# Rh(III)-Catalyzed Chelation-Assisted Intermolecular Carbenoid Functionaliztion of α-Imino $Csp^3$-H Bonds

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## Supporting Information

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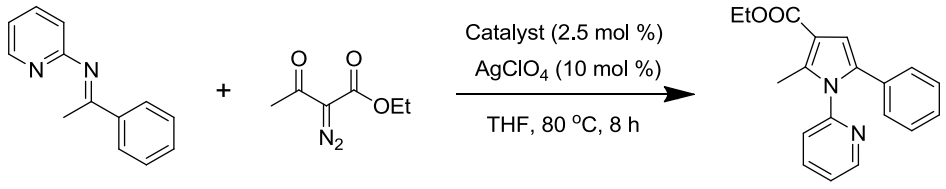
# 1. General experimental information

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or Strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. The starting ketoimine substrates **1a-1t** were prepared according to our previously reported procedures.[1] Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (40-63 mm). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers ($cm^{-1}$). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz for $^{1}H$ NMR and 100 MHz for $^{13}C$ NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

**1.1. Table 1. Catalyst screening for intermolecular carbenoid functionaliztion of α-imino Csp$^3$-H bonds** [a]

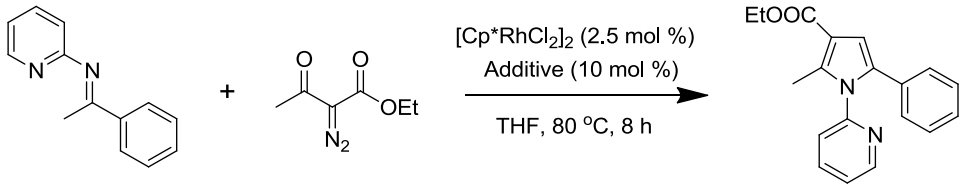



**1a** **2a** **3a**

| entry | catalyst | yield (%) [b] |
|---|---|---|
| 1 | $Pd(OAc)_2$ | 0 |
| 2 | CuI | 0 |
| 3 | $Cu(OAc)_2$ | 0 |
| 4 | $[\{RuCl_2(p\text{-cymene})\}_2]$ | 0 |
| 5 | $[Cp^*IrCl_2]_2$ | 21 |
| 6 | $RhCl_3$ | 0 |
| 7 | $Rh_2(COD)_2Cl_2$ | 0 |
| 8 | $[Cp^*RhCl_2]_2$ | 27 |

[a] All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.2 mmol), catalyst (2.5 mol %), $AgClO_4$ (10 mol %) in THF (2.0 mL) at 80 °C for 8 h in a sealed reaction tube, followed by flash chromatography on $SiO_2$. [b] Isolated yield.

**1.2. Table 2. The effect of additives on the intermolecular carbenoid functionaliztion of α-imino Csp$^3$-H bonds** [a]

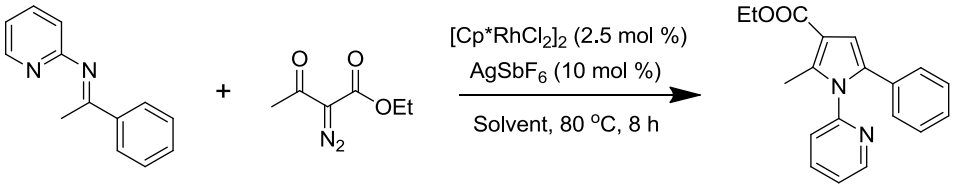



**1a** **2a** **3a**

| entry | additive | yield (%) [b] |
|---|---|---|
| 1 | $AgClO_4$ | 27 |
| 2 | $AgBF_4$ | 31 |
| 3 | $AgNTf_2$ | 34 |
| 4 | AgOAc | 29 |
| 5 | $AgSbF_6$ | 36 |

[a] All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), additive (10 mol %) in THF (2.0 mL) at 80 °C for 8 h in a sealed reaction tube , followed by flash chromatography on $SiO_2$. [b] Isolated yield.

**1.3. Table 3. The effect of solvents on the intermolecular carbenoid functionaliztion of α-imino Csp$^3$-H bonds** [a]

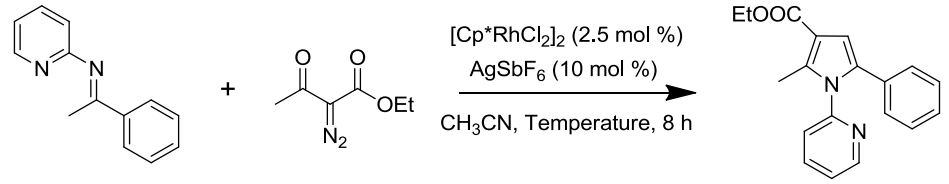



**1a** **2a** **3a**

| entry | solvent | yield (%) [b] |
|---|---|---|
| 1 | THF | 36 |
| 2 | EtOH | 23 |
| 3 | DCE | 85 |
| 4 | Toluene | trace |
| 5 | Dioxane | 52 |
| 6 | $CH_3CN$ | 90 |
| 7 | DMSO | 26 |

[a] All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %), $AgSbF_6$ (10 mol %) in solvent (2.0 mL) at 80 °C for 8 h in a sealed reaction tube , followed by flash chromatography on $SiO_2$. [b] Isolated yield.

**1.4. Table 4. The effect of the reaction temperature on the intermolecular carbenoid functionaliztion of α-imino $Csp^3$-H bonds [a]**

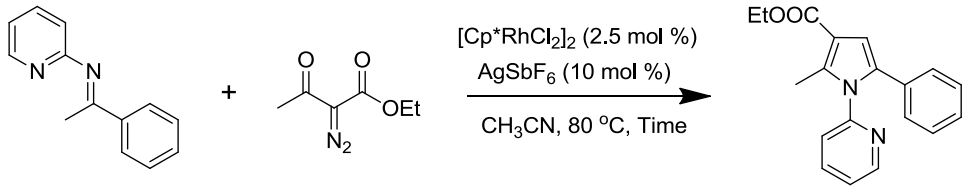



**1a** **2a** **3a**

| entry | temp. (°C) | yield (%) [b] |
|---|---|---|
| 1 | 60 | 81 |
| 2 | 80 | 90 |
| 3 | 100 | 87 |

[a] All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %) in $CH_3CN$ (2.0 mL) at the given temperature for 8 h in a sealed reaction tube, followed by flash chromatography on $SiO_2$. [b] Isolated yield.

**1.5. Table 5. The effect of the reaction time on the intermolecular carbenoid functionaliztion of α-imino $Csp^3$-H bonds [a]**



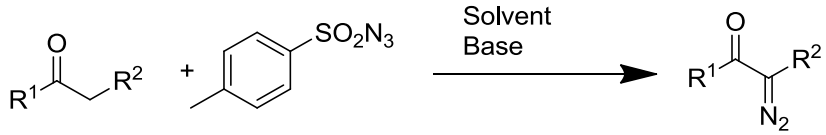

**1a** **2a** **3a**

| entry | time (h) | yield (%) [b] |
|---|---|---|
| 1 | 6 | 88 |
| 2 | 8 | 90 |
| 3 | 12 | 90 |

[a] All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %) in $CH_3CN$ (2.0 mL) at 80 °C for the given

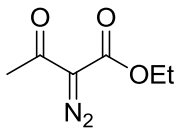
time in a sealed reaction tube , followed by flash chromatography on $SiO_2$. [b] Isolated yield.

**1.6. General procedures for the preparation of diazo compounds (2a-2j)**




**Method A**: To a solution of β-ketoester or β-diketone (1.0 equiv.) and 4-methylbenzenesulfonyl azide (1.2 equiv.) in $CH_3CN$ at 0 $^oC$ was added triethylamine (1.2 equiv.). The resulting solution was stirred at 0 $^oC$ for 3 h and slowly brought to RT. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous $MgSO_4$. The reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography.

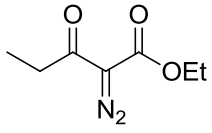
**Method B**: To a cold suspension of NaH (1.2 equiv.) in benzene (50 mL) and THF (8 mL) was added β-ketoester (1.0 equiv.) in benzene (20 mL) and the suspension stirred at 0 $^oC$ for 45 min. 4-methylbenzenesulfonyl azide (1.2 equiv.) in benzene (10 mL) was slowly added and the reaction mixture was stirred for 2 h, then warming to room temperature. The mixture was then filtered on a pad of celite and concentrated under reduced pressure, and the crude product was purified by column chromatography.




**2a**

**Ethyl 2-diazo-3-oxobutanoate (2a)** [2]

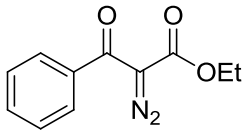
The title compound was prepared according to Method A. The product was obtained as yellow oil in 91% yield. $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 190.2, 161.4, 61.4, 28.2, 14.3. IR (KBr): 2989, 2876, 2135, 1720, 1658, 1469, 1375, 1072 $cm^{-1}$.




**2b**

**Ethyl 2-diazo-3-oxopentanoate (2b)** [2]

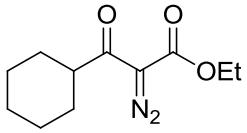
The title compound was prepared according to Method A. The product was obtained as yellow oil in 88% yield. $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.30 (q, *J* = 6.9 Hz, 2H), 2.86 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 193.5, 161.4, 61.3, 33.7, 14.3, 8.2. IR (KBr): 2981, 2844, 2138, 1721, 1650, 1458, 1373, 1065 $cm^{-1}$.




**2c**

**Ethyl 2-diazo-3-oxo-3-phenylpropanoate (2c)** [3]

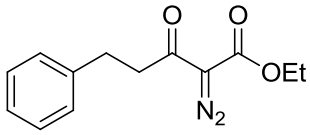
The title compound was prepared according to Method A. The product was obtained as yellow oil in 90% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 186.9, 161.0, 137.1, 132.2, 128.3, 127.8, 61.6, 14.2. IR (KBr): 3013, 2976, 2838, 2144, 1720, 1656, 1625, 1448, 1371, 1308, 1045 cm $^{-1}$.




**2d**

**Ethyl 3-cyclohexyl-2-diazo-3-oxopropanoate (2d)** [3]

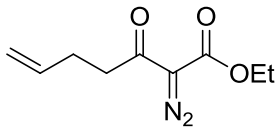
The title compound was prepared according to Method A. The product was obtained as yellow oil in 81% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, *J* = 6.9 Hz, 2H), 3.32 (t, *J* = 9.8 Hz, 1H), 1.80 (d, *J* = 7.7 Hz, 4H), 1.69 (d, *J* = 12.3 Hz, 1H), 1.46 - 1.38 (m, 2H), 1.37 - 1.30 (m, 5H), 1.24 (d, *J* = 11.7 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.0, 161.2, 61.2, 46.7, 28.7, 25.7, 14.3. IR (KBr): 2979, 2856, 2138, 1715, 1651, 1371, 1318, 1146, 1077, 1044 cm $^{-1}$.




**2e**

**Ethyl 2-diazo-3-oxo-5-phenylpentanoate (2e)** [3]

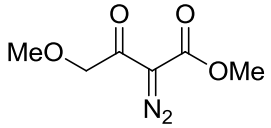
The title compound was prepared according to Method A. The product was obtained as yellow oil in 78% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 9.9 Hz, 4H), 7.19 (d, *J* = 5.5 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 191.9, 161.3, 140.8, 128.4, 126.1, 61.4, 41.7, 30.2, 14.3. IR (KBr): 3011, 2983, 2140, 1714, 1651, 1454, 1374, 1313, 1052 cm $^{-1}$.




**2f**

**Ethyl 2-diazo-3-oxohept-6-enoate (2f)** [4]

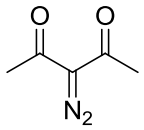
The title compound was prepared according to Method A. The product was obtained as yellow oil in 78% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.92 - 5.77 (m, 1H), 5.03 (dd, *J* = 29.0, 13.6 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.43 - 2.34 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.0, 161.3, 136.9, 115.3, 61.3, 39.3, 28.1, 14.3; IR (KBr): 3061, 2980, 2930, 2136, 1718, 1657, 1434, 1370, 1050 cm $^{-1}$.




**2g**

**Methyl 2-diazo-4-methoxy-3-oxobutanoate (2g)** [4]

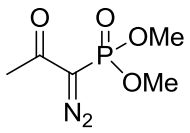
The title compound was prepared according to Method A. The product was obtained as yellow oil in 86% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H), 3.85 (s, 3H), 3.47 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.7, 161.5, 75.7, 59.4, 52.3; IR (KBr): 2976, 2837, 2115, 1713, 1648, 1469, 1375, 1065cm $^{-1}$.




**2h**

**3-Diazopentane-2,4-dione (2h)** [4]

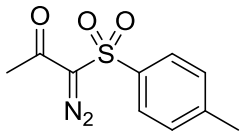
The title compound was prepared according to Method A. The product was obtained as yellow oil in 85% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.1, 84.5, 28.3; IR (KBr): 2960, 2875, 2140, 1727, 1463, 1365 cm $^{-1}$.




**2i**

**Dimethyl (1-diazo-2-oxopropyl)phosphonate (2i)** [5]

The title compound was prepared according to Method B. The product was obtained as white oil in 72% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.84 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 189.8, 53.5, 27.1; IR (KBr): 2961, 2856, 2127, 1722, 1646, 1439, 1369, 1038 cm $^{-1}$.



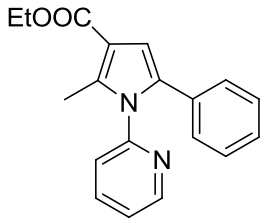
**2j**

**1-Diazo-1-tosylpropan-2-one (2j)** [4]

The title compound was prepared according to Method A. The product was obtained as yellow solid in 75% yield; mp 102 - 104 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 2.28 (d, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 185.8, 145.5, 139.1, 130.1, 127.3, 27.0, 21.6; IR (KBr): 3060, 2974, 2923, 2119, 1720, 1660, 1593, 1432, 1370, 1020 cm $^{-1}$.

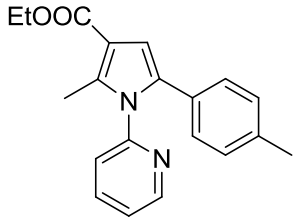
**1.7 General procedure for the synthesis of pyrrole derivatives (3a-3y)**

A 10 mL of reaction tube was charged with $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %), $AgSbF_6$ (3.4 mg, 10 mol %), ketoimines **1** (0.1 mmol) and $CH_3CN$ (1.5 mL) under Ar atmosphere. Then diazo compound **2** (0.2 mmol) in $CH_3CN$ (0.5 mL) was added in one-pot under Ar and the mixture was stirred at 80 ℃ for 8 h. The corresponding reaction mixture was cooled to room temperature and then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silical gel using ethyl acetate/petroleum ether as eluent to afford the desired product **3**.



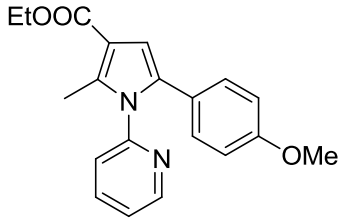
**3a**

**Ethyl 2-methyl-5-phenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3a)**: Yellow oil; 27.5 mg, 90% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.33 - 7.28 (m, 1H), 7.14 (d, *J* = 6.3 Hz, 3H), 7.02 (d, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.78 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.5, 151.5, 149.4, 138.4, 138.1, 133.6, 132.4, 128.1, 126.7, 123.4, 113.4, 110.5, 59.6, 14.6, 12.4; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{19}H_{19}N_2O_2$: 307.1441, found: 307.1444; IR (KBr): 3062, 2980, 2928, 1701, 1573, 1469, 1439, 1375, 1228, 1076 cm $^{-1}$.



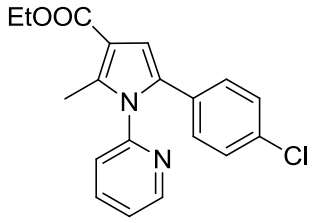

**3b**

**Ethyl 2-methyl-1-(pyridin-2-yl)-5-(p-tolyl)-1H-pyrrole-3-carboxylate (3b)**: Yellow oil; 26.2 mg, 82% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.0 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 5.4 Hz, 1H), 6.98 - 6.89 (m, 5H), 6.74 (s, 1H), 4.32 (q, *J* = 6.9 Hz, 2H), 2.47 (s, 3H), 2.25 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.5, 151.6, 149.35, 138.1, 136.4, 133.6, 129.4, 128.8, 127.9, 123.4, 123.2, 113.2, 110.0, 59.5, 21.0, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{20}H_{21}N_2O_2$: 321.1598, found: 321.1607; IR (KBr): 3130, 2983, 2926, 1702, 1580, 1534, 1469, 1331, 1228, 1076 cm $^{-1}$.




**3c**

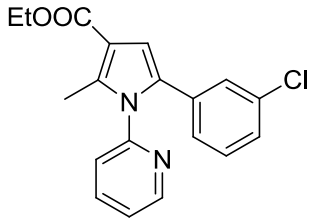
**Ethyl 5-(4-methoxyphenyl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3c)**: Yellow oil; 24.2 mg, 72% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.9 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.33 - 7.27 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 3H), 6.70 (d, *J* = 4.2 Hz, 3H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 2.47 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.5, 158.46, 151.5, 149.3, 138.0, 137.8, 133.3, 129.4, 125.0, 123.4, 123.2, 113.6, 113.1, 109.5, 59.5, 55.1, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{20}H_{21}N_2O_3$: 337.1547, found: 337.1552; IR (KBr): 3148, 2978, 2927, 1700, 1571, 1535, 1468, 1333, 1376, 1227, 1076 cm $^{-1}$.




**3d**

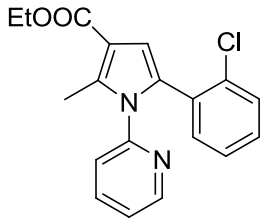
**Ethyl 5-(4-chlorophenyl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3d)**: Yellow oil; 30.9 mg, 91% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 3.9 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.36 - 7.32 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.95 (t, *J* = 8.2 Hz, 3H), 6.78 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.3, 151.2,

149.5, 138.6, 138.3, 132.5, 132.3, 130.8, 129.1, 128.4, 123.4, 113.5, 110.8, 59.6, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{19}H_{18}ClN_2O_2$: 341.1051, found: 341.1054; IR (KBr): 3129, 2986, 1701, 1580, 1473, 1400, 1228, 1082 $cm^{-1}$.



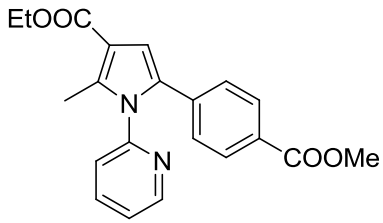

**3e**

**Ethyl 5-(3-chlorophenyl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3e)**: Yellow oil; 28.9 mg, 85% yield. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.0 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.39 - 7.32 (m, 1H), 7.11 - 7.02 (m, 3H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.32 (q, *J* = 6.9 Hz, 2H), 2.47 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 165.3, 151.1, 149.5, 138.8, 138.3, 134.0, 132.0, 129.3, 127.8, 126.6, 125.9, 123.5, 123.3, 113.5, 111.2, 59.6, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{19}H_{18}ClN_2O_2$: 341.1051, found: 341.1057; IR (KBr): 3063, 2980, 2932, 1702, 1586, 1523, 1464, 1376, 1228, 1081 $cm^{-1}$.



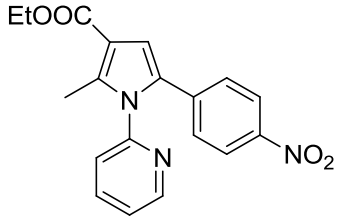

**3f**

**Ethyl 5-(2-chlorophenyl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3f)**: Yellow oil; 21.1 mg, 62% yield. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.0 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 5.4 Hz, 1H), 6.98 - 6.89 (m, 5H), 6.74 (s, 1H), 4.32 (q, *J* = 6.9 Hz, 2H), 2.47 (s, 3H), 2.25 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 165.5, 151.6, 149.3, 138.1, 136.4, 133.6, 129.4, 128.8, 127.9, 123.4, 123.2, 113.2, 110.0, 59.5, 21.0, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{19}H_{18}ClN_2O_2$: 341.1051, found: 341.1068; IR (KBr): 3129, 2984, 2930, 1701, 1576, 1467, 1402, 1333, 1227, 1083 $cm^{-1}$.



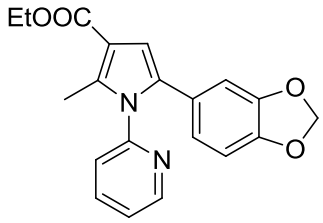

**3g**

**Ethyl 5-(4-(methoxycarbonyl)phenyl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3g)**: Yellow oil; 31.3 mg, 86% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 3.4 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 5.9 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.90 (s, 1H), 4.33 (q, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 2.49 (s, 3H), 1.38 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.7, 165.2, 151.2, 149.6, 139.4, 138.3, 136.7, 132.4, 129.5, 127.8, 127.3, 123.5, 123.3, 113.8, 111.9, 59.6, 52.0, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{21}H_{21}N_2O_4$: 365.1496, found: 365.1514; IR (KBr): 3059, 2983, 1712, 1606, 1468, 1435, 1376, 1230, 1106 cm $^{-1}$.



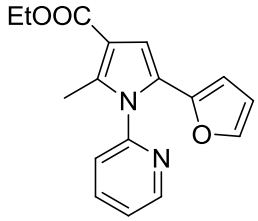

**3h**

**Ethyl 2-methyl-5-(4-nitrophenyl)-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3h)**: Reddish oil; 33.3 mg, 95% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 3.8 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.43 - 7.38 (m, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.9, 150.8, 149.8, 145.7, 140.3, 138.6, 131.2, 127.5, 123.9, 123.6, 123.1, 114.2, 113.2, 59.8, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{19}H_{18}N_3O_4$: 352.1292, found: 352.1305; IR (KBr): 3125, 2986, 2931, 1703, 1594, 1517, 1466, 1338, 1230, 1105 cm $^{-1}$.



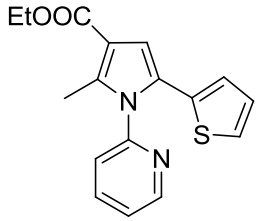

**3i**

**Ethyl 5-(benzo[d][1,3]dioxol-5-yl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3i)**: Yellow oil; 21.3 mg, 61% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.3 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.34 - 7.28 (m, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.69 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 9.2 Hz, 2H), 5.88 (s, 2H), 4.31 (q, *J* = 7.0 Hz, 2H), 2.46 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.5, 151.4, 149.4, 147.3, 146.5, 138.1, 137.9, 133.2, 126.4, 123.3, 122.0, 113.1, 109.9, 108.7, 108.1, 100.9, 59.5, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{19}N_2O_4$: 351.1339, found: 351.1342; IR (KBr): 3134, 2985, 2898, 1700, 1578, 1532, 1476, 1437, 1346, 1225, 1086 cm $^{-1}$.



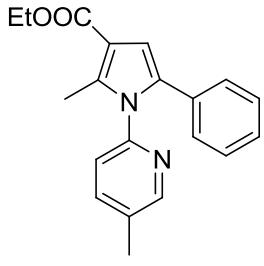

**3j**

**Ethyl 5-(furan-2-yl)-2-methyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3j)**: Yellow oil; 18.0 mg, 61% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.0 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.46 - 7.39 (m, 1H), 7.24 - 7.18 (m, 2H), 6.93 (s, 1H), 6.19 (d, *J* = 1.4 Hz, 1H), 5.49 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.29, 151.2, 149.6, 146.5, 141.2, 138.4, 138.1, 124.5, 123.9, 123.2, 113.3, 110.7, 109.7, 105.6, 59.6, 14.5, 12.0; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{17}H_{17}N_2O_3$: 297.1234, found: 297.1242; IR (KBr): 3128, 2984, 2927, 1703, 1587, 1554, 1470, 1400, 1376, 1237, 1078 cm $^{-1}$.




**3k**

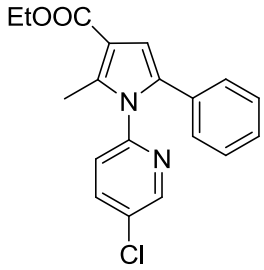
**Ethyl 2-methyl-1-(pyridin-2-yl)-5-(thiophen-2-yl)-1H-pyrrole-3-carboxylate (3k)**: Yellow oil; 18.1 mg, 58% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 3.9 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.42 - 7.36 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 4.6 Hz, 1H), 6.83 (s, 1H), 6.80 (t, *J* = 4.2 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.9, 149.6, 138.3, 134.1, 126.9, 125.0, 124.5, 123.9, 123.7, 113.2, 110.8, 59.6, 14.5, 12.2; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{17}H_{17}N_2O_2S$: 313.1005, found: 313.1016; IR (KBr): 3064, 2979, 2929, 1702, 1580, 1468, 1435, 1378, 1232, 1081 cm $^{-1}$.




**3l**

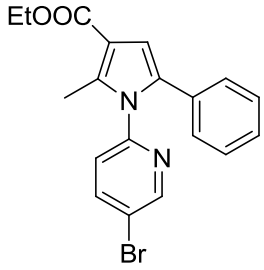
**Ethyl 2-methyl-1-(5-methylpyridin-2-yl)-5-phenyl-1H-pyrrole-3-carboxylate (3l)**: Yellow oil; 25.9 mg, 81% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.19 - 7.11 (m, 3H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 4.32 (q, *J* = 7.1 Hz,

2H), 2.46 (s, 3H), 2.38 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.5, 149.6, 149.1, 138.6, 138.4, 133.5, 133.1, 132.4, 128.0, 126.5, 122.7, 113.2, 110.3, 59.5, 18.1, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{21}N_2O_2$: 321.1598, found: 321.1607; IR (KBr): 3063, 2977, 2926, 1702, 1570, 1529, 1481, 1400, 1332, 1228, 1075 cm $^{-1}$.



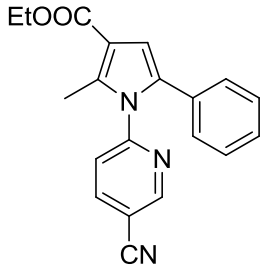

**3m**

**Ethyl 1-(5-chloropyridin-2-yl)-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (3m)**: Yellow oil; 26.5 mg, 78% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 6.3 Hz, 3H), 7.02 (d, *J* = 6.7 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.77 (s, 1H), 4.32 (q, *J* = 7.0 Hz, 2H), 2.48 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.3, 149.6, 148.1, 138.3, 137.8, 133.5, 132.1, 131.5, 128.3, 128.1, 126.9, 124.0, 113.7, 110.8, 59.6, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{19}H_{18}ClN_2O_2$: 341.1051, found: 341.1056; IR (KBr): 3062, 2980, 2928, 1704, 1568, 1530, 1466, 1400, 1380, 1229, 1074 cm $^{-1}$.



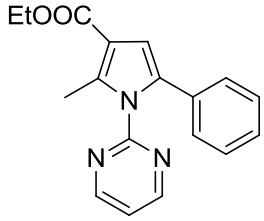

**3n**

**Ethyl 1-(5-bromopyridin-2-yl)-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (3n)**: Yellow oil; 28.8 mg, 75% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.18 (d, *J* = 6.8 Hz, 3H), 7.03 (d, *J* = 6.6 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.77 (s, 1H), 4.32 (q, *J* = 7.0 Hz, 2H), 2.49 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.3, 150.4, 150.1, 140.68, 138.2, 133.5, 132.1, 128.3, 128.1, 126.9, 124.5, 120.0, 113.7, 110.8, 59.6, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{19}H_{18}BrN_2O_2$: 385.0546, found: 385.0550; IR (KBr): 3141, 2982, 2925, 1703, 1567, 1531, 1464, 1328, 1229, 1078 cm $^{-1}$.



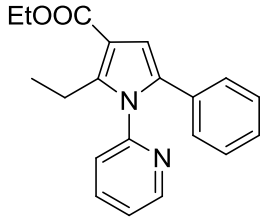

**3o**

**Ethyl 1-(5-cyanopyridin-2-yl)-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (3o)**: Yellow oil; 26.1 mg, 79% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.20 (s, 3H), 6.98 (t, *J* = 6.1 Hz, 3H), 6.79 (s, 1H), 4.33 (q, *J* = 6.6 Hz, 2H), 2.55 (s, 3H), 1.38 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.1, 154.1, 152.2, 140.9, 138.3, 133.4, 131.7, 128.5, 128.2, 127.2, 123.3, 115.8, 114.6, 111.8, 108.9, 59.8, 14.5, 12.5; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{18}N_3O_2$: 332.1394, found: 332.1398; IR (KBr): 3103, 2983, 2929, 2234, 1703, 1586, 1478, 1448, 1330, 1231, 1074 cm $^{-1}$.




**3p**

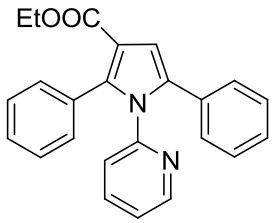
**Ethyl 2-methyl-5-phenyl-1-(pyrimidin-2-yl)-1H-pyrrole-3-carboxylate (3p)**: Yellow oil; 23.9 mg, 78% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.8 Hz, 2H), 7.30 - 7.26 (m, 1H), 7.17 (d, *J* = 7.0 Hz, 3H), 7.01 (d, *J* = 7.1 Hz, 2H), 6.77 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.4, 158.6, 158.2, 138.4, 133.8, 132.8, 128.3, 127.8, 126.6, 119.7, 113.8, 111.1, 59.6, 14.5, 12.3; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{18}H_{18}N_3O_2$: 308.1394, found: 308.1397; IR (KBr): 3060, 2978, 2926, 1702, 1564, 1486, 1423, 1375, 1231, 1071 cm $^{-1}$.




**3q**

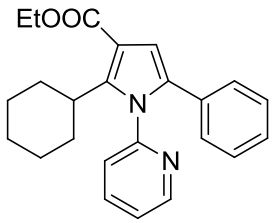
**Ethyl 2-ethyl-5-phenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3q)**: Yellow oil; 27.8 mg, 87% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.32 (s, 1H), 7.13 (s, 3H), 7.02 (d, *J* = 6.0 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 4.33 (q, *J* = 6.9 Hz, 2H),

2.93 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.2, 151.5, 149.3, 144.4, 138.0, 133.5, 132.3, 128.1, 126.6, 123.6, 123.4, 112.5, 110.5, 59.5, 19.2, 14.5, 14.2; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{20}H_{21}N_2O_2$: 321.1598, found: 321.1605; IR (KBr): 3150, 2980, 2932, 1702, 1586, 1524, 1468, 1401, 1376, 1220, 1085 cm $^{-1}$.



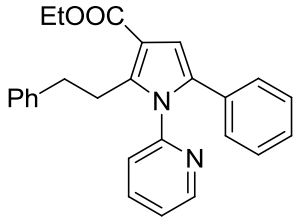

**3r**

**Ethyl 2,5-diphenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3r)**: White solid, 26.5 mg, 72% yield, m.p. 87-89 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 3.9 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.19 (dd, *J* = 18.0, 7.5 Hz, 8H), 7.12 (d, *J* = 7.4 Hz, 3H), 6.94 (s, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.6, 151.3, 148.9, 139.8, 137.5, 134.8, 132.2, 131.5, 131.2, 128.4, 128.1, 127.8, 127.2, 126.9, 123.7, 122.9, 114.6, 111.1, 59.6, 14.1; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{24}H_{21}N_2O_2$: 369.1598, found: 369.1605; IR (KBr): 3103, 2988, 2926, 1702, 1585, 1534, 1477, 1378, 1239, 1081 cm $^{-1}$.



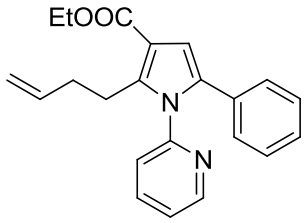

**3s**

**Ethyl 2-cyclohexyl-5-phenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3s)**: White oil; 27.7 mg, 74% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.2 Hz, 1H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 5.6 Hz, 1H), 7.11 (s, 3H), 7.03 - 6.96 (m, 3H), 6.79 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.86 (t, *J* = 11.4 Hz, 1H), 1.95 (s, 2H), 1.70 (s, 4H), 1.57 (d, *J* = 11.6 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.14 (dd, *J* = 25.7, 12.4 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.2, 152.1, 149.1, 146.4, 137.9, 133.2, 132.4, 128.3, 128.0, 126.5, 124.1, 123.6, 112.6, 111.5, 59.6, 37.7, 30.0, 27.0, 25.6, 14.5; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{24}H_{27}N_2O_2$: 375.2067, found: 375.2069; IR (KBr): 3100, 2926, 2854, 1704, 1585, 1517, 1465, 1397, 1224, 1087 cm $^{-1}$.



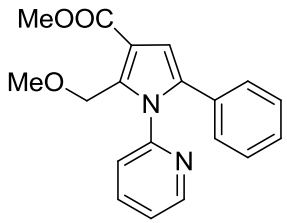

**3t**

**Ethyl 2-phenethyl-5-phenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3t)**: Yellow oil; 33.3 mg, 84% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.30 (s, 1H), 7.17 (dd, *J* = 16.6, 7.8 Hz, 6H), 7.02 (s, 4H), 6.82 (s, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 4.36 (q, *J* = 6.7 Hz, 2H), 3.21 - 3.15 (m, 2H), 2.91 - 2.84 (m, 2H), 1.40 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.1, 151.3, 149.1, 141.8, 138.0, 133.6, 132.3, 128.6, 128.0, 126.7, 125.8, 123.6, 123.3, 113.29, 110.7, 59.6, 36.1, 28.4, 14.6; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{26}H_{25}N_2O_2$: 397.1911, found: 397.1917; IR (KBr): 3068, 2979, 2931, 2858, 1701, 1582, 1525, 1442, 1230, 1237, 1080 cm $^{-1}$.




**3u**

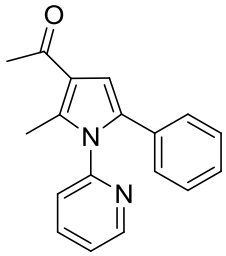
**Ethyl 2-(but-3-en-1-yl)-5-phenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3u)**: Yellow oil; 24.6 mg, 71% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 3.3 Hz, 1H), 7.13 (s, 3H), 7.02 (d, *J* = 5.6 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.80 (s, 1H), 5.70 (td, *J* = 14.5, 7.0 Hz, 1H), 4.87 (t, *J* = 13.6 Hz, 2H), 4.33 (q, *J* = 6.5 Hz, 2H), 3.01 (t, *J* = 7.1 Hz, 2H), 2.25 (d, *J* = 6.8 Hz, 2H), 1.37 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.2, 151.4, 149.2, 142.0, 137.9, 133.6, 132.3, 128.1, 126.6, 123.7, 123.3, 114.6, 113.2, 110.6, 59.5, 33.9, 25.5, 14.5; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{22}H_{23}N_2O_2$: 347.1754, found: 347.1756; IR (KBr): 3066, 2979, 2854, 1702, 1569, 1522, 1436, 1371, 1232, 1079 cm $^{-1}$.




**3v**

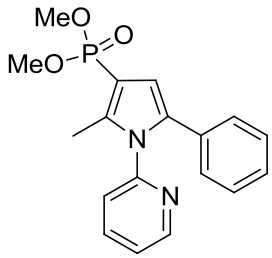
**Methyl 2-(methoxymethyl)-5-phenyl-1-(pyridin-2-yl)-1H-pyrrole-3-carboxylate (3v)**: Yellow oil; 29.6 mg, 92% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.7 Hz, 1H), 7.70 (t, *J* = 7.7

Hz, 1H), 7.30 (d, *J* = 5.9 Hz, 1H), 7.17 (d, *J* = 6.1 Hz, 4H), 7.05 (s, 2H), 6.81 (s, 1H), 4.78 (s, 2H), 3.87 (s, 3H), 3.19 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.3, 151.2, 149.1, 138.0, 136.2, 135.3, 132.0, 128.2, 127.0, 123.3, 115.7, 110.7, 62.9, 57.6, 51.2; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{19}H_{19}N_2O_3$: 323.1390, found: 323.1387; IR (KBr): 3102, 2942, 2818, 1710, 1586, 1525, 1471, 1402, 1226, 1083 cm $^{-1}$.



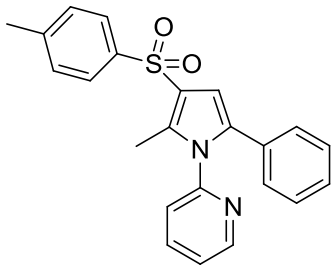

**3w**

**1-(2-Methyl-5-phenyl-1-(pyridin-2-yl)-1H-pyrrol-3-yl)ethanone (3w)**: Yellow oil, 20.9 mg, 76% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.1 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.35 - 7.30 (m, 1H), 7.16 (d, *J* = 5.6 Hz, 3H), 7.03 (d, *J* = 6.5 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.71 (s, 1H), 2.49 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.3, 151.2, 149.4, 138.1, 137.7, 133.5, 132.2, 128.1, 126.8, 123.4, 121.8, 110.7, 28.9, 12.8; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{18}H_{17}N_2O$: 277.1335, found: 277.1340; IR (KBr): 3163, 2923, 2853, 1723, 1659, 1590, 1519, 1471, 1436, 1345, 1231, 1072 cm $^{-1}$.




**3x**

**Dimethyl (2-methyl-5-phenyl-1-(pyridin-2-yl)-1H-pyrrol-3-yl)phosphonate (3x)**: White oil, 18.8 mg, 55% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.33 (s, 1H), 7.15 (s, 3H), 7.04 - 6.99 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.4, 149.4, 139.5, 139.2, 138.2, 134.8, 132.0, 128.2, 127.9, 126.8, 123.3, 112.4, 106.1, 103.9, 52.3, 12.4; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{18}H_{20}N_2O_3P$: 343.1206, found: 343.1215; IR (KBr): 3131, 2951, 2850, 1589, 1516, 1469, 1398, 1240, 1028 cm $^{-1}$.

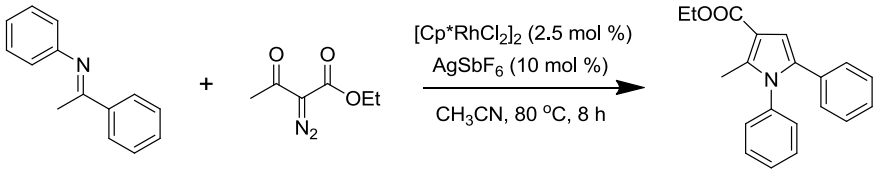


**3y**

**2-(2-Methyl-5-phenyl-3-tosyl-1H-pyrrol-1-yl)pyridine (3y)**: White solid; 24.4 mg, 63% yield; m.p. 122-124 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.34 - 7.27 (m, 3H), 7.15 (s, 3H), 6.98 (s, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.73 (s, 1H), 2.41 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.8, 149.4, 143.1, 140.8, 138.4, 134.9, 134.2, 131.4, 129.6, 128.2, 127.2, 126.8, 123.7, 123.5, 122.0, 109.3, 21.5, 11.5; HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{23}H_{21}N_2O_2S$: 389.1318, found: 389.1321; IR (KBr): 3133, 3008, 2984, 2924, 2854, 1677, 1590, 1518, 1470, 1438, 1399, 1300, 1237, 1150 cm $^{-1}$.

