Supporting information

for

Cu(II)-catalyzed C–H (SP^3) oxidation and C–N cleavage: base-switched methylenation and formylation using tetramethylethylenediamine as carbon source

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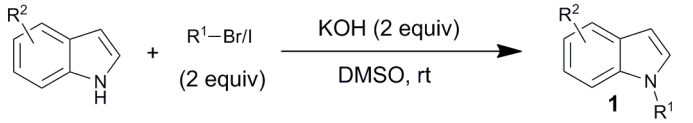
1. General Information

All reagents and solvents were used as supplied without further purification. ^{1}H NMR and ^{13}C NMR were determined in $CDCl_3$ or DMSO-d_6 on a Brucker 300 or 400 MHz spectrometer at room temperature, respectively, and tetramethylsilane (TMS) served as an internal standard. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as brs (broad). Coupling constants (*J*) are given in hertz (Hz). ESI-MS were carried out on a LCMS-2020 (Shimadzu, Japan). EI-MS was taken on a QP2010 GC-MS instrument (Shimadzu, Japan). All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Qingdao Haiyang Chemical Co., Ltd).

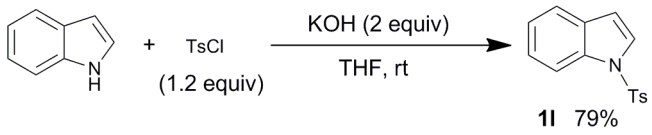
2. General Procedure for Synthesis of Substrates and products

2.1 General procedure for the synthesis of *N*-protected indoles (1a-j) from substituted indoles with alkyl bromides (iodomethane used for methyl-protected reagent) (5 mmol scale). A 50 mL flask equipped with a stir-bar was charged with substituted indole (5 mmol) and KOH (10.0 mmol). 20 mL of DMSO was added to the flask and the solution was stirred under room temperature, then alkyl bromides (10.0 mmol) was added. The reaction mixture was stirred at room temperature and monitored by TLC. Upon finished the reaction mixture was quenched by water (20 mL) and extracted by ethyl acetate (3×30 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by ^{1}H- and ^{13}C-NMR and MS (EI or ESI).

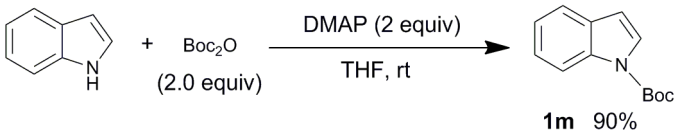


	R^1	R^2	Yield %		R^1	R^2	Yield %
1a	Et	H	95	**1f**	Et	5-Cl	90
1b	Me	H	97	**1g**	Et	5-CN	86
1c	Bn	H	91	**1h**	Et	2-Me	94
1d	PMB	H	88	**1i**	Et	4-Me	83
1e	Et	5-OMe	87	**1j**	Et	7-Me	82

2.2 Synthesis of 1-Tosylindole (1l) from indole with 4-methylbenzene-1-sulfonyl chloride (5 mmol scale) was according to the literature method.[1]



2.3 Synthesis of 1-Bocindole (1l) from indole with di-*tert*-butyl dicarbonate (5 mmol scale) was according to the literature method.[2]



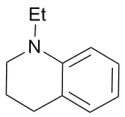
2.4 General procedure for the synthesis of *N*-protected anilines (5b-l, 5n-p) from substituted anilines with alkyl bromides (iodomethane used for methyl-protected reagent) (5 mmol scale). A 50 mL flask equipped with a stir-bar was charged with substituted anilines (5 mmol) and KOH (10.0 mmol). 20 mL of DMSO was added to the flask and the solution was stirred under room temperature. Followed alkyl bromides (2.0 equiv for **5c-e**, **5n**; 4.0 equiv for **5b**, **5f-l**, **5o-p**) was added. The reaction mixture was stirred at 50 ^{o}C and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and extracted by ethyl acetate (3×30 mL).

Combined organic phase were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by ^{1}H- and ^{13}C-NMR and MS (EI or ESI).

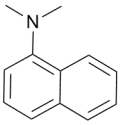
for **5c-d**: R = Me
others: R = H

5

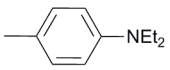
	R^1	R^2	R^3	R^4	R^5	Yield %
5b	H	H	H	Et	Et	93
5c	H	H	H	Me	Bn	90
5d	H	H	H	Me	PMB	86
5e	H	H	H	Me	Allyl	94
5f	H	OMe	OMe	Et	Et	76
5g	H	Me	Me	Et	Et	83
5h	H	H	OMe	Et	Et	88
5i	H	H	Me	Et	Et	90
5j	H	H	Cl	Et	Et	73
5k	OMe	H	OMe	Et	Et	91
5l	Me	H	H	Et	Et	86



5n (88%)



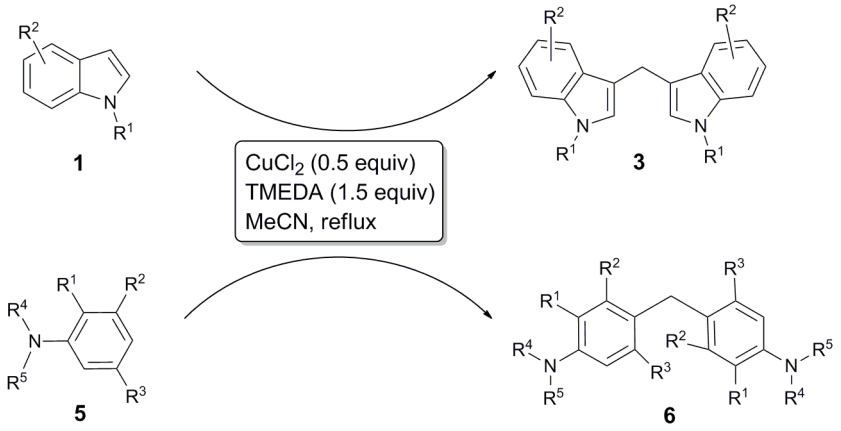
5o (93%)



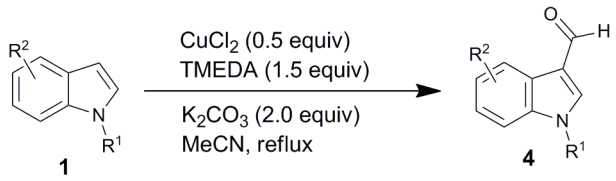
5p (89%)

2.5 General procedure for the synthesis of 3,3′-bisindolylmethanes (3a-j) and 4,4′-diaminodiphenylmethanes (6a-p). A 15 mL flask equipped with a stir-bar and condenser was charged with $CuCl_2$ (0.5 mmol, 68.0 mg) and MeCN (5.0 mL, for **6c-e** DMA was use as solvent). TMEDA (1.5 mmol, 230 μL) was added to the flask while stirring at room temperature. Followed indoles or anilines (1.0 mmol) was added. The reaction mixture was stirred at refluxing (or **6c-e** was heated to 140 °C) and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and ammonia water (25%, 1.0 mL) and extracted by ethyl acetate (3×30 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and concentrated under reduced

pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by ^{1}H- and ^{13}C-NMR and MS (EI or ESI).

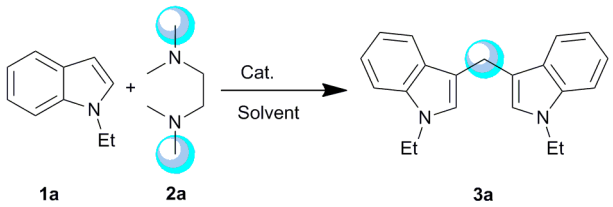


2.6 General procedure for the synthesis of 3-formylindoles (4a-k). A 15 mL flask equipped with a stir-bar and condenser was charged with $CuCl_2$ (0.5 mmol, 68.0 mg) and MeCN (5 mL). TMEDA (1.5 mmol, 230 μL) was added to the flask while stirring at room temperature. Followed indoles (1.0 mmol) and K_2CO_3 (2 mmol, 276 mg) was added. The reaction mixture was stirred at refluxing and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and ammonia water (25%, 1.0 mL) and extracted by ethyl acetate (3×50 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by ^{1}H- and ^{13}C-NMR and MS (EI or ESI).



3. Optimization of reaction conditions and other Information

3.1 Table S1 Optimization of reaction conditions for TMEDA (**2a**) as methylene donor[a]



Entry	Cat. (mol%)	Equiv. **2a**	Solvent	T (°C)	*t* (h)	Yield (%)[b]
1	None	2.5	MeCN	Reflux	3	0
2	$CuCl_2$ (50%)	2.5	MeCN	Reflux	3	87[c]
3	$CuBr_2$ (50%)	2,5	MeCN	Reflux	3	56
4	$Cu(OAc)_2$ (50%)	2.5	MeCN	Reflux	3	44
5	CuBr (50%)	2.5	MeCN	Reflux	3	Trace
6	$FeCl_3$ (50%)	2.5	MeCN	Reflux	3	Messy
7	$RuCl_3$ (50%)	2.5	MeCN	Reflux	3	Trace
8	$CuCl_2$ (50%)	0	MeCN	Reflux	3	0
9	$CuCl_2$ (50%)	1.5	MeCN	Reflux	3	86[c]
10[d]	$CuCl_2$ (50%)	1.5	MeCN	Reflux	3	11
11	$CuCl_2$ (50%)	1.5	MeCN	50	3	Trace
12	$CuCl_2$ (50%)	1.5	MeCN	Reflux	6	62[c]
13	$CuCl_2$ (30%)	1.5	MeCN	Reflux	6	39
14	$CuCl_2$ (50%)	1.5	DMA	90	3	79[c]
15	$CuCl_2$ (50%)	1.5	Dioxane	90	3	Trace

[a] Reaction condition: **1a** (1.0 mmol) was added to a mixture of catalyst, **2a**, and a solvent (5 mL) heated to indicated temperature and time. [b] Isolated yield. [c] Trace amount of N-ethyl-3-formylindole (**4a**) were observed. [d] Reaction under nitrogen atmosphere .

3.2 Selection of other amines as methylene donor

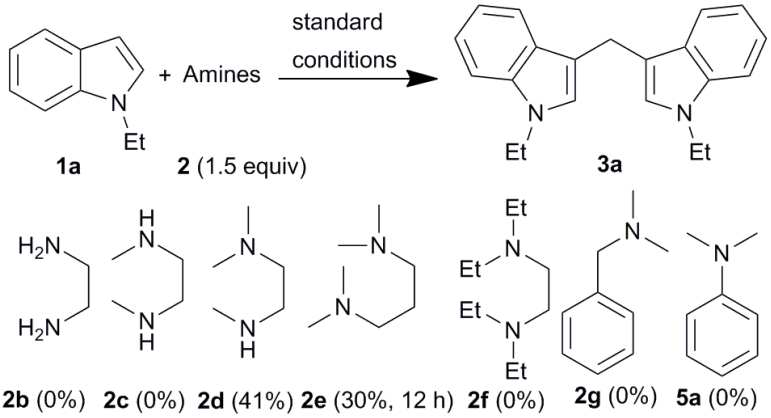


Figure **S1** Selection of other amines as methylene donor

3.3 To detect TMEDA (**2a**) transferred to **2d,** an experiment using MeCN-d_3 was carried under standard conditions. The signals of **2d** and **2a** were identified by comparing with their standard compound ^{1}HNMR spectra (300MHz, MeCN-d_3, figure S2). It was noted that the signals of **2d** or **2a** appeared to be one broad peak in the presentation of $CuCl_2$ in MeCN-d_3.

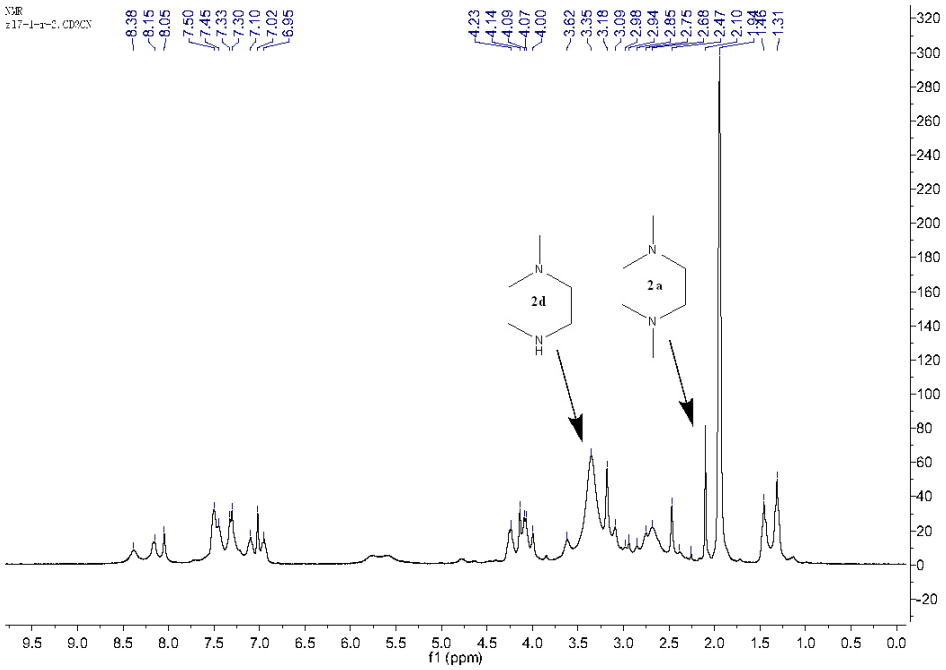
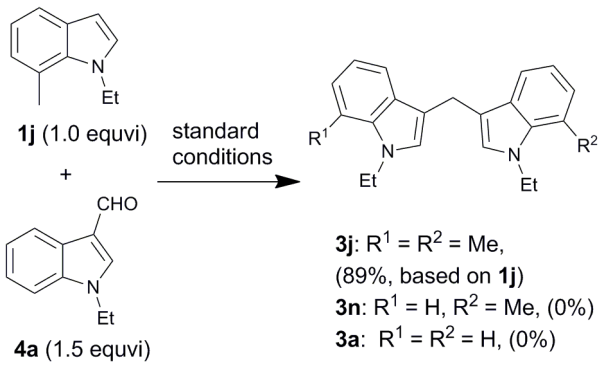


Figure **S2** ^{1}H-NMR analysis of the reaction mixture using MeCN-d_3 as the solvent

3.4 To exclude the possibility of 3-formylindole as an intermediate for methylenation, **4a** was treated with indole **1j** under standard conditions, upon isolation and GC-MS analysis, no heterobisindolylmethane **3n** and **3a** was detected (Fig. **S3**). Homobisindolylmethane **3j** was isolated in 89% yield based on **1j.**



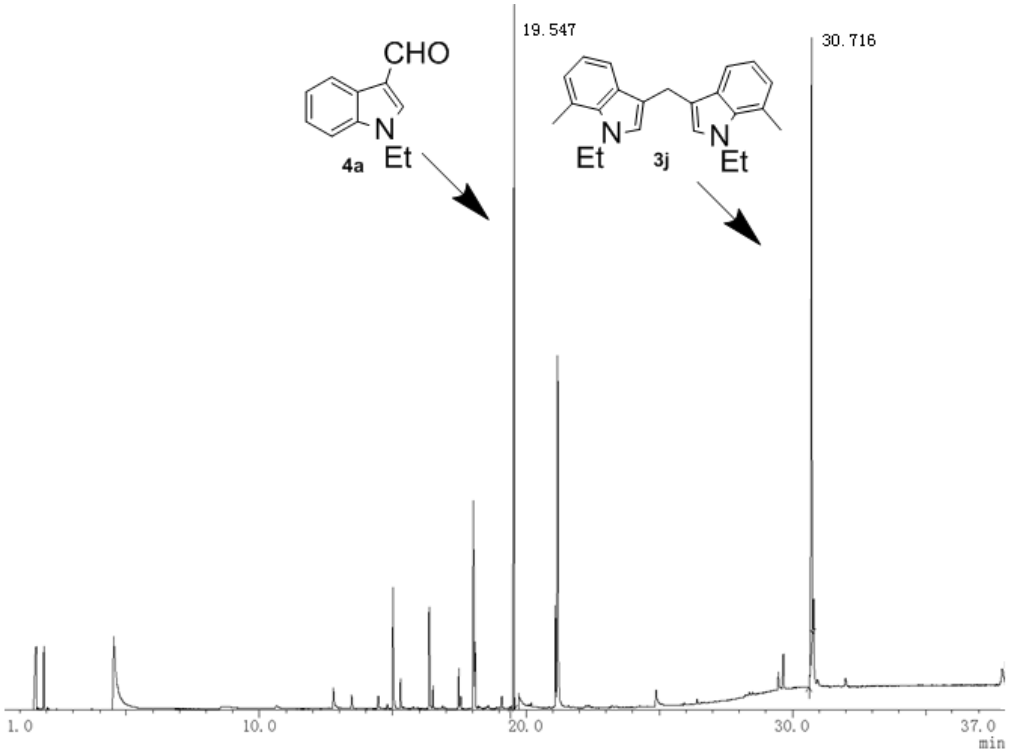
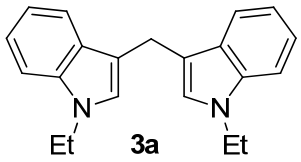


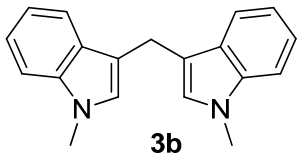
Figure **S3** GC-MS analysis of reaction mixture

4. Characterization data of Products and Substrates

4.1 Characterization of products

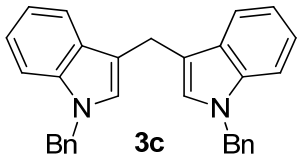


Bis(1-ethyl-1*H*-indol-3-yl)methane[3] (Table 1, 3a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.19 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.89 (s, 2H), 4.27 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 4H), 1.43 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 128.2, 125.3, 121.2, 119.5, 118.5, 114.4, 109.2, 40.7, 21.1, 15.5; EI-MS *m*/*z* (rel. int., %): 302 (100), 301 (92), 273 (26).



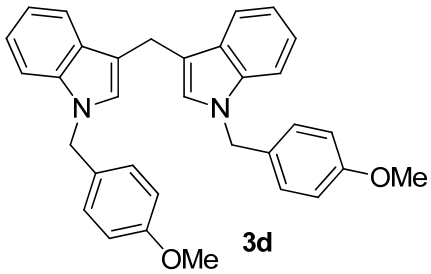
Bis(1-methyl-1*H*-indol-3-yl)methane[3] (Table 1, 3b): ^{1}H NMR (300 MHz, $CDCl_3$)

δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.80 (s, 2H), 4.23 (s, 2H), 3.72 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 127.8, 126.9, 121.3, 119.2, 118.5, 114.2, 109.0, 32.5, 20.8; EI-MS *m*/*z* (rel. int., %): 274 (100), 273 (98), 144 (20).



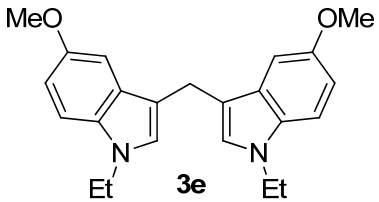
3c

Bis(1-benzyl-1*H*-indol-3-yl)methane[4] (Table 1, 3c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.22 (m, 8H), 7.21 – 7.15 (m, 2H), 7.14 – 7.05 (m, 6H), 6.94 (s, 2H), 5.26 (s, 4H), 4.29 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 136.8, 128.6, 128.2, 127.4, 126.6, 126.5, 121.6, 119.4, 118.8, 114.8, 109.6, 49.8, 21.2; EI-MS *m*/*z* (rel. int., %): 426 (100), 425 (19), 335 (88).



3d

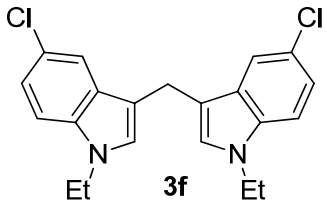
Bis(1-(4-methoxybenzyl)-1*H*-indol-3-yl)methane (Table 1, 3d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 2H), 7.11 – 7.00 (m, 6H), 6.90 (s, 2H), 6.84 – 6.77 (m, 4H), 5.18 (s, 4H), 4.25 (s, 2H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 136.7, 129.8, 128.2, 128.0, 126.3, 121.5, 119.4, 118.7, 114.6, 114.0, 109.6, 55.2, 49.3, 21.2; MS (ESI): 487.20 $[M+H]^+$.



