Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Electrochemically driven reductive coupling of nitroarenes with alkyl bromides

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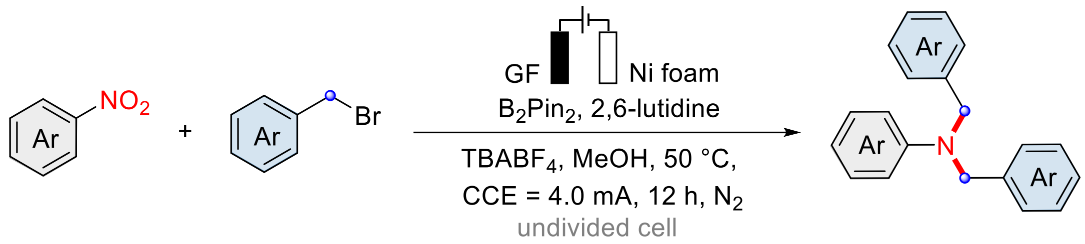
1. General Remarks

Unless otherwise noted, catalytic reactions were carried out in undivided electrochemical cells (10 mL) using pre-dried glassware. All reagents and solvents were purchased from commercial suppliers (Energy Chemical, Adamas-beta, Bidepharm, General Reagent) and used without further purification. Nickel foam (10 mm × 20 mm × 1.5 mm, 99.9%; obtained from Kunshan City Yushan town Wulife electronic material management department, China) and graphite felt electrodes (10 mm × 20 mm × 3.0 mm, Anhui Senrise Technologies, China) were connected using stainless steel adapters. The electrocatalytic reactions were conducted at constant current modes using a HSPY-600 as power supply. Thin-layer chromatography (TLC) was performed on 200 ± 50 μm glass-backed silica gel plates purchased from Shanghai Titan Technology Co., Ltd., China. Column chromatography was carried out on silica gel (200–300 mesh) purchased from Yantai Xinnuo Chemical Co., Ltd., China. NMR spectra were recorded on Bruker Avance NEO 600 or Avance 400 instrument. Chemical shifts (δ) are given in ppm relative to the solvent residual peak, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (J) are in Hertz (Hz). GC-MS analysis was performed on a Shimadzu GC-2030AM or a Hexin EI-Q 1000. High revolution mass spectra (HR-MS) were obtained on Waters Xevo G3 QTof UPLC/MS spectrometer. All IR spectra were recorded on Thermo Nicolet is20 device in the range from 4000 to 400 cm^{-1}. Melting point ranges were taken with Melting Point Apparatus X-5 (Beijing Unitedvision Technology Co., Ltd., China).

2. General Procedure for Electrochemical Reduction.



Scheme S1. General procedure for electrochemical reduction.

General Procedure A: The electrocatalysis was carried out in an undivided cell under N_2 with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene (0.40 mmol), benzyl bromide (1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 µL, 1.20 mmol), B_2Pin_2 (203 mg, 0.80 mmol) and MeOH (4.0 mL). Electrocatalysis was performed at 50 °C with a constant current of 4.0 mA maintained for 12 h. The electrodes were washed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. The residue was purified by chromatography on silica gel to afford the the desired products.

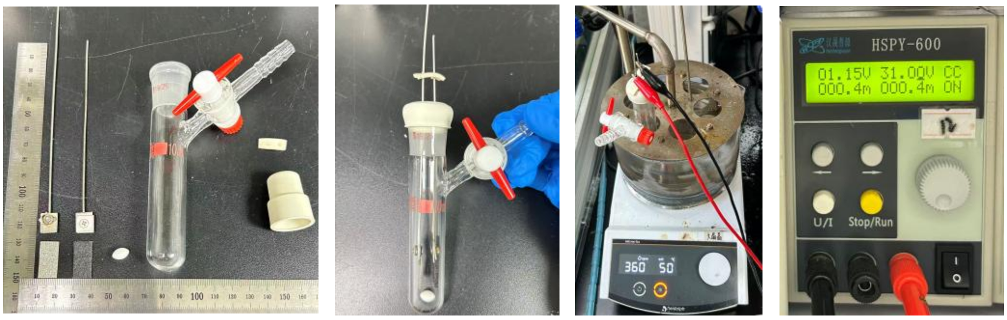
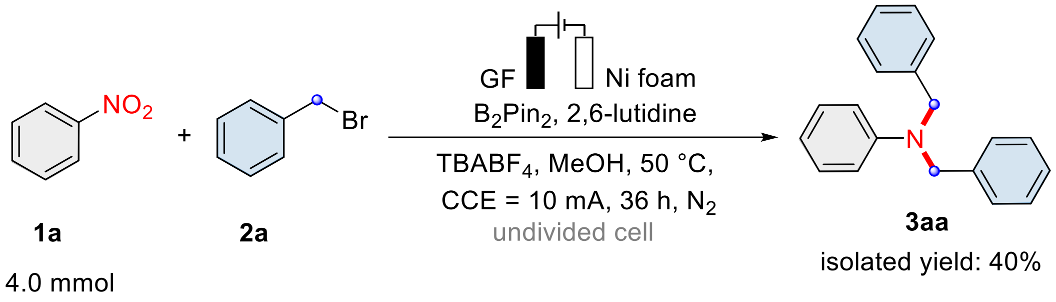


Figure S1. Pictures of the setup of electrolysis.

General Procedure B (for Scale-up reaction)



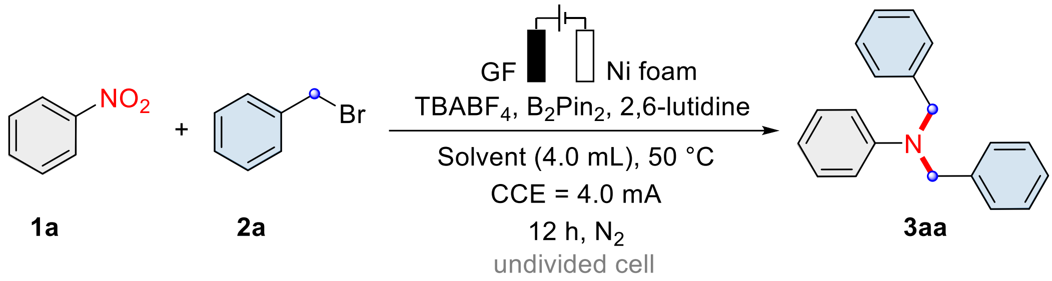
Scheme S2. General procedure for scale-up reaction.

The electrocatalysis was carried out in an undivided cell under N_2 with a GF anode (20 mm × 50 mm × 3.0 mm) and a Ni foam cathode (20 mm × 50 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (492 mg, 4.0 mmol), benzyl bromide **2a** (2.05 g, 12 mmol), $TBABF_4$ (1.98 g, 6.0 mmol), 2,6-lutidine (1.40 mL, 12 mmol), B_2Pin_2 (2.03 g, 8.0 mmol) and MeOH solvent (40.0 mL). Electrocatalysis was performed at 50 °C with a constant current of 10 mA maintained for 36 h. The electrodes were washed with dichloromethane (3 × 8.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. The residue was purified by chromatography on silica gel (PE/DCM = 50:1) to afford product **3aa** (433 mg, 40%) as white solid.

Figure S2. Pictures of the scale-up reaction setups.

3. Optimization of the Reaction Conditions

Table S1. The effect of solvent.[a]

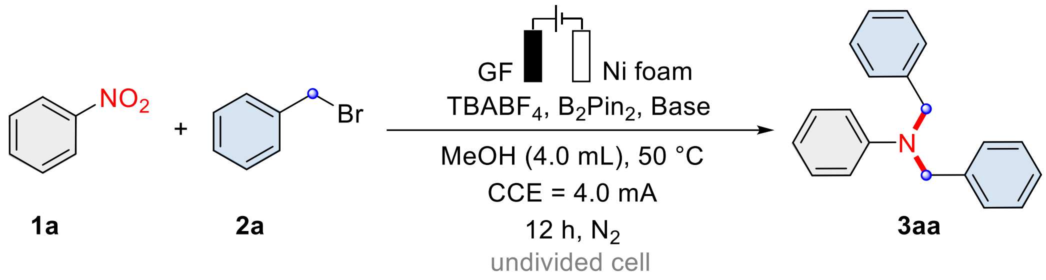


Scheme S3. The effect of solvent.

Entry	Solvent	Yield (%)
1	MeOH	92%, 85[b]
2	HFIP	trace
3	DMA	27
4	CH_3CN	47
5	THF	trace
6	H_2O	NR
7	DMF	45

[a] Reaction conditions: undivided cell, GF as anode, Ni Foam as cathode, constant current electrolysis (CCE) = 4.0 mA, **1a** (41 µL, 0.40 mmol), **2a** (143 µL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), B_2Pin_2 (203 mg, 0.80 mmol), 2,6-lutidine (140 µL, 1.20 mmol), solvent (4.0 mL), 50 °C, 12 h, under N_2 atmosphere. GC yields with 1,3,5-trimethoxybenzene as the internal standard. [b] Isolated yield of **3aa**.

Table S2. The effect of base.[a]



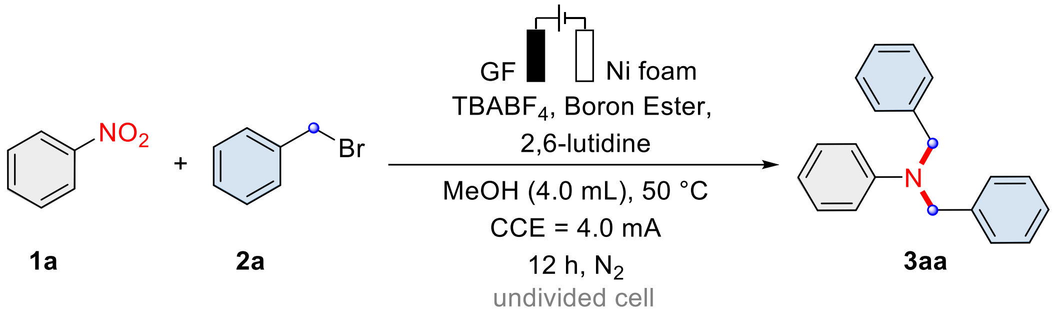
Scheme S4. The effect of base.

Entry	Base	Yield (%)
1	2,6-lutidine	92%, 85[b]
2	Et_3N	44
3	pyridine	trace
4	DMAP	trace
5	DBU	50
6	DBN	27
7	DIPEA	57
8	2,4,6-collidine	64
9	2,6-di-tert-butylpyridine	NR
10	K_2CO_3	NR

[a] Reaction conditions: undivided cell, GF as anode, Ni Foam as cathode, constant current electrolysis (CCE) = 4.0 mA, **1a** (41 μL, 0.40 mmol), **2a** (143 μL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), B_2Pin_2 (203 mg, 0.80 mmol), base (1.20 mmol), MeOH (4.0 mL), 50 °C, 12 h, under N_2 atmosphere. GC yields with 1,3,5-trimethoxybenzene as the internal standard.

[b] Isolated yield of **3aa**.

Table S3. The effect of boron ester.[a]

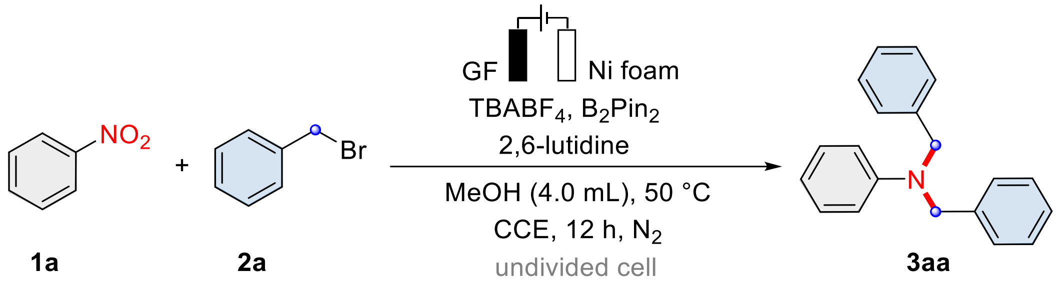


Scheme S5. The effect of boron ester.

Entry	Boron Ester	Yield (%)
1	B_2Pin_2	92%, 85[b]
2	B_2Cat_2	64
3	Cy-Bpin	11

[a] Reaction conditions: undivided cell, GF as anode, Ni Foam as cathode, constant current electrolysis (CCE) = 4.0 mA, **1a** (41 µL, 0.40 mmol), **2a** (143 µL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), boron ester (0.80 mmol), 2,6-lutidine (140 µL, 1.20 mmol), MeOH (4.0 mL), 50 °C, 12 h, under N_2 atmosphere. GC yields with 1,3,5-trimethoxybenzene as the internal standard. [b] Isolated yield of **3aa**.

Table S4. The effect of current density.



Scheme S6. The effect of current density.

Entry	CCE	Yield (%)
1	4.0 mA	85
2	2.0 mA	58
3	6.0 mA	74
4	8.0 mA	62

[a] Reaction conditions: undivided cell, GF as anode, Ni Foam as cathode, **1a** (41 μL, 0.40 mmol), **2a** (143 μL, 1.20 mmol), TBABF4 (198 mg, 0.60 mmol), B_2pin_2 (203 mg, 0.80 mmol), 2,6-lutidine (140 μL, 1.20 mmol), MeOH (4.0 mL). After that, the reaction was electrolyzed at a constant current of 2.0 mA (0.5 mA/cm^2), 4.0 mA (1.0 mA/cm^2), 6.0 mA (1.5 mA/cm^2), 8.0 mA (4.0 mA/cm^2), 50 °C, 12 h, under N_2 atmosphere. Isolated yield of **3aa**.

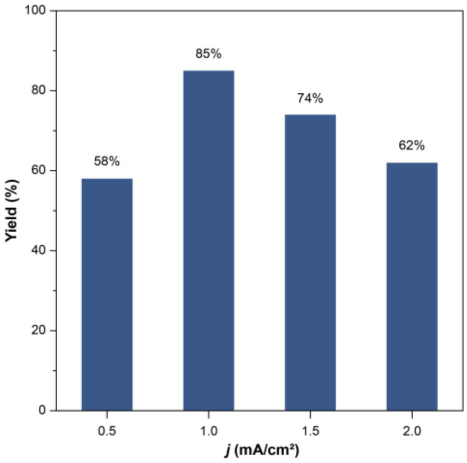
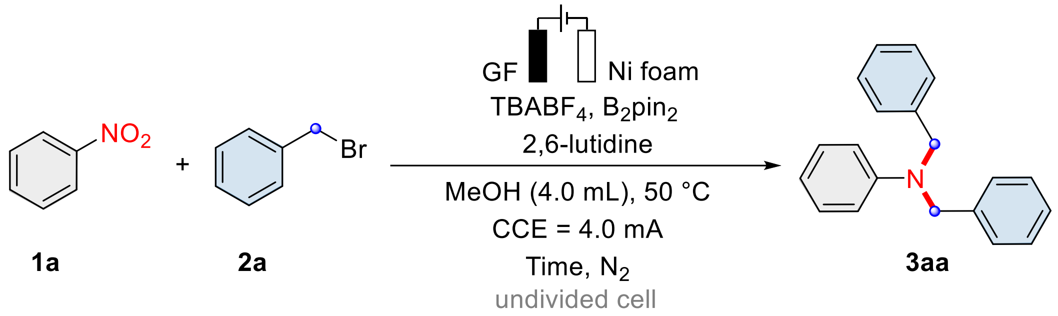


Figure S3. The effect of current density.

Table S5. The effect of applied charge.



Scheme S7. The effect of applied charge.

Entry	Time	Yield (%)
1	12 h	85
2	4 h	37
3	6 h	44
4	8 h	71
5	16 h	66
6	18 h	65

[a] Reaction conditions: undivided cell, GF as anode, Ni Foam as cathode, **1a** (41 μL, 0.40 mmol), **2a** (143 μL, 1.20 mmol), TBABF$_4$ (198 mg, 0.60 mmol), B$_2$pin$_2$ (203 mg, 0.80 mmol), 2,6-lutidine (140 μL, 1.20 mmol), MeOH (4.0 mL). After that, the reaction mixture was electrolyzed under a constant current electrolysis at 4.0 mA for different time: 4 h (1.49 F/mol), 6 h (2.24 F/mol), 8 h (2.98 F/mol), 12 h (4.48 F/mol), 16 h (5.97 F/mol), 18 h (6.72 F/mol), 50 °C, under N$_2$ atmosphere. Isolated yield of **3aa**.

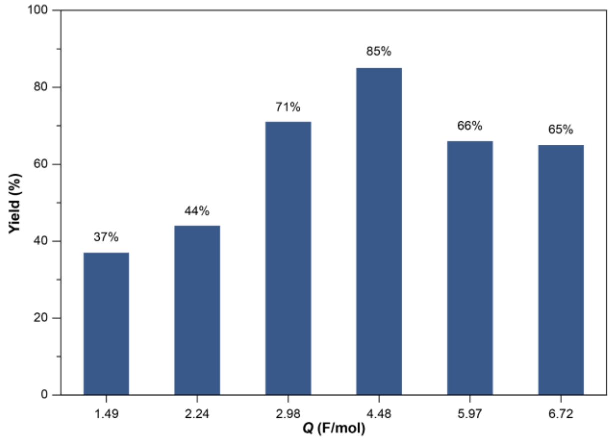
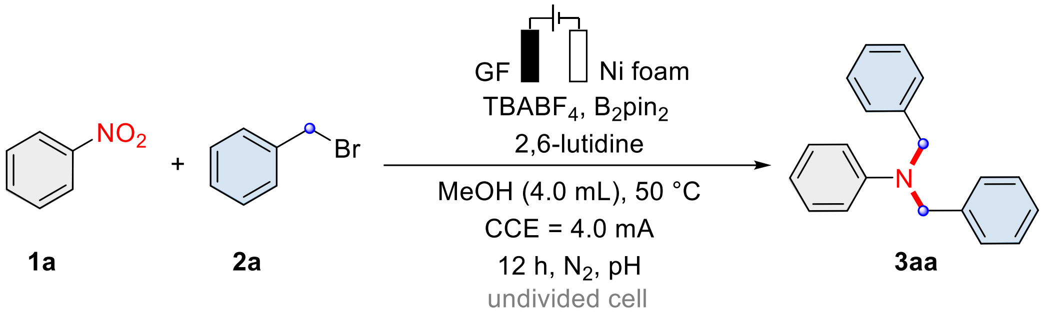


Figure S4. The effect of applied charge.

Table S6. The effect of pH.



Scheme S8. The effect of pH.

Entry	pH	Yield (%)
1	8.35	85
2	7.35	66
3	9.35	59

[a] Reaction conditions: undivided cell, GF as anode, Ni Foam as cathode, **1a** (41 µL, 0.40 mmol), **2a** (143 µL, 1.20 mmol), TBABF$_4$ (198 mg, 0.60 mmol), B$_2$pin$_2$ (203 mg, 0.80 mmol), 2,6-lutidine (140 µL, 1.20 mmol), MeOH (4.0 mL). We first measured the pH (8.35) of the reaction mixture. Subsequently, we adjusted the pH of the reaction mixture using hydrochloric acid methanol solution and sodium hydroxide methanol solution, respectively: 1.25 M methanolic hydrochloric acid methanol solution was added to adjust the pH to 7.35, while 1.0 M methanolic sodium hydroxide methanol solution was added to adjust the pH to 9.35, 50 ℃, under N$_2$ atmosphere. Isolated yield of **3aa**.

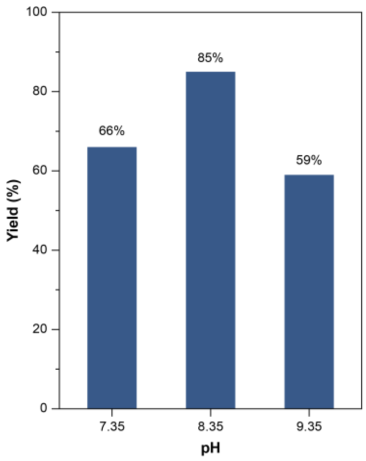
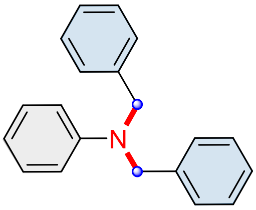
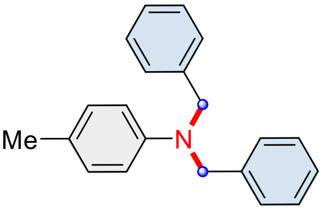


Figure S5. The effect of pH.

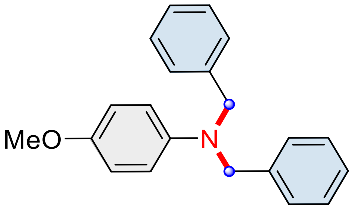
4. Characterization Data of Products



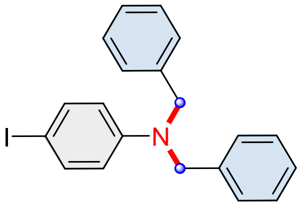
***N,N*-dibenzylaniline (3aa):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3aa** (92.8 mg, 85%) as white solid. **M.p.** = 67–68 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.34 (t, J = 7.5 Hz, 4H), 7.28 (d, J = 7.4 Hz, 6H), 7.19 (t, J = 7.7 Hz, 2H), 6.77 (d, J = 8.1 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 4.68 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.3 (C_q), 138.7 (C_q), 129.3 (CH), 128.8 (CH), 127.0 (CH), 126.8 (CH), 116.9 (CH), 112.6 (CH), 54.3 (CH_2). **IR** (KBr): 3020, 1597, 1505, 1450, 1398, 1229, 1026, 957, 750, 731, 693 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 274 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{19}N$ $[M+H]^+$ 274.1590, found 274.1593. The data are in agreement with those reported in literature.[1]



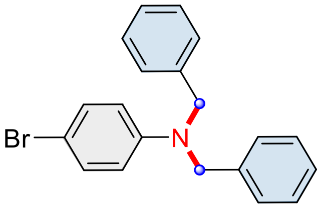
***N,N*-dibenzyl-4-methylaniline (3ba):** The general procedure A was followed using **1b** (54.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ba** (72.6 mg, 63%) as white solid. **M.p.** = 68–69 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.35 (t, J = 7.5 Hz, 4H), 7.30–7.27 (m, 6H), 7.01 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 8.3 Hz, 2H), 4.65 (s, 4H), 2.26 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 147.2 (C_q), 139.0 (C_q), 129.9 (C_q), 128.7 (CH), 126.9 (CH), 126.8 (CH), 126.0 (CH), 112.8 (CH), 54.5 (CH_2), 20.4 (CH_3). **IR** (KBr): 3022, 2920, 1618, 1521, 1362, 1238, 1074, 951, 800, 738, 695 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 288 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{21}N$ $[M+H]^+$ 288.1747, found 288.1747. The data are in agreement with those reported in literature.[2]



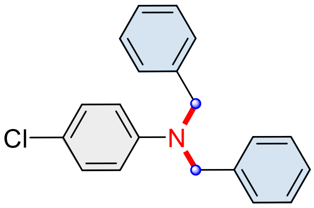
***N,N*-dibenzyl-4-methoxyaniline (3ca):** The general procedure A was followed using **1c** (61.2 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ca** (91.2 mg, 75%) as white solid. **M.p.** = 64–65 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.35 (t, J = 7.5 Hz, 4H), 7.30–7.27 (m, 6H), 6.80 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 4.60 (s, 4H), 3.76 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 151.8 (C_q), 144.0 (C_q), 139.1 (C_q), 128.7 (CH), 127.1 (CH), 127.0 (CH), 114.9 (CH), 114.7 (CH), 55.8 (CH_3), 55.3 (CH_2). **IR** (KBr): 3027, 2924, 1602, 1512, 1355, 1232, 1081, 965, 805, 735, 694 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 304 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{21}NO$ $[M+H]^+$ 304.1696, found 304.1695. The data are in agreement with those reported in literature.[3]



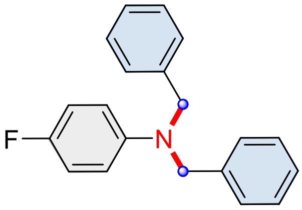
***N,N*-dibenzyl-4-iodoaniline (3da):** The general procedure A was followed using **1d** (99.6 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3da** (68.8 mg, 68%) as white solid. **M.p.** = 65–66 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.40 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 4H), 7.27 (t, J = 6.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 4H), 6.51 (d, J = 8.5 Hz, 2H), 4.64 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.8 (C_q), 138.1 (C_q), 137.9 (CH), 128.9 (CH), 127.2 (CH), 126.6 (CH), 114.9 (CH), 77.7 (C_q), 54.4 (CH_2). **IR** (KBr): 3022, 2924, 1589, 1493, 1350, 1242, 1070, 961, 799, 728, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 400 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}IN$ $[M+H]^+$ 400.0557, found 400.0562. The data are in agreement with those reported in literature.[4]



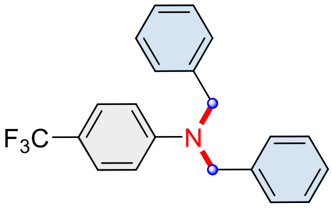
***N,N*-dibenzyl-4-bromoaniline (3ea):** The general procedure A was followed using **1e** (80.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ea** (99.9 mg, 71%) as white solid. **M.p.** = 190–191 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.33 (t, J = 7.5 Hz, 4H), 7.26 (t, J = 7.1 Hz, 2H), 7.25–7.21 (m, 6H), 6.59 (d, J = 9.0 Hz, 2H), 4.63 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.2 (C_q), 138.1 (C_q), 132.0 (CH), 128.9 (CH), 127.2 (CH), 126.7 (CH), 114.3 (CH), 108.7 (C_q), 54.6 (CH_2). **IR** (KBr): 2924, 1591, 1497, 1380, 1241, 1082, 965, 801, 729, 691 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 352 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}{}^{79}BrN$ $[M+H]^+$ 352.0695, found 352.0695. The data are in agreement with those reported in literature.[5]



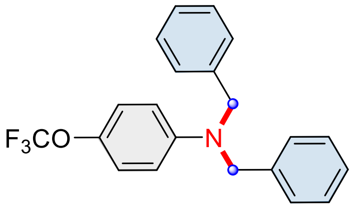
***N,N*-dibenzyl-4-chloroaniline (3fa):** The general procedure A was followed using **1f** (63.2 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3fa** (85.3 mg, 69%) as white solid. **M.p.** = 92–93 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ =7.34 (t, J = 7.7 Hz, 4H), 7.27 (t, J = 7.3 Hz, 2H), 7.23 (d, J = 7.1 Hz, 4H), 7.10 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 4.64 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 147.8 (C_q), 138.2 (C_q), 129.1 (CH), 128.9 (CH), 127.2 (CH), 126.7 (CH), 121.7 (C_q), 113.8 (CH), 54.6 (CH_2). **IR** (KBr): 2924, 1591, 1497, 1351, 1241, 1190, 1082, 965, 801, 729, 691 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 308 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}{}^{35}ClN$ $[M+H]^+$ 308.1201, found 308.1202. The data are in agreement with those reported in literature.[5]



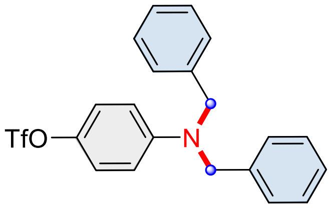
***N,N*-dibenzyl-4-fluoroaniline (3ga):** The general procedure A was followed using **1g** (56.4 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ga** (71.9 mg, 62%) as brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.32 (t, J = 7.5 Hz, 4H), 7.25–7.23 (m, 6H), 6.85 (t, J = 8.7 Hz, 2H), 6.64 (dd, J = 9.0, 4.3 Hz, 2H), 4.60 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 155.6 (d, $^1J_{C\text{–}F}$ = 235.6 Hz, C_q), 145.8 (d, $^4J_{C\text{–}F}$ = 1.9 Hz, C_q), 138.6 (C_q), 128.8 (CH), 127.1 (CH), 126.8 (CH), 115.7 (d, $^2J_{C\text{–}F}$ = 21.1 Hz, CH), 113.9 (d, $^3J_{C\text{–}F}$ = 6.0 Hz, CH), 55.2 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -128.87. **IR** (KBr): 3027, 2924, 1602, 1512, 1355, 1232, 1081, 965, 805, 735, 694 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 292 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}FN$ $[M+H]^+$ 292.1496, found 292.1494. The data are in agreement with those reported in literature.[6]



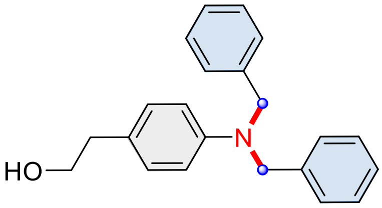
***N,N*-dibenzyl-4-(trifluoromethyl)aniline (3ha):** The general procedure A was followed using **1h** (76.4 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ha** (69.8 mg, 51%) as white solid. **M.p.** = 80–81 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.39 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.5 Hz, 4H), 7.28 (t, J = 7.4 Hz, 2H), 7.22 (d, J = 8.7 Hz, 4H), 6.74 (d, J = 8.7 Hz, 2H), 4.71 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 151.4 (C_q), 137.6 (C_q), 129.0 (CH), 127.4 (CH), 126.7 (q, $^3J_{C\text{–}F}$ = 3.0 Hz, CH), 126.6 (CH), 125.2 (q, $^1J_{C\text{–}F}$ = 270.3 Hz, C_q), 118.4 (q, $^2J_{C\text{–}F}$ = 33.2 Hz, C_q), 111.7 (CH), 54.3 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -60.99. **IR** (KBr): 3026, 2923, 1617, 1493, 1390, 1296, 1069, 963, 813, 741, 694 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{18}F_3N$ $[M+H]^+$ 342.1464, found 342.1468. The data are in agreement with those reported in literature.[7]



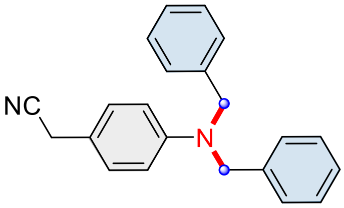
***N,N*-dibenzyl-4-(trifluoromethoxy)aniline (3ia):** The general procedure A was followed using **1i** (82.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ia** (88.7 mg, 62%) as white solid. **M.p.** = 71–72 °C. **^{1}H NMR (**600 MHz, $CDCl_3$) $\delta = 7.36$ (t, $J = 7.4$ Hz, 4H), 7.30–7.26 (m, 3H), 7.26–7.23 (m, 3H), 7.02 (d, $J = 8.5$ Hz, 2H), 6.68 (d, $J = 8.5$ Hz, 2H), 4.67 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) $\delta = 147.9$ (C_q), 140.3 (C_q), 138.1 (C_q), 128.9 (CH), 127.3 (CH), 126.7 (CH), 122.5 (q, $^1J_{C\text{–}F} = 255.2$ Hz, C_q), 118.3 (CH), 113.0 (CH), 54.8 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) $\delta = -58.37$. **IR** (KBr): 3026, 2922, 1605, 1517, 1362, 1234, 1150, 953, 808, 732, 695 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 358 (100) $[M+H]^+$.**HR-MS** (ESI) *m/z* calcd for $C_{21}H_{18}F_3NO$ $[M+H]^+$ 358.1413, found 358.1414**.** The data are in agreement with those reported in literature.[8]



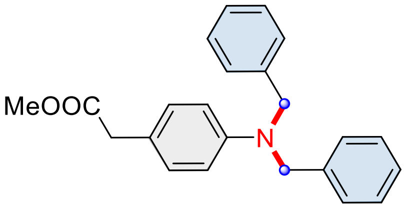
4-(Dibenzylamino)phenyl trifluoromethanesulfonate (3ja): The general procedure A was followed using **1j** (108 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ja** (108 mg, 64%) as pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) $\delta = 7.34$ (t, $J = 7.5$ Hz, 4H), 7.27 (t, $J = 7.3$ Hz, 2H), 7.22 (d, $J = 7.4$ Hz, 4H), 7.02 (d, $J = 9.2$ Hz, 2H), 6.66 (d, $J = 9.2$ Hz, 2H), 4.66 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) $\delta = 148.9$ (C_q), 140.6 (C_q), 137.7 (C_q), 129.0 (CH), 127.3 (CH), 126.5 (CH), 122.1 (CH), 118.9 (q, $^1J_{C\text{–}F} = 321.0$ Hz, C_q), 112.9 (CH), 54.7 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) $\delta = -72.85$. **IR** (KBr): 3055, 1509, 1418, 1249, 1211, 1141, 883, 818, 736, 697, 608 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 422 (100) [M+H]$^+$. **HR-MS** (ESI) m/z calcd for $C_{21}H_{18}F_3NO_3S$ [M+H]$^+$ 422.1032, found 422.1030.



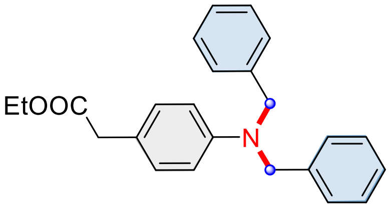
2-(4-(Dibenzylamino)phenyl)ethan-1-ol (3ka): The general procedure A was followed using **1k** (66.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ka** (63.5 mg, 50%) as pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.33 (t, J = 7.5 Hz, 4H), 7.27–7.24 (m, 6H), 7.02 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 4.64 (s, 4H), 3.80 (t, J = 6.5 Hz, 2H), 2.75 (t, J = 6.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 147.9 (C_q), 138.7 (C_q), 129.9 (CH), 128.7 (CH), 127.0 (CH), 126.7 (CH), 126.2 (C_q), 112.7 (CH), 64.0 (CH_2), 54.4 (CH_2), 38.2 (CH_2). **IR** (KBr): 3027, 2926, 1615, 1520, 1452, 1360, 1231, 1045, 809, 731, 697 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 318 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{23}NO$ [M+H]$^+$ 318.1852, found 318.1850. The data are in agreement with those reported in literature.[9]



2-(4-(Dibenzylamino)phenyl)acetonitrile (3la): The general procedure A was followed using **1l** (64.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3la** (56.6 mg, 45%) as pale yellow solid. **M.p.** = 75–76 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.35 (t, J = 7.4 Hz, 4H), 7.30–7.25 (m, 6H), 7.12 (d, J = 8.2 Hz, 2H), 6.74 (d, J = 8.2 Hz, 2H), 4.68 (s, 4H), 3.63 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.7 (C_q), 138.1 (C_q), 129.0 (CH), 128.9 (CH), 127.2 (CH), 126.7 (CH), 118.7 (C_q), 117.7 (C_q), 113.1 (CH), 54.6 (CH_2), 22.8 (CH_2). **IR** (KBr): 3026, 2921, 2246, 1615, 1523, 1449, 1237, 958, 802, 730, 695 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 318 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{23}NO$ [M+H]$^+$ 318.1852, found 318.1850. The data are in agreement with those reported in literature.[1]

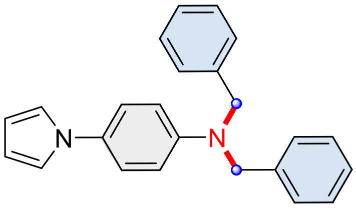


Methyl 2-(4-(dibenzylamino)phenyl)acetate (3ma): The general procedure A was followed using **1m** (78.0 mg, 0.40 mmol) and **2a** (143 μL, 1.20 mmol). Purification by column chromatography (PE/EA = 20:1) yielded **3ma** (58 mg, 42%) as brown solid. **M.p.** = 82–83 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.32 (t, J = 7.2 Hz, 4H), 7.26–7.24 (m, 6H), 7.07 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 4.64 (s, 4H), 3.67 (s, 3H), 3.50 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.8 (C_q), 148.3 (C_q), 138.6 (C_q), 130.1 (CH), 128.8 (CH), 127.0 (CH), 126.8 (CH), 122.0 (C_q), 112.7 (CH), 54.4 (CH_2), 52.0 (CH_3), 40.3 (CH_2). **IR** (KBr): 3014, 2924, 1732, 1615, 1523, 1400, 1230, 958, 813, 737, 696 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 346 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{23}NO_2$ [M+H]$^+$ 346.1802, found 346.1803. The data are in agreement with those reported in literature.[1]

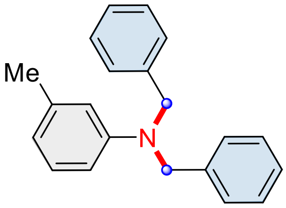


Ethyl 2-(4-(dibenzylamino)phenyl)acetate (3na): The general procedure A was followed using **1n** (83.6 mg, 0.40 mmol) and **2a** (143 μL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3na** (76.5 mg, 53%) as pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.32 (t, J = 6.7 Hz, 4H), 7.26–7.24 (m, 6H), 7.08 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 4.64 (s, 4H), 4.13 (q, J = 7.1 Hz, 2H), 3.48 (s, 2H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.4 (C_q), 148.3 (C_q), 138.7 (C_q), 130.1 (CH), 128.8

(CH), 127.0 (CH), 126.8 (CH), 122.2 (C_q), 112.7 (CH), 60.8 (CH_2), 54.4 (CH_2), 40.5 (CH_2), 14.3 (CH_3). **IR** (KBr): 2982, 1734, 1615, 1521, 1393, 1150, 1030, 957, 810, 733, 696 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 360 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{25}NO_2$ $[M+H]^+$ 360.1958, found 360.1958. The data are in agreement with those reported in literature.[10]

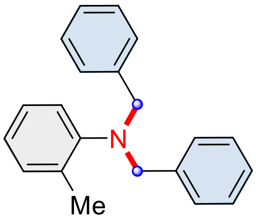


***N,N*-dibenzyl-4-(1*H*-pyrrol-1-yl)aniline (3oa):** The general procedure A was followed using **1o** (75.2 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 20:1) yielded **3oa** (56.8 mg, 42%) as brown solid. **M.p.** = 66–67 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.32 (t, J = 7.8 Hz, 4H), 7.26–7.24 (m, 6H), 7.14 (d, J = 9.3 Hz, 2H), 6.92 (t, J = 2.2 Hz, 2H), 6.74 (d, J = 9.3 Hz, 2H), 6.26 (t, J = 2.2 Hz, 2H), 4.65 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 147.5 (C_q), 138.4 (C_q), 131.5 (C_q), 128.8 (CH), 127.2 (CH), 126.7 (CH), 122.4 (CH), 119.8 (CH), 113.2 (CH), 109.4 (CH), 54.7 (CH_2). **IR** (KBr): 3026, 2918, 1617, 1522, 1390, 1243, 1075, 955, 812, 728, 694 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 339 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_2$ $[M+H]^+$ 339.1856, found 339.1856.

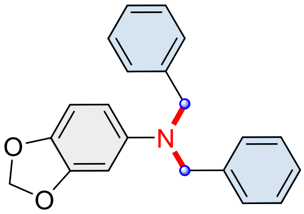


***N,N*-dibenzyl-3-methylaniline (3pa):** The general procedure A was followed using **1p** (54.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3pa** (70.7 mg, 62%) as white solid. **M.p.** = 71–72 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.33 (t, J = 7.5 Hz, 4H), 7.26–7.25 (m, 6H), 7.07 (t, J = 7.8 Hz, 1H), 6.60 (s, 1H), 6.56 (t, J = 8.6 Hz, 2H), 4.64 (s, 4H), 2.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.5

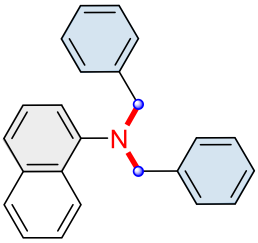
(C_q), 139.1 (C_q), 138.8 (C_q), 129.2 (CH), 128.7 (CH), 127.0 (CH), 126.8 (CH), 117.9 (CH), 113.1 (CH), 109.8 (CH), 54.1 (CH_2), 22.1 (CH_3). **IR** (KBr): 3020, 2857, 1603, 1493, 1381, 1253, 1072, 959, 838, 770, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 288 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{21}N$ $[M+H]^+$ 288.1747, found 288.1749. The data are in agreement with those reported in literature.[11]



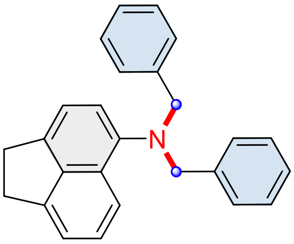
***N,N*-dibenzyl-2-methylaniline (3qa):** The general procedure A was followed using **1q** (121 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3qa** (48.3 mg, 42%) as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.27–7.25 (m, 8H), 7.22–7.16 (m, 3H), 7.05 (q, J = 6.4 Hz, 1H), 6.94 (dd, J = 9.7, 4.1 Hz, 2H), 4.06 (dd, J = 5.8, 2.6 Hz, 4H), 2.45–2.44 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 150.0 (C_q), 138.7 (C_q), 133.9 (C_q), 131.2 (CH), 128.8 (CH), 128.3 (CH), 127.0 (CH), 126.2 (CH), 123.6 (CH), 122.6 (CH), 57.0 (CH_2), 18.7 (CH_3). **IR** (KBr): 3061, 2923, 1597, 1493, 1361, 1212, 1005, 1029, 766, 722, 697 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 288 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{21}N$ $[M+H]^+$ 288.1747, found 288.1748. The data are in agreement with those reported in literature.[11]



***N,N*-dibenzylbenzo[*d*][1,3]dioxol-5-amine (3ra):** The general procedure A was followed using **1r** (66.8 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ra** (72.3 mg, 57%) as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.35 (t, J = 8.5 Hz, 4H), 7.28 (d, J = 7.2 Hz, 6H), 6.66 (d, J = 8.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 6.18 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.82 (s, 2H), 4.58 (s, 4H). **^{13}C NMR** (151 MHz, CDCl$_3$) *δ* = 148.5 (C$_q$), 145.4 (C$_q$), 139.3 (C$_q$), 138.8 (C$_q$), 128.7 (CH), 127.0 (CH), 126.9 (CH), 108.5 (CH), 105.2 (CH), 100.7 (CH$_2$), 96.3 (CH), 55.4 (CH$_2$). **IR** (KBr): 3060, 2924, 1608, 1503, 1343, 1275, 1037, 919, 870, 724, 686 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 318 (100) [M+H]$^+$.**HR-MS** (ESI) *m/z* calcd for $C_{21}H_{19}NO_2$ [M+H]$^+$ 318.1489, found 318.1488.

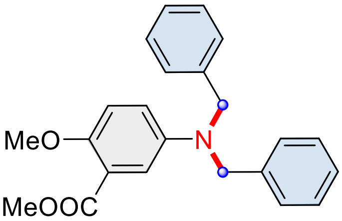


***N,N*-dibenzylnaphthalen-1-amine (3sa):** The general procedure A was followed using **1s** (69.2 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/EA = 50:1) yielded **3sa** (46.6 mg, 36%) as brown oil. **^{1}H NMR** (600 MHz, CDCl$_3$) *δ* = 8.52 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.28–7.26 (m, 4H), 7.26–7.17 (m, 7H), 6.91 (d, *J* = 7.4 Hz, 1H), 4.29 (s, 4H)**. ^{13}C NMR** (151 MHz, CDCl$_3$) *δ* = 147.6 (C$_q$), 138.3 (C$_q$), 135.1 (C$_q$), 129.8 (C$_q$), 128.7 (CH), 128.6 (CH), 128.3 (CH), 127.1 (CH), 125.9 (CH), 125.7 (CH), 125.6 (CH), 123.9 (CH), 123.7 (CH), 118.6 (CH), 57.3 (CH$_2$). **IR** (KBr): 3059, 2923, 1575, 1493, 1452, 1400, 1223, 1028, 774, 751, 698 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 324 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{21}N$ [M+H]$^+$ 324.1747, found 324.1747. The data are in agreement with those reported in literature.[12]

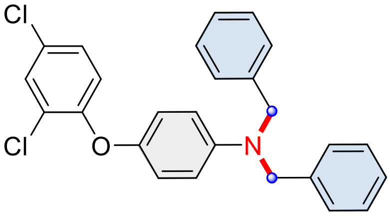


***N,N*-Dibenzyl-1,2-dihydroacenaphthylen-5-amine (3ta):** The general procedure A was followed using **1t** (80.5 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ta** (55.0 mg, 39%) as colorless oli. **^{1}H NMR** (600

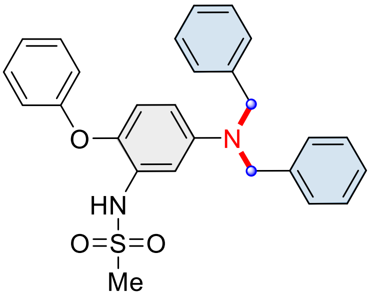
MHz, $CDCl_3$) δ = 8.10 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 6.7 Hz, 1H), 7.39 (d, J = 8.1 Hz, 4H), 7.36–7.30 (m, 5H), 7.29–7.24 (m, 2H), 7.12 (d, J = 8.7 Hz, 1H), 6.92 (d, J = 5.6 Hz, 1H), 3.47–3.42 (m, 2H), 3.37–3.32 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 146.6 (C_q), 143.9 (C_q), 140.8(C_q), 140.7 (C_q), 138.7 (C_q), 128.5 (CH), 128.3 (CH), 128.0 (C_q), 127.3 (CH), 127.0 (CH), 119.4 (CH), 119.3 (CH), 119.2 (CH), 118.9 (CH), 57.1 (CH_2), 31.0 (CH_2), 29.78 (CH_2). **IR** (KBr): 3026, 2921, 1735, 1590, 1430, 1216, 1173, 1028, 958, 832, 697 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 350 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{26}H_{23}N$ $[M+H]^+$ 350.1903, found 349.1883.



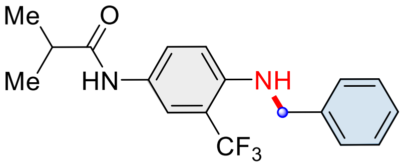
5-(Dibenzylamino)-2-methoxyphenyl acetate (3ua): The general procedure A was followed using **1u** (84.5 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/EA = 20:1) yielded **3ua** (93.3 mg, 65%) as yellow oli. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30–7.26 (m, 3H), 7.26–7.19 (m, 8H), 6.82–6.75 (m, 2H), 4.53 (s, 4H), 3.79 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.1 (C_q), 151.2 (C_q), 143.2 (C_q), 138.4 (C_q), 138.4 (C_q), 128.6 (CH), 127.0 (CH), 120.7 (CH), 118.5 (CH), 116.2 (CH), 114.1 (CH), 56.8 (CH_3), 54.9 (CH_2), 29.7 (CH_3). **IR** (KBr): 2924, 1730, 1506, 1435, 1245, 1082, 1026, 807, 742, 697 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 362 (100) $[M+H]^+$, 384 (21) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{23}NO_3$ $[M+H]^+$ 362.1751, found 362.1751. The data are in agreement with those reported in literature.[13]



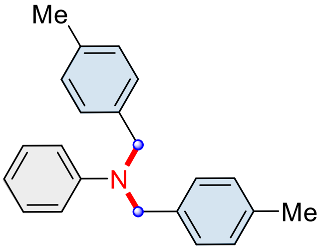
***N,N*-dibenzyl-4-(2,4-dichlorophenoxy) aniline (3va):** The general procedure A was followed using **1v** (114 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3va** (128 mg, 74%) as white solid. **M.p.** = 64–65 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, J = 2.5 Hz, 1H), 7.34 (t, J = 7.6 Hz, 4H), 7.28–7.26 (m, 6H), 7.09 (dd, J = 8.8, 2.5 Hz, 1H), 6.83 (d, J = 9.0 Hz, 2H), 6.76 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 5.4 Hz, 2H), 4.64 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 153.4 (C_q), 146.9 (C_q), 146.5 (C_q), 138.5 (C_q), 130.3 (CH), 128.8 (CH), 127.8 (CH), 127.6 (C_q), 127.2 (CH), 126.9 (CH), 125.0 (C_q), 120.5 (CH), 119.1 (CH), 113.9 (CH), 55.0 (CH_2). **IR** (KBr): 2922, 1603, 1511, 1470, 1231, 1053, 954, 812, 728, 696 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 434 (100) $[M+H]^+$, 472 (3) $[M+K]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{26}H_{21}Cl_2NO$ $[M+H]^+$ 434.1070, found 434.1073.



***N*-(4-(dibenzylamino)-2-phenoxyphenyl) methanesulfonamide (3wa):** The general procedure A was followed using **3w** (123 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/EA = 10:1) yielded **3wa** (97.9 mg, 53%) as white solid. **M.p.** = 100–101 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.35 (d, J = 9.0 Hz, 1H), 7.30 (t, J = 7.4 Hz, 4H), 7.25 (t, J = 7.1 Hz, 2H), 7.22 (t, J = 7.9 Hz, 2H), 7.16 (d, J = 6.9 Hz, 4H), 7.07 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.9 Hz, 2H), 6.53 (dd, J = 9.0, 2.8 Hz, 1H), 6.22 (s, 1H), 6.21 (d, J = 2.8 Hz, 1H), 4.56 (s, 4H), 2.88 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 155.9 (C_q), 150.2 (C_q), 148.6 (C_q), 137.8 (C_q), 130.1 (CH), 128.9 (CH), 127.5 (CH), 127.3 (CH), 126.8 (CH), 123.9 (CH), 118.2 (CH), 116.5 (C_q), 108.7 (CH), 103.2 (CH), 55.1 (CH_2), 39.2 (CH_3). **IR** (KBr): 3061, 1615, 1515, 1489, 1393, 1155, 961, 749, 702, 691 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 459 (100) $[M+H]^+$, 481 (38) $[M+Na]^+$, 497 (1) $[M+K]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{26}N_2O_3S$ $[M+H]^+$ 459.1737, found 459.1739.