**2. Controlled experiments for mechanism studies**

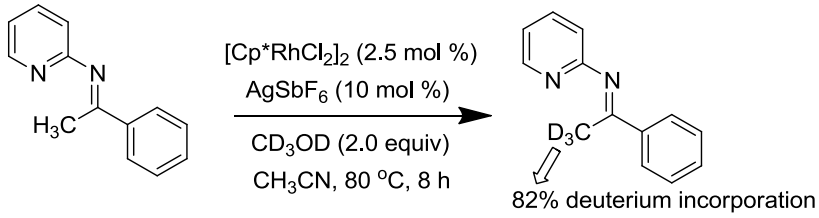
**(a)**. **Rh(III)-catalyzed intermolecular cyclization cascade of *N*-phenyl ketoimine 1q with diazo compound 2a**




**1q** **2a** **3z (not observed)**

A 10 mL of reaction tube was charged with $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol%), $AgSbF_6$ (3.4 mg, 10 mol%), ketoimines **1q** (20 mg, 0.1 mmol) and $CH_3CN$ (1.5 mL) under Ar. Diazo compound **2a** (31 mg, 0.2 mmol) in $CH_3CN$ (0.5 mL) was then added in one-pot under Ar and the mixture was stirred at 80 ℃ for 8 h. Afterwards, the reaction mixture was cooled to room temperature, no product **3z** was observed by $^{1}$H NMR and GC-MS analysis, this result indicated that the pyridyl group played a significant chelation-directing role in this transformation.

**(b) H/D Exchange of *N*-(2-pyridyl) ketoimine (1a)**

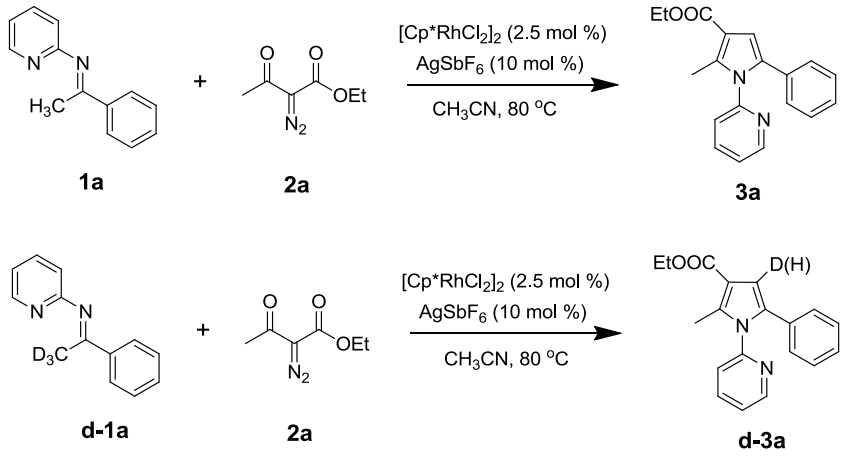



**1a** **d-1a**

To the solution of ketoimine **1a** (20 mg, 0.1 mmol) in $CH_3CN$ (1.0 mL) were added $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %), $AgSbF_6$ (3.4 mg, 10 mol %) and $CD_3OD$ (2.0 equiv) under Ar. The reaction

mixture was stirred at 80 ℃ for 8 h and then cooled down to room temperature. After removal of solvent the resulted crude was quickly purified by flash column chromatography to give the desired compound ***d*-1a** (51% yield) as oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.00 (d, *J* = 6.7 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 3H), 7.02 (s, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 2.25 (s, 0.55H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.7, 163.5, 148.9, 139.0, 137.7, 130.9, 128.3, 127.5, 118.9, 115.2. HR-MS (ESI) calcd for $[M + 1]^+$ : $C_{13}H_{10}D_3N_2$: 200.1262, found: 200.1262.

**(c): Kinetic isotope effect of this transformation**




A 10 mL of reaction tube was charged with ketoimines **(1a:** 20 mg**,** 0.1 mmol; or ***d*-1a:** 20 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol%), $AgSbF_6$ (3.4 mg, 10 mol%) and $CH_3CN$ (1.5 mL) under Ar. Diazo compound **2a** (31 mg, 0.2 mmol) in $CH_3CN$ (0.5 mL) was then added in one-pot under Ar and the mixture was stirred at 80 ℃. Aliquots (0.4 mL) were extracted at 1hour intervals for the first 4 hours of the reaction. After the solvent of each aliquot (0.4 mL) was removed under reduced pressure conditions and analyzed by $^{1}$H NMR spectrum (see **Figure 1** and **Figure 2**). A sample plot of the initial rate data for the reactionn of both **1a** and ***d*-1a** was shown in **Figure 3.** The reaction progress in the early stage (0-4 hours) indicated a kinetic isotope effect (KIE) of 2.3.

***d*-3a**: Yellow liquid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 4.3 Hz, 1H), 7.14 (s, 3H), 7.03 (d, *J* = 6.3 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 0.22H), 4.32 (q, *J* = 6.7 Hz, 2H), 2.48 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.5 (s), 151.5 (s), 149.3 (s), 138.3 (s), 138.1 (s), 133.4 (s), 132.3 (s), 128.0 (d, *J* = 13.8 Hz), 126.6 (s), 123.3 (d, *J* = 16.1 Hz), 113.3 (s), 110.5 (s), 59.5 (s), 14.5 (s), 12.3 (s). HR-MS (ESI) calcd for $[M + 1]^+$: $C_{19}H_{18}DN_2O_2$: 308.1504, found: 308.1512.

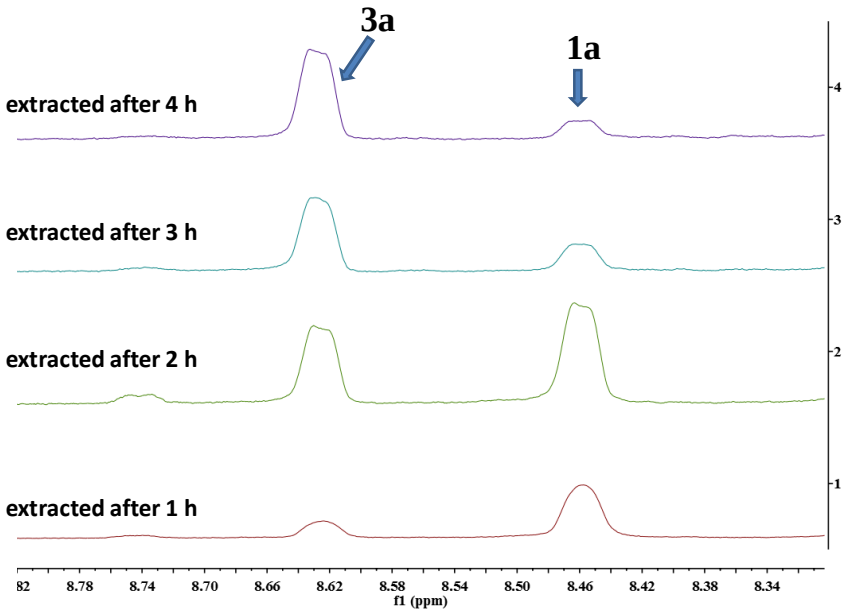



**Figure 1,** The conversion of **1a** was monitored by $^{1}$H NMR method

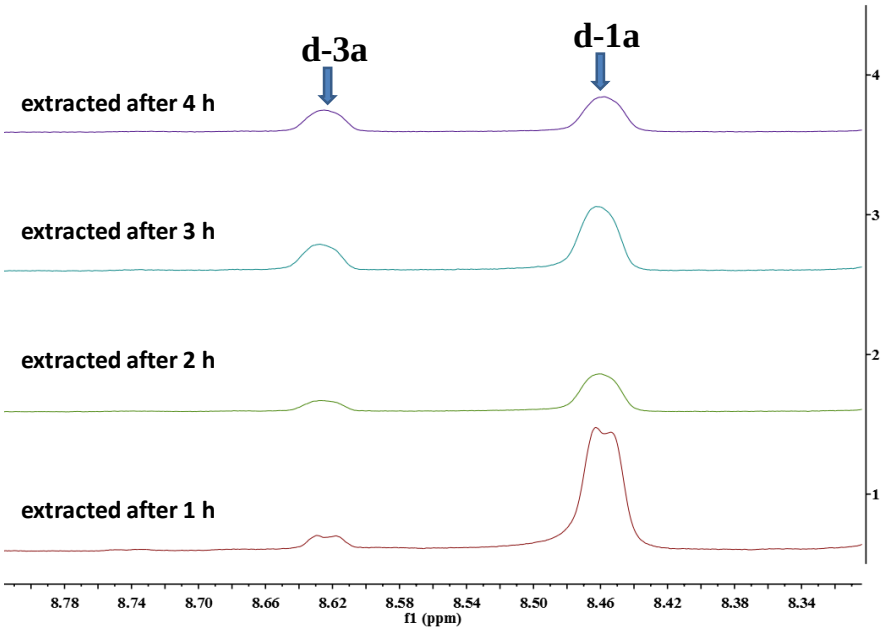



**Figure 2**. The conversion of ***d*-1a** was monitored by $^{1}$H NMR method

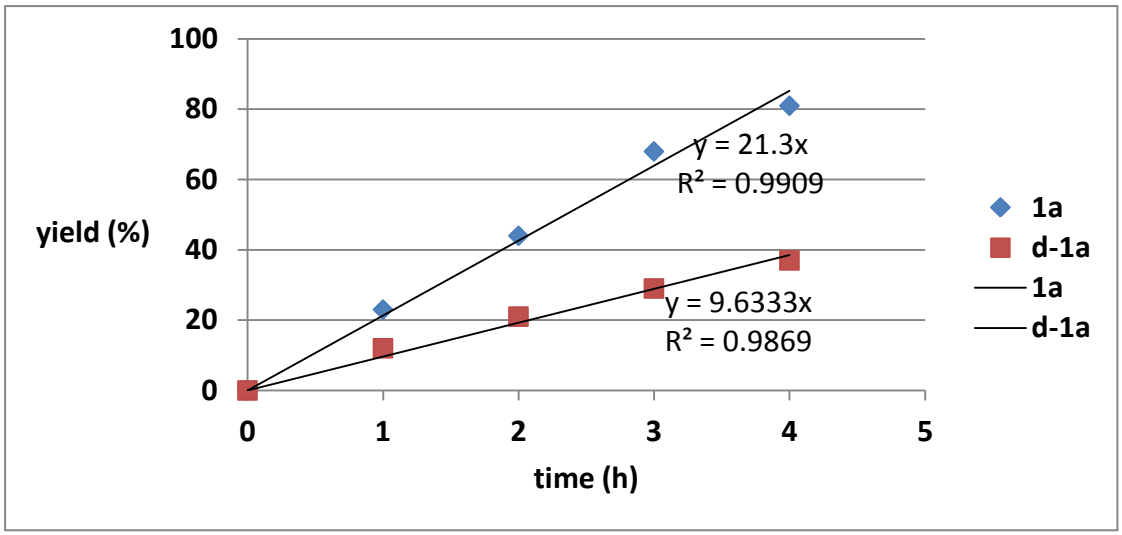



**Figure 3**, The plot of initial rates for KIE measurements.

### 3.1 Singlerystal structure and crystallographic data for 3r

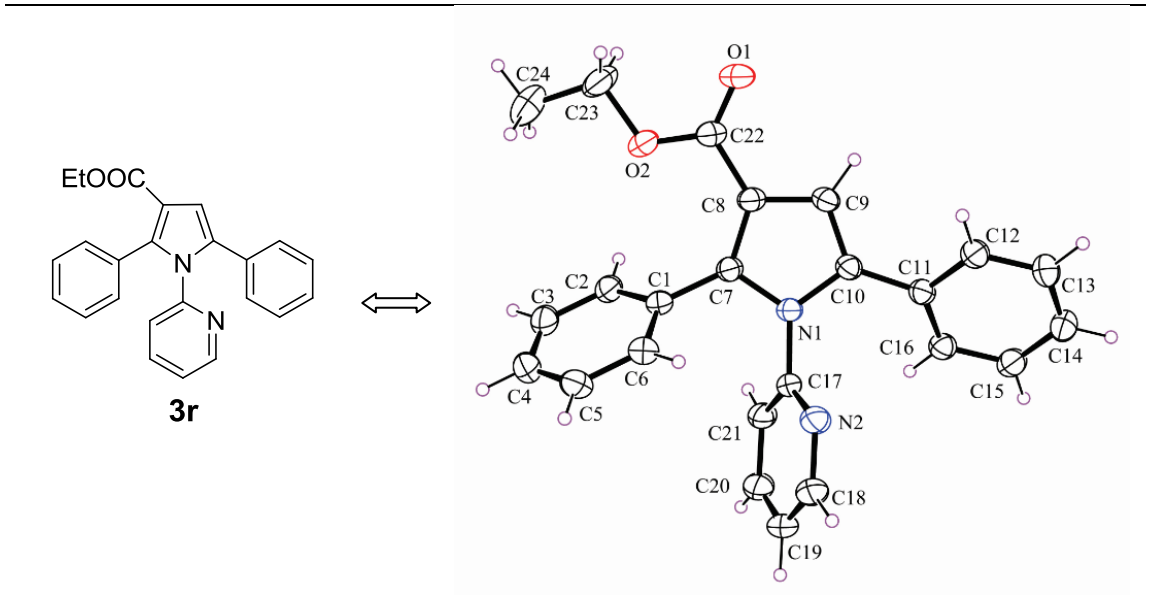



**Figure 1. The Single crystal structure of compound 3r**

**Table 6. Crystal data and structure refinement for 3r.**

| | |
|---|---|
| Identification code | 3r |
| Empirical formula | $C_{24}H_{21}N_2O_2$ |
| Formula weight | 369.43 |
| Temperature | 571(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, C2/C |
| Unit cell dimensions | a = 29.4790(8) A alpha = 90 deg. |

| | |
|---|---|
| | b = 12.0530(3) A beta = 108.029(2) deg. |
| | c = 11.6531(3) A gamma = 90 deg. |
| Volume | 3937.17(18) A^3 |
| Z, Calculated density | 8, 1.246 Mg/m^3 |
| Absorption coefficient | 0.635 mm^-1 |
| F(000) | 61560 |
| Crystal size | 0.28 x 0.24 x 0.20 $mm^3$ |
| Theta range for data collection | 5.99 to 62.68 deg. |
| Limiting indices | -33<=h<=33, -11<=k<=13, -13<=l<=12 |
| Reflections collected / unique | 8227 / 3109 [R(int) = 0.0228] |
| Completeness to theta = 27.45 | 98.3 % |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3109 / 0 / 253 |
| Goodness-of-fit on F^2 | 0.674 |
| Final R indices [I>2sigma(I)] | R1 = 0.0396, wR2 = 0.1129 |
| R indices (all data) | R1 = 0.0439, wR2 = 0.1192 |
| Largest diff. peak and hole | 0.172 and -0.162 e.A^-3 |

**Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 3r**.

U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor**.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 3796(1) | 3824(1) | 757(1) | 75(1) |
| O(2) | 4133(1) | 4806(1) | -380(1) | 65(1) |
| N(1) | 3503(1) | 7512(1) | 876(1) | 43(1) |
| C(17) | 3504(1) | 8702(1) | 816(1) | 44(1) |
| C(1) | 4143(1) | 7335(1) | -83(1) | 47(1) |
| C(2) | 4160(1) | 7090(1) | -1237(1) | 54(1) |
| C(3) | 4504(1) | 7563(1) | -1658(2) | 66(1) |
| C(4) | 4831(1) | 8287(2) | -956(2) | 73(1) |
| C(5) | 4820(1) | 8541(1) | 191(2) | 70(1) |
| C(6) | 4479(1) | 8065(1) | 625(2) | 57(1) |
| C(7) | 3780(1) | 6840(1) | 401(1) | 43(1) |
| C(8) | 3675(1) | 5752(1) | 620(1) | 45(1) |
| C(9) | 3334(1) | 5789(1) | 1246(1) | 48(1) |
| C(10) | 3230(1) | 6867(1) | 1403(1) | 44(1) |

| | | | | |
|---|---|---|---|---|
| C(11) | 2885(1) | 7292(1) | 1977(1) | 45(1) |
| C(12) | 2844(1) | 6726(1) | 2984(1) | 54(1) |
| C(13) | 2502(1) | 7019(2) | 3507(2) | 63(1) |
| C(14) | 2200(1) | 7897(1) | 3058(2) | 62(1) |
| C(15) | 2242(1) | 8474(1) | 2082(1) | 57(1) |
| C(16) | 2580(1) | 8177(1) | 1538(1) | 49(1) |
| N(2) | 3670(1) | 9217(1) | 1870(1) | 57(1) |
| C(18) | 3691(1) | 10323(1) | 1814(2) | 73(1) |
| C(19) | 3563(1) | 10921(1) | 756(2) | 76(1) |
| C(20) | 3386(1) | 10362(1) | -312(2) | 70(1) |
| C(21) | 3350(1) | 9220(1) | -286(1) | 54(1) |
| C(22) | 3870(1) | 4701(1) | 358(1) | 50(1) |
| C(23) | 4331(1) | 3804(2) | -714(2) | 81(1) |
| C(24) | 4620(1) | 4134(2) | -1495(2) | 88(1) |

**Table 8. Bond lengths [A] and angles [deg] for 3r.**

| | |
|---|---|
| O(1)-C(22) | 1.2023(18) |
| O(2)-C(22) | 1.3290(19) |
| O(2)-C(23) | 1.4468(19) |
| N(1)-C(7) | 1.3806(17) |
| N(1)-C(10) | 1.3904(17) |
| N(1)-C(17) | 1.4359(17) |
| C(17)-N(2) | 1.3268(18) |
| C(17)-C(21) | 1.373(2) |
| C(1)-C(6) | 1.389(2) |
| C(1)-C(2) | 1.392(2) |
| C(1)-C(7) | 1.4812(19) |
| C(2)-C(3) | 1.380(2) |
| C(2)-H(2A) | 0.9300 |
| C(3)-C(4) | 1.368(3) |
| C(3)-H(3A) | 0.9300 |
| C(4)-C(5) | 1.382(3) |
| C(4)-H(4A) | 0.9300 |
| C(5)-C(6) | 1.384(2) |
| C(5)-H(5A) | 0.9300 |
| C(6)-H(6A) | 0.9300 |

| | |
|---|---|
| C(7)-C(8) | 1.3884(19) |
| C(8)-C(9) | 1.414(2) |
| C(8)-C(22) | 1.4618(19) |
| C(9)-C(10) | 1.3597(19) |
| C(9)-H(9A) | 0.9300 |
| C(10)-C(11) | 1.4715(19) |
| C(11)-C(16) | 1.388(2) |
| C(11)-C(12) | 1.3951(19) |
| C(12)-C(13) | 1.377(2) |
| C(12)-H(12A) | 0.9300 |
| C(13)-C(14) | 1.378(2) |
| C(13)-H(13A) | 0.9300 |
| C(14)-C(15) | 1.372(2) |
| C(14)-H(14A) | 0.9300 |
| C(15)-C(16) | 1.383(2) |
| C(15)-H(15A) | 0.9300 |
| C(16)-H(16A) | 0.9300 |
| N(2)-C(18) | 1.338(2) |
| C(18)-C(19) | 1.375(3) |
| C(18)-H(18A) | 0.9300 |
| C(19)-C(20) | 1.369(3) |
| C(19)-H(19A) | 0.9300 |
| C(20)-C(21) | 1.381(2) |
| C(20)-H(20A) | 0.9300 |
| C(21)-H(21A) | 0.9300 |
| C(23)-C(24) | 1.479(3) |
| C(23)-H(23B) | 0.9700 |
| C(23)-H(23C) | 0.9700 |
| C(24)-H(24C) | 0.9600 |
| C(24)-H(24D) | 0.9600 |
| C(24)-H(24A) | 0.9600 |

| | |
|---|---|
| C(22)-O(2)-C(23) | 117.38(13) |
| C(7)-N(1)-C(10) | 110.08(11) |
| C(7)-N(1)-C(17) | 123.80(11) |
| C(10)-N(1)-C(17) | 126.12(11) |
| N(2)-C(17)-C(21) | 124.95(13) |
| N(2)-C(17)-N(1) | 115.33(12) |

| | |
|---|---|
| C(21)-C(17)-N(1) | 119.69(12) |
| C(6)-C(1)-C(2) | 118.48(14) |
| C(6)-C(1)-C(7) | 119.66(13) |
| C(2)-C(1)-C(7) | 121.86(13) |
| C(3)-C(2)-C(1) | 120.37(16) |
| C(3)-C(2)-H(2A) | 119.8 |
| C(1)-C(2)-H(2A) | 119.8 |
| C(4)-C(3)-C(2) | 120.73(17) |
| C(4)-C(3)-H(3A) | 119.6 |
| C(2)-C(3)-H(3A) | 119.6 |
| C(3)-C(4)-C(5) | 119.78(16) |
| C(3)-C(4)-H(4A) | 120.1 |
| C(5)-C(4)-H(4A) | 120.1 |
| C(6)-C(5)-C(4) | 119.96(17) |
| C(6)-C(5)-H(5A) | 120.0 |
| C(4)-C(5)-H(5A) | 120.0 |
| C(5)-C(6)-C(1) | 120.68(16) |
| C(5)-C(6)-H(6A) | 119.7 |
| C(1)-C(6)-H(6A) | 119.7 |
| N(1)-C(7)-C(8) | 106.71(11) |
| N(1)-C(7)-C(1) | 120.14(12) |
| C(8)-C(7)-C(1) | 132.73(12) |
| C(7)-C(8)-C(9) | 107.41(11) |
| C(7)-C(8)-C(22) | 130.96(13) |
| C(9)-C(8)-C(22) | 121.58(12) |
| C(10)-C(9)-C(8) | 108.92(12) |
| C(10)-C(9)-H(9A) | 125.5 |
| C(8)-C(9)-H(9A) | 125.5 |
| C(9)-C(10)-N(1) | 106.87(12) |
| C(9)-C(10)-C(11) | 127.50(12) |
| N(1)-C(10)-C(11) | 125.60(12) |
| C(16)-C(11)-C(12) | 118.07(13) |
| C(16)-C(11)-C(10) | 124.11(12) |
| C(12)-C(11)-C(10) | 117.70(13) |
| C(13)-C(12)-C(11) | 120.90(15) |
| C(13)-C(12)-H(12A) | 119.5 |
| C(11)-C(12)-H(12A) | 119.5 |
| C(14)-C(13)-C(12) | 120.34(14) |

| | |
|---|---|
| C(14)-C(13)-H(13A) | 119.8 |
| C(12)-C(13)-H(13A) | 119.8 |
| C(15)-C(14)-C(13) | 119.40(14) |
| C(15)-C(14)-H(14A) | 120.3 |
| C(13)-C(14)-H(14A) | 120.3 |
| C(14)-C(15)-C(16) | 120.78(15) |
| C(14)-C(15)-H(15A) | 119.6 |
| C(16)-C(15)-H(15A) | 119.6 |
| C(15)-C(16)-C(11) | 120.47(13) |
| C(15)-C(16)-H(16A) | 119.8 |
| C(11)-C(16)-H(16A) | 119.8 |
| C(17)-N(2)-C(18) | 115.51(14) |
| N(2)-C(18)-C(19) | 124.16(16) |
| N(2)-C(18)-H(18A) | 117.9 |
| C(19)-C(18)-H(18A) | 117.9 |
| C(20)-C(19)-C(18) | 118.62(15) |
| C(20)-C(19)-H(19A) | 120.7 |
| C(18)-C(19)-H(19A) | 120.7 |
| C(19)-C(20)-C(21) | 118.69(16) |
| C(19)-C(20)-H(20A) | 120.7 |
| C(21)-C(20)-H(20A) | 120.7 |
| C(17)-C(21)-C(20) | 117.98(15) |
| C(17)-C(21)-H(21A) | 121.0 |
| C(20)-C(21)-H(21A) | 121.0 |
| O(1)-C(22)-O(2) | 123.09(13) |
| O(1)-C(22)-C(8) | 123.42(14) |
| O(2)-C(22)-C(8) | 113.48(12) |
| O(2)-C(23)-C(24) | 107.38(16) |
| O(2)-C(23)-H(23B) | 110.2 |
| C(24)-C(23)-H(23B) | 110.2 |
| O(2)-C(23)-H(23C) | 110.2 |
| C(24)-C(23)-H(23C) | 110.2 |
| H(23B)-C(23)-H(23C) | 108.5 |
| C(23)-C(24)-H(24C) | 109.5 |
| C(23)-C(24)-H(24D) | 109.5 |
| H(24C)-C(24)-H(24D) | 109.5 |
| C(23)-C(24)-H(24A) | 109.5 |
| H(24C)-C(24)-H(24A) | 109.5 |

H(24D)-C(24)-H(24A) 109.5

---

Symmetry transformations used to generate equivalent atoms:

**Table 9. Anisotropic displacement parameters (A^2 x 10^3) for 3r. The anisotropic displacement factor exponent takes the form:** $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2\ hka^*b^*U^{12}]$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 106(1) | 37(1) | 94(1) | 8(1) | 47(1) | 8(1) |
| O(2) | 83(1) | 45(1) | 80(1) | 3(1) | 41(1) | 17(1) |
| N(1) | 54(1) | 33(1) | 45(1) | 1(1) | 21(1) | 1(1) |
| C(17) | 54(1) | 34(1) | 51(1) | -2(1) | 26(1) | -1(1) |
| C(1) | 52(1) | 36(1) | 55(1) | 6(1) | 22(1) | 7(1) |
| C(2) | 62(1) | 48(1) | 57(1) | 5(1) | 27(1) | 10(1) |
| C(3) | 79(1) | 59(1) | 75(1) | 12(1) | 45(1) | 13(1) |
| C(4) | 76(1) | 58(1) | 103(1) | 17(1) | 54(1) | 7(1) |
| C(5) | 65(1) | 48(1) | 101(1) | 1(1) | 33(1) | -7(1) |
| C(6) | 63(1) | 45(1) | 67(1) | 0(1) | 27(1) | -1(1) |
| C(7) | 50(1) | 38(1) | 42(1) | 0(1) | 16(1) | 3(1) |
| C(8) | 54(1) | 36(1) | 45(1) | 1(1) | 15(1) | 3(1) |
| C(9) | 59(1) | 37(1) | 50(1) | 5(1) | 22(1) | -3(1) |
| C(10) | 54(1) | 40(1) | 42(1) | 2(1) | 18(1) | -2(1) |
| C(11) | 53(1) | 41(1) | 42(1) | -2(1) | 17(1) | -5(1) |
| C(12) | 67(1) | 50(1) | 49(1) | 6(1) | 24(1) | 5(1) |
| C(13) | 82(1) | 65(1) | 54(1) | 3(1) | 37(1) | -2(1) |
| C(14) | 67(1) | 63(1) | 64(1) | -10(1) | 34(1) | -2(1) |
| C(15) | 58(1) | 52(1) | 63(1) | -6(1) | 21(1) | 4(1) |
| C(16) | 57(1) | 45(1) | 46(1) | 1(1) | 17(1) | -1(1) |
| N(2) | 78(1) | 47(1) | 54(1) | -10(1) | 29(1) | -11(1) |
| C(18) | 100(1) | 48(1) | 84(1) | -23(1) | 49(1) | -19(1) |
| C(19) | 107(2) | 34(1) | 109(2) | -2(1) | 65(1) | -3(1) |
| C(20) | 97(1) | 45(1) | 80(1) | 18(1) | 47(1) | 14(1) |
| C(21) | 73(1) | 42(1) | 52(1) | 5(1) | 26(1) | 6(1) |
| C(22) | 58(1) | 39(1) | 50(1) | 1(1) | 14(1) | 4(1) |
| C(23) | 92(1) | 60(1) | 96(1) | -7(1) | 38(1) | 29(1) |
| C(24) | 89(1) | 105(2) | 72(1) | -11(1) | 27(1) | 36(1) |

**Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3r.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 3938 | 6604 | -1726 | 64 |
| H(3A) | 4514 | 7387 | -2427 | 79 |
| H(4A) | 5060 | 8607 | -1251 | 88 |
| H(5A) | 5042 | 9032 | 671 | 84 |
| H(6A) | 4474 | 8236 | 1400 | 68 |
| H(9A) | 3202 | 5176 | 1508 | 57 |
| H(12A) | 3051 | 6143 | 3307 | 65 |
| H(13A) | 2474 | 6622 | 4167 | 76 |
| H(14A) | 1970 | 8097 | 3415 | 74 |
| H(15A) | 2041 | 9072 | 1782 | 69 |
| H(16A) | 2602 | 8574 | 873 | 59 |
| H(18A) | 3798 | 10714 | 2536 | 87 |
| H(19A) | 3597 | 11688 | 767 | 91 |
| H(20A) | 3291 | 10744 | -1041 | 84 |
| H(21A) | 3227 | 8815 | -993 | 65 |
| H(23B) | 4077 | 3306 | -1146 | 97 |
| H(23C) | 4529 | 3427 | 1 | 97 |
| H(24C) | 4757 | 3486 | -1733 | 133 |
| H(24D) | 4870 | 4626 | -1058 | 133 |
| H(24A) | 4420 | 4505 | -2199 | 133 |

### 3.2 Single crystal structure and crystallographic data for 3y

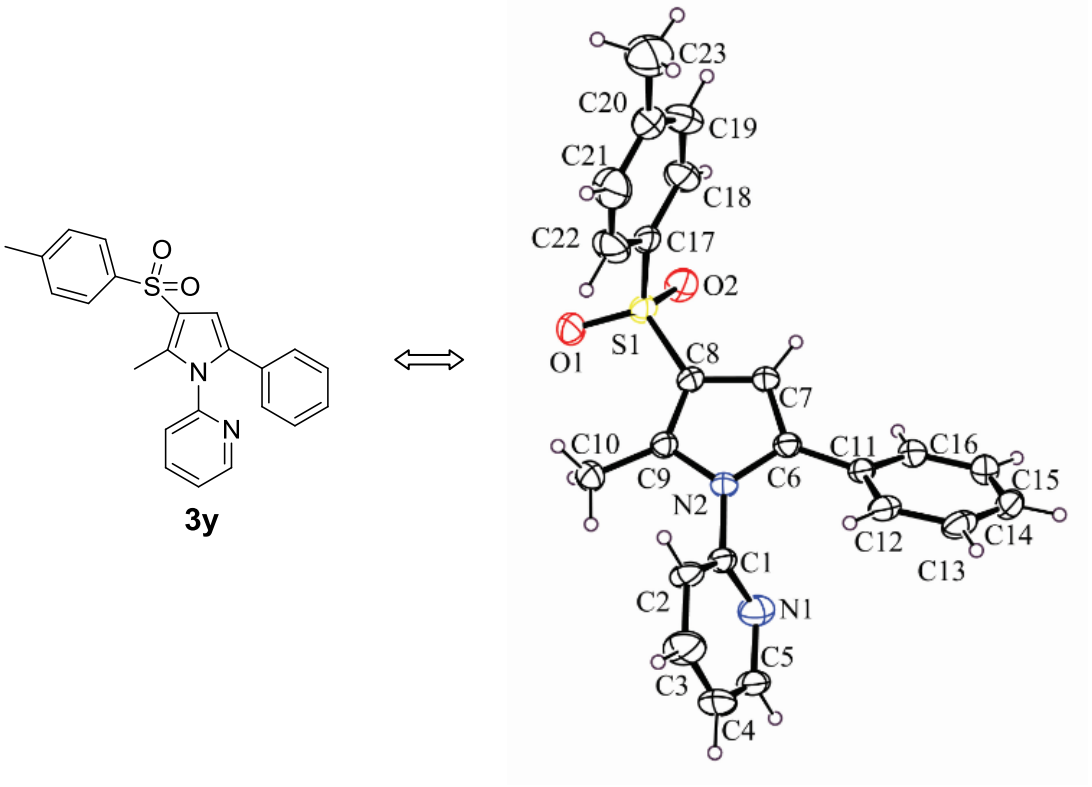



**Figure 2. The Single crystal structure of compound 3y**

**Table 11. Crystal data and structure refinement for 3y.**

| | |
|---|---|
| Identification code | 3y |
| Empirical formula | $C_{23}H_{20}N_2O_2S$ |
| Formula weight | 388.47 |
| Temperature | 571(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P21/C |
| Unit cell dimensions | a = 15.4468(4) A alpha = 90 deg. |
| | b = 12.2137(3) A beta = 90.313(3) deg. |
| | c = 10.5709(3) A gamma = 90 deg. |
| Volume | 1994.30(9) A^3 |
| Z, Calculated density | 4, 1.294 Mg/m^3 |
| Absorption coefficient | 1.606 mm^-1 |
| F(000) | 816 |
| Crystal size | 0.26 x 0.22 x 0.21 $mm^3$ |
| Theta range for data collection | 4.62 to 62.60 deg. |

| | |
|---|---|
| Limiting indices | -17<=h<=17, -14<=k<=13, -12<=l<=6 |
| Reflections collected / unique | 5045 / 2672 [R(int) = 0.0233] |
| Completeness to theta = 27.45 | 83.7 % |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2672 / 0 / 254 |
| Goodness-of-fit on F^2 | 1.023 |
| Final R indices [I>2sigma(I)] | R1 = 0.0542, wR2 = 0.1537 |
| R indices (all data) | R1 = 0.0585, wR2 = 0.1591 |
| Largest diff. peak and hole | 0.434 and -0.386 e.A^-3 |

**Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 3y**.

U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor**.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 7161(1) | 9647(1) | 370(1) | 51(1) |
| O(1) | 6583(2) | 9823(2) | 1399(2) | 67(1) |
| O(2) | 7851(2) | 8868(2) | 530(2) | 66(1) |
| N(1) | 8794(2) | 14207(2) | 453(3) | 66(1) |
| N(2) | 7978(1) | 12617(2) | -255(2) | 40(1) |
| C(1) | 8034(2) | 13777(2) | -27(3) | 42(1) |
| C(2) | 7338(2) | 14341(2) | -317(3) | 52(1) |
| C(3) | 7382(3) | 15427(3) | -106(5) | 85(1) |
| C(4) | 8097(3) | 15939(3) | 362(4) | 74(1) |
| C(5) | 8812(2) | 15329(2) | 647(3) | 58(1) |
| C(6) | 8528(2) | 12032(2) | -1052(3) | 42(1) |
| C(7) | 8298(2) | 10955(2) | -956(3) | 45(1) |
| C(8) | 7616(2) | 10884(2) | -81(3) | 44(1) |
| C(9) | 7418(2) | 11921(2) | 356(3) | 42(1) |
| C(10) | 6812(2) | 12310(3) | 1345(3) | 56(1) |
| C(11) | 9204(2) | 12510(2) | -1849(3) | 43(1) |
| C(12) | 9073(2) | 13444(2) | -2585(3) | 49(1) |
| C(13) | 9712(2) | 13781(3) | -3412(3) | 61(1) |
| C(14) | 10484(2) | 13216(3) | -3511(3) | 63(1) |
| C(15) | 10630(2) | 12316(3) | -2760(3) | 60(1) |
| C(16) | 9991(2) | 11969(2) | -1938(3) | 52(1) |
| C(17) | 6543(2) | 9225(2) | -954(3) | 53(1) |

| | | | | |
|---|---|---|---|---|
| C(18) | 6760(3) | 8287(3) | -1605(4) | 74(1) |
| C(19) | 6256(3) | 7952(3) | -2604(5) | 90(1) |
| C(20) | 5542(2) | 8528(4) | -2984(4) | 83(1) |
| C(21) | 5335(2) | 9459(4) | -2323(5) | 91(1) |
| C(22) | 5828(2) | 9806(3) | -1315(4) | 78(1) |
| C(23) | 4991(4) | 8149(6) | -4079(6) | 128(2) |

