Supporting Information

Copper(II)-catalyzed C–H (sp^3) oxidation and C–N cleavage: synthesis of methylene-bridged compounds using TMEDA as a carbon source in water

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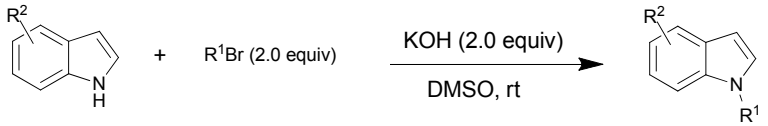
1. General Information

All reagents and solvents were used as supplied without further purification. ^{1}H NMR and ^{13}C NMR were determined in $CDCl_3$ on a Bruker DPX 300 MHz or a Bruker AVANCE Ⅲ 400MHz spectrometerat room temperature, respectively, and tetramethylsilane (TMS) served as an internal standard. Spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet) 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). The absorption spectrum were carried out on VarioskanFlash. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Qingdao Haiyang Chemical Co., Ltd).

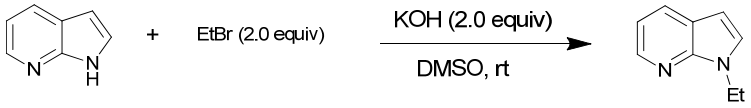
2. General Procedure for Synthesis of Substrates and Products

2.1 General procedure for the synthesis of N-protected indoles (1a–k, 1m–q) from substituted indoles with alkyl bromides.

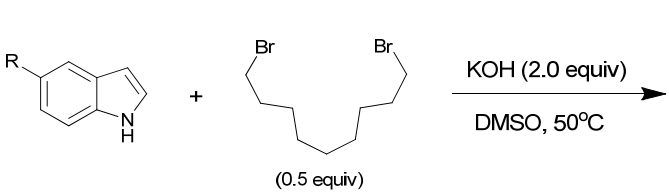
To a solution of substituted indole (5 mmol) in DMSO (20 mL) was added KOH (10.0 mmol) and alkyl bromides (2.0 equiv for **1a**–**k** and **1q**; 0.5 equiv for **1m**–**p**). The reaction mixture was stirred (room temperature for **1a**–**k** and **1q**; 50 °C for **1m**–**p**) and monitored by TLC. 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 in vacuo. The residue was then purified by chromatography on silica gel with a eluent of petroleum ether, ethyl acetate. Products were characterized by ^{1}H, ^{13}C NMR and MS (EI or ESI).



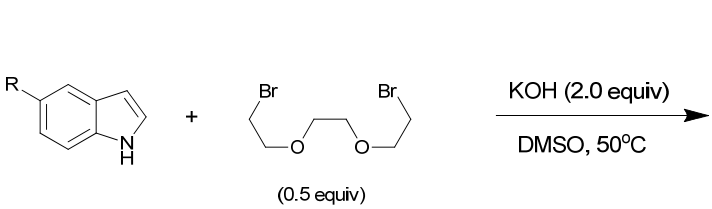
	R^1	R^2	Yield %		R^1	R^2	Yield %
1a	Et	H	95	**1f**	Et	4-Me	83
1b	Bn	H	91	**1g**	Et	7-Me	82
1c	Et	5-Cl	90	**1h**	Et	5-CN	86
1d	Et	5-OMe	87	**1i**	Et	6-COOMe	92
1e	Et	2-Me	94	**1j**	Et	6-NO_2	85
				1q	Et	3-CHO	98



1k, 88%

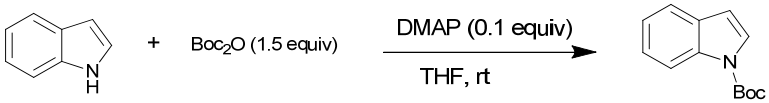


	R	Yield %
1m	H	96
1n	OMe	84



	R	Yield %
1o	H	89
1p	OMe	92

2.2 Synthesis of 1-bocindole (1l) from indole with di-*tert*-butyl dicarbonate was according to the reported method.[1]

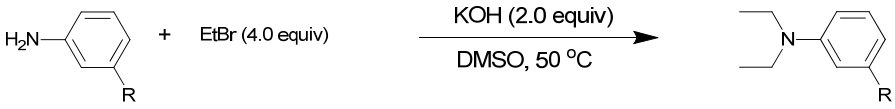


1l, 90%

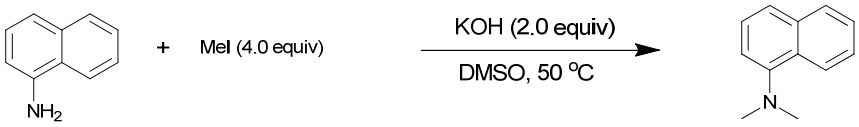
2.3 General procedure for the synthesis of N-protected anilines (4b–f) from substituted anilines with alkyl bromides (iodomethane used for methyl-protected reagent).

To a solution of substituted anilines (5 mmol) in DMSO (20 mL) was added KOH (10.0 mmol) and alkyl bromides (2.0 equiv for **4f**; 4.0 equiv for **4b**–**e**). The reaction mixture was stirred at 50°C and monitored by TLC. Upon finished the reaction, the mixture was treated as described in **2.1** to obtain a

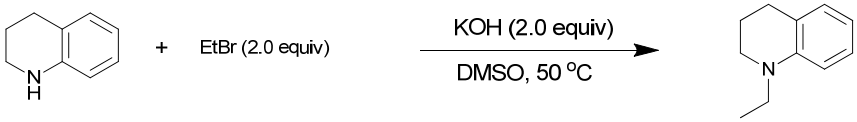
residue. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by ^{1}H, ^{13}C NMR and MS (EI or ESI).



	R	Yield %
4b	H	93
4c	Me	90
4d	OMe	88



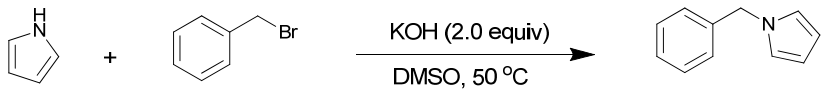
4e (93%)



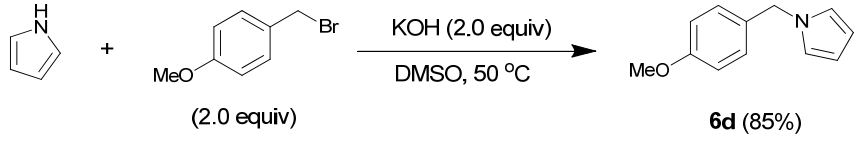
4f (88%)

2.4 General procedure for the synthesis of N-protected pyrroles (6c–d) from pyrroles with alkyl bromides.

To a solution of pyrrole (5 mmol) in DMSO (20 mL) was added KOH (10.0 mmol) and alkyl bromides (2.0 equiv). The reaction mixture was stirred at 50°C and monitored by TLC. Upon finished the reaction, the mixture was treated as described in **2.1** to obtain a residue. 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, ^{13}C NMR and MS (EI or ESI).



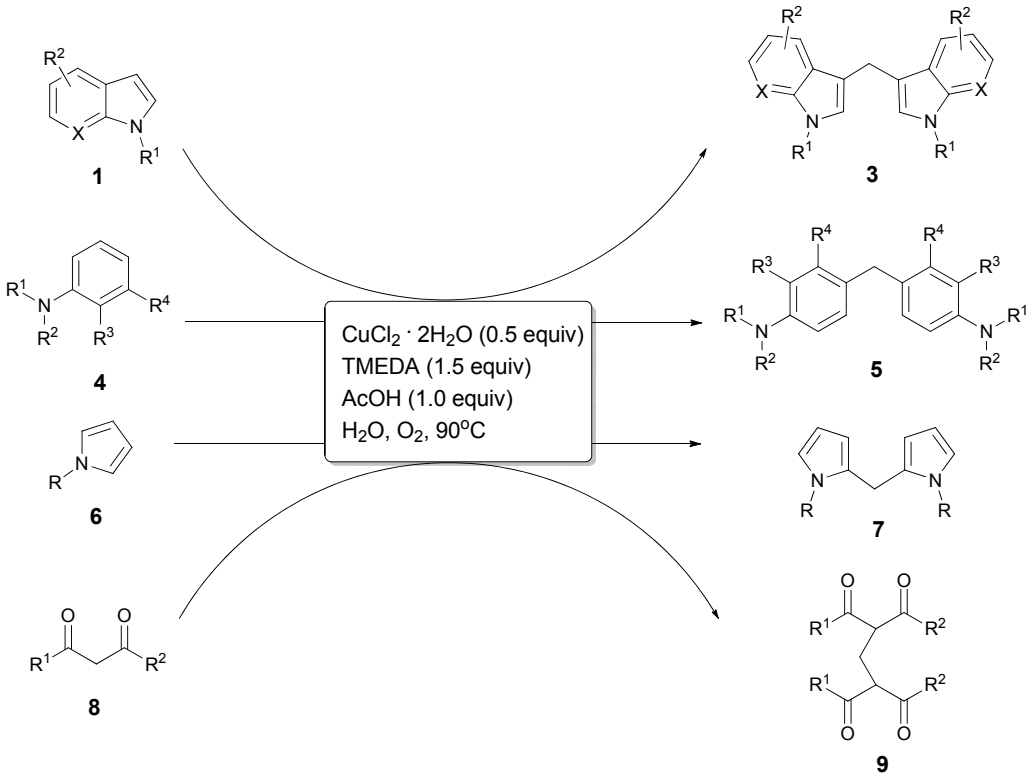
6c (90%)



6d (85%)

2.5 General procedure for the synthesis of 3,3′-bisindolylmethanes (3a–p) , 4,4′-diaminodiphenylmethanes (5a–f), 2,2′-bispyrrolylmethanes (7a–d) and 2,2′-bis-1,3-dicarbonylmethanes (9a–b).

To a solution of $CuCl_2 \cdot 2H_2O$ (0.5 mmol, 85 mg) in solvent (30 mL 80% acetonitrile aqueous solution for **1m–p**; 10 mL water for other substrates) was added TMEDA (1.5 mmol, 230 μL) while stirring at room temperature. Followed indoles, anilines, pyrroles or 1,3-dicarbonyl compounds (1.0 mmol) and acetic acid (1.0 mmol) was added. The reaction mixture was stirred at 90°C and monitored by TLC. Upon finished the reaction mixture was extracted by ethyl acetate (3×10 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by ^1H, ^{13}C NMR and MS (EI or ESI).



3. Experimental Details for Nash Test

General procedure for Nash Test: Formaldehyde formation was assessed using the Nash Test. The Nash reagent was prepared by dissolving NH_4OAc (15 g, 0.19 mol), 2,4-pentanedione (0.2 mL, 2 mmol) and acetic acid (0.3 mL, 5 mmol) in 100 mL of water.

Reaction:

1. preparation of sample A in water: An Schlenk tube was charged with TMEDA (1 mmol), $CuCl_2 \cdot 2H_2O$ (0.3 mmol), acetic acid (0.7 mmol) and 10 mL water under oxygen. The reaction mixture was stirred at 90°C for 4h. After cooled to room temperature, 1 mL of the mixture in water was added to 10 mL Nash reagent and incubated at 60 °C for 10 min.
2. preparation of sample B in water: A flask was charged with TMEDA (1 mmol), $CuCl_2 \cdot 2H_2O$ (0.3 mmol), acetic acid (0.7 mmol) and 10 mL water under oxygen. The reaction mixture was stirred at room temperature for 2 min. Then, 1 mL of the mixture in water was added to 10 mL Nash reagent and incubated at 60 °C for 10 min.
3. preparation of sample C in water: A flask was charged with TMEDA (1 mmol), $CuCl_2 \cdot 2H_2O$ (0.3 mmol), acetic acid (0.7 mmol) and 10 mL water under oxygen. The reaction mixture was stirred at room temperature for 2 min. Then, 1 mL of the mixture in water was added to 10 mL Nash reagent and stirred at room temperature for 2 min.
4. preparation of control in water: 1 mL 0.01 M formaldehyde aqueous solution was added to 10 mL Nash reagent and incubated at 60 °C for 10 min.
5. preparation of sample A, B,C and control in EtOAc: 1 mL sample or control in water above was extracted by EtOAc (1 mL) to give sample A, B, C and control in EtOAc, respectively.

The existence of formaldehyde was determined by measuring the absorption spectrum of the samples from 350 to 600 nm.

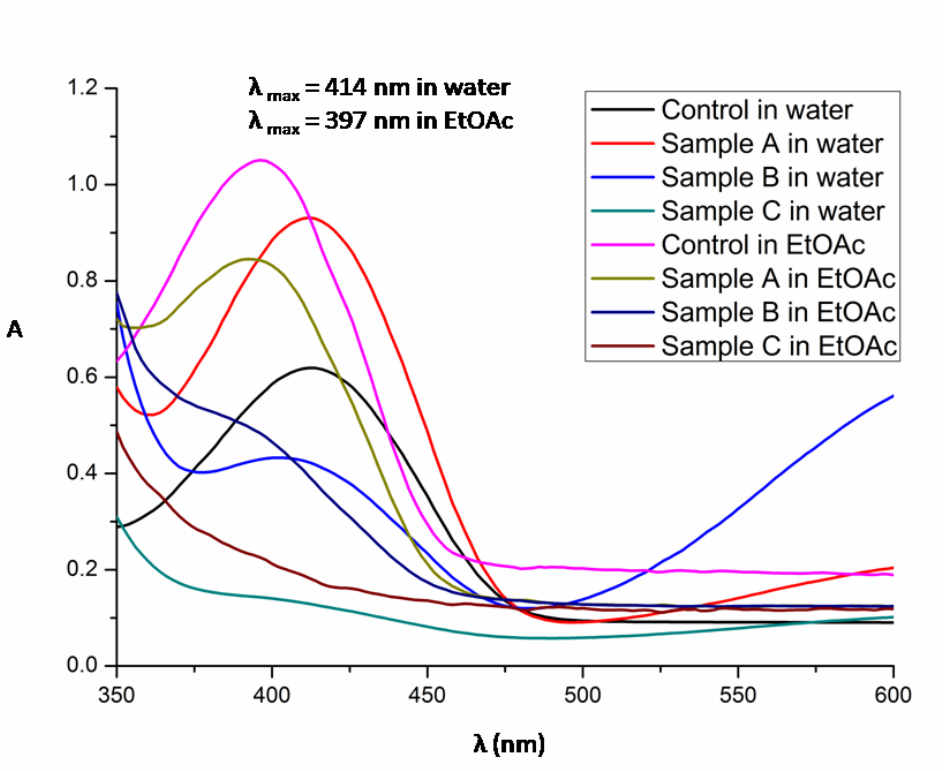


Figure 1. The absorption spectrum of the samples and control.

