Supporting Information for

Synthesis of trisubstituted hydroxylamines by visible light-promoted multicomponent reaction

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1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. THF was freshly distilled from Na under argon. All other solvents and reagents were purified according to standard procedures or were used as received from chemical suppliers. The starting materials were synthesized according to literature procedures. The light employed in this work was bought from GeAo Chemical: model H106062, 24 W blue LEDs. All reactions involving heating are carried out in an oil bath.

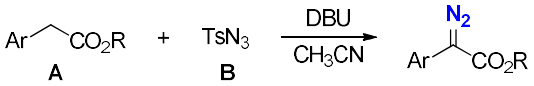
Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silica gel 60 F254). Visualisation was by ultraviolet fluorescence (λ = 254 nm) and/or staining with phosphomolybdic acid or potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

^{1}H NMR and **^{13}C NMR** spectra were recorded on a JEOL JNM ECZ000R at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment.

High Resolution Mass Spectrometry (HRMS): All were recorded on LTQ Orbitrap XL using a positive electrospray ionization (ESI^+). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

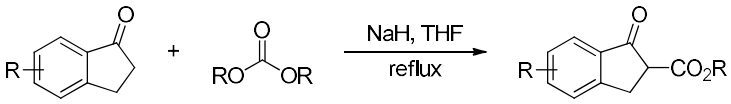
2. Preparation of Starting Materials

The aryldiazoacetates are prepared by the following procedure according to literature reports.[1-4]



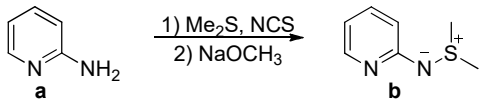
To a mixture of esters **A** (1.0 equiv.) and *p*-toluenesulfonyl azide (TsN_3) **B** (1.2 equiv.) in anhydrous acetonitrile (3 mL/mmol), DBU (1.4 equiv.) was added. The reaction mixture was stirred at room temperature for overnight. Upon the complete consumption of the starting materials, the reaction mixture was diluted with appropriate water, followed by extraction with ethyl acetate. After washing with 10% NH_4Cl solution and brine, the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 60/1 to 30/1) to afford the aryldiazoacetate.

The β-keto ester are prepared by the following procedure according to literature reports.[5]

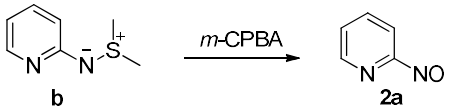


A solution of ketone (1.0 equiv.) in THF (1 L/mol) was added dropwise to a stirred solution of dialkyl carbonate (5.0-10 equiv.) in THF (2 L/mol) containing NaH (60% dispersion in mineral oil, 2.1 equiv.) under a nitrogen atmosphere. The mixture was heated to reflux (4 h), cooled in an ice-bath and then acidified with 1 mol/L hydrochloric acid (1.5 L/mol). The residue was then extracted with Et_2O (3 x 5 L/mol). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography to give the β-keto ester.

The 2-nitrosopyridine are prepared by the following procedure according to literature reports.[6]



To a solution of 9.40 g (0.10 mol) of 2-aminopyridine **a** and 6.80 g (8.0 mL, 0.11 mol) of dimethyl sulfide in 100 mL of DCM was added dropwise, over a period of 1 h, 13.3 g (0.10 mol) of *N*-chlorosuccinimide in 250 mL of DCM, while the temperature was maintained at -20 °C. After the addition was complete, the reaction mixture was stirred at -20 °C for 1 h and then for an additional hour at room temperature. A solution of sodium methoxide in methanol (from 4.05 g, 0.17 mol, of sodium and 75 mL of methanol) was then added, the mixture stirred for 10 min, 150 mL of water added, and stirring continued for 4 h. The organic layer was separated, and the aqueous layer was extracted with two 50-mL portions of methylene chloride. The combined organic extracts were washed with 50 mL of water, dried, and evaporated to give a thick gum which solidified upon being chilled; yield 11 g (71%). Recrystallization from diethyl ether gave a cream-colored solid.



To a solution of 20.1 g (0.119 mol, 80-90%) of m-chloroperbenzoic acid in 500 mL of dry DCM,

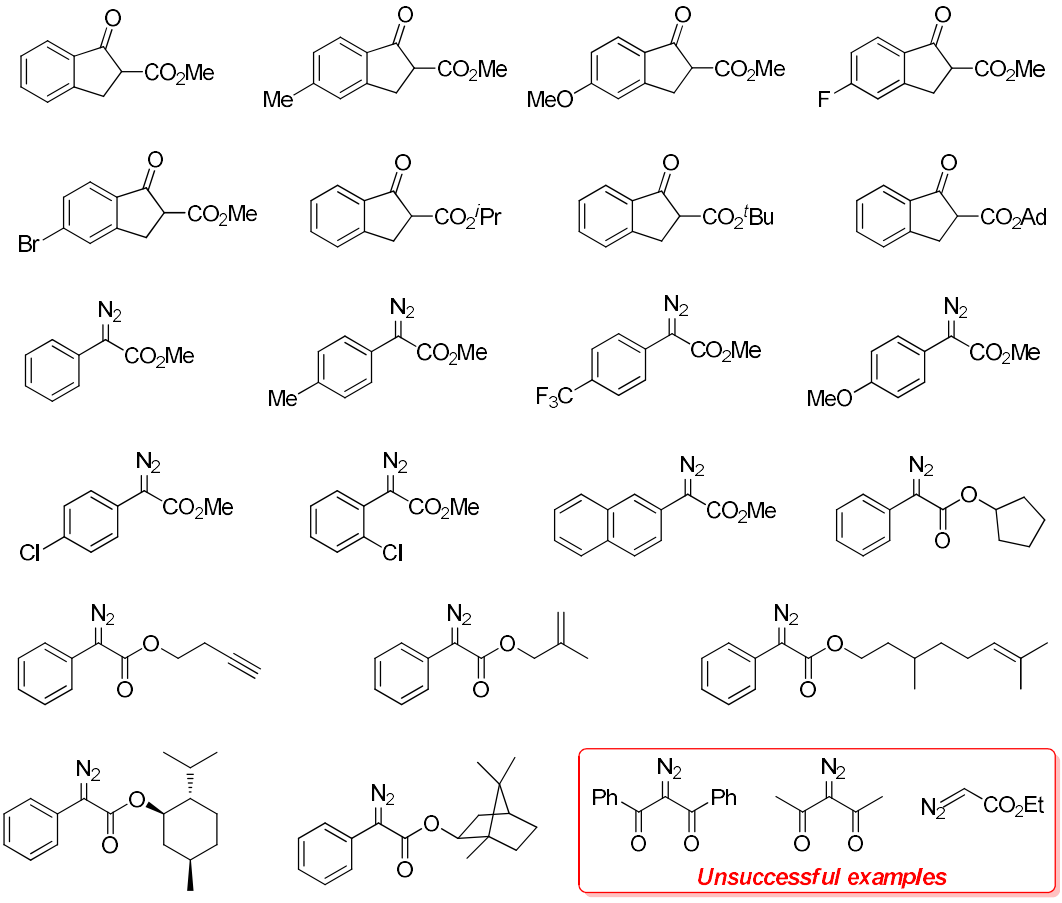
cooled to 0 °C, was added, all at once, a solution of 10.9 g (0.07 mol) of **b** in 100 mL of DCM. The mixture was stirred at 0-5 °C for 90 min, 3-4 mL of dimethyl sulfide added, and stirring continued for an additional 30 min. To the reaction mixture was then added 500 mL of a saturated aqueous solution of sodium carbonate, the layers were separated, and the green organic layer was washed with water and dried (Na_2SO_4). Evaporation of the dried extracts gave a light tan solid which was recrystallized from ethanol to give product as a light yellow solid.

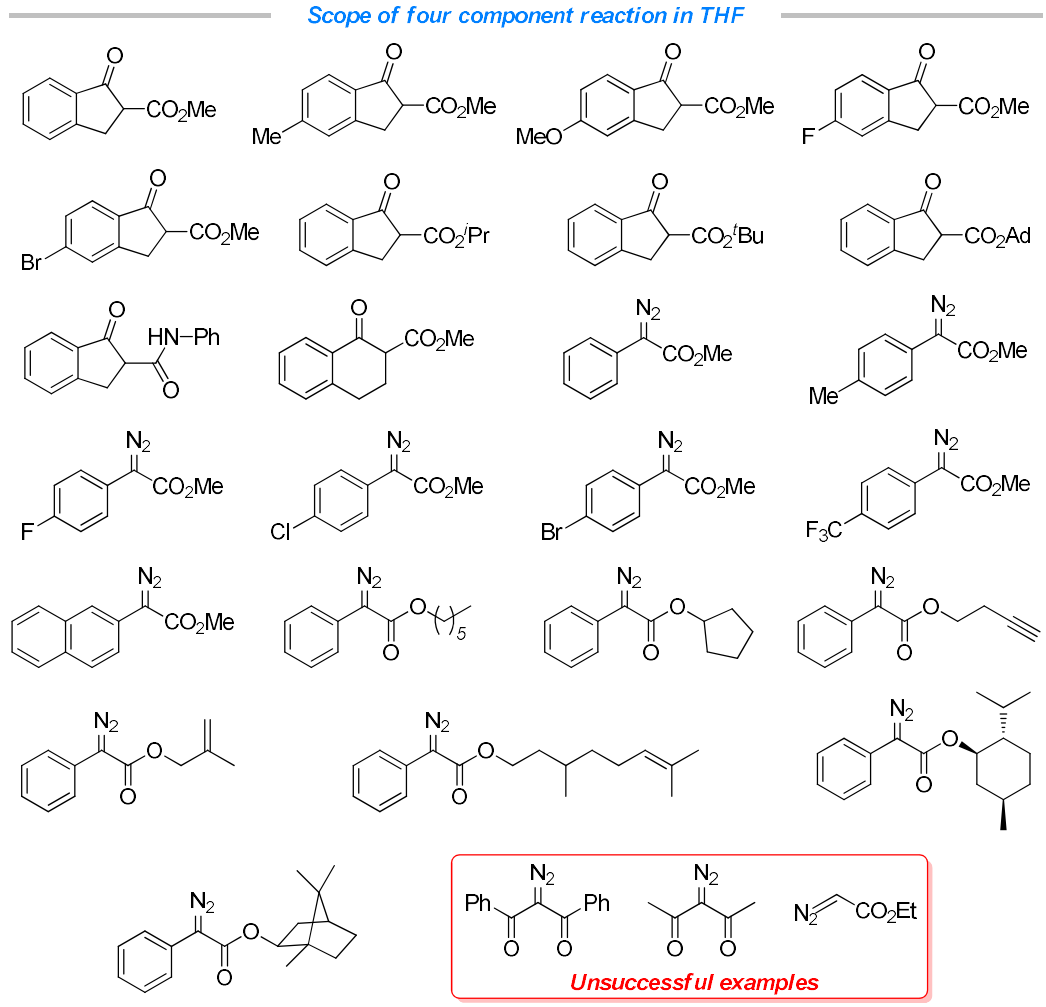
Reference:

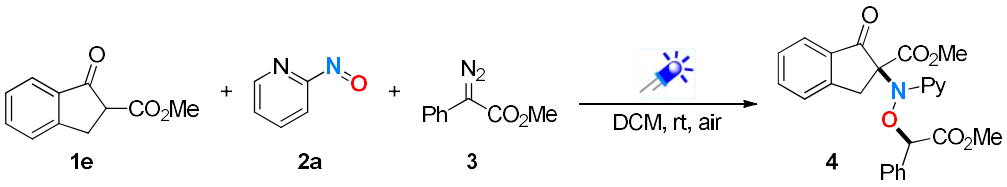
1. E. N. Bess, D. M. Guptill, H. M. L. Davies, M. S. Sigman, *Chem. Sci.* **2015**, *6*, 3057.
2. X. Cheng, B.-G. Cai,, H. Mao, J. Lu, L. Li, K. Wang, J. Xuan, *Org. Lett.* **2021**, *23*, 4109.
3. C. Ye, B.-G. Cai, J. Lu, X. Cheng, L. Li, Z.-W. Pan, J. Xuan, *J. Org. Chem.* **2021**, *86*, 1012.
4. B.-G. Cai, S.-S. Luo, L. Li, L. Li, J. Xuan, W.-J. Xiao, *CCS Chem.* **2020**, *2*, 2764.
5. S. Jones, P. Zhao, *Tetrahedron: Asymmetry*. **2014**, *25*, 238.
6. W. Lin, A. Gupta, K. H. Kim, D. Mendel, M. J. Miller, *Org. Lett.* **2009**, *11*, 449.

3. General Procedure and Spectral Data of Products

Scope of three component reaction in DCM

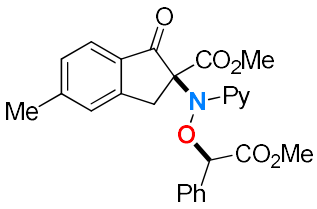






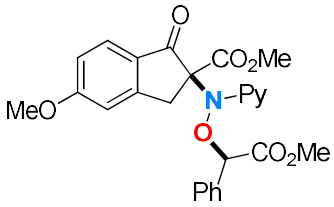
General procedure (*GP1*): To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1e** (0.1 mmol), **2a** (0.1 mmol), **3** (0.15 mmol), dry DCM (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 w blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **4** as a yellow oil in 91% yield (40.6 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 – 7.95 (m, 1H), 7.63 – 7.18 (m, 11H), 6.92 – 6.72 (m, 1H), 6.04 (s, 0.5 H), 5.98 (s, 0.5 H), 4.06 (dd, *J* = 39.1, 17.1 Hz, 1H), 3.77 – 3.57 (m, 6H), 3.20 (dd, *J* = 48.0, 17.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.4, 195.3, 171.1, 169.9, 167.6, 167.2, 160.8, 153.3, 152.7, 145.9, 145.7, 137.6, 137.4, 135.7, 135.6, 135.2, 134.9, 134.4, 134.4, 129.1, 128.8, 128.7, 128.3, 128.2, 127.7, 127.5, 127.3, 126.3, 125.9, 124.9, 124.8, 118.6, 118.1, 113.8, 112.7, 87.4, 86.3, 81.3, 81.2, 53.2, 53.1, 52.1, 52.0, 34.9, 34.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}N_2O_6$: 447.1551; Found: 447.1544.

Methyl 2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-5-methyl-1-oxo-2,3 -dihydro-1*H*-indene-2-carboxylate (6)



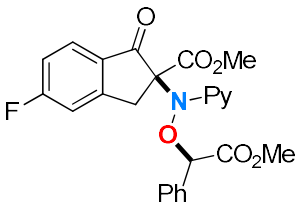
According to *GP1* with β-keto ester (20.4 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **6** and as a yellow oil in 74% yield (34.1 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.05 (d, *J* = 5.0 Hz, 1H), 7.69 – 7.03 (m, 10H), 6.91 – 6.73 (m, 1H), 6.05 (s, 0.5 H), 5.98 (s, 0.5 H), 4.00 (dd, *J* = 46.9, 17.1 Hz, 1H), 3.78 – 3.58 (m, 6H), 3.14 (dd, *J* = 55.8, 17.1 Hz, 1H), 2.40 (d, *J* = 28.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.1, 195.1, 171.4, 170.1, 167.9, 167.6, 161.1, 154.2, 153.4, 147.3, 146.9, 146.1, 146.0, 137.8, 137.6, 136.0, 135.1, 132.3, 132.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 128.0, 126.9, 126.5, 125.0, 124.9, 118.7, 118.2, 114.0, 112.8, 87.6, 86.4, 81.8, 81.6, 53.4, 53.3, 52.3, 52.1, 34.9, 34.7, 22.4, 22.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_6$: 461.1707; Found: 461.1696.

Methyl 5-methoxy-2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (7)



According to *GP1* with β-keto ester (22.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **7** and as a yellow oil in 63% yield (30.2 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.12 – 8.03 (m, 1H), 7.73 – 7.21 (m, 8H), 6.94 – 6.74 (m, 3H), 6.06 (s, 0.5H), 5.98 (s, 0.5H), 4.07 (d, *J* = 17.0 Hz, 1H), 3.88 – 3.60 (m, 9H), 3.13 (dd, *J* = 59.1, 17.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.6, 193.7, 171.3, 170.0, 167.8, 167.7, 166.1, 165.9, 161.0, 156.6, 156.2, 146.0, 145.9, 137.6, 137.4, 135.9, 134.9, 129.1, 128.8, 128.7, 128.3, 127.8, 127.6, 126.8, 126.7, 118.6, 118.0, 116.0, 115.8, 114.0, 112.7, 109.3, 108.9, 87.5, 86.1, 81.7, 81.4, 55.6, 55.6, 53.2, 53.1, 52.1, 52.0, 35.0, 34.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_7$: 477.1656; Found: 477.1637.

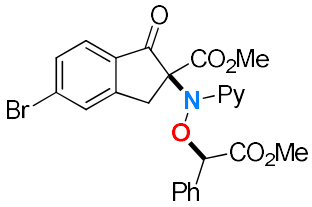
Methyl 5-fluoro-2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1*H*-indene-2-carboxylate (8)



According to *GP1* with β-keto ester (20.8 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **8** and as a yellow oil in 82% yield (38.0 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.03 (s, 1H), 7.81 – 7.23 (m, 8H), 7.13 – 6.76 (m, 3H), 6.01 (s, 0.5H), 5.97 (s, 0.5H) 4.06 (dd, *J* = 37.7, 17.4 Hz, 1H), 3.68 (dd, *J* = 35.1, 29.3 Hz, 6H), 3.19 (dd, *J* = 47.3, 17.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.7, 171.1, 169.9, 168.9, 168.6, 167.4, 167.1, 166.0, 160.7, 156.4, 155.7, 145.9, 145.7, 137.8, 137.5, 135.7, 134.9, 130.8, 129.1, 128.8, 128.7, 128.5, 128.3, 128.1, 127.6, 127.4, 127.3, 127.2, 127.1, 126.5, 118.8, 118.3, 116.1, 115.9, 115.8, 115.6, 113.9, 113.2, 113.0, 112.8, 112.7, 112.6,

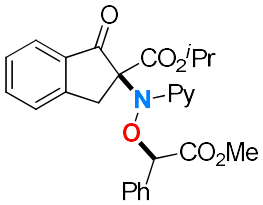
87.4, 86.4, 81.4, 81.3, 53.3, 53.2, 52.1, 52.0, 34.8, 34.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}FN_2O_6$: 465.1456; Found: 465.1430.

Methyl 5-bromo-2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1*H*-indene-2-carboxylate (9)



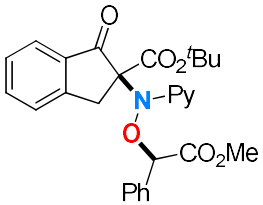
According to *GP1* with β-keto ester (26.8 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **9** and as a yellow oil in 72% yield (37.6 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 18.9 Hz, 1H), 7.65 – 7.26 (m, 10H), 6.82 (d, *J* = 30.7 Hz, 1H), 6.01 (s, 1H), 4.05 (dd, *J* = 33.7, 17.4 Hz, 1H), 3.76 – 3.59 (m, 6H), 3.19 (dd, *J* = 46.1, 17.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.0, 169.9, 167.3, 166.9, 160.6, 154.7, 154.0, 145.9, 145.6, 137.8, 137.5, 135.6, 135.0, 133.4, 133.3, 131.2, 130.9, 129.6, 129.2, 129.1, 128.9, 128.7, 128.4, 128.0, 127.6, 126.0, 125.9, 118.8, 118.3, 113.8, 112.8, 87.4, 86.6, 81.1, 77.3, 53.3, 53.2, 52.1, 52.1, 34.5, 34.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}BrN_2O_6$: 525.0656; Found: 525.0625.

Isopropyl 2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1*H*-indene-2-carboxylate (10)



According to *GP1* with β-keto ester (21.8 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **10** and as a yellow oil in 75% yield (35.4 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (s, 1H), 7.81 – 7.22 (m, 11H), 6.80 (d, *J* = 45.2 Hz, 1H), 6.07 (s, 0.5H), 6.03 (s, 0.5H), 5.07 – 4.94 (m, 1H), 4.05 (dd, *J* = 36.7, 17.2 Hz, 1H), 3.63 (d, *J* = 29.2 Hz, 3H), 3.18 (dd, *J* = 35.2, 17.2 Hz, 1H), 1.27 (d, *J* = 7.7 Hz, 3H), 1.12 – 1.06 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.1, 169.9, 166.3, 166.0, 160.7, 153.4, 152.8, 145.6, 145.4, 137.4, 137.0, 135.5, 135.4, 134.9, 134.6, 134.4, 129.0, 128.6, 128.5, 128.2, 127.6, 127.3, 127.1, 126.1, 125.7, 124.7, 124.6, 118.4, 117.8, 113.7, 112.5, 86.8, 86.2, 81.2, 81.2, 69.5, 69.4, 52.0, 51.9, 35.1, 35.0, 21.3, 21.3, 20.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}N_2O_6$: 475.1864; Found: 475.1840.

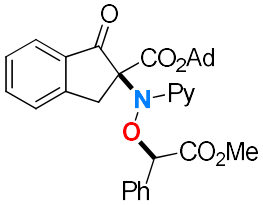
Tert-butyl 2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1*H*-indene-2-carboxylate (11)



According to *GP1* with β-keto ester (23.2 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **11** and as a yellow oil in 78% yield (38.3 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (s, 1H), 7.80 – 7.24 (m, 11H), 6.79 (d, *J* = 43.2 Hz, 1H), 6.11 (s, 0.5H), 6.04 (s, 0.5H), 4.01 (dd, *J* = 42.6, 17.1 Hz, 1H), 3.63 (d, *J* = 18.4 Hz, 3H), 3.13 (dd, *J* = 33.1, 17.2 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.7, 171.2, 170.0, 165.7, 165.3, 161.0, 160.9, 153.6, 152.9, 145.7, 145.5, 137.3, 137.1, 135.5, 135.4, 135.0,

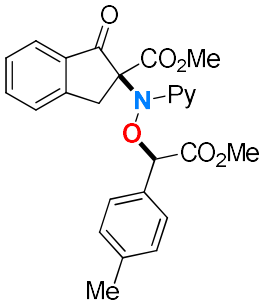
134.9, 134.6, 129.0, 128.8, 128.7, 128.6, 128.4, 127.8, 127.3, 127.1, 126.1, 125.7, 124.7, 124.6, 118.3, 117.8, 113.7, 112.4, 86.8, 86.3, 82.0, 81.9, 81.8, 52.0, 51.9, 35.4, 35.3, 27.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{29}N_2O_6$: 489.2020; Found: 489.1994.

Adamantan-1-yl 2-((2-methoxy-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1*H*-indene-2-carboxylate (12)



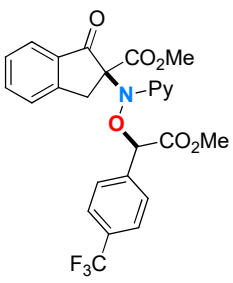
According to *GP1* with β-keto ester (31.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **12** and as a yellow oil in 89% yield (50.1 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.03 (d, *J* = 16.7 Hz, 1H), 7.80 – 7.24 (m, 11H), 6.78 (d, *J* = 38.3 Hz, 1H), 6.12 (s, 0.5H), 6.05 (s, 0.5H), 4.00 (dd, *J* = 39.1, 17.2 Hz, 1H), 3.63 (d, *J* = 21.1 Hz, 3H), 3.13 (dd, *J* = 30.0, 17.2 Hz, 1H), 2.07 (d, *J* = 20.7 Hz, 9H), 1.59 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.6, 171.1, 170.0, 165.3, 164.9, 160.8, 153.5, 152.8, 145.7, 145.5, 137.3, 137.0, 135.5, 135.3, 135.1, 134.9, 134.8, 134.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.8, 127.3, 127.0, 126.0, 125.6, 124.7, 124.5, 118.3, 117.7, 113.7, 112.4, 86.7, 86.3, 81.9, 81.9, 81.8, 51.9, 51.9, 40.6, 36.0, 35.4, 35.3, 30.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{35}N_2O_6$: 567.2490; Found: 567.2466.

Methyl 2-((2-methoxy-2-oxo-1-(p-tolyl)ethoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1H-indene-2-carboxylate (13)



According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (28.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **13** and as a yellow oil in 82% yield (37.7 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (d, *J* = 11.9 Hz, 1H), 7.79 – 7.03 (m, 10H), 6.90 – 6.73 (m, 1H), 6.01 (s, 0.5H), 5.94 (s, 0.5H), 4.05 (dd, *J* = 44.0, 17.1 Hz, 1H), 3.67 (dd, *J* = 41.0, 31.7 Hz, 6H), 3.19 (dd, *J* = 51.7, 17.1 Hz, 1H), 2.31 (d, *J* = 24.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.5, 171.3, 170.1, 167.6, 160.9, 153.4, 152.7, 145.9, 145.7, 139.0, 138.8, 137.6, 137.4, 135.6, 135.2, 134.5, 134.4, 132.7, 131.9, 129.4, 129.1, 128.1, 127.7, 127.5, 127.2, 126.3, 125.9, 124.9, 124.8, 118.6, 118.1, 113.9, 112.7, 87.2, 86.1, 81.4, 81.2, 53.2, 53.1, 52.0, 51.9, 34.9, 34.7, 21.2, 21.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_6$: 461.1707; Found: 461.1680.

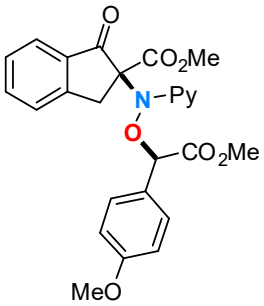
Methyl 2-((2-methoxy-2-oxo-1-(4-(trifluoromethyl)phenyl)ethoxy)(pyridin-2-yl) amino)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (14)



According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (36.6 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **14** and as a yellow oil in 47% yield (24.1 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.21 (m, 10H), 6.93 (s, 0.5H), 6.82 (s,

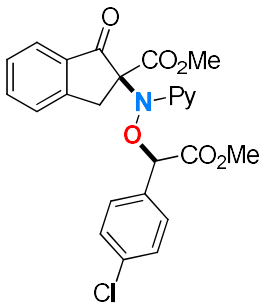
0.5H), 6.07 (d, J = 11.0 Hz, 1H), 4.15 – 4.03 (m, 1H), 3.77 – 3.60 (m, 6H), 3.23 (dd, J = 42.1, 17.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.6, 169.4, 167.3, 167.1, 160.6, 153.4, 153.1, 146.2, 146.1, 139.5, 139.0, 137.9, 137.6, 135.8, 135.6, 134.4, 134.2, 128.5, 127.8, 127.6, 127.4, 126.9, 126.4, 126.0, 125.7, 125.7, 125.2, 125.0, 124.7, 119.0, 118.5, 113.9, 112.6, 86.6, 85.9, 81.3, 81.2, 53.3, 53.2, 52.4, 52.3, 34.9, 34.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}F_3N_2O_6$: 515.1424; Found: 515.1402.

Methyl 2-((2-methoxy-1-(4-methoxyphenyl)-2-oxoethoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (15)



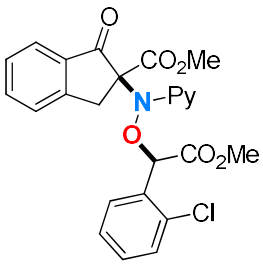
According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (30.9 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **15** and as a yellow oil in 91% yield (43.2 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, J = 9.6 Hz, 1H), 7.76 – 7.24 (m, 8H), 6.79 (dd, J = 46.1, 6.6 Hz, 3H), 5.97 (s, 0.5H), 5.90 (s, 0.5H), 4.03 (dd, J = 45.6, 17.1 Hz, 1H), 3.75 – 3.67 (m, 6H), 3.59 (d, J = 30.4 Hz, 3H), 3.15 (dd, J = 50.5, 17.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.4, 171.3, 170.0, 167.5, 167.2, 160.9, 160.1, 159.9, 153.4, 152.7, 145.9, 145.6, 137.6, 137.4, 135.6, 135.2, 134.4, 134.3, 129.7, 129.3, 127.8, 127.5, 127.2, 126.3, 125.9, 124.8, 124.7, 118.5, 118.0, 114.0, 113.7, 112.6, 86.7, 85.7, 81.3, 81.1, 55.1, 55.1, 53.1, 53.1, 52.0, 51.8, 34.9, 34.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_7$: 477.1656; Found: 477.1634.

Methyl 2-((1-(4-chlorophenyl)-2-methoxy-2-oxoethoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (16)



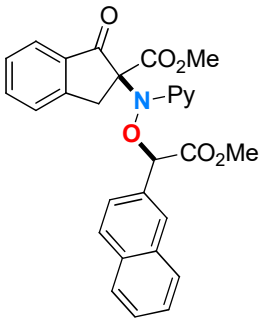
According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (31.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **16** and as a yellow oil in 84% yield (40.3 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.05 (s, 1H), 7.80 – 7.16 (m, 10H), 6.85 (d, J = 37.9 Hz, 1H), 6.02 (s, 0.5H), 5.97 (s, 0.5H), 4.06 (dd, J = 32.4, 17.1 Hz, 1H), 3.67 (dd, J = 35.5, 30.7 Hz, 6H), 3.19 (dd, J = 44.7, 17.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.4, 170.8, 169.5, 167.3=4, 167.1, 160.7, 153.3, 152.9, 146.1, 145.8, 137.7, 137.5, 135.7, 135.4, 135.1, 134.7, 134.3, 134.1, 133.5, 129.6, 129.0, 128.9, 128.6, 128.5, 127.9, 127.5, 127.3, 126.3, 125.9, 124.9, 124.7, 118.8, 118.3, 113.8, 112.5, 86.4, 85.6, 81.2, 53.2, 53.1, 52.2, 52.1, 34.9, 34.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_6$: 481.1161; Found: 481.1144.

Methyl 2-((1-(2-chlorophenyl)-2-methoxy-2-oxoethoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (17)



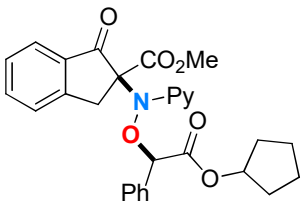
According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (31.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **17** and as a yellow oil in 52% yield (24.9 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (d, *J* = 18.9 Hz, 1H), 7.80 – 7.06 (m, 10H), 6.87 (s, 0.5H), 6.79 (s, 0.5H), 6.38 (s, 1H), 4.07 (t, *J* = 15.3 Hz, 1H), 3.76 – 3.59 (m, 6H), 3.23 (t, *J* = 19.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.4, 169.3, 167.7, 167.4, 160.9, 153.2, 152.5, 146.1, 145.8, 137.7, 137.6, 135.6, 135.1, 134.7, 134.5, 134.1, 133.8, 133.6, 133.4, 130.9, 130.3, 129.9, 129.9, 129.6, 129.4, 127.5, 127.3, 127.2, 126.7, 126.3, 125.9, 125.0, 124.8, 118.7, 118.2, 113.6, 112.1, 84.5, 83.3, 81.4, 81.0, 53.2, 53.2, 52.3, 52.2, 34.9, 34.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_6$: 481.1161; Found: 481.1133.

Methyl 2-((2-methoxy-1-(naphthalen-2-yl)-2-oxoethoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (18)



According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (33.9 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **18** and as a yellow oil in 70% yield (34.5 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.04 – 7.41 (m, 12H), 7.33 – 6.52 (m, 3H), 6.72 (s, 0.5H), 6.59 (s, 0.5H), 6.21 (d, *J* = 2.5 Hz, 1H), 4.09 (dd, *J* = 37.2, 17.2 Hz, 1H), 3.78 – 3.58 (m, 6H), 3.25 (dd, *J* = 49.7, 17.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 197.4, 171.2, 170.0, 167.6, 167.2, 160.8, 153.4, 152.7, 145.9, 145.7, 137.7, 137.5, 135.7, 135.2, 134.4, 133.4, 133.2, 133.1, 133.0, 132.8, 132.4, 128.6, 128.3, 128.2, 128.0, 127.6, 127.5, 127.5, 127.3, 127.2, 126.6, 126.5, 126.4, 126.3, 126.3, 126.1, 125.8, 125.1, 124.9, 124.8, 124.7, 118.7, 118.2, 113.9, 112.8, 87.6, 86.5, 81.3, 81.2, 53.2, 53.1, 52.2, 52.0, 34.9, 34.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}N_2O_6$: 497.1707; Found: 497.1684.

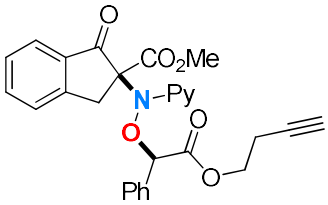
Methyl 2-((2-(cyclopentyloxy)-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (19)



According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (34.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **19** and as a yellow oil in 75% yield (37.6 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (s, 1H), 7.79 – 7.19 (m, 11H), 6.86 (s, 0.5H), 6.75 (s, 0.5H), 5.95 (d, *J* = 11.4 Hz, 1H), 5.12 (d, *J* = 40.1 Hz, 1H), 4.07 (dd, *J* = 28.8, 17.1 Hz, 1H), 3.70 (d, *J* = 47.8 Hz, 3H), 3.21 (dd, *J* = 45.7, 17.1 Hz, 1H), 1.83 – 1.42 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.3, 169.2, 167.5, 167.2, 160.8, 153.2, 152.7, 145.8, 145.7, 137.6, 137.3, 136.1, 135.5, 135.3, 135.1, 134.4, 134.4, 128.8, 128.5, 128.4, 128.1, 128.0, 127.5, 127.4, 127.2, 126.2, 125.8, 124.9, 124.7, 118.5, 118.0, 113.8, 112.7, 87.4,

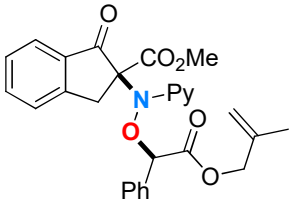
86.6, 81.3, 81.1, 78.1, 78.0, 53.1, 53.1, 34.8, 34.7, 32.4, 32.3, 32.3, 32.2, 32.0, 23.5, 23.4, 23.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{29}N_2O_6$: 501.2020; Found: 501.1996.

Methyl 2-((2-(but-3-yn-1-yloxy)-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (20)



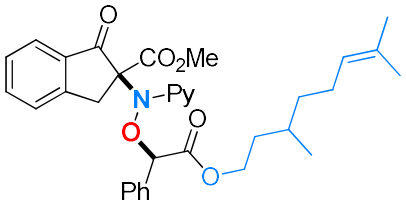
According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (32.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **20** and as a yellow oil in 63% yield (30.6 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.03 (s, 1H), 7.65 – 7.22 (m, 11H), 6.82 (d, *J* = 38.6 Hz, 1H), 6.05 (s, 0.5H), 5.99 (s, 0.5H), 4.25 – 3.98 (m, 3H), 3.71 (d, *J* = 39.3 Hz, 3H), 3.21 (dd, *J* = 49.6, 17.1 Hz, 1H), 2.41 (dt, *J* = 33.6, 7.3 Hz, 2H), 1.92 – 1.86 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.4, 169.2, 167.5, 167.1, 160.8, 153.4, 152.7, 145.9, 145.7, 137.6, 137.4, 135.7, 135.6, 135.2, 134.9, 134.4, 134.3, 129.1, 128.7, 128.7, 128.3, 128.1, 127.6, 127.6, 127.3, 126.5, 126.3, 125.9, 124.9, 124.8, 118.7, 118.2, 113.8, 112.7, 87.4, 86.4, 81.3, 81.3, 79.4, 79.3, 70.0, 69.9, 63.4, 62.6, 62.5, 53.2, 53.1, 34.8, 34.7, 18.6, 18.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}N_2O_6$: 485.1707; Found: 485.1683.

Methyl 2-((2-((2-methylallyl)oxy)-2-oxo-1-phenylethoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (21)



According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (32.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **21** and as a yellow oil in 64% yield (31.0 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (s, 1H), 7.77 – 7.23 (m, 11H), 6.90 (s, 0.5H), 6.77 (s, 0.5H), 6.05 (d, *J* = 22.3 Hz, 1H), 4.79 (d, *J* = 12.2 Hz, 2H), 4.44 (d, *J* = 55.8 Hz, 2H), 4.07 (dd, *J* = 31.9, 17.1 Hz, 1H), 3.71 (d, *J* = 39.3 Hz, 3H), 3.21 (dd, *J* = 48.6, 17.2 Hz, 1H), 1.58 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.4, 169.1, 167.6, 167.3, 160.9, 153.3, 152.8, 145.9, 145.7, 139.3, 139.2, 137.7, 137.4, 135.9, 135.6, 135.2, 134.5, 134.4, 129.0, 128.7, 128.7, 128.5, 128.3, 128.2, 127.7, 127.5, 127.3, 126.5, 126.3, 125.9, 125.0, 124.8, 118.6, 118.2, 113.9, 113.0, 112.9, 112.8, 87.3, 86.5, 81.3, 81.3, 68.1, 67.9, 53.2, 53.1, 34.9, 34.8, 19.1, 19.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}N_2O_6$: 487.1864; Found: 487.1844.

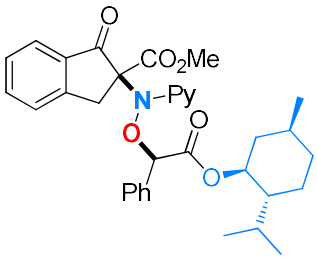
Methyl 2-((2-((3,7-dimethyloct-6-en-1-yl)oxy)-2-oxo-1-phenylethoxy)(pyridin-2-yl) amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (22)



According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (45.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **22** and as a yellow oil in 60% yield (34.2 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (s, 1H), 7.82 – 7.45 (m, 5H), 7.33 (d, *J* = 9.8 Hz, 4H), 7.21 (d, *J* =

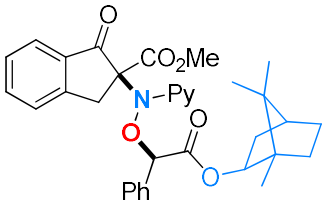
6.6 Hz, 2H), 6.82 (d, *J* = 34.9 Hz, 1H), 5.99 (d, *J* = 15.5 Hz, 1H), 5.04 (d, *J* = 7.7 Hz, 1H), 4.10 (d, *J* = 15.0 Hz, 2H), 3.77 (d, *J* = 10.4 Hz, 2H), 3.66 (s, 2H), 3.21 (dd, *J* = 48.4, 17.2 Hz, 1H), 1.94 – 1.81 (m, 2H), 1.67 (s, 3H), 1.57 (s, 3H), 1.24 (t, *J* = 56.2 Hz, 5H), 0.80 (t, *J* = 9.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.9, 169.6, 167., 167.3, 160.9, 153.3, 152.8, 145.8, 145.7, 137.6, 137.4, 136.0, 135.6, 135.4, 135.2, 134.4, 131.1, 128.9, 128.6, 128.4, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 126.5, 126.4, 126.3, 125.9, 124.9, 124.8, 124.6, 124.5, 124.5, 118.6, 118.1, 113.9, 112.8, 87.4, 86.6, 81.3, 81.2, 63.6, 63.5, 53.2, 53.1, 53.1, 52.7, 36.8, 36.8, 35.1, 35.0, 35.0, 34.8, 34.7, 30.2, 29.2, 25.6, 25.3, 19.1, 19.1, 19.0, 17.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{39}N_2O_6$: 571.2803; Found: 571.2777.