3e

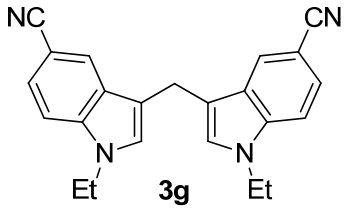
Bis(1-ethyl-5-methoxy-1*H*-indol-3-yl)methane (Table 1, 3e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 1.9 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.0 Hz,

2H), 6.87 (s, 2H), 4.20 (s, 2H), 4.09 (q, *J* = 7.2 Hz, 4H), 3.85 (s, 6H), 1.42 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 131.5, 128.3, 125.8, 113.6, 111.5, 109.9, 101.2, 55.9, 40.8, 21.2, 15.5; EI-MS *m*/*z* (rel. int., %): 362 (100), 361 (71), 333 (19).



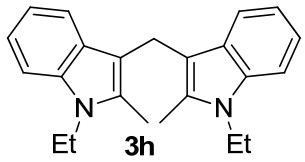
3f

Bis(5-chloro-1-ethyl-1*H*-indol-3-yl)methane (Table 1, 3f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.8 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.15 (dd, *J* = 8.7, 1.9 Hz, 2H), 6.88 (s, 2H), 4.13 – 4.05 (m, 6H), 1.41 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5, 128.9, 126.4, 124.3, 121.5, 118.7, 113.5, 110.2, 40.9, 20.9, 15.4; EI-MS *m*/*z* (rel. int., %): 370 (100), 369 (84), 341 (18).



3g

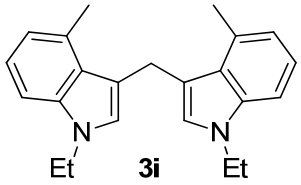
Bis(5-cyano-1-ethyl-1*H*-indol-3-yl)methane (Table 1, 3g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.43 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.02 (s, 2H), 4.21 (s, 2H), 4.16 (q, *J* = 7.3 Hz, 4H), 1.45 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 127.5, 127.2, 124.9, 124.4, 120.8, 114.6, 110.1, 101.6, 41.1, 21.0, 15.4; EI-MS *m*/*z* (rel. int., %): 352 (100), 351 (89), 323 (20).



3h

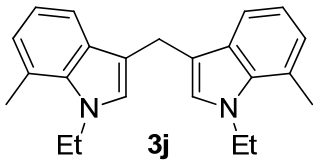
Bis(1-ethyl-2-methyl-1*H*-indol-3-yl)methane (Table 1, 3h): ^{1}H NMR (300 MHz, MeOD) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 7.9 Hz, 2H), 4.20 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 4H), 2.39 (s, 6H), 1.34 (t, *J*

= 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 131.8, 128.3, 120.1, 118.5, 118.4, 110.4, 108.3, 37.5, 19.9, 15.3, 10.1; EI-MS *m*/*z* (rel. int., %): 330 (78), 315 (36), 171 (100).



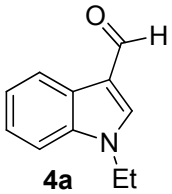
3i

Bis(1-ethyl-4-methyl-1*H*-indol-3-yl)methane (Table 1, 3i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 6.7 Hz, 2H), 6.69 (s, 2H), 4.60 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 4H), 2.70 (s, 6H), 1.39 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 131.6, 126.6, 126.2, 121.4, 120.2, 116.2, 107.2, 40.8, 25.7, 20.2, 15.5; EI-MS *m*/*z* (rel. int., %): 330 (42), 171 (100).



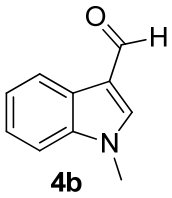
3j

Bis(1-ethyl-7-methyl-1*H*-indol-3-yl)methane (Table 1, 3j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.06 – 6.88 (m, 4H), 6.78 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 4H), 4.18 (s, 2H), 2.73 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 129.4, 127.2, 124.4, 120.7, 118.9, 117.6, 114.6, 43.2, 21.2, 20.0, 18.1; EI-MS *m*/*z* (rel. int., %): 330 (100), 329 (49), 301 (60).



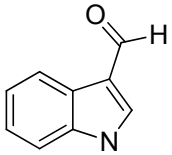
4a

1-Ethyl-3-formylindole[5] (Table 1, 4a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.35 – 8.27 (m, 1H), 7.75 (s, 1H), 7.44 – 7.28 (m, 3H), 4.24 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 137.4, 136.9, 125.4, 123.8, 122.8, 122.0, 118.1, 109.8, 41.8, 15.0; MS (ESI): 174.10$[M+H]^+$.



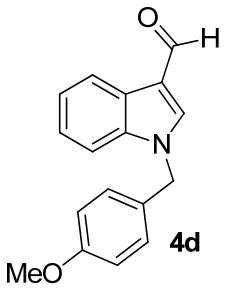
4b

1-Methyl-3-formylindole[6] (Table 1, 4b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.49 – 8.14 (m, 1H), 7.64 (s, 1H), 7.38 – 7.28 (m, 3H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 139.2, 137.8, 125.1, 123.9, 122.8, 121.9, 117.9, 109.8, 33.6; MS (ESI): 160.10$[M+H]^+$.



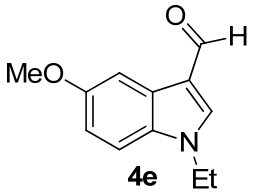
4c Bn

1-Benzyl-3-formylindole[5] (Table 1, 4c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.47 – 8.22 (m, 1H), 7.70 (s, 1H), 7.40 – 7.27 (m, 6H), 7.22 – 7.14 (m, 2H), 5.35 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.5, 138.4, 137.4, 135.2, 129.0, 128.3, 127.1, 125.4, 124.1, 123.0, 122.1, 118.4, 110.3, 50.8; MS (ESI): 236.10$[M+H]^+$.



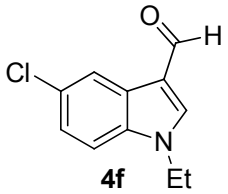
4d

1-(4-Methoxybenzyl)-3-formylindole[7] (Table 1, 4d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.48 – 8.21 (m, 1H), 7.67 (s, 1H), 7.41 – 7.28 (m, 3H), 7.15 (d, J = 8.8 Hz, 2H), 6.93 – 6.85 (m, 2H), 5.28 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 159.5, 138.4, 137.3, 128.8, 127.0, 125.4, 124.0, 123.0 (s), 122.0, 118.2, 114.4, 110.3, 55.2, 50.3; MS (ESI): 266.10$[M+H]^+$.



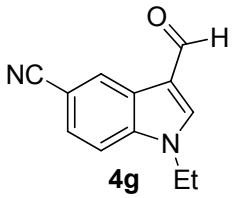
4e

1-Ethyl-3-formyl-5-methoxyindole[8] (Table 1, 4e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.67 (s, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 3.89 (s, 3H), 1.52 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 156.5, 137.5, 131.8, 126.1, 117.8, 114.3, 110.7, 103.3, 55.7, 41.9, 15.0; MS (ESI): 204.10$[M+H]^+$.



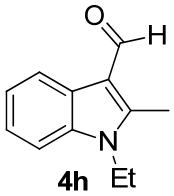
4f

5-Chloro-1-ethyl-3-formylindole (Table 1, 4f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.29 (s, 1H), 7.75 (s, 1H), 7.29 (s, 2H), 4.21 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.1, 138.0, 135.2, 128.8, 126.3, 124.2, 121.7, 117.5, 110.9, 42.0, 14.9; MS (ESI): 208.05$[M+H]^+$.



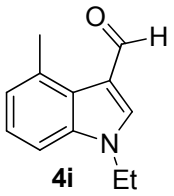
4g

5-Cyano-1-ethyl-3-formylindole (Table 1, 4g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.65 (d, *J* = 0.8 Hz, 1H), 7.87 (s, 1H), 7.56 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 4.28 (q, *J* = 7.3 Hz, 2H), 1.58 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.1, 138.9, 138.4, 127.5, 126.8, 125.0, 119.7, 118.2, 110.9, 106.1, 42.2, 15.0; MS (ESI): 199.10$[M+H]^+$.



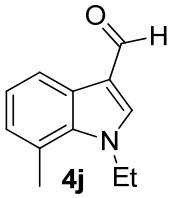
4h

1-Ethyl-3-formyl-2-methylindole (Table 1, 4h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.43 – 8.10 (m, 1H), 7.46 – 7.15 (m, 3H), 4.14 (q, *J* = 7.3 Hz, 2H), 2.66 (s, 3H), 1.38 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.0, 146.8, 135.8, 125.9, 123.0, 122.6, 120.8, 114.2, 109.2, 38.0, 14.6, 10.2; MS (ESI): 188.10$[M+H]^+$.



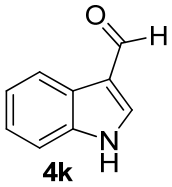
4i

1-Ethyl-3-formyl-4-methylindole (Table 1, 4i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.89 (s, 1H), 7.25 – 7.21 (m, 2H), 7.10 – 7.08 (m, 1H), 4.22 (q, *J* = 7.3 Hz, 2H), 2.84 (s, 3H), 1.54 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 137.2, 136.3, 132.3, 125.2, 124.1, 123.3, 119.5, 107.8, 41.8, 22.5, 14.8; MS (ESI): 188.10$[M+H]^+$.



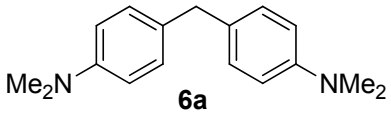
4j

1-Ethyl-3-formyl-7-methylindole (Table 1, 4j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.69 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 2.74 (s, 3H), 1.54 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 139.0, 135.7, 126.9, 126.5, 122.9, 121.2, 119.9, 117.9, 44.4, 19.5, 17.2; MS (ESI): 188.10$[M+H]^+$.



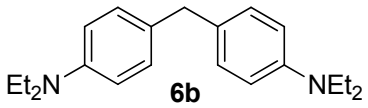
4k

3-Formylindole[9] (Table 1, 4k): ^{1}H NMR (300 MHz, DMSO) δ 12.13 (s, 1H), 9.93 (s, 1H), 8.28 (d, *J* = 3.1 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.27 – 7.18 (m, *J* = 7.1, 1.3 Hz, 2H); ^{13}C NMR (75 MHz, DMSO) δ 185.3, 138.8, 137.4, 124.5, 123.8, 122.5, 121.2, 118.5, 112.8; MS (ESI): 146.05$[M+H]^{+}$.



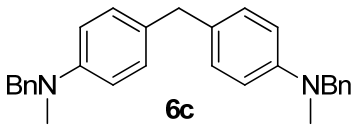
6a

4,4'-Methylenebis(*N*,*N*-dimethylaniline)[10] (Table 2, 6a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 4H), 6.70 (d, *J* = 8.6 Hz, 4H), 3.82 (s, 2H), 2.91 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 130.3, 129.4, 113.0, 40.9, 39.8; MS (ESI): 255.15$[M+H]^{+}$.



6b

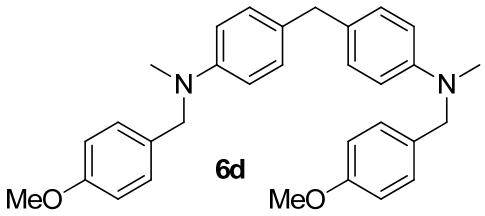
4,4'-Methylenebis(*N*,*N*-diethylaniline)[11] (Table 2, 6b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.6 Hz, 4H), 6.61 (d, *J* = 8.6 Hz, 4H), 3.77 (s, 2H), 3.30 (q, *J* = 7.0 Hz, 8H), 1.12 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 129.5, 129.0, 112.1, 44.4, 39.7, 12.6; MS (ESI): 311.20$[M+H]^{+}$.



6c

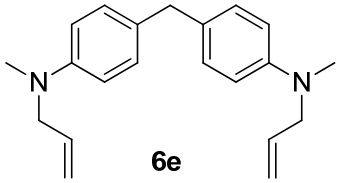
4,4'-Methylenebis(*N*-benzyl-*N*-methylaniline) (Table 2, 6c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.28 – 7.22 (m, 6H), 7.06 (d, *J* = 8.5 Hz, 4H), 6.71 (d, *J* = 8.0 Hz, 4H), 4.50 (s, 4H), 3.81 (s, 2H), 2.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 139.2, 130.1, 129.5, 128.5, 126.8, 112.6, 56.9, 39.8, 38.6; MS (ESI):

407.20[M+H]$^+$.



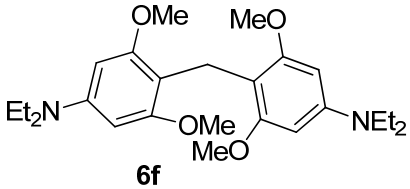
6d

4,4'-Methylenebis(*N*-(4-methoxybenzyl)-*N*-methylaniline) (Table 2, 6d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 4H), 7.04 (d, *J* = 8.5 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 6.69 (d, *J* = 8.6 Hz, 4H), 4.41 (s, 4H), 3.79 (s, 8H), 2.93 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 148.0, 131.0, 130.0, 129.4, 128.0, 113.8, 112.6, 56.3, 55.2, 39.8, 38.4; MS (ESI): 467.25[M+H]$^+$.



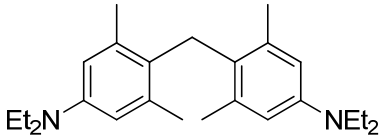
6e

4,4'-Methylenebis(*N*-allyl-*N*-methylaniline) (Table 2, 6e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.6 Hz, 4H), 6.66 (d, *J* = 8.4 Hz, 4H), 5.88 – 5.79 (m, 2H), 5.29 – 4.99 (m, 4H), 3.94 – 3.83 (m, 4H), 3.79 (s, 2H), 2.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 134.0, 130.0, 129.3, 116.1, 112.6, 55.5, 39.7, 38.0; MS (ESI): 307.20[M+H]$^+$.



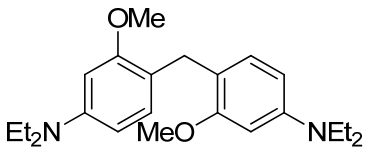
6f

4,4'-Methylenebis(*N*,*N*-diethyl-3,5-dimethoxyaniline) (Table 2, 6f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (s, 4H), 3.80 (s, 2H), 3.71 (s, 12H), 3.30 (q, *J* = 7.1 Hz, 8H), 1.14 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 146.9, 108.8, 91.0, 56.2, 44.6, 16.2, 12.6; MS (ESI): 431.25[M+H]$^+$.



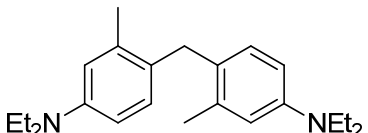
6g

4,4'-Methylenebis(*N*,*N*-diethyl-3,5-dimethylaniline) (Table 2, 6g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (s, 4H), 3.89 (s, 2H), 3.30 (q, *J* = 7.0 Hz, 8H), 2.11 (s, 12H), 1.13 (d, *J* = 7.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 137.5, 126.1, 112.8, 44.1, 29.8, 21.4, 12.6; MS (ESI): 367.30$[M+H]^+$.



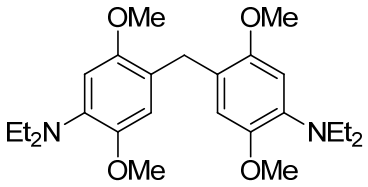
6h

4,4'-Methylenebis(*N*,*N*-diethyl-3-methoxyaniline) (Table 2, 6h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, *J* = 8.3 Hz, 2H), 6.42 – 6.06 (m, 4H), 3.83 (s, 6H), 3.77 (s, 2H), 3.34 (q, *J* = 7.0 Hz, 8H), 1.17 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 147.4, 130.6, 117.4, 104.4, 96.0, 55.3, 44.6, 27.8, 12.6; MS (ESI): 371.25$[M+H]^+$.



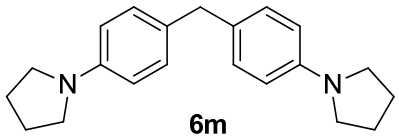
6i

4,4'-Methylenebis(*N*,*N*-diethyl-3-methylaniline) (Table 2, 6i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, *J* = 8.3 Hz, 2H), 6.56 (s, 2H), 6.47 (d, *J* = 7.5 Hz, 2H), 3.73 (s, 2H), 3.33 (q, *J* = 7.0 Hz, 8H), 2.25 (s, 6H), 1.16 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 137.2, 130.1, 126.5, 114.0, 109.9, 44.4, 34.7, 20.3, 12.7; MS (ESI): 339.25 $[M+H]^+$.



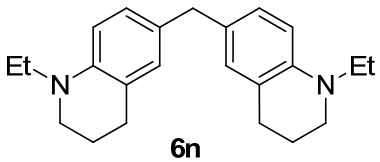
6k

4,4'-Methylenebis(*N*,*N*-diethyl-2,5-dimethoxyaniline) (Table 2, 6k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61 (s, 2H), 6.58 (s, 2H), 3.86 (s, 2H), 3.79 (s, 6H), 3.71 (s, 6H), 3.13 (q, *J* = 6.8 Hz, 8H), 1.02 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 148.0, 137.3, 123.3, 114.2, 106.4, 56.4, 55.7, 46.4, 29.0, 12.0; MS (ESI): 431.25$[M+H]^+$.



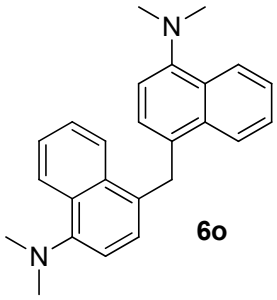
6m

Bis(4-(pyrrolidin-1-yl)phenyl)methane (Table 2, 6m): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.8 Hz, 4H), 6.50 (d, *J* = 7.8 Hz, 4H), 3.80 (s, 2H), 3.25 (s, 8H), 1.98 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 129.5, 129.0, 111.6, 47.7, 39.9, 25.4; MS (ESI): 307.20$[M+H]^+$.



6n

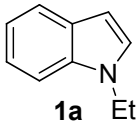
Bis(1-ethyl-1,2,3,4-tetrahydroquinolin-6-yl)methane (Table 2, 6n): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.3 Hz, 2H), 6.78 (s, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 3.68 (s, 2H), 3.31 (q, *J* = 7.0 Hz, 4H), 3.25 – 3.17 (m, 4H), 2.70 (t, *J* = 6.4 Hz, 4H), 2.04 – 1.82 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 129.6, 129.0, 127.2, 122.4, 110.6, 48.3, 45.3, 39.9, 28.1, 22.4, 10.7; MS (ESI): 335.20$[M+H]^+$.



6o

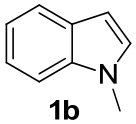
4,4'-Methylenebis(*N*,*N*-dimethylnaphthalen-1-amine)[10] (Table 2, 6o): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.41 (m, 4H), 7.01 – 6.94 (m, 4H), 4.76 (s, 2H), 2.89 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 133.3, 130.9, 129.0, 126.9, 125.8, 124.9, 124.7, 124.5, 113.8, 45.3, 35.2; MS (ESI): 355.20$[M+H]^+$.

4.2 Characterization of substrates



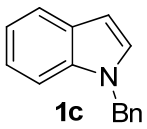
1a Et

1-Ethylindole (1a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.38 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.24 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.15 – 7.10 (m,2H), 6.52 (dd, *J* = 3.1, 0.8 Hz, 1H), 4.20 (q, *J* = 7.3 Hz, 2H), 1.49 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 128.6, 127.0, 121.3, 121.0, 119.2, 109.3, 101.0, 40.9, 15.4; EI-MS *m*/*z* (rel. int., %): 145 (65), 130 (100).

