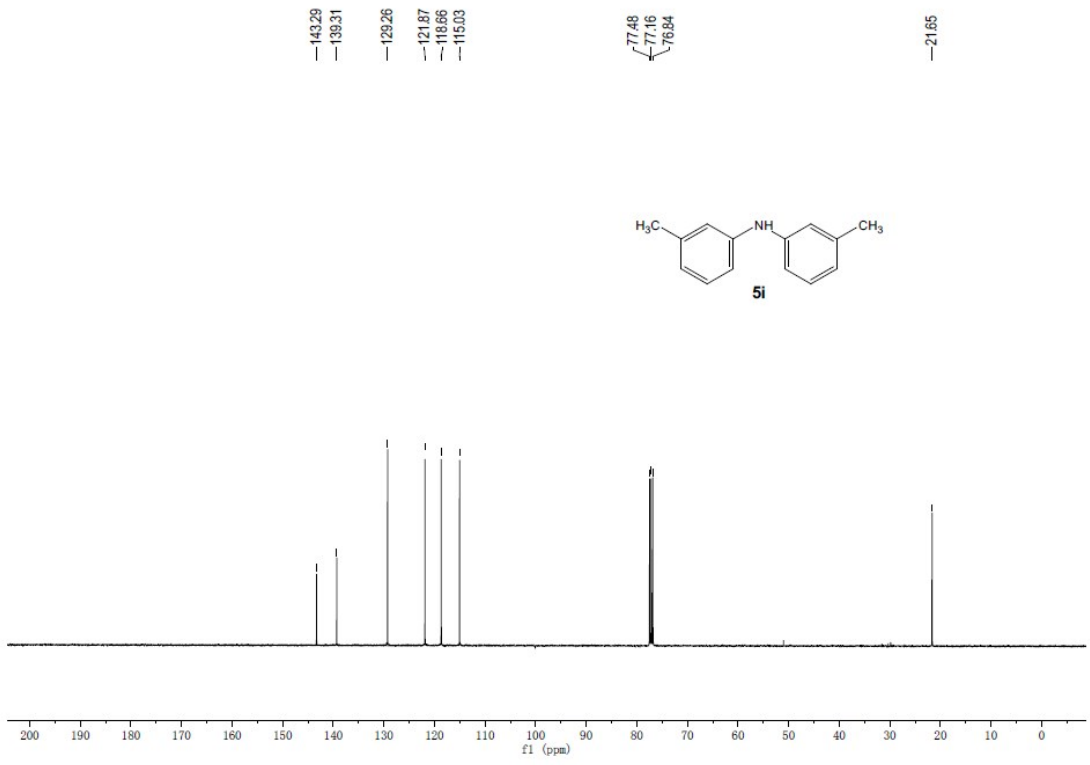
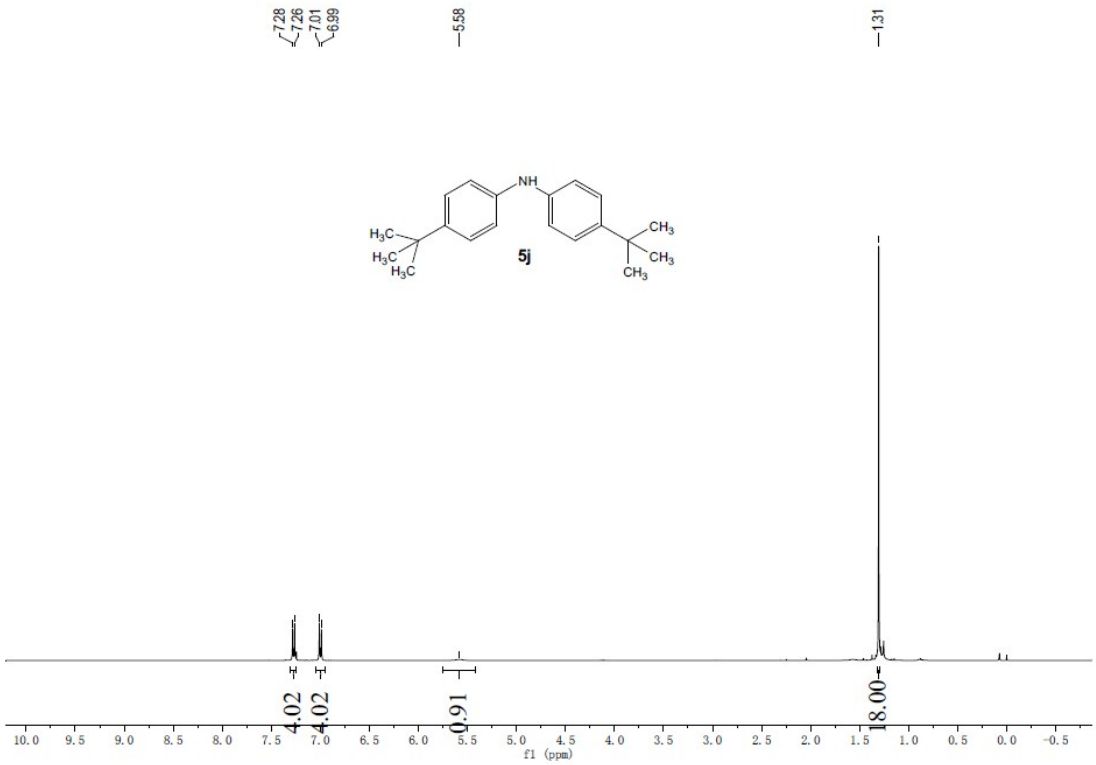
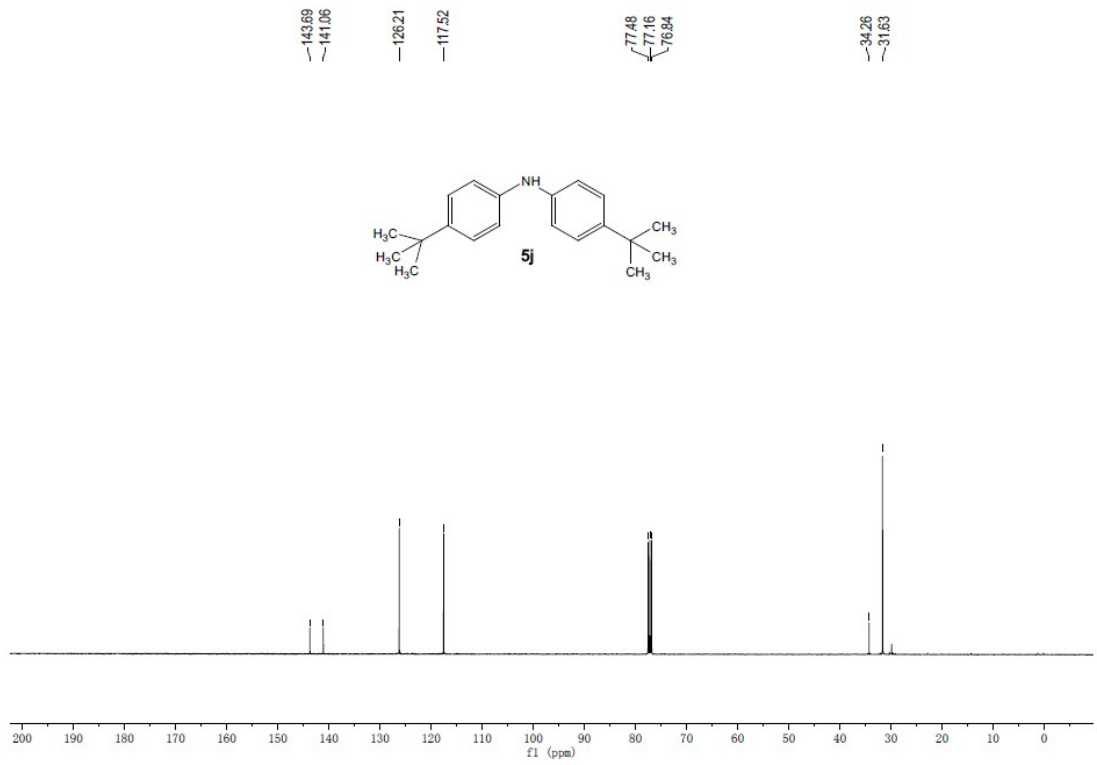
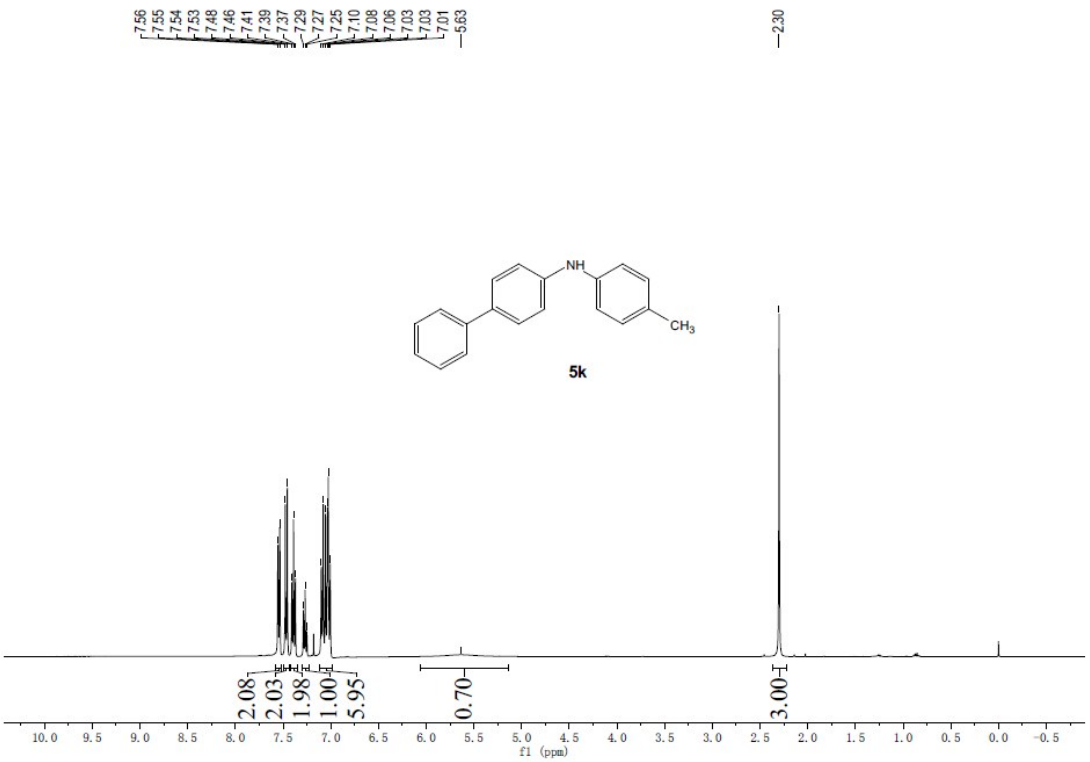
76.84
21.61
NH
Br
CH3
5h
f1 (ppm)

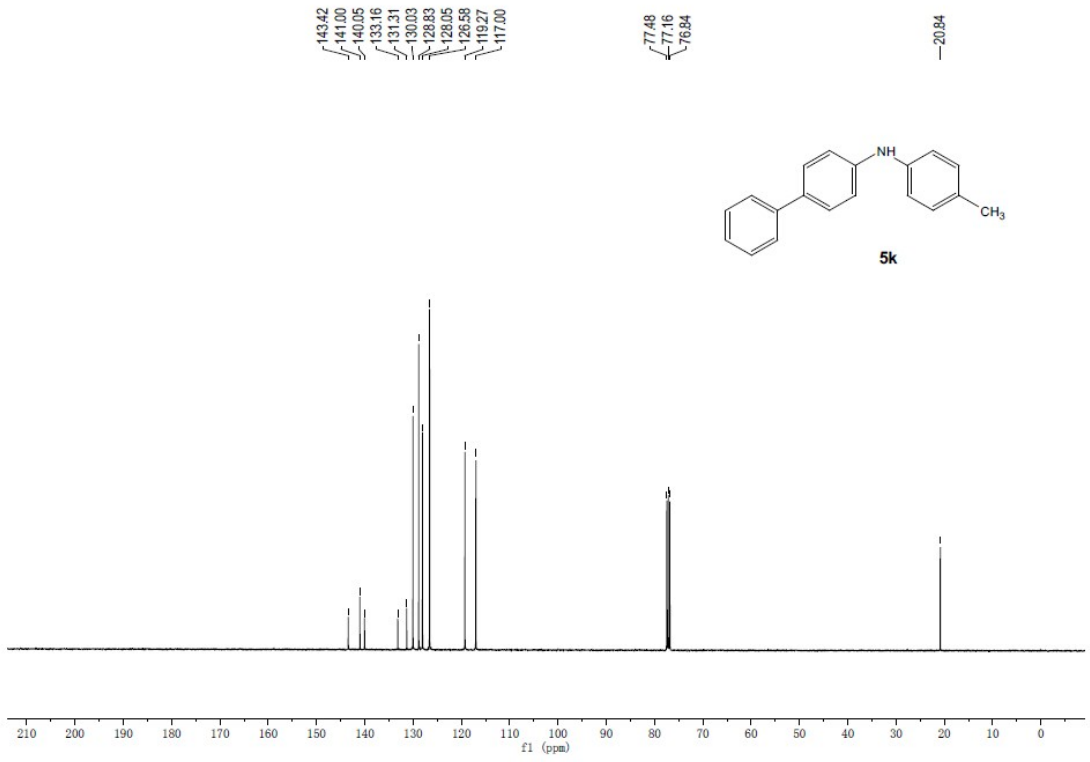

7.16
7.14
7.12
6.88
6.87
6.75
6.73
2.30
H3C
NH
CH3
5i
2.03
3.86
1.95
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.29
139.31
129.26
121.87
118.66
115.03
77.48
77.16
76.84
21.65
H3C
NH
CH3
5i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.28
7.26
7.01
6.99
5.58
1.31
NH
H3C