Methyl 2-((2-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxo-1 -phenylethoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (23)



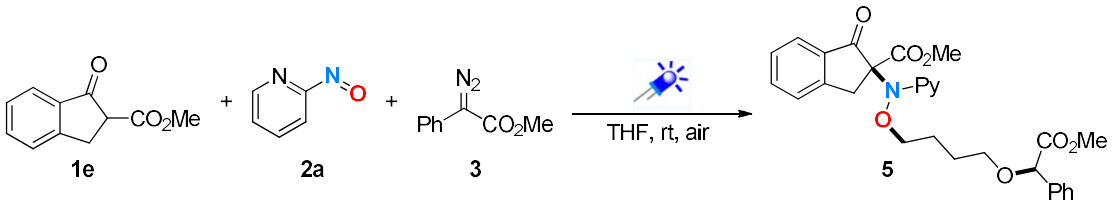
According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (45.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **23** and as a yellow oil in 62% yield (35.3 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.03 (s, 1H), 7.78 – 7.17 (m, 11H), 6.80 (d, *J* = 49.7 Hz, 1H), 6.07 – 5.91 (m, 1H), 4.74 – 4.47 (m, 1H), 4.15 – 3.98 (m, 1H), 3.78 – 3.60 (m, 3H), 3.21 (dd, *J* = 45.7, 17.2 Hz, 1H), 2.22 – 1.89 (m, 1H), 1.66 – 1.34 (m, 3H), 1.27 – 0.70 (m, 10H), 0.62 – 0.29 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.1, 167.6, 167.3, 160.9, 153.4, 145.8, 145.8, 137.6, 137.5, 137.4, 137.3, 136.2, 135.6, 135.5, 135.1, 134.4, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 128.0, 127.7, 127.5, 127.4, 127.3, 127.2, 126.3, 126.2, 125.9, 125.8, 125.0, 124.9, 124.7, 118.5, 118.0, 114.1, 113.7, 112.7, 112.6, 87.6, 87.1, 86.8, 86.7, 81.4, 81.3, 81.0, 75.3, 75.1, 74.9, 53.1, 53.1, 45.0, 46.8, 46.6, 40.8, 40.6, 40.0, 39.8, 35.0, 34.9, 34.7, 34.1, 34.0, 31.3, 31.3, 31.2, 31.1, 25.6, 25.4, 25.2, 23.1, 23.0, 22.8, 22.1, 21.9, 21.8, 20.8, 20.4, 20.3, 16.1, 15.8, 15.6, 15.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{39}N_2O_6$: 571.2803; Found: 571.2786.

Methyl 1-oxo-2-((2-oxo-1-phenyl-2-(((1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan -2-yl)oxy)ethoxy)(pyridin-2-yl)amino)-2,3-dihydro-1H-indene-2-carboxylate (24)



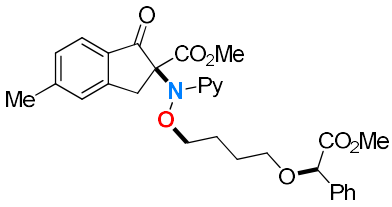
According to *GP1* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (44.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL DCM for 12 h. Purification by silica gel chromatography afforded the desired **24** and as a yellow oil in 71% yield (40.1 mg, d.r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (s, 1H), 7.79 – 7.19 (m, 11H), 6.81 (d, *J* = 35.0 Hz, 1H), 6.03 (d, *J* = 8.5 Hz, 1H), 4.98 – 4.69 (m, 1H), 4.08 (t, *J* = 17.2 Hz, 1H), 3.69 (d, *J* = 52.9 Hz, 3H), 3.23 (dd, *J* = 44.8, 17.1 Hz, 1H), 2.39 – 2.09 (m, 1H), 1.92 – 1.04 (m, 6H), 0.81 (d, *J* = 11.5 Hz, 7H), 0.57 – 0.42 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.1, 167.6, 167.3, 160.8, 145.8, 145.6, 137.8, 137.7, 137.5, 136.2, 135.5, 135.1, 134.5, 128.8, 128.6, 128.4, 128.2, 128.1, 127.9, 127.5, 127.4, 127.4, 127.2, 127.2, 126.2, 125.9, 125.9, 125.0, 124.8, 118.6, 118.1, 113.9, 112.9, 112.8, 87.5, 87.2, 86.9, 81.3, 81.0, 80.6, 53.2, 53.2, 53.1, 49.0, 48.8, 48.8, 48.7, 47.8, 47.7, 44.8, 44.8, 44.6, 36.1, 36.1, 36.0, 34.8,

34.8, 34.7, 34.7, 27.8, 27.7, 27.6, 27.6, 26.9, 26.8, 26.7, 19.6, 19.5, 18.8, 18.7, 18.7, 13.3, 13.2, 13.0, 12.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{37}N_2O_6$: 569.2652; Found: 569.2639.



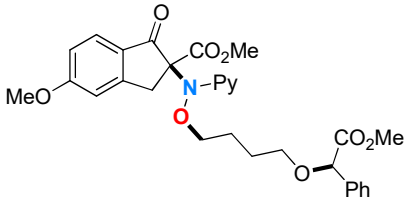
General procedure (*GP2*): To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1e** (0.1 mmol), **2a** (0.1 mmol), **3** (0.15 mmol), dry THF (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 w blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **5** as a yellow oil in 99% yield (51.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.78 (t, *J* = 9.7 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.31 (m, 7H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.87 (s, 1H), 4.79 (s, 1H), 4.33 – 4.07 (m, 3H), 3.73 (d, *J* = 33.7 Hz, 6H), 3.39 (d, *J* = 35.4 Hz, 2H), 3.07 (dd, *J* = 17.3, 9.0 Hz, 1H), 1.58 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 171.3, 167.5, 161.4, 153.3, 146.6, 137.8, 136.5, 135.6, 134.3, 128.6, 128.5, 127.6, 127.1, 126.3, 124.9, 117.8, 111.0, 111.0, 81.0, 79.8, 79.8, 75.5, 69.4, 69.3, 53.2, 52.1, 34.9, 26.0, 24.8, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{31}N_2O_7$: 519.2126; Found: 519.2090.

Methyl 2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-5-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (25)



According to *GP2* with β-keto ester (20.4 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **25** and as a colorless oil in 88% yield (46.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.63 (dt, *J* = 27.4, 8.5 Hz, 2H), 7.37 (dd, *J* = 25.1, 6.7 Hz, 5H), 7.17 (dd, *J* = 19.1, 11.6 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 4.79 (s, 1H), 4.24 (d, *J* = 55.1 Hz, 2H), 4.05 (d, *J* = 14.1 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.39 (d, *J* = 34.8 Hz, 2H), 3.02 (dd, *J* = 17.3, 8.7 Hz, 1H), 2.42 (s, 3H), 1.57 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.1, 171.3, 167.6, 161.5, 153.8, 147.0, 146.6, 137.8, 136.5, 132.0, 128.9, 128.6, 128.5, 127.0, 126.6, 124.8, 117.7, 111.0, 111.0, 80.9, 80.0, 80.0, 75.5, 69.4, 69.3, 53.2, 52.1, 34.7, 26.0, 24.7, 24.7, 22.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_7$: 533.2287; Found: 533.2260.

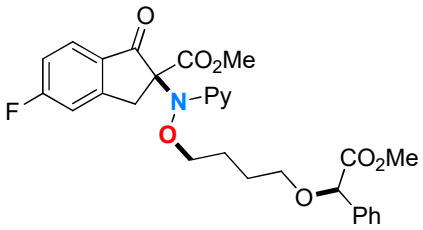
Methyl 5-methoxy-2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (26)



According to *GP2* with β-keto ester (22.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **26** and as a colorless

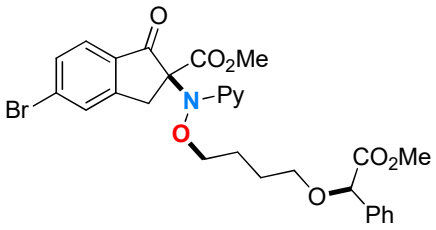
oil in 94% yield (51.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.12 (s, 1H), 7.75 – 7.67 (m, 1H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 29.4, 6.7 Hz, 5H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 3H), 4.79 (s, 1H), 4.25 (d, *J* = 62.4 Hz, 2H), 4.06 (d, *J* = 17.3 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.69 (s, 3H), 3.39 (d, *J* = 35.8 Hz, 2H), 3.02 (dd, *J* = 17.4, 8.7 Hz, 1H), 1.58 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.8, 171.3, 167.8, 166.0, 161.6, 156.4, 146.6, 137.7, 136.5, 136.5, 128.5, 128.5, 127.5, 127.0, 126.7, 117.7, 115.9, 111.1, 111.0, 109.3, 80.9, 80.0, 80.0, 75.5, 69.4, 69.3, 55.6, 53.1, 52.1, 34.9, 26.0, 24.7, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_8$: 549.2231; Found: 549.2213.

methyl 5-fluoro-2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (27)



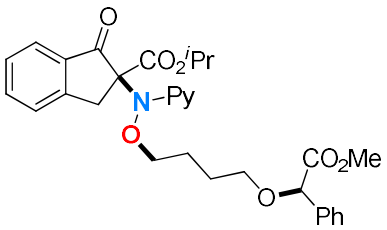
According to *GP2* with β-keto ester (20.8 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **27** and as a colorless oil in 88% yield (47.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (s, 1H), 7.79 (dt, *J* = 14.3, 6.8 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.42 – 7.31 (m, 5H), 7.05 (dd, *J* = 18.1, 8.5 Hz, 3H), 6.88 (s, 1H), 4.79 (s, 1H), 4.24 (d, *J* = 38.5 Hz, 2H), 4.09 (d, *J* = 17.3 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.40 (d, *J* = 36.8 Hz, 2H), 3.05 (dd, *J* = 17.6, 8.3 Hz, 1H), 1.58 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5, 171.3, 167.1, 161.2, 154.7, 146.6, 137.9, 136.5, 133.2, 131.3, 131.1, 129.6, 128.6, 128.6, 127.1, 126.1, 126.1, 118.0, 111.1, 111.0, 81.0, 79.9, 79.8, 75.6, 69.4, 69.3, 53.3, 52.2, 34.5, 26.0, 24.8, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}FN_2O_7$: 537.2032; Found: 537.2018.

Methyl 5-bromo-2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (28)



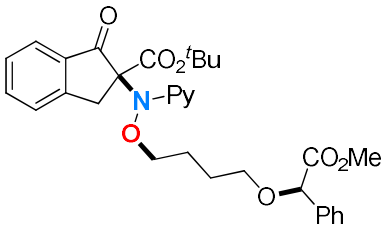
According to *GP2* with β-keto ester (26.8 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **28** and as a colorless oil in 89% yield (53.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 (s, 1H), 7.67 – 7.58 (m, 3H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.32 (m, 5H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.87 (s, 1H), 4.80 (s, 1H), 4.23 (d, *J* = 27.4 Hz, 2H), 4.07 (d, *J* = 17.3 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.41 (d, *J* = 37.0 Hz, 2H), 3.04 (dd, *J* = 17.6, 9.4 Hz, 1H), 1.58 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5, 171.3, 167.1, 161.2, 154.7, 146.6, 137.9, 136.5, 133.2, 131.3, 131.1, 129.6, 128.6, 128.6, 127.1, 126.1, 126.1, 118.0, 111.1, 111.0, 81.0, 79.9, 79.8, 75.6, 69.4, 69.3, 53.3, 52.2, 34.5, 26.0, 24.8, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}BrN_2O_7$: 597.1231; Found: 597.1204.

Isopropyl 2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1H-indene-2-carboxylate (29)



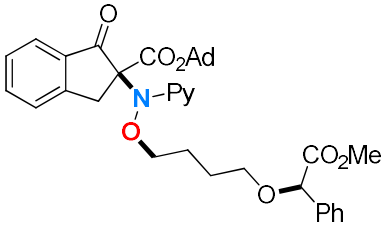
According to *GP2* with β-keto ester (21.8 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **29** and as a colorless oil in 94% yield (51.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (s, 1H), 7.78 (t, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.31 (m, 7H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 5.12 – 5.00 (m, 1H), 4.80 (s, 1H), 4.25 (d, *J* = 32.2 Hz, 2H), 4.09 (d, *J* = 17.3 Hz, 1H), 3.69 (s, 3H), 3.40 (d, *J* = 37.5 Hz, 2H), 3.05 (dd, *J* = 17.3, 7.9 Hz, 1H), 1.58 (s, 4H), 1.26 (d, *J* = 5.4 Hz, 3H), 1.13 (d, *J* = 5.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.4, 171.3, 166.3, 161.3, 153.3, 146.3, 137.6, 136.5, 135.2, 134.6, 128.5, 128.5, 127.4, 127.1, 126.1, 124.8, 117.6, 110.9, 80.9, 79.9, 75.4, 69.6, 69.4, 69.4, 52.1, 35.2, 26.0, 24.8, 24.7, 21.5, 21.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{35}N_2O_7$: 547.2439; Found: 547.2417.

Tert-butyl 2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1H-indene-2-carboxylate (30)



According to *GP2* with β-keto ester (23.2 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **30** and as a colorless oil in 91% yield (51.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.05 (s, 1H), 7.76 (t, *J* = 8.7 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.41 – 7.29 (m, 7H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 6.7 Hz, 1H), 4.79 (s, 1H), 4.22 (d, *J* = 34.2 Hz, 2H), 4.03 (d, *J* = 17.3 Hz, 1H), 3.67 (s, 3H), 3.40 (d, *J* = 34.6 Hz, 2H), 3.00 (dd, *J* = 17.3, 7.3 Hz, 1H), 1.58 (s, 4H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.5, 171.3, 165.5, 161.3, 153.2, 146.4, 137.6, 136.5, 135.1, 134.8, 128.5, 127.3, 127.1, 126.0, 124.7, 117.4, 110.7, 81.9, 80.9, 80.4, 75.4, 69.4, 69.4, 52.1, 35.4, 27.6, 26.1, 24.8, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{37}N_2O_7$: 561.2595; Found: 561.2582.

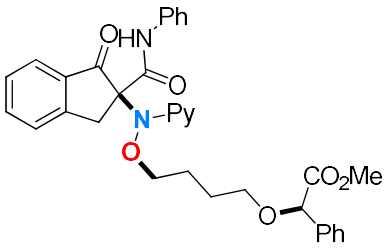
Adamantan-1-yl 2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo -2,3-dihydro-1H-indene-2-carboxylate (31)



According to *GP2* with β-keto ester (31.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **31** and as a colorless oil in 88% yield (56.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (s, 1H), 7.78 (t, *J* = 8.7 Hz, 1H), 7.56 (q, *J* = 6.8 Hz, 2H), 7.43 – 7.31 (m, 7H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.82 (s, 1H), 4.81 (s, 1H), 4.25 (d, *J* = 21.9 Hz, 2H), 4.03 (d, *J* = 17.2 Hz, 1H), 3.69 (s, 3H), 3.42 (d, *J* = 32.5 Hz, 2H), 3.01 (dd, *J* = 17.4, 6.8 Hz, 1H), 2.08 (d, *J* = 13.8 Hz, 9H), 1.60 (s, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.5, 171.4, 165.2, 161.2, 153.2, 146.4,

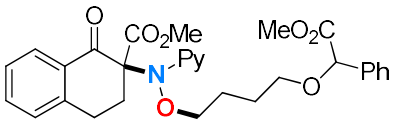
137.6, 136.5, 135.0, 134.8, 128.5, 127.3, 127.1, 126.0, 124.7, 117.4, 110.7, 82.0, 81.0, 80.6, 75.4, 69.5, 69.4, 52.1, 40.8, 36.1, 35.4, 30.8, 26.1, 24.8, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{43}N_2O_7$: 639.3065; Found: 639.3023.

Methyl 2-(4-(((1-oxo-2-(phenylcarbamoyl)-2,3-dihydro-1H-inden-2-yl)(pyridin-2-yl)amino) oxy)butoxy)-2-phenylacetate (32)



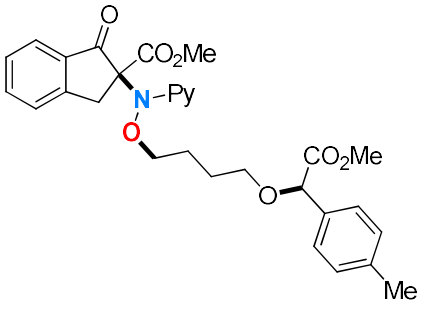
According to *GP2* with β-keto ester (25.1 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **32** and as a brown oil in 97% yield (56.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.70 (s, 1H), 8.11 (s, 1H), 7.76 (t, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 43.4, 8.0 Hz, 4H), 7.43 – 7.26 (m, 9H), 7.10 – 7.03 (m, 2H), 6.88 (s, 1H), 4.79 (s, 1H), 4.40 – 4.12 (m, 3H), 3.69 (d, *J* = 4.1 Hz, 3H), 3.41 (d, *J* = 38.7 Hz, 2H), 2.91 (d, *J* = 22.7 Hz, 1H), 1.64 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 197.3, 171.3, 163.9, 161.1, 153.8, 147.3, 138.1, 138.0, 136.5, 135.5, 134.3, 128.8, 128.6, 128.5, 127.5, 127.1, 126.3, 124.8, 124.0, 119.8, 118.4, 111.0, 81.3, 80.9, 75.6, 69.3, 69.3, 52.2, 32.8, 26.0, 24.8, 24.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{34}N_3O_7$: 580.2442; Found: 580.2425.

Methyl 2-((4-(2-methoxy-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo -1,2,3,4-tetrahydronaphthalene-2-carboxylate (33)



According to *GP2* with β-keto ester (20.4 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (26.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **33** and as a colorless oil in 92% yield (49.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.48 – 7.40 (m, 3H), 7.35 – 7.21 (m, 5H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.79 (t, *J* = 5.8 Hz, 1H), 4.82 (s, 1H), 3.96 (d, *J* = 8.1 Hz, 1H), 3.71 (d, *J* = 10.6 Hz, 7H), 3.42 (dd, *J* = 38.0, 6.2 Hz, 2H), 3.20 – 2.98 (m, 3H), 2.78 (d, *J* = 15.3 Hz, 1H), 1.64 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.8, 171.3, 169.4, 146.6, 142.9, 137.9, 136.5, 133.2, 133.0, 128.6, 128.6, 128.5, 128.1, 127.1, 126.6, 116.6, 109.0, 81.0, 77.6, 75.1, 69.4, 52.5, 52.2, 26.2, 26.0, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_7$: 533.2282; Found: 533.2253.

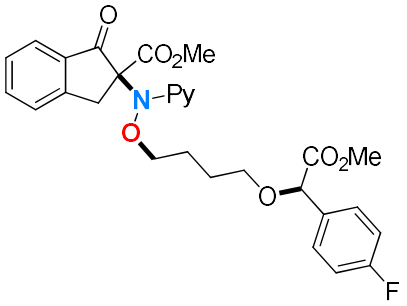
Methyl 2-((4-(2-methoxy-2-oxo-1-(p-tolyl)ethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3 -dihydro-1H-indene-2-carboxylate (34)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (28.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **34** and as a colorless oil in 87% yield (46.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (s, 1H), 7.78 (t, *J* = 9.0 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.44 – 7.32 (m, 2H), 7.28 (d, *J* = 8.3

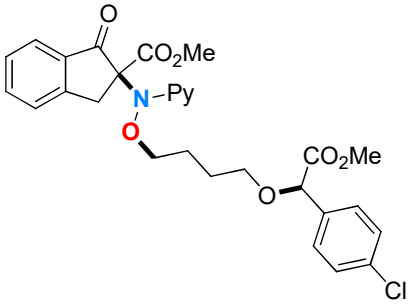
Hz, 2H), 7.15 (d, *J* = 6.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 5.7 Hz, 1H), 4.75 (s, 1H), 4.34 – 4.06 (m, 3H), 3.77 (s, 3H), 3.68 (s, 3H), 3.45 – 3.27 (m, 2H), 3.12 – 3.01 (m, 1H), 2.33 (s, 3H), 1.56 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 171.5, 167.5, 161.4, 153.3, 146.6, 138.4, 137.8, 135.6, 134.3, 133.6, 129.2, 127.6, 127.1, 126.3, 124.9, 117.8, 111.0, 111.0, 80.8, 79.9, 79.8, 75.6, 69.2, 69.2, 53.2, 52.1, 34.9, 26.0, 24.8, 24.7, 21.14. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_7$: 533.2282; Found: 533.2256.

Methyl 2-((4-(1-(4-fluorophenyl)-2-methoxy-2-oxoethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (35)



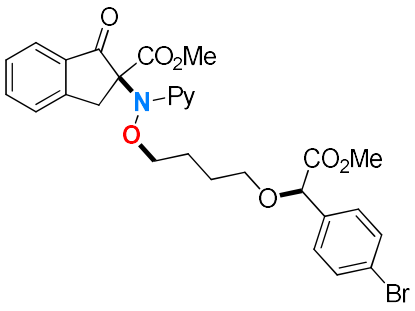
According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (29.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **35** and as a colorless oil in 94% yield (50.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.81 – 7.74 (m, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 21.7, 7.3 Hz, 4H), 7.02 (d, *J* = 7.9 Hz, 3H), 6.87 (t, *J* = 6.5 Hz, 1H), 4.76 (s, 1H), 4.35 – 4.07 (m, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.48 – 3.27 (m, 2H), 3.07 (dd, *J* = 17.5, 8.1 Hz, 1H), 1.58 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 171.2, 167.4, 164.0, 161.6, 161.4, 153.4, 146.7, 137.8, 135.6, 134.3, 132.4, 128.9, 128.8, 127.6, 126.3, 124.9, 117.8, 115.6, 115.4, 111.0, 110.9, 80.2, 79.9, 75.5, 69.4, 69.4, 53.2, 52.2, 34.9, 26.0, 24.7, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}FN_2O_7$: 537.2032; Found: 537.2014.

Methyl 2-((4-(1-(4-chlorophenyl)-2-methoxy-2-oxoethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (36)



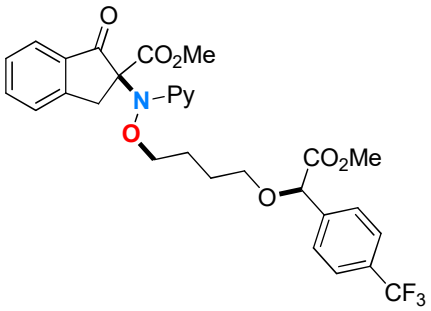
According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (29.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **36** and as a colorless oil in 86% yield (47.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (s, 1H), 7.77 (dd, *J* = 14.5, 6.5 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.44 – 7.29 (m, 6H), 7.02 (d, *J* = 11.0 Hz, 1H), 6.87 (s, 1H), 4.75 (s, 1H), 4.34 – 4.07 (m, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.38 (d, *J* = 44.2 Hz, 2H), 3.06 (dd, *J* = 17.6, 9.3 Hz, 1H), 1.57 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 171.0, 167.4, 161.4, 153.4, 146.7, 137.8, 135.6, 135.1, 134.5, 134.3, 128.7, 128.4, 127.6, 126.3, 124.9, 117.9, 111.0, 80.2, 79.9, 75.5, 69.5, 69.4, 53.2, 52.3, 34.9, 26.0, 24.7, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}ClN_2O_7$: 553.1736; Found: 553.1717.

Methyl 2-((4-(1-(4-bromophenyl)-2-methoxy-2-oxoethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (37)



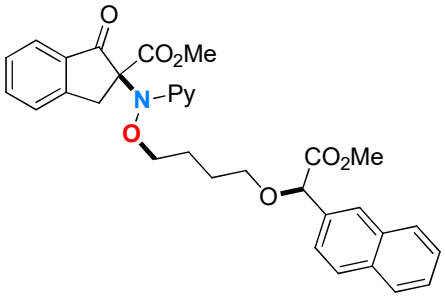
According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (38.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **37** and as a colorless oil in 88% yield (52.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.12 (s, 1H), 7.77 (dd, *J* = 15.3, 7.7 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.50 – 7.32 (m, 4H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 6.4 Hz, 1H), 4.74 (s, 1H), 4.35 – 4.07 (m, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.39 (dd, *J* = 46.5, 6.4 Hz, 2H), 3.06 (dd, *J* = 17.3, 10.2 Hz, 1H), 1.57 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 170.9, 167.4, 161.4, 153.4, 146.7, 137.8, 135.6, 134.3, 131.7, 128.7, 127.6, 126.3, 124.9, 124.9, 122.6, 117.9, 111.0, 80.3, 79.9, 79.8, 75.5, 69.5, 69.4, 53.2, 52.3, 26.0, 24.7, 24.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}BrN_2O_7$: 597.1231; Found: 597.1222.

Methyl 2-((4-(2-methoxy-2-oxo-1-(4-(trifluoromethyl)phenyl)ethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (38)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (36.6 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **38** and as a colorless oil in 75% yield (44.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.12 (s, 1H), 7.77 (dd, *J* = 17.5, 7.8 Hz, 1H), 7.63 – 7.52 (m, 6H), 7.45 – 7.32 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 3.7 Hz, 1H), 4.85 (s, 1H), 4.35 – 4.08 (m, 3H), 3.77 (s, 3H), 3.70 (d, *J* = 2.2 Hz, 3H), 3.52 – 3.45 (m, 1H), 3.34 (s, 1H), 3.12 – 2.99 (m, 1H), 1.59 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 170.7, 167.4, 161.4, 153.4, 146.7, 140.5, 137.8, 135.6, 134.3, 127.6, 127.3, 126.3, 125.5, 125.5, 124.9, 117.9, 110.9, 80.4, 79.9, 75.5, 69.8, 69.7, 53.2, 52.4, 34.9, 26.0, 24.7, 24.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{30}F_3N_2O_7$: 587.2000; Found: 587.1982.

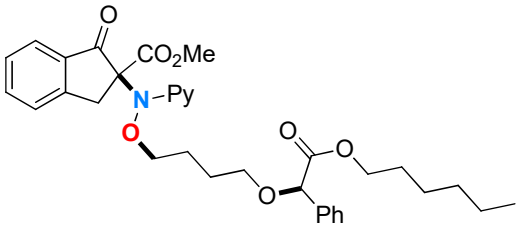
Methyl 2-((4-(2-methoxy-1-(naphthalen-2-yl)-2-oxoethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (39)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (33.9 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **39** and as a colorless oil in 88% yield (50.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.09 (s, 1H), 7.82 (q, *J* = 9.4, 7.2 Hz, 5H), 7.59 – 7.29 (m, 7H), 7.02 (d, *J* = 8.4

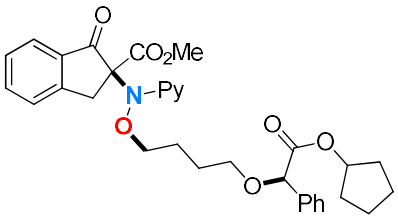
Hz, 1H), 6.84 (d, *J* = 6.6 Hz, 1H), 4.95 (s, 1H), 4.33 – 4.04 (m, 3H), 3.76 (s, 3H), 3.68 (s, 3H), 3.52 – 3.33 (m, 2H), 3.05 (t, *J* = 18.0 Hz, 1H), 1.60 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.6, 171.2, 167.4, 161.4, 153.3, 146.6, 137.8, 135.5, 134.3, 133.9, 133.3, 133.0, 128.4, 128.0, 127.6, 127.5, 126.6, 126.3, 126.3, 126.2, 124.9, 124.9, 124.4, 117.8, 111.0, 110.9, 81.1, 79.8, 79.8, 75.6, 69.4, 69.3, 53.2, 52.2, 34.9, 26.0, 24.8, 24.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{33}N_2O_7$: 569.2282; Found: 569.2263.

Methyl 2-((4-(2-(hexyloxy)-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (40)



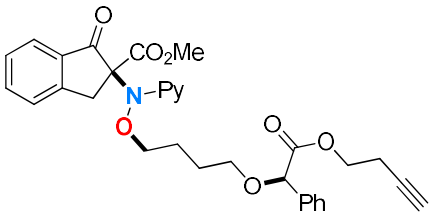
According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (36.9 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **40** and as a colorless oil in 89% yield (52.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.78 (t, *J* = 9.5 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.30 (m, 7H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 5.7 Hz, 1H), 4.77 (s, 1H), 4.33 – 4.06 (m, 5H), 3.76 (s, 3H), 3.40 (d, *J* = 39.3 Hz, 2H), 3.13 – 3.01 (m, 1H), 1.59 (d, *J* = 19.8 Hz, 6H), 1.20 (s, 6H), 0.83 (d, *J* = 7.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 171.0, 167.5, 161.4, 153.3, 146.6, 137.8, 136.7, 135.5, 134.3, 128.4, 127.6, 127.0, 127.0, 126.3, 124.9, 117.8, 111.0, 111.0, 81.0, 79.8, 75.6, 69.3, 69.3, 65.1, 53.2, 34.9, 31.2, 28.4, 26.0, 25.3, 24.8, 24.7, 22.4, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{41}N_2O_7$: 589.2908; Found: 589.2878.

Methyl 2-((4-(2-(cyclopentyloxy)-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (41)



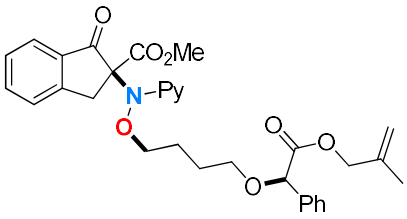
According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (34.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **41** and as a colorless oil in 81% yield (46.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.78 (t, *J* = 9.3 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.36 (dd, *J* = 25.1, 9.1 Hz, 7H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.86 (t, *J* = 6.4 Hz, 1H), 5.17 (s, 1H), 4.73 (s, 1H), 4.35 – 4.07 (m, 3H), 3.76 (s, 3H), 3.40 (d, *J* = 35.9 Hz, 2H), 3.07 (dd, *J* = 17.4, 8.8 Hz, 1H), 1.82 – 1.48 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 170.6, 167.5, 161.4, 153.3, 146.6, 137.8, 136.8, 135.5, 134.3, 128.4, 128.3, 127.5, 127.0, 126.9, 126.2, 124.9, 117.8, 111.0, 111.0, 81.0, 79.8, 77.9, 75.6, 69.3, 69.2, 53.2, 34.9, 32.4, 32.4, 26.0, 24.8, 24.8, 23.5, 23.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{37}N_2O_7$: 573.2595; Found: 573.2566.

Methyl 2-((4-(2-(but-3-yn-1-yloxy)-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (42)



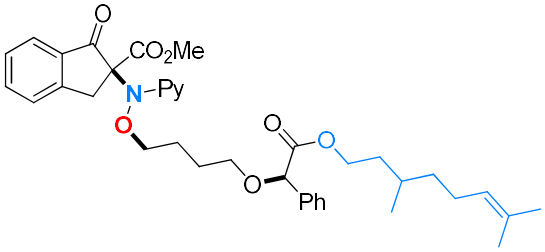
According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (32.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **42** and as a colorless oil in 97% yield (54.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.83 – 7.75 (m, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 32.8, 6.6 Hz, 7H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 6.4 Hz, 1H), 4.80 (s, 1H), 4.33 – 4.07 (m, 5H), 3.76 (s, 3H), 3.41 (d, *J* = 36.5 Hz, 2H), 3.07 (dd, *J* = 17.3, 8.9 Hz, 1H), 2.45 (s, 2H), 1.92 (d, *J* = 5.6 Hz, 1H), 1.59 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 170.7, 167.5, 161.4, 153.4, 146.7, 137.8, 136.4, 135.6, 134.3, 128.6, 128.5, 127.6, 127.1, 126.3, 124.9, 117.8, 111.0, 80.9, 79.8, 79.5, 75.6, 70.0, 69.4, 69.3, 62.6, 53.2, 34.9, 26.0, 24.8, 24.7, 18.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_7$: 557.2282; Found: 557.2260.

Methyl 2-((4-(2-((2-methylallyl)oxy)-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (43)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (32.4 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **43** and as a colorless oil in 94% yield (52.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (d, *J* = 4.8 Hz, 1H), 7.78 (t, *J* = 9.3 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.37 (dd, *J* = 36.8, 7.4 Hz, 7H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.86 (t, *J* = 4.2 Hz, 1H), 4.81 (s, 3H), 4.50 (t, *J* = 15.9 Hz, 2H), 4.34 – 4.06 (m, 3H), 3.77 (s, 3H), 3.41 (d, *J* = 38.4 Hz, 2H), 3.07 (dd, *J* = 17.5, 9.1 Hz, 1H), 1.60 (s, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 170.5, 167.5, 161.4, 153.4, 146.6, 139.4, 137.8, 136.6, 135.6, 134.4, 128.6, 128.5, 127.6, 127.1, 126.3, 124.9, 117.8, 113.0, 111.0, 81.00, 79.8, 75.6, 69.4, 69.3, 68.0, 53.2, 34.9, 26.0, 24.8, 24.7, 19.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{35}N_2O_7$: 559.2439; Found: 559.2412.

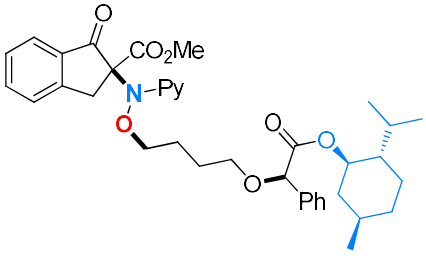
Methyl 2-((4-(2-((3,7-dimethyloct-6-en-1-yl)oxy)-2-oxo-1-phenylethoxy)butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (44)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (45.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **44** and as a colorless oil in 92% yield (59.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (s, 1H), 7.78 (t, *J* = 9.8 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.30 (m, 7H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 6.1 Hz, 1H), 5.04 (s, 1H), 4.76 (s, 1H), 4.37 – 4.05 (m, 5H), 3.76 (s, 3H), 3.39 (d, *J* = 42.0 Hz, 2H), 3.07 (dd, *J* = 17.3, 9.1 Hz,

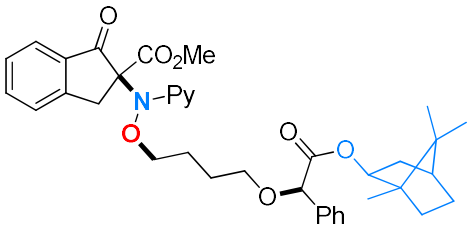
1H), 1.97 – 1.81 (m, 2H), 1.67 (s, 3H), 1.57 (s, 7H), 1.42 – 1.05 (m, 5H), 0.81 (dd, J = 7.3, 4.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 170.9, 167.5, 161.4, 153.3, 146.6, 137.8, 136.7, 135.5, 134.3, 131.2, 128.4, 127.6, 127.0, 126.3, 124.9, 124.5, 117.8, 111.0, 81.0, 79.8, 69.3, 69.3, 63.6, 53.2, 36.8, 36.8, 35.3, 34.9, 29.3, 29.3, 26.0, 25.6, 25.3, 24.8, 24.7, 19.2, 19.1, 17.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{47}N_2O_7$: 643.3378; Found: 643.3354.

Methyl 2-((4-(2-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxo-1-phenylethoxy) butoxy)(pyridin-2-yl)amino)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (45)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (45.1 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **45** and as a colorless oil in 98% yield (63.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (s, 1H), 7.78 (t, *J* = 9.3 Hz, 1H), 7.59 (t, *J* = 7.1 Hz, 2H), 7.44 – 7.29 (m, 7H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 6.4 Hz, 1H), 4.78 – 4.56 (m, 2H), 4.36 – 4.05 (m, 3H), 3.77 (s, 3H), 3.40 (d, *J* = 35.3 Hz, 2H), 3.07 (dd, *J* = 17.3, 8.7 Hz, 1H), 1.80 – 1.54 (m, 8H), 1.48 – 1.13 (m, 3H), 1.05 – 0.80 (m, 7H), 0.64 (dd, *J* = 23.1, 4.1 Hz, 3H), 0.43 – 0.40 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.5, 167.5, 161.5, 153.4, 146.6, 137.8, 135.6, 134.4, 128.4, 128.4, 127.6, 127.2, 126.9, 126.9, 126.3, 124.9, 117.8, 111.0, 81.2, 79.9, 75.6, 75.1, 75.0, 69.3, 69.2, 53.2, 47.1, 46.9, 40.8, 40.2, 34.9, 34.1, 31.3, 31.3, 26.1, 26.1, 25.4, 24.9, 23.3, 22.9, 22.0, 21.9, 20.6, 20.5, 16.1, 15.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{47}N_2O_7$: 643.3378; Found: 643.3354.