Conclusion:

1. The sample A, B and control have the same λ_{max} in water and EtOAc, respectively, and λ_{max} in water was 414 nm which revealed the existence of formaldehyde[2].
2. The formaldehyde concentration of sample A was far higher than that of sample B, which showed

that TMEDA reacted with $CuCl_2$ in water to afford formaldehyde intermediate. Otherwise, the formaldehyde concentration of these two samples could be same, due to the same reaction time with Nash reagent.

3. If the formaldehyde concentration was within the linear range (Beer–Lambert law), we also can give a rough estimate of the transformation rate of TMEDA to formaldehyde in water: $\eta(CH_2O)$ = (0.93-0.09) / (0.62-0.09) / 10 × 100% = 16%.

4. Proof of 1q as A Possible Intermediate *via* ^{1}H NMR

Reaction: To a solution of $CuCl_2 \cdot 2H_2O$ (0.5 mmol) in 10 mL water was added TMEDA (1.5 mmol) while stirring at room temperature. Followed **1a** (1 mmol) was added. The reaction mixture was stirred at 90°C for 12h. Upon finished the reaction mixture was extracted by ethyl acetate (3×10 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was characterized by ^{1}H NMR. The only difference between this reaction and standard conditions was absence of acetic acid, which was beneficial for **1q** in the formation of the byproduct as shown in proposed reaction mechanism. Figure 2–4 proved the existence of **1q** in the reaction system.

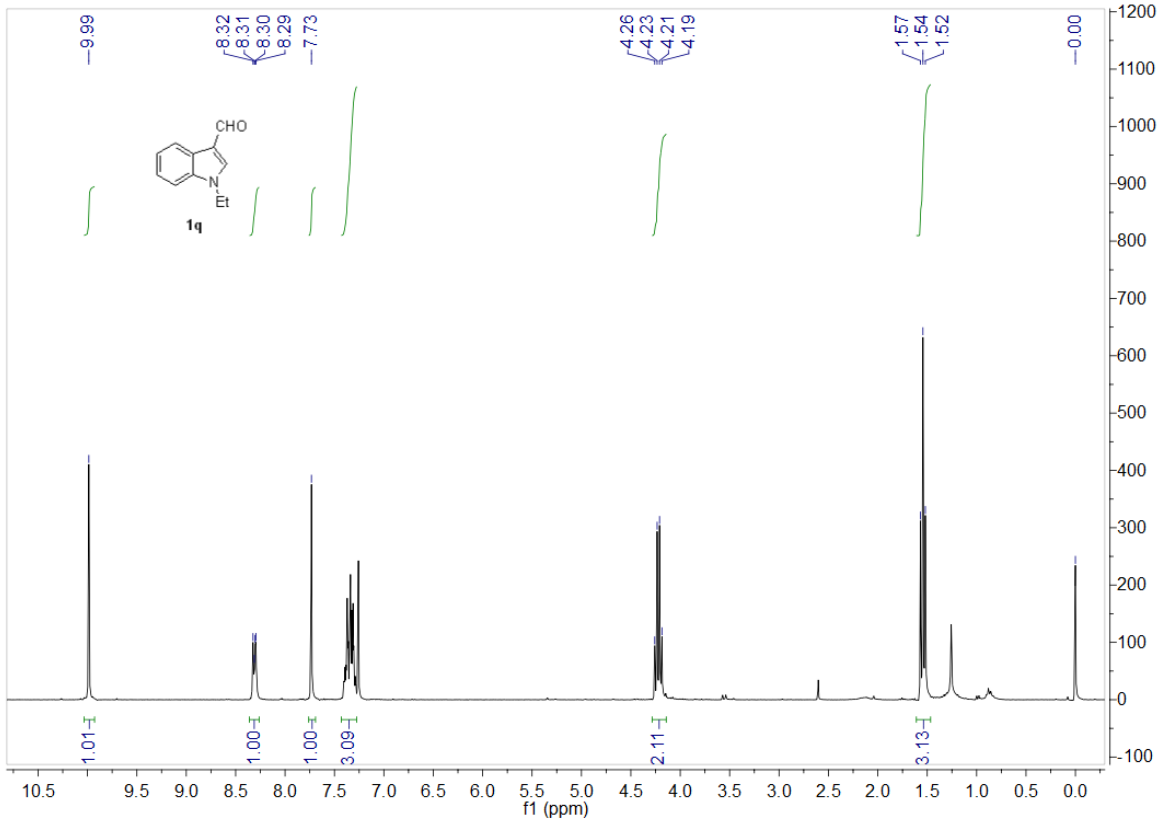


Figure 2. ^{1}H NMR of compound **1q** in $CDCl_3$.

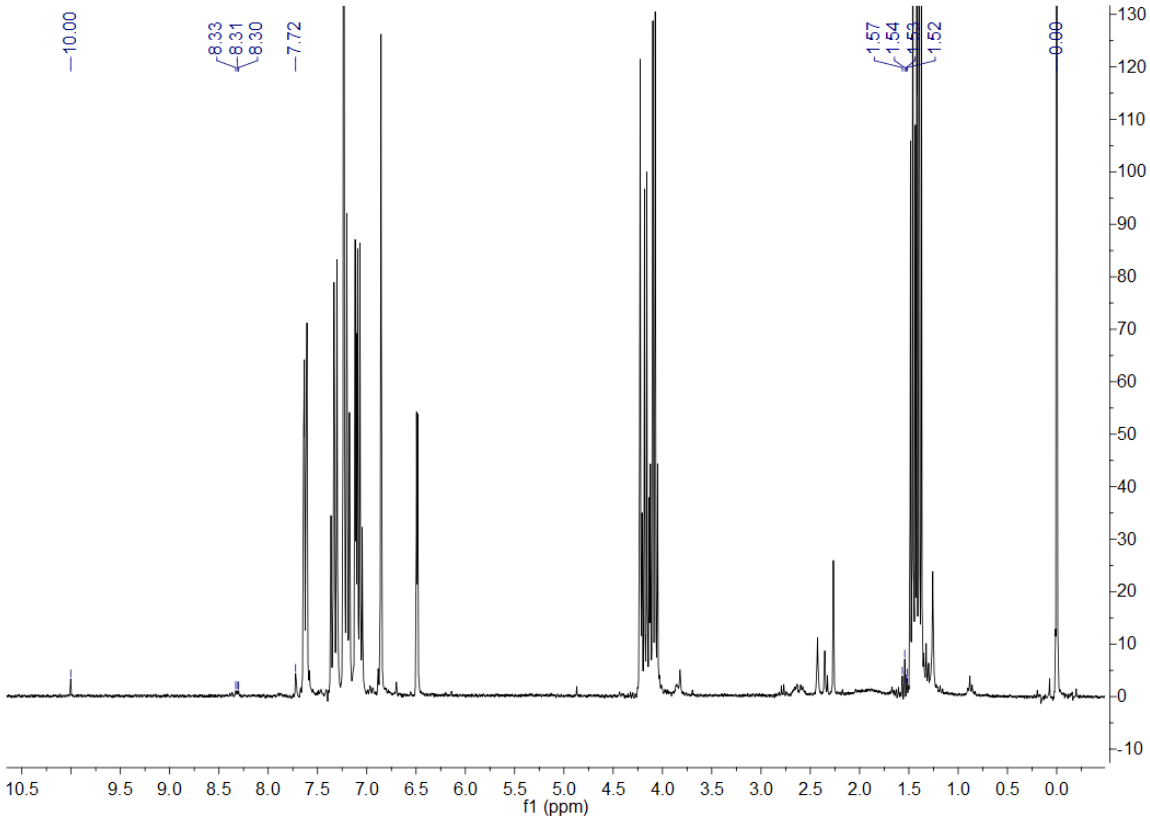


Figure 3. ^{1}H NMR of residue in $CDCl_3$.

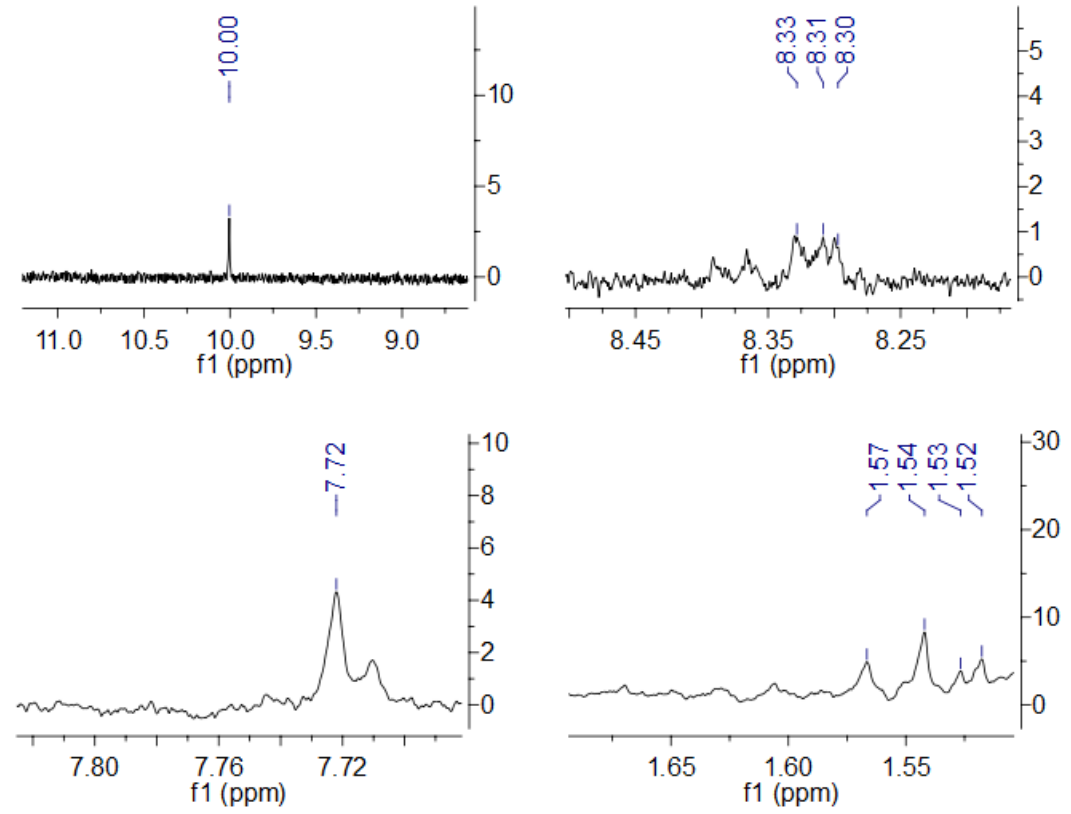
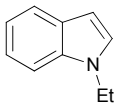


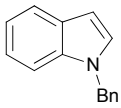
Figure 4. An expanded view of ^{1}H NMR of residue in $CDCl_3$.

5. Characterization Data of the Substrates and Products



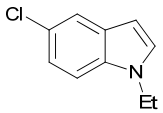
1a

1-Ethyl-1*H*-indole (1a) Yield: 95 % ; ^{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).



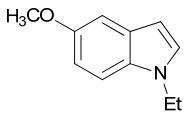
1b

1-Benzyl-1*H*-indole (1b) Yield: 91 % ; ^{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 $[M+H]^+$.



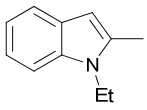
1c

5-Chloro-1-ethyl-1*H*-indole (1c) Yield: 90 % ; ^{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 $[M+H]^+$.



1d

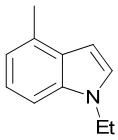
1-Ethyl-5-methoxy-1*H*-indole (1d) Yield: 87 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.10 (d, *J* = 2.2 Hz, 2H), 6.88 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.15 (q, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 1.46 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 131.1, 128.9, 127.4, 111.7, 101.0, 102.6, 100.5, 55.8, 41.0, 15.4; MS (ESI): 176.10 $[M+H]^+$.



1e

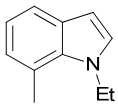
1-Ethyl-2-methyl-1*H*-indole (1e) Yield: 94 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.06 (td, *J* = 7.5, 1.1 Hz, 1H), 6.24 (s, 1H), 4.14

(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 $[M+H]^+$.



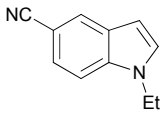
1f

1-Ethyl-4-methyl-1*H*-indole (1f) Yield: 83 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 1H), 7.19 – 7.08 (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 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 130.5, 128.6, 126.5, 121.6, 119.5, 107.0, 99.6, 41.1, 18.9, 15.6; MS (ESI): 160.10 $[M+H]^+$.



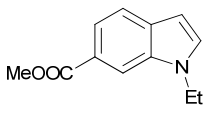
1g

1-Ethyl-7-methyl-1*H*-indole (1g) Yield: 82 % ; ^{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, 120.7, 119.6, 119.2, 101.7, 43.5, 19.9, 18.0; MS (ESI): 160.15 $[M+H]^+$.



