Supporting Information

**Aminocyclopropenium as a new class of hydrogen bonding catalyst in Friedel–Crafts alkylation**

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General Information

Organic solutions were concentrated using Buchi rotary evaporator or IKA rotary evaporator. 1H NMR spectra were recorded on a Bruker-AV-400 (400 MHz) at ambient temperature, using the chemical shift of a residual protic solvent (CHCl3 at 7.26 ppm or DMSO at 2.50 ppm) as an internal reference. 13C NMR spectra were recorded on a Bruker AV-400 (100 MHz) using the central resonance of the triplet of CHCl3 at δ77.16 ppm or DMSO at δ 39.52 ppm as an internal reference.

All operations were performed using standard Schlenk techniques with an argon atmosphere to reduce exposure to water. Dichloromethane was distilled over CaH2 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.

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; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C16H14N2O2H 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; 1H NMR (400 MHz, CDCl3) 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). 13C NMR (100 MHz, CDCl3) 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 C17H16N2O2H 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; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C17H16N2O3H 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; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C16H13ClN2O2H 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; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C17H16N2O2H 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; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C17H16N2O2H 281.1285; Found 281.1274.

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

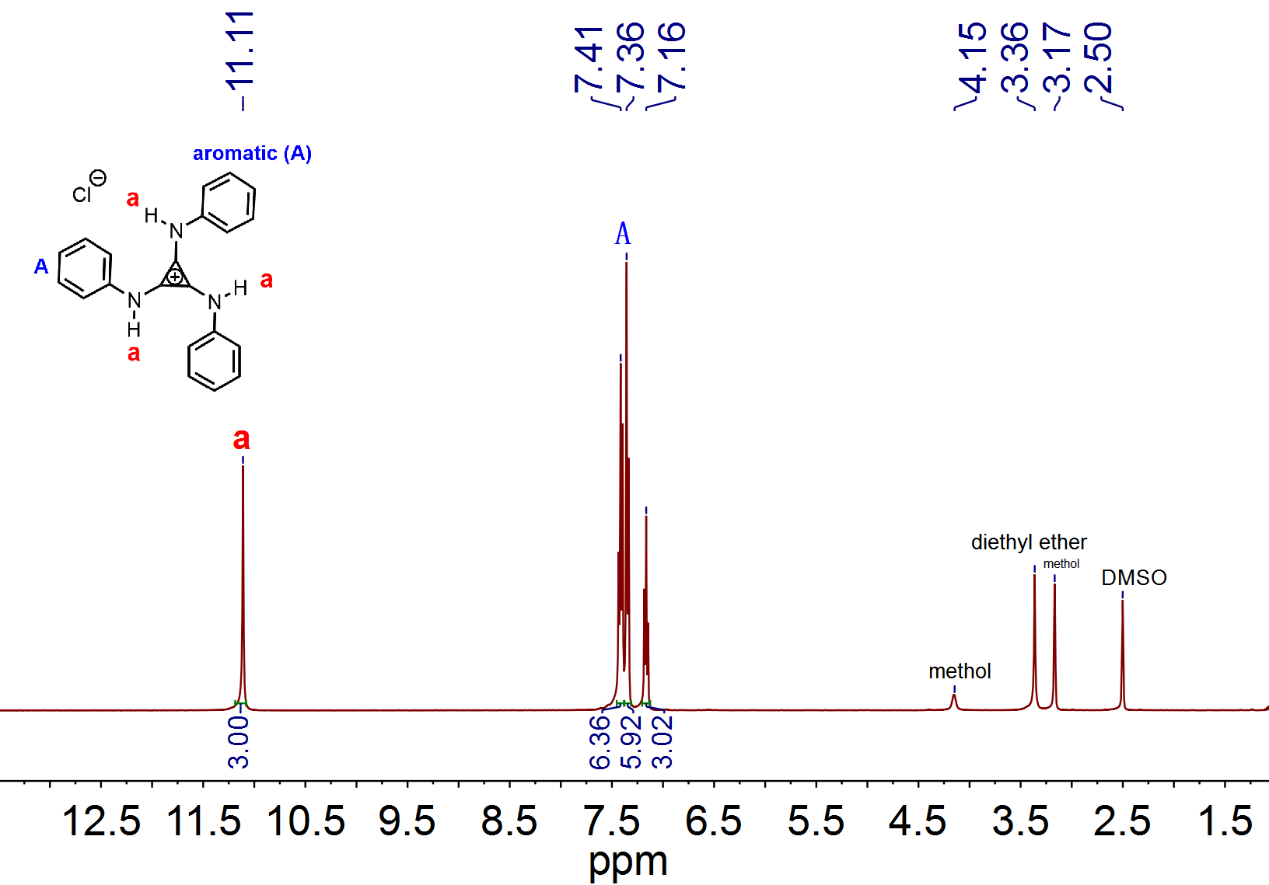
A white solid was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.16 g, 55 % yield; m.p. 148.2 – 150.1 oC; 1H NMR (400 MHz, CDCl3) δ 8.08 (brs, 1H), 7.44 (dd, J = 7.9, 1.1 Hz, 1H), 7.36 (dt, J = 8.2, 1.0 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.10 – 7.02 (m, 2H), 6.86 – 6.84 (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); 13C NMR (100 MHz, CDCl3) 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 C17H16N2O3H 297.1234; Found 297.1267.

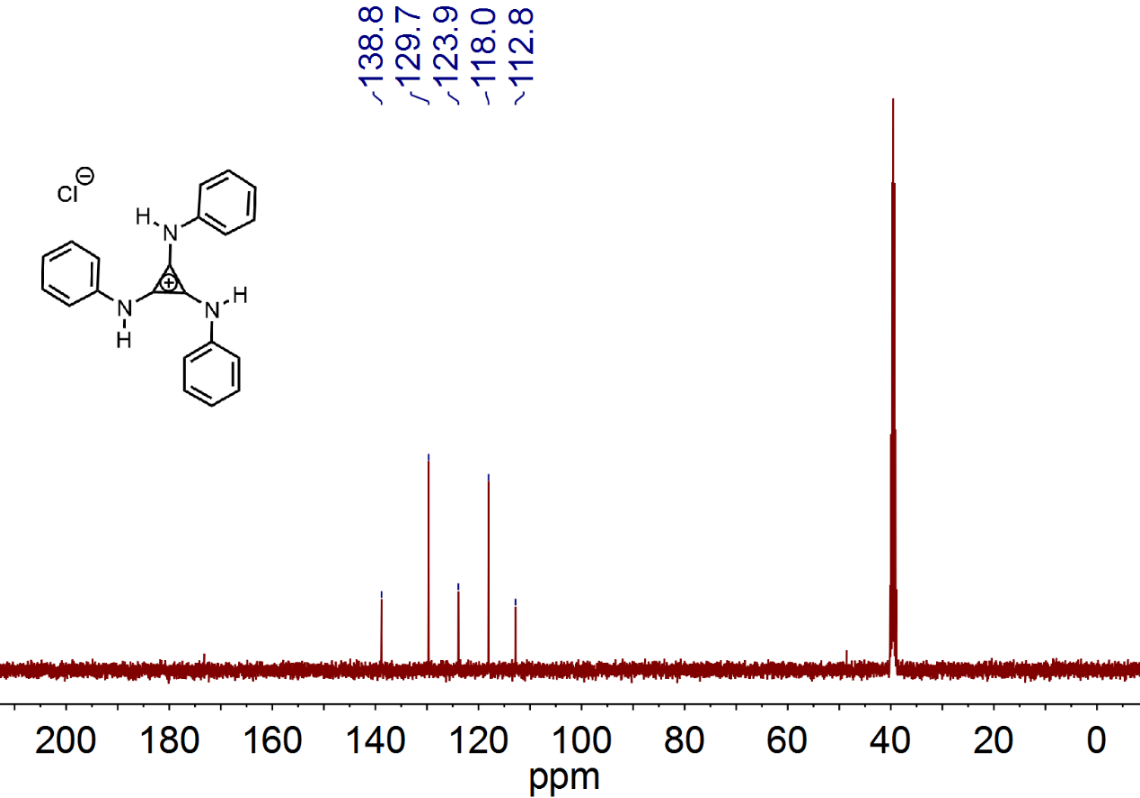
*3-(2-Nitro-1-thiophen-2-yl-ethyl)-1H-indole* ***3ad***