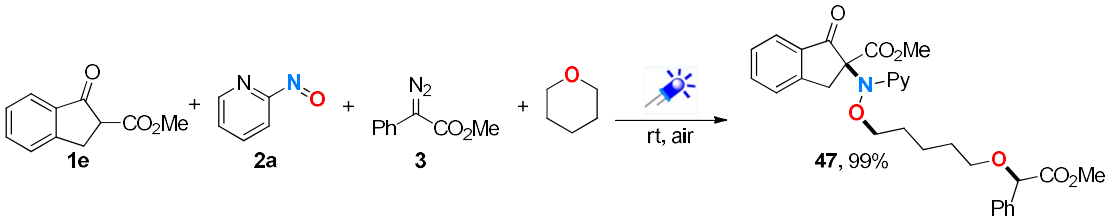
Methyl 1-oxo-2-((4-(2-oxo-1-phenyl-2-(((4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy) ethoxy)butoxy)(pyridin-2-yl)amino)-2,3-dihydro-1H-indene-2-carboxylate (46)



According to *GP2* with β-keto ester (19.0 mg, 0.10 mmol, 1.0 equiv.), 2-nitrosopyridine (10.8 mg, 0.10 mmol, 1.0 equiv.), aryldiazoacetates (44.5 mg, 0.15 mmol, 1.5 equiv.) in 1.0 mL THF for 12 h. Purification by silica gel chromatography afforded the desired **46** and as a colorless oil in 94% yield (60.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (s, 1H), 7.84 – 7.73 (m, 1H), 7.66 – 7.54 (m, 2H), 7.44 – 7.29 (m, 7H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.86 (s, 1H), 4.94 – 4.82 (m, 1H), 4.79 (s, 1H), 4.35 – 4.06 (m, 3H), 3.77 (s, 3H), 3.42 (d, *J* = 33.2 Hz, 2H), 3.07 (dd, *J* = 17.4, 8.9 Hz, 1H), 2.28 (dd, *J* = 26.9, 16.2 Hz, 1H), 1.86 – 1.57 (m, 7H), 1.29 – 1.11 (m, 2H), 0.96 – 0.79 (m, 8H), 0.56 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 171.2, 171.1, 167.5, 161.4, 153.4, 146.6, 137.8, 137.1, 136.9, 135.5, 134.4, 128.4, 128.3, 127.6, 127.1, 127.0, 126.9, 126.9, 126.3, 124.9, 117.8, 111.0, 81.2, 81.1, 80.7, 80.4, 79.8, 69.3, 53.2, 48.9, 48.7, 47.8, 44.8, 44.6, 36.4, 36.4, 34.9, 27.9, 27.7, 27.0, 26.8, 26.1, 24.8, 19.6, 18.7, 13.4, 13.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{45}N_2O_7$: 641.3221; Found: 641.3182.

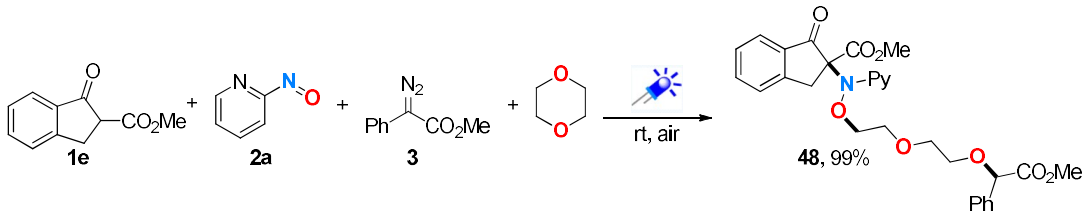
4. Follow-up chemistry

(a) Four-component trisubstituted hydroxylamines formation in tetrahydropyran



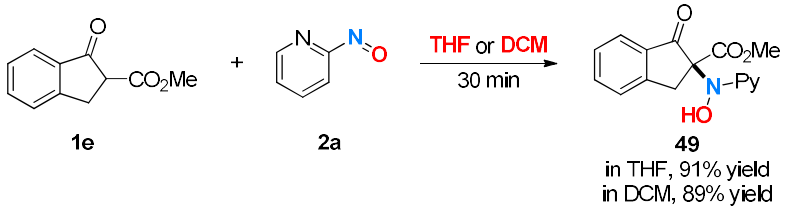
To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1e** (0.1 mmol), **2a** (0.1 mmol), **3** (0.15 mmol), tetrahydropyran (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 w blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **47** as a colorless oil in 99% yield (52.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 1H), 7.80 – 7.74 (m, 1H), 7.59 (p, *J* = 7.3, 6.7 Hz, 2H), 7.38 (dd, *J* = 31.9, 6.3 Hz, 7H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.86 (t, *J* = 6.4 Hz, 1H), 4.82 (s, 1H), 4.33 – 4.08 (m, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.38 – 3.26 (m, 2H), 3.08 (d, *J* = 17.2 Hz, 1H), 1.61 – 1.44 (m, 4H), 1.37 – 1.23 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.6, 171.3, 167.5, 161.4, 153.3, 146.6, 137.8, 136.6, 135.5, 134.3, 128.6, 128.5, 127.5, 127.0, 126.2, 124.9, 117.8, 111.0, 81.0, 79.7, 75.8, 69.5, 53.2, 52.1, 34.9, 29.2, 27.8, 22.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_7$: 533.2282; Found: 533.2274.

(b) Four-component trisubstituted hydroxylamines formation in 1,4-dioxane

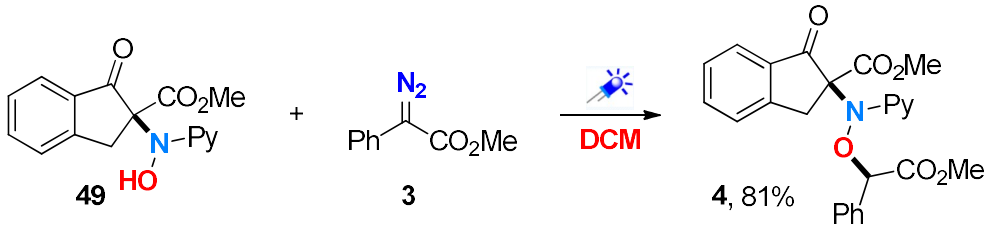


To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1e** (0.1 mmol), **2a** (0.1 mmol), **3** (0.15 mmol), 1,4-dioxane (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 w blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **48** as a colorless oil in 99% yield (53.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.09 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.44 – 7.29 (m, 8H), 6.85 (s, 1H), 4.98 (s, 1H), 4.38 (s, 2H), 4.09 (d, *J* = 17.0 Hz, 1H), 3.77 (s, 3H), 3.68 – 3.46 (m, 9H), 3.10 (d, *J* = 17.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.8, 171.2, 167.4, 161.5, 153.4, 146.4, 138.0, 136.3, 135.6, 134.3, 128.6, 128.5, 127.5, 127.2, 126.3, 124.9, 117.9, 111.4, 81.2, 80.1, 75.6, 70.5, 70.4, 69.1, 69.1, 68.9, 68.8, 53.2, 52.1, 34.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{31}N_2O_8$: 535.2075; Found: 535.2052.

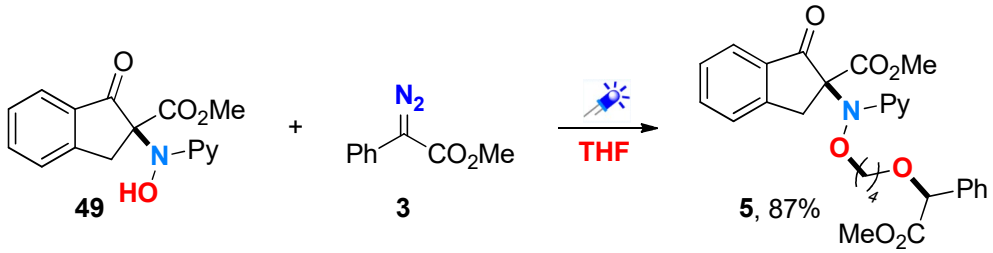
5. Mechanism studies



To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1e** (0.1 mmol) and **2a** (0.1 mmol) in THF or DCM (1.0 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **49** as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.44 (dd, *J* = 19.6, 10.1 Hz, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.76 (t, *J* = 4.2 Hz, 1H), 4.09 (d, *J* = 16.5 Hz, 1H), 3.75 (s, 3H), 3.19 (d, *J* = 16.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.6, 167.7, 160.5, 153.3, 145.6, 137.4, 135.6, 134.4, 127.6, 126.3, 125.1, 117.6, 112.5, 80.3, 53.3, 34.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_4$: 299.1026; Found: 299.1013.



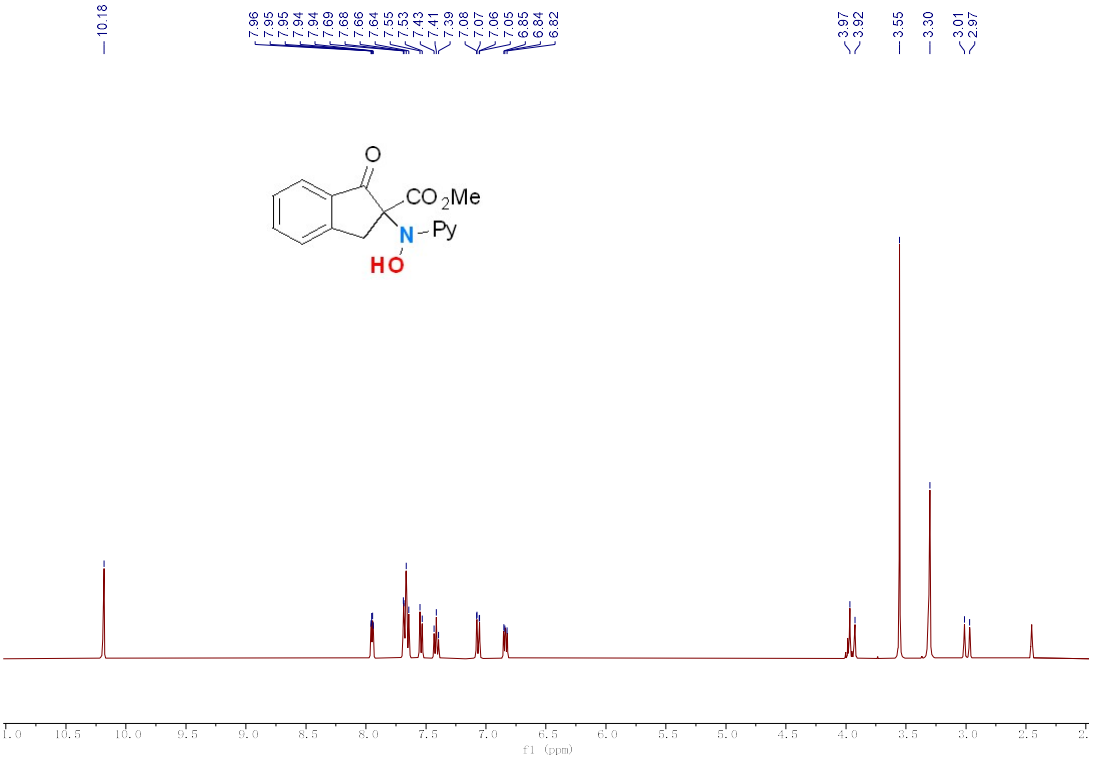
To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **49** (0.1 mmol) and **3** (0.15 mmol) in DCM (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 w blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **4** as a yellow oil in 81% yield (36.2 mg).



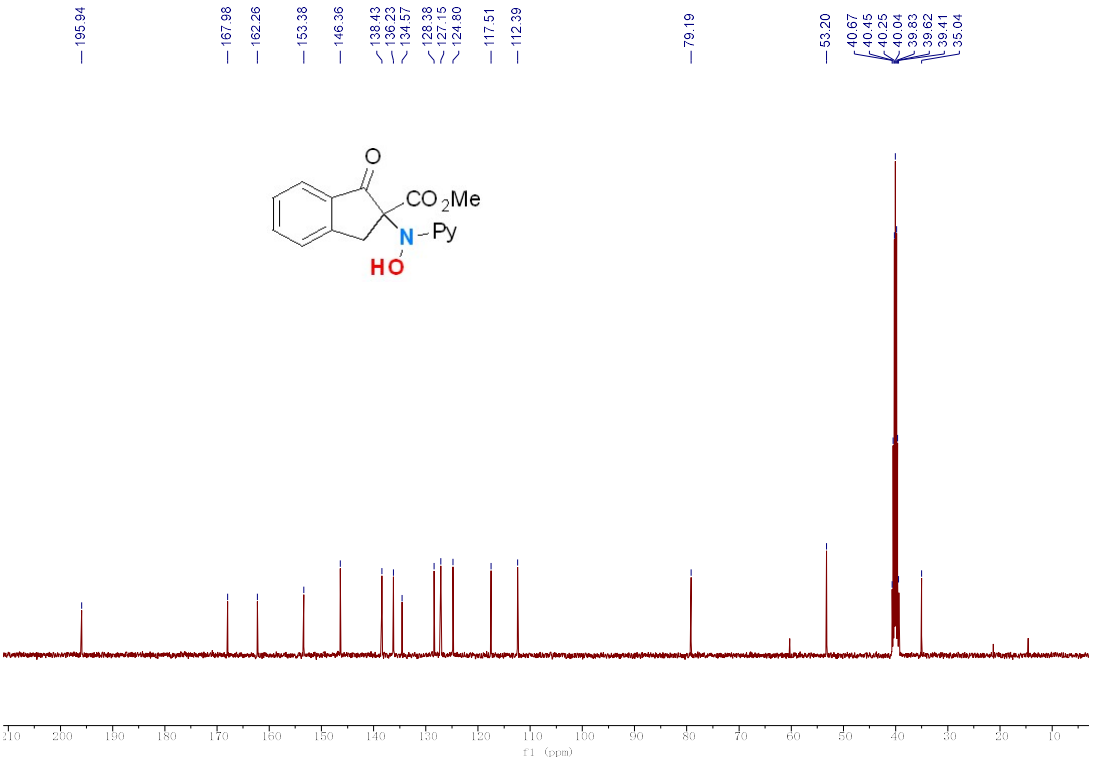
To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **49** (0.1 mmol) and **3** (0.15 mmol) in THF (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 w blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (20:1~5:1) to provide pure product **5** as a colorless oil in 87% yield (45.1 mg).

Information on chemical shift studies

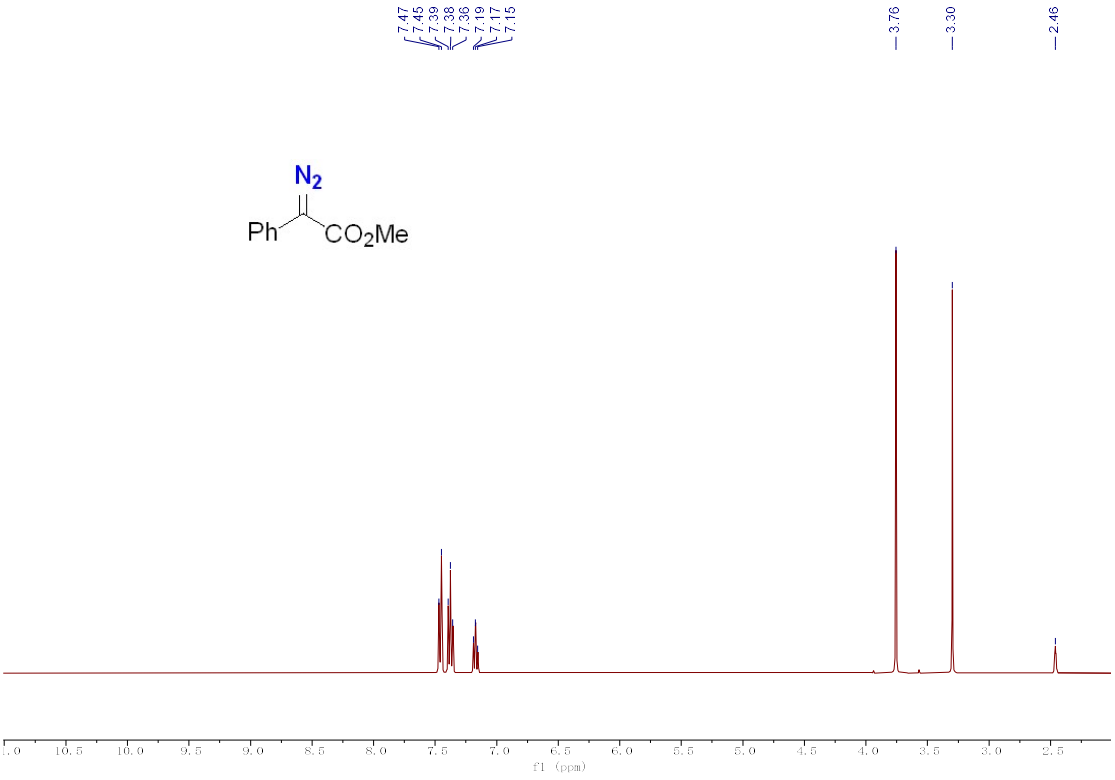
^{1}H NMR (400 MHz) Spectrum of 49 in $(CD_3)_2SO$



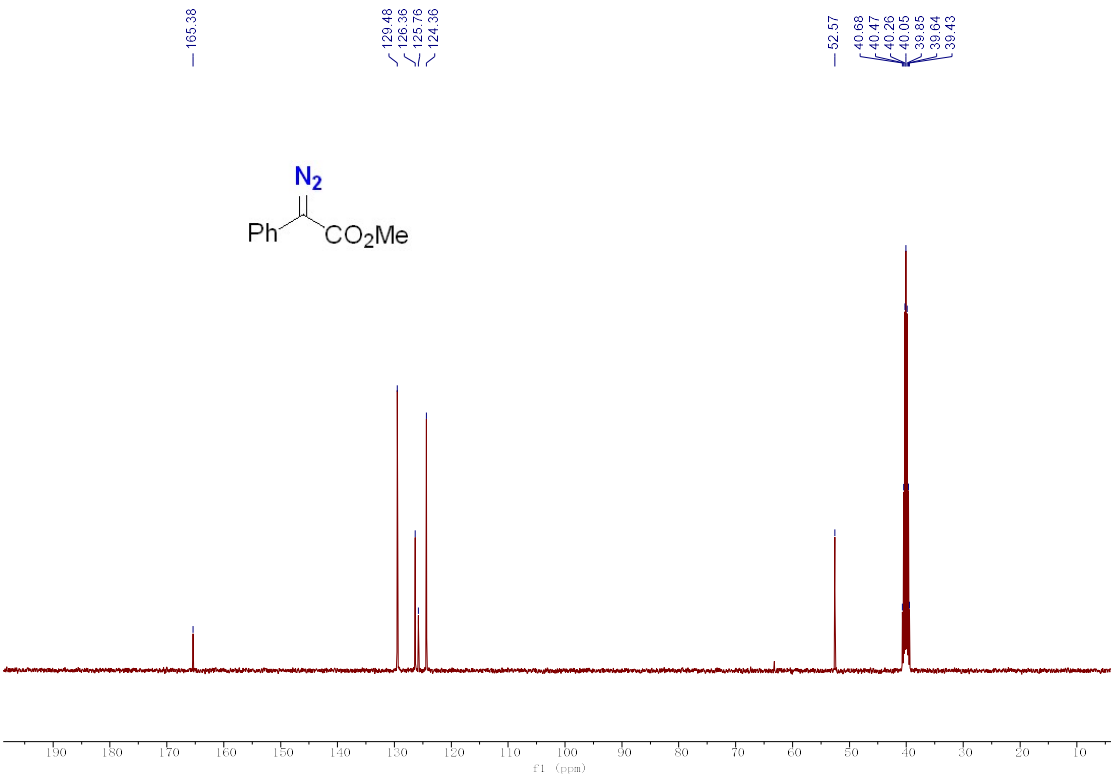
^{13}C NMR (100 MHz) Spectrum of 49 in $(CD_3)_2SO$



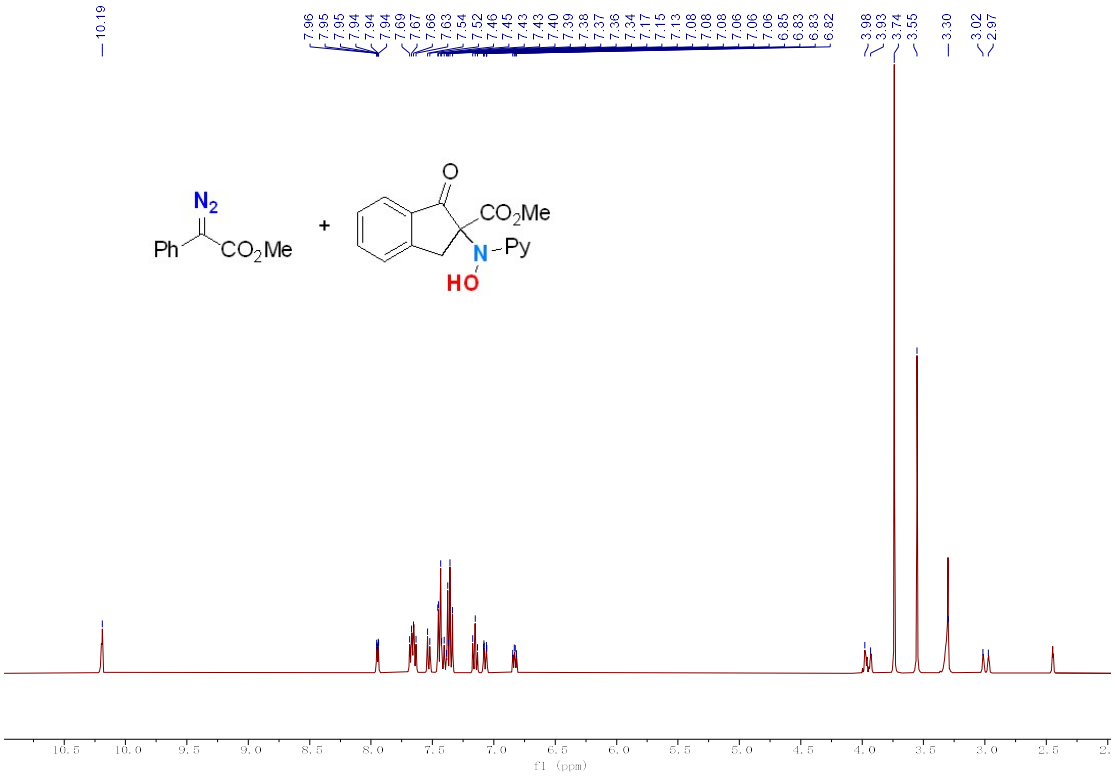
^{1}H NMR (400 MHz) Spectrum of 3 in $(CD_3)_2SO$



^{13}C NMR (100 MHz) Spectrum of 3 in $(CD_3)_2SO$



^{1}H NMR (400 MHz) Spectrum of 3 and 49 in $(CD_3)_2SO$



^{13}C NMR (100 MHz) Spectrum of 3 and 49 in $(CD_3)_2SO$

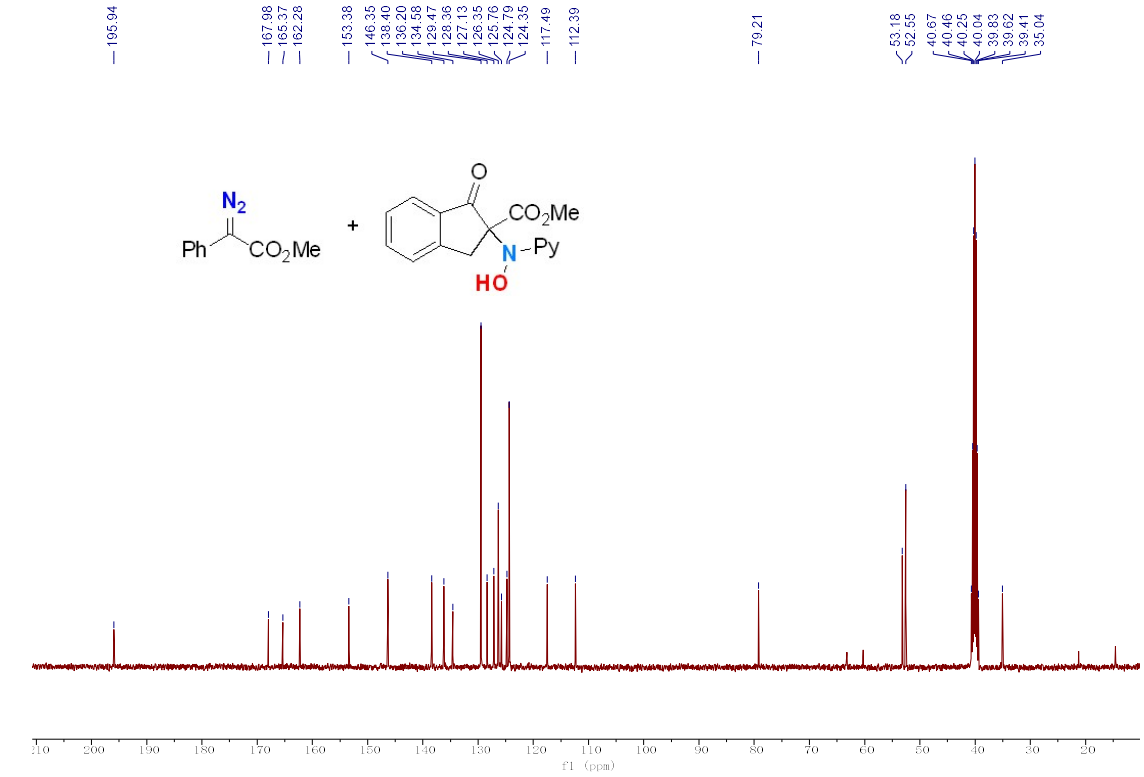
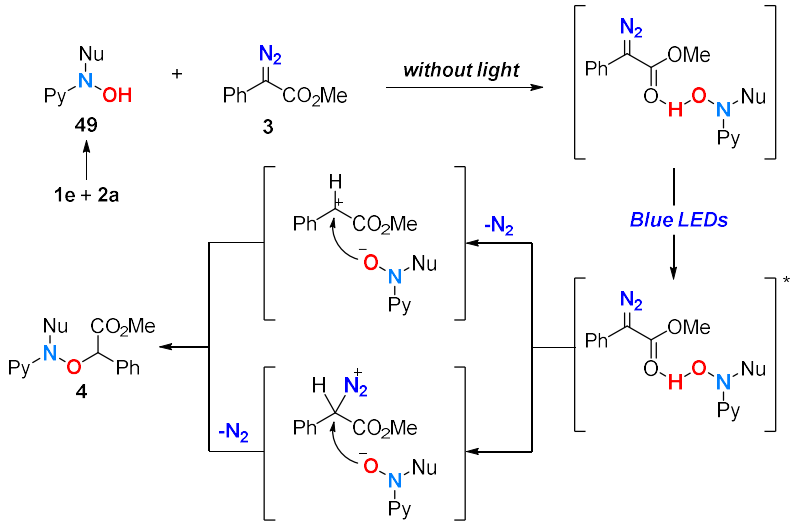
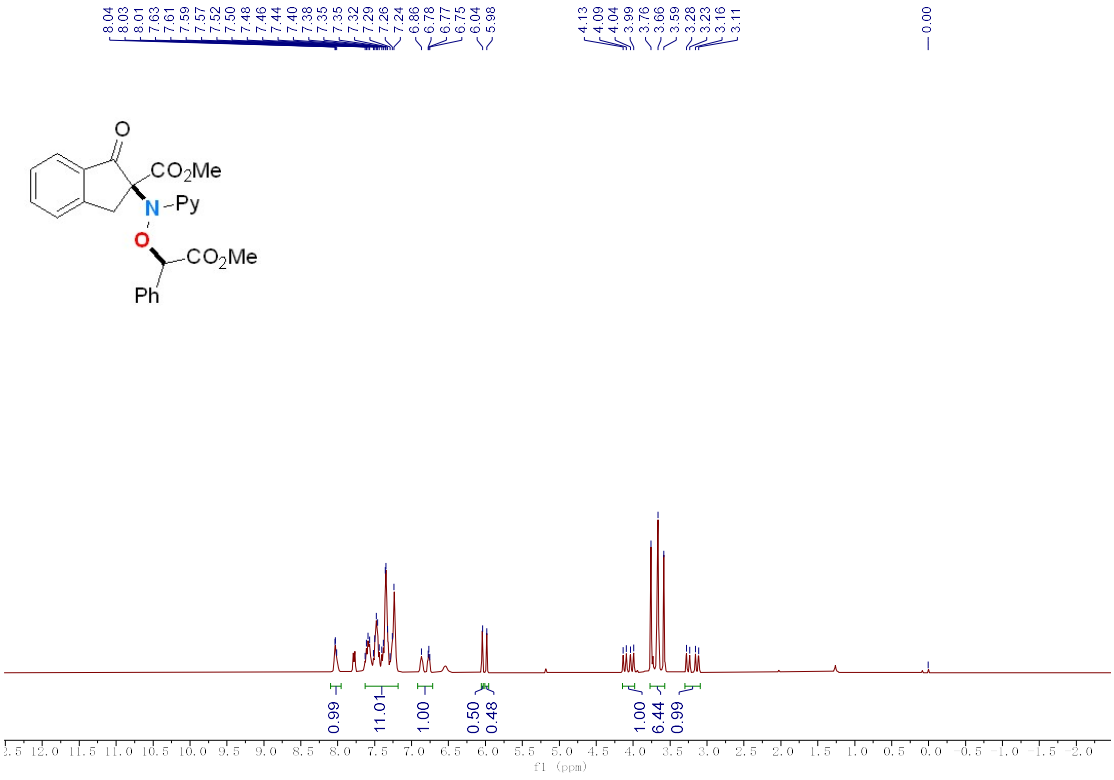


Photo-induced proton transfer mechanism

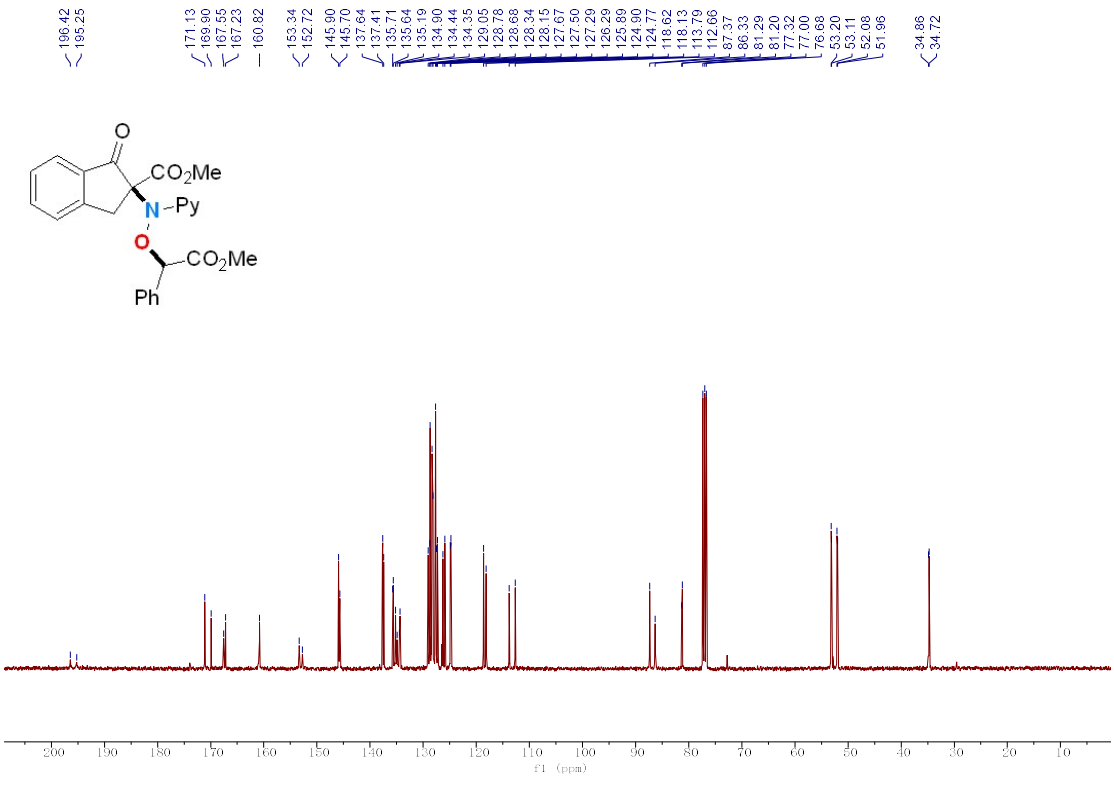


6. Copies of ^{1}H NMR and ^{13}C NMR Spectra

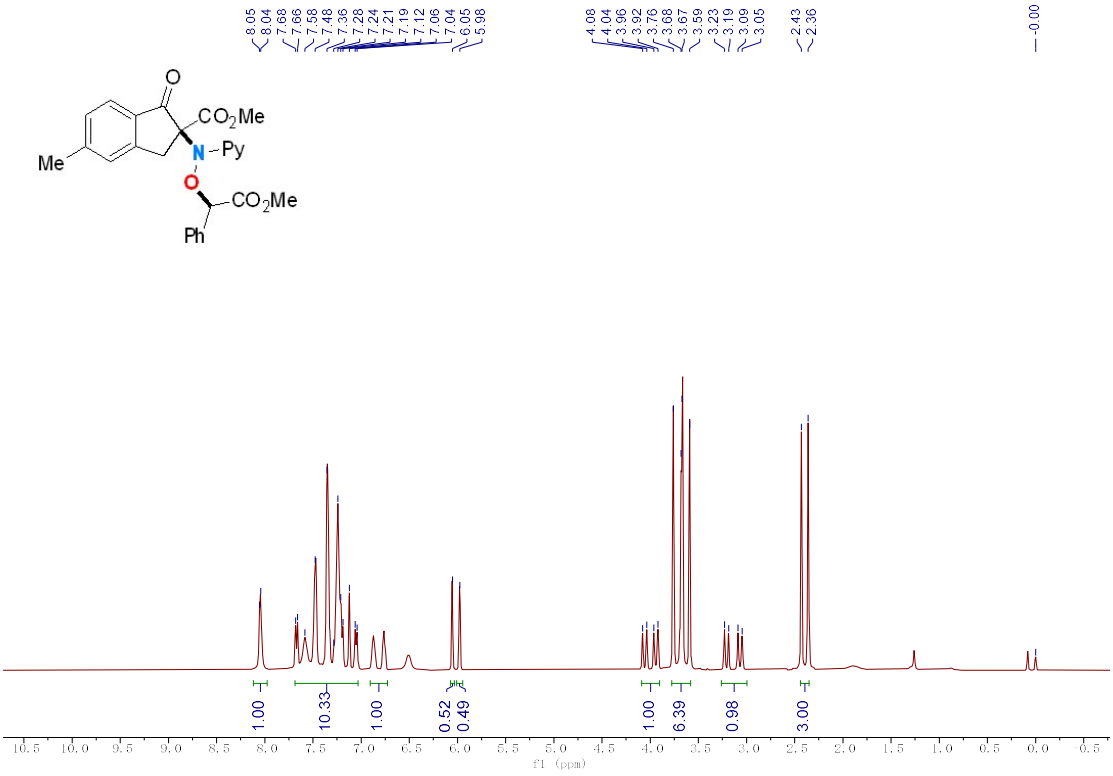
^{1}H NMR (400 MHz) Spectrum of 4 in $CDCl_3$



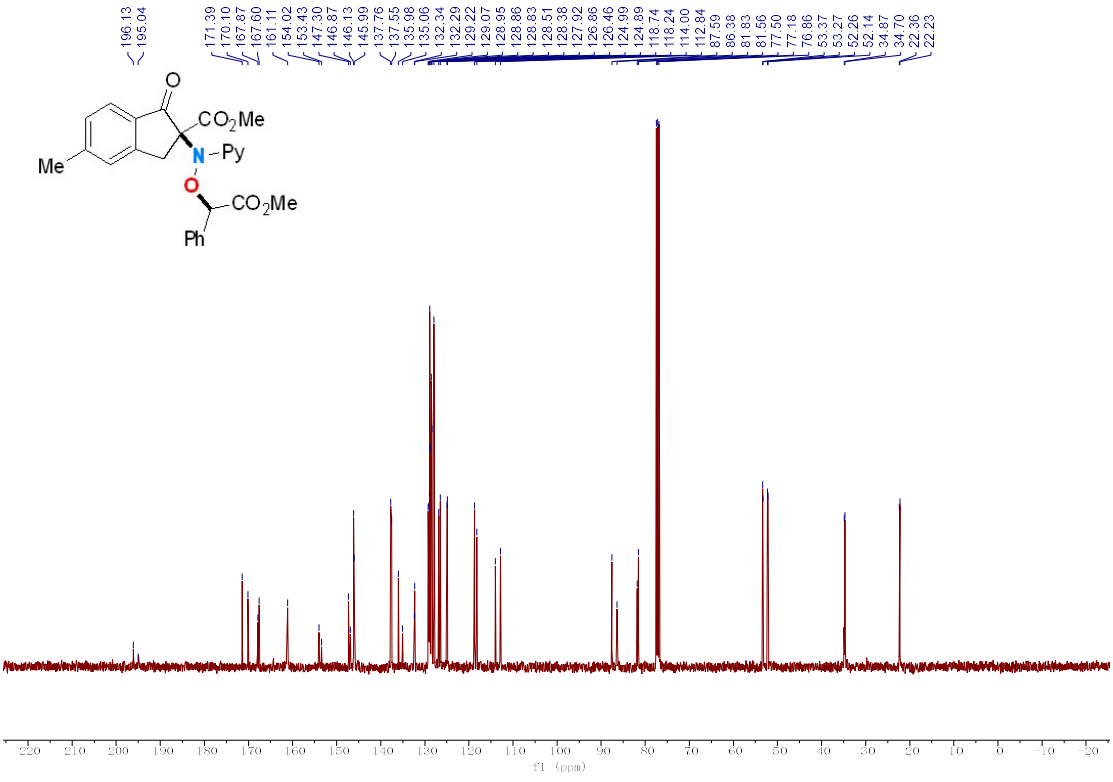
^{13}CNMR (100 MHz) Spectrum of 4 in $CDCl_3$



