catalysts

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Supporting Information

Aminocyclopropenium as a New Class of Hydrogen Bonding Catalyst in Friedel–Crafts Alkylation

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General Information

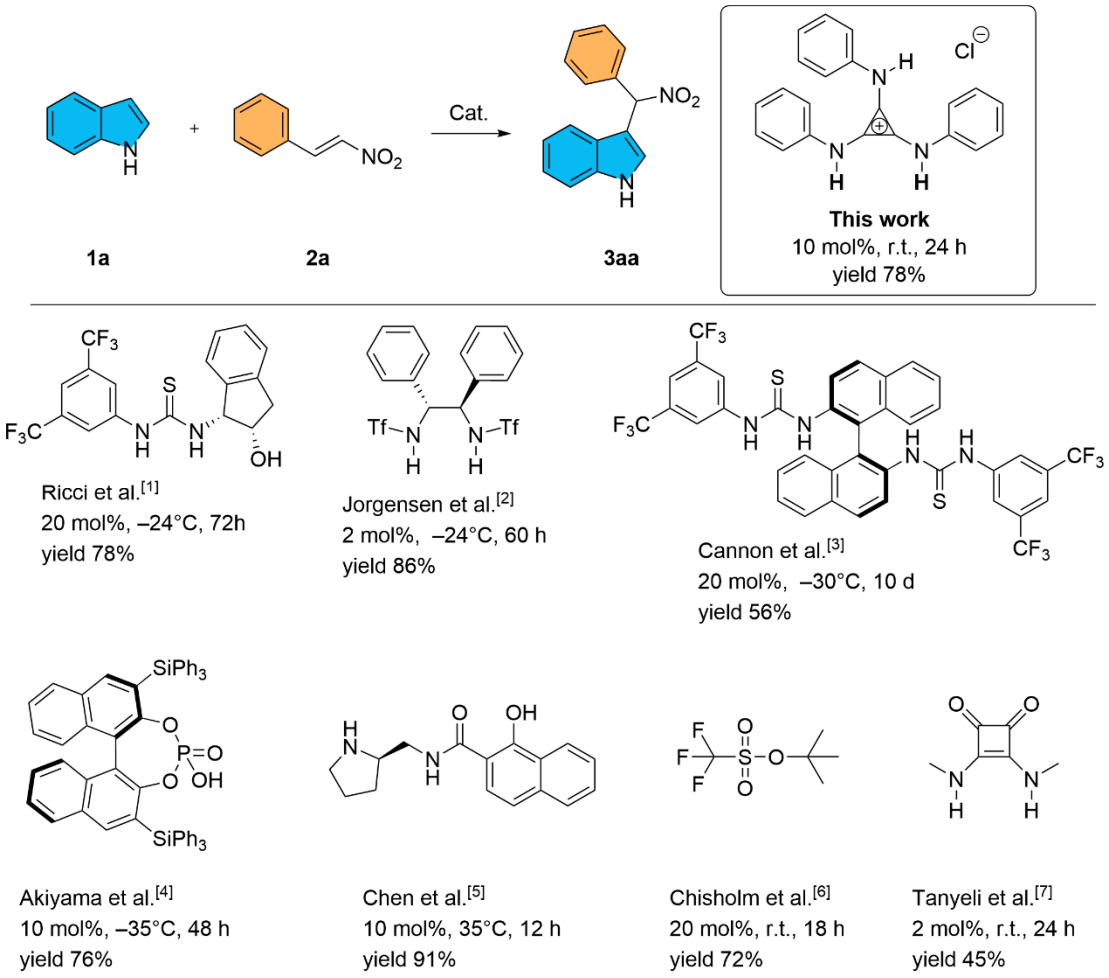
NMR spectra were recorded at room temperature on a Bruker AVANCE 400 spectrometer in deuterated solvents as noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to a residual solvent resonance as the internal standard (^{1}H δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6; ^{13}C δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-d_6). NMR peak multiplicities are abbreviated as follows: brs = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6520 Q-TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. XRD data were obtained on X-ray diffractometer (Bruker SMART APEX II).

All operations were performed using standard Schlenk techniques with an argon atmosphere to reduce exposure to water. Dichloromethane was distilled over CaH_2 under an argon atmosphere, and further dried over 3 Å molecular sieve pellets for 48 h before use. Benzene was purified by refluxing on sodium under an argon atmosphere, and further dried over 3 Å molecular sieve pellets for 48 h before use.

Catalysts **TPAC·Cl**, **TPAC·F**, **TDAC·Cl**, and **TDAC·F** were prepared according to the reported procedure[1]. Catalysts **TBA·Cl** and **TBA·F** were purchased from Sigma Aldrich without additional purification.

Reaction conditions had been screened in the initial attempts to verify the feasibility of this reaction. In pre-experiments, low catalyst loading was found that could not realize the Friedel-Crafts alkylation reaction of indoles with nitroalkenes. To ensure that the reaction is homogeneous, the solubility of the solvent must be carefully considered. Dichloromethane was found to be the optimal solvent after the experiment examination.

Comparsion of organocatalysts used in the F–C alkylation of indole and nitroalkene

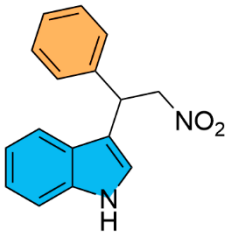


Scheme S1. A comparison between organocatalysts utilized to catalyze the F–C alkylation of indole and nitroalkene.

A comparison between related organocatalysts utilized to catalyze the F–C alkylation reaction of indole and nitroalkene was shown in Scheme S1. The amino-cyclopropenium ion pair could facilitate the coupling of indole to nitroalkene at room temperature with 10 mol% catalyst loading in 24 h, a 78% yield of the corresponding product was given.

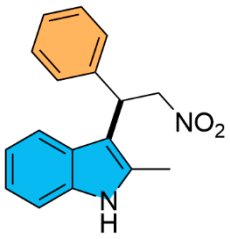
Characterization Data

3. -(2-Nitro-1-phenylethyl)-1H-indole (3aa)



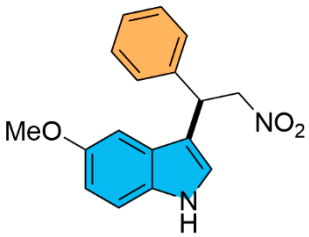
A colorless oil was obtained after purification by flash column chromatography (*n*-hexane-EtOAc, 10:1): 0.21 g, 78 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (brs, 1H), 7.37(d, *J* = 8.0 Hz, 1H), 7.29-7.18 (m, 6H), 7.12 (m, 1H), 7.02 – 6.95 (m, 2H), 5.12 (t, *J* = 7.9 Hz, 1H), 4.99 (dd, *J* = 12.5, 7.6 Hz, 1H), 4.89 (dd, *J* = 12.5, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.6, 129.0, 127.9,127.7, 126.2, 122.8, 121.7, 120.0, 119.0, 114.5, 111.5, 79.6, 41.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}N_2O_2H$ 267.1128; Found 267.1127.

2. -Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (3ba)



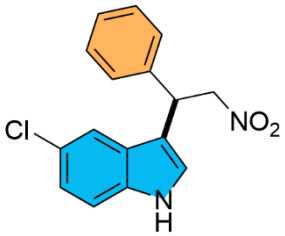
A colorless oil was obtained after purification by flash column chromatography (*n*-hexane-EtOAc, 9:1): 0.24 g, 86 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.16 (m, 6H), 7.08 – 7.04 (m, 1H), 6.99 – 6.96 (m, 1H), 5.20 – 5.12 (m, 2H), 5.10 – 5.04 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.3, 132.9, 128.9, 127.4, 127.2, 127.0, 121.5, 119.9, 118.7, 110.8, 109.0, 78.8, 40.6, 12.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}N_2O_2H$ 281.1285; Found 281.1274.

5. -Methoxy-3-(2-nitro-1-phenylethyl)-1H-indole (3ca)



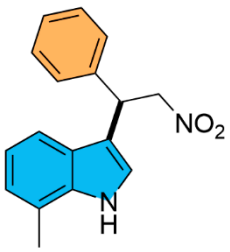
A white solid was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.26 g, 88 % yield; m.p. 138.2 – 140.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (brs, 1H), 7.27 – 7.15 (m, 6H), 6.92-6.91 (m, 1H), 6.79 – 6.76 (m, 2H), 5.06 (t, J = 7.9 Hz, 1H), 4.97 (dd, J = 12.4, 7.5 Hz, 1H), 4.86 (dd, J = 12.4, 8.4 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 139.3, 131.7, 129.1, 127.9, 127.7, 126.7, 122.4, 114.3, 112.9, 112.2, 101.0, 79.6, 56.0, 41.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}N_2O_3H$ 297.1234; Found 297.1267.