A colorless oil was obtained after purification by flash column chromatography (n-hexane-EtOAc, 9:1): 0.19 g, 71 % yield; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C14H12N2O2SH 273.0692; Found 273.0645.

NMR Spectra of Compounds

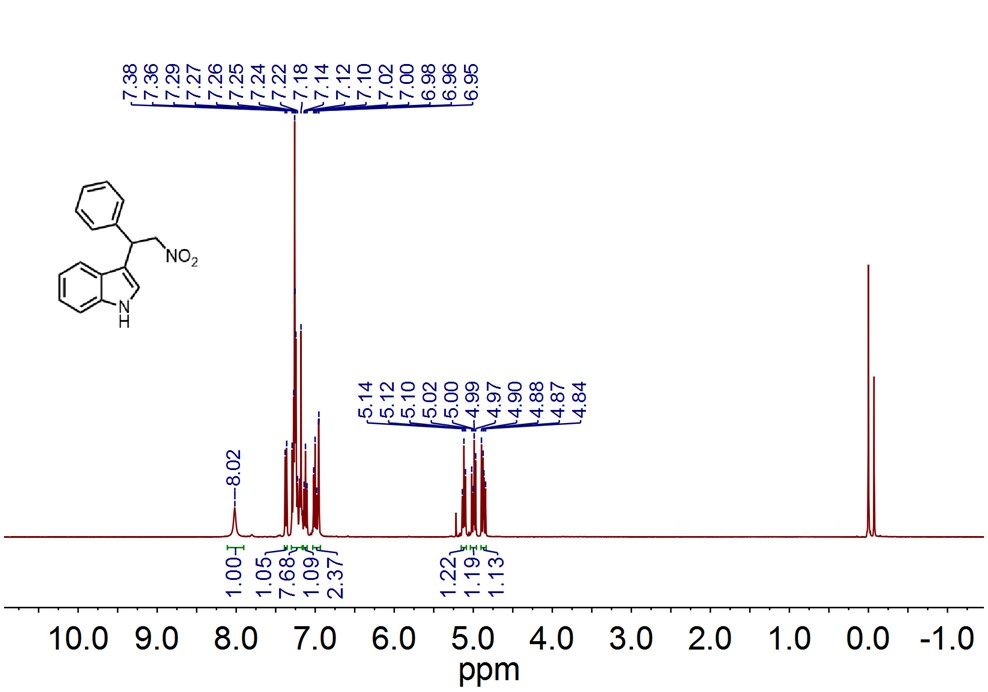
**Copies of NMR spectra of catalysts**

****1H NMR Spectrum of Compound **TPAC·Cl**

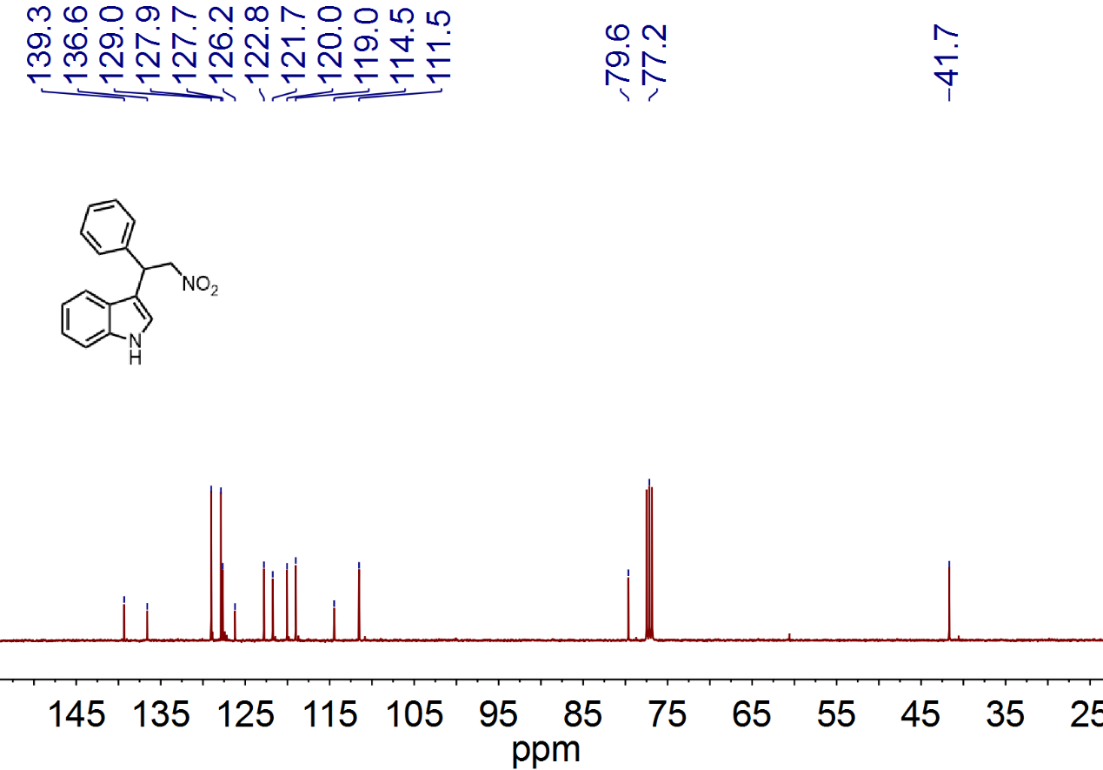
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13C NMR Spectrum of Compound **TPAC·Cl**