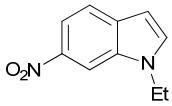
1h

1-Ethyl-1*H*-indole-5-carbonitrile (1h) Yield: 86 % ; ^{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, 101.0, 102.2, 60.3, 41.2, 15.3; MS (ESI): 171.10 $[M+H]^+$.



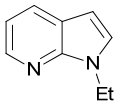
1i

Methyl 1-ethyl-1*H*-indole-6-carboxylate (1i) Yield: 92 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.80 (dd, J = 8.4, 1.3 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 3.0 Hz, 1H), 6.54 (d, J = 3.1 Hz, 1H), 4.25 (q, J = 7.3 Hz, 2H), 3.95 (s, 3H), 1.50 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 135.0, 132.2, 130.2, 122.9, 120.4, 120.2, 111.6, 101.4, 51.8, 41.1, 15.5; MS (ESI): 204.90 $[M+H]^+$.



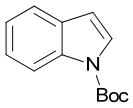
1j

1-Ethyl-6-nitro-1*H*-indole (1j) Yield: 85 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.01 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 3.1 Hz, 1H), 6.60 (d, *J* = 3.1 Hz, 1H), 4.27 (q, *J* = 7.3 Hz, 2H), 1.53 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 134.2, 133.3, 132. 8, 120.6, 114.7, 106.2, 102.2, 41.4, 15.4; MS (ESI): 190.95 $[M+H]^+$.



1k

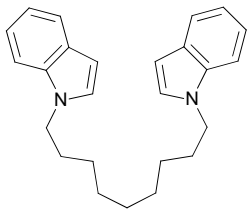
1-Ethyl-1*H*-pyrrolo[2,3-*b*]pyridine (1k) Yield: 88 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.05 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.46 (d, *J* = 3.5 Hz, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 1.49 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 142.5, 128.6, 127.2, 120.6, 115.4, 99.2, 39.2, 15.6; EI-MS m/z (rel. int., %): 146 (58), 131 (51), 118 (100).



1l

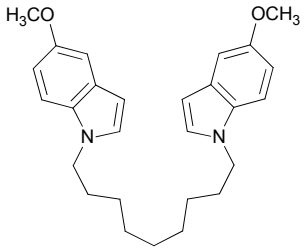
***Tert*-butyl 1*H*-indole-1-carboxylate (1l)**

To a solution of indole (5 mmol) in THF (20mL) was added 4-DMAP (0.5 mmol) and Boc_2O (7.5 mmol). The reaction mixture was stirred at room temperature and monitored by TLC. Upon finished the reaction mixture was concentrated in vacuo. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Yield: 90 % ;^{1}H NMR (300 MHz, $CDCl_3$) 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 $[M+H]^+$.



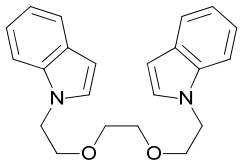
1m

1,9-Di(1*H*-indol-1-yl)nonane (1m) Yield: 96 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 3.1 Hz, 2H), 6.60 (d, *J* = 3.1 Hz, 2H), 4.16 (t, *J* = 7.1 Hz, 4H), 1.94 – 1.82 (m, 4H), 1.46 –1.28 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 128.6, 127.8, 121.3, 121.0, 119.2, 109.4, 100.8, 46.4, 30.2, 29.3, 29.1, 26.9; EI-MS m/z (rel. int., %): 358 (100), 281 (44).



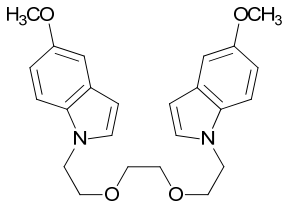
1n

1,9-Bis(5-methoxy-1*H*-indol-1-yl)nonane (1n) Yield: 84 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 2.4 Hz, 2H), 7.04 (d, *J* = 3.0 Hz, 2H), 6.86 (dd, *J* = 8.9, 2.4 Hz, 2H), 6.39 (d, *J* = 2.8 Hz, 2H), 4.04 (t, *J* = 7.1 Hz, 4H), 3.84 (s, 6H), 1.82 – 1.73 (m, 4H), 1.32 –1.17 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 131.3, 128.9, 128.3, 111.7, 110.1, 102.5, 100.3, 55.9, 46.5, 30.2, 29.3, 29.1, 26.9; MS (ESI): 419.15 $[M+H]^+$.



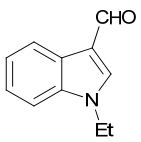
1o

1,2-Bis(2-(1*H*-indol-1-yl)ethoxy)ethane (1o) Yield: 89 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.15 – 7.07 (m, 4H), 6.49 (dd, *J* = 3.1, 0.6 Hz, 2H), 4.22 (t, *J* = 5.6 Hz, 4H), 3.70 (t, *J* = 5.6 Hz, 4H), 3.44 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 128.5, 128.4, 121.3, 120.9, 119.3, 109.3, 101.1, 70.7, 70.1, 46.2; EI-MS m/z (rel. int., %): 349 (23), 348 (100).



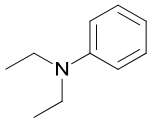
1p

1,2-Bis(2-(5-methoxy-1*H*-indol-1-yl)ethoxy)ethane (1p) Yield: 92 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.9 Hz, 2H), 7.12– 7.06 (m, 4H), 6.86 (dd, *J* = 8.9, 2.4 Hz, 2H), 6.39 (d, *J* = 2.9 Hz, 2H), 4.18 (t, *J* = 5.6 Hz, 4H), 3.85 (s, 6H), 3.68 (t, *J* = 5.6 Hz, 4H), 3.42 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 131.8, 129.3, 129.2, 111. 9, 110.5, 102.7, 101.0, 70.7, 70.3, 55.9, 46.4 ; MS (ESI): 409.15 $[M+H]^+$.



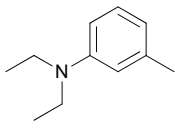
1q

1-Ethyl-1*H*-indole-3-carbaldehyde1 (1q) Yield: 98 %; H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.36 – 8.26 (m, 1H), 7.74 (s, 1H), 7.42 – 7.28 (m, 3H), 4.23 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 137.4, 136.9, 125.4, 123.8, 122.8, 122.0, 118.1, 109.9, 41.8, 14.9; EI-MS m/z (rel. int., %): 173 (100), 172 (99), 158 (51).



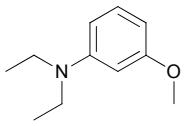
4b

***N*,*N*-Diethylaniline (4b)** Yield: 93 % ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.74 – 6.62 (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, 111.8, 44.2, 12.5 ; MS (ESI): 150.15 $[M+H]^+$.



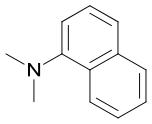
4c

***N*,*N*-Diethyl-3-methylaniline (4c)** Yield: 90 % ; ^1H 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 $[M+H]^+$.



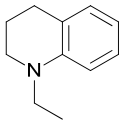
4d

***N*,*N*-Diethyl-3-methoxyaniline (4d)** Yield: 88 % ; ^1H 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, 149.1, 129.8, 105.0, 99.9, 98.3, 55.0, 44.4, 12.6; MS (ESI): 180.15 $[M+H]^+$.



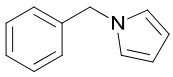
4e

***N*,*N*-Dimethylnaphthalen-1-amine (4e)** Yield: 93 % ; ^1H NMR (300 MHz, $CDCl_3$) δ 8.35 – 8.20 (m, 1H), 7.83 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.60 – 7.44 (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 $[M+H]^+$.



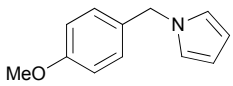
4f

1-Ethyl-1,2,3,4-tetrahydroquinoline (4f) Yield: 88 % ; ^{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), 3.34 – 3.23 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.12 – 1.93 (m, 2H), 1.19 (dd, *J* = 7.3, 6.8 Hz, 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, 28.1, 22.2, 10.7 ; MS (ESI): 162.15 $[M+H]^+$.



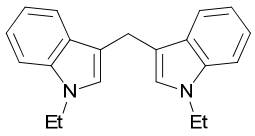
6c

1-Benzyl-1*H*-pyrrole (6c) Yield: 90 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 3H), 7.13 (d, *J* = 6.5 Hz, 2H), 6.71 (t, *J* = 2.1 Hz, 2H), 6.21 (t, *J* = 2.1 Hz, 2H), 5.09 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 128.7, 127.6, 127.0, 121.1, 108.5, 53.3; MS (ESI): 158.10 $[M+H]^+$.



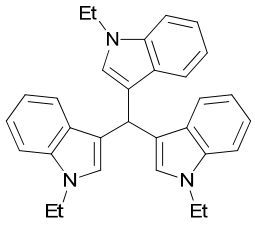
6d

1-(4-Methoxybenzyl)-1*H*-pyrrole (6d) Yield: 85 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.68 (t, *J* = 2.0 Hz, 2H), 6.18 (t, *J* = 1.9 Hz, 2H), 5.01 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 130.1, 128.5, 120.9, 114.0, 108.4, 55.2, 52.8; MS (ESI): 188.10 $[M+H]^+$.



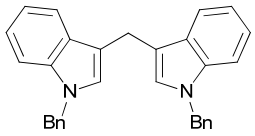
3a

Bis(1-ethyl-1*H*-indol-3-yl)methane[3] (3a) Yield: 88 % ; ^{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 – 7.20 (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).



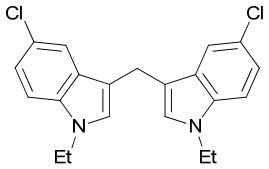
3aa

Tris(1-ethyl-1*H*-indol-3-yl)methane[4] (3aa) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 3H), 7.32 (d, *J* = 8.2 Hz, 3H), 7.17 (t, *J* = 7.1 Hz, 3H), 6.97 (t, *J* = 7.5 Hz, 3H), 6.71 (s, 3H), 6.15 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 6H), 1.36 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 127.8, 126.5, 120.9, 120.4, 118.3, 118.1, 109.0, 40.8, 31.2, 15.6; MS (ESI): 444.25 $[M-H]^-$.



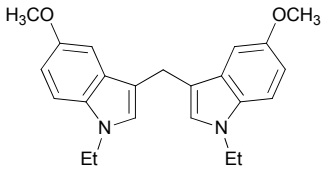
3b

Bis(1-benzyl-1*H*-indol-3-yl)methane[5] (3b) Yield: 53 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.31– 7.25 (m, 8H), 7.22 – 7.14 (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).



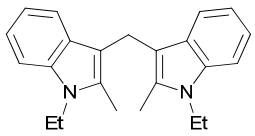
3c

Bis(5-chloro-1-ethyl-1*H*-indol-3-yl)methane[6] (3c) Yield: 72 % ; ^{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).



3d

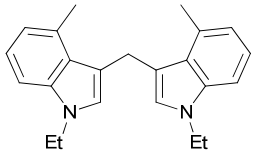
Bis(1-ethyl-5-methoxy-1*H*-indol-3-yl)methane[6] (3d) Yield: 82 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 1.9 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.87 (s, 2H), 4.20 (s, 2H), 4.09 (q, *J* = 7.2 Hz, 4H), 3.85 (s, 6H), 1.42 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 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).



3e

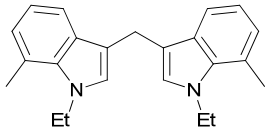
Bis(1-ethyl-2-methyl-1*H*-indol-3-yl)methane[6] (3e) Yield: 95 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.09 (m, 2H), 7.06 – 6.96 (m, 2H), 4.20 (s, 2H),

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).



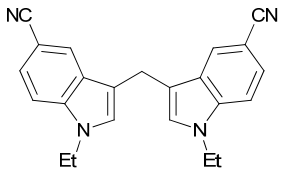
3f

Bis(1-ethyl-4-methyl-1*H*-indol-3-yl)methane[6] (3f) Yield: 72 % ; ^{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).



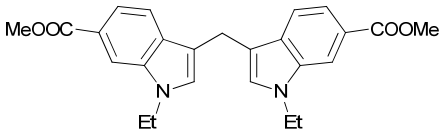
3g

Bis(1-ethyl-7-methyl-1*H*-indol-3-yl)methane[6] (3g) Yield: 82 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.01 – 6.92 (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).



3h

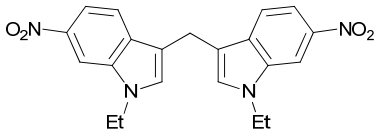
3,3'-Methylenebis(1-ethyl-1*H*-indole-5-carbonitrile)[6] (3h) Yield: 61 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.43 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.02 (s, 2H), 4.21 (s, 2H), 4.16 (q, *J* = 7.3 Hz, 4H), 1.45 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 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).



3i

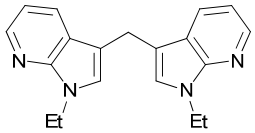
Dimethyl 3,3'-methylenebis(1-ethyl-1*H*-indole-6-carboxylate) (3i) Yield: 35 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.77 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 2H), 4.23 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 4H), 3.95 (s, 6H), 1.43 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

168.3, 135.6, 131.4, 128.7, 123.0, 119.8, 118.8, 114.5, 111.8, 51.9, 41.0, 21.0, 15.7 ; MS (ESI): 419.10 $[M+H]^+$.



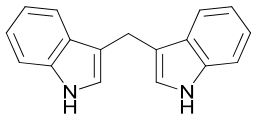
3j

Dis(1-ethyl-6-nitro-1*H*-indol-3-yl)methane (3j) Yield: 30 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.9 Hz, 2H), 7.97 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.15 (s, 2H), 4.24 (s, 2H), 4.21 (q, *J* = 7.3 Hz, 4H), 1.48 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 134.7, 132.1, 131.0, 119.0, 114.7, 114.3, 106.4, 41.3, 20.7, 15.6 ; MS (ESI): 393.05 $[M+H]^+$.