**Table 13. Bond lengths [A] and angles [deg] for 3y.**

| | |
|---|---|
| S(1)-O(1) | 1.427(3) |
| S(1)-O(2) | 1.438(2) |
| S(1)-C(8) | 1.734(3) |
| S(1)-C(17) | 1.767(3) |
| N(1)-C(1) | 1.381(4) |
| N(1)-C(5) | 1.386(4) |
| N(2)-C(9) | 1.377(3) |
| N(2)-C(6) | 1.397(4) |
| N(2)-C(1) | 1.440(3) |
| C(1)-C(2) | 1.312(4) |
| C(2)-C(3) | 1.346(4) |
| C(2)-H(2A) | 0.9300 |
| C(3)-C(4) | 1.360(6) |
| C(3)-H(3A) | 0.9300 |
| C(4)-C(5) | 1.364(5) |
| C(4)-H(4A) | 0.9300 |
| C(5)-H(5A) | 0.9300 |
| C(6)-C(7) | 1.366(4) |
| C(6)-C(11) | 1.466(4) |
| C(7)-C(8) | 1.409(4) |
| C(7)-H(7A) | 0.9300 |
| C(8)-C(9) | 1.383(4) |
| C(9)-C(10) | 1.485(4) |
| C(10)-H(10A) | 0.9600 |
| C(10)-H(10B) | 0.9600 |
| C(10)-H(10C) | 0.9600 |
| C(11)-C(16) | 1.387(4) |
| C(11)-C(12) | 1.396(4) |

| | |
|---|---|
| C(12)-C(13) | 1.384(4) |
| C(12)-H(12A) | 0.9300 |
| C(13)-C(14) | 1.383(5) |
| C(13)-H(13A) | 0.9300 |
| C(14)-C(15) | 1.374(5) |
| C(14)-H(14A) | 0.9300 |
| C(15)-C(16) | 1.384(4) |
| C(15)-H(15A) | 0.9300 |
| C(16)-H(16A) | 0.9300 |
| C(17)-C(22) | 1.365(5) |
| C(17)-C(18) | 1.378(4) |
| C(18)-C(19) | 1.371(6) |
| C(18)-H(18A) | 0.9300 |
| C(19)-C(20) | 1.367(6) |
| C(19)-H(19A) | 0.9300 |
| C(20)-C(21) | 1.373(6) |
| C(20)-C(23) | 1.506(7) |
| C(21)-C(22) | 1.374(6) |
| C(21)-H(21A) | 0.9300 |
| C(22)-H(22A) | 0.9300 |
| C(23)-H(23A) | 0.9600 |
| C(23)-H(23B) | 0.9600 |
| C(23)-H(23C) | 0.9600 |

| | |
|---|---|
| O(1)-S(1)-O(2) | 118.42(15) |
| O(1)-S(1)-C(8) | 109.52(14) |
| O(2)-S(1)-C(8) | 107.94(13) |
| O(1)-S(1)-C(17) | 108.04(15) |
| O(2)-S(1)-C(17) | 107.30(14) |
| C(8)-S(1)-C(17) | 104.76(14) |
| C(1)-N(1)-C(5) | 116.5(3) |
| C(9)-N(2)-C(6) | 110.6(2) |
| C(9)-N(2)-C(1) | 124.5(2) |
| C(6)-N(2)-C(1) | 124.7(2) |
| C(2)-C(1)-N(1) | 125.5(3) |
| C(2)-C(1)-N(2) | 115.5(2) |
| N(1)-C(1)-N(2) | 119.0(2) |
| C(1)-C(2)-C(3) | 115.9(3) |

| | |
|---|---|
| C(1)-C(2)-H(2A) | 122.0 |
| C(3)-C(2)-H(2A) | 122.0 |
| C(2)-C(3)-C(4) | 123.6(3) |
| C(2)-C(3)-H(3A) | 118.2 |
| C(4)-C(3)-H(3A) | 118.2 |
| C(3)-C(4)-C(5) | 118.9(3) |
| C(3)-C(4)-H(4A) | 120.5 |
| C(5)-C(4)-H(4A) | 120.5 |
| C(4)-C(5)-N(1) | 119.5(3) |
| C(4)-C(5)-H(5A) | 120.2 |
| N(1)-C(5)-H(5A) | 120.2 |
| C(7)-C(6)-N(2) | 106.8(2) |
| C(7)-C(6)-C(11) | 127.8(3) |
| N(2)-C(6)-C(11) | 125.4(2) |
| C(6)-C(7)-C(8) | 107.7(2) |
| C(6)-C(7)-H(7A) | 126.1 |
| C(8)-C(7)-H(7A) | 126.1 |
| C(9)-C(8)-C(7) | 109.3(2) |
| C(9)-C(8)-S(1) | 128.0(2) |
| C(7)-C(8)-S(1) | 122.7(2) |
| N(2)-C(9)-C(8) | 105.6(2) |
| N(2)-C(9)-C(10) | 122.2(2) |
| C(8)-C(9)-C(10) | 132.0(3) |
| C(9)-C(10)-H(10A) | 109.5 |
| C(9)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(9)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| C(16)-C(11)-C(12) | 118.4(3) |
| C(16)-C(11)-C(6) | 118.4(3) |
| C(12)-C(11)-C(6) | 123.0(3) |
| C(13)-C(12)-C(11) | 119.5(3) |
| C(13)-C(12)-H(12A) | 120.2 |
| C(11)-C(12)-H(12A) | 120.2 |
| C(14)-C(13)-C(12) | 121.2(3) |
| C(14)-C(13)-H(13A) | 119.4 |

| | |
|---|---|
| C(12)-C(13)-H(13A) | 119.4 |
| C(15)-C(14)-C(13) | 119.6(3) |
| C(15)-C(14)-H(14A) | 120.2 |
| C(13)-C(14)-H(14A) | 120.2 |
| C(14)-C(15)-C(16) | 119.5(3) |
| C(14)-C(15)-H(15A) | 120.3 |
| C(16)-C(15)-H(15A) | 120.3 |
| C(15)-C(16)-C(11) | 121.7(3) |
| C(15)-C(16)-H(16A) | 119.2 |
| C(11)-C(16)-H(16A) | 119.2 |
| C(22)-C(17)-C(18) | 119.4(3) |
| C(22)-C(17)-S(1) | 120.2(3) |
| C(18)-C(17)-S(1) | 120.4(3) |
| C(19)-C(18)-C(17) | 119.6(4) |
| C(19)-C(18)-H(18A) | 120.2 |
| C(17)-C(18)-H(18A) | 120.2 |
| C(20)-C(19)-C(18) | 121.8(4) |
| C(20)-C(19)-H(19A) | 119.1 |
| C(18)-C(19)-H(19A) | 119.1 |
| C(19)-C(20)-C(21) | 117.8(4) |
| C(19)-C(20)-C(23) | 121.3(4) |
| C(21)-C(20)-C(23) | 120.8(5) |
| C(20)-C(21)-C(22) | 121.3(4) |
| C(20)-C(21)-H(21A) | 119.3 |
| C(22)-C(21)-H(21A) | 119.3 |
| C(17)-C(22)-C(21) | 120.1(3) |
| C(17)-C(22)-H(22A) | 120.0 |
| C(21)-C(22)-H(22A) | 120.0 |
| C(20)-C(23)-H(23A) | 109.5 |
| C(20)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(20)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(16)-C(11)-C(10) | 124.11(12) |
| C(12)-C(11)-C(10) | 117.70(13) |
| C(13)-C(12)-C(11) | 120.90(15) |
| C(13)-C(12)-H(12A) | 119.5 |

| | |
|---|---|
| C(11)-C(12)-H(12A) | 119.5 |
| C(14)-C(13)-C(12) | 120.34(14) |
| C(14)-C(13)-H(13A) | 119.8 |
| C(12)-C(13)-H(13A) | 119.8 |
| C(15)-C(14)-C(13) | 119.40(14) |
| C(15)-C(14)-H(14A) | 120.3 |
| C(13)-C(14)-H(14A) | 120.3 |
| C(14)-C(15)-C(16) | 120.78(15) |
| C(14)-C(15)-H(15A) | 119.6 |
| C(16)-C(15)-H(15A) | 119.6 |
| C(15)-C(16)-C(11) | 120.47(13) |
| C(15)-C(16)-H(16A) | 119.8 |
| C(11)-C(16)-H(16A) | 119.8 |
| C(17)-N(2)-C(18) | 115.51(14) |
| N(2)-C(18)-C(19) | 124.16(16) |
| N(2)-C(18)-H(18A) | 117.9 |
| C(19)-C(18)-H(18A) | 117.9 |
| C(20)-C(19)-C(18) | 118.62(15) |
| C(20)-C(19)-H(19A) | 120.7 |
| C(18)-C(19)-H(19A) | 120.7 |
| C(19)-C(20)-C(21) | 118.69(16) |
| C(19)-C(20)-H(20A) | 120.7 |
| C(21)-C(20)-H(20A) | 120.7 |
| C(17)-C(21)-C(20) | 117.98(15) |
| C(17)-C(21)-H(21A) | 121.0 |
| C(20)-C(21)-H(21A) | 121.0 |
| O(1)-C(22)-O(2) | 123.09(13) |
| O(1)-C(22)-C(8) | 123.42(14) |
| O(2)-C(22)-C(8) | 113.48(12) |
| O(2)-C(23)-C(24) | 107.38(16) |
| O(2)-C(23)-H(23B) | 110.2 |
| C(24)-C(23)-H(23B) | 110.2 |
| O(2)-C(23)-H(23C) | 110.2 |
| C(24)-C(23)-H(23C) | 110.2 |
| H(23B)-C(23)-H(23C) | 108.5 |
| C(23)-C(24)-H(24C) | 109.5 |
| C(23)-C(24)-H(24D) | 109.5 |
| H(24C)-C(24)-H(24D) | 109.5 |

| | |
|---|---|
| C(23)-C(24)-H(24A) | 109.5 |
| H(24C)-C(24)-H(24A) | 109.5 |
| H(24D)-C(24)-H(24A) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

**Table 14. Anisotropic displacement parameters (A^2 x 10^3) for 3y. The anisotropic displacement factor exponent takes the form:** $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\,hka^*b^*U^{12}]$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| S(1) | 52(1) | 33(1) | 67(1) | 6(1) | 12(1) | -1(1) |
| O(1) | 79(2) | 51(1) | 72(2) | 4(1) | 30(1) | -6(1) |
| O(2) | 65(1) | 43(1) | 90(2) | 16(1) | 5(1) | 9(1) |
| N(1) | 79(2) | 60(2) | 60(2) | -2(1) | -8(2) | -10(1) |
| N(2) | 45(1) | 31(1) | 45(1) | 0(1) | 3(1) | 1(1) |
| C(1) | 49(2) | 33(1) | 45(2) | 0(1) | 1(1) | -4(1) |
| C(2) | 41(1) | 27(1) | 87(2) | 1(1) | -7(2) | 4(1) |
| C(3) | 73(2) | 43(2) | 139(4) | 2(2) | -2(3) | 15(2) |
| C(4) | 97(3) | 35(2) | 90(3) | -7(2) | 13(2) | -3(2) |
| C(5) | 76(2) | 44(2) | 56(2) | -9(1) | 2(2) | -17(2) |
| C(6) | 49(2) | 35(1) | 44(2) | -1(1) | 1(1) | -3(1) |
| C(7) | 52(2) | 34(1) | 51(2) | -2(1) | 9(1) | -1(1) |
| C(8) | 46(2) | 36(1) | 50(2) | 2(1) | 4(1) | -5(1) |
| C(9) | 42(1) | 37(1) | 47(2) | 1(1) | 2(1) | -1(1) |
| C(10) | 53(2) | 49(2) | 67(2) | -2(2) | 12(2) | 5(1) |
| C(11) | 50(2) | 38(1) | 39(2) | -3(1) | 3(1) | -9(1) |
| C(12) | 61(2) | 40(1) | 46(2) | -1(1) | -7(2) | -12(1) |
| C(13) | 89(3) | 49(2) | 45(2) | 7(1) | -4(2) | -27(2) |
| C(14) | 63(2) | 71(2) | 54(2) | -10(2) | 11(2) | -29(2) |
| C(15) | 56(2) | 65(2) | 59(2) | -12(2) | 11(2) | -10(2) |
| C(16) | 58(2) | 45(2) | 52(2) | -3(1) | 6(2) | -4(1) |
| C(17) | 44(2) | 35(1) | 79(2) | -5(1) | 13(2) | -2(1) |
| C(18) | 74(2) | 48(2) | 99(3) | -16(2) | 8(2) | 12(2) |
| C(19) | 92(3) | 66(2) | 114(3) | -40(2) | 9(3) | -4(2) |
| C(20) | 59(2) | 89(3) | 100(3) | -32(2) | 13(2) | -18(2) |
| C(21) | 51(2) | 108(3) | 114(3) | -25(3) | -8(2) | 15(2) |
| C(22) | 62(2) | 68(2) | 106(3) | -31(2) | -1(2) | 18(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(23) | 98(3) | 159(6) | 127(4) | -54(4) | -14(3) | -21(4) |

**Table 15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3y.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 6843 | 14011 | -647 | 62 |
| H(3A) | 6897 | 15850 | -291 | 102 |
| H(4A) | 8099 | 16693 | 486 | 89 |
| H(5A) | 9307 | 15664 | 968 | 70 |
| H(7A) | 8547 | 10374 | -1391 | 55 |
| H(10A) | 6838 | 13094 | 1398 | 84 |
| H(10B) | 6972 | 11998 | 2146 | 84 |
| H(10C) | 6233 | 12089 | 1130 | 84 |
| H(12A) | 8559 | 13838 | -2521 | 59 |
| H(13A) | 9620 | 14399 | -3910 | 73 |
| H(14A) | 10903 | 13445 | -4083 | 75 |
| H(15A) | 11153 | 11942 | -2804 | 72 |
| H(16A) | 10092 | 11359 | -1433 | 62 |
| H(18A) | 7245 | 7884 | -1367 | 89 |
| H(19A) | 6404 | 7315 | -3034 | 108 |
| H(21A) | 4850 | 9862 | -2563 | 109 |
| H(22A) | 5675 | 10437 | -879 | 94 |
| H(23A) | 5229 | 7487 | -4422 | 192 |
| H(23B) | 4980 | 8705 | -4721 | 192 |
| H(23C) | 4412 | 8014 | -3791 | 192 |

## 4. References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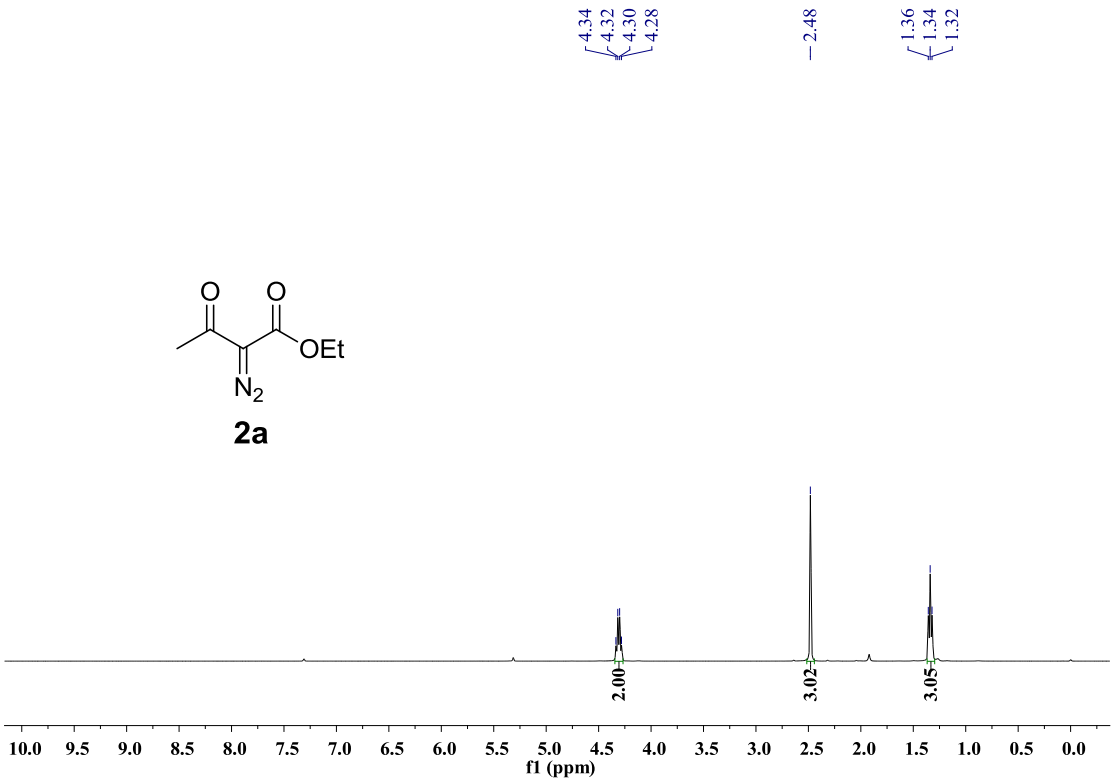
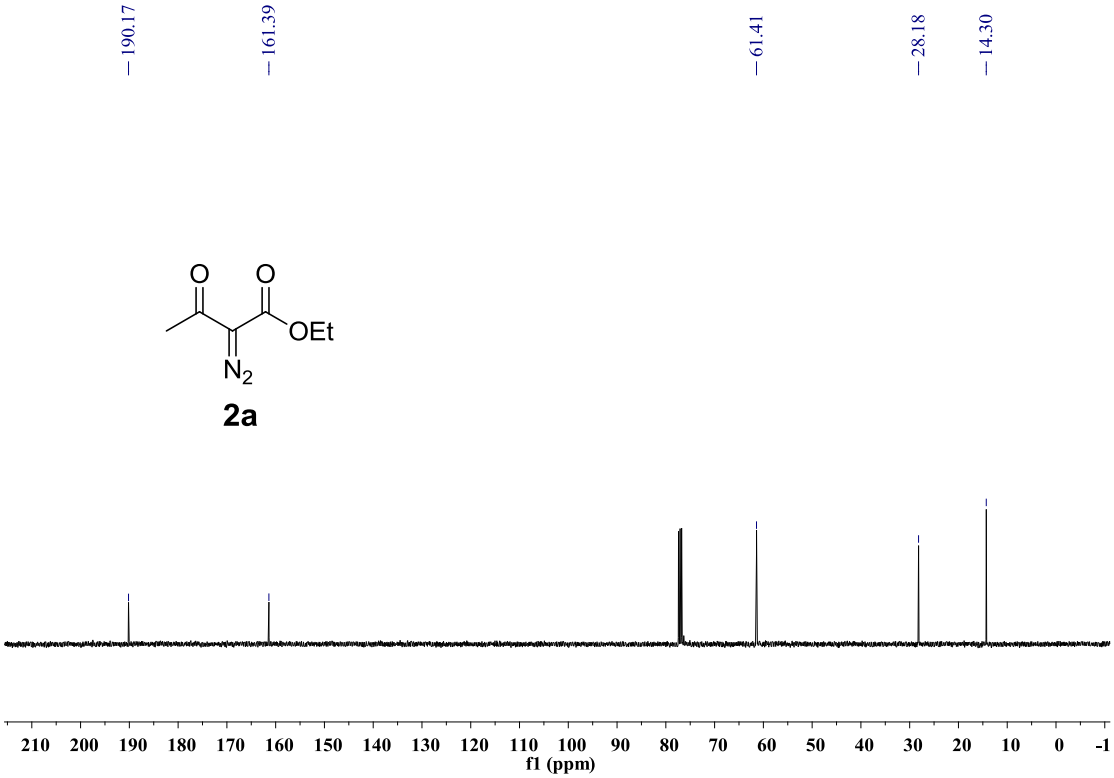
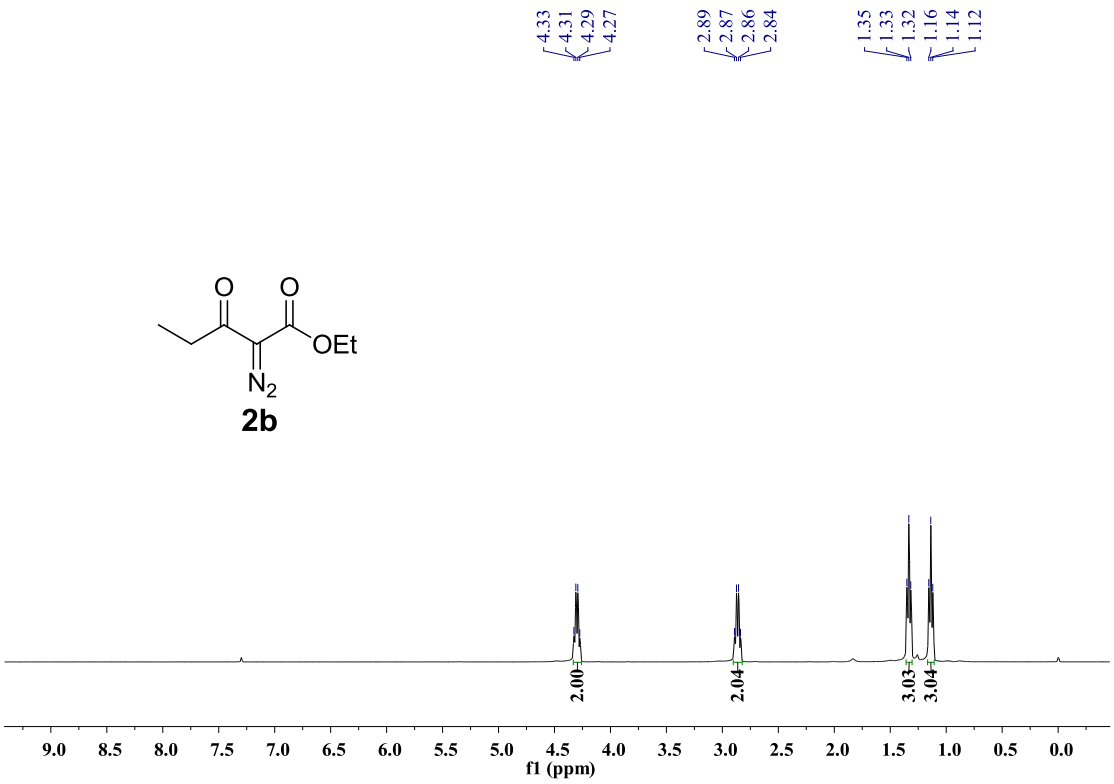
**5. $^{1}$H NMR and $^{13}$C NMR spectrum for all isolated products.**

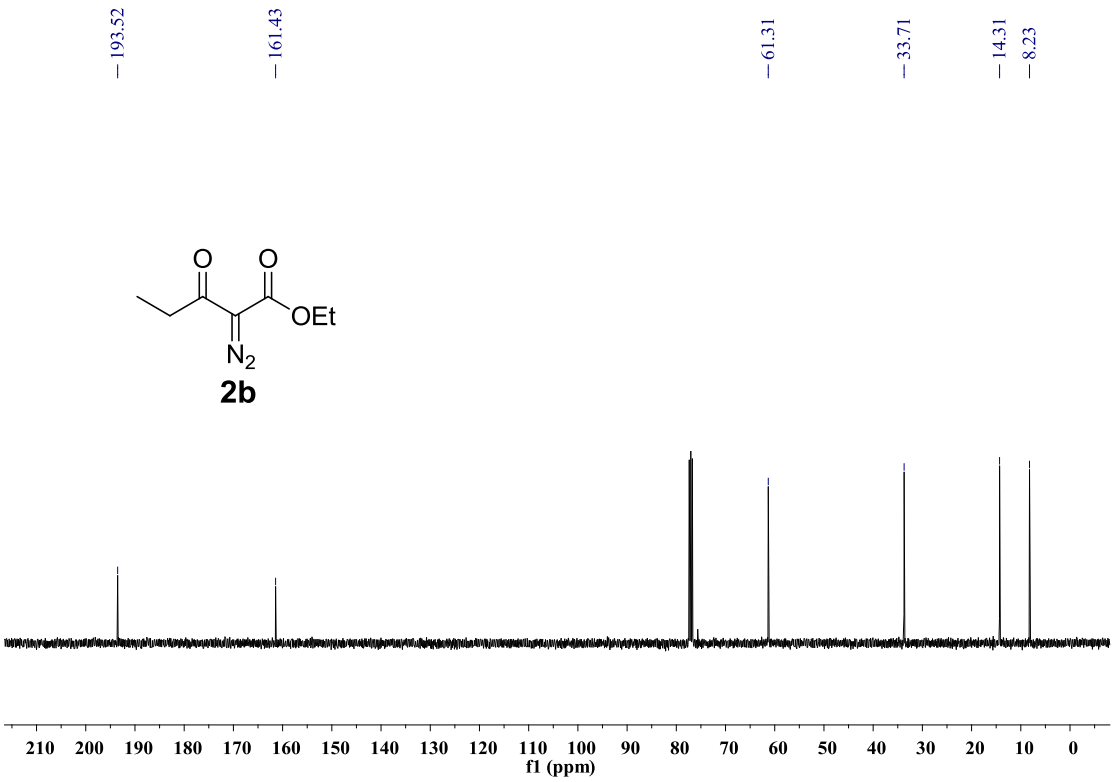
(1) The $^{1}$H NMR and $^{13}$C NMR spectrum for **2a** (using $CDCl_3$ as solvent)



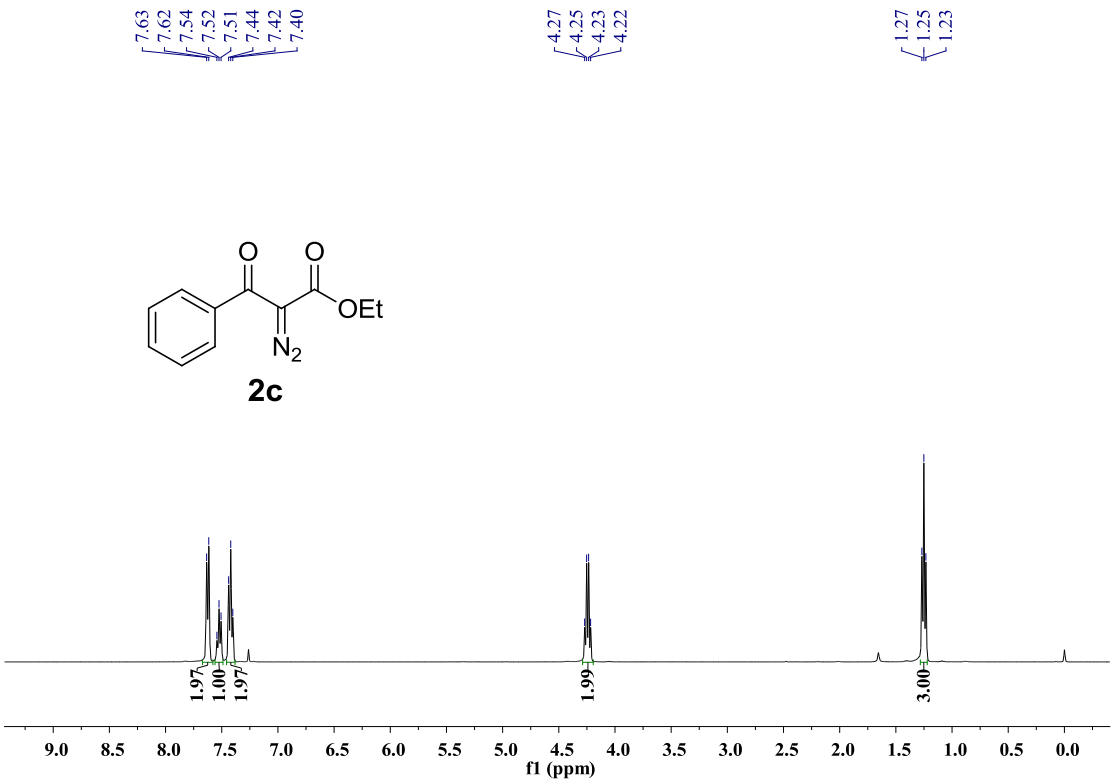



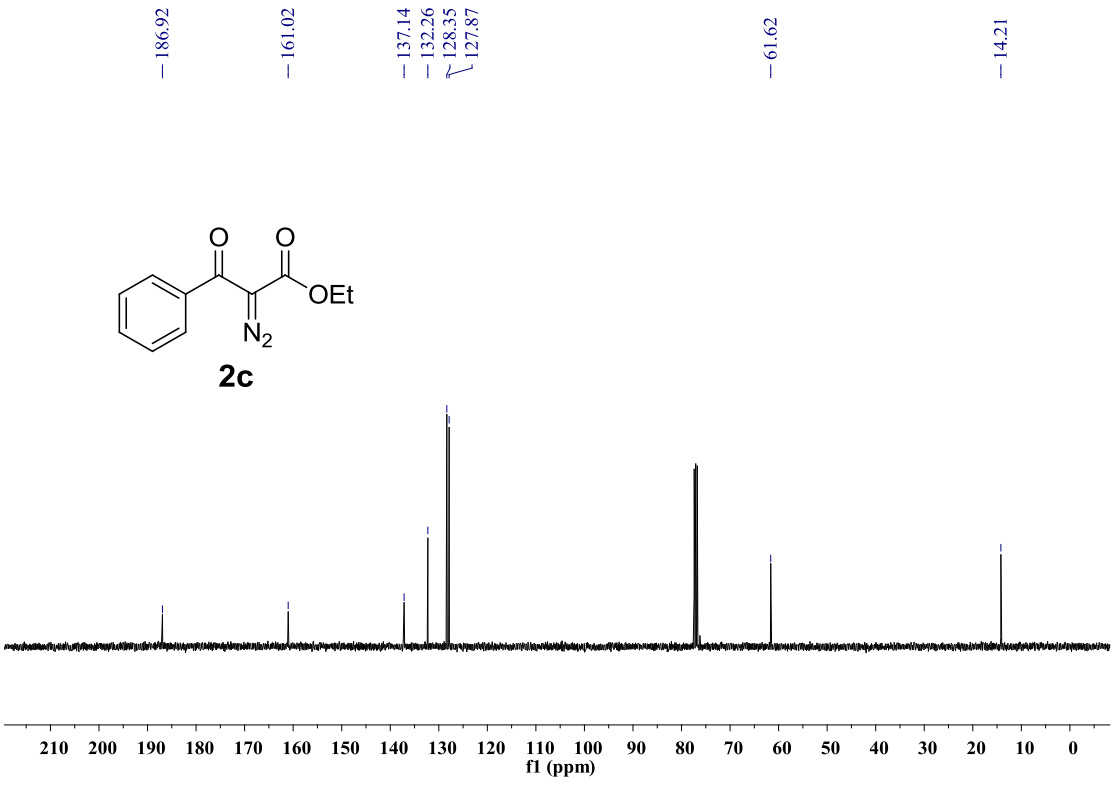
(2) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2b** (using $CDCl_3$ as solvent)



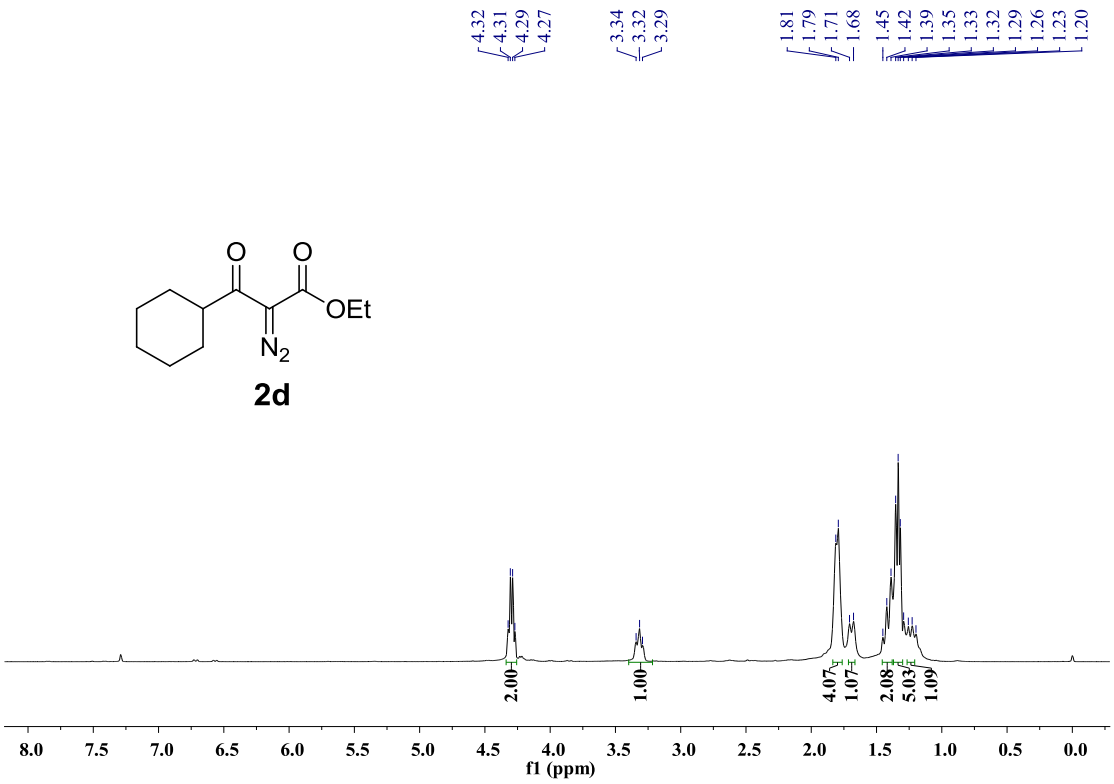



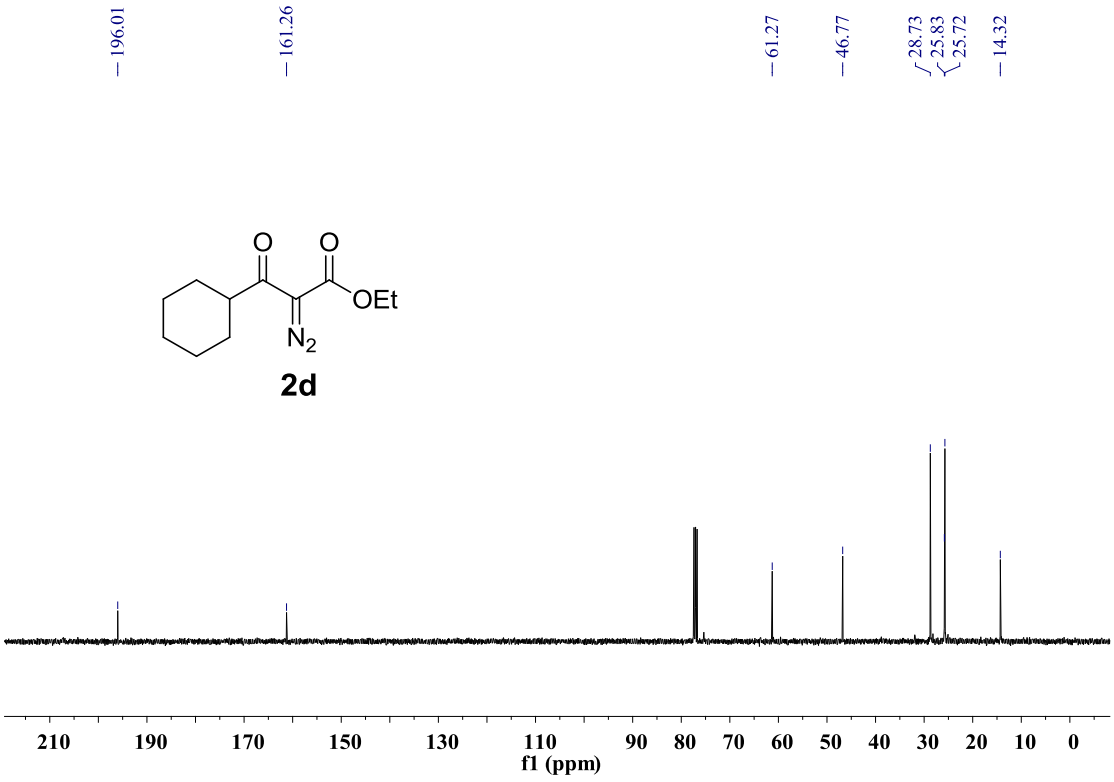
(3) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2c** (using $CDCl_3$ as solvent)



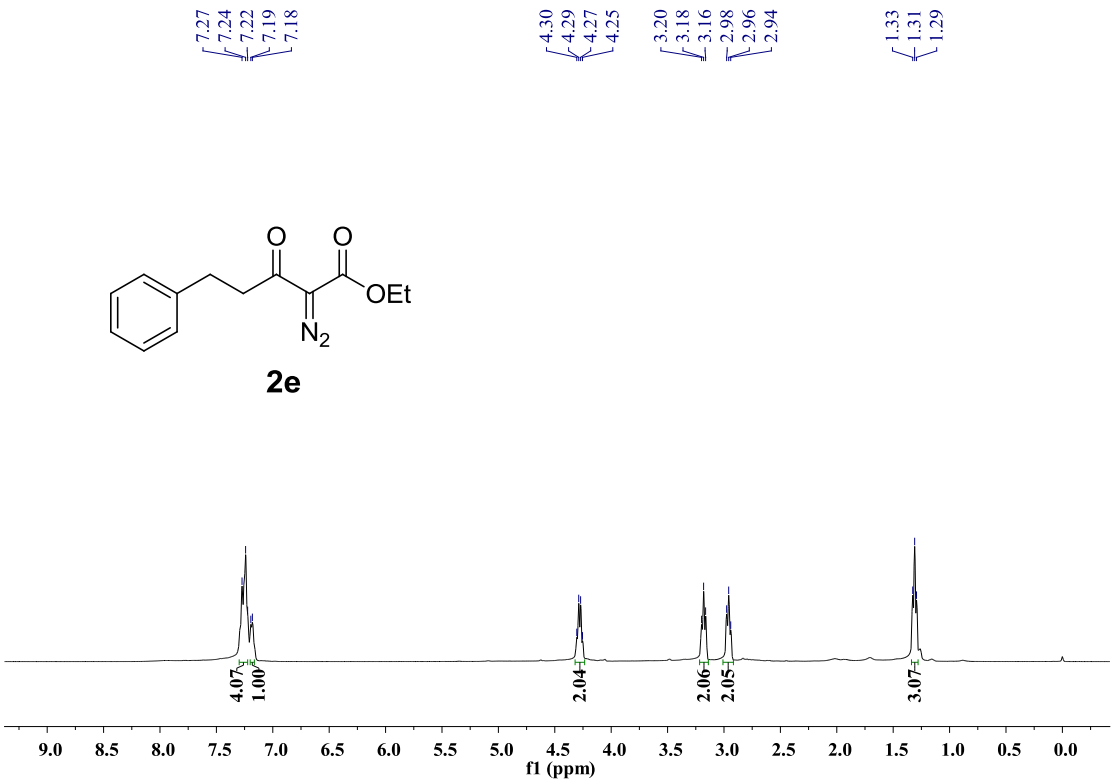



(4) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2d** (using $CDCl_3$ as solvent)

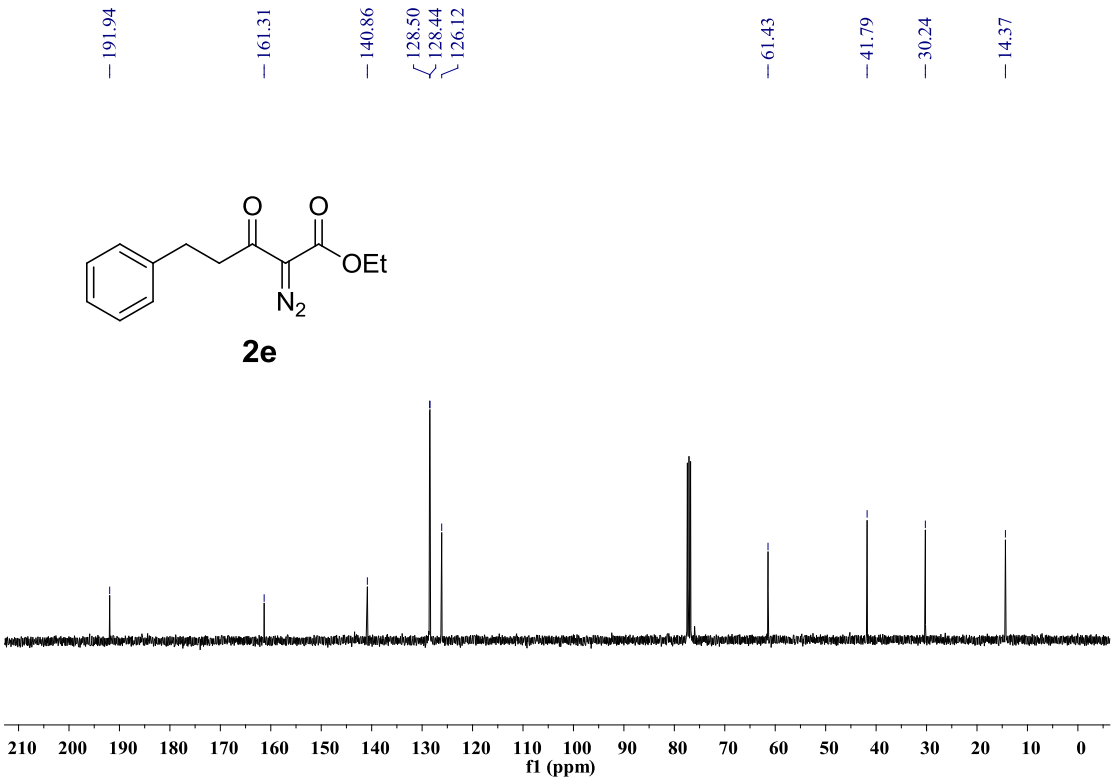


(5) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2e** (using $CDCl_3$ as solvent)