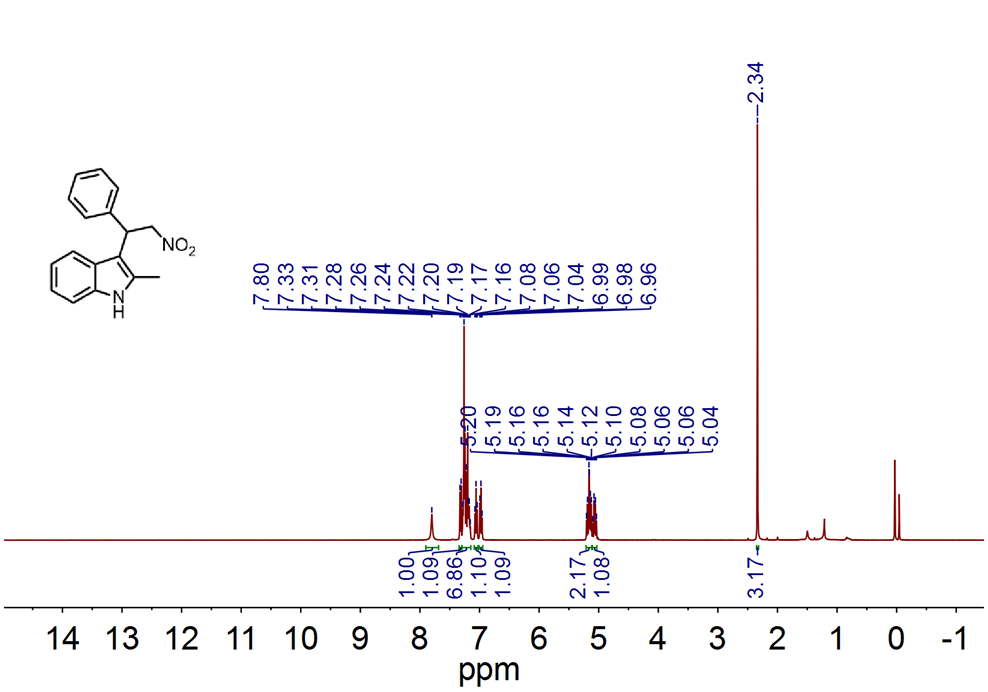
**Copies of NMR spectra of products**



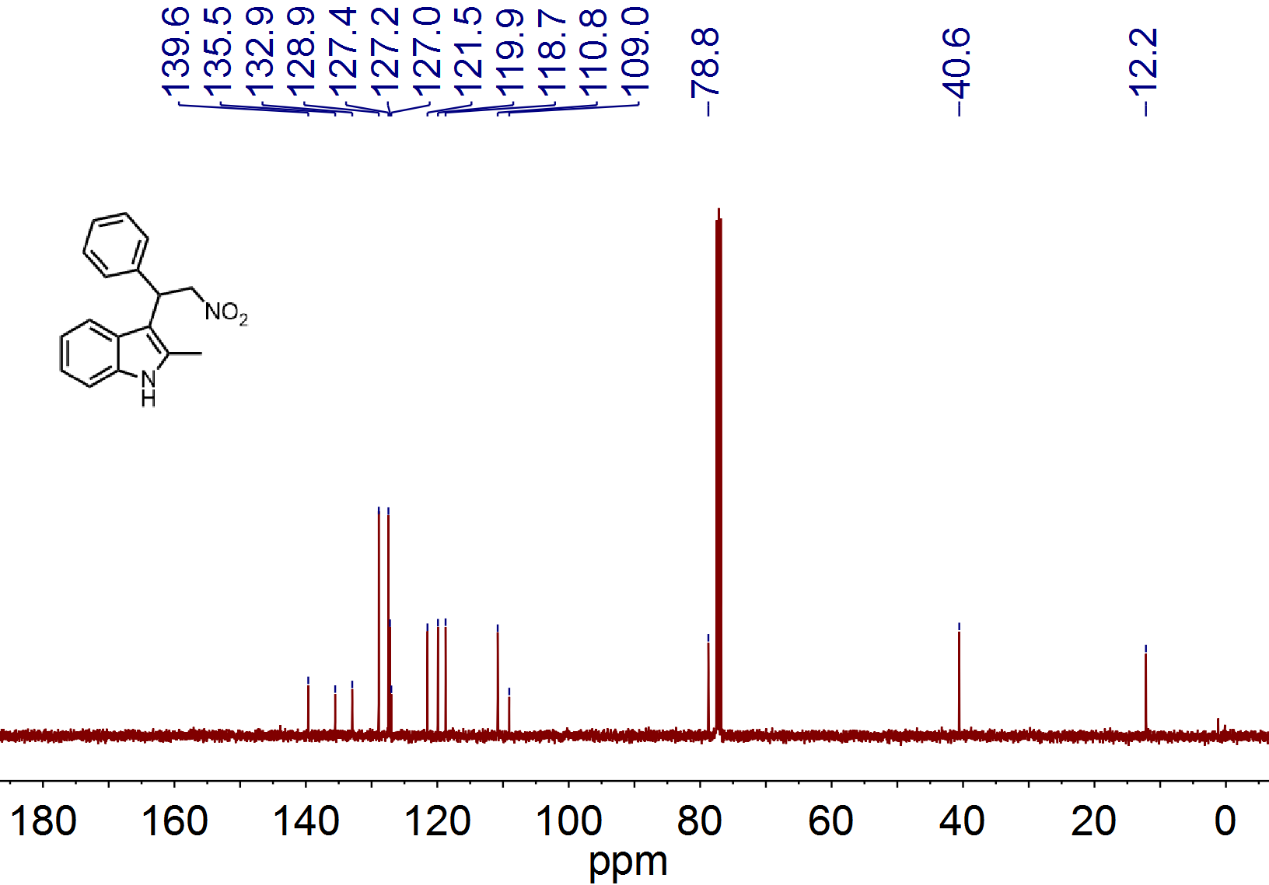
1H NMR Spectrum of Compound **3aa**



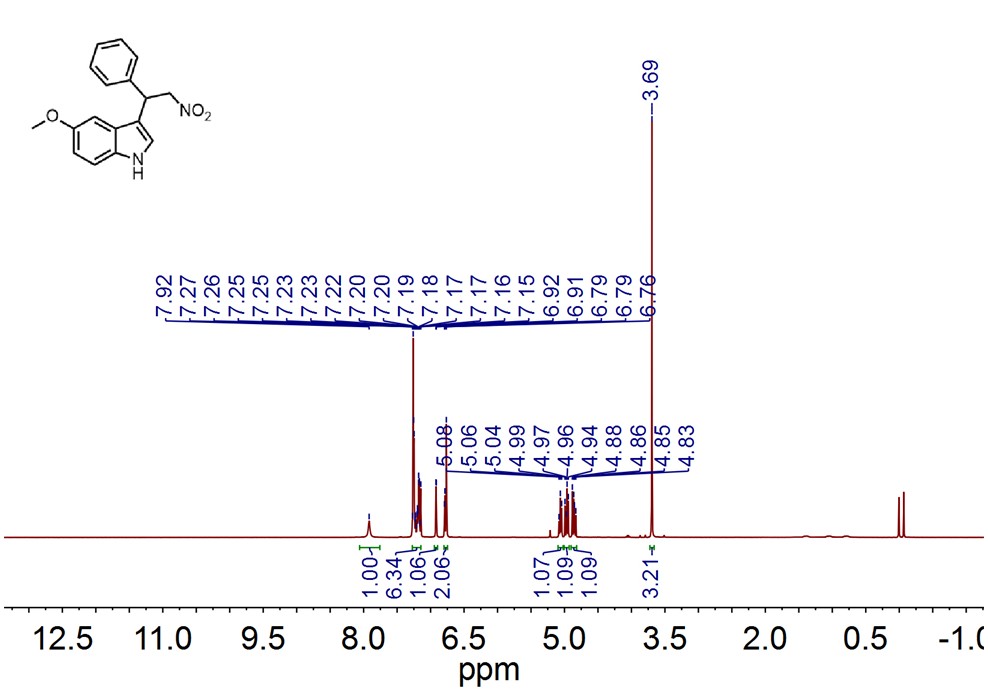
13C NMR Spectrum of Compound **3aa**



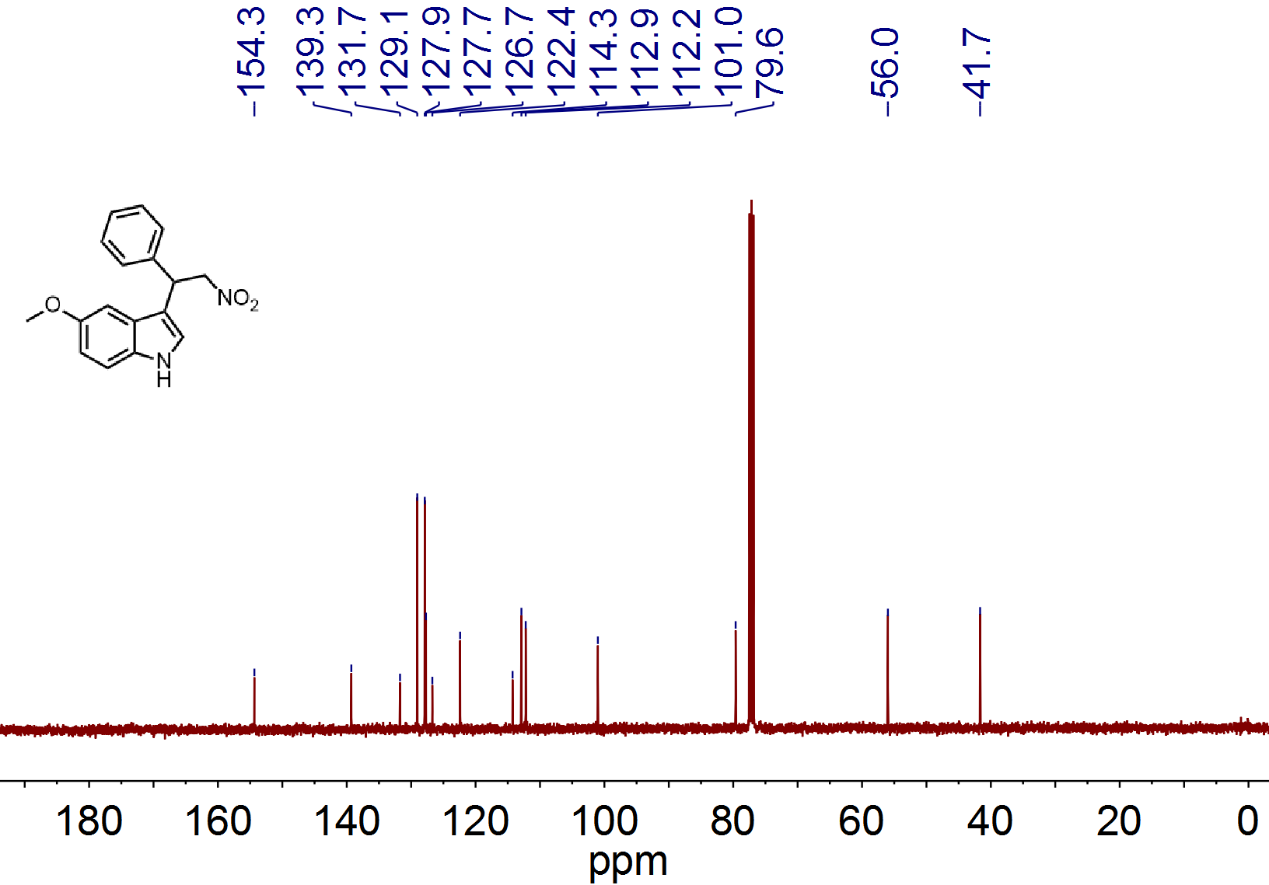
