Selective Kumada Biaryl Cross-Coupling Reaction Enabled by an Iron(III) Alkoxide/*N*-heterocyclic Carbene Catalyst System

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Supporting Information

Contents

General information. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF was dried over alumina under N_2 using a Grubbs-type solvent purification system. *p*-tolylmagnesium bromide in THF and phenylmagnesium bromide in THF were purchased from Aldrich and titrated before use. Other arylmagnesium bromides were prepared from the corresponding aryl bromides and magnesium (turnings) using diisobutylaluminum hydride for activation.[1] $Fe_2(O^tBu)_6$,[2] **1f,**[3] **1l**,[4] **1o**,[5] **1r**,[6] **1q**,[7] and **1t**[8] were prepared according to the literature procedures. Yields refer to chromatographically and spectroscopically (1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by Agilent GC Series 6890N and GCMS 7890A. Merck silica gel plates (60F-254) using UV light as visualizing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-400 calibrated using residual deuterated solvent ($CDCl_3$: δH = 7.26 ppm, δC = 77.10 ppm) as an internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Perkin−Elmer Spectrum 100 FT-IR spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Series 1969A ESI-TOF (time of flight) mass spectrometer using EI (electron ionization) or ESI (electrospray ionization).

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(1) U. Tilstam, H. Weinmann, *Org. Process Res. Dev.* **2002**, *6*, 906.

(2) J. Spandl, M. Kusserow, I. Z. Brüdgam, *Anorg. Allg. Chem.* **2003**, *629*, 968.

(3) M. Iwao, *J. Org. Chem.* **1990**, *55*, 3622.

(4) J. Yang, S. Liu, J.-F. Zheng, J. Zhou, *Eur. J. Org. Chem.* **2012**, *31*, 6248.

(5) J. P. Brand, S. Ganss, G. L. Tolnai, J. Waser, *Org. Lett.* **2013**, *15*, 112.

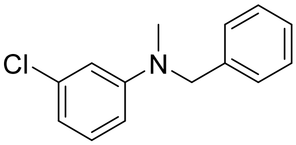
(6) X. Dai, Y. Chen, S. Garrell, H. Liu, L.-K. Zhang, A. Palani, G. Hughes, R. Nargund, *J. Org. Chem.***2013**, *78*, 7758.

(7) O. M. Kuzmina, A. K. Steib, D. Flubacher, P. Knochel, *Org. Lett.* **2012**, *14*, 4818.

(8) C. M. Gothard, S. Soh, N. A. Gothard, B. Kowalczyk, Y. Wei, B. Baytekin, B. A. Grzybowski, *Angew. Chem. Int Ed.***2012**, *51*, 7922.

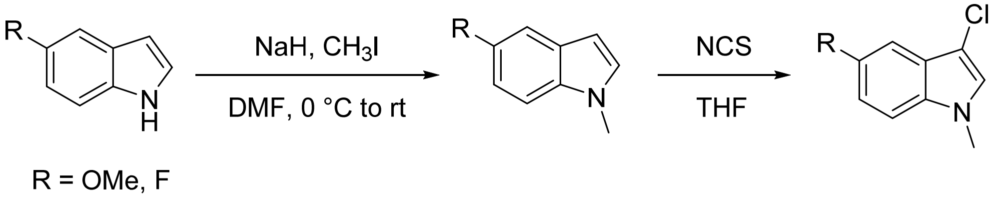
Synthesis and Characterization of Starting Material

N-Benzyl-3-chloro-N-methylaniline (1g)

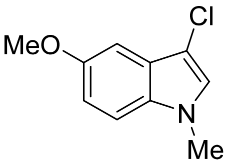


To a 2-necked flask was charged with *N*-methyl-3-chloroaniline (425 mg, 3.0 mmol, 1.0 eq) and heated at 90 °C under Ar atmosphere. Benzyl chloride (380 mg, 3.0 mmol, 1.0 eq) was added dropwise into the flask. The reaction mixture was allowed to stir for 2 h. White precipitate was observed and the mixture was allowed to stand at room temperature overnight. The reaction mixture was diluted with Et_2O and 0.5 mL of 1.0M aq NaOH was added. The resulting mixture was allowed to stir for another 5 mins before H_2O was added. Organic layer was separated and aqueous layer was washed several times with Et_2O. Combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude was purified by flash column chromatography eluting 10% Et_2O/petroleum ether to afford *N*-Benzyl-3-chloro-*N*-methylaniline **1g** as a yellow oil (419 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 6.5 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.73 (t, *J* = 2.2 Hz, 1H), 6.70 – 6.66 (m, 1H), 6.61 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.53 (s, 2H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 138.3, 135.2, 130.2, 128.8, 127.2, 126.8, 116.6, 112.3, 110.7, 56.5, 38.7. IR ν_{max} (neat): 1595, 1496, 1453, 1353, 1101, 908, 828, 730 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_{14}H_{15}ClN^+$ $[M+H]^+$ 232.0888, found 232.0884.

Synthesis of N-Methyl-3-chloroindole

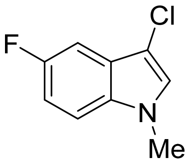


3-Chloro-5-methoxy-1-methyl-1H-indole (1m)



5-Methoxy-1-methyl-1*H*-indole was prepared according to the reported literature procedure[9]. To a solution of 5-methoxy-1-methyl-1*H*-indole (322 mg, 2.0 mmol, 1.0 eq) in THF (0.2 M) was added *N*-chlorosuccinimide (280 mg, 2.1 mmol, 1.05 eq). The reaction mixture was allowed to stir at room temperature for 1 h before the addition of brine. Organic layer was separated and the aqueous layer was washed several times with EtOAc. Combined organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated in vacuo. The resulting crude mixture was purified using flash column chromatography eluting 20% Et_2O/petroleum ether to afford 3-chloro-5-methoxy-1-methyl-1*H*-indole **1m** as a white solid (290 mg, 74%). Mp 81.4 °C – 83.0 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.9 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.99 (s, 1H), 6.92 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.88 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 131.2, 126.1, 125.7, 113.6, 110.6 , 103.9, 99.6, 55.9, 33.2. IR ν_{max} (neat): 2949, 1626, 1494, 1222, 1034, 909, 733 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_{10}H_{11}ClNO^+$ $[M+H]^+$ 196.0524, found 196.0519.

3-Chloro-5-fluoro-1-methyl-1*H*-indole (1n)



5-Fluoro-1-methyl-1*H*-indole was prepared according to the reported literature procedure[9]. To a solution of 5-fluoro-1-methyl-1*H*-indole (298 mg, 2.0 mmol, 1.0 eq) in THF (0.2 M) was added *N*-chlorosuccinimide (280 mg, 2.1 mmol, 1.05 eq). The reaction mixture was allowed to stir at room temperature overnight before the addition of brine. Organic layer was separated and the aqueous layer was washed several times with EtOAc. Combined organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated in vacuo. The resulting crude mixture was purified using flash column chromatography eluting 20% Et_2O/petroleum ether to afford 3-chloro-5-fluoro-1-methyl-1*H*-indole **1n** as a yellow oil (311 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 1H), 7.21 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.05 (s, 1H), 7.01 (td,

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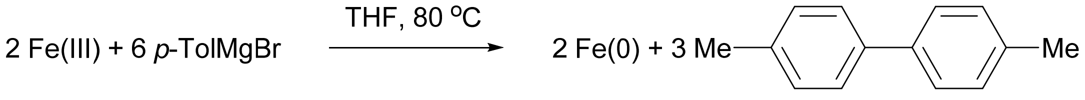
[9] M. Chen, Z.-T. Huang, Q.-Y. Zheng, *Chem. Commun.* **2012**, *48*, 11686.

J = 9.1, 2.5 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3 (d, J = 236.0 Hz), 132.6, 126.9, 126.2 (d, J = 10.5 Hz), 111.4 (d, J = 26.7 Hz), 110.5 (d, J = 9.7 Hz), 104.3 (d, J = 5.0 Hz), 103.5 (d, J = 24.6 Hz), 33.3. IR ν_{max} (neat): 1492, 1426, 1281, 1191, 1161, 909, 876, 734 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_9H_8ClFN^+$ $[M+H]^+$ 184.0324, found 184.0325.

Effects of *tert*-butoxide on the reduction of Fe(III) to Fe(0):



3a'

In a glovebox, a mixture of the iron complex ($FeBr_3$ or $Fe_2(O^tBu)_6$), SIPr and dodecane in THF was stirred at rt for 1h. *p*-Tolylmagnesium bromide was added and the mixture was heated at 80 °C for the specified time. The yield of **3a**' was determined by GC analysis.

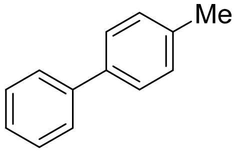
[Fe]	SIPr	*p*-TolMgBr	Dodecane	t (min)	3a' (mmol)	3a' (%)
0.03 mmol $FeBr_3$	0.09 mmol	0.3 mmol	0.03 mmol	15	0.041	91
				60	0.045	100
0.015 mmol $Fe_2(O^tBu)_6$	0.09 mmol	0.3 mmol	0.03 mmol	60	0.006	13
				120	0.006	13

Synthesis and Characterization of Fe-catalyzed Biaryl Cross-coupling Reaction

General Procedure for Iron-catalyzed Biaryl Cross-coupling Reaction:

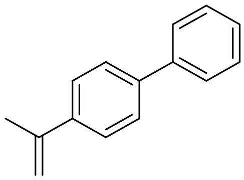
In a glovebox, $Fe_2(O^tBu)_6$ (8 mg, 0.015 mmol, 1.5 mol%), SIPr•HCl (38 mg, 0.090 mmol, 9 mol%) and NaO^tBu (9 mg, 0.09 mmol, 9 mol%) in THF (0.5 mL) were charge to a reaction tube. The mixture was allowed to stir at rt for 1 h before a solution of chlorobenzene **1a** (113 mg, 1 mmol) and *p*-tolylmagnesium bromide **2a** (1.28mL, 0.94 M in THF, 1.2 mmol) was added. The tube was sealed, taken out of the glovebox and stirred at 80 °C for 16h. The reaction progress was monitored by GC. Once completed, the mixture was quenched with brine and exacted with CH_2Cl_2 several times. The combined organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3a** as a white solid (166 mg, 99%, >97% pure on GC analysis).

4-Methyl-1,1'-biphenyl[10] (3a)



3a was prepared from chlorobenzene **1a** and *p*-tolylmagnesium bromide **2a** in 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79-7.77 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.50 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.3, 138.5, 137.1, 129.6, 128.8, 127.1 (2C), 127.0, 21.2.

4-(Prop-1-en-2-yl)-1,1'-biphenyl[11] (3b)



3b was prepared from 1-chloro-4-(prop-1-en-2-yl)benzene (153 mg, 1.0 mmol) **1j**, phenylmagnesium bromide **2b** (1.38 mL, 0.87M in THF, 1.2 mmol), $Fe_2(O^tBu)_6$ (8 mg, 0.015 mmol, 1.5 mol%), SIPr.HCl (38 mg, 0.090 mmol, 9 mol%), NaO^tBu (9 mg, 0.09 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3b** as a white solid (178mg, 92%, >96% pure on GC analysis). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.71 – 7.57 (m, 6H), 7.48-7.43 (m, 2H), 7.39 – 7.32 (m, 1H), 5.47 (dd, *J* = 1.5, 0.8 Hz, 1H), 5.13-5.12 (m, 1H), 2.18 (dd, *J* = 1.5, 0.8 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 143.7, 141.4, 140.9, 129.7, 128.2, 127.6, 126.8, 112.8, 21.9.

4-Methoxy-1,1'-biphenyl[12] (3c)

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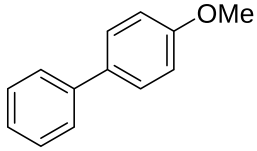
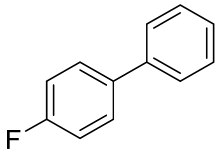
(10) T. Hatakeyama, S. Hashimoto, K. Ishizuka, M. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 11949-11963.
(11) A. L. Hansen, J.-P. Ebran, T. Skrydstrup, *J. Org. Chem.* **2007**, *72*, 6464.
(12) H. Liu, B. Yin, Z. Gao, Y. Li, H. Jiang, *Chem. Comm.* **2012**, *48*, 2033.



3c was prepared from chlorobenzene (113 mg, 1mmol) **1a** and (4-anisylmagnesium bromide **2c** (1.40 mL, 0.86 M in THF, 1.2 mmol), $Fe_2(O^tBu)_6$ (8 mg, 0.015 mmol, 1.5 mol%), SIPr.HCl (38 mg, 0.090 mmol, 9 mol%), NaO^tBu (9 mg, 0.09 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (20% CH_2Cl_2/petroleum ether) to afford **3c** as a white solid (151 mg, 82%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.55 (m, 4H), 7.50 – 7.43 (m, 2H), 7.38 – 7.32 (m, 1H), 7.07 – 7.00 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4.

4-Fluoro-1,1'-biphenyl[13] (3d)



3d was prepared from chlorobenzene **1a** (56 mg, 0.5 mmol), (4-fluorophenyl)magnesium bromide **2d** (0.65 mL, 0.93 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3d** as a white solid (75mg, 87%, >99% pure on GC analysis). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57-7.54 (m, 4H), 7.46-7.42 (m, 2H), 7.38 – 7.32 (m, 1H), 7.17 – 7.10 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6 (d, J = 246.2 Hz), 140.4, 137.5 (d, J = 3.2 Hz), 128.9, 128.8 (d, J = 7.9 Hz), 127.3, 127.1, 115.7 (d, J = 21.5 Hz).

4-([1,1'-Biphenyl]-4-yl)morpholine[14] (3e)

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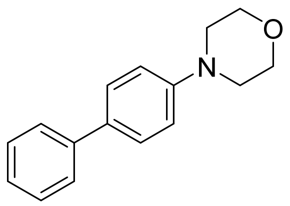
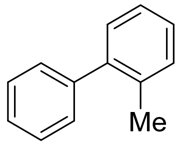
(13) K. Tanimoro, M. Ueno, K. Takeda, M. Kirihata, S. Tanimori, *J. Org. Chem.* **2012**, *77*, 7844.

(14) B. H. Lipshutz, D. M. Nihan, E. Vinogradova, B. R. Taft, *Org. Lett.* **2008**, *10*, 4279.



3e was prepared from chlorobenzene **1a** (57 mg, 0.5 mmol), (4-morpholinophenyl)magnesium bromide **2e** (0.78 mL, 0.77 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (4 mg, 0.0075 mmol, 1.5 mol%), SIPr.HCl (19 mg, 0.045 mmol, 9 mol%), NaO^tBu (4.5 mg, 0.045 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (1-5% CH_2Cl_2/petroleum ether) to afford **3e** as a white solid (106 mg, 89%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62-7.55 (m, 4H), 7.49 – 7.41 (m, 2H), 7.36 – 7.30 (m, 1H), 7.04 – 6.99 (m, 2H), 3.91 (t, *J* = 4.8 Hz, 4H), 3.23 (t, *J* = 4.8 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6, 140.9, 132.7, 128.7, 127.8, 126.6, 115.8, 66.9, 49.2.

2-Methyl-1,1'-biphenyl[15] (3f)



3f was prepared from chlorobenzene **1a** (57 mg, 0.5 mmol), *o*-tolylmagnesium bromide **2f** (0.78 mL, 0.77 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (4 mg, 0.0075 mmol, 1.5 mol%), SIPr.HCl (19 mg, 0.045 mmol, 9 mol%), NaO^tBu (4.5 mg, 0.045 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3e** as a colorless oil (79 mg, 94%, >97% pure on GC analysis). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.25 (m, 2H), 7.25 – 7.18 (m, 3H), 7.18 – 7.09 (m, 4H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.1, 142.0, 135.4, 130.4, 129.9, 129.3, 128.1, 127.3, 126.8, 125.8, 20.5.

5-(4-Methoxyphenyl)benzo[*d*][1,3]dioxole[16] (3g)

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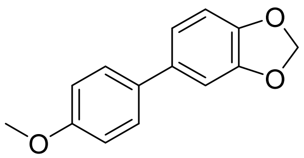
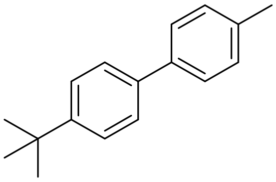
[15] O. Kobayashi, D. Uraguchi, T. Yamakawa, *Org. Lett.* **2009**, *11*, 2679.

[16] V. Colombel, M. Presset, D. Oehlrich, F. Rombouts, G. A. Molander, *Org. Lett.* **2012**, *14*, 1680.



3g was prepared from 1-chloro-4-methoxybenzene **1c** (71 mg, 0.5 mmol), benzo[*d*][1,3]dioxol-5-ylmagnesium bromide **2g** (0.78 mL, 0.77 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (4 mg, 0.0075 mmol, 1.5 mol%), SIPr.HCl (19 mg, 0.045 mmol, 9 mol%), NaO^tBu (4.5 mg, 0.045 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (20% CH_2Cl_2/petroleum ether) followed by recrystallization from petroleum ether to afford **3g** as a white solid (87 mg, 76%). ^1H NMR (400 MHz, Acetone-d_6) δ 7.55 – 7.47 (m, 2H), 7.12 – 7.03 (m, 2H), 7.02 – 6.94 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 160.0, 149.2, 147.6, 136.0, 134.1, 128.5, 120.7, 115.0, 109.3, 107.8, 102.0, 55.6.

4-(*tert*-Butyl)-4'-methyl-1,1'-biphenyl[17] (3h)



3h was prepared from 1-(tert-butyl)-4-chlorobenzene **1b** (169 mg, 1 mmol), *p*-tolylmagnesium bromide **2a** (1.28mL, 0.94 M in THF, 1.2 mmol), $Fe_2(O^tBu)_6$ (14 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (64 mg, 0.090 mmol, 15 mol%), NaO^tBu (15 mg, 0.09 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3h** as a white solid (211 mg, 94%, >97% pure on GC analysis). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.46 (m, 6H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 1.40 (s, 9H). ^{113}C NMR (101 MHz, Chloroform-*d*) δ 150.0, 138.4, 138.3, 136.8, 129.5, 126.9, 126.7, 125.7, 34.6, 31.5, 21.2.

4-Methoxy-4'-methyl-1,1'-biphenyl[10] (3i)

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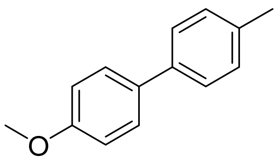
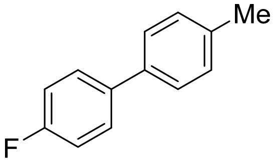
[17] F. Zhou, M.-O. Simon, C.-J. Li, *Chem. Eur. J.* **2013**, *19*, 7151.



3i was prepared from 4-methoxyphenyl chloride **1c** (143 mg, 1 mmol), *p*-tolylmagnesium bromide **2a** (1.28mL, 0.94 M in THF, 1.2 mmol), $Fe_2(O^tBu)_6$ (14 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (64 mg, 0.090 mmol, 15 mol%), NaO^tBu (15 mg, 0.09 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (5% Et_2O/petroleum ether) to afford **3i** as a white solid (162 mg, 82%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 (td, *J* = 8.8, 2.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.85 (td, *J* = 8.8, 2.8 Hz, 2H), 3.71 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 138.0, 136.4, 133.8, 129.5, 128.0, 126.6, 114.3, 55.4, 21.1.

4-Fluoro-4'-methyl-1,1'-biphenyl[18] (3j)



3j was prepared from 1-chloro-4-fluorobenzene **1d** (65mg, 0.5 mmol) *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 2.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3j** as a white solid in (86 mg, 92%, >97% pure on GC analysis). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.46 – 7.42 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.15 – 7.07 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 245.7 Hz), 137.5, 137.4 (d, *J* = 3.2 Hz), 137.1, 129.6, 128.6 (d, *J* = 8.0 Hz), 127.0, 115.6 (d, *J* = 21.3 Hz), 21.1.

3,4'-dimethyl-1,1'-biphenyl[19] (3k)

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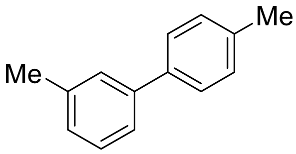
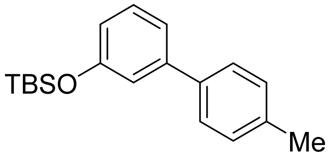
(18) Z.-Y. Wang, G.-Q. Chen, L.-X. Shao, *J. Org. Chem.* **2012**, *77*, 6608.

(19) M. a. J. Iglesias, A. Prieto, M. C. Nicasio, *Org. Lett.***2012**, *14*, 4318.



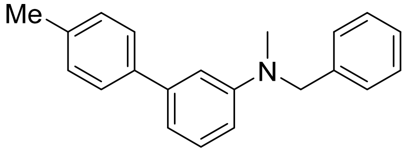
3k was prepared from 1-chloro-3-methylbenzene **1e** (63 mg, 0.5 mmol) and *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3k** as a colorless oil (89 mg, 98%, >95% pure on GC analysis). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.3, 138.3, 137.0, 129.5, 128.7, 127.9, 127.8, 127.1, 126.9, 124.2, 21.6, 21.2.

***Tert*-Butyldimethyl((4'-methyl-[1,1'-biphenyl]-3-yl)oxy)silane (3l)**



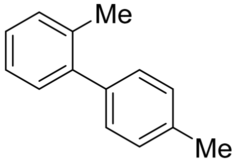
3l was prepared from *tert*-butyl(3-chlorophenoxy)dimethylsilane **1f** (121 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3l** as a colourless oil (127 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.31 – 7.23 (m, 3H), 7.18 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.82 (ddd, *J* = 8.0, 2.4, 1.0 Hz, 1H), 2.41 (s, 3H), 1.03 (s, 9H), 0.25 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.1, 142.7, 138.3, 137.2, 129.7, 129.5, 127.0, 120.1, 118.8, 118.7, 25.8, 21.2, 18.3, -4.2. IR ν_{max} (neat): 2957, 2930, 2859, 1601, 1479, 1309, 1259, 1206, 937, 835, 784 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_{19}H_{27}OSi^+$ $[M+H]^+$ 299.1826, found 299.1825.

***N*-Benzyl-*N*,4'-dimethyl-[1,1'-biphenyl]-3-amine (3m)**



3m was prepared from *N*-benzyl-3-chloro-*N*-methylaniline **1g** (116 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (10% Et_2O/petroleum ether) to afford **3m** as a yellow oil (117 mg, 81%,). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50-7.46 (m, 2H), 7.36 – 7.20 (m, 8H), 6.99 – 6.93 (m, 2H), 6.75 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.59 (s, 2H), 3.07 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 142.4, 139.4, 139.1, 136.9, 129.5, 129.5, 129.4, 128.7, 127.2, 127.0, 126.9, 115.8, 111.4, 56.9, 38.7, 21.2. IR ν_{max} (neat): 3025, 1601, 1494, 1452, 1354, 1206, 1114, 909, 817, 773, 731 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747, found 288.1753.

2,4'-Dimethyl-1,1'-biphenyl[20] (3n)



3n was prepared from 1-chloro-2-methylbenzene **1h** (63 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3n** as a colourless oil (80 mg, 88%, >94% pure on GC analysis). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.15 (m, 8H), 2.41 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 139.2, 136.4, 135.5, 130.4, 129.9, 129.2, 128.9, 127.1, 125.8, 21.2, 20.6.

4-Methyl-4'-vinyl-1,1'-biphenyl[21] (3o)

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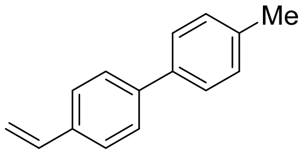
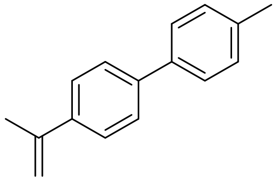
(20) T. Hoshi, I. Saitoh, T. Nakazawa, T. Suzuki, J.-i. Sakai, H. Hagiwara, *J. Org. Chem.* **2009**, *74*, 4013.
(21) Y. Liu, J. Wang, *Syn.Commun.* **2009**, *40*, 196.



3o was prepared from 1-chloro-4-vinylbenzene **1i** (70 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 2.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3o** as a white solid (77 mg, 79%, >95% pure on GC analysis). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 2H), 7.52 – 7.43 (m, 4H), 7.25 (d, *J* = 9.2 Hz, 2H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.26 (dd, *J* = 10.9, 0.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.7, 138.0, 137.2, 136.6, 136.5, 129.6, 127.1, 126.9, 126.7, 113.8, 21.2.