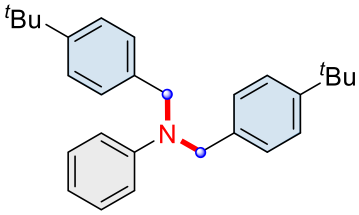


***N*-(4-(benzylamino)-3-(trifluoromethyl)phenyl)isobutyramide (3xa):** The general procedure A was followed using **1x** (111 mg, 0.40 mmol) and **2a** (143 µL, 1.20 mmol). Purification by column chromatography (PE/EA = 10:1) yielded **3xa** (74.3 mg, 44%) as white solid. **M.p.** = 126–127 °C. **^{1}H NMR** (600 MHz, d_6-DMSO) δ = 9.66 (s, 1H), 7.82 (d, J = 2.5 Hz, 1H), 7.40 (dd, J = 8.9, 2.5 Hz, 1H), 7.33–7.29 (m, 4H), 7.20 (m, 1H), 6.58 (d, J = 9.0 Hz, 1H), 6.07 (t, J = 6.1 Hz, 1H), 4.42 (d, J = 6.0 Hz, 2H), 3.37 (s, 1H), 1.06 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (151 MHz, d_6-DMSO) δ = 174.7 (C_q), 141.2 (C_q), 139.8 (C_q), 128.4 (CH), 128.2 (C_q), 126.7 (CH), 126.7 (CH), 125.4 (q, $^1J_{C-F}$ = 271.8 Hz, C_q), 124.9 (CH), 117.60 (q, $^3J_{C-F}$ = 6.0 Hz, CH), 112.8 (CH), 111.2 (q, $^2J_{C-F}$ = 28.7 Hz, C_q), 45.9 (CH_2), 34.8 (CH), 19.5 (CH_3). **^{19}F NMR** (565 MHz, d_6-DMSO) δ = -61.38. **IR** (KBr): 3267, 2970, 1658, 1549, 1426, 1337, 1251, 1107, 1048, 701 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 337 (100) [M+H]$^+$, 359 (90) [M+Na]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{19}F_3N_2O$ [M+H]$^+$ 337.1522, found 337.1526.

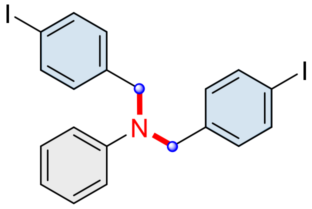


***N,N*-bis(4-methylbenzyl)aniline (3ab):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2b** (222 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **5a** (68.3 mg, 56%) as white solid. **M.p.** = 92–93 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.20–7.16 (m, 3H), 7.16–7.14 (m, 7H), 6.76 (d, J = 8.1 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 4.62 (s, 4H), 2.35 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.4 (C_q), 136.6 (C_q), 135.7 (C_q), 129.4 (CH), 129.3 (CH), 126.8 (CH), 116.7 (CH), 112.6 (CH), 54.0 (CH_2), 21.2 (CH_3). **IR** (KBr): 3017, 2921, 1597, 1506, 1430, 1387, 1237, 1174, 792, 745, 688 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 302 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{23}N$ [M+H]$^+$

302.1903, found 302.1903. The data are in agreement with those reported in literature.[2]

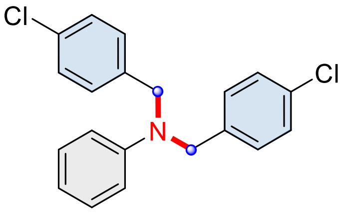


***N,N*-bis(4-(*tert*-butyl)benzyl)aniline (3ac):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2c** (272 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ac** (55.4 mg, 36%) as white solid. **M.p.** = 105–106 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.27 (d, J = 7.8 Hz, 4H), 7.13–7.07 (m, 6H), 6.68 (d, J = 8.1 Hz, 2H), 6.61 (t, J = 7.3 Hz, 1H), 4.55 (s, 4H), 1.25 (s, 18H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.8 (C_q), 149.5 (C_q), 135.7 (C_q), 129.3 (CH), 126.5 (CH), 125.6 (CH), 116.6 (CH), 112.5 (CH), 53.9 (CH_2), 34.6 (C_q), 31.6 (CH_3). **IR** (KBr): 3022, 2956, 1599, 1505, 1412, 1268, 1016, 937, 819, 748, 690 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 386 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{28}H_{35}N$ $[M+H]^+$ 386.2842, found 386.2842. The data are in agreement with those reported in literature.[14]

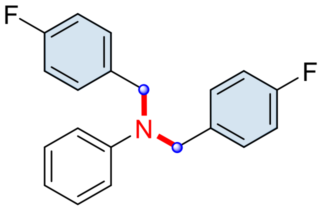


***N,N*-bis(4-iodobenzyl)aniline (3ad):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2d** (356 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ad** (140.8 mg, 67%) as white solid. **M.p.** = 98–99 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.64 (d, J = 8.1 Hz, 4H), 7.19 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 8.1 Hz, 4H), 6.75 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 8.2 Hz, 2H), 4.55 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.7 (C_q), 138.2 (C_q), 137.8 (CH), 129.5 (CH), 128.8 (CH), 117.7 (CH), 112.9 (CH), 92.3 (C_q), 54.1 (CH_2). **IR** (KBr): 3036, 2923, 1597, 1504, 1390, 1234, 1006, 960, 800, 744, 689 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 525 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for

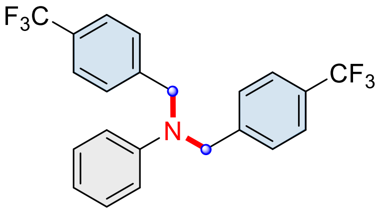
$C_{20}H_{17}I_2N$ [M+H]$^+$ 525.9523, found 525.9537. The data are in agreement with those reported in literature.[15]



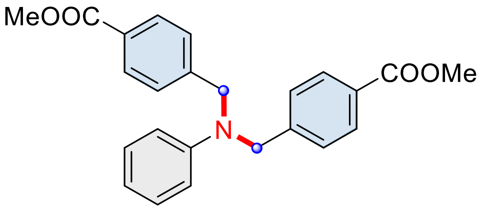
***N,N*-bis(4-chlorobenzyl)aniline (3ae):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2e** (246 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ae** (89.7 mg, 66%) as white solid. **M.p.** = 120–121 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.29 (d, J = 8.2 Hz, 4H), 7.19–7.15 (m, 6H), 6.74 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 8.2 Hz, 2H), 4.57 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.8 (C_q), 137.0 (C_q), 132.8 (C_q), 129.5 (CH), 129.0 (CH), 128.1 (CH), 117.5 (CH), 112.9 (CH), 53.9 (CH_2). **IR** (KBr): 2924, 1597, 1505, 1487, 1384, 1237, 1090, 1014, 812, 746, 687 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}{}^{35}Cl_2N$ [M+H]$^+$ 342.0811, found 342.0814. The data are in agreement with those reported in literature.[1]



***N,N*-bis(4-fluorobenzyl)aniline (3af):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2f** (226 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3af** (71.7 mg, 58%) as brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.22–7.19 (m, 6H), 7.05–6.98 (m, 4H), 6.75 (t, J = 8.7 Hz, 3H), 4.59 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 162.0 (d, $^1J_{C–F}$ = 244.6 Hz , C_q), 149.0 (C_q), 134.1 (C_q), 129.4 (CH), 128.4 (d, $^3J_{C–F}$ = 8.2 Hz, CH), 117.4 (CH), 115.6 (d, $^2J_{C–F}$ = 21.3 Hz , CH), 112.9 (CH), 53.7 (CH_2). **^{19}F NMR** (565 MHz, DMSO-d_6) δ = -116.39. **IR** (KBr): 3039, 2922, 1599, 1507, 1354, 1222, 1154, 1094, 822, 748, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 310 (100) [M+H]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}F_2N$ $[M+H]^+$ 310.1402, found 310.1407. The data are in agreement with those reported in literature.[2]

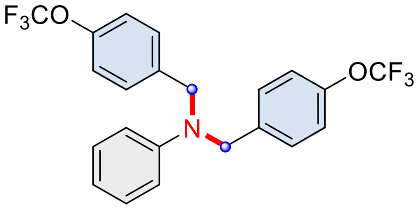


***N,N*-bis(4-(trifluoromethyl)benzyl)aniline (3ag):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2g** (286 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ag** (108 mg, 66%) as white solid. **M.p.** = 74–75 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.60 (d, J = 8.1 Hz, 4H), 7.38 (d, J = 8.1 Hz, 4H), 7.21 (t, J = 7.8 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 8.2 Hz, 2H), 4.71 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.6 (C_q), 142.7 (C_q), 129.7 (q, $^2J_{C-F}$ = 33.2 Hz, C_q), 129.6 (CH), 127.1 (CH), 125.8 (q, $^3J_{C-F}$ = 3.7 Hz, CH), 124.3 (q, $^1J_{C-F}$ = 271.8 Hz, C_q), 118.0 (CH), 112.9 (CH), 54.4 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -62.44. **IR** (KBr): 2924, 1601, 1507, 1418, 1325, 1131, 1065, 1016, 825, 747, 690 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 410 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}F_6N$ $[M+H]^+$ 410.1338, found 410.1339. The data are in agreement with those reported in literature.[15]

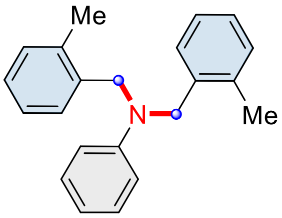


Dimethyl 4,4'-((phenylazanediyl)bis(methylene))dibenzoate (3ah): The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2h** (275 mg, 1.20 mmol). Purification by column chromatography (PE/EA = 20:1) yielded **3ah** (79.4 mg, 58%) as white solid. **M.p.** = 96–97 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.00 (d, J = 8.1 Hz, 4H), 7.32 (d, J = 8.1 Hz, 4H), 7.18 (t, J = 8.2 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 8.1 Hz, 2H), 4.69 (s, 4H), 3.91 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 167.0 (C_q), 148.6 (C_q), 144.0 (C_q), 130.2 (CH), 129.5

(CH), 129.2 (C_q), 126.8 (CH), 117.7 (CH), 112.9 (CH), 54.6 (CH_2), 52.2 (CH_3). **IR** (KBr): 2949, 2923, 1708, 1598, 1506, 1430, 1283, 1105, 885, 753, 694 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 390 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{23}NO_4$ $[M+H]^+$ 390.1700, found 390.1699. The data are in agreement with those reported in literature.[16]

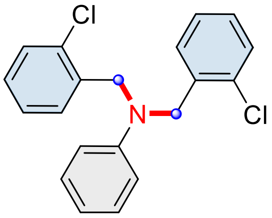


***N,N*-bis(4-(trifluoromethoxy)benzyl)aniline (3ai):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2i** (306 mg, 1.20 mmol). Purification by column chromatography (PE/EA = 50:1) yielded **3ai** (128 mg, 73%) as colorless liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.28 (d, J = 8.2 Hz, 4H), 7.23–7.20 (m, 2H), 7.19 (d, J = 8.2 Hz, 4H), 6.77 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 8.2 Hz, 2H), 4.64 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.8 (C_q), 148.3 (C_q), 137.2 (C_q), 129.6 (CH), 128.1 (CH), 120.6 (q, $^1J_{C-F}$ = 256.7 Hz, C_q), 121.4 (CH), 117.6 (CH), 112.8 (CH), 53.81 (CH_2). **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -57.89. **IR** (KBr): 3444, 2920, 2849, 1643, 1507, 1384, 1265, 1018, 746, 706 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 442 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}F_6NO_2$ $[M+H]^+$ 442.1236, found 442.1238.

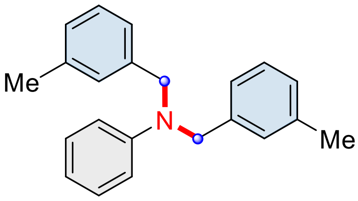


***N,N*-bis(2-methylbenzyl)aniline (3aj):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2j** (222 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3aj** (60.0 mg, 50%) as white solid. **M.p.** = 141–142 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.34–7.30 (m, 6H), 7.30–7.27 (m, 4H), 6.81 (t, J = 7.2 Hz, 1H), 6.73 (d, J = 8.1 Hz, 2H), 4.70 (s, 4H), 2.39 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.1 (C_q), 135.7

(C_q), 135.1 (C_q), 130.5 (CH), 129.3 (CH), 126.9 (CH), 126.3 (CH), 125.9 (CH), 116.6 (CH), 112.2 (CH), 52.5 (CH_2), 19.0 (CH_3). **IR** (KBr): 3025, 2923, 1597, 1507, 1352, 1265, 1049, 989, 859, 743, 690 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 302 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{23}N$ $[M+H]^+$ 302.1903, found 302.1902. The data are in agreement with those reported in literature.[15]

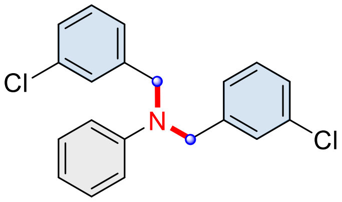


***N,N*-bis(2-chlorobenzyl)aniline (3ak):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2k** (246 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ak** (86.3 mg, 63%) as white solid. **M.p.** = 128–129 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.46–7.43 (m, 2H), 7.31–7.26 (m, 6H), 7.22 (t, J = 8.5 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 8.4 Hz, 2H), 4.76 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.3 (C_q), 135.2 (C_q), 133.1 (C_q), 129.8 (CH), 129.5 (CH), 128.4 (CH), 127.8 (CH), 127.2 (CH), 117.3 (CH), 112.2 (CH), 52.9 (CH_2). **IR** (KBr): 2926, 1598, 1505, 1441, 1356, 1235, 1047, 960, 755, 743, 699 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}{}^{35}Cl_2N$ $[M+H]^+$ 342.0811, found 342.0812. The data are in agreement with those reported in literature.[2]

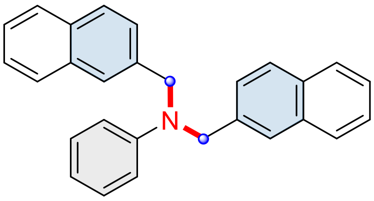


***N,N*-bis(3-methylbenzyl)aniline (3al):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2l** (222 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3al** (66.5 mg, 55%) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.26–7.20 (m, 4H), 7.13–7.08 (m, 6H), 6.83 (d, J = 8.2 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 4.66 (s, 4H), 2.38 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.6 (C_q), 138.9 (C_q), 138.4 (C_q), 129.3

(CH), 128.6 (CH), 127.8 (CH), 127.6 (CH), 124.1 (CH), 116.9 (CH), 112.9 (CH), 54.5 (CH_2), 21.6 (CH_3). **IR** (KBr): 3024, 2918, 1598, 1506, 1349, 1227, 1091, 989, 776, 747, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 302 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{23}N$ $[M+H]^+$ 302.1903, found 302.1906. The data are in agreement with those reported in literature.[15]

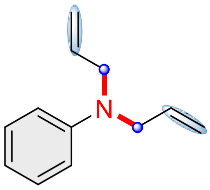


***N,N*-bis(3-chlorobenzyl)aniline (3am):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2m** (246 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3am** (83.2 mg, 61%) as colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.25–7.21 (m, 6H), 7.19 (t, J = 8.1 Hz, 2H), 7.12 (d, J = 6.7 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 7.8 Hz, 2H), 4.60 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.6 (C_q), 140.8 (C_q), 134.8 (C_q), 130.1 (CH), 129.5 (CH), 127.4 (CH), 126.8 (CH), 124.9 (CH), 117.6 (CH), 112.7 (CH), 54.0 (CH_2). **IR** (KBr): 3060, 2924, 1596, 1505, 1348, 1198, 1076, 958, 779, 748, 682 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}{}^{35}Cl_2N$ $[M+H]^+$ 342.0811, found 342.0811.

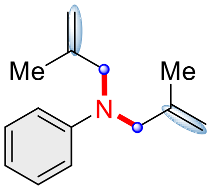


***N,N*-bis(naphthalen-2-ylmethyl)aniline (3an):** The general procedure A was followed using **1a** (41 µL, 0.40 mmol) and **2n** (265 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3an** (82.4 mg, 55%) as white solid. **M.p.** = 154–155 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.85–7.81 (m, 4H), 7.78 (d, J = 7.6 Hz, 2H), 7.72 (s, 2H), 7.49–7.44 (m, 4H), 7.41 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.7 Hz, 2H), 6.87 (d, J = 8.1 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 4.88 (s, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.4 (C_q), 136.2 (C_q), 133.7 (C_q), 132.8 (C_q), 129.5 (CH), 128.6 (CH), 127.9 (CH), 127.8 (CH), 126.3 (CH), 125.8 (CH), 125.3

(CH), 125.2 (CH), 117.1 (CH), 112.9 (CH), 54.6 (CH_2). **IR** (KBr): 3043, 2923, 1599, 1505, 1372, 1189, 963, 875, 807, 748, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 374 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{28}H_{23}N$ $[M+H]^+$ 374.1903, found 374.1909.

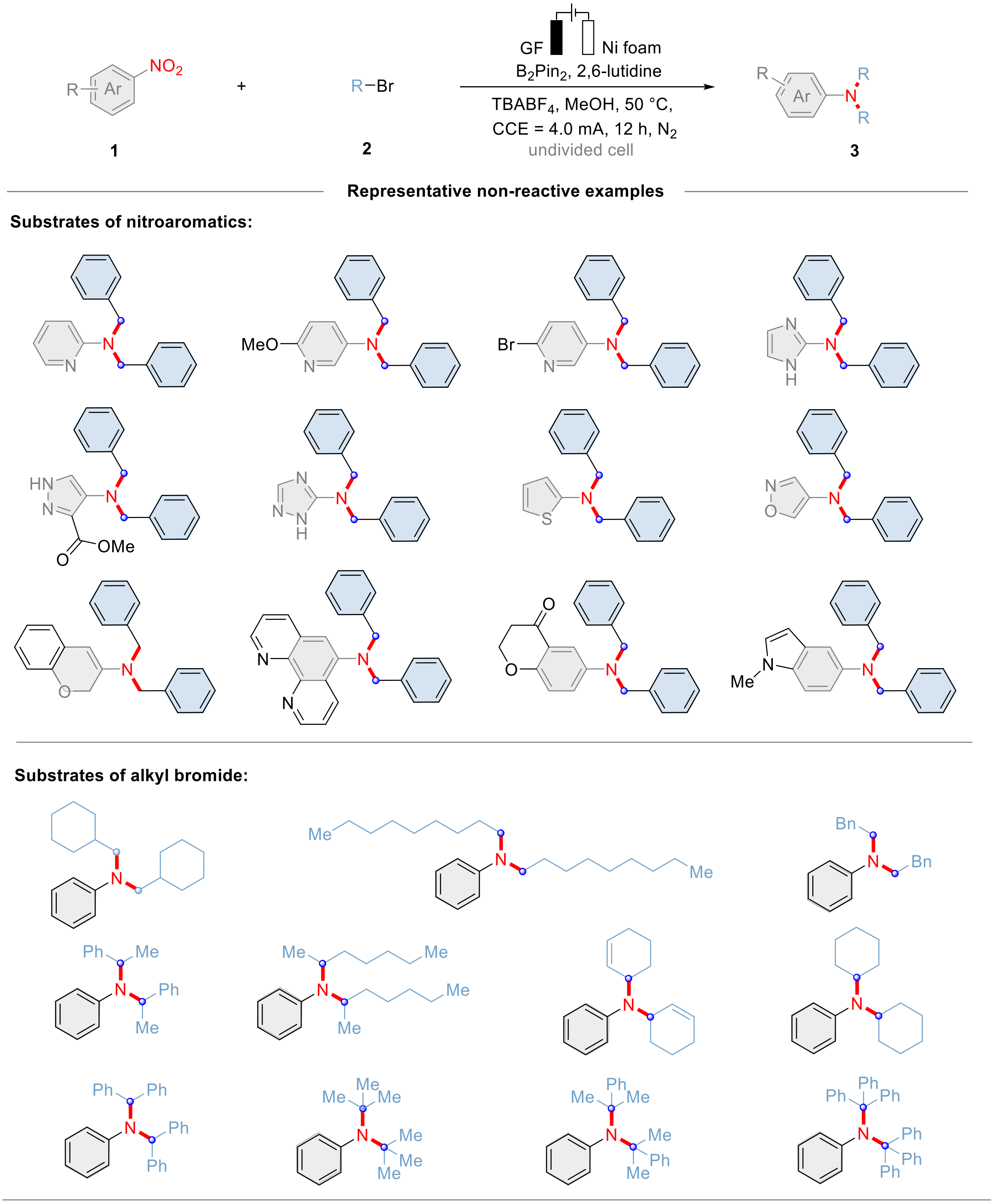


***N,N*-diallylaniline (3ao):** The general procedure A was followed using **1a** (41 μL, 0.40 mmol) and **2o** (145 mg, 1.20 mmol). Purification by column chromatography (PE/DCM = 50:1) yielded **3ao** (24.5 mg, 35%) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.24 (t, J = 7.9 Hz, 2H), 6.76–6.71 (m, 3H), 5.93–5.87 (m, 2H), 5.24–5.19 (m, 4H), 3.97 (d, J = 4.9 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.8 (C_q), 134.2 (CH), 129.2 (CH), 116.4 (CH), 116.1 (CH_2), 112.5 (CH), 52.9 (CH_2). **IR** (KBr): 3061, 2924, 1599, 1505, 1388, 1233, 1182, 989, 919, 747, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 174 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{12}H_{15}N$ $[M+H]^+$ 174.1277, found 174.1272. The data are in agreement with those reported in literature.[3]



***N,N*-bis(2-methylallyl)aniline (3ap):** The general procedure A was followed using **1a** (41 μL, 0.40 mmol) and **2p** (162 mg, 1.20 mmol). Purification by column chromatography (PE/EA = 50:1) yielded **3ap** (34.3 mg, 43%) as colorless oli. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.18 (t, J = 8.3 Hz, 2H), 6.66 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 8.2 Hz, 2H), 4.85 (s, 2H), 4.79 (s, 2H), 3.81 (s, 4H), 1.74 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 149.0 (C_q), 140.7 (C_q), 129.0 (CH), 116.1 (CH), 112.0 (CH), 110.3 (CH_2), 56.4 (CH_2), 20.2 (CH_3). **IR** (KBr): 2924, 1599, 1505, 1389, 1229, 1186, 894, 746, 690, 512 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 202 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{14}H_{19}N$ $[M+H]^+$ 202.1590, found 202.1586. The data are in agreement with those reported in literature.[17]

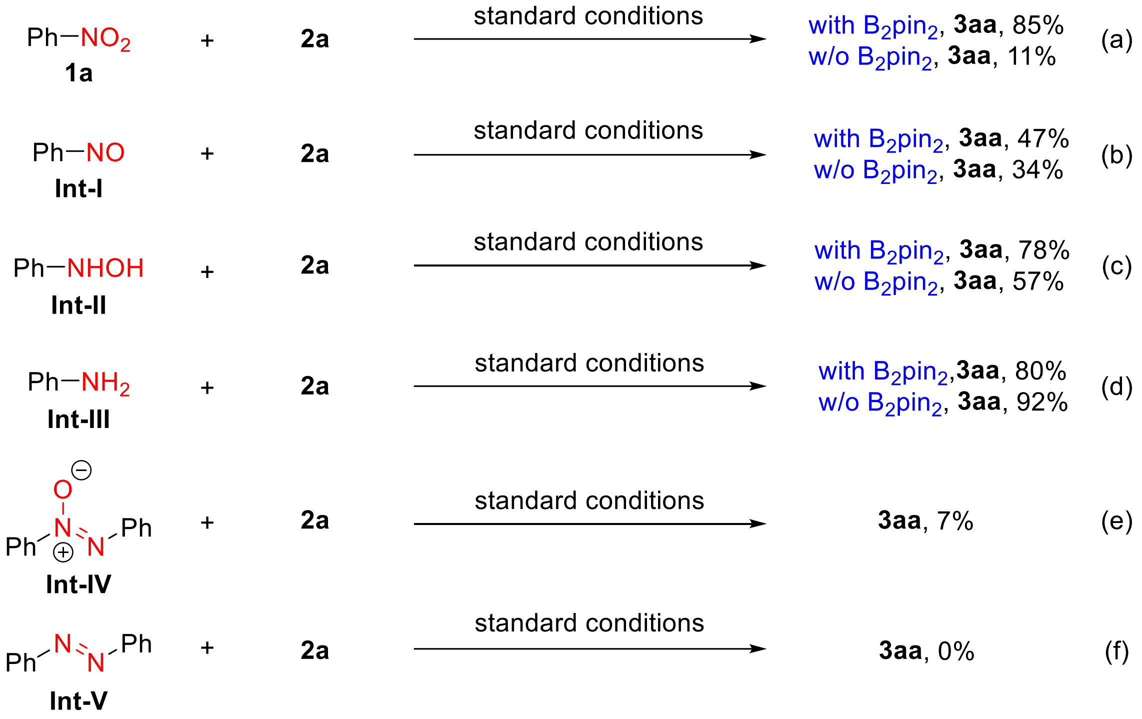
Unsuccessful Substrates:



Scheme S9. Unsuccessful substrates.

5. Mechanistic Studies

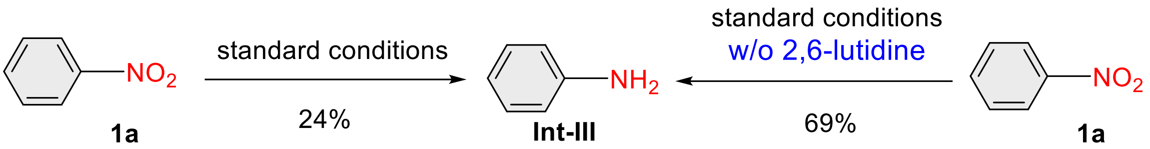
5.1 Control Experiments



Scheme S10. Control experiments for potential intermediate.

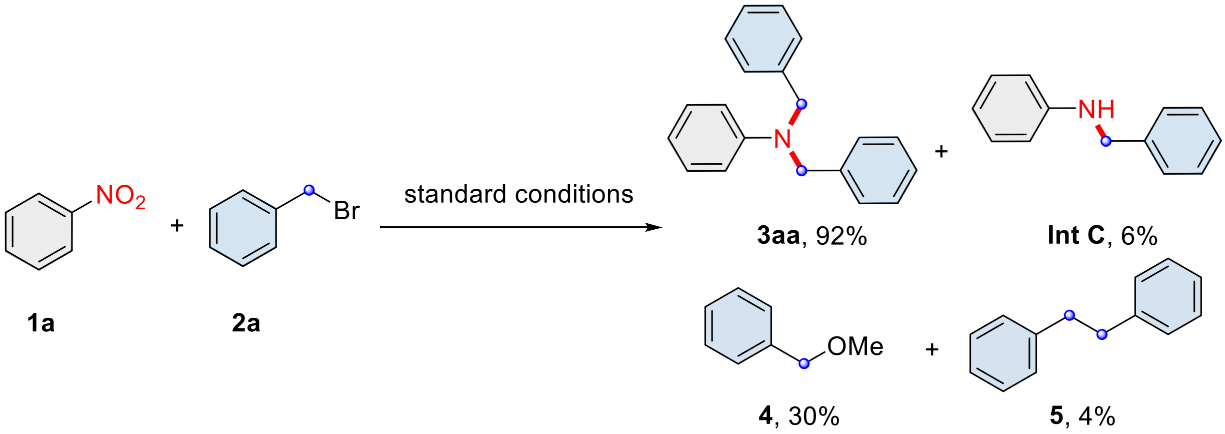
The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with potential intermediate (0.4 mmol), benzyl bromide **2a** (143 µL, 1.20 mmol), TBABF$_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 µL, 1.20 mmol), B$_2$Pin$_2$ (203 mg, 0.80 mmol, if used) and MeOH (4.0 mL), the reaction cells were performed at 50 °C with a constant current of 4.0 mA maintained for 12 h. The electrodes were washed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. The residue was purified by chromatography on silica gel (PE/DCM) to afford the corresponding products **3aa**.

5.2 Investigation on the Role of 2,6-Lutidine



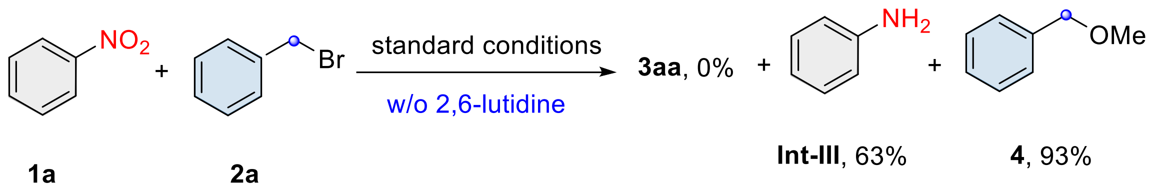
Scheme S11. Investigation on the role of 2,6-lutidine.

The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (41 µL, 0.40 mmol), $TBABF_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 µL, 1.20 mmol, if used), B_2Pin_2 (203 mg, 0.80 mmol) and MeOH (4.0 mL). Electrocatalysis was performed at 50 °C with a constant current of 4.0 mA maintained for 12 h. The yields of aniline **Int-III** were determined by GC-MS analysis using 1,3,5-trimethoxybenzene as the internal standard.



Scheme S12. GC-MS monitors compounds in the reaction system.

The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (41µL, 0.4 mmol), benzyl bromide **2a** (143 µL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 µL, 1.20 mmol), B_2Pin_2 (203 mg, 0.80 mmol) and MeOH (4.0 mL), the reaction cells were performed at 50 °C with a constant current of 4.0 mA maintained for 12 h. The yields of corresponding products were determined by GC-MS analysis using 1,3,5-trimethoxybenzene as the internal standard.



Scheme S13. Investigation of the products without 2,6-lutidine.

The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (41μL, 0.4 mmol), benzyl bromide **2a** (143 μL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), B_2Pin_2 (203 mg, 0.80 mmol) and MeOH (4.0 mL), the reaction cells were performed at 50 °C with a constant current of 4.0 mA maintained for 12 h. The yields of corresponding products were determined by GC-MS analysis using 1,3,5-trimethoxybenzene as the internal standard.

5.3 Cyclic Voltammetry Experiments

The cyclic voltammetry measurements were conducted with a Lanlike LK98BII electrochemical workstation and following analysis was performed with LK98BII software. A glassy-carbon (GC) electrode (3.0 mm-diameter, disc-electrode) was used as the working electrode, polished with 0.3 and 0.05 μm aluminum oxide, and then washed with distilled water and acetone before air drying. A platinum plate (1.0 cm × 1.0 cm × 0.1 cm) was used as the auxiliary electrode and an Ag/AgCl electrode was used as the reference. The voltammograms were recorded at room temperature under N_2 atmosphere. The solution was degassed by nitrogen gas bubbling for 5 mins before each measurement. The scan rate was 100 mVs^{-1}. Details of measurements are indicated in the respective figures and descriptions.

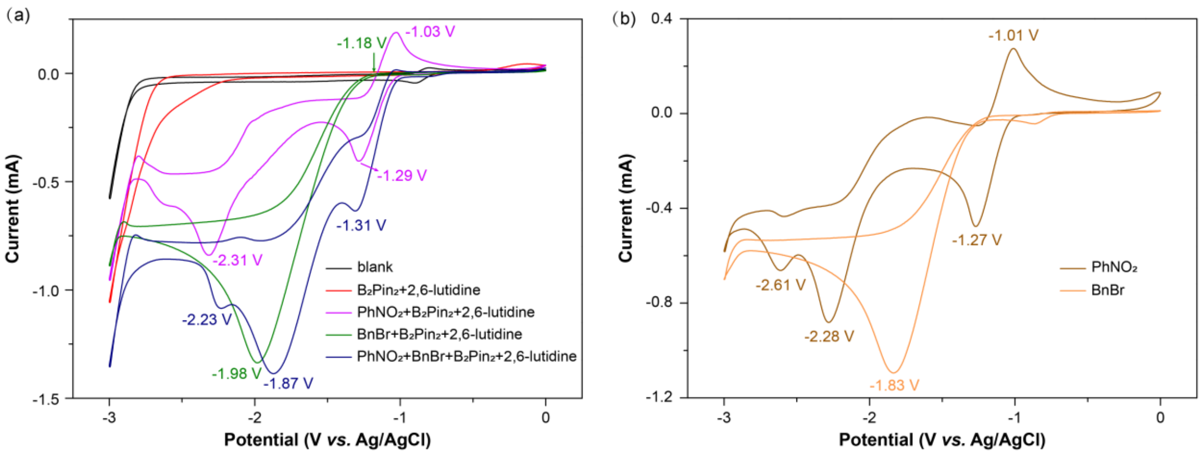


Figure S6. Cyclic voltammograms at 100 mVs^{-1} using MeCN (4.0 mL) as solvent and TBABF$_4$ (0.10 M) as the electrolyte; blank (black), B$_2$Pin$_2$ (40 mM) + 2,6-lutidine (60 mM) (red line), PhNO$_2$ (20 mM) + B$_2$Pin$_2$ (40 mM) + 2,6-lutidine (60 mM) (purple line), BnBr (60 mM) + B$_2$Pin$_2$ (40 mM) + 2,6-lutidine (60 mM) (green line), PhNO$_2$ (20 mM) + BnBr (60 mM) + B$_2$Pin$_2$ (40 mM) + 2,6-lutidine (60 mM) (blue line), PhNO$_2$ (20 mM) (brown line), BnBr (60 mM) (orange line). The scan rate is 100 mVs^{-1}, ranging from 0.0 V to -3.0 V. Initial scan direction: negative.

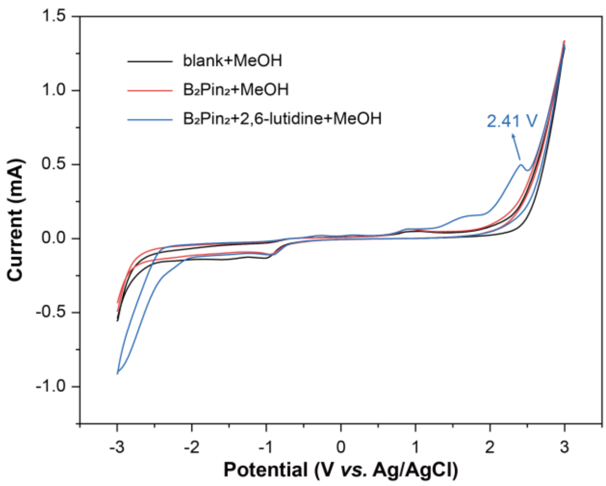


Figure S7. Cyclic voltammograms at 100 mVs^{-1} using MeCN (4.0 mL) as solvent and TBABF$_4$ (0.10 M) as the electrolyte; blank + MeOH (0.8 mL) (black), B$_2$Pin$_2$ (40 mM) + MeOH (0.8 mL) (red), B$_2$Pin$_2$ (40 mM) + 2,6-lutidine (60 mM) + MeOH (0.8 mL) (blue line). The scan rate is 100 mVs^{-1}, with scanning direction from -3.0 V to 3.0 V.

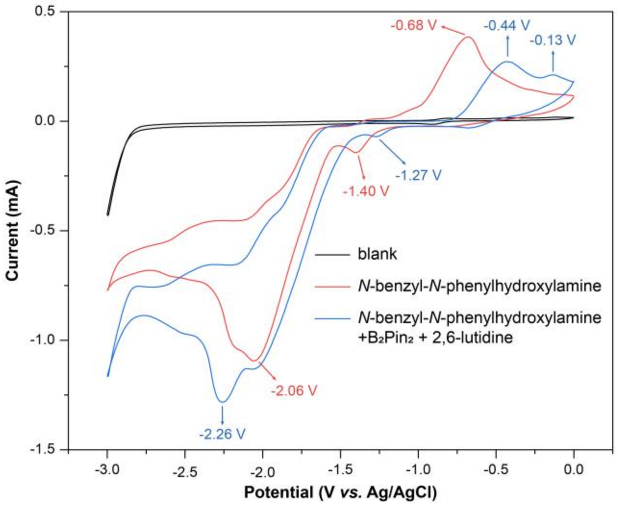
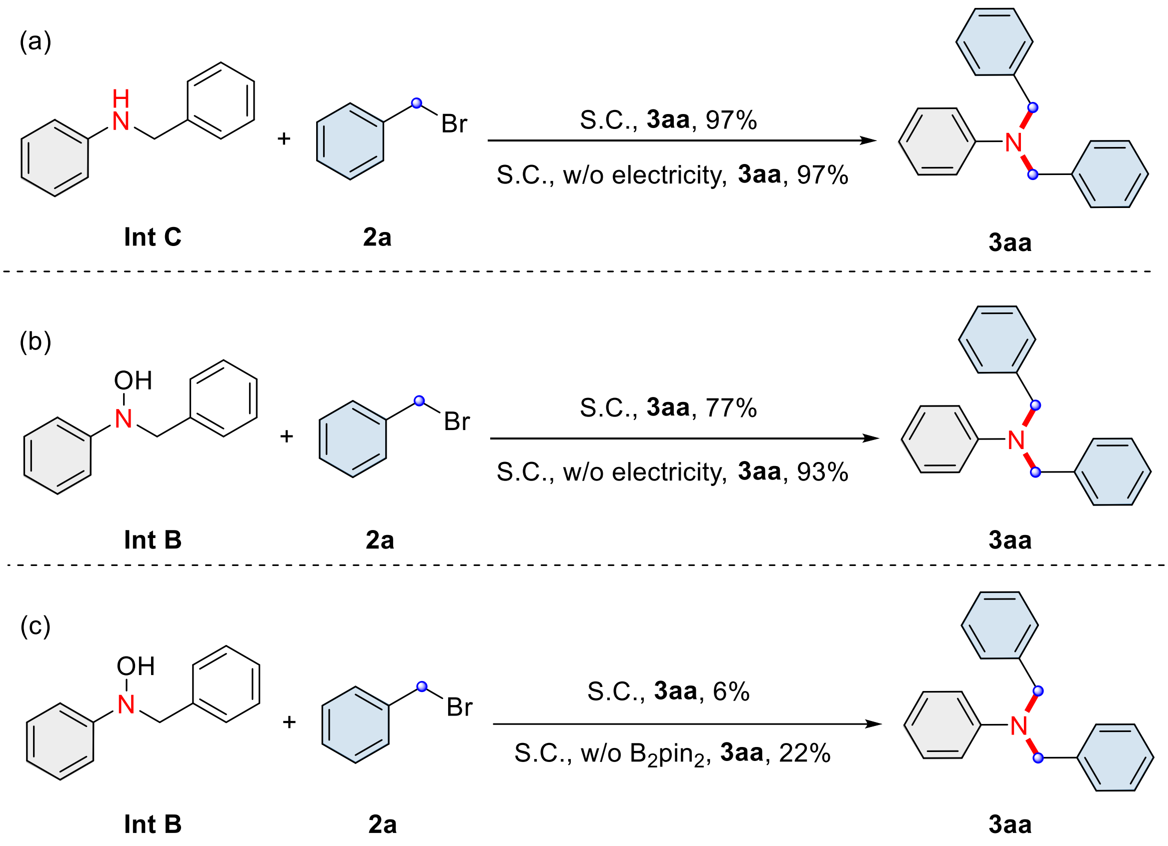


Figure S8. Cyclic voltammograms at 100 mVs^{-1} using MeCN (4.0 mL) as solvent and TBABF$_4$ (0.10 M) as the electrolyte; blank (black), *N*-benzyl-*N*-phenylhydroxylamine (20 mM) (red line), *N*-benzyl-*N*-phenylhydroxylamine (20 mM) + B$_2$Pin$_2$ (40 mM) + 2,6-lutidine (60 mM) (blue line).

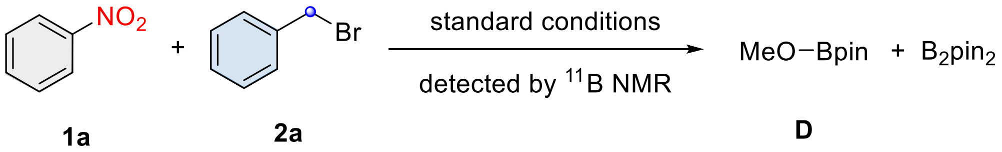
5.4 Control Experiments



Scheme S14. Studies on *N*-benzylaniline and *N*-benzylhydroxylamine as substrates.

The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with potential intermediate (0.4 mmol), benzyl bromide **2a** (143 μL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 μL, 1.20 mmol), B_2Pin_2 (203 mg, 0.80 mmol, if used) and MeOH (4.0 mL), the reaction cells were performed at 50 °C with a constant current of 4.0 mA maintained for 12 h, or without electricity for control experiments. The electrodes were washed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. The residue was purified by chromatography on silica gel (PE/DCM) to afford the corresponding products **3aa**.

5.5 ^{11}B NMR Analysis on the Reaction Components



Scheme S15. ^{11}B NMR analysis on the reaction components.

The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (41μL, 0.4 mmol), benzyl bromide **2a** (143 μL, 1.20 mmol), $TBABF_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 μL, 1.20 mmol), B_2Pin_2 (203 mg, 0.80 mmol) and MeOH (4.0 mL), the reaction cells were performed at 50 °C with a constant current of 4.0 mA maintained for 12 h. When the electrolysis was done, the resultant reaction mixture was cooled to room temperature. Transfer the reaction to a nitrogen-filled glovebox to open the reaction. A 200 μL aliquot of the solution was diluted with 400 μL $CDCl_3$. Then 600 μL of the resultant solution was added to an NMR sample tube, and the sample was analyzed by ^{11}B NMR spectroscopy[18-19].

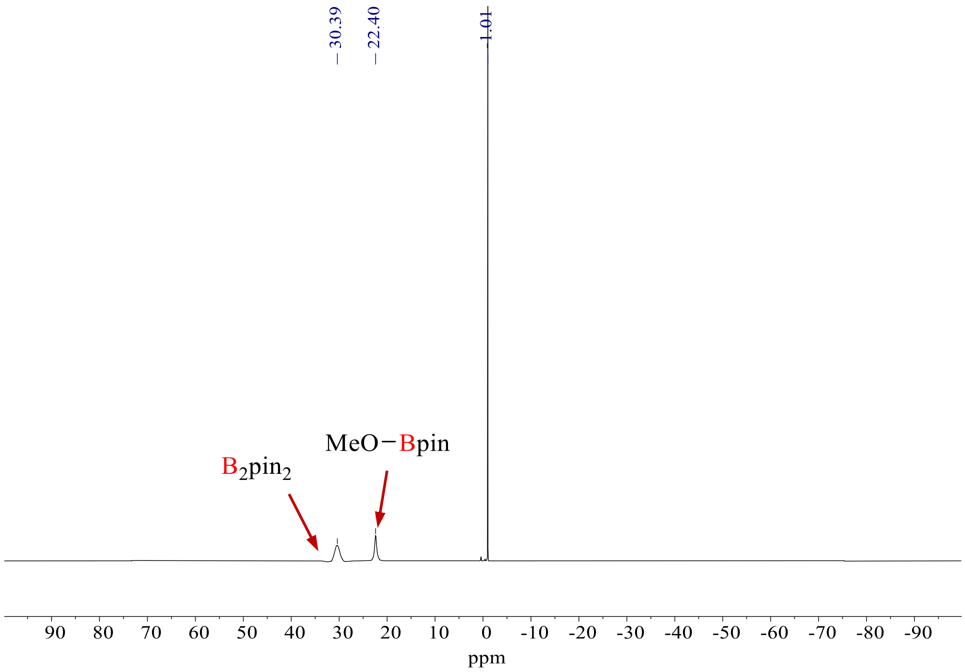
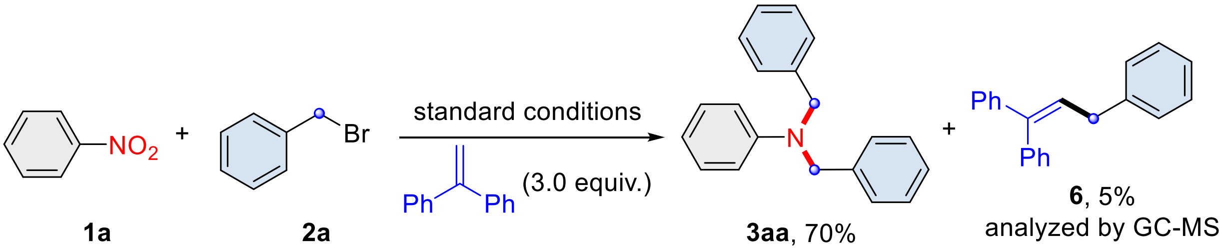


Figure S9. The ^{11}B NMR spectrum of the reaction.

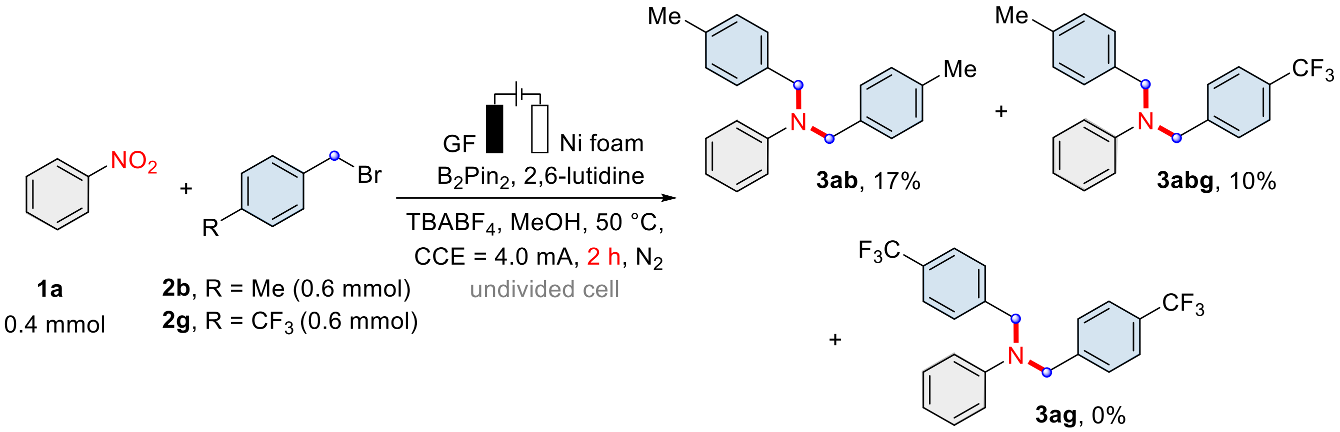
5.6 Radical Trapping Experiments



Scheme S16. Radical trapping experiments.

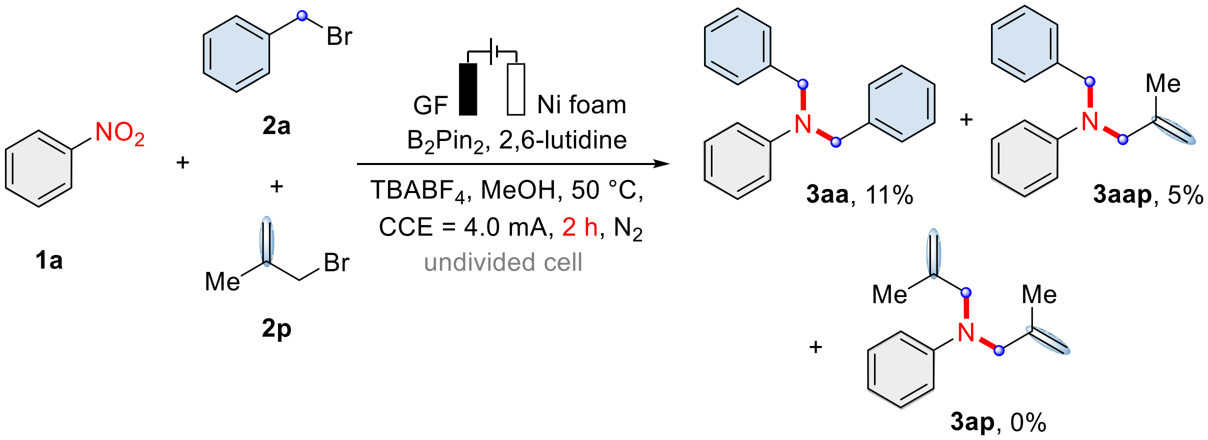
In order to confirm whether the reaction undergoes a radical mechanism, radical trapping experiments were performed. The yields of corresponding products were determined by GC-MS analysis using 1,3,5-trimethoxybenzene as the internal standard. When the radical scavenger 1,1-diphenylethylene was added, the yield of product 3aa slightly decreased to 70%. The radical generated from 2a in the reaction could be captured by 1,1-diphenylethylene (detected by GC-MS). This result suggested that the reaction mainly proceed through two-electron process.

5.7 Competition Experiments



Scheme S17. Competition experiments electron-donating/withdrawing benzyl bromide

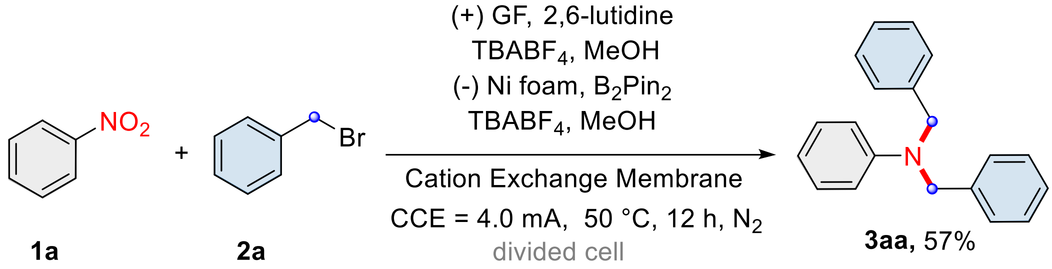
The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (41 µL, 0.40 mmol), 1-(bromomethyl)-4-methylbenzene **2b** (111 mg, 0.60 mmol), 1-(bromomethyl)-4-(trifluoromethyl)benzene **2g** (143 mg, 0.60 mmol), $TBABF_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 µL, 1.20 mmol), B_2Pin_2 (203 mg, 0.80 mmol) and MeOH (4.0 mL). Electrocatalysis was performed at 50 °C with a constant current of 4.0 mA maintained for 2 h. The electrodes were washed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. Upon GC analysis, the residue gave the corresponding products **3aa**, **3abg** in yields of 17% and 10%, respectively. The yields of corresponding products were determined by GC-MS analysis using 1,3,5-trimethoxybenzene as the internal standard.