1H NMR Spectrum of Compound **3ba**



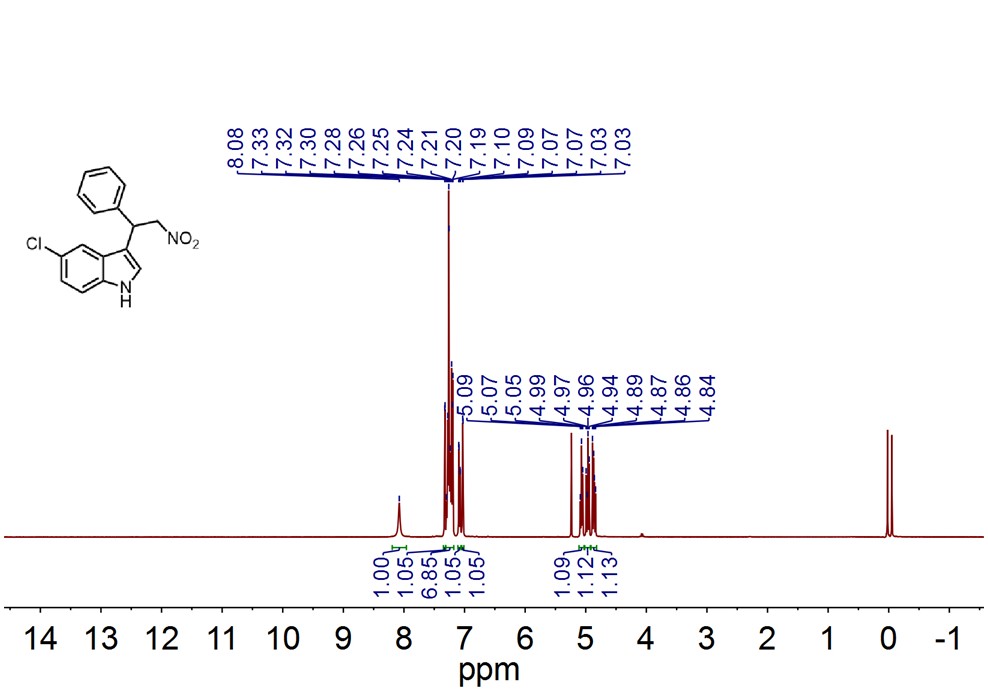
13C NMR Spectrum of Compound **3ba**



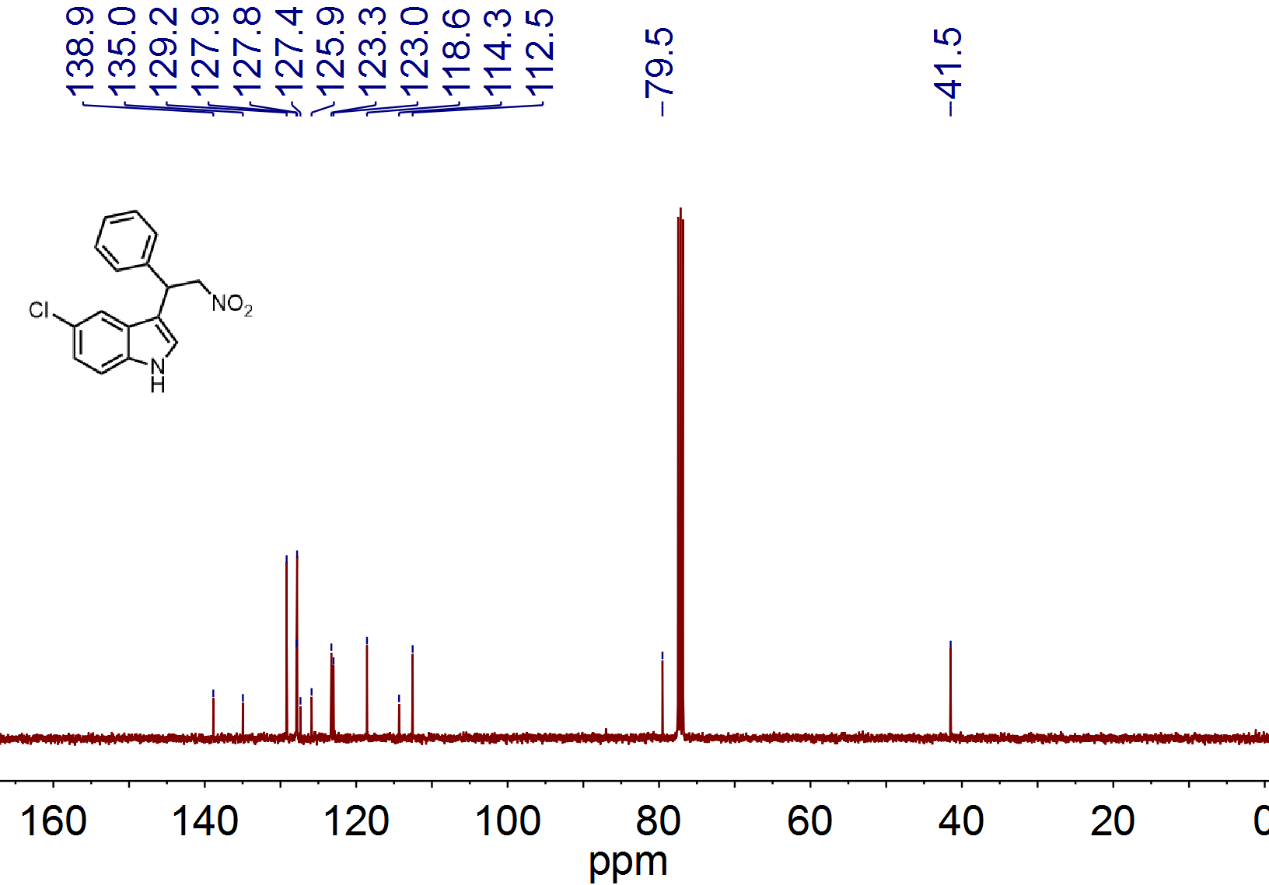
1H NMR Spectrum of Compound **3ca**

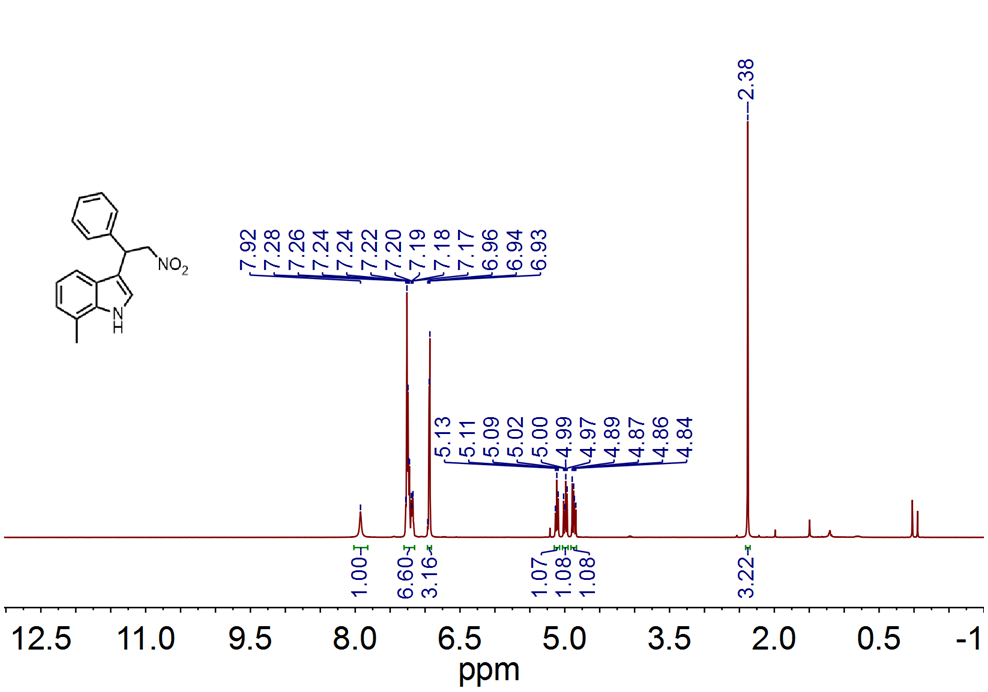


13C NMR Spectrum of Compound **3ca**