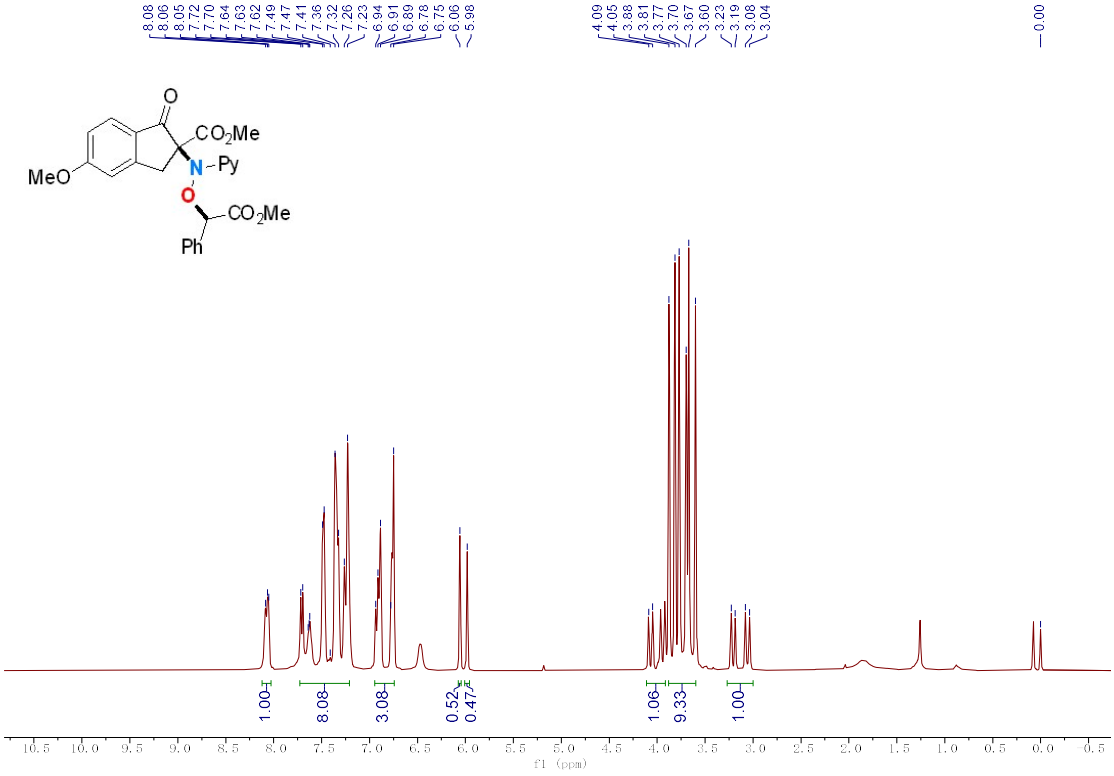
^{1}H NMR (400 MHz) Spectrum of 6 in $CDCl_3$



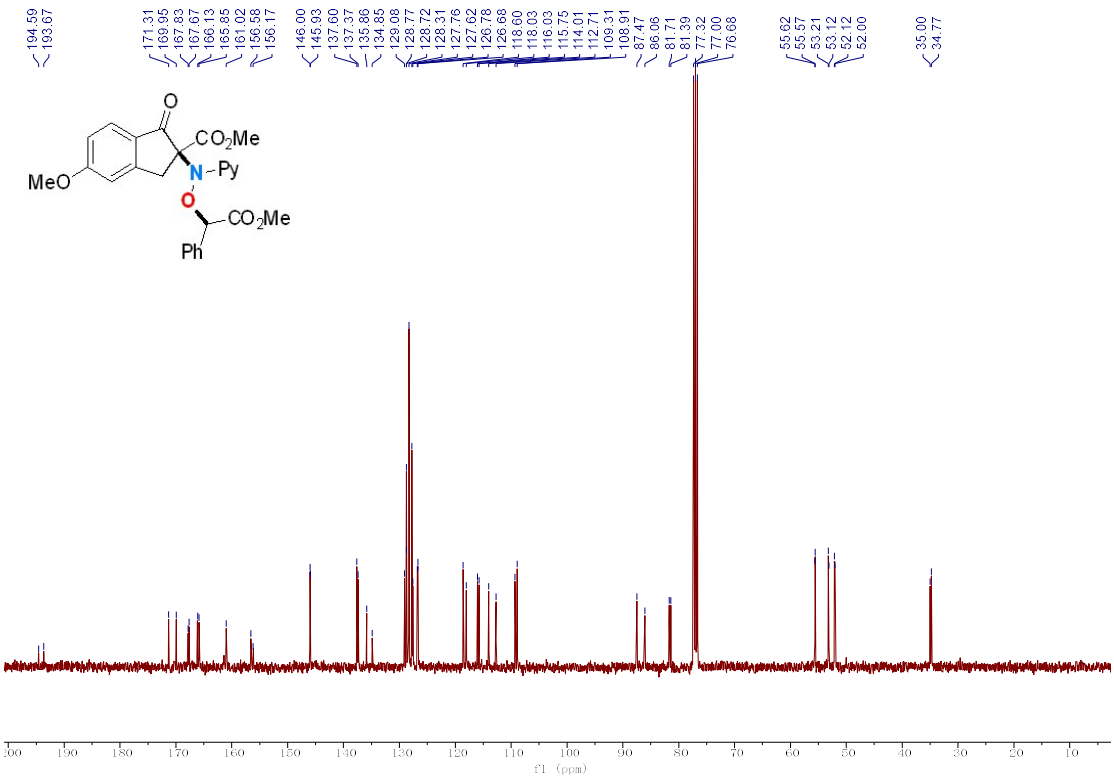
^{13}CNMR (100 MHz) Spectrum of 6 in $CDCl_3$



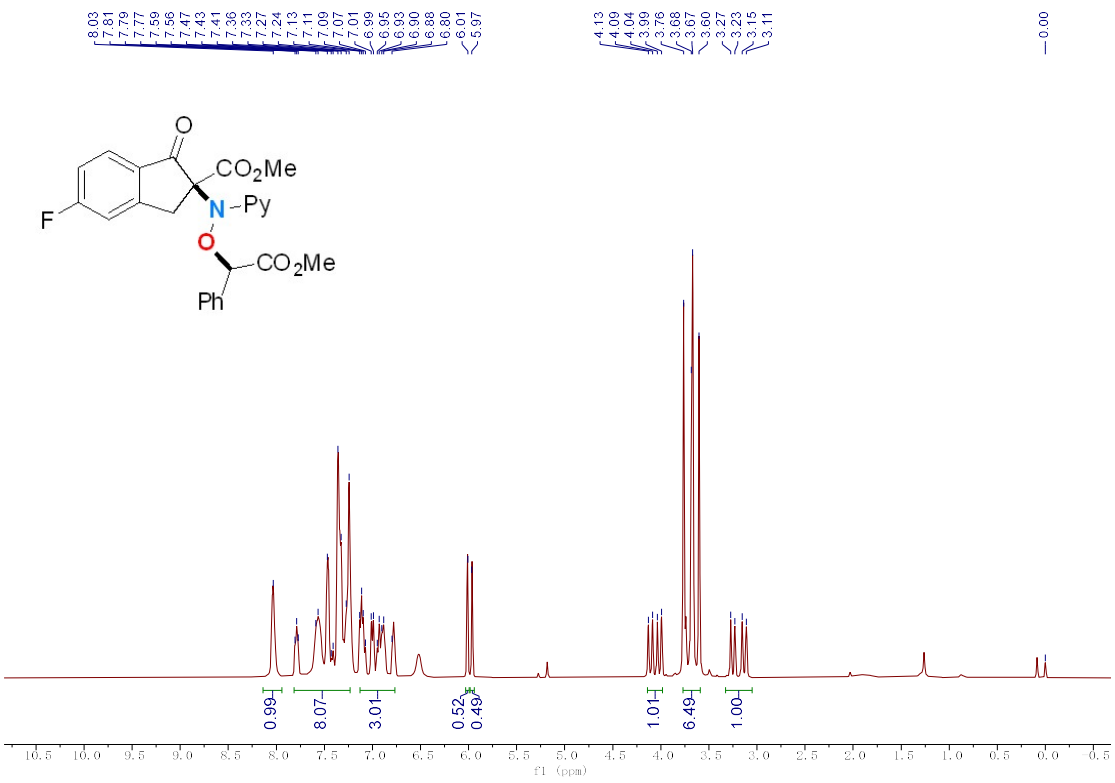
^{1}H NMR (400 MHz) Spectrum of 7 in $CDCl_3$



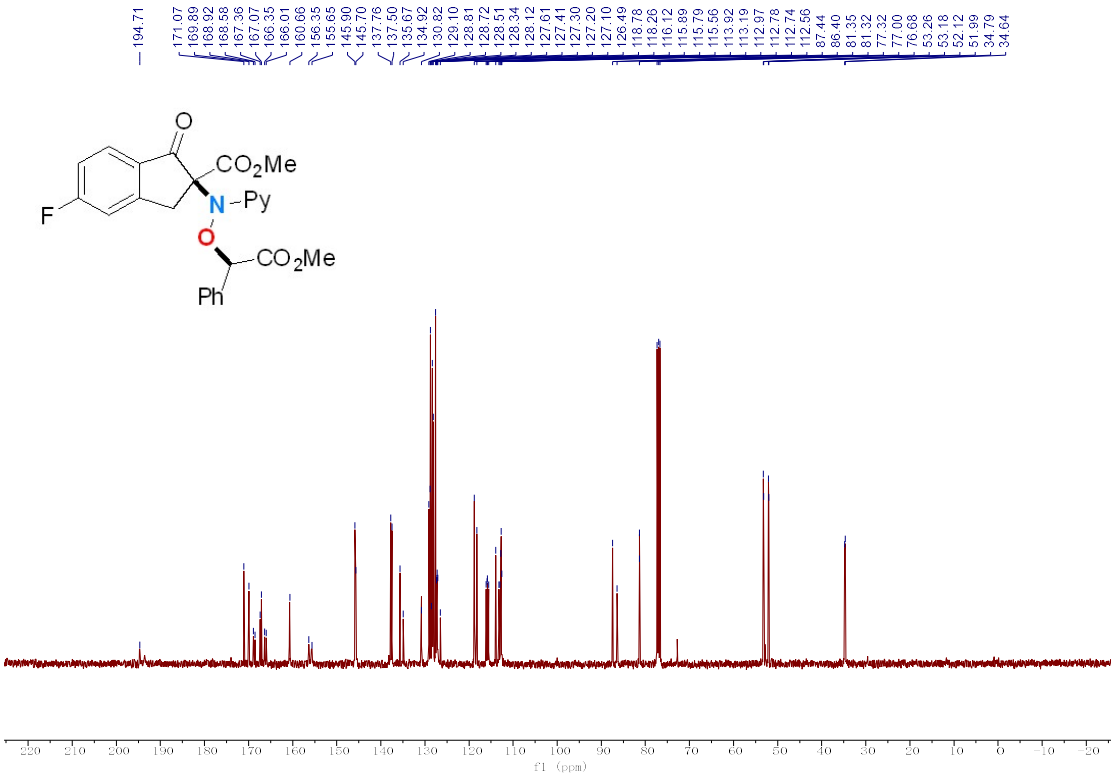
^{13}CNMR (100 MHz) Spectrum of 7 in $CDCl_3$



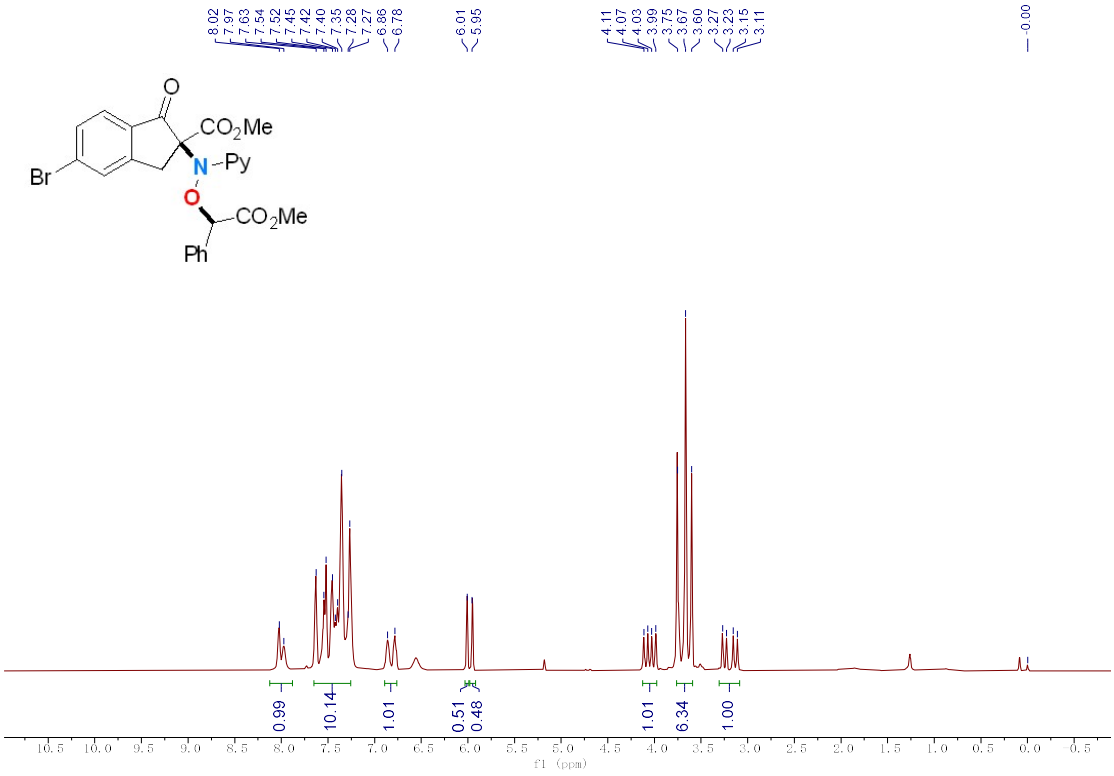
^{1}H NMR (400 MHz) Spectrum of 8 in $CDCl_3$



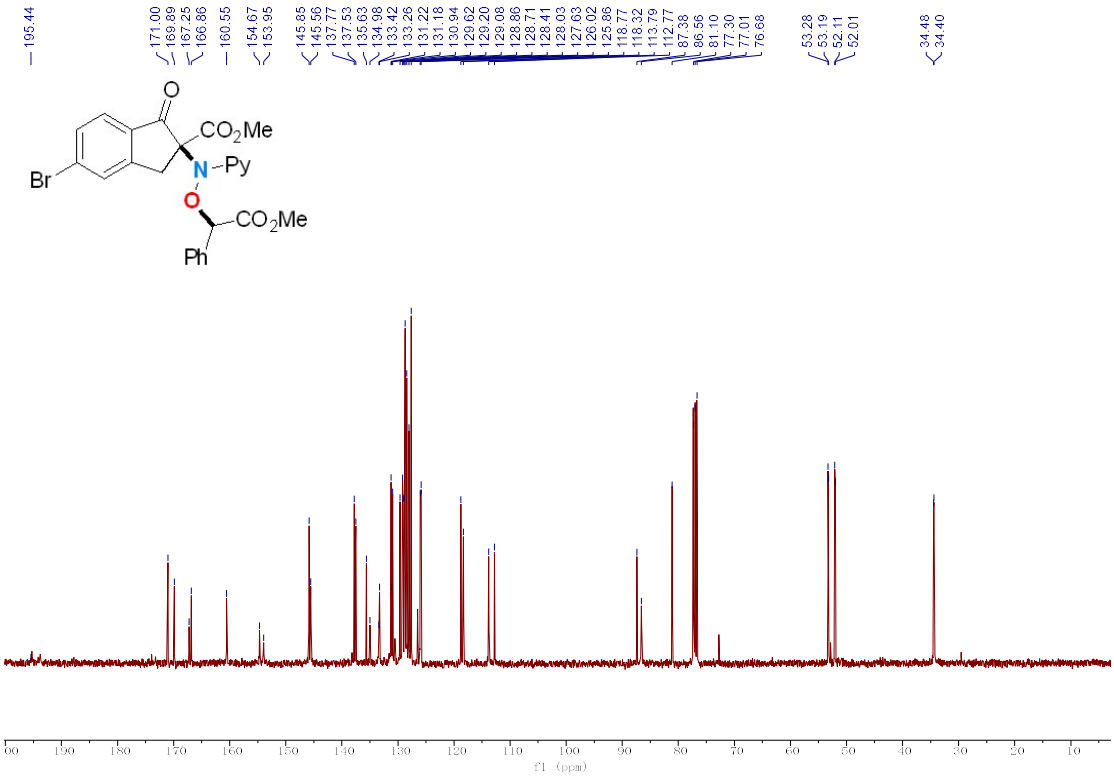
^{13}CNMR (100 MHz) Spectrum of 8 in $CDCl_3$



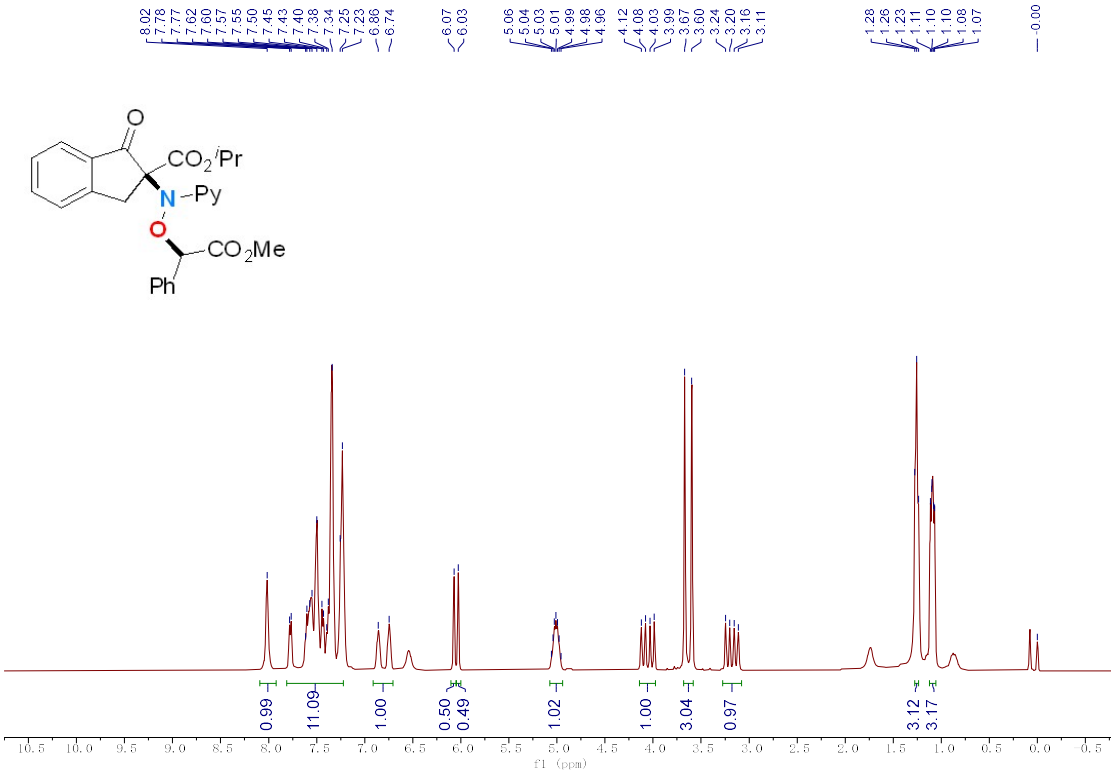
^{1}H NMR (400 MHz) Spectrum of 9 in $CDCl_3$



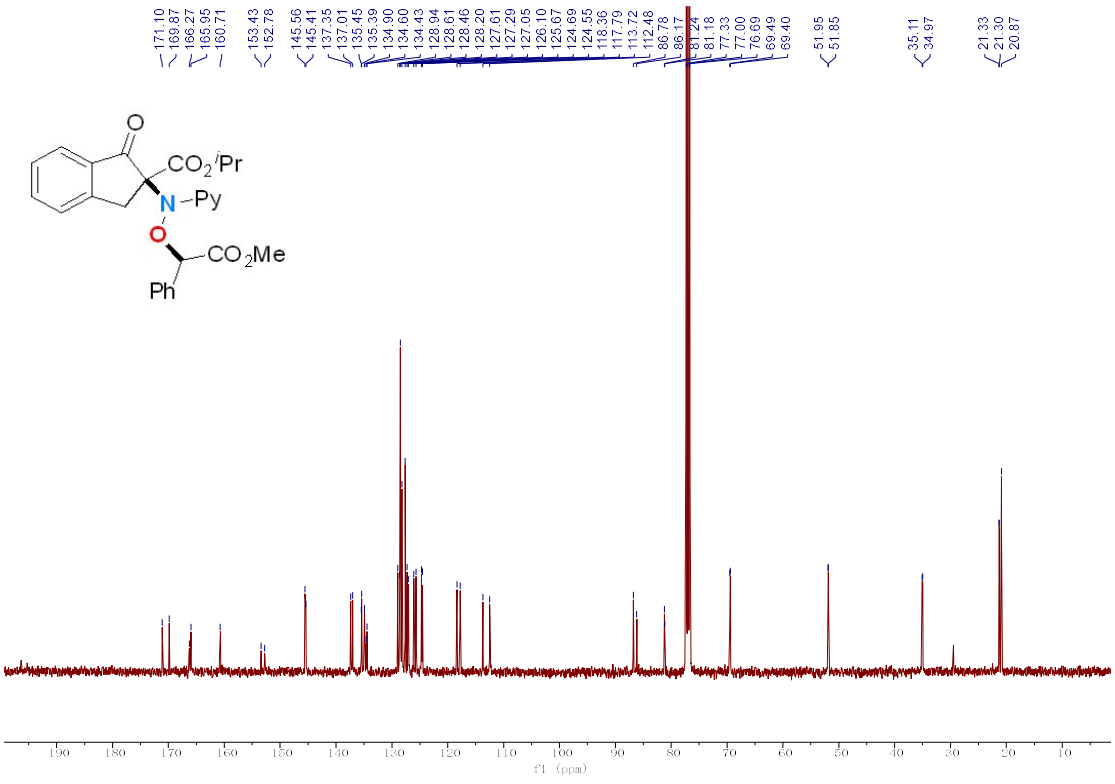
^{13}CNMR (100 MHz) Spectrum of 9 in $CDCl_3$



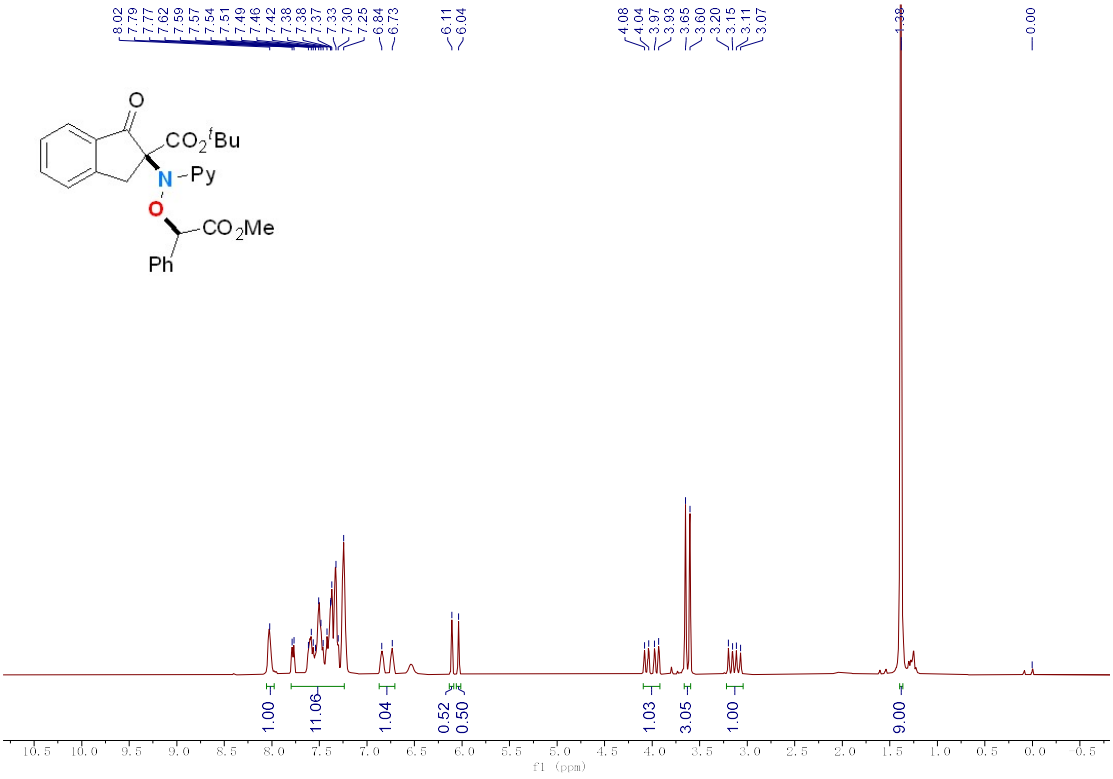
^{1}H NMR (400 MHz) Spectrum of 10 in $CDCl_3$



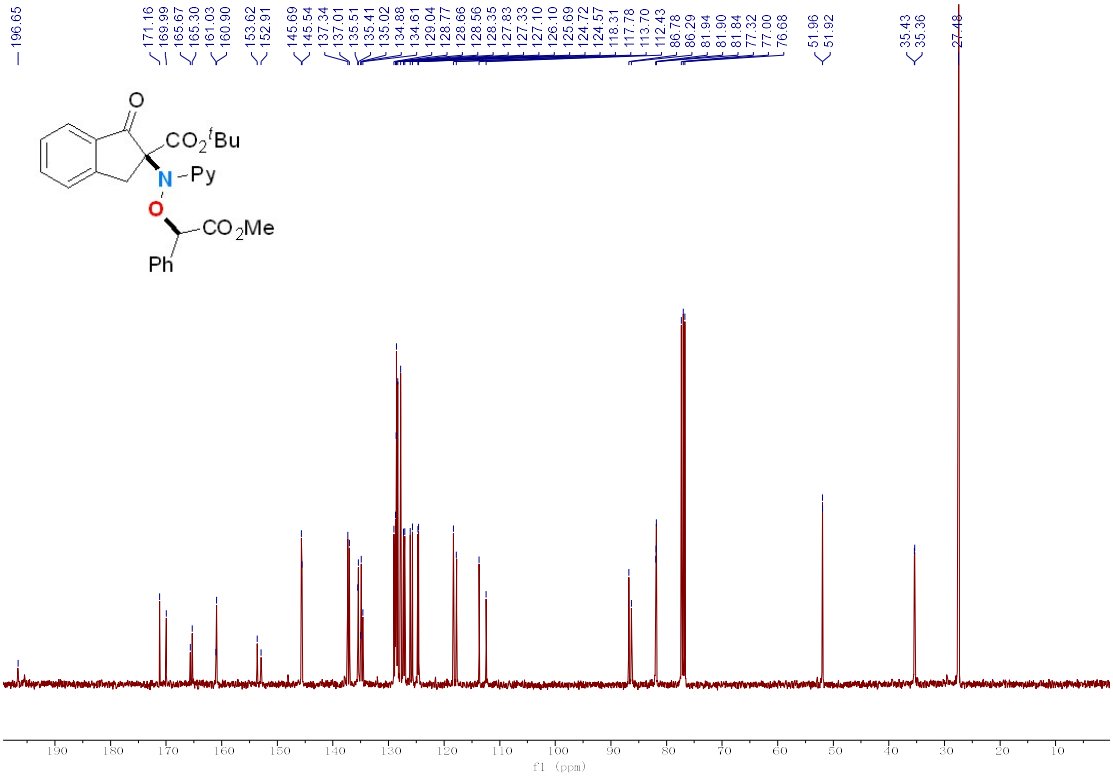
^{13}CNMR (100 MHz) Spectrum of 10 in $CDCl_3$



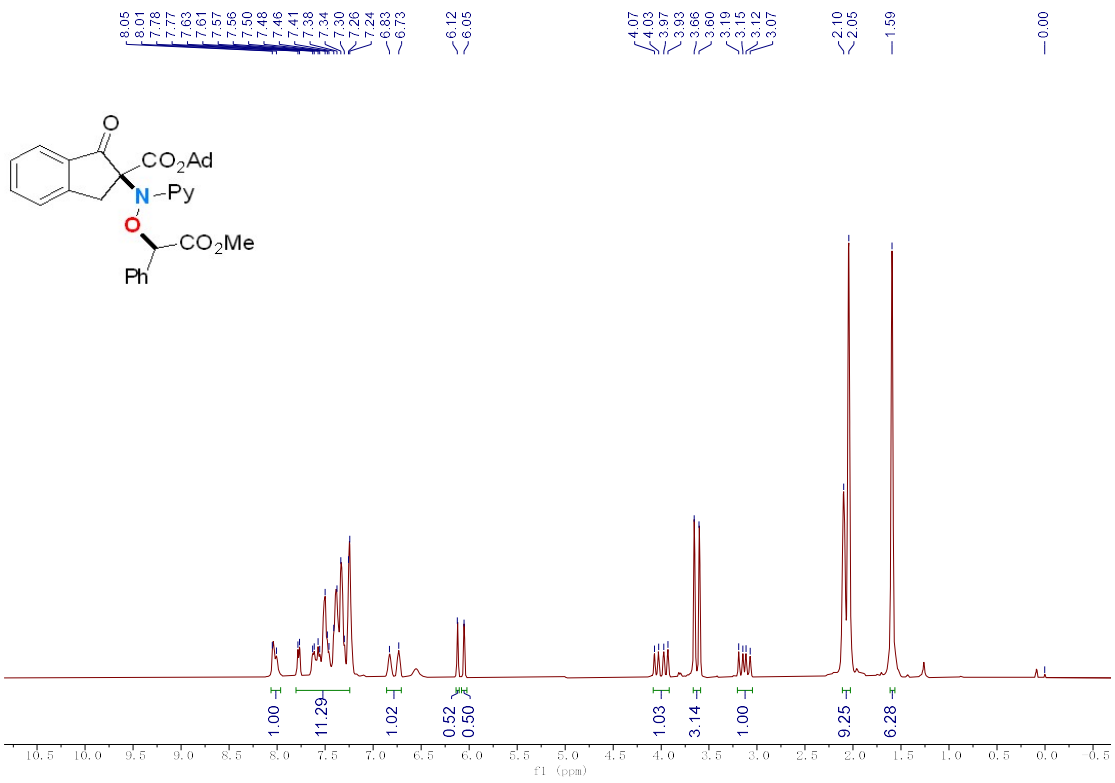
^{1}H NMR (400 MHz) Spectrum of 11 in $CDCl_3$



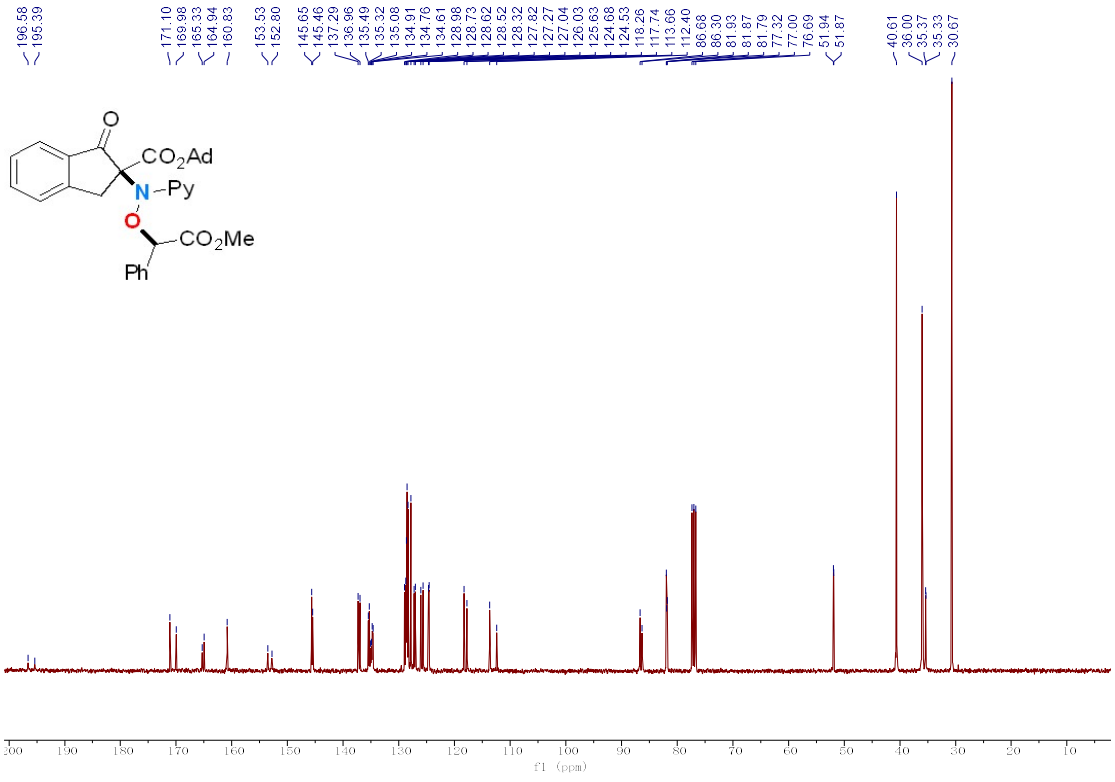
^{13}CNMR (100 MHz) Spectrum of 11 in $CDCl_3$



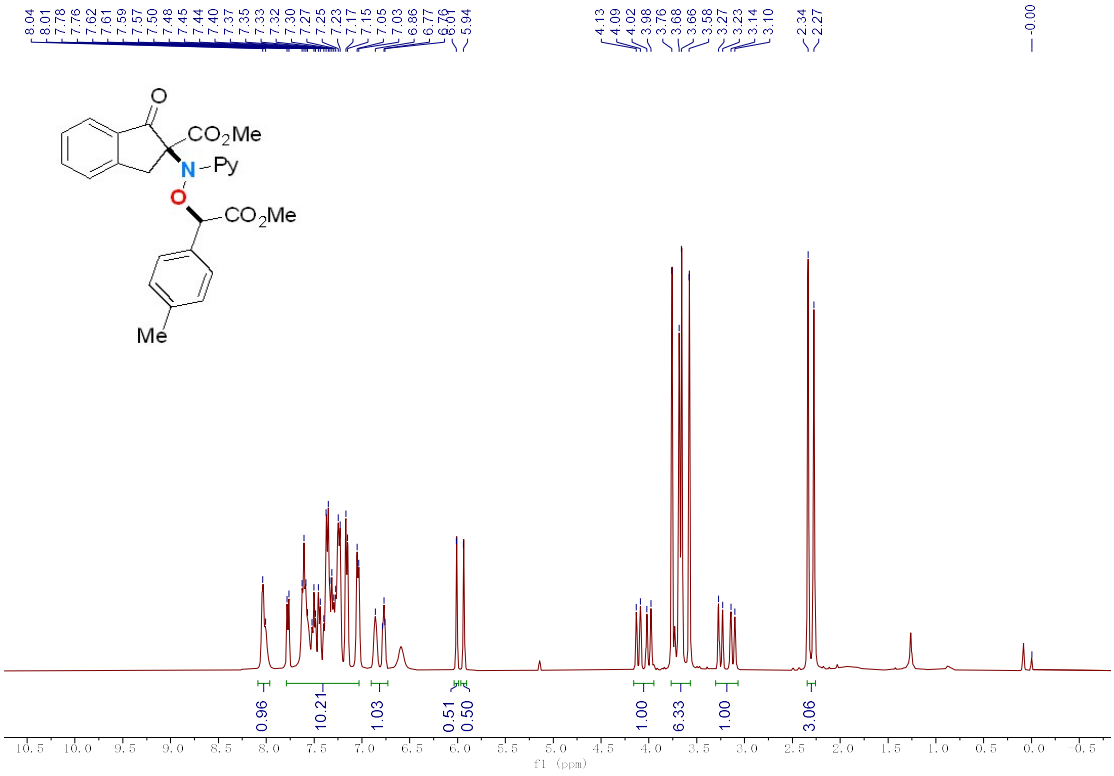
^{1}H NMR (400 MHz) Spectrum of 12 in $CDCl_3$



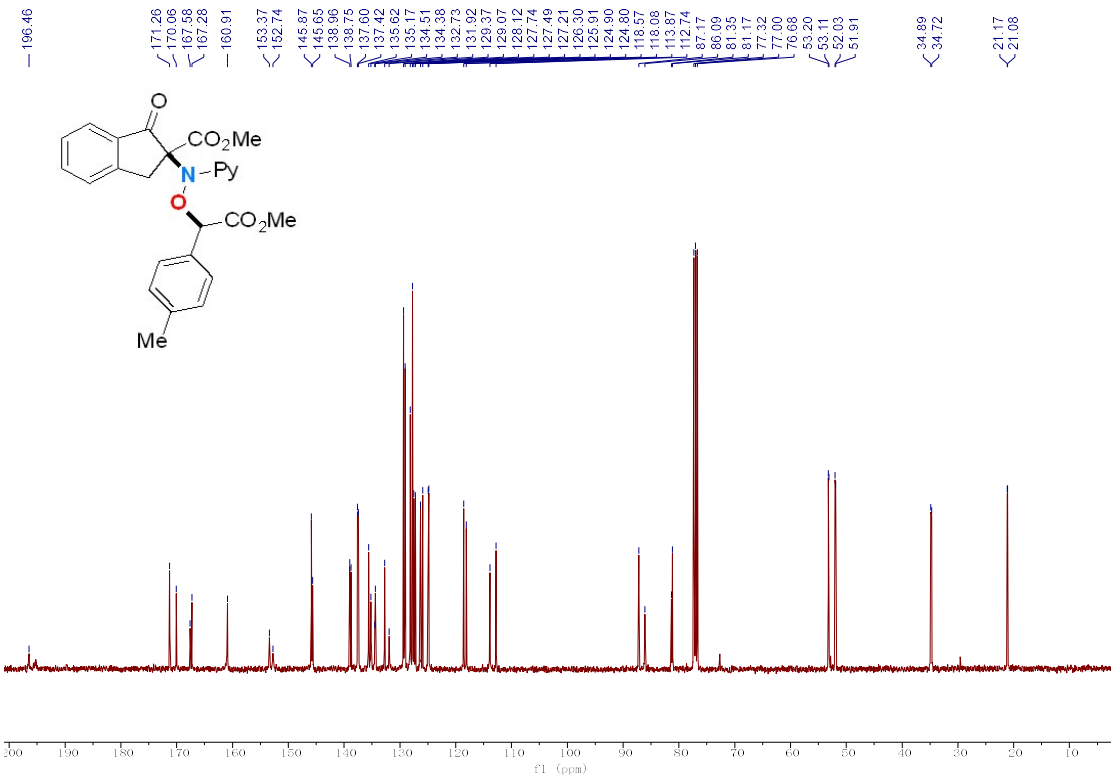
^{13}CNMR (100 MHz) Spectrum of 12 in $CDCl_3$