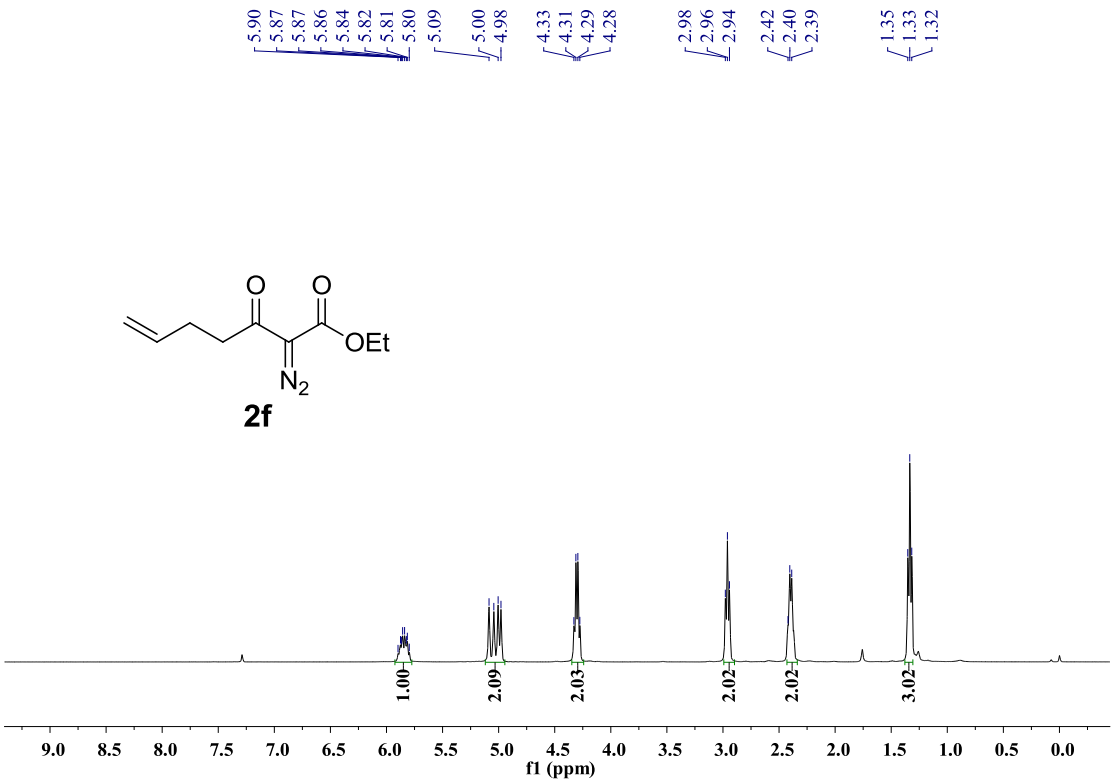


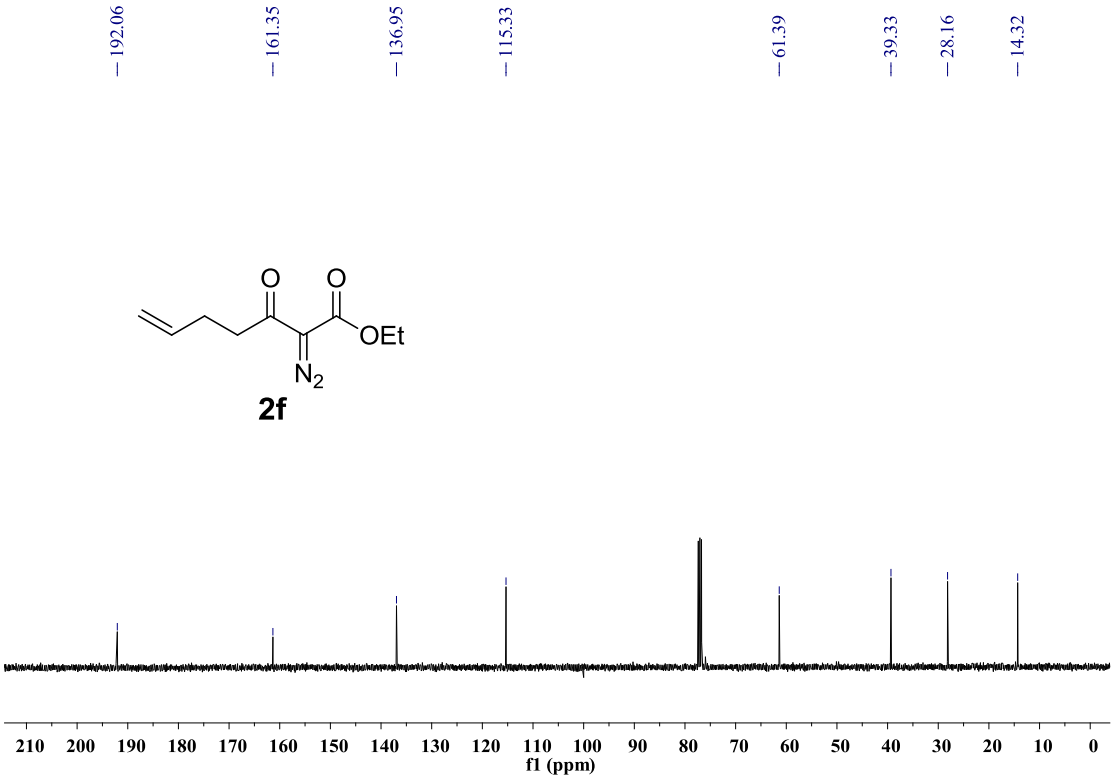

**2e**



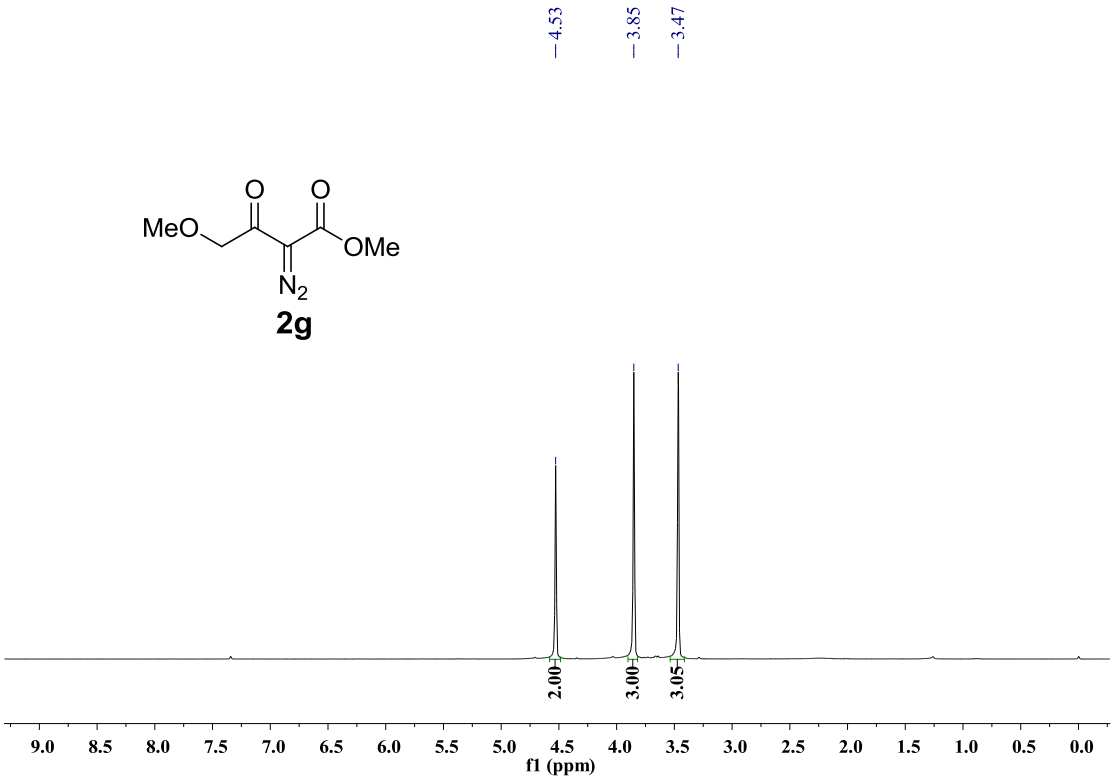

**2e**

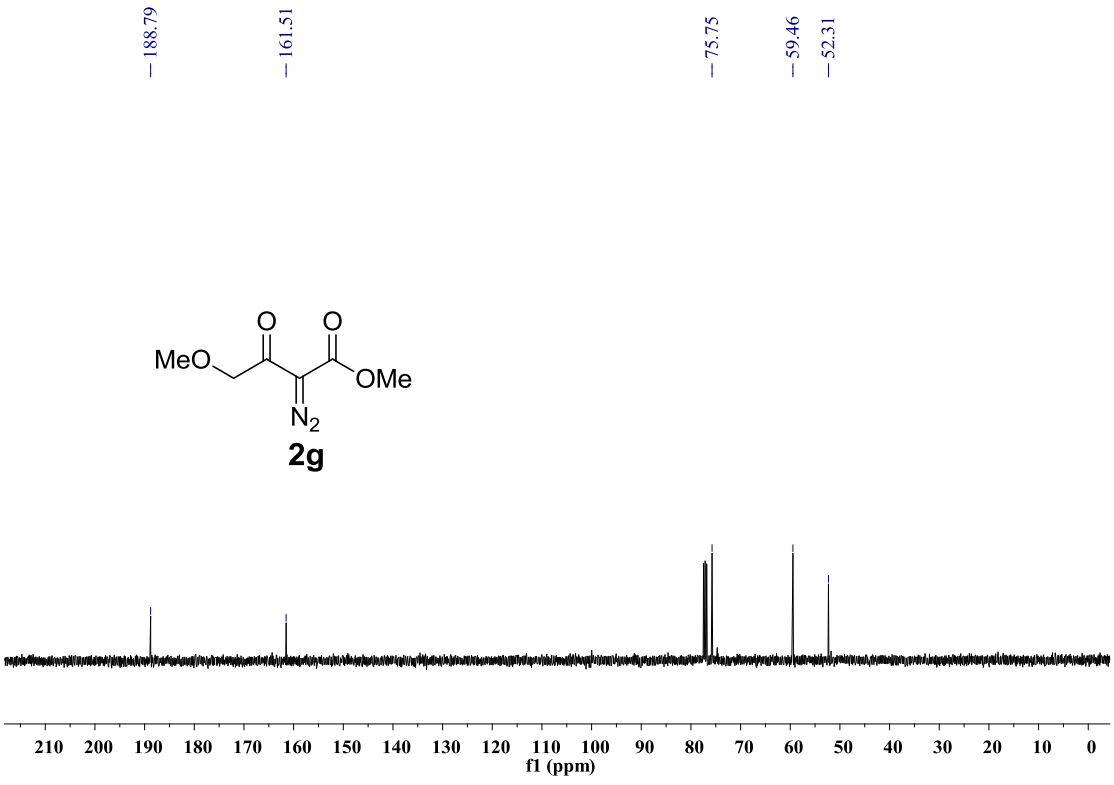
(6) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2f** (using $CDCl_3$ as solvent)



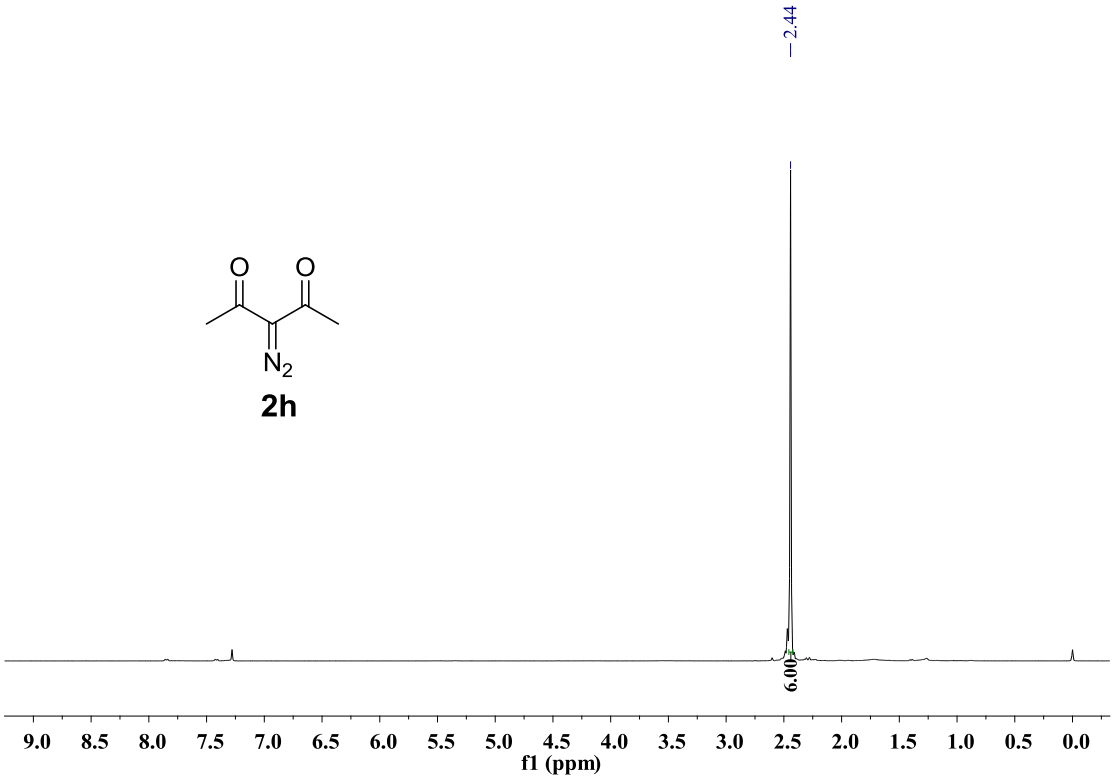



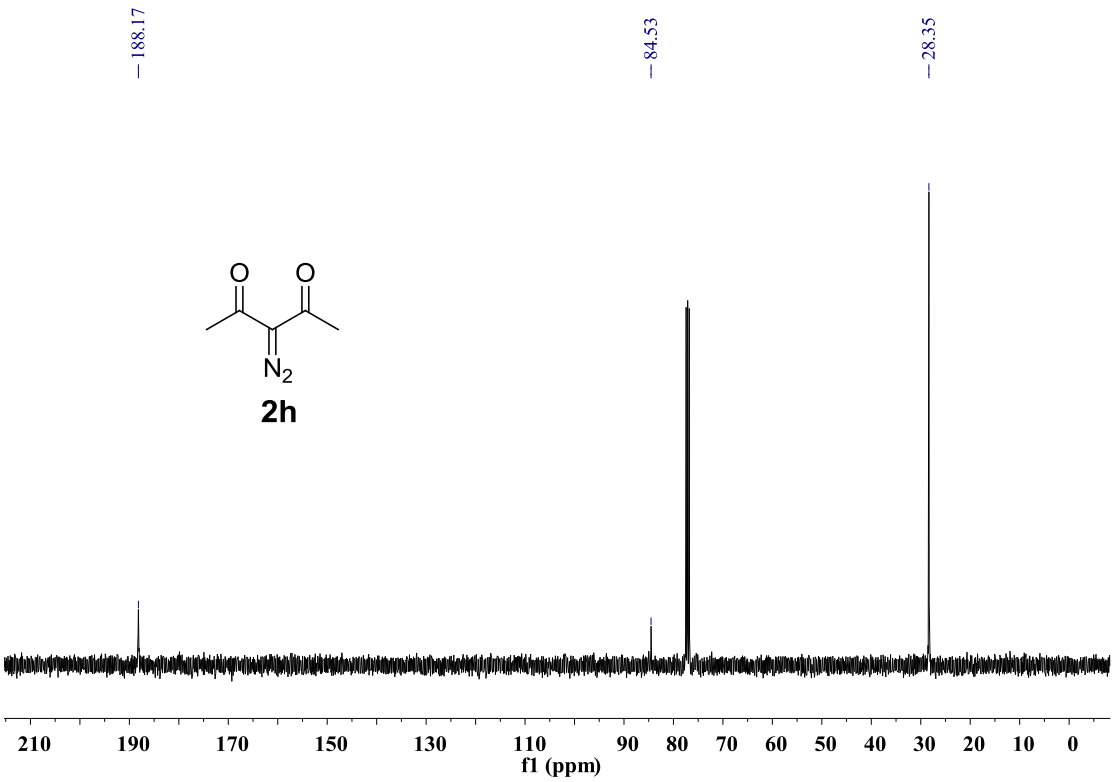
(7) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2g** (using $CDCl_3$ as solvent)



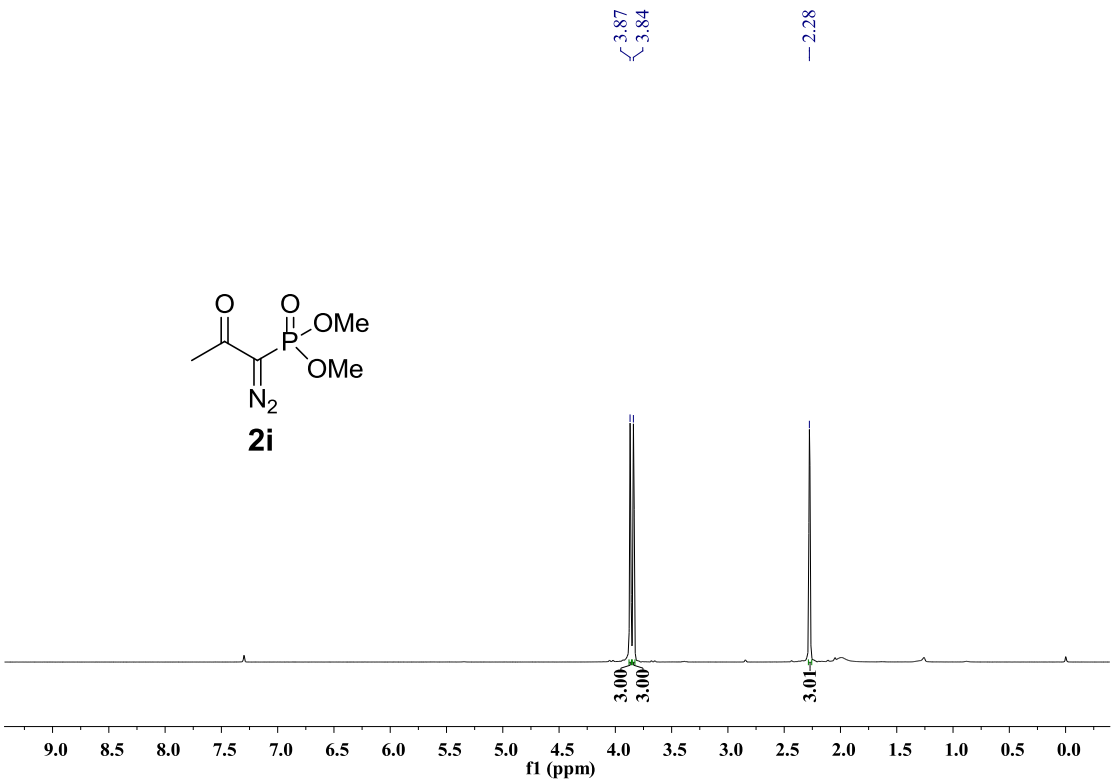



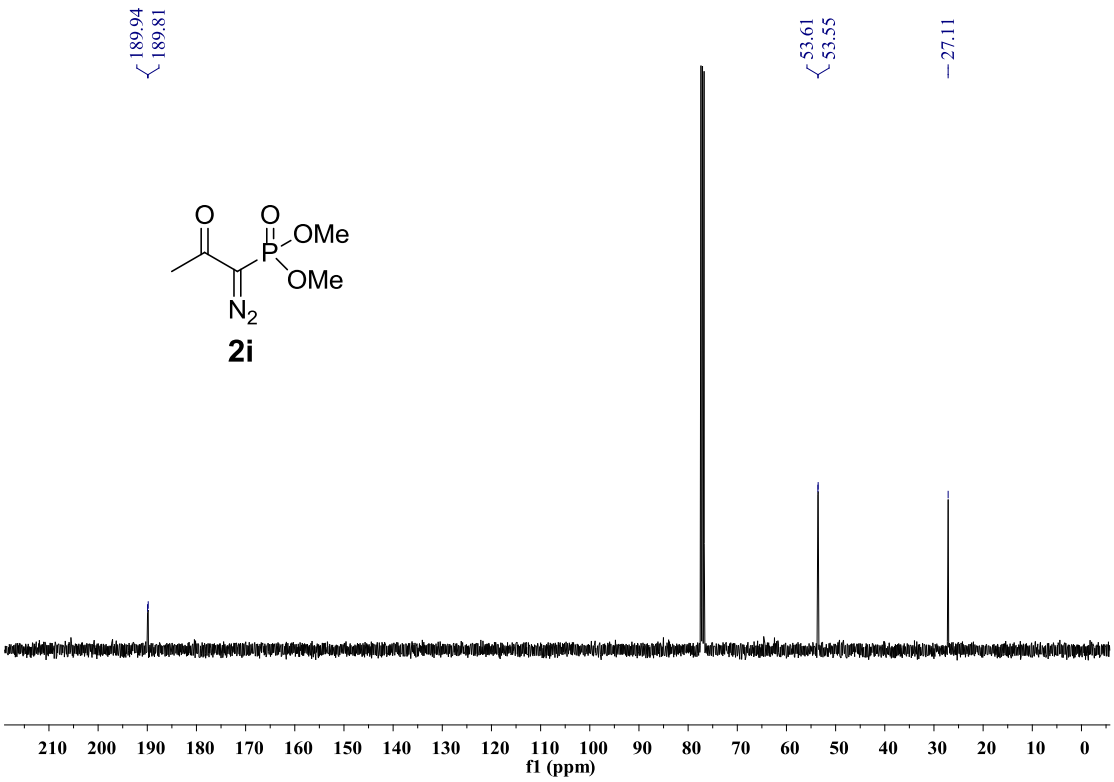
(8) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2h** (using $CDCl_3$ as solvent)



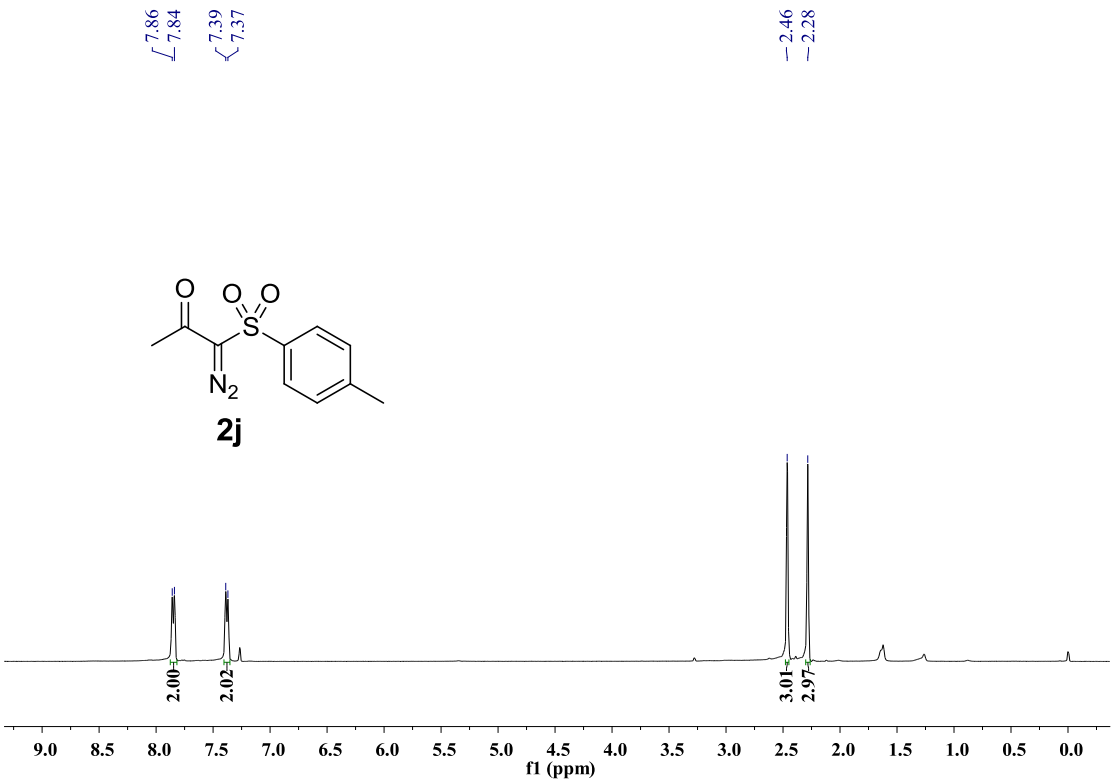



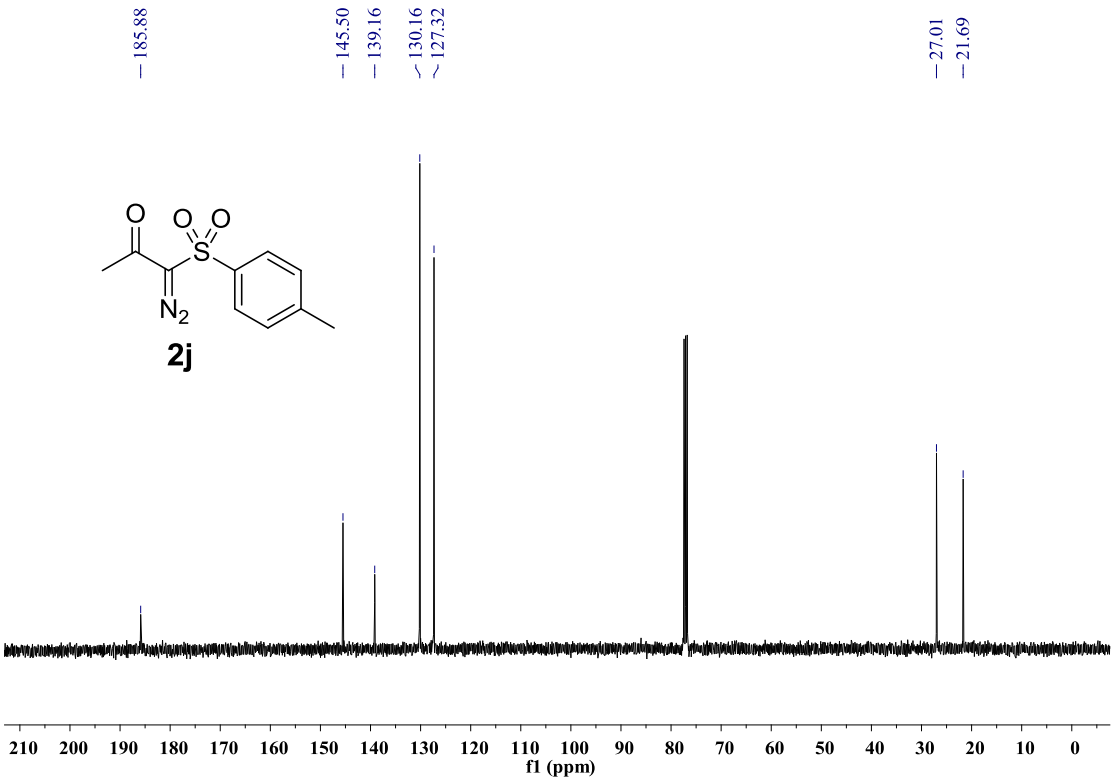
(9) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2i** (using $CDCl_3$ as solvent)



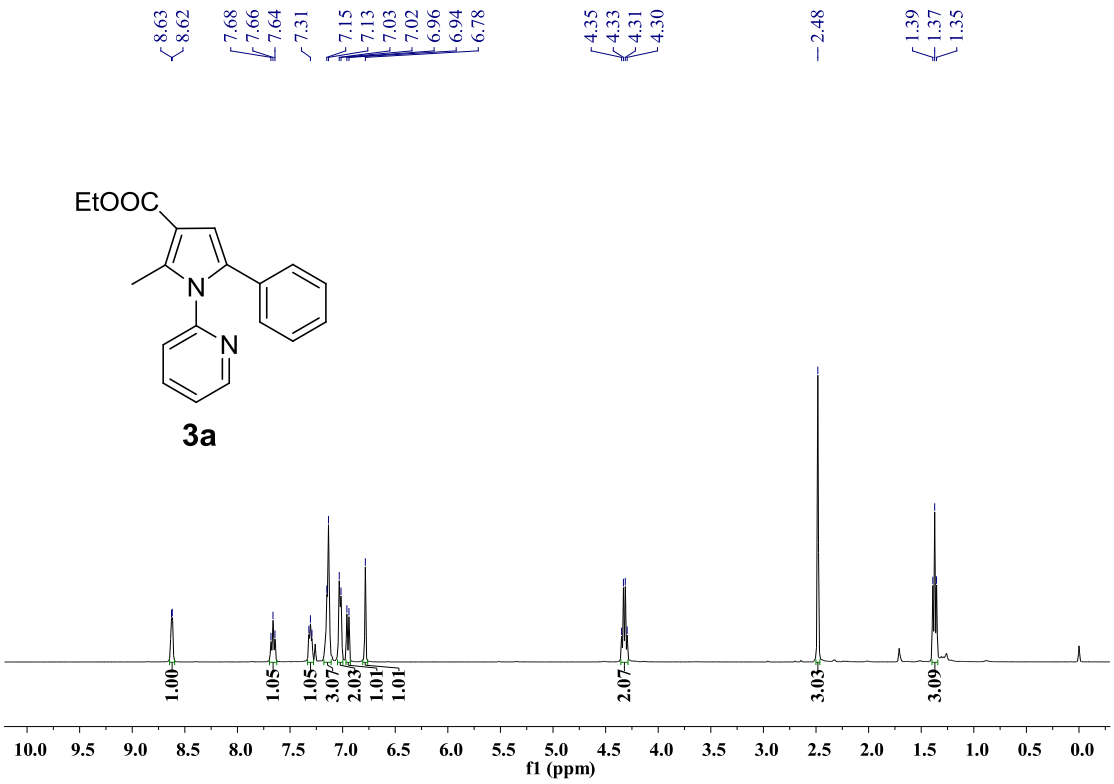



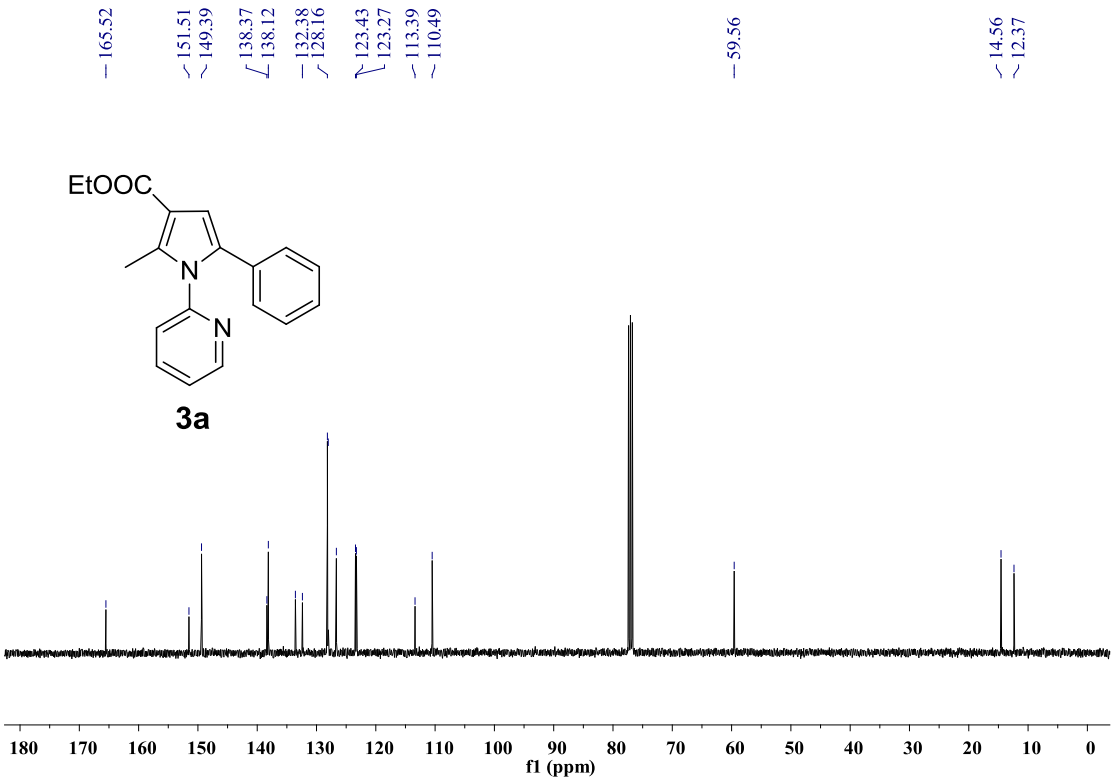
(10) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **2j** (using $CDCl_3$ as solvent)



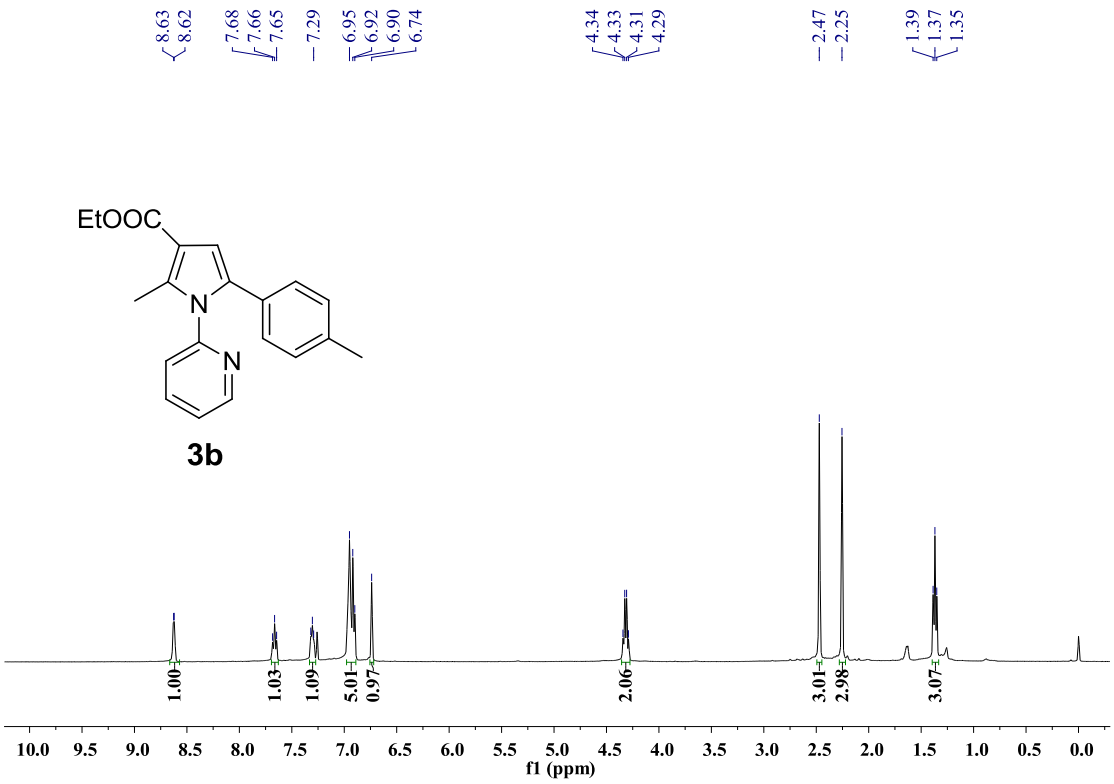



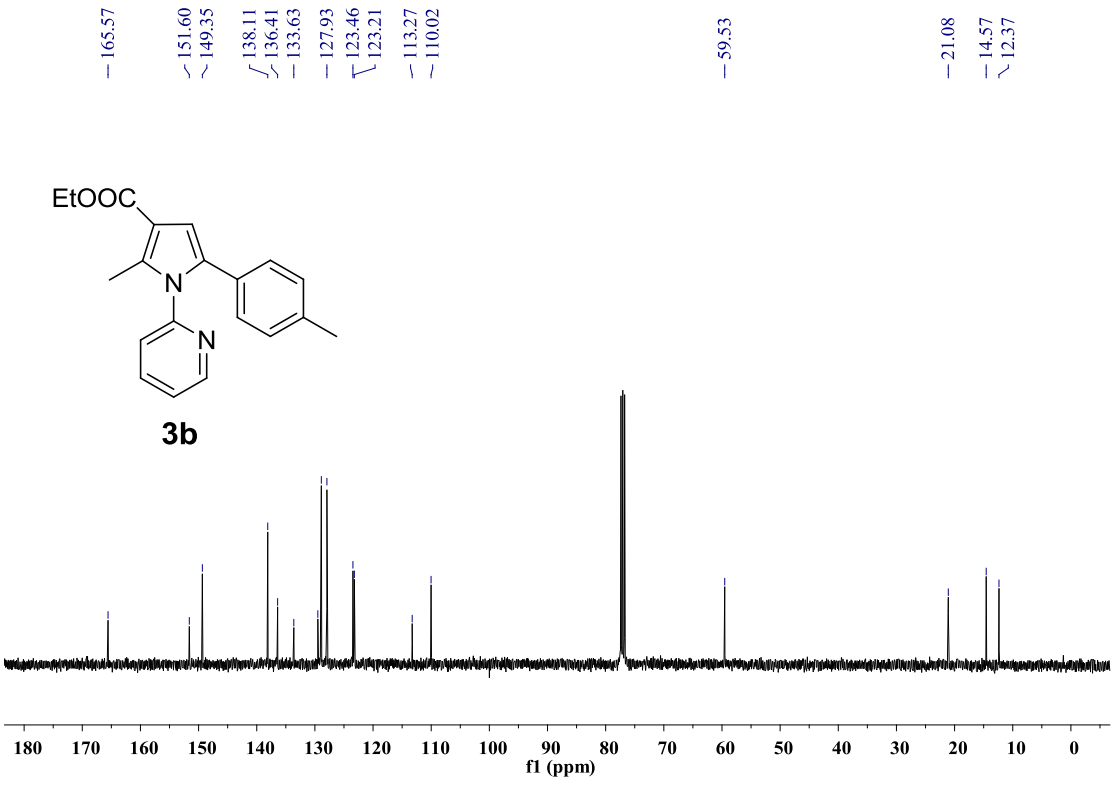
(11) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3a** (using $CDCl_3$ as solvent)



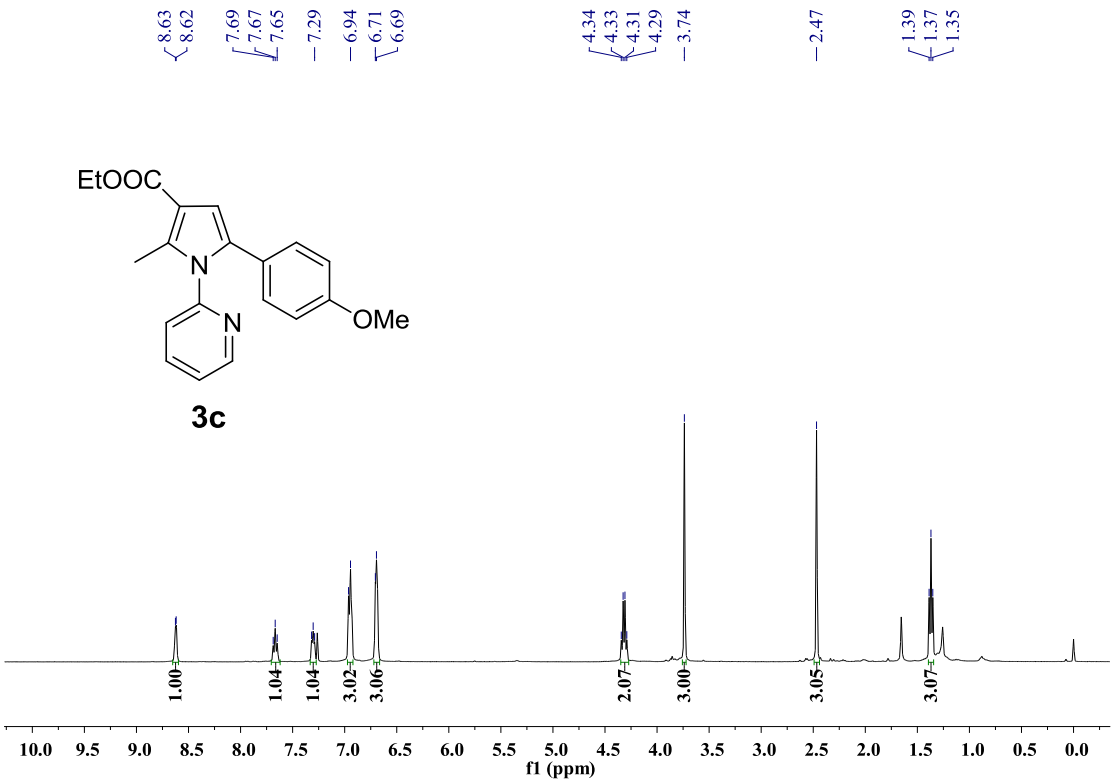



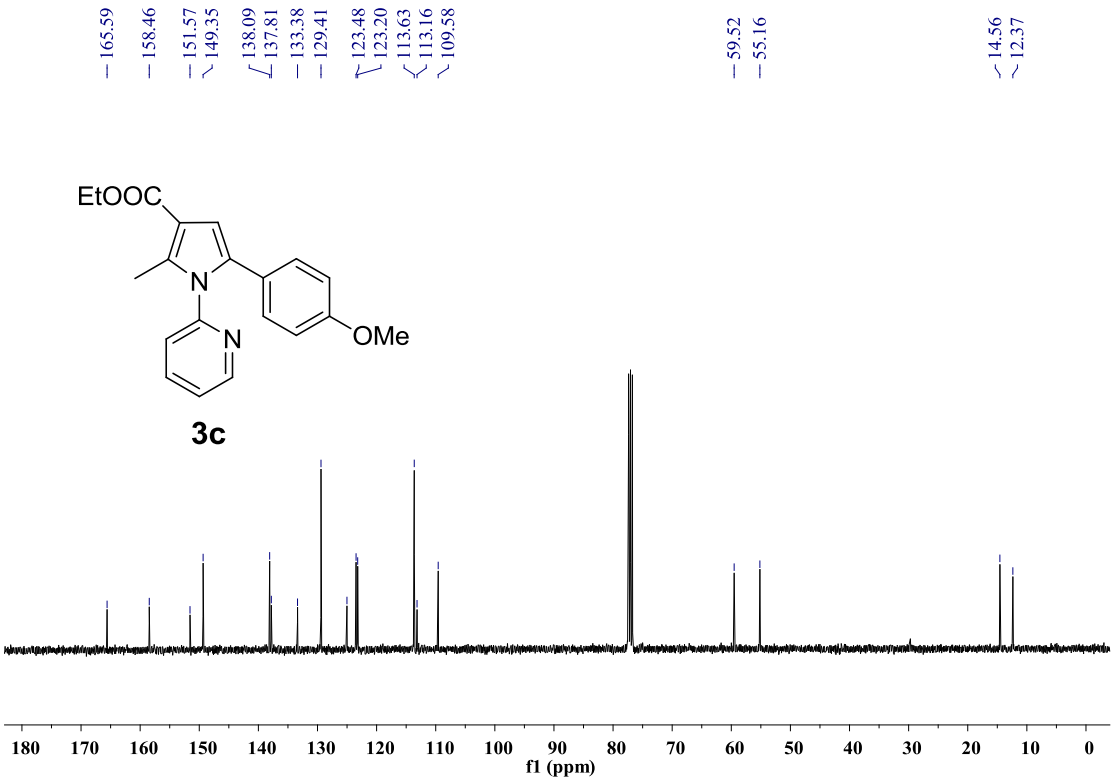
(12) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3b** (using $CDCl_3$ as solvent)