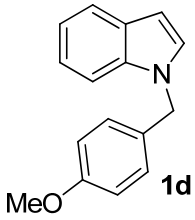


1b

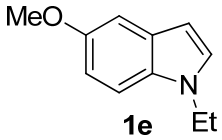
1-Methylindole (1b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.15 – 7.09 (m, 1H), 7.06 (d, *J* = 3.0 Hz, 1H), 6.50 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 128.7, 128.4, 121.4, 120.8, 119.2, 109.1, 100.8, 32.7; MS (ESI): 132.10$[M+H]^+$.



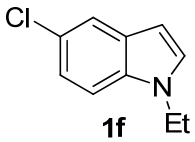
1-Benzylindole (1c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.36 – 7.24 (m, 4H), 7.23 – 7.07 (m, 5H), 6.58 (d, *J* = 2.7 Hz, 1H), 5.34 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 136.3, 128.7, 128.2, 127.6, 126.8, 124.6, 121.7, 121.0, 119.5, 109.7, 101.7, 50.0; MS (ESI): 208.10$[M+H]^+$.



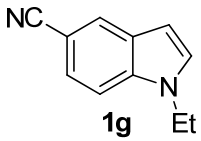
1-(4-Methoxybenzyl)indole (1d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.18 – 7.12 (m, 2H), 7.12 – 7.06 (m, 2H), 6.90 – 6.82 (m, 1H), 6.58 (d, *J* = 3.1 Hz, 1H), 5.28 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 136.2, 129.4, 128.2, 128.1, 121.6, 120.9, 119.5, 114.1, 113.8, 109.7, 101.5, 55.2, 49.5; MS (ESI): 238.15$[M+H]^+$.



1-Ethyl-5-methoxyindole (1e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.10 (d, *J* = 2.2 Hz, 2H), 6.88 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.15 (q, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 1.46 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 131.1, 128.9, 127.4, 111.7, 109.9, 102.6, 100.5, 55.8, 41.0, 15.4; MS (ESI): 176.10$[M+H]^+$.

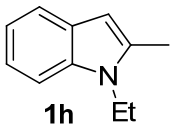


5-Chloro-1-ethylindole (1f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.7 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.18 – 7.12 (m, 2H), 6.43 (dd, *J* = 3.1, 0.7 Hz, 1H), 4.16 (q, *J* = 7.3 Hz, 2H), 1.46 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.1, 129.6, 128.3, 124.9, 121.6, 120.2, 110.2, 100.7, 41.1, 15.3; MS (ESI): 180.10$[M+H]^+$.



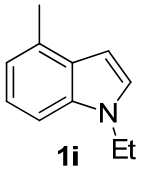
1g

5-Cyano-1-ethylindole (1g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.43 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 4.21 (q, *J* = 7.3 Hz, 2H), 1.48 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 129.2, 128.2, 126.5, 124.2, 120.8, 110.0, 102.2, 60.3, 41.2, 15.3; MS (ESI): 171.10$[M+H]^+$.



1h

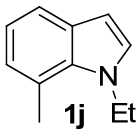
1-Ethyl-2-methylindole (1h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.19 – 7.10 (m, 1H), 7.07 (dd, *J* = 10.7, 4.1 Hz, 1H), 6.24 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 136.0, 128.3, 120.5, 119.8, 119.2, 108.9, 99.9, 37.7, 15.3, 12.6; MS (ESI): 160.15$[M+H]^+$.



1i

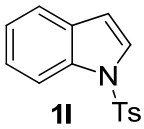
1-Ethyl-4-methylindole (1i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.53 (dd, *J* = 3.1, 0.7 Hz, 1H), 4.19 (q, *J* = 7.3 Hz, 2H), 2.59 (s, 3H), 1.48 (dd, *J* = 9.2, 5.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 130.5, 128.6, 126.5, 121.6, 119.5, 107.0, 99.6, 41.1, 18.9, 15.6; MS (ESI):

160.10$[M+H]^+$.



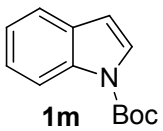
1j

1-Ethyl-7-methylindole (1j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 6.9 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.77 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5, 129.9, 128.7, 124.5, 120.8, 119.6, 119.2, 101.7, 43.5, 19.9, 18.0; MS (ESI): 160.15$[M+H]^+$.



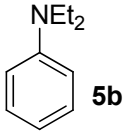
1l

1-Tosylindole (1l): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 3.7 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.20 (m, 3H), 6.65 (d, *J* = 3.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 135.2, 134.7, 130.7, 129.8, 126.7, 126.2, 124.5, 123.2, 121.3, 113.4, 109.0, 21.5; MS (ESI): 272.05$[M+H]^+$.



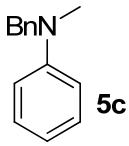
1m

1-*tert*-Butoxycarbonylindole (1m): ^{1}H NMR (300 MHz, DMSO) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.54 (m,2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.25 – 7.19 (m, 1H), 1.68 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 135.1, 130.5, 125.8, 124.1, 122.6, 120.8, 115.1, 107.2, 28.1, 27.8; MS (ESI): 218.10$[M+H]^+$.



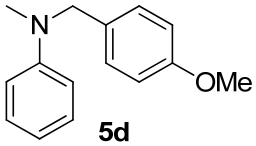
5b

***N,N*-Diethylaniline (5b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.1 Hz, 2H), 6.72 – 6.64 (m,3H), 3.37 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 129.2, 115.2, 111.7, 44.2, 12.5; MS (ESI): 150.15$[M+H]^+$.



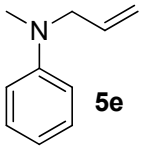
5c

***N*-Benzyl-*N*-methylaniline (5c):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.27 – 7.22 (m,5H), 6.79 – 7.72 (m, 3H), 4.56 (s, 2H), 3.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 139.0, 129.2, 128.6, 126.8, 126.7, 116.5, 112.3, 56.6, 38.5; MS (ESI): 198.15$[M+H]^+$.



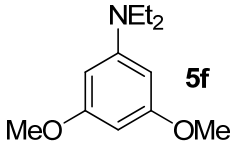
5d

***N*-(4-Methoxybenzyl)-*N*-methylaniline (5d):**^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.82 – 6.73 (m,3H), 4.51 (s, 2H), 3.82 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 149.7, 130.8, 129.1, 127.9, 116.4, 113.9, 112.4, 56.0, 55.2, 38.3; MS (ESI): 228.15$[M+H]^+$.



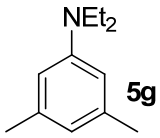
5e

***N*-Allyl-*N*-methylaniline (5e):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 2H), 6.77 – 6.71 (m,3H), 5.92 – 5.83 (m, 1H), 5.23 – 5.15 (m, 2H), 3.96 – 3.94 (m,2H), 2.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 133.8, 129.1, 116.4, 116.1, 112.4, 55.2, 38.0; MS (ESI): 148.15$[M+H]^+$.



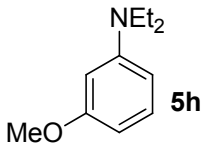
5f

***N,N*-Diethyl-3,5-dimethoxyaniline (5f):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (brs, 3H), 3.78 (s, 6H), 3.32 (q, *J* = 7.0 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 149.5, 91.0, 87.3, 55.0, 44.4, 12.6; MS (ESI): 210.15 $[M+H]^+$.



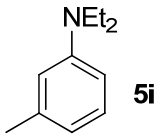
5g

***N,N*-Diethyl-3,5-dimethylaniline (5g):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.33 (brs, 3H), 3.31 (q, *J* = 7.1, 4H), 2.27 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 117.5, 112.0, 109.8, 44.3, 24.3, 12.5; MS (ESI): 178.15$[M+H]^+$.



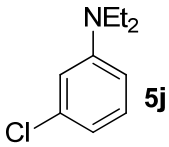
5h

***N,N*-Diethyl-3-methoxyaniline (5h):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 8.6 Hz, 1H), 6.24 – 6.20 (m, 2H), 3.80 (s, 3H), 3.34 (q, *J* = 7.1 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 149.10, 129.8, 105.0, 99.9, 98.3, 55.0, 44.4, 12.6; MS (ESI): 180.15$[M+H]^+$.



5i

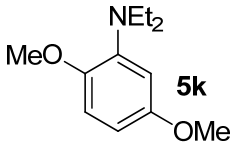
***N,N*-Diethyl-3-methylaniline (5i):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 9.1, 7.3 Hz, 1H), 6.53 – 6.47 (m, 3H), 3.35 (q, *J* = 7.0 Hz, 4H), 2.32 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 138.8, 129.1, 116.3, 112.5, 109.0, 44.2, 22.0, 12.6; MS (ESI): 164.15$[M+H]^+$.



5j

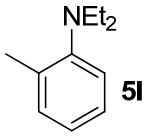
3-Chloro-*N,N*-diethylaniline (5j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.0 Hz,

1H), 6.64 – 6.49 (m, 3H), 3.33 (q, *J* = 7.1 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 135.1, 130.1, 114.9, 111.3, 109.7, 44.3, 12.4; MS (ESI): 184.10$[M+H]^+$.



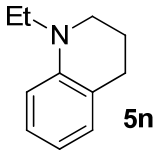
5k

***N,N*-Diethyl-2,5-dimethoxyaniline (5k):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 2.8 Hz, 1H), 6.47 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.16 (q, *J* = 7.1 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 148.0, 140.1, 111.8, 109.0, 105.0, 55.8, 55.4, 45.9, 11.8; MS (ESI): 210.10$[M+H]^+$.



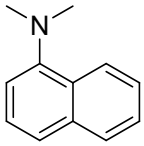
5l

***N,N*-Diethyl-2-methylaniline (5l):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.13 (m,2H), 7.10 – 6.94 (m, 2H), 2.99 (q, *J* = 7.1 Hz, 4H), 2.31 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 135.3, 130.8, 125.9, 123.1, 122.1, 47.5, 18.3, 12.5; MS (ESI): 164.15$[M+H]^+$.



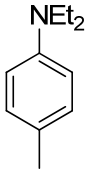
5n

1-Ethyl-1,2,3,4-tetrahydroquinoline (5n): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.67 – 6.58 (m, 2H), 3.40 (q, *J* = 7.0 Hz, 2H), 3.35 – 3.26 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.24 – 1.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 129.1, 127.0, 122.4, 115.3, 110.4, 48.3, 45.2, 28.2, 22.2, 10.7; MS (ESI): 162.15$[M+H]^+$.



5o

***N,N*-Dimethylnaphthalen-1-amine (5o):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 1H), 7.83 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 2.92 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 134.8, 128.8, 128.4, 125.8, 125.7, 125.2, 124.2, 122.9, 113.9, 45.2; MS (ESI): 172.10$[M+H]^+$.



5p

***N,N*-Diethyl-4-methylaniline (5p):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 3.32 (q, *J* = 7.0 Hz, 4H), 2.25 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 129.7, 124.7, 112.4, 44.5, 20.1, 12.5; MS (ESI): 164.15$[M+H]^+$.

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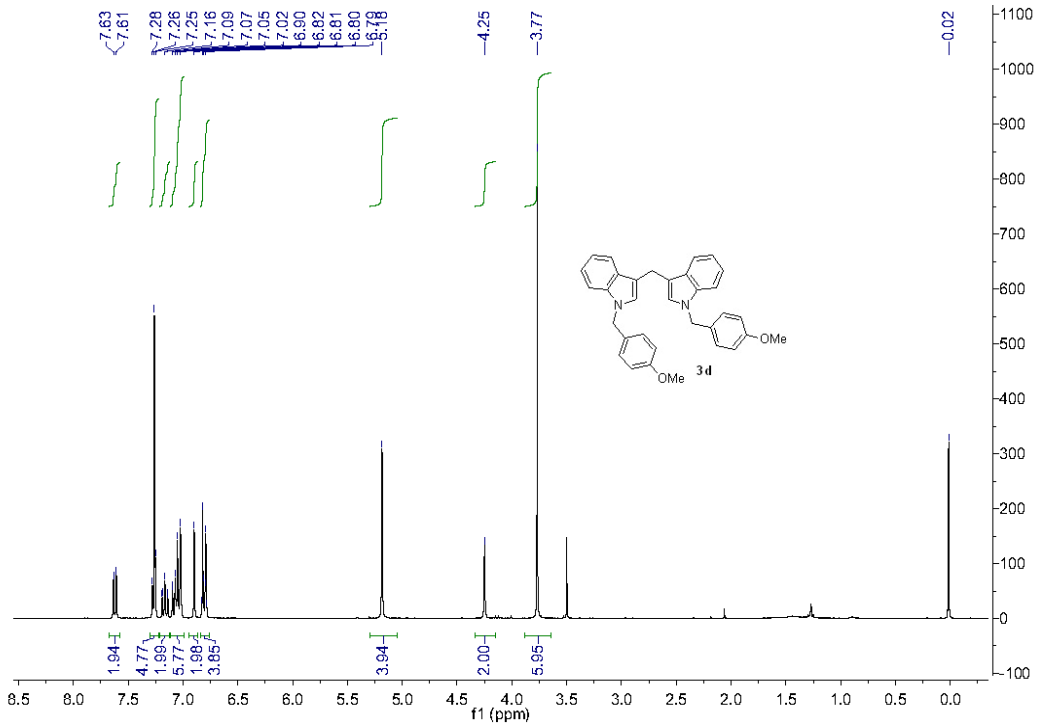
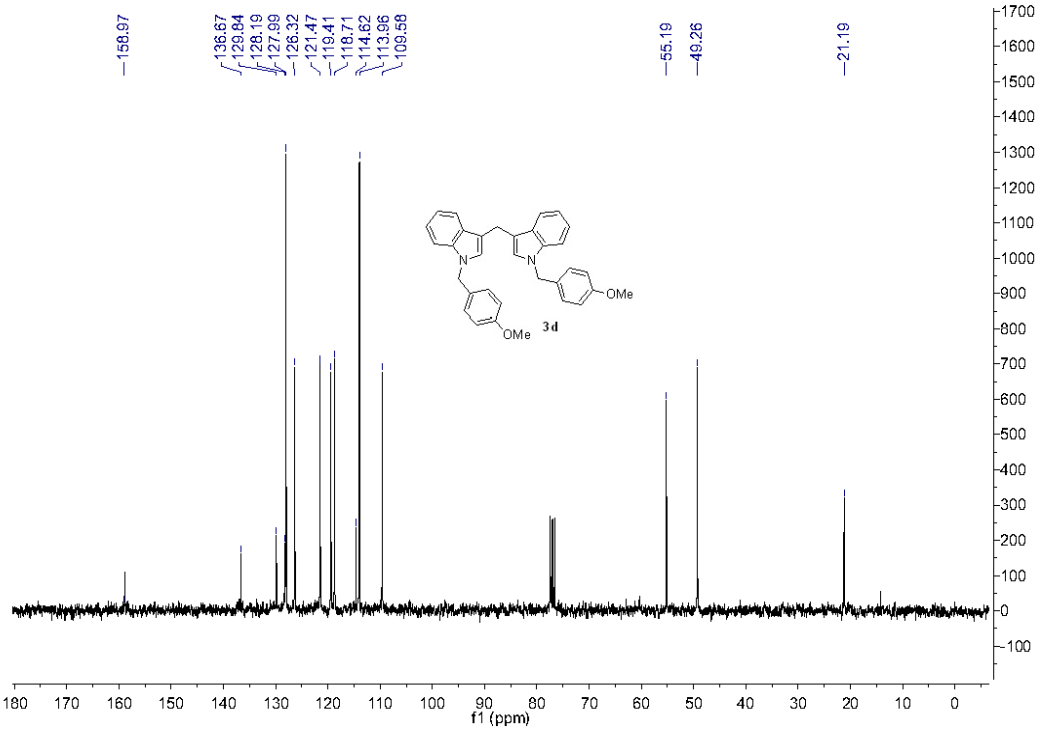
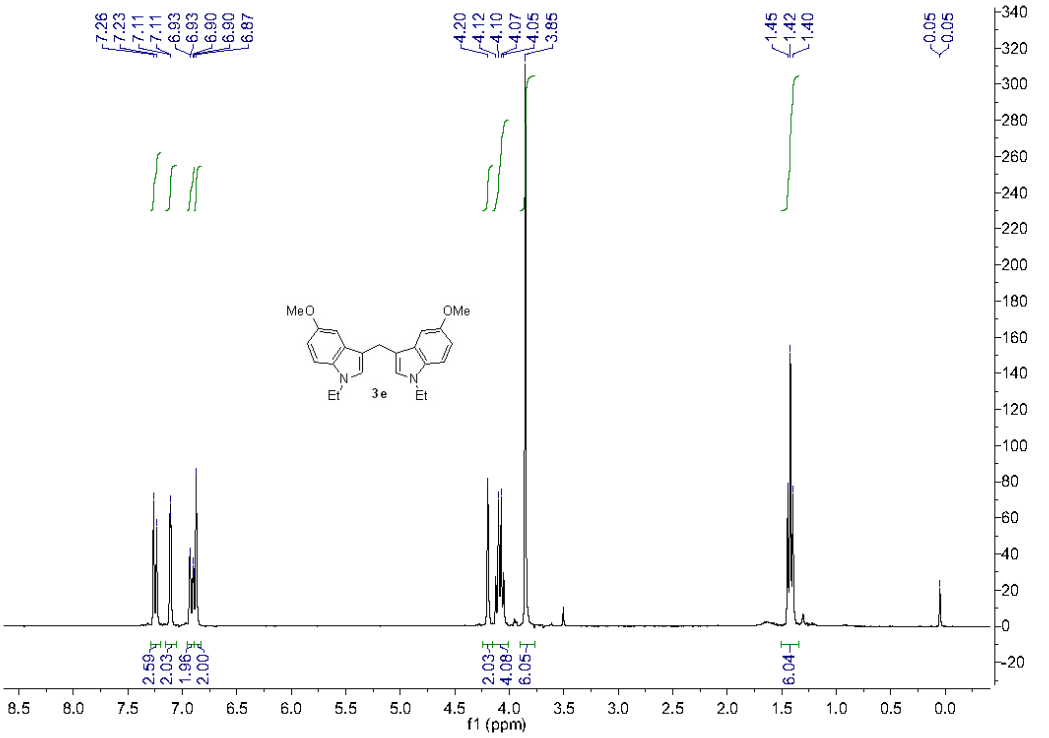
5. NMR Spectra of unknow Products