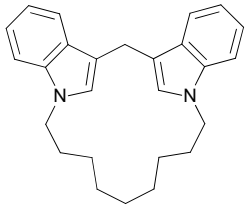
3k

Bis(1-ethyl-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)methane (3k) Yield: 45 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 4.7, 1.5 Hz, 2H), 7.80 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.00 – 6.97 (m, 4H), 4.28 (q, *J* = 7.3 Hz, 4H), 4.18 (s, 2H), 1.43 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 142.5, 127.2, 125.1, 120.2, 114.8, 112.1, 39.0, 21.4, 15.6 ; MS (ESI): 305.10 $[M+H]^+$.



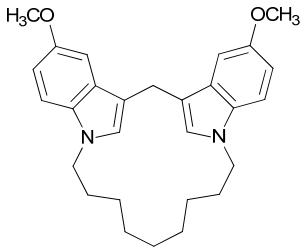
3l

Di(1*H*-indol-3-yl)methane[7] (3l) Yield: 45 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (brs, 2H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.91 (s, 2H), 4.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 127.6, 122.2, 121.9, 119.2, 119.2, 115.7, 111.0, 21.2; MS (ESI): 247.05 $[M+H]^+$.



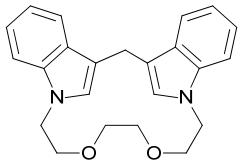
3m

(3m) Yield: 32 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26– 7.20 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 6.68 (s, 2H), 4.23 (s, 2H), 4.15 – 3.94 (m, 4H), 1.86 – 1.66 (m, 4H), 1.26 – 0.95 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 128.0, 126.4, 121.1, 118.9, 118.5, 115.0, 109.2, 44.7, 29.4, 28.8, 27.0, 25.6, 20.0; MS (ESI): 371.10 $[M+H]^+$.



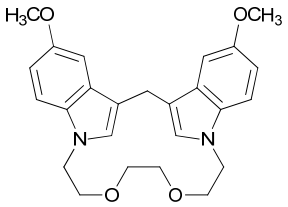
3n

(3n) Yield: 41 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 2.4 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 2H), 6.65 (s, 2H), 4.15 (s, 2H), 4.09 – 3.99 (m, 4H), 3.87 (s, 6H), 1.85 – 1.68 (m, 4H), 1.22 – 0.91 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 131.4, 128.1, 127.0, 114.3, 111.5, 110.1, 100.5, 55.8, 44.8, 29.4, 28.8, 26.9, 25.6, 20.2; MS (ESI): 431.20 $[M+H]^+$.



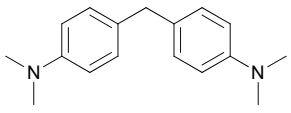
3o

(3o) Yield: 34 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.18 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 2H), 4.24 (s, 2H), 4.24 – 4.19 (m, 4H), 3.69 (t, *J* = 4.3 Hz, 4H), 3.53 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 129.1, 128.3, 120.9, 118.7, 118.5, 114.4, 108.7, 70.5, 70.2, 45.4, 19.6 ; MS (ESI): 361.05 $[M+H]^+$.



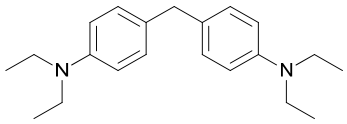
3p

(3p) Yield: 64 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 6H), 6.87 (dd, *J* = 8.7, 2.5 Hz, 2H), 4.21 – 4.16 (m, 4H), 4.14 (s, 2H), 3.89 (s,6H), 3.69 – 3.64 (m, 4H), 3.53 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 131.3, 129.8, 128.5, 113.8, 111.2, 109.4, 100.6, 70.5, 70.1, 56.0, 45.6, 19.7; MS (ESI): 421.10 $[M+H]^+$.



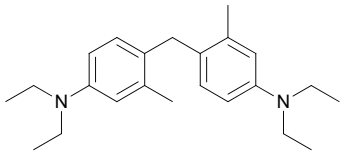
5a

4,4'-Methylenebis(*N*,*N*-dimethylaniline)[8] (5a) Yield: 82 % ; ^{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, 129.3, 113.0, 40.9, 39.8; MS (ESI): 255.15 $[M+H]^+$.



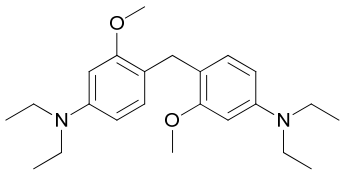
5b

4,4'-Methylenebis(*N*,*N*-diethylaniline)[9] (5b) Yield: 65 % ; ^{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 $[M+H]^+$.



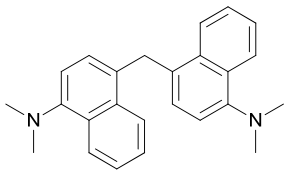
5c

4,4'-Methylenebis(*N*,*N*-diethyl-3-methylaniline)[10] (5c) Yield: 95 % ; ^{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 $[M+H]^+$.



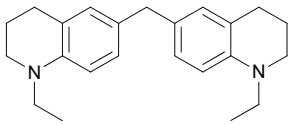
5d

4,4'-Methylenebis(*N*,*N*-diethyl-3-methoxyaniline)[6] (5d) Yield: 92 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, *J* = 8.3 Hz, 2H), 6.35 – 6.14 (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 $[M+H]^+$.



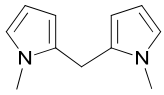
5e

4,4'-Methylenebis(*N*,*N*-dimethylnaphthalen-1-amine)[11] (5e) Yield: 71 % ; ^{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 $[M+H]^+$.



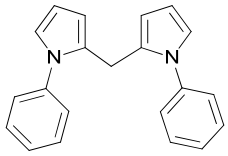
5f

Bis(1-ethyl-1,2,3,4-tetrahydroquinolin-6-yl)methane[6] (5f) Yield: 68 % ; ^{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 – 3.18 (m, 4H), 2.70 (t, *J* = 6.4 Hz, 4H), 2.00 – 1.87 (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 $[M+H]^+$.



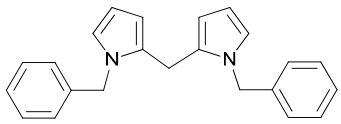
7a

Bis(1-methyl-1*H*-pyrrol-2-yl)methane[12] (7a) Yield: 43 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 2H), 6.05 (t, *J* = 3.1 Hz, 2H), 5.84 (s, 2H), 3.88 (s, 2H), 3.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.8, 121.7, 107.5, 106.6, 33.8, 24.6; MS (ESI): 175.10 $[M+H]^+$.



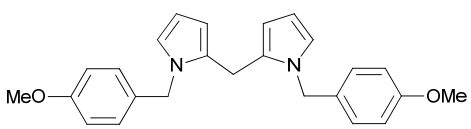
7b

Bis(1-phenyl-1*H*-pyrrol-2-yl)methane (7b) Yield: 48 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 –7.29 (m, 6H), 7.13 – 7.09 (m, 4H), 6.73 (dd, *J* = 2.6, 1.9 Hz, 2H), 6.19 (t, *J* = 3.1 Hz, 2H), 5.97 – 5.95 (m, 2H), 3.75 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 131.0, 128.8, 126.9, 125.9, 121.6, 108.9, 108.0, 24.6; MS (ESI): 299.05 $[M+H]^+$.



7c

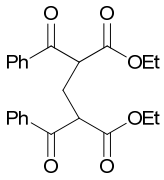
Bis(1-benzyl-1*H*-pyrrol-2-yl)methane[13] (7c) Yield: 50 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 6H), 6.91 – 6.83 (m, 4H), 6.64 (s, 2H), 6.11 (t, *J* = 2.9 Hz, 2H), 5.88 (s, 2H), 4.92 (s, 4H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 129.8, 128.6, 127.3, 126.4, 121.7, 108.3, 107.1, 50.4, 24.6; MS (ESI): 327.10 $[M+H]^+$.



7d

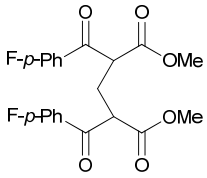
Bis(1-(4-methoxybenzyl)-1*H*-pyrrol-2-yl)methane (7d) Yield: 54 % ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 – 6.75 (m, 8H), 6.64 – 6.60 (m, 2H), 6.09 (t, *J* = 3.1 Hz, 2H), 5.86 (s, 2H), 4.84 (s, 4H), 3.77 (s,

6H), 3.66 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 130.2, 129.7, 127.8, 121.4, 113.9, 108.1, 106.9, 55.2, 49.8, 24.5; MS (ESI): 387.10 $[M+H]^+$.



9a

Diethyl 2,4-dibenzoylpentanedioate[14] (9a) Yield: 19% ; The ratio of two diastereomers is 1.1:1. **Two diastereomers:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 4H), 7.64 – 7.54 (m, 2H), 7.54 – 7.44(m, 4H), 4.63 (t, J = 7.3 Hz, 1H), 4.55 (t, J = 7.3 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.16 – 4.06(m, 2H), 2.84 – 2.32 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 194.8, 169.7, 169.3, 135.9, 135.5, 133.80, 133.79, 128.9, 128.8, 61.7, 61.6, 51.6, 51.3, 28.2, 27.7, 14.0, 13.9; MS (ESI): 397.15 $[M+H]^+$.



9b

Dimethyl 2,4-bis(4-fluorobenzoyl)pentanedioate (9b) Yield: 15% ; The ratio of two diastereomers is 1.3:1. **Two diastereomers:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.05 (m, 4H), 7.24 – 7.11(m, 4H), 4.69 – 4.57 (m, 1H), 4.52 (t, J = 7.2 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 2.79 – 2.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 193.1, 170.1, 169.6, 167.6, 165.0, 131.84, 131.75, 131.7, 131.6, 116.2, 116.0, 52.8, 51.2, 51.0, 28.3, 27.7; MS (ESI): 405.10 $[M+H]^+$.

6. References

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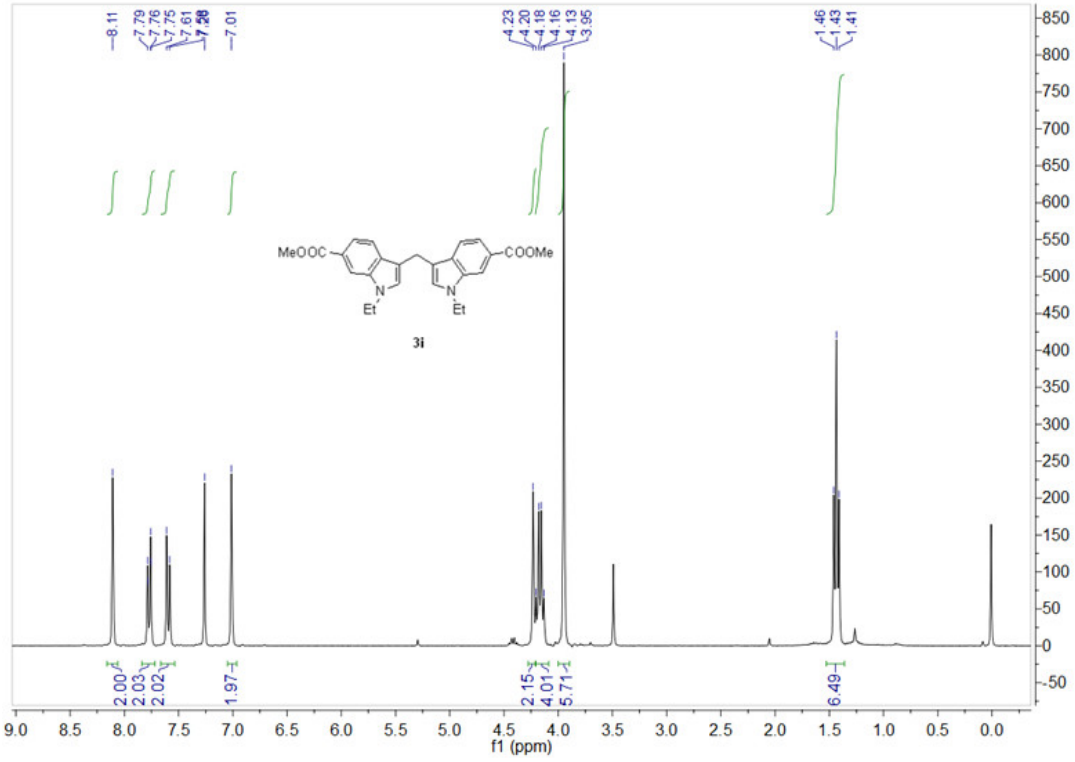
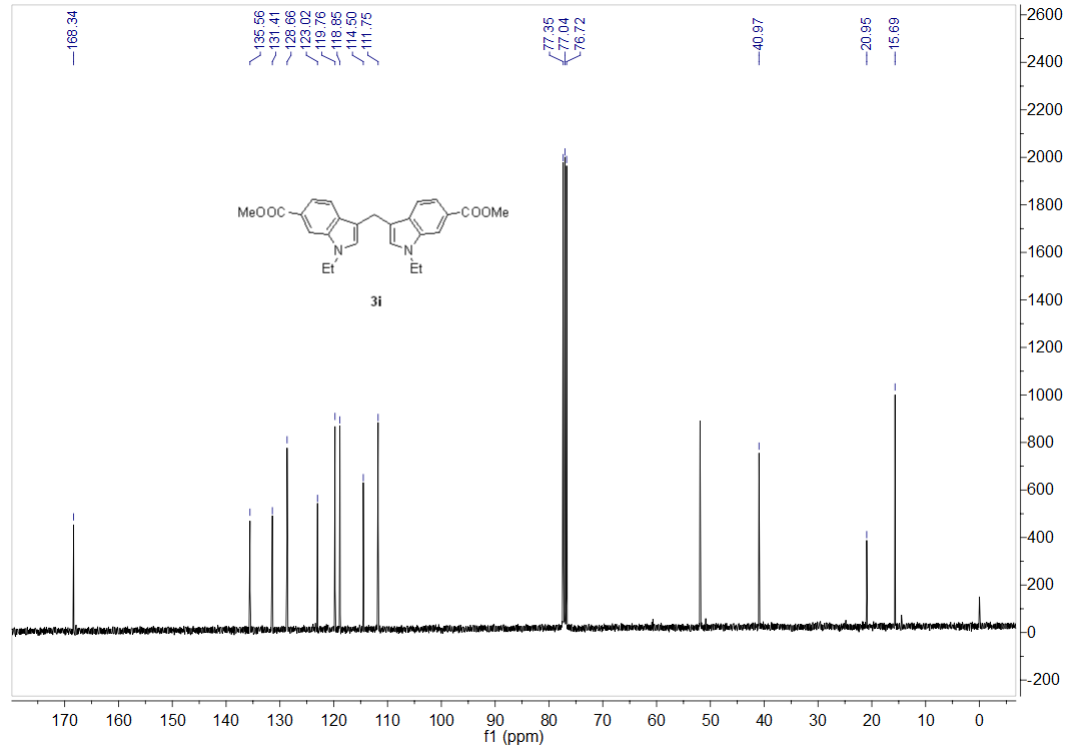
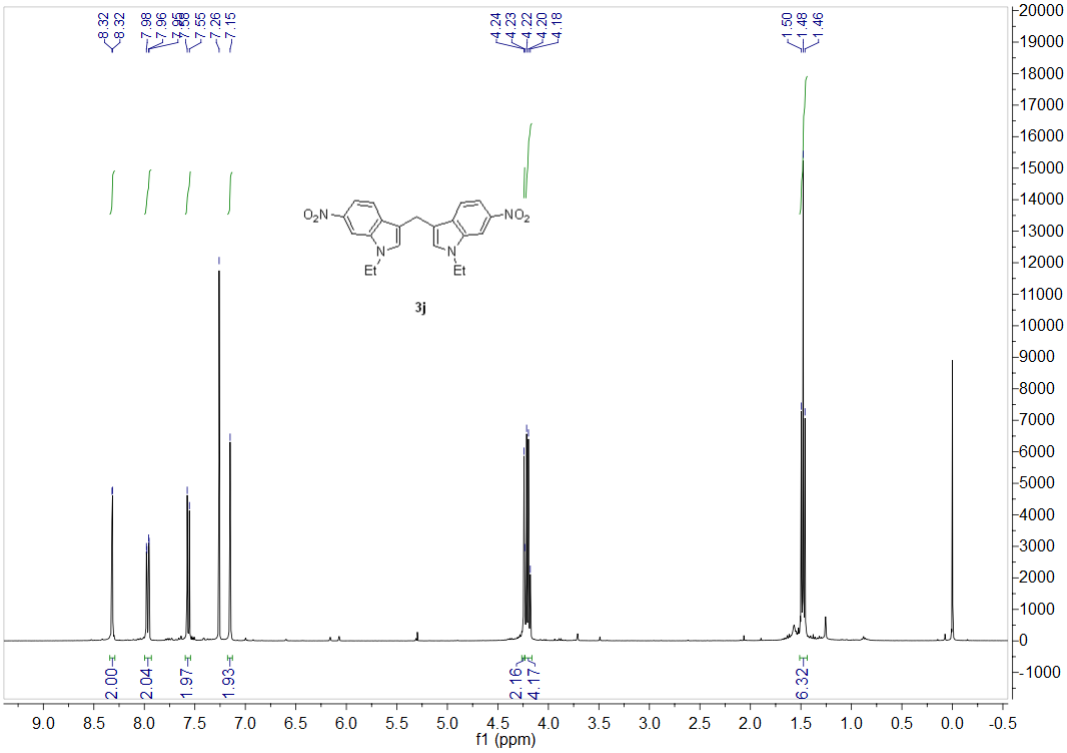
7. NMR Spectra of Unknown Products