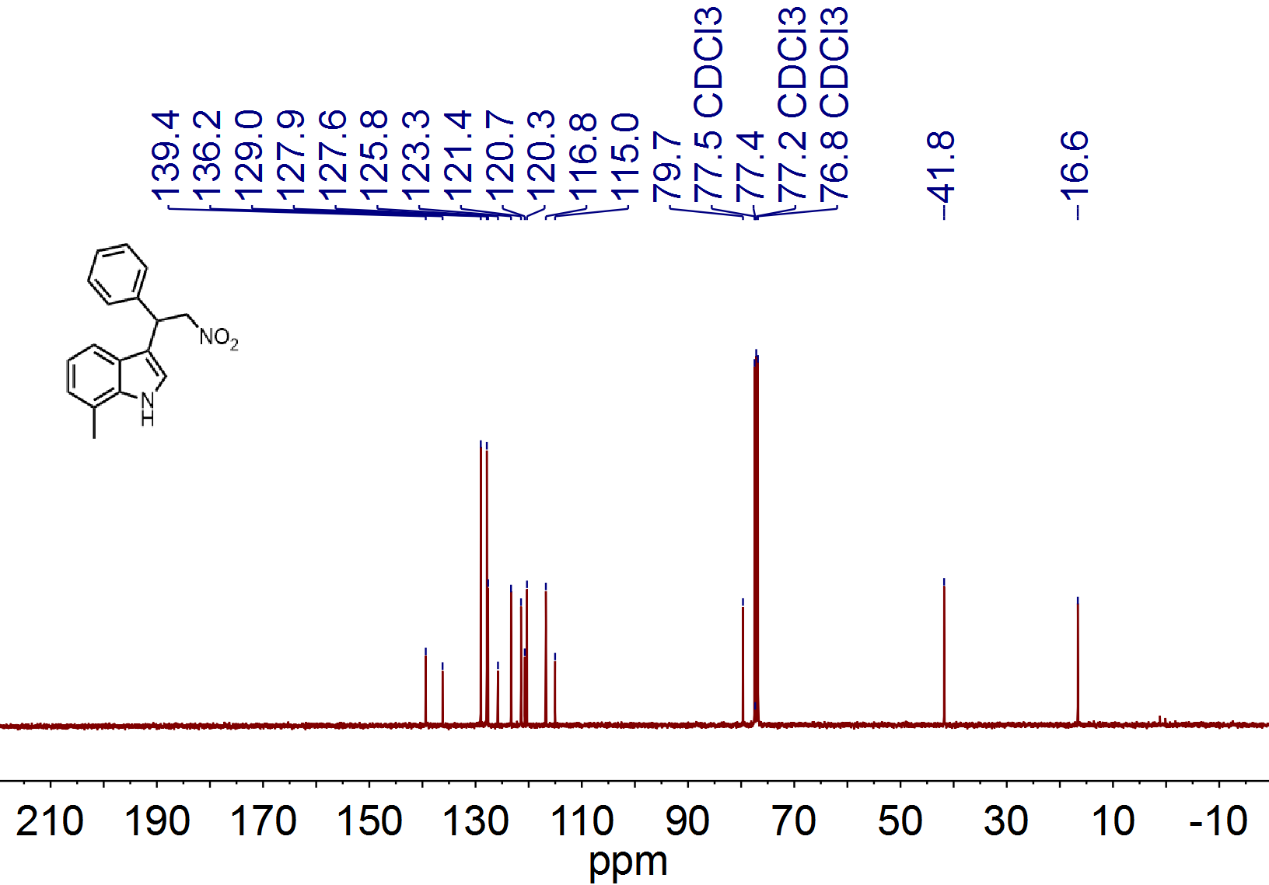


1H NMR Spectrum of Compound **3da**

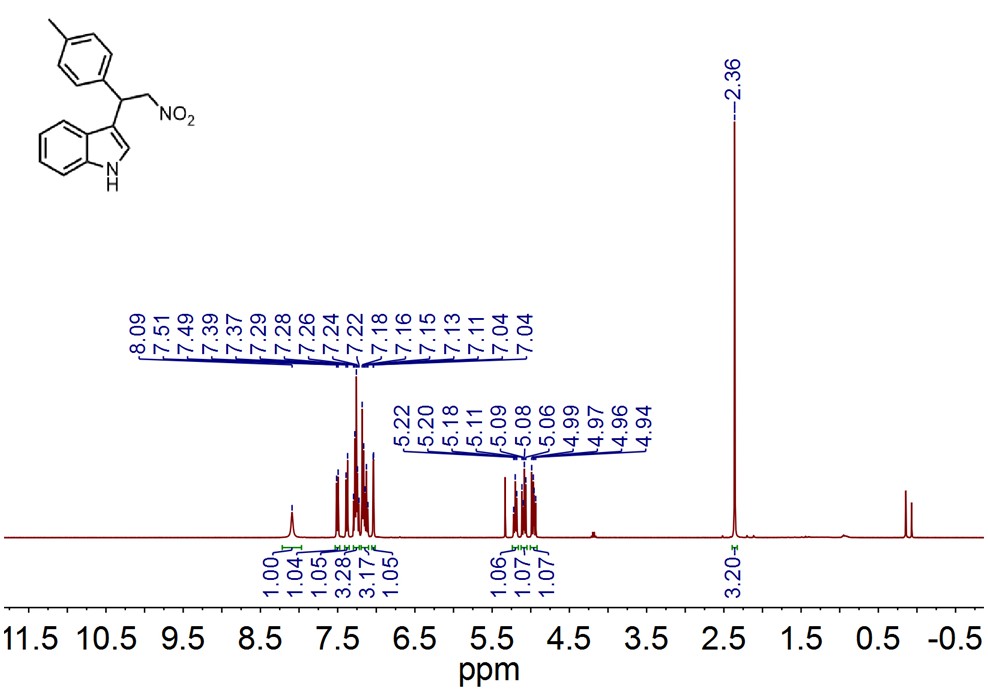


13C NMR Spectrum of Compound **3da**

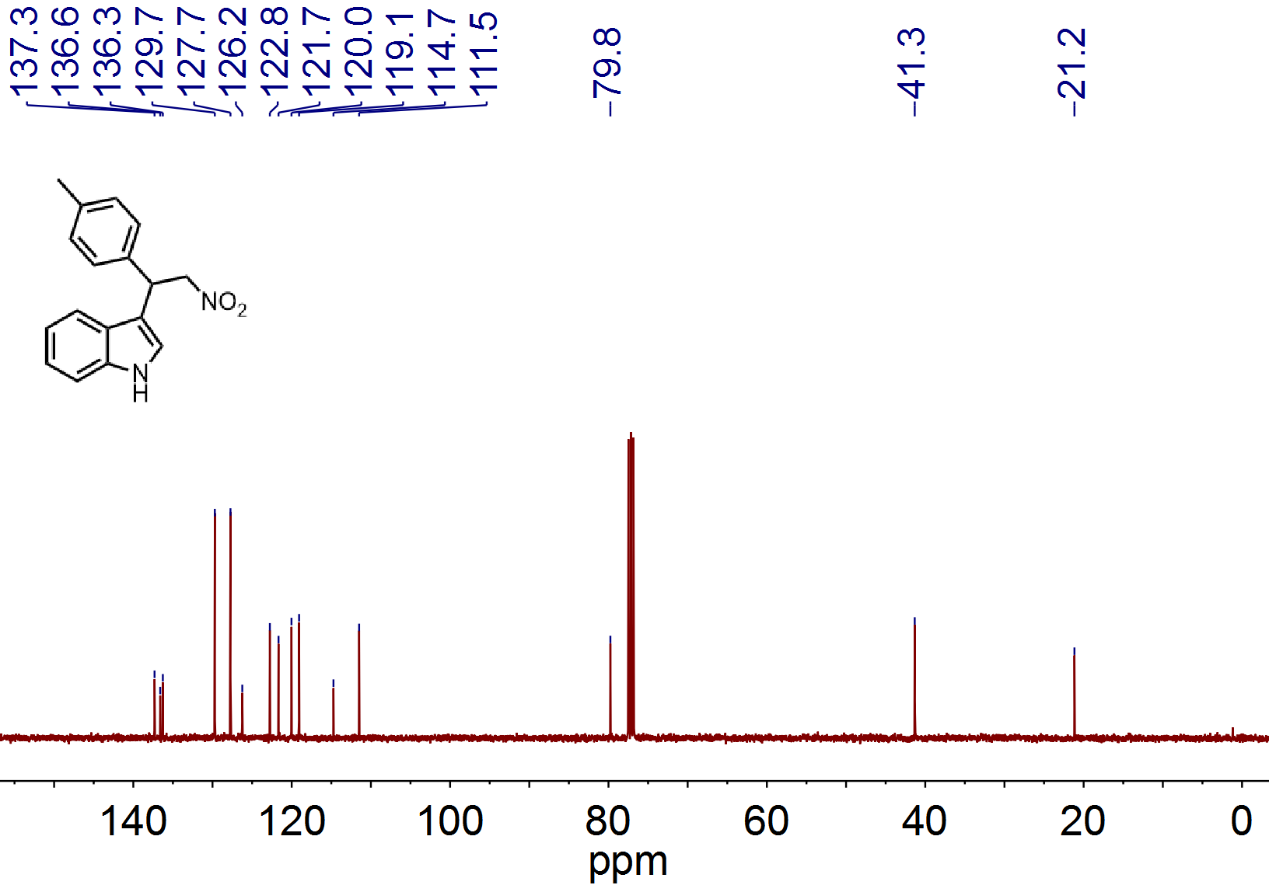
1H NMR Spectrum of Compound **3ea**



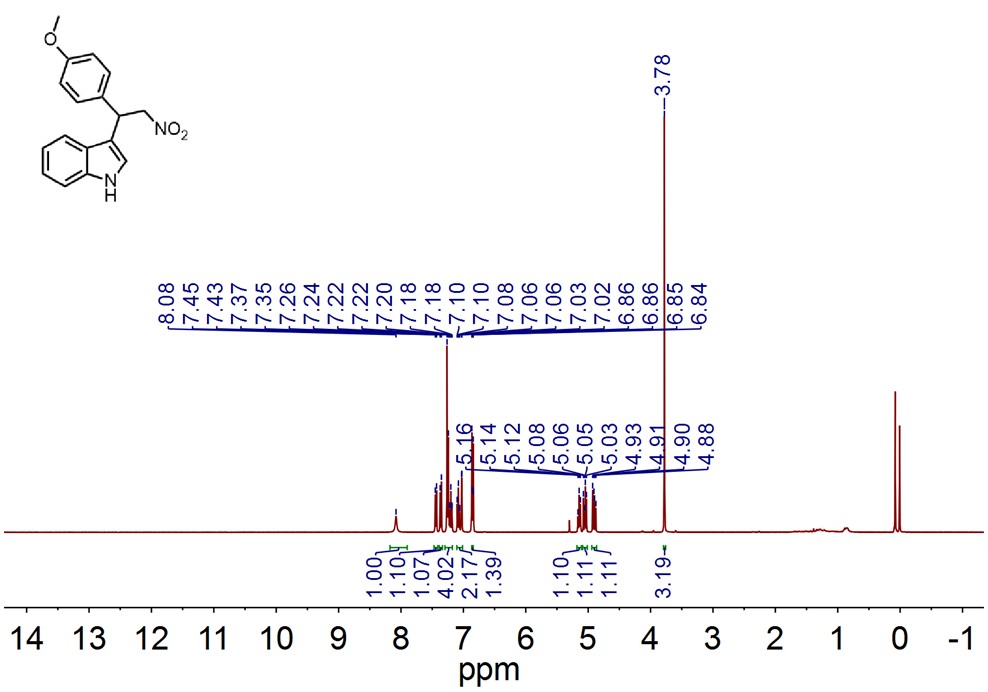