Scheme S18. Comparative reactions between: aliphatic bromides and aromatic bromides.

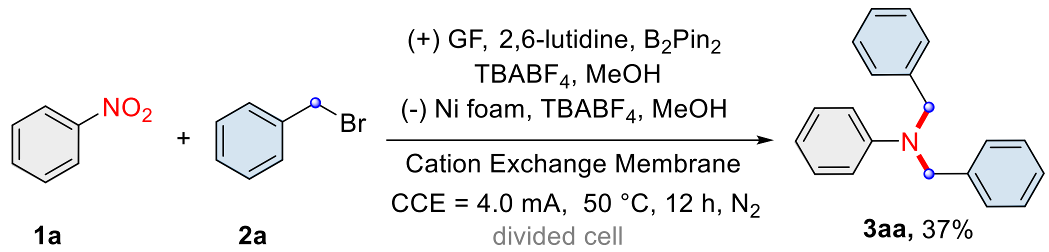
The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm) and a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The cell was charged with nitrobenzene **1a** (41 μL, 0.40 mmol), benzyl bromide **2a** (71 μL, 0.60 mmol), 3-bromo-2-methylprop-1-ene **2p** (61 μL, 0.60 mmol), TBABF$_4$ (198 mg, 0.60 mmol), 2,6-lutidine (140 μL, 1.20 mmol), B$_2$Pin$_2$ (203 mg, 0.80 mmol) and MeOH (4.0 mL). Electrocatalysis was performed at 50 °C with a constant current of 4.0 mA maintained for 2 h. The electrodes were washed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. Upon GC analysis, the residue gave the corresponding products **3aa**, **3abg** in yields of 11% and 5%, respectively. The yields of corresponding products were determined by GC-MS analysis using 1,3,5-trimethoxybenzene as the internal standard.

5.8 Divided Cell Experiments



Scheme S19. Divided cell experiments with B$_2$Pin$_2$ at the cathode.

In a N$_2$-filled glovebox, a pre-assembled Cation Exchange Membrane (1.5×1.5 cm^2) divided H-type cell was equipped with a magnetic stir bar in each 10 mL chamber. The anodic chamber was charged with TBABF$_4$ (198 mg, 0.15 M), 2,6-lutidine (140 μL, 1.20 mmol), and MeOH (4.0 mL). The anodic chamber was sealed by rubber septum cap with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm). The cathodic chamber was charged with nitrobenzene **1a** (49.2 mg, 0.4 mmol), benzyl bromide **2a** (143 μL, 1.20 mmol), B$_2$Pin$_2$ (203 mg, 0.8 mmol) TBABF$_4$ (198 mg, 0.15 M) and MeOH (4.0 mL). The cathodic chamber was sealed by rubber septum cap with a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The distance between the anode and cathode was almost 5.5 cm. The cell was transferred out from the glovebox. After that, constant current of 4.0 mA was conducted for 12 h at 50 °C with stirring. Upon completion of the electrolysis, the solution in the cathodic chamber of the cell was transferred to a 100 mL round-bottomed flask. The Ni foam cathode and cathodic chamber were rinsed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. The residue was purified by chromatography on silica gel (PE/DCM = 50:1) to afford the corresponding products **3aa**.



Scheme S20. Divided cell experiments with B_2Pin_2 at the anode.

In a N_2-filled glovebox, a pre-assembled Cation Exchange Membrane (1.5×1.5 cm^2) divided H-type cell was equipped with a magnetic stir bar in each 10 mL chamber. The anodic chamber was charged with $TBABF_4$ (198 mg, 0.15 M), B_2Pin_2 (203 mg, 0.8 mmol), 2,6-lutidine (140 µL, 1.20 mmol), and MeOH (4.0 mL). The anodic chamber was sealed by rubber septum cap with a graphite felt (GF) anode (10 mm × 20 mm × 3.0 mm). The cathodic chamber was charged with nitrobenzene **1a** (49.2 mg, 0.4 mmol), benzyl bromide **2a** (143 µL, 1.20 mmol), $TBABF_4$ (198 mg, 0.15 M) and MeOH (4.0 mL). The cathodic chamber was sealed by rubber septum cap with a nickel foam (Ni foam) cathode (10 mm × 20 mm × 1.5 mm). The distance between the anode and cathode was almost 5.5 cm. The cell was transferred out from the glovebox. After that, constant current of 4.0 mA was conducted for 12 h at 50 °C with stirring. Upon completion of the electrolysis, the solution in the cathodic chamber of the cell was transferred to a 100 mL round-bottomed flask. The Ni foam cathode and cathodic chamber were rinsed with dichloromethane (3 × 4.0 mL) in an ultrasonic bath. The combined mixtures were filtered and concentrated under reduced pressure at 50 °C. The residue was purified by chromatography on silica gel (PE/DCM = 50:1) to afford the corresponding products **3aa**.

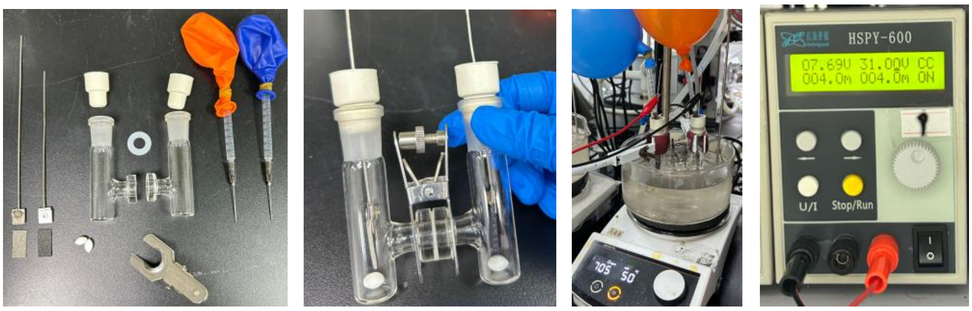


Figure S10. Pictures of the divided cell reaction setups.

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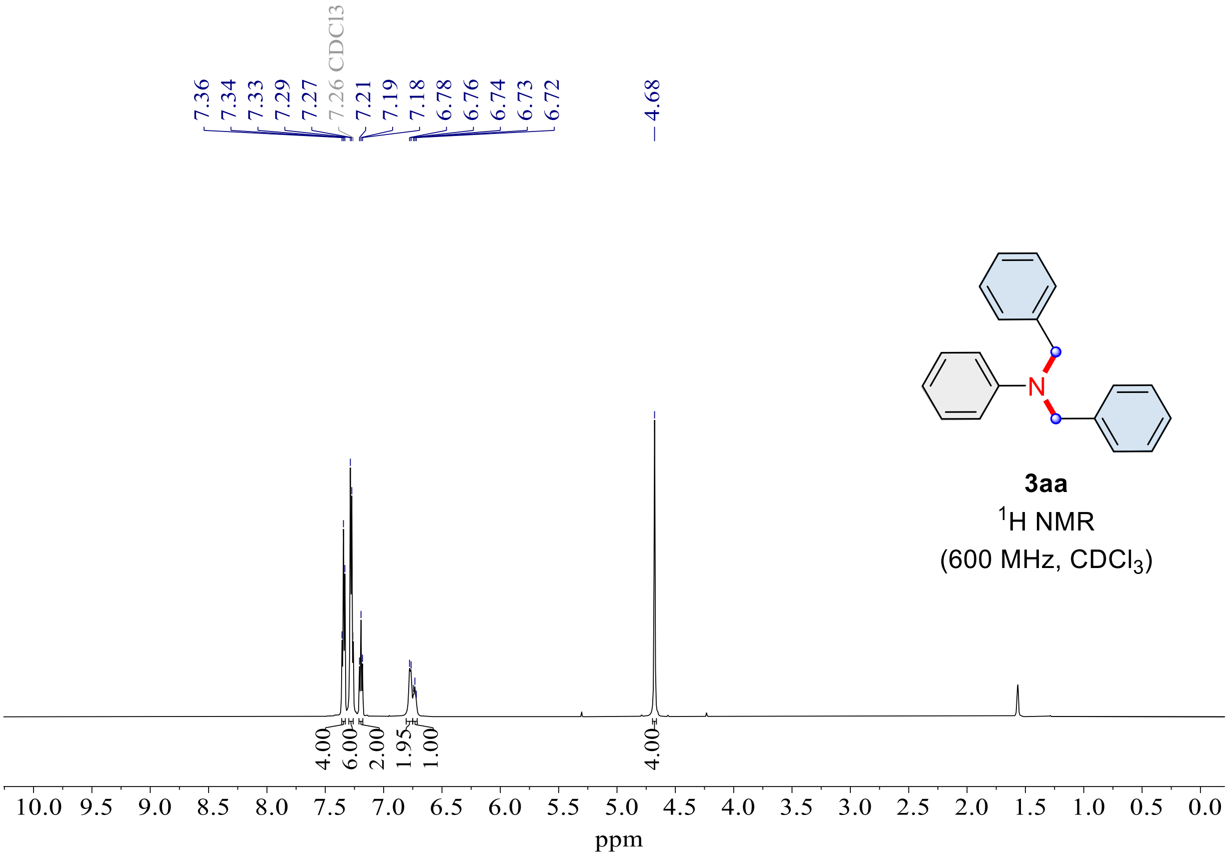
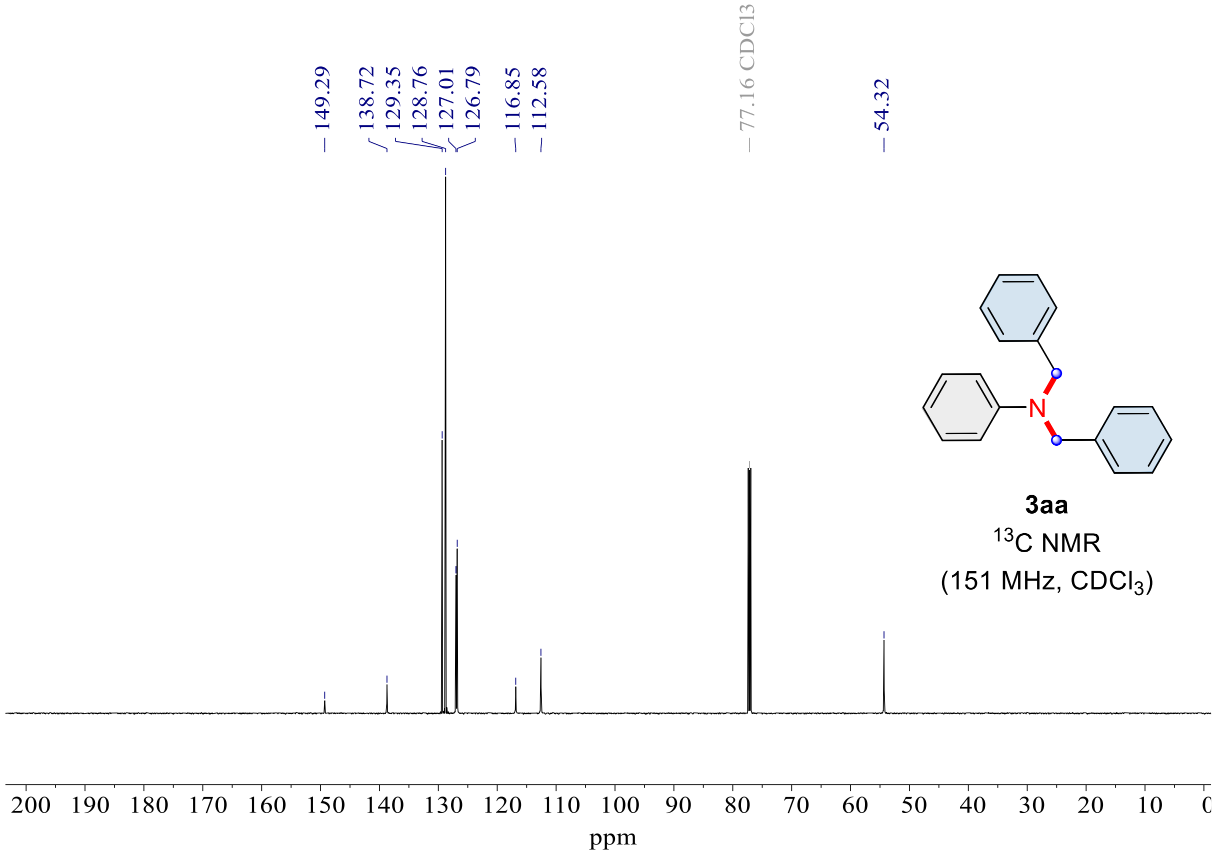
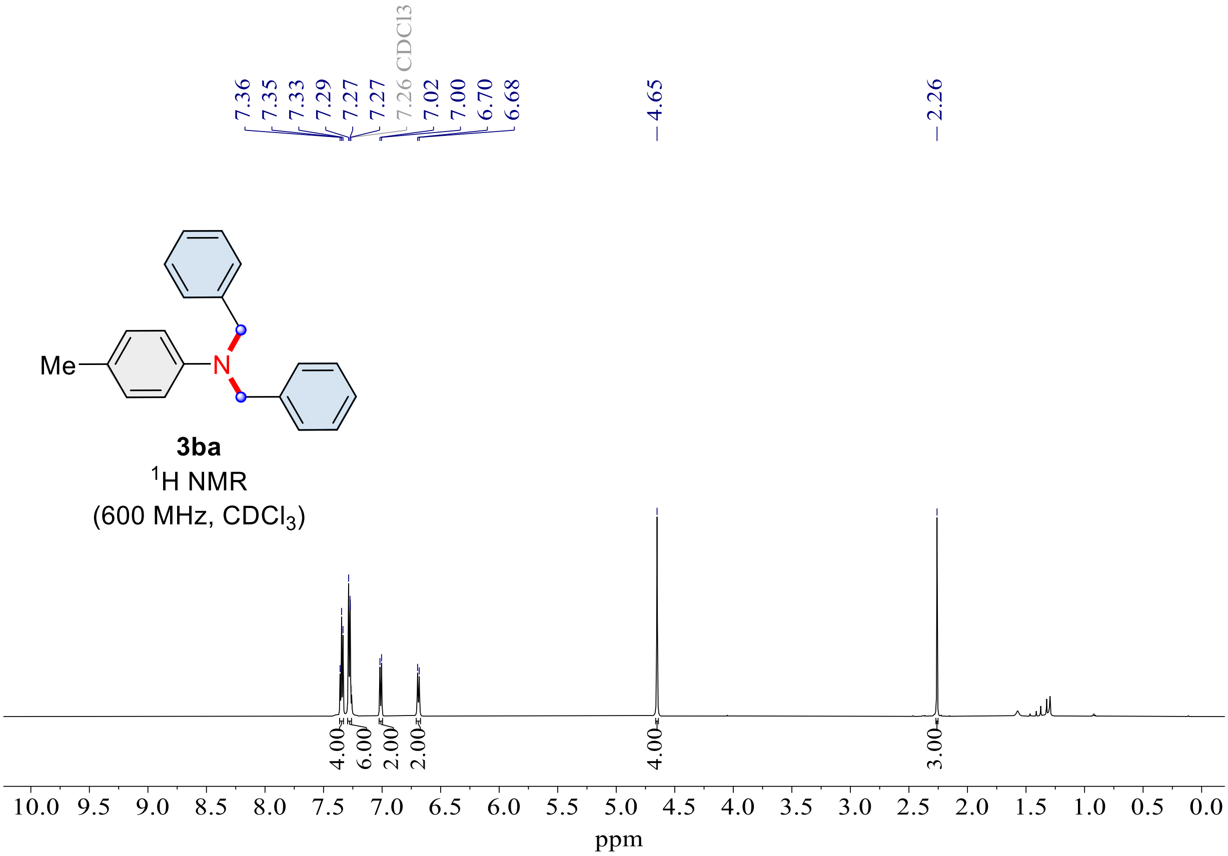
7. NMR Spectra



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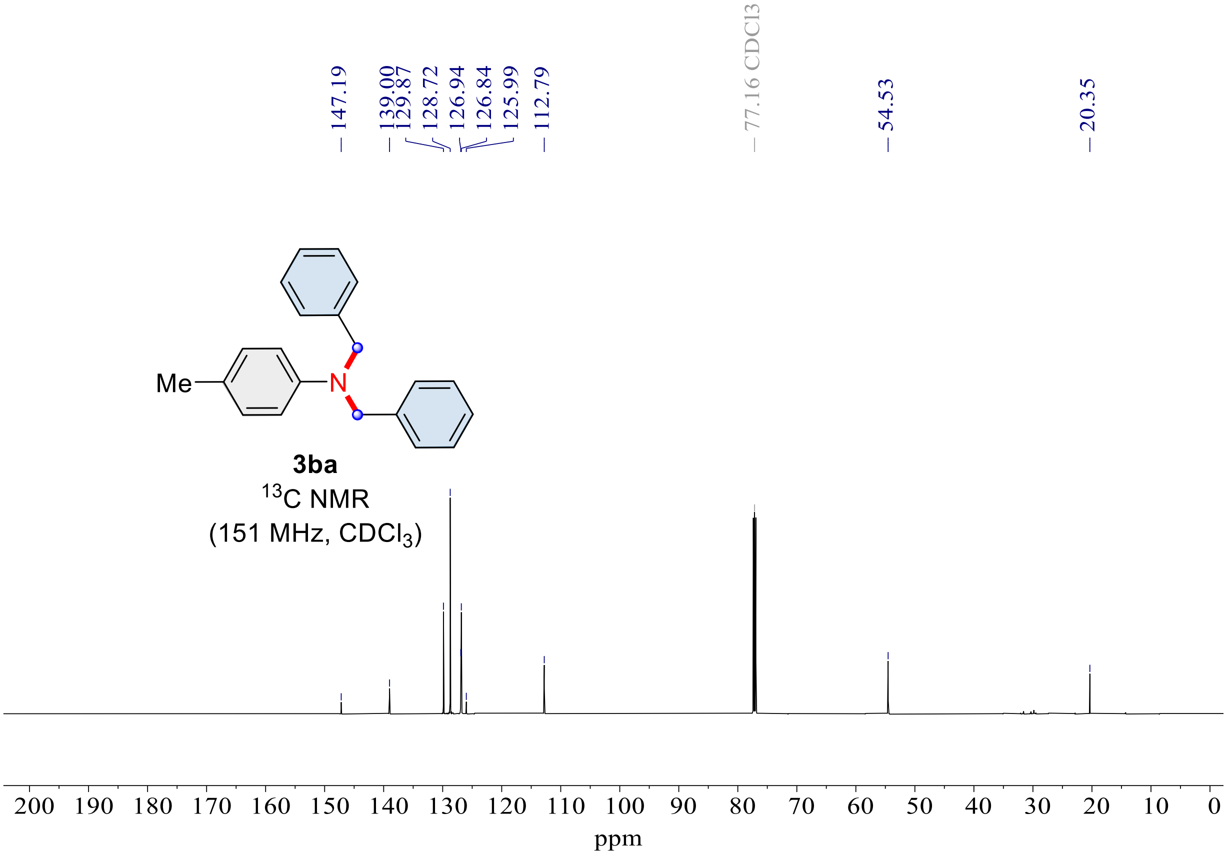
7.33
7.29
7.27
7.27
7.26 CDCl3
7.02
7.00
6.70
6.68
4.65
2.26
Me
N
3ba
^{1}H NMR
(600 MHz, $CDCl_3$)
4.00
6.00
2.00
2.00
4.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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129.87
128.72
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125.99
112.79
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54.53
20.35
Me
N
3ba
^{13}C NMR
(151 MHz, $CDCl_3$)
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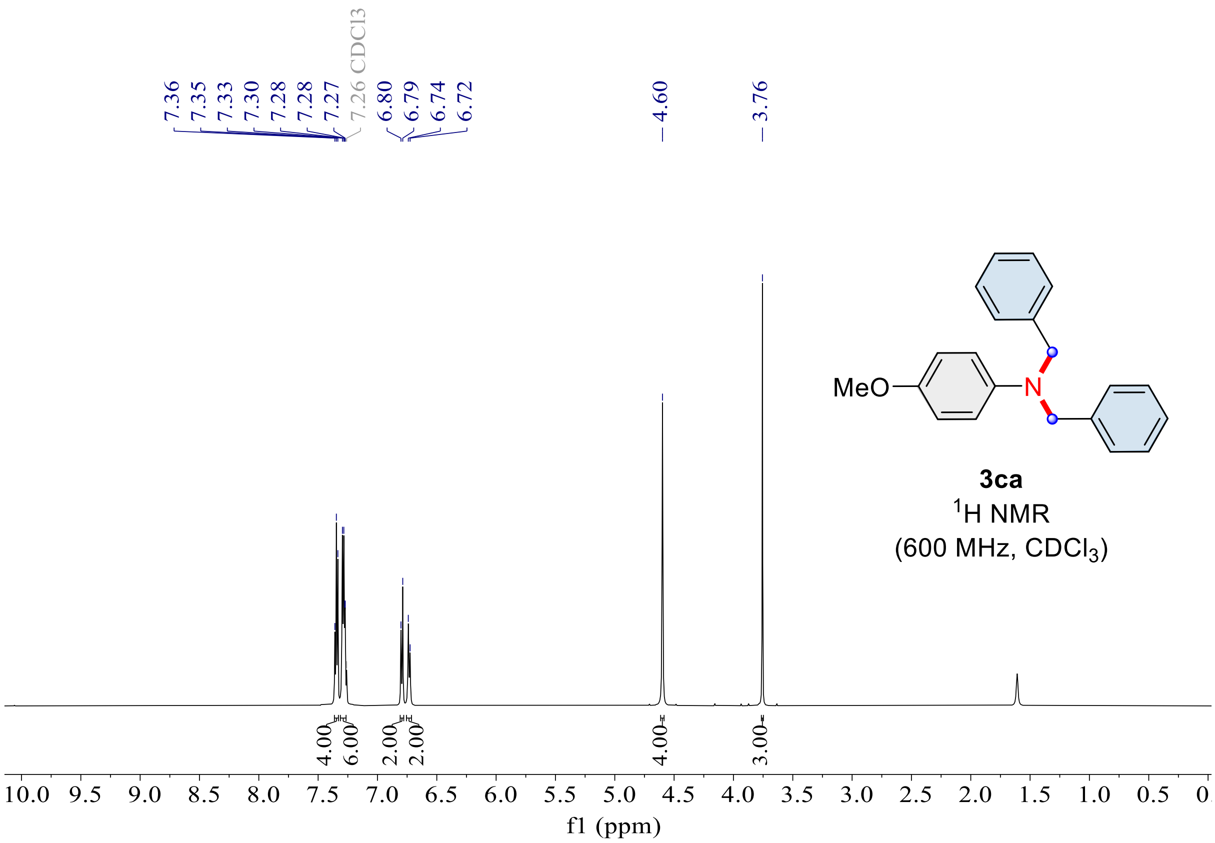
ppm



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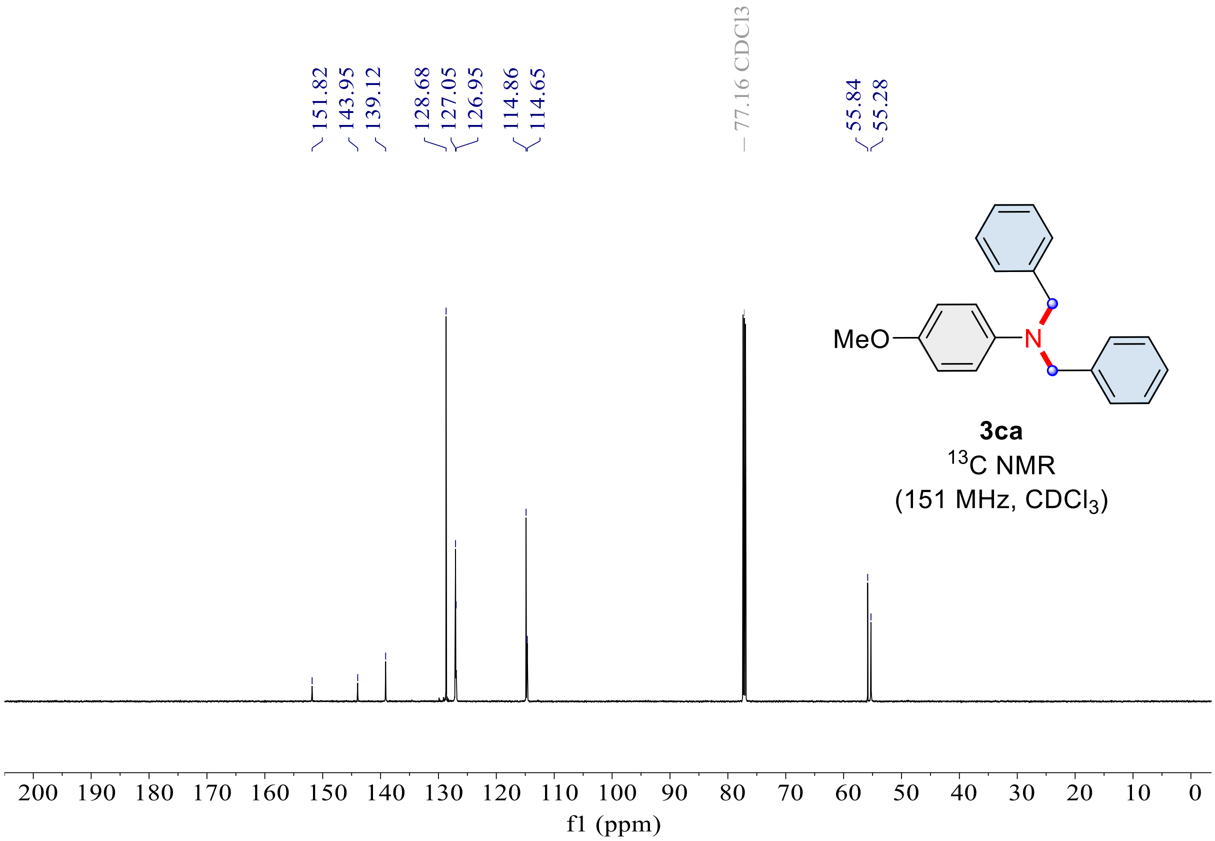
^1H NMR
(600 MHz, $CDCl_3$)



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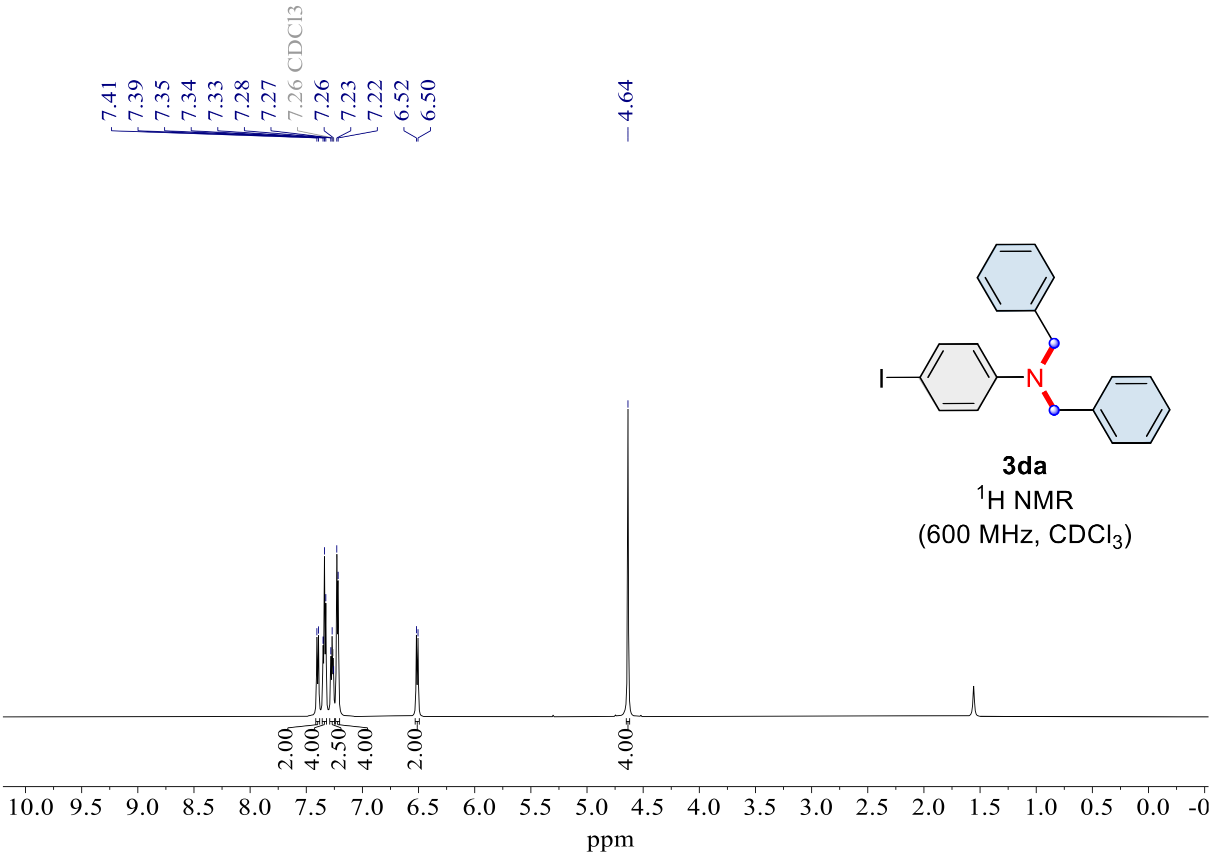
^{13}C NMR
(151 MHz, $CDCl_3$)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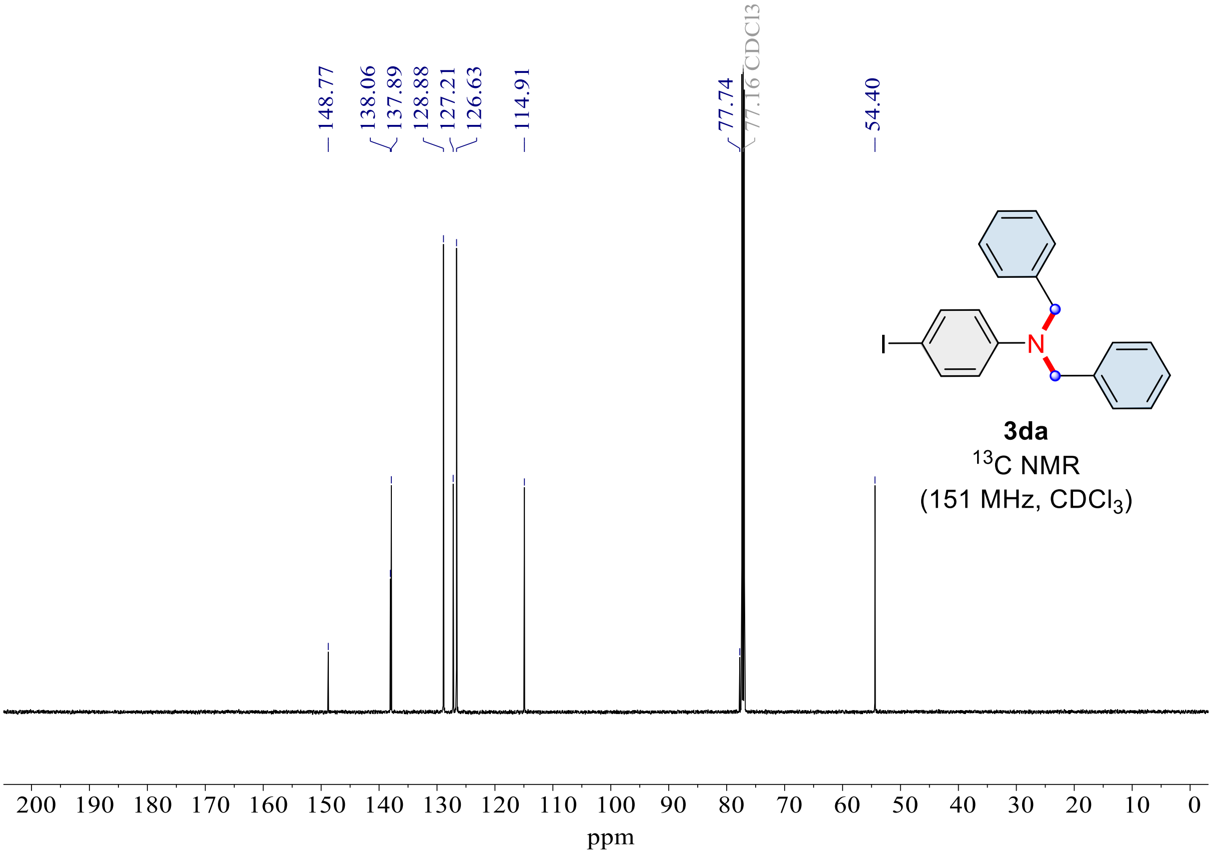
7.35
7.34
7.33
7.28
7.27
7.26 CDCl3
7.26
7.23
7.22
6.52
6.50
4.64
I
N
3da
^{1}H NMR
(600 MHz, CDCl$_3$)
2.00
4.00
2.50
4.00
2.00
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm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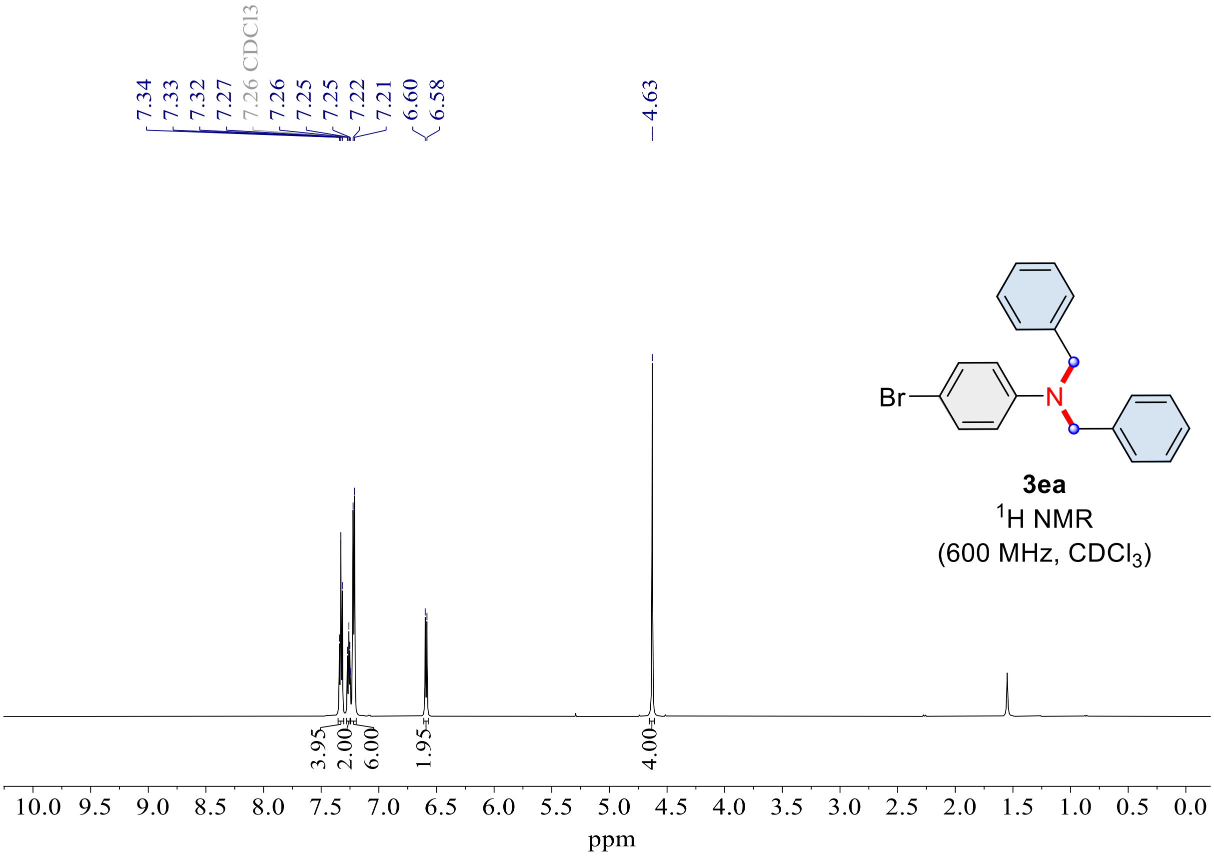
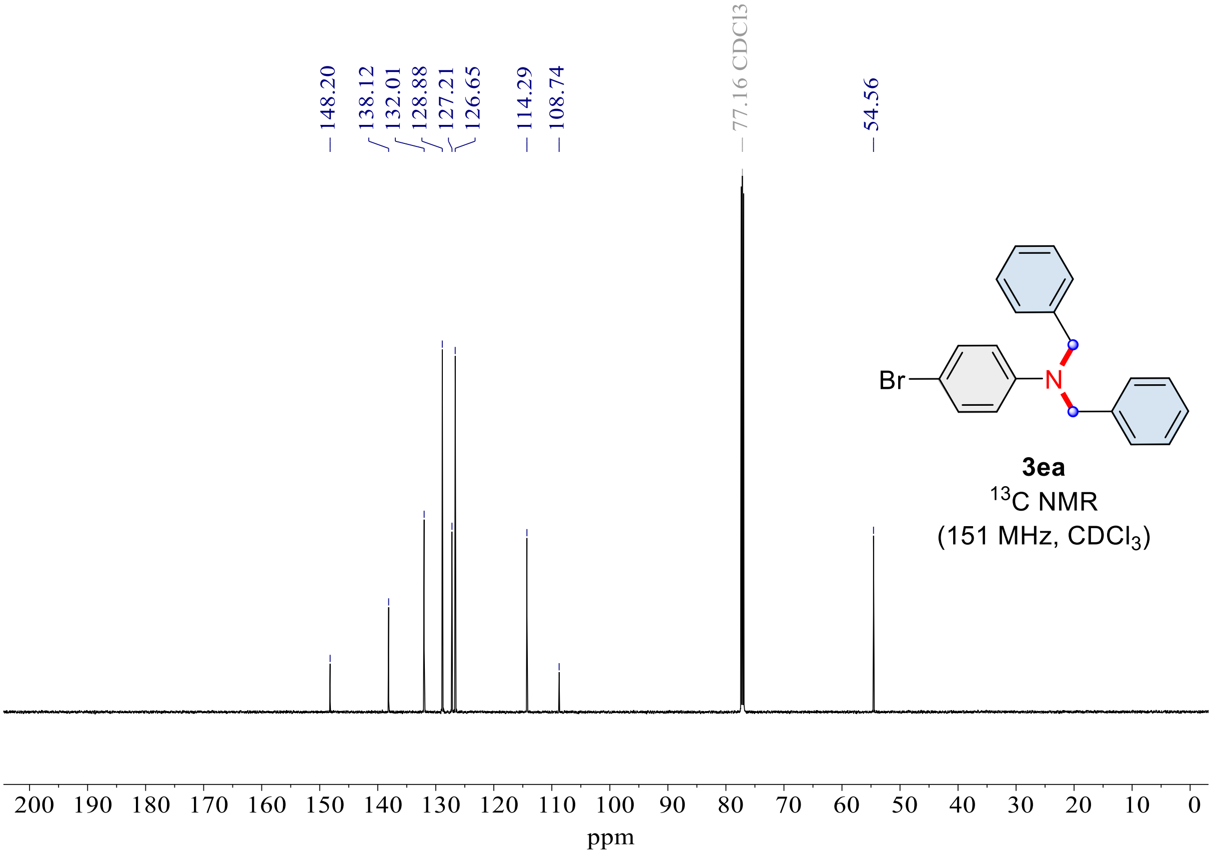
127.21
126.63
114.91
77.74
77.16 CDCl3
54.40
I
N
3da
^{13}C NMR
(151 MHz, CDCl$_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3ea

^{1}H NMR

(600 MHz, $CDCl_3$)



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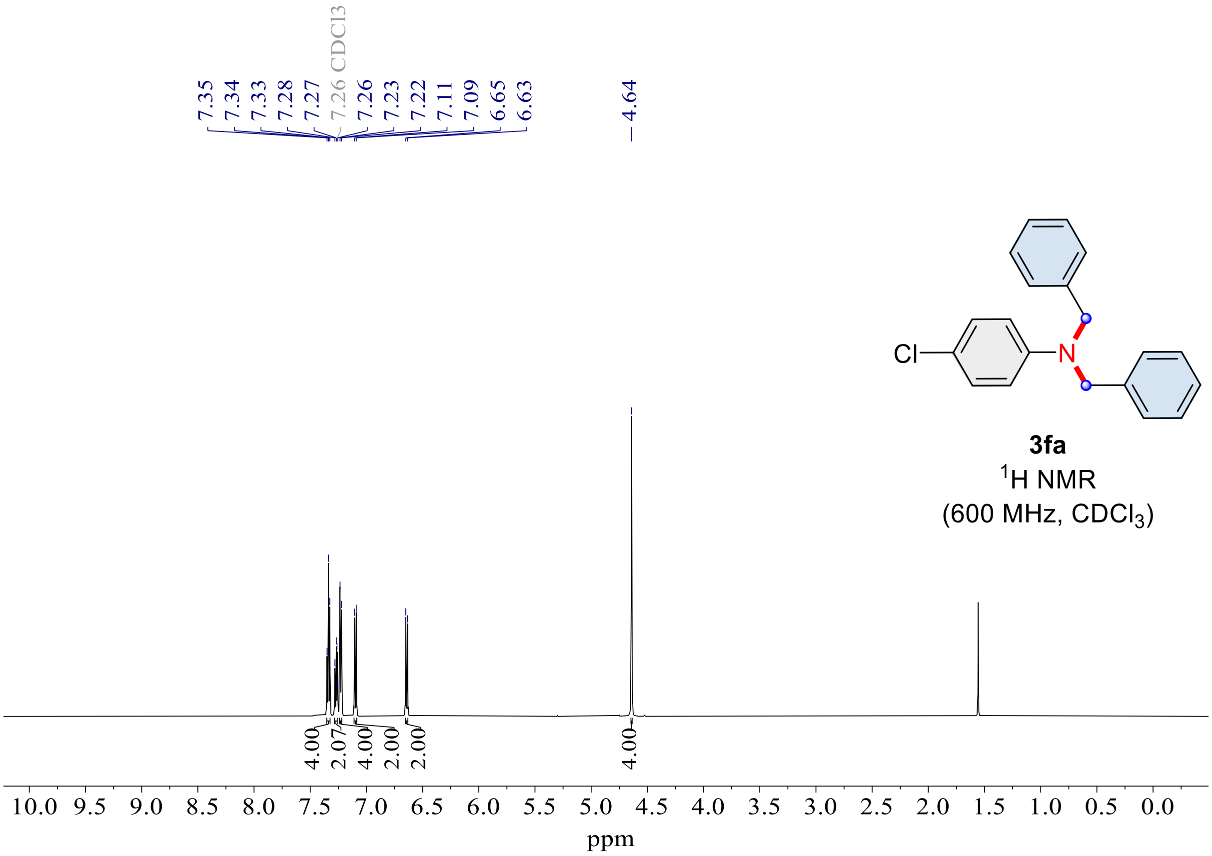
(151 MHz, $CDCl_3$)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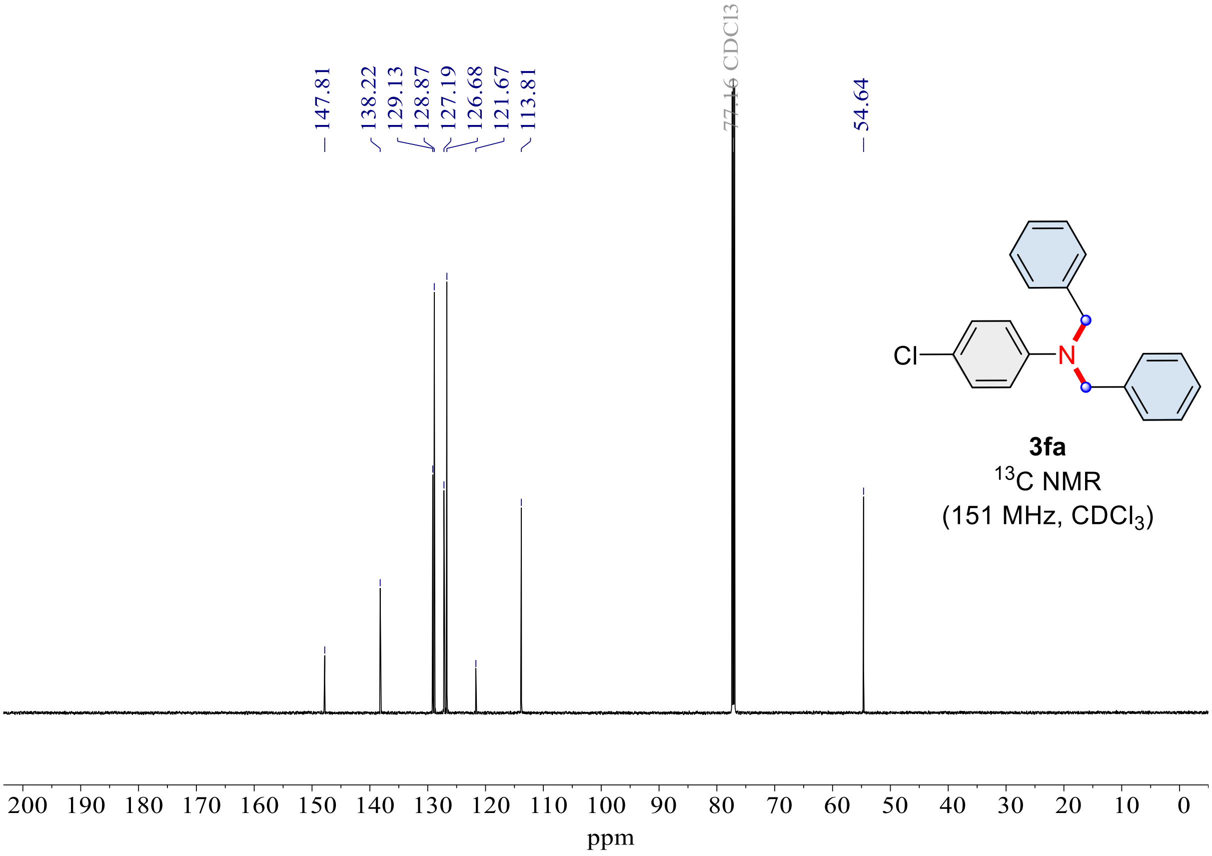
7.33
7.28
7.27
7.26 CDCl3
7.26
7.23
7.22
7.11
7.09
6.65
6.63
4.64
Cl
N
3fa
^{1}H NMR
(600 MHz, CDCl$_3$)
4.00
2.07
4.00
2.00
2.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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128.87
127.19
126.68
121.67
113.81
77.16 CDCl3
54.64
Cl
N
3fa
^{13}C NMR
(151 MHz, CDCl$_3$)
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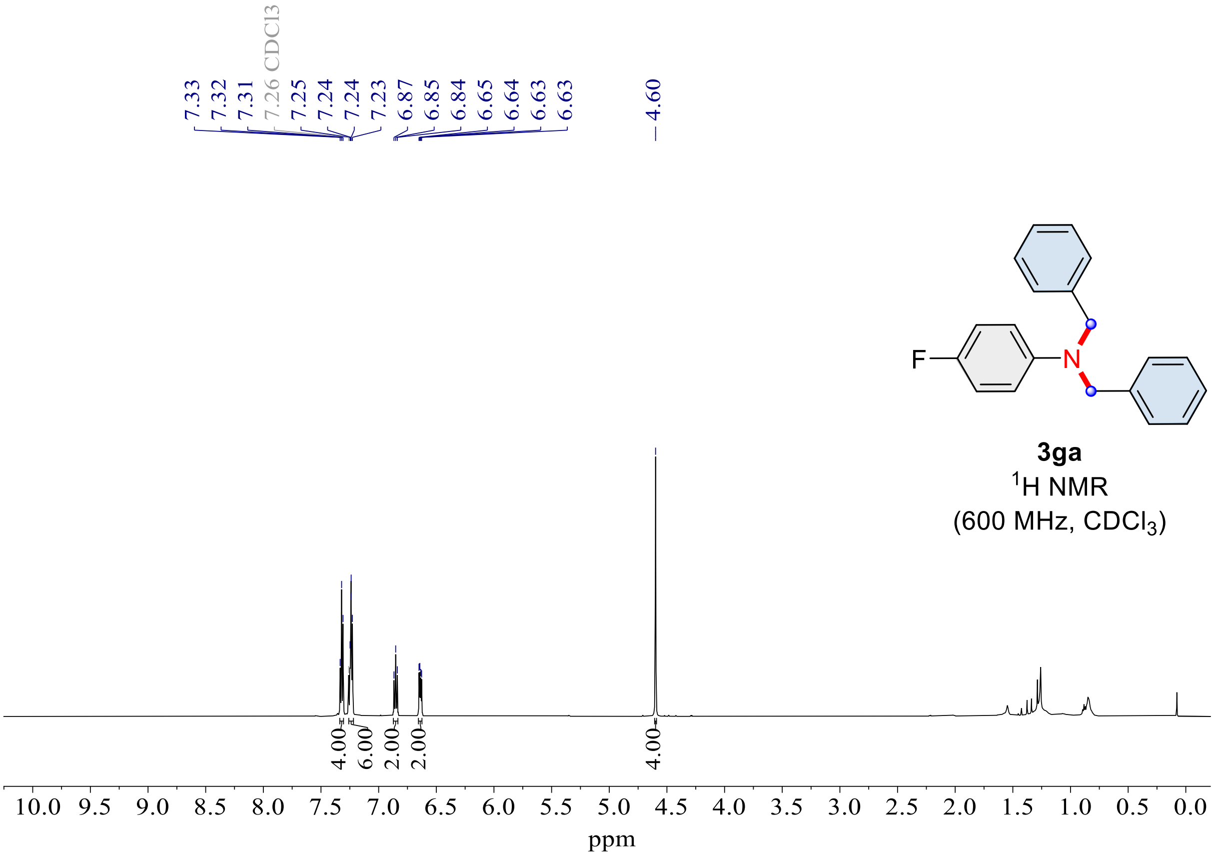
ppm