4-Methyl-4'-(prop-1-en-2-yl)-1,1'-biphenyl[22] (3p)



3p was prepared from 1-chloro-4-(prop-1-en-2-yl)benzene **1j** (153 mg, 1 mmol), *p*-tolylmagnesium bromide **2a** (1.28mL, 0.94 M in THF, 1.2 mmol), $Fe_2(O^tBu)_6$ (8 mg, 0.015 mmol, 1.5 mol%), SIPr.HCl (38 mg, 0.09 mmol, 9 mol%), NaO^tBu (9 mg, 0.09 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (petroleum ether) to afford **3p** as a white solid (188 mg, 90%, >96% pure on GC analysis). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48-7.38 (m, 6H), 7.16-7.13 (m, 2H), 5.33 (dd, *J* = 1.4, 0.8 Hz, 1H), 5.02-5.01 (p, *J* = 1.4 Hz, 1H), 2.30 (s, 3H), 2.10 (dd, *J* = 1.4, 0.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9, 140.2, 140.0, 138.0, 137.1, 129.6, 126.9, 126.8, 126.0, 112.4, 21.87, 21.2.

5-Methoxy-1-methyl-3-(*p*-tolyl)-1*H*-indole (3s)

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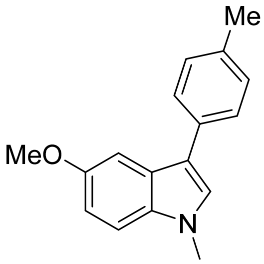
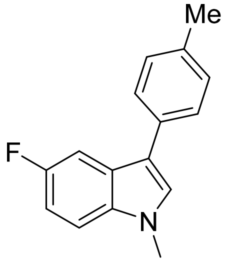
[22] M. Jiang, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2010**, 3307.



3s was prepared from 3-chloro-5-methoxy-1-methyl-1*H*-indole **1m** (98 mg, 0.5 mmol), *p*-tolylmagnesium bromide (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (20% DCM/petroleum ether) to afford **3s** as a yellow solid (107 mg, 85%). Mp 91.6 °C – 92.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.28 (t, *J* = 3.9 Hz, 3H), 7.19 (s, 1H), 6.97 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 135.3, 133.0, 132.9, 129.6, 127.2 , 127.0 , 126.6 , 116.4 , 112.3, 110.3, 102.0, 56.2, 33.1, 21.2. IR ν_{max} (neat): 2945, 2918, 2832, 1619, 1489, 1423, 1217, 1208, 1088, 1035, 864, 791 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_{17}H_{18}NO^+$ $[M+H]^+$ 252.1383, found 252.1378.

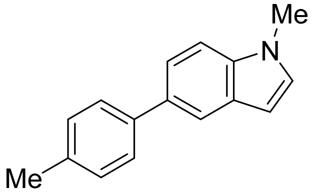
5-Fluoro-1-methyl-3-(*p*-tolyl)-1*H*-indole (3t)



3t was prepared from 3-chloro-5-fluoro-1-methyl-1*H*-indole **1n** (92 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (10% Et_2O/petroleum ether) to afford **3t** as a brown oil (110 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.28 – 7.21 (m, 4H), 7.01 (td, *J* = 9.0, 2.5 Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.43 (d, *J* = 234.3 Hz), 135.6, 134.2, 132.3, 129.6, 127.9, 127.1, 126.6 (d, *J* = 9.8 Hz), 116.8 (d, *J* = 4.8 Hz), 110.4 (d, *J* = 26.3 Hz), 110.1, 105.0 (d, *J* = 24.1 Hz), 33.2, 21.2.

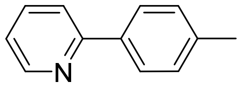
IR ν_{max} (neat): 2920, 1622, 1555, 1488, 1191, 1129, 871, 792 cm^{-1}. HRMS (ESI+) *m/z* calc for $C_{16}H_{15}FN^+$ $[M+H]^+$ 240.1183, found 240.1192.

1-Methyl-5-(*p*-tolyl)-1*H*-indole (3u)



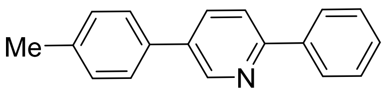
3u was prepared from 5-chloro-1-methyl-1*H*-indole **1o** (83 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.0125 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (0-5% Et_2O/petroleum ether) to afford **3u** as a white solid (89 mg, 80%). Mp 164.7 °C – 166.4 °C. ^1H NMR (400 MHz, Methylene Chloride-*d*$_2$) δ 7.83 (dd, *J* = 1.7, 0.6 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.48 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 3.1 Hz, 1H), 6.53 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Methylene Chloride-*d*$_2$) δ 140.0, 136.7, 136.4, 132.9, 130.0, 129.8, 129.5, 127.4, 121.4, 119.2, 109.9, 101.5, 33.2, 21.2. IR ν_{max} (neat): 2924, 1510, 1485, 1424, 1336, 1246, 1112, 889, 830, 799, 728 cm^{-1}. HRMS (ESI+) m/z calc for $C_{16}H_{16}N^+$ $[M+H]^+$ 222.1277, found 222.1270.

2-(*p*-Tolyl)pyridine[19] (3v)



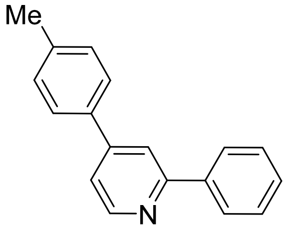
3v was prepared from 2-chloropyridine **1p** (113 mg, 1 mmol), *p*-tolylmagnesium bromide **2a** (1.28mL, 0.94 M in THF, 1.2 mmol), $Fe_2(O^tBu)_6$ (8 mg, 0.015 mmol, 1.5 mol%), SIPr.HCl (38 mg, 0.09 mmol, 9 mol%), NaO^tBu (9 mg, 0.09 mmol, 9 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (0-5% ethyl acetate/petroleum ether) to afford **3v** as a colorless oil (104 mg, 62%).^1H NMR (400 MHz, Chloroform-*d*) δ 8.68 (td, *J* = 4.8, 1.2 Hz, 1H), 7.93-7.90 (m, 2H), 7.69-7.68 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20-7.14 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.4, 149.5, 138.9, 136.6, 129.4, 126.7, 121.7, 120.2, 21.2.

2-Phenyl-5-(*p*-tolyl)pyridine[23] (3w)



3w was prepared from 5-chloro-2-phenylpyridine **1q** (95 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (10% Et_2O/petroleum ether) to afford **3w** as a white solid (98 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.94 – 8.91 (m, 1H), 8.08 – 8.02 (m, 2H), 7.94 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.46 – 7.39 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 148.0, 139.1, 138.1, 135.0, 129.9, 129.0, 128.9, 126.9, 120.4, 21.3.

2-Phenyl-4-(*p*-tolyl)pyridine[24] (3x)



3x was prepared from 4-chloro-2-phenylpyridine **1r** (95 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (10% Et_2O/petroleum ether) to afford **3x** as a white solid (79 mg, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.6 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.94 – 7.90 (m, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.45-7.41 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C

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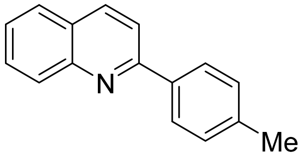
[23] A. Gheorghe, B. a. Quiclet-Sire, X. Vila, S. Z. Zard, *Org. Lett.* **2005**, *7*, 1653.

[24] X.-F. Duan, X.-H. Li, F.-Y. Li, X.-H. Huang, *Synthesis* **2004**, 2614.

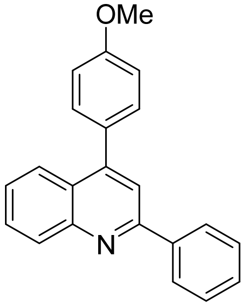
NMR (101 MHz, Chloroform-*d*) δ 158.2, 150.1, 149.3, 139.7, 139.3, 135.7, 129.9, 129.1, 128.8, 127.2, 127.0, 120.1, 118.6, 21.3.

2-(*p*-Tolyl)quinoline[19] (3y)



3y was prepared from 2-chloroquinoline **1s** (82 mg, 0.5 mmol), *p*-tolylmagnesium bromide **2a** (0.64 mL, 0.94 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (10% Et_2O/petroleum ether) to afford **3y** as a white solid (69 mg, 63%,). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (t, *J* = 8.2 Hz, 2H), 8.10 – 8.06 (m, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.82 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.74-7.70 (m, 1H), 7.54-7.50 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.4, 148.2, 139.6, 136.9, 136.8, 129.8, 129.7, 129.6, 127.6, 127.5, 127.2, 126.2, 119.0, 21.4.

4-(4-Methoxyphenyl)-2-phenylquinoline[25] (3z)



3z was prepared from 4-chloro-2-phenylquinoline **1t** (120 mg, 0.5 mmol), (4-methoxyphenyl)magnesium bromide **2c** (1.5 mL, 0.4 M in THF, 0.6 mmol), $Fe_2(O^tBu)_6$ (7 mg, 0.025 mmol, 2.5 mol%), SIPr.HCl (32 mg, 0.075 mmol, 15 mol%), NaO^tBu (7 mg, 0.075 mmol, 15 mol%) and 0.5 mL THF. The crude mixture was purified by silica gel column chromatography (10% Et_2O/petroleum ether) to afford **3z** as a white solid (83 mg, 53%, >96% pure on NMR analysis).^1H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.22 –

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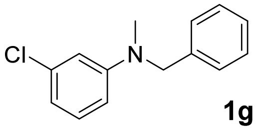
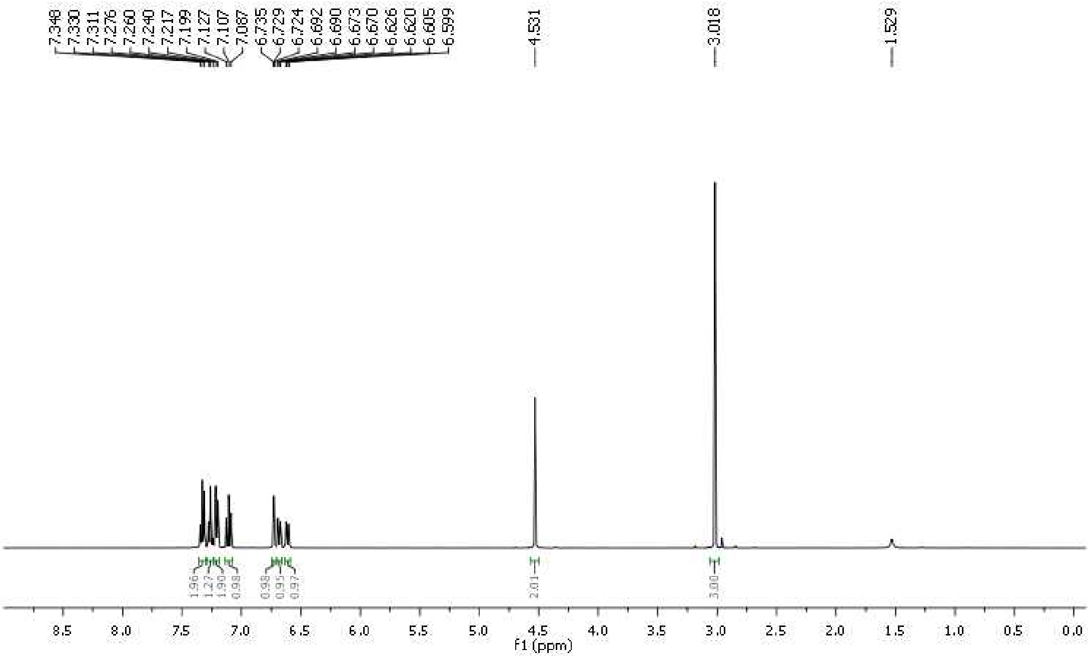
(25) K. Cao, F.-M. Zhang, Y.-Q. Tu, X.-T. Zhuo, C.-A. Fan, *Chem. Eur. J.* **2009,** *15*, 6332.

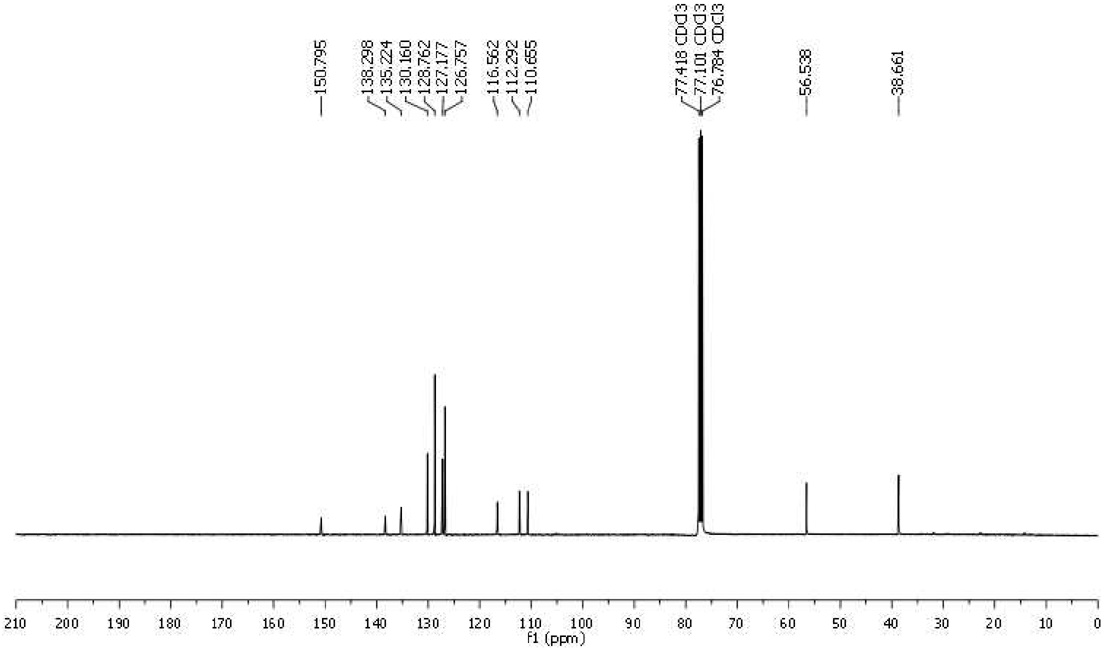
8.18 (m, 2H), 7.97 – 7.93 (m, 1H), 7.80 (s, 1H), 7.75-7.71 (m, 1H), 7.56 – 7.43 (m, 6H), 7.12 – 7.06 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 157.0, 149.0 (2C), 139.8, 130.9, 130.8, 130.2, 129.5, 129.4, 128.9, 127.7, 126.3, 126.1, 125.8, 119.4, 114.2, 55.5.

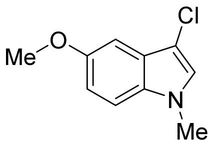
NMR Spectra



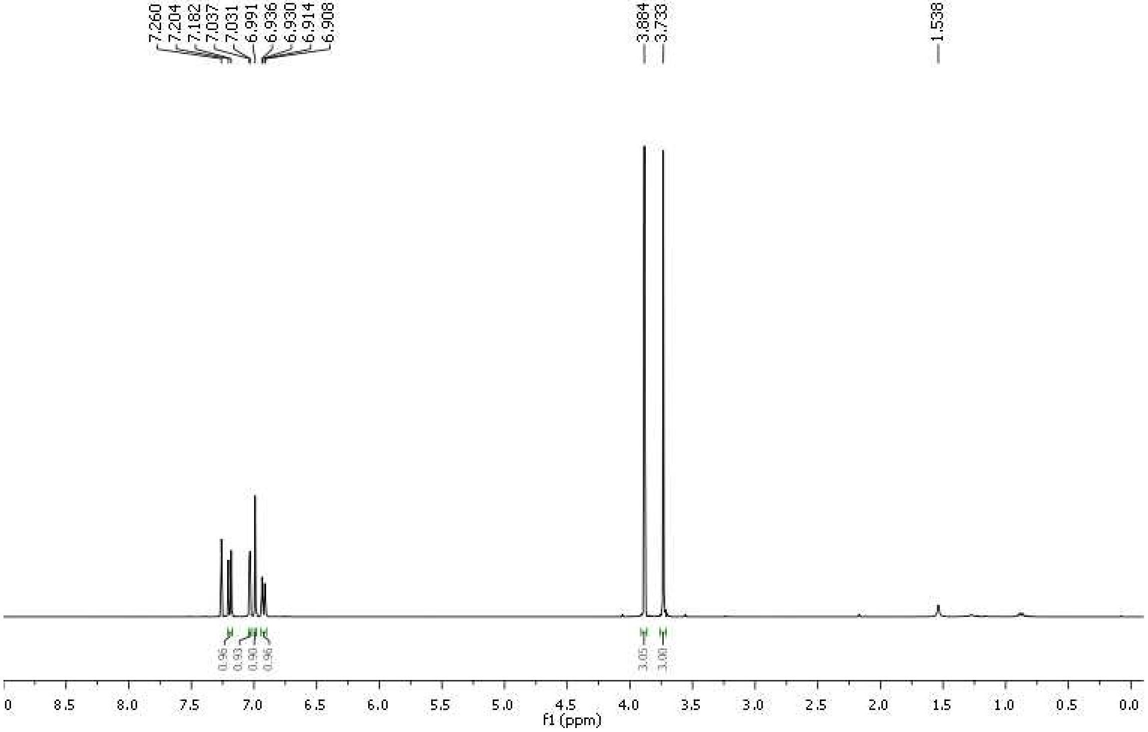
1g






Cl
Me
O
N
Me

1m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7.182
7.037
7.031
6.991
6.936
6.930
6.914
6.908
3.884
3.733
1.538
0.96
0.93
0.90
0.96
3.05
3.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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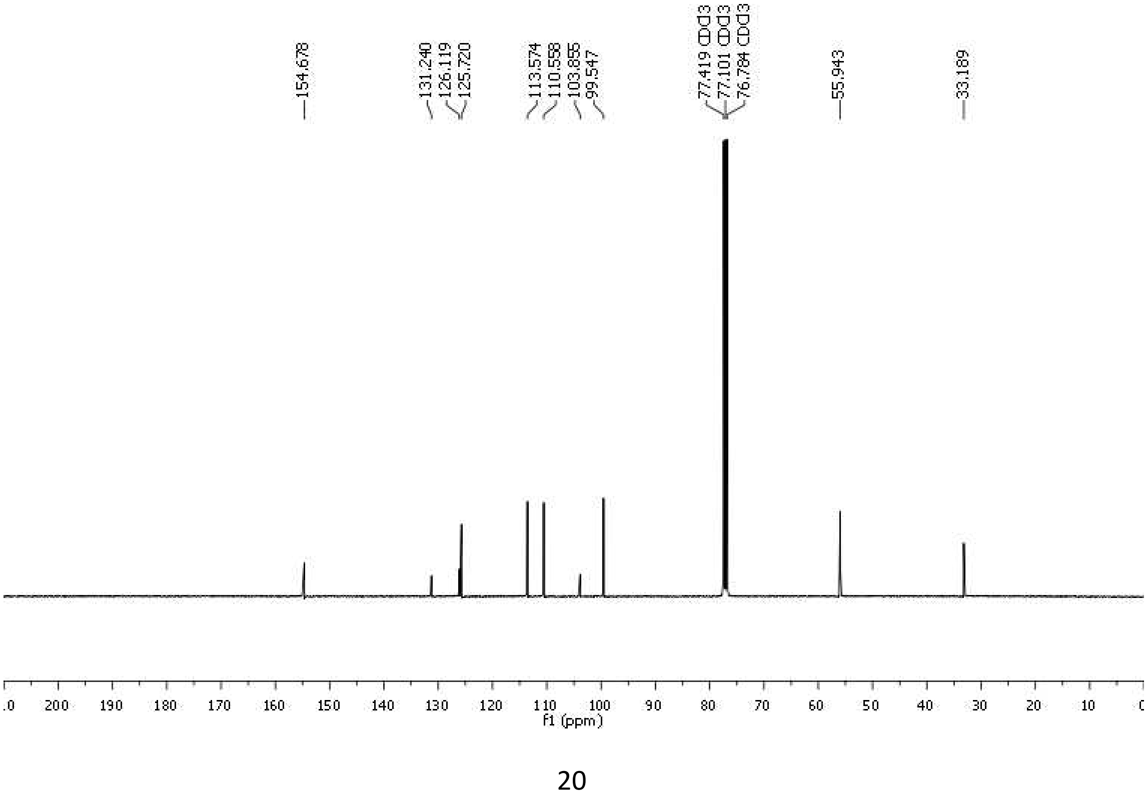
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.240
126.119
125.720
113.574
110.558
103.855
99.547
77.419 CDCl3
77.101 CDCl3
76.784 CDCl3
55.943
33.189
.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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30
20
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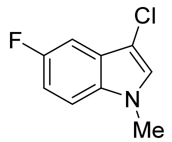
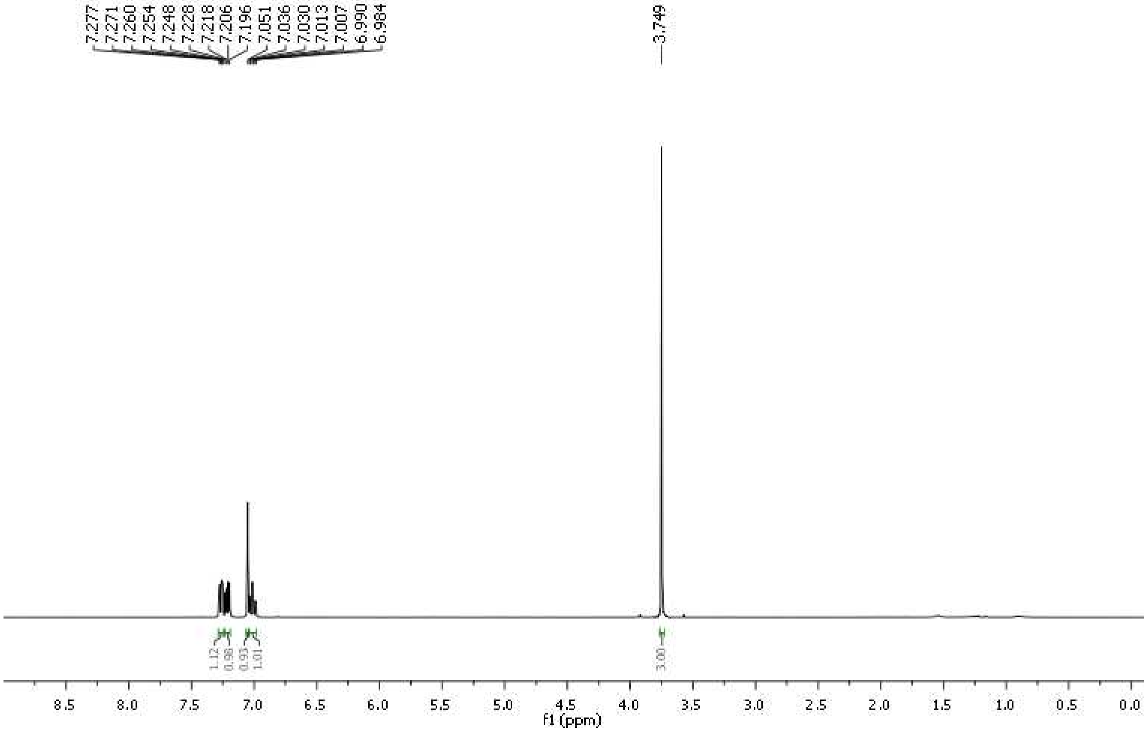
f1 (ppm)