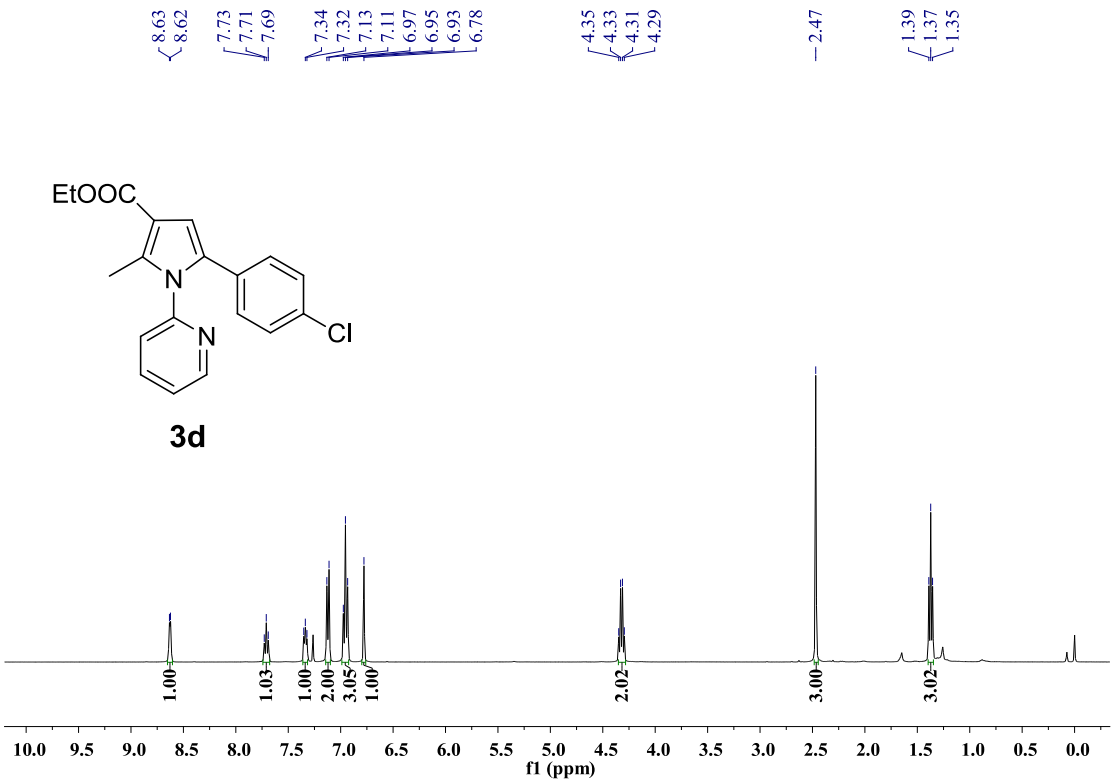



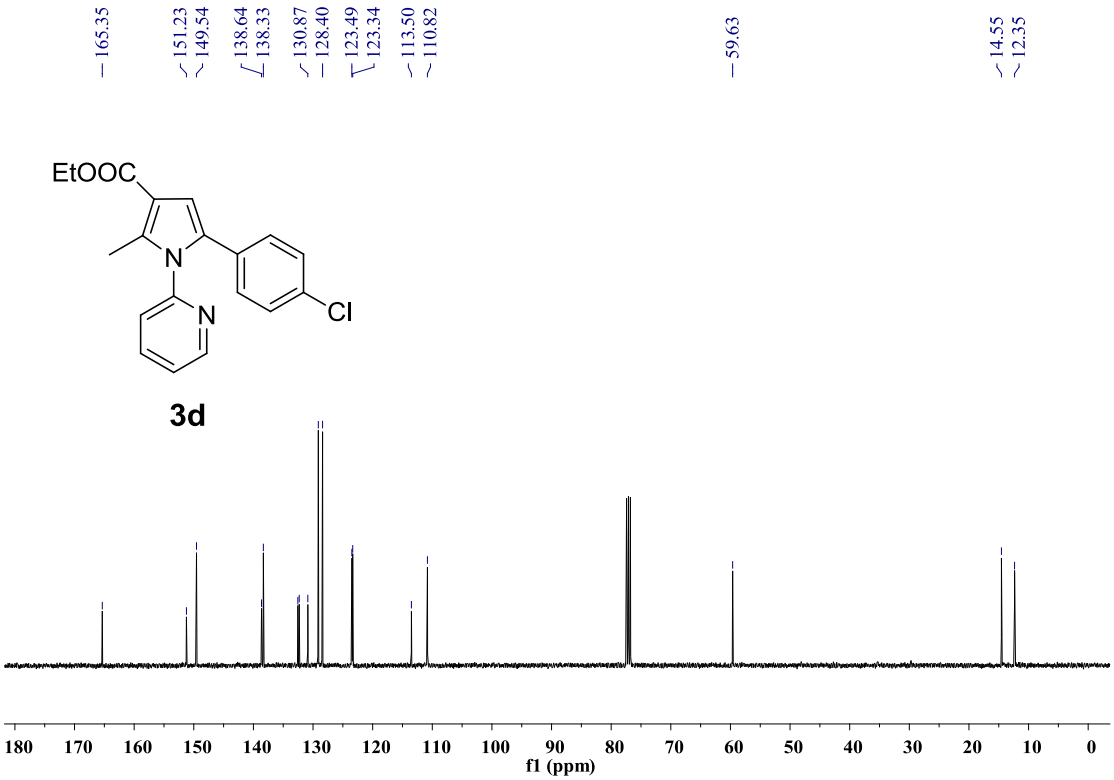
(13) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3c** (using $CDCl_3$ as solvent)



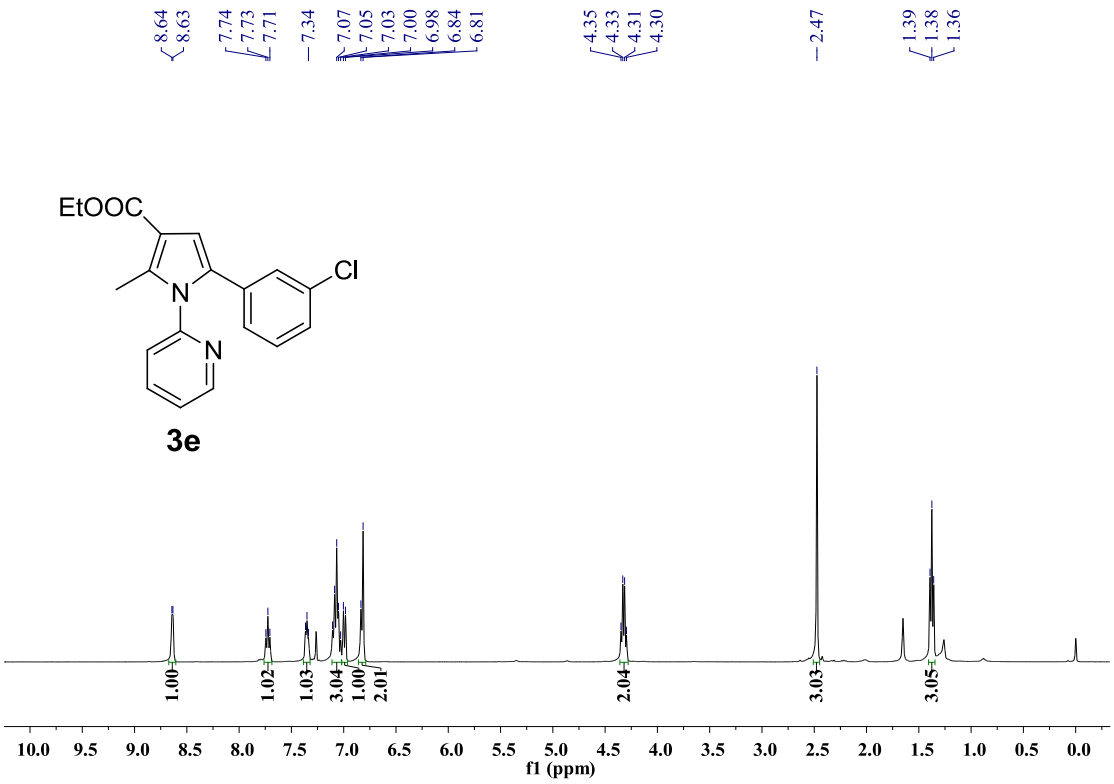



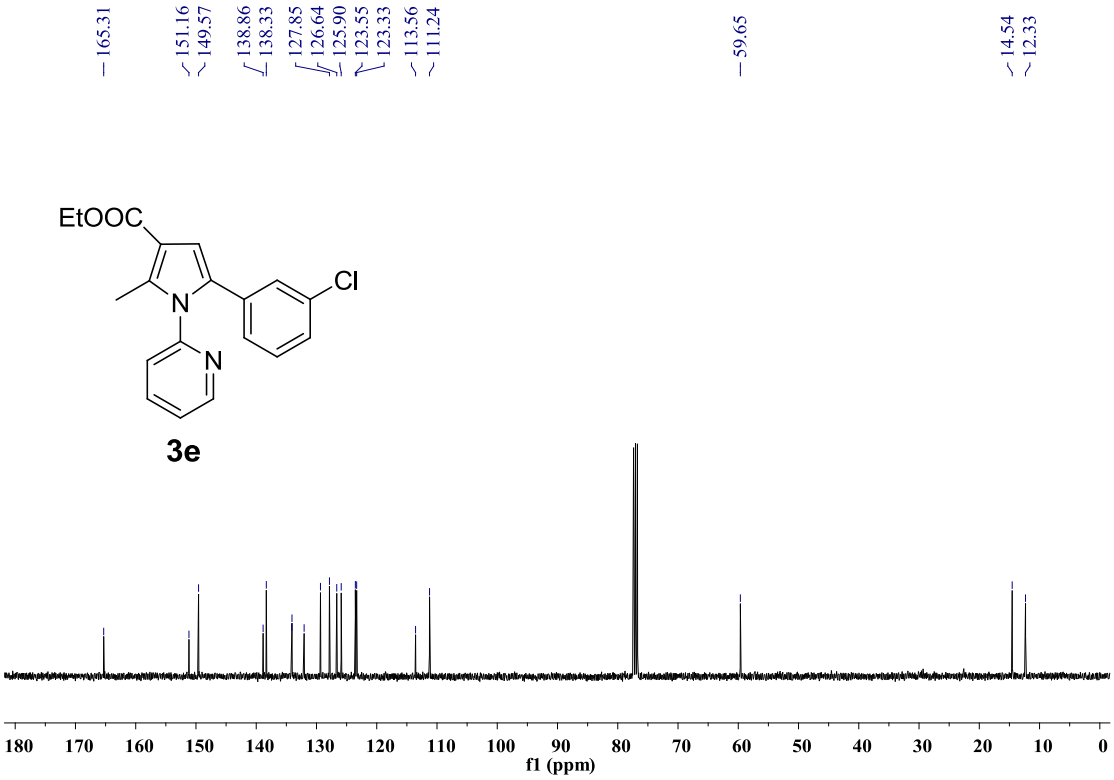
(14) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3d** (using $CDCl_3$ as solvent)



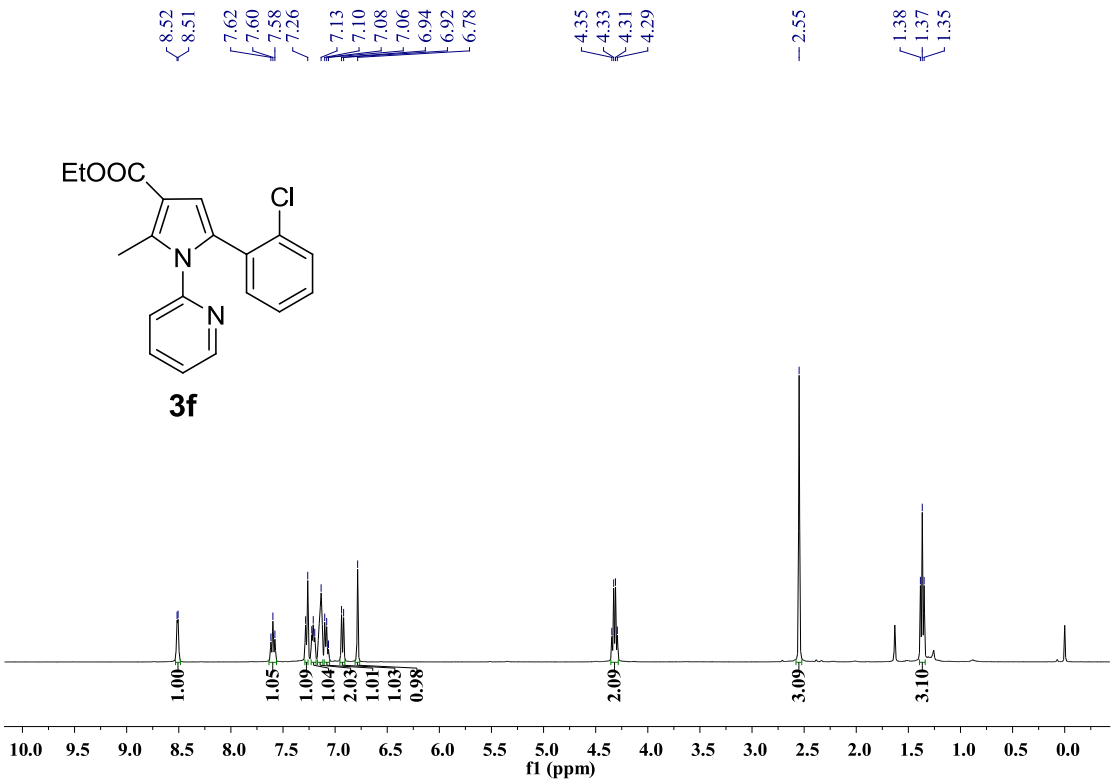



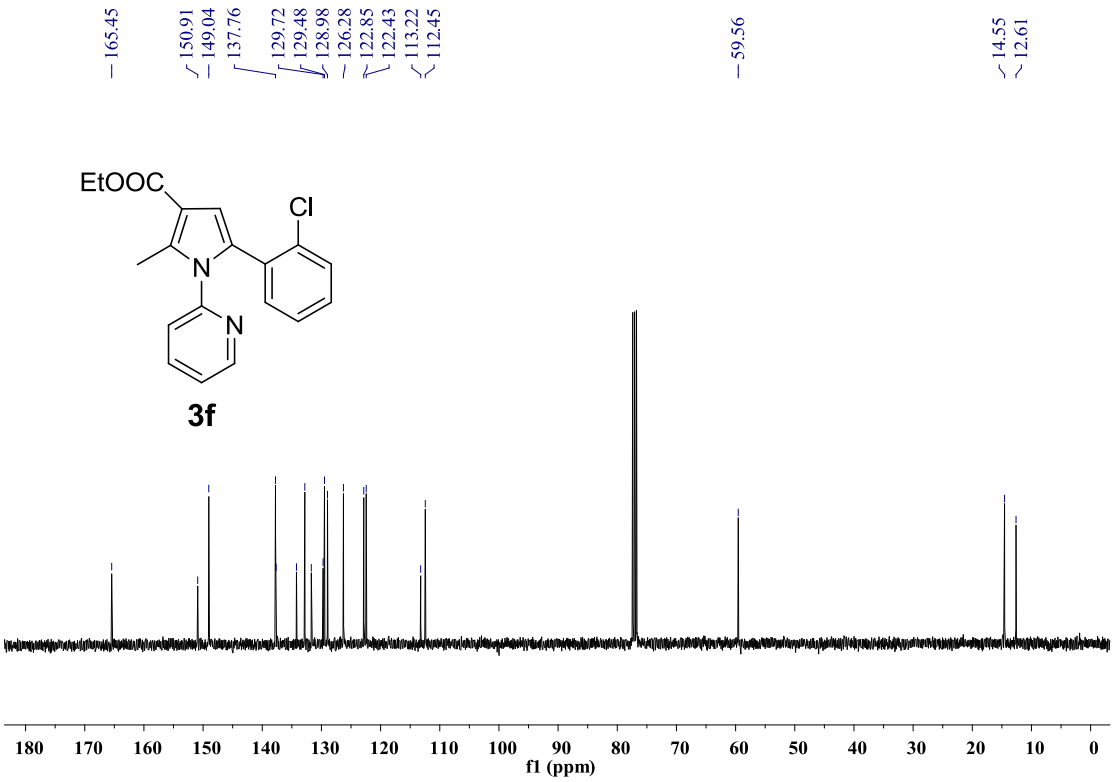
(15) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3e** (using $CDCl_3$ as solvent)



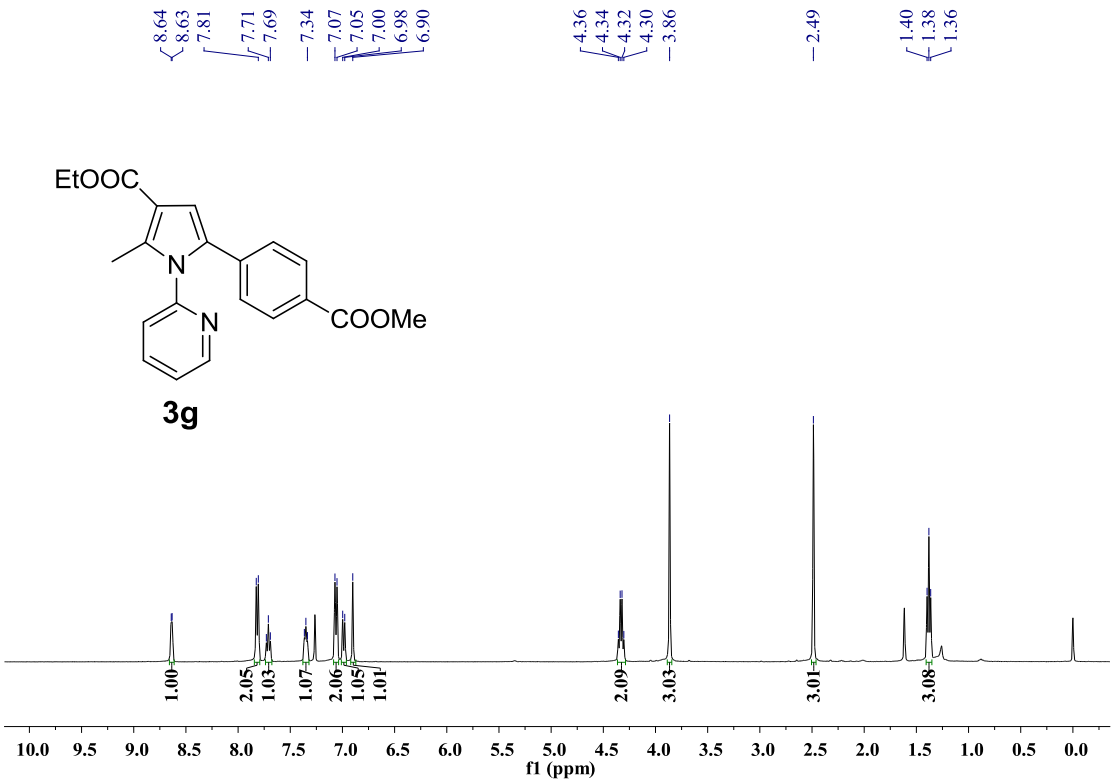



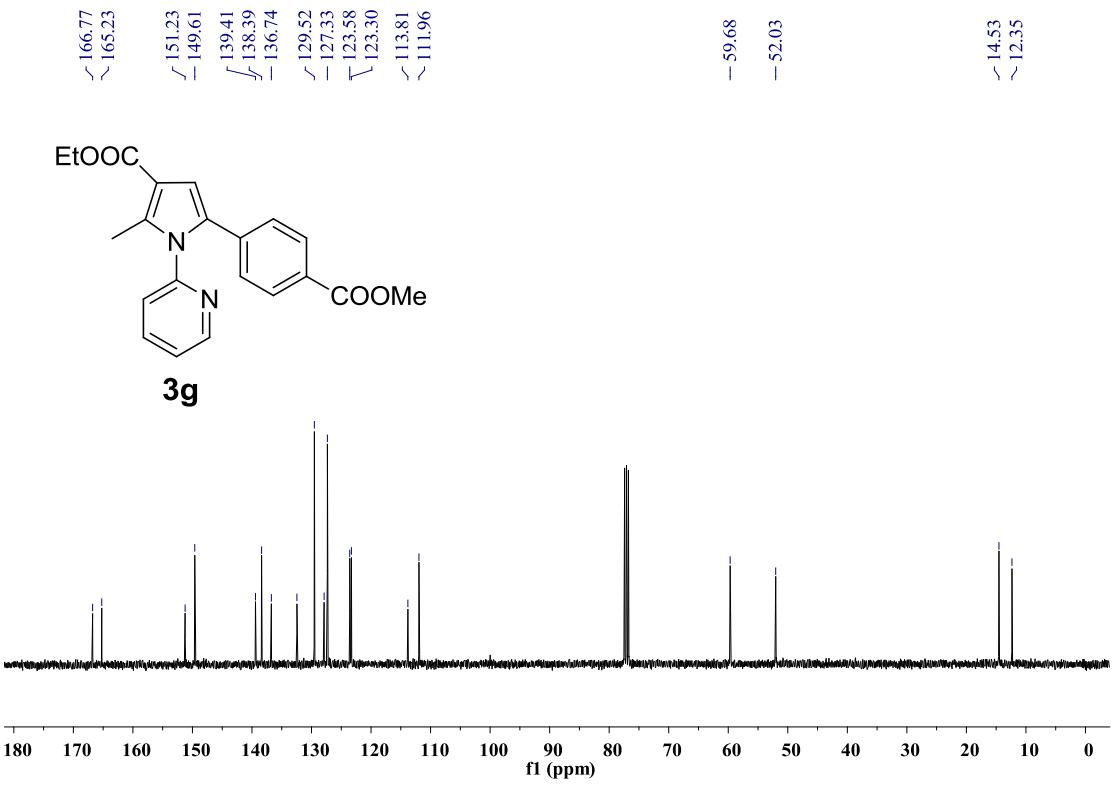
(16) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3f** (using $CDCl_3$ as solvent)



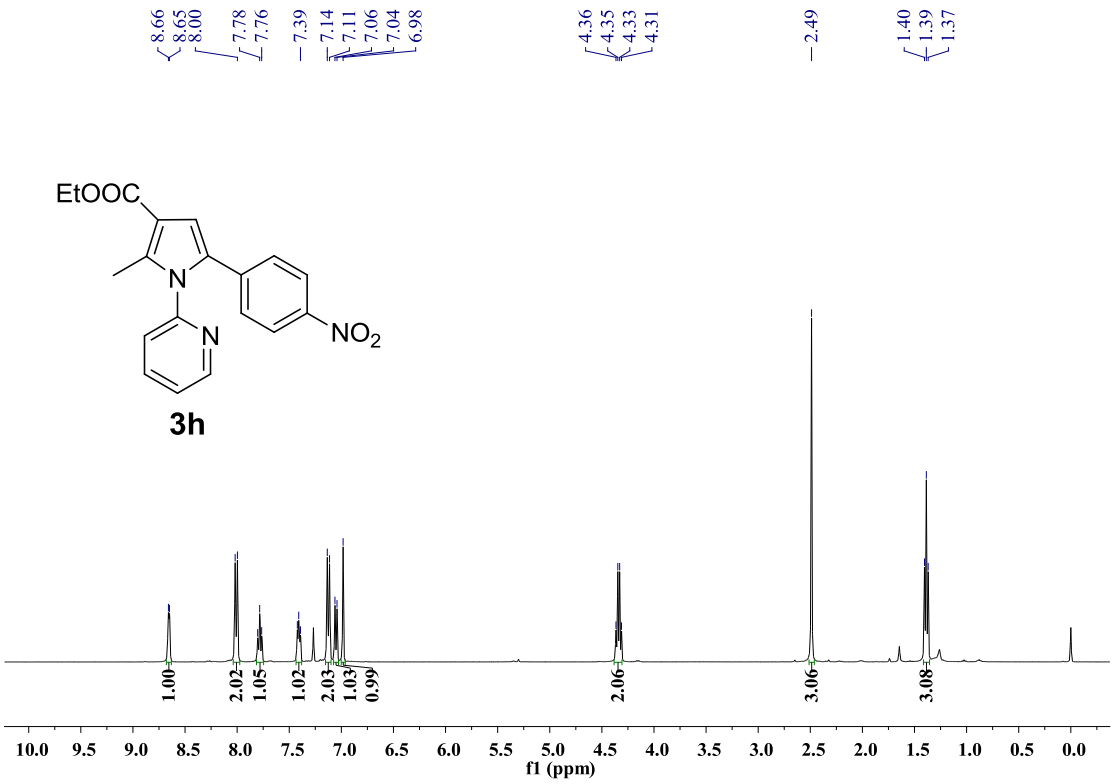



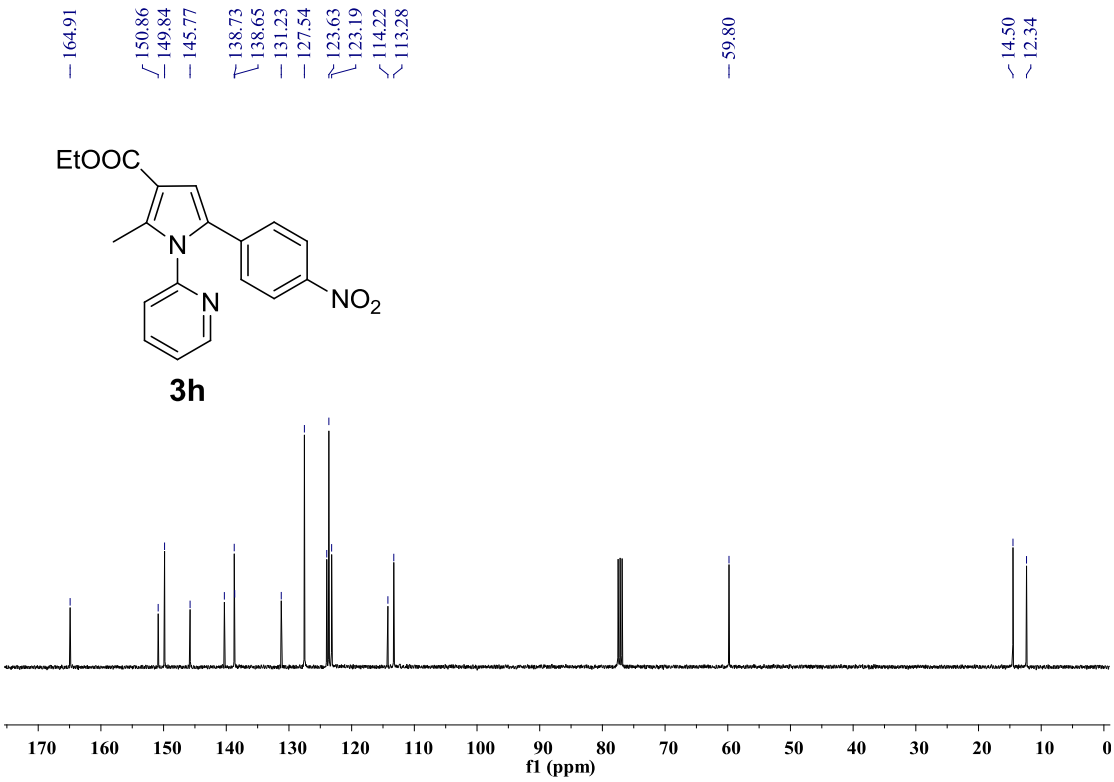
(17) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3g** (using $CDCl_3$ as solvent)



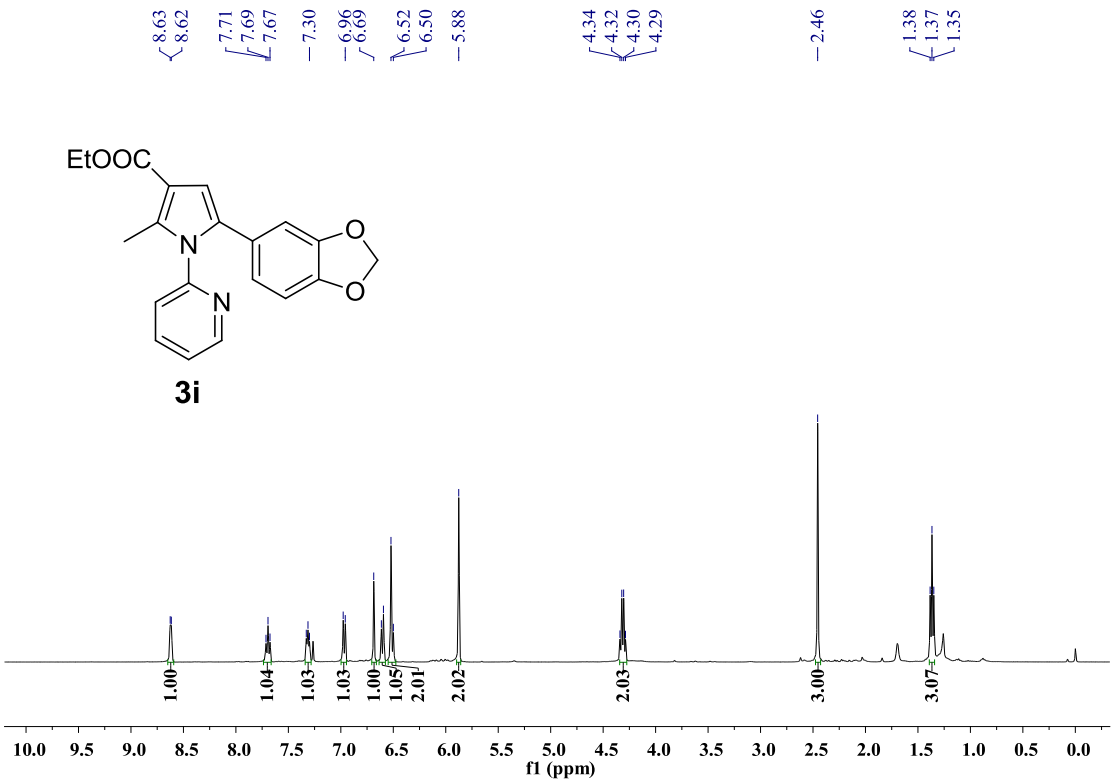



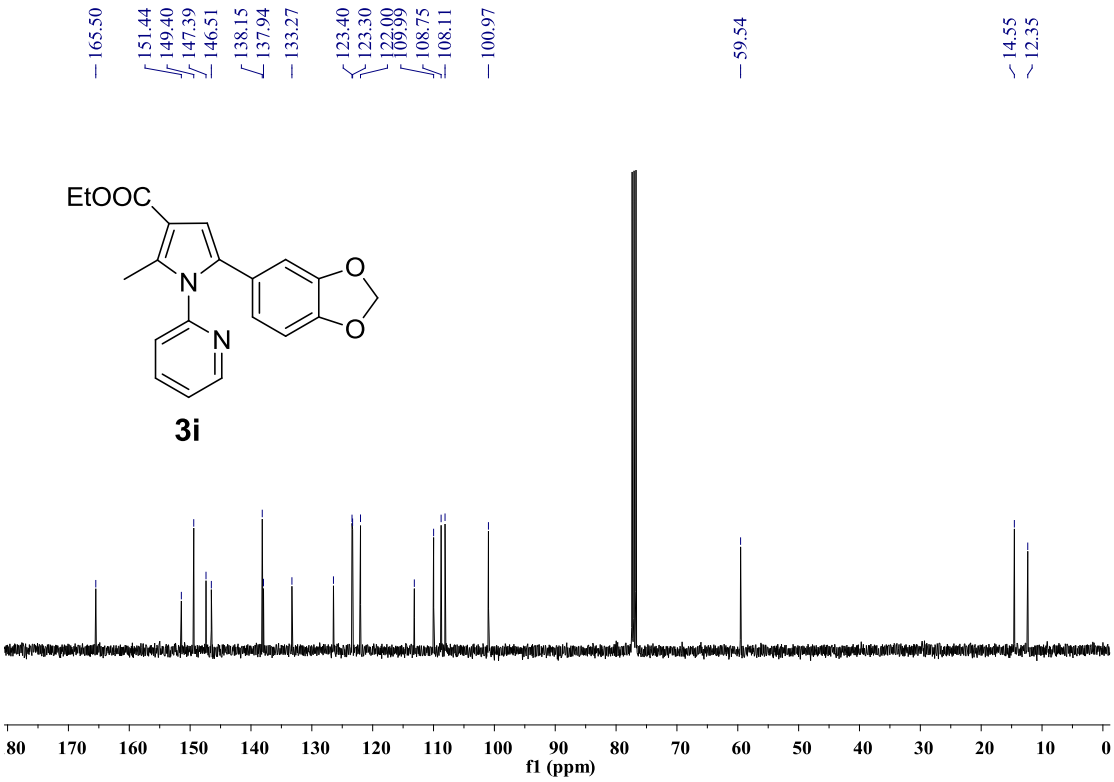
(18) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3h** (using $CDCl_3$ as solvent)



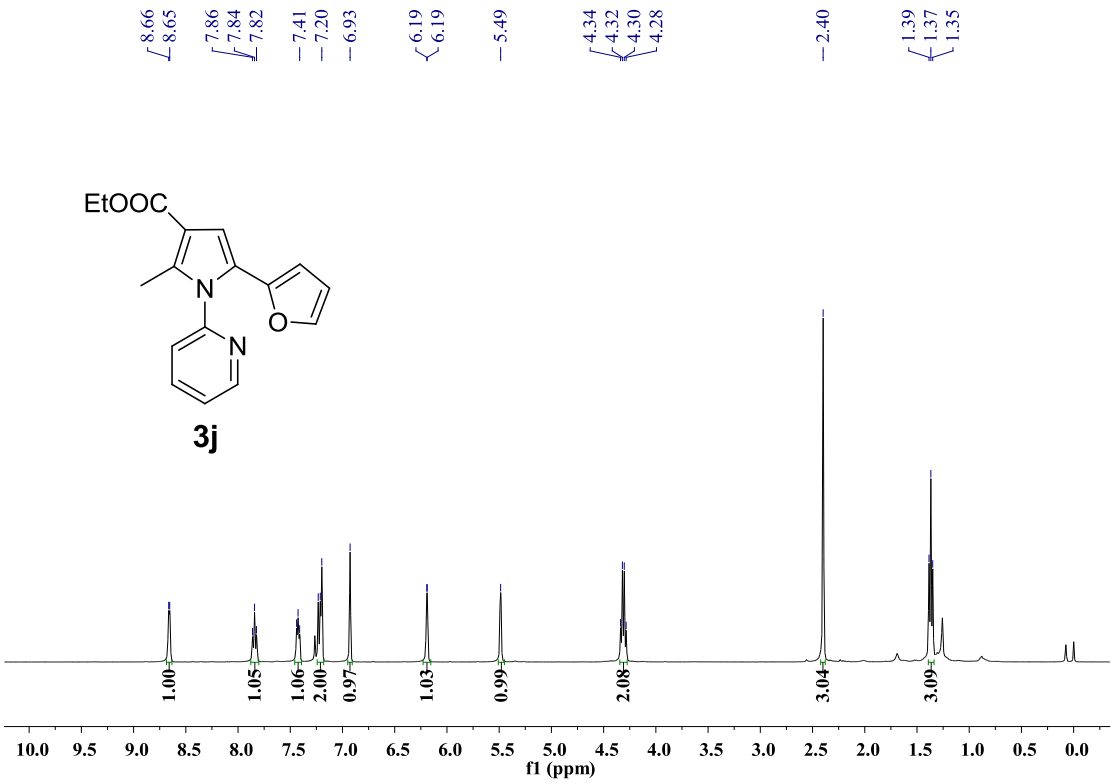



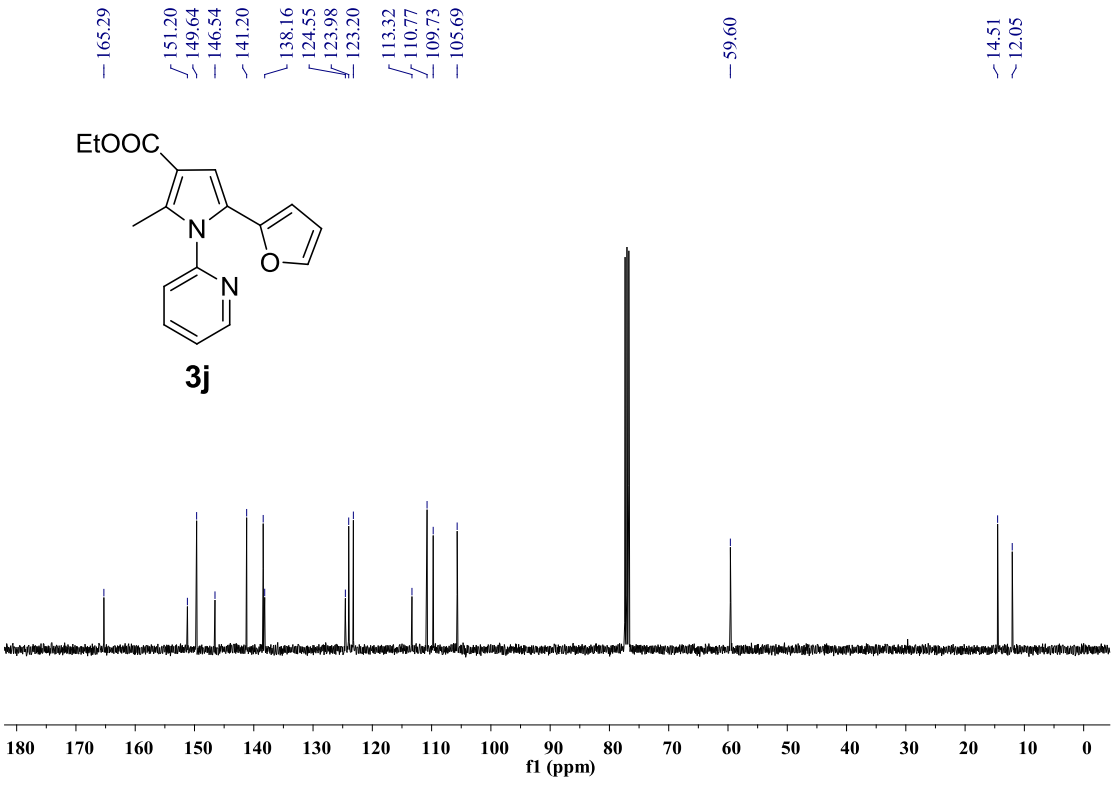
(19) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3i** (using $CDCl_3$ as solvent)