13C NMR Spectrum of Compound **3ea**



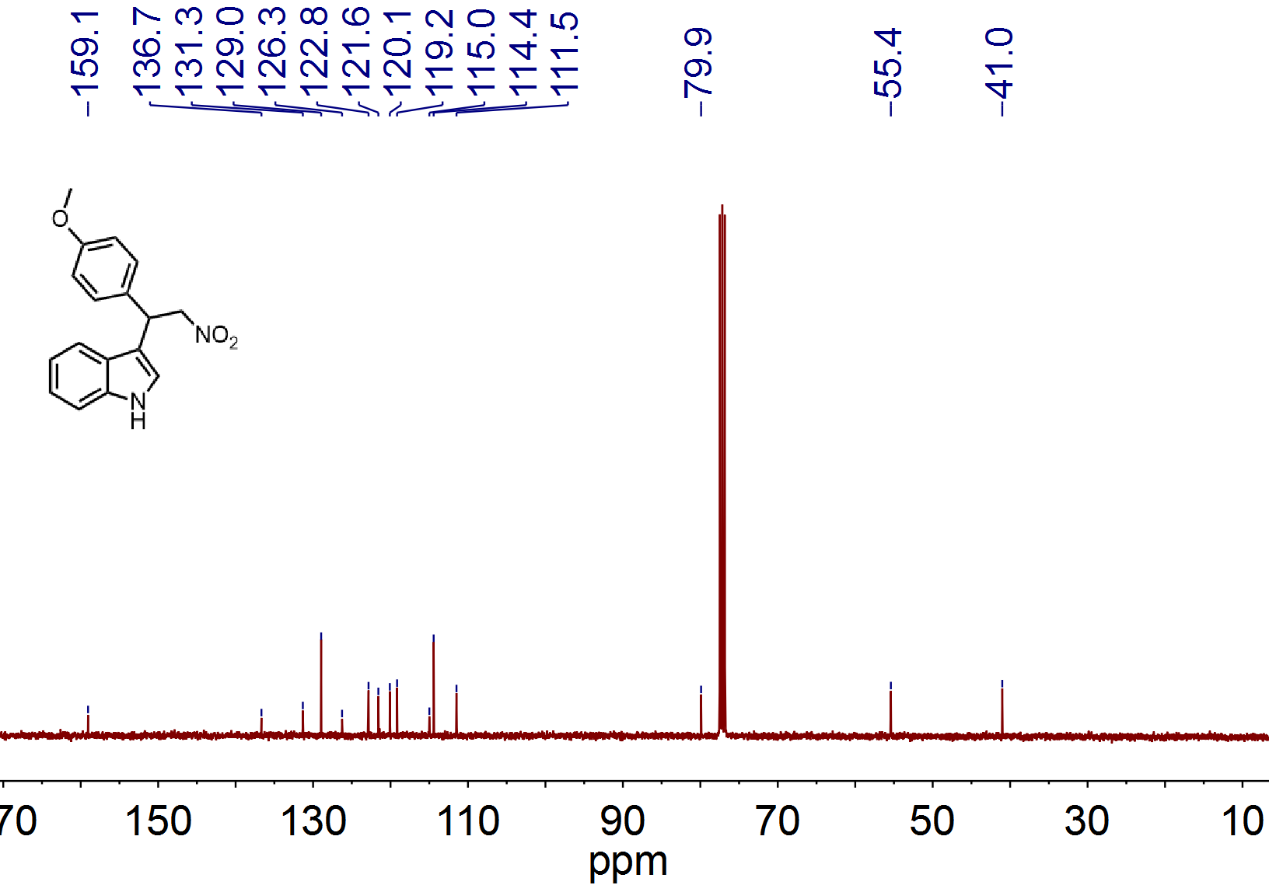
1H NMR Spectrum of Compound **3ab**



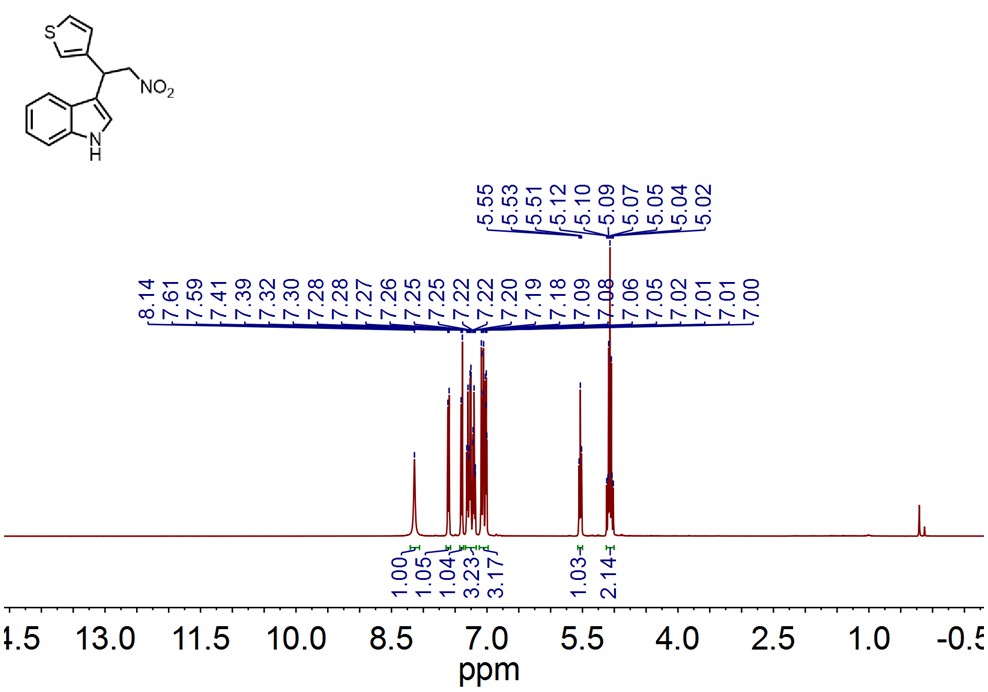
13C NMR Spectrum of Compound **3ab**



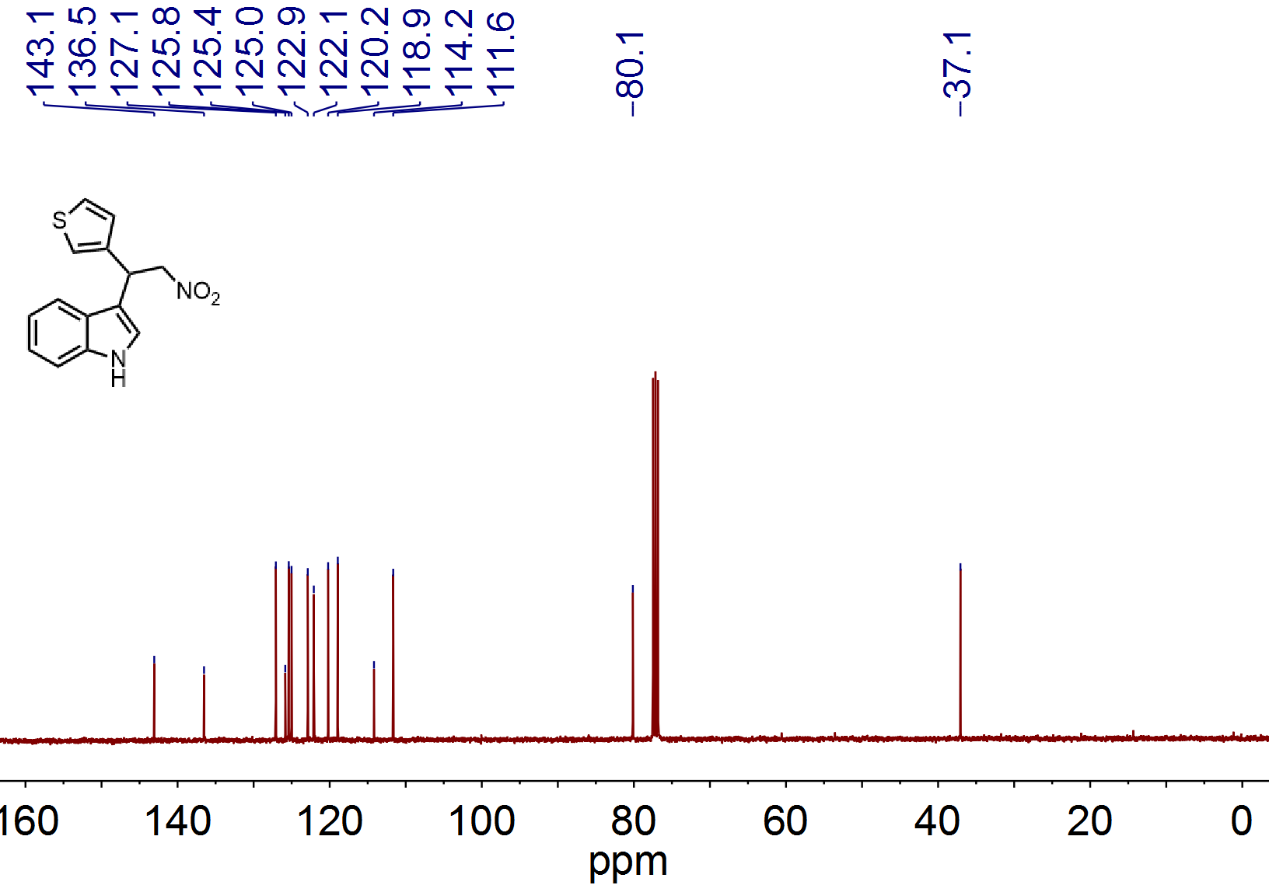
1H NMR Spectrum of Compound **3ac**



13C NMR Spectrum of Compound **3ac**



1H NMR Spectrum of Compound **3ad**



13C NMR Spectrum of Compound **3ac**

X-ray crystal structure of TPAC·Cl



**Table 1.** Crystal data and structure refinement for TPAC·Cl

|  |  |
| --- | --- |
| 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(Å3) | 2451.6(4) |
| *Z* | 4 |
| *T* (K) | 296(2) |
| *D*calcd (g/m3) | 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)]  CCDC NO. | 0.3079a  1509942 |

a *w* =1/[*σ*2(*F*0)2+(0.1820*P*)2 +3.4136*P*], where P = (*F*02 + 2*F*c2)/3;