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OMe
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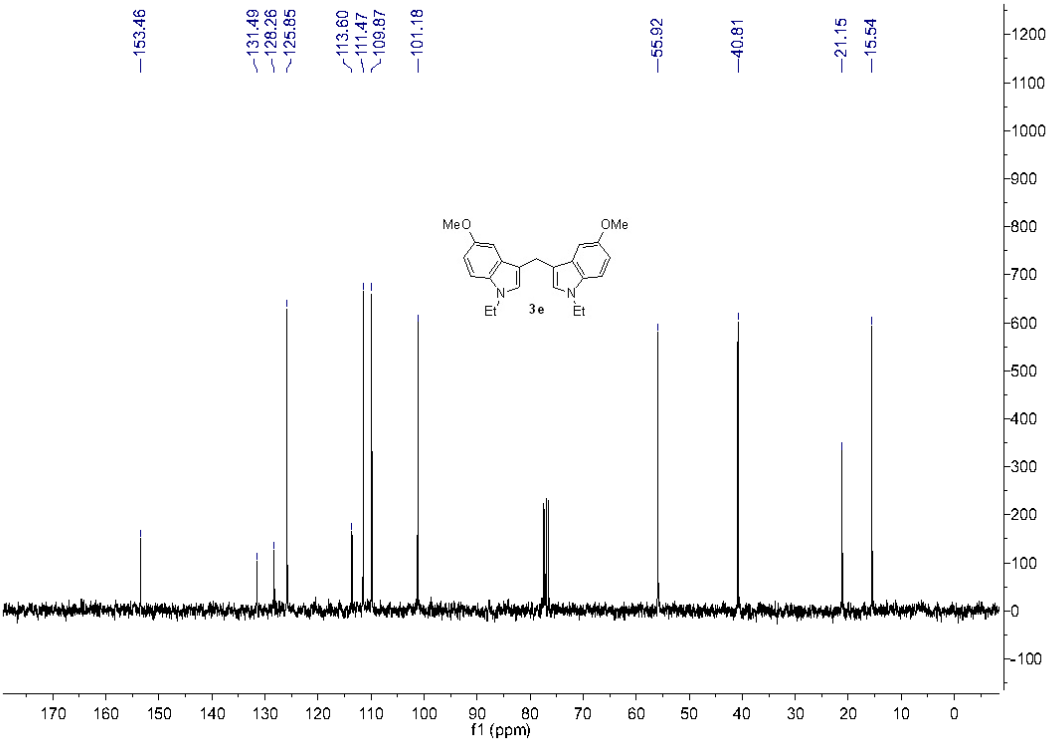
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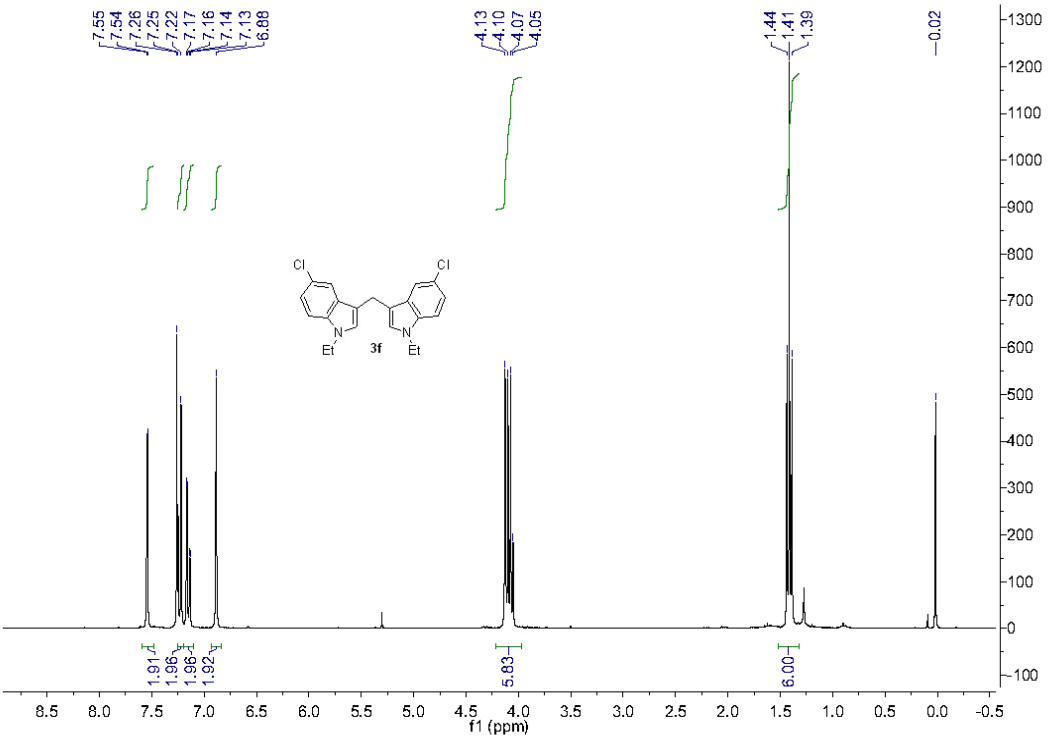
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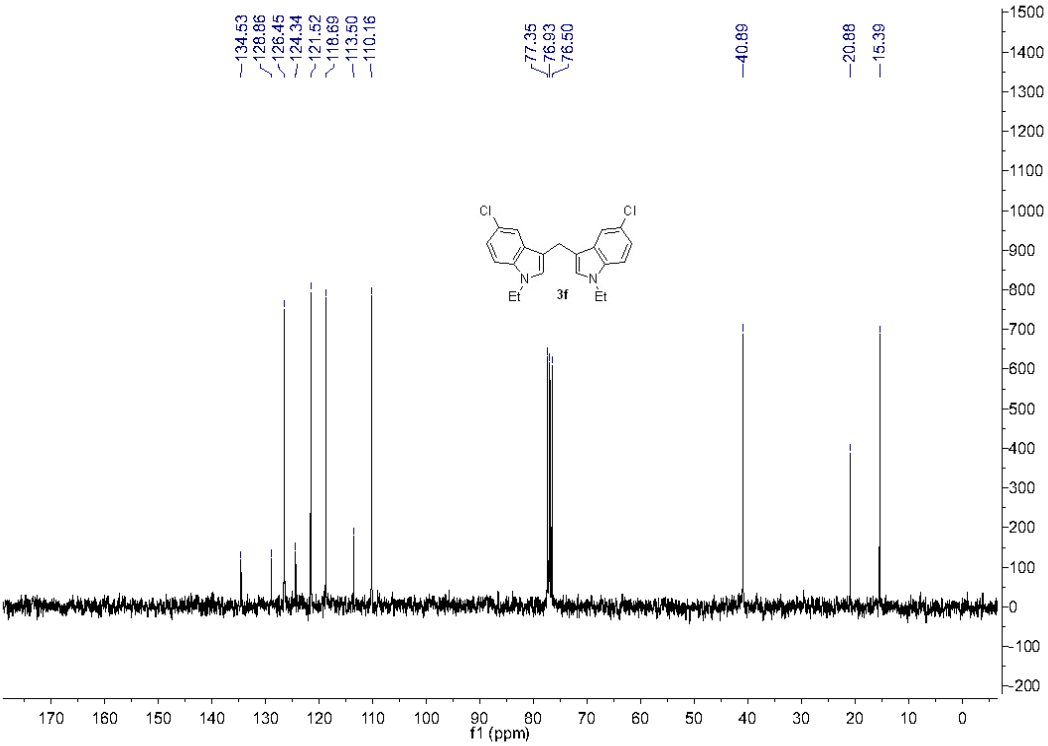
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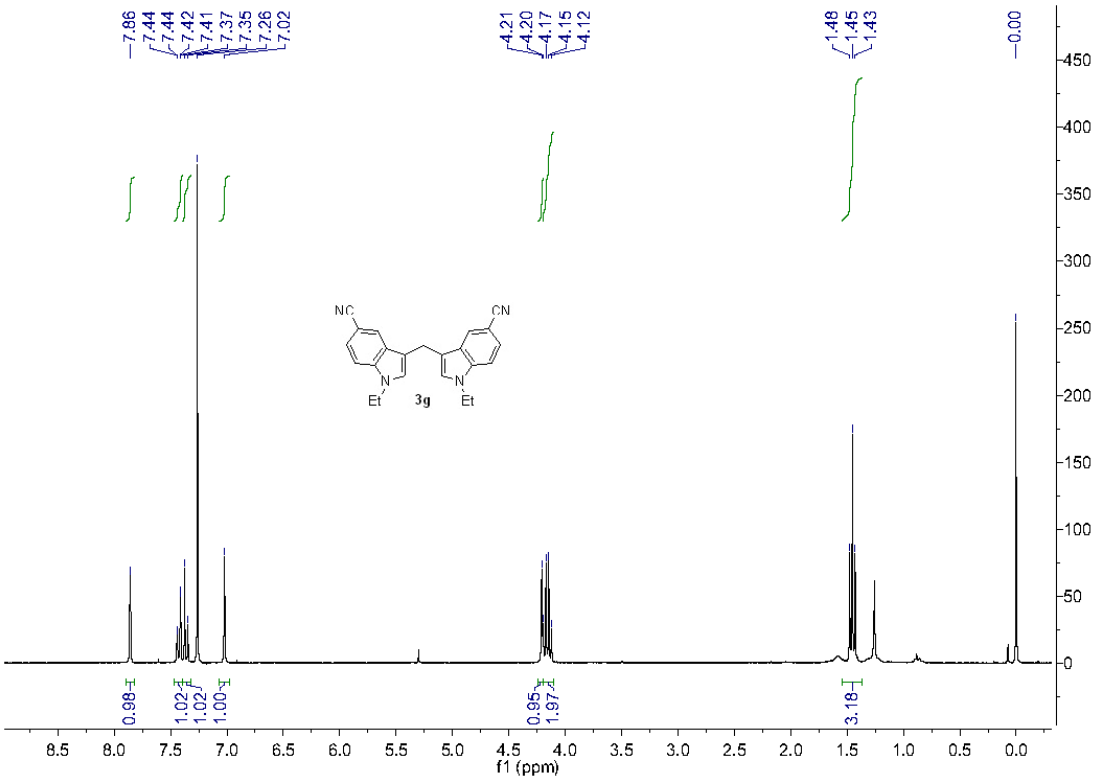
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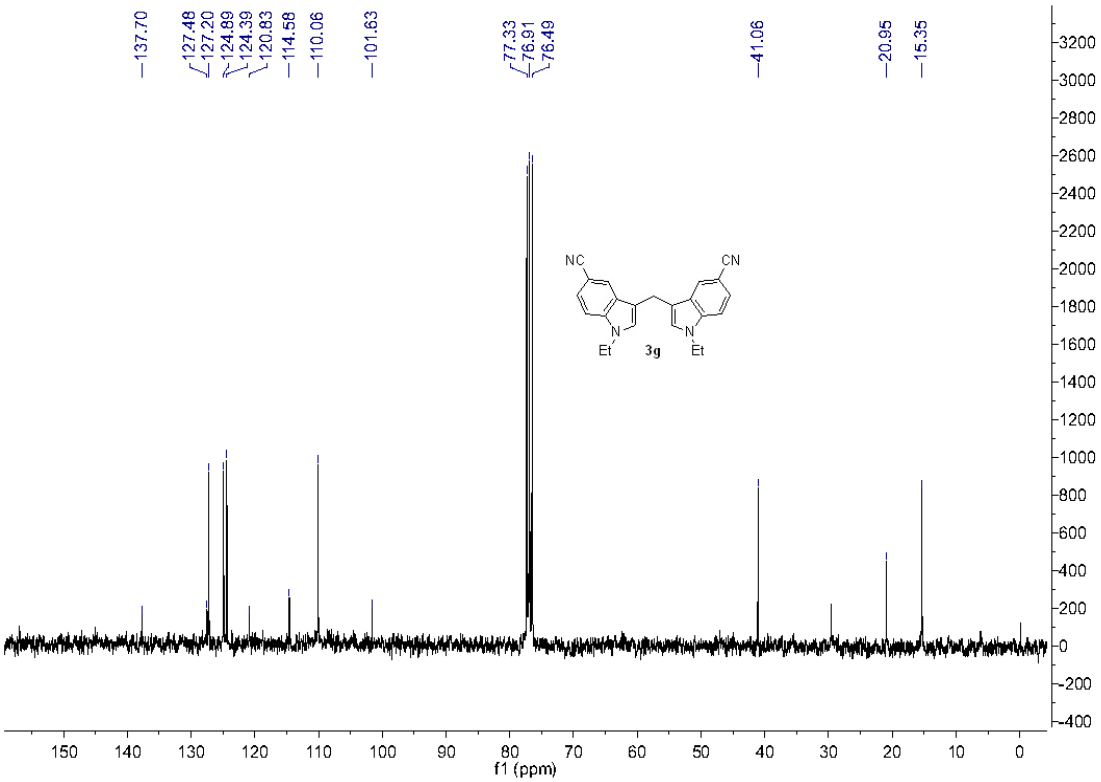
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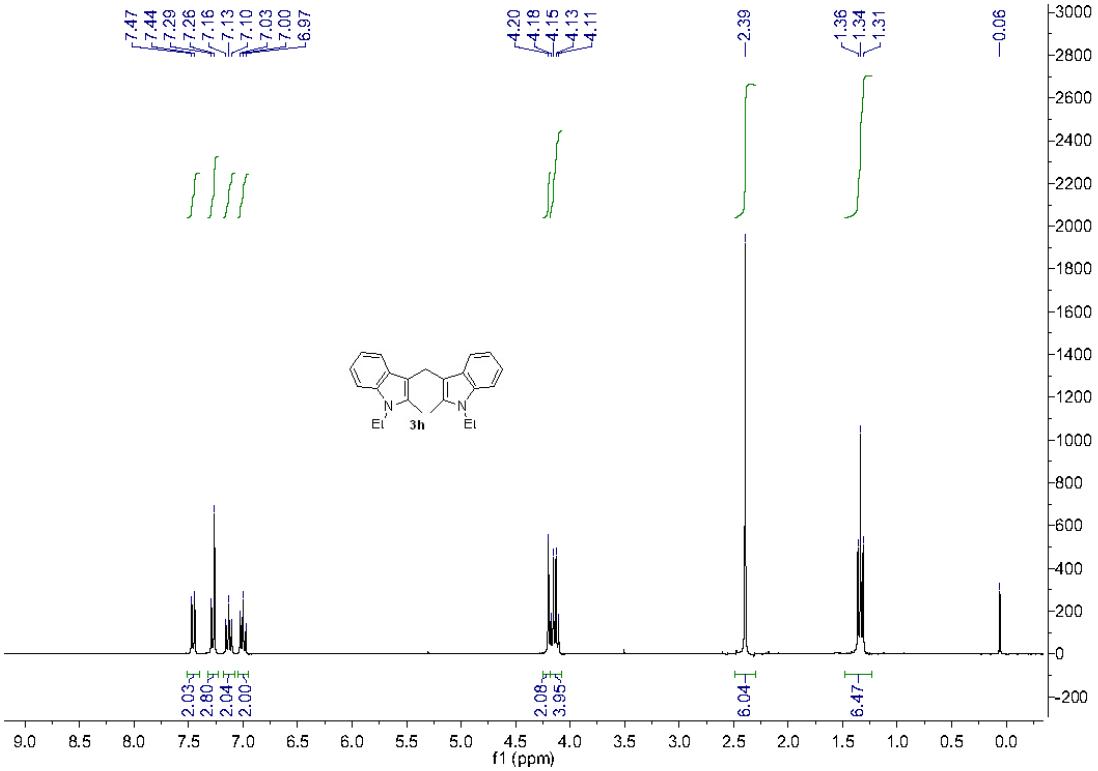
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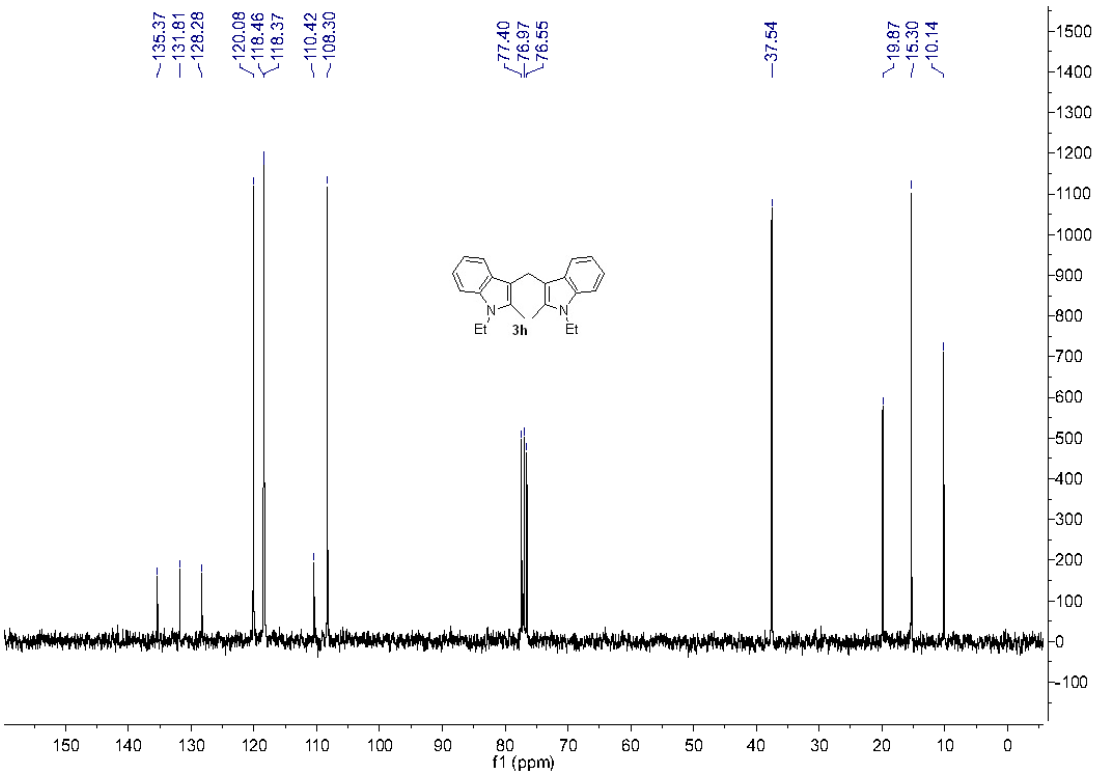
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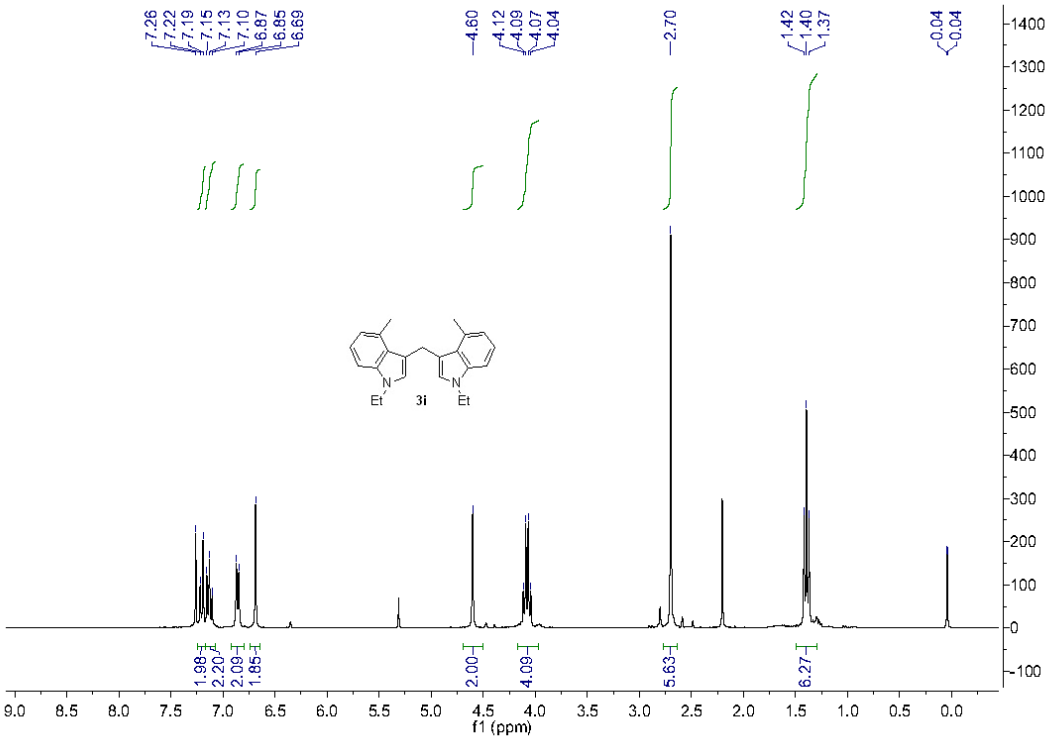