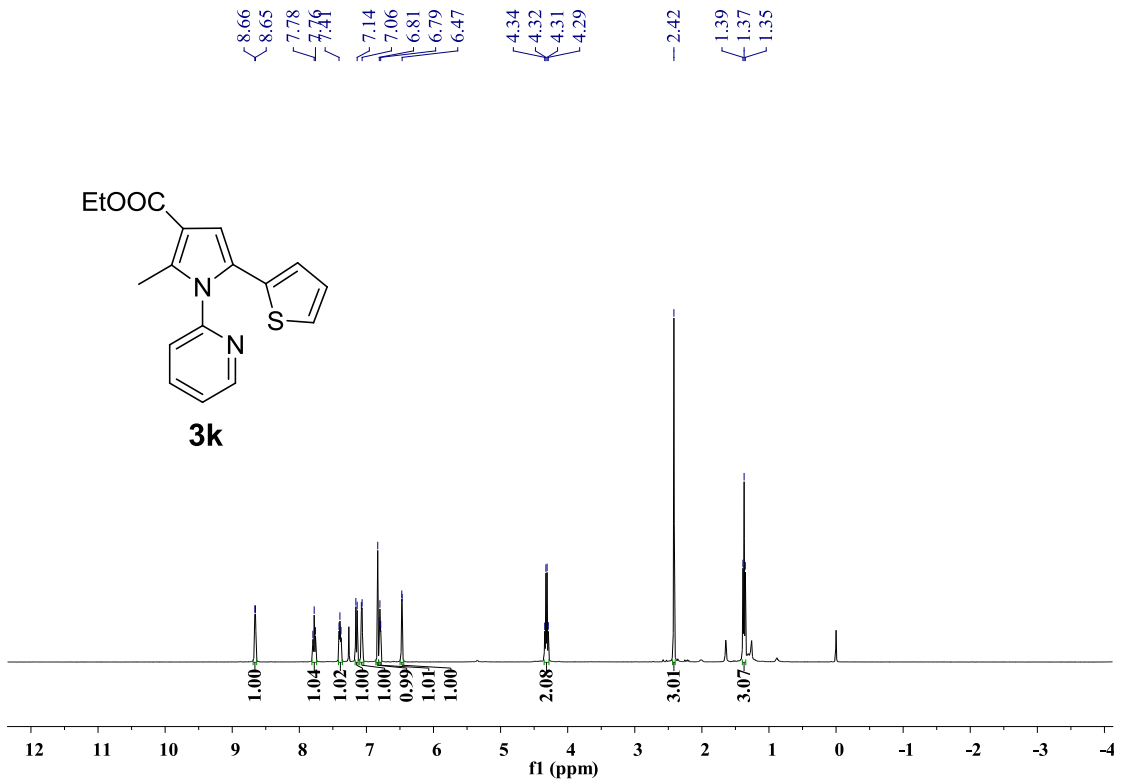



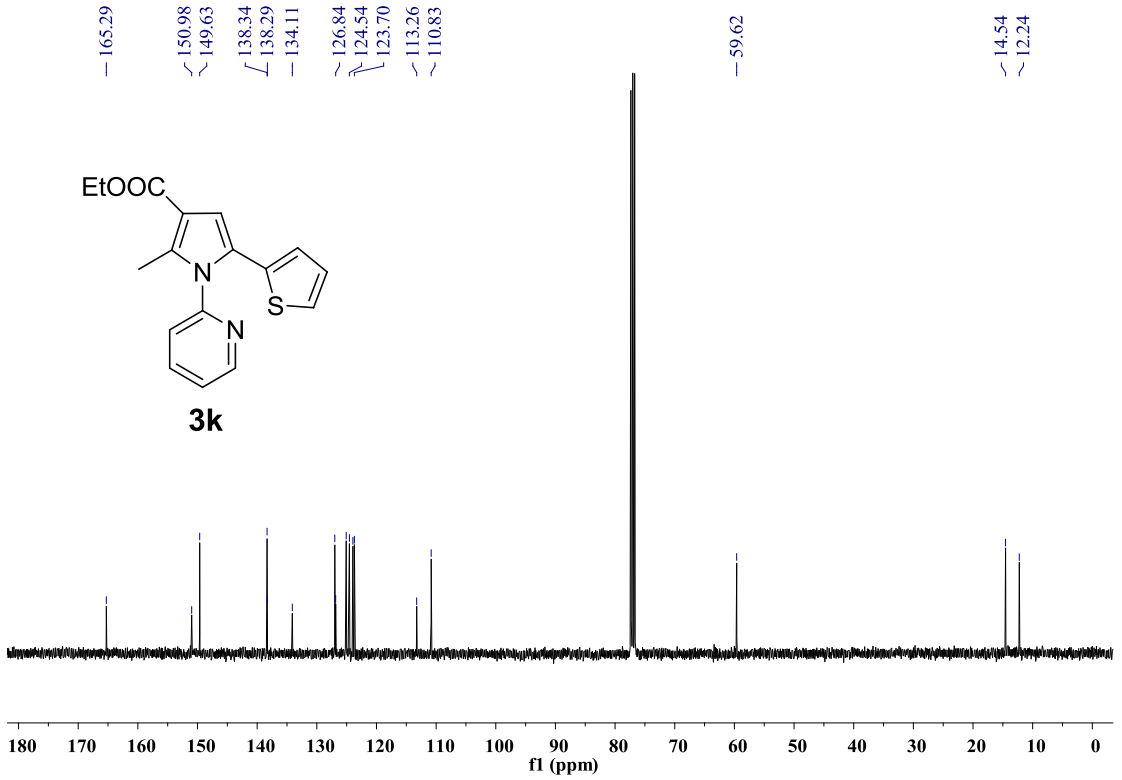
(20) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3j** (using $CDCl_3$ as solvent)



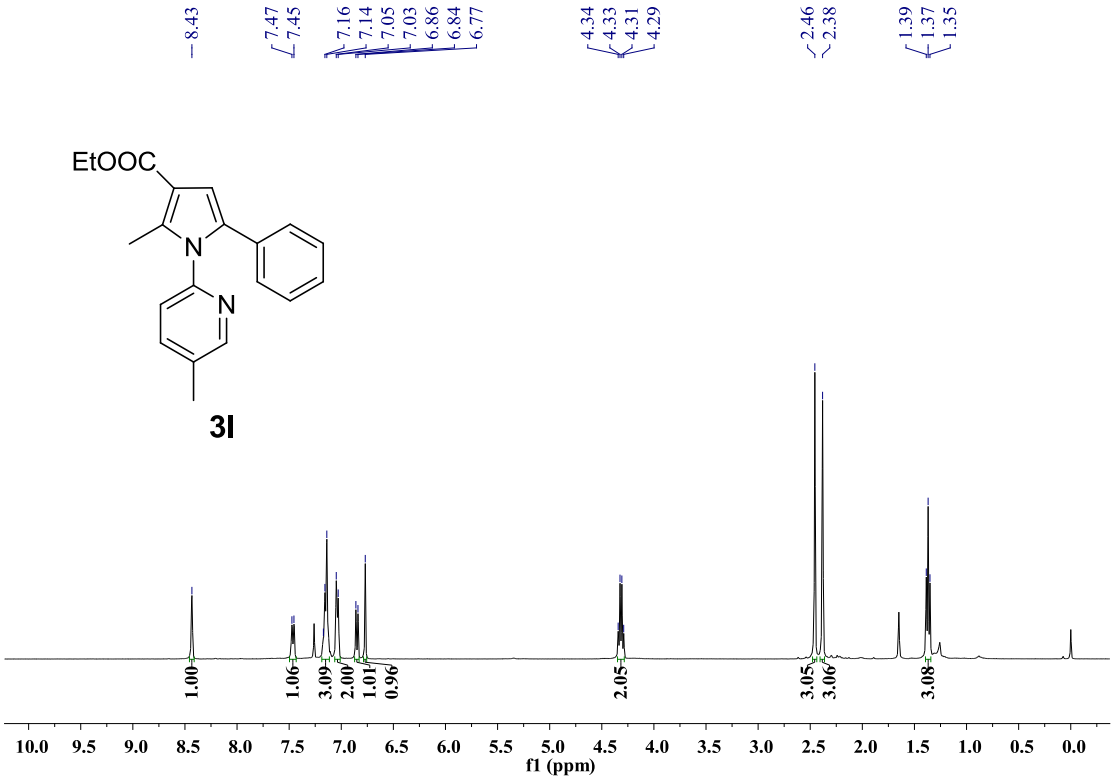



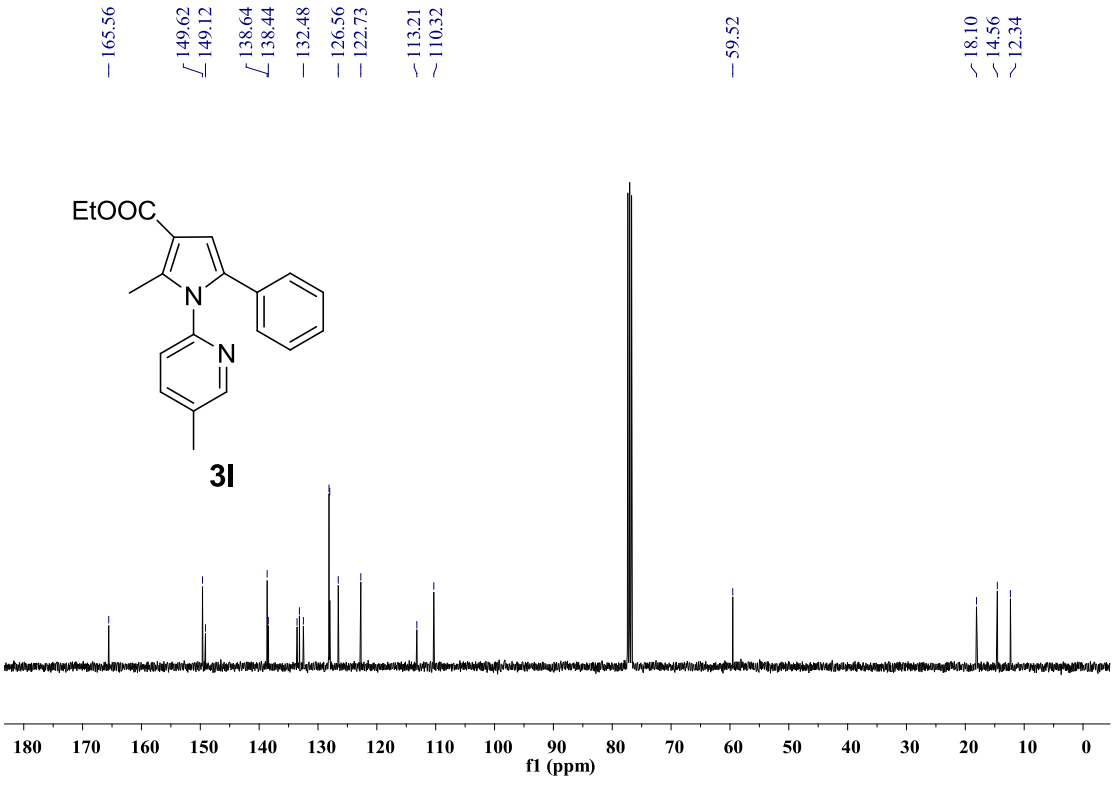
(21) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3k** (using $CDCl_3$ as solvent)



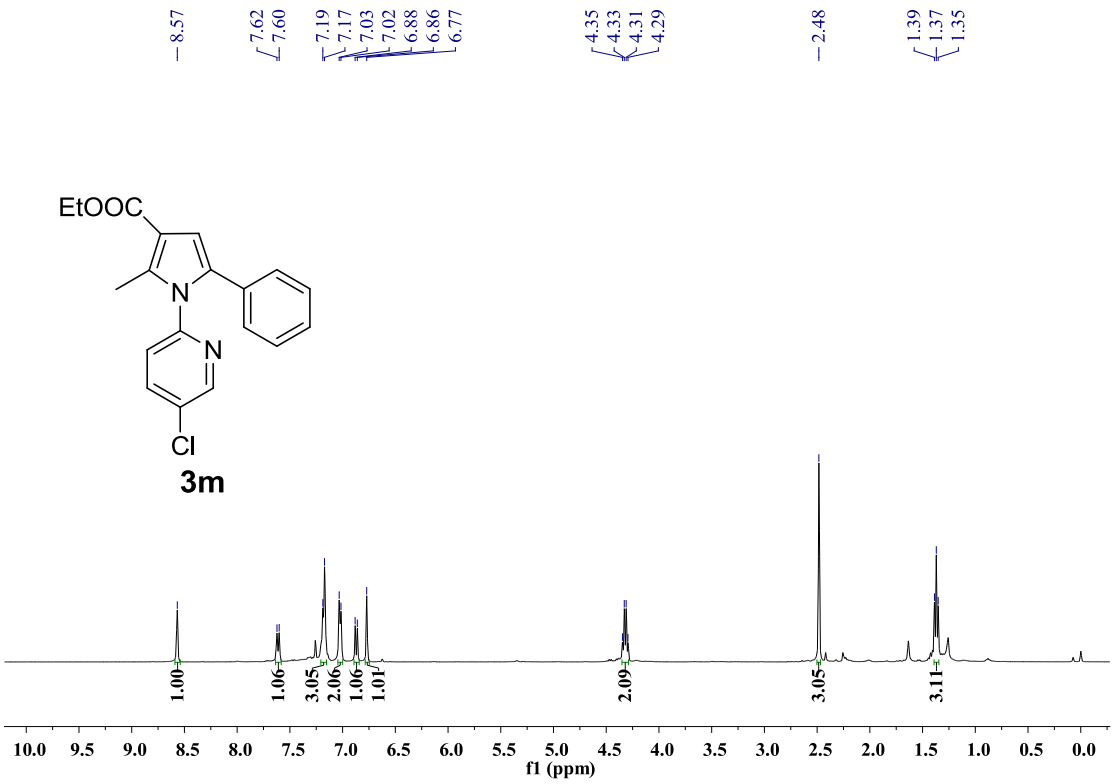



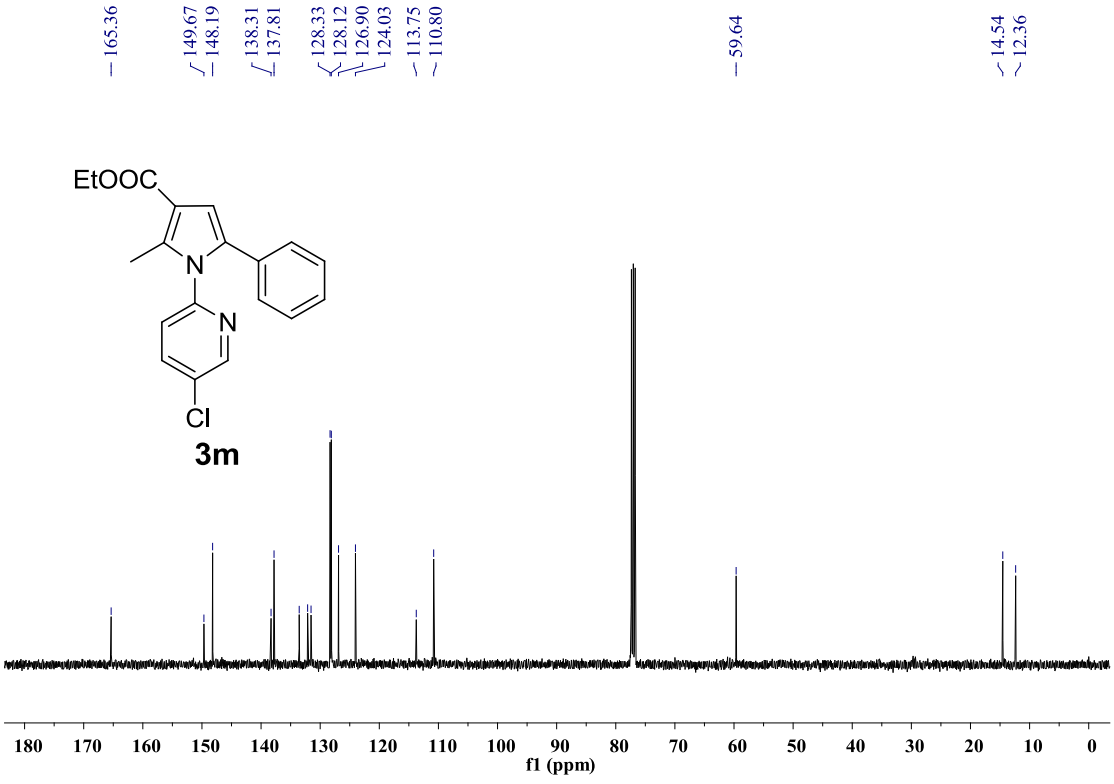
(22) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3l** (using $CDCl_3$ as solvent)



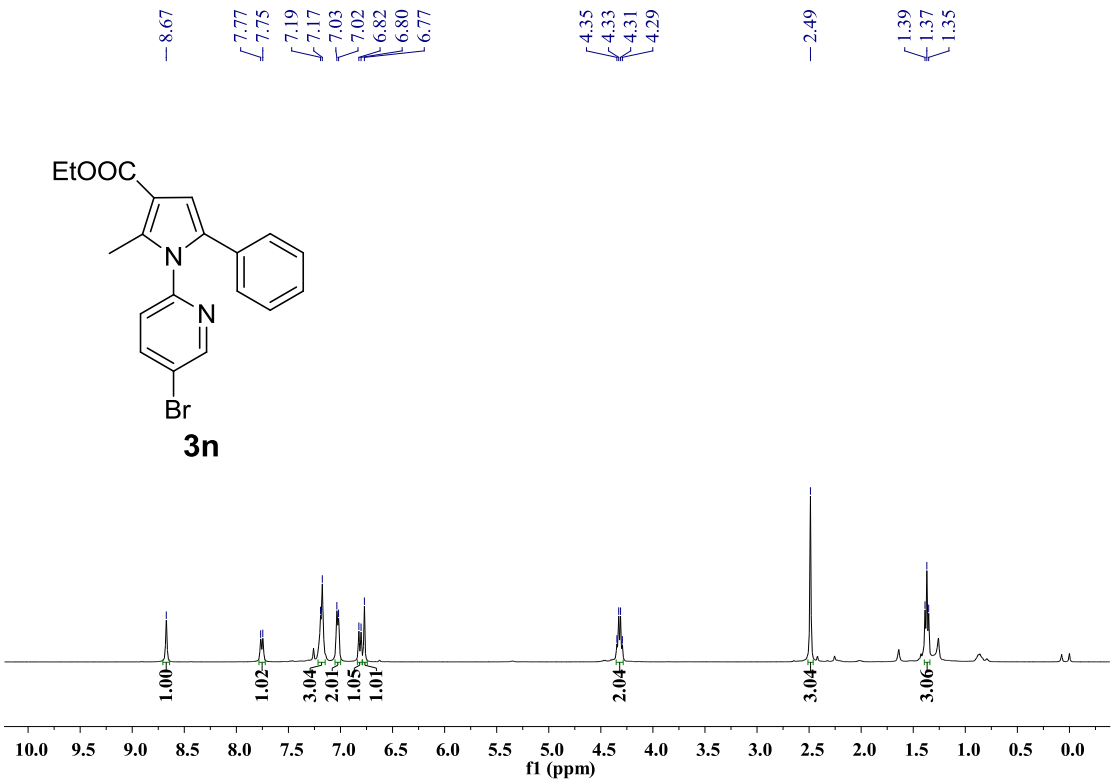



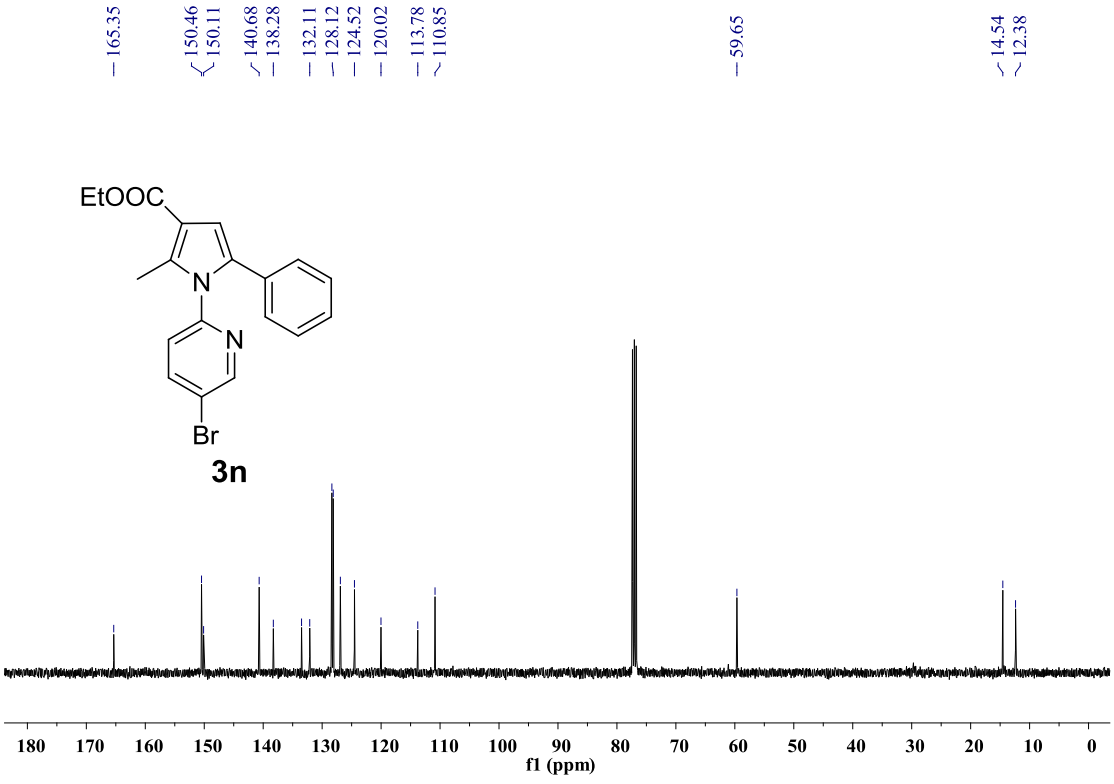
(23) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3m** (using $CDCl_3$ as solvent)



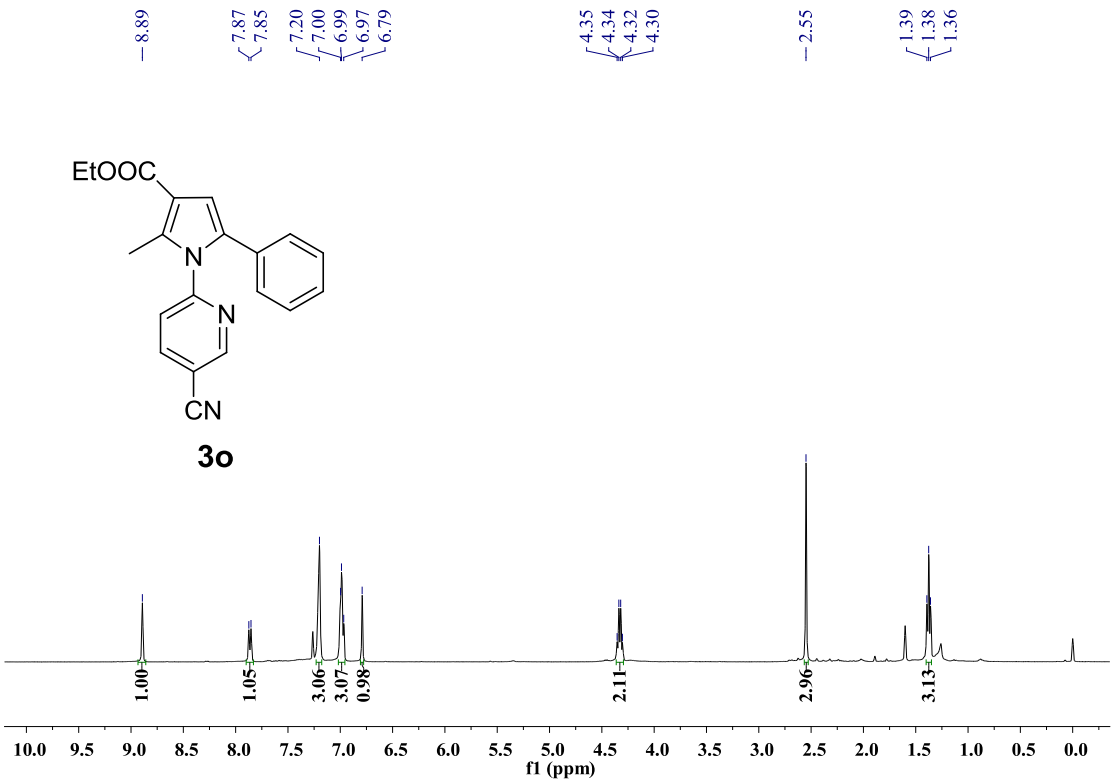



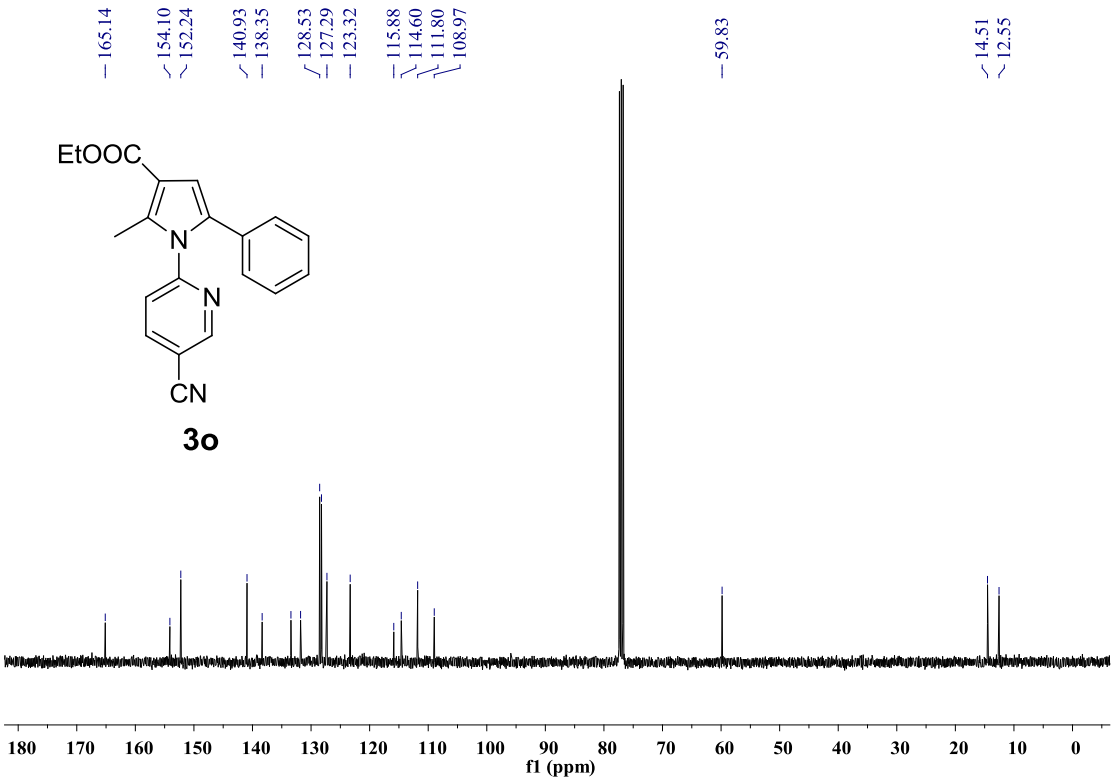
(24) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3n** (using $CDCl_3$ as solvent)



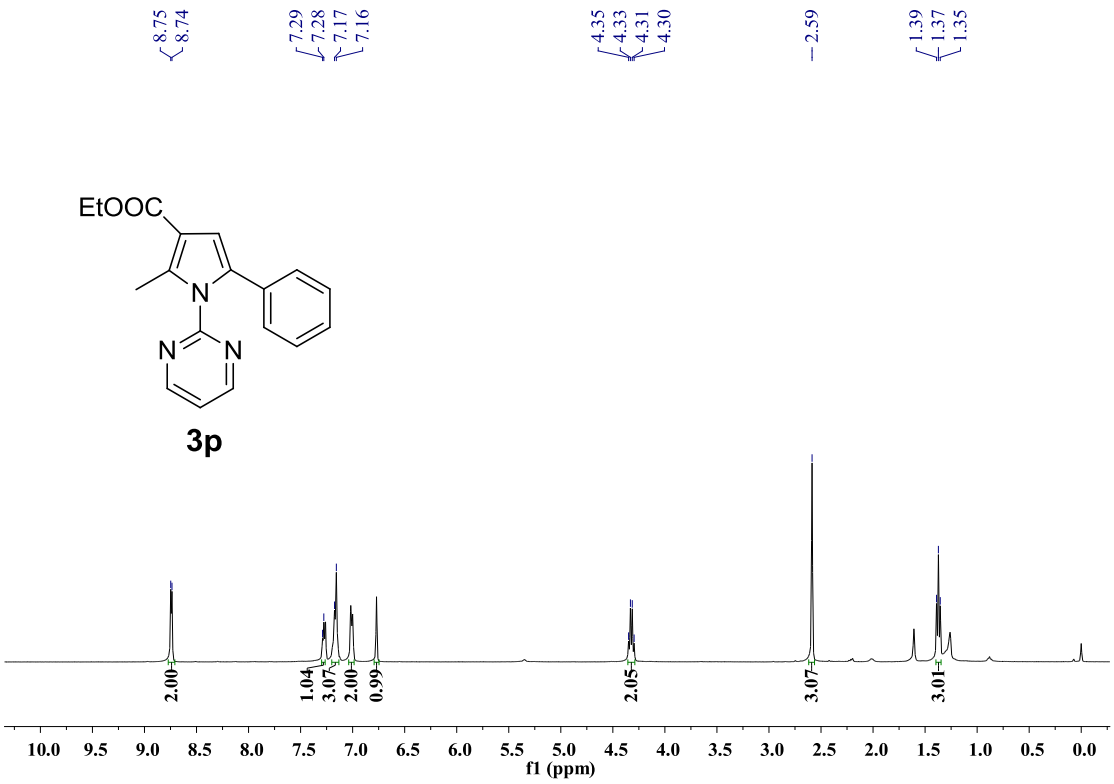



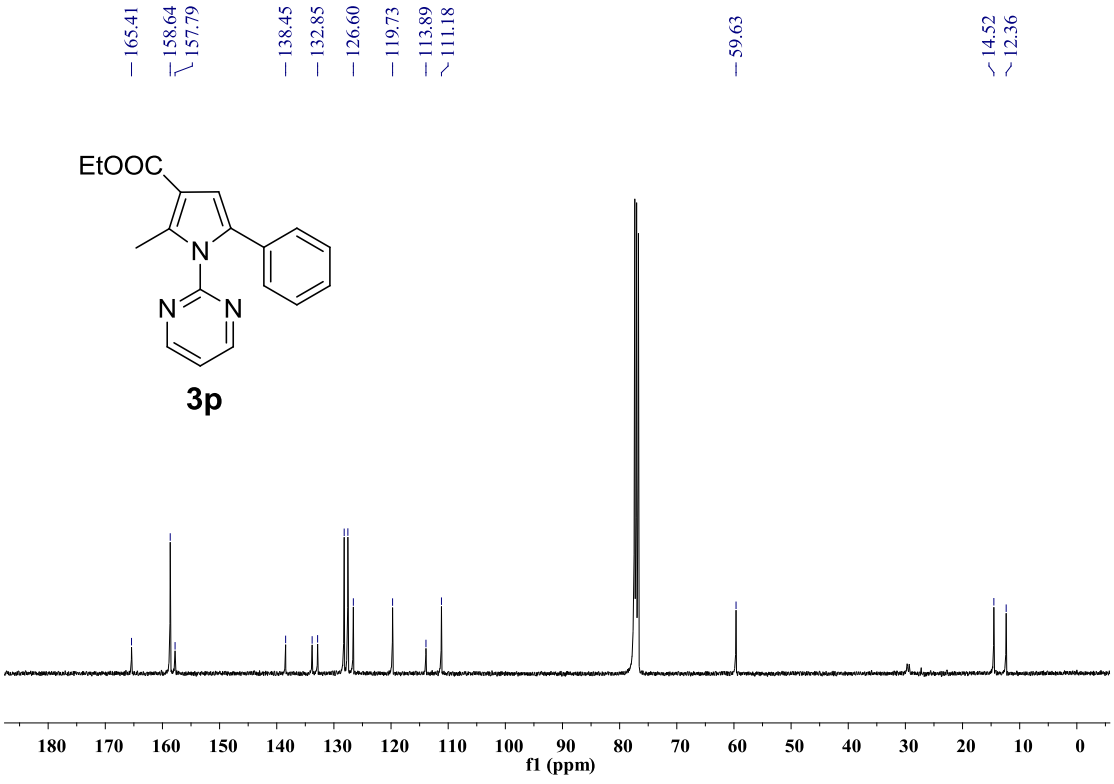
(25) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3o** (using $CDCl_3$ as solvent)



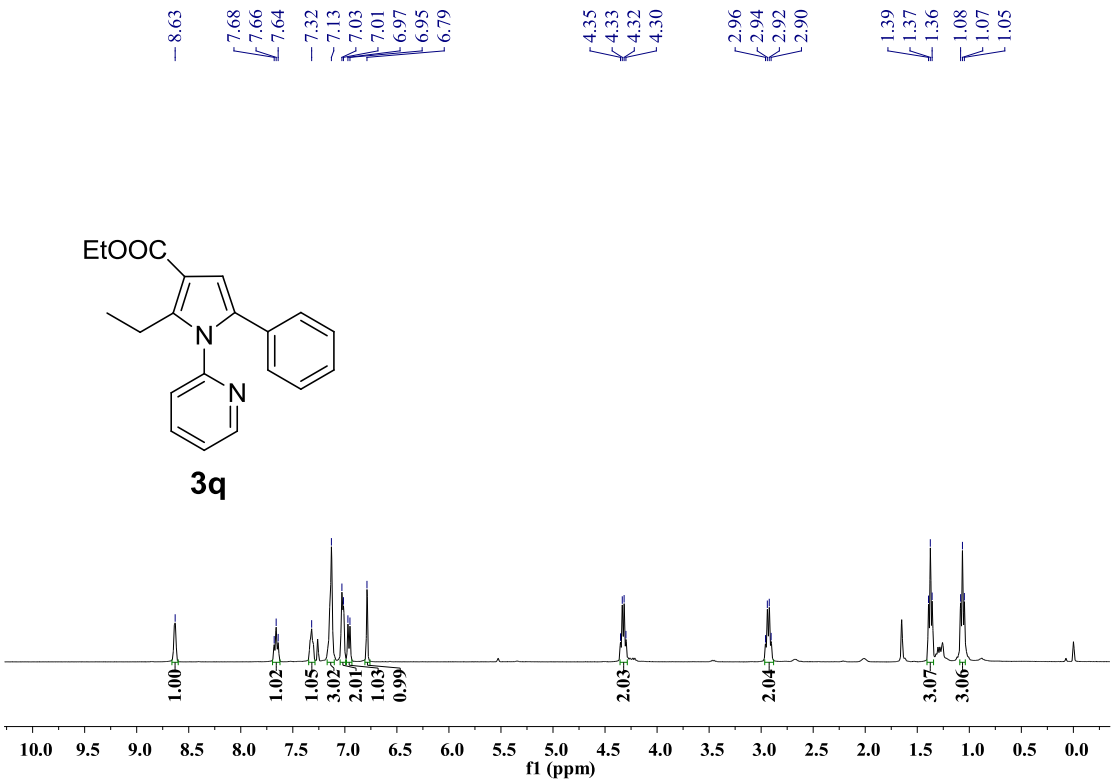



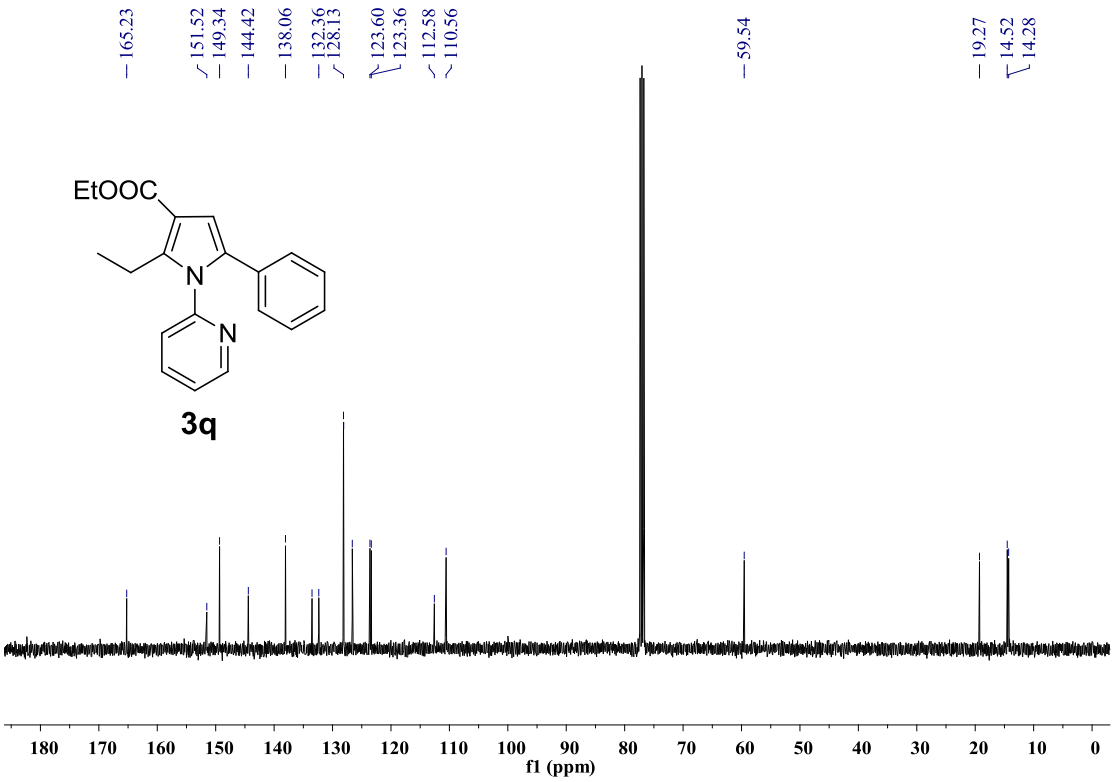
(26) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3p** (using $CDCl_3$ as solvent)