5. -Chloro-3-(2-nitro-1-phenylethyl)-1H-indole (3da)



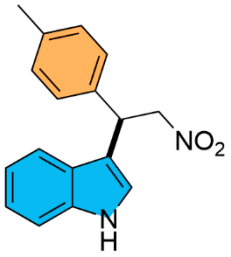
A colorless oil was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.16 g, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (brs, 1H), 7.32 (d, J = 1.6 Hz, 1H), 7.30 – 7.19 (m, 6H), 7.08 (dd, J = 8.6, 1.9 Hz, 1H), 7.03 (d, J = 2.1 Hz, 1H), 5.07 (t, J = 8.0 Hz, 1H), 4.99 – 4.94 (m, 1H), 4.89 – 4.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 135.0, 129.2, 127.9, 127.8, 127.4, 125.9, 123.3, 123.0, 118.6, 114.3, 112.5, 79.5, 41.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}ClN_2O_2H$ 301.0738; Found 301.0765.

7. -Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (3ea)



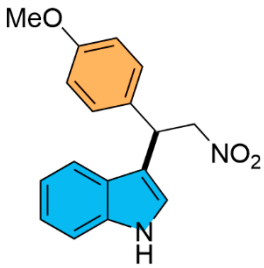
A colorless oil was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.16 g, 57 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (brs, 1H), 7.28 – 7.17 (m, 6H), 6.96 – 6.93 (m, 3H), 5.13-5,09 (m, 1H), 4.99 (dd, J = 12.5, 7.6 Hz, 1H), 4.87 (dd, J = 12.5, 8.3 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 136.2, 129.0, 127.9, 127.6, 125.8, 123.3, 121.4, 120.7, 120.3, 116.8, 115.0, 79.7, 41.8, 16.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}N_2O_2H$ 281.1285; Found 281.1276.

3. -(2-nitro-1-(p-tolyl)ethyl)-1H-indole (3ab)



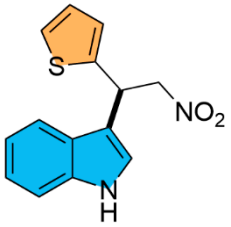
A colorless oil was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.09 g, 33 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (brs, 1H), 7.51 (dd, J = 8.0, 1.0 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.29 – 7.22 (m, 3H), 7.18 – 7.11 (m, 3H), 7.04 (m, 1H), 5.20 (t, J = 8.0 Hz, 1H), 5.09 (dd, J = 12.4, 7.6 Hz, 1H), 4.96 (dd, J = 12.4, 8.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.6, 136.3, 129.7, 127.7, 126.2, 122.8, 121.7, 120.0, 119.1, 114.7, 111.5, 79.8, 41.3, 21.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}N_2O_2H$ 281.1285; Found 281.1274.

3. -(1-(4-methoxyphenyl)-2-nitroethyl)-1H-indole (3ac)



A white solid was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.16 g, 55 % yield; m.p. 148.2 – 150.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (brs, 1H), 7.44 (dd, J = 7.9, 1.1 Hz, 1H), 7.36 (dt, J = 8.2, 1.0 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.10 – 7.02 (m, 2H), 6.86 – 6.84 (m, 1H), 5.14 (t, J = 8.0 Hz, 1H), 5.05 (dd, J = 12.2, 7.5 Hz, 1H), 4.90 (dd, J = 12.2, 8.4 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 136.7, 131.3, 129.0, 126.3, 122.8, 121.6, 120.1, 119.2, 115.0, 114.4, 111.5, 79.9, 55.4, 41.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}N_2O_3H$ 297.1234; Found 297.1267.

3. -(2-Nitro-1-thiophen-2-yl-ethyl)-1H-indole (3ad)



A colorless oil was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.19 g, 71 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.61 – 7.59 (m, 1H), 7.41-7.39 (m, 1H), 7.32 – 7.18 (m, 3H), 7.09 – 7.00 (m, 3H), 5.53 (t, J = 7.9 Hz, 1H), 5.12-5.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.5, 127.1, 125.8, 125.4, 125.0, 122.9, 122.1, 120.2, 118.9, 114.2, 111.6, 80.1, 37.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}N_2O_2SH$ 273.0692; Found 273.0645.

Tri(phenylamino)cyclopropenium chloride **TPAC·Cl**

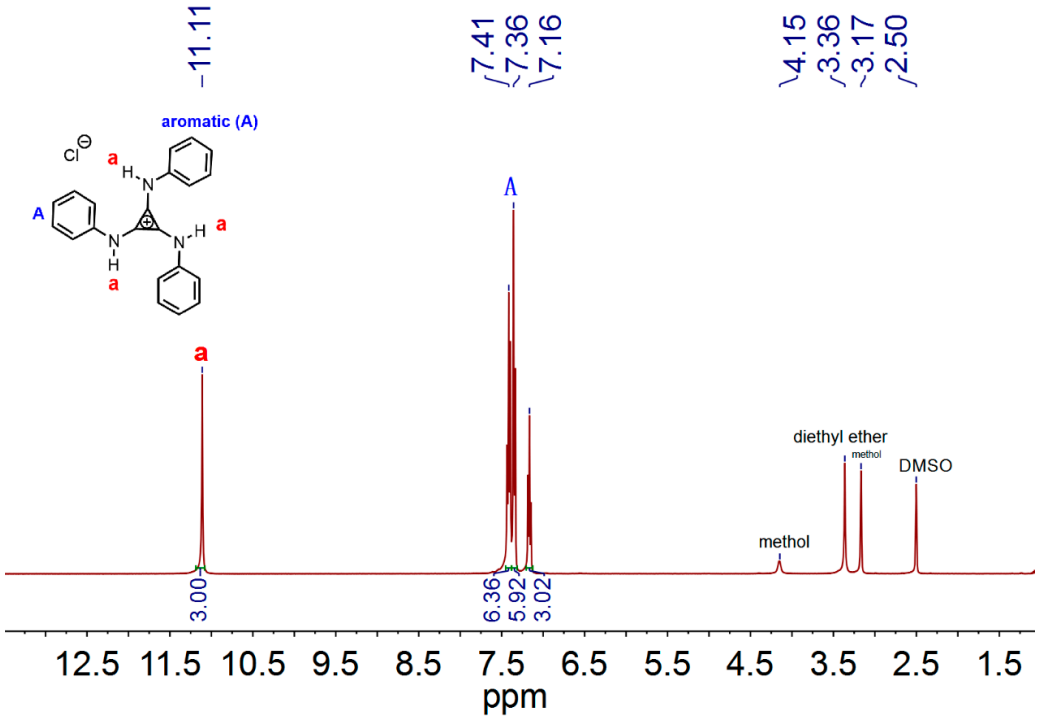
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.1 (s, 3H), 7.48 – 7.41 (m, 6H), 7.36 – 7.27 (m, 6H), 7.22 – 7.16 (m, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 139.28, 130.22, 124.48, 118.47, 113.32. HRMS (ESI-ToF) m / z [M]+ calcd for C21H18N3 312.1495, found 312.1497. The spectral data were consistent with values reported in the literature[8].

Tris(dimethylamino)cyclopropenium chloride **TDAC·Cl**

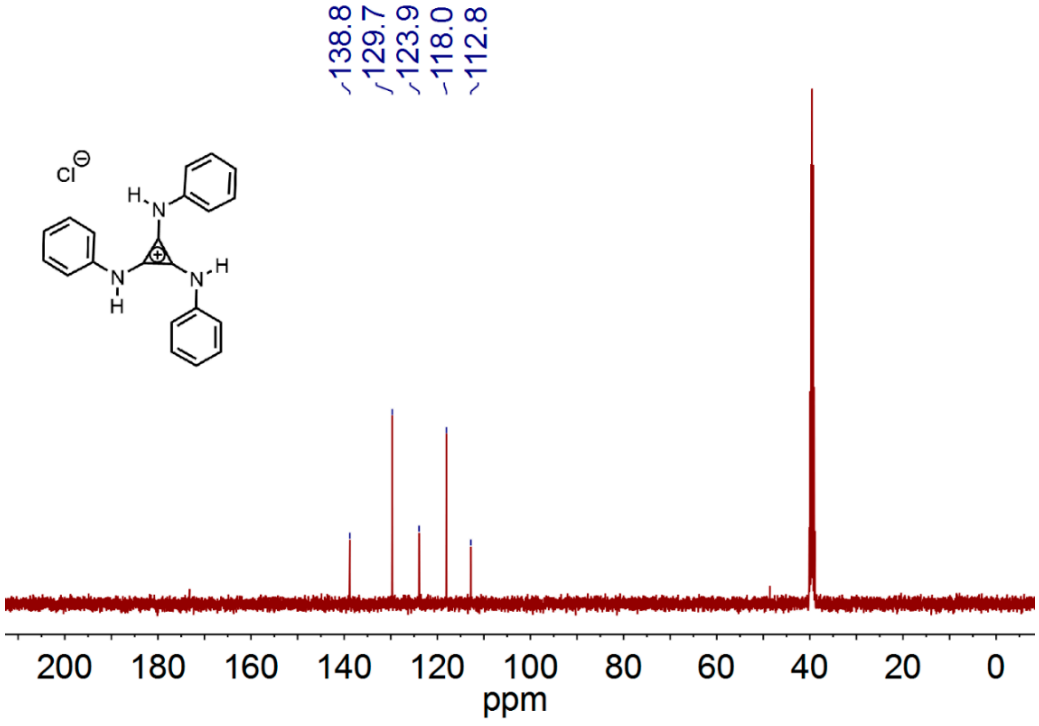
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.19 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 117.81, 42.53. **HRMS** (ESI-TOF) m / z [M]+ calcd for C9H18N3 168.1495, found 168.1434. The spectral data were consistent with values reported in the literature[8].