Cl
F
N
Me

1n



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7.271
7.260
7.254
7.248
7.228
7.218
7.206
7.196
7.051
7.036
7.030
7.013
7.007
6.990
6.984
3.749
1.12
0.98
0.93
1.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
1.0
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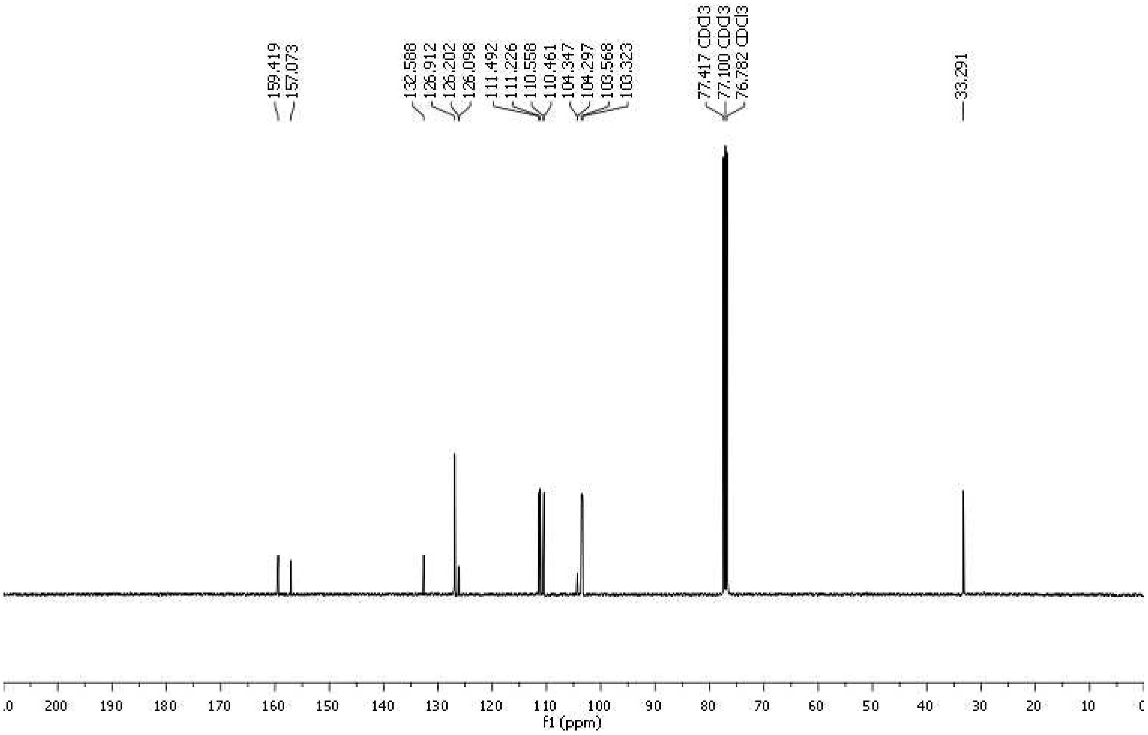
0.0
f1 (ppm)



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157.073
132.588
126.912
126.202
126.098
111.492
111.226
110.558
110.461
104.347
104.297
103.568
103.323
77.417 CDCl3
77.100 CDCl3
76.782 CDCl3
33.291
200
190
180
170
160
150
140
130
120
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100
90
80
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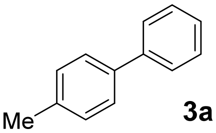
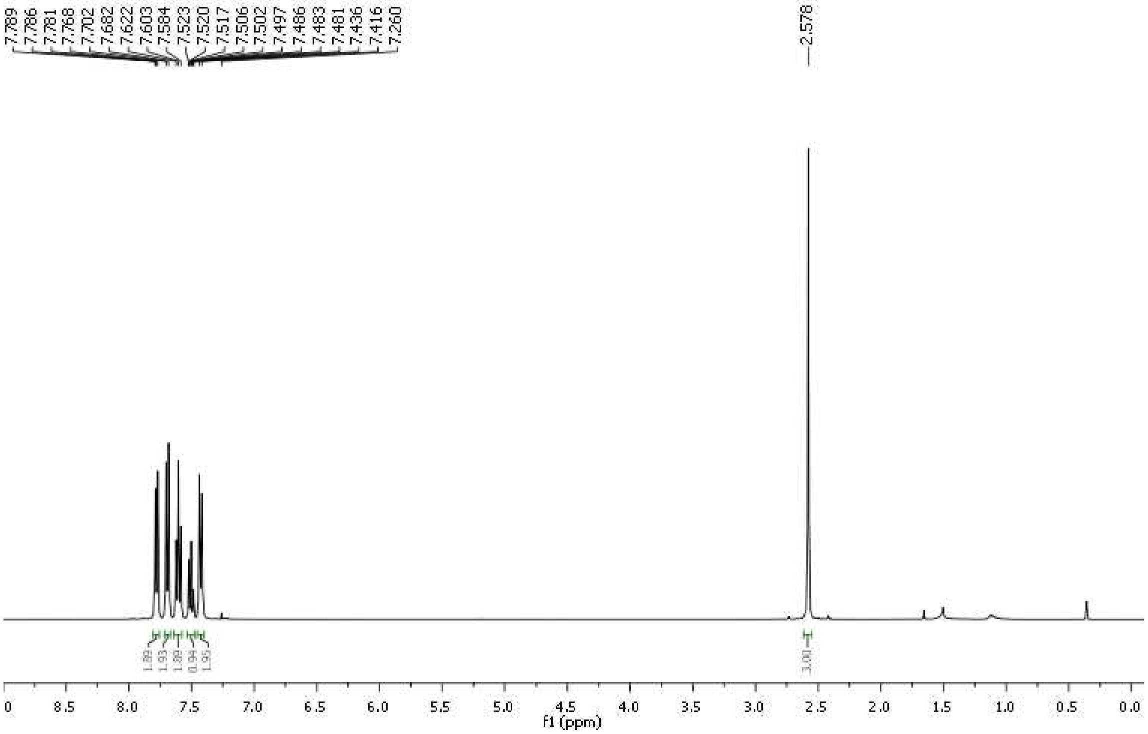
f1 (ppm)


Me

3a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7.768
7.702
7.682
7.622
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7.584
7.523
7.520
7.517
7.506
7.502
7.497
7.486
7.483
7.481
7.436
7.416
7.260
2.578
1.89
1.93
1.89
0.94
1.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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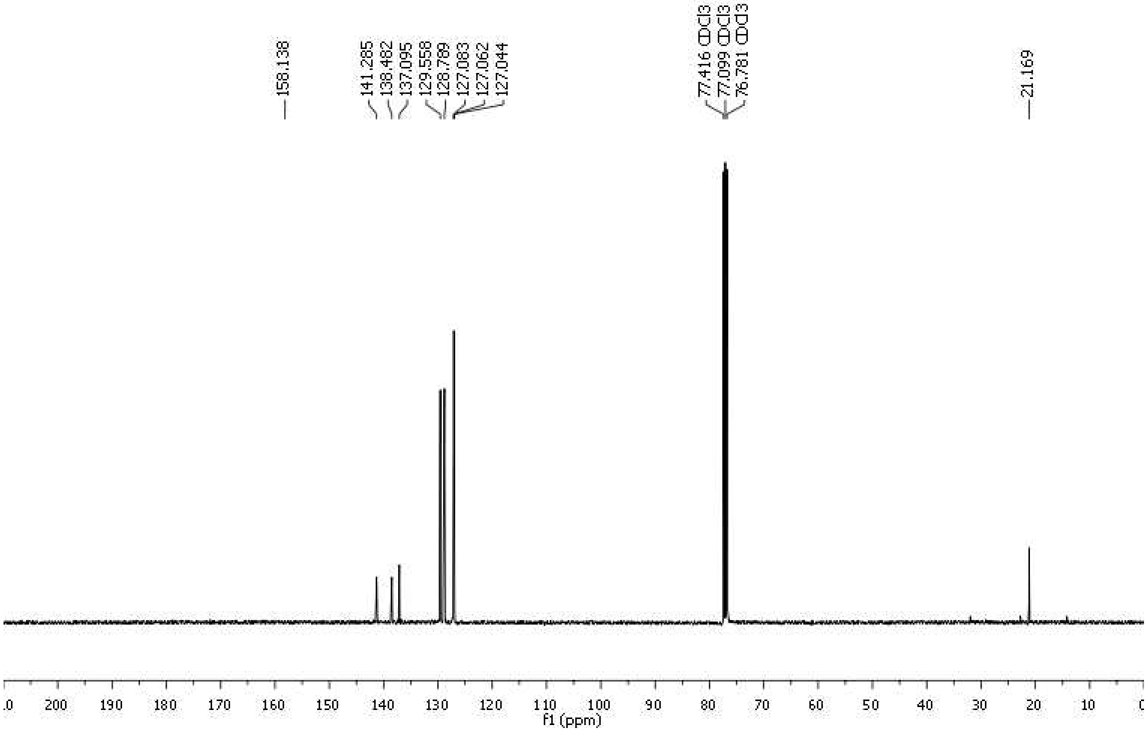
0.0
f1 (ppm)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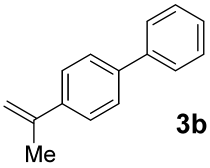
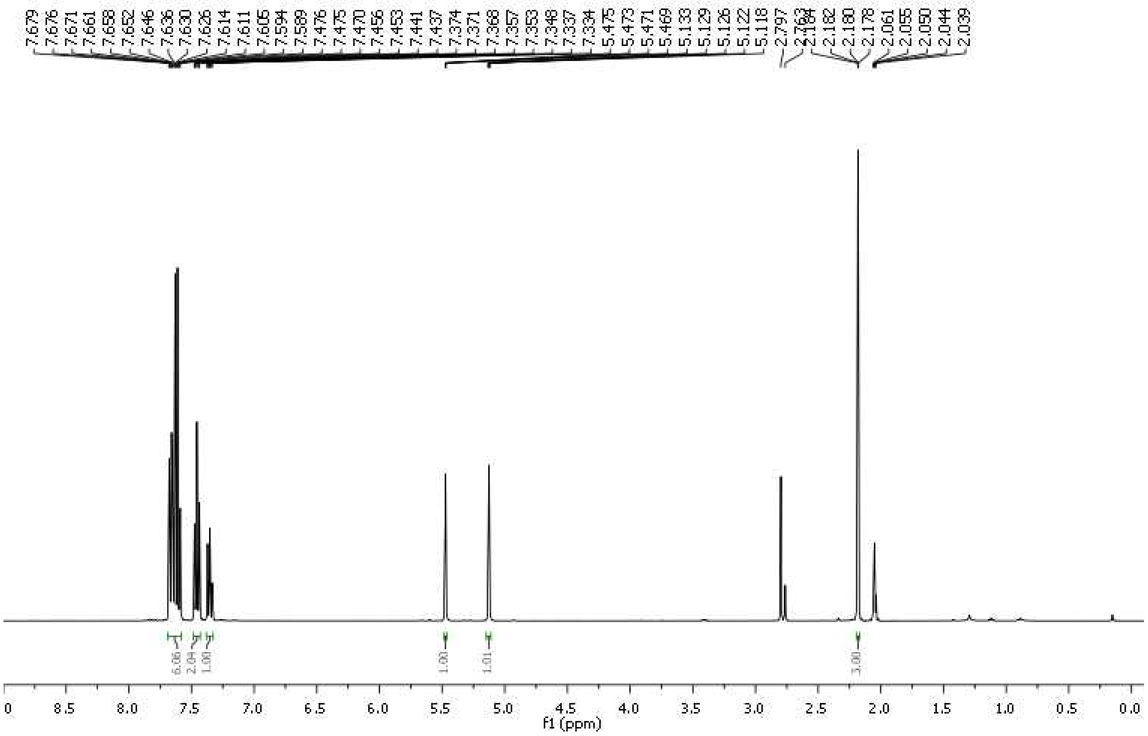
138.482
137.095
129.558
128.789
127.083
127.062
127.044
77.416 CDCl3
77.099 CDCl3
76.781 CDCl3
21.169
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me

3b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7.636
7.630
7.626
7.614
7.611
7.605
7.594
7.589
7.476
7.475
7.470
7.456
7.453
7.441
7.437
7.374
7.371
7.368
7.357
7.353
7.348
7.337
7.334
5.475
5.473
5.471
5.469
5.133
5.129
5.126
5.122
5.118
2.797
2.763
2.184
2.182
2.180
2.178
2.061
2.055
2.050
2.044
2.039
6.06
2.04
1.00
1.00
1.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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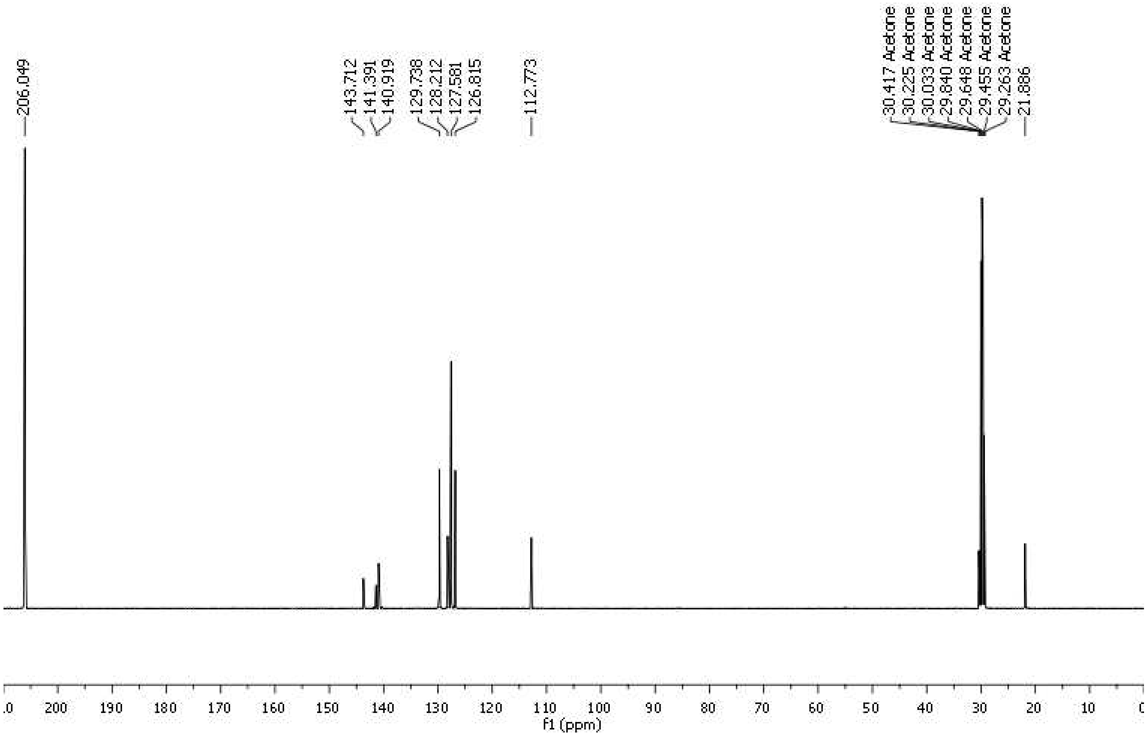
0.0
f1 (ppm)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141.391
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128.212
127.581
126.815
112.773
30.417 Acetone
30.225 Acetone
30.033 Acetone
29.840 Acetone
29.648 Acetone
29.455 Acetone
29.263 Acetone
21.886
200
190
180
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160
150
140
130
120
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100
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80
70
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40
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20
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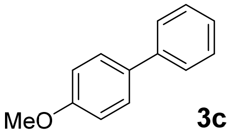
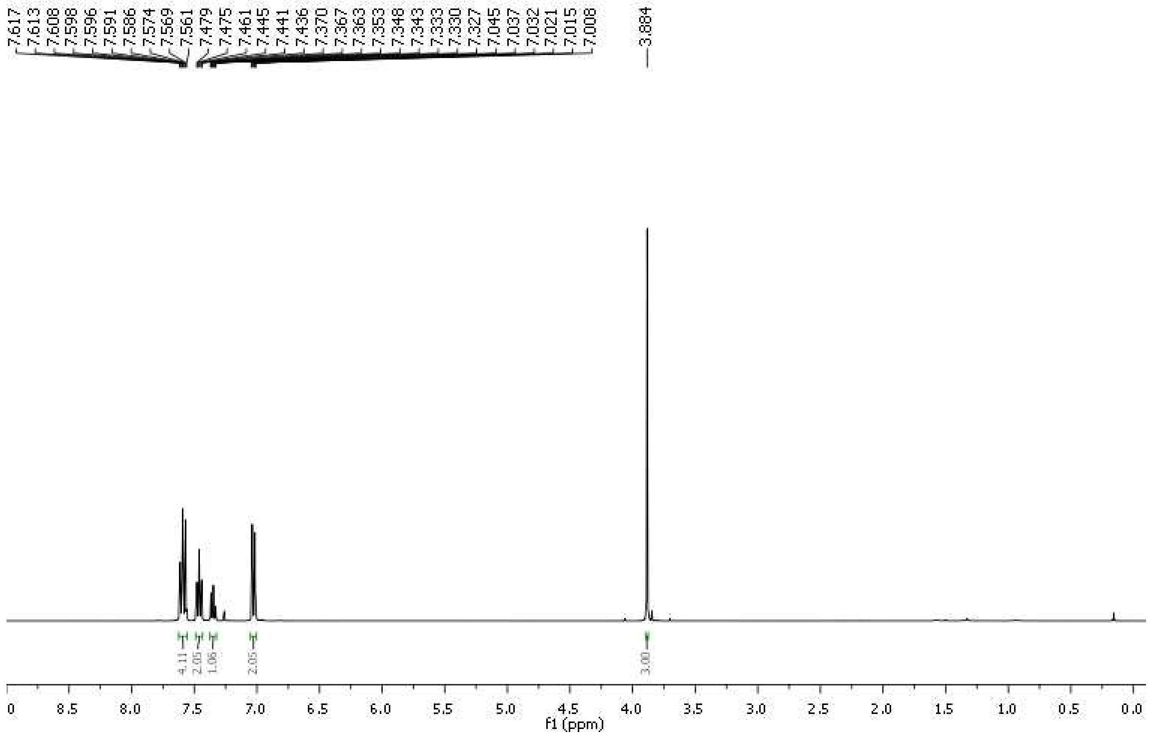
f1 (ppm)


MeO

3c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7.591
7.586
7.574
7.569
7.561
7.479
7.475
7.461
7.445
7.441
7.436
7.370
7.367
7.363
7.353
7.348
7.343
7.333
7.330
7.327
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7.037
7.032
7.021
7.015
7.008
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1.06
2.05
3.00
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7.0
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6.0
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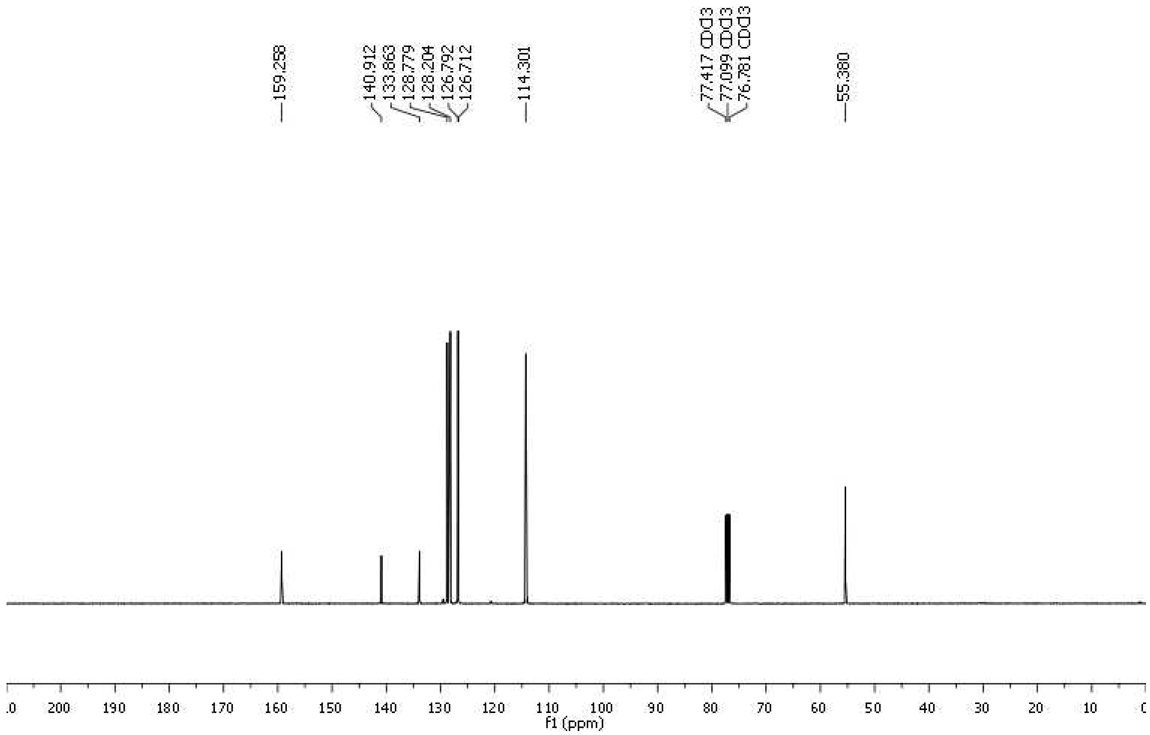
0.0
f1 (ppm)


159.258
140.912
133.863
128.779
128.204
126.792
126.712
114.301
77.417 CDCl3
77.099 CDCl3
76.781 CDCl3
55.380
.0
200
190
180
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130
120
110
100
90
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70
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50
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30
20
10
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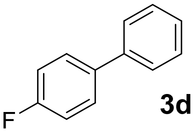
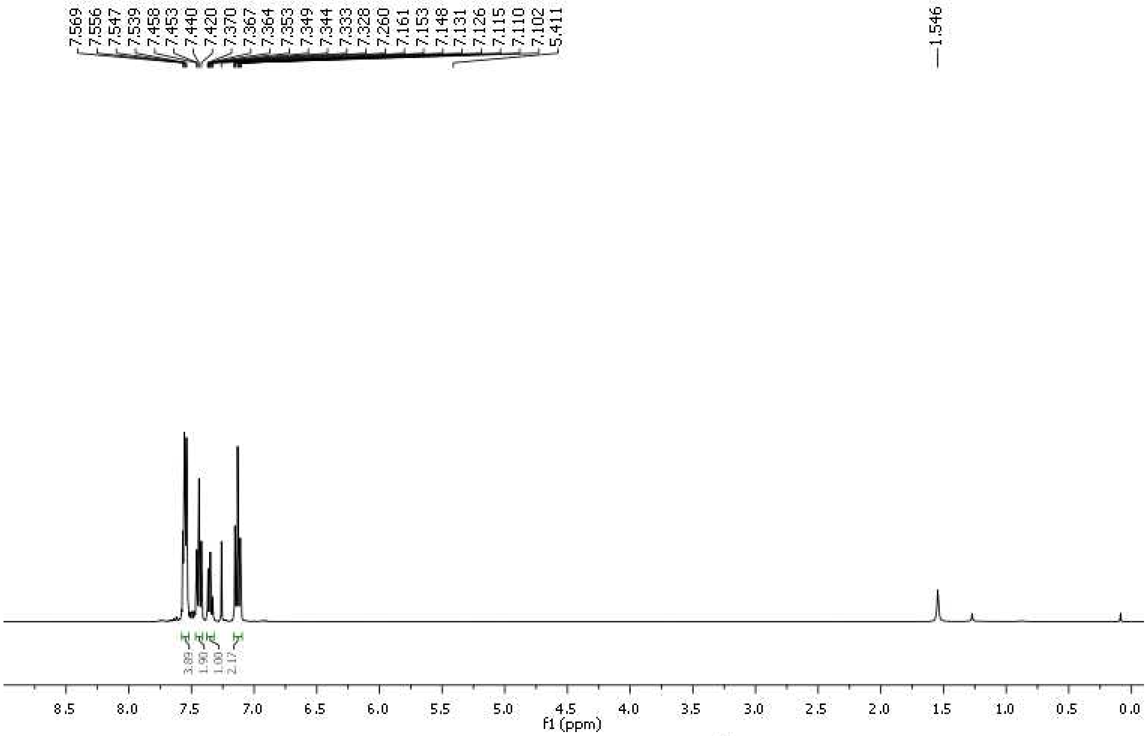
f1 (ppm)