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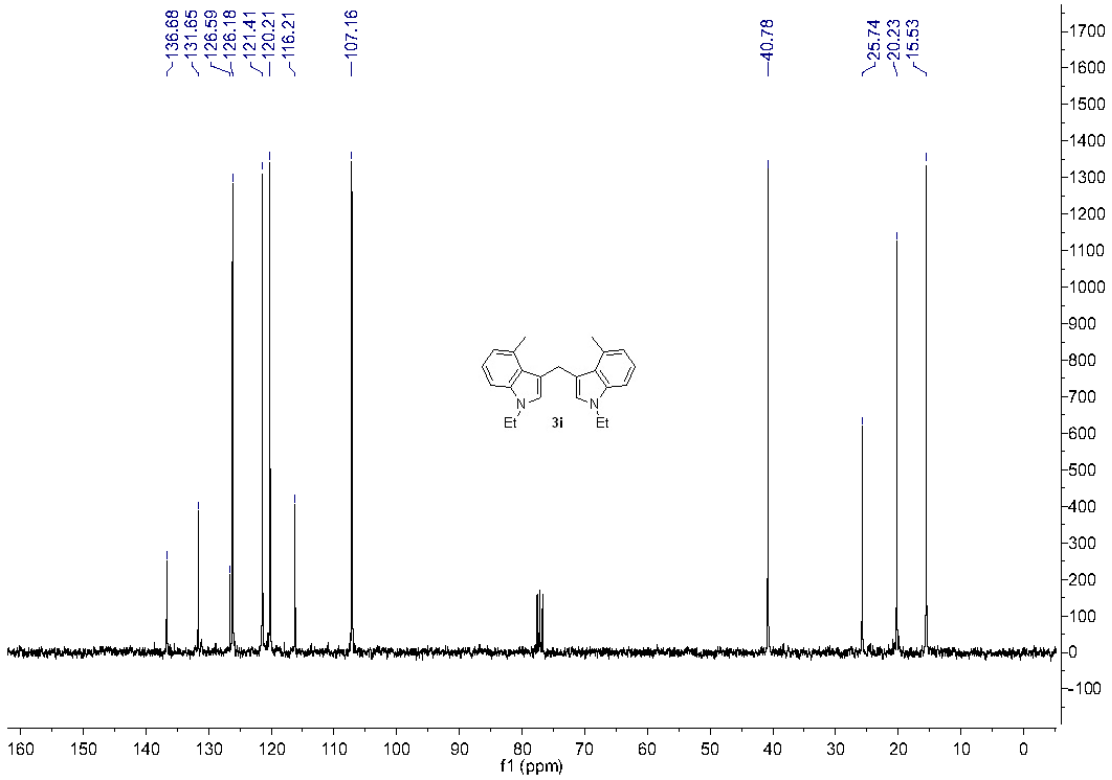
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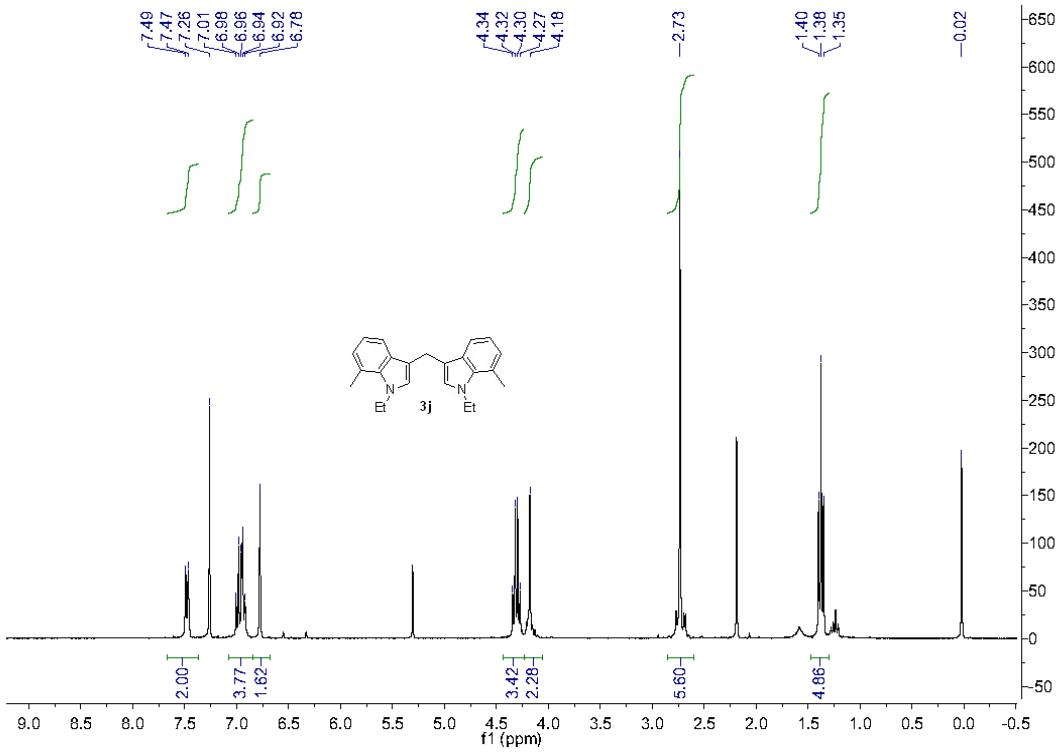
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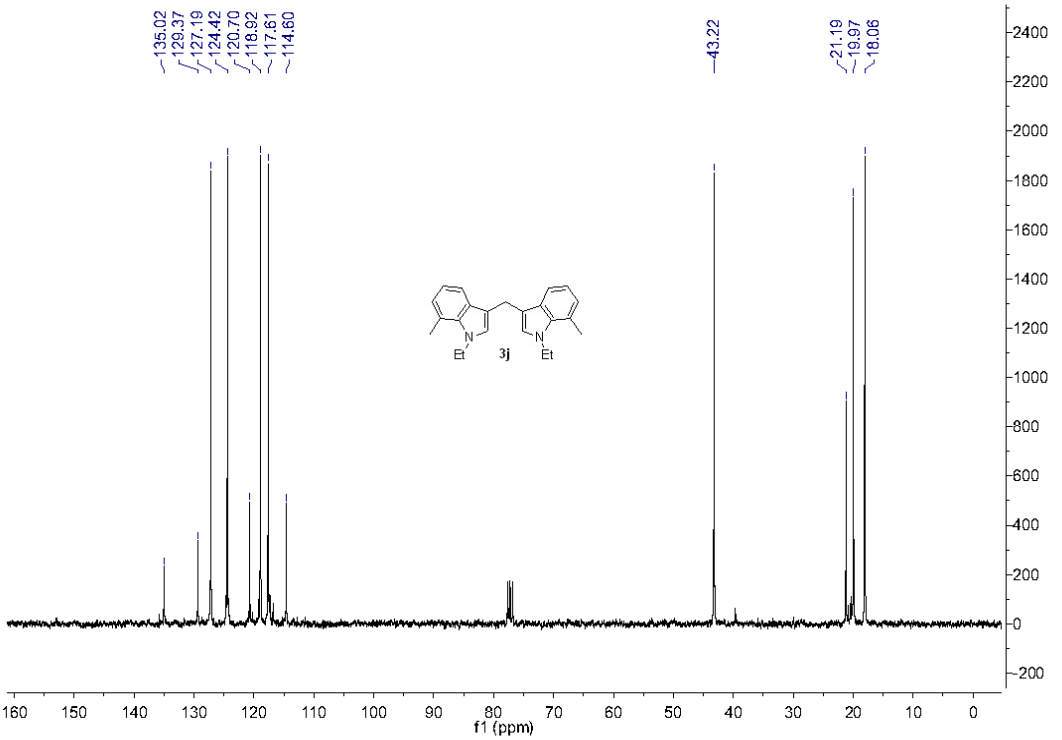
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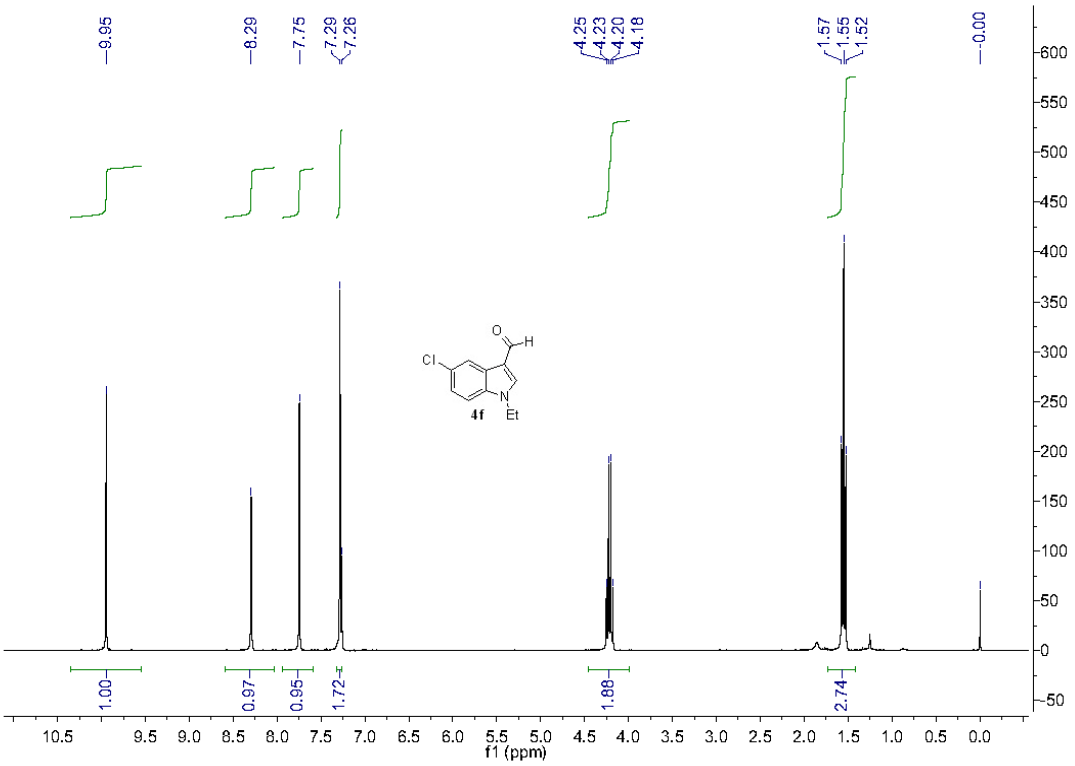
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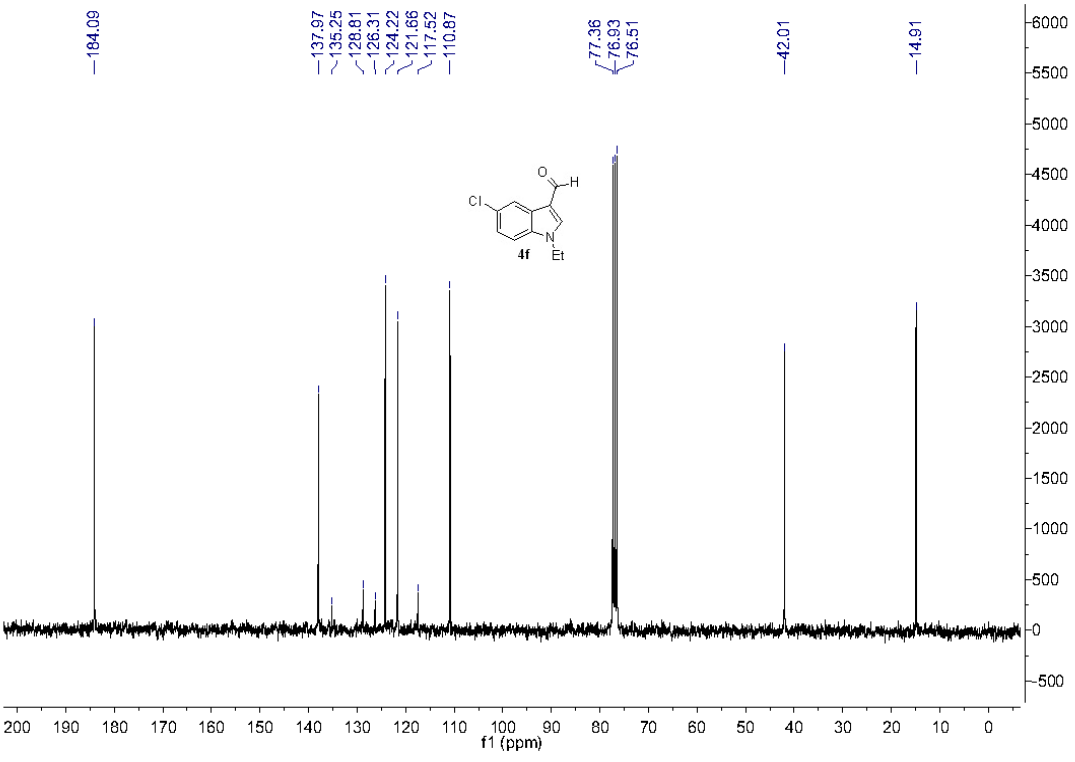
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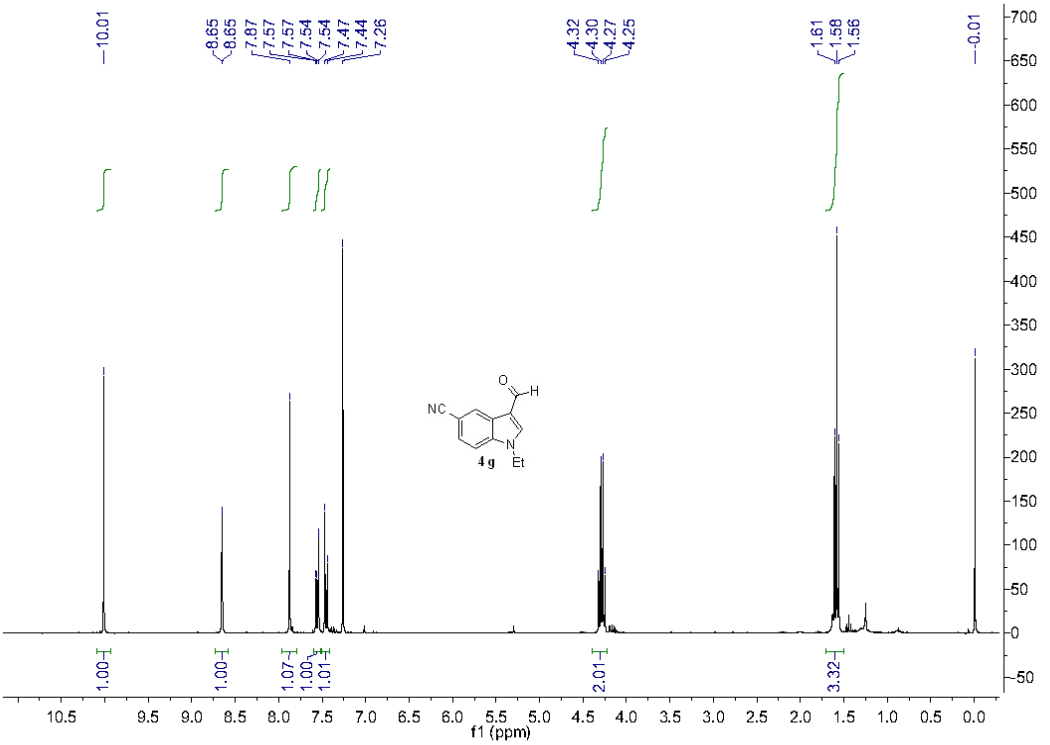
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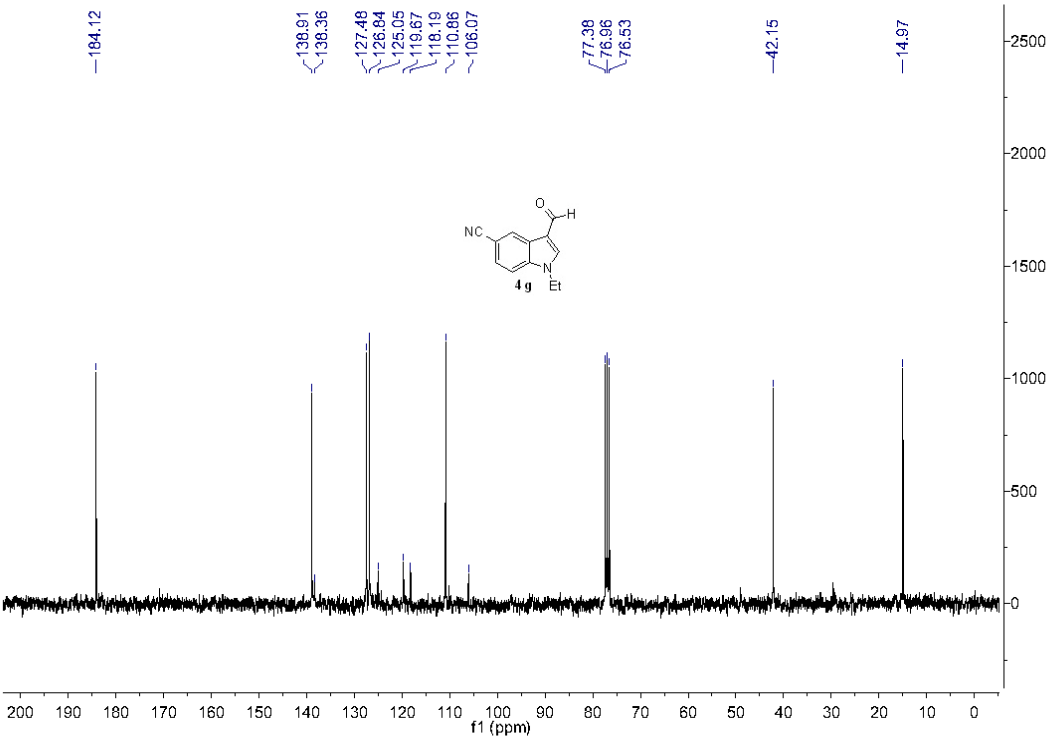
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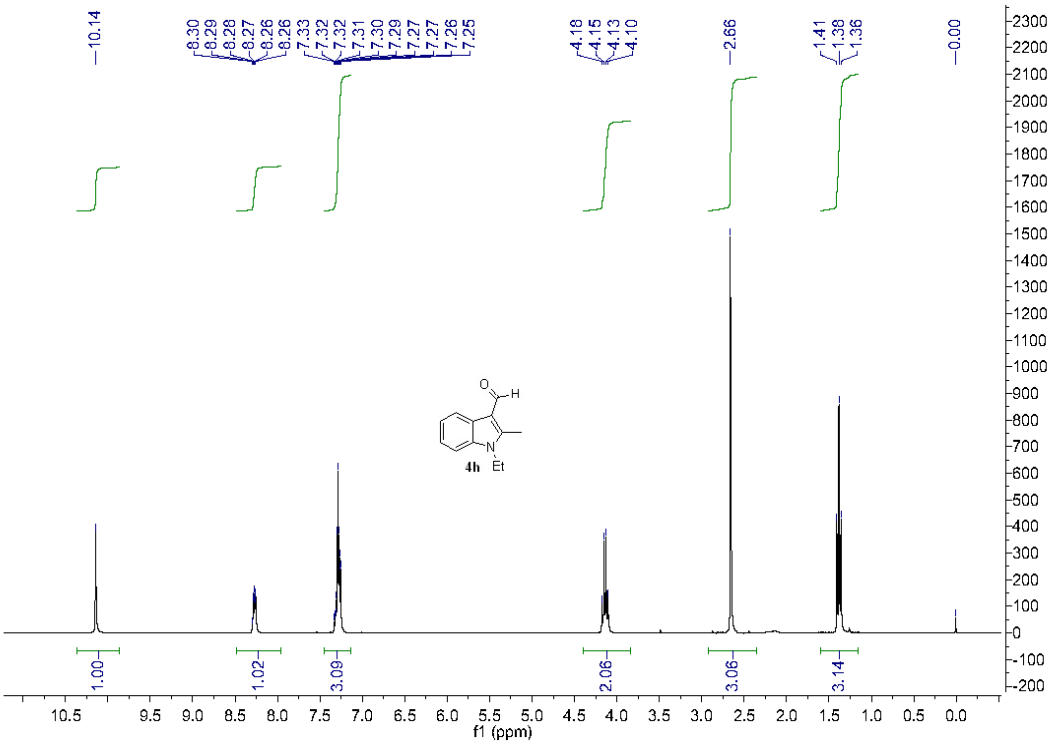