H3C
H3C
CH3
CH3
CH3
5j
4.02
4.02
0.91
18.00
f1 (ppm)


143.69
141.06
126.21
117.52
77.48
77.16
76.84
34.26
31.63
NH
H3C
H3C
H3C
CH3
CH3
CH3
5j
f1 (ppm)


7.56
7.55
7.54
7.53
7.48
7.46
7.41
7.39
7.37
7.29
7.27
7.25
7.10
7.08
7.06
7.03
7.03
7.01
5.63
2.30
NH
CH3
5k
2.08
2.03
1.98
1.00
5.95
0.70
3.00
f1 (ppm)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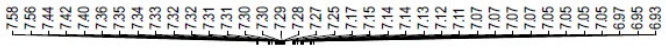
131.31
130.03
128.83
128.05
126.58
119.27
117.00
77.48
77.16
76.84
20.84
NH
CH3
5k
f1 (ppm)


7.58
7.56
7.44
7.42
7.40
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.25
7.17
7.15
7.14
7.14
7.13
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7.07
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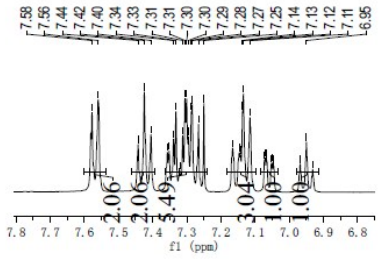
7.05
7.05
7.05
6.97
6.95
6.93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7.31
7.31
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7.28
7.27
7.25
7.14
7.13
7.12
7.11
6.95
2.06
2.06
3.49
3.04
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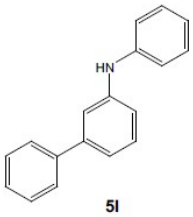