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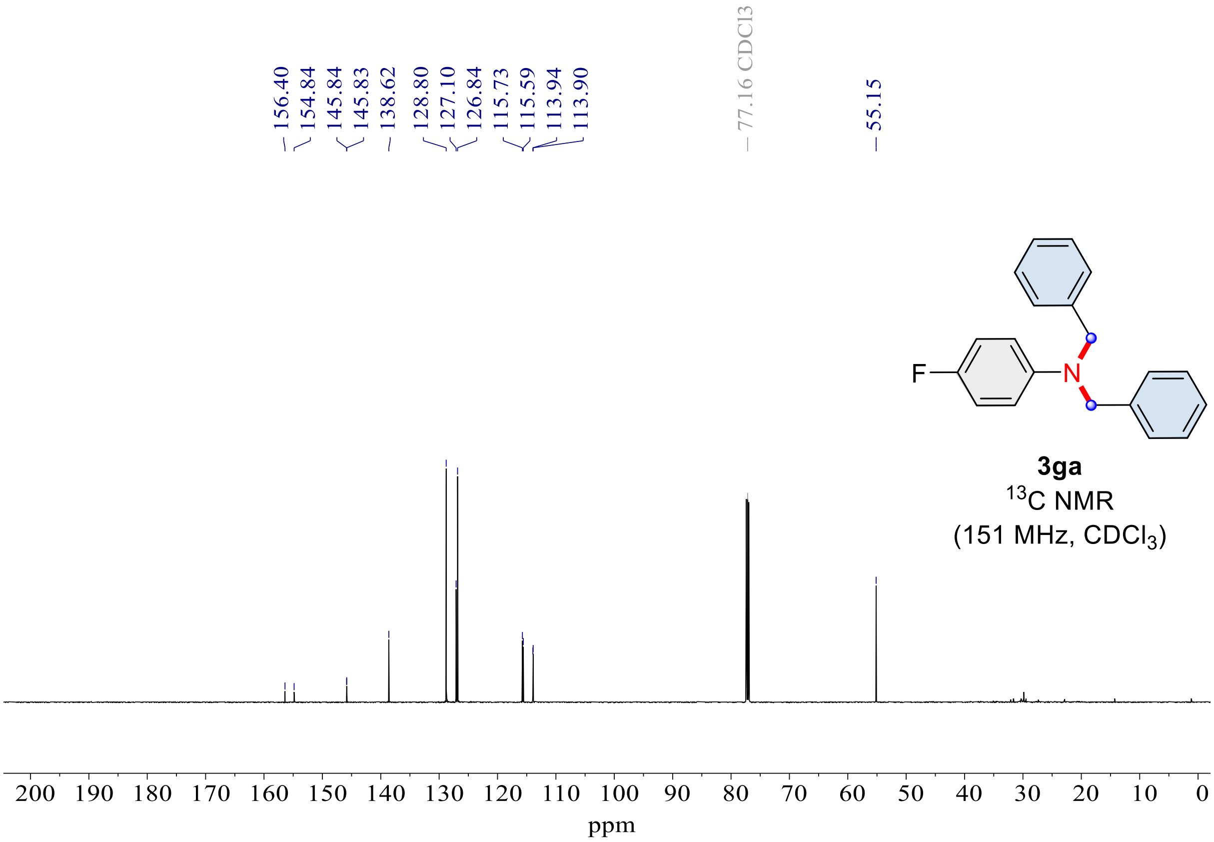
^{1}H NMR

(600 MHz, $CDCl_3$)



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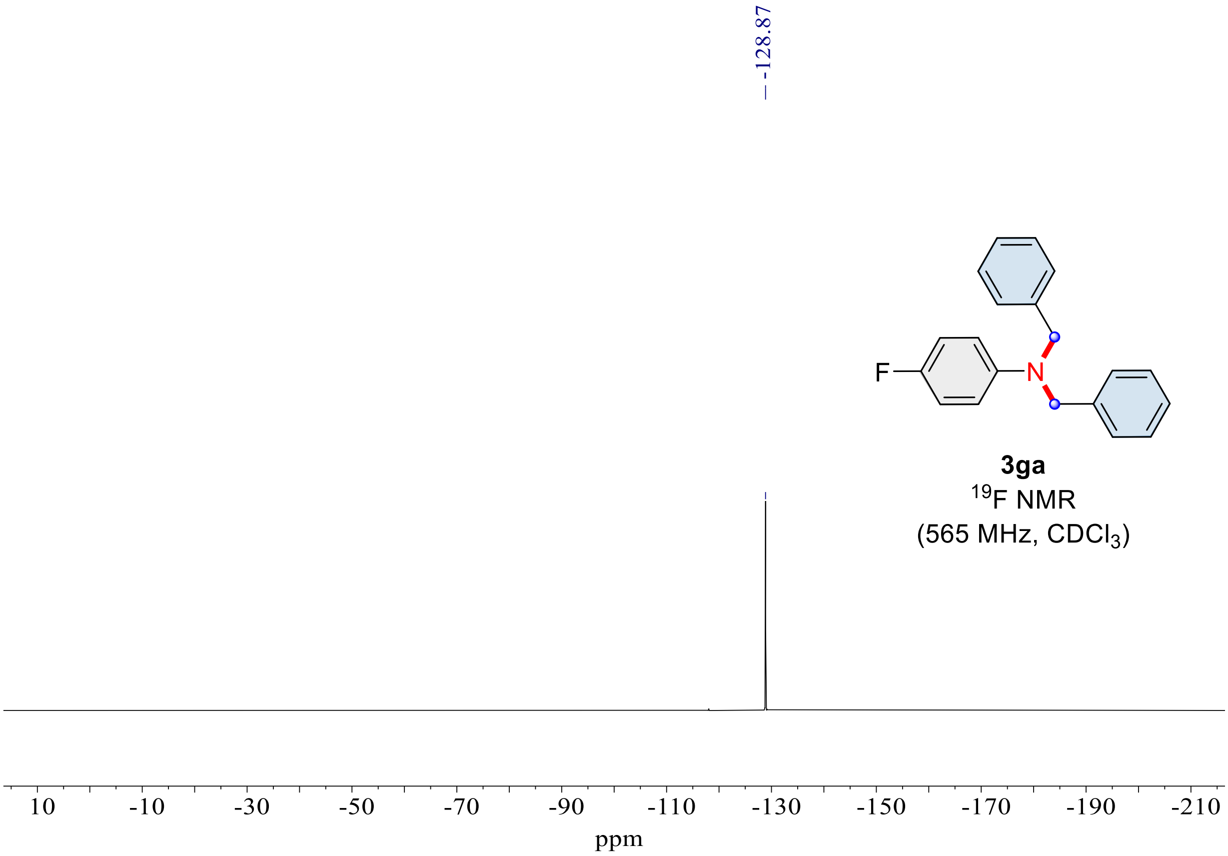

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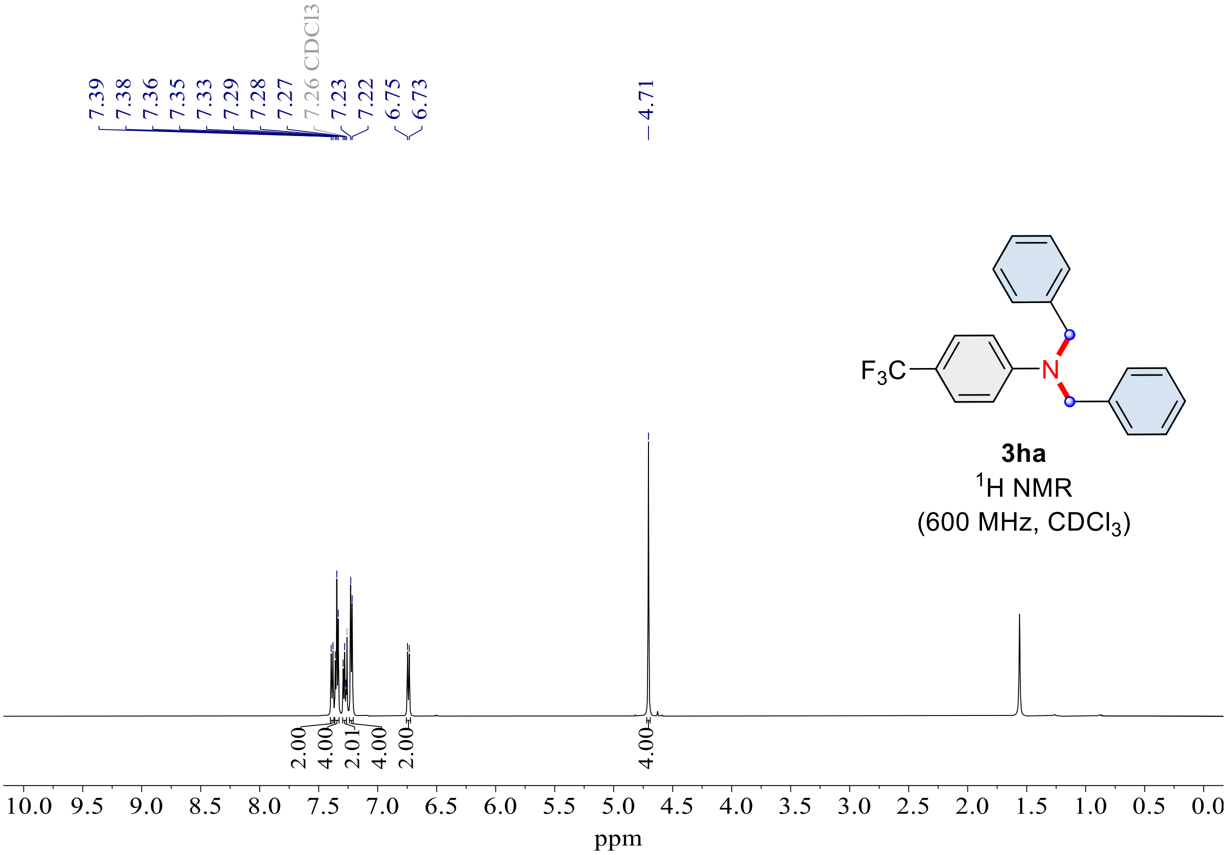
(565 MHz, $CDCl_3$)



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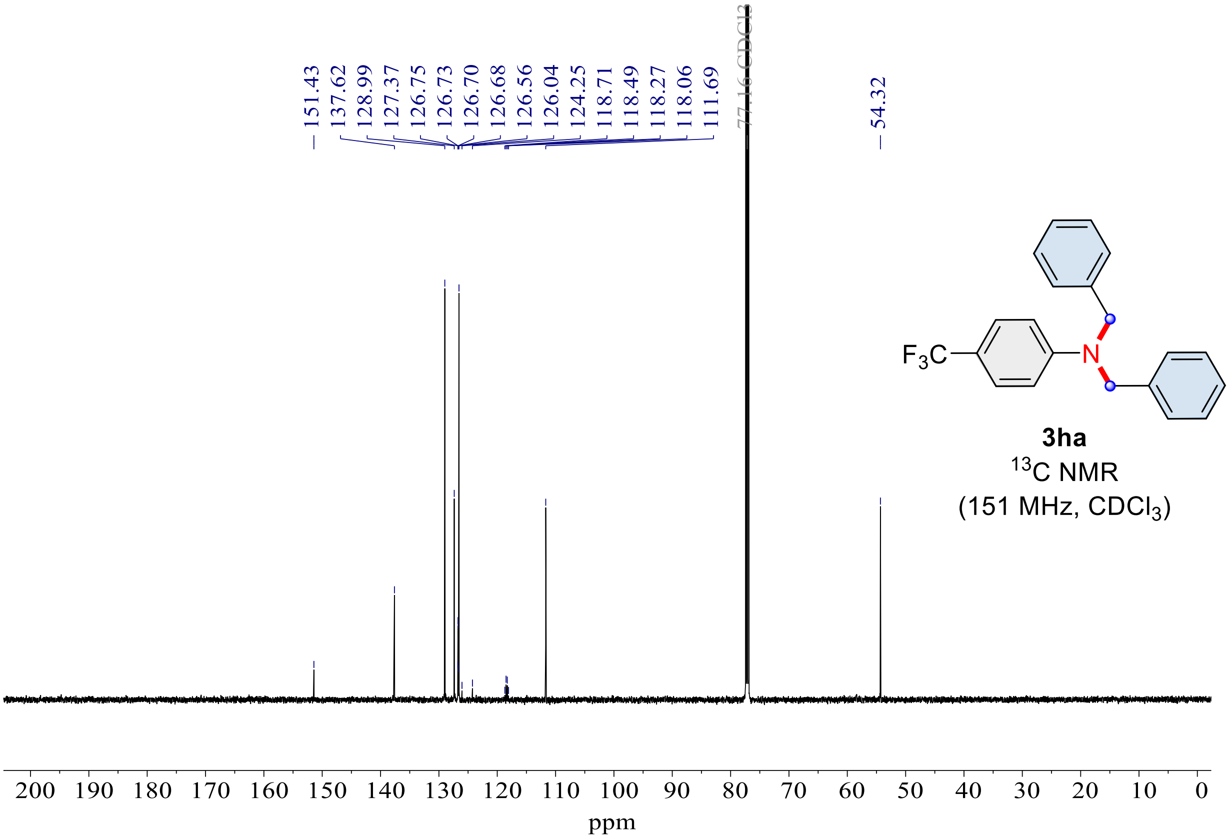
(600 MHz, $CDCl_3$)



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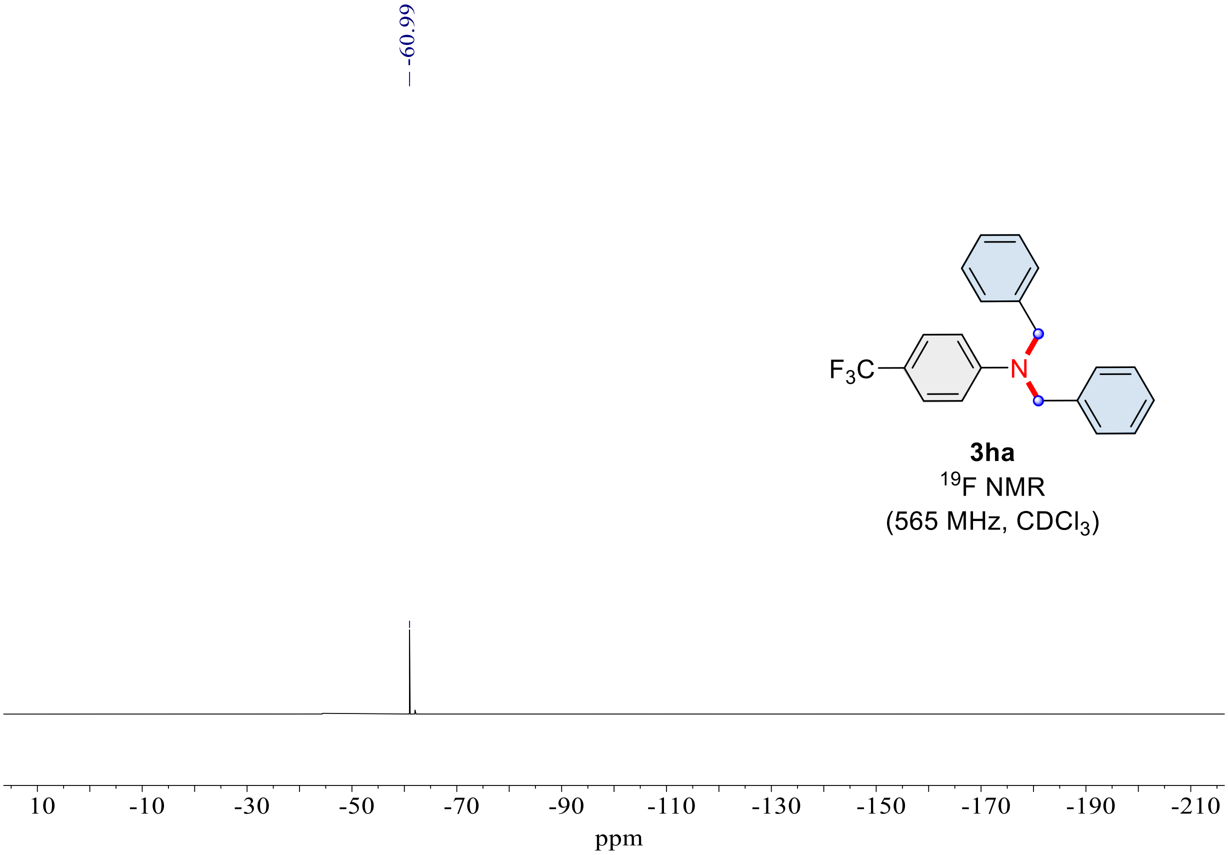
(151 MHz, $CDCl_3$)



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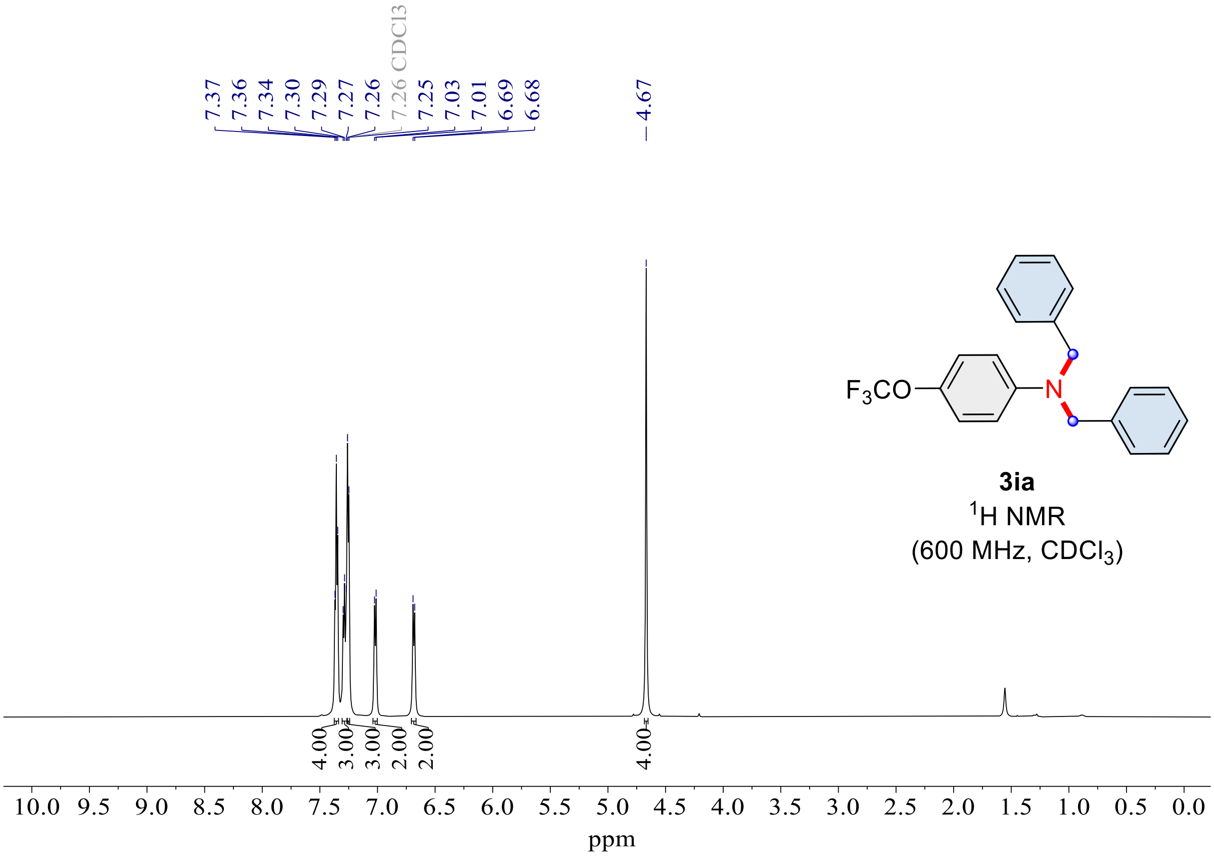
^{19}F NMR
(565 MHz, $CDCl_3$)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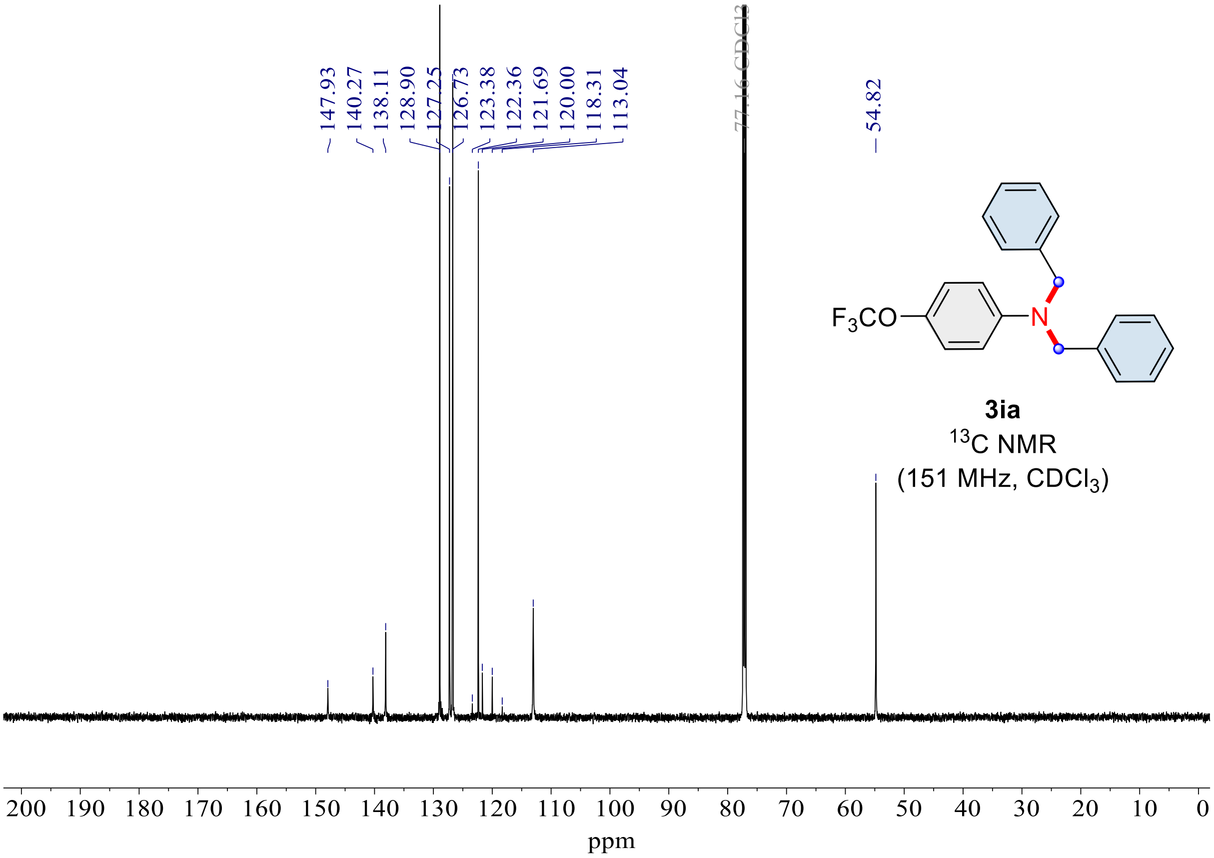
7.29
7.27
7.26
7.26 CDCl3
7.25
7.03
7.01
6.69
6.68
4.67
F3CO
N
3ia
^{1}H NMR
(600 MHz, CDCl$_3$)
4.00
3.00
3.00
2.00
2.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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77.16 CDCl3
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F3CO
N
3ia
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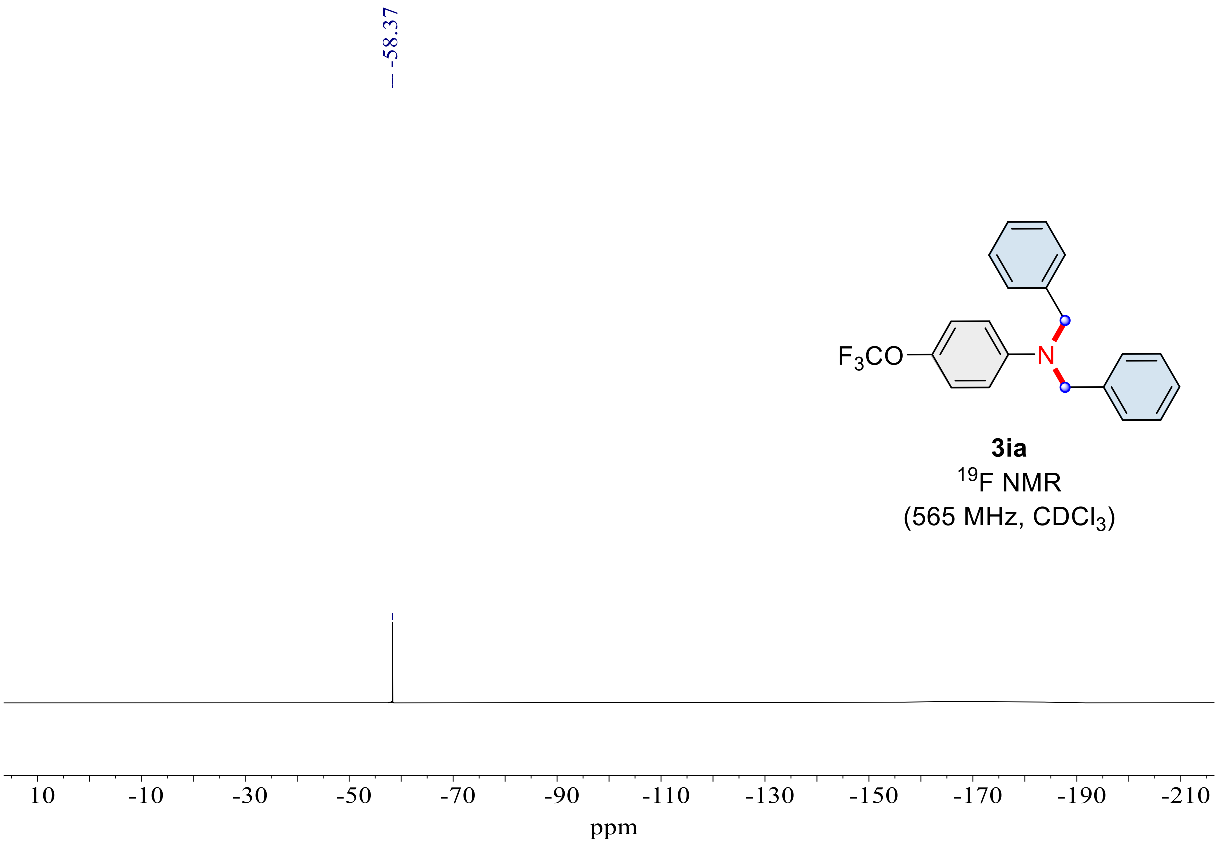
ppm



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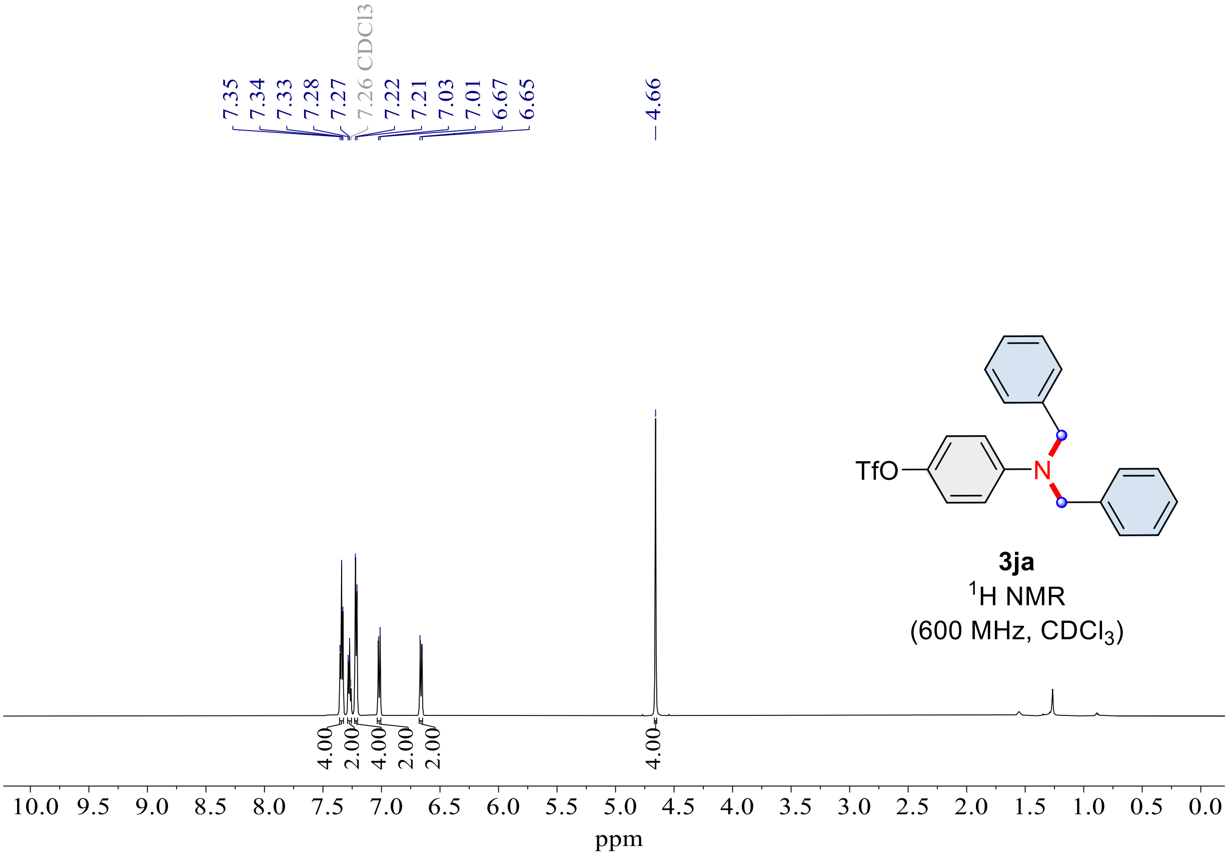
^{19}F NMR
(565 MHz, $CDCl_3$)



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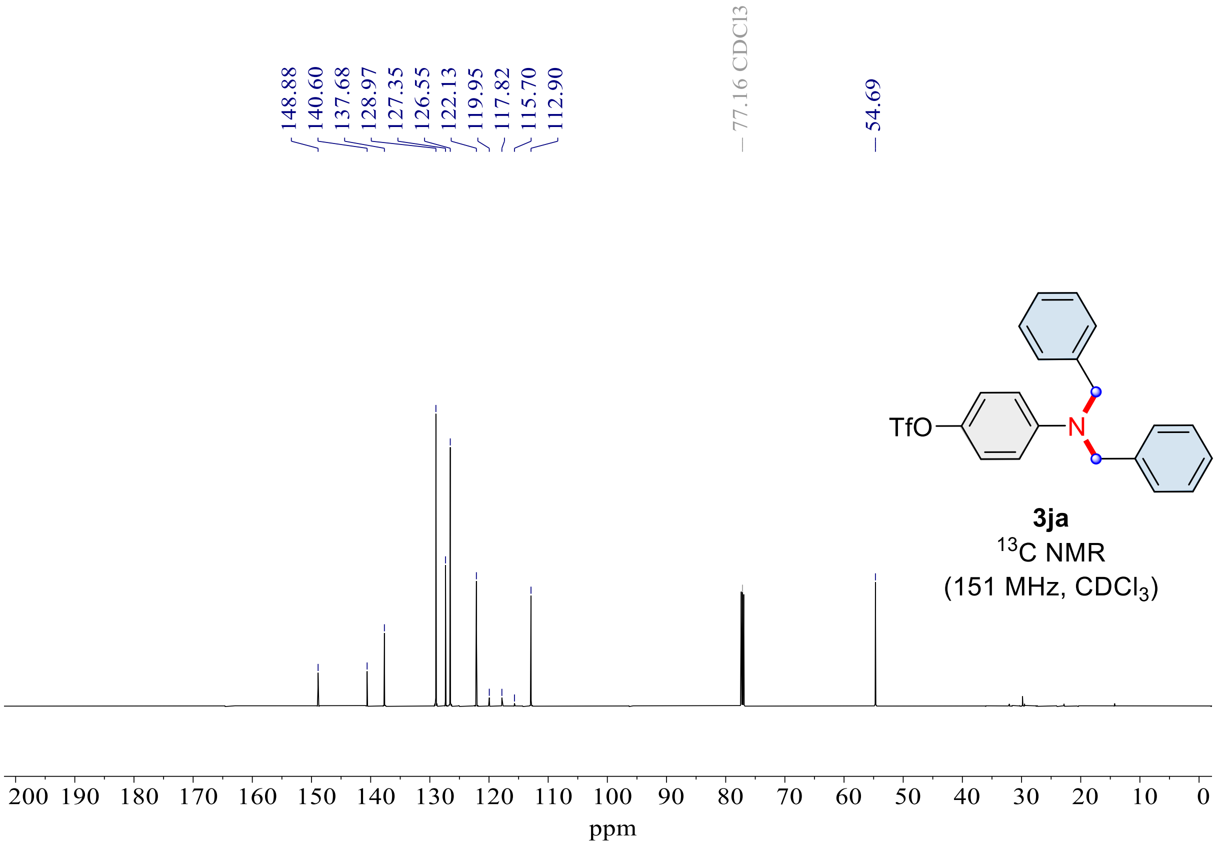
(600 MHz, $CDCl_3$)



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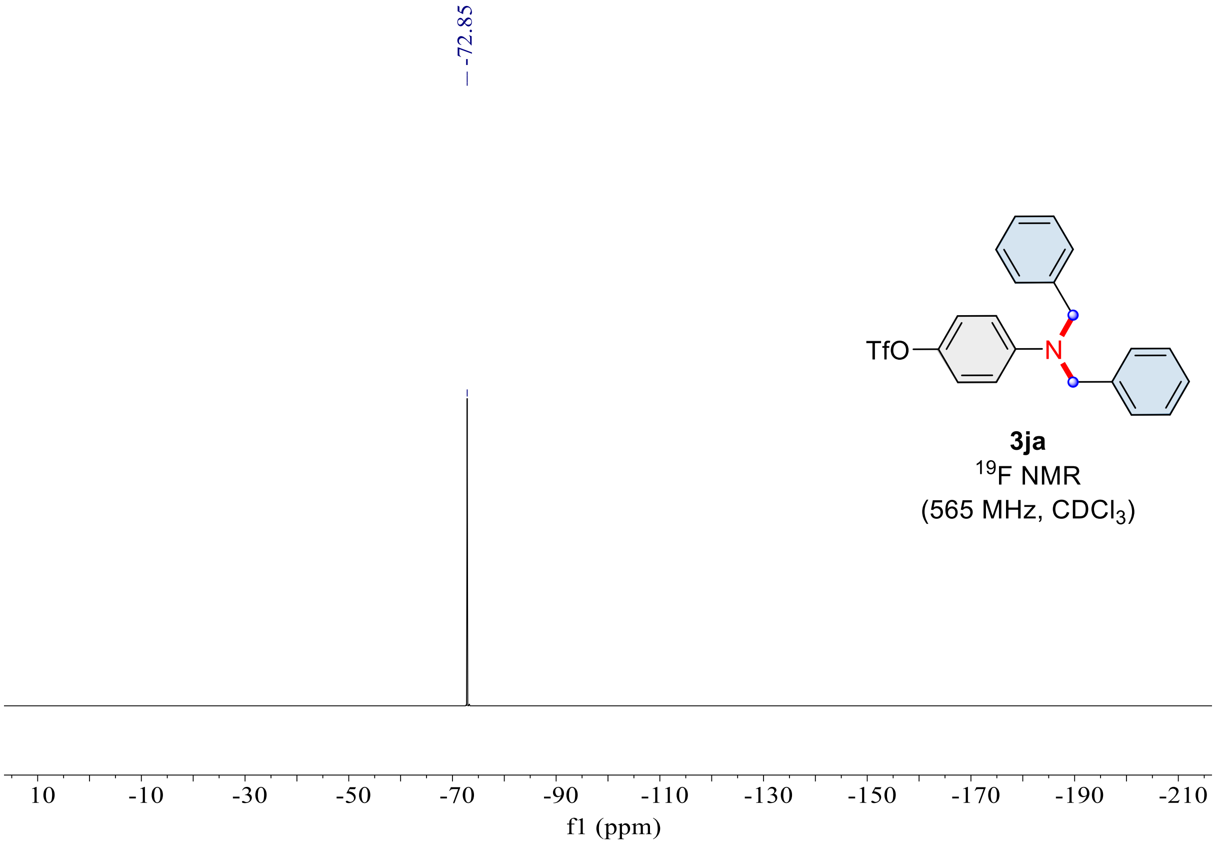

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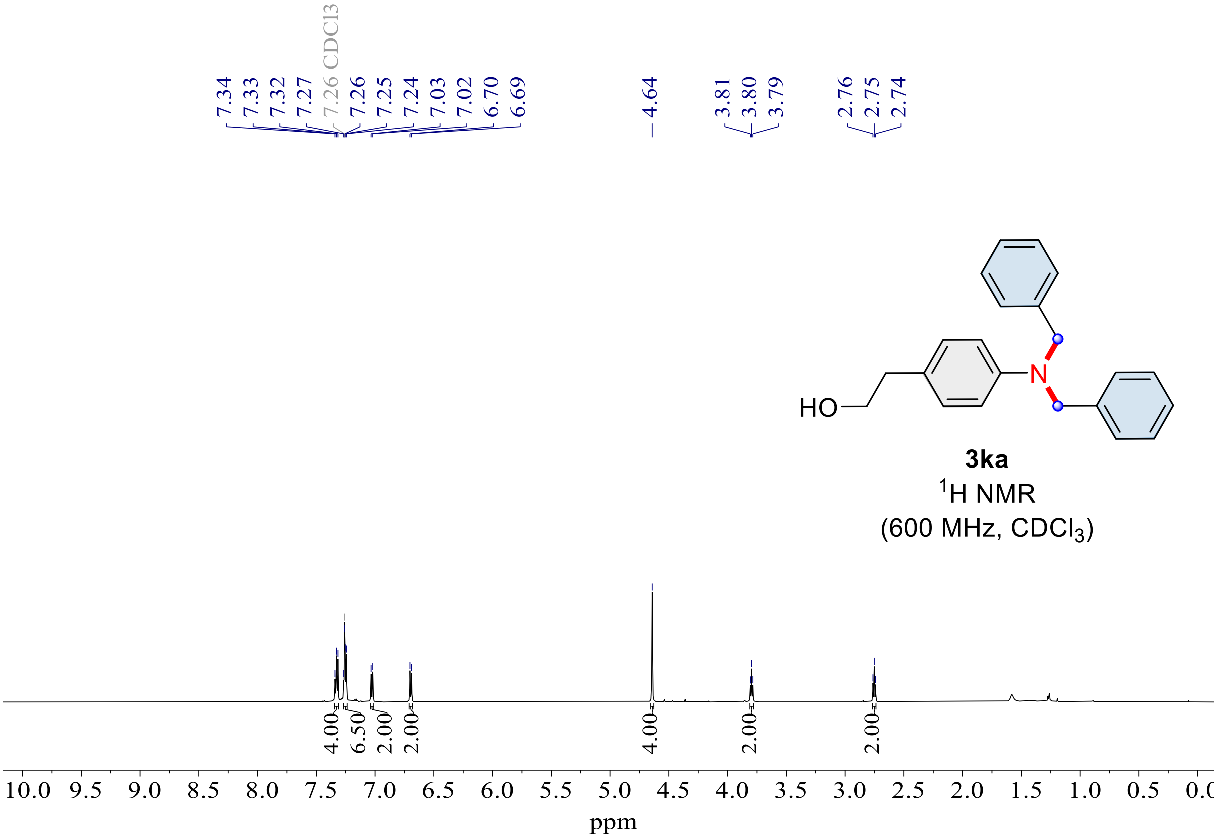

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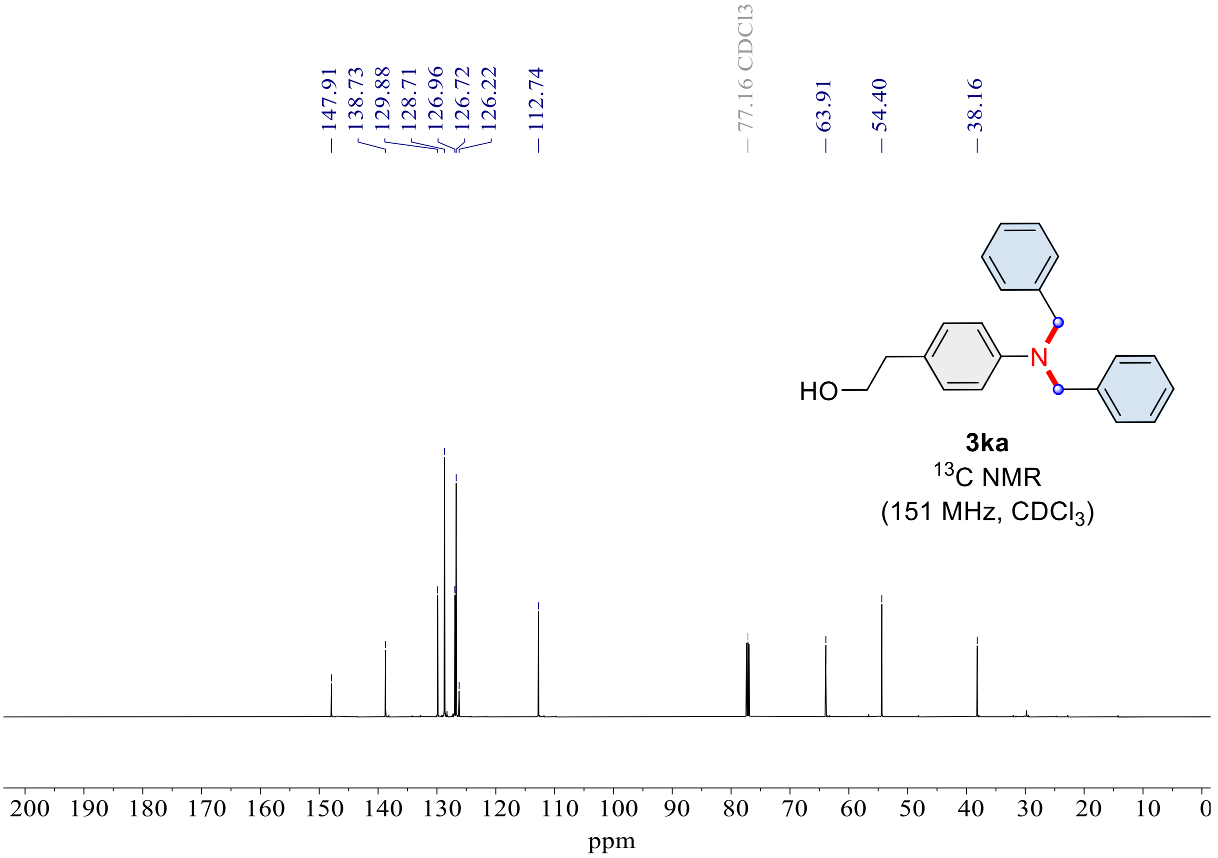

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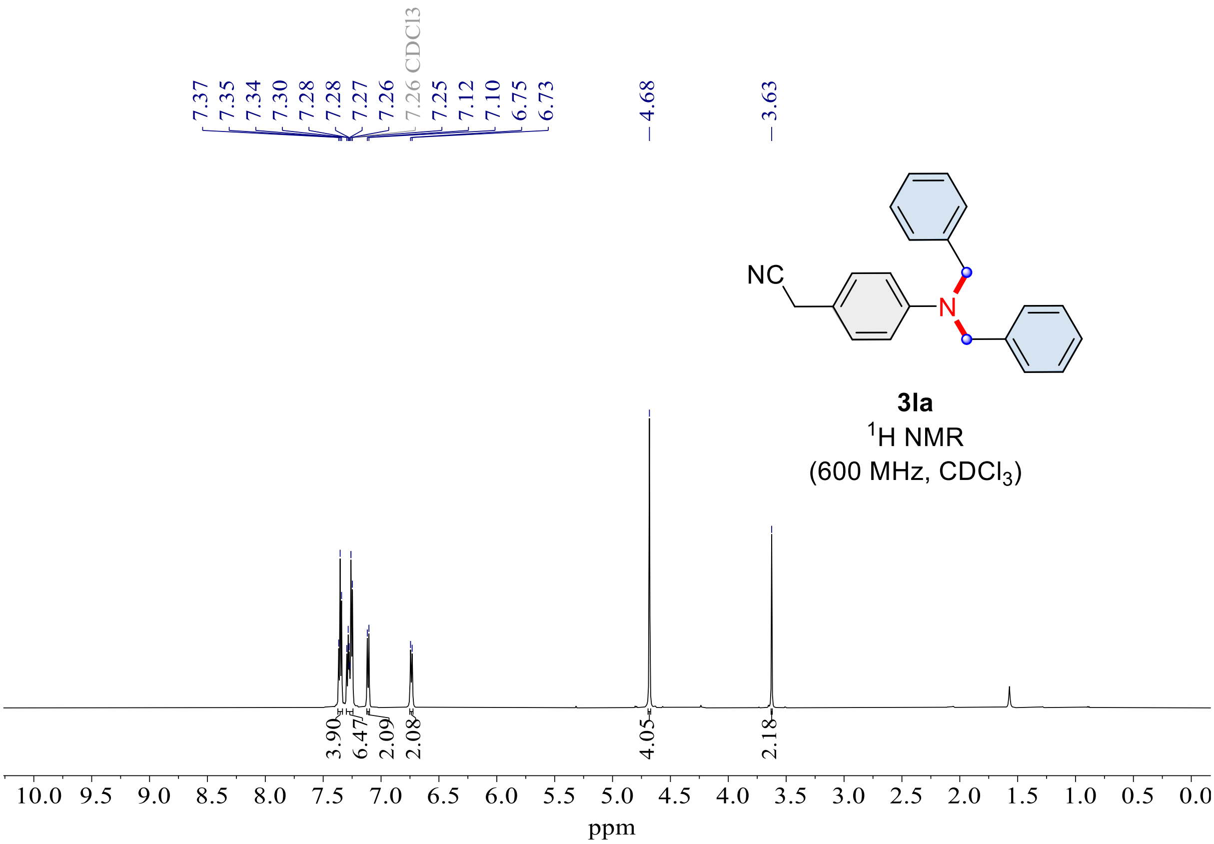

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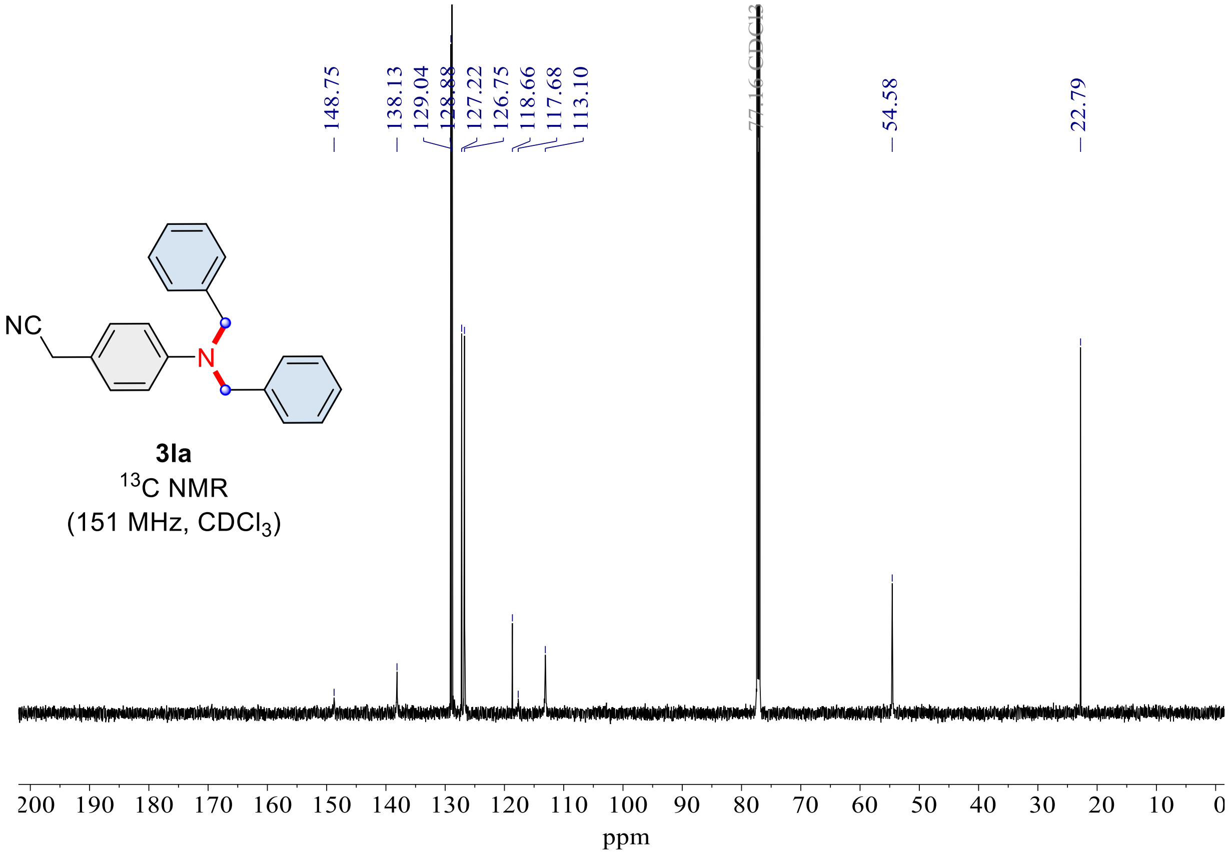
^{1}H NMR