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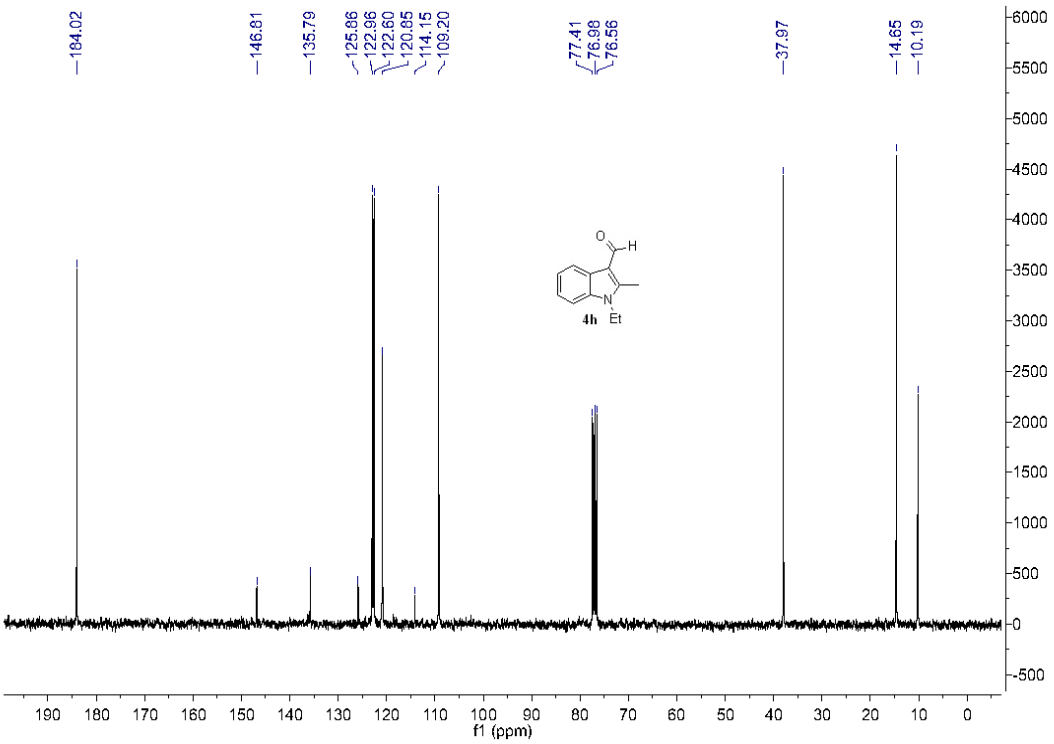
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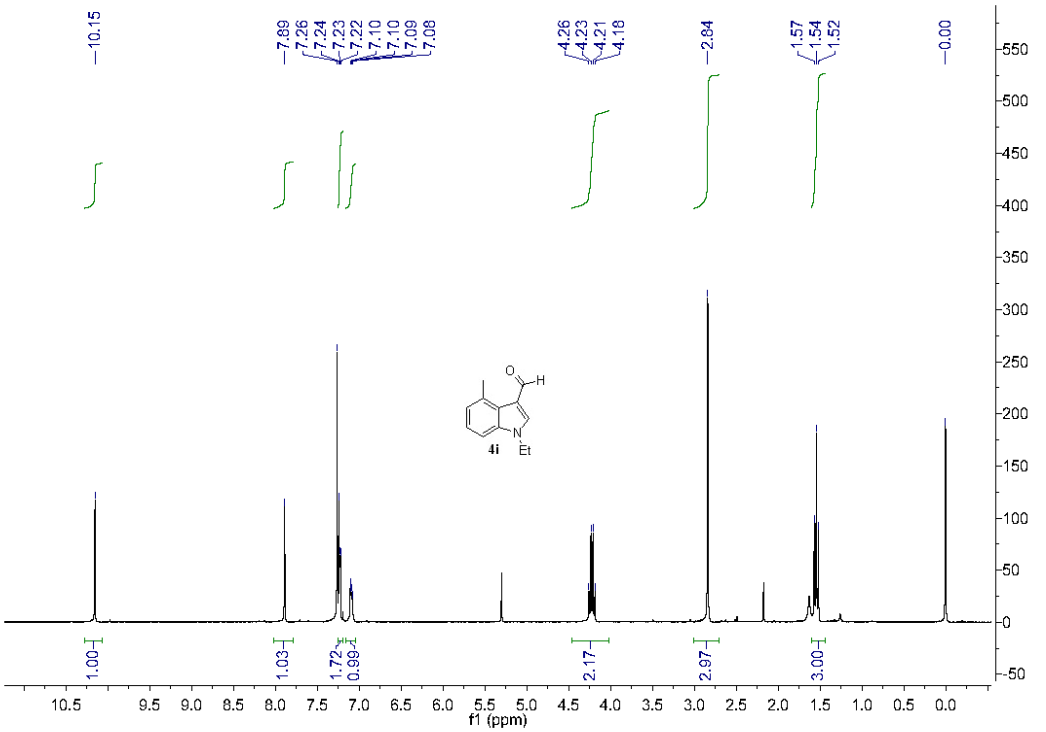
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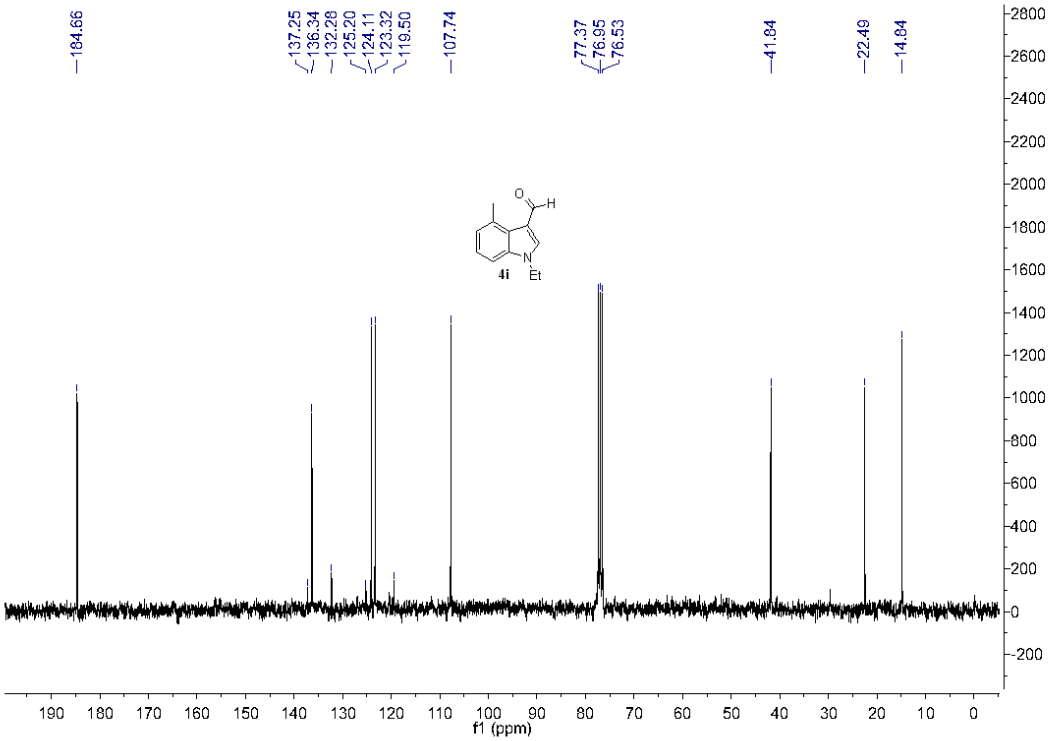
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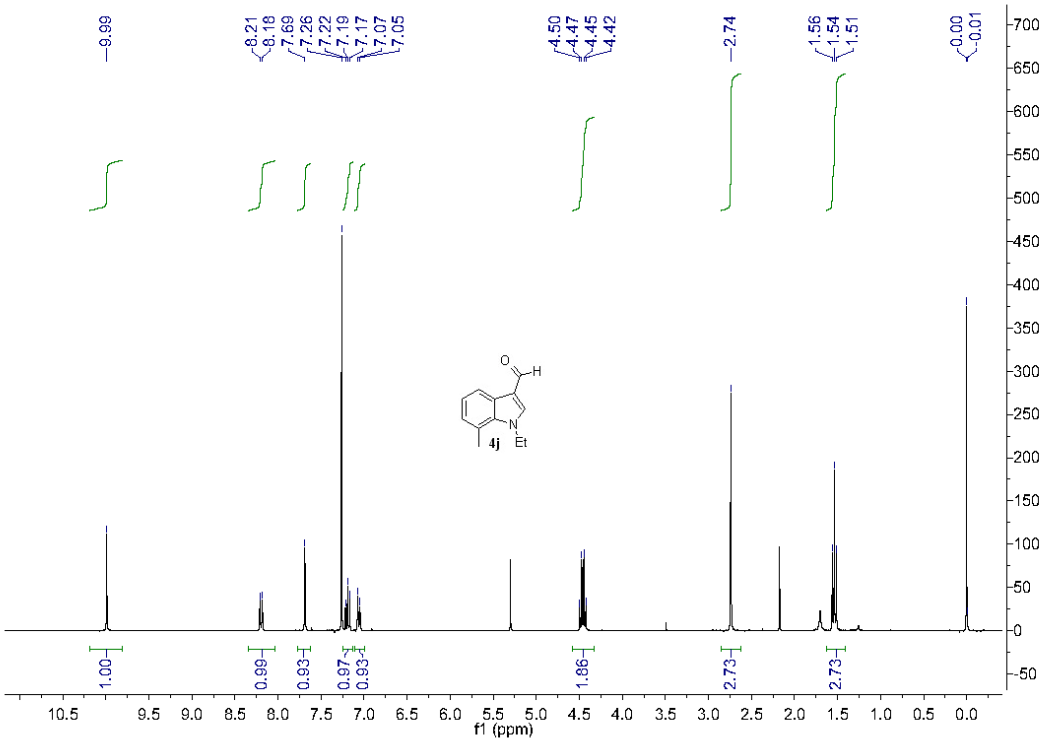
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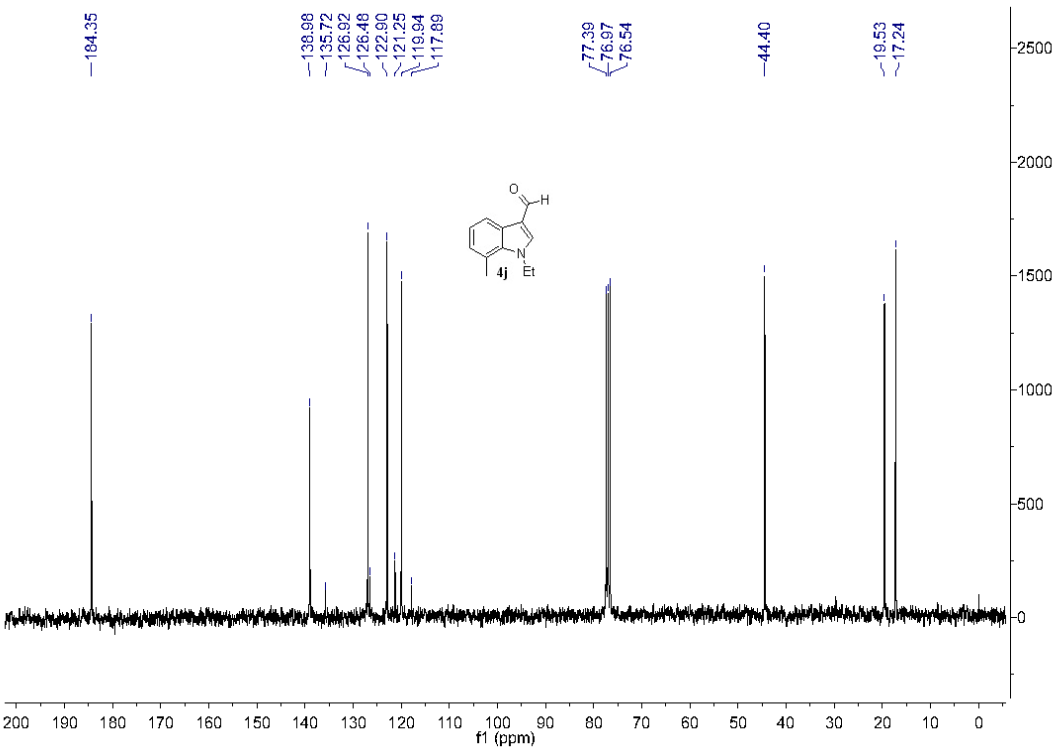
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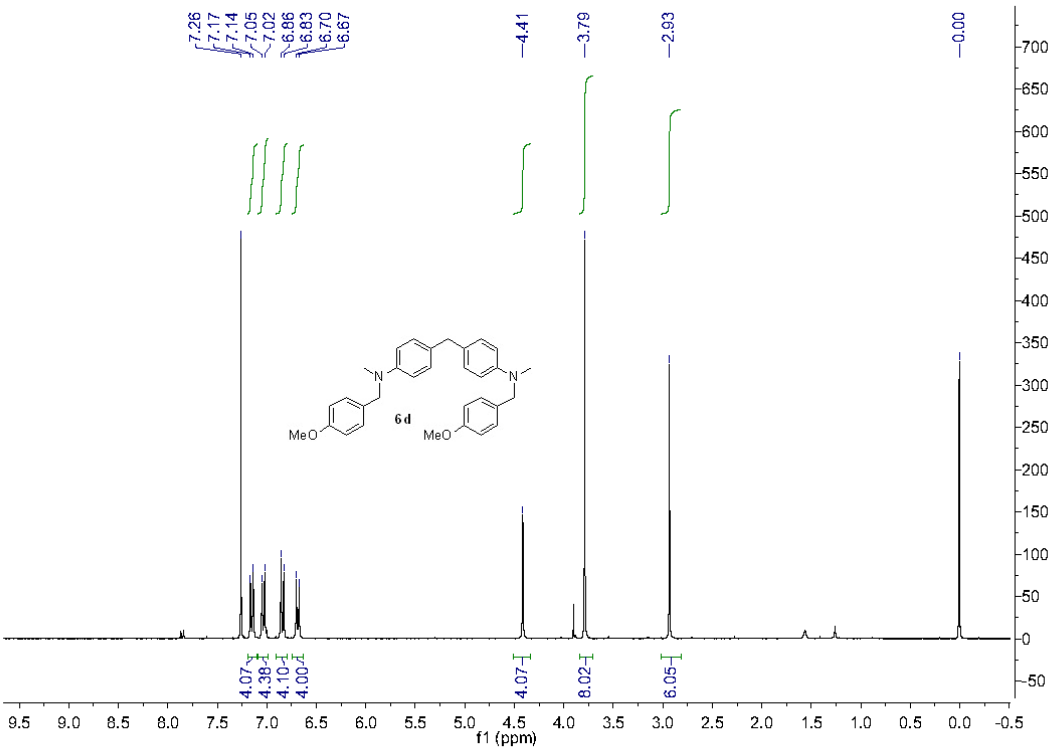
4j Et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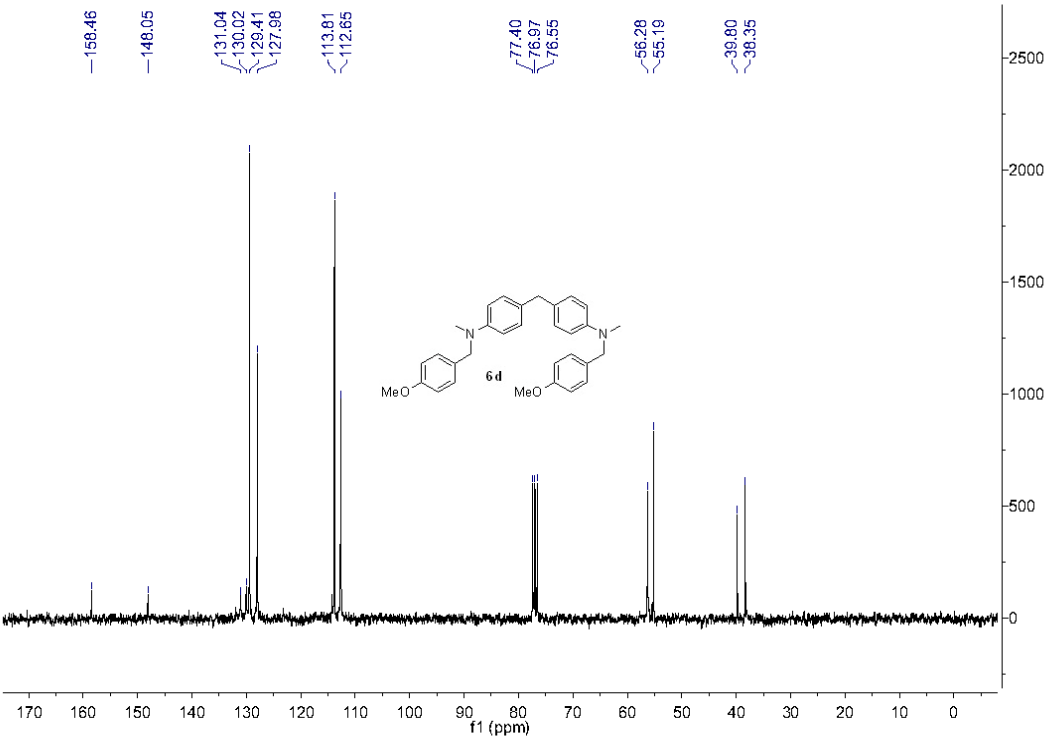
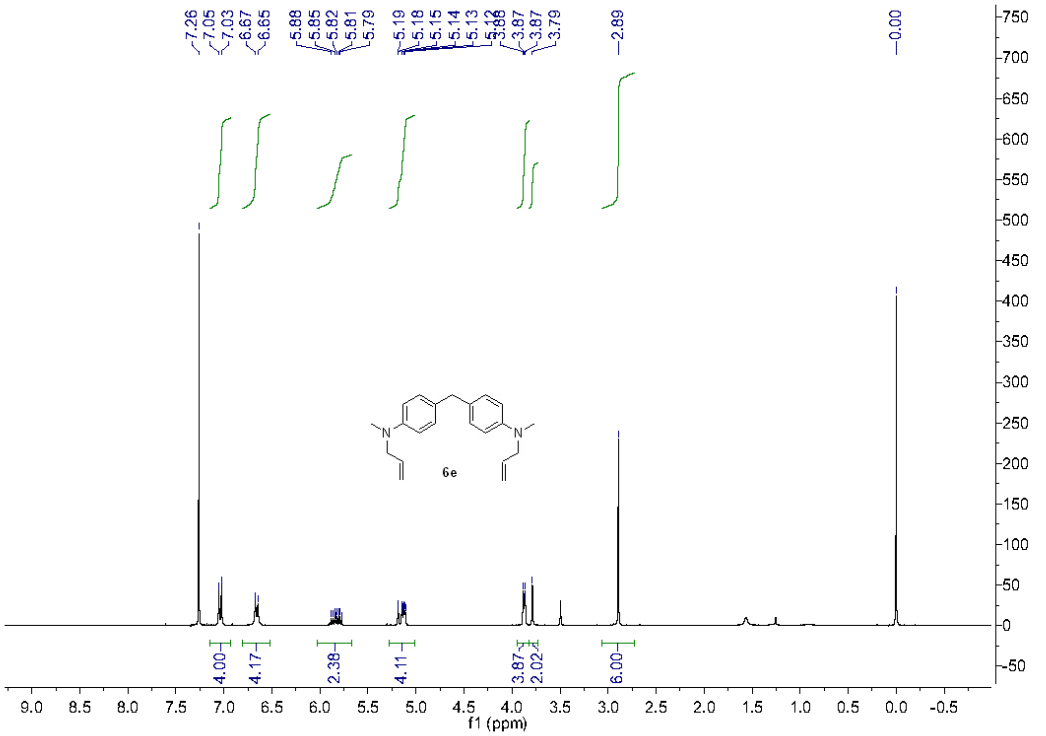
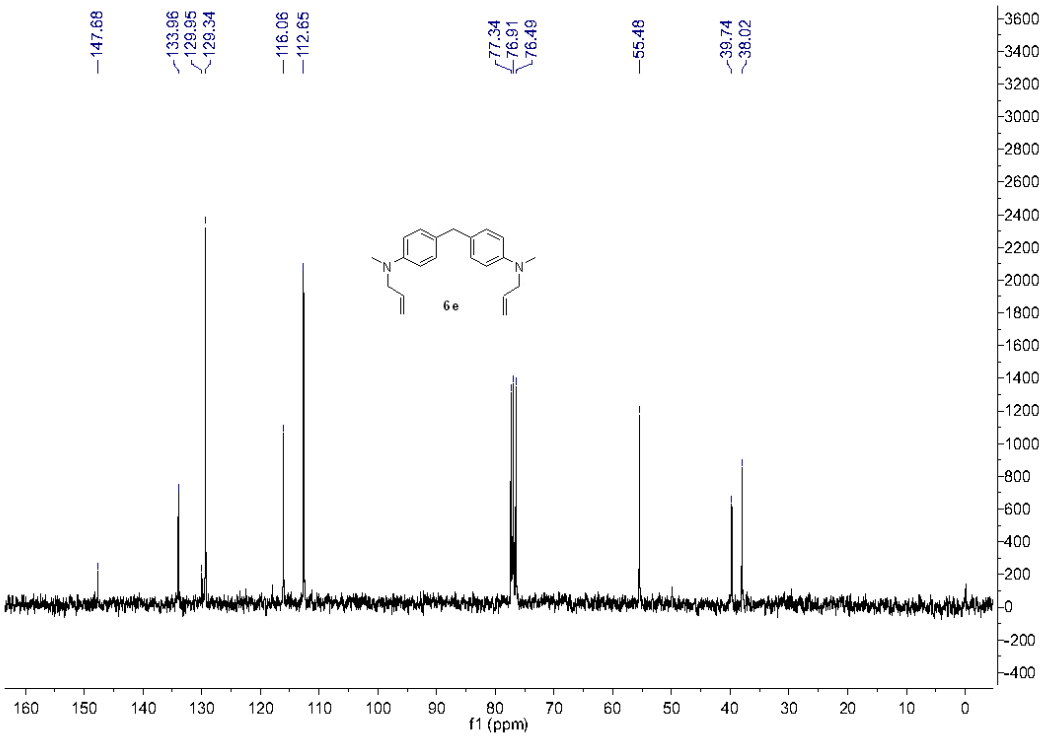
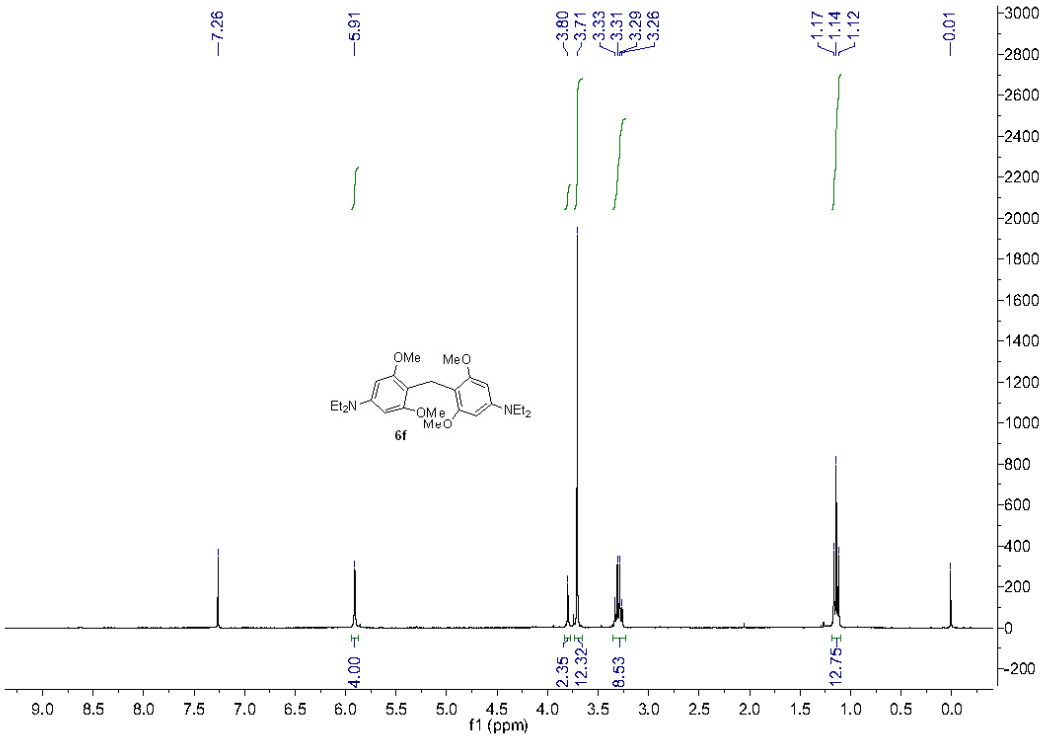
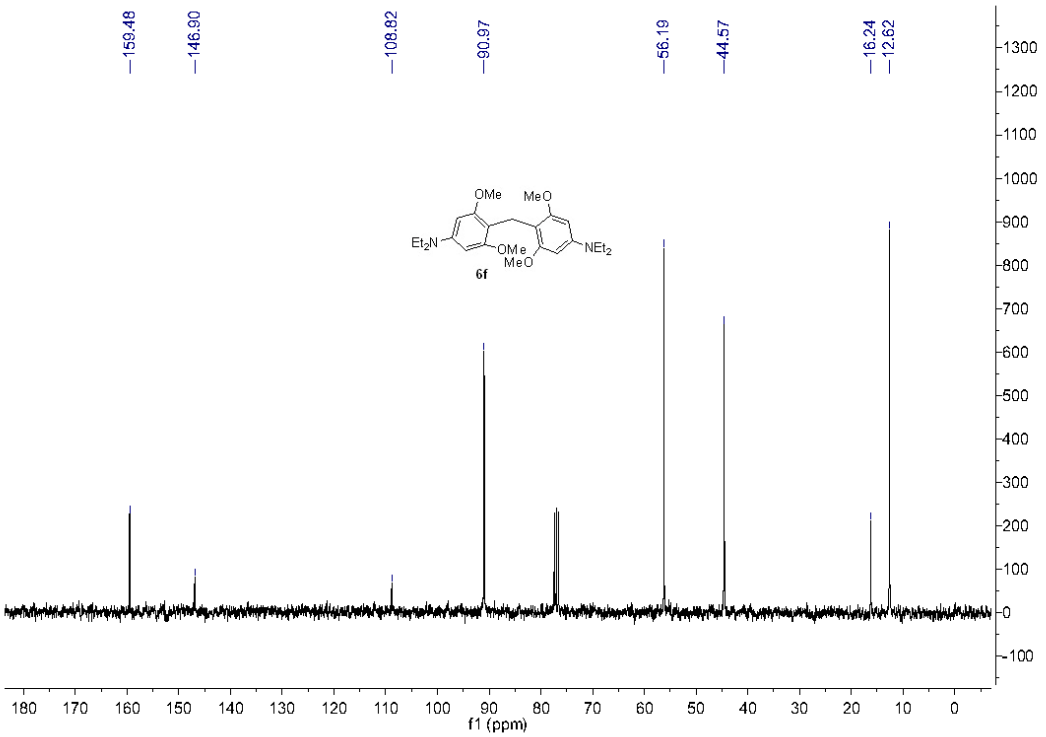
6.05
f1 (ppm)