NMR Spectra of Compounds

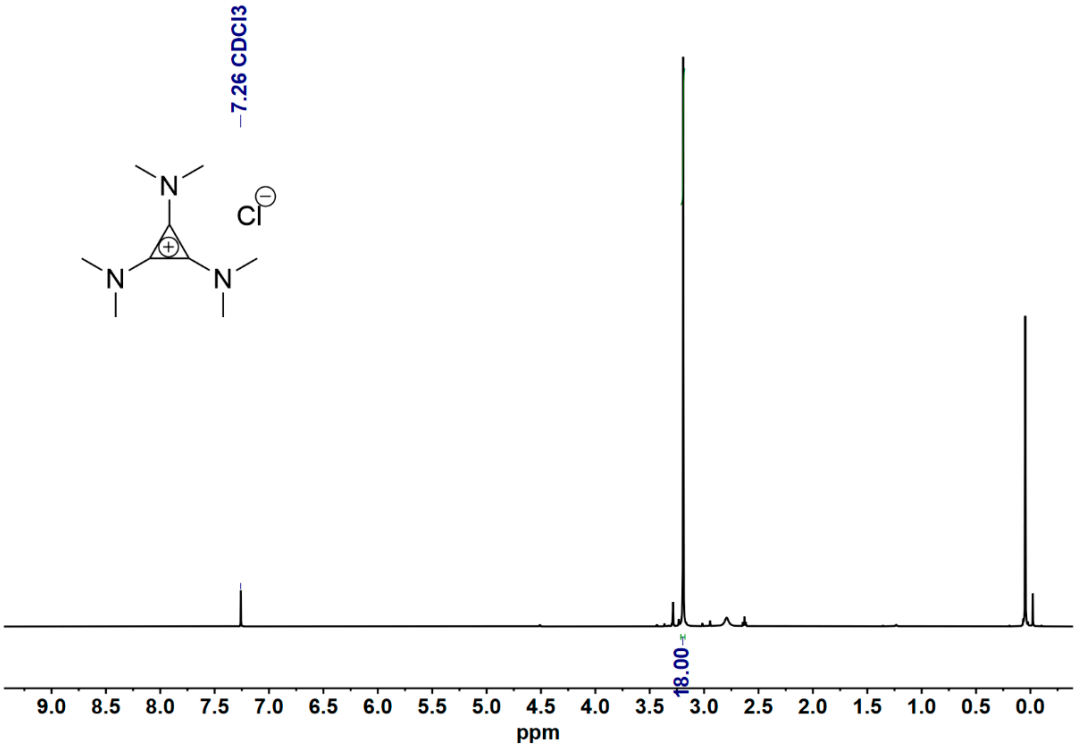
Copies of NMR spectra of catalysts



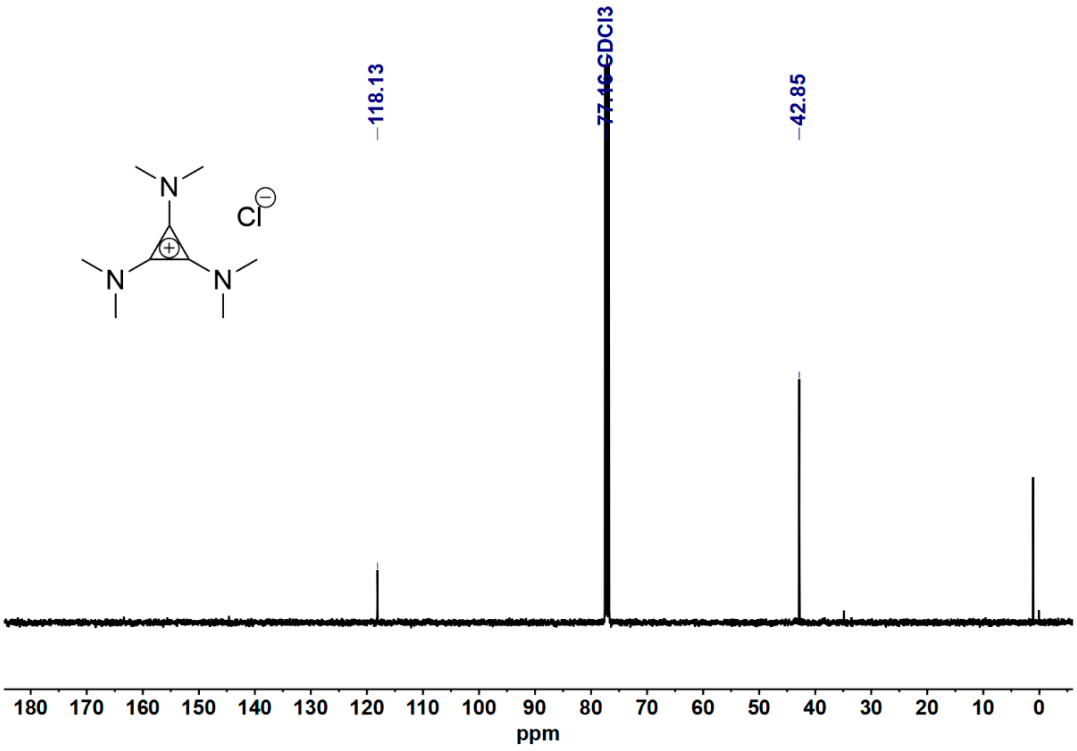
^{1}H NMR Spectrum of Compound **TPAC·Cl**