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7.15
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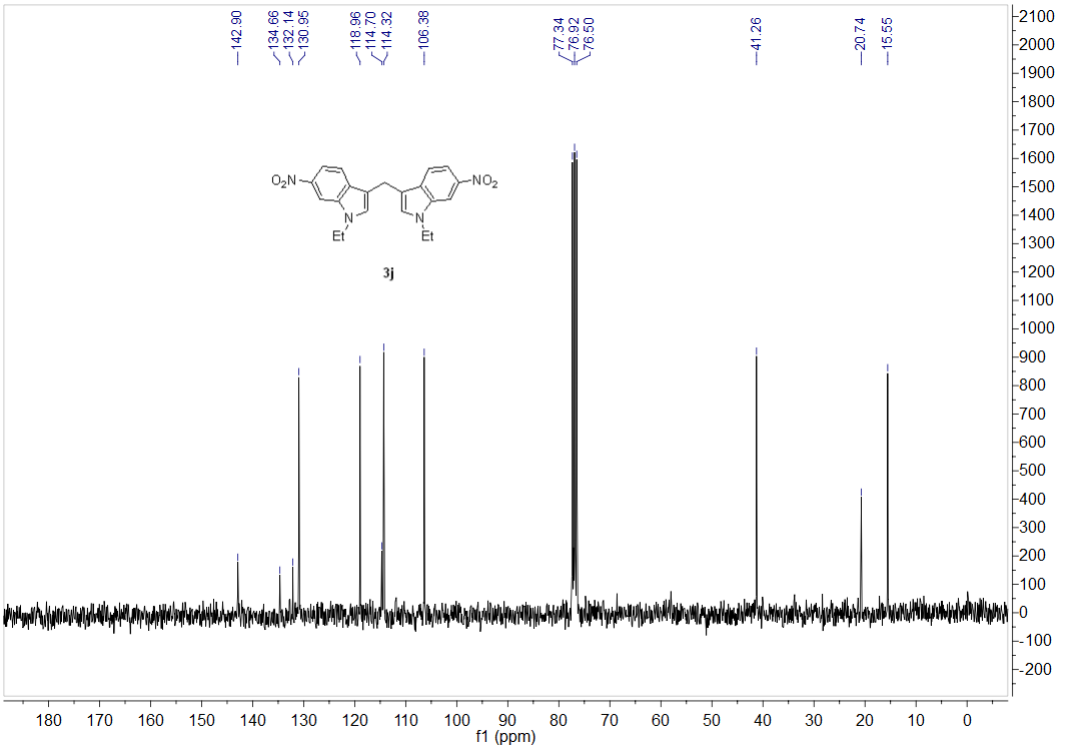
1.50
1.48
1.46
O_2N
NO_2
Et
Et
3j
2.00
2.04
1.97
1.93
2.16
4.17
6.32
f1 (ppm)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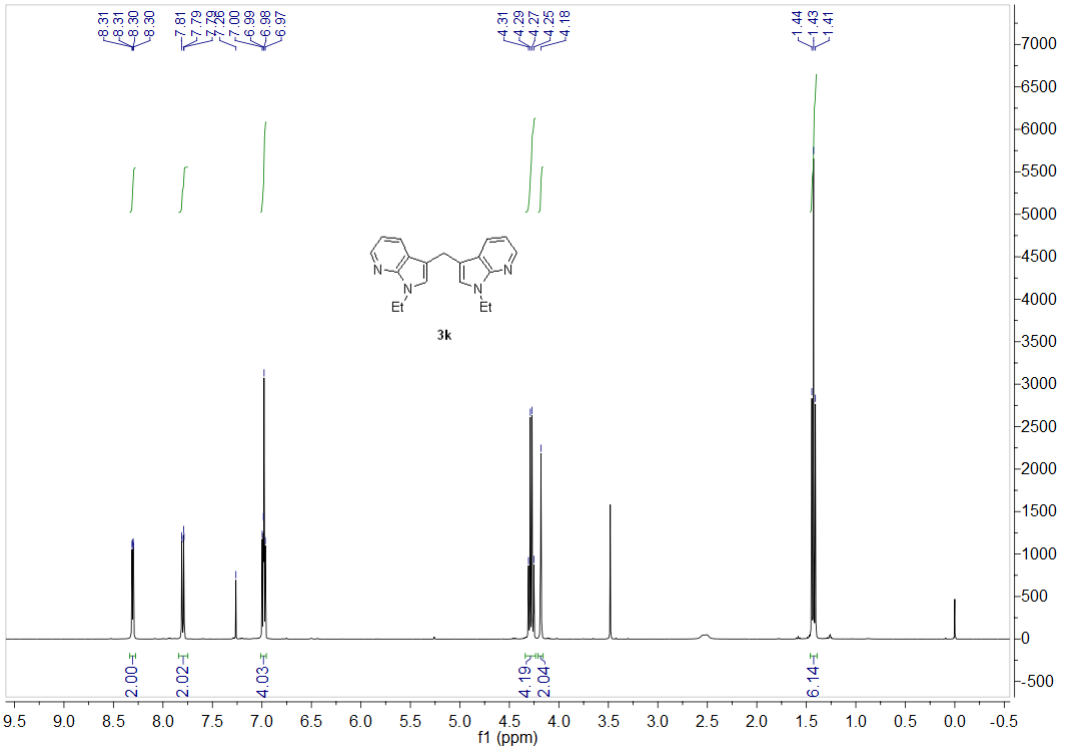
20.74
15.55
O_2N
NO_2
Et
Et
3j
f1 (ppm)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4.31
4.29
4.27
4.25
4.18
1.44
1.43
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Et
Et
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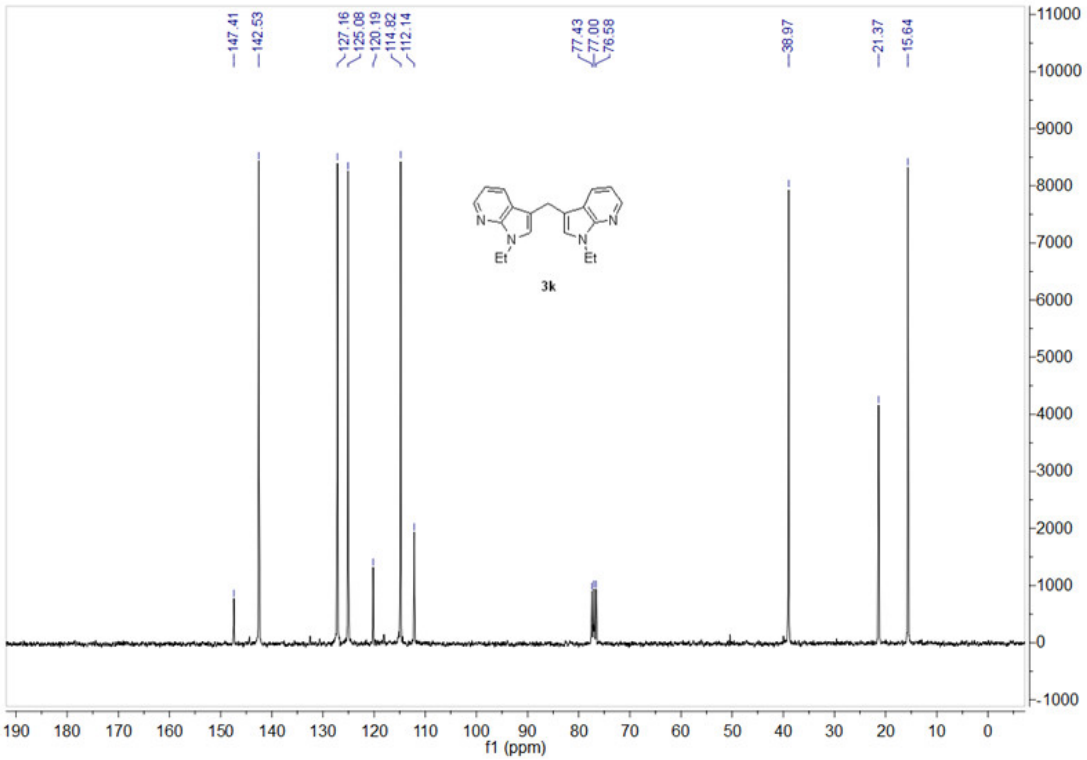
4.03
4.19
2.04
6.14