F

3d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7.440
7.420
7.370
7.367
7.364
7.353
7.349
7.344
7.333
7.328
7.260
7.161
7.153
7.148
7.131
7.126
7.115
7.110
7.102
5.411
1.546
3.89
1.90
1.00
2.17
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7.0
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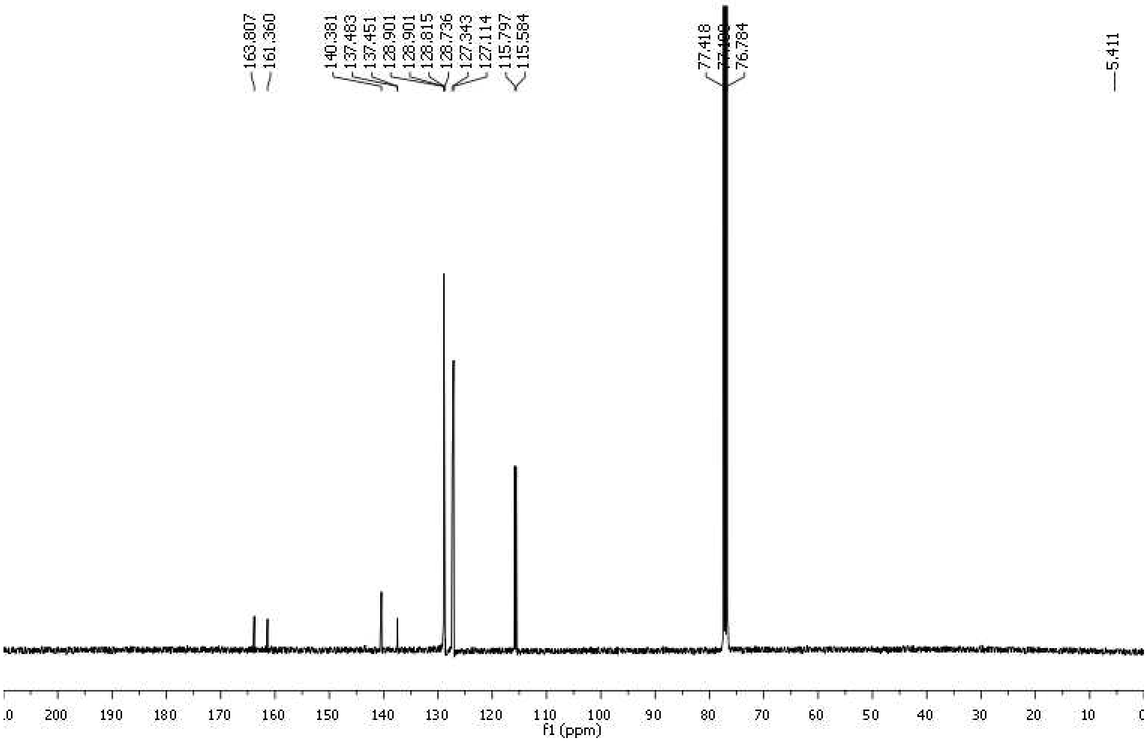
f1 (ppm)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127.343
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115.584
77.418
77.100
76.784
5.411
200
190
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40
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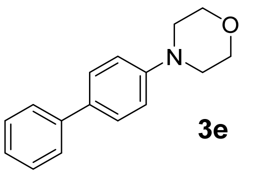
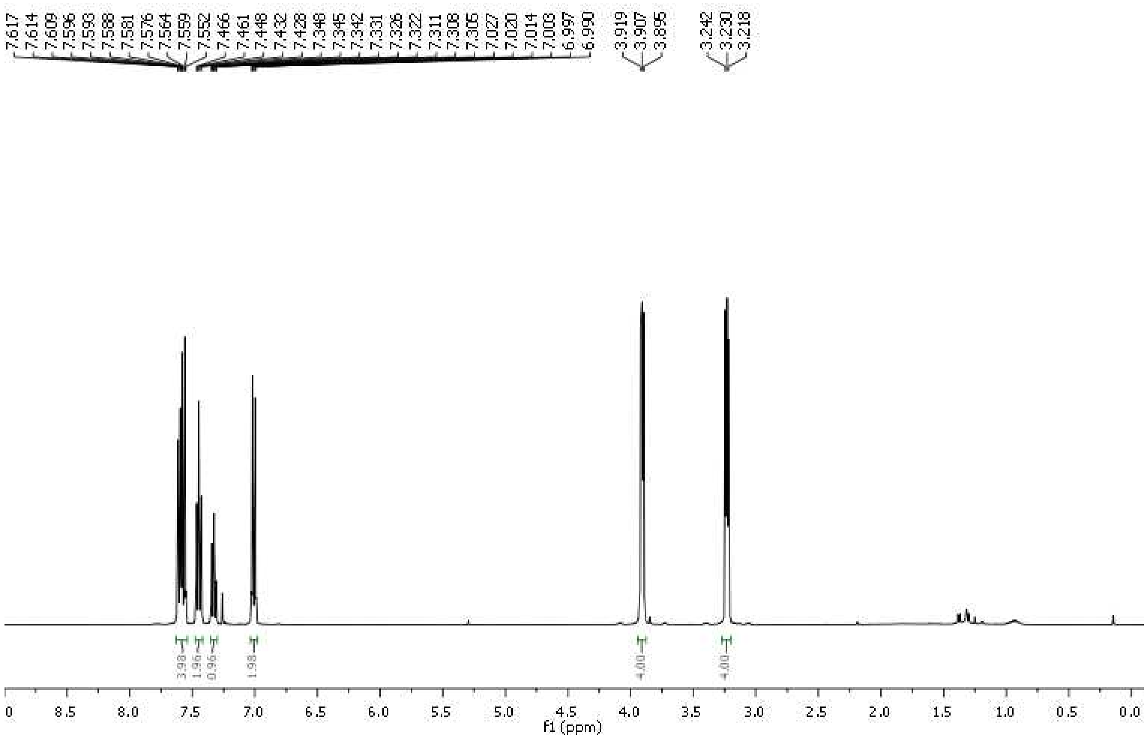
10
f1 (ppm)


N
O

3e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7.461
7.448
7.432
7.428
7.348
7.345
7.342
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7.305
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7.003
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6.990
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3.907
3.895
3.242
3.230
3.218
3.98
1.96
0.96
1.98
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4.00
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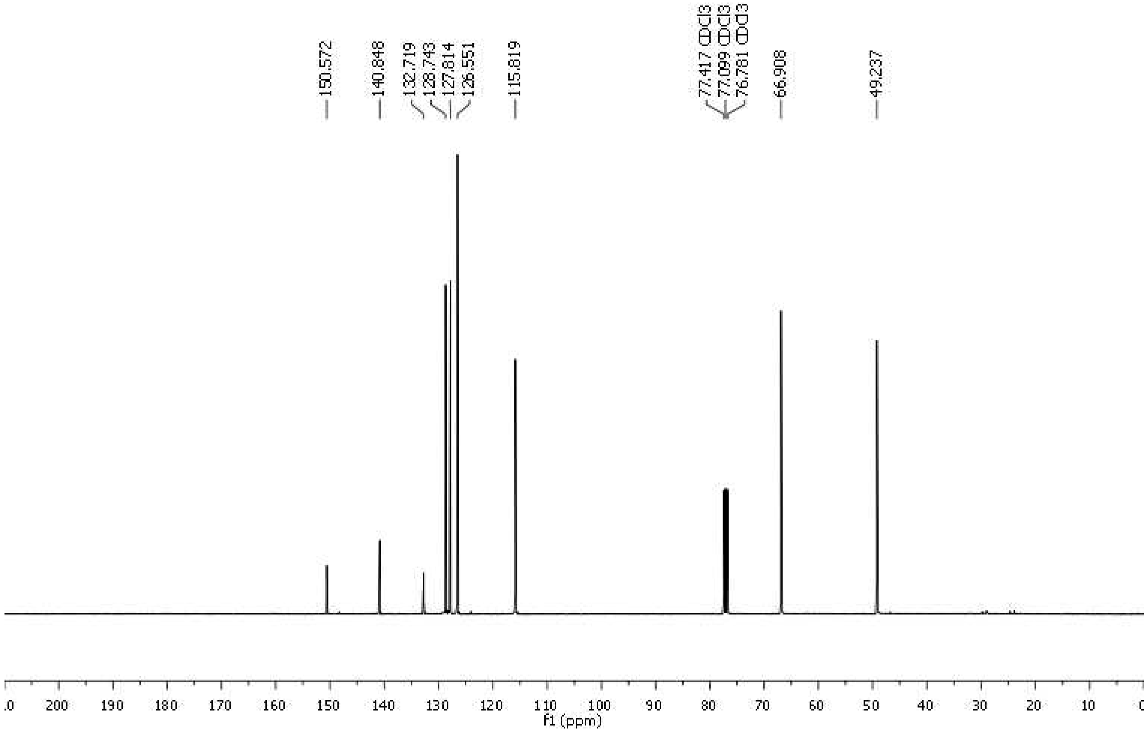
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77.099 CDCl3
76.781 CDCl3
66.908
49.237
200
190
180
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150
140
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20
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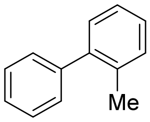
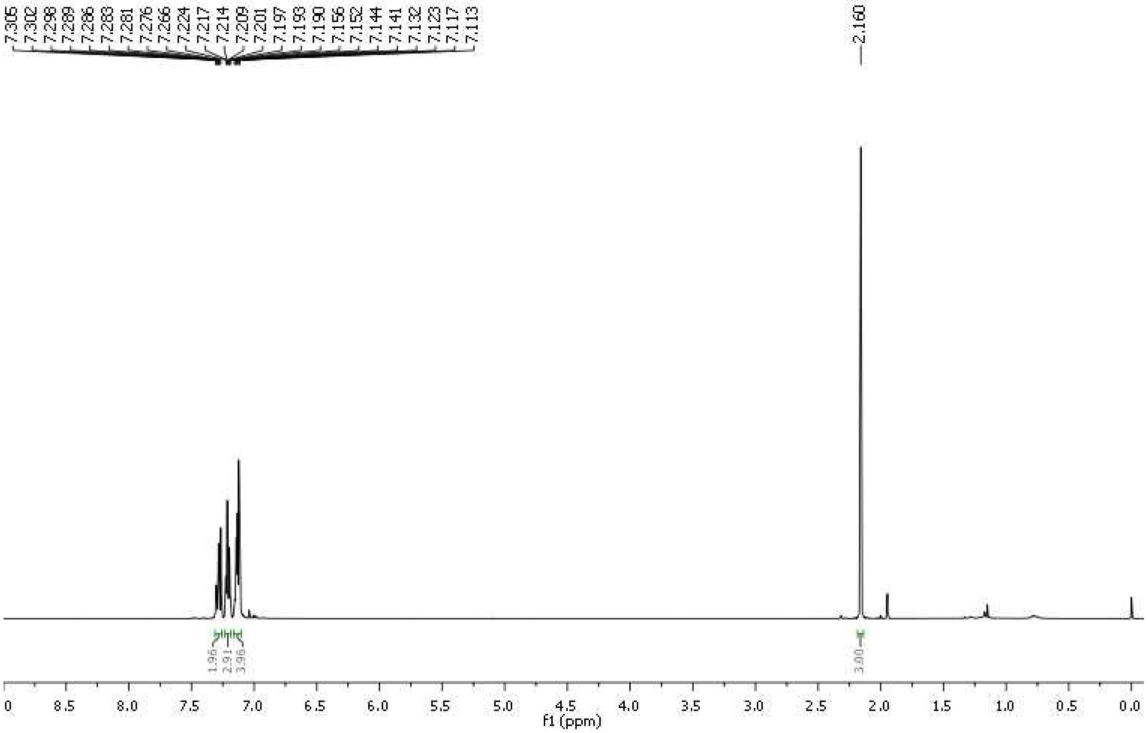
f1 (ppm)


Me

3f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7.201
7.197
7.193
7.190
7.156
7.152
7.144
7.141
7.132
7.123
7.117
7.113
2.160
1.96
2.91
3.96
3.00
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7.5
7.0
6.5
6.0
5.5
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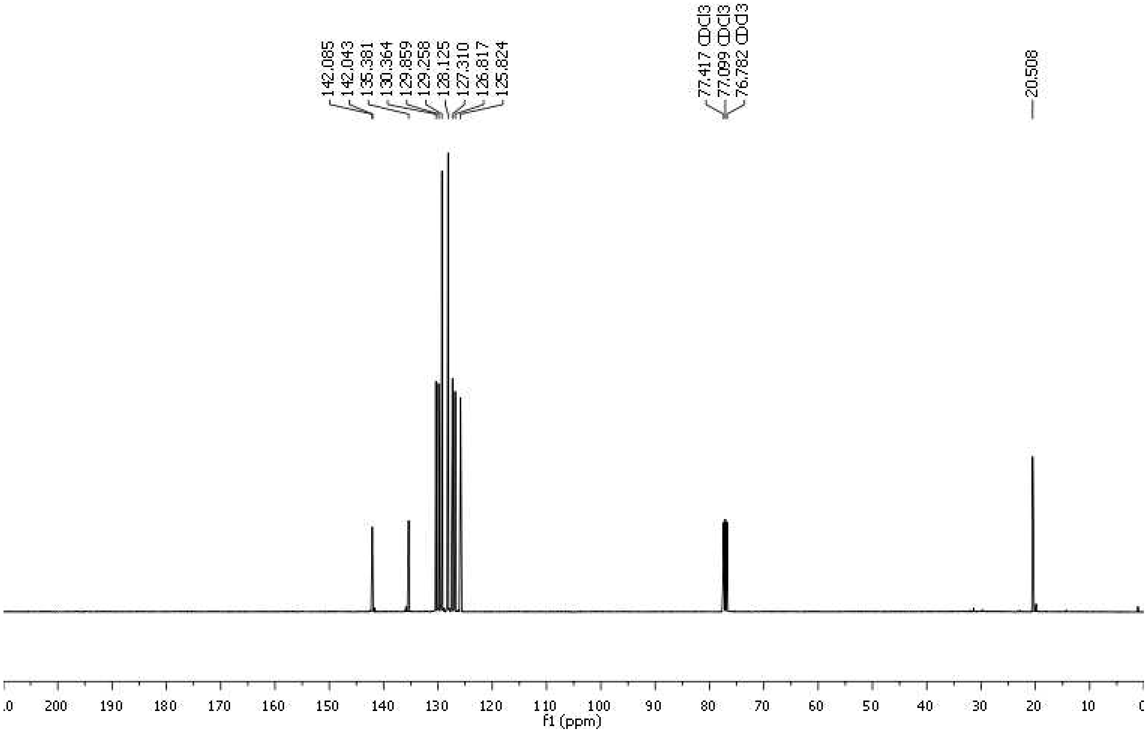
0.0
f1 (ppm)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135.381
130.364
129.859
129.258
128.125
127.310
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125.824
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77.099 CDCl3
76.782 CDCl3
20.508
200
190
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120
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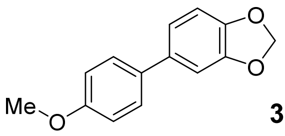
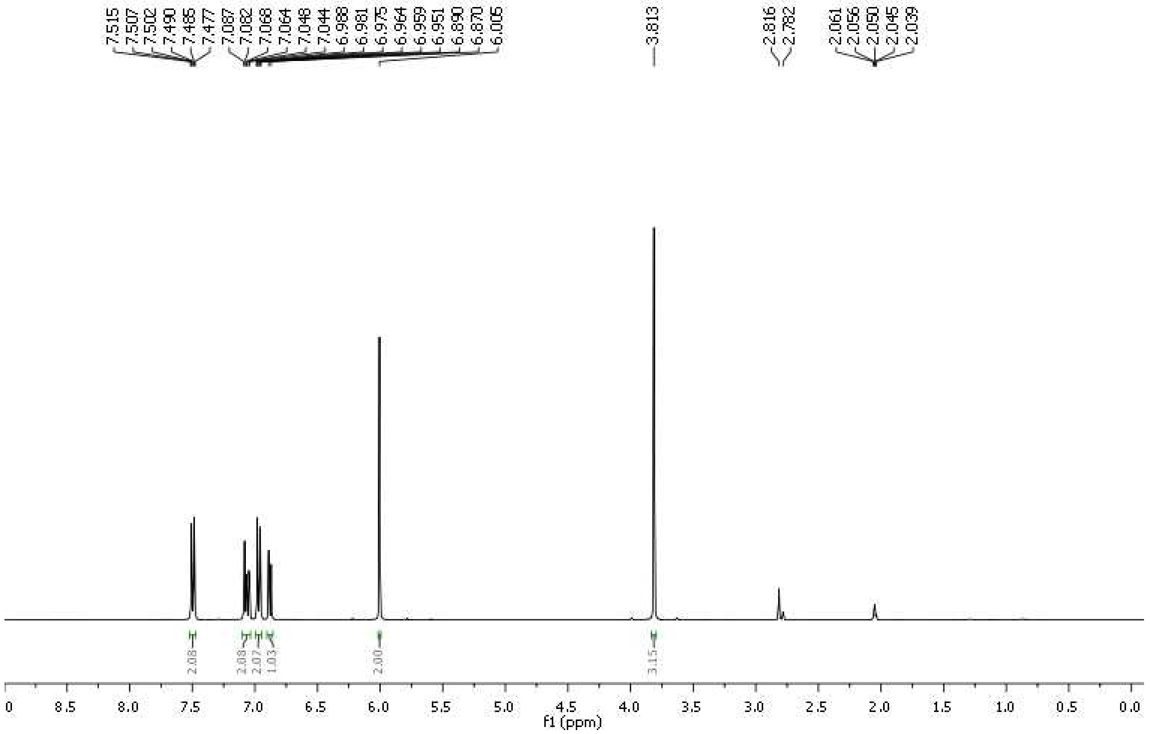
f1 (ppm)


Me
O
O
O

3g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7.064
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7.044
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6.981
6.975
6.964
6.959
6.951
6.890
6.870
6.005
3.813
2.816
2.782
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2.056
2.050
2.045
2.039
2.08
2.08
2.07
1.03
2.00
3.15
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8.5
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6.5
6.0
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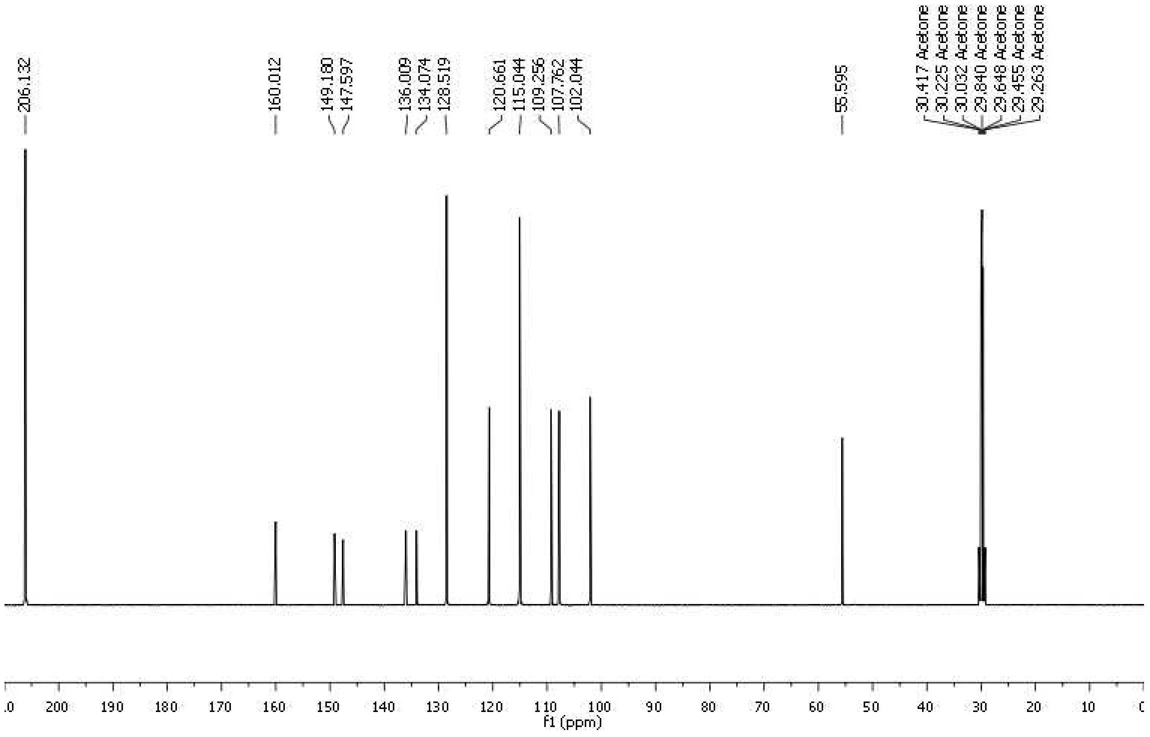
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134.074
128.519
120.661
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109.256
107.762
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55.595
30.417 Acetone
30.225 Acetone
30.032 Acetone
29.840 Acetone
29.648 Acetone
29.455 Acetone
29.263 Acetone
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200
190
180
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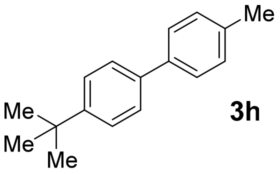
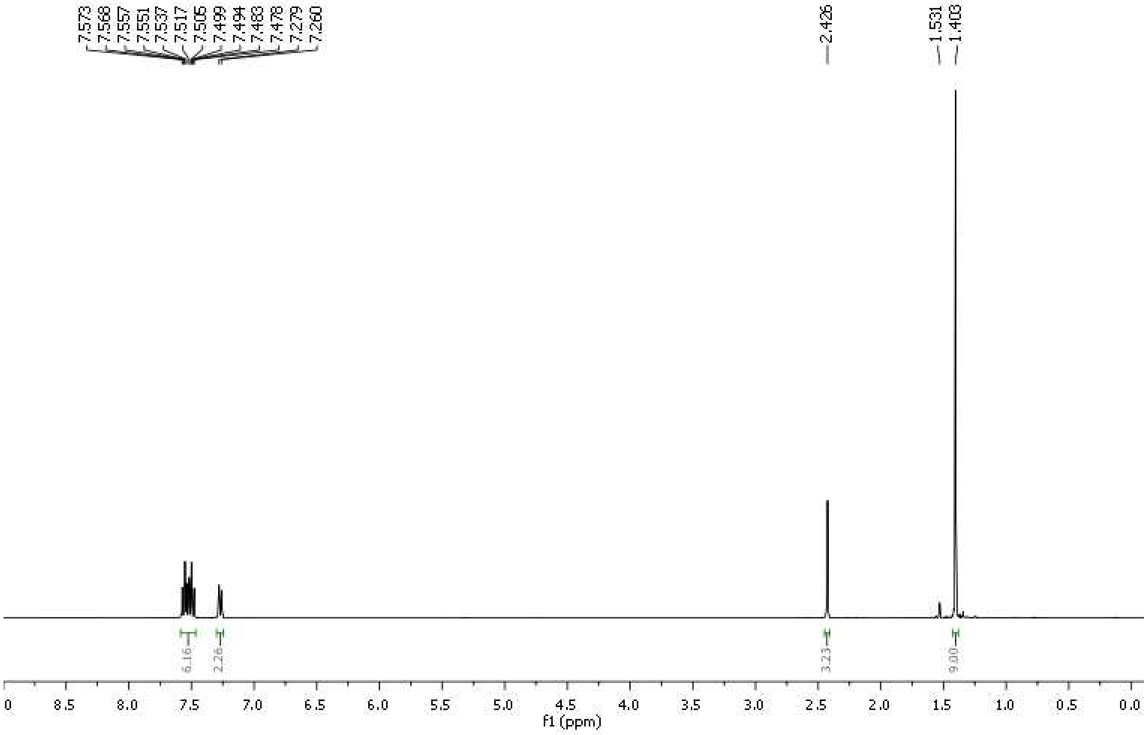
f1 (ppm)