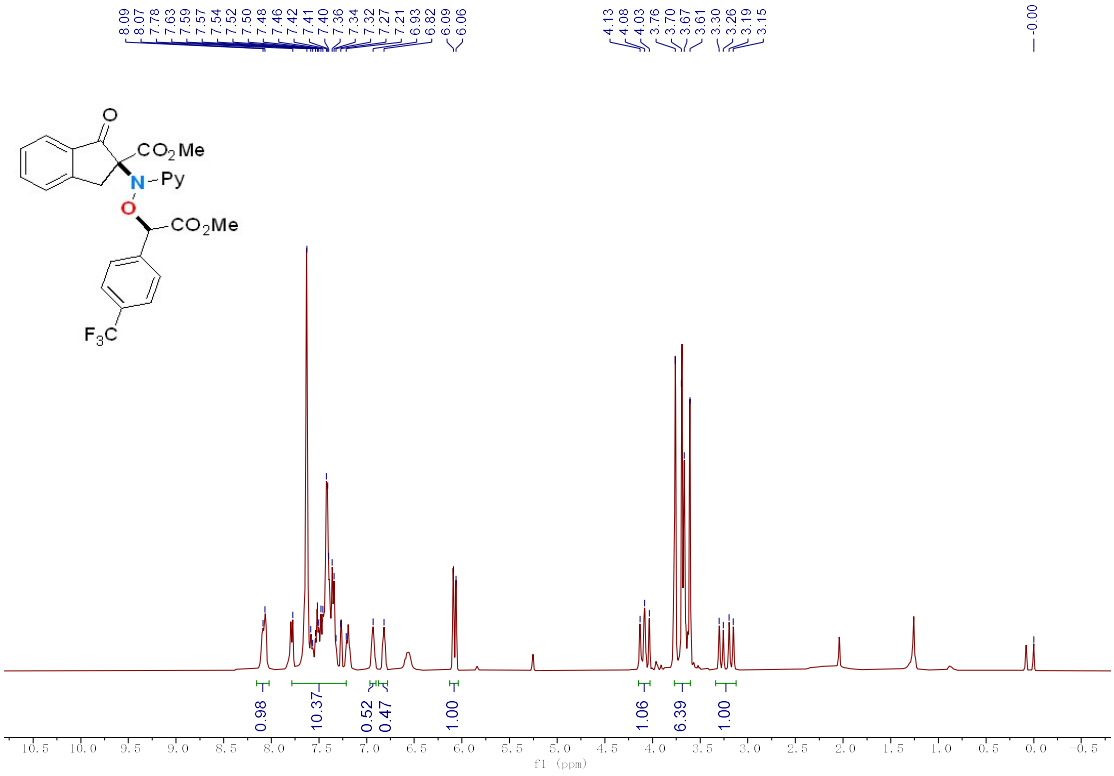
^{1}H NMR (400 MHz) Spectrum of 13 in $CDCl_3$



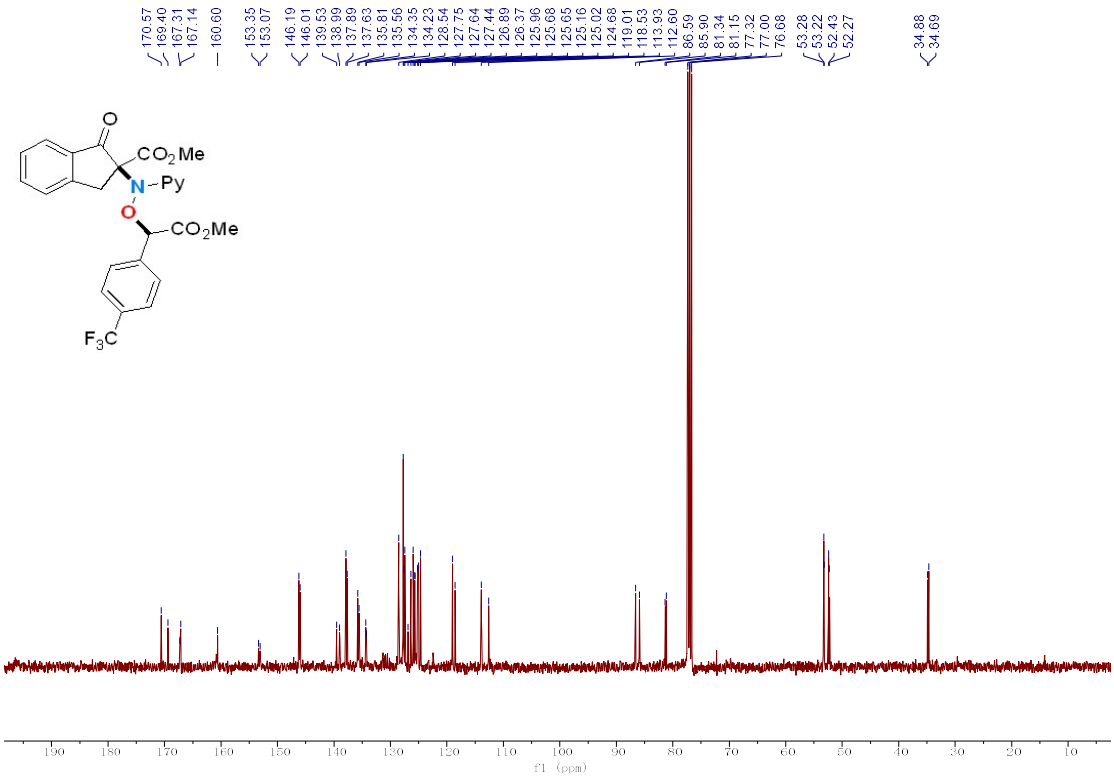
^{13}CNMR (100 MHz) Spectrum of 13 in $CDCl_3$



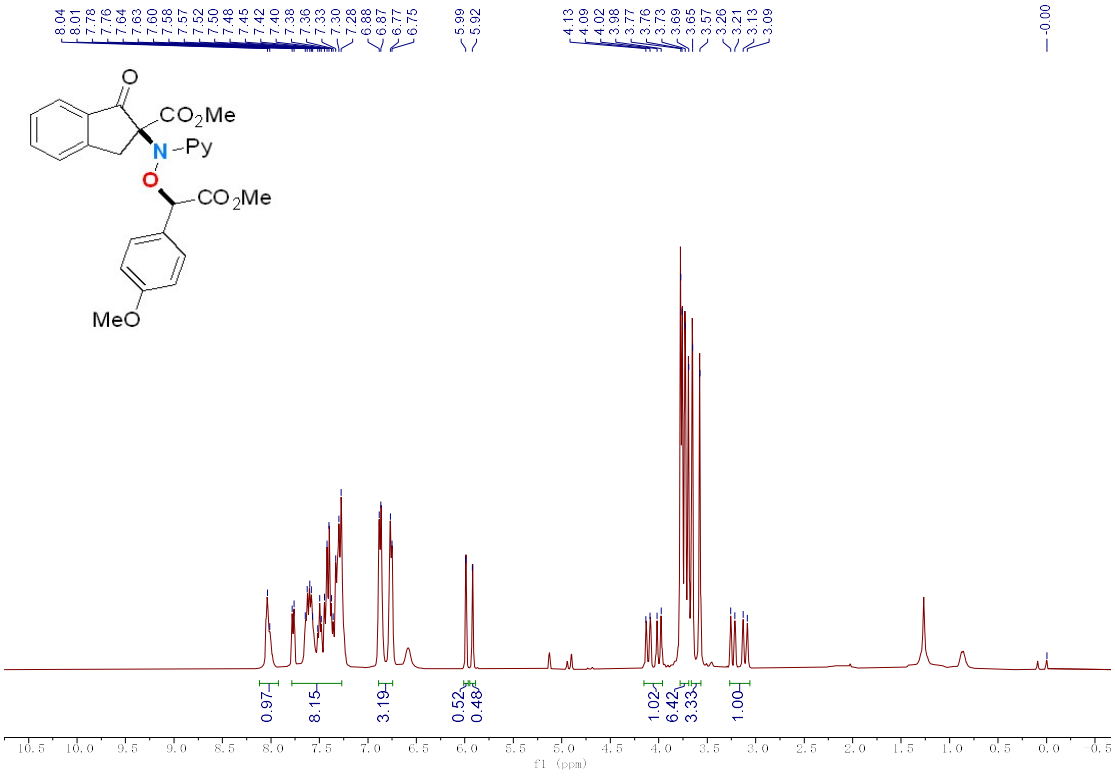
^{1}H NMR (400 MHz) Spectrum of 14 in $CDCl_3$



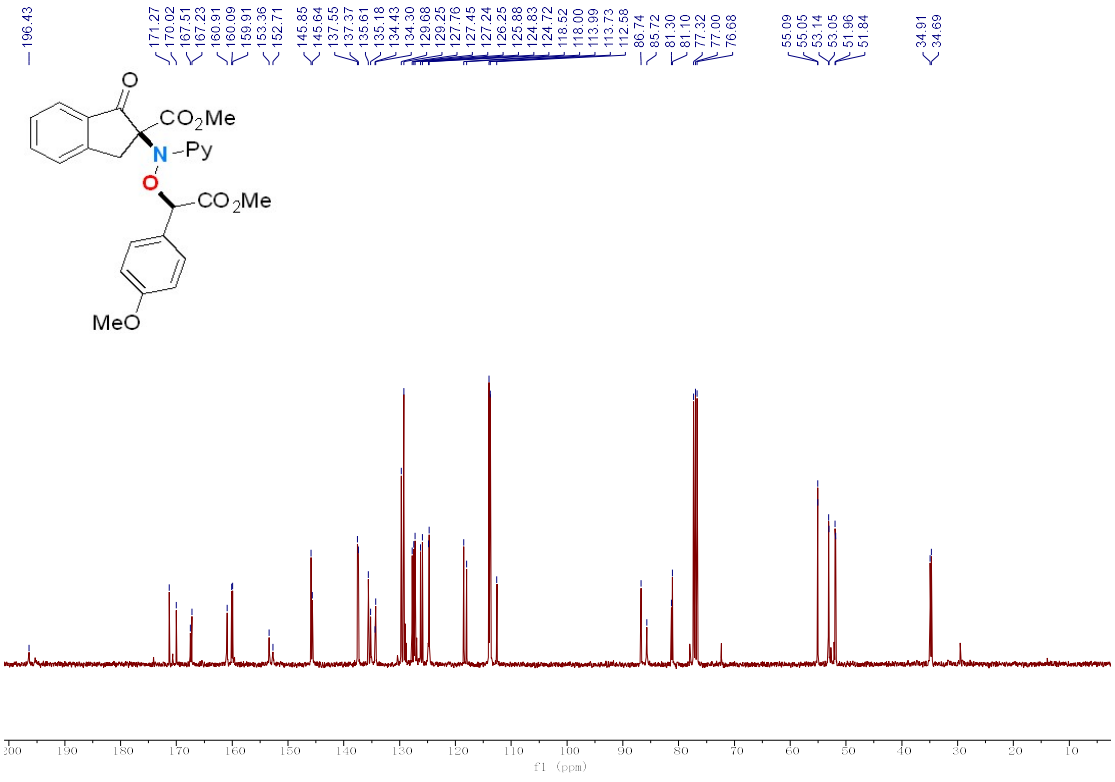
^{13}CNMR (100 MHz) Spectrum of 14 in $CDCl_3$



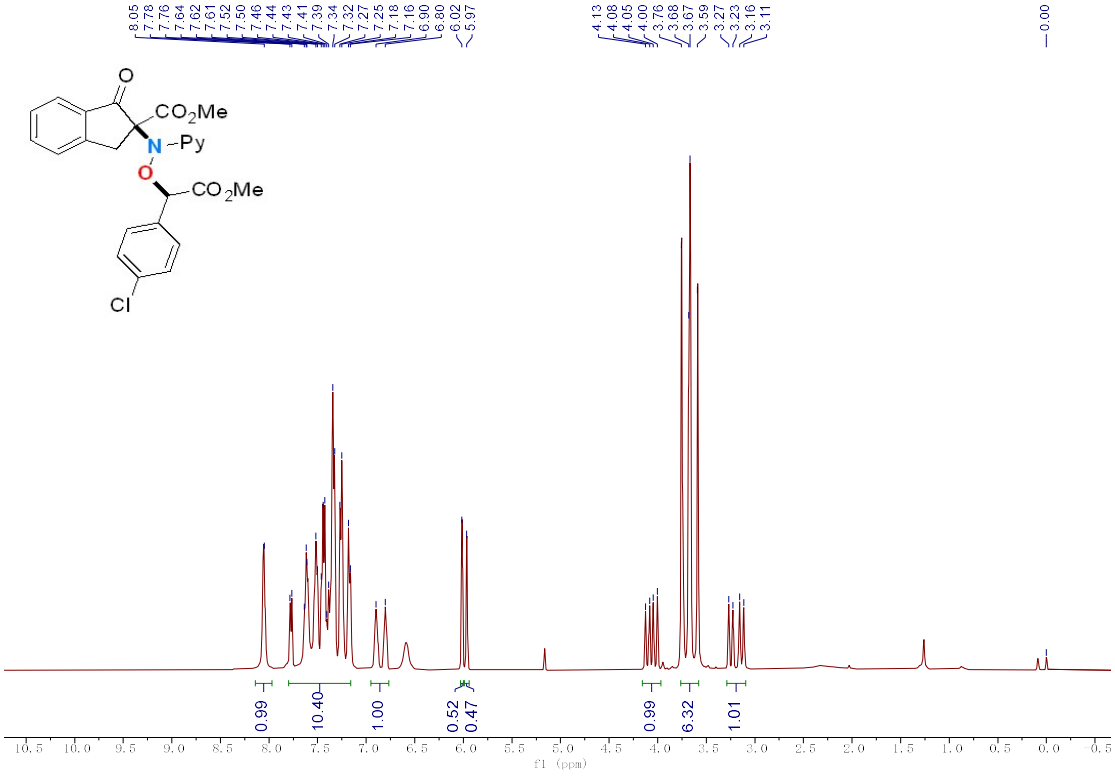
^{1}H NMR (400 MHz) Spectrum of 15 in $CDCl_3$



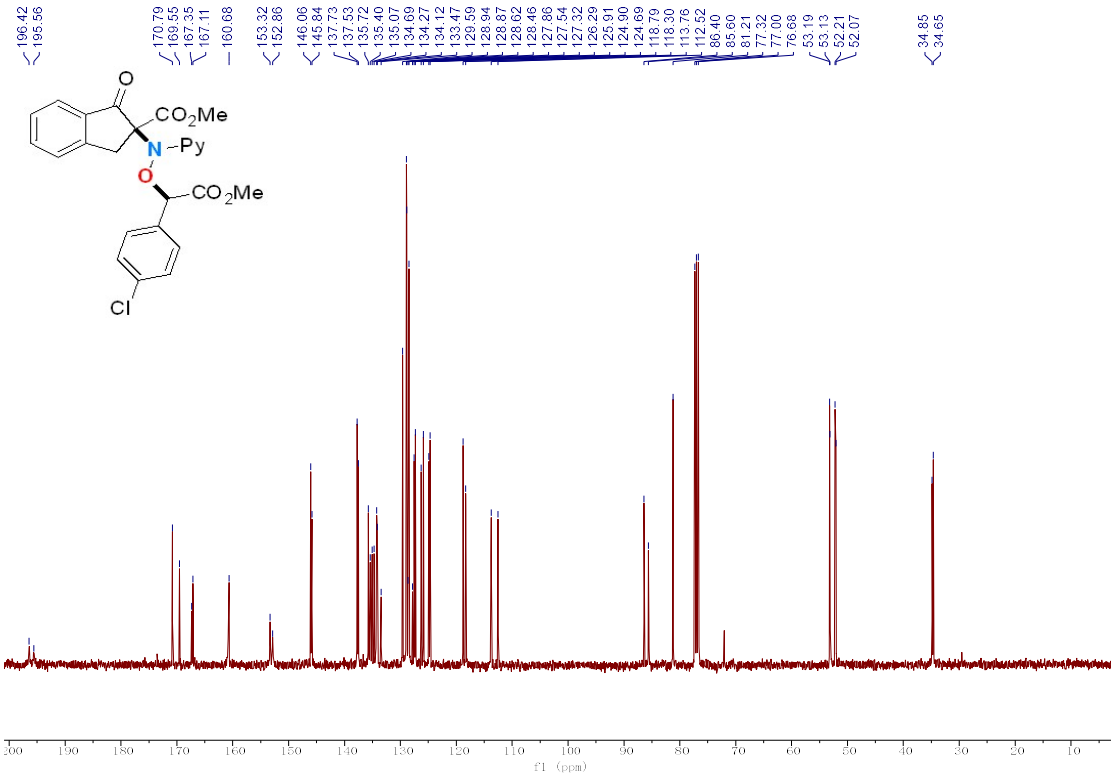
^{13}CNMR (100 MHz) Spectrum of 15 in $CDCl_3$



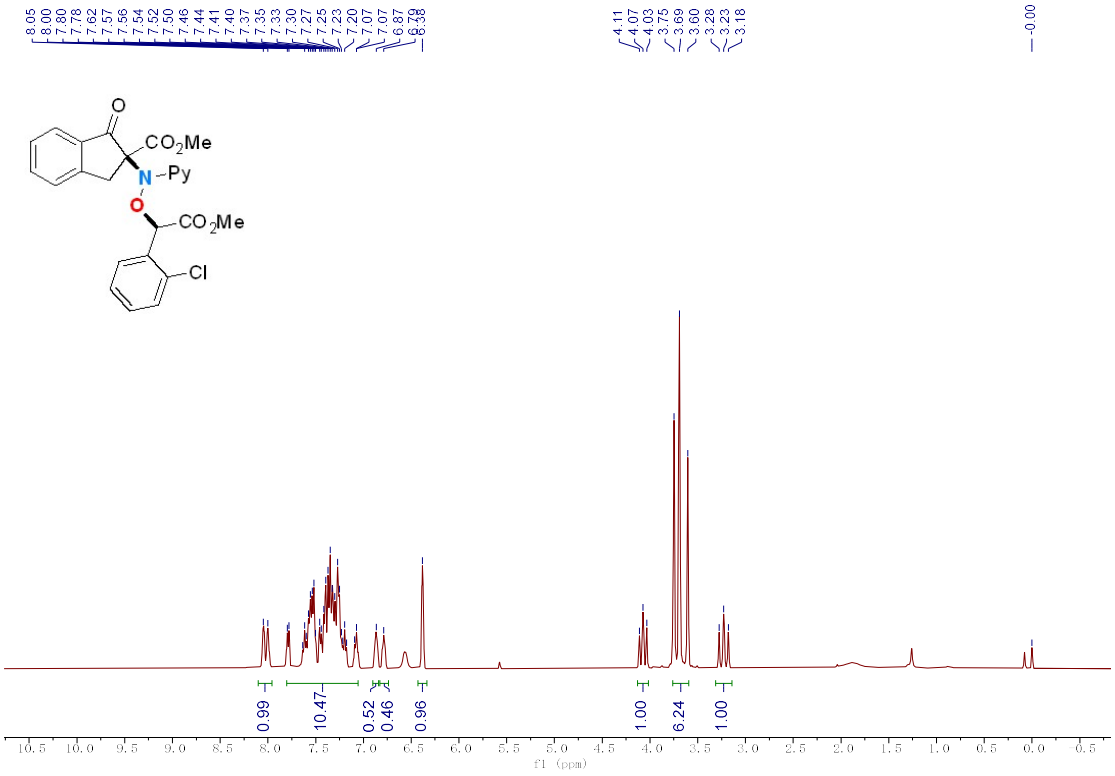
^{1}H NMR (400 MHz) Spectrum of 16 in $CDCl_3$



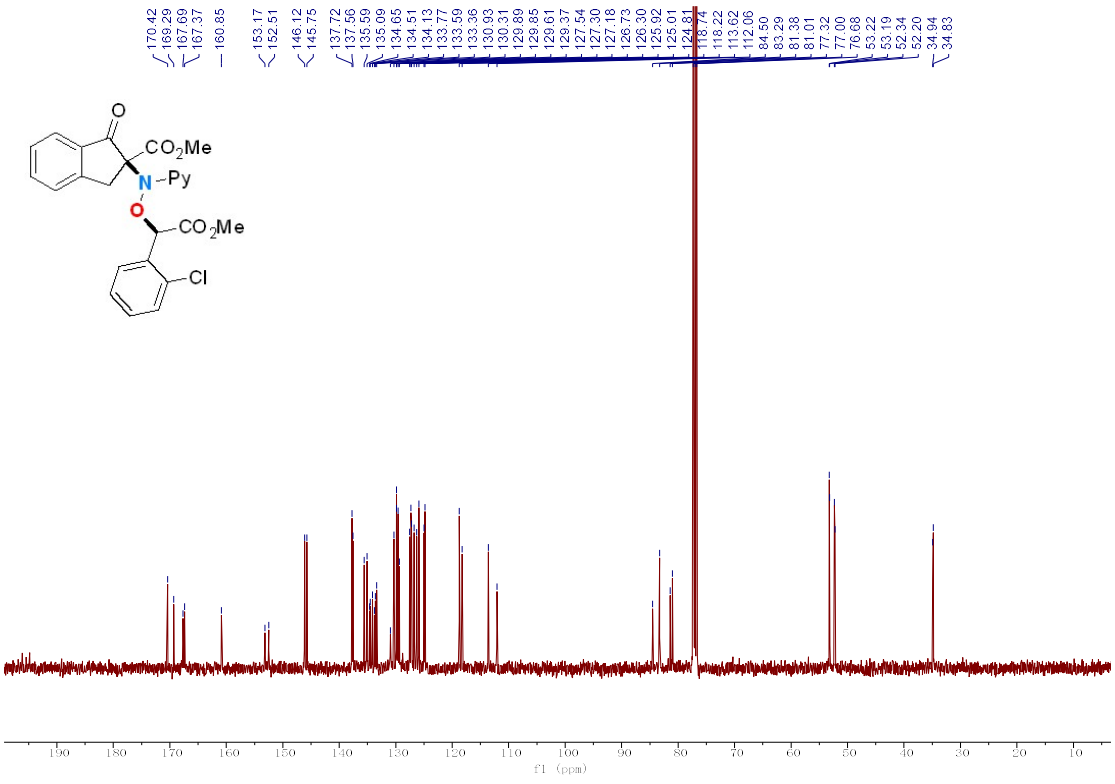
^{13}CNMR (100 MHz) Spectrum of 16 in $CDCl_3$



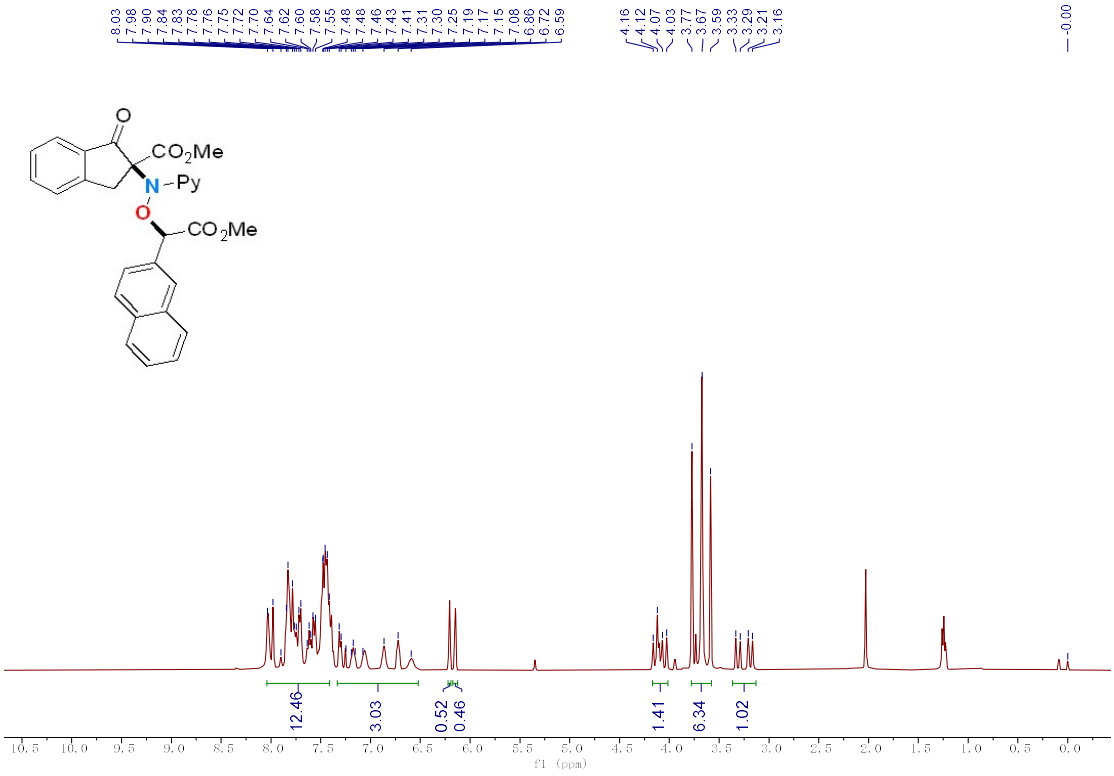
^{1}H NMR (400 MHz) Spectrum of 17 in $CDCl_3$



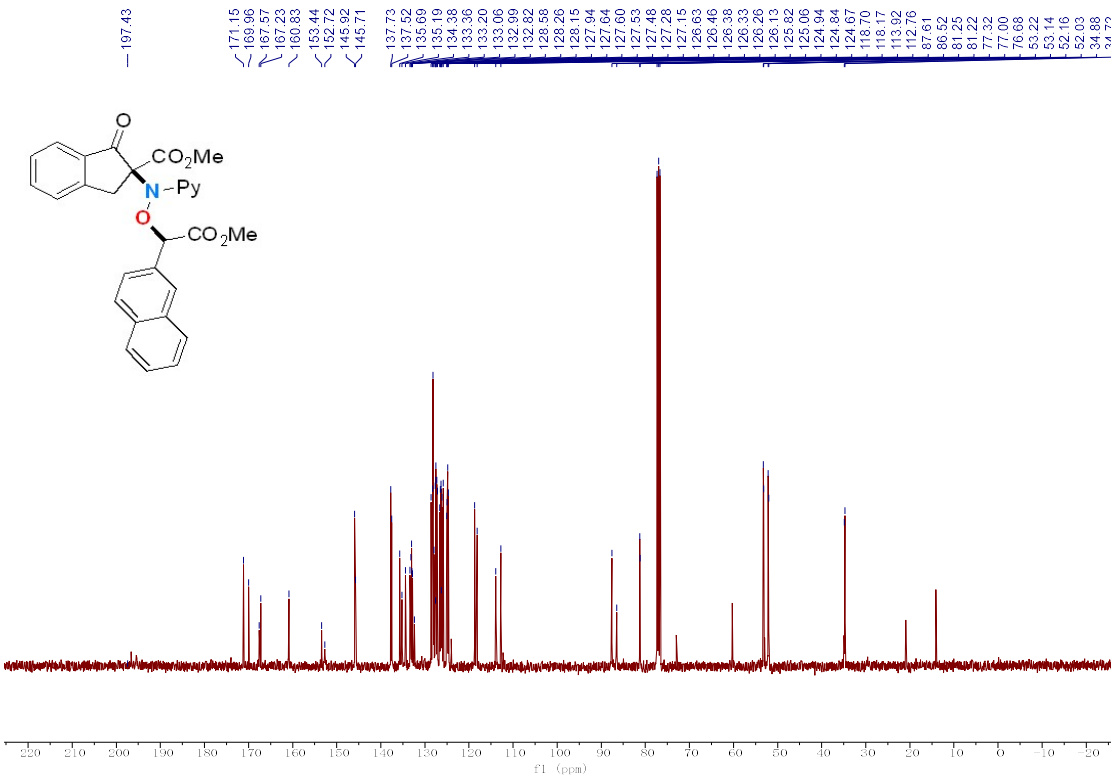
^{13}CNMR (100 MHz) Spectrum of 17 in $CDCl_3$



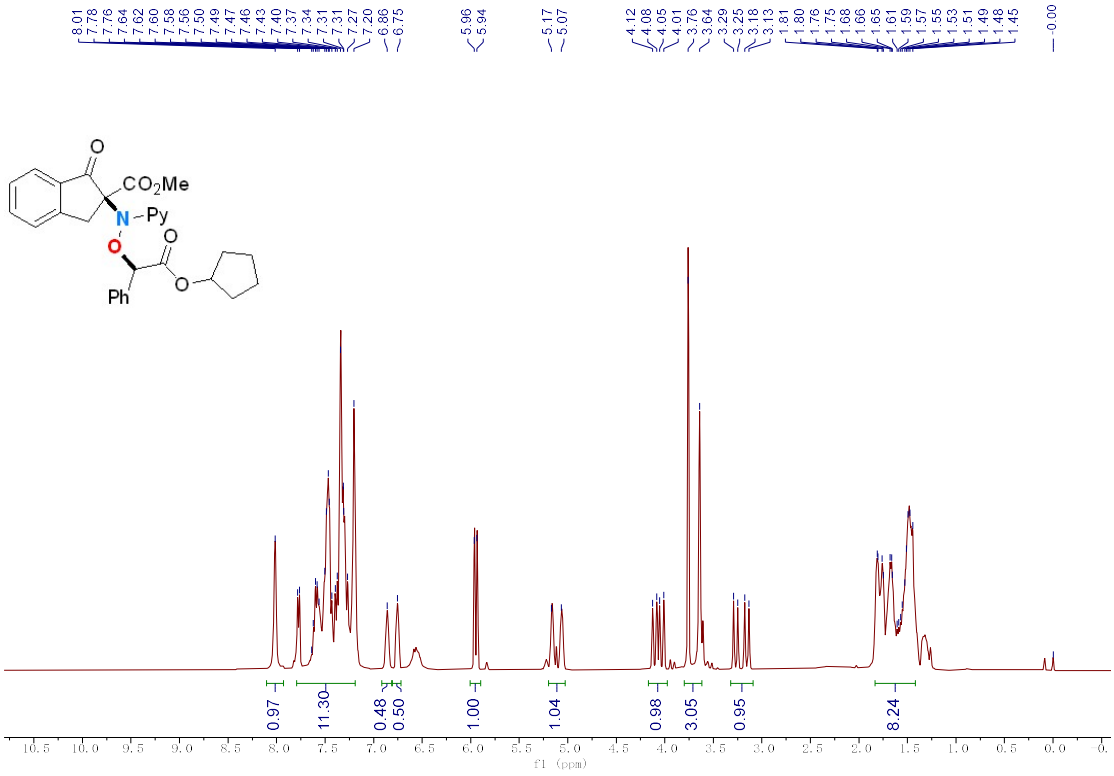
^{1}H NMR (400 MHz) Spectrum of 18 in $CDCl_3$



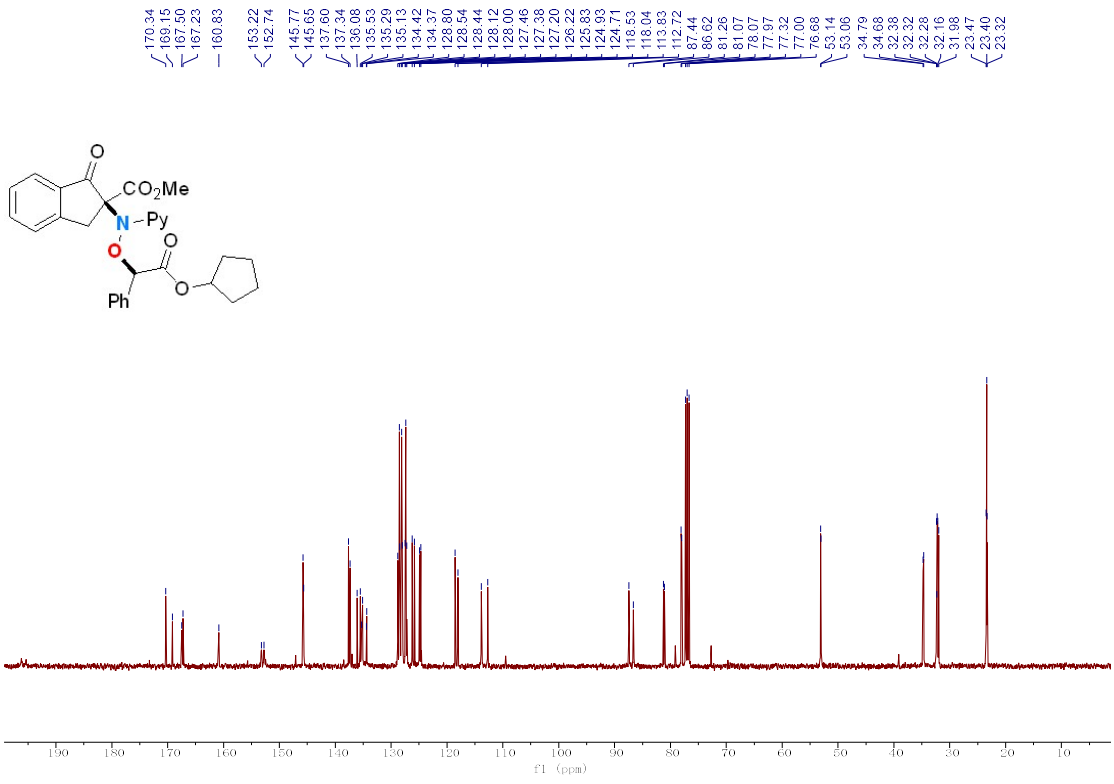
^{13}CNMR (100 MHz) Spectrum of 18 in $CDCl_3$



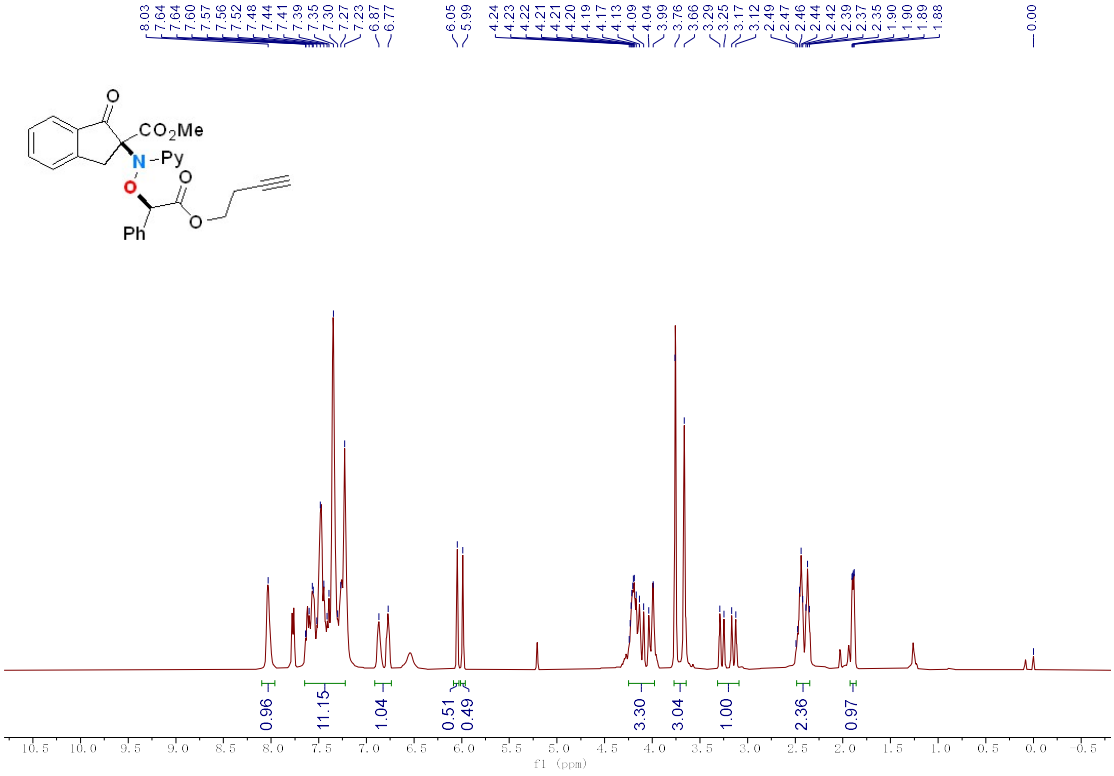
^{1}H NMR (400 MHz) Spectrum of 19 in $CDCl_3$



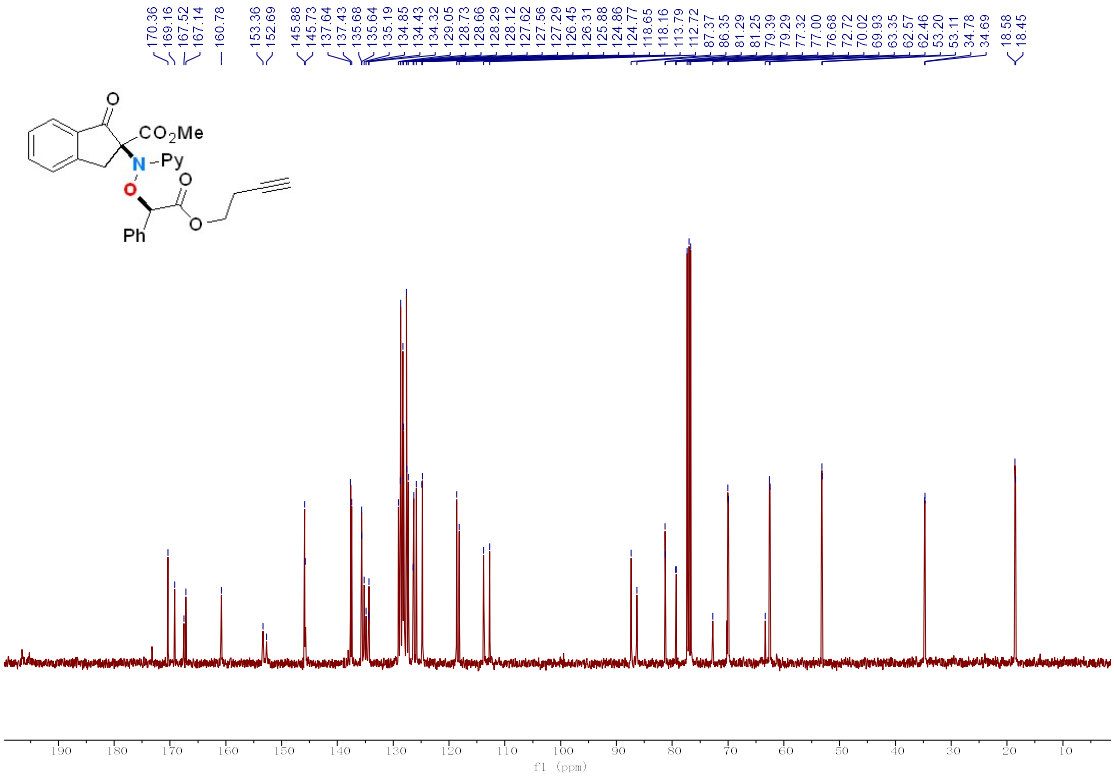
^{13}CNMR (100 MHz) Spectrum of 19 in $CDCl_3$