f1 (ppm)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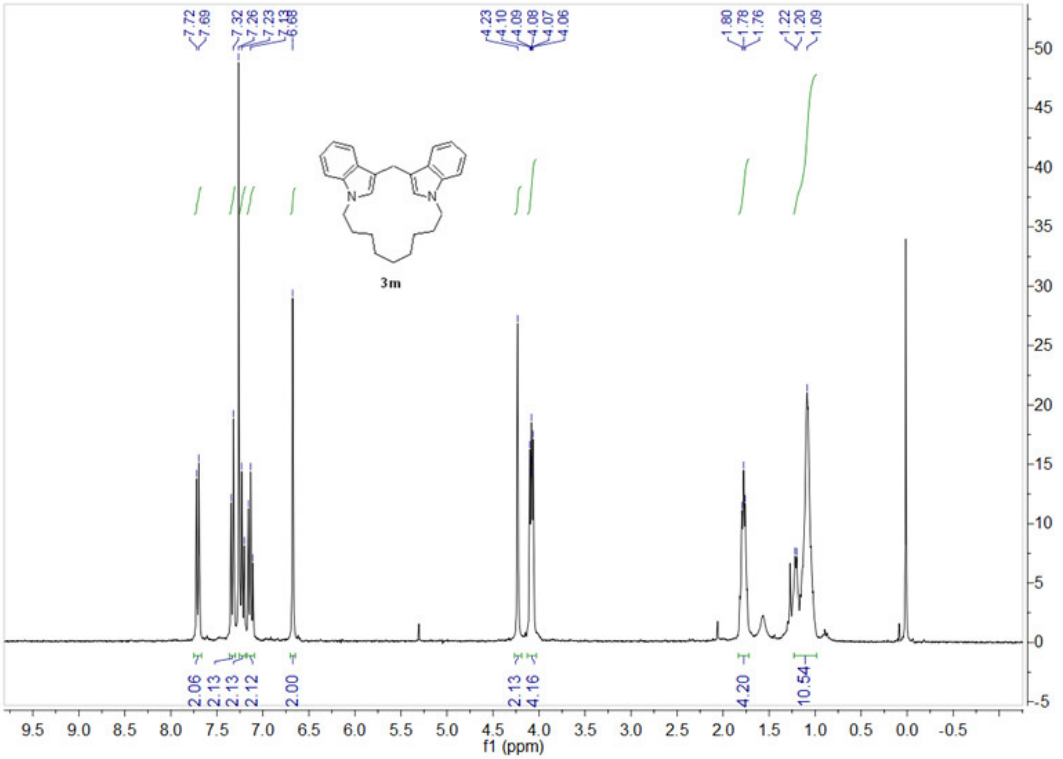
Et
Et
3k
f1 (ppm)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1.80
1.78
1.76
1.22
1.20
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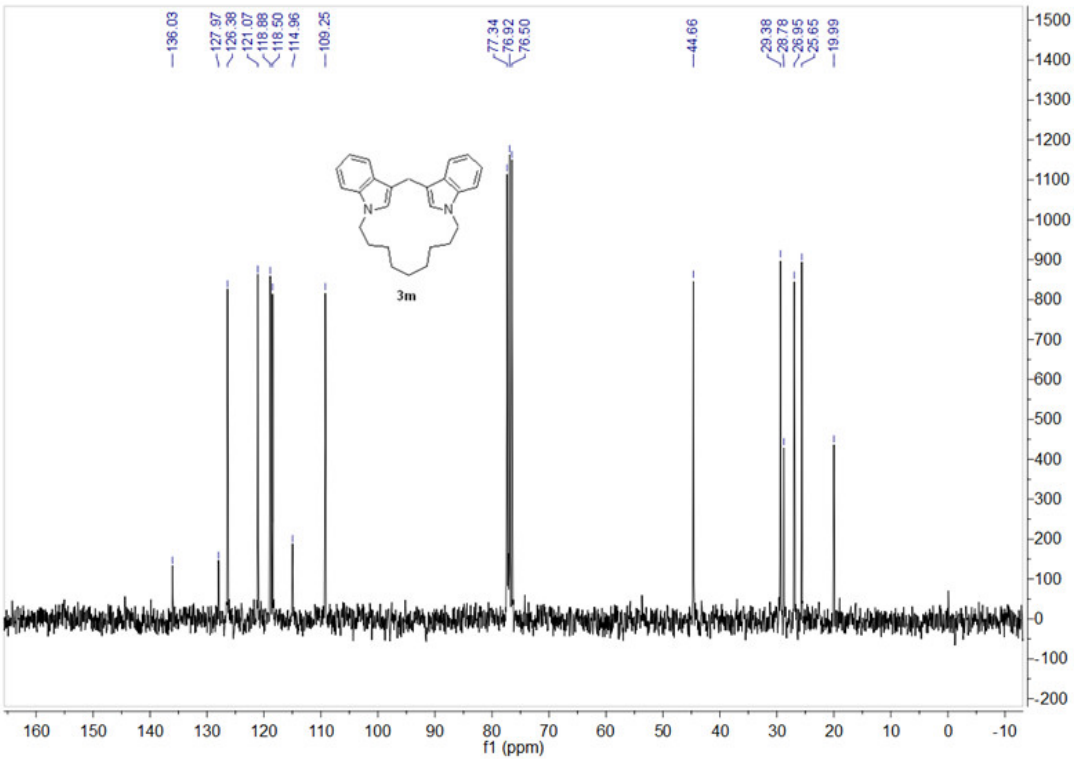
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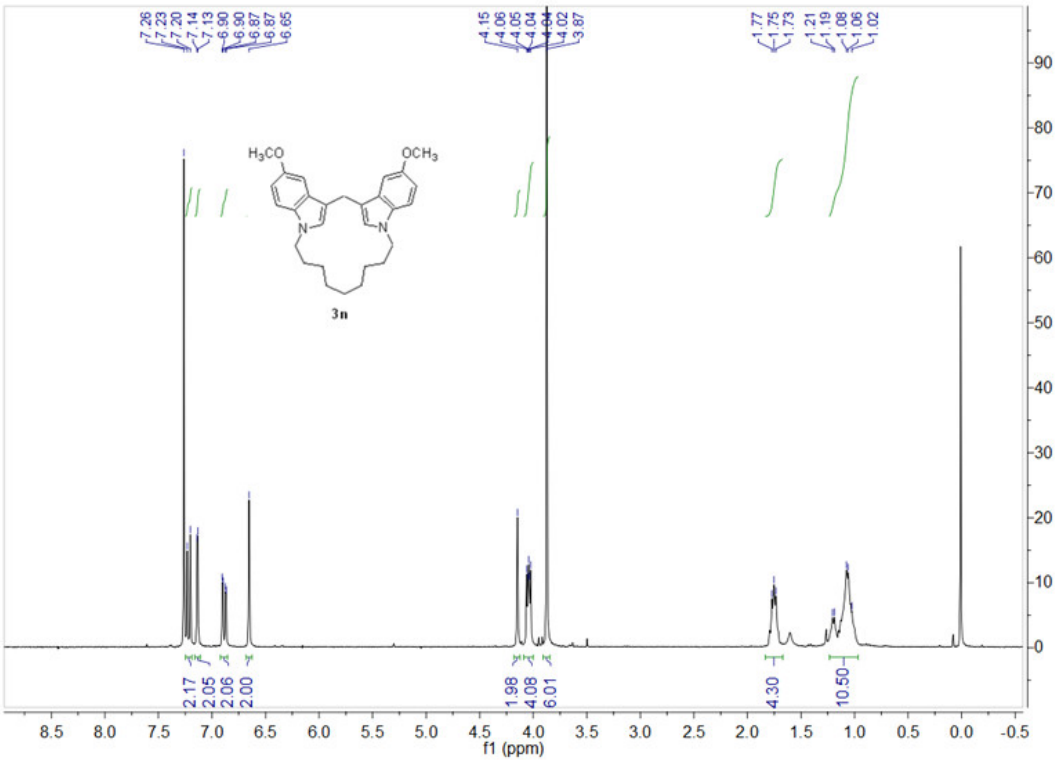
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4.04
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1.19
1.08
1.06
1.02
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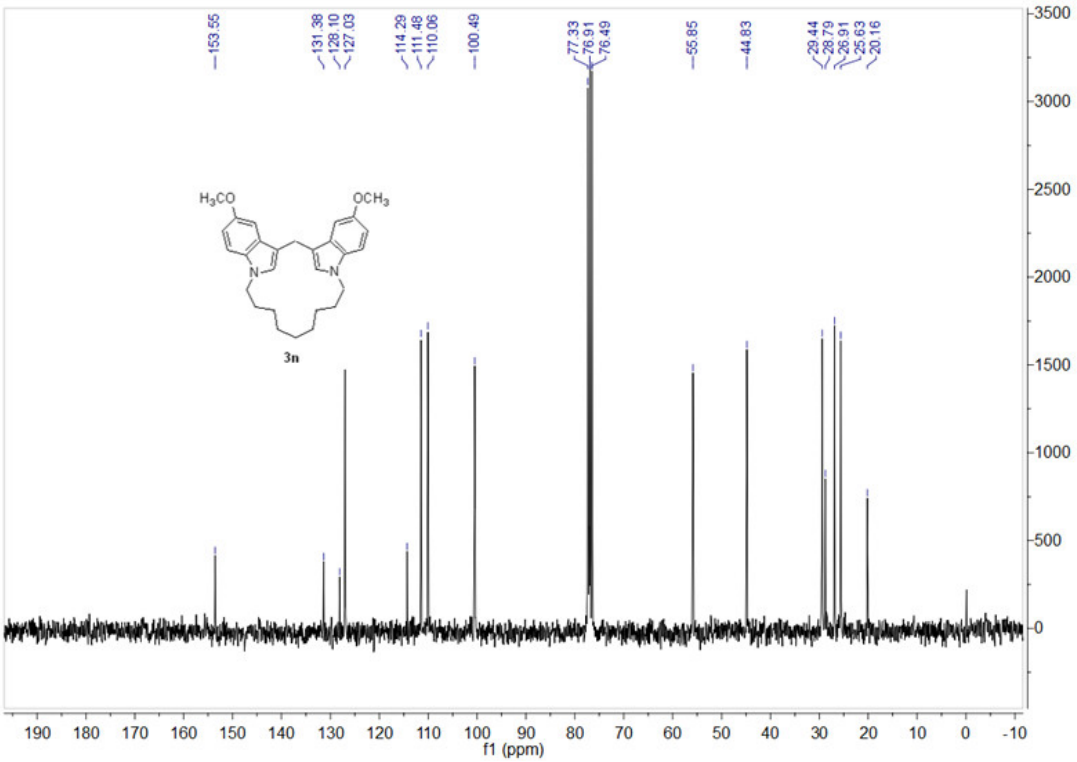
f1 (ppm)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20.16