Me
Me
Me
Me

3h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7.499
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7.483
7.478
7.279
7.260
2.426
1.531
1.403
6.16
2.26
3.23
9.00
0
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8.0
7.5
7.0
6.5
6.0
5.5
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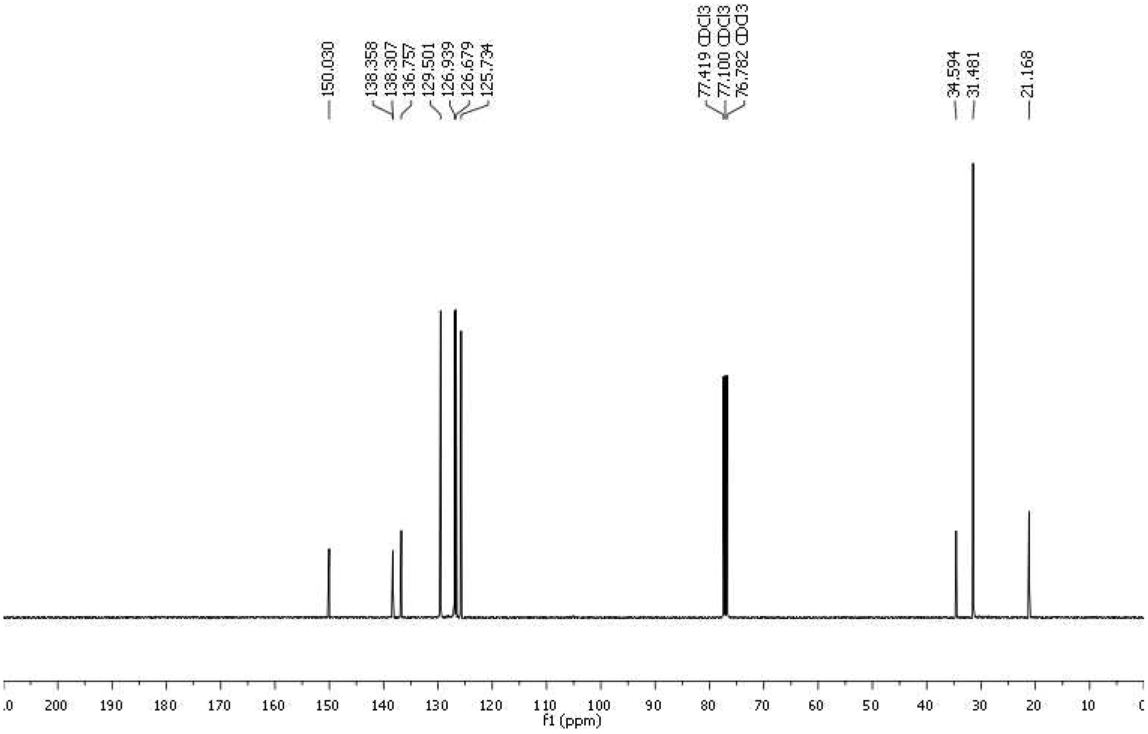
0.5
0.0
f1 (ppm)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138.358
138.307
136.757
129.501
126.939
126.679
125.734
77.419 CDCl3
77.100 CDCl3
76.782 CDCl3
34.594
31.481
21.168
.0
200
190
180
170
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40
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20
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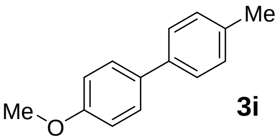
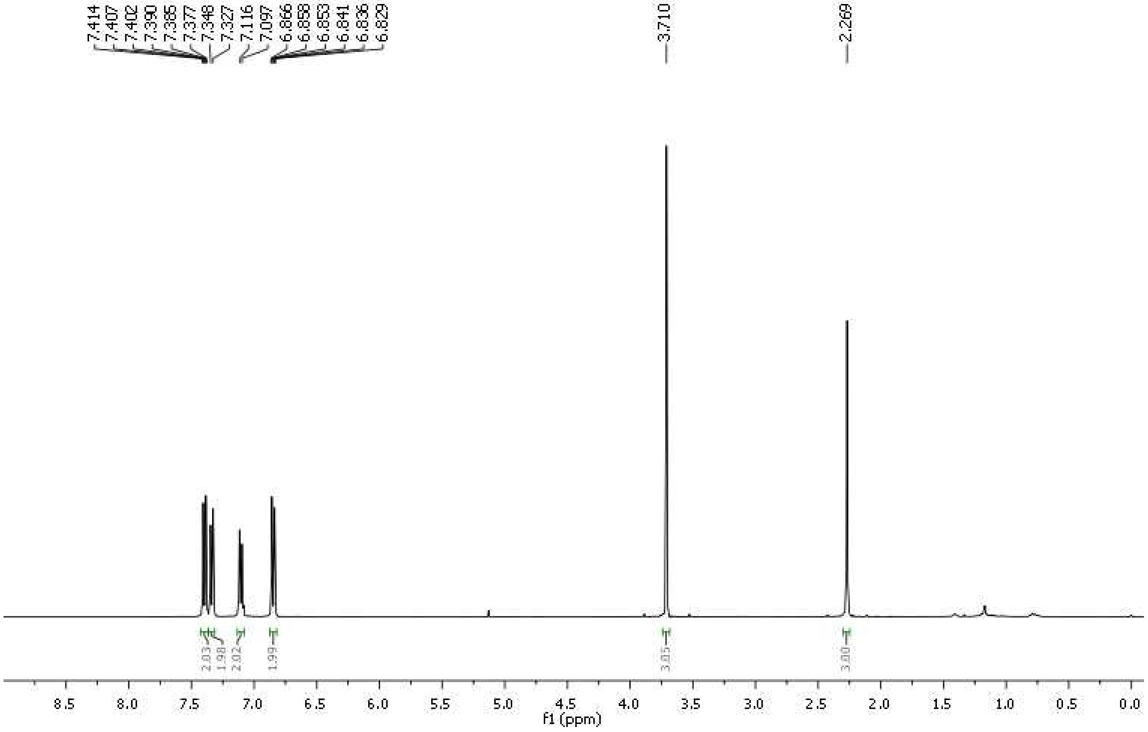
0
f1 (ppm)


Me
Me
O

3i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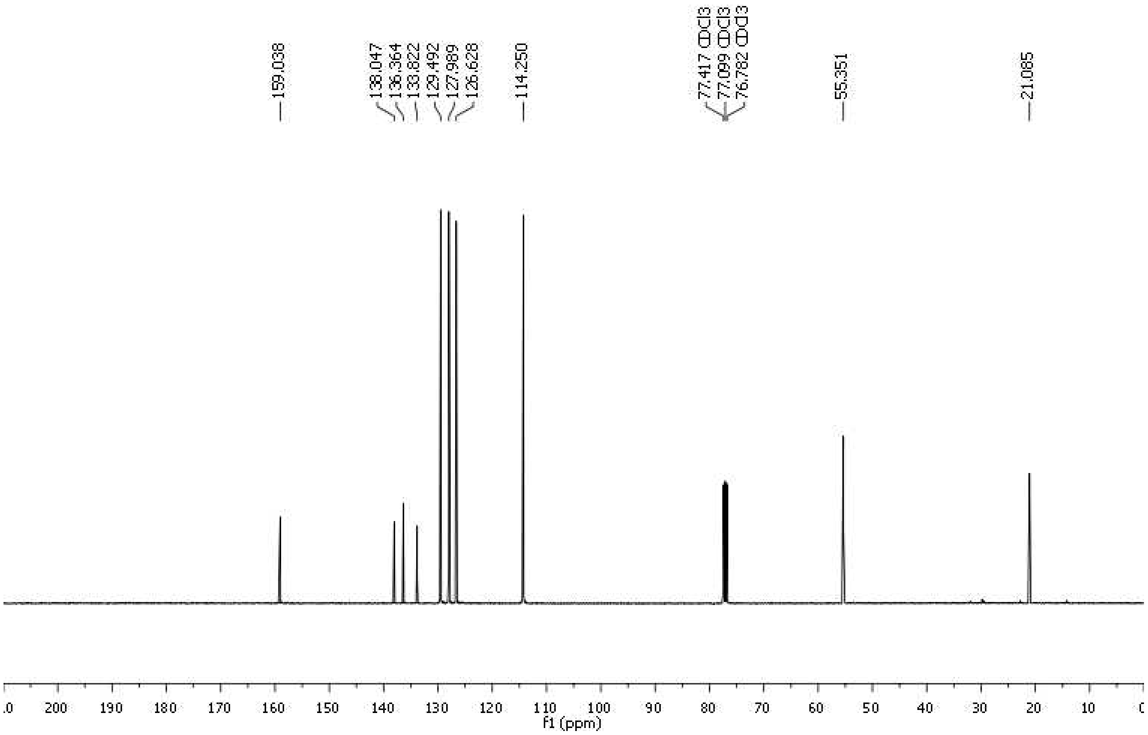
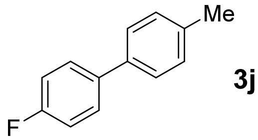
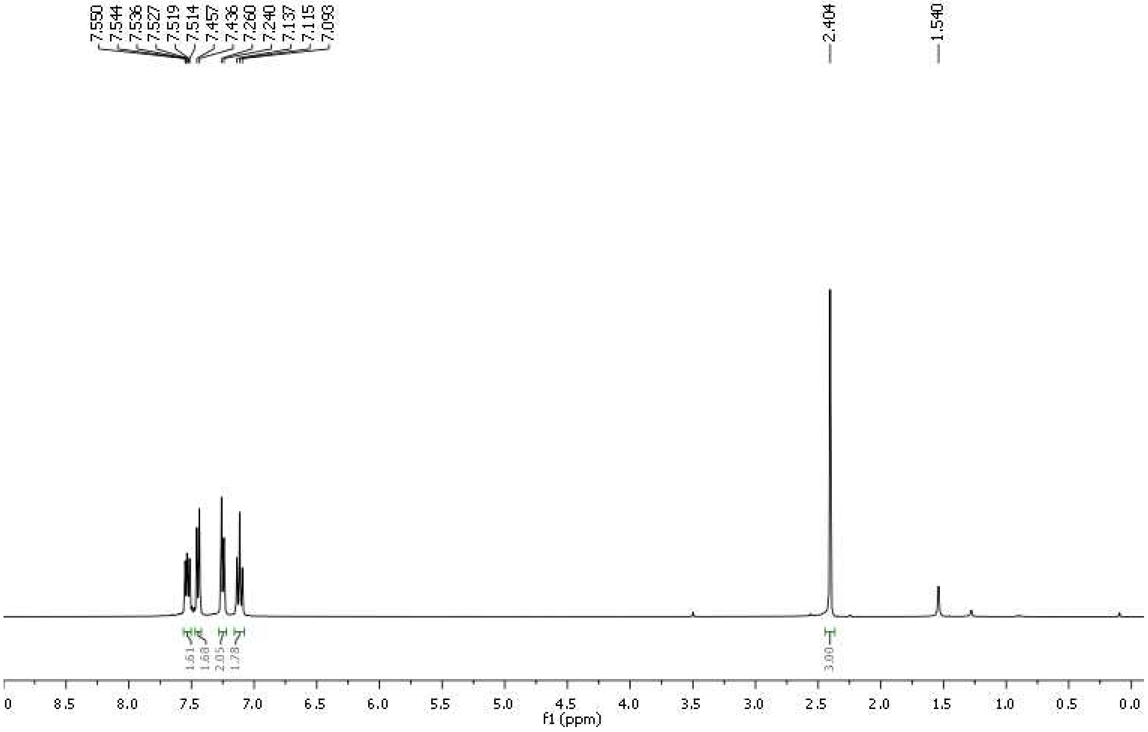
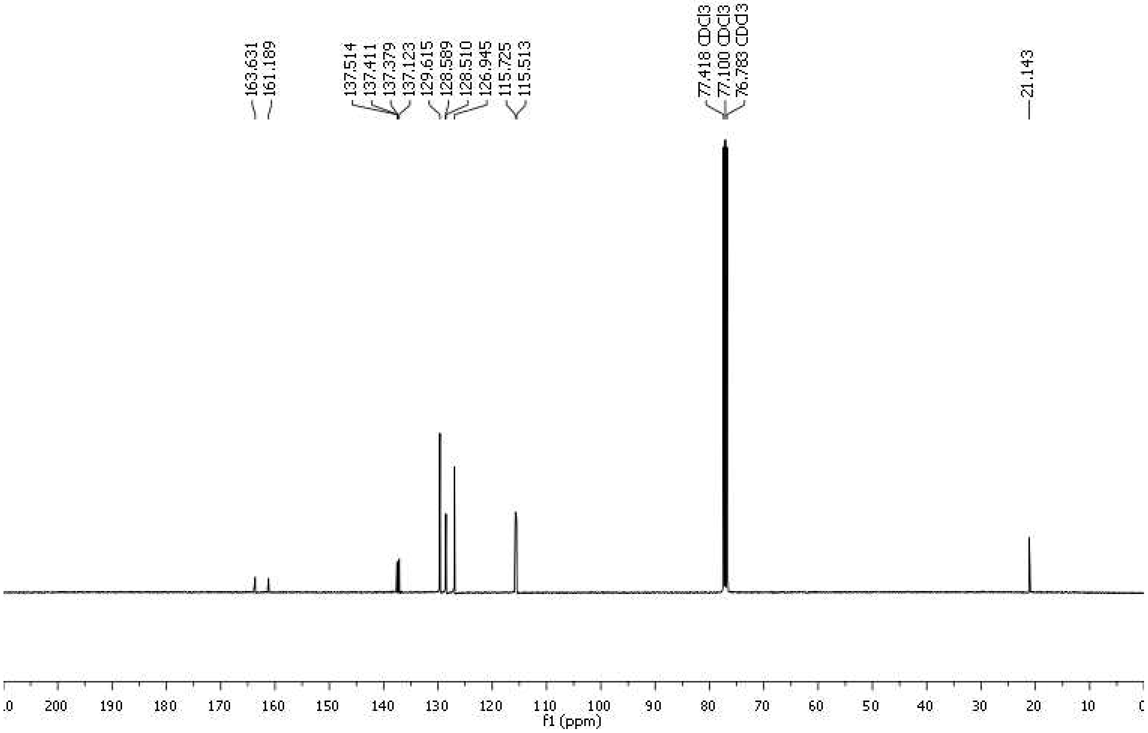
7.407
7.402
7.390
7.385
7.377
7.348
7.327
7.116
7.097
6.866
6.858
6.853
6.841
6.836
6.829
3.710
2.269
2.03
1.98
2.02
1.99
3.05
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

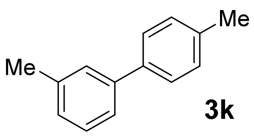

159.038
138.047
136.364
133.822
129.492
127.989
126.628
114.250
77.417 CDCl3
77.099 CDCl3
76.782 CDCl3
55.351
21.085
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
F

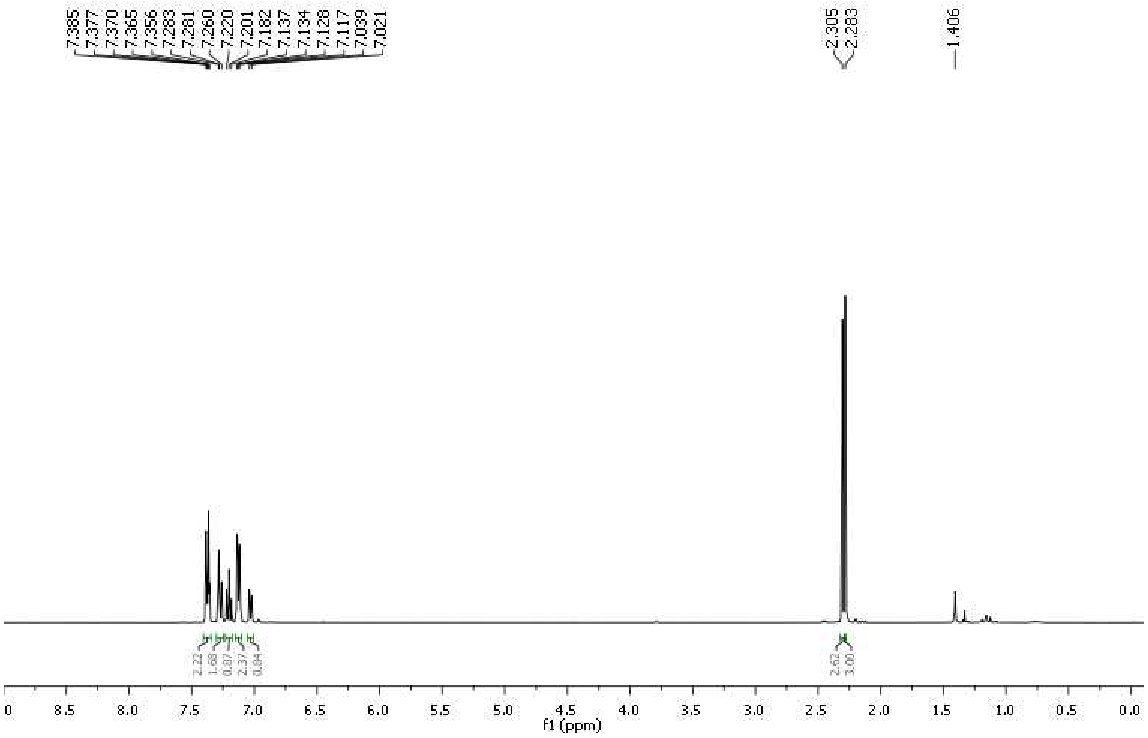
3j

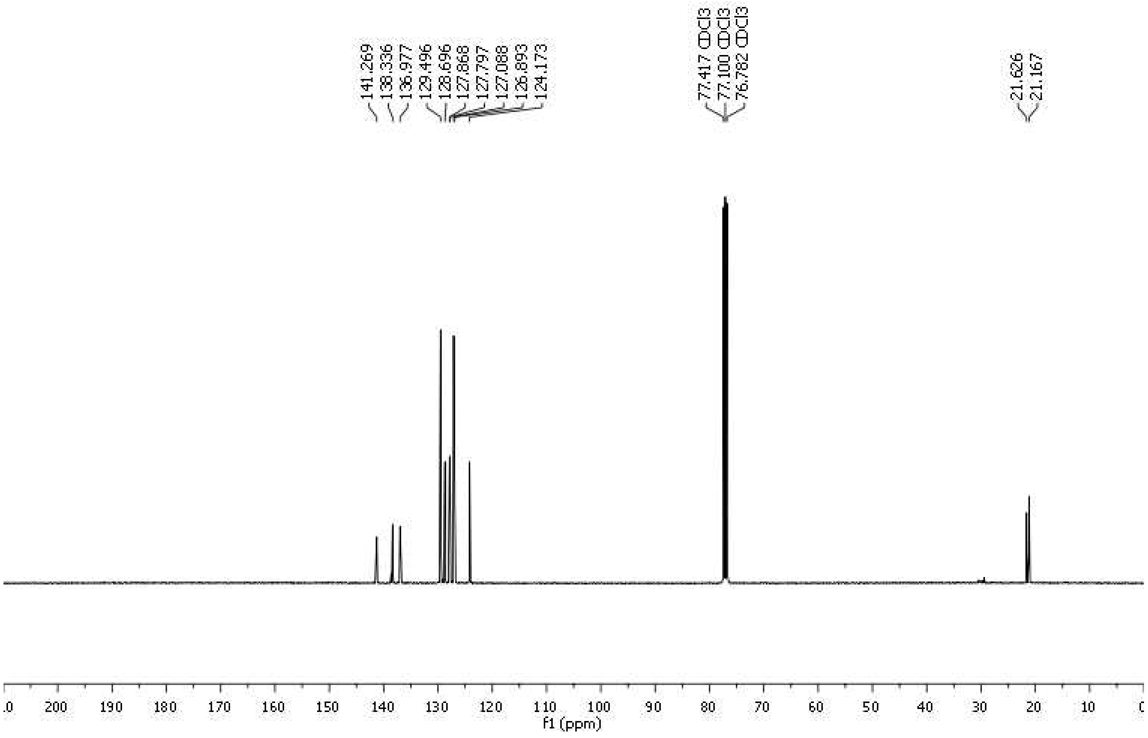

7.550
7.544
7.536
7.527
7.519
7.514
7.457
7.436
7.260
7.240
7.137
7.115
7.093
2.404
1.540
1.61
1.68
2.05
1.78
3.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

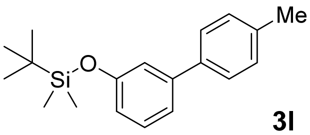

163.631
161.189
137.514
137.411
137.379
137.123
129.615
128.589
128.510
126.945
115.725
115.513
77.418 CDCl3
77.100 CDCl3
76.783 CDCl3
21.143
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me

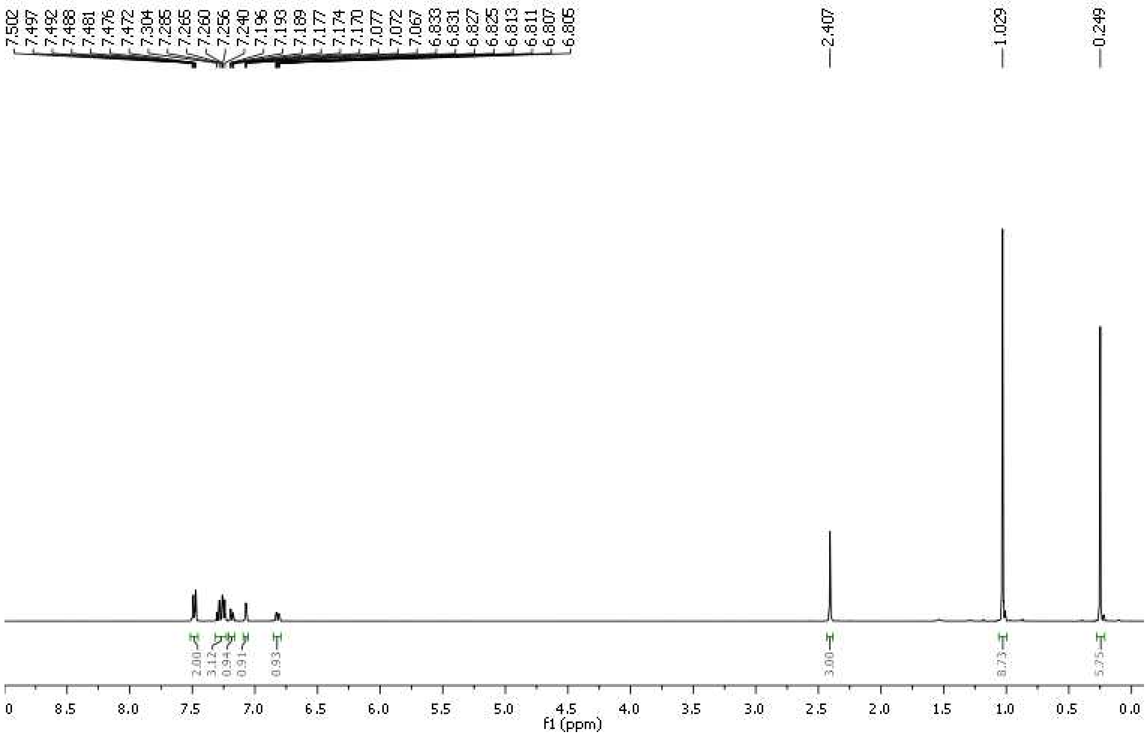
3k

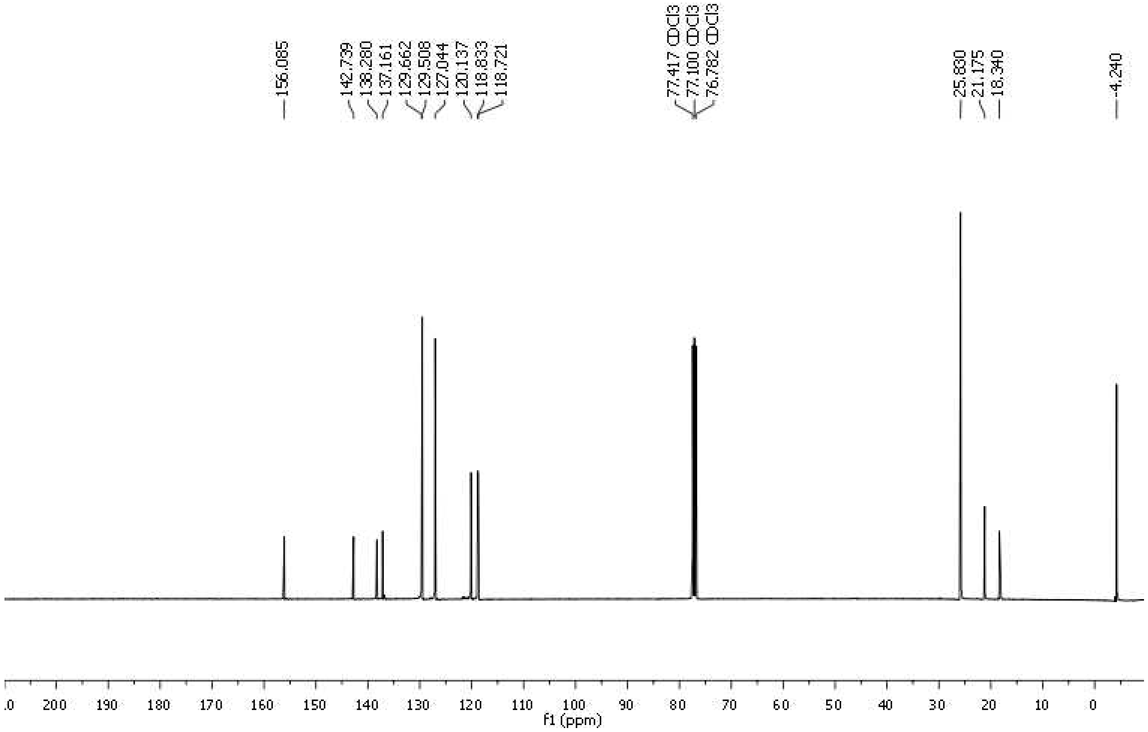

7.385
7.377
7.370
7.365
7.356
7.283
7.281
7.260
7.220
7.201
7.182
7.137
7.134
7.128
7.117
7.039
7.021
2.305
2.283
1.406
2.22
1.68
0.87
2.37
0.84
2.62
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