(600 MHz, CDCl$_3$)



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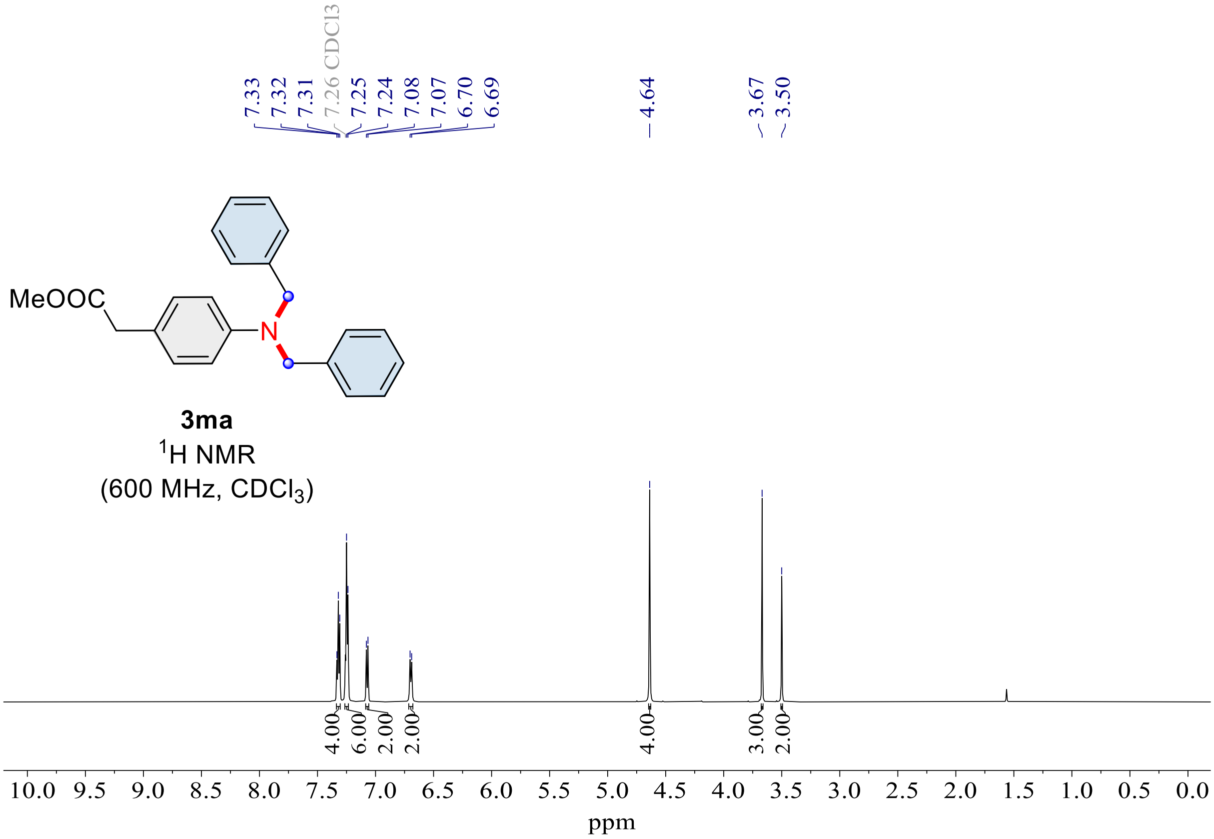
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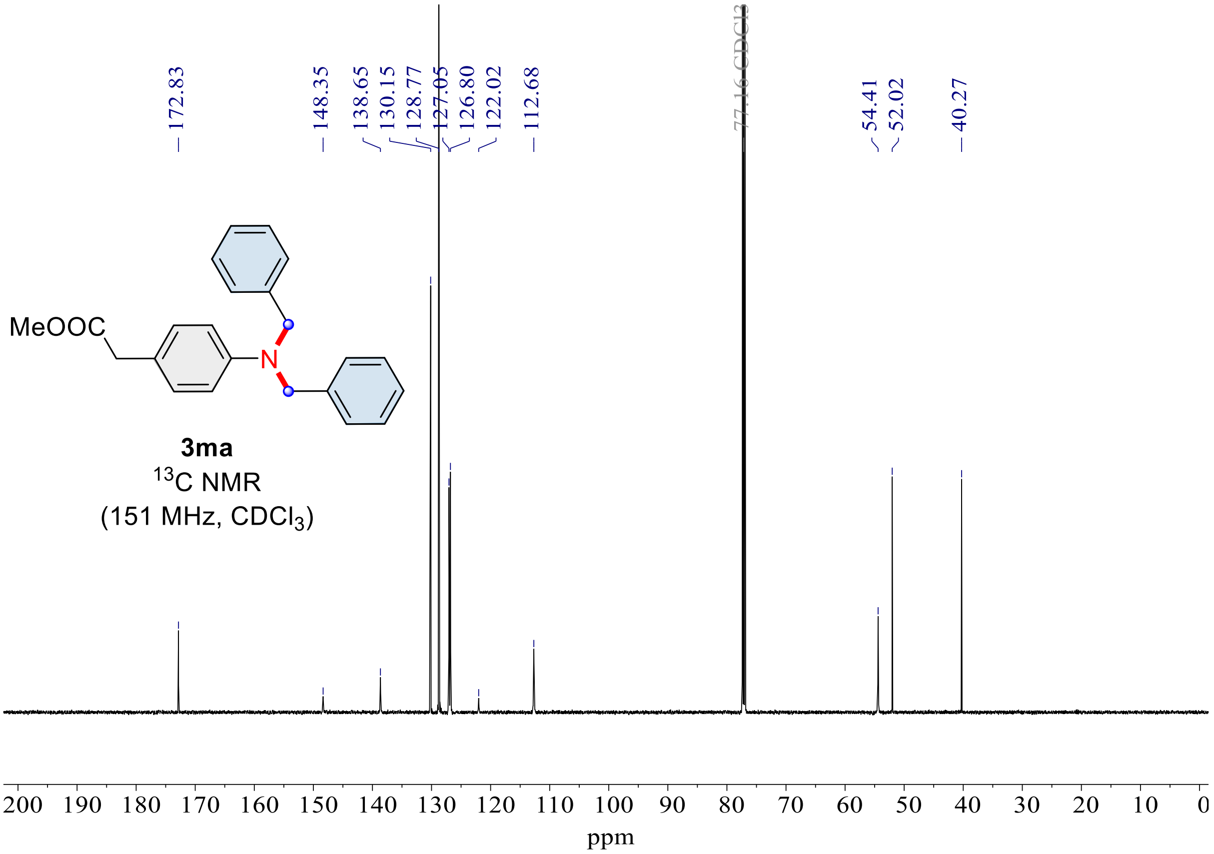
3.67
3.50
MeOOC
N
3ma
^{1}H NMR
(600 MHz, CDCl$_3$)
4.00
6.00
2.00
2.00
4.00
3.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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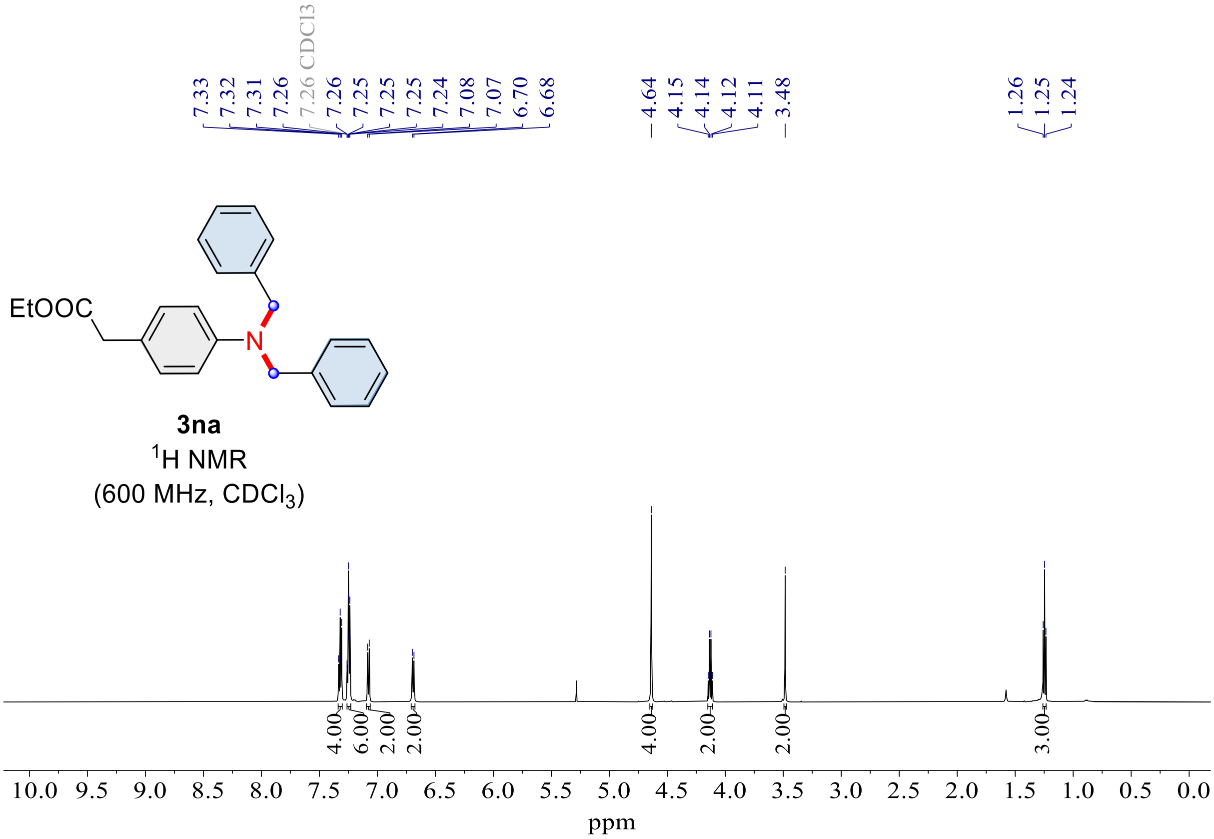
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6.68
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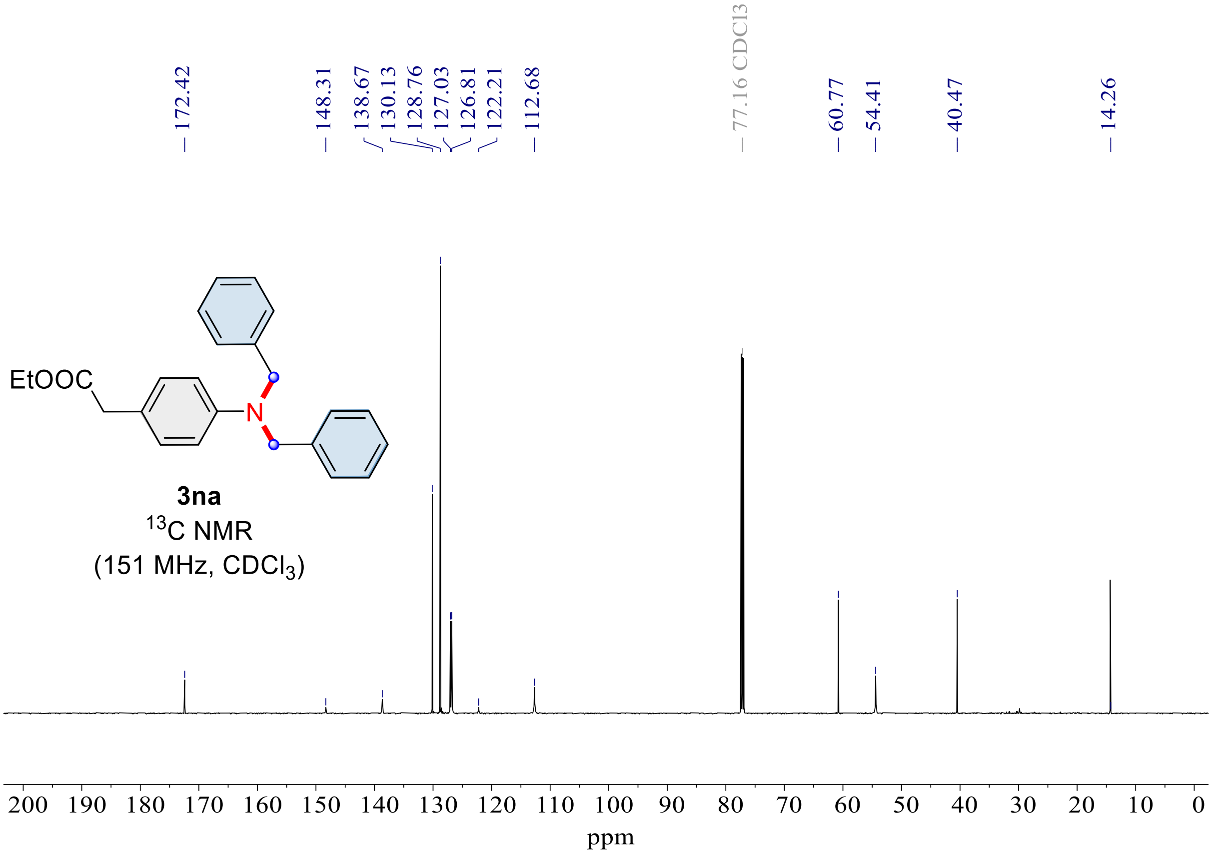
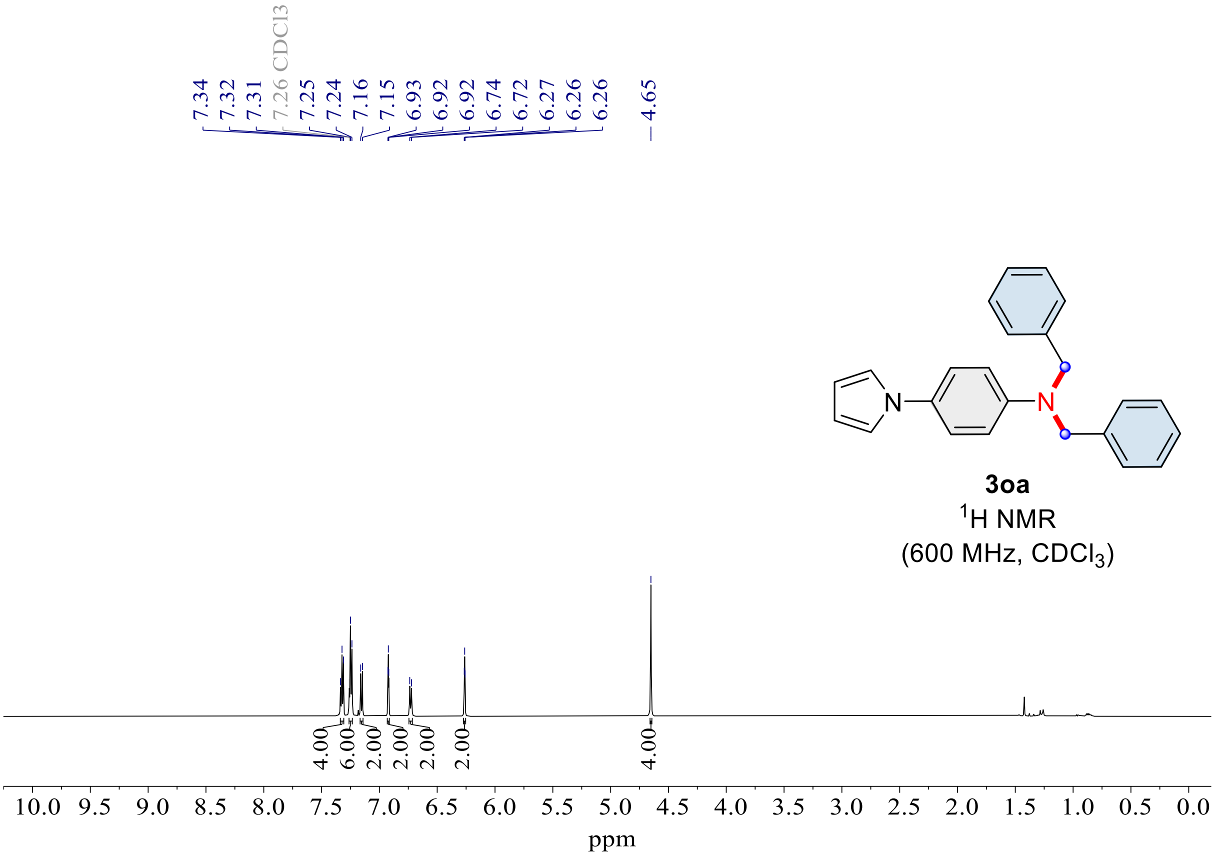
4.15
4.14
4.12
4.11
3.48
1.26
1.25
1.24
EtOOC
N
3na
^{1}H NMR
(600 MHz, $CDCl_3$)
4.00
6.00
2.00
2.00
4.00
2.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

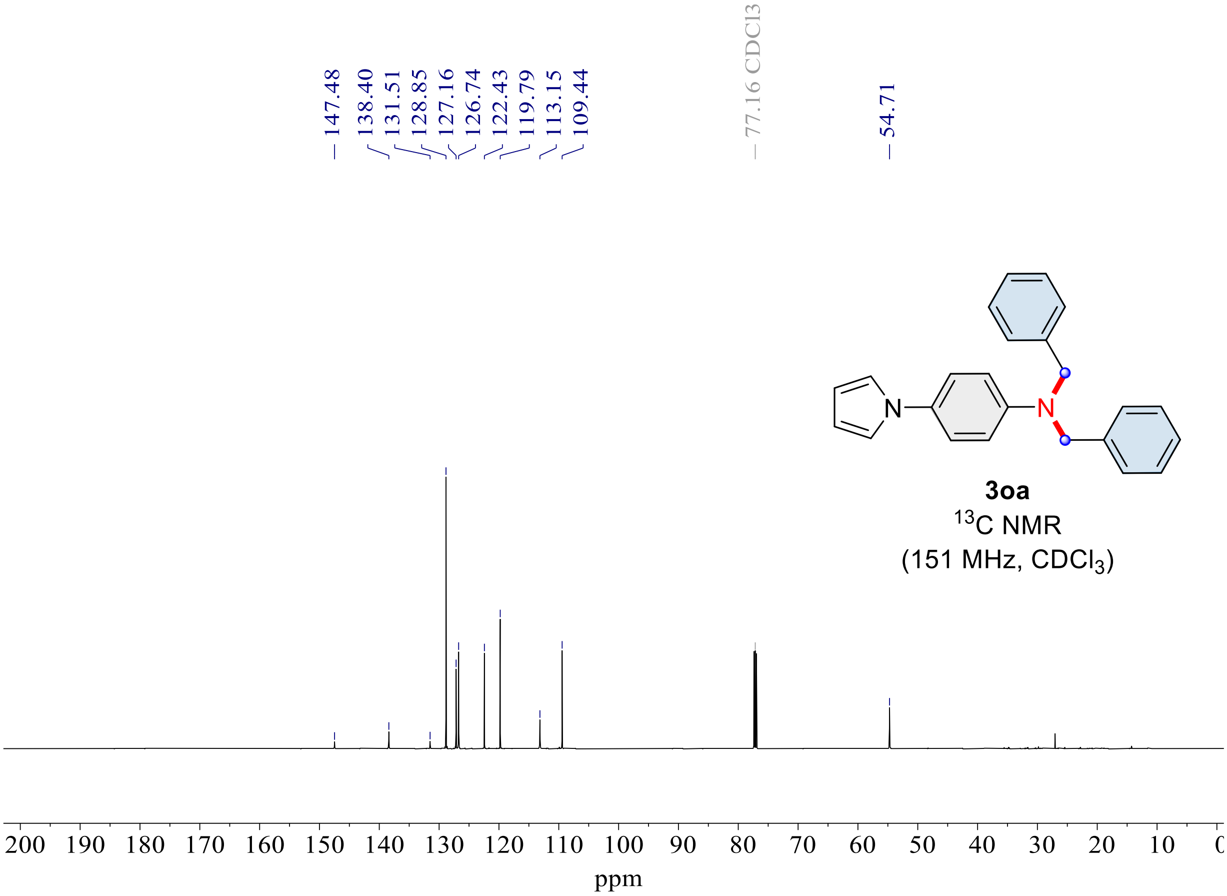

172.42
148.31
138.67
130.13
128.76
127.03
126.81
122.21
112.68
77.16 CDCl3
60.77
54.41
40.47
14.26
EtOOC
N
3na
^{13}C NMR
(151 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3oa

^{1}H NMR

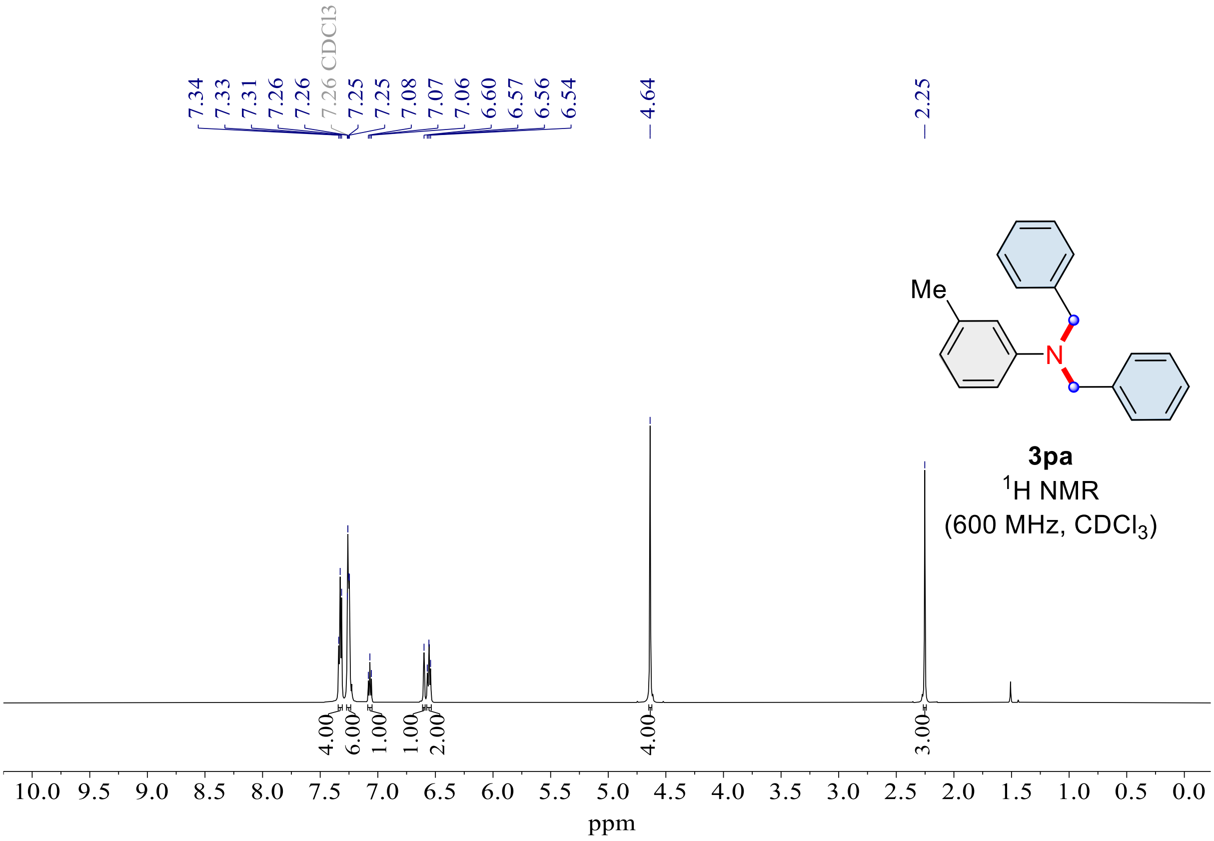
(600 MHz, $CDCl_3$)



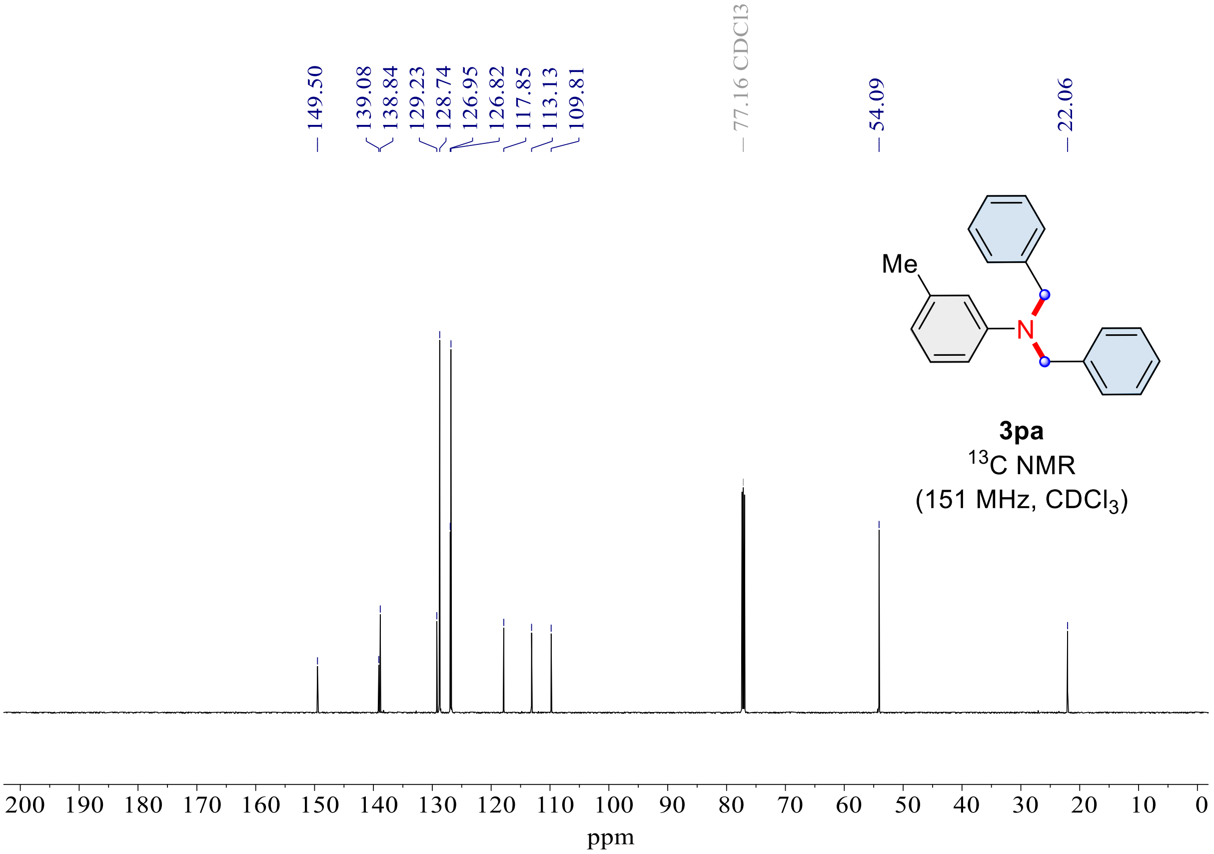
3oa

^{13}C NMR

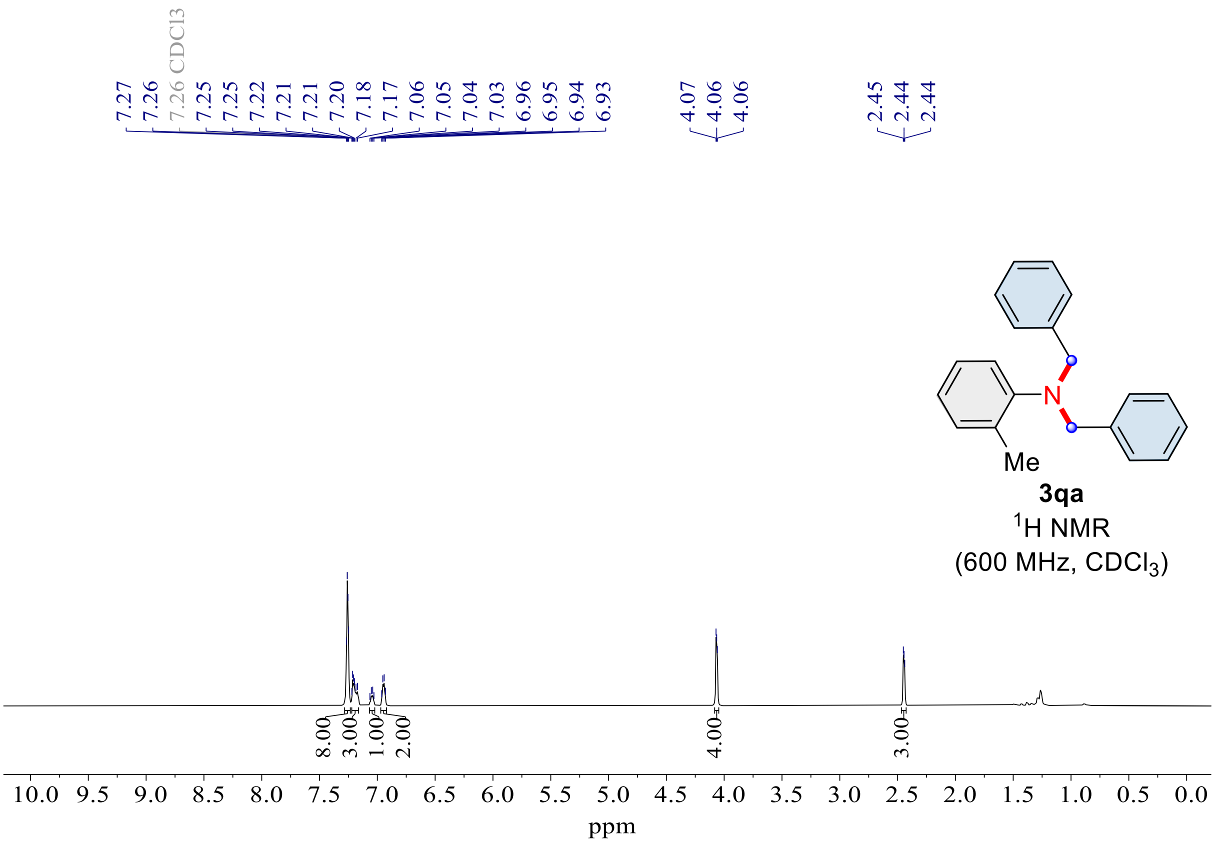
(151 MHz, $CDCl_3$)



3pa
^{1}H NMR
(600 MHz, $CDCl_3$)



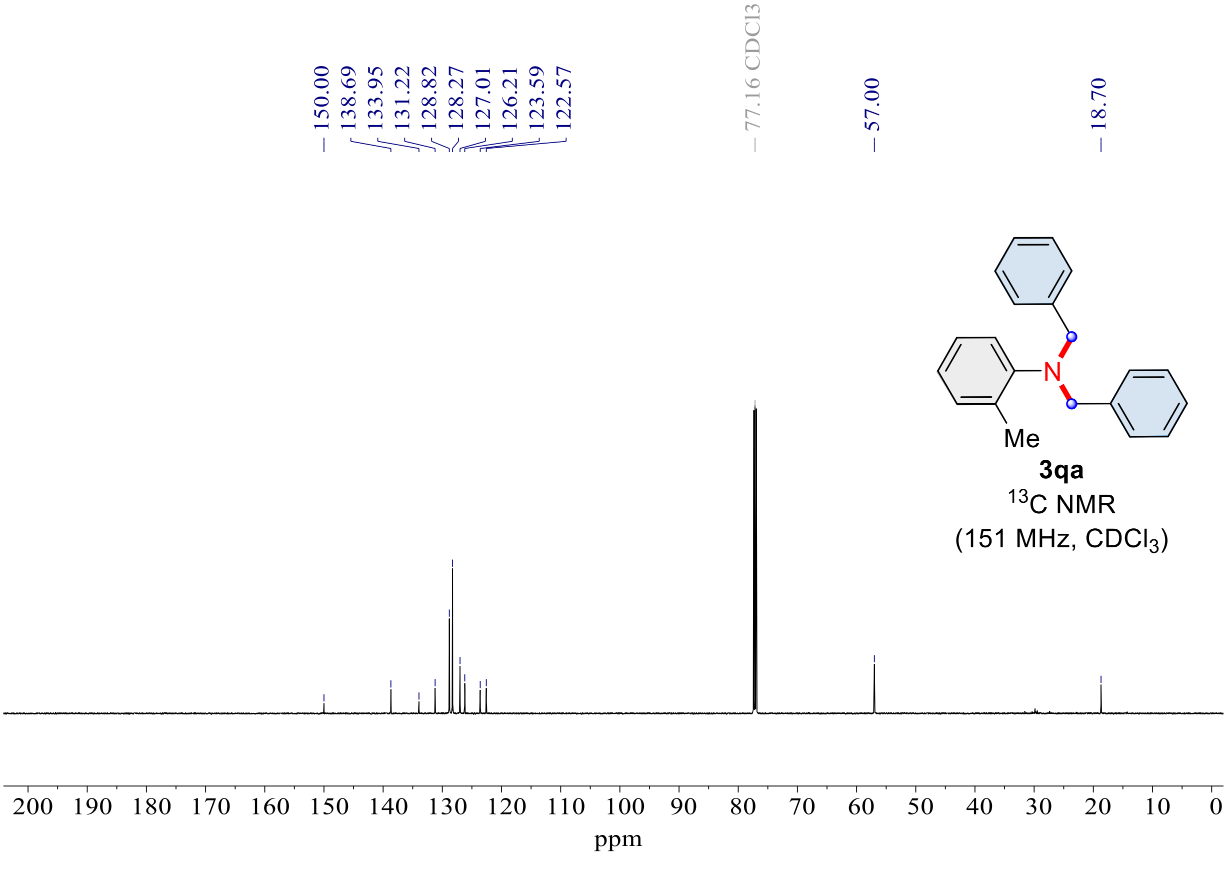
3pa
^{13}C NMR
(151 MHz, $CDCl_3$)



3qa

^{1}H NMR

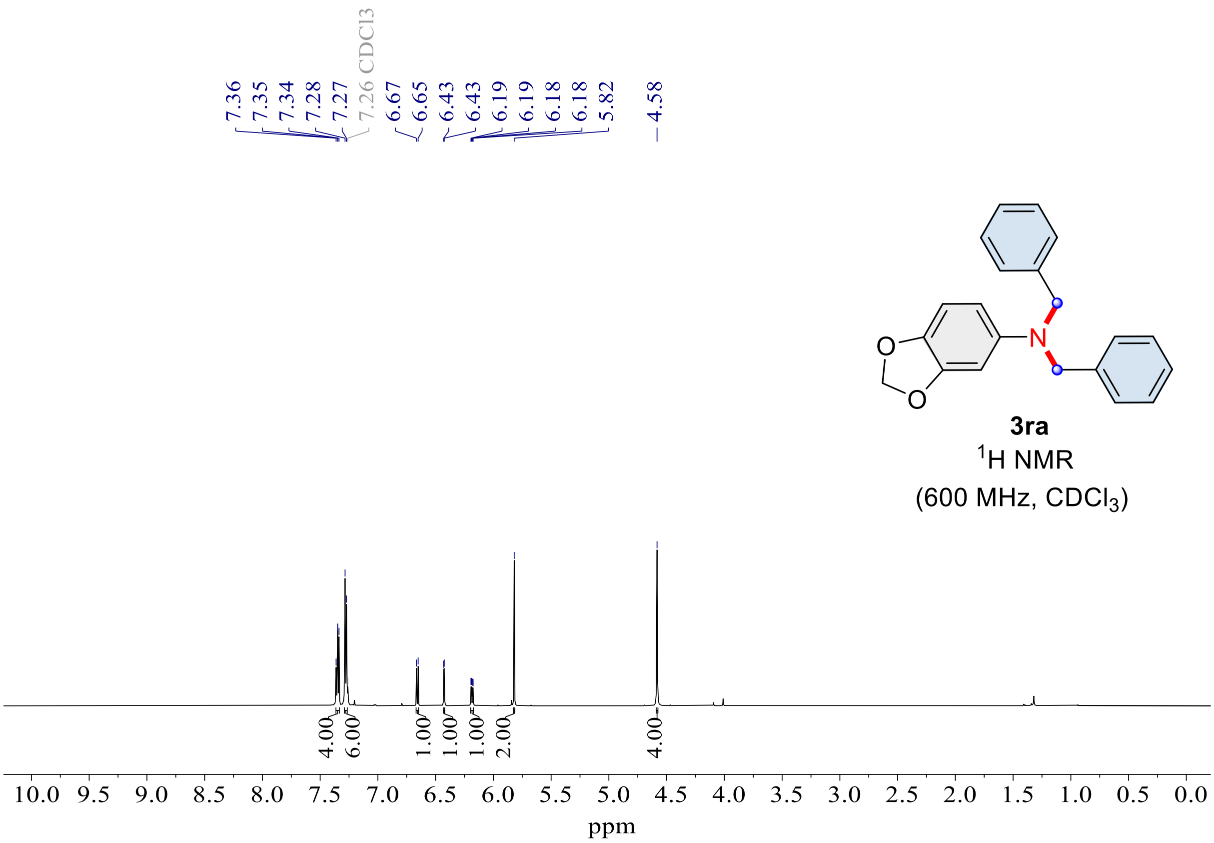
(600 MHz, $CDCl_3$)



3qa

^{13}C NMR

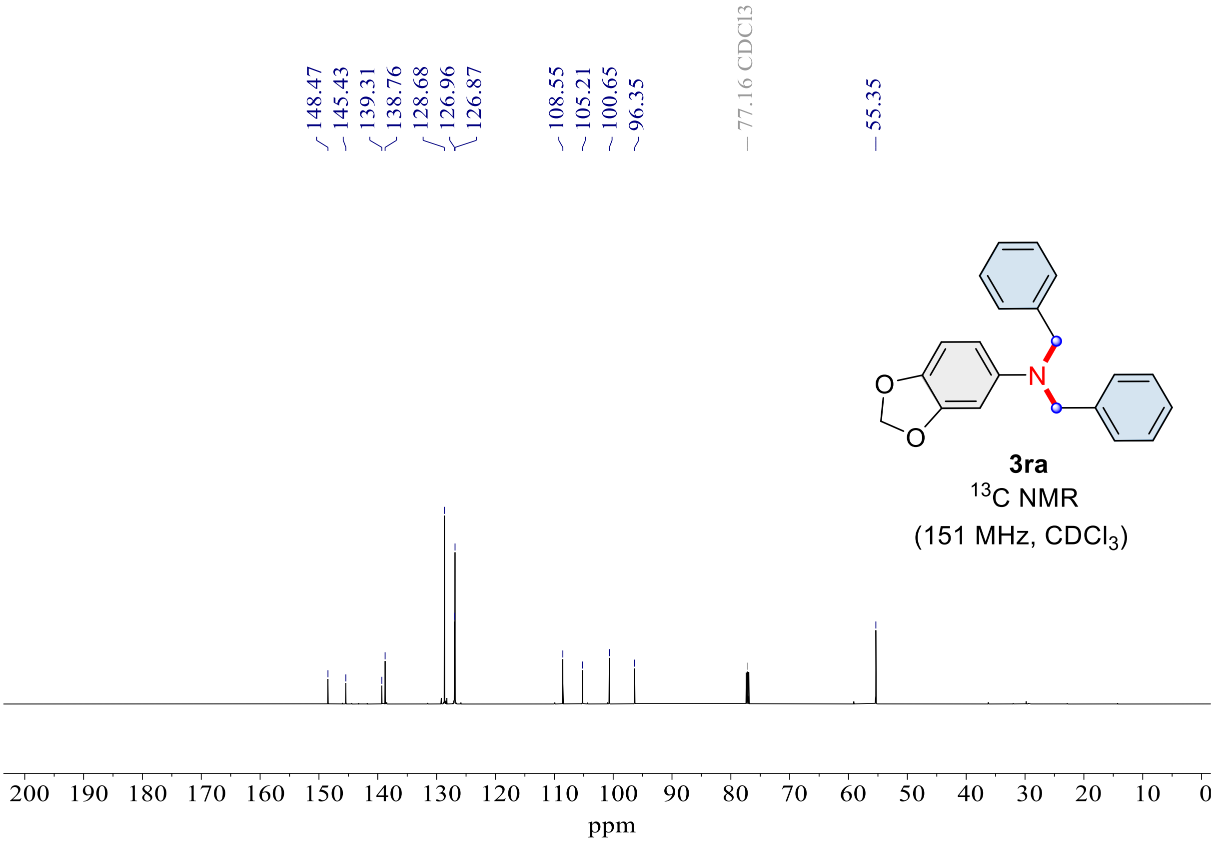
(151 MHz, $CDCl_3$)



3ra

^{1}H NMR

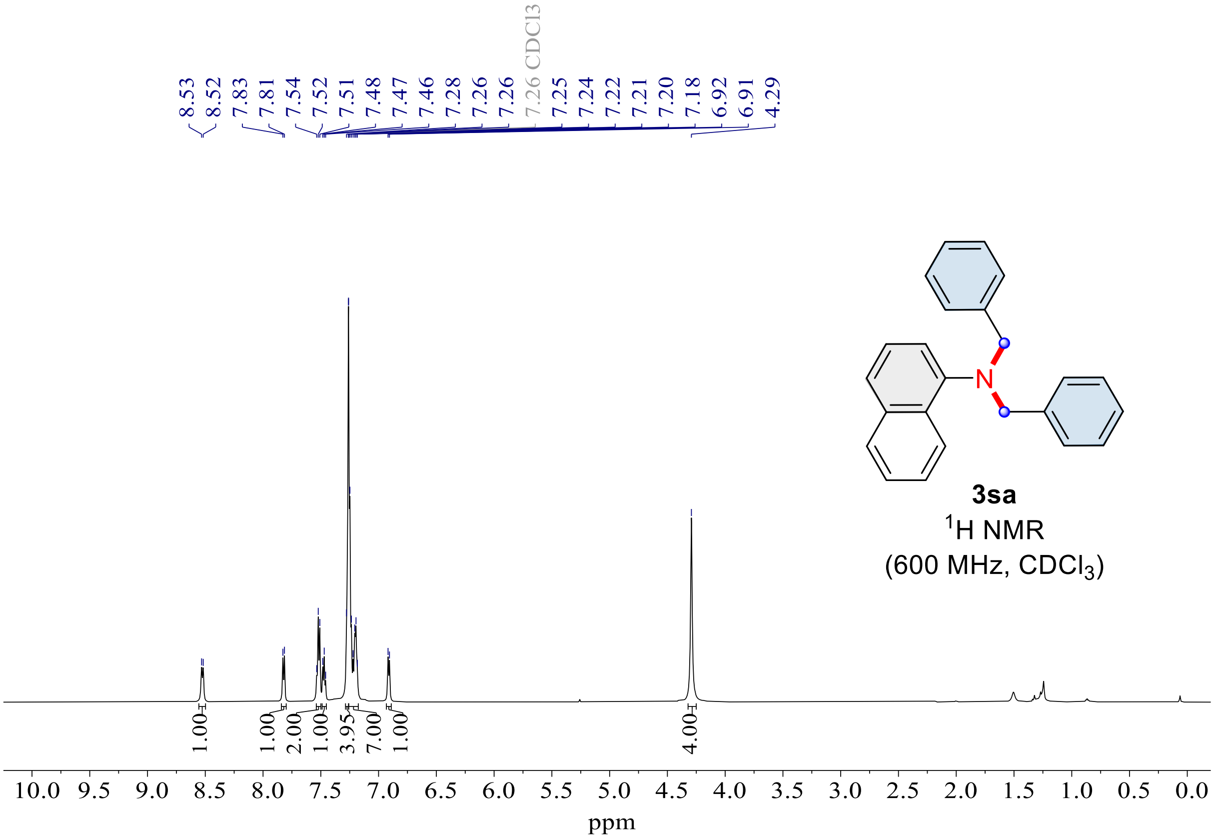
(600 MHz, $CDCl_3$)