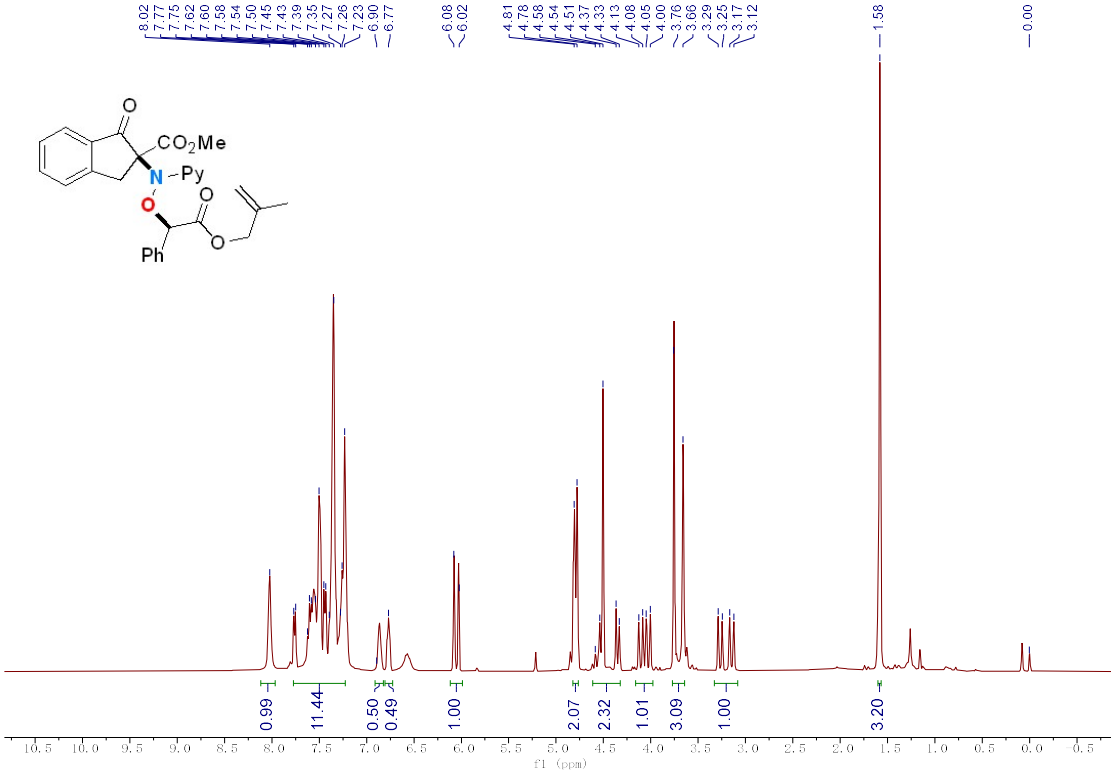
^{1}H NMR (400 MHz) Spectrum of 20 in $CDCl_3$



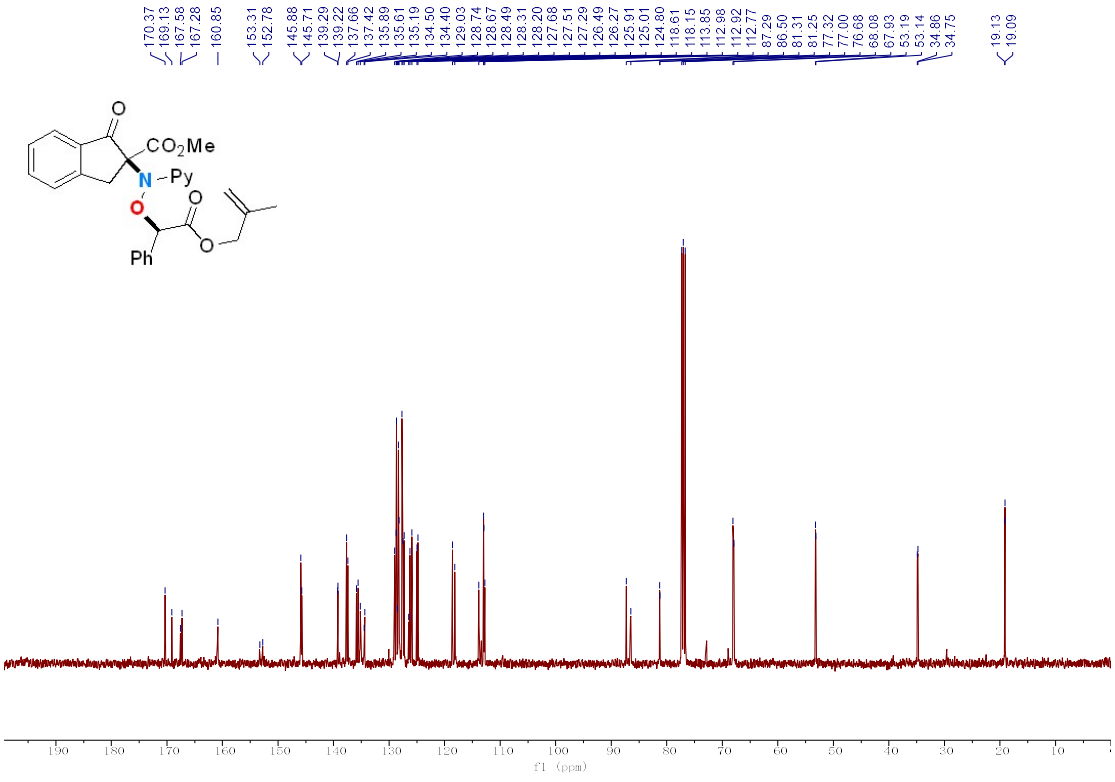
^{13}CNMR (100 MHz) Spectrum of 20 in $CDCl_3$



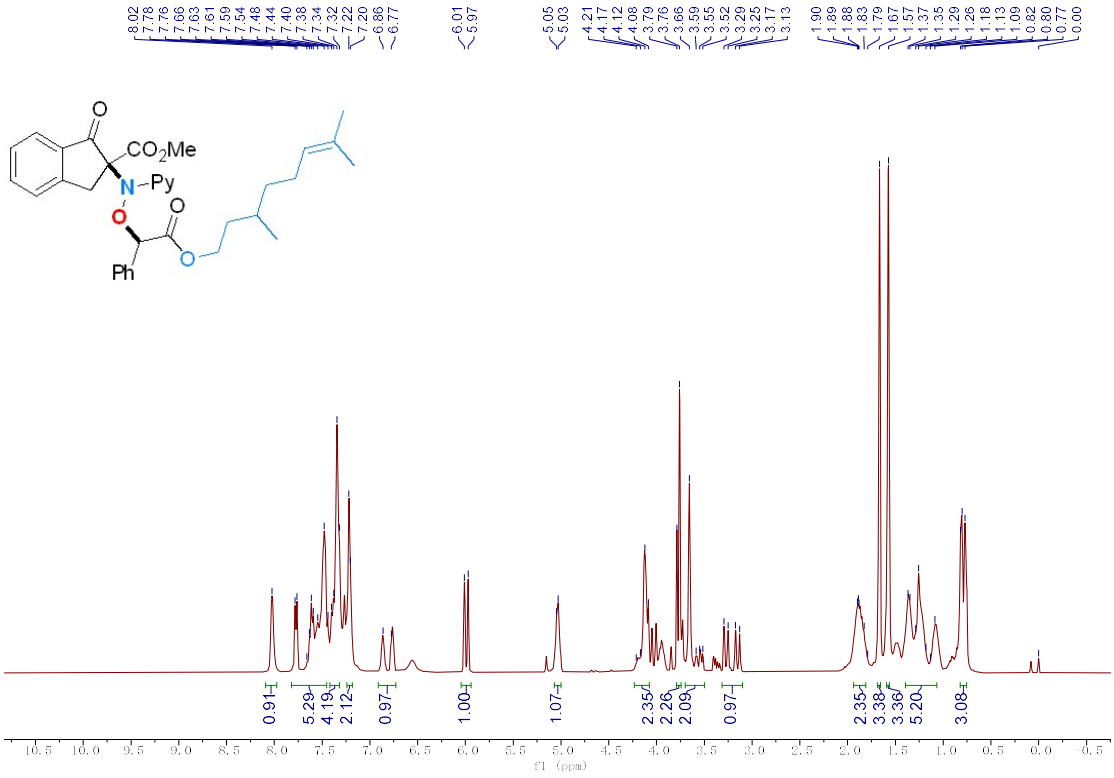
^{1}H NMR (400 MHz) Spectrum of 21 in $CDCl_3$



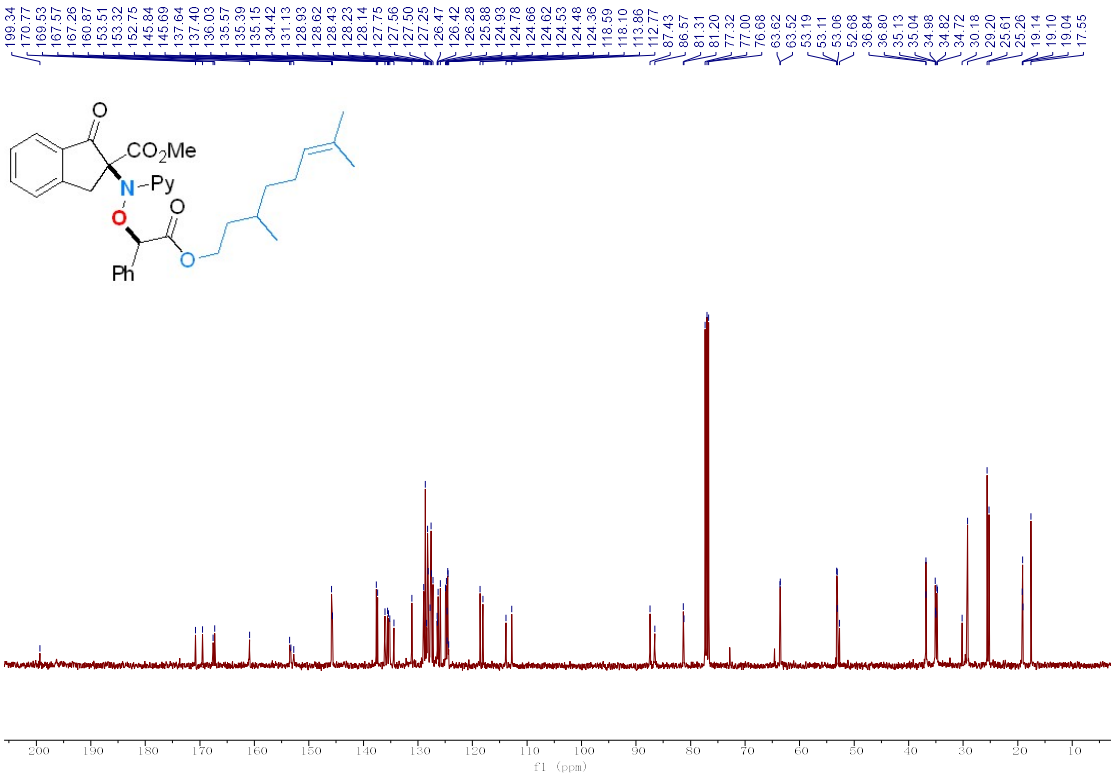
^{13}CNMR (100 MHz) Spectrum of 21 in $CDCl_3$



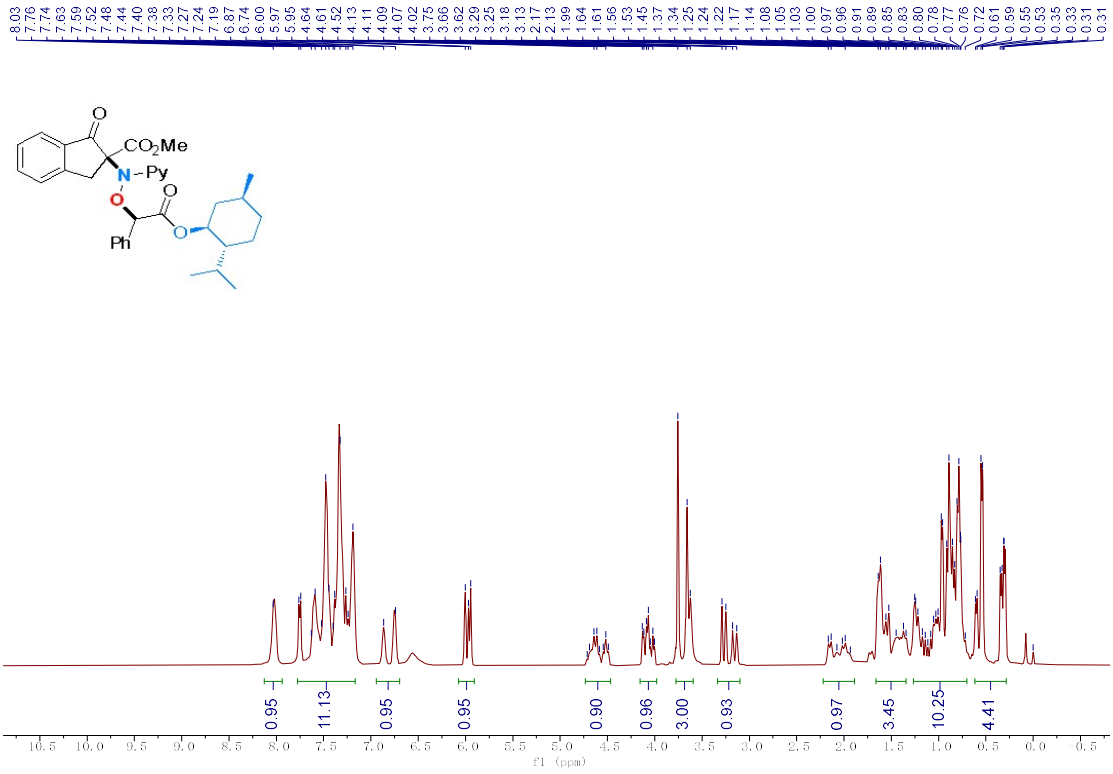
^{1}H NMR (400 MHz) Spectrum of 22 in $CDCl_3$



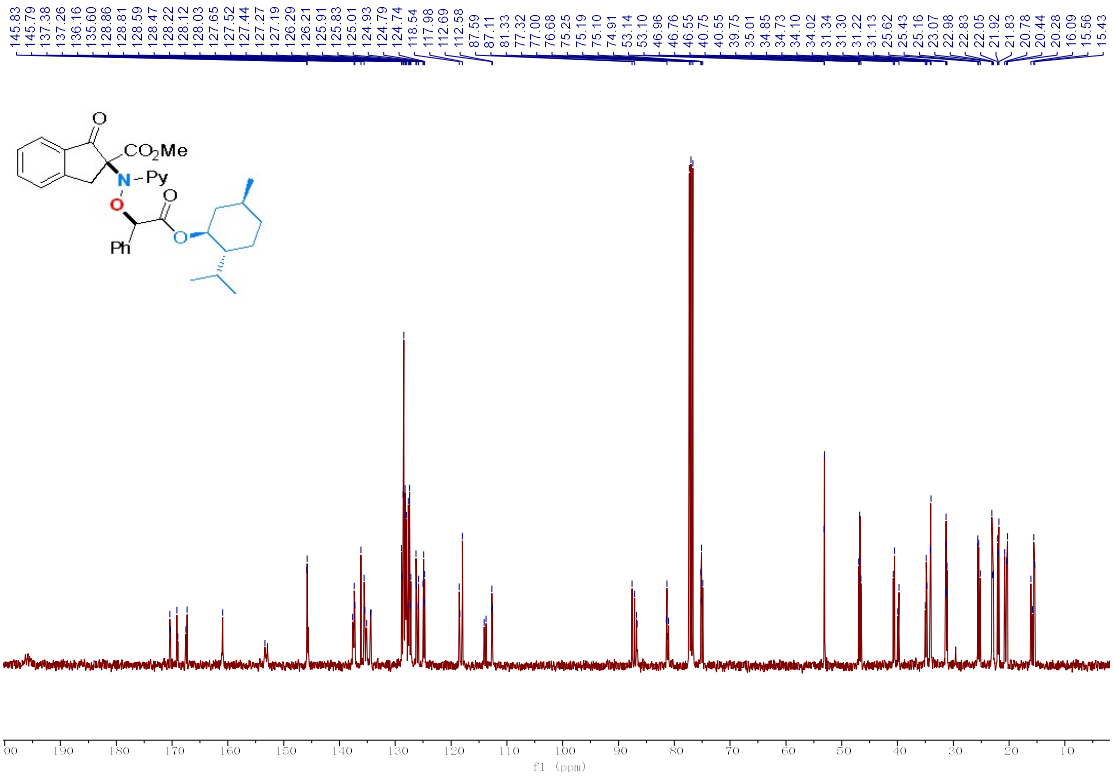
^{13}CNMR (100 MHz) Spectrum of 22 in $CDCl_3$



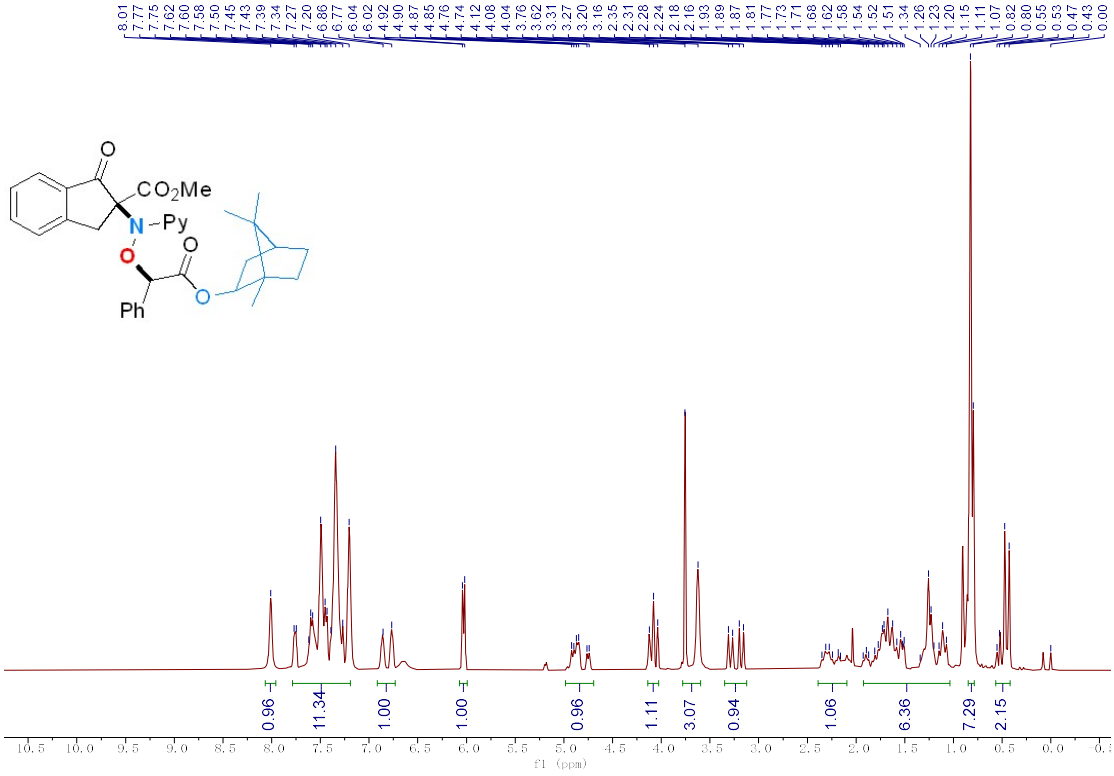
^{1}H NMR (400 MHz) Spectrum of 23 in $CDCl_3$



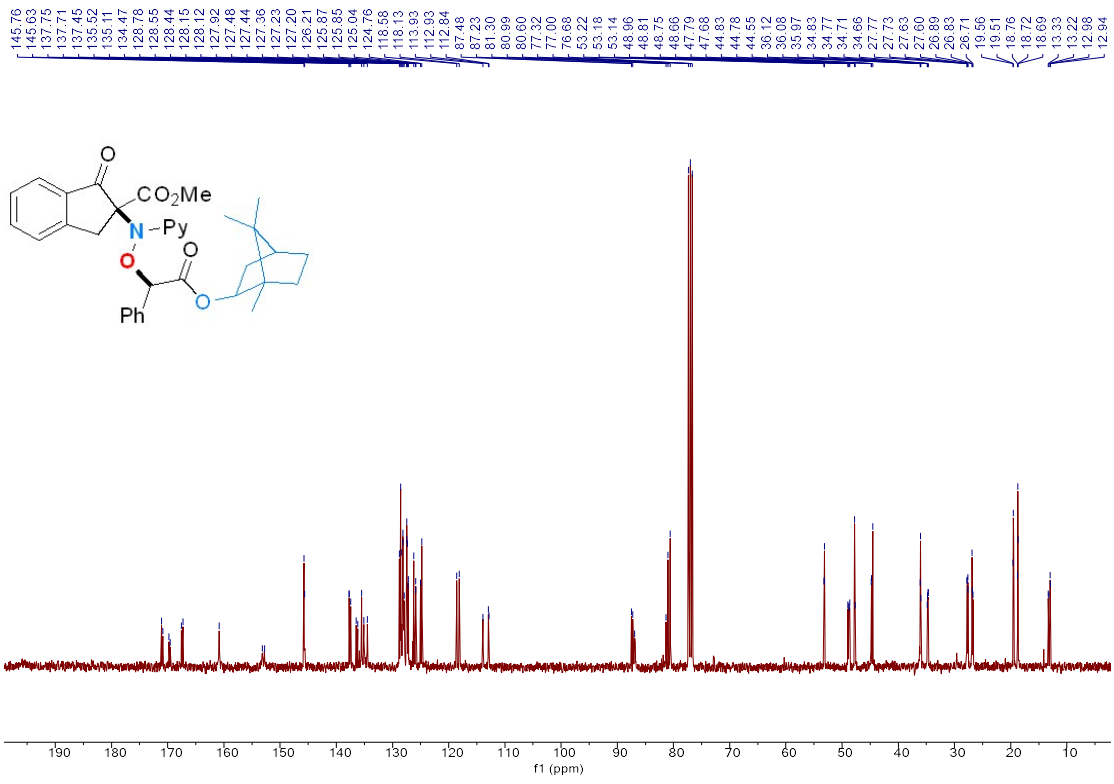
^{13}CNMR (100 MHz) Spectrum of 23 in $CDCl_3$



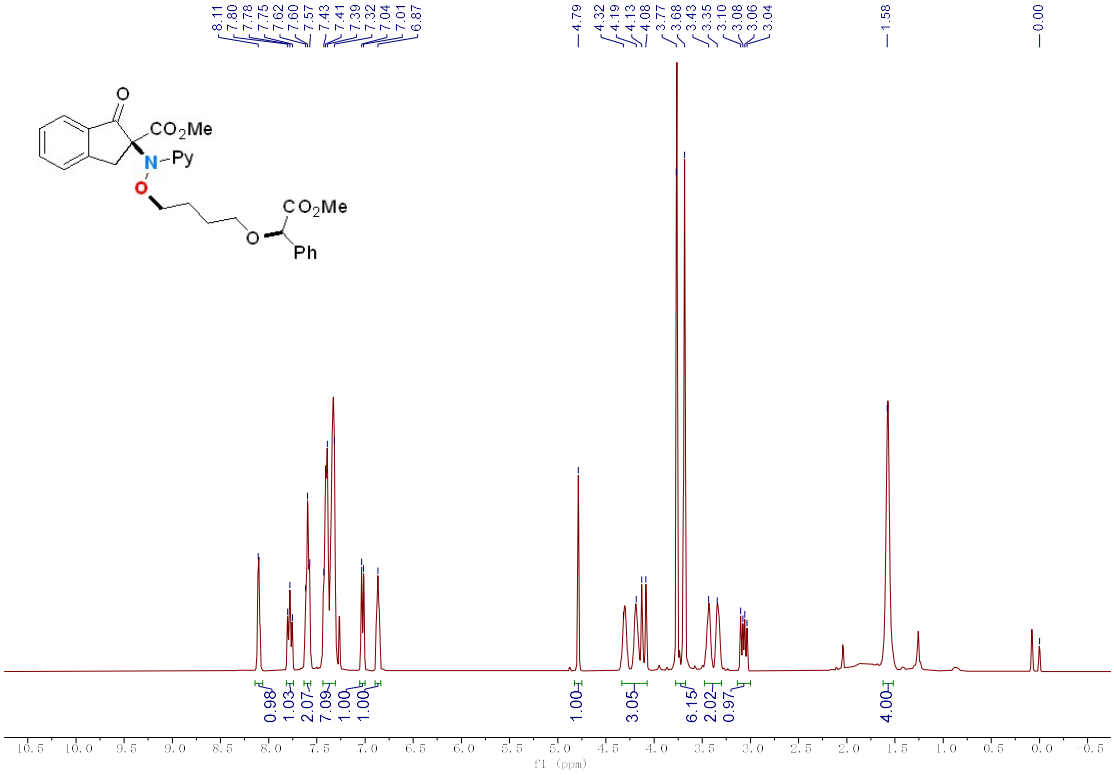
^{1}H NMR (400 MHz) Spectrum of 24 in $CDCl_3$



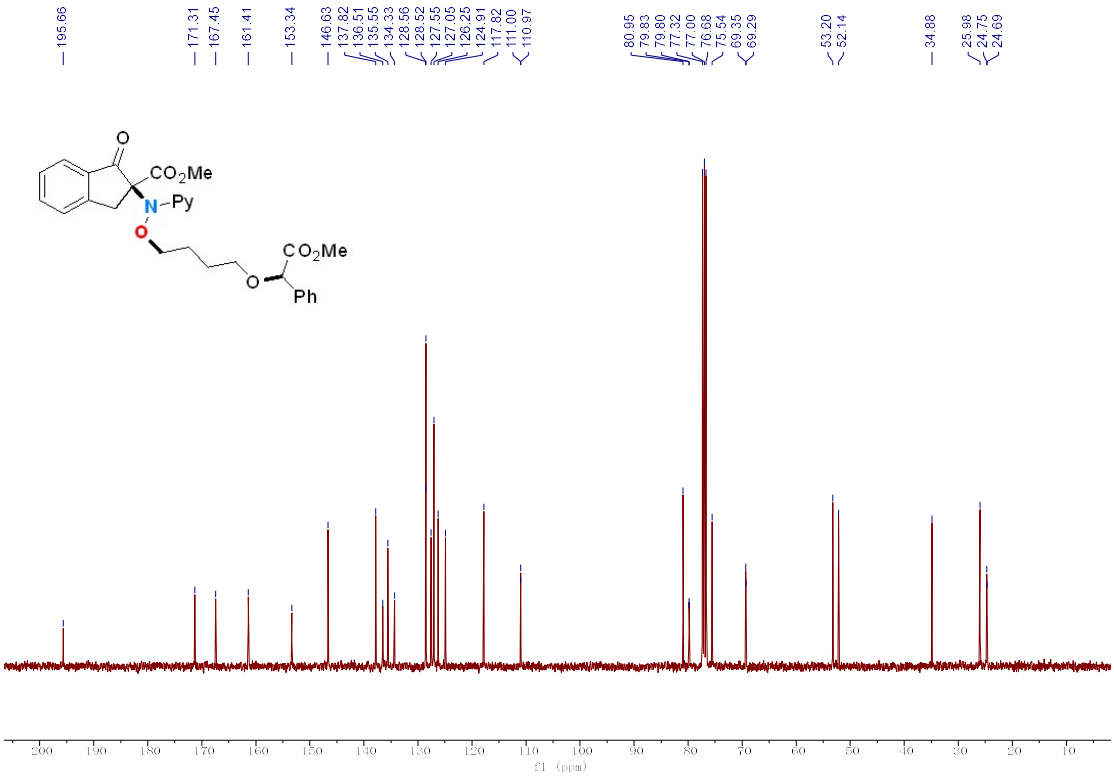
^{13}CNMR (100 MHz) Spectrum of 24 in $CDCl_3$



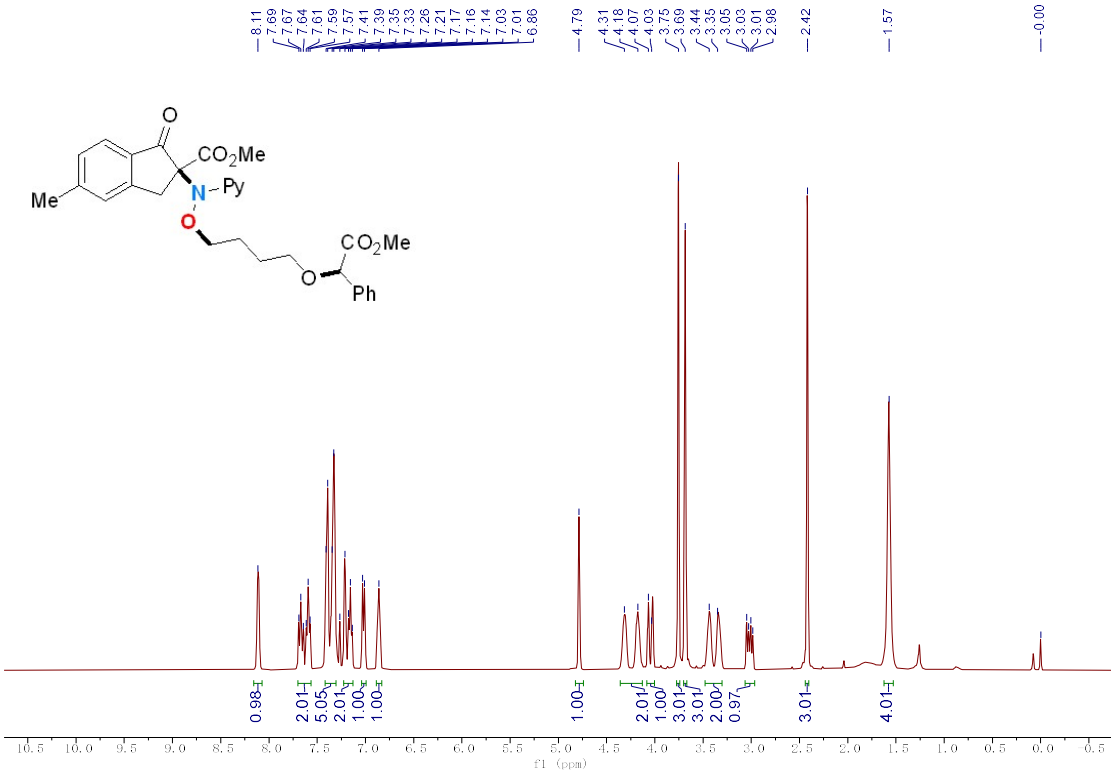
^{1}H NMR (400 MHz) Spectrum of 5 in $CDCl_3$



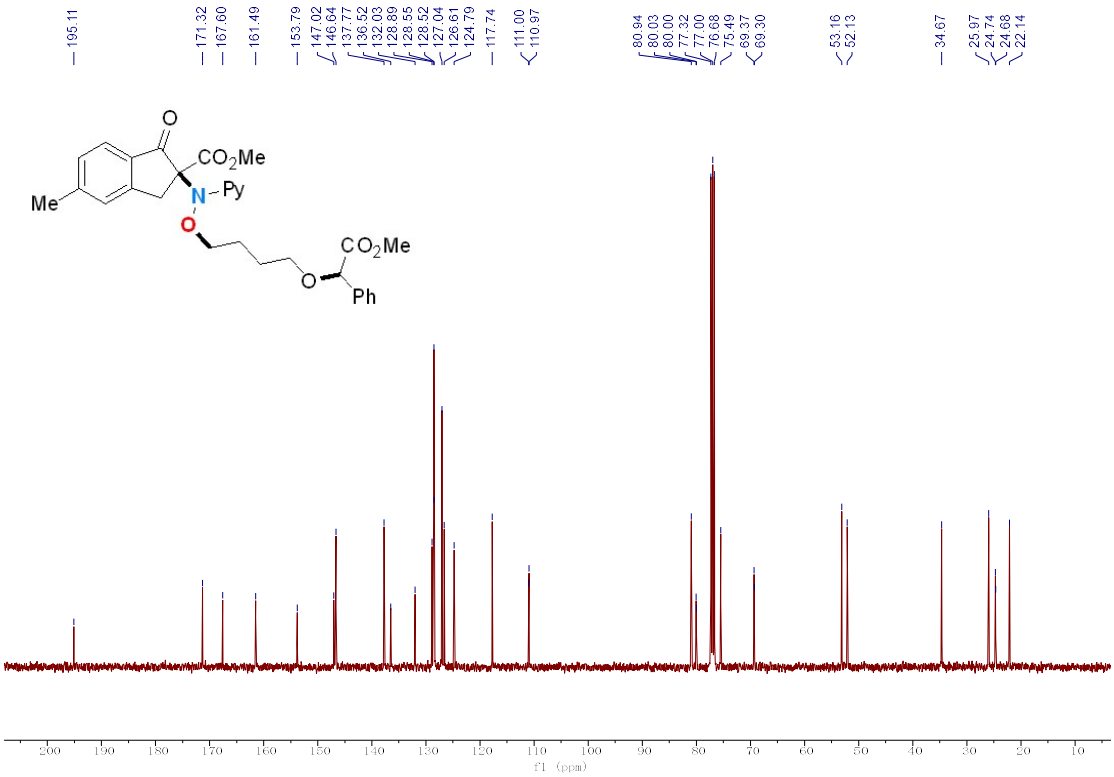
^{13}CNMR (100 MHz) Spectrum of 5 in $CDCl_3$



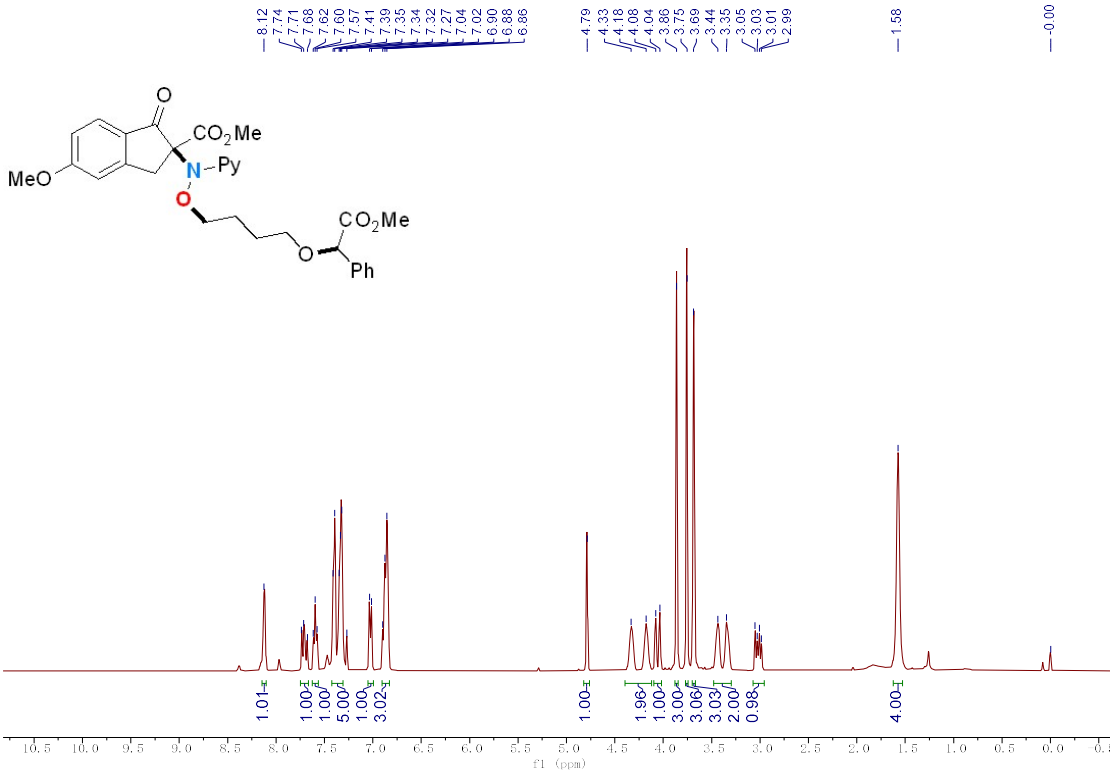
^{1}H NMR (400 MHz) Spectrum of 25 in $CDCl_3$



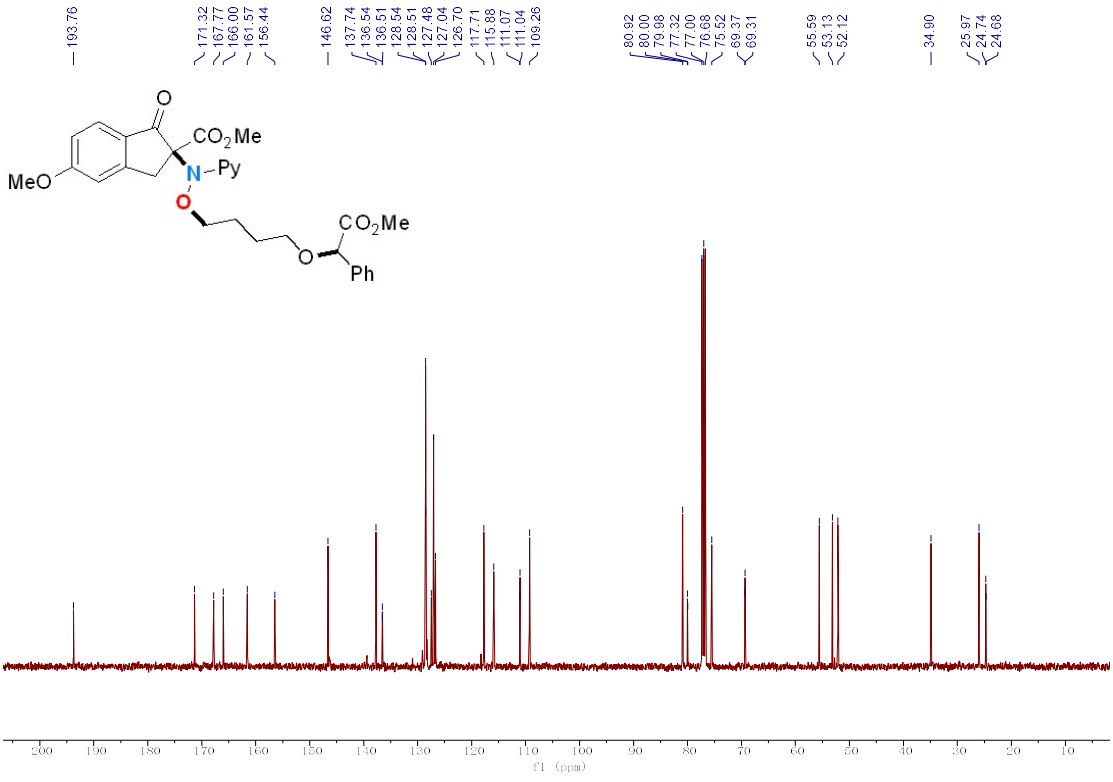
^{13}CNMR (100 MHz) Spectrum of 25 in $CDCl_3$