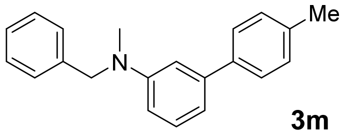

141.269
138.336
136.977
129.496
128.696
127.868
127.797
127.088
126.893
124.173
77.417 CDCl3
77.100 CDCl3
76.782 CDCl3
21.626
21.167
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Si
O

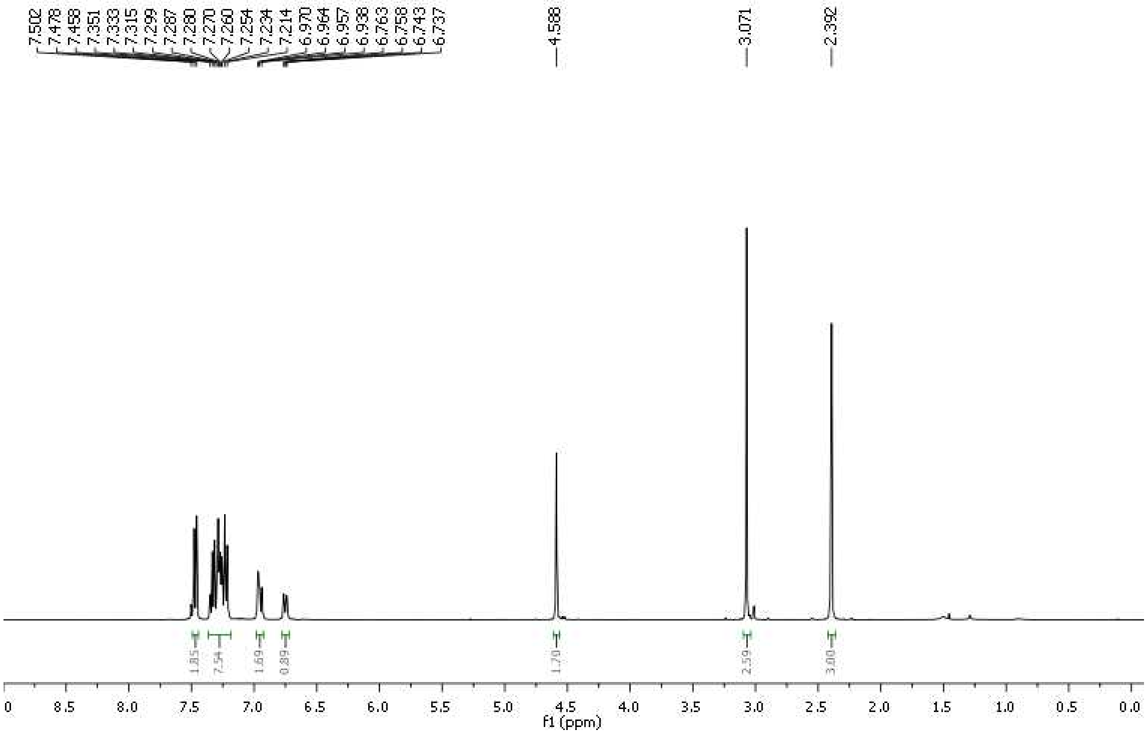
3l

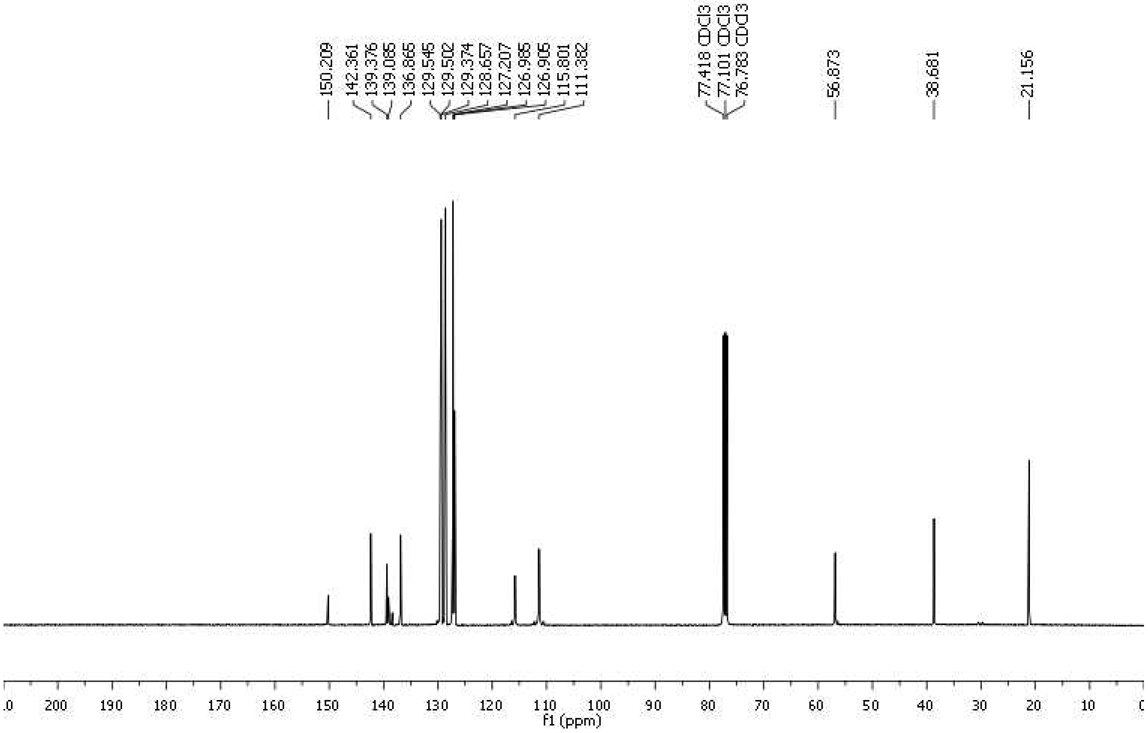

7.502
7.497
7.492
7.488
7.481
7.476
7.472
7.304
7.285
7.265
7.260
7.256
7.240
7.196
7.193
7.189
7.177
7.174
7.170
7.077
7.072
7.067
6.833
6.831
6.827
6.825
6.813
6.811
6.807
6.805
2.407
1.029
0.249
2.00
3.12
0.94
0.91
0.93
3.00
8.73
5.75
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.085
142.739
138.280
137.161
129.662
129.508
127.044
120.137
118.833
118.721
77.417 CDCl3
77.100 CDCl3
76.782 CDCl3
25.830
21.175
18.340
-4.240
.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
N

3m


7.502
7.478
7.458
7.351
7.333
7.315
7.299
7.287
7.280
7.270
7.260
7.254
7.234
7.214
6.970
6.964
6.957
6.938
6.763
6.758
6.743
6.737
4.588
3.071
2.392
1.85
7.54
1.69
0.89
1.70
2.59
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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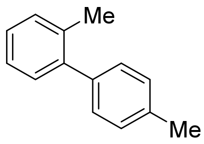
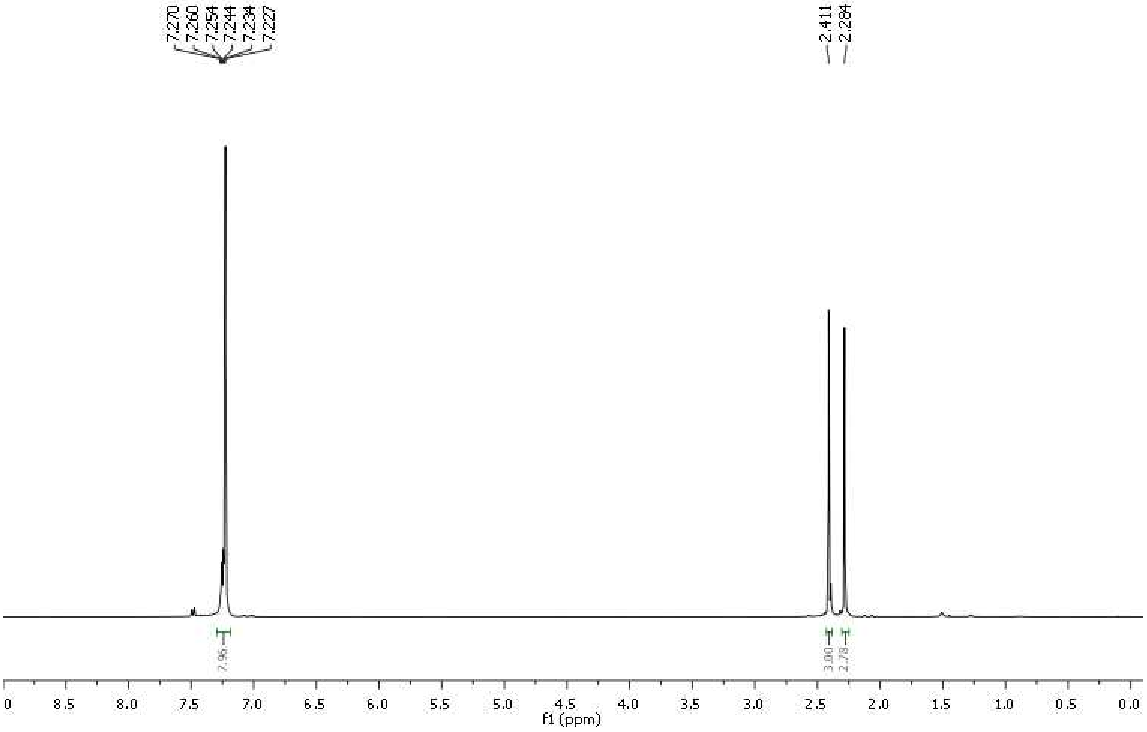
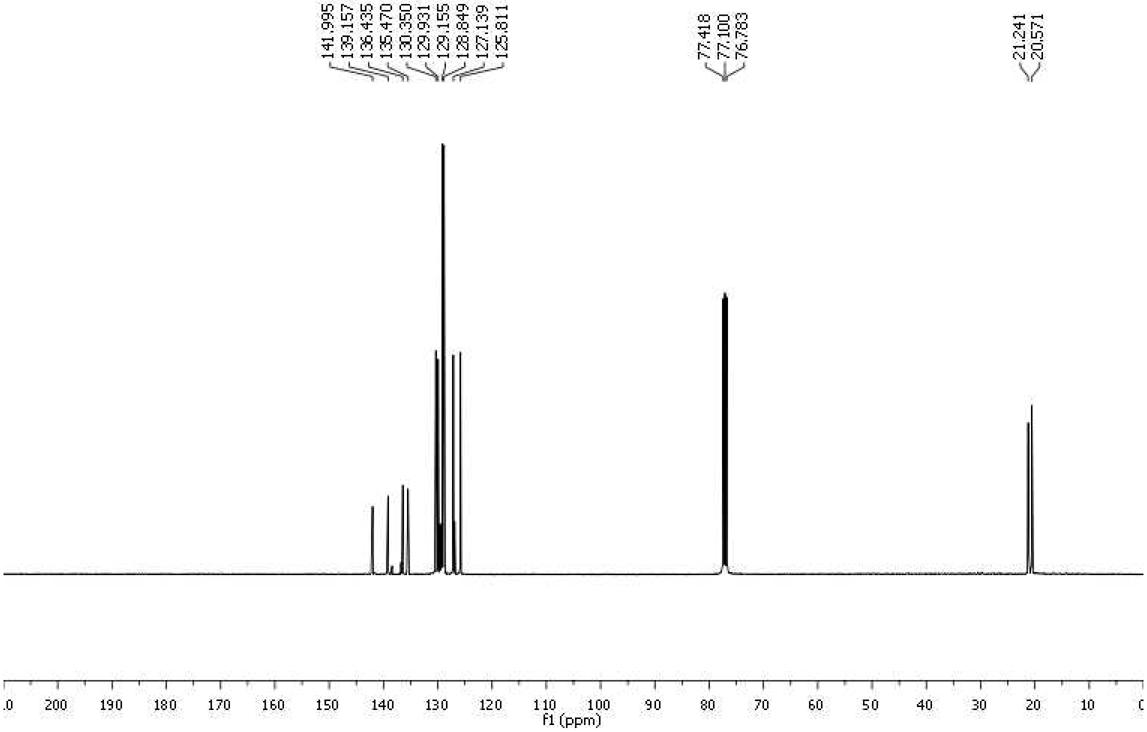
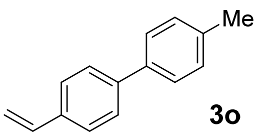
142.361
139.376
139.085
136.865
129.545
129.502
129.374
128.657
127.207
126.985
126.905
115.801
111.382
77.418 CDCl3
77.101 CDCl3
76.783 CDCl3
56.873
38.681
21.156
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me

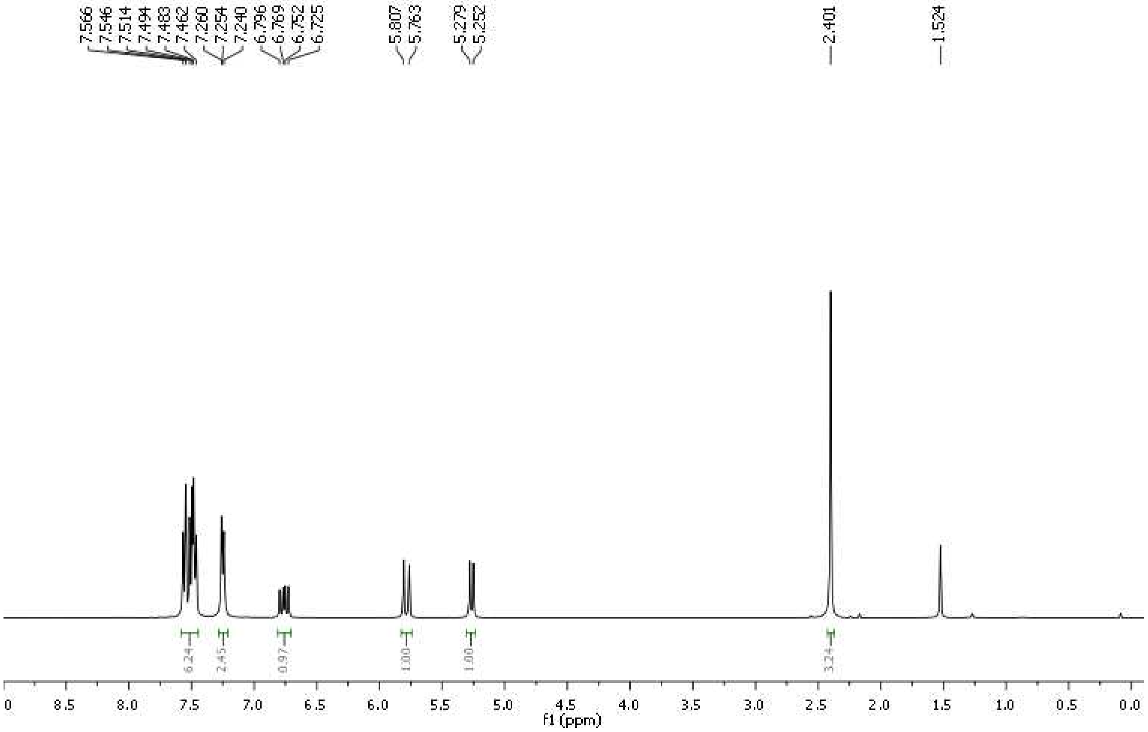
3n

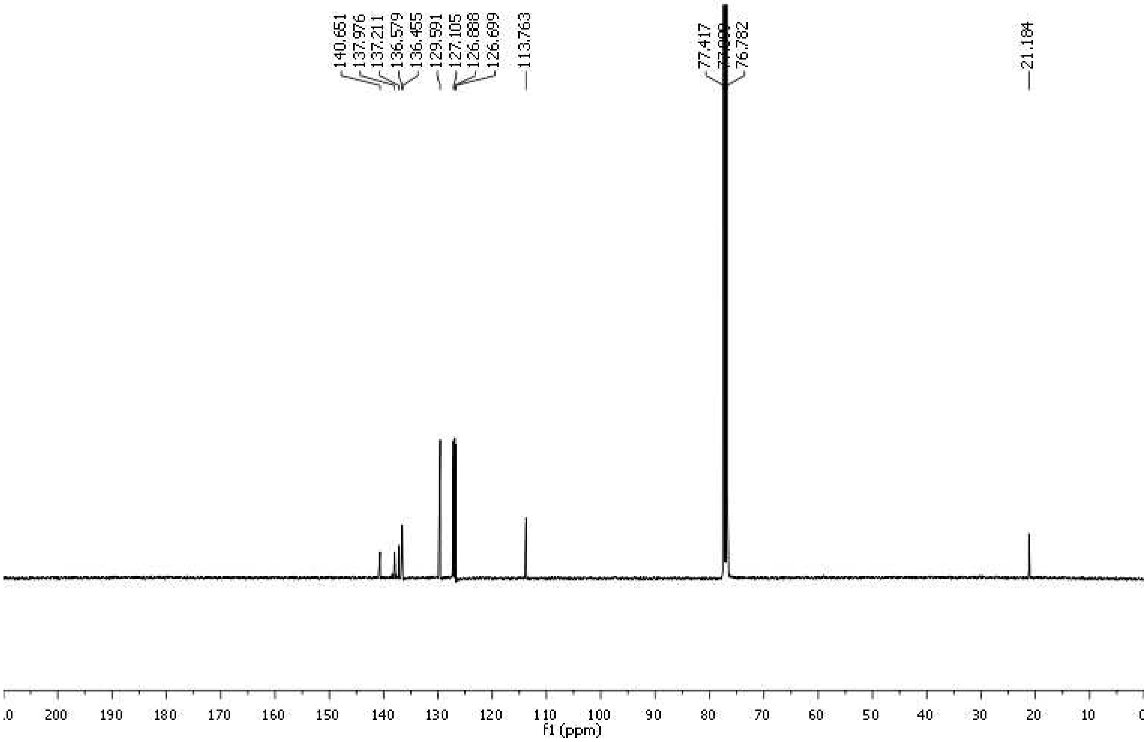

7.270
7.260
7.254
7.244
7.234
7.227
2.411
2.284
2.96
3.00
2.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

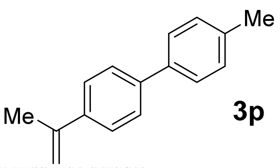

141.995
139.157
136.435
135.470
130.350
129.931
129.155
128.849
127.139
125.811
77.418
77.100
76.783
21.241
20.571
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me

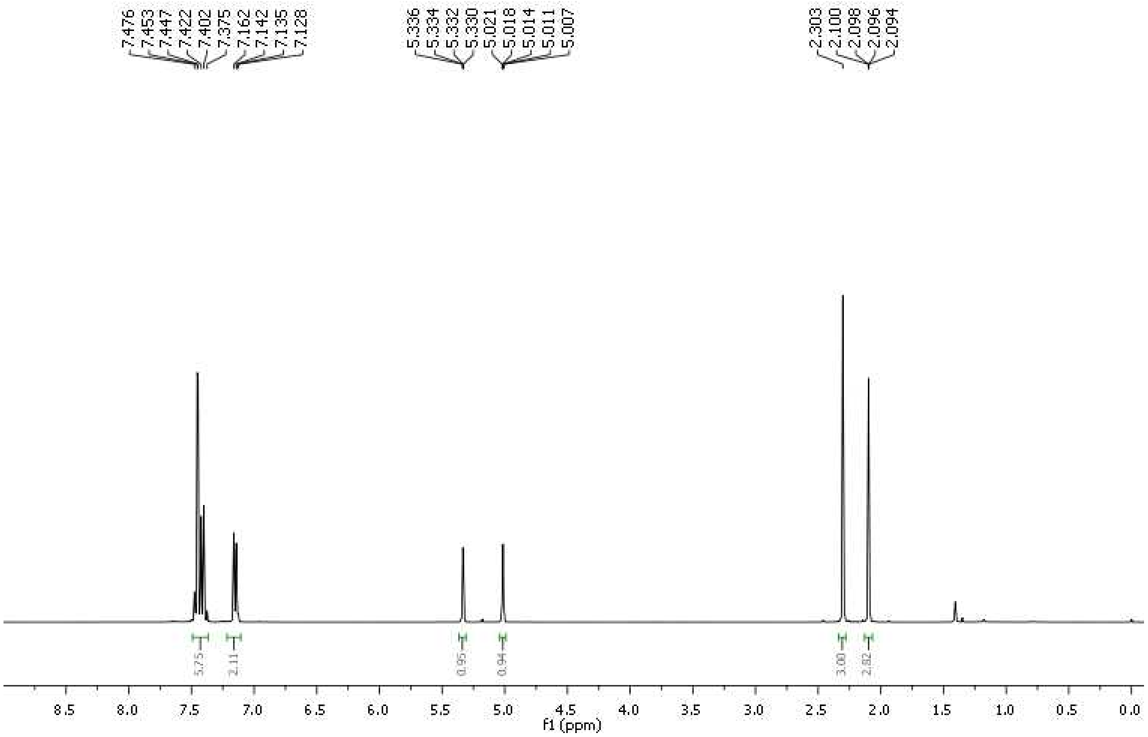
3o


7.566
7.546
7.514
7.494
7.483
7.462
7.260
7.254
7.240
6.796
6.769
6.752
6.725
5.807
5.763
5.279
5.252
2.401
1.524
6.24
2.45
0.97
1.00
1.00
3.24
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)


140.651
137.976
137.211
136.579
136.455
129.591
127.105
126.888
126.699
113.763
77.417
77.000
76.782
21.184
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me