^{13}C NMR Spectrum of Compound **TPAC·Cl**

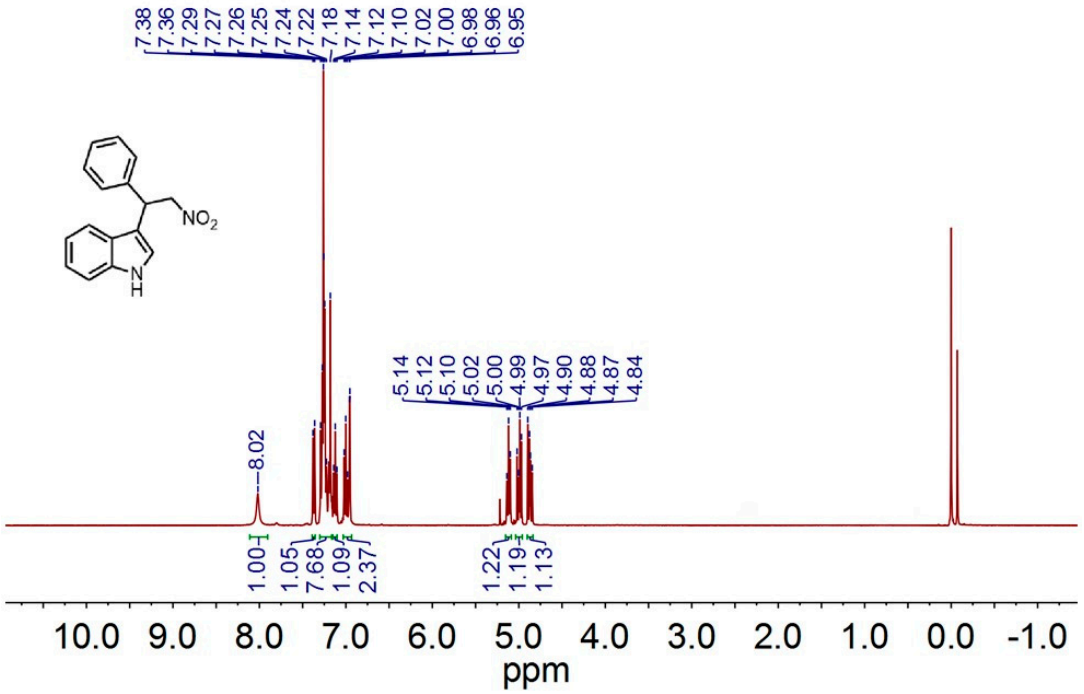


^{1}H NMR Spectrum of Compound **TPAC·Cl**

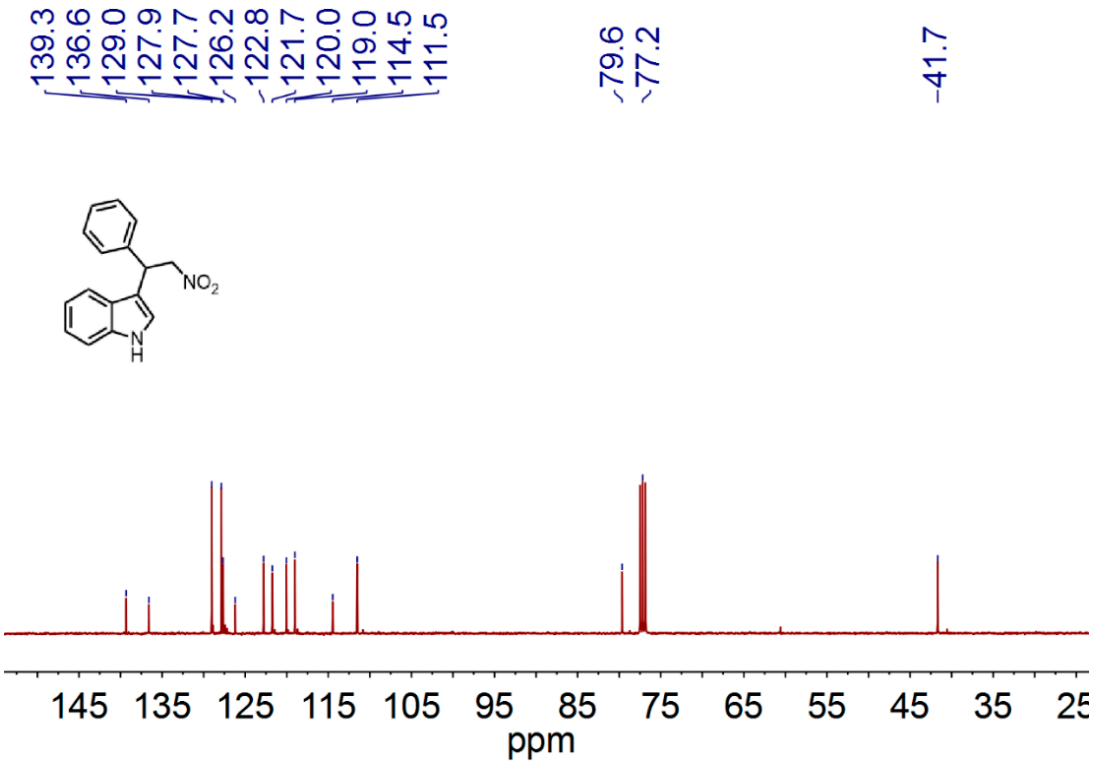


^{1}H NMR Spectrum of Compound **TPAC·Cl**

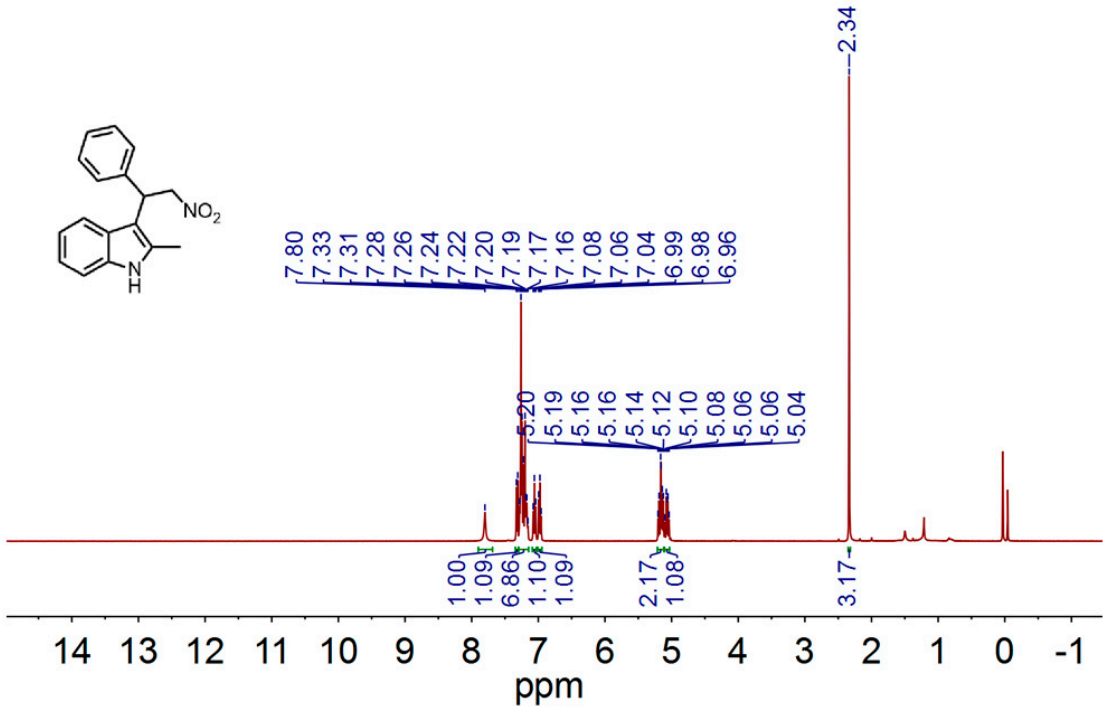
Copies of NMR spectra of products



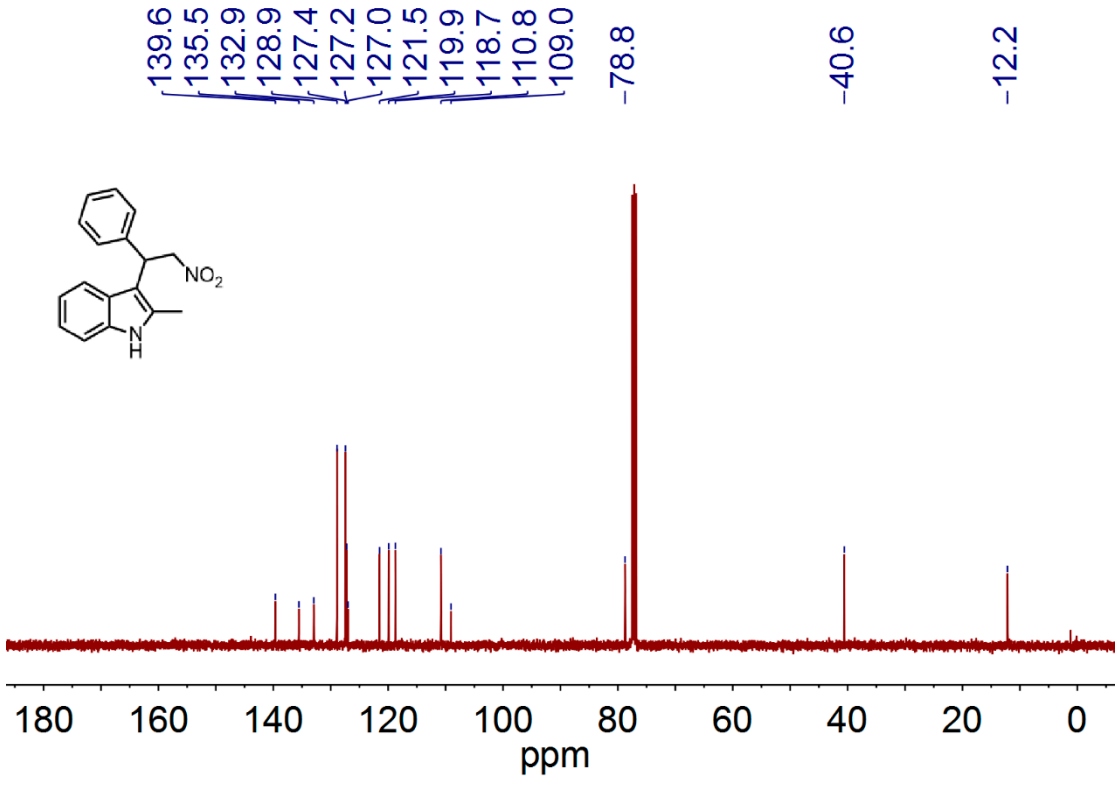
^{1}H NMR Spectrum of Compound **3aa**



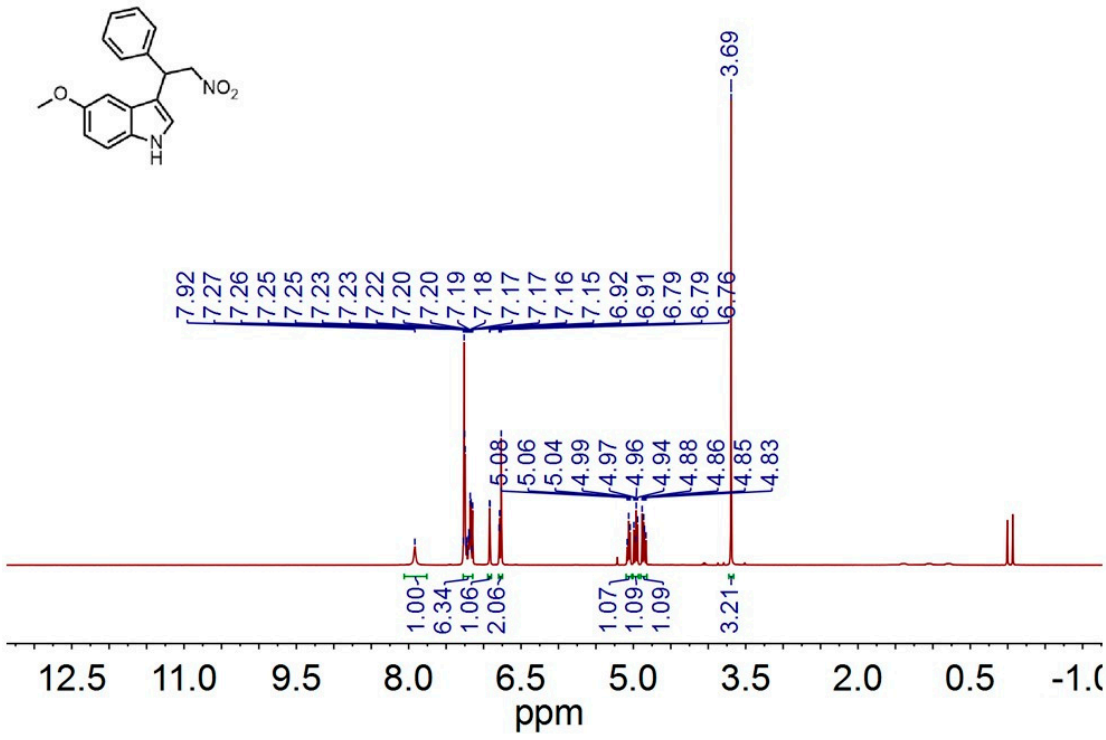