1.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)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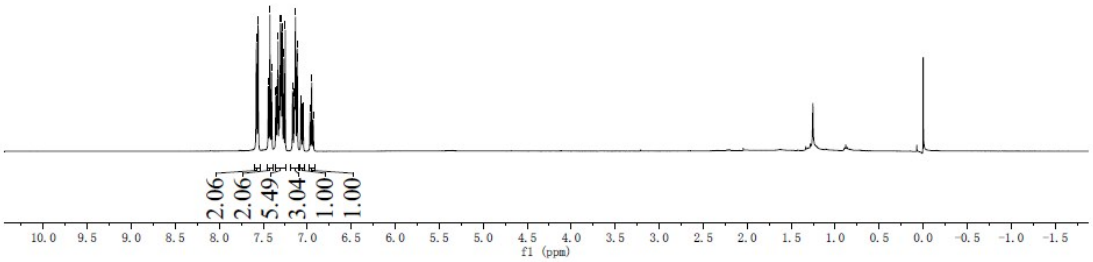
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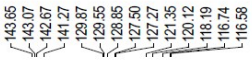
2.06
5.49
3.04
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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143.07
142.67
141.27
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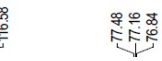
129.55
128.85
127.50
127.27
121.35
120.12
118.19