3p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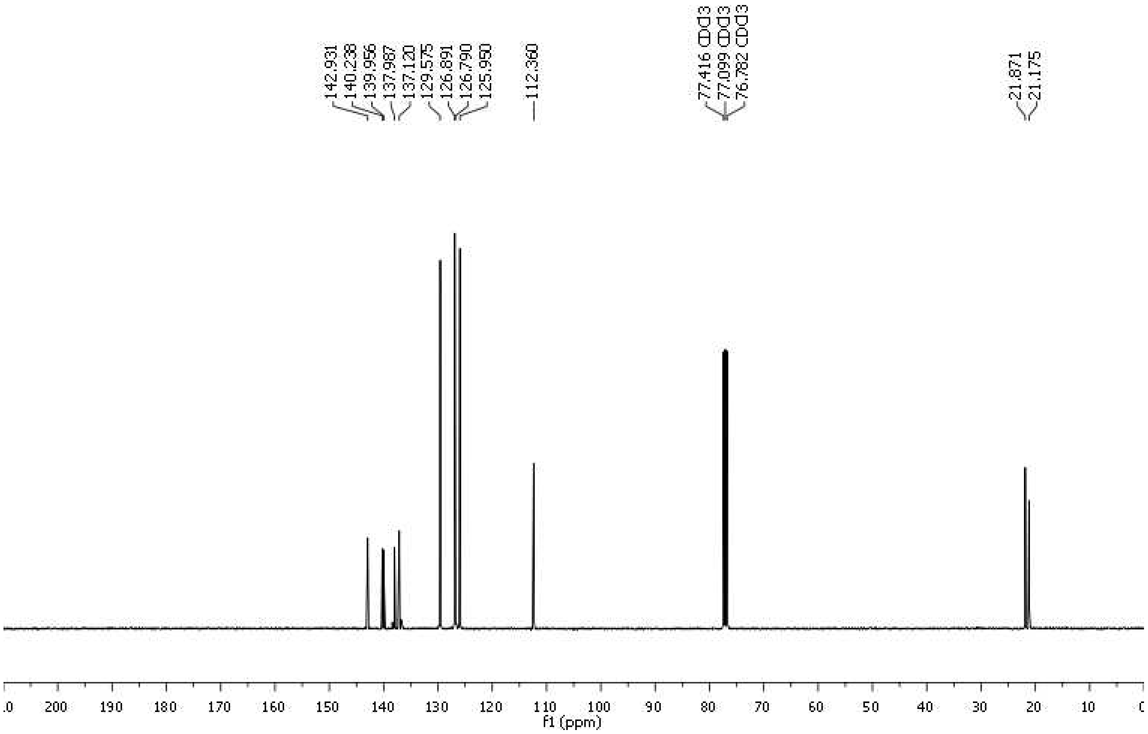
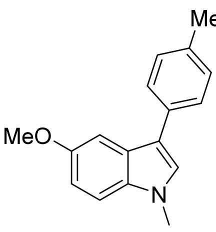
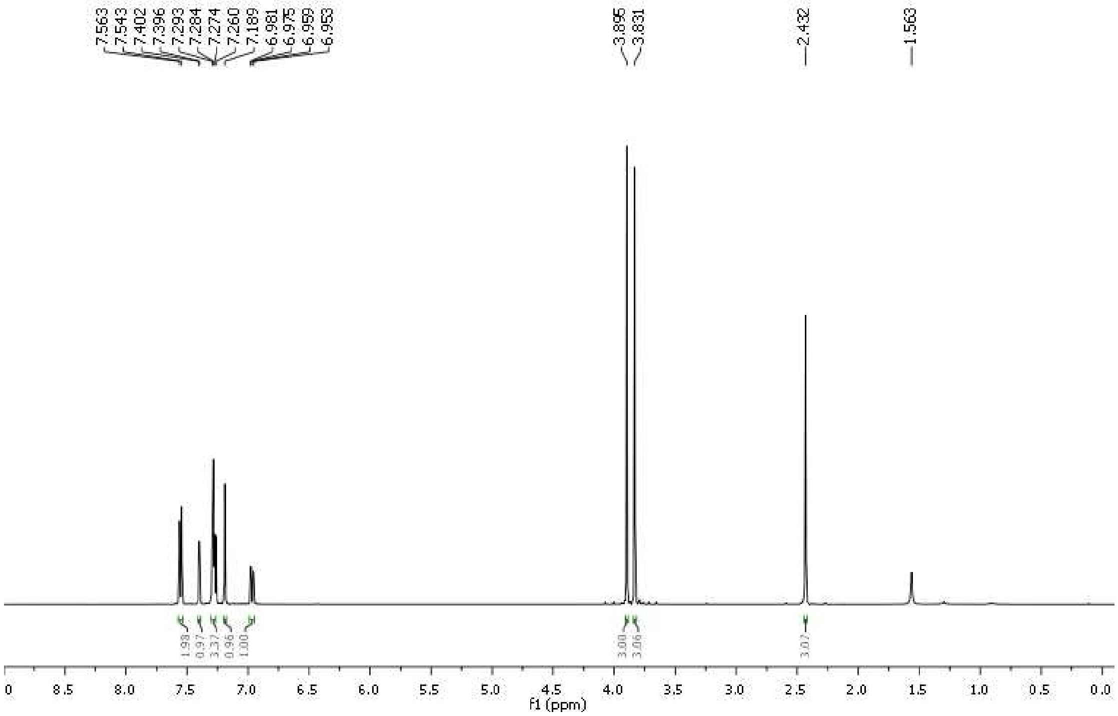
7.447
7.422
7.402
7.375
7.162
7.142
7.135
7.128
5.336
5.334
5.332
5.330
5.021
5.018
5.014
5.011
5.007
2.303
2.100
2.098
2.096
2.094
5.75
2.11
0.95
0.94
3.00
2.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.931
140.238
139.956
137.987
137.120
129.575
126.891
126.790
125.950
112.360
77.416 CDCl3
77.099 CDCl3
76.782 CDCl3
21.871
21.175
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
MeO
N

3s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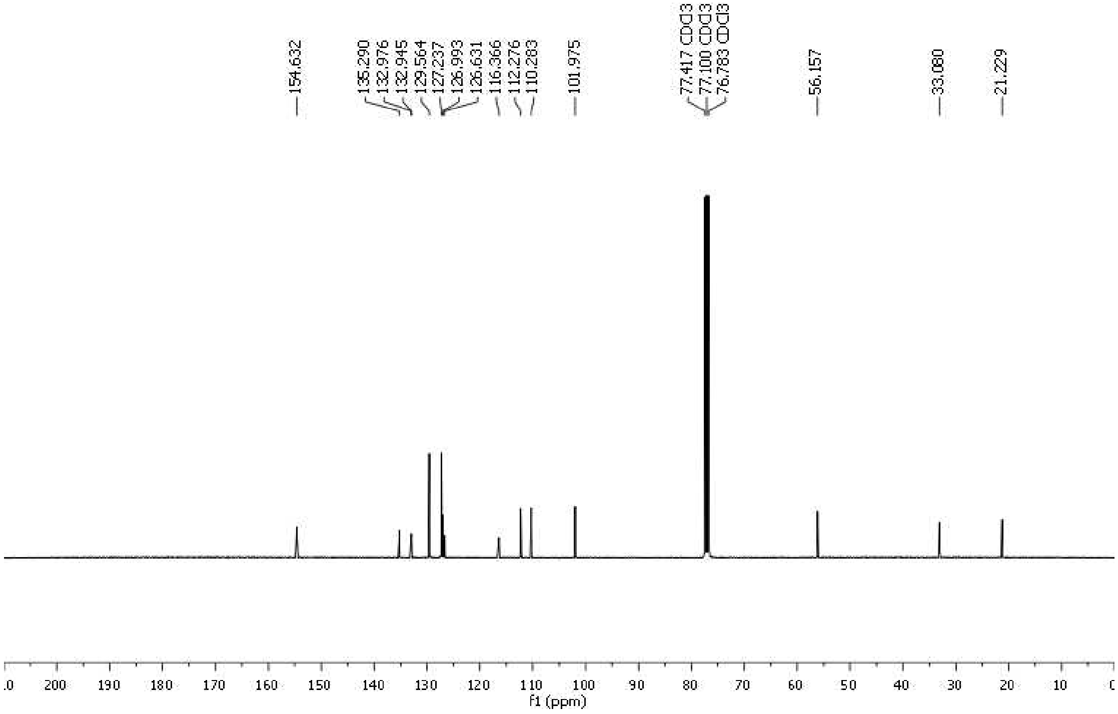
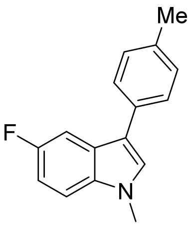
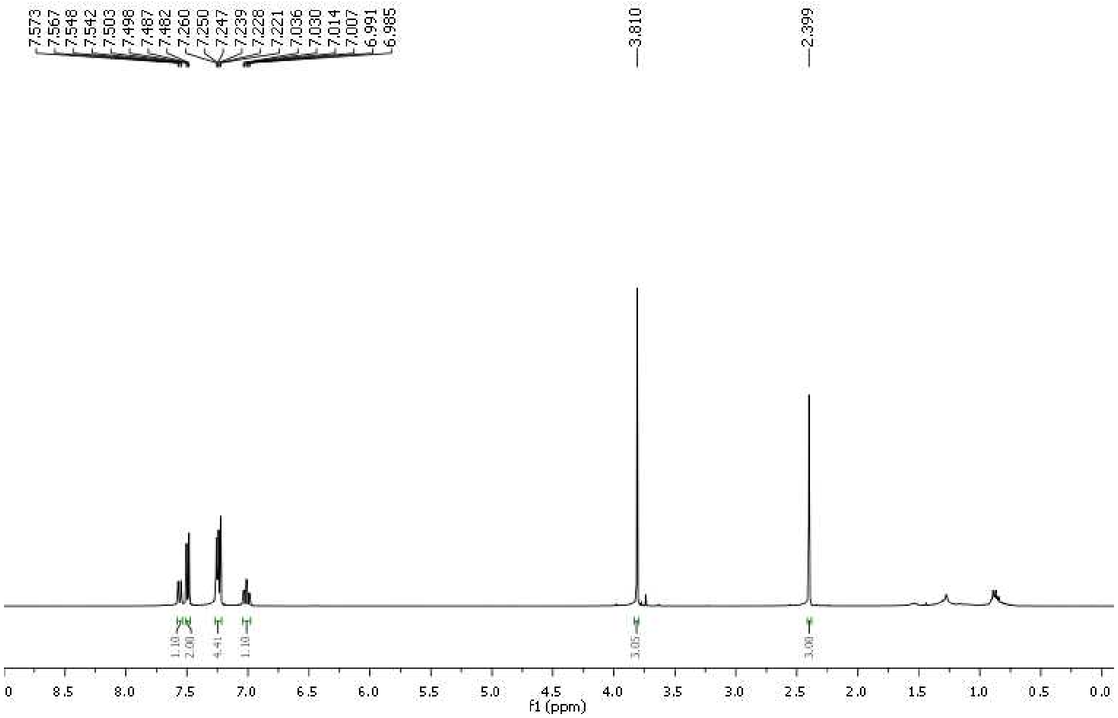
7.402
7.396
7.293
7.284
7.274
7.260
7.189
6.981
6.975
6.959
6.953
3.895
3.831
2.432
1.563
1.98
0.97
3.37
0.96
1.00
3.00
3.06
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.632
135.290
132.976
132.945
129.564
127.237
126.993
126.631
116.366
112.276
110.283
101.975
77.417 CDCl3
77.100 CDCl3
76.783 CDCl3
56.157
33.080
21.229
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
F
N

3t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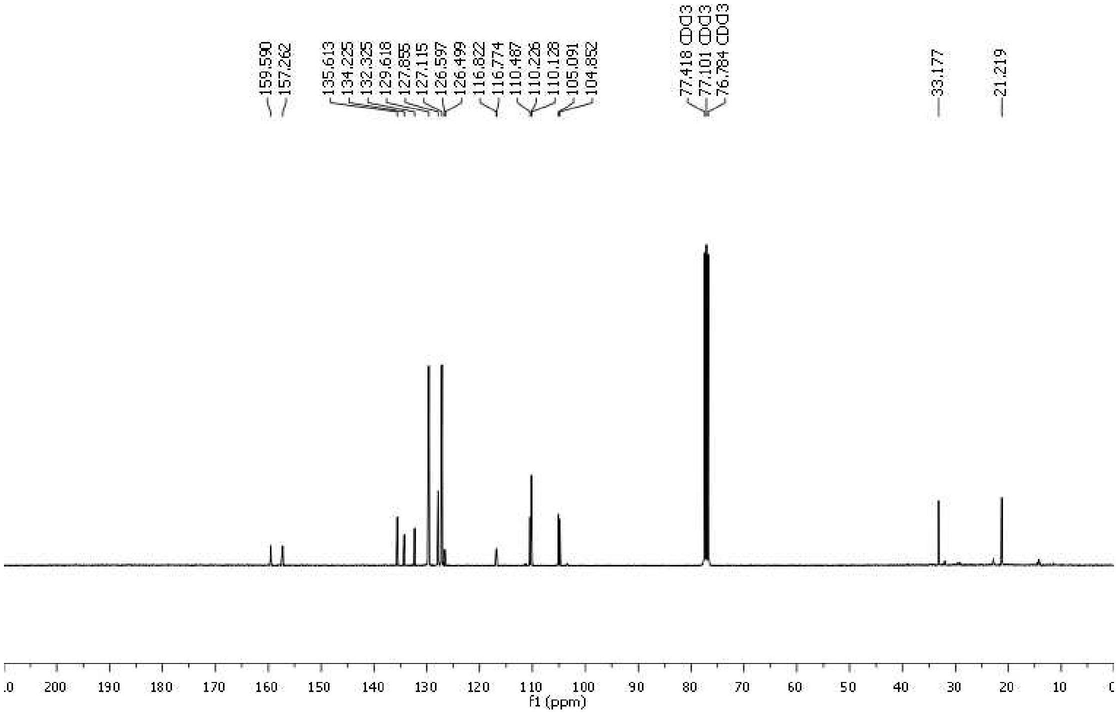
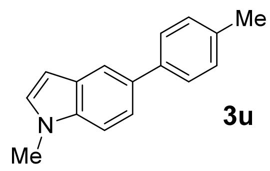
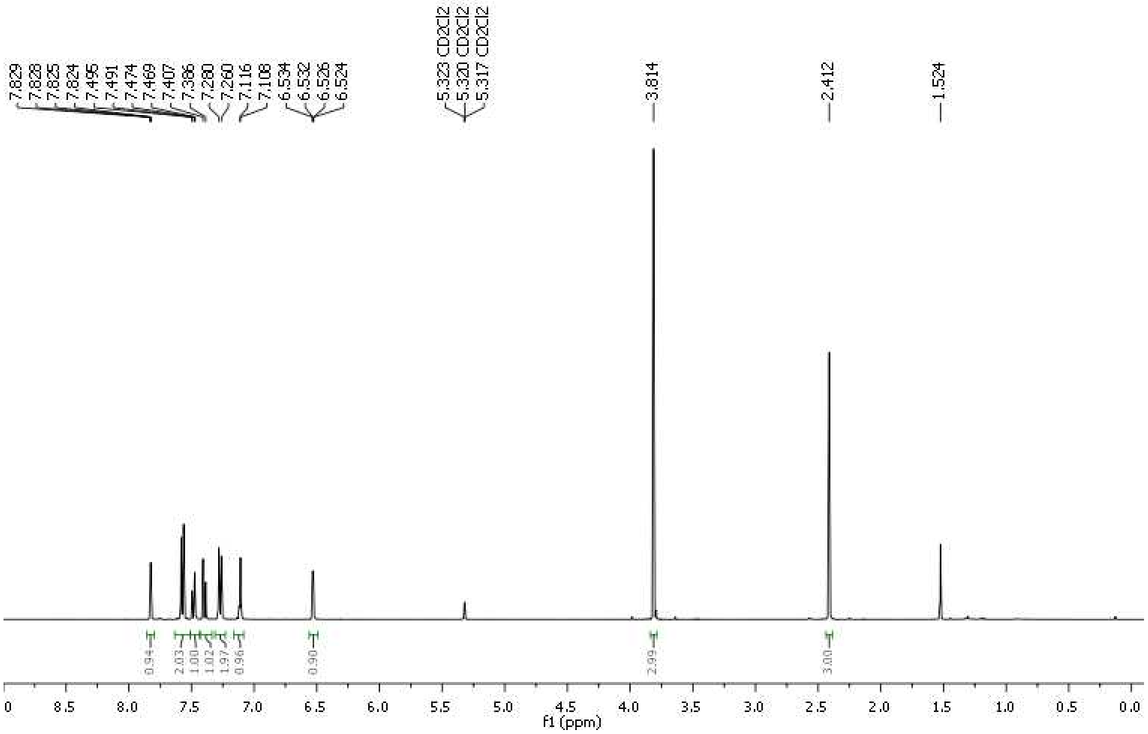
7.487
7.482
7.260
7.250
7.247
7.239
7.228
7.221
7.036
7.030
7.014
7.007
6.991
6.985
3.810
2.399
1.10
2.00
4.41
1.10
3.05
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.590
157.262
135.613
134.225
132.325
129.618
127.855
127.115
126.597
126.499
116.822
116.774
110.487
110.226
110.128
105.091
104.852
77.418 CDCl3
77.101 CDCl3
76.784 CDCl3
33.177
21.219
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
N
Me

3u


7.829
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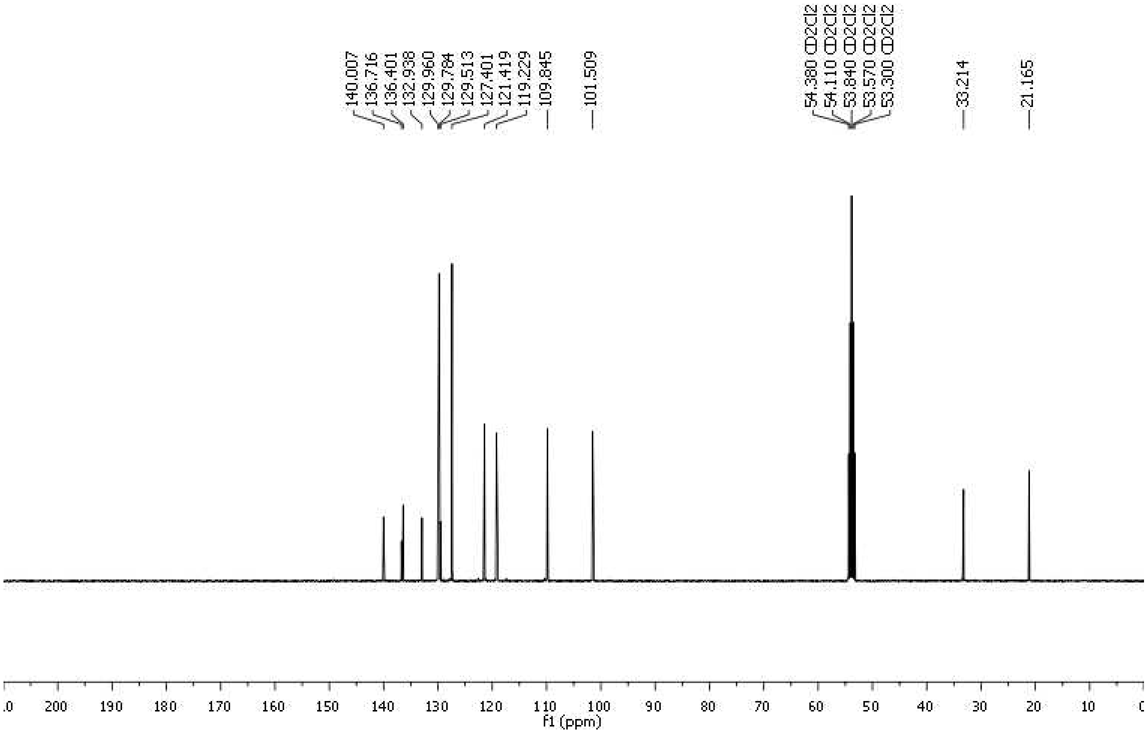
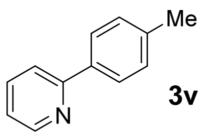
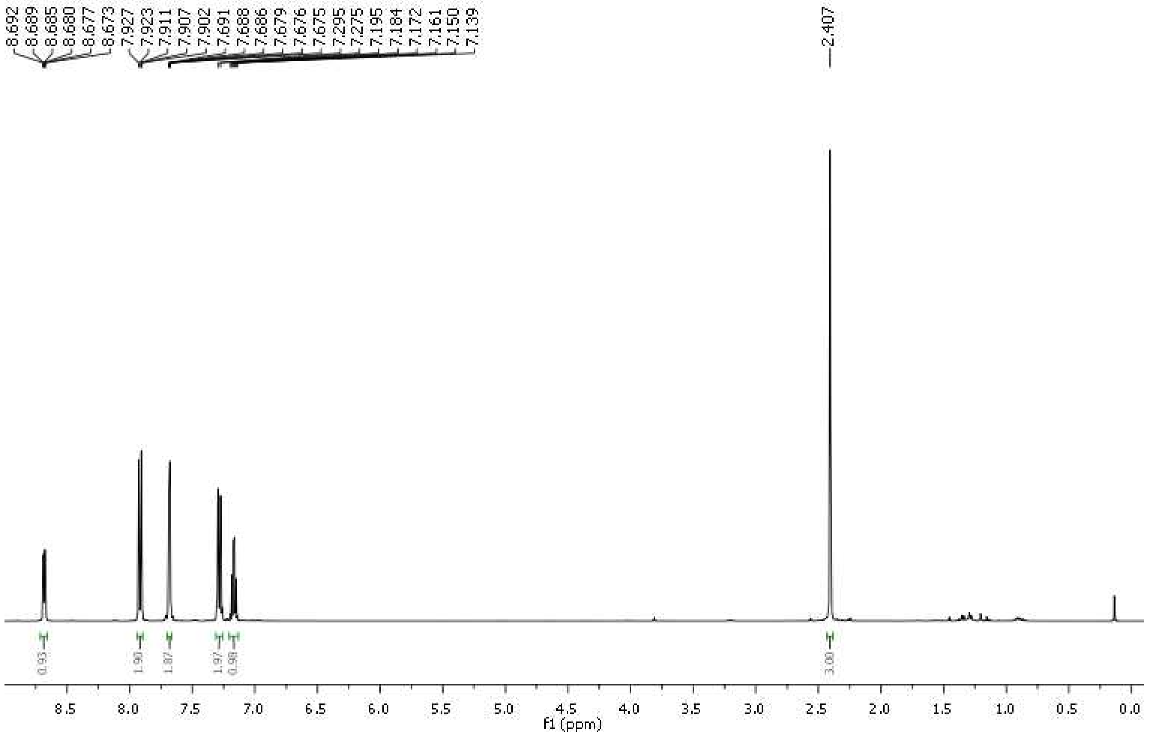
7.825
7.824
7.495
7.491
7.474
7.469
7.407
7.386
7.280
7.260
7.116
7.108
6.534
6.532
6.526
6.524
5.323 CD2Cl2
5.320 CD2Cl2
5.317 CD2Cl2
3.814
2.412
1.524
0.94
2.03
1.00
1.02
1.97
0.96
0.90
2.99
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.007
136.716
136.401
132.938
129.960
129.784
129.513
127.401
121.419
119.229
109.845
101.509
54.380 CD2Cl2
54.110 CD2Cl2
53.840 CD2Cl2
53.570 CD2Cl2
53.300 CD2Cl2
33.214
21.165
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
N

3v


8.692
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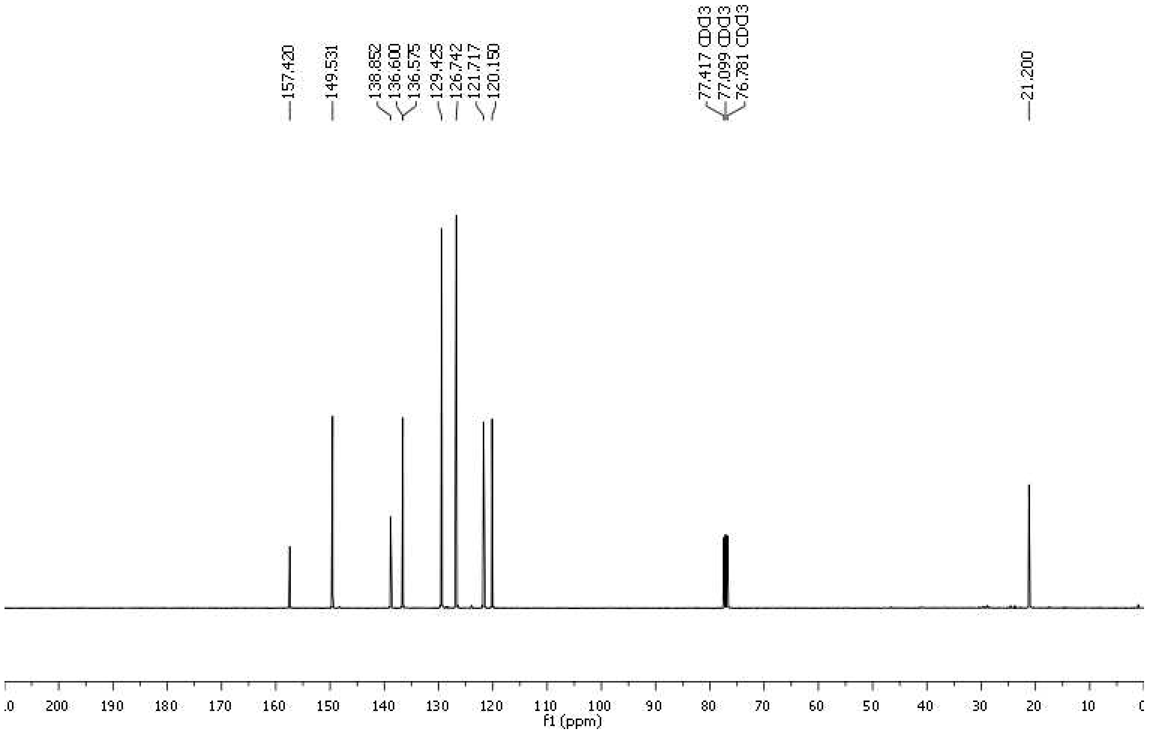
8.680
8.677
8.673
7.927
7.923
7.911
7.907
7.902
7.691
7.688
7.686
7.679
7.676
7.675
7.295
7.275
7.195
7.184
7.172
7.161
7.150
7.139
2.407
0.93
1.90
1.87
1.97
0.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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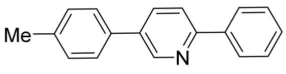
149.531
138.852
136.600
136.575
129.425
126.742
121.717
120.150
77.417 CDCl3
77.099 CDCl3
76.781 CDCl3
21.200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