^{13}C NMR Spectrum of Compound **3aa**



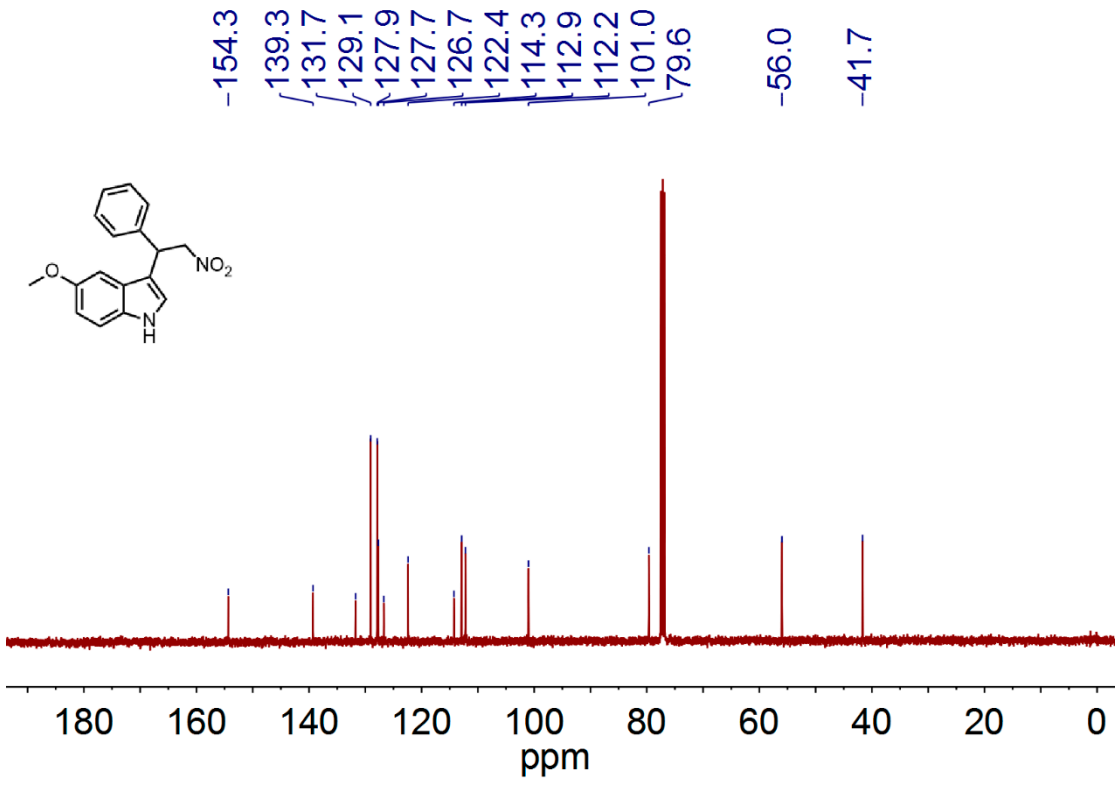
^{1}H NMR Spectrum of Compound **3ba**



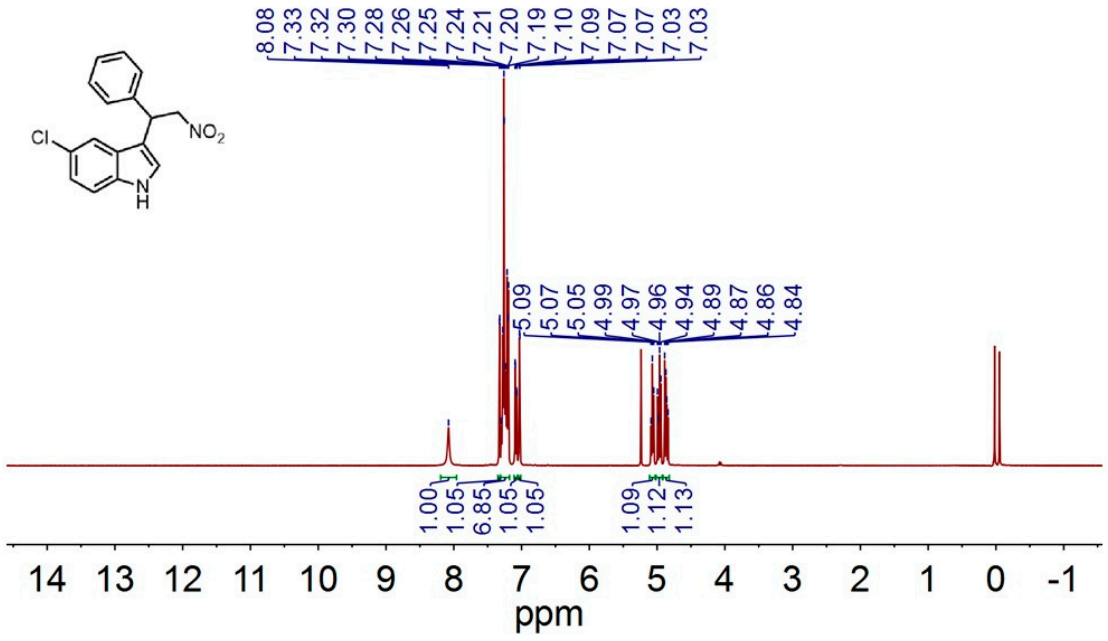
^{13}C NMR Spectrum of Compound **3ba**



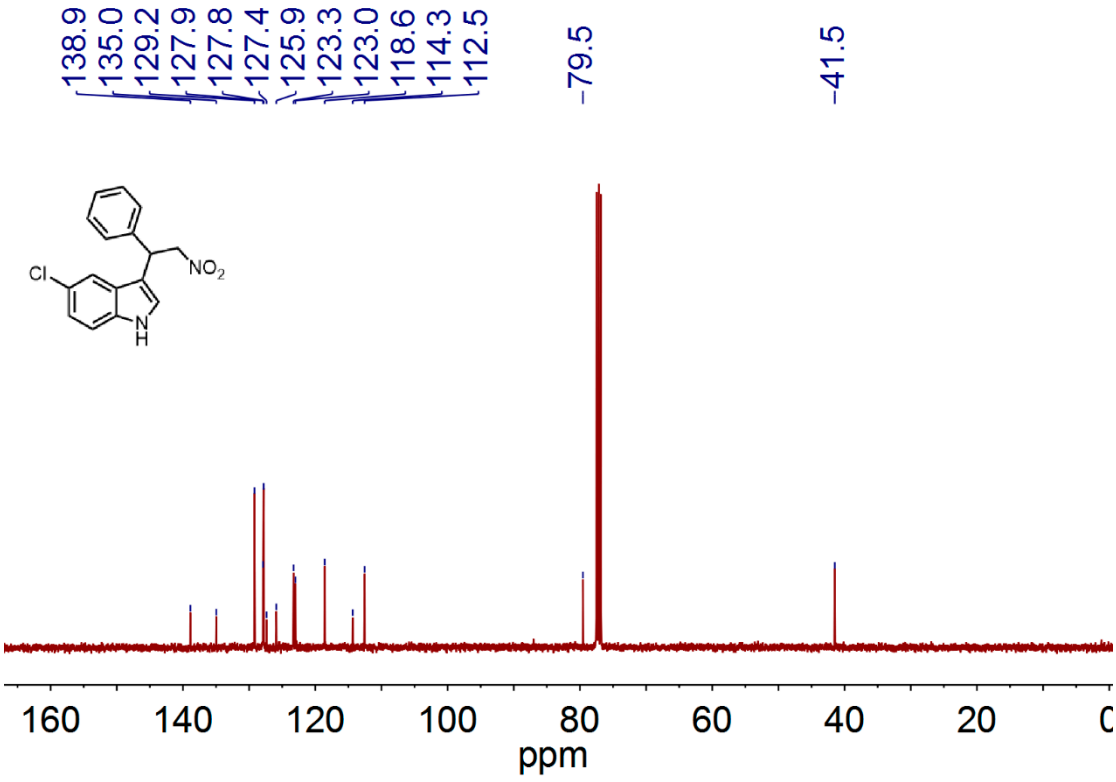
^{1}H NMR Spectrum of Compound **3ca**



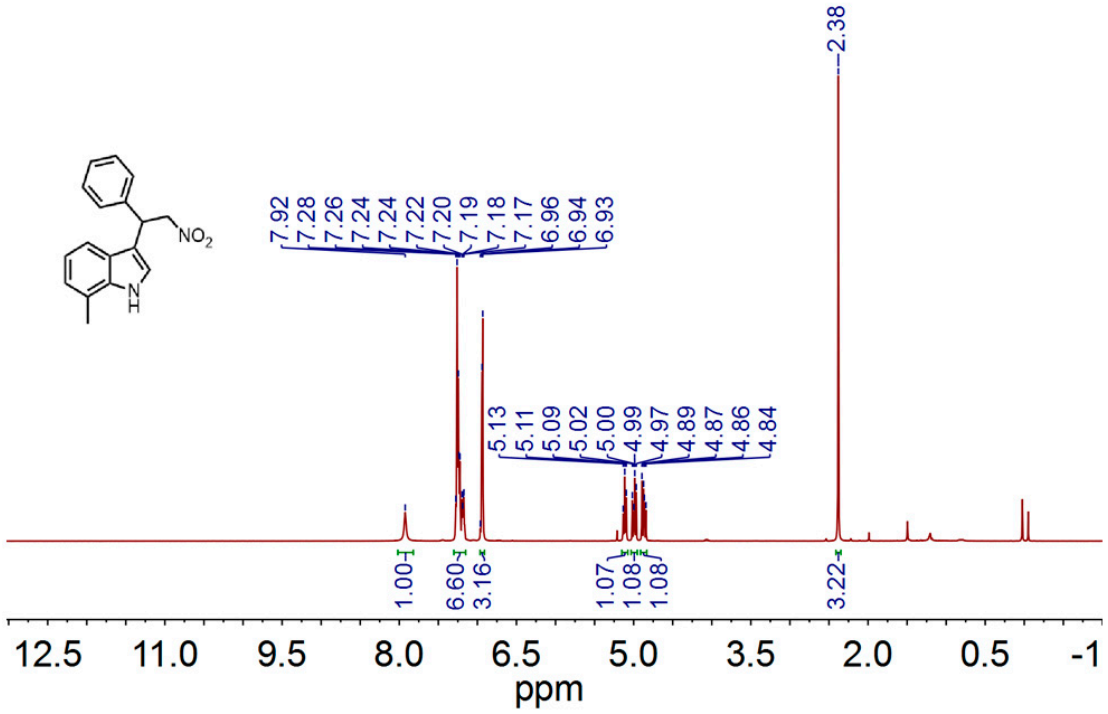
^{13}C NMR Spectrum of Compound **3ca**



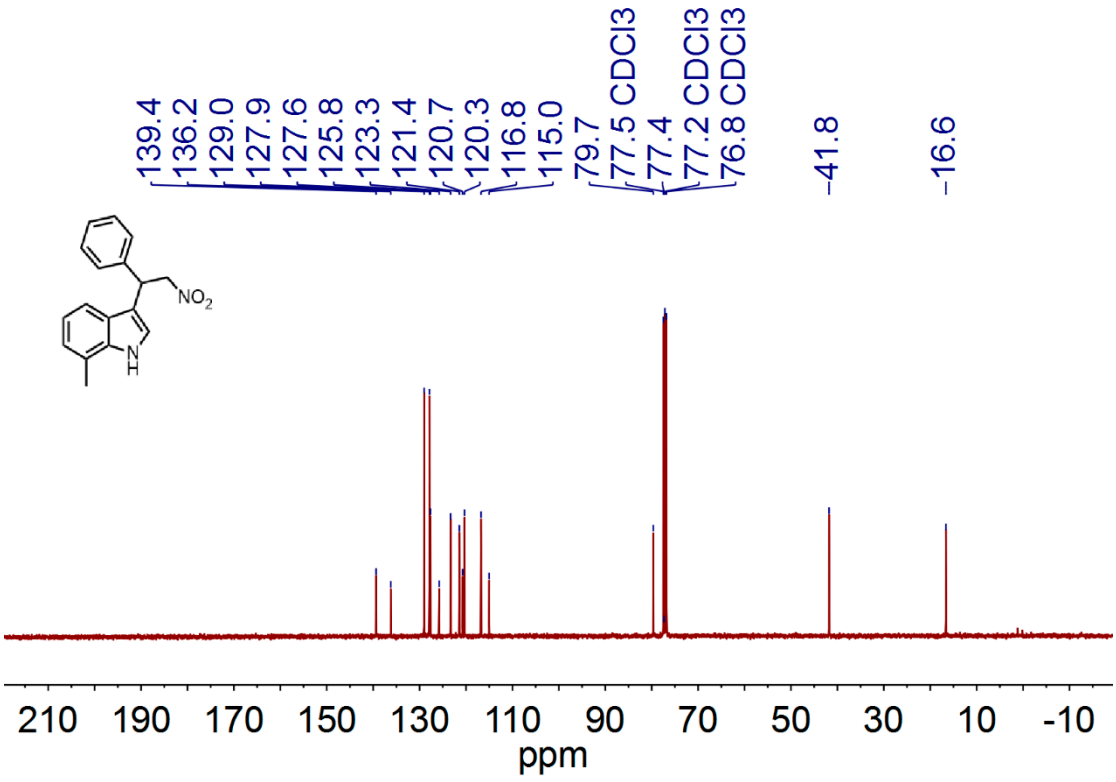
^{1}H NMR Spectrum of Compound **3da**