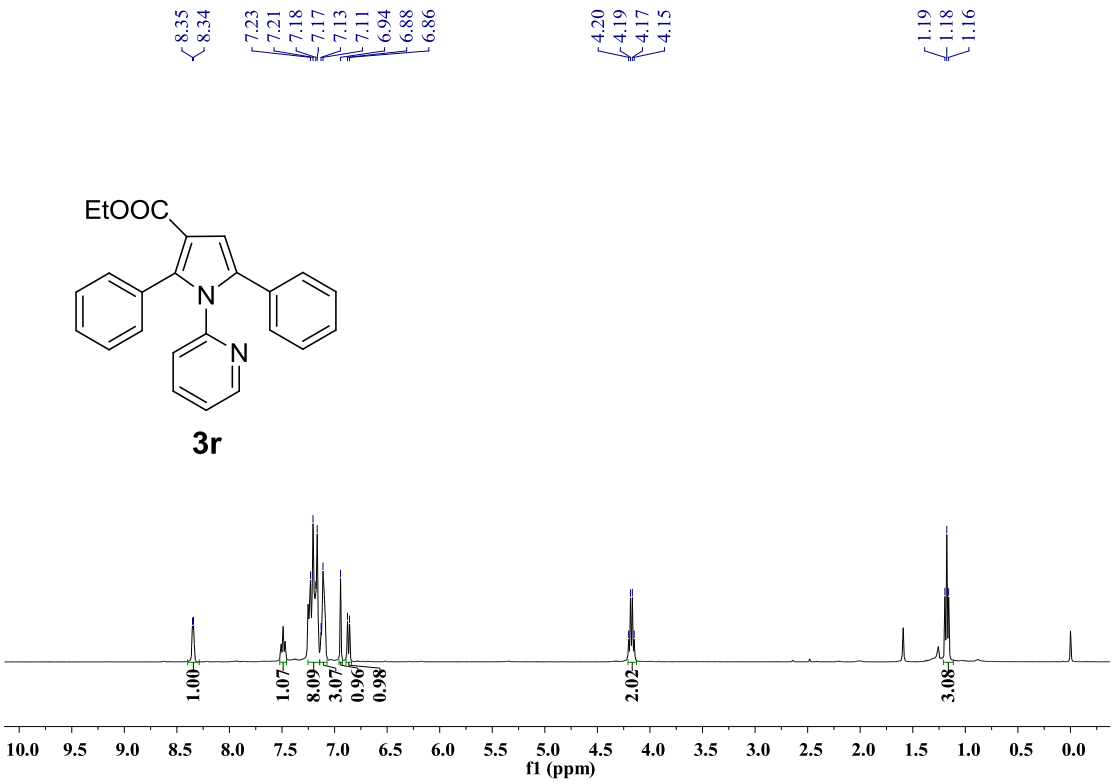



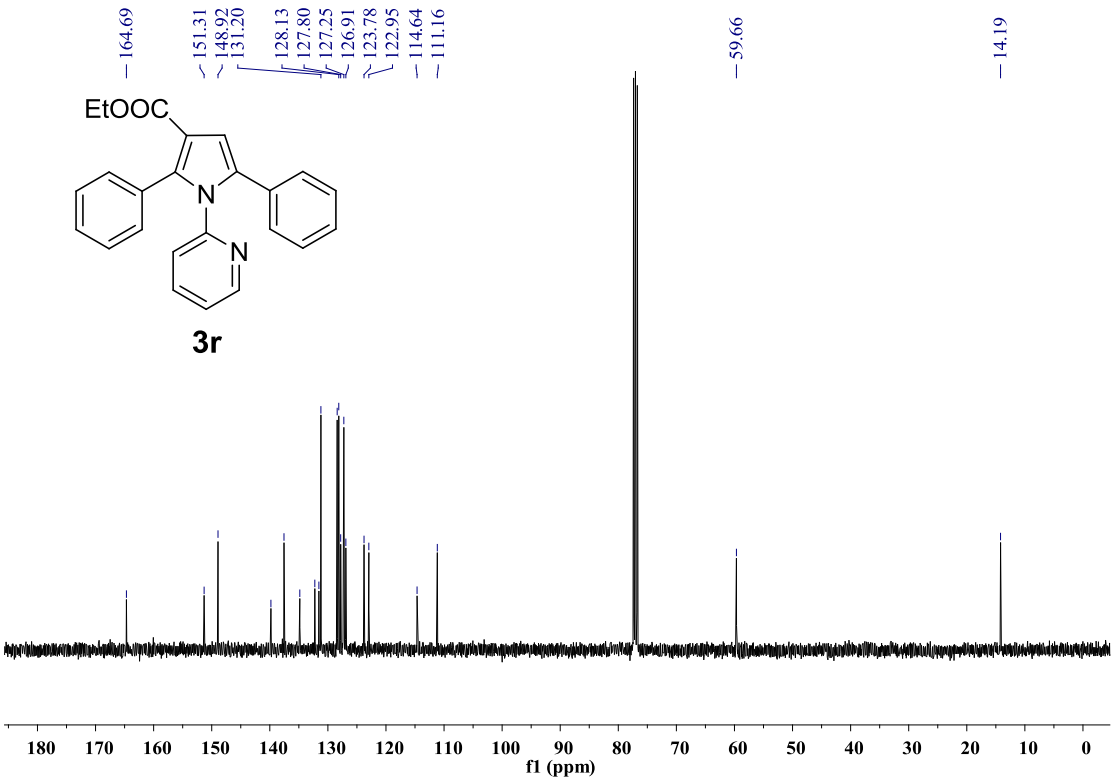
(27) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3q** (using $CDCl_3$ as solvent)



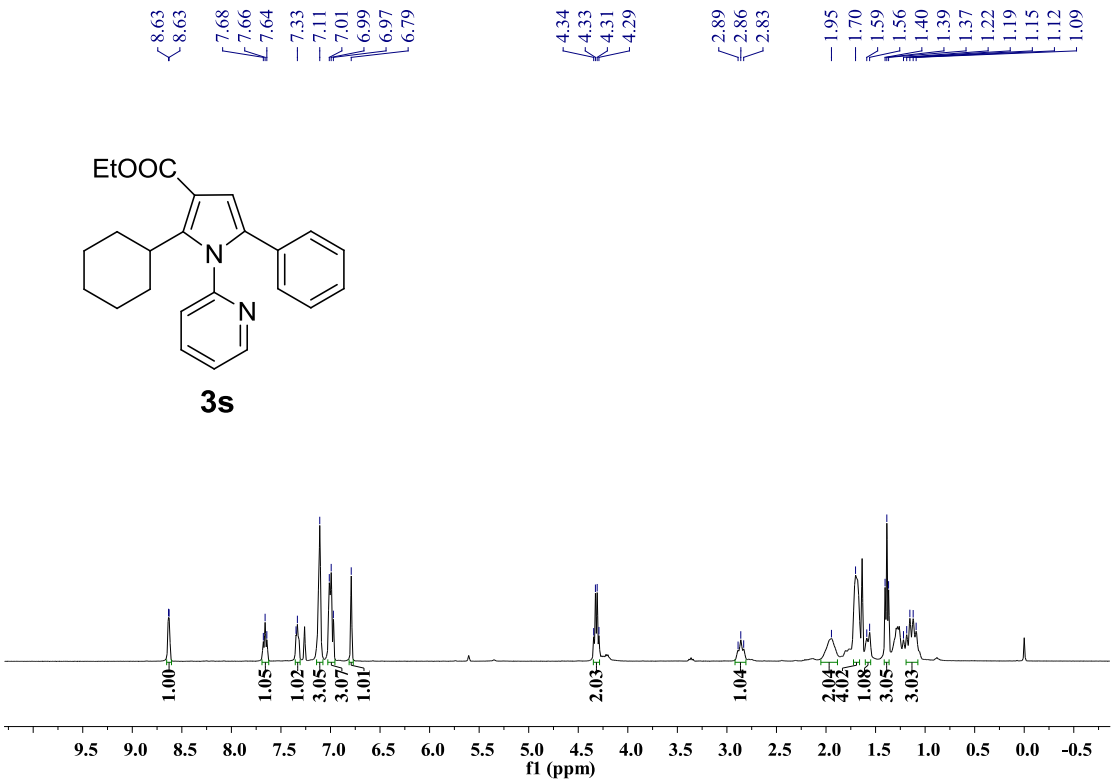



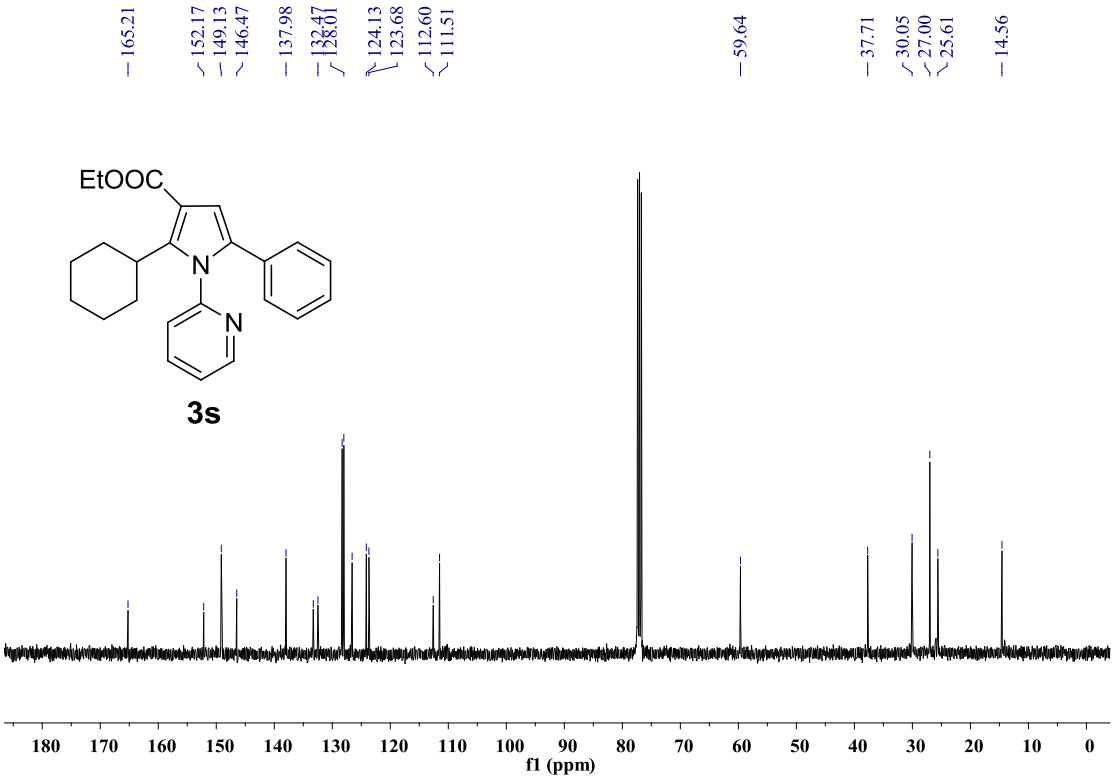
(28) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3r** (using $CDCl_3$ as solvent)



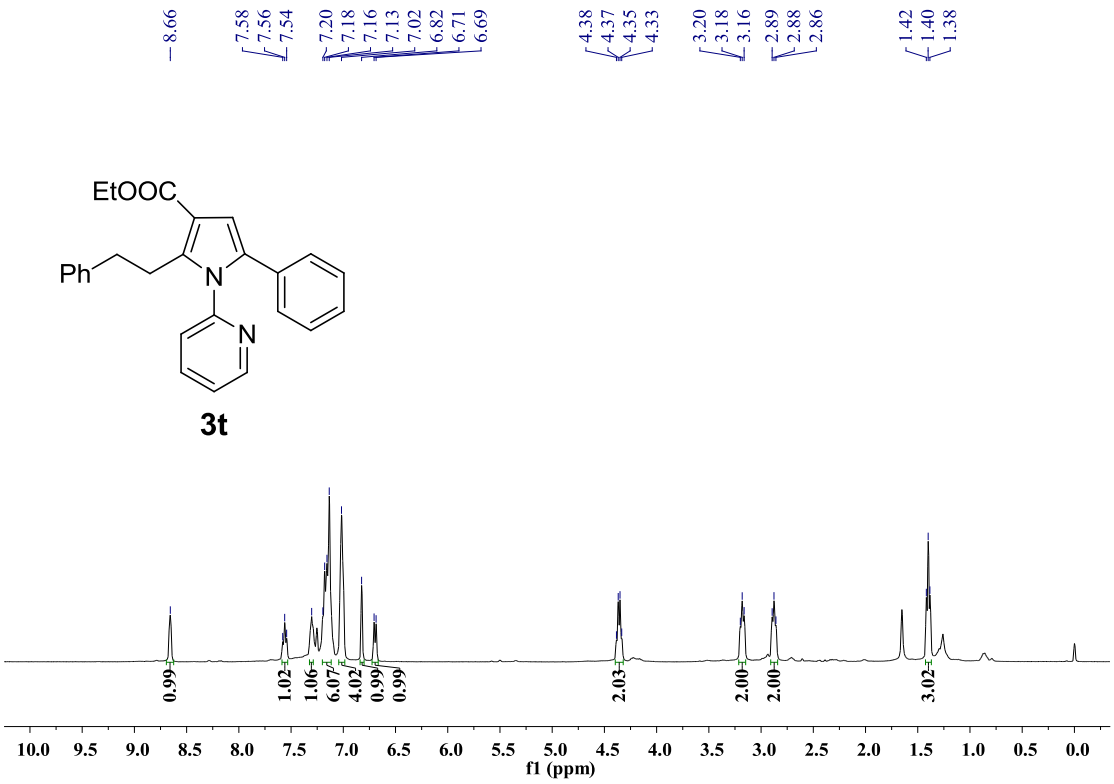



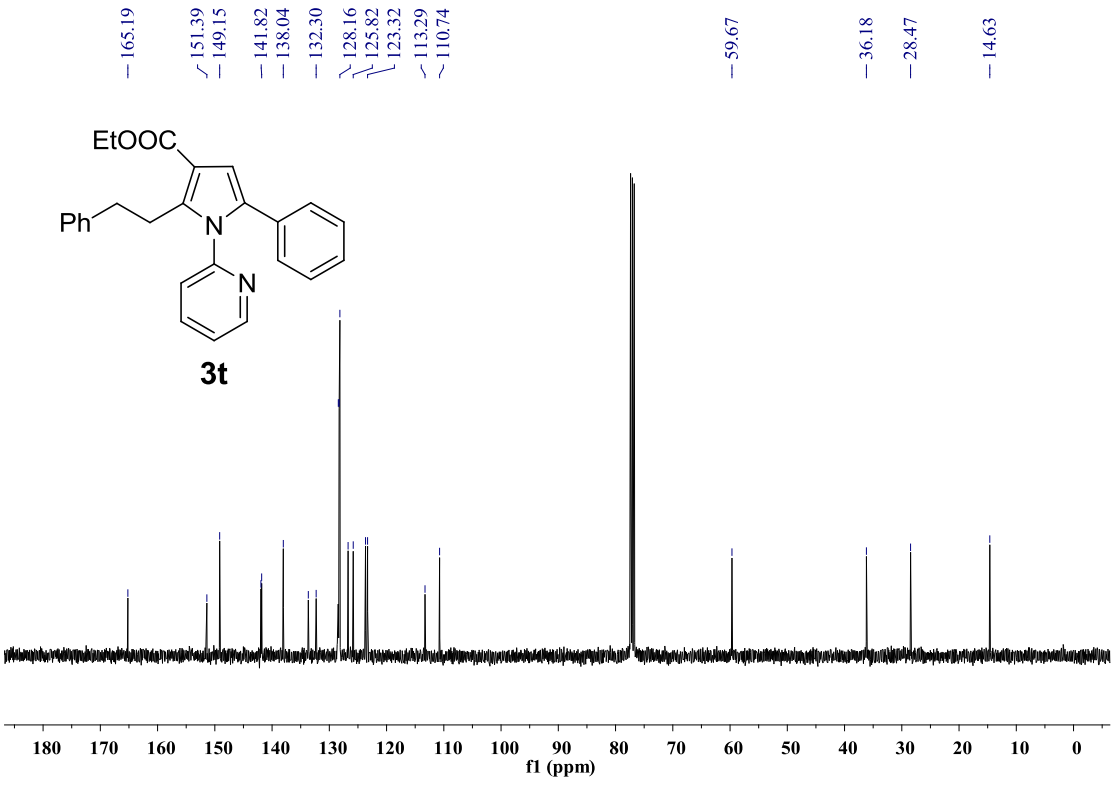
(29) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3s** (using $CDCl_3$ as solvent)



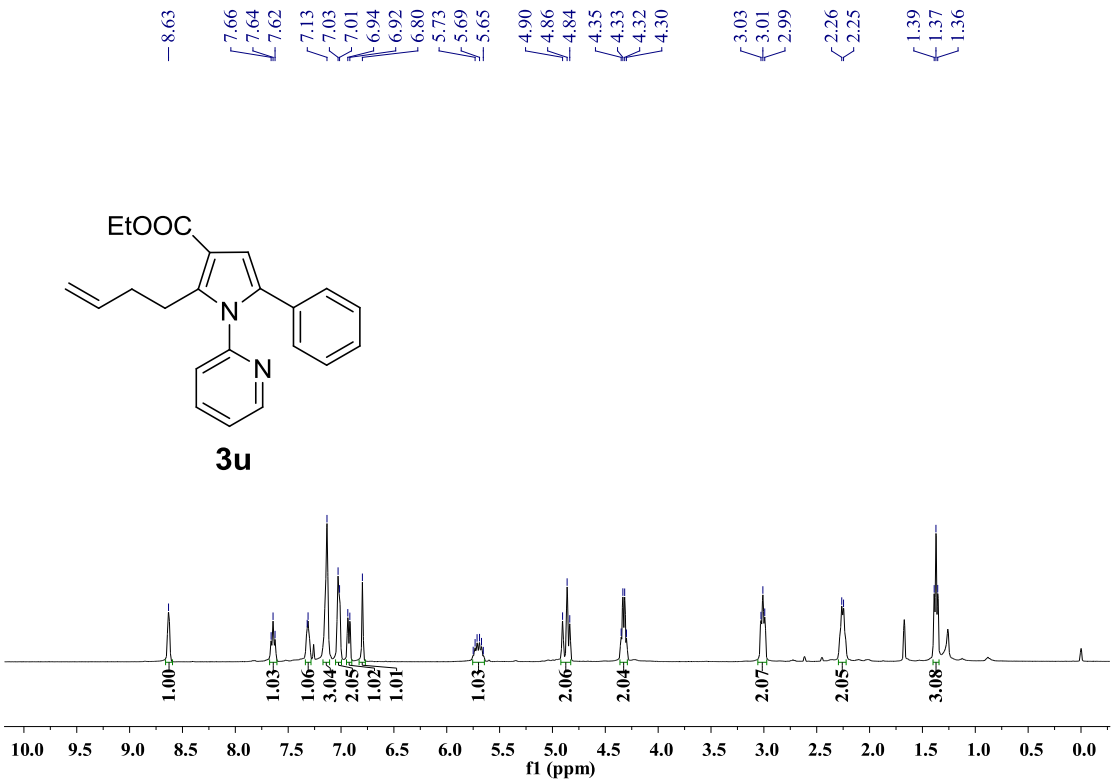



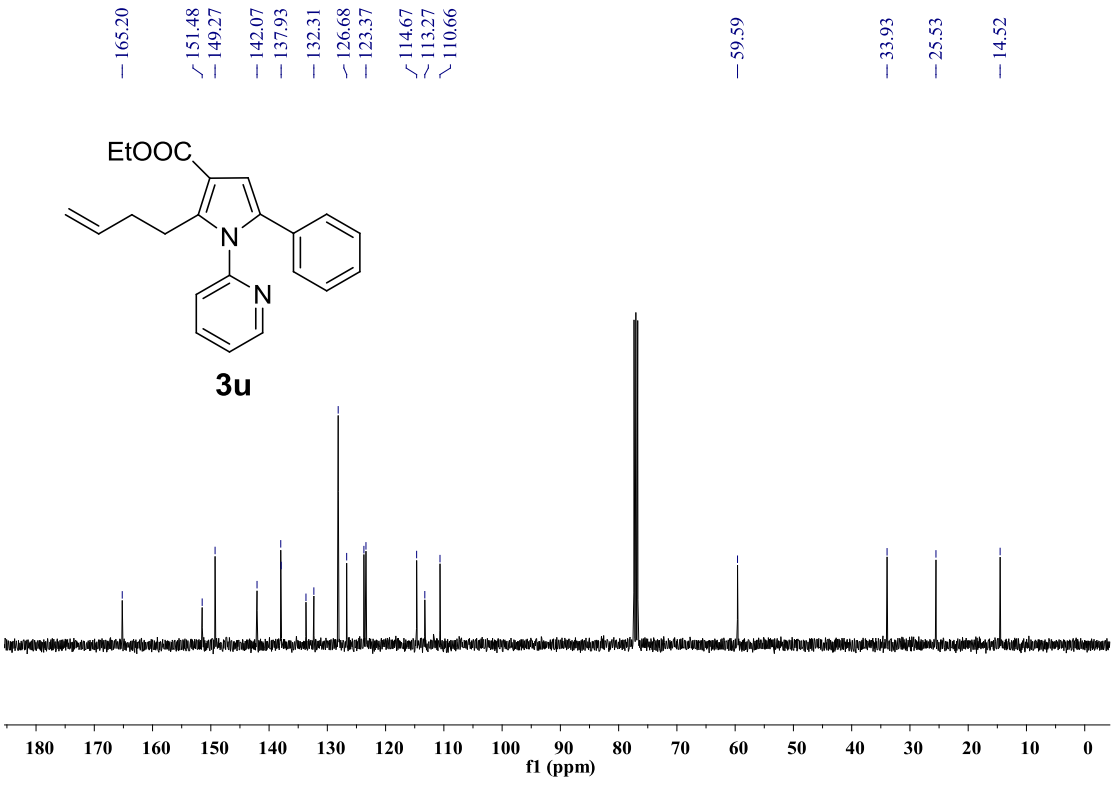
(30) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3t** (using $CDCl_3$ as solvent)



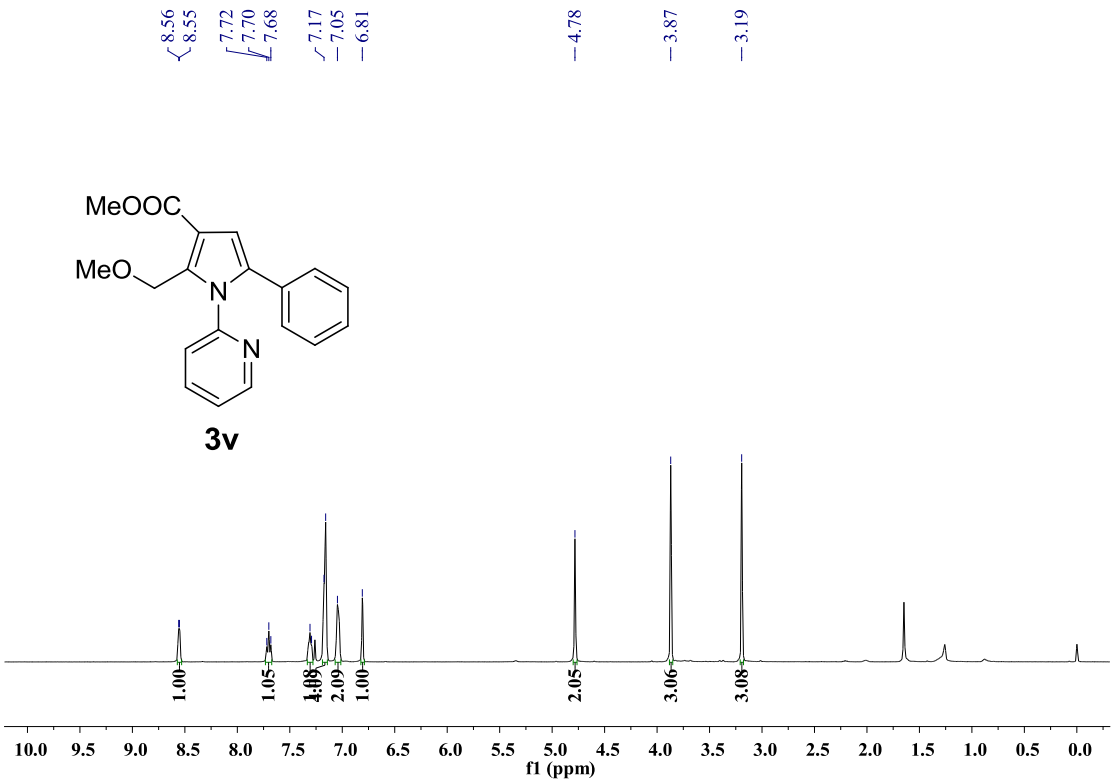



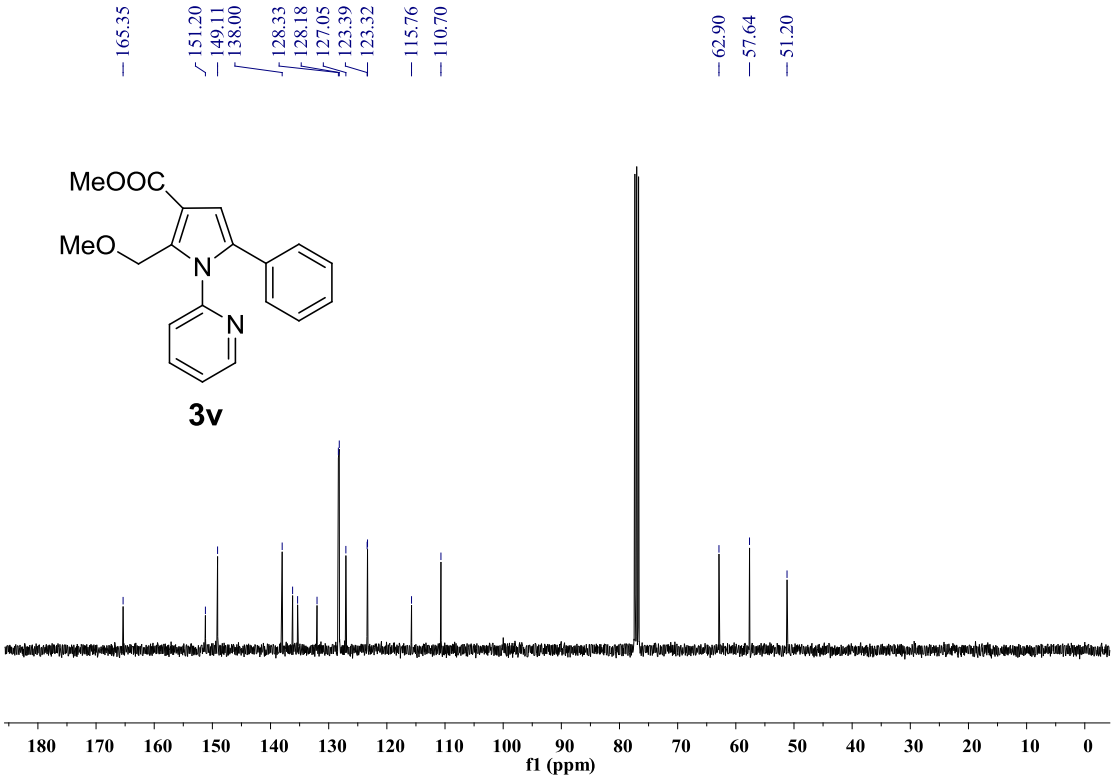
(31) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3u** (using $CDCl_3$ as solvent)



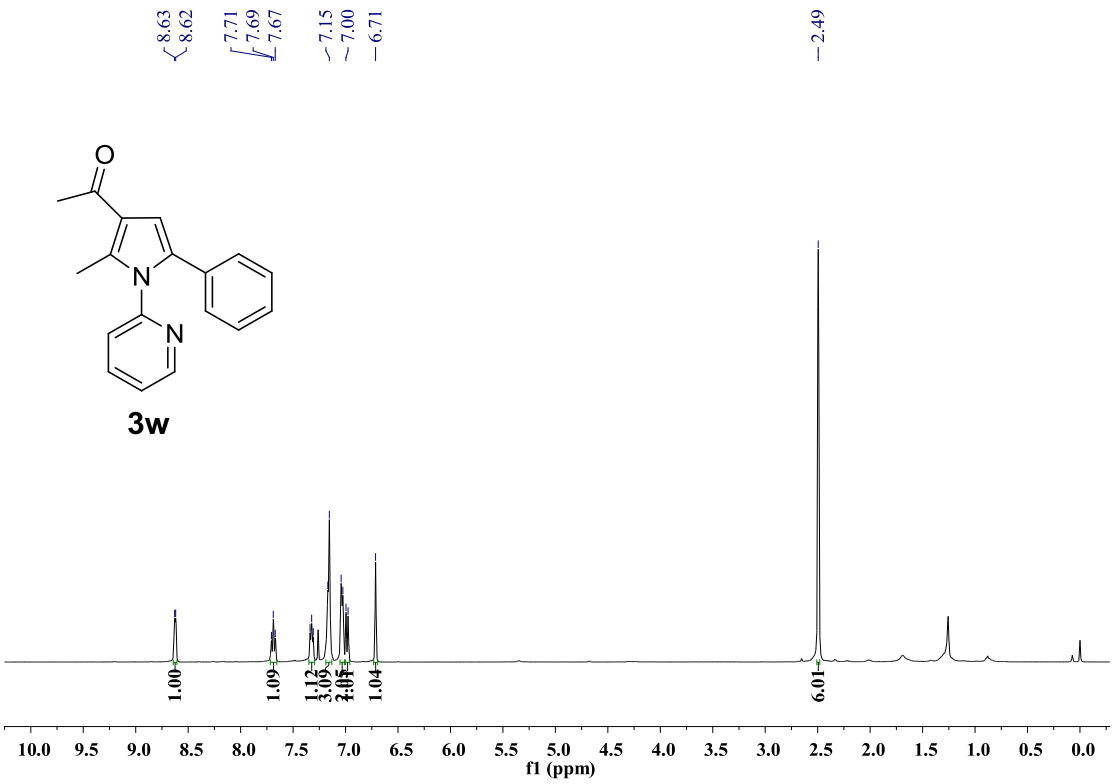



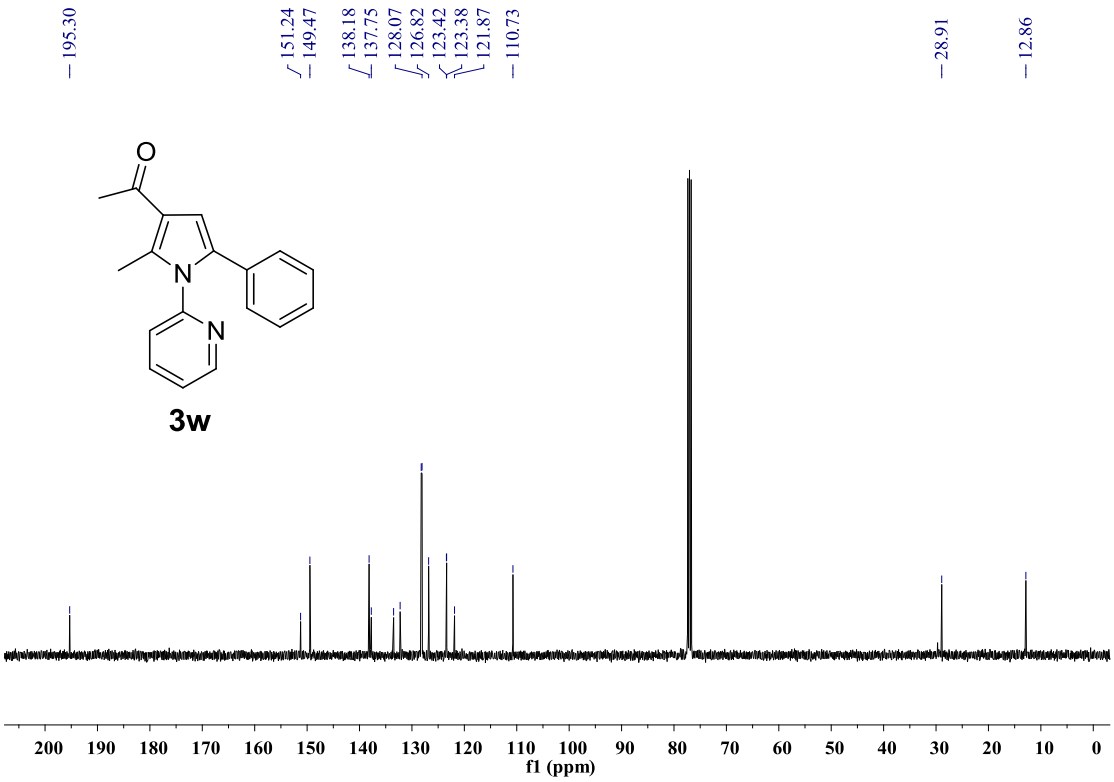
(32) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3v** (using $CDCl_3$ as solvent)



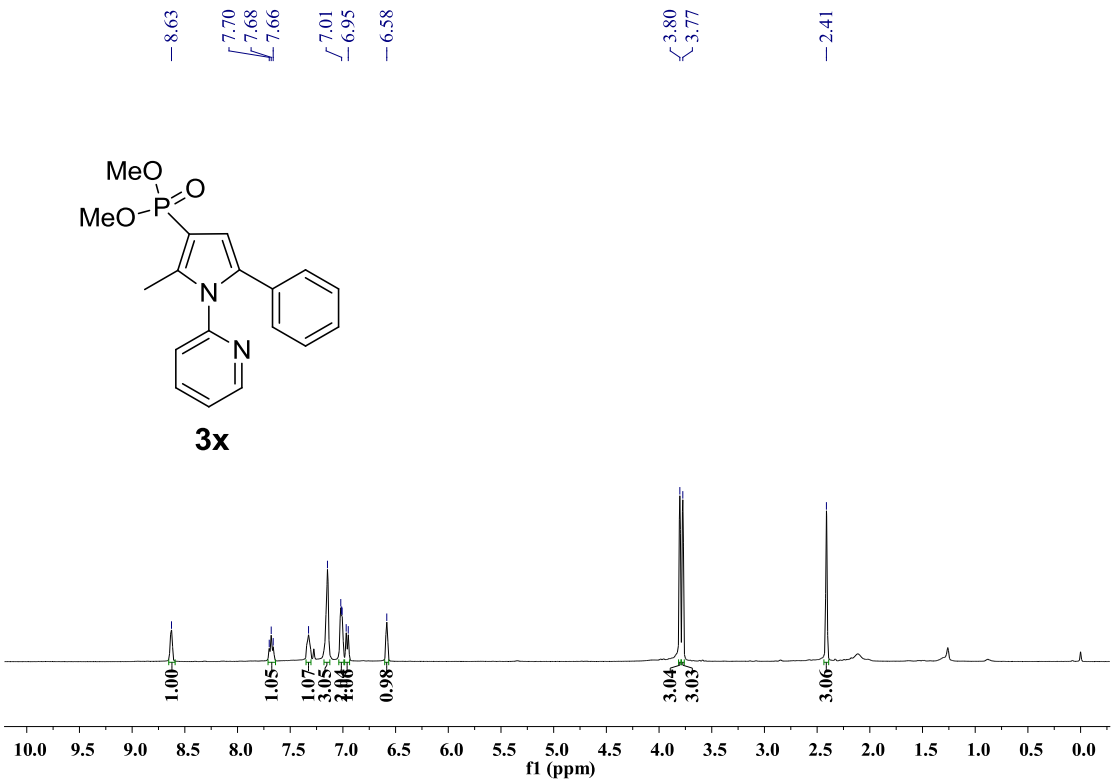



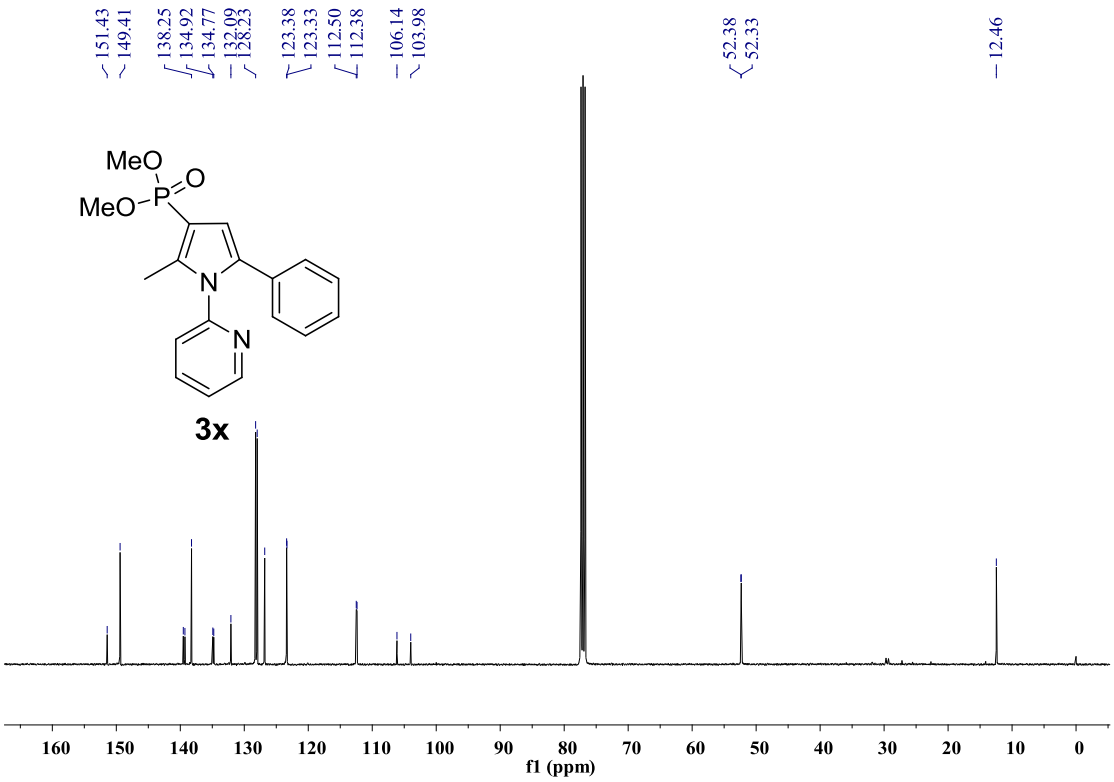
(33) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3w** (using $CDCl_3$ as solvent)