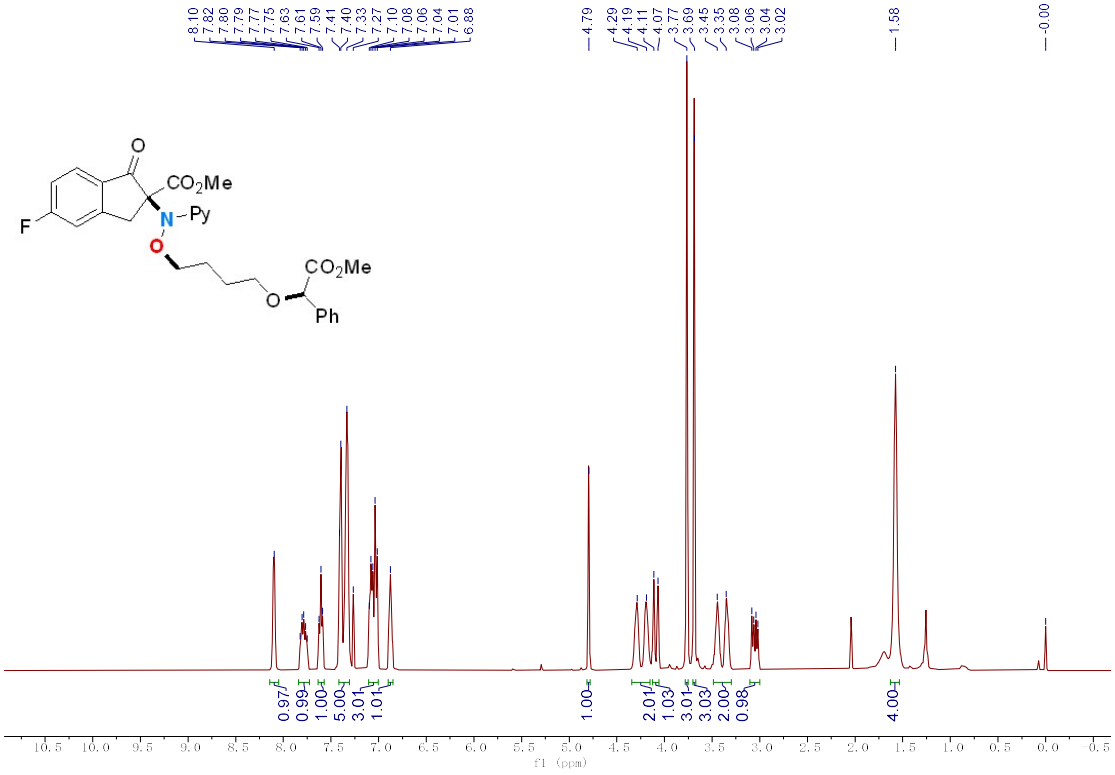
^{1}H NMR (400 MHz) Spectrum of 26 in $CDCl_3$



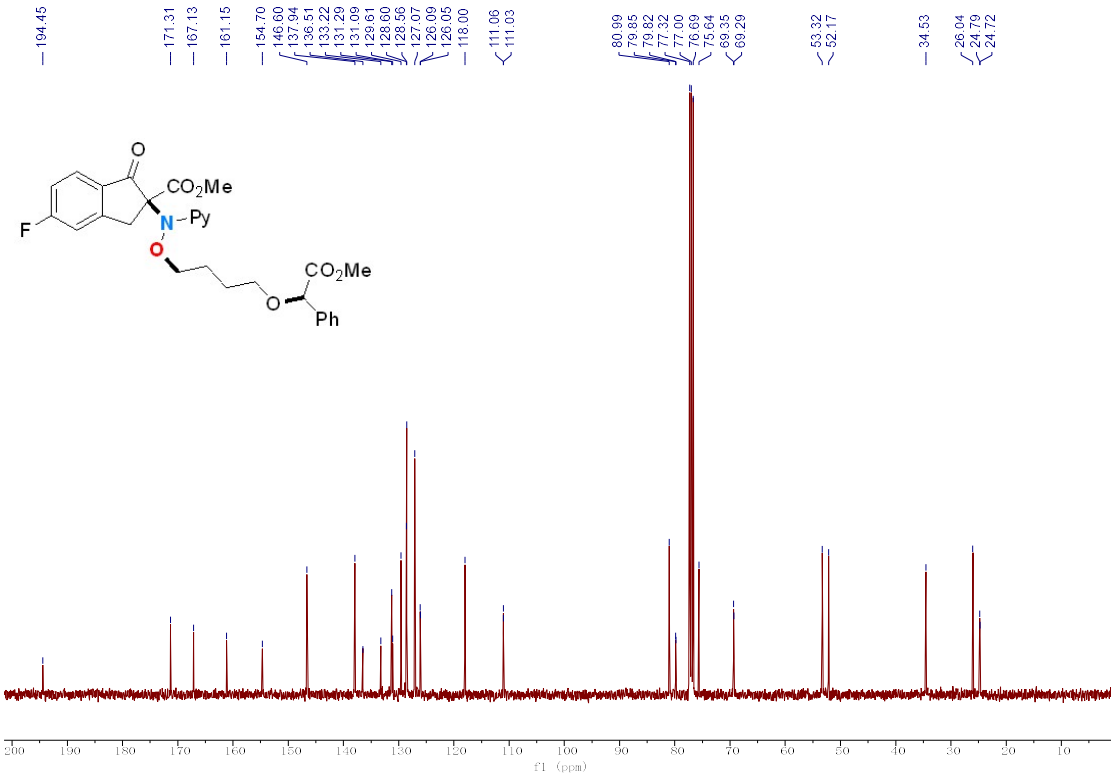
^{13}CNMR (100 MHz) Spectrum of 26 in $CDCl_3$



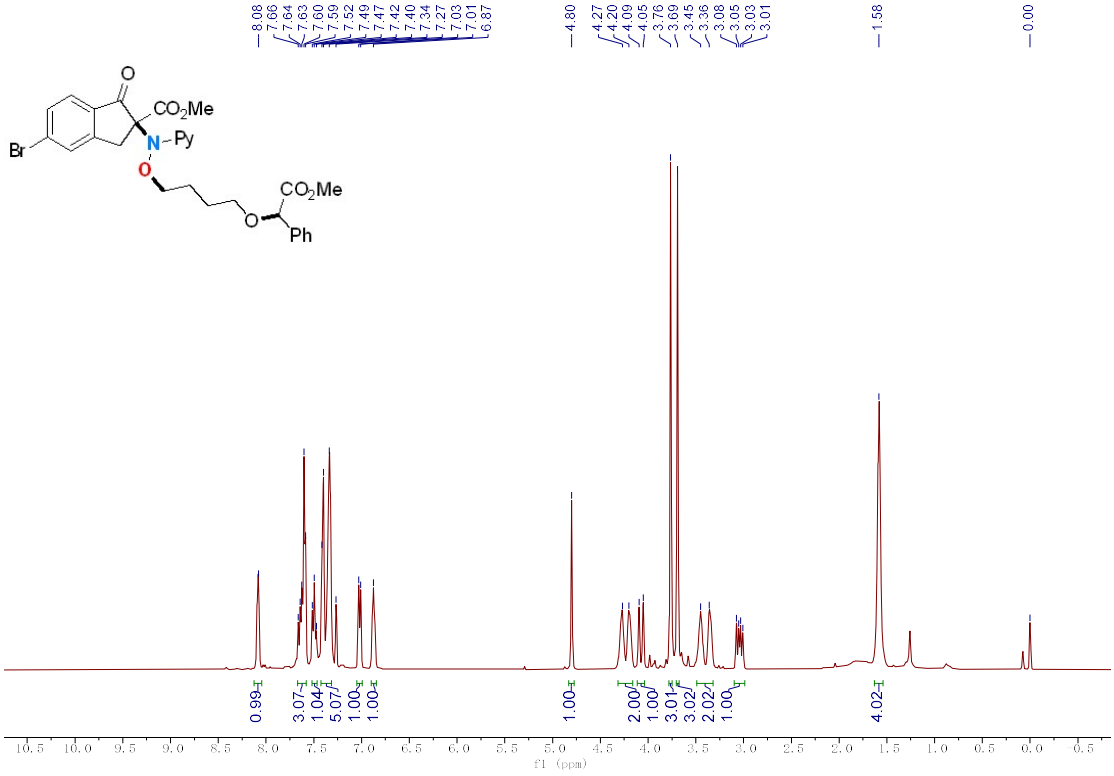
^{1}H NMR (400 MHz) Spectrum of 27 in $CDCl_3$



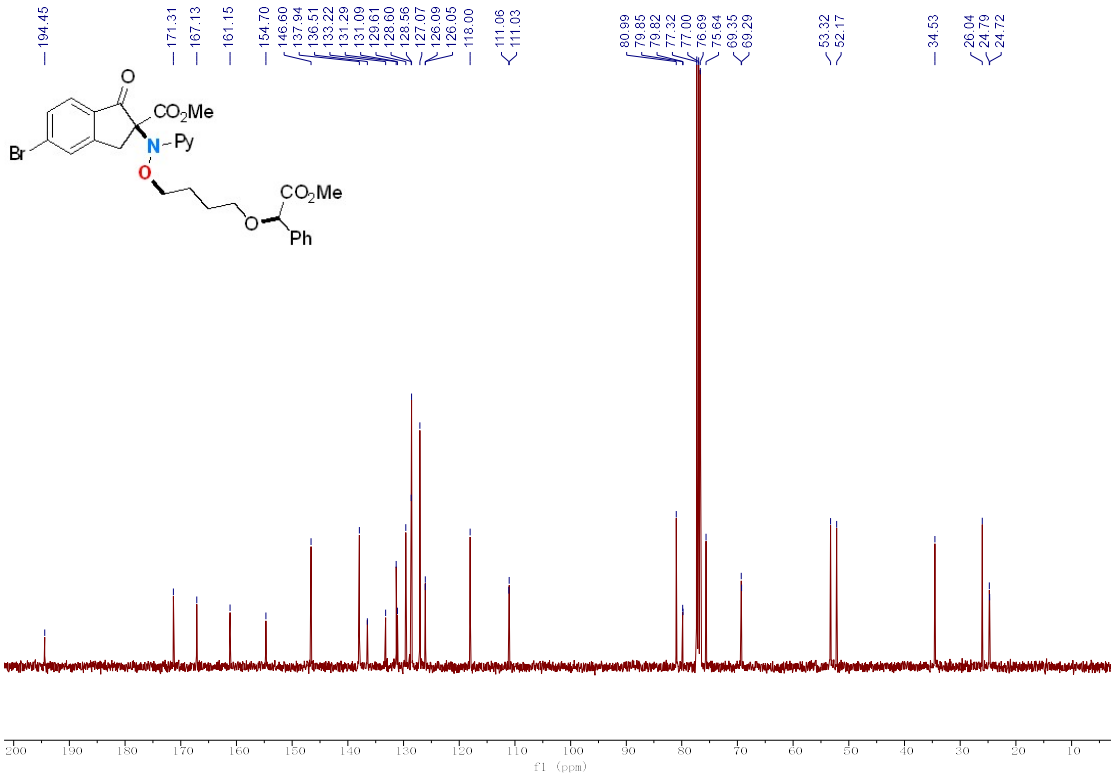
^{13}CNMR (100 MHz) Spectrum of 27 in $CDCl_3$



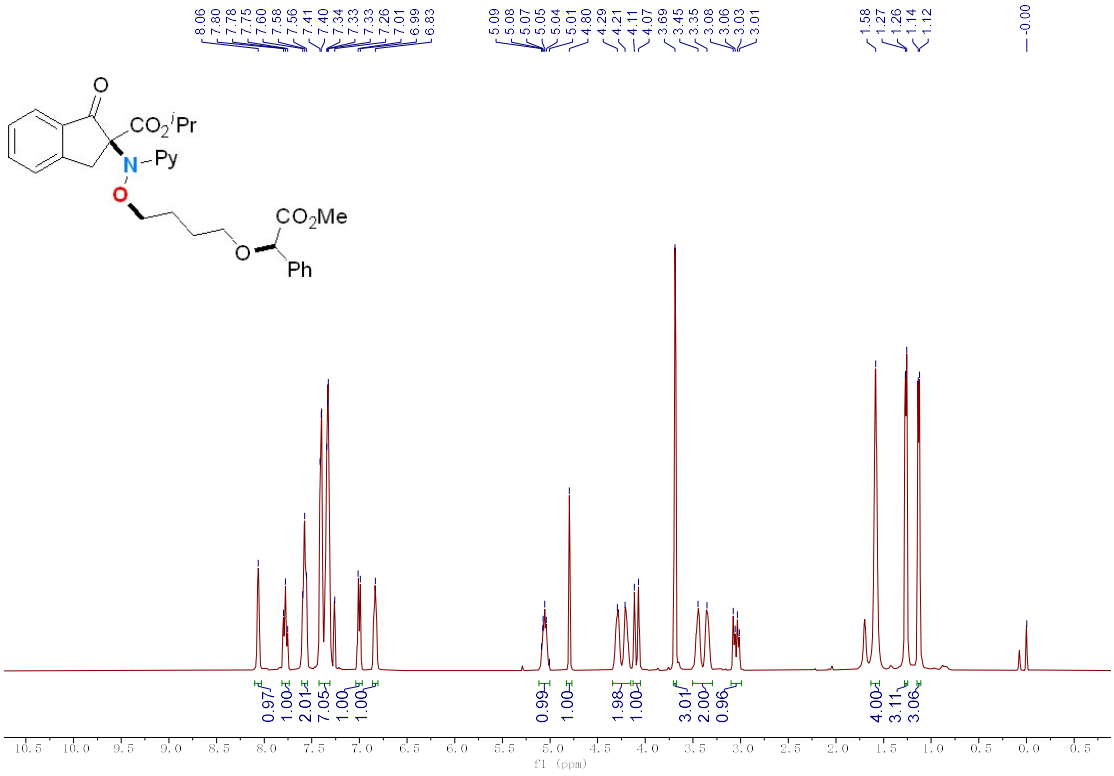
^{1}H NMR (400 MHz) Spectrum of 28 in $CDCl_3$



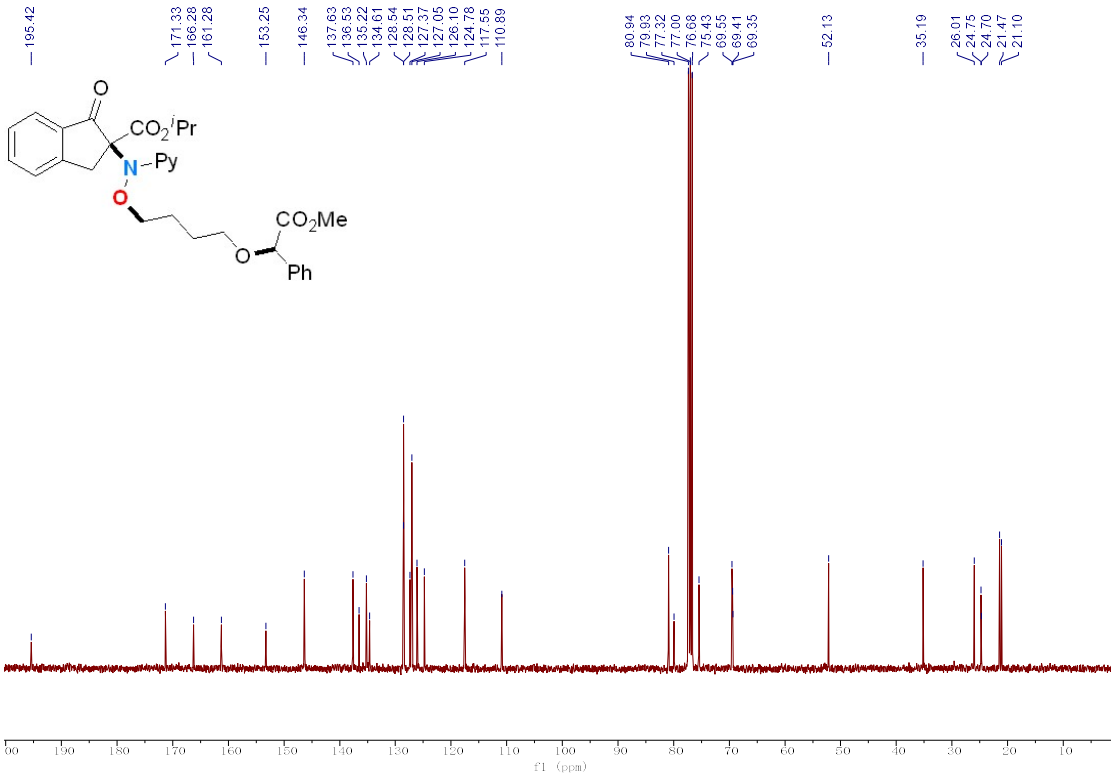
^{13}CNMR (100 MHz) Spectrum of 28 in $CDCl_3$



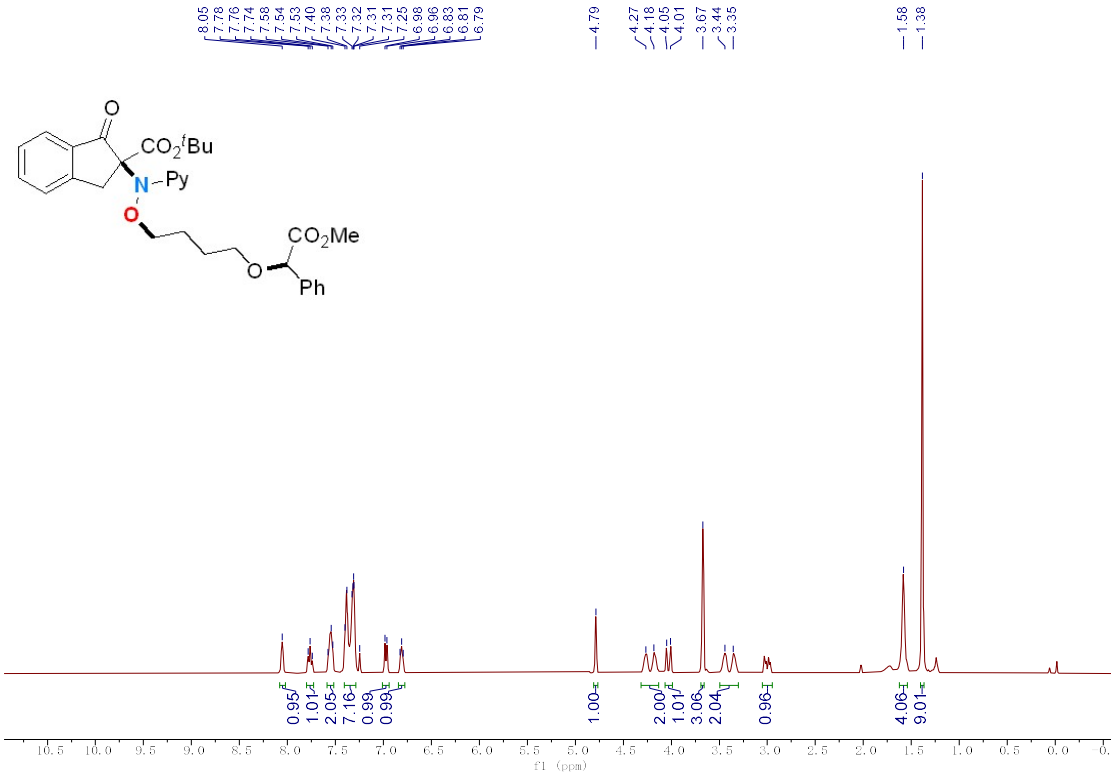
^{1}H NMR (400 MHz) Spectrum of 29 in $CDCl_3$



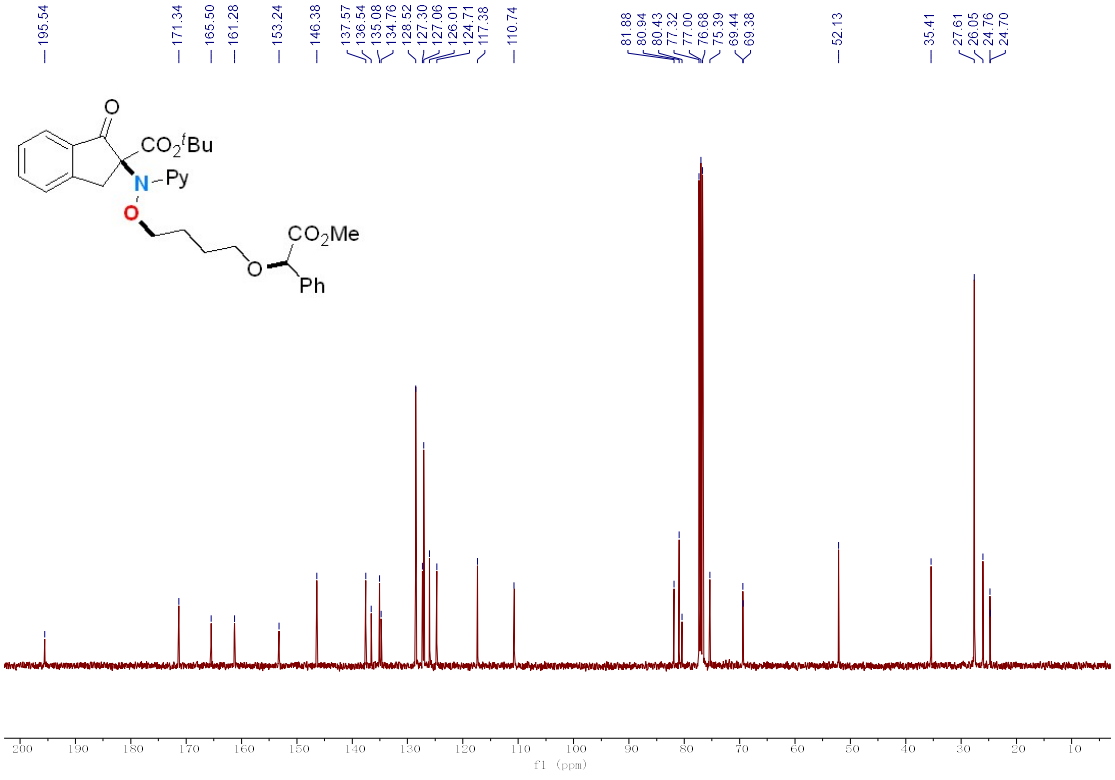
^{13}CNMR (100 MHz) Spectrum of 29 in $CDCl_3$



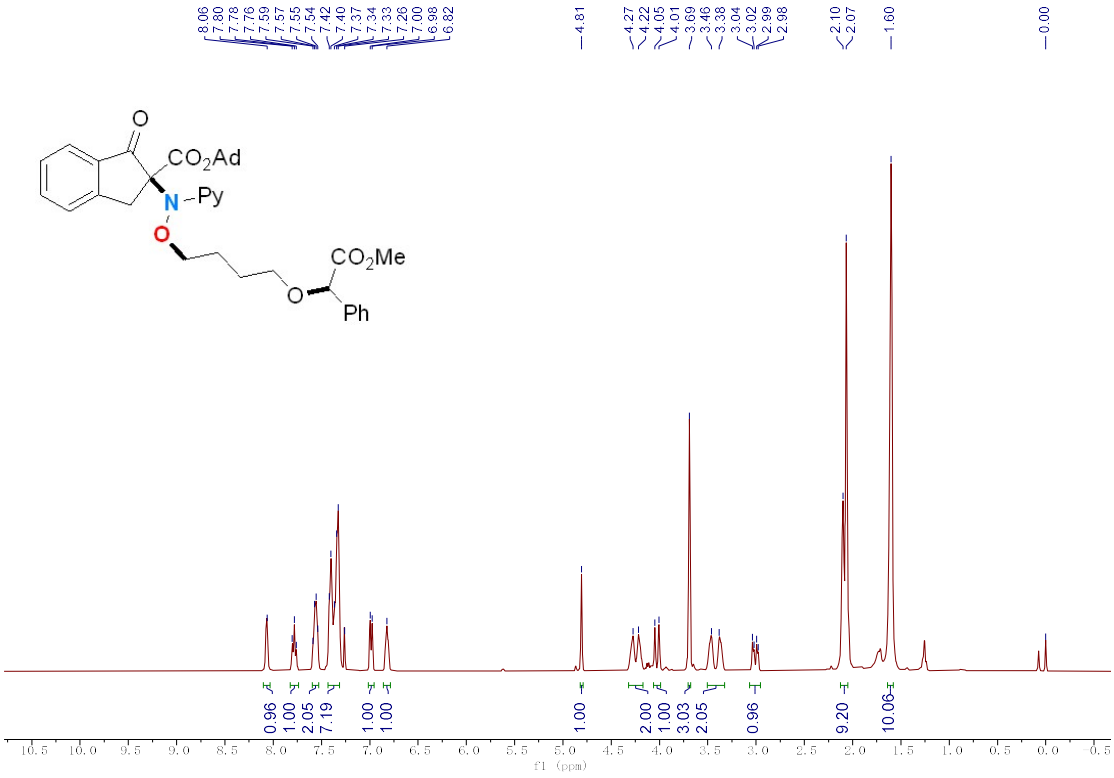
^{1}H NMR (400 MHz) Spectrum of 30 in $CDCl_3$



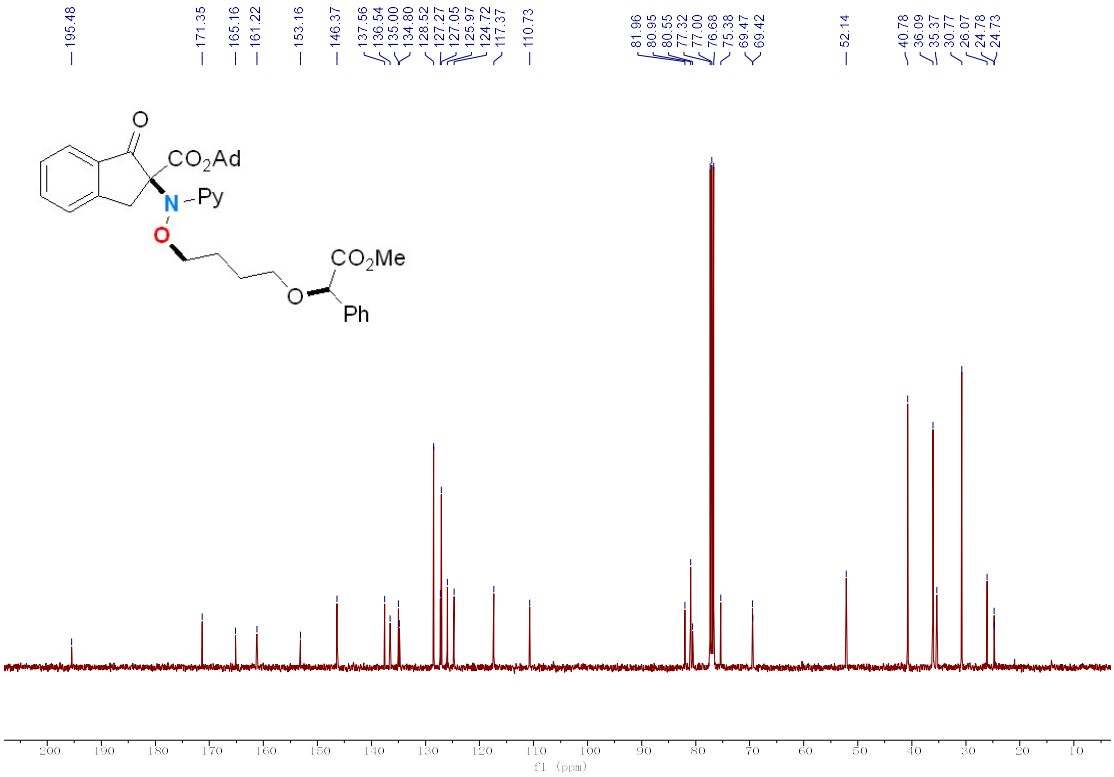
^{13}CNMR (100 MHz) Spectrum of 30 in $CDCl_3$



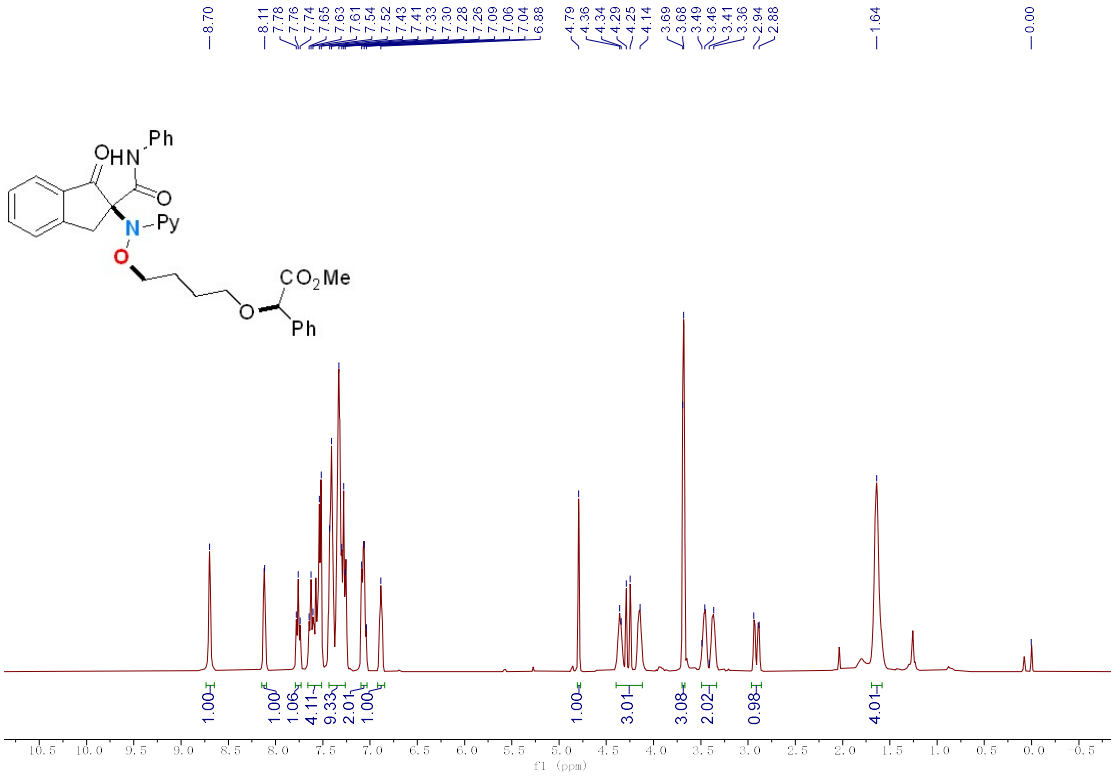
^{1}H NMR (400 MHz) Spectrum of 31 in $CDCl_3$



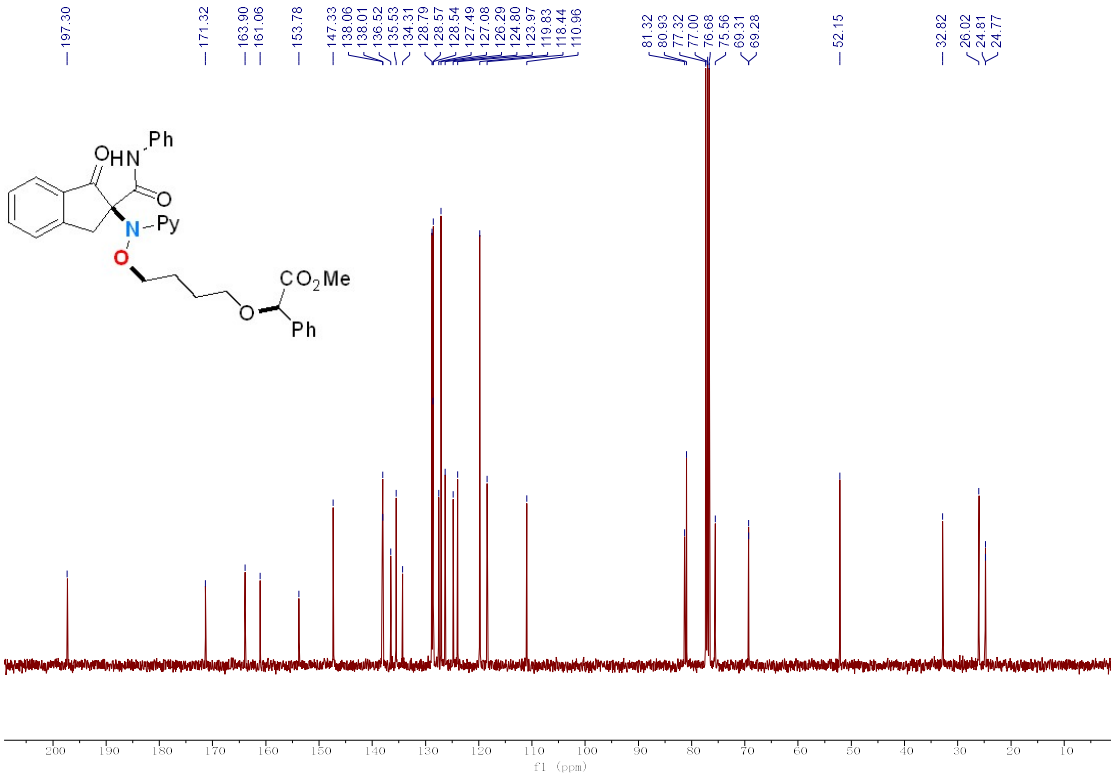
^{13}CNMR (100 MHz) Spectrum of 31 in $CDCl_3$



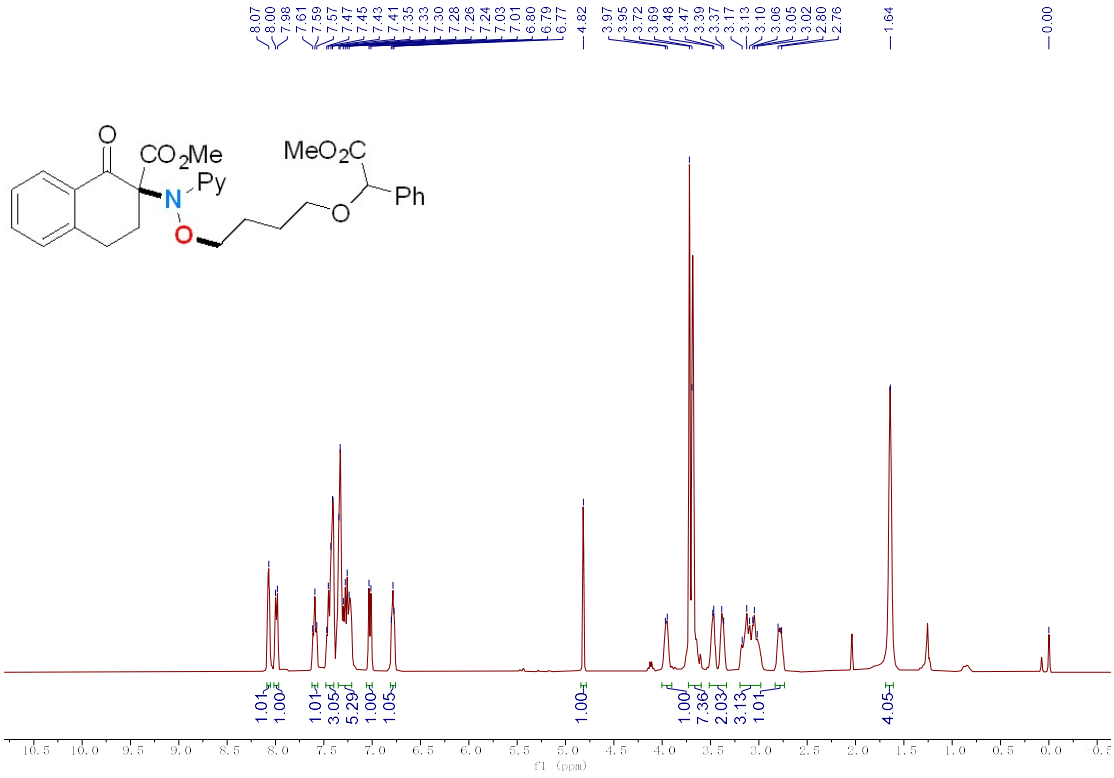
^{1}H NMR (400 MHz) Spectrum of 32 in $CDCl_3$