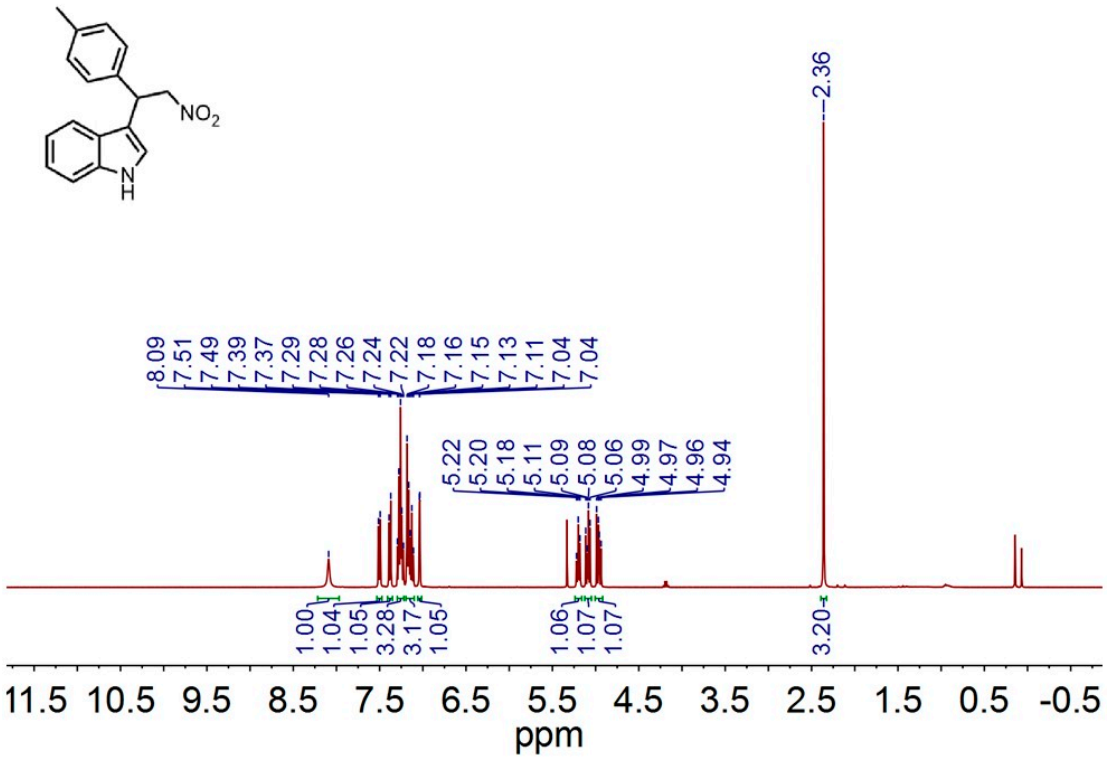
^{13}C NMR Spectrum of Compound **3da**



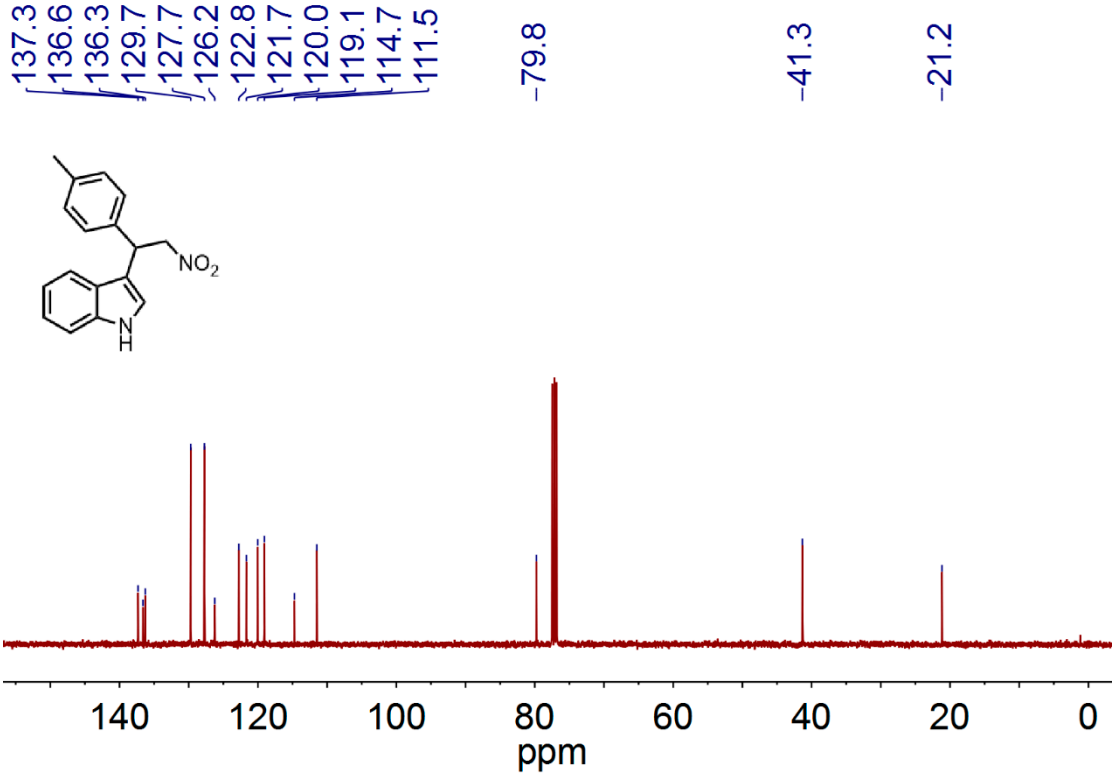
^{1}H NMR Spectrum of Compound **3ea**



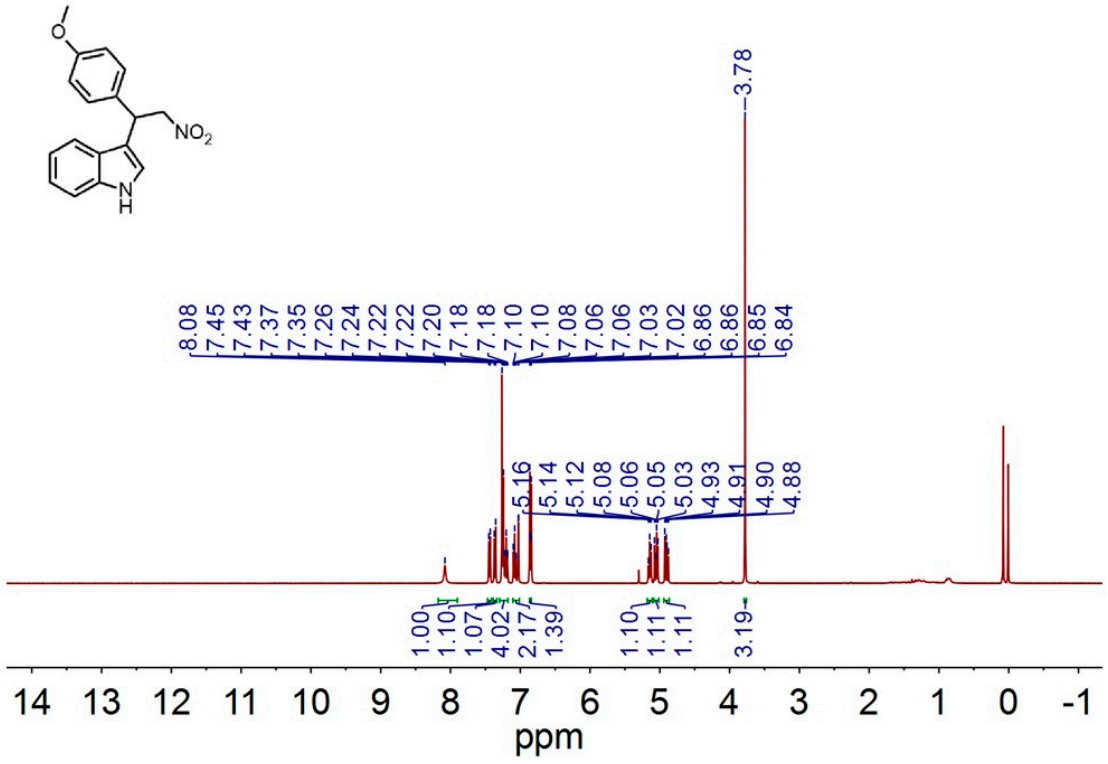
^{13}C NMR Spectrum of Compound **3ea**



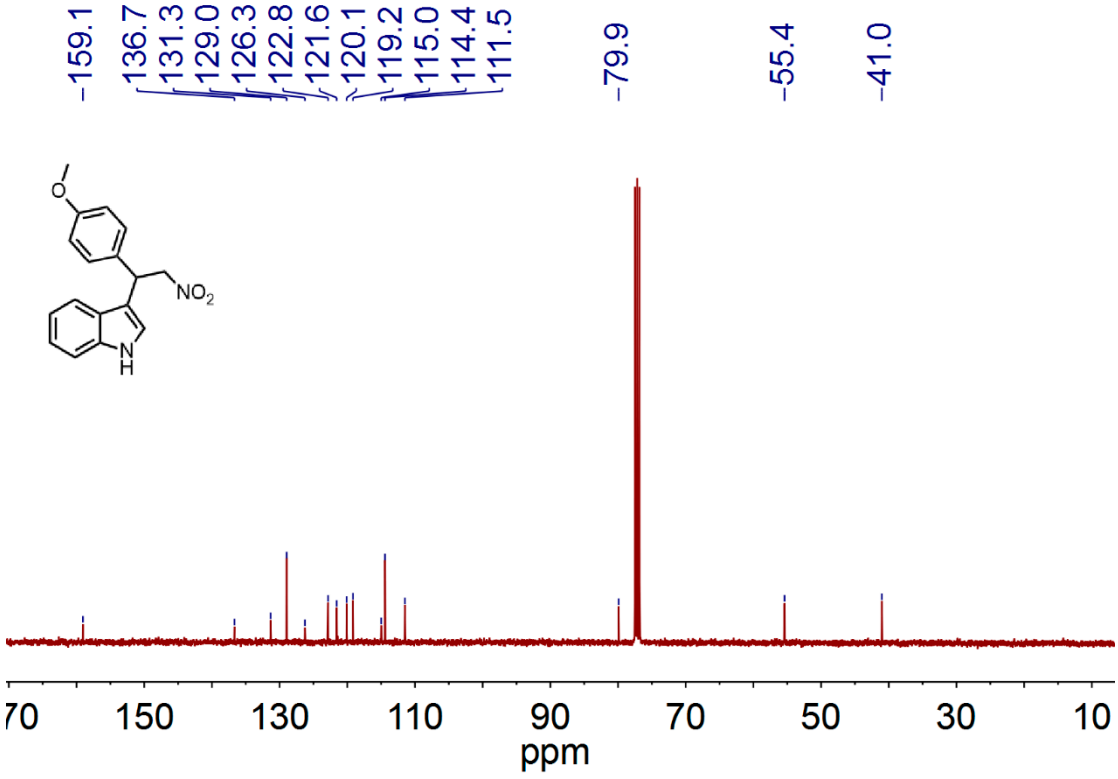
^{1}H NMR Spectrum of Compound **3ab**



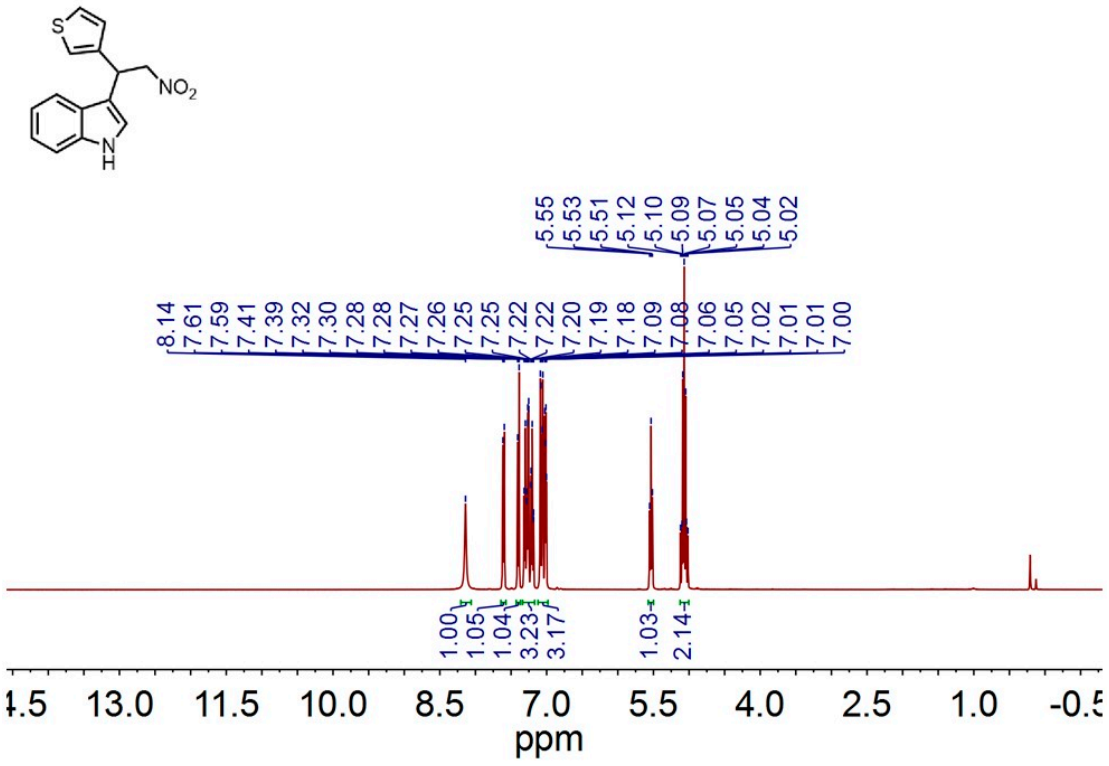
^{13}C NMR Spectrum of Compound **3ab**