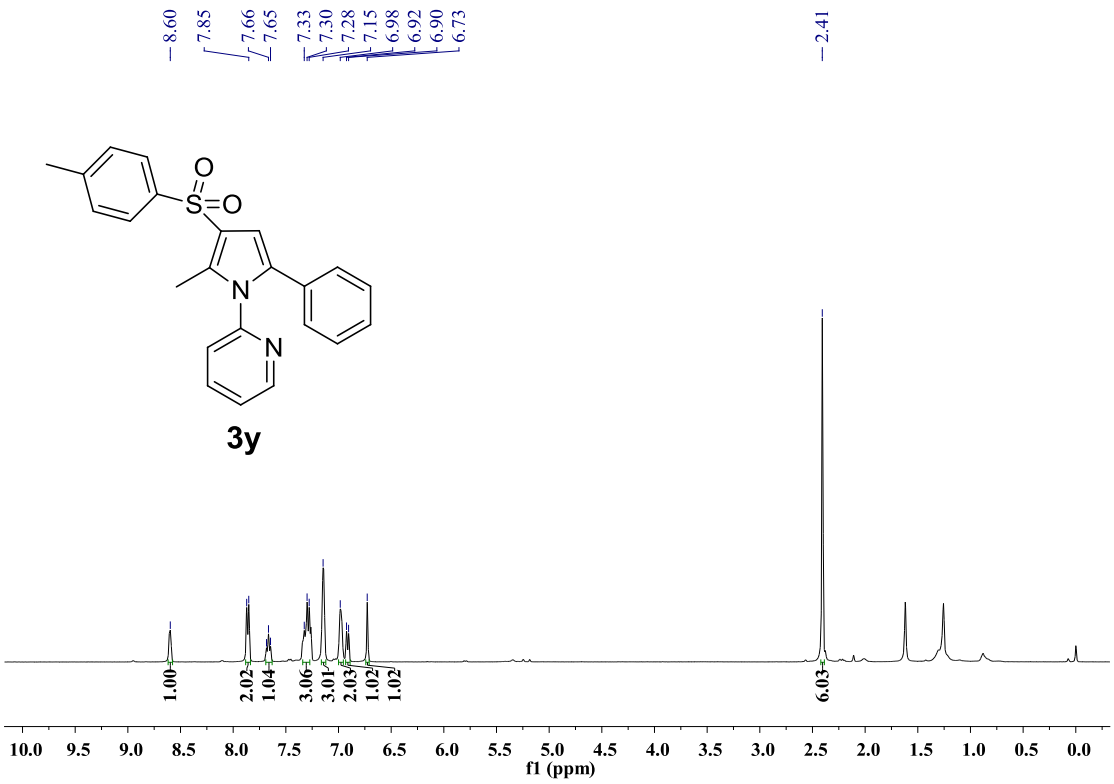



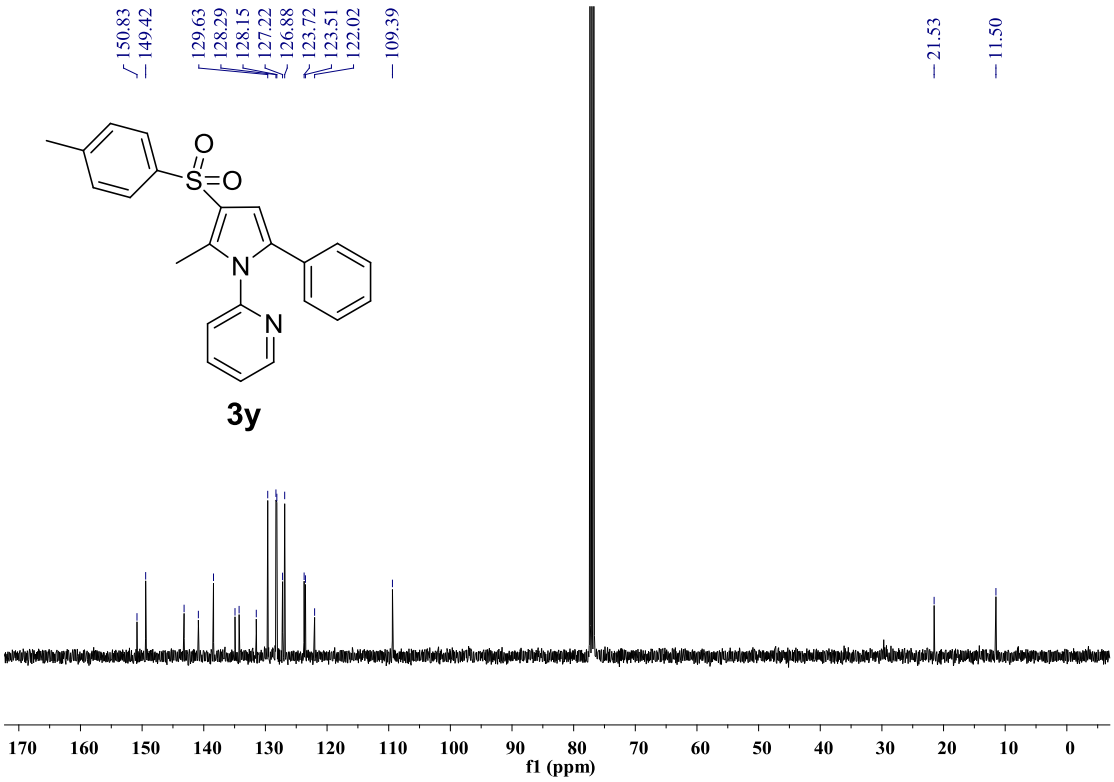
(34) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3x** (using $CDCl_3$ as solvent)



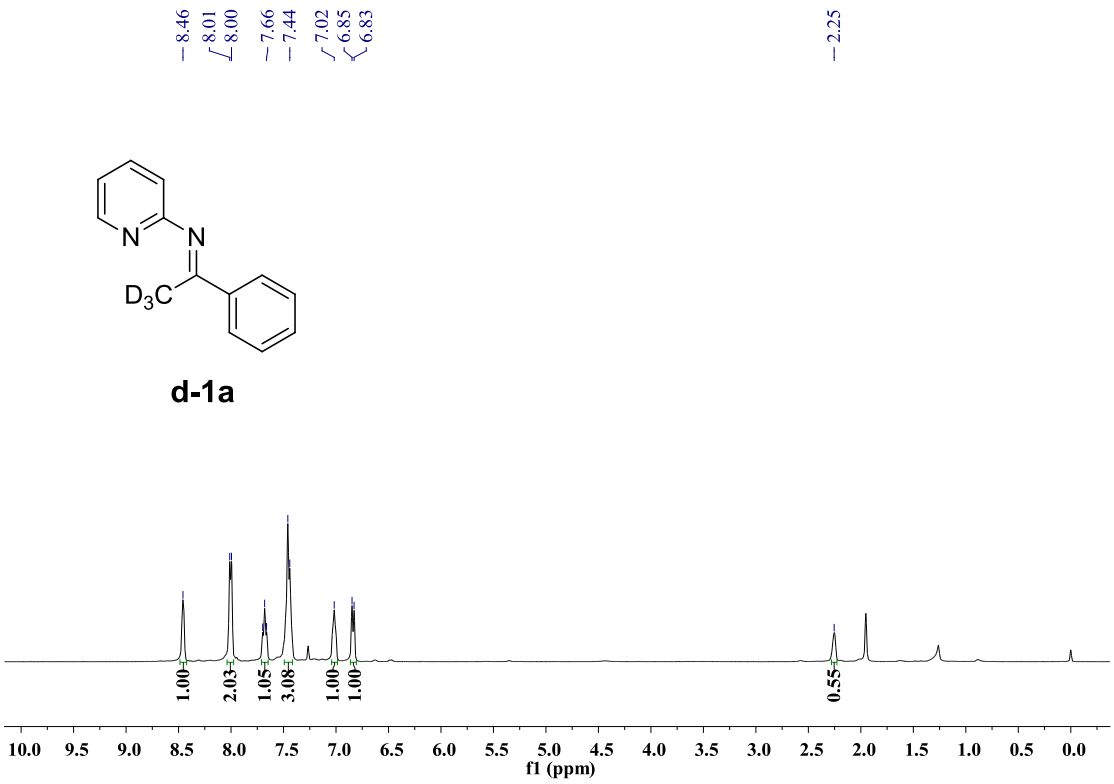



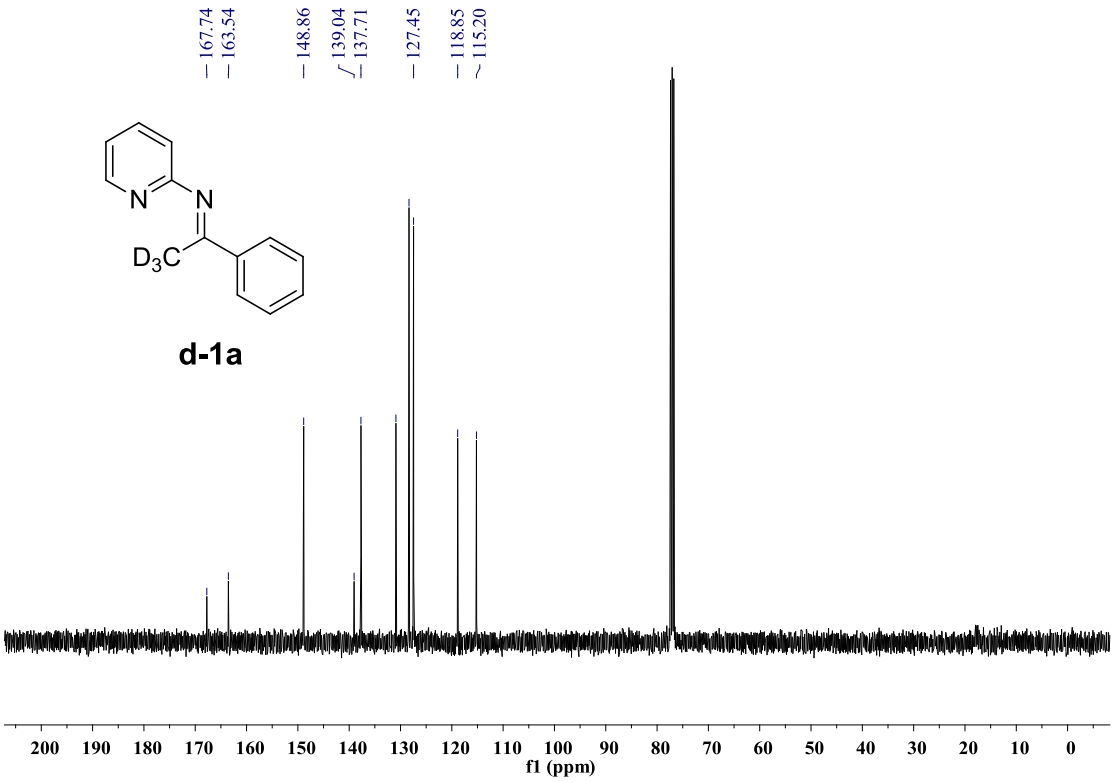
(35) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **3y** (using $CDCl_3$ as solvent)



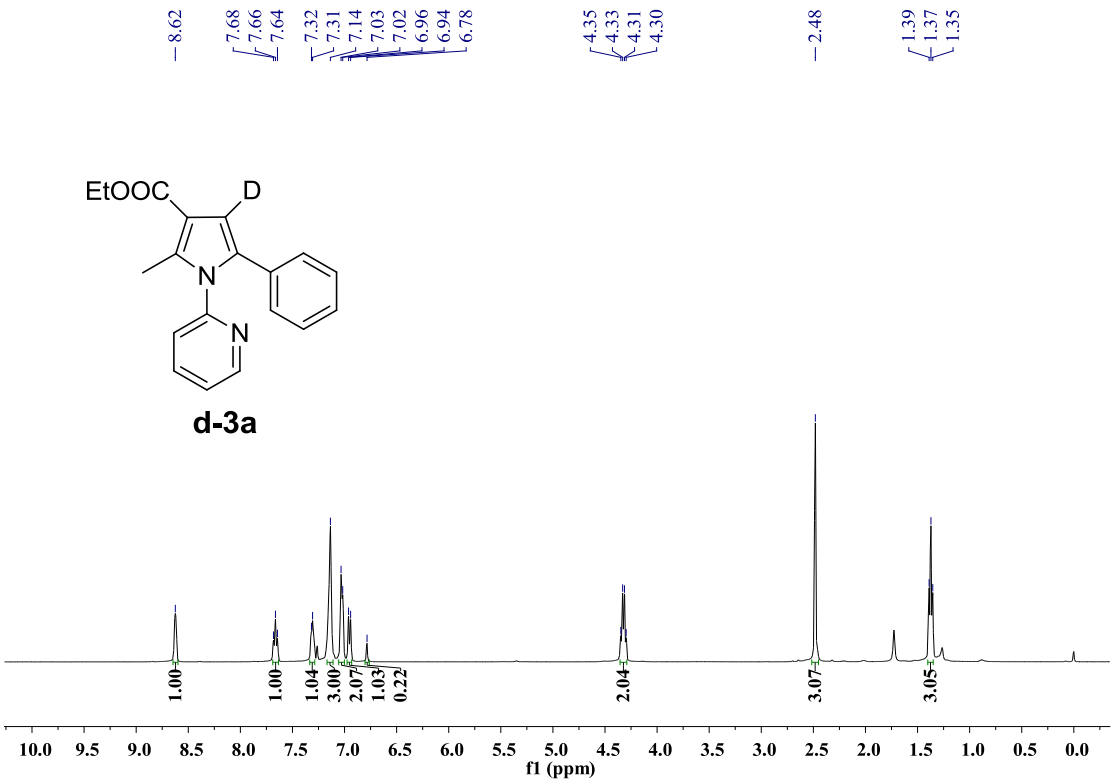



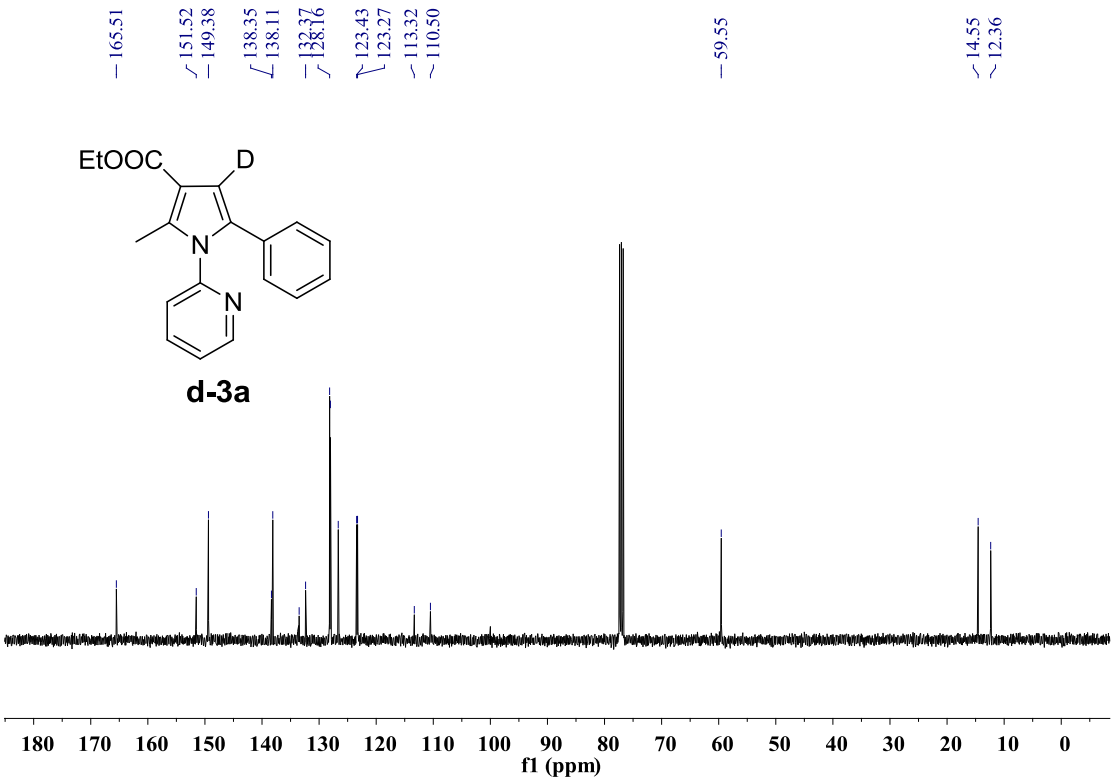
(36) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **d-1a** (using $CDCl_3$ as solvent)



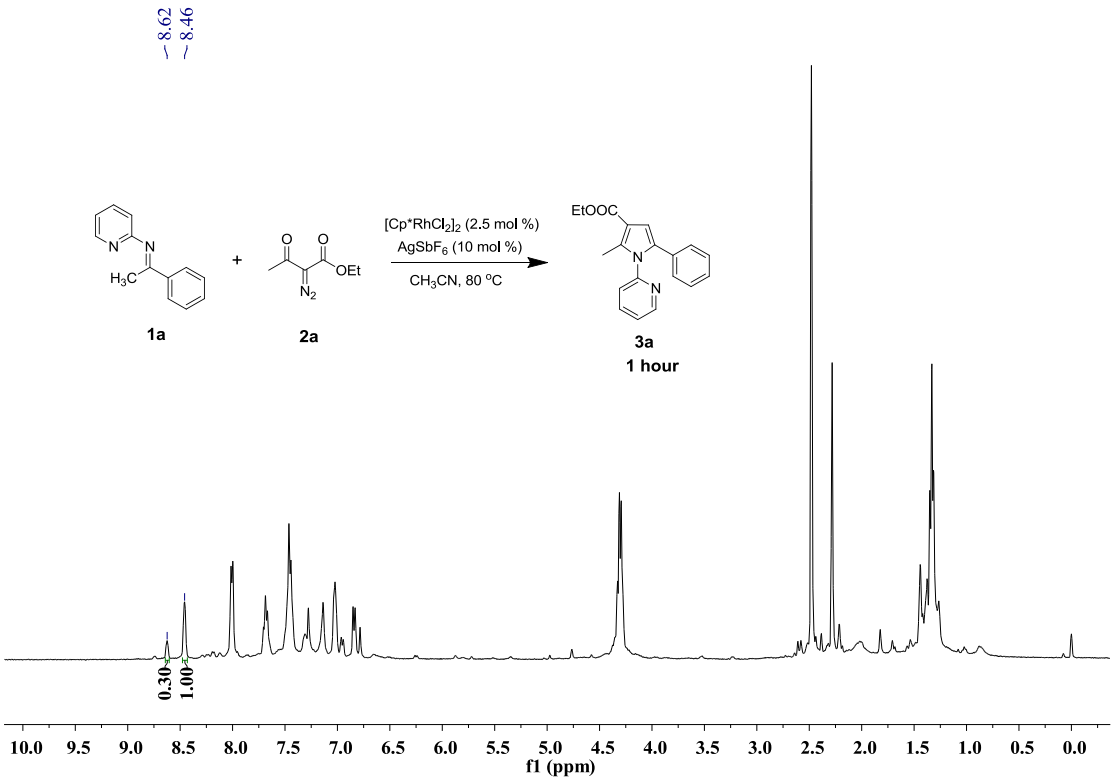



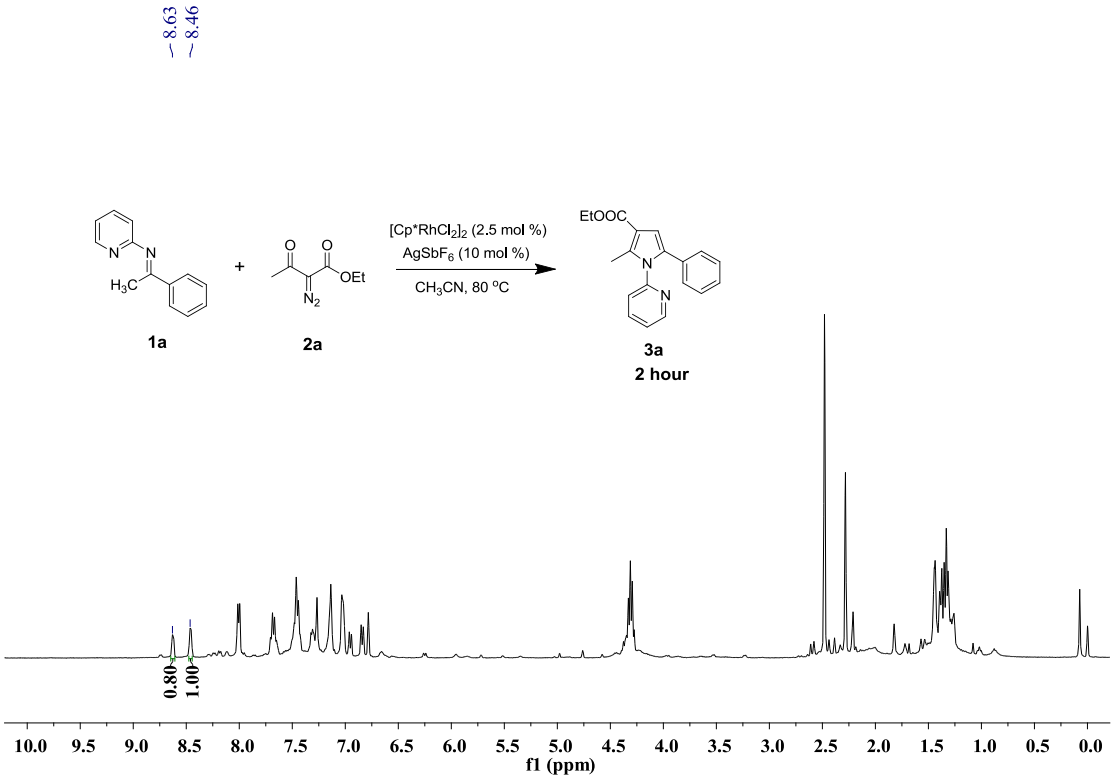
(37) The $^{1}H$ NMR and $^{13}C$ NMR spectrum for **d-3a** (using $CDCl_3$ as solvent)

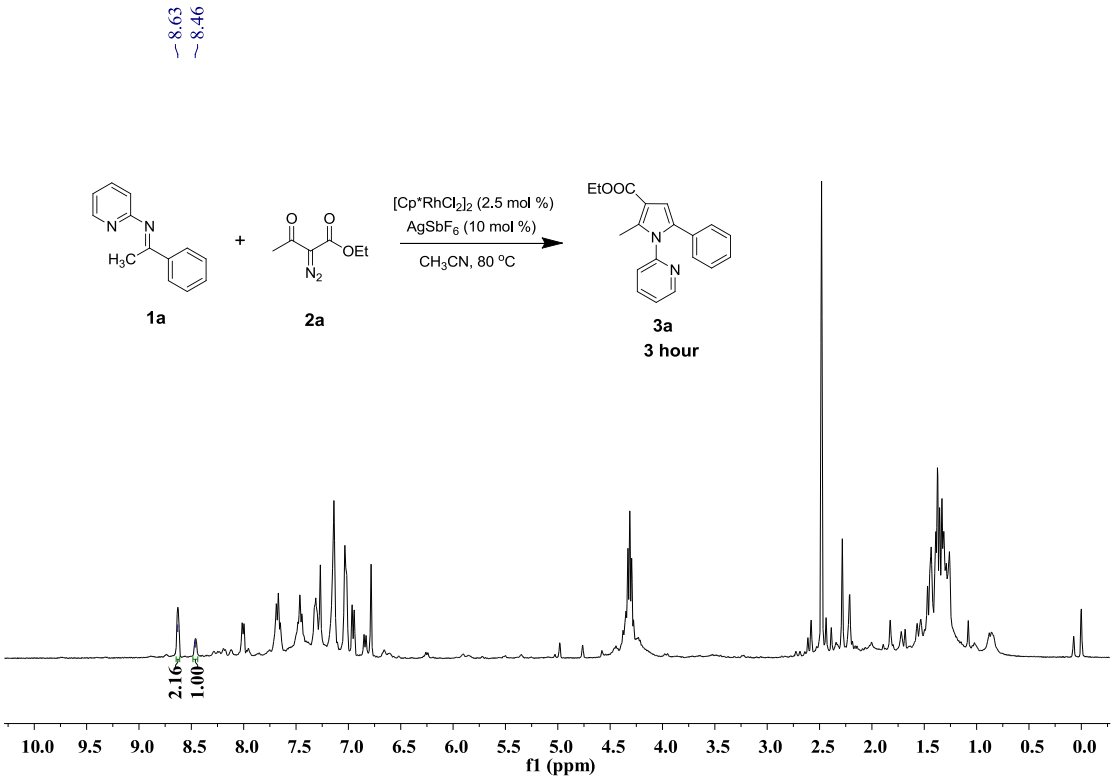


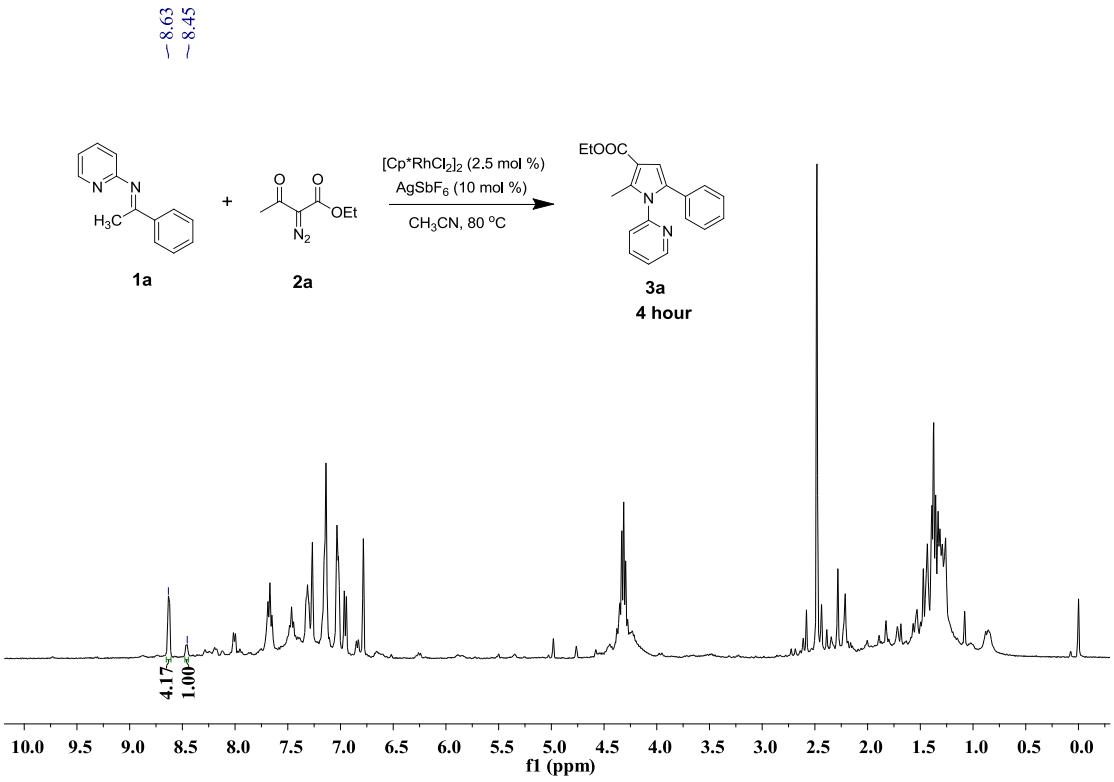



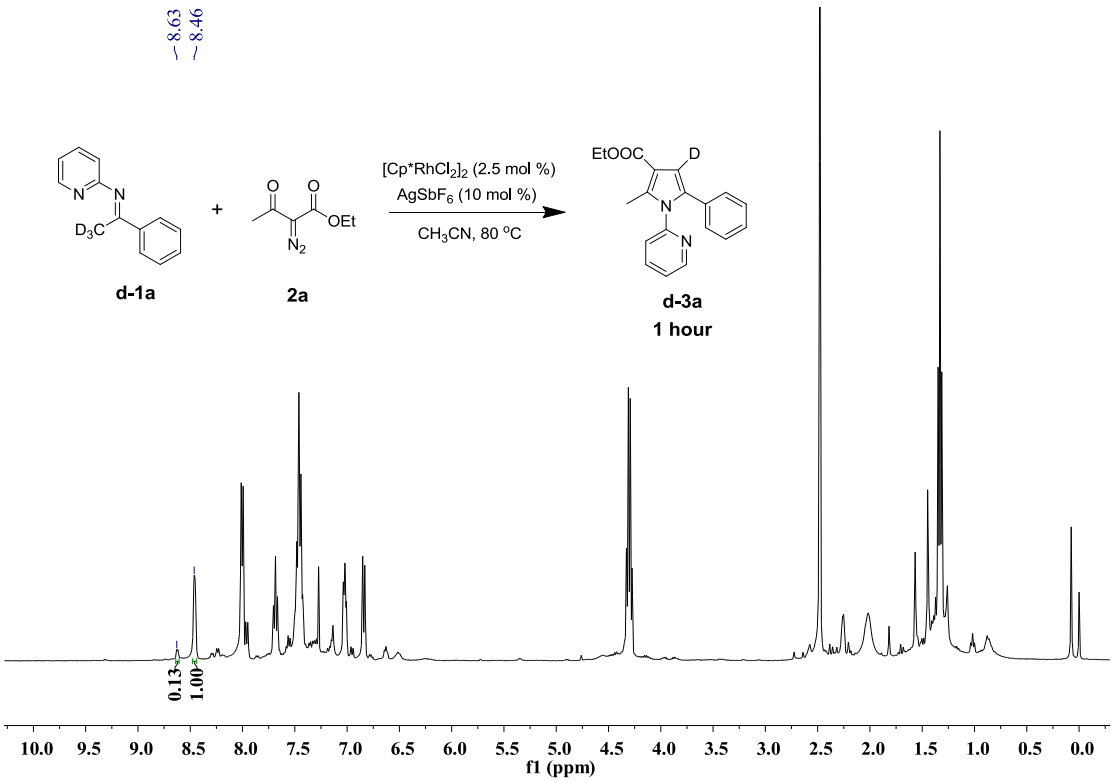
(38) The crude $^{1}H$ NMR spectrum for calculating KIE value via parallel reactions.

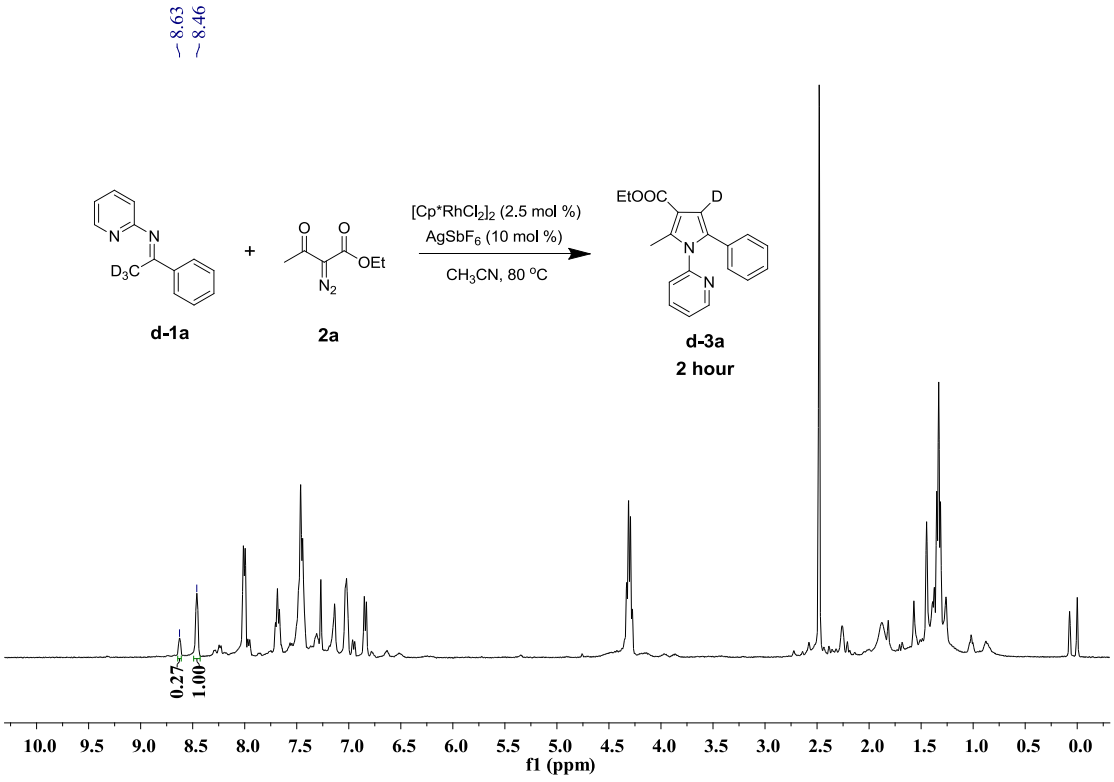


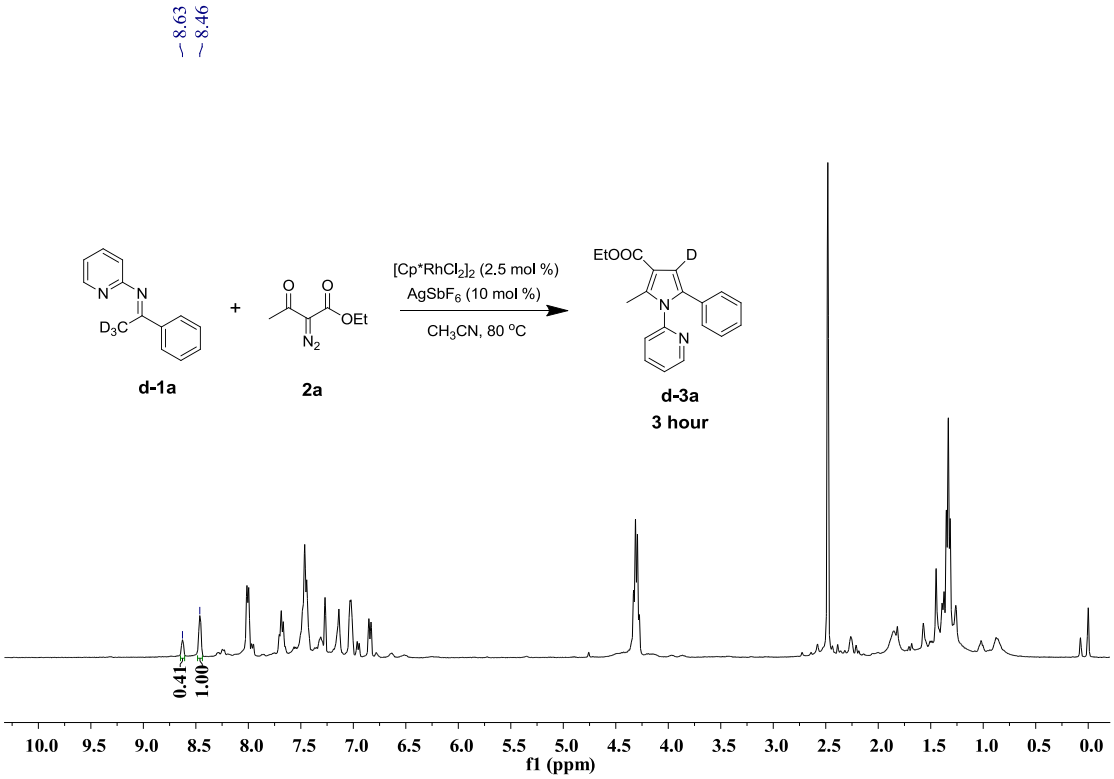



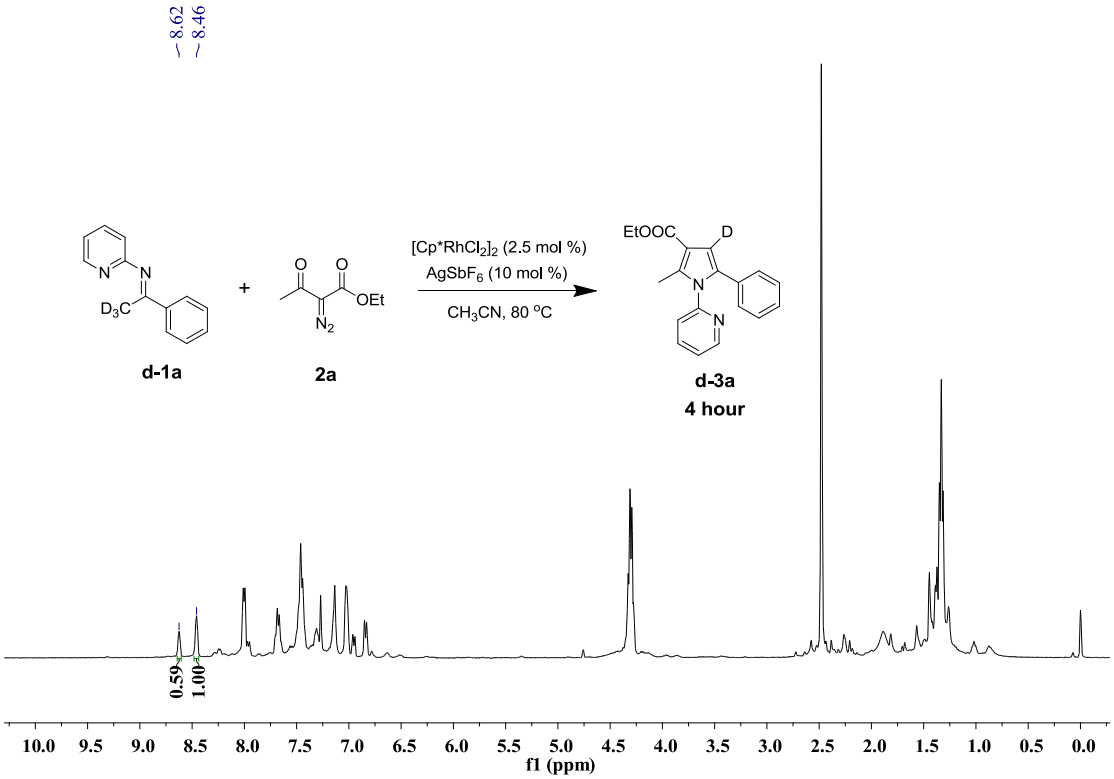

8.63
8.46
[Cp*RhCl2]2 (2.5 mol %)
AgSbF6 (10 mol %)
CH3CN, 80 °C
EtOOC
OEt
1a
2a
3a
3 hour
2.16
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.63
8.45
[Cp*RhCl2]2 (2.5 mol %)
AgSbF6 (10 mol %)
CH3CN, 80 °C
EtOOC
OEt
1a
2a
3a
4 hour
4.17
1.00
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
f1 (ppm)


8.63
8.46
[Cp*RhCl2]2 (2.5 mol %)
AgSbF6 (10 mol %)
CH3CN, 80 °C
EtOOC
D
OEt
d-1a
2a
d-3a
1 hour
0.13
1.00
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
f1 (ppm)


8.63
8.46
[Cp*RhCl2]2 (2.5 mol %)
AgSbF6 (10 mol %)
CH3CN, 80 °C
EtOOC
D
OEt
d-1a
2a
d-3a
2 hour
0.27
1.00
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
f1 (ppm)


~ 8.63
~ 8.46
[Cp*RhCl2]2 (2.5 mol %)
AgSbF6 (10 mol %)
CH3CN, 80 °C
EtOOC
D
OEt
N2
D3C
d-1a
2a
d-3a
3 hour
0.41
1.00
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
f1 (ppm)


~ 8.62
~ 8.46
[Cp*RhCl2]2 (2.5 mol %)
AgSbF6 (10 mol %)
CH3CN, 80 °C
EtOOC
D
OEt
N2
D3C
d-1a
2a
d-3a
4 hour
0.59
1.00
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
f1 (ppm)