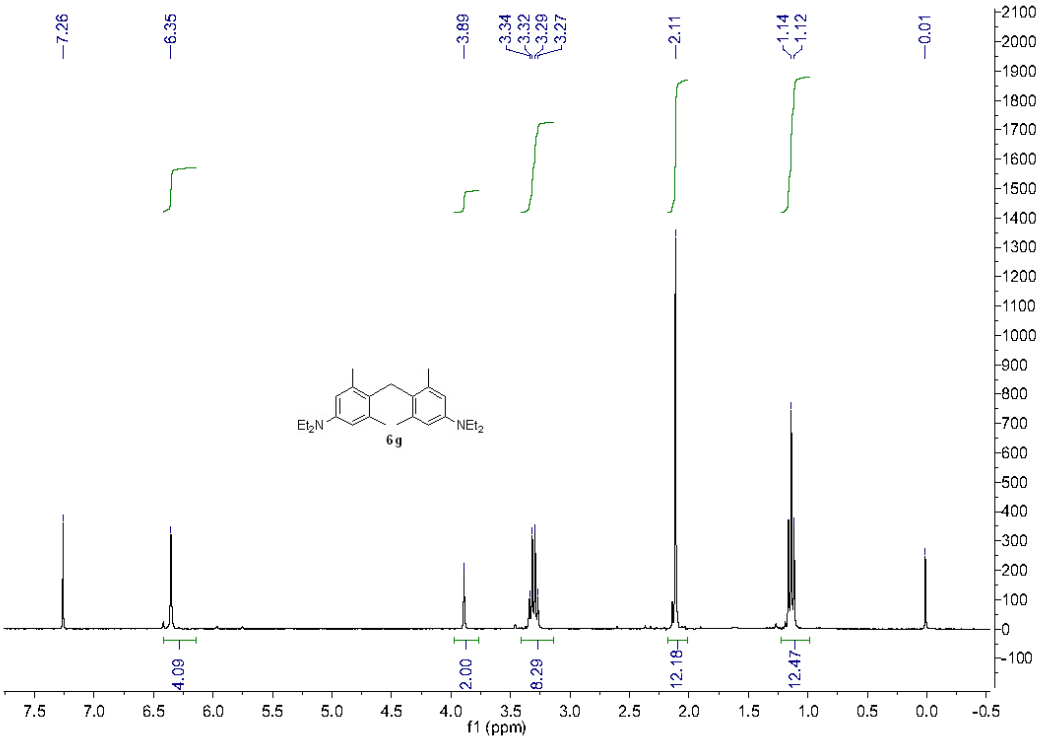

158.46
148.05
131.04
130.02
129.41
127.98
113.81
112.65
77.40
76.97
76.55
56.28
55.19
39.80
38.35
MeO
6d
MeO
f1 (ppm)

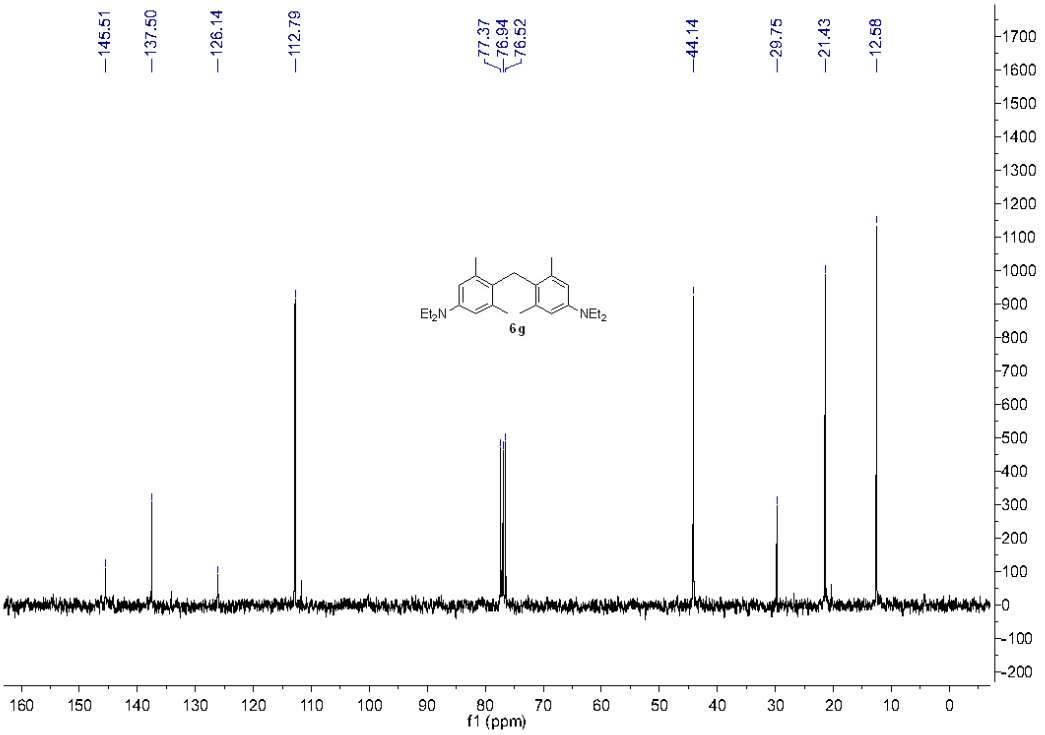

7.26
7.05
7.03
6.67
6.65
5.88
5.85
5.82
5.81
5.79
5.19
5.18
5.15
5.14
5.13
5.12
3.88
3.87
3.87
3.79
2.89
0.00
6e
4.00
4.17
2.38
4.11
3.87
2.02
6.00
f1 (ppm)

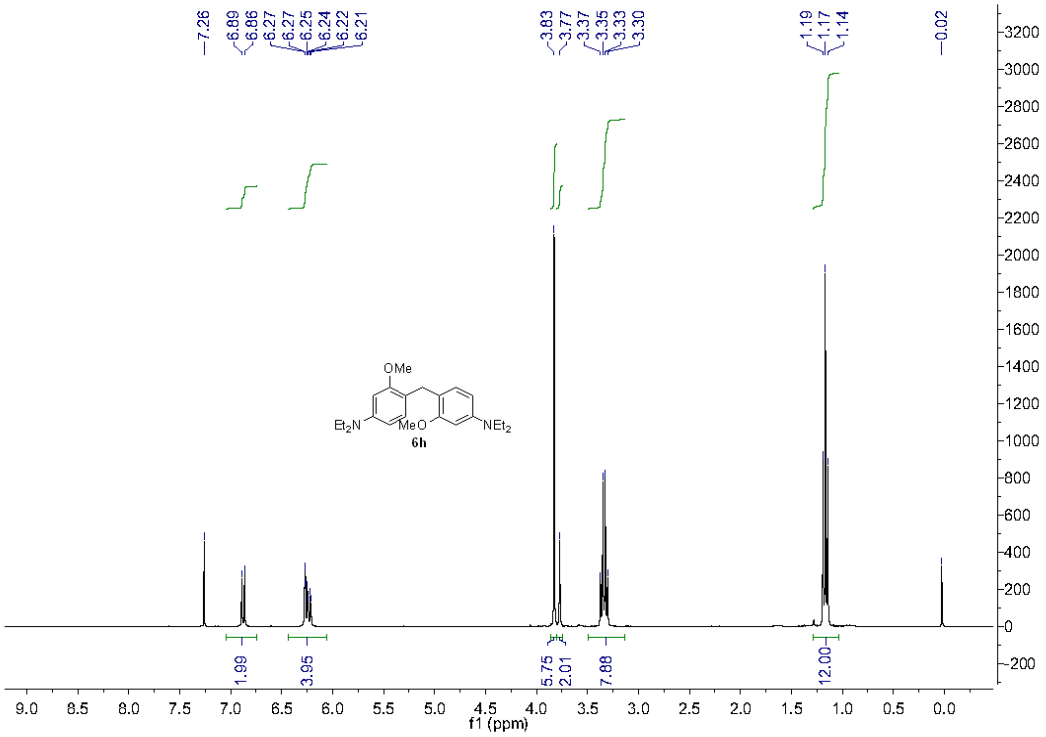

147.68
133.96
129.95
129.34
116.06
112.65
77.34
76.91
76.49
55.48
39.74
38.02
6e
f1 (ppm)

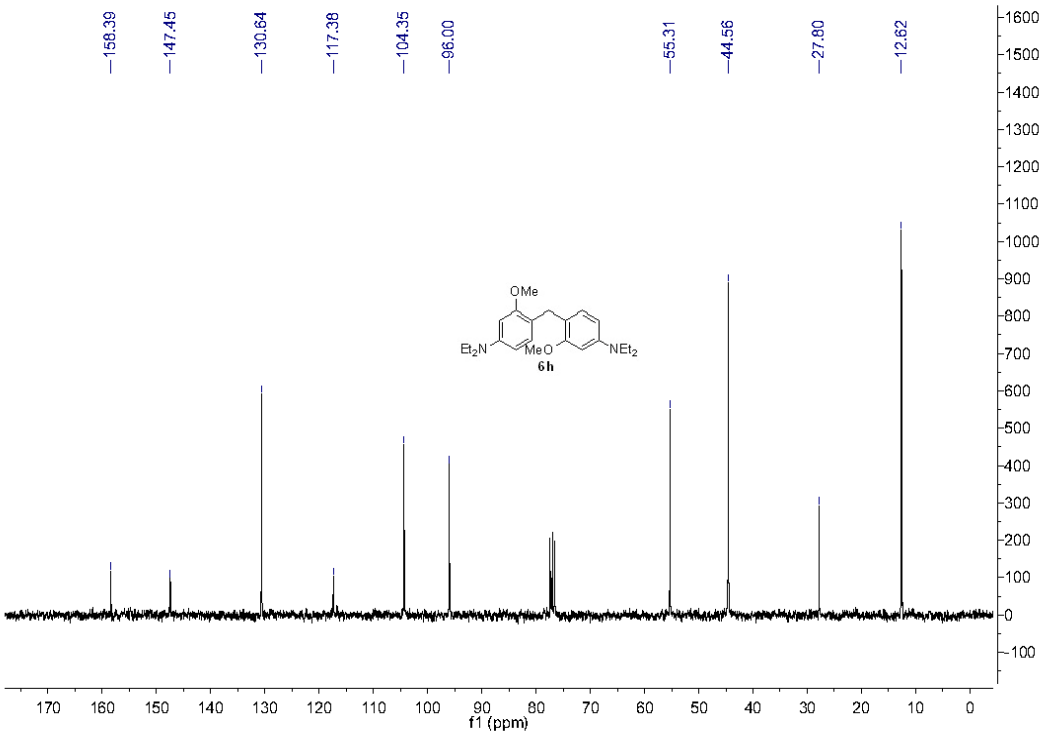

7.26
5.91
3.80
3.71
3.33
3.31
3.29
3.26
1.17
1.14
1.12
0.01
OMe
MeO
Et2N
NEt2
OMe
MeO
6f
4.00
2.35
12.32
8.53
12.75
f1 (ppm)

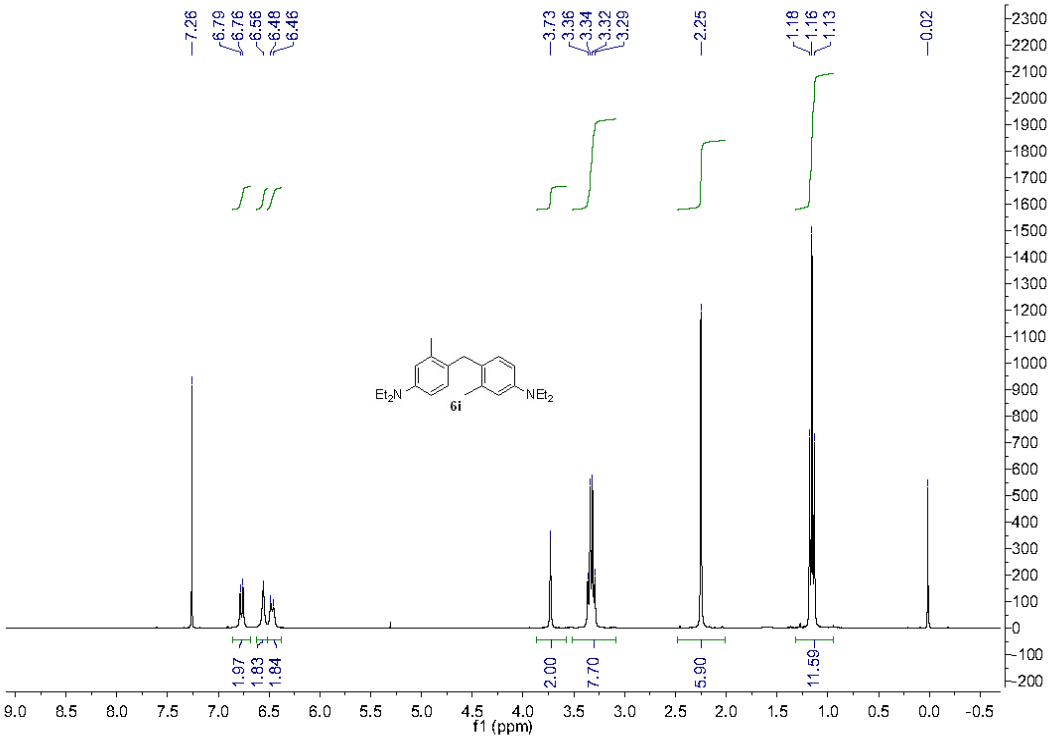

159.48
146.90
108.82
90.97
56.19
44.57
16.24
12.62
OMe
MeO
Et2N
NEt2
OMe
MeO
6f
f1 (ppm)