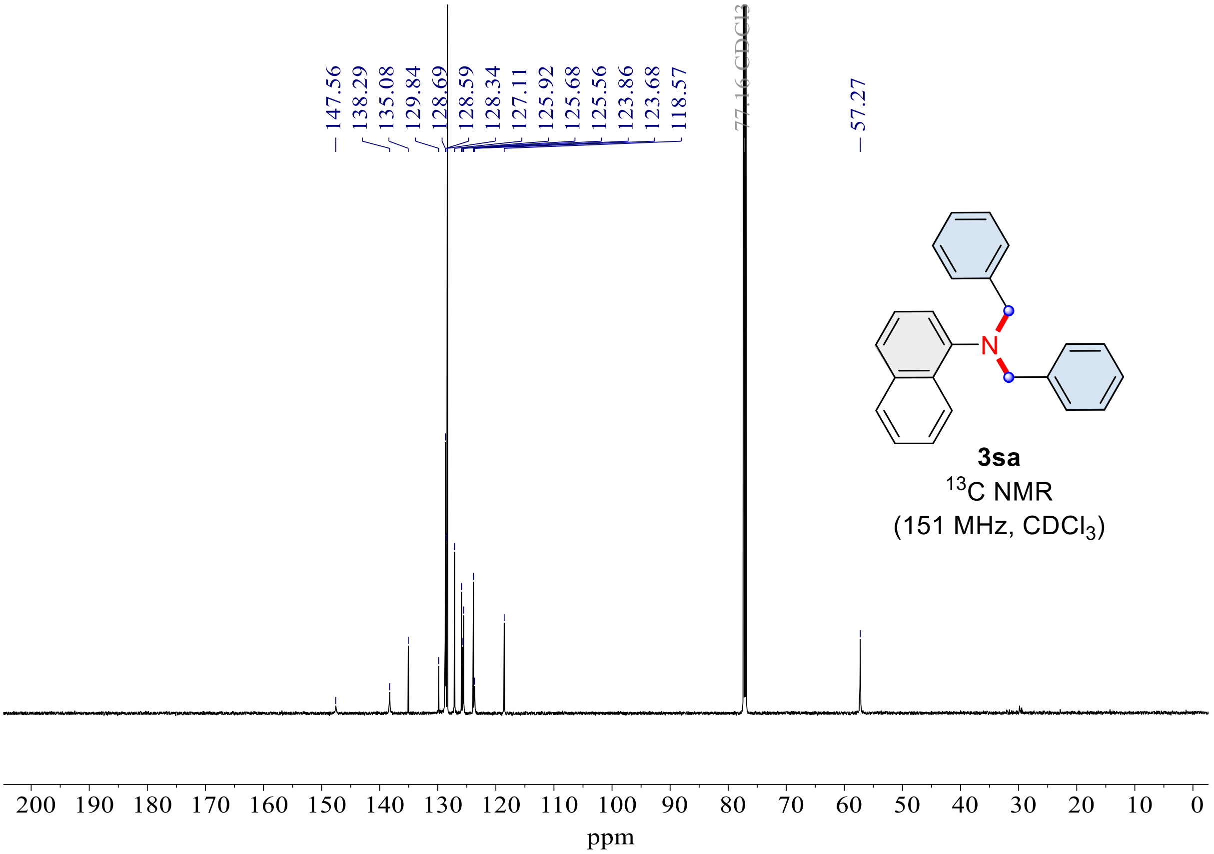


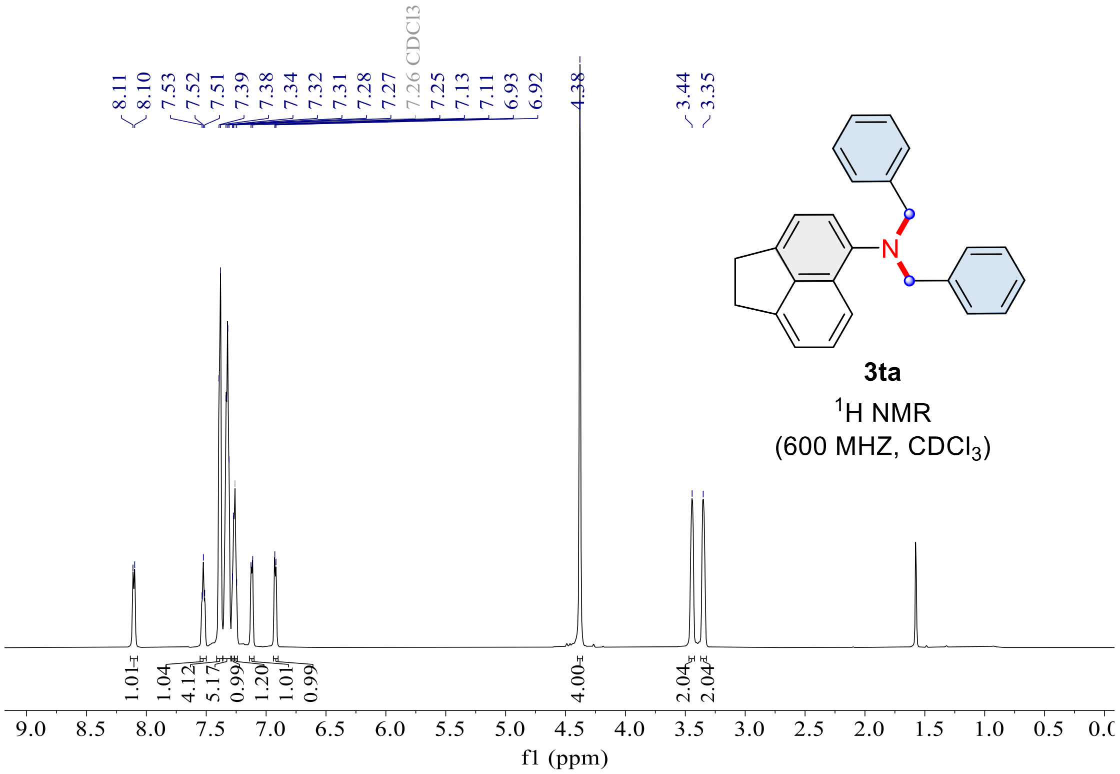
3ra

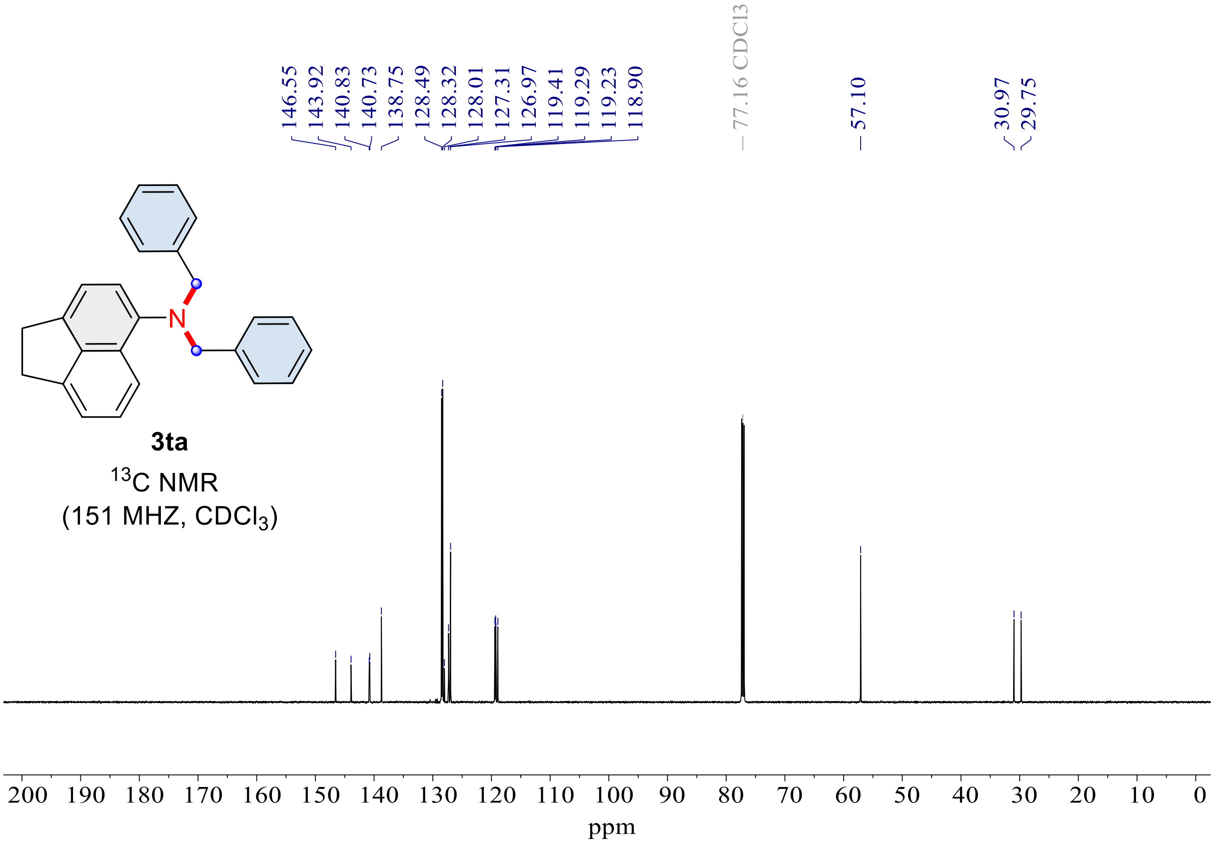
^{13}C NMR

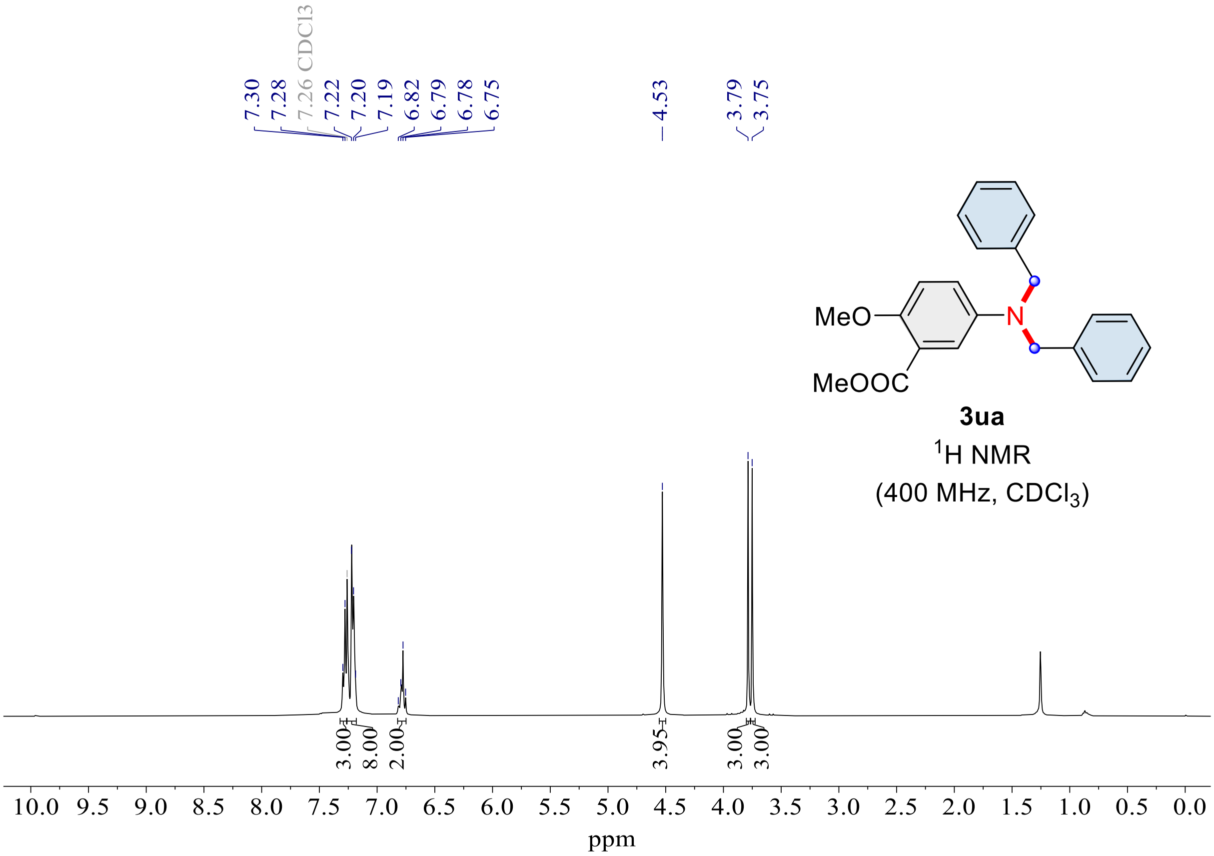
(151 MHz, $CDCl_3$)

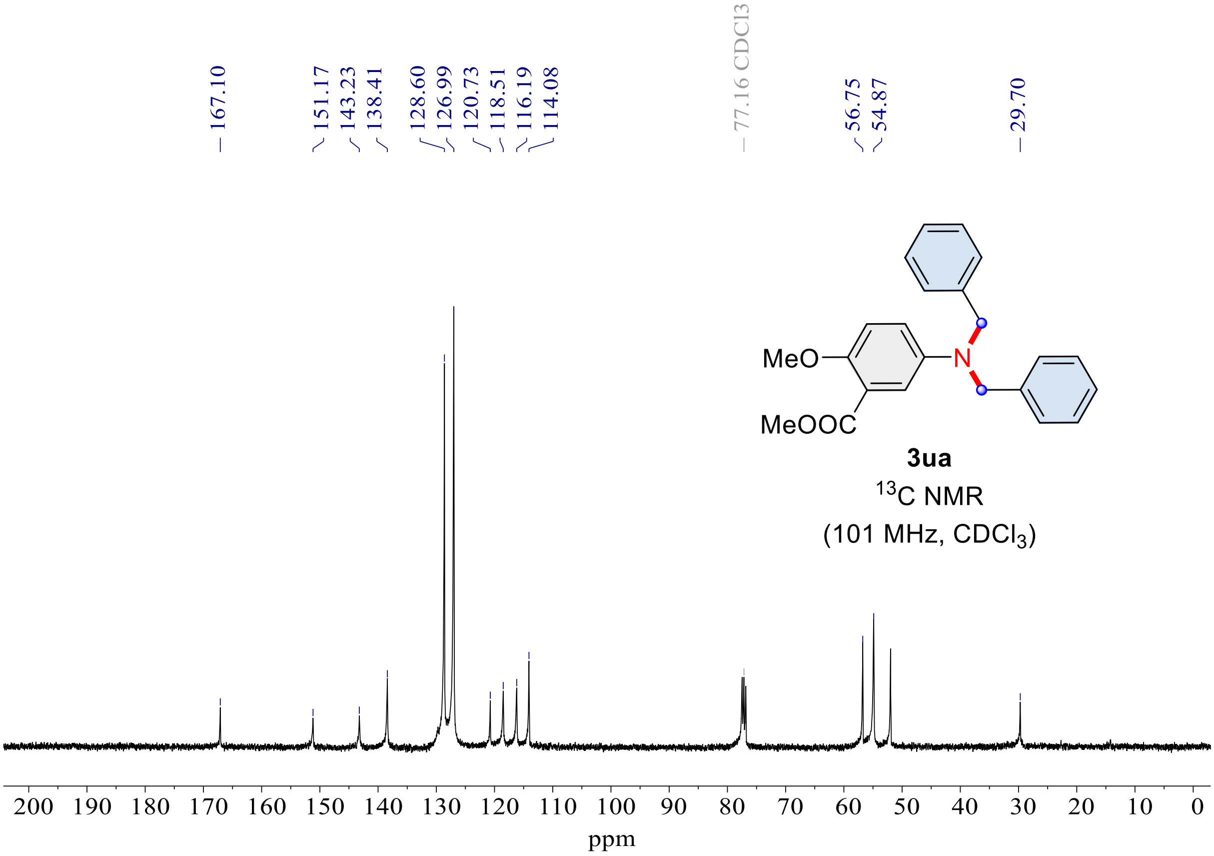

8.53
8.52
7.83
7.81
7.54
7.52
7.51
7.48
7.47
7.46
7.28
7.26
7.26
7.26 CDCl3
7.25
7.24
7.22
7.21
7.20
7.18
6.92
6.91
4.29
N
3sa
^{1}H NMR
(600 MHz, $CDCl_3$)
1.00
1.00
2.00
1.00
3.95
7.00
1.00
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

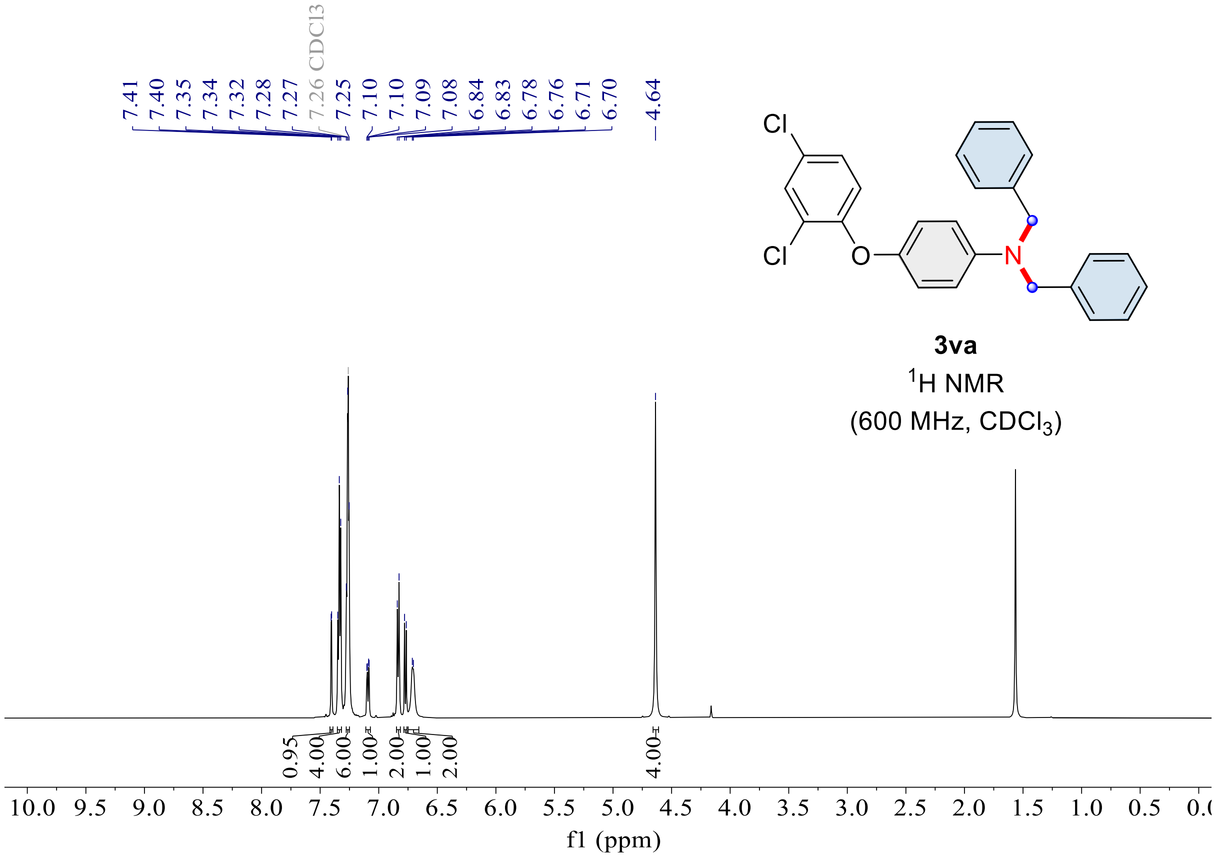

147.56
138.29
135.08
129.84
128.69
128.59
128.34
127.11
125.92
125.68
125.56
123.86
123.68
118.57
77.16 CDCl3
57.27
N
3sa
^{13}C NMR
(151 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.11
8.10
7.53
7.52
7.51
7.39
7.38
7.34
7.32
7.31
7.28
7.27
7.26 CDCl3
7.25
7.13
7.11
6.93
6.92
4.38
3.44
3.35
N
3ta
^{1}H NMR
(600 MHZ, $CDCl_3$)
1.01
1.04
4.12
5.17
0.99
1.20
1.01
0.99
4.00
2.04
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.55
143.92
140.83
140.73
138.75
128.49
128.32
128.01
127.31
126.97
119.41
119.29
119.23
118.90
77.16 CDCl3
57.10
30.97
29.75
N
3ta
^{13}C NMR
(151 MHZ, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.30
7.28
7.26 CDCl3
7.22
7.20
7.19
6.82
6.79
6.78
6.75
4.53
3.79
3.75
MeO
N
MeOOC
3ua
^{1}H NMR
(400 MHz, CDCl$_3$)
3.00
8.00
2.00
3.95
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

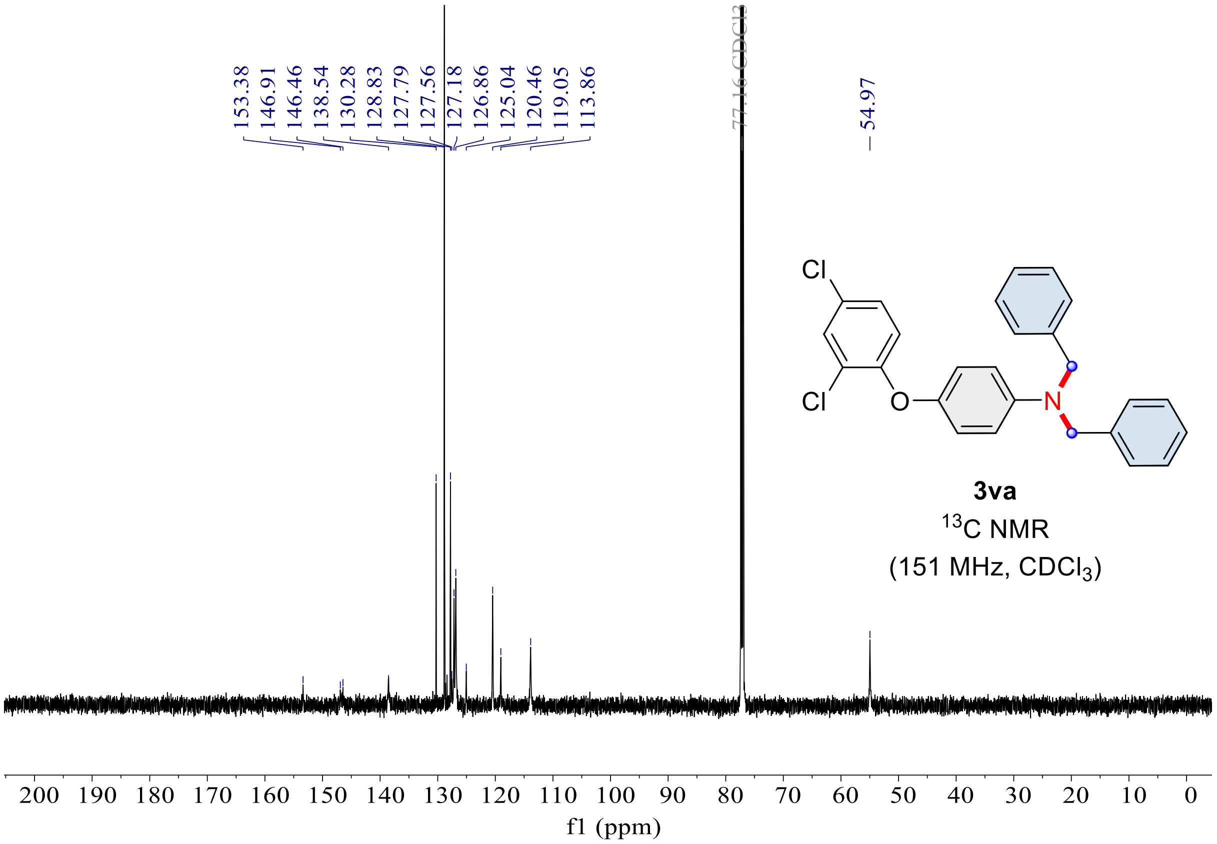

167.10
151.17
143.23
138.41
128.60
126.99
120.73
118.51
116.19
114.08
77.16 CDCl3
56.75
54.87
29.70
MeO
N
MeOOC
3ua
^{13}C NMR
(101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



3va

^{1}H NMR

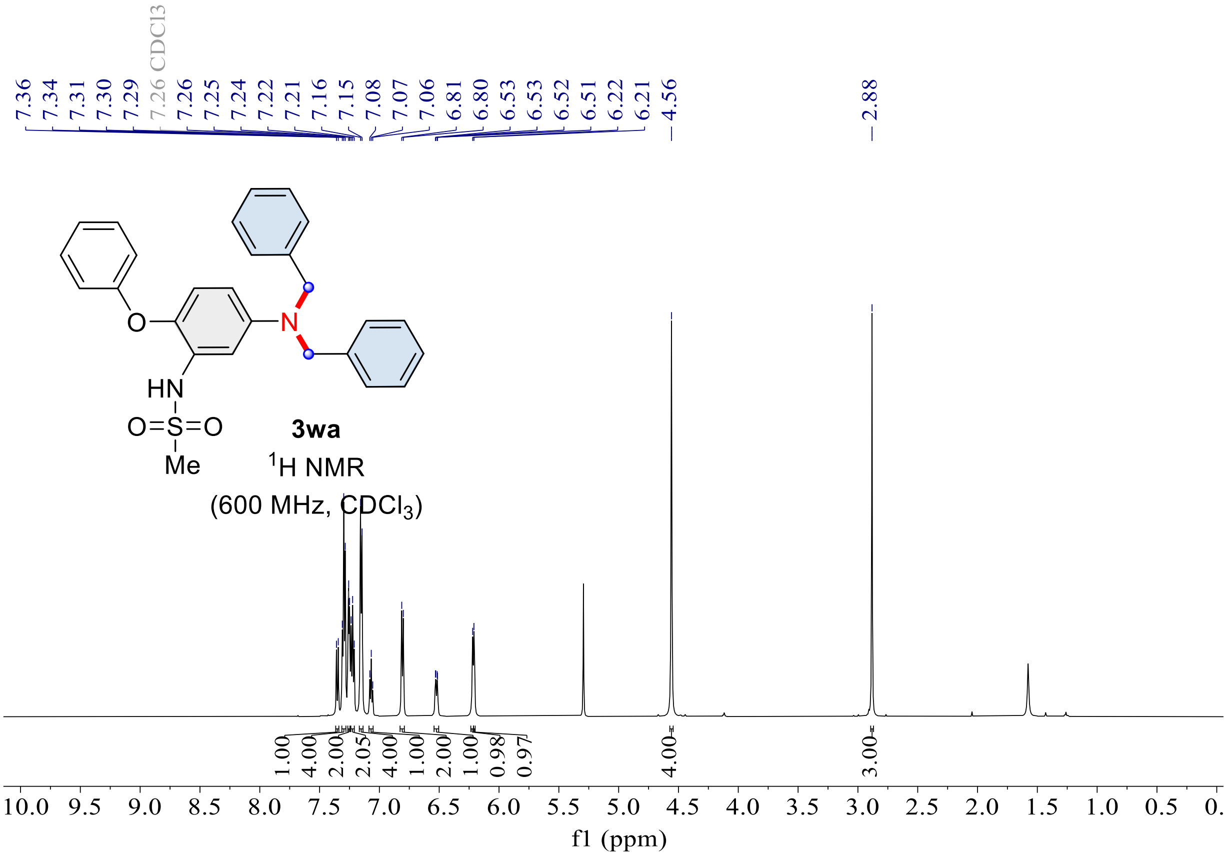
(600 MHz, $CDCl_3$)



3va

^{13}C NMR

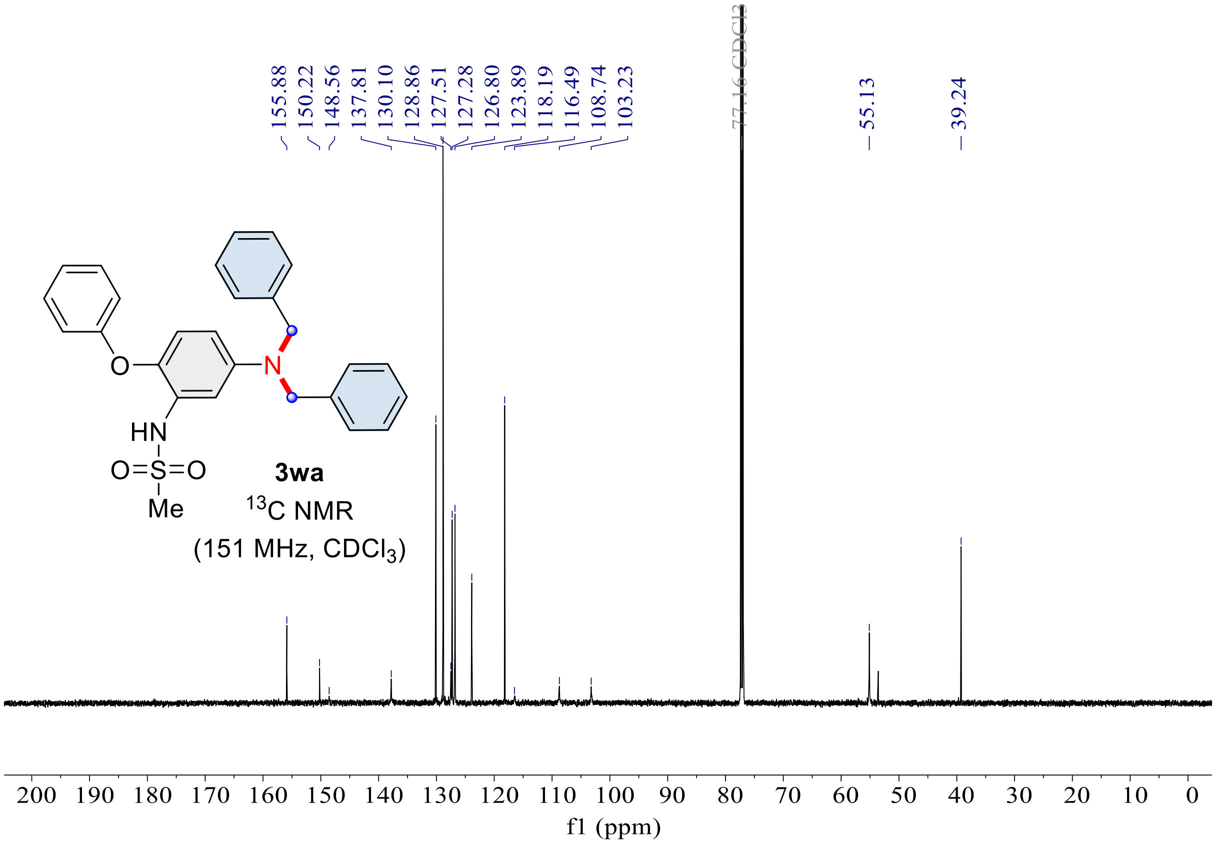
(151 MHz, $CDCl_3$)



3wa

^{1}H NMR

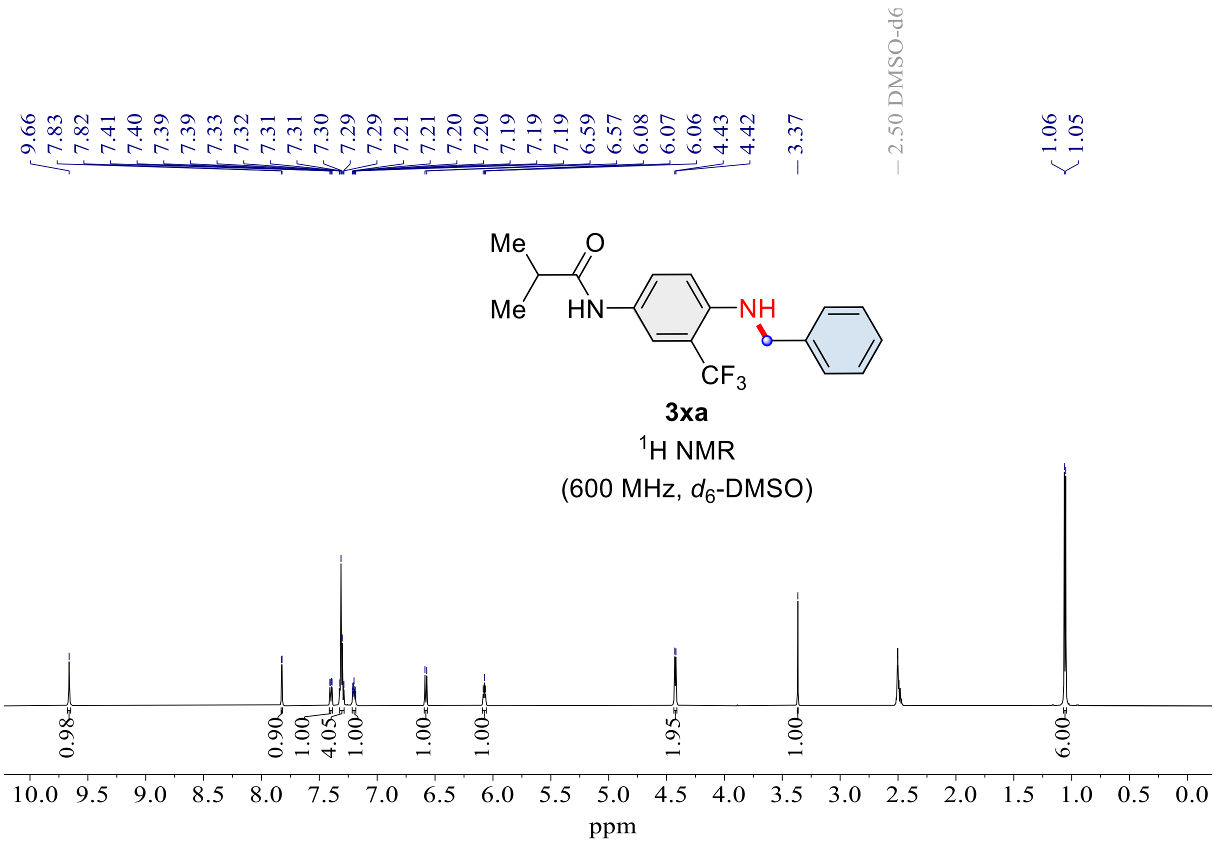
(600 MHz, $CDCl_3$)



3wa

^{13}C NMR

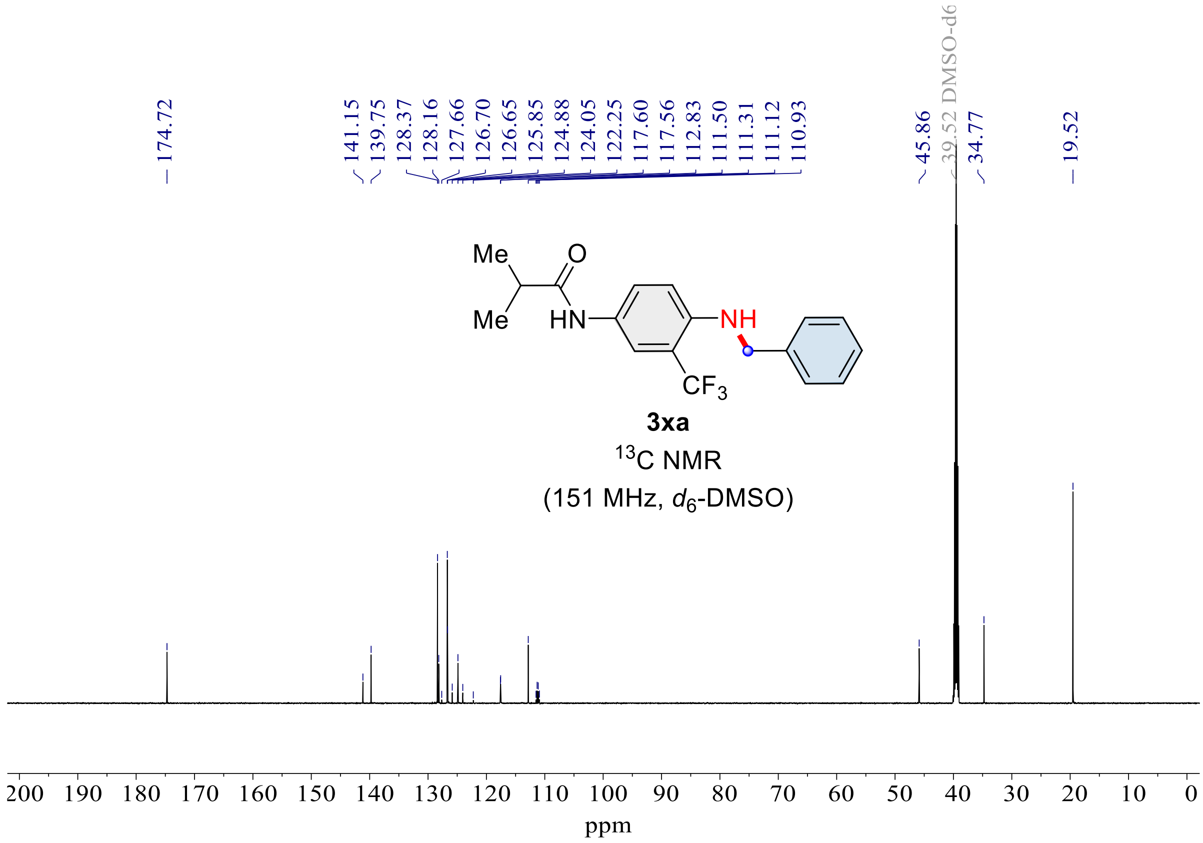
(151 MHz, $CDCl_3$)



3xa

^{1}H NMR

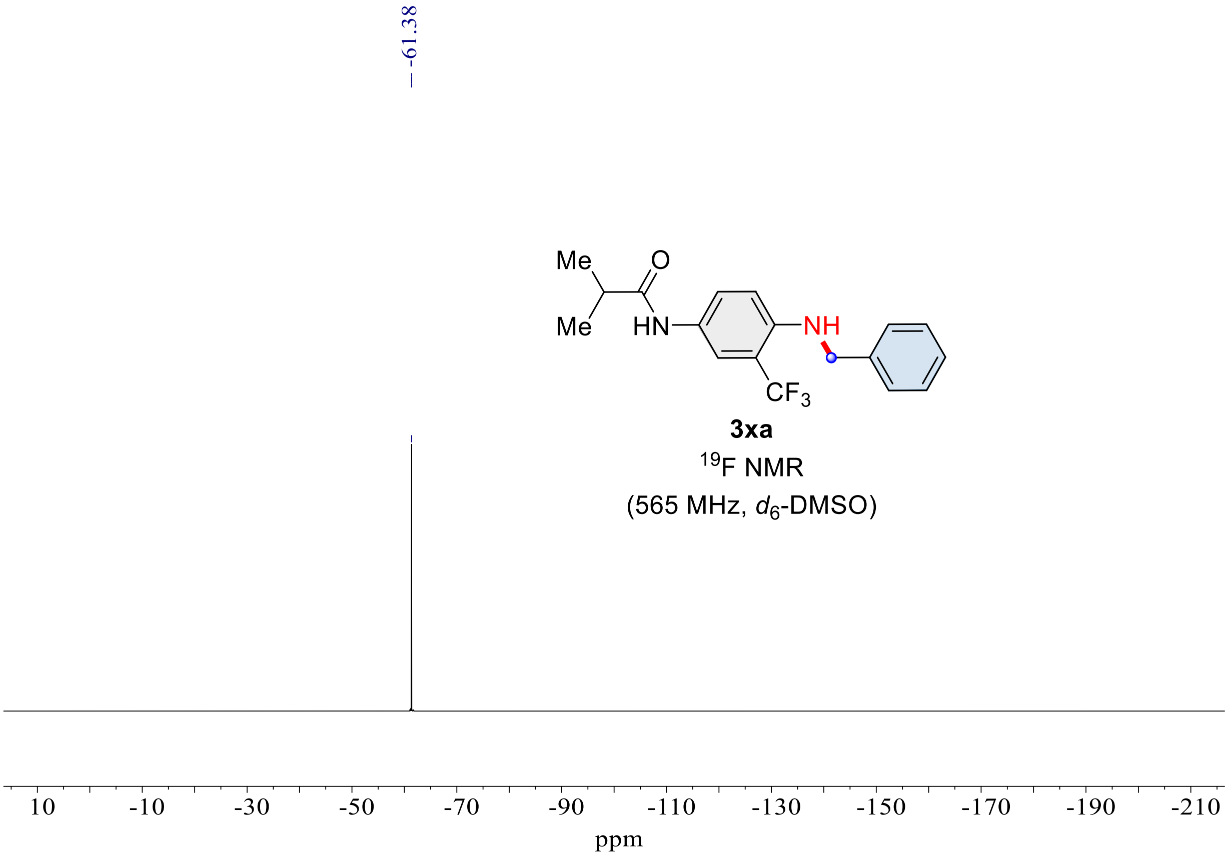
(600 MHz, d_6-DMSO)

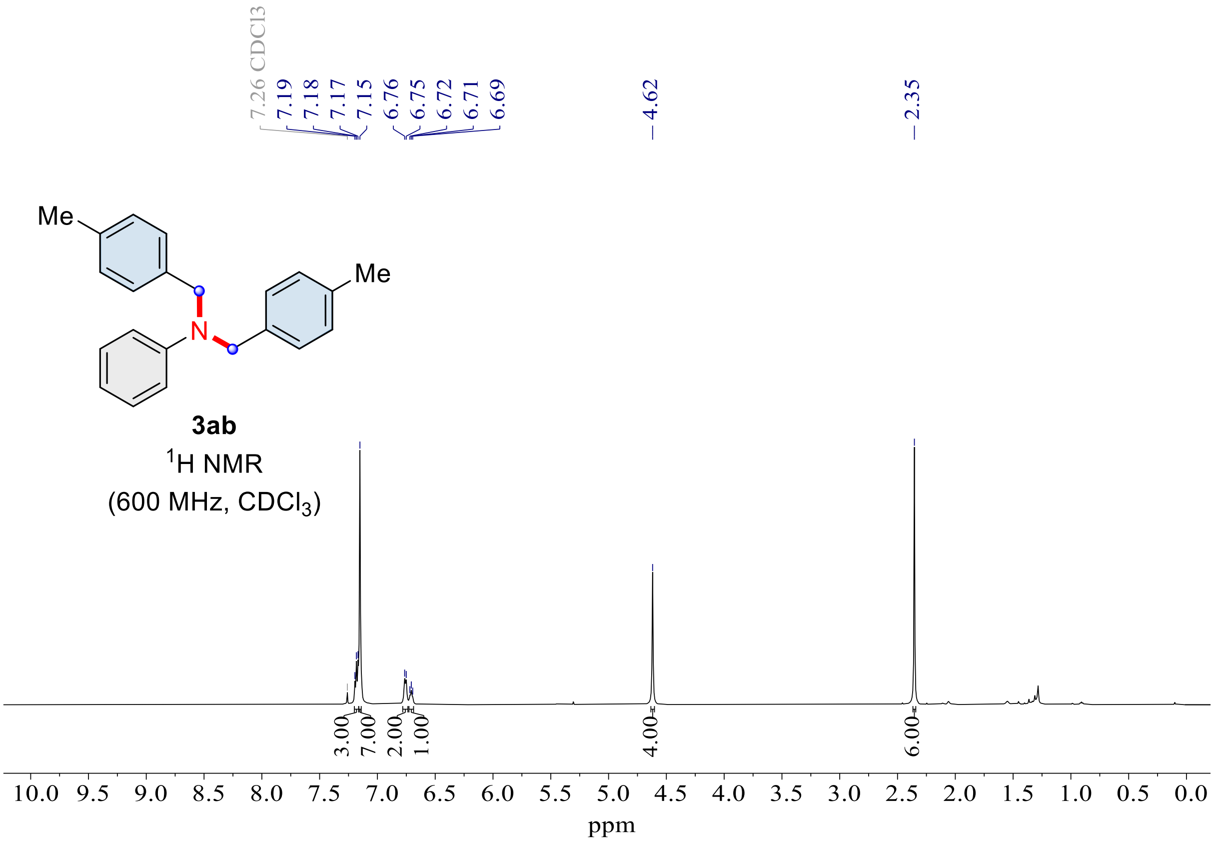


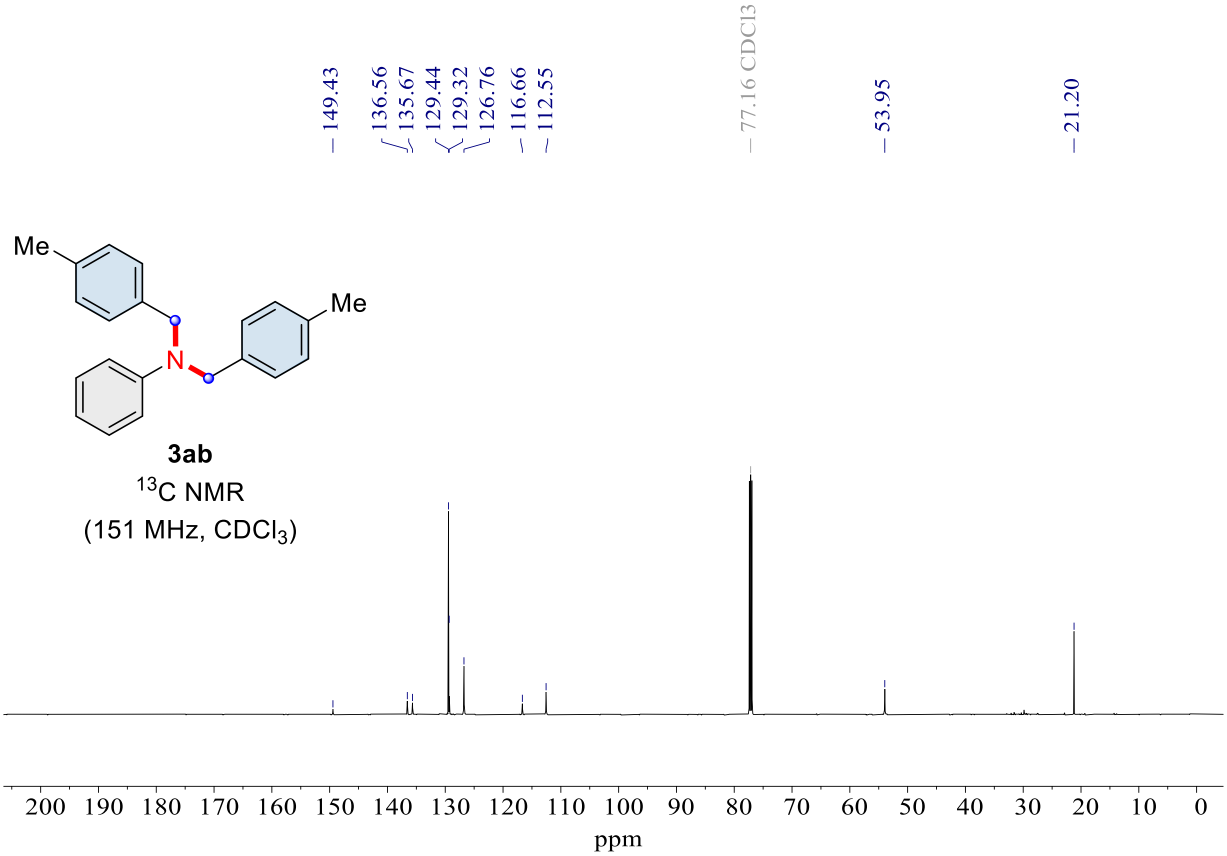
3xa

^{13}C NMR

(151 MHz, d_6-DMSO)


-61.38
Me
O
Me
HN
NH
CF$_3$
3xa
^{19}F NMR
(565 MHz, d_6-DMSO)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
ppm

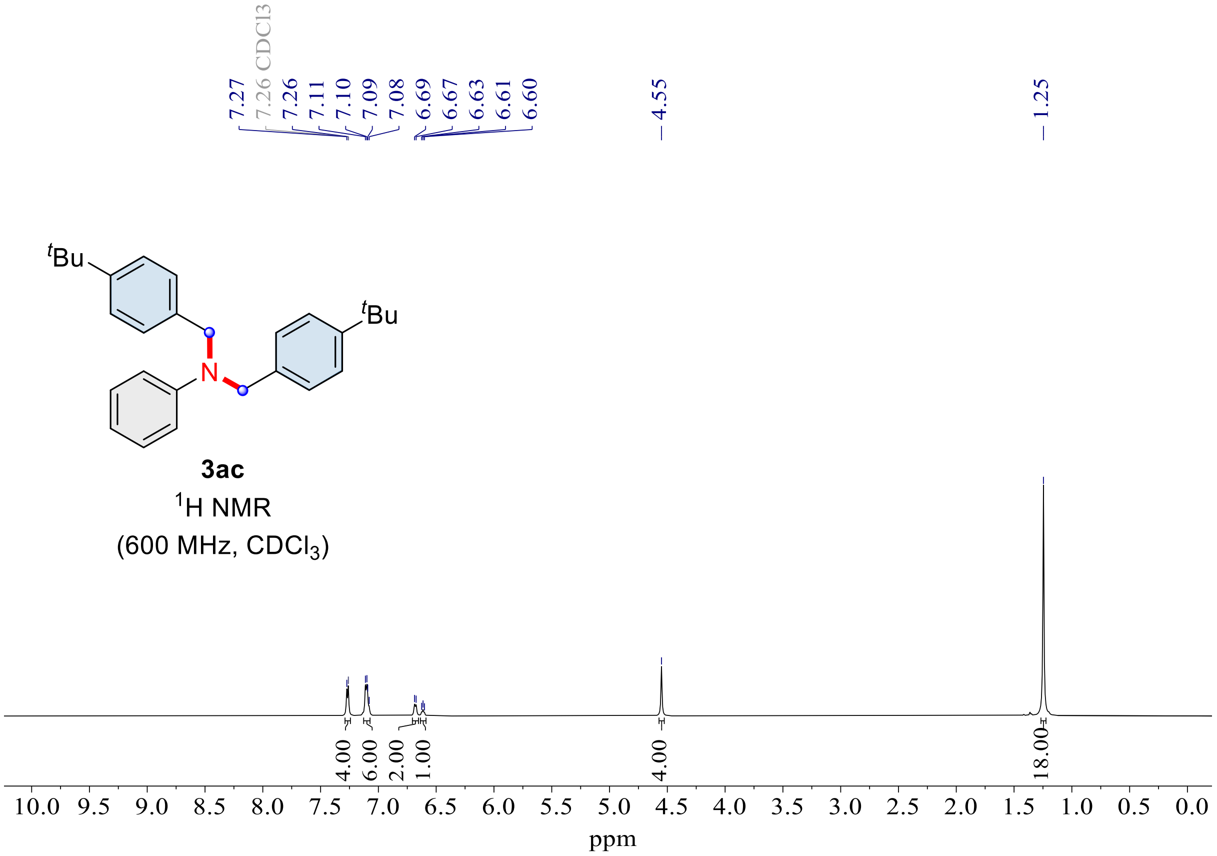

7.26 CDCl3
7.19
7.18
7.17
7.15
6.76
6.75
6.72
6.71
6.69
4.62
2.35
Me
Me
N
3ab
^{1}H NMR
(600 MHz, CDCl$_3$)
3.00
7.00
2.00
1.00
4.00
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



3ab

^{13}C NMR

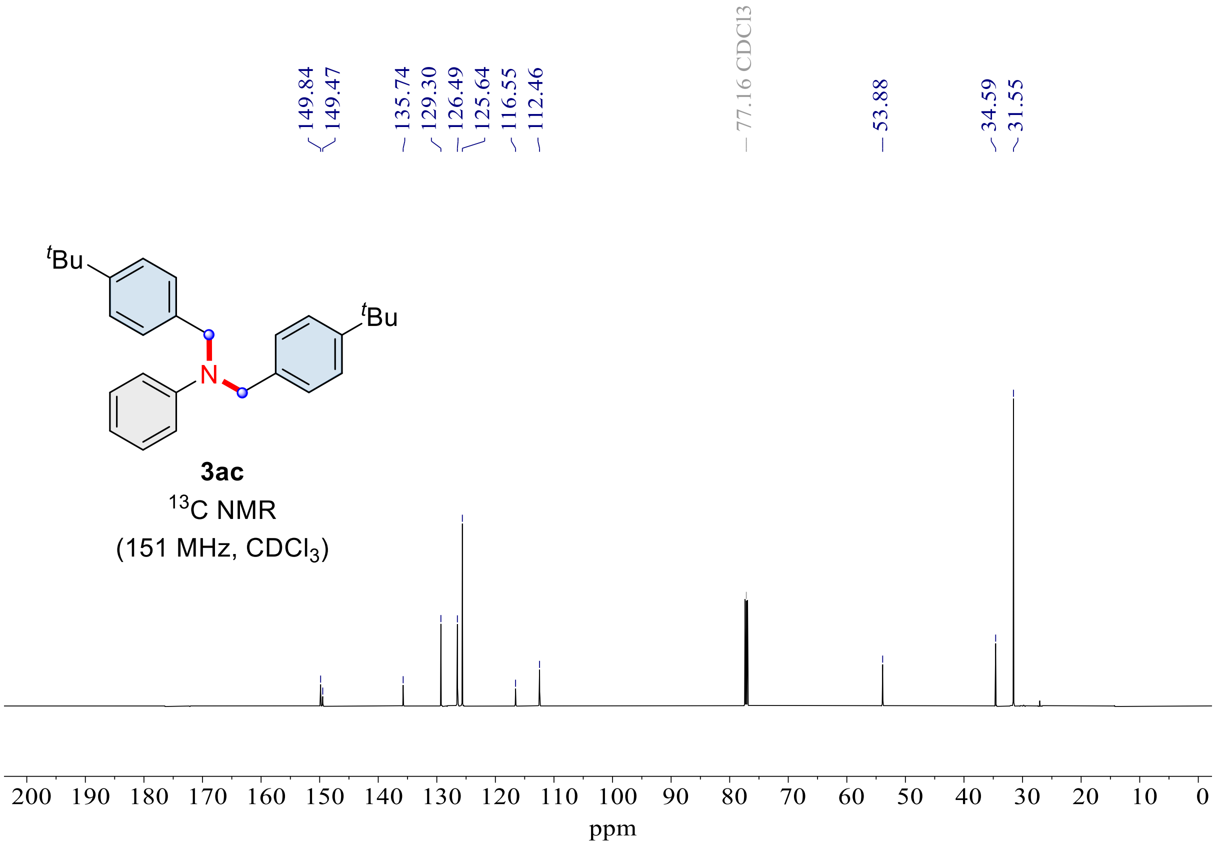
(151 MHz, $CDCl_3$)