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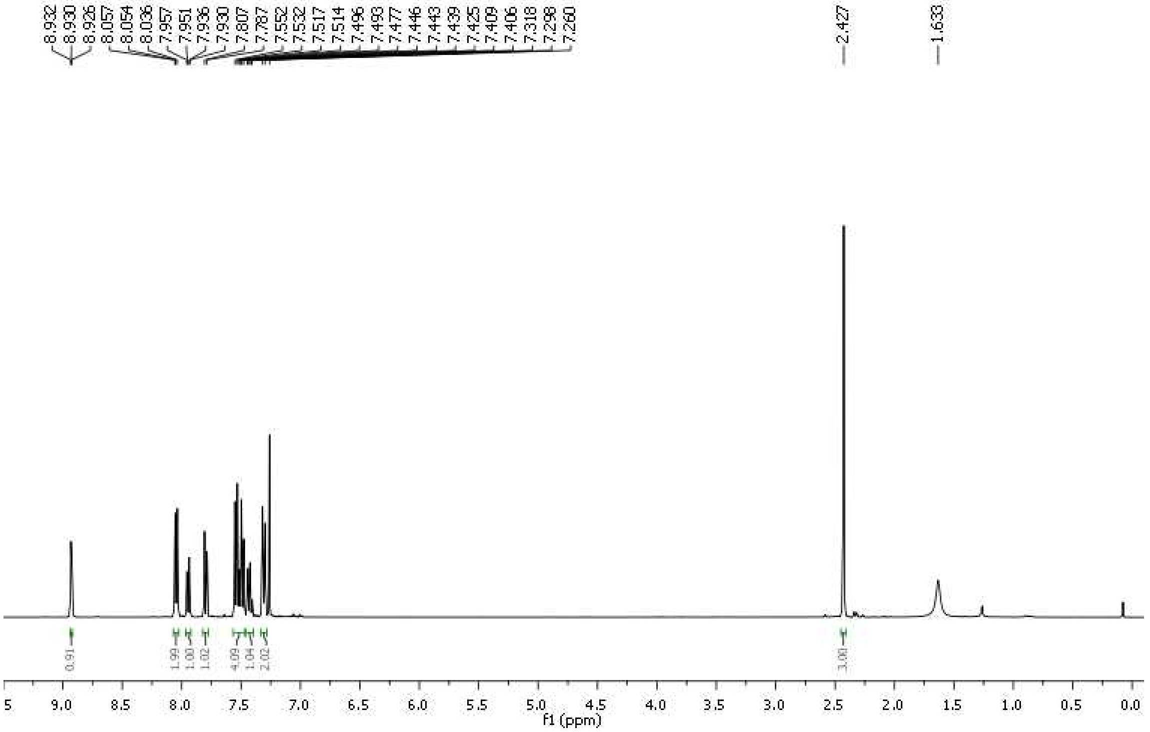
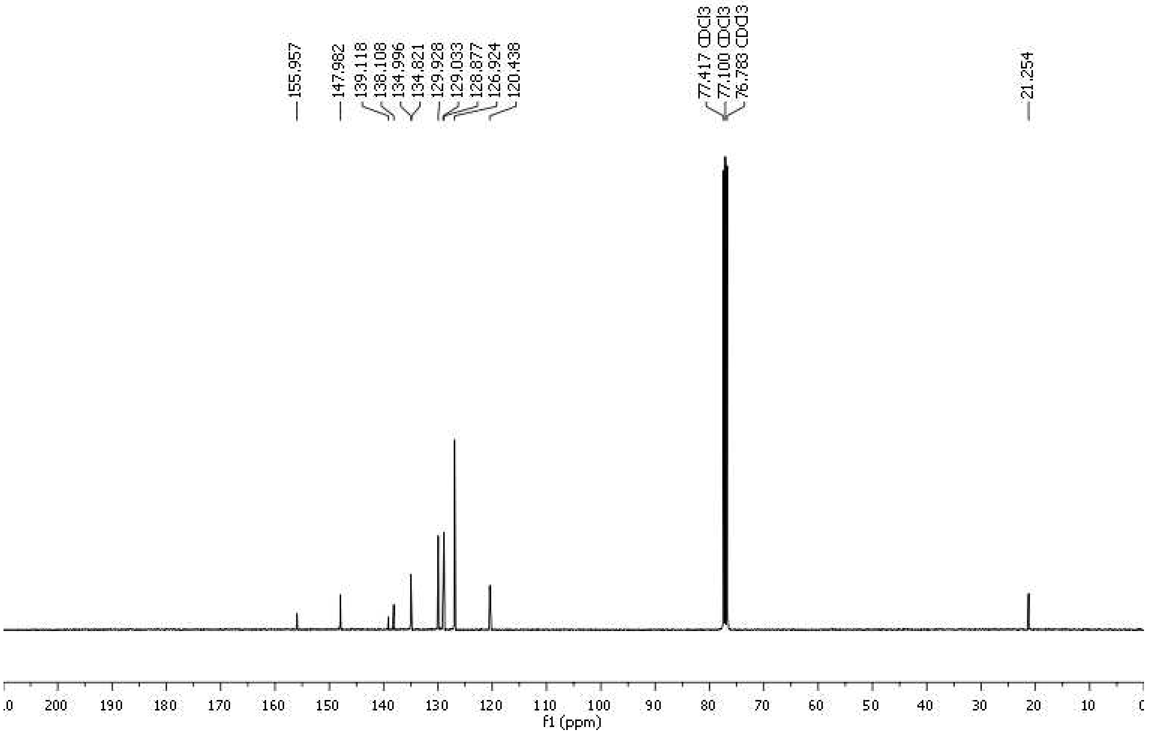
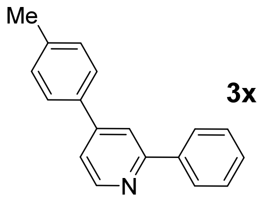


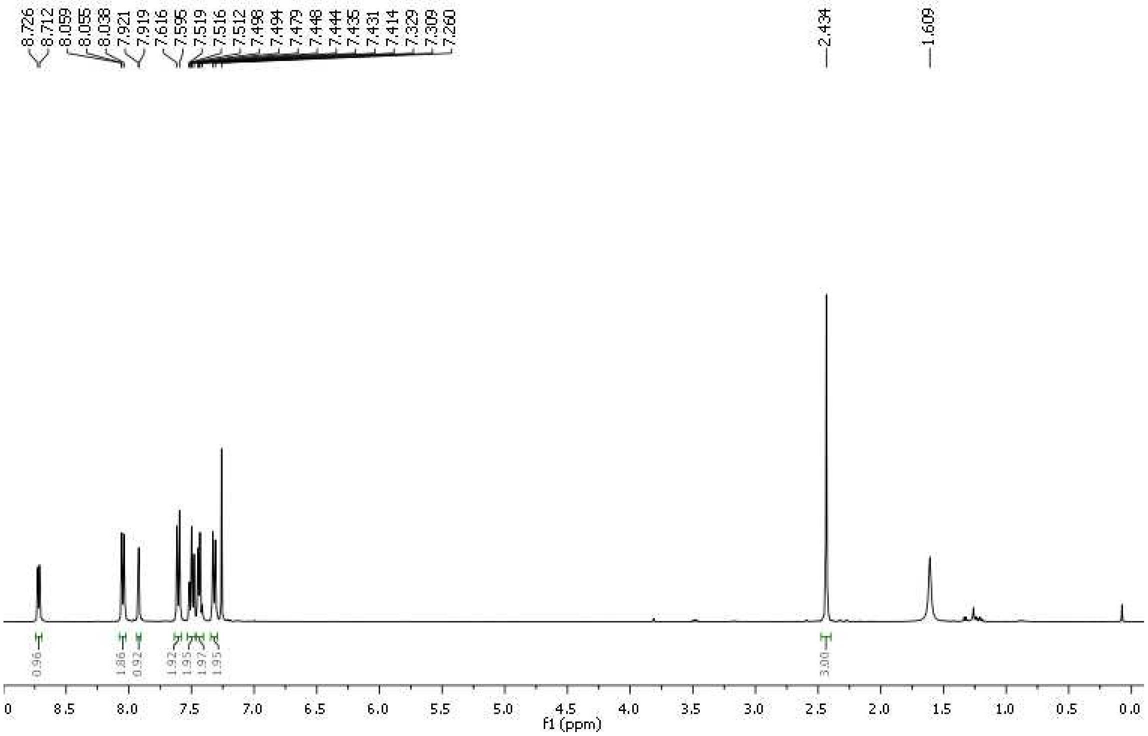
8.932
8.930
8.926
8.057
8.054
8.036
7.957
7.951
7.936
7.930
7.807
7.787
7.552
7.532
7.517
7.514
7.496
7.493
7.477
7.446
7.443
7.439
7.425
7.409
7.406
7.318
7.298
7.260
2.427
1.633
0.91
1.99
1.00
1.02
4.09
1.04
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

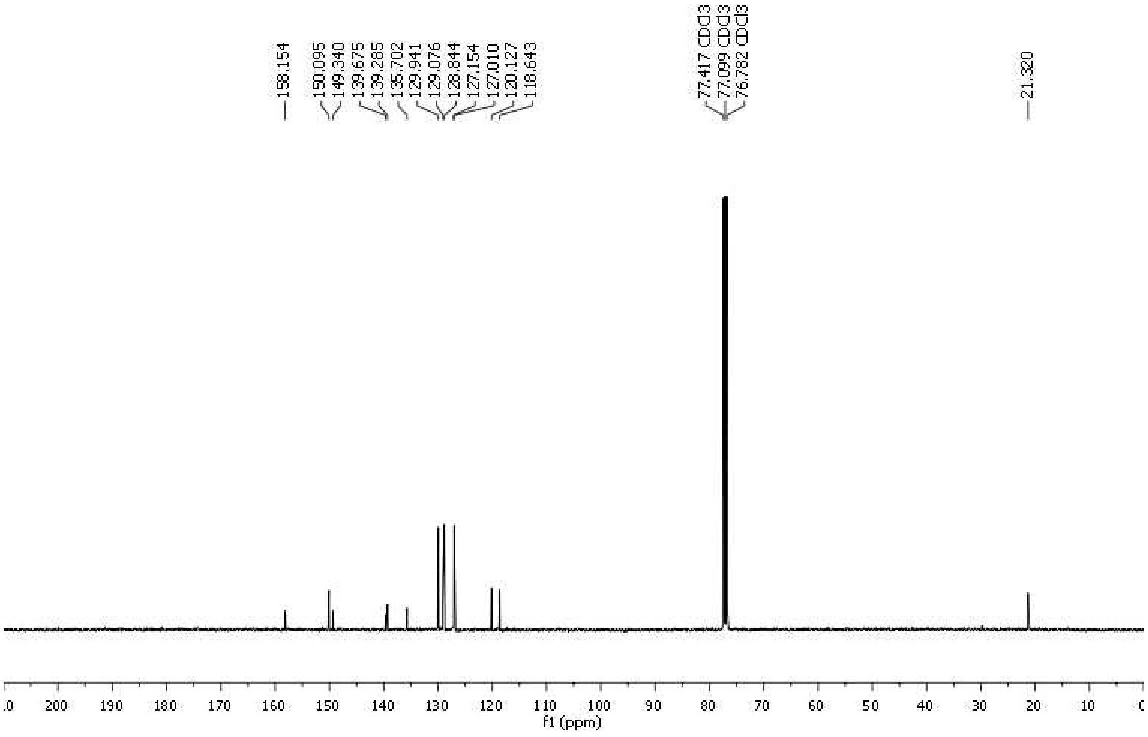


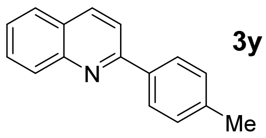
155.957
147.982
139.118
138.108
134.996
134.821
129.928
129.033
128.877
126.924
120.438
77.417 CDCl3
77.100 CDCl3
76.783 CDCl3
21.254
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
N

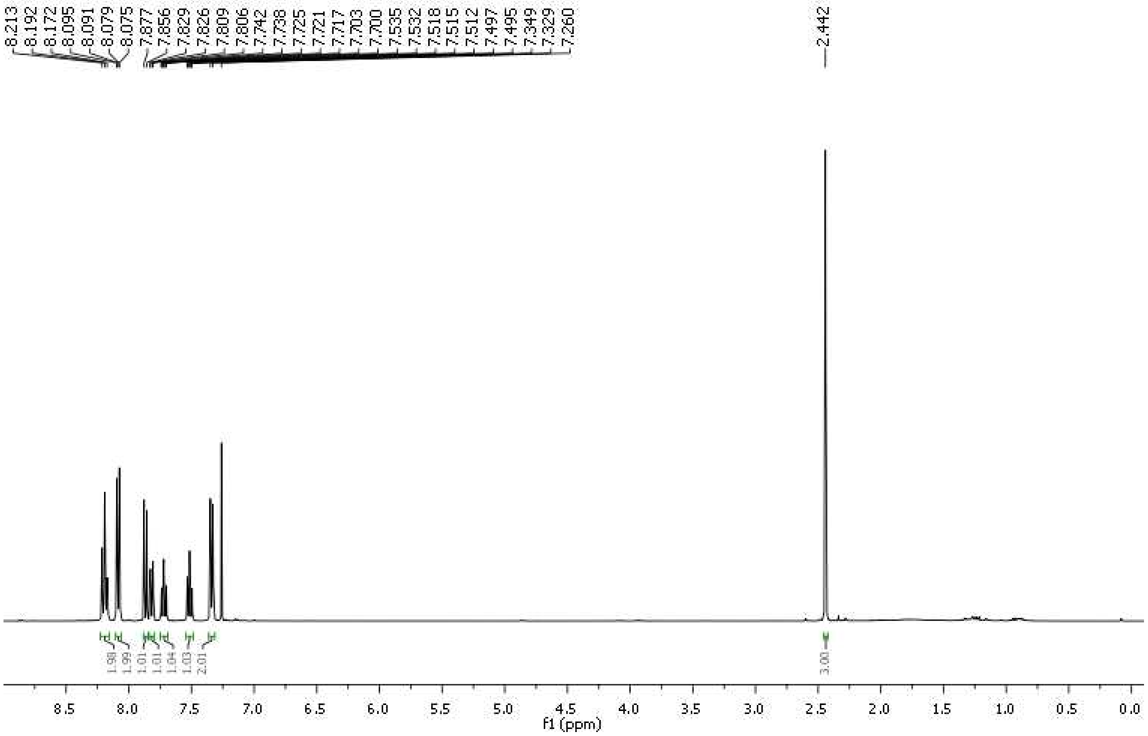
3x

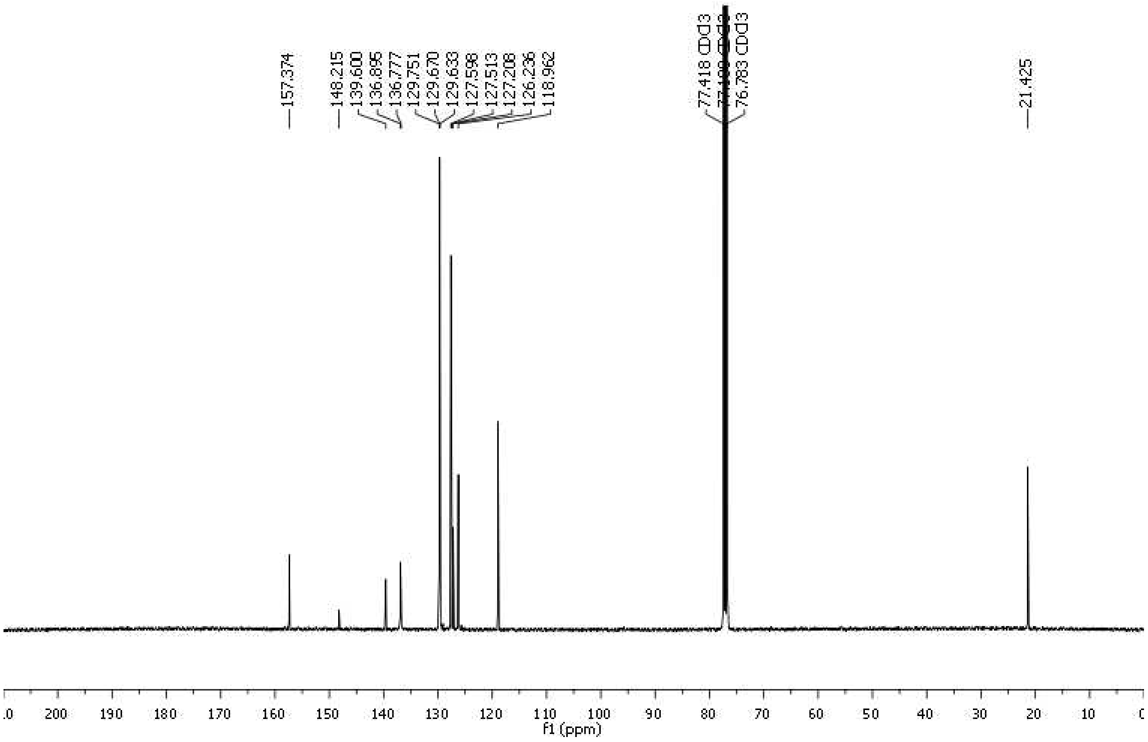

8.726
8.712
8.059
8.055
8.038
7.921
7.919
7.616
7.596
7.519
7.516
7.512
7.498
7.494
7.479
7.448
7.444
7.435
7.431
7.414
7.329
7.309
7.260
2.434
1.609
0.96
1.86
0.92
1.92
1.95
1.97
1.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

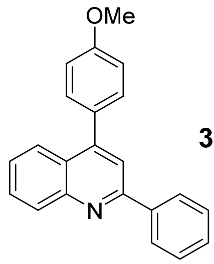

158.154
150.095
149.340
139.675
139.285
135.702
129.941
129.076
128.844
127.154
127.010
120.127
118.643
77.417 CDCl3
77.099 CDCl3
76.782 CDCl3
21.320
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


N
Me

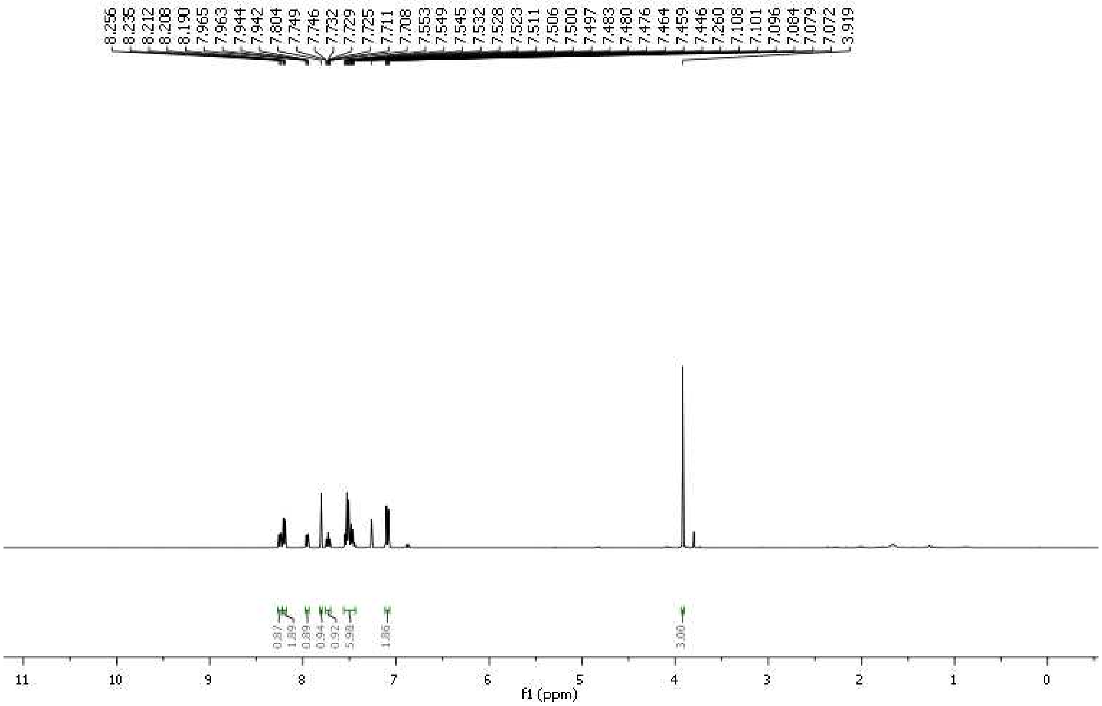
3y

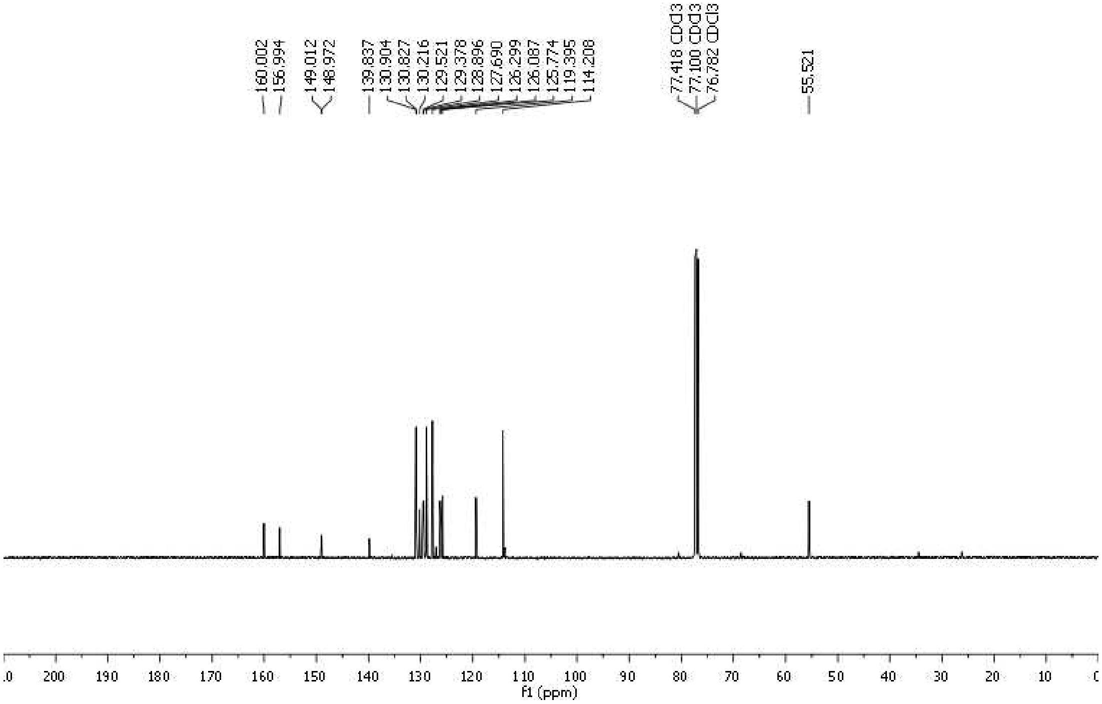

8.213
8.192
8.172
8.095
8.091
8.079
8.075
7.877
7.856
7.829
7.826
7.809
7.806
7.742
7.738
7.725
7.721
7.717
7.703
7.700
7.535
7.532
7.518
7.515
7.512
7.497
7.495
7.349
7.329
7.260
2.442
1.98
1.99
1.01
1.01
1.04
1.03
2.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.374
148.215
139.600
136.895
136.777
129.751
129.670
129.633
127.598
127.513
127.208
126.236
118.962
77.418 CDCl3
77.100 CDCl3
76.783 CDCl3
21.425
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OMe
N

3z


8.256
8.235
8.212
8.208
8.190
7.965
7.963
7.944
7.942
7.804
7.749
7.746
7.732
7.729
7.725
7.711
7.708
7.553
7.549
7.545
7.532
7.528
7.523
7.511
7.506
7.500
7.497
7.483
7.480
7.476
7.464
7.459
7.446
7.260
7.108
7.101
7.096
7.084
7.079
7.072
3.919
0.87
1.89
0.89
0.94
0.92
5.98
1.86
3.00
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


160.002
156.994
149.012
148.972
139.837
130.904
130.827
130.216
129.521
129.378
128.896
127.690
126.299
126.087
125.774
119.395
114.208
77.418 CDCl3
77.100 CDCl3
76.782 CDCl3
55.521
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)