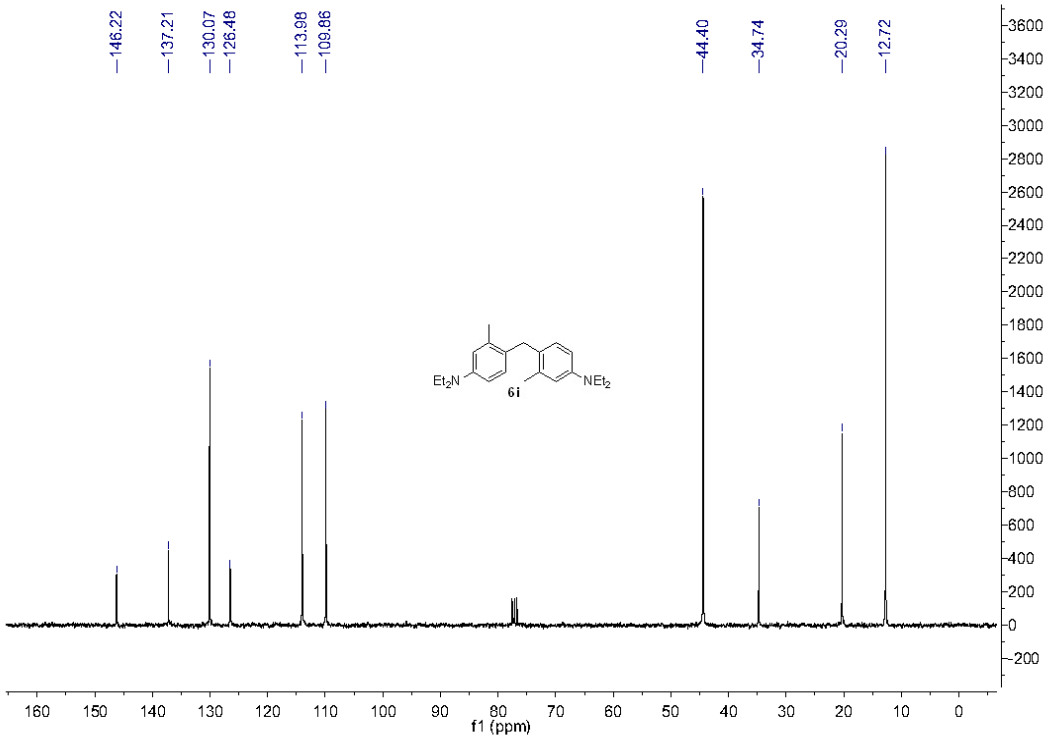

7.26
6.35
3.89
3.34
3.32
3.29
3.27
2.11
1.14
1.12
0.01
Et2N
NEt2
6g
4.09
2.00
8.29
12.18
12.47
f1 (ppm)

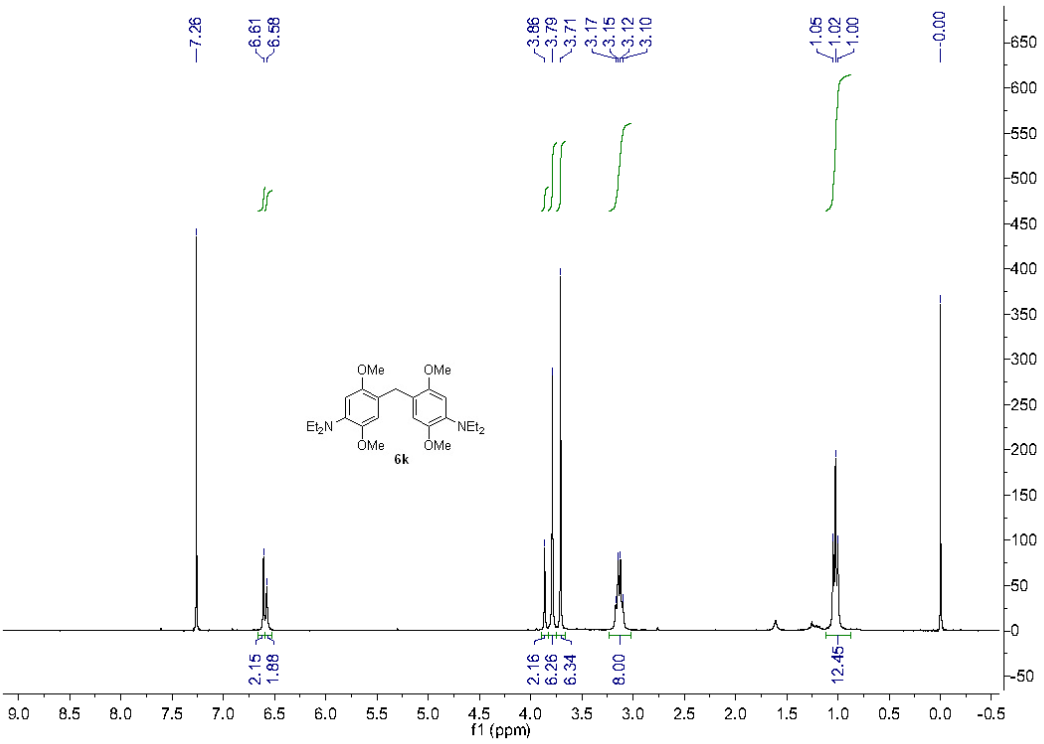

145.51
137.50
126.14
112.79
77.37
76.94
76.52
44.14
29.75
21.43
12.58
Et2N
NEt2
6g
f1 (ppm)

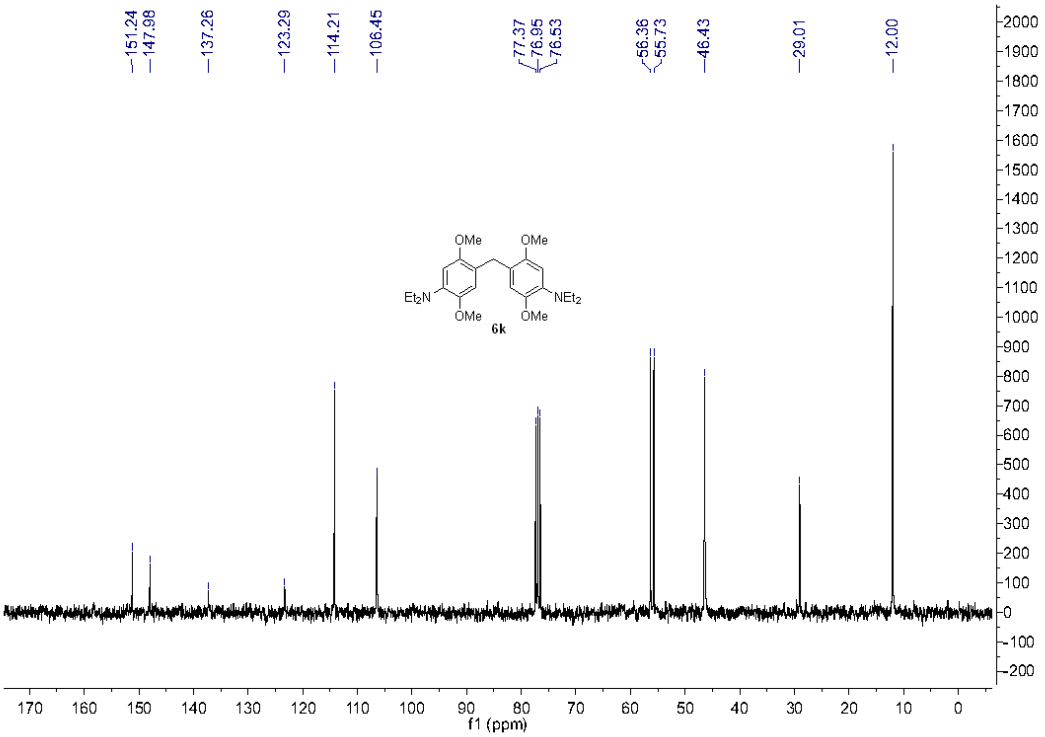

7.26
6.89
6.86
6.27
6.27
6.25
6.24
6.22
6.21
3.83
3.77
3.37
3.35
3.33
3.30
1.19
1.17
1.14
0.02
OMe
Et2N
MeO
NEt2
6h
1.99
3.95
5.75
2.01
7.88
12.00
f1 (ppm)


158.39
147.45
130.64
117.38
104.35
96.00
55.31
44.56
27.80
12.62
OMe
Et2N
MeO
NEt2
6h
f1 (ppm)


7.26
6.79
6.76
6.56
6.48
6.46
3.73
3.36
3.34
3.32
3.29
2.25
1.18
1.16
1.13
0.02
1.97
1.83
1.84
2.00
7.70
5.90
11.59
Et2N
NEt2
6i
f1 (ppm)


146.22
137.21
130.07
126.48
113.98
109.86
44.40
34.74
20.29
12.72
Et2N
NEt2
6i
f1 (ppm)


7.26
6.61
6.58
3.86
3.79
3.71
3.17
3.15
3.12
3.10
1.05
1.02
1.00
0.00
OMe
OMe
Et2N
NEt2
OMe
OMe
6k
2.15
1.88
2.16
6.26
6.34
8.00
12.45
f1 (ppm)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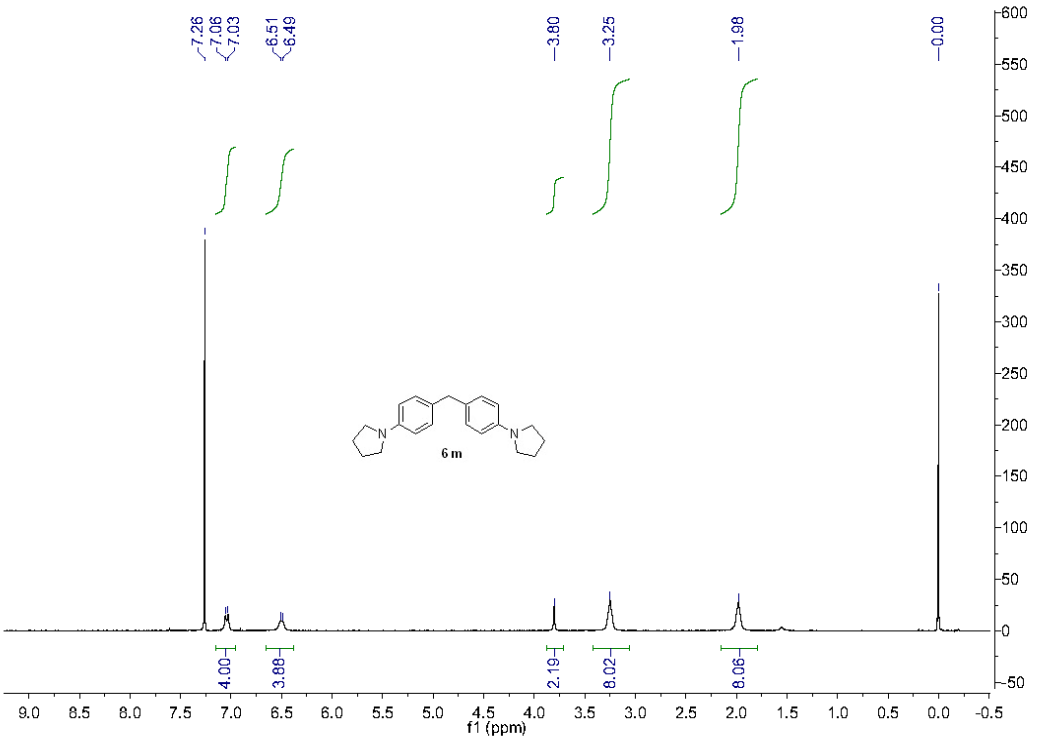
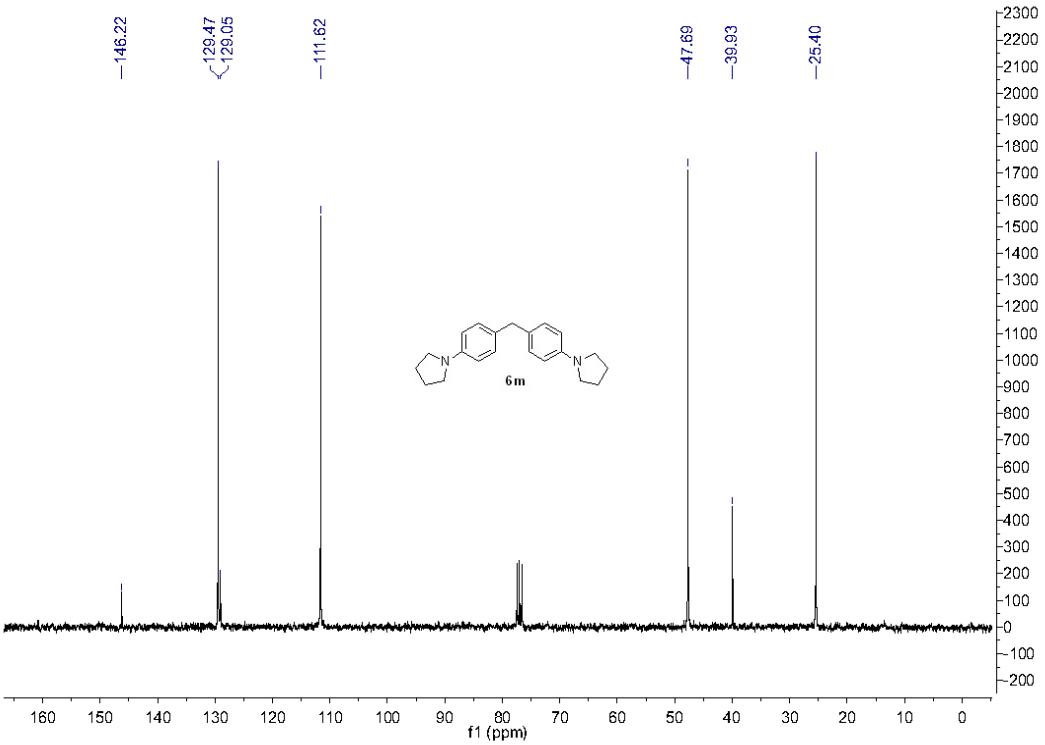
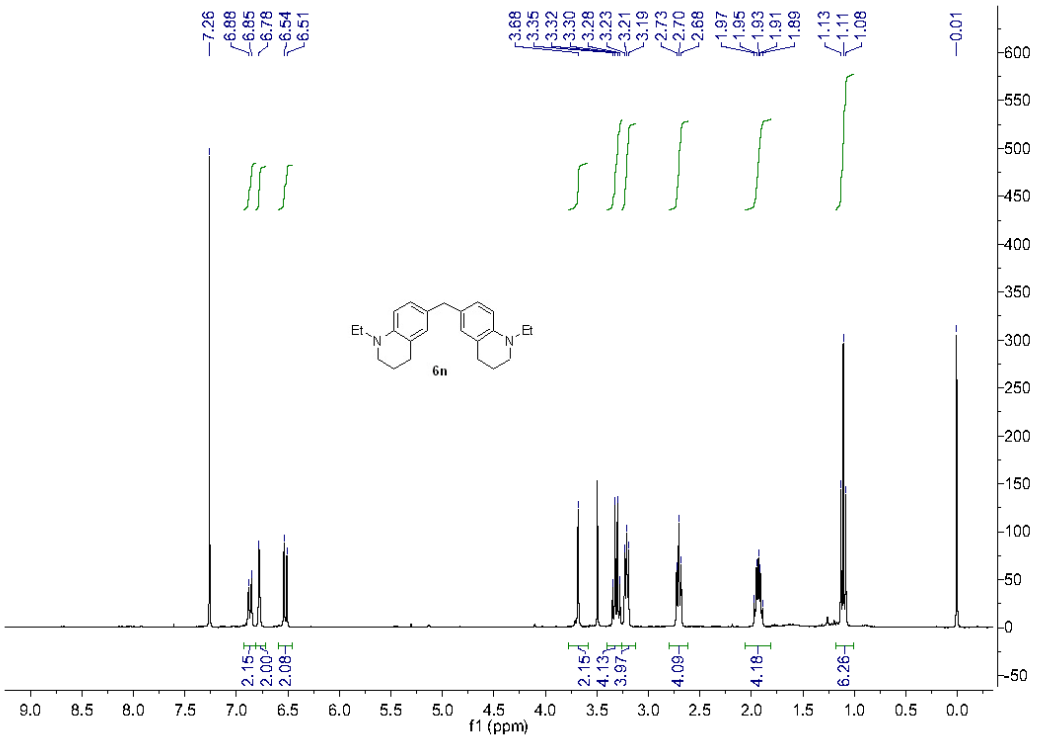
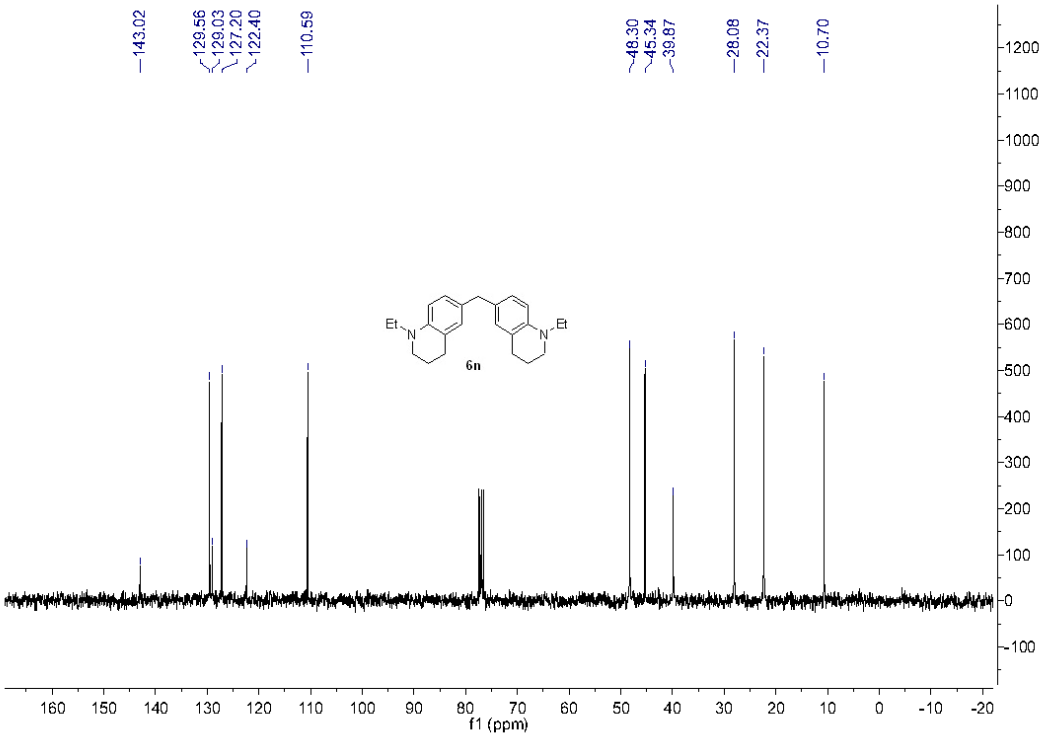
147.98
137.26
123.29
114.21
106.45
77.37
76.95
76.53
56.36
55.73
46.43
29.01
12.00
OMe
OMe
Et2N
NEt2
OMe
OMe
6k
f1 (ppm)


7.26
7.06
7.03
6.51
6.49
3.80
3.25
1.98
0.00
6m
4.00
3.88
2.19
8.02
8.06
f1 (ppm)


146.22
129.47
129.05
111.62
47.69
39.93
25.40
6m
f1 (ppm)


7.26
6.88
6.85
6.78
6.54
6.51
3.68
3.35
3.32
3.30
3.28
3.23
3.21
3.19
2.73
2.70
2.68
1.97
1.95
1.93
1.91
1.89
1.13
1.11
1.08
0.01
Et
N
N
Et
6n
2.15
2.00
2.08
2.15
4.13
3.97
4.09
4.18
6.26
f1 (ppm)


143.02
129.56
129.03
127.20
122.40
110.59
48.30
45.34
39.87
28.08
22.37
10.70
Et
N
N
Et
6n
f1 (ppm)