116.74
116.58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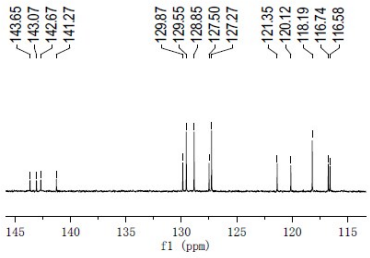
143.65
143.07
142.67
141.27
129.87
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127.50
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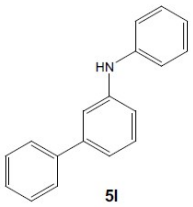
121.35
120.12
118.19
116.74
116.58
145 140 135 130 125 120 115
f1 (ppm)


HN
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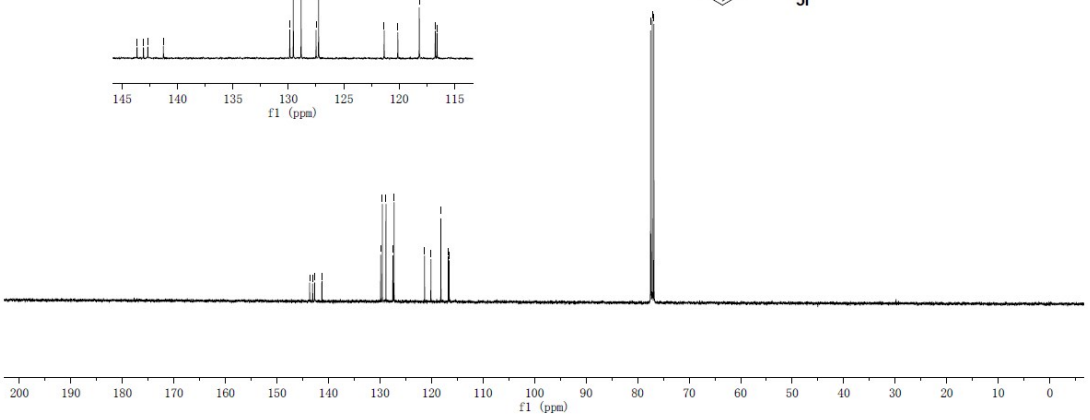
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f1 (ppm)