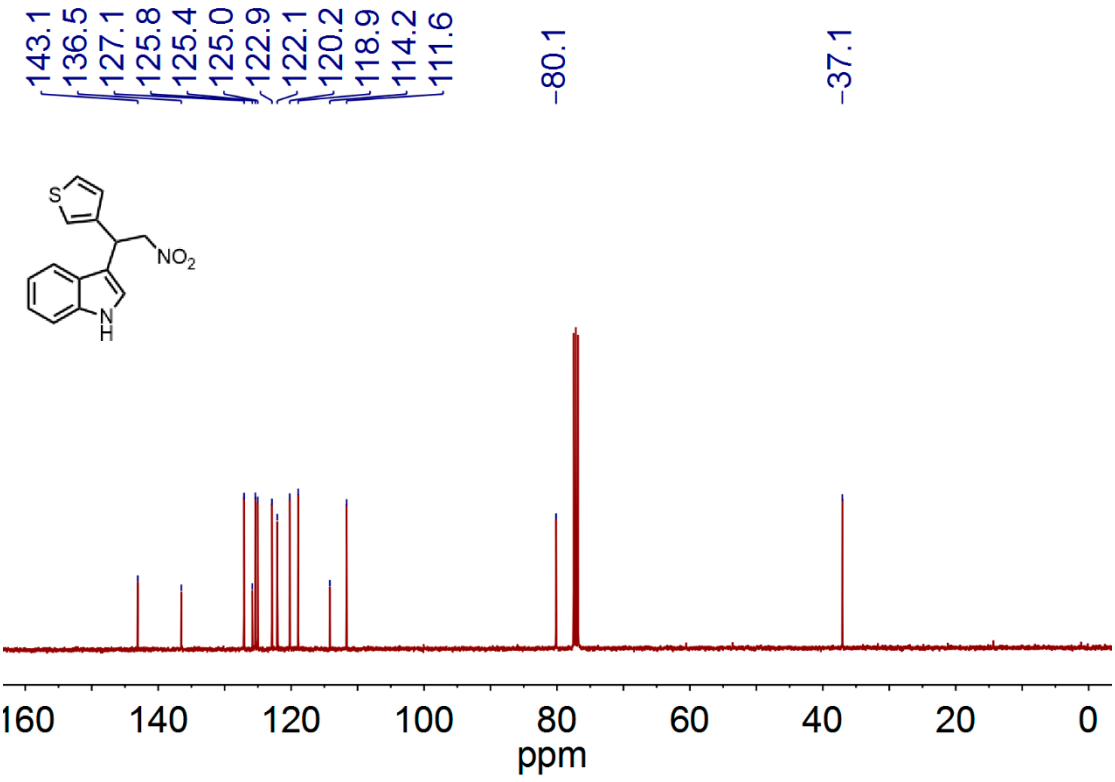
^{1}H NMR Spectrum of Compound **3ac**



^{13}C NMR Spectrum of Compound **3ac**



^{1}H NMR Spectrum of Compound **3ad**



^{13}C NMR Spectrum of Compound **3ac**

X-ray crystal structure of TPAC·Cl

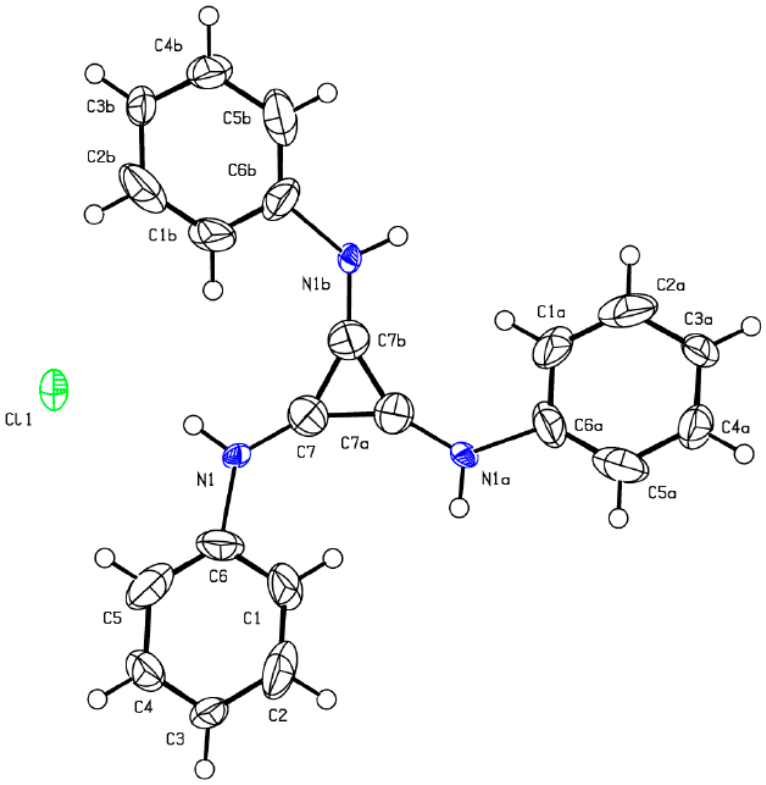


Table S1. Crystal data and structure refinement for TPAC·Cl[8].

complex	**1**
Formula	C21H18ClN3
Formula weight	347.83
Crystal system	Cubic
space group	*P*213
a (Å)	13.484(8)
b (Å)	13.484(8)
c (Å)	13.484(8)
α (º)	90
β (º)	90
γ (º)	90
Volume(Å^3)	2451.6(4)
Z	4
T (K)	296(2)
D_{calcd} (g/m^3)	1.573
F(000)	728
Reflections collected	2045
Unique reflections	1846
Goof	1.140

R_1[I> 2σ(I)]	0.1082
wR_2[I>2σ(I)]	0.3079[a]
CCDC NO.	1509942

[a] w =1/[$\sigma^2(F_0)^2$+(0.1820P)^2 +3.4136P], where P = (F_0^2 + 2F_c^2)/3;.

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