3ac

^{1}H NMR

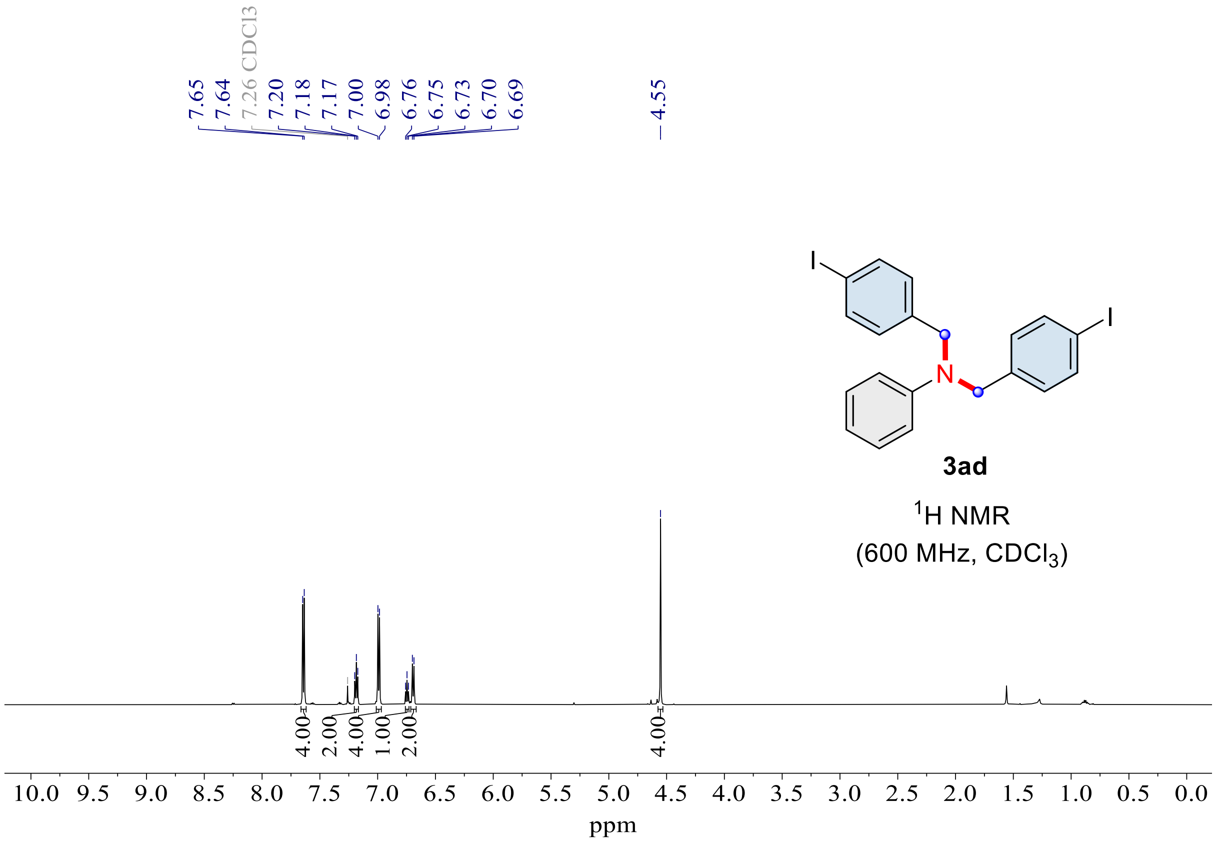
(600 MHz, $CDCl_3$)



3ac

^{13}C NMR

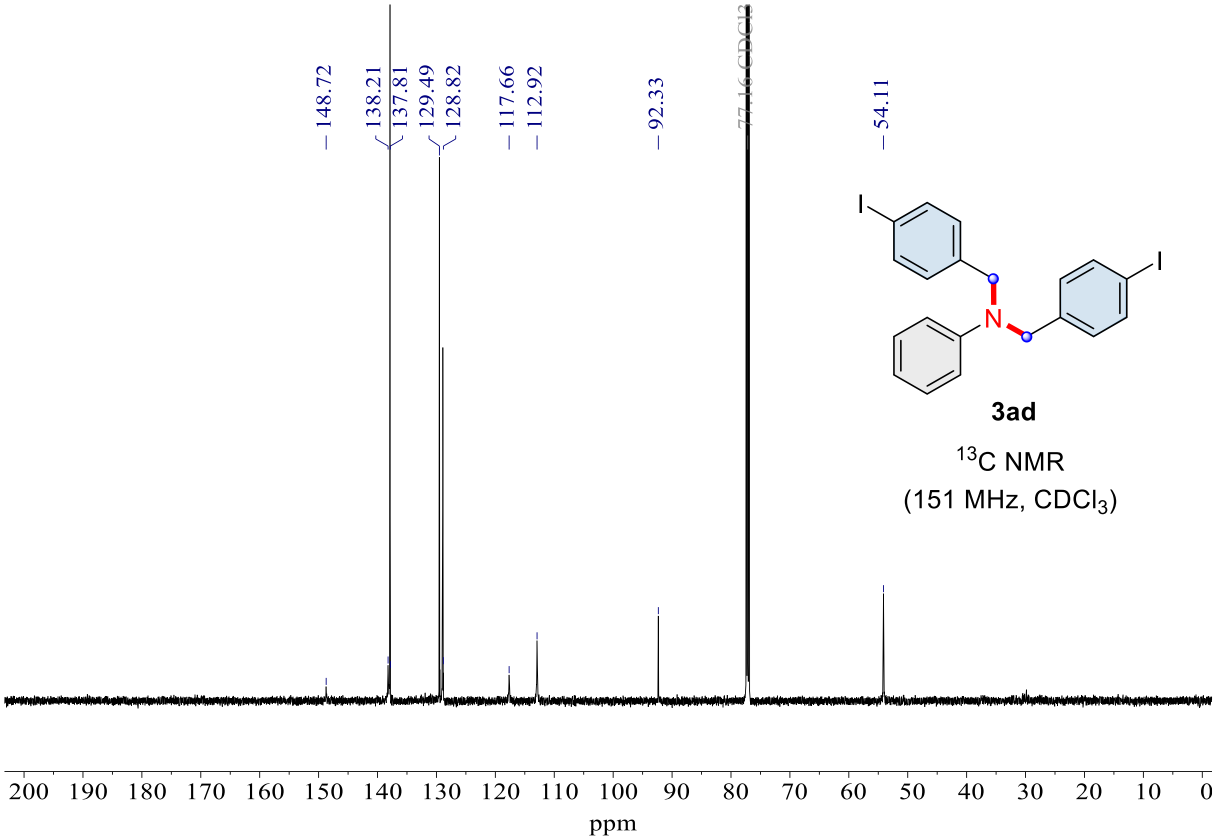
(151 MHz, CDCl$_3$)



3ad

^{1}H NMR

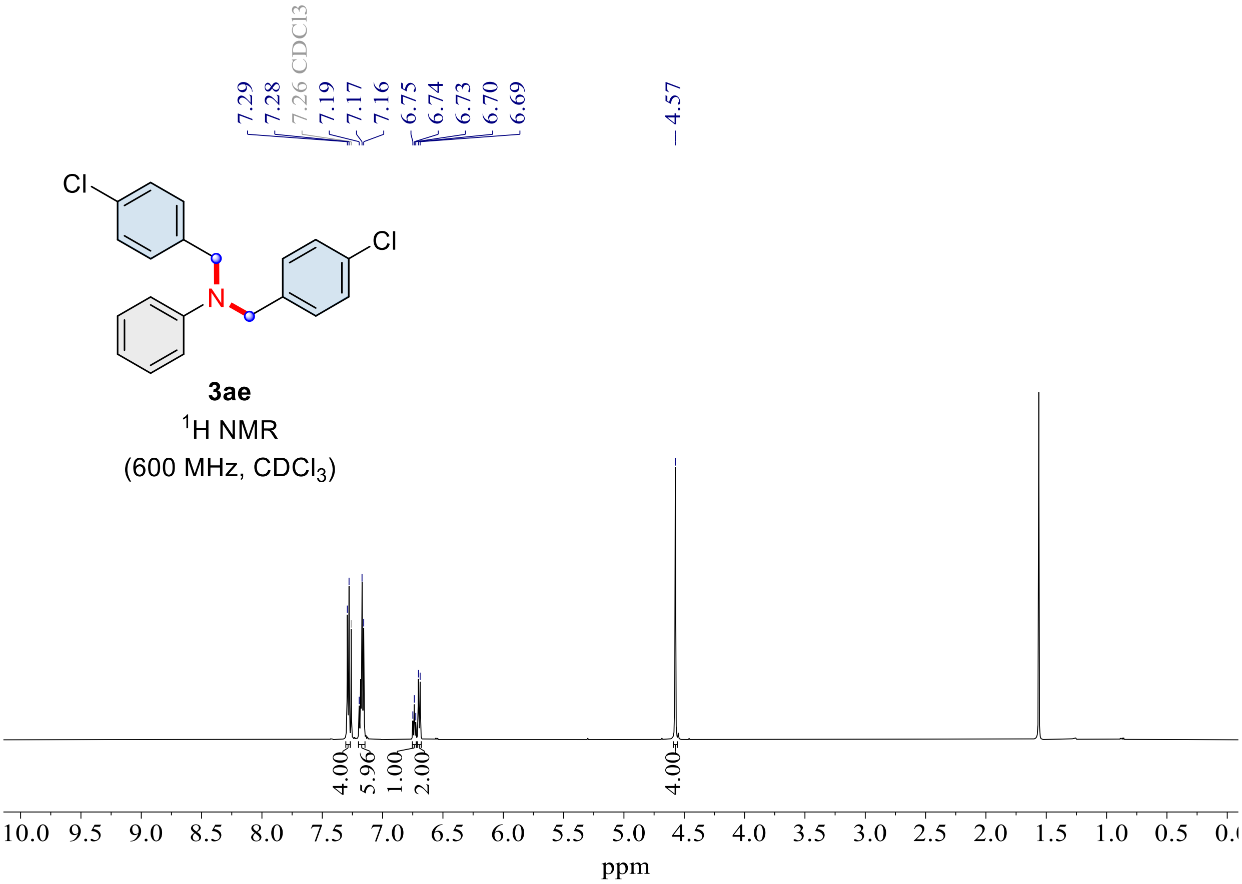
(600 MHz, CDCl$_3$)



3ad

^{13}C NMR

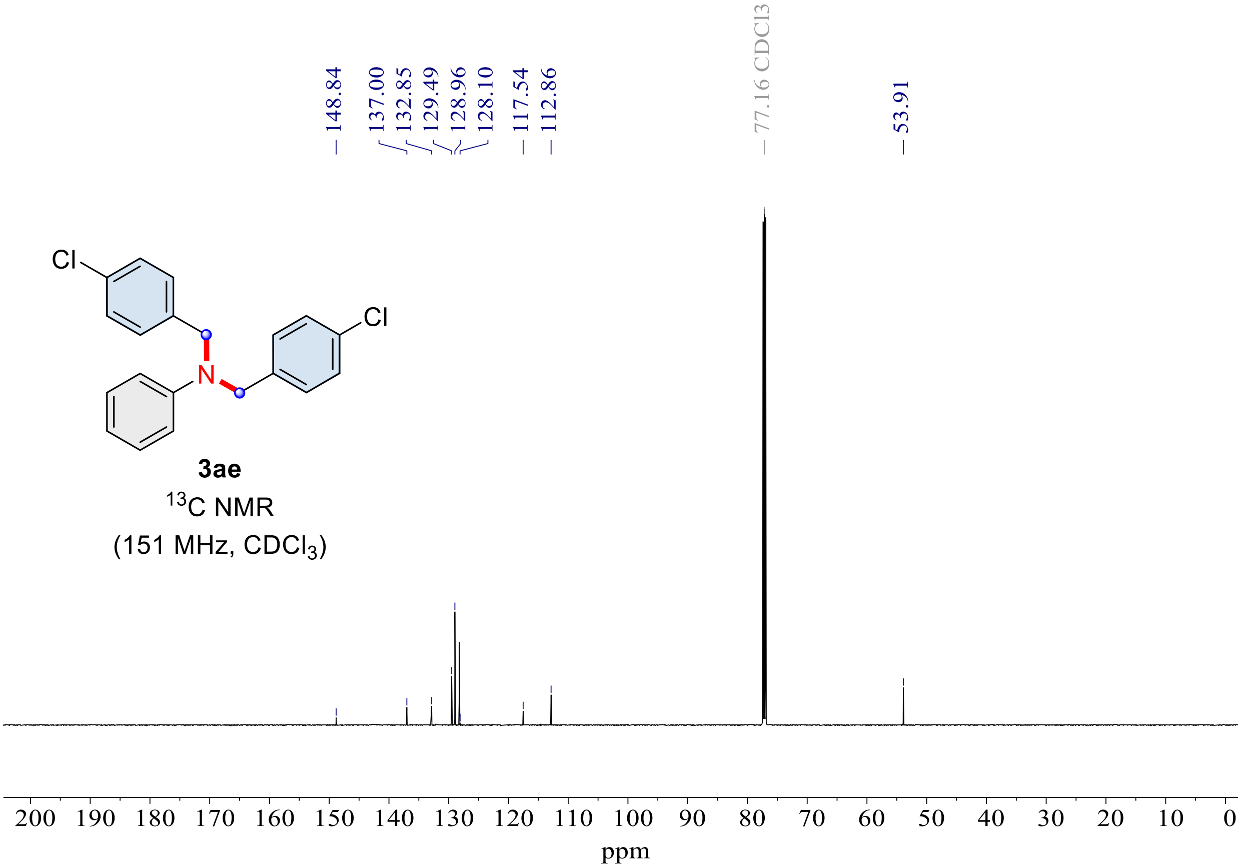
(151 MHz, CDCl$_3$)



3ae

^{1}H NMR

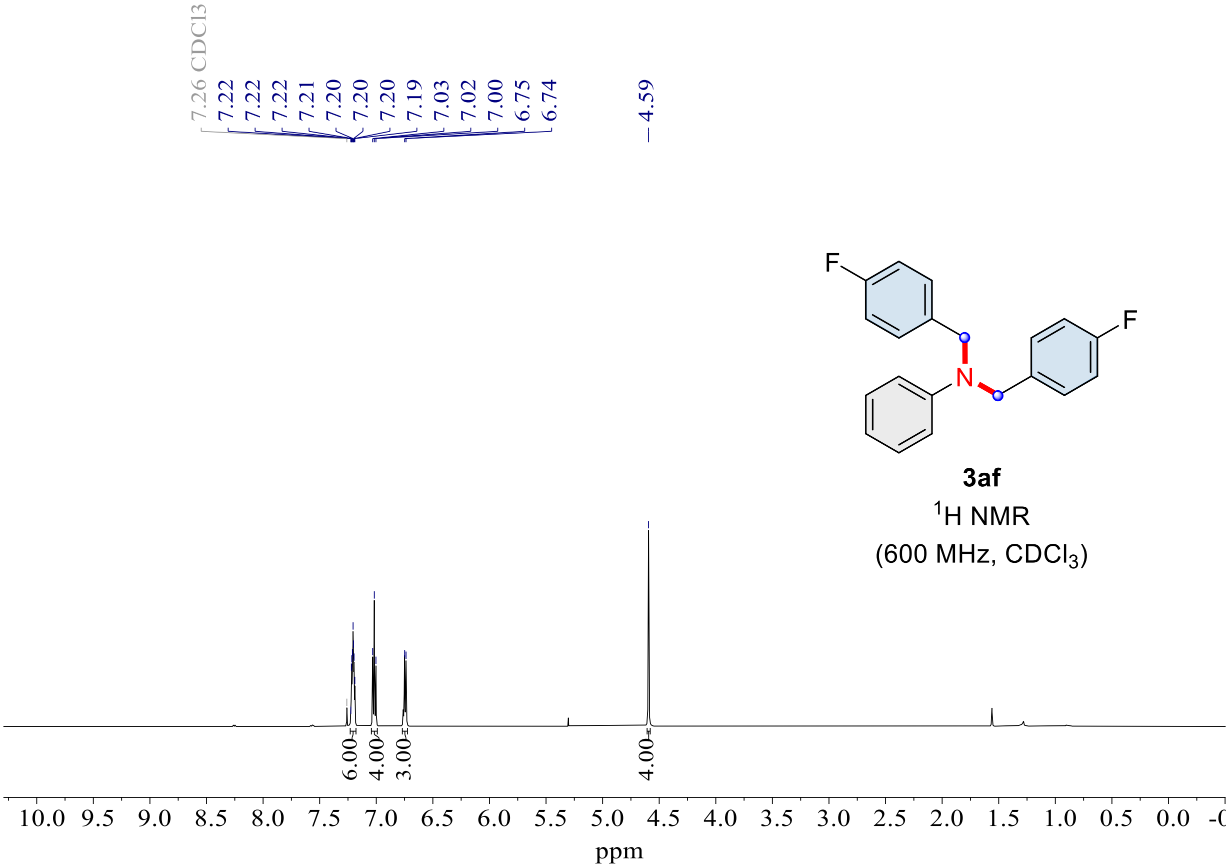
(600 MHz, CDCl$_3$)



3ae

^{13}C NMR

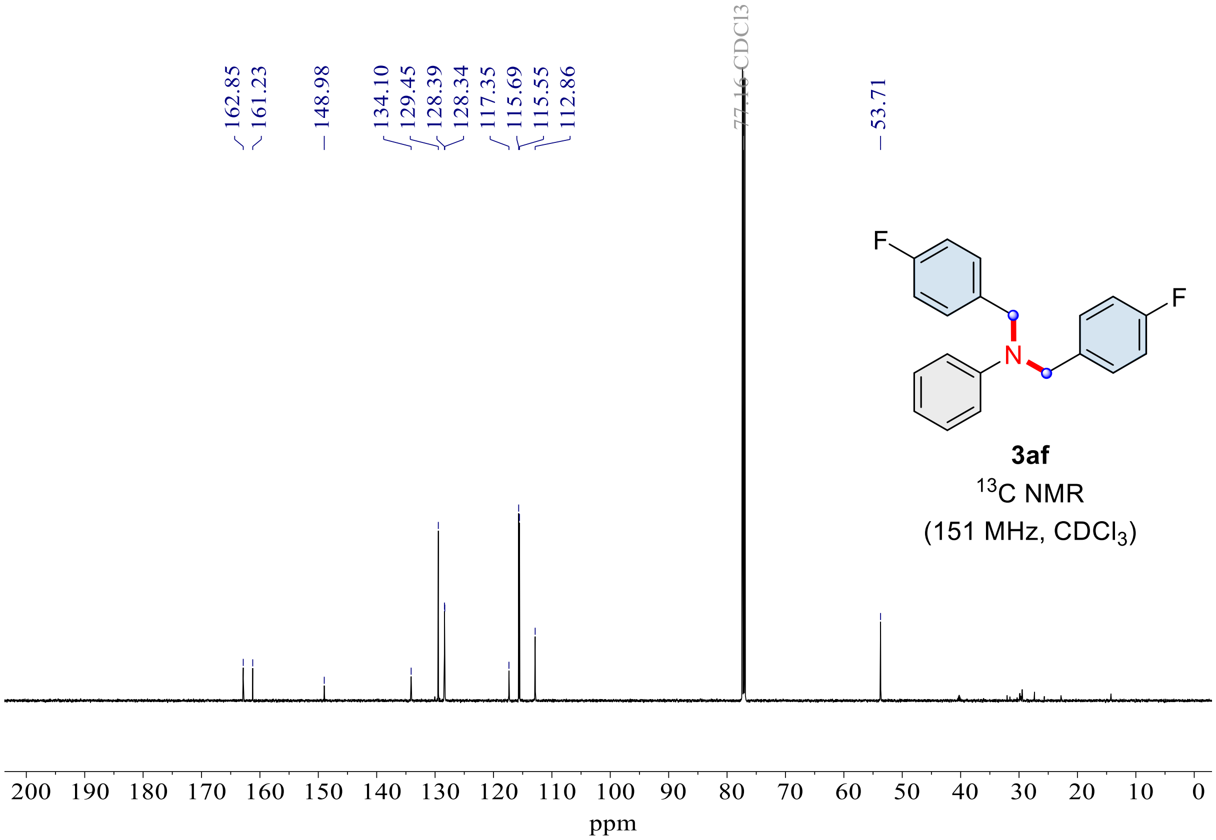
(151 MHz, $CDCl_3$)

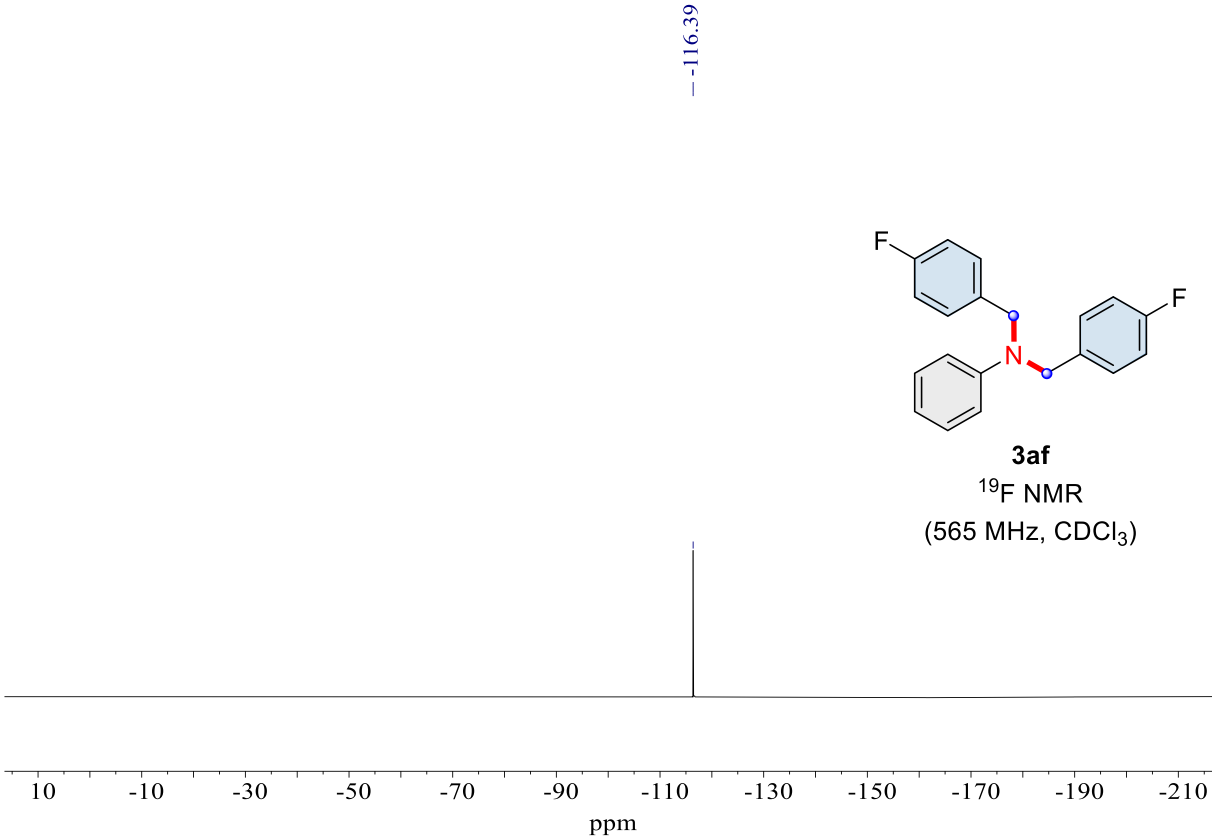


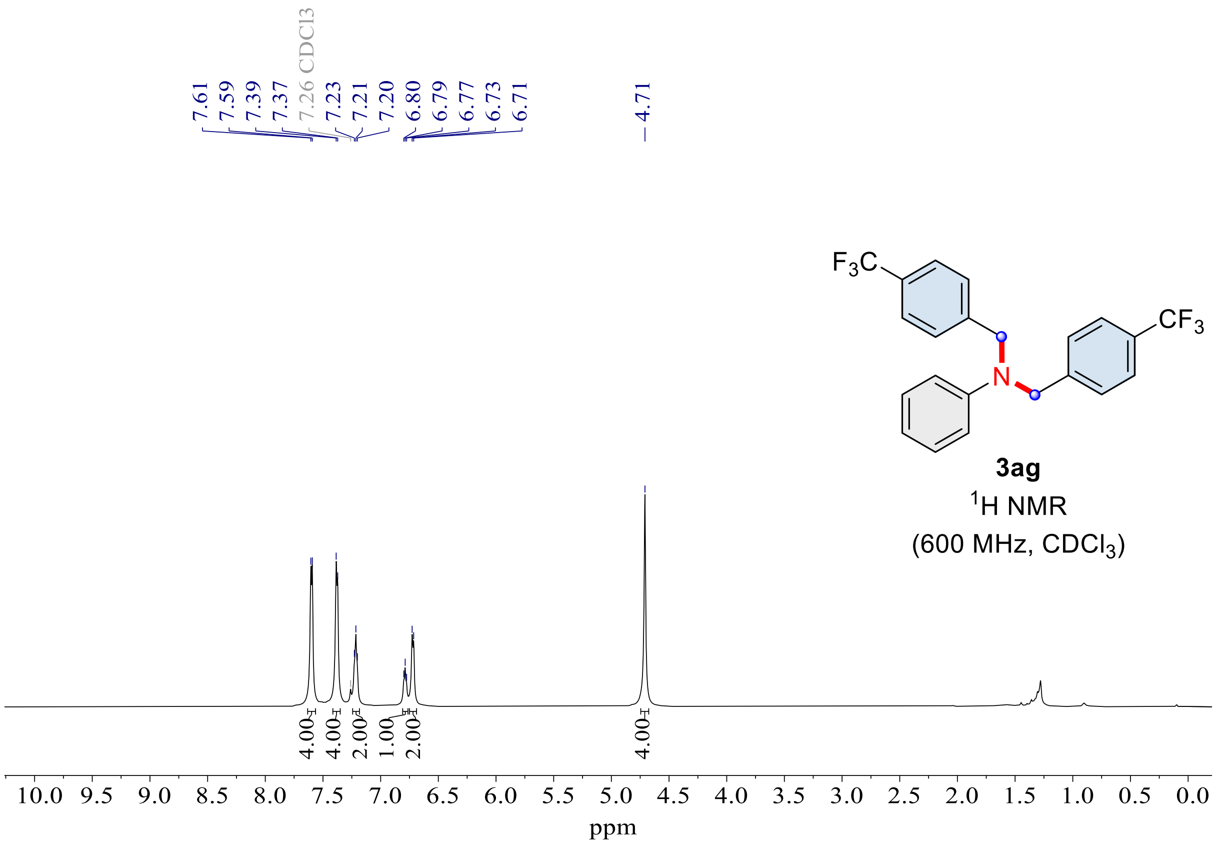
3af

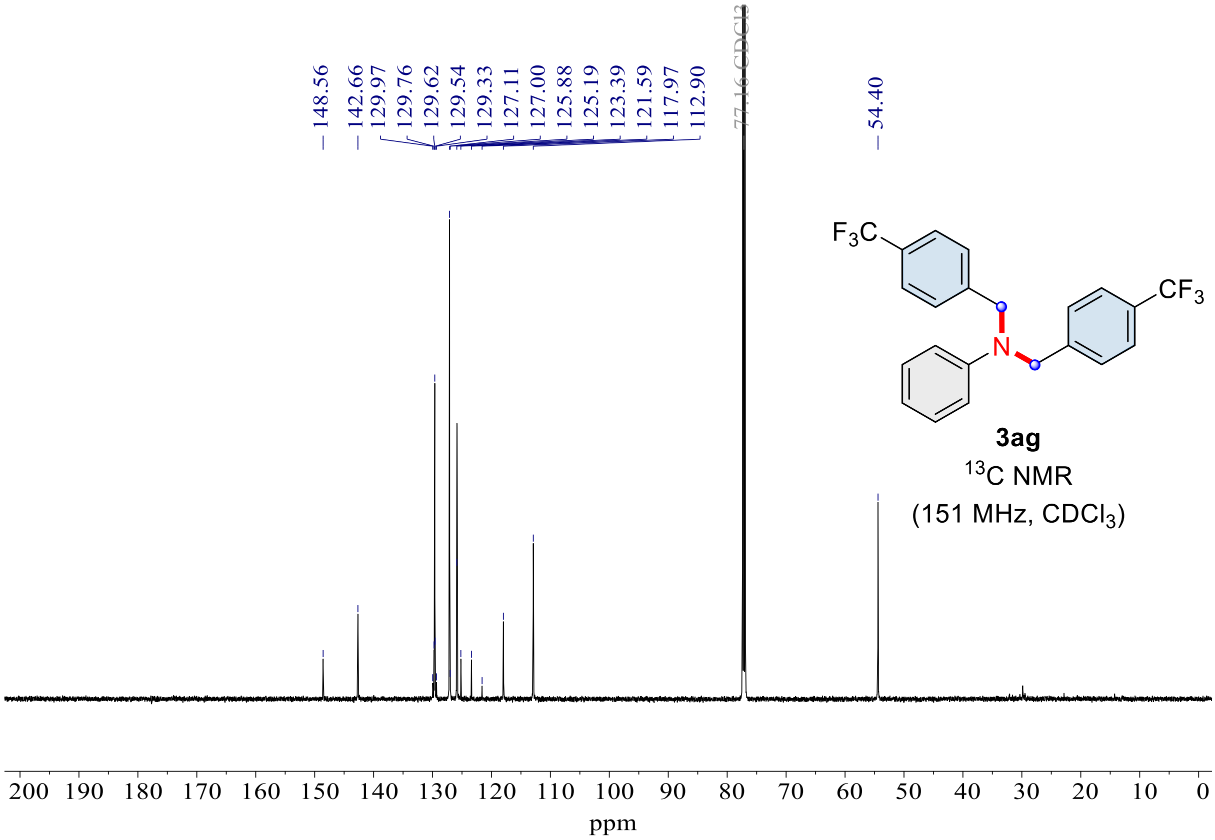
^{1}H NMR

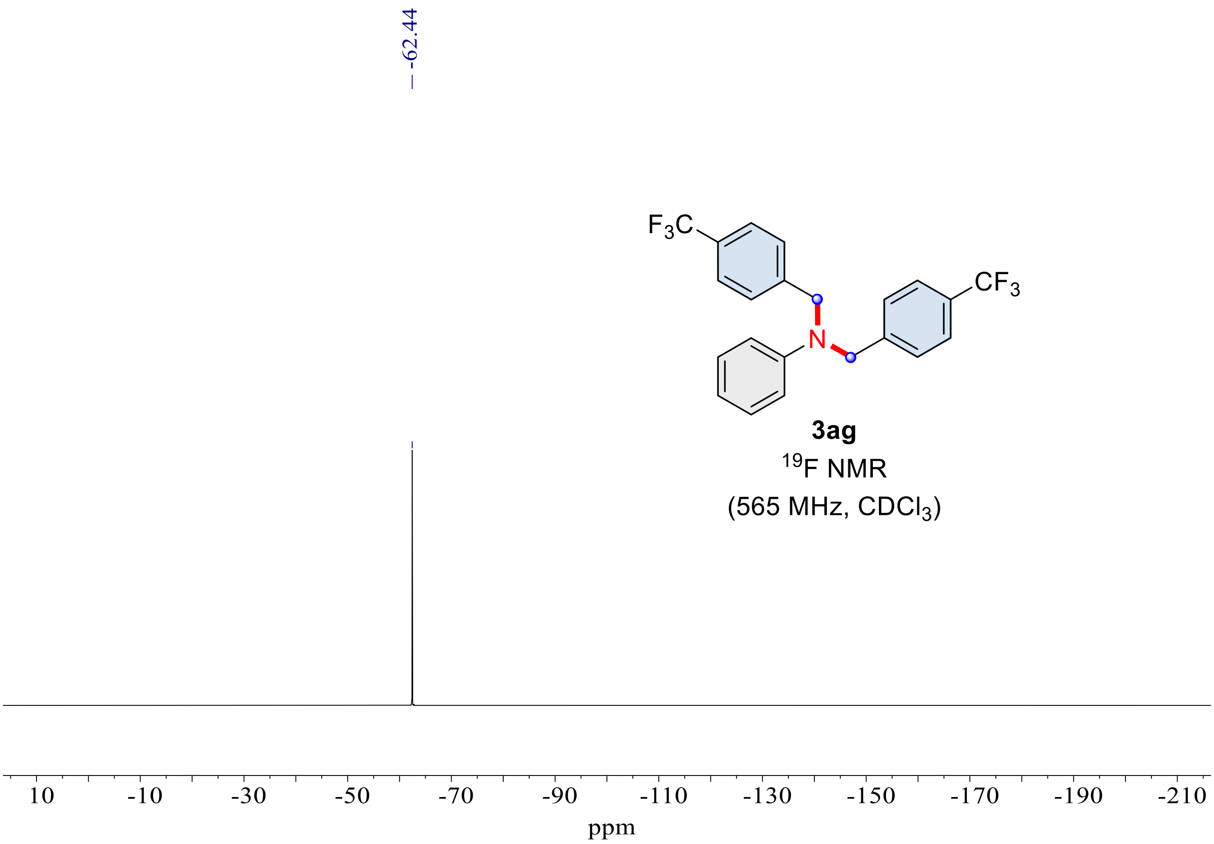
(600 MHz, $CDCl_3$)


162.85
161.23
148.98
134.10
129.45
128.39
128.34
117.35
115.69
115.55
112.86
77.16 CDCl3
53.71
F
F
N
3af
^{13}C NMR
(151 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-116.39
F
F
N
3af
^{19}F NMR
(565 MHz, CDCl$_3$)
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
ppm


7.61
7.59
7.39
7.37
7.26 CDCl3
7.23
7.21
7.20
6.80
6.79
6.77
6.73
6.71
4.71
F$_3$C
CF$_3$
N
3ag
^{1}H NMR
(600 MHz, CDCl$_3$)
4.00
4.00
2.00
1.00
2.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

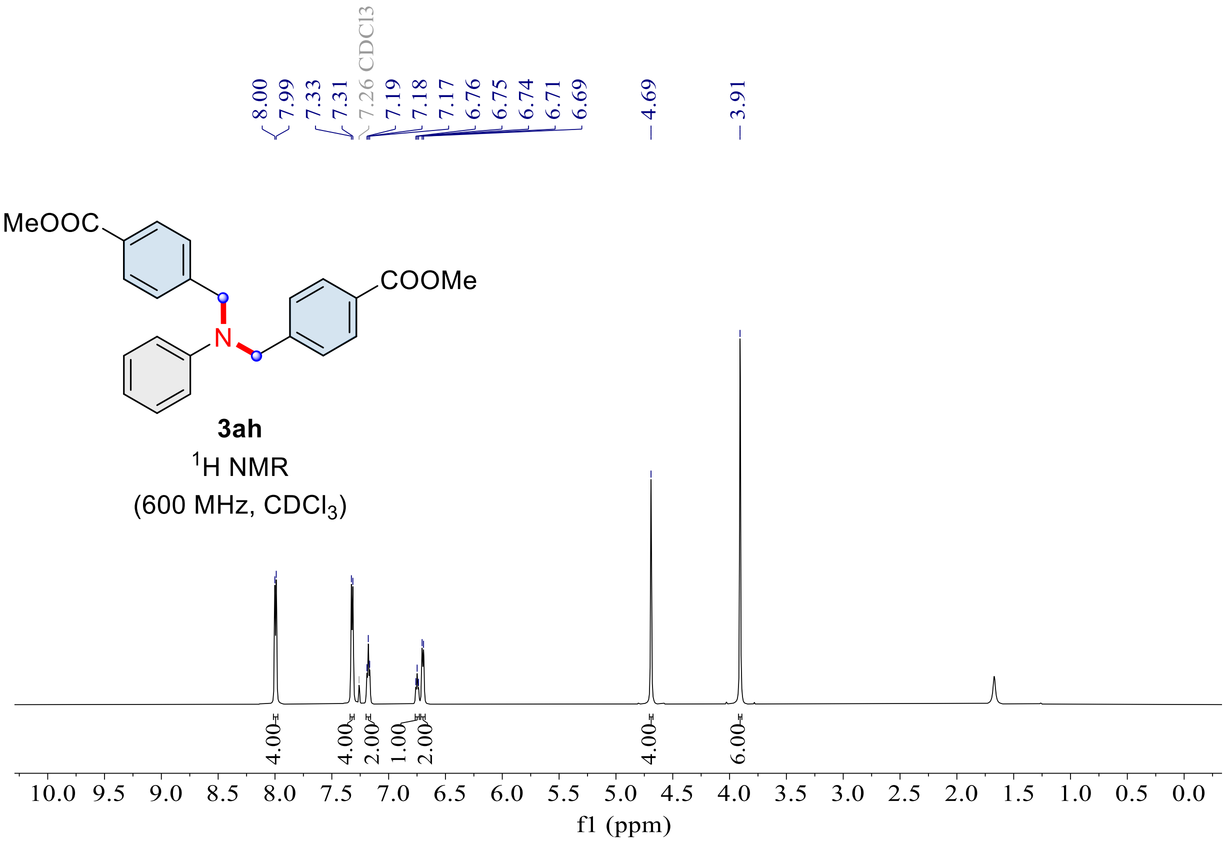

148.56
142.66
129.97
129.76
129.62
129.54
129.33
127.11
127.00
125.88
125.19
123.39
121.59
117.97
112.90
77.16 CDCl3
54.40
F$_3$C
CF$_3$
N
3ag
^{13}C NMR
(151 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



3ag

^{19}F NMR

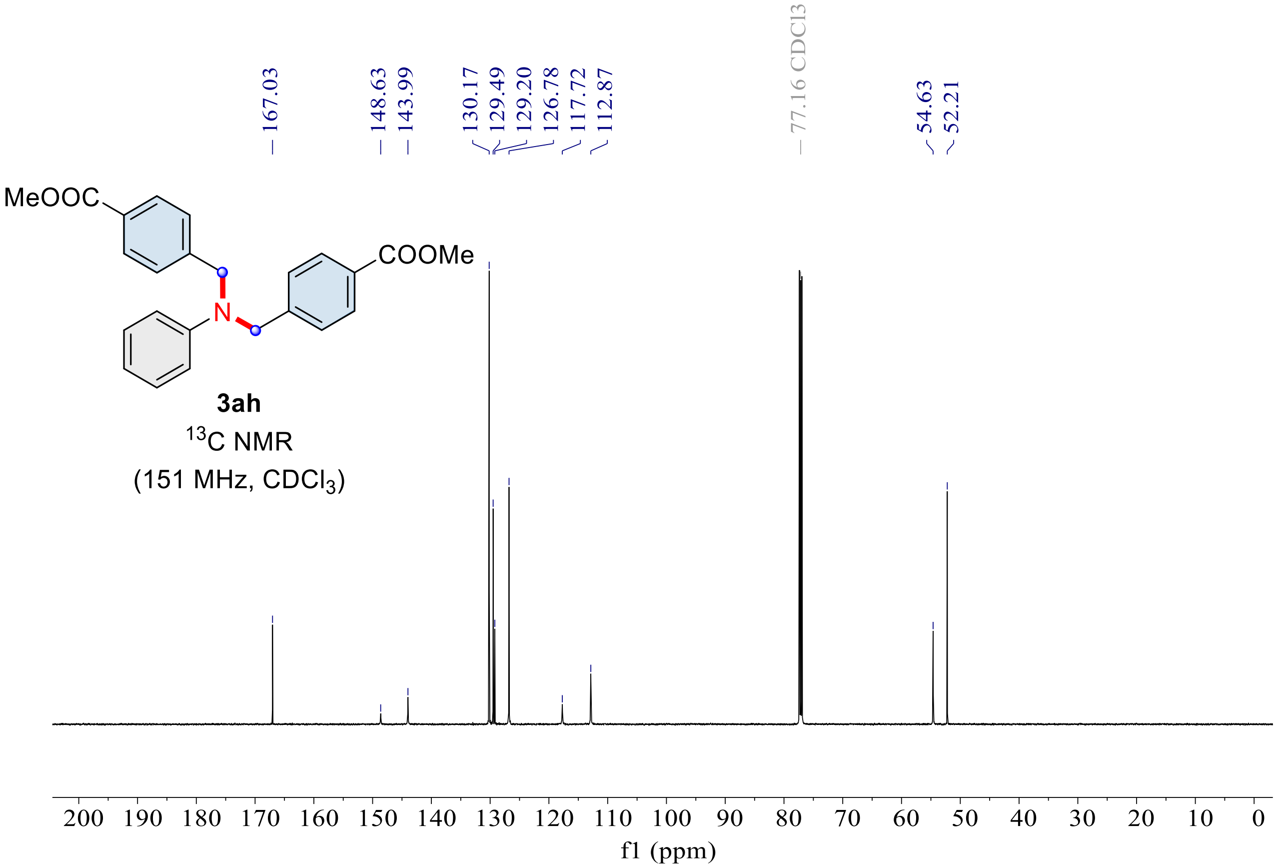
(565 MHz, $CDCl_3$)

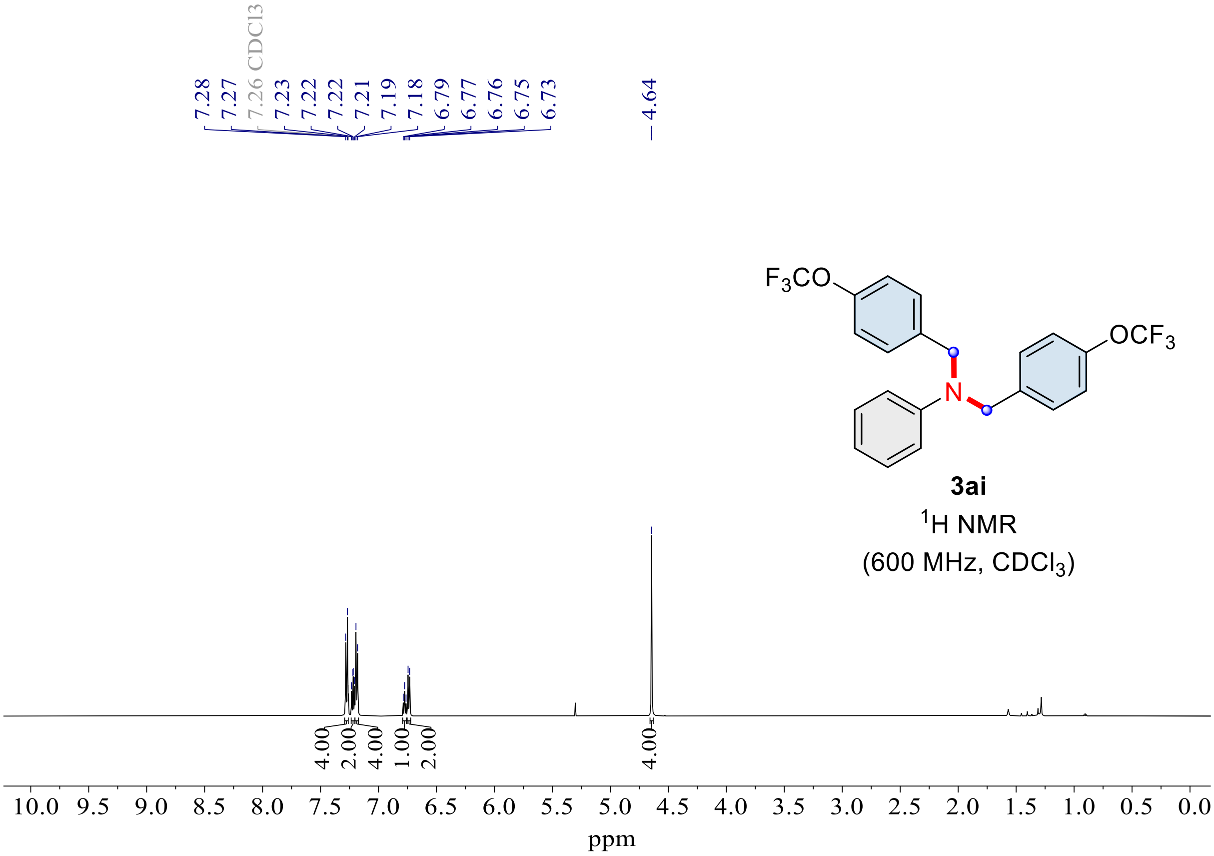


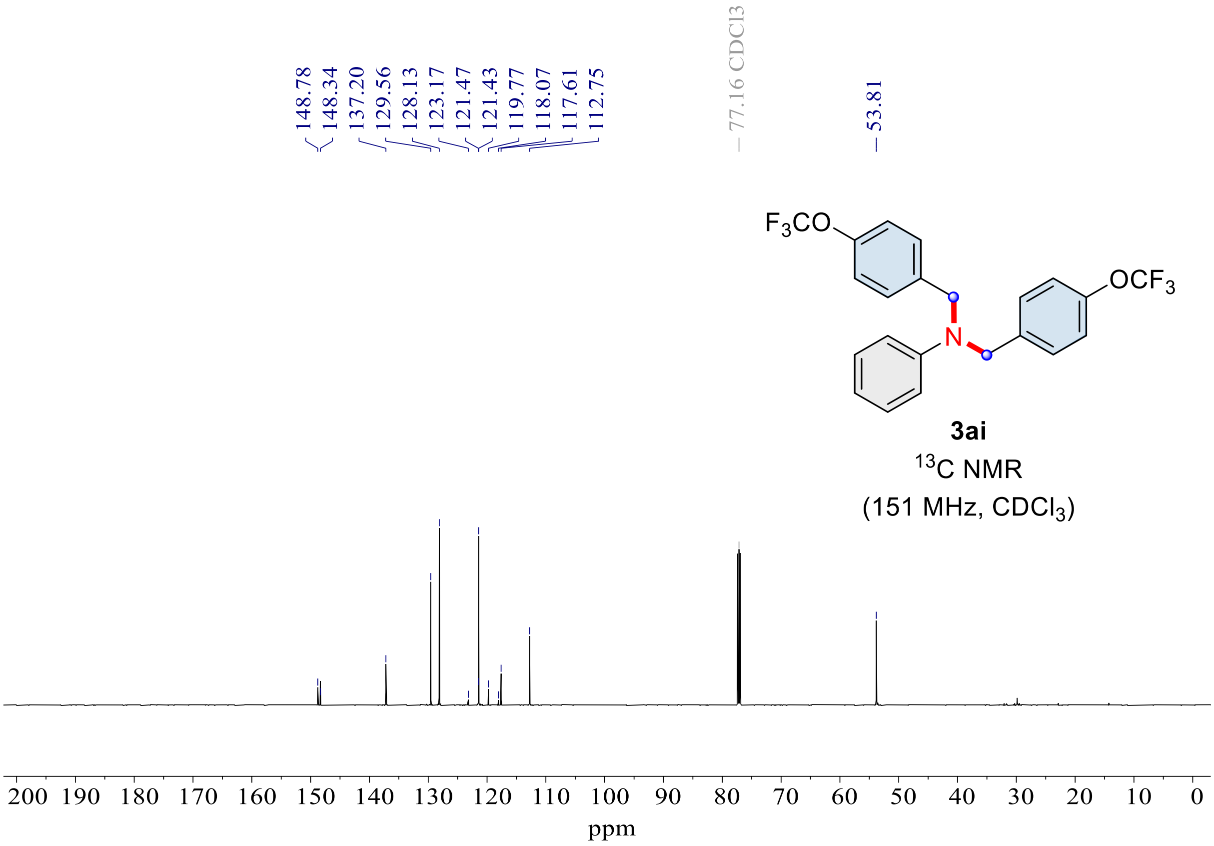
3ah

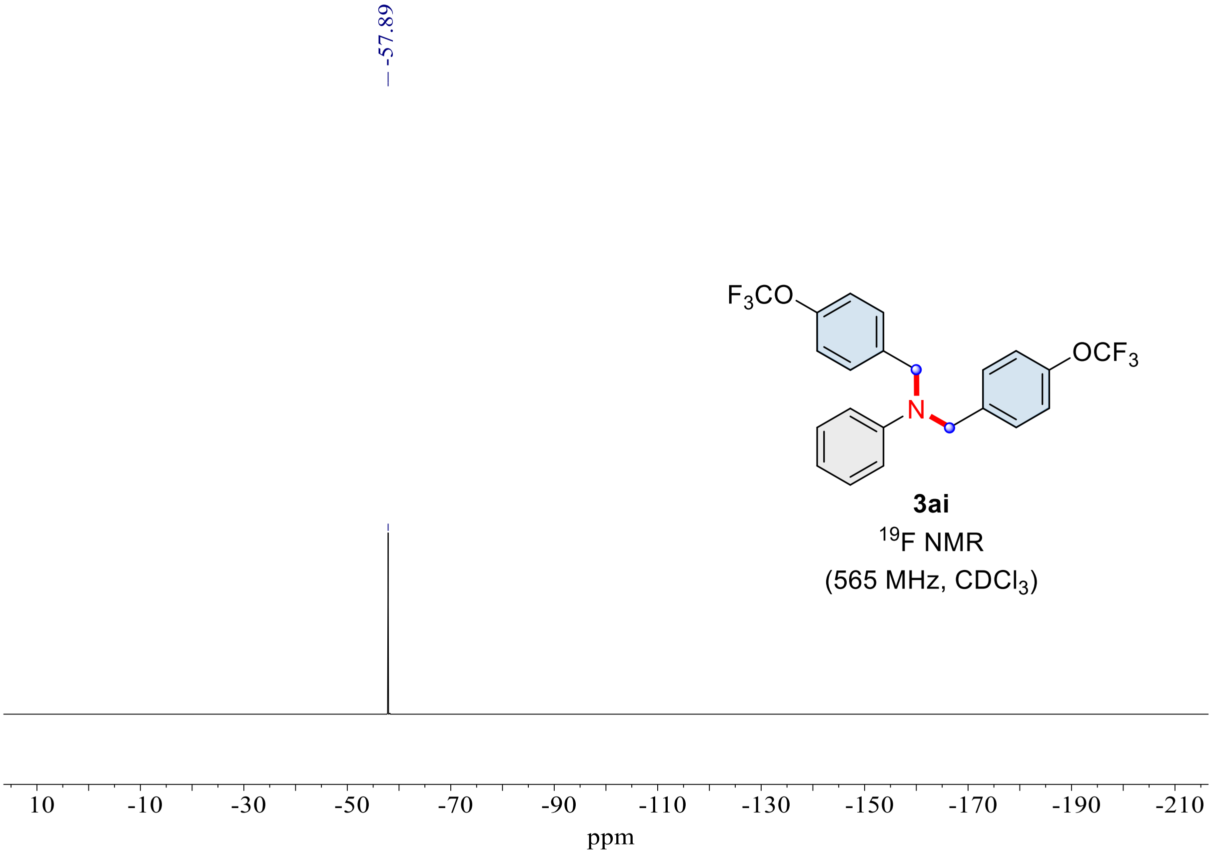
^{1}H NMR

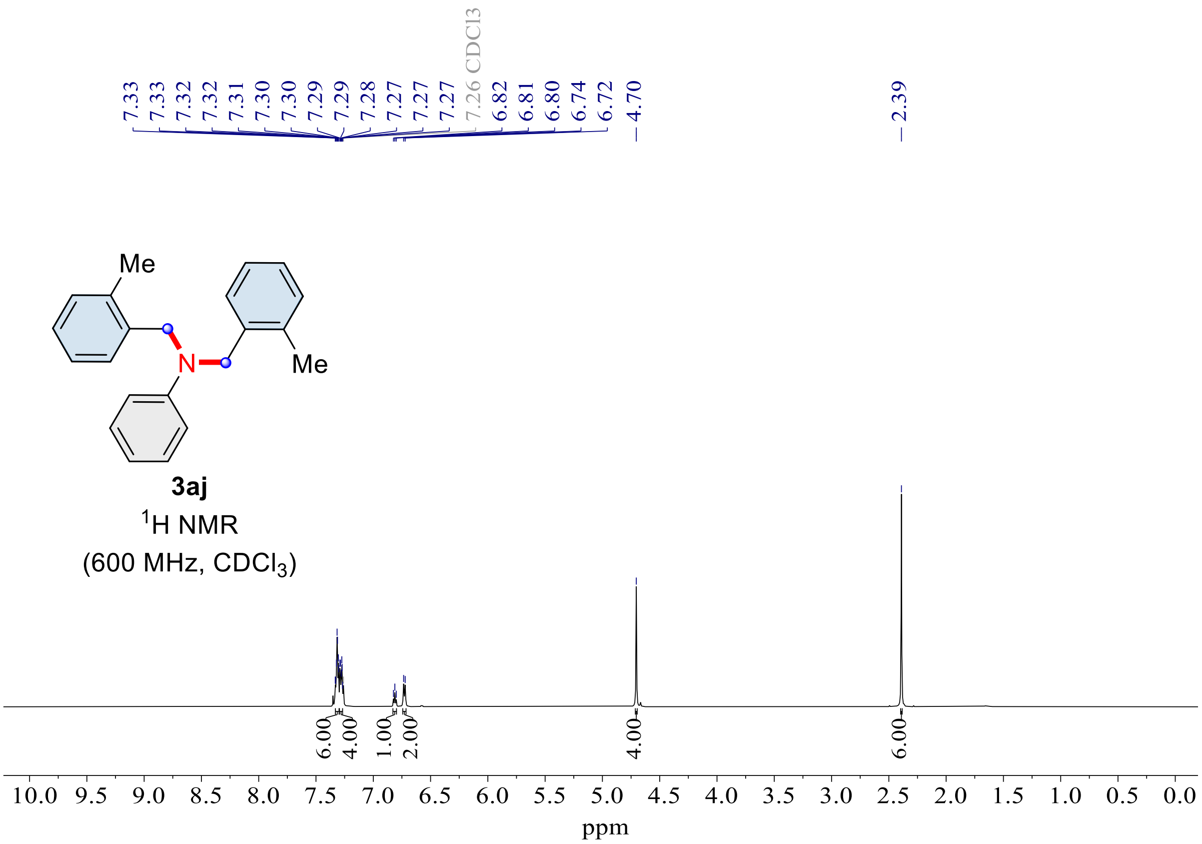
(600 MHz, $CDCl_3$)