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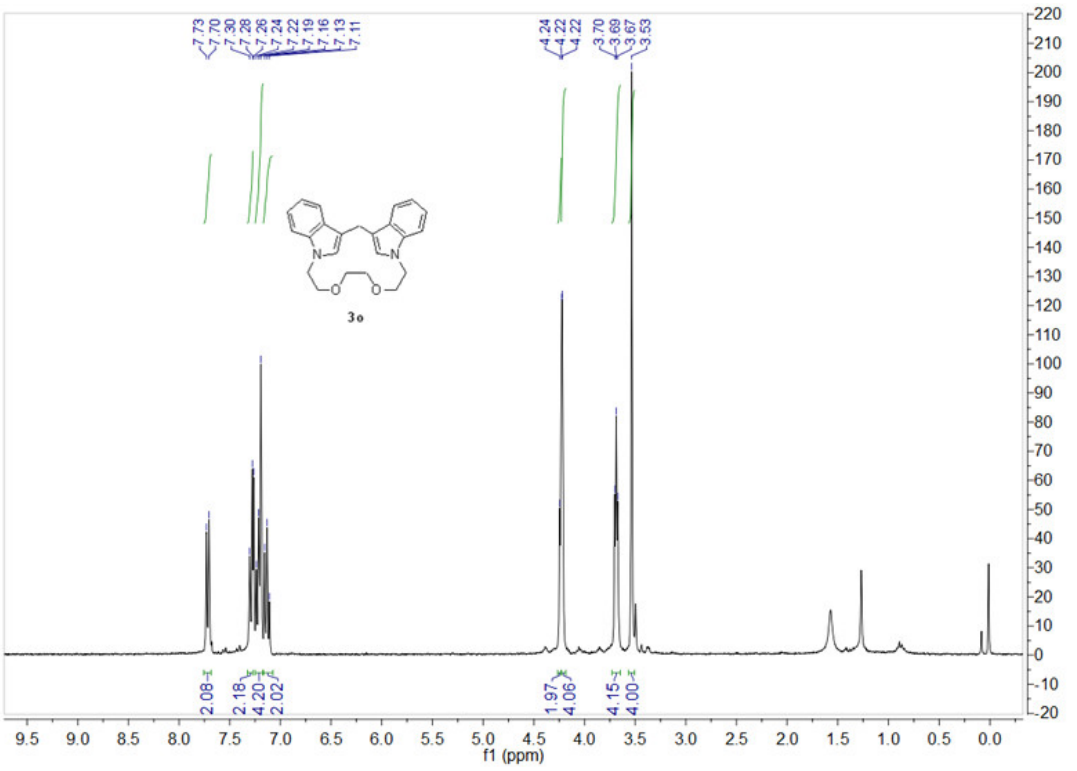
OCH3
3n
f1 (ppm)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4.22
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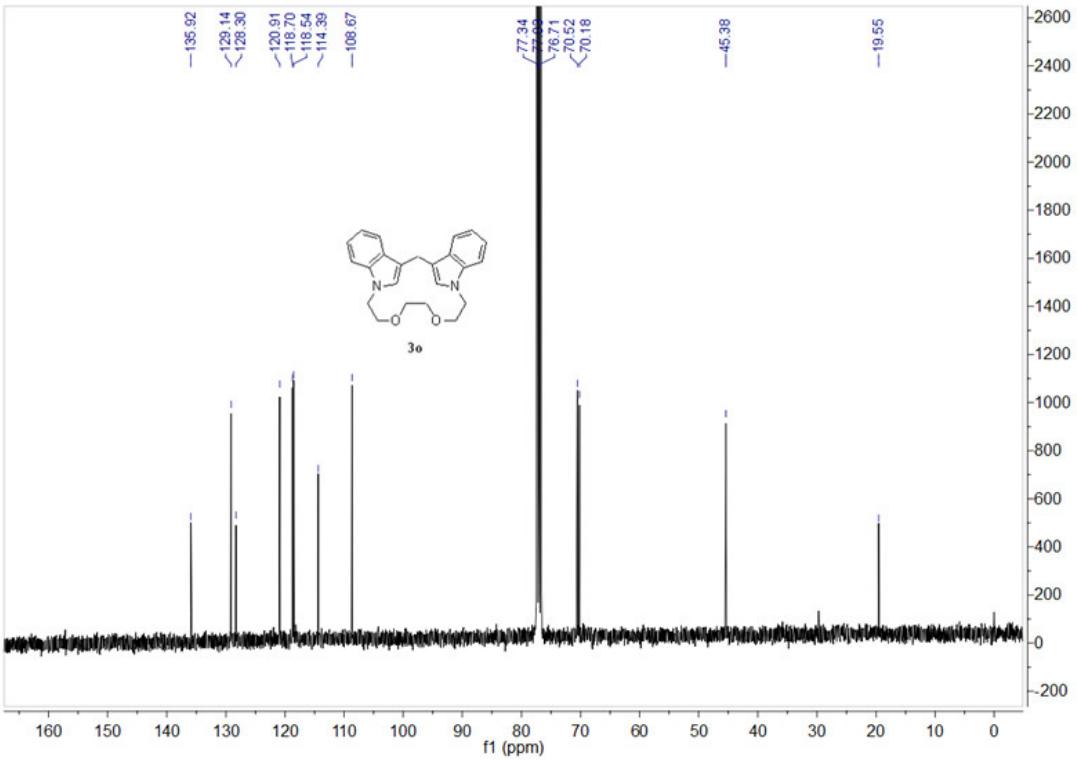
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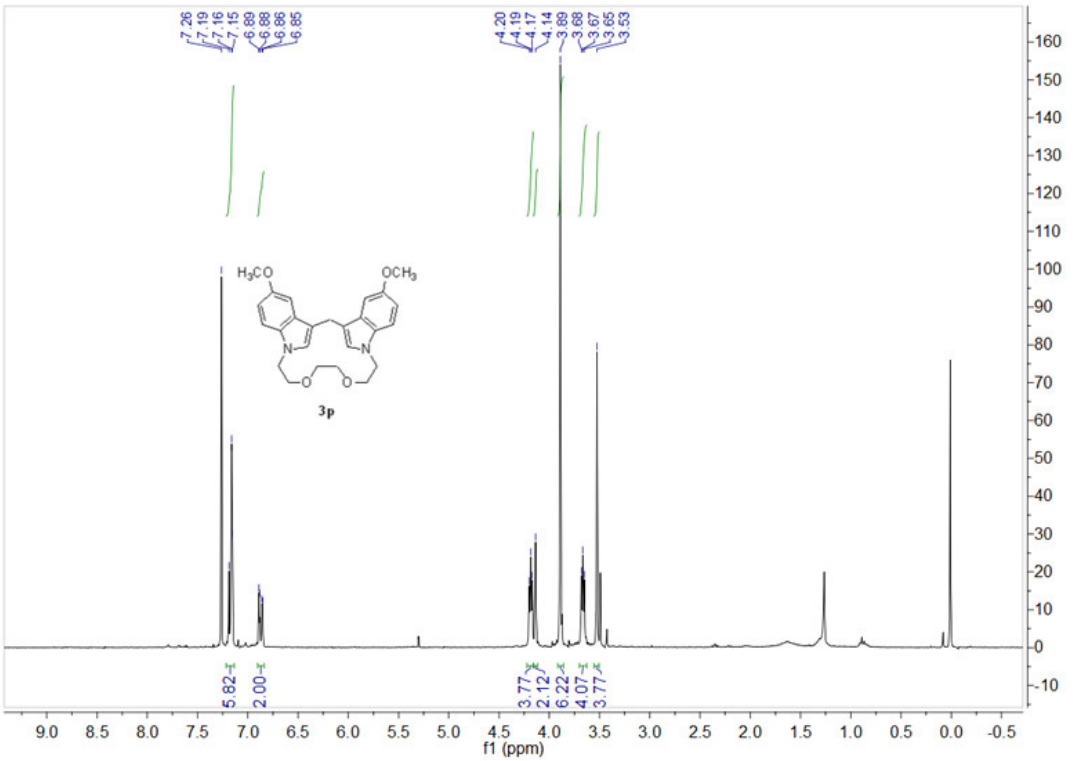
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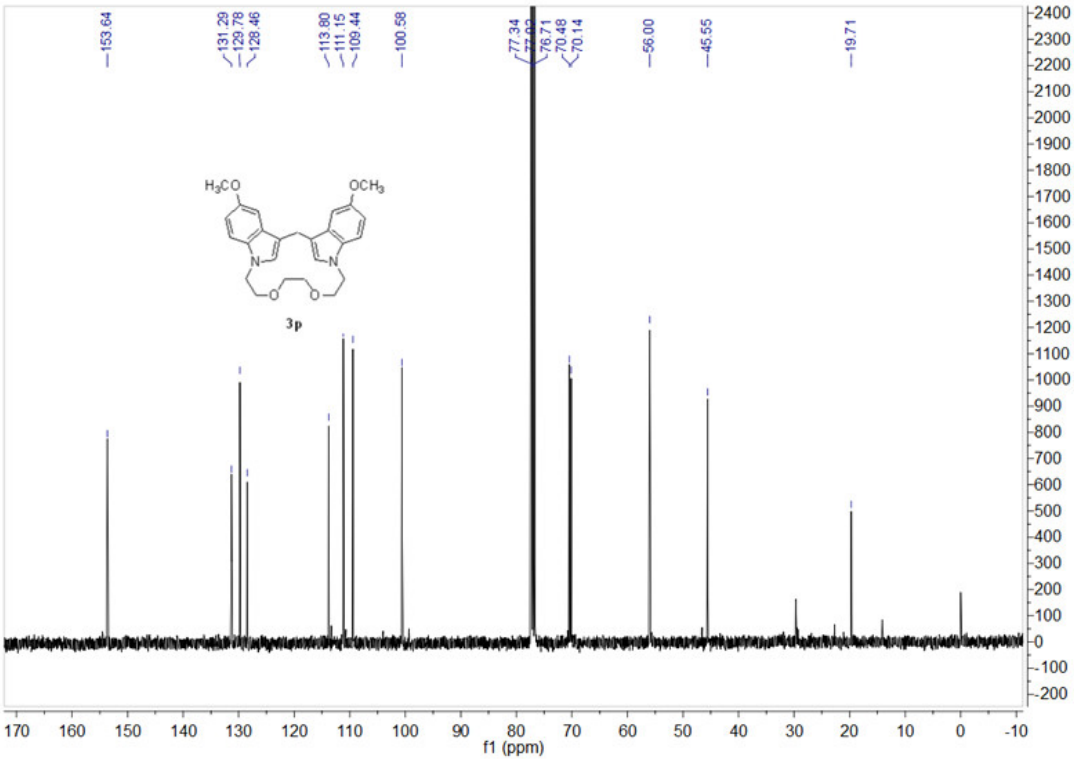
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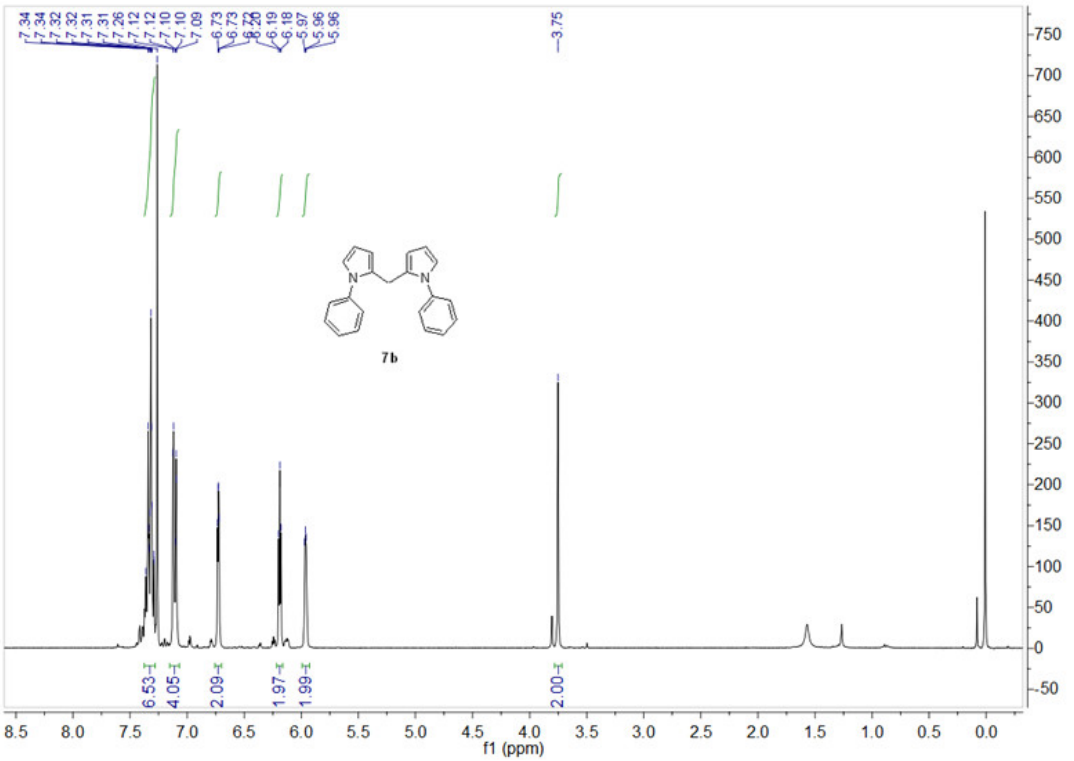
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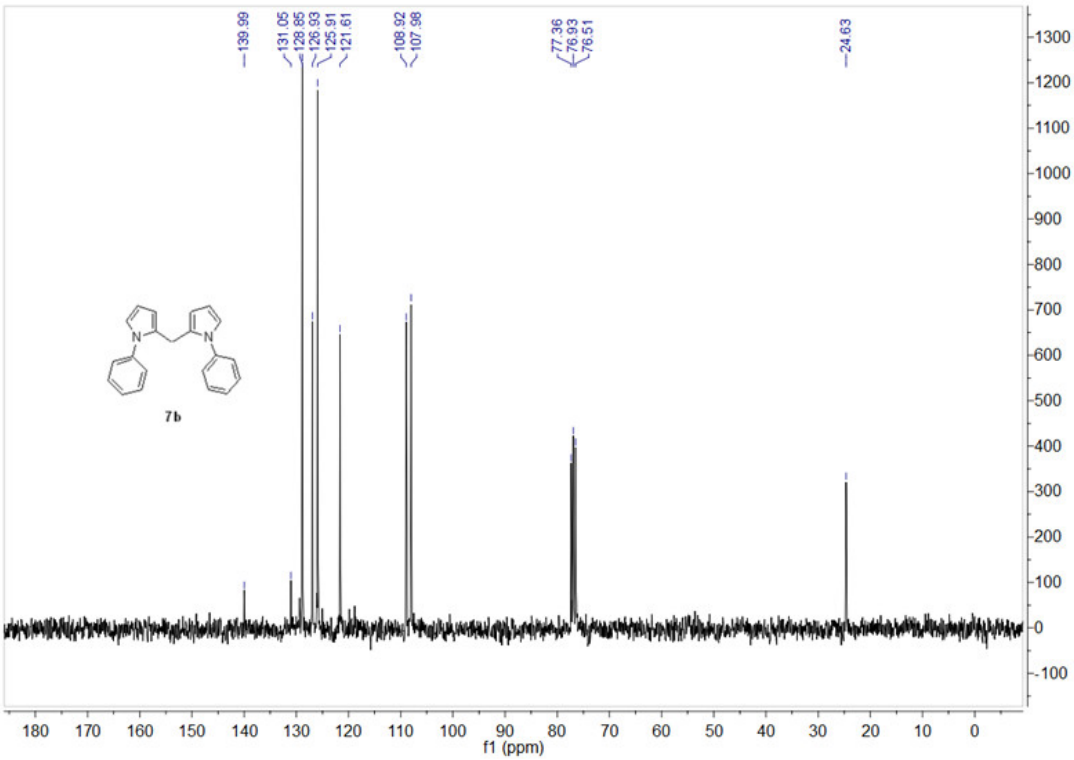
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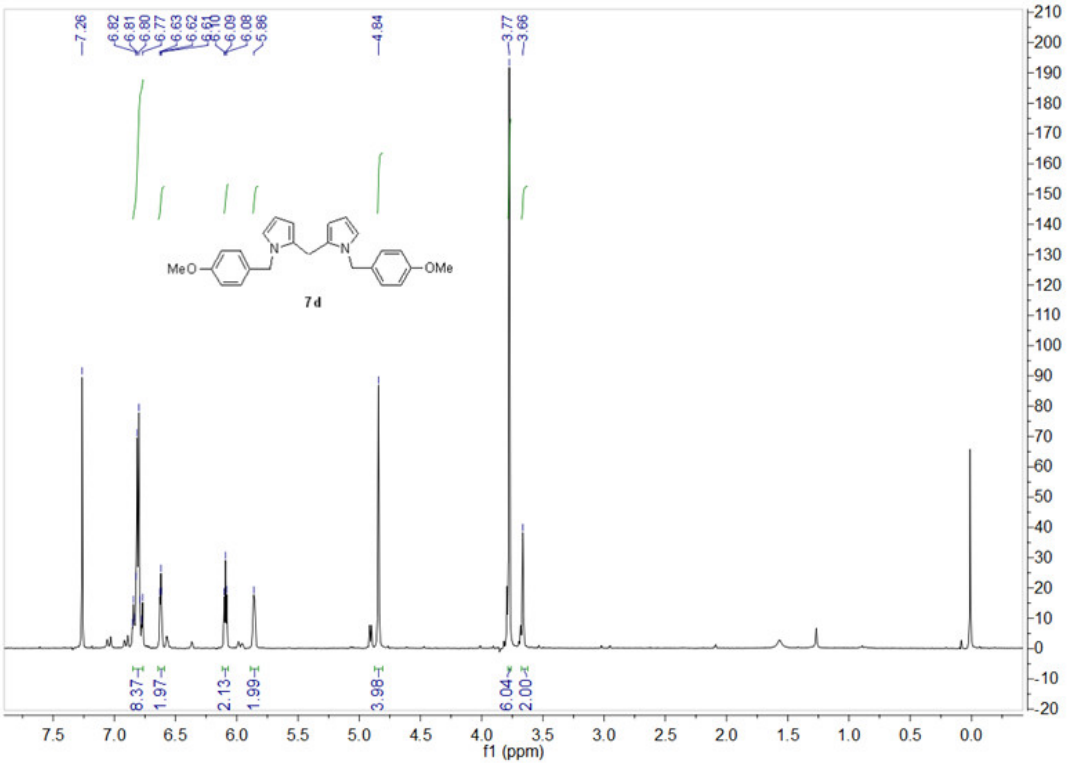
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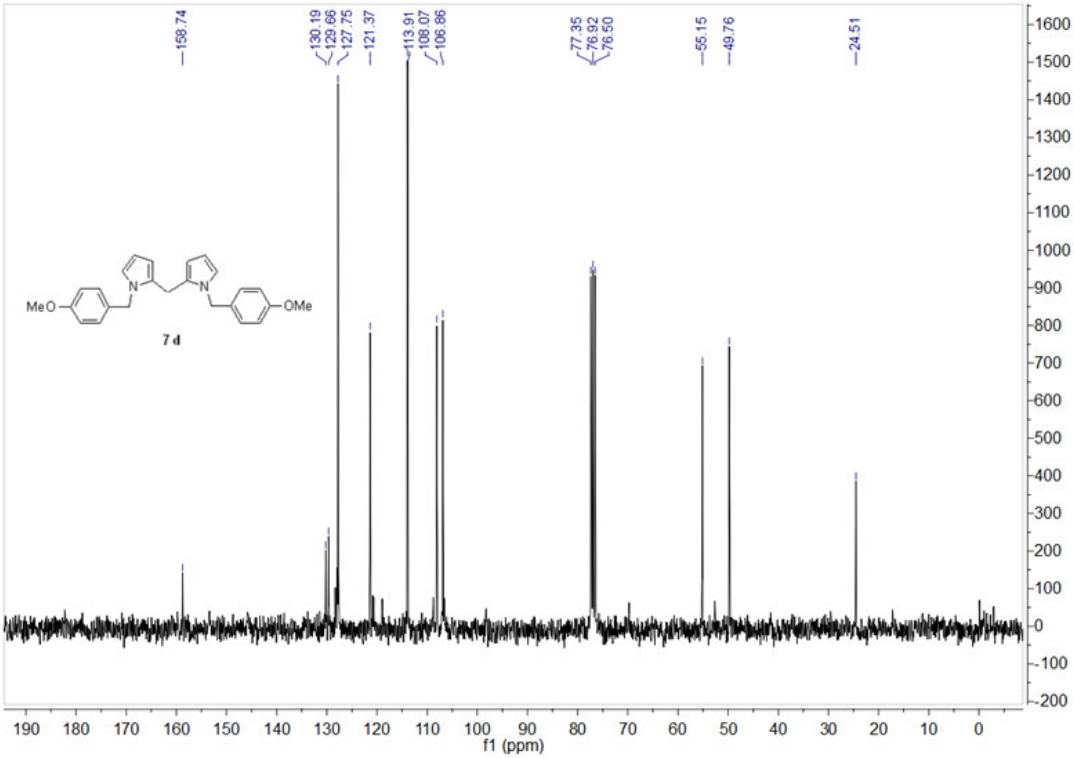
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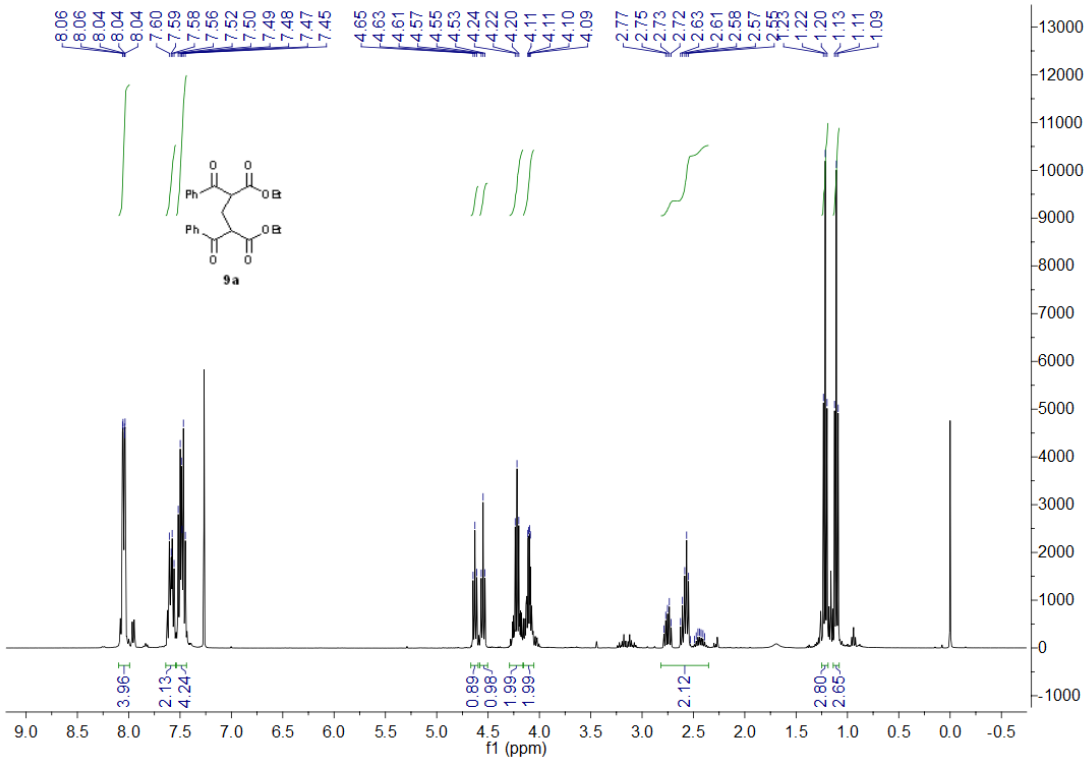
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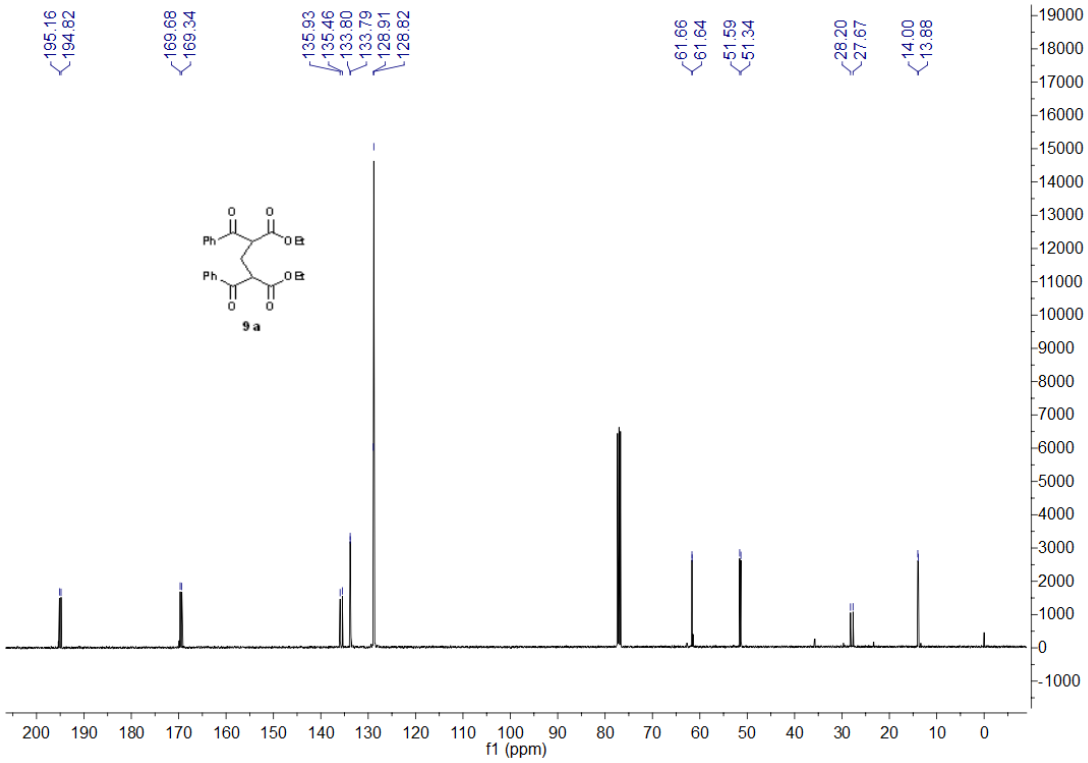
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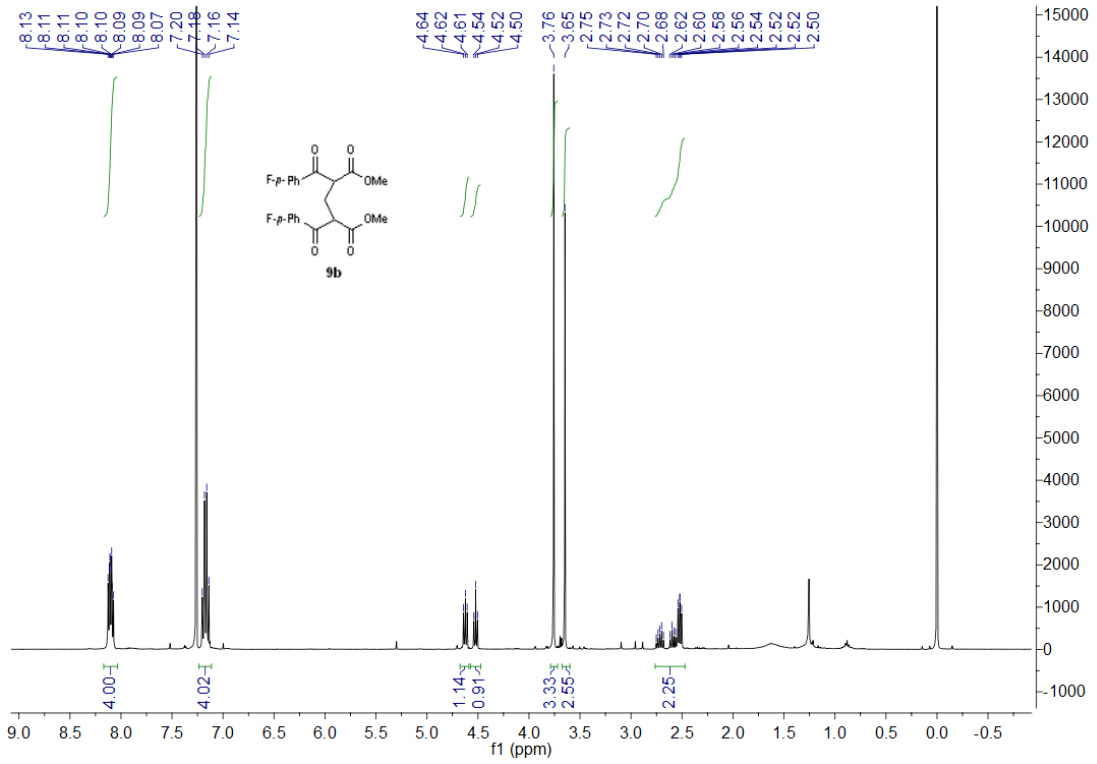
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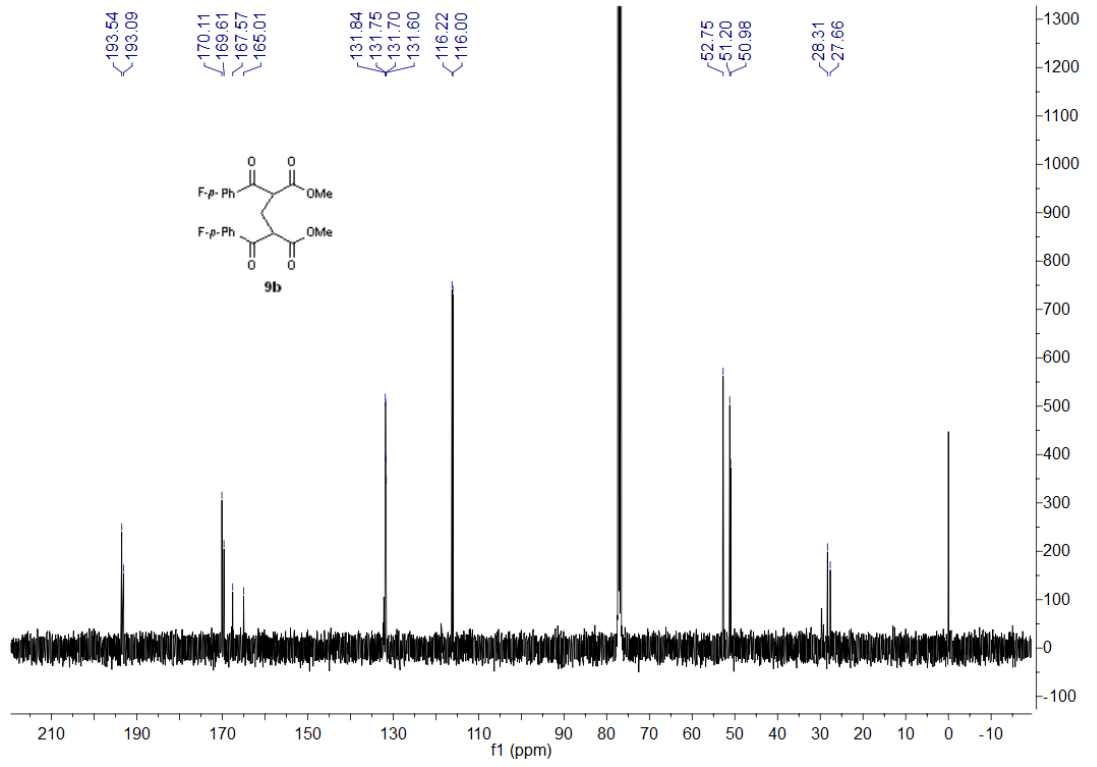
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