167.03
148.63
143.99
130.17
129.49
129.20
126.78
117.72
112.87
77.16 CDCl3
54.63
52.21
MeOOC
COOMe
N
3ah
^{13}C NMR
(151 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.28
7.27
7.26 CDCl3
7.23
7.22
7.22
7.21
7.19
7.18
6.79
6.77
6.76
6.75
6.73
4.64
F_3CO
OCF_3
N
3ai
^{1}H NMR
(600 MHz, $CDCl_3$)
4.00
2.00
4.00
1.00
2.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


148.78
148.34
137.20
129.56
128.13
123.17
121.47
121.43
119.77
118.07
117.61
112.75
77.16 CDCl3
53.81
F3CO
OCF3
N
3ai
13C NMR
(151 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

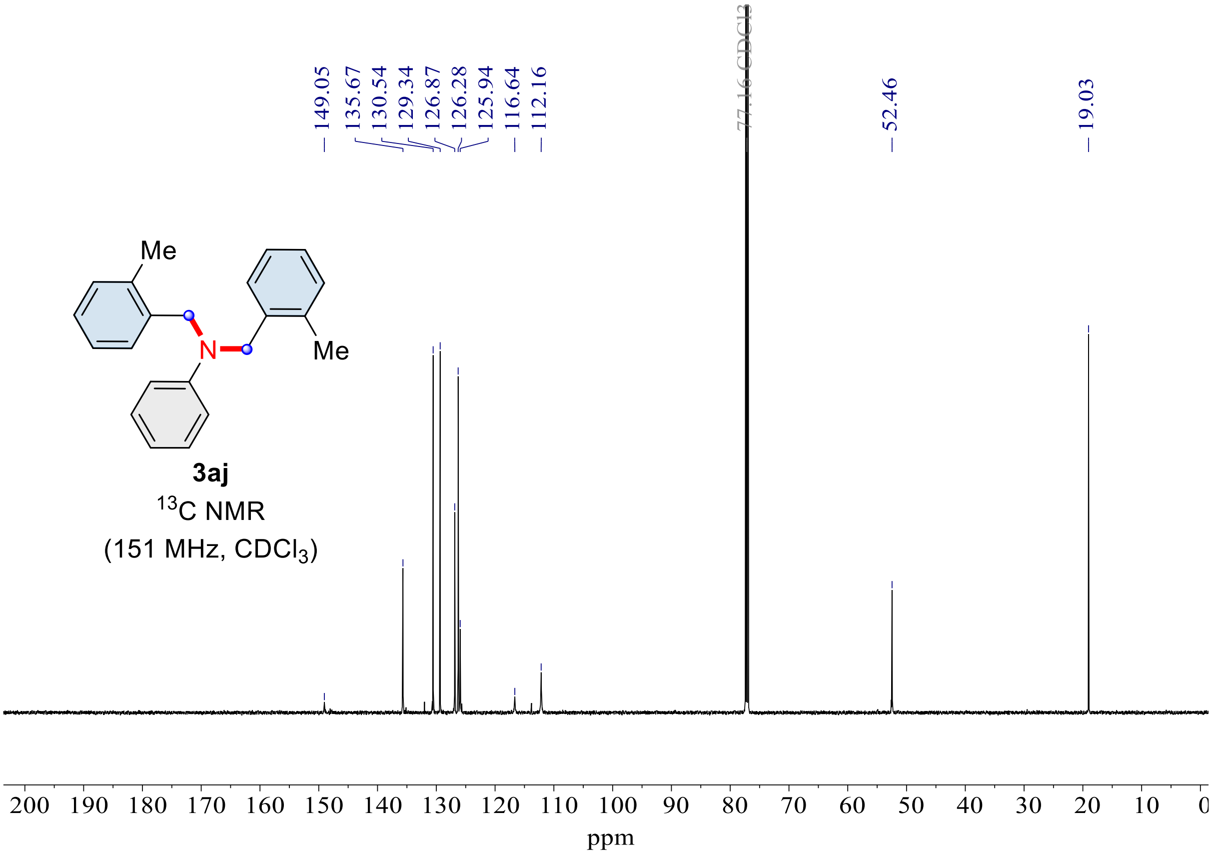

-57.89
F3CO
OCF3
N
3ai
19F NMR
(565 MHz, CDCl3)
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
ppm



3aj

^{1}H NMR

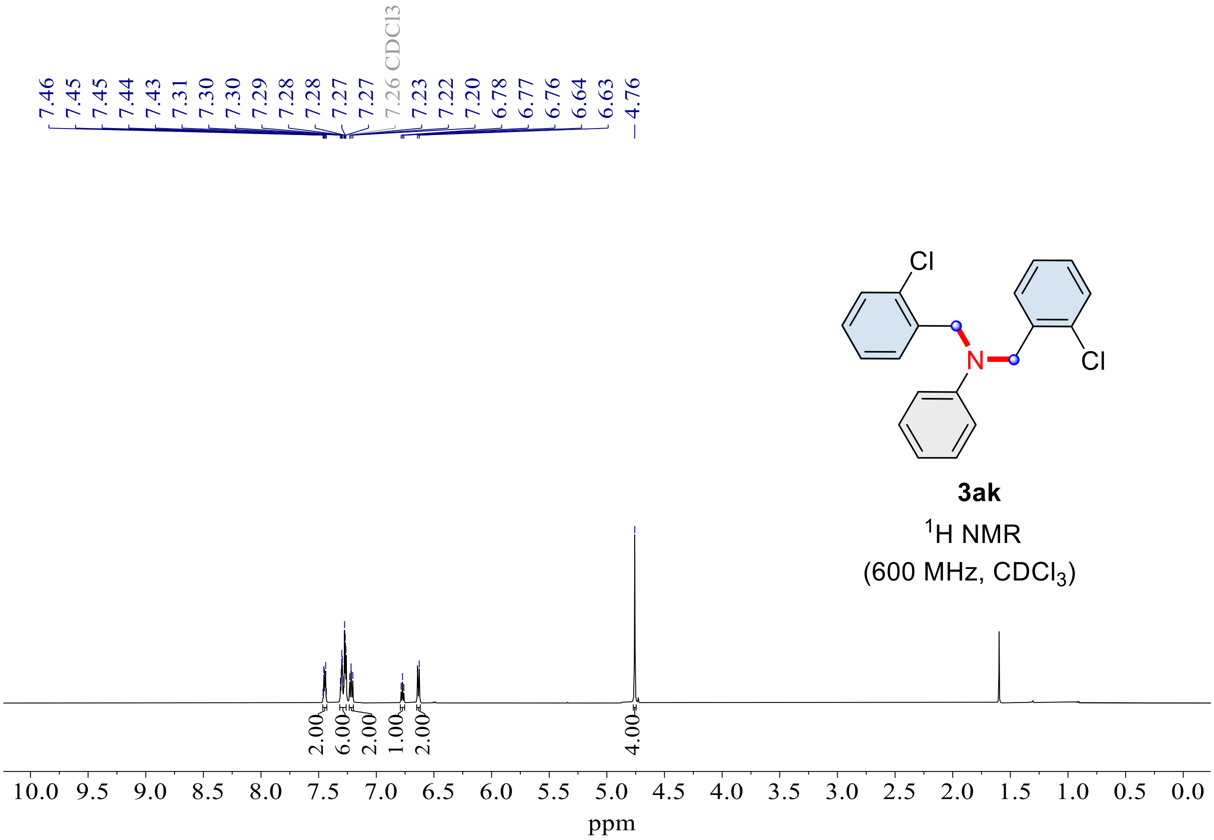
(600 MHz, $CDCl_3$)

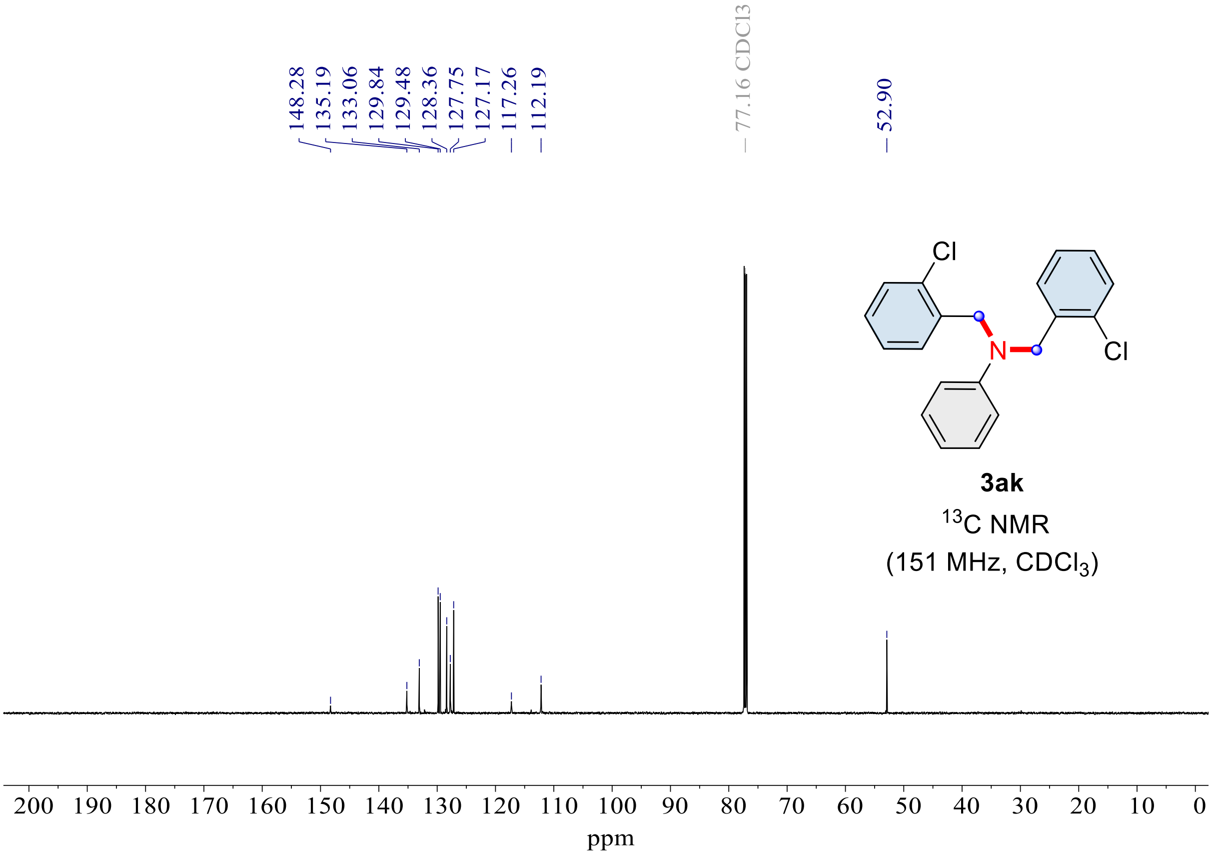


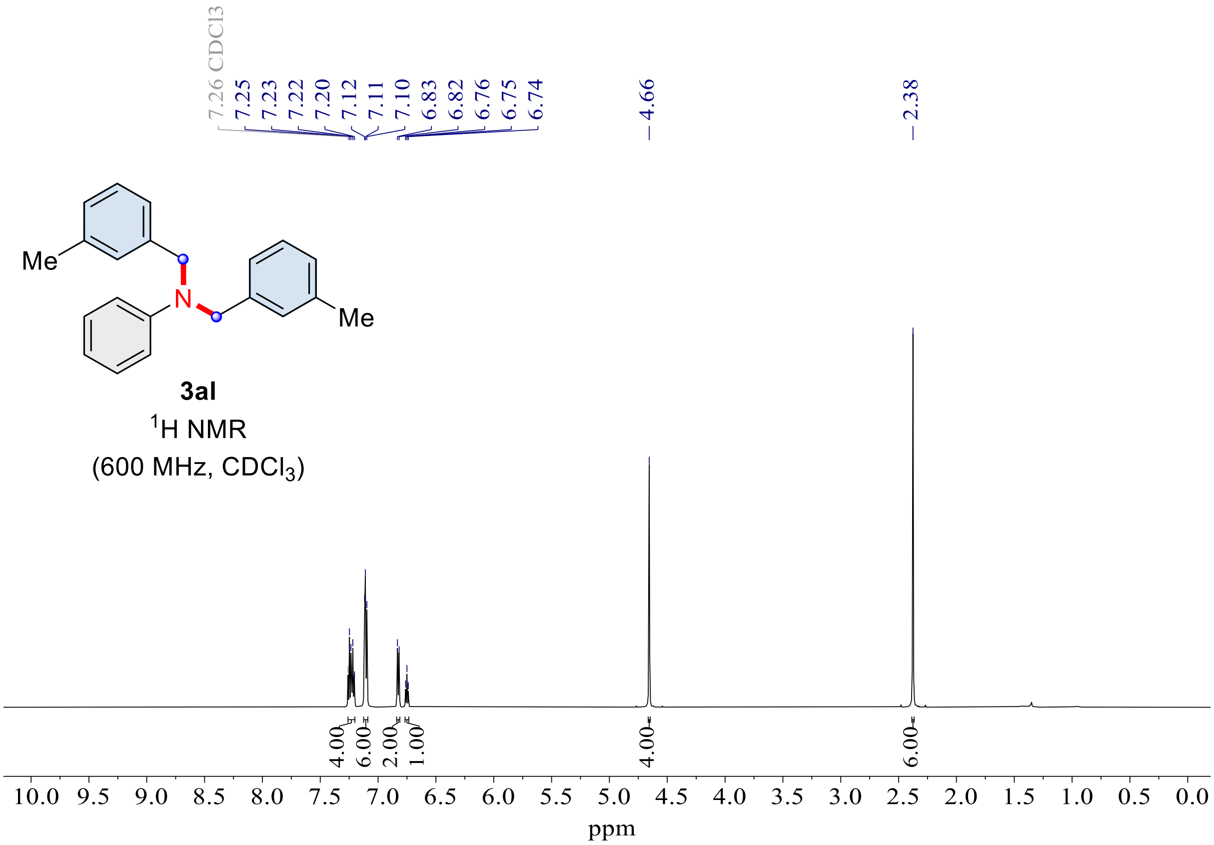
3aj

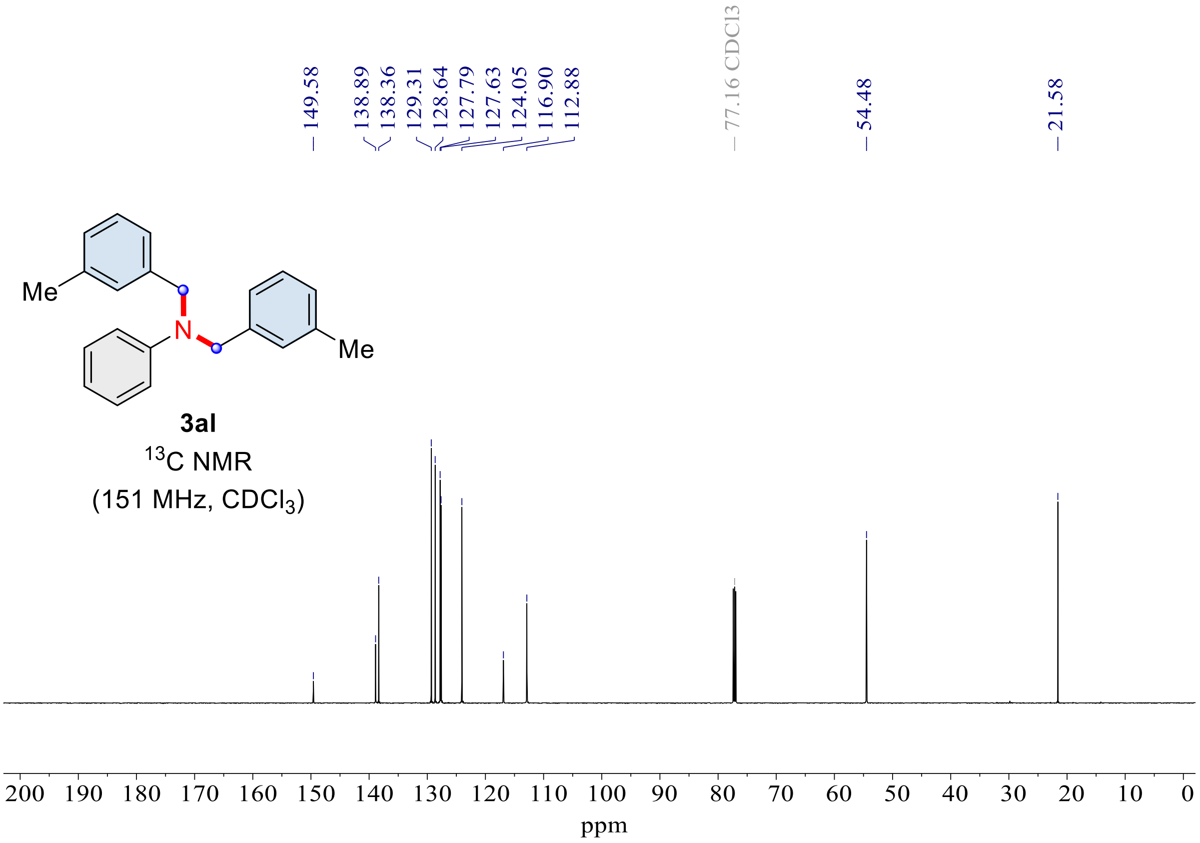
^{13}C NMR

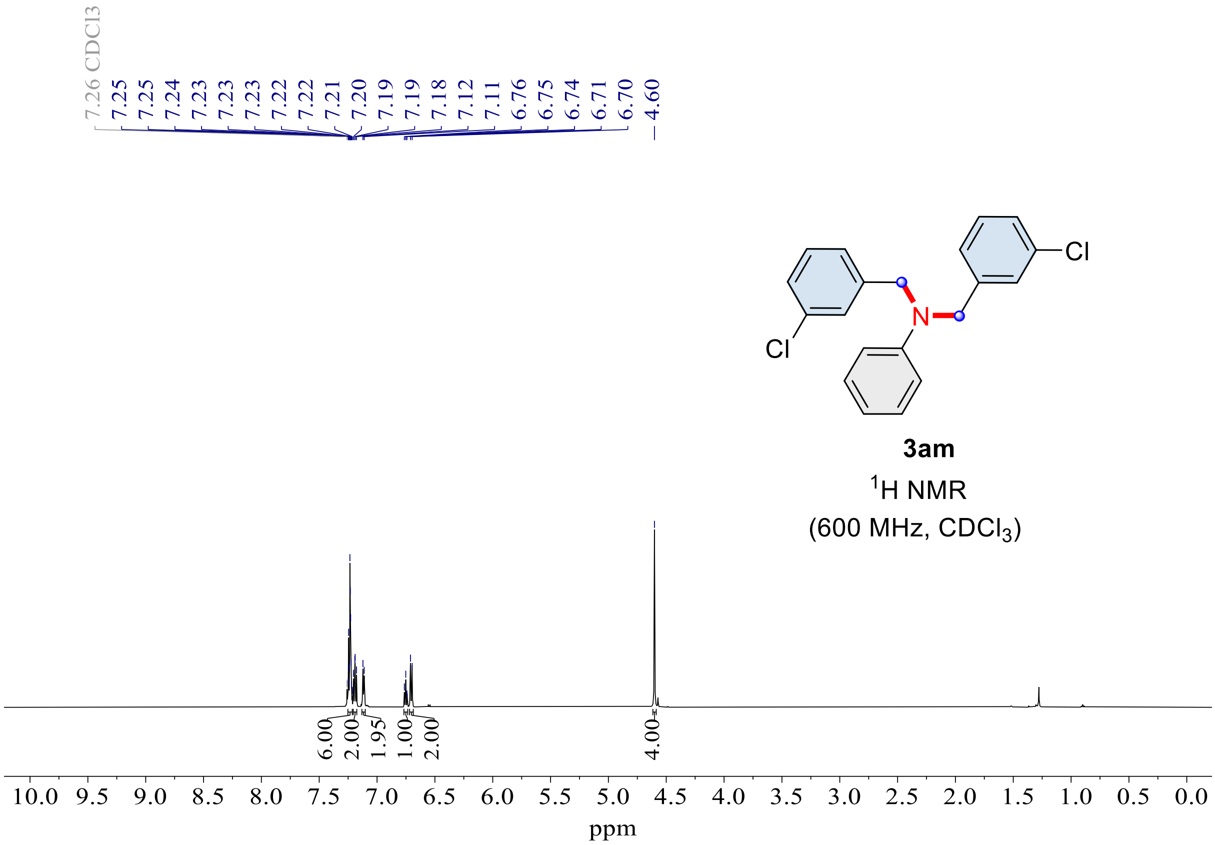
(151 MHz, $CDCl_3$)


7.46
7.45
7.45
7.44
7.43
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26 CDCl3
7.23
7.22
7.20
6.78
6.77
6.76
6.64
6.63
4.76
Cl
N
Cl
3ak
^{1}H NMR
(600 MHz, CDCl$_3$)
2.00
6.00
2.00
1.00
2.00
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


148.28
135.19
133.06
129.84
129.48
128.36
127.75
127.17
117.26
112.19
77.16 CDCl3
52.90
Cl
N
Cl
3ak
^{13}C NMR
(151 MHz, CDCl$_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.26 CDCl3
7.25
7.23
7.22
7.20
7.12
7.11
7.10
6.83
6.82
6.76
6.75
6.74
4.66
2.38
Me
N
Me
3al
1H NMR
(600 MHz, CDCl3)
4.00
6.00
2.00
1.00
4.00
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

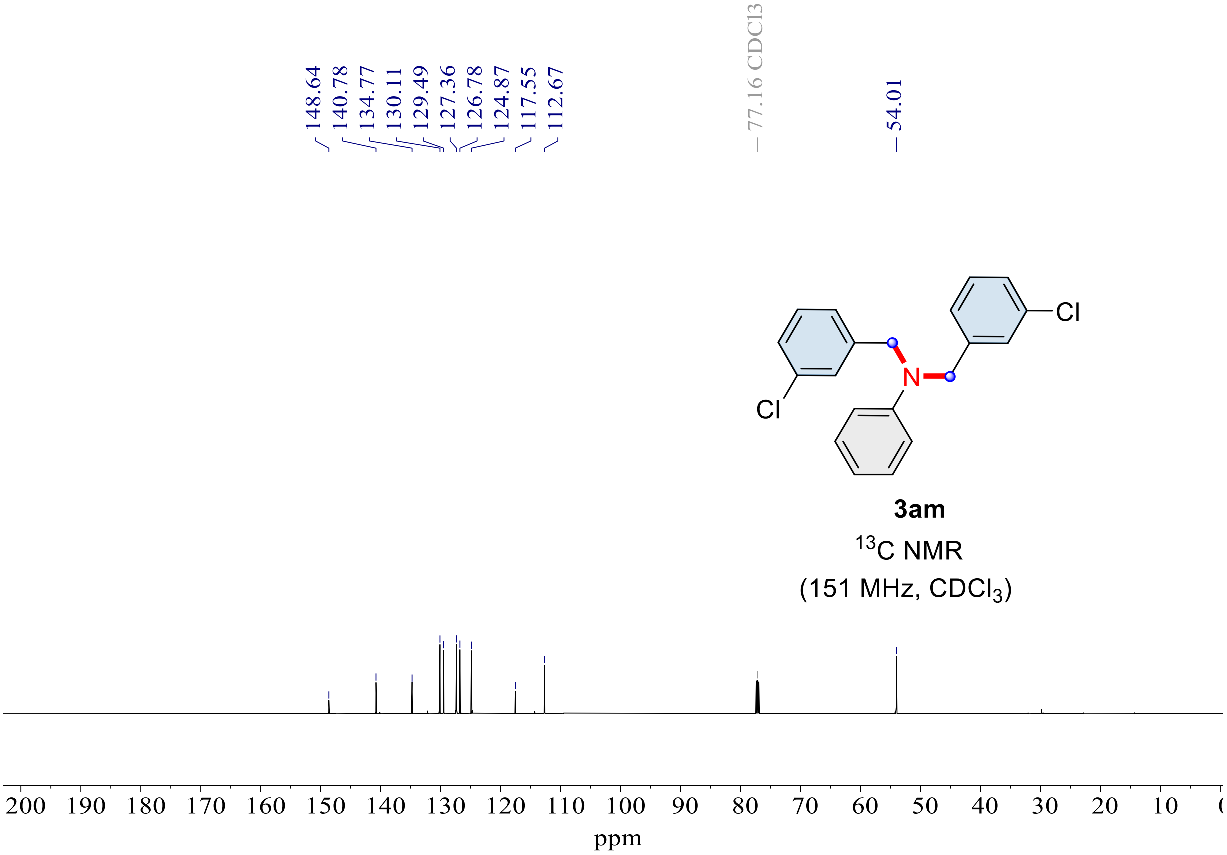

149.58
138.89
138.36
129.31
128.64
127.79
127.63
124.05
116.90
112.88
77.16 CDCl3
54.48
21.58
Me
N
Me
3al
13C NMR
(151 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3am

^{1}H NMR

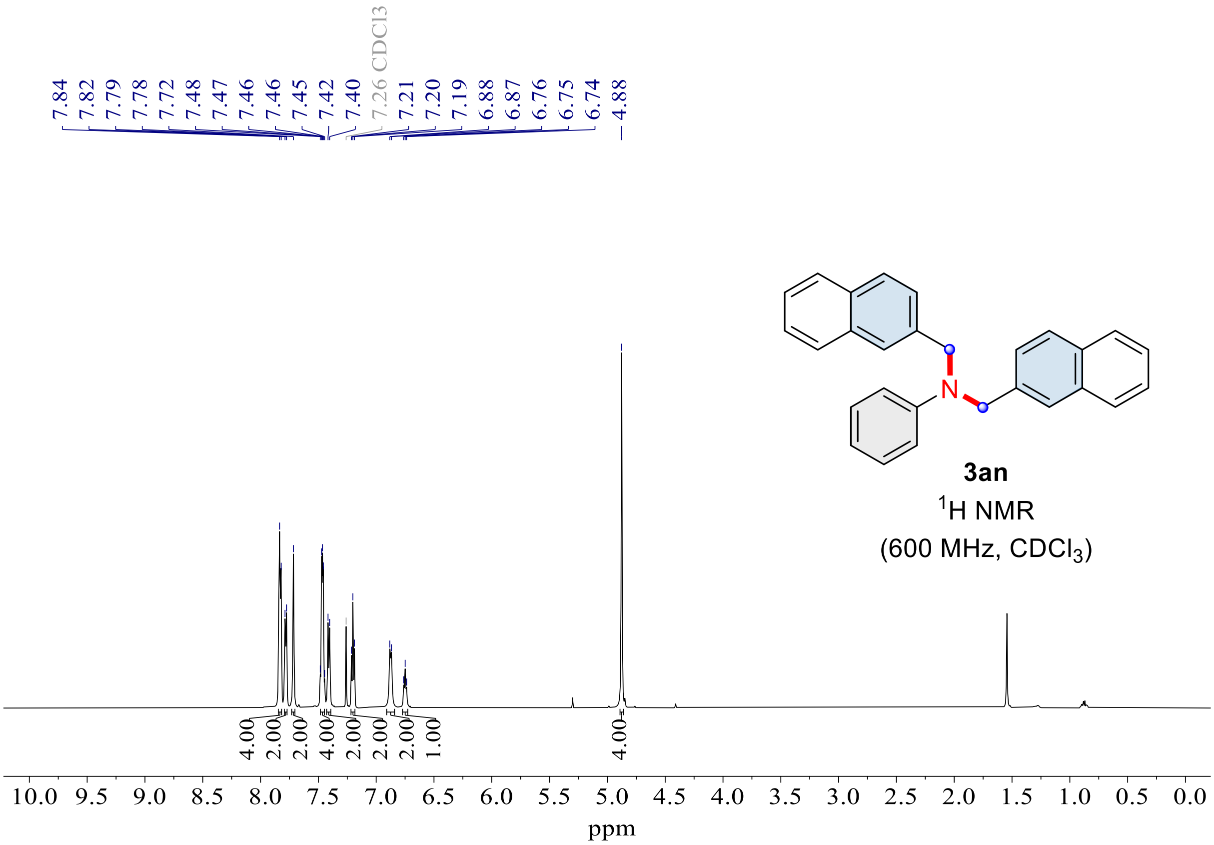
(600 MHz, $CDCl_3$)

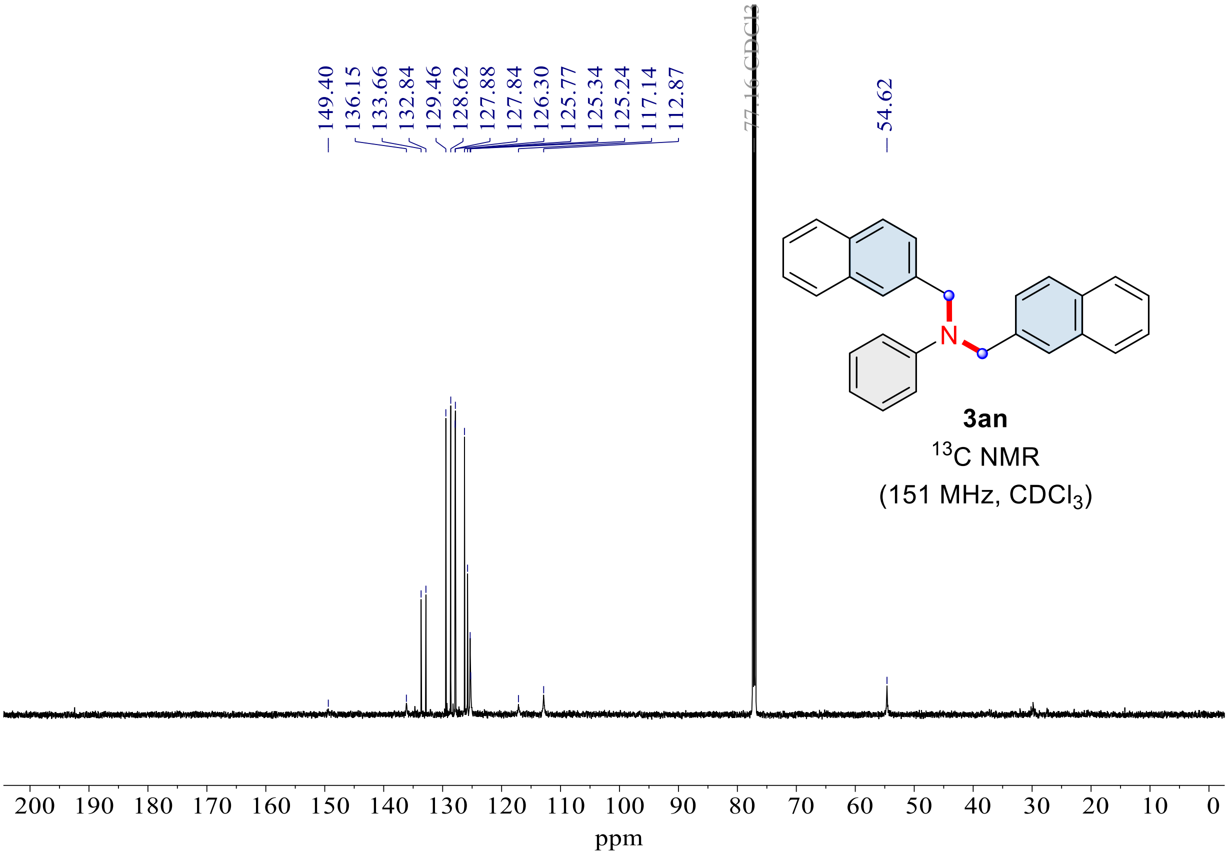


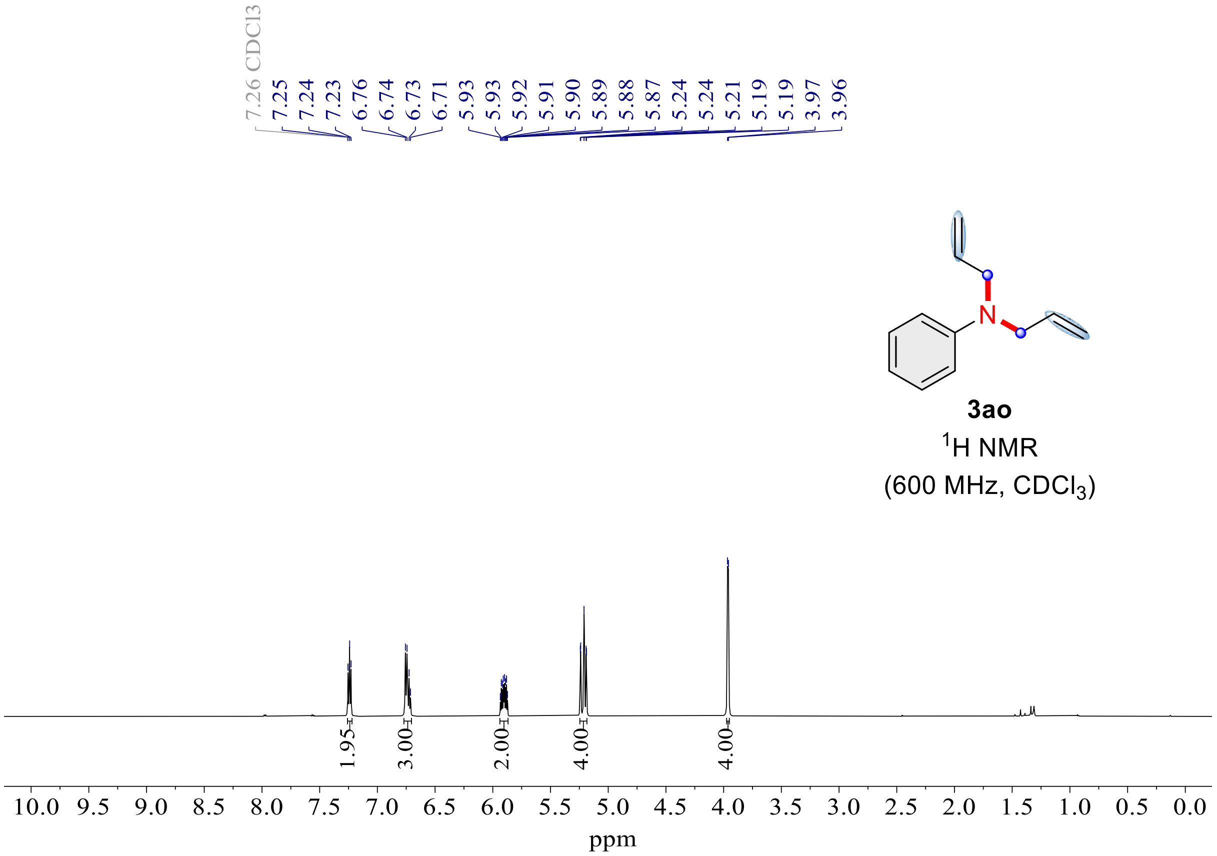
3am

^{13}C NMR

(151 MHz, $CDCl_3$)


7.84
7.82
7.79
7.78
7.72
7.48
7.47
7.46
7.46
7.45
7.42
7.40
7.26 CDCl3
7.21
7.20
7.19
6.88
6.87
6.76
6.75
6.74
4.88
4.00
2.00
2.00
4.00
2.00
2.00
2.00
1.00
4.00
N
3an
^{1}H NMR
(600 MHz, $CDCl_3$)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

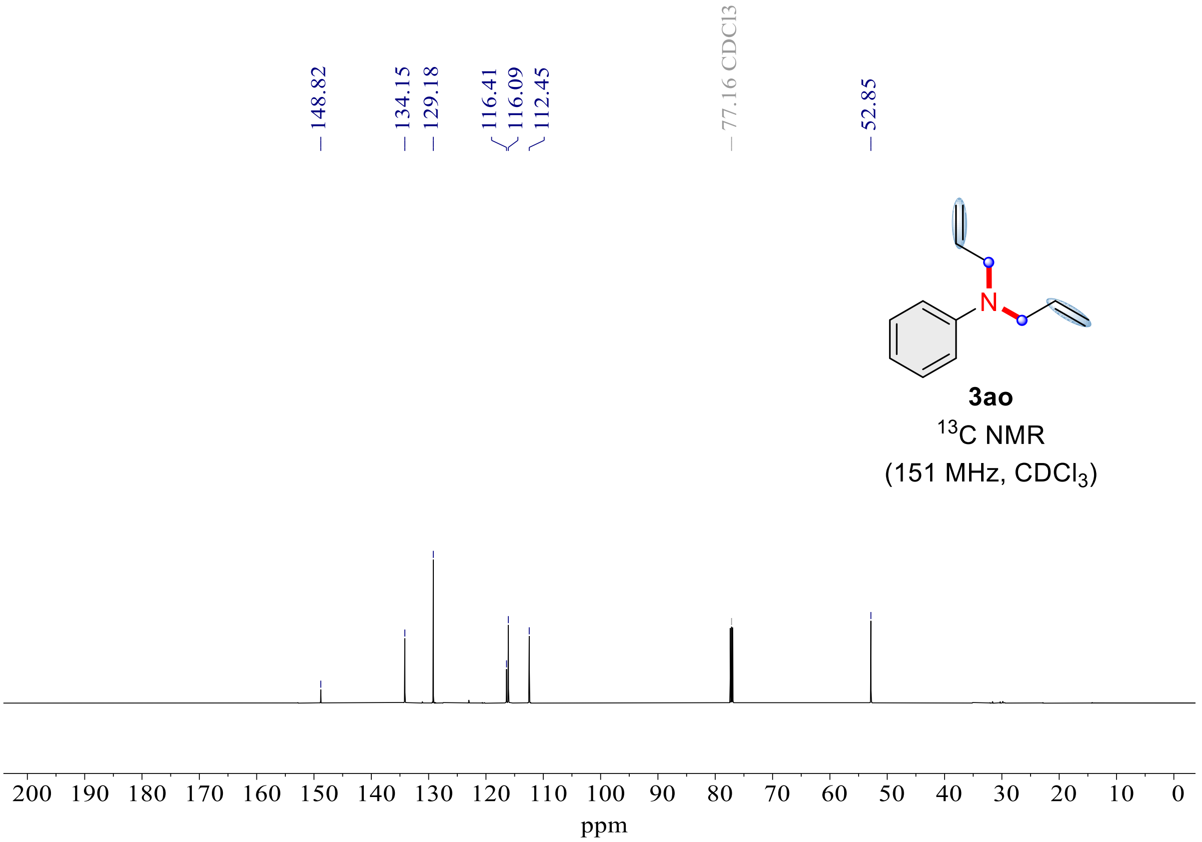

149.40
136.15
133.66
132.84
129.46
128.62
127.88
127.84
126.30
125.77
125.34
125.24
117.14
112.87
77.16 CDCl3
54.62
N
3an
^{13}C NMR
(151 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



3ao

^{1}H NMR

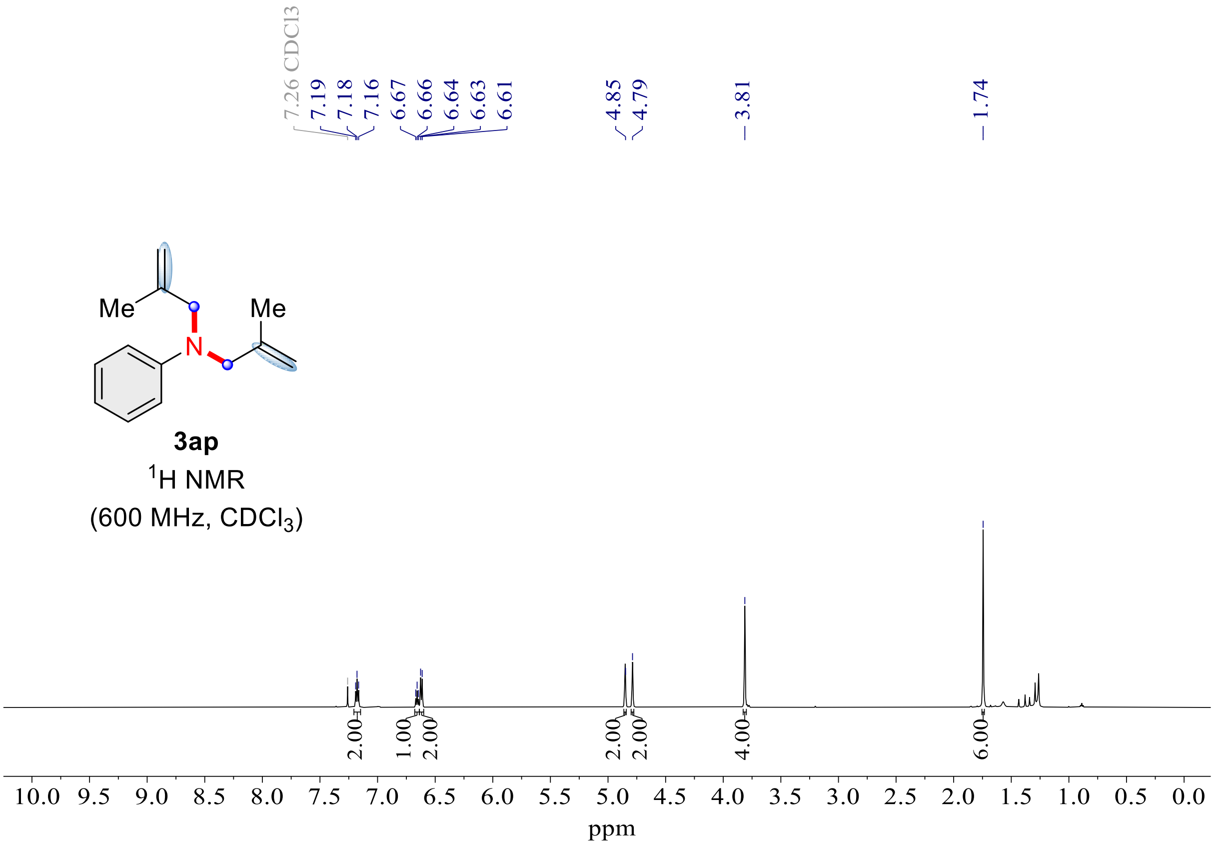
(600 MHz, $CDCl_3$)



3ao

^{13}C NMR

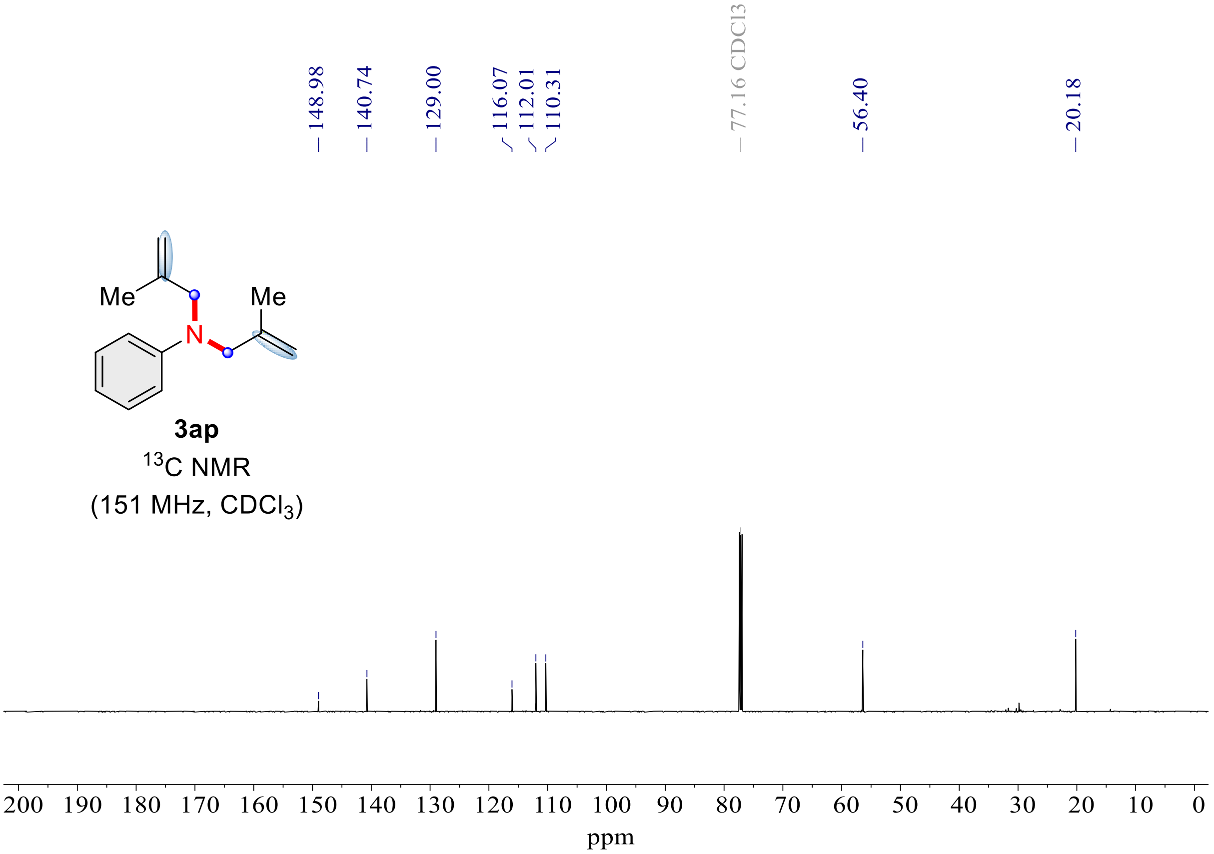
(151 MHz, $CDCl_3$)



3ap

^{1}H NMR

(600 MHz, $CDCl_3$)



3ap

^{13}C NMR

(151 MHz, $CDCl_3$)