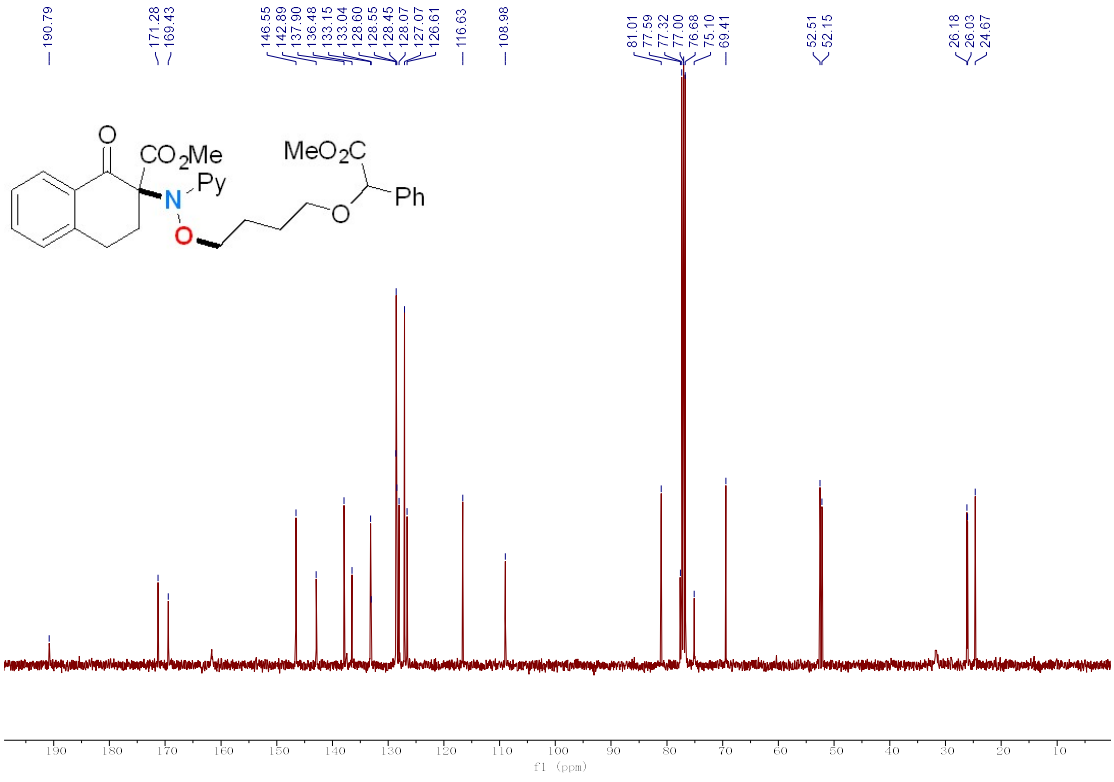
^{13}CNMR (100 MHz) Spectrum of 32 in $CDCl_3$



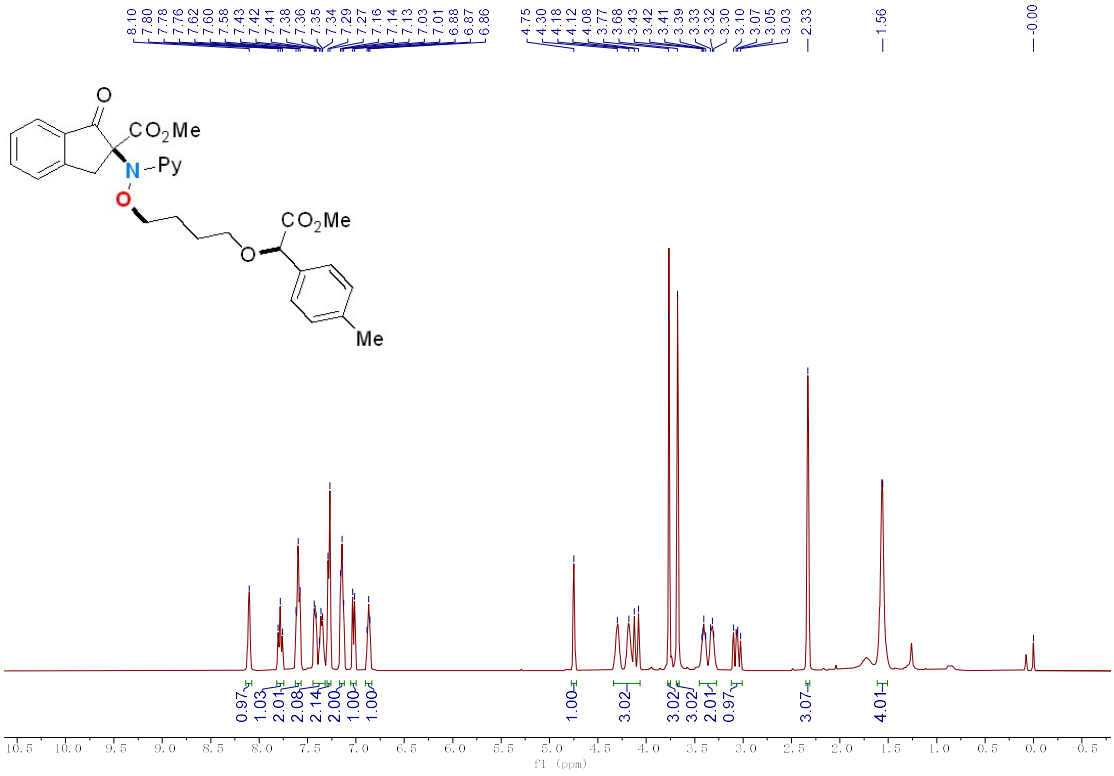
^{1}H NMR (400 MHz) Spectrum of 33 in $CDCl_3$



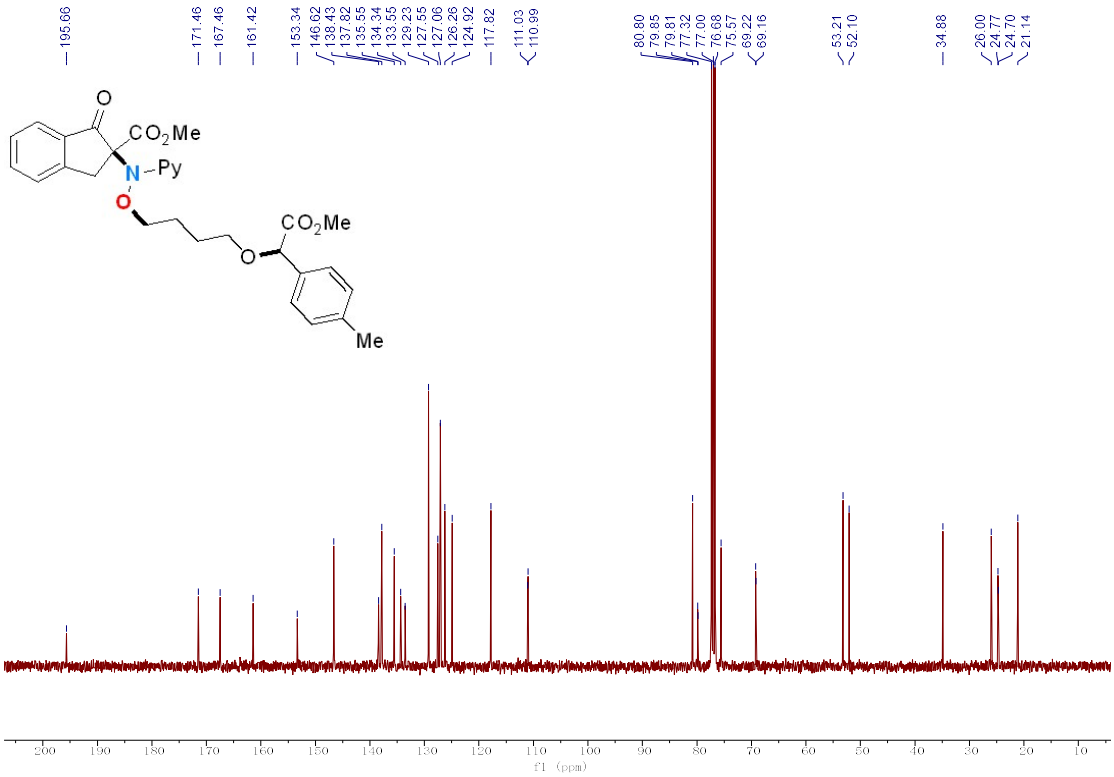
^{13}CNMR (100 MHz) Spectrum of 33 in $CDCl_3$



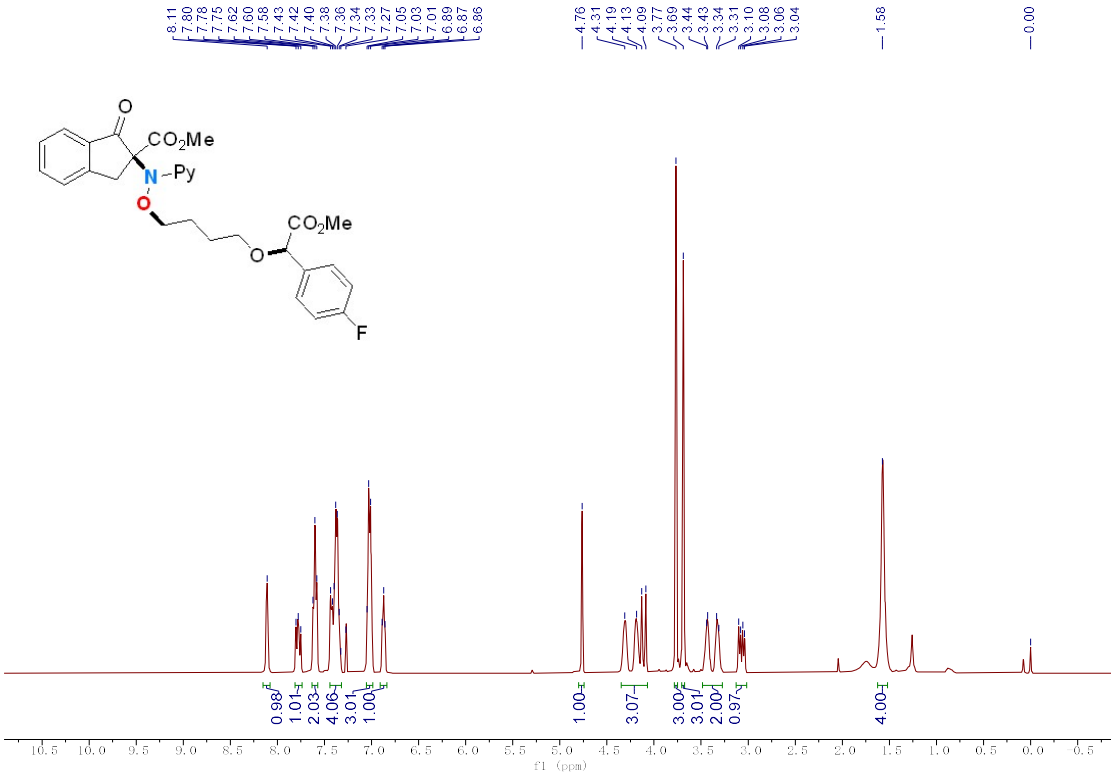
^{1}H NMR (400 MHz) Spectrum of 34 in $CDCl_3$



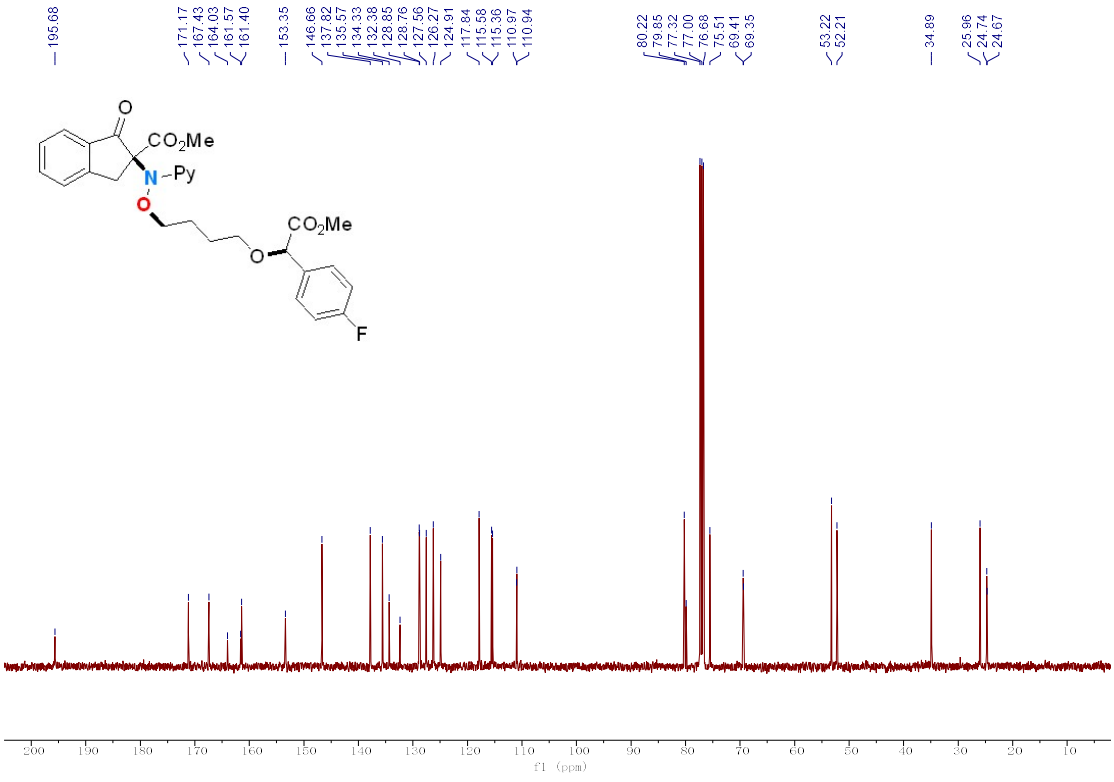
^{13}CNMR (100 MHz) Spectrum of 34 in $CDCl_3$



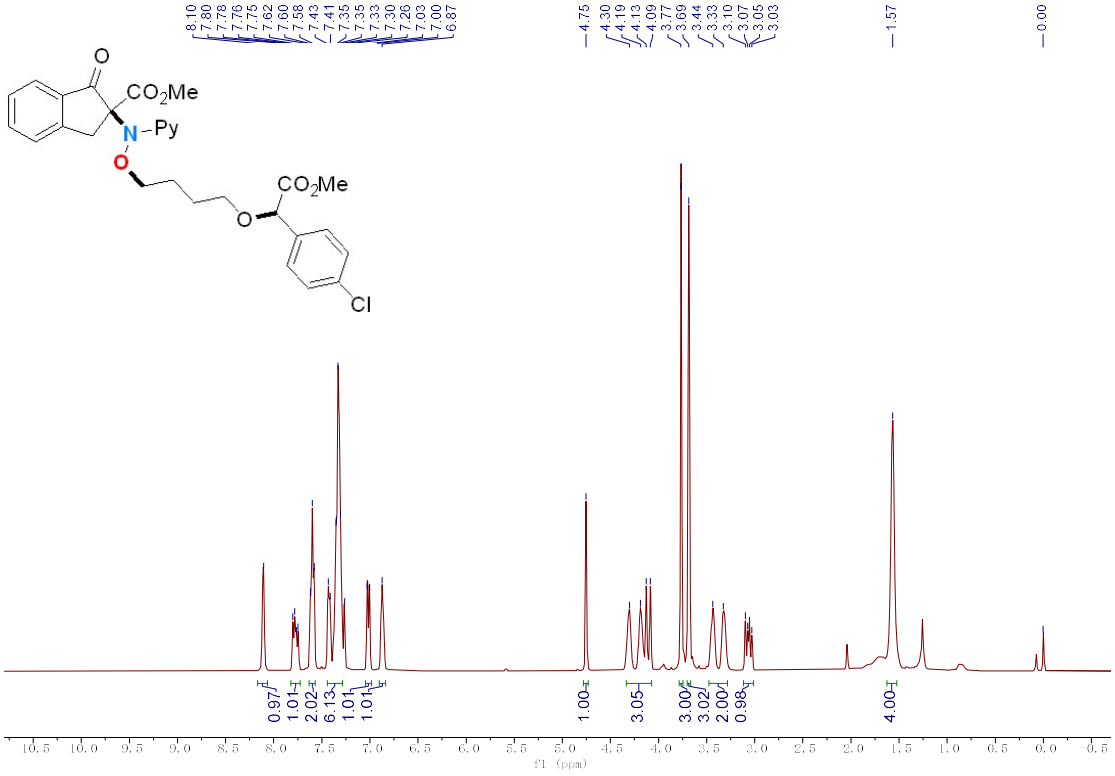
^{1}H NMR (400 MHz) Spectrum of 35 in $CDCl_3$



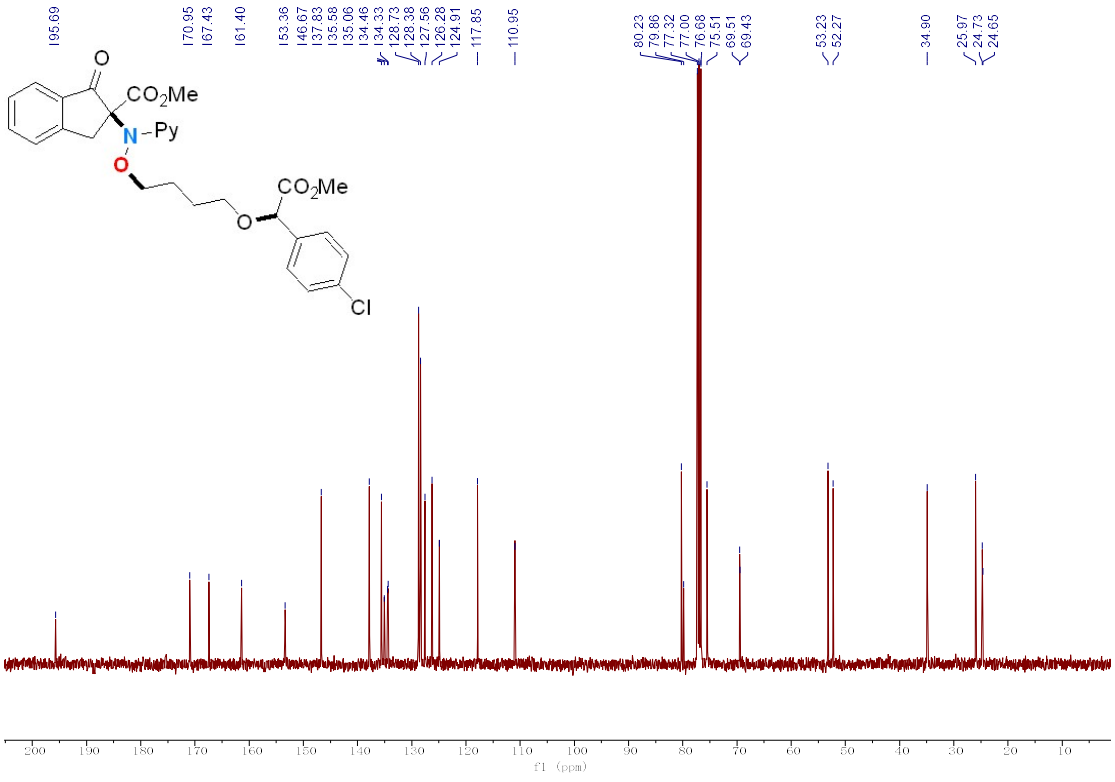
^{13}CNMR (100 MHz) Spectrum of 35 in $CDCl_3$



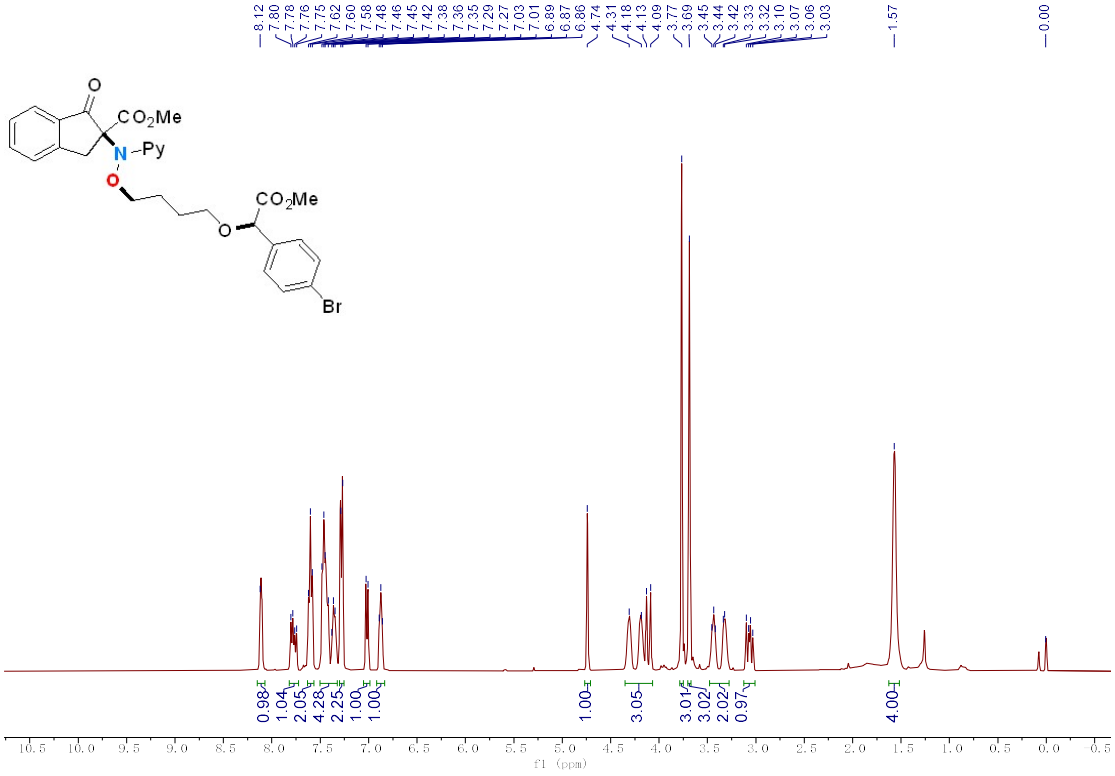
^{1}H NMR (400 MHz) Spectrum of 36 in $CDCl_3$



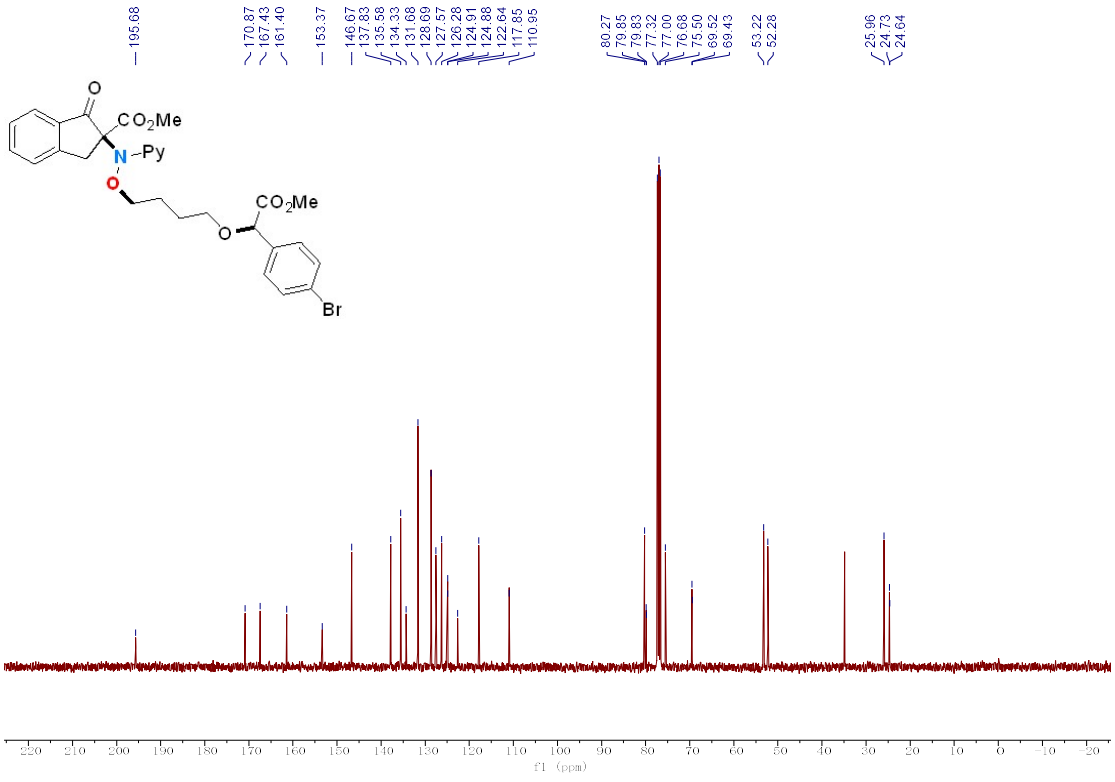
^{13}CNMR (100 MHz) Spectrum of 36 in $CDCl_3$



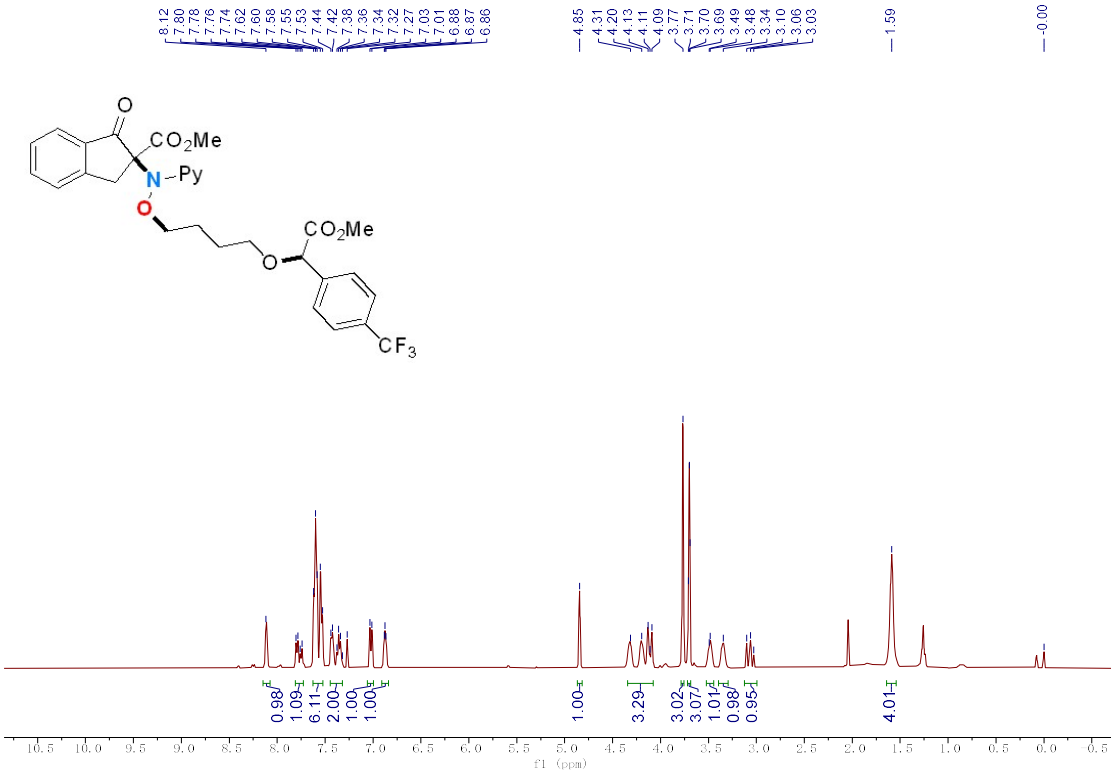
^{1}H NMR (400 MHz) Spectrum of 37 in $CDCl_3$



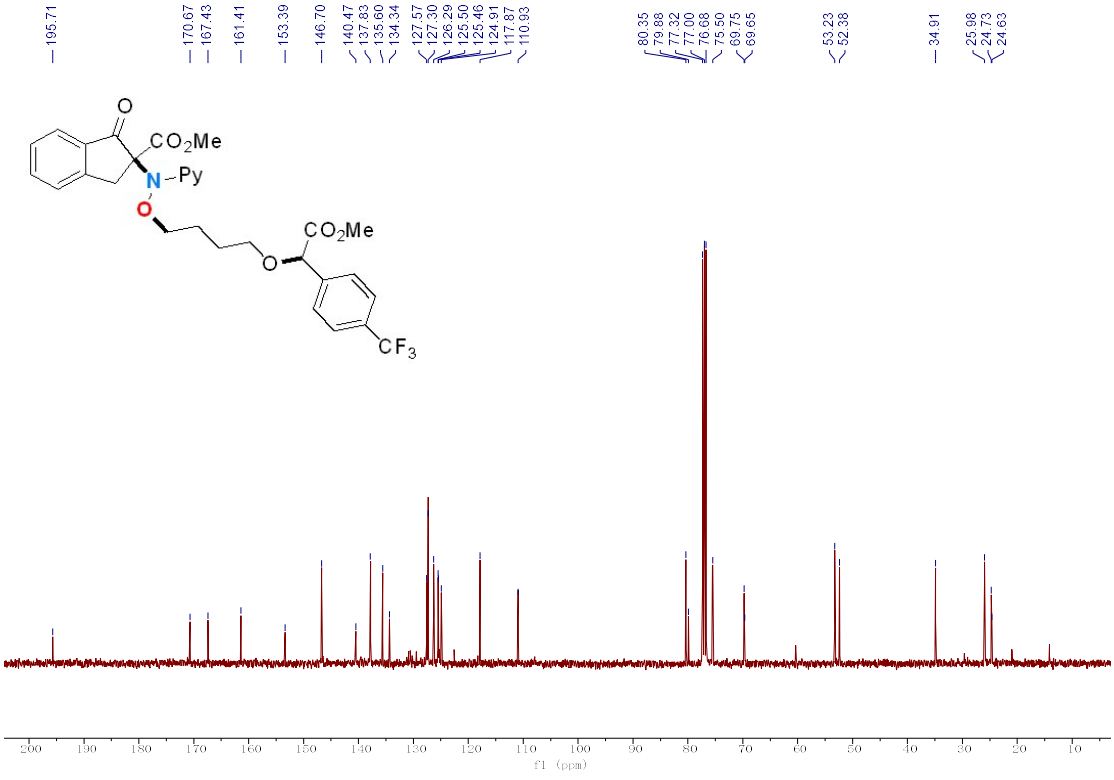
^{13}CNMR (100 MHz) Spectrum of 37 in $CDCl_3$



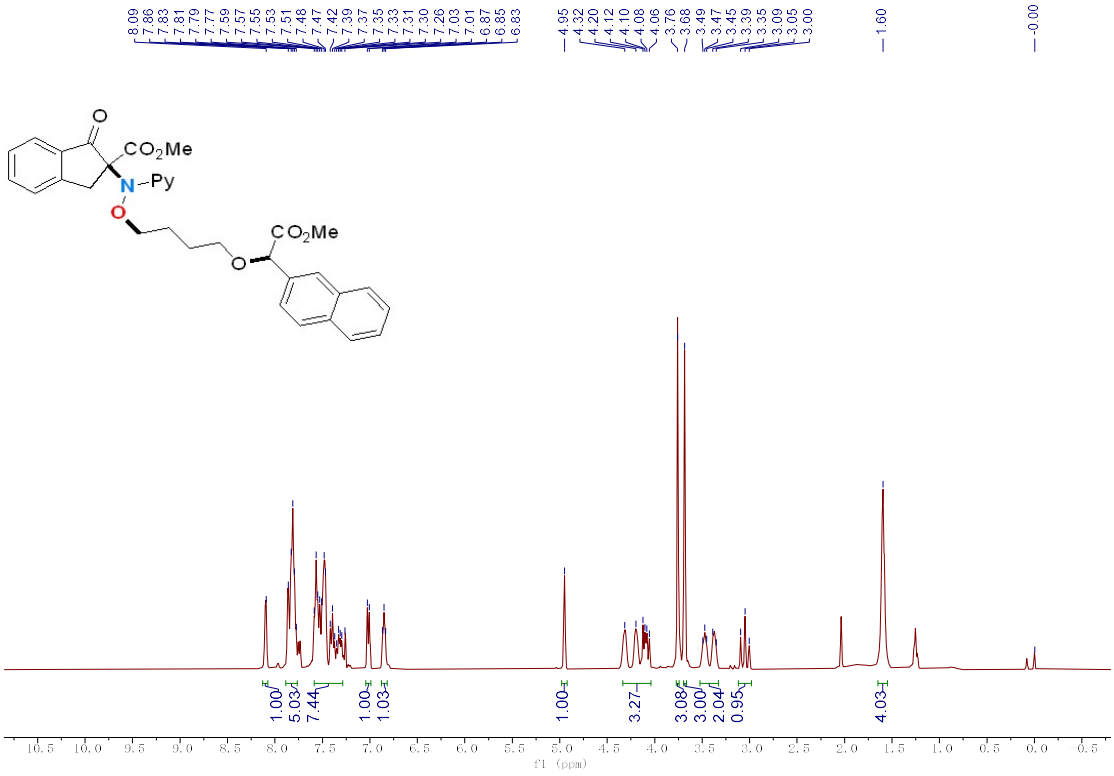
^{1}H NMR (400 MHz) Spectrum of 38 in $CDCl_3$



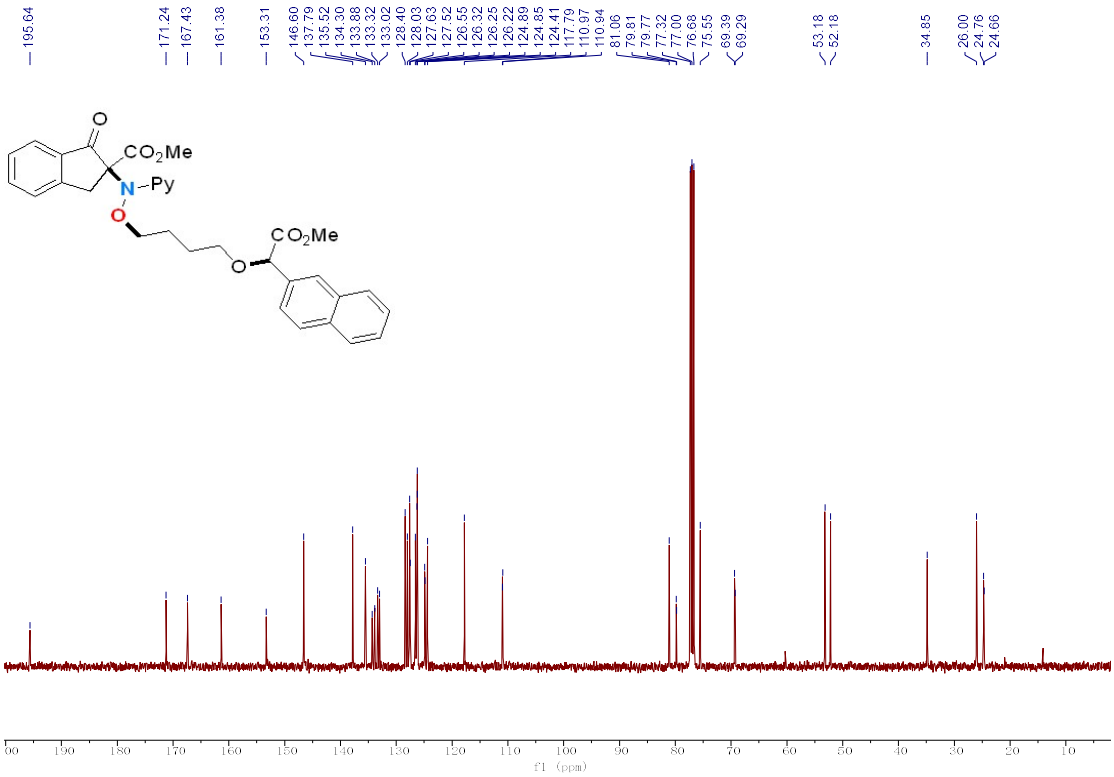
^{13}CNMR (100 MHz) Spectrum of 38 in $CDCl_3$



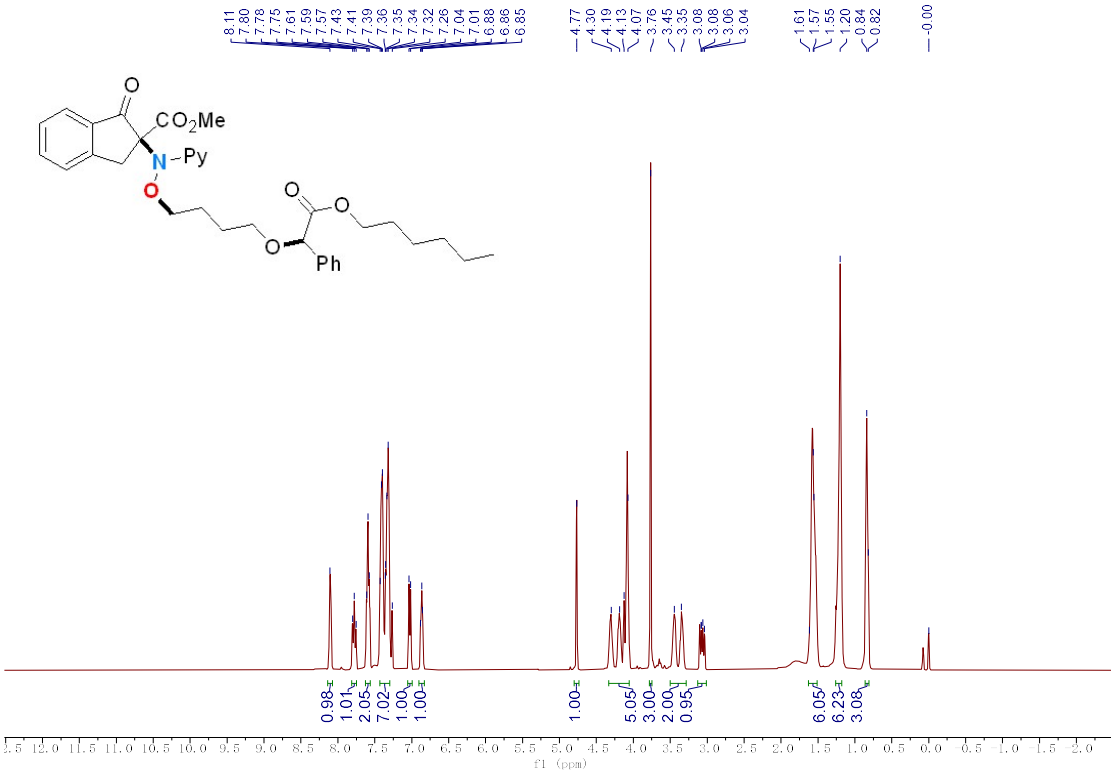
^{1}H NMR (400 MHz) Spectrum of 39 in $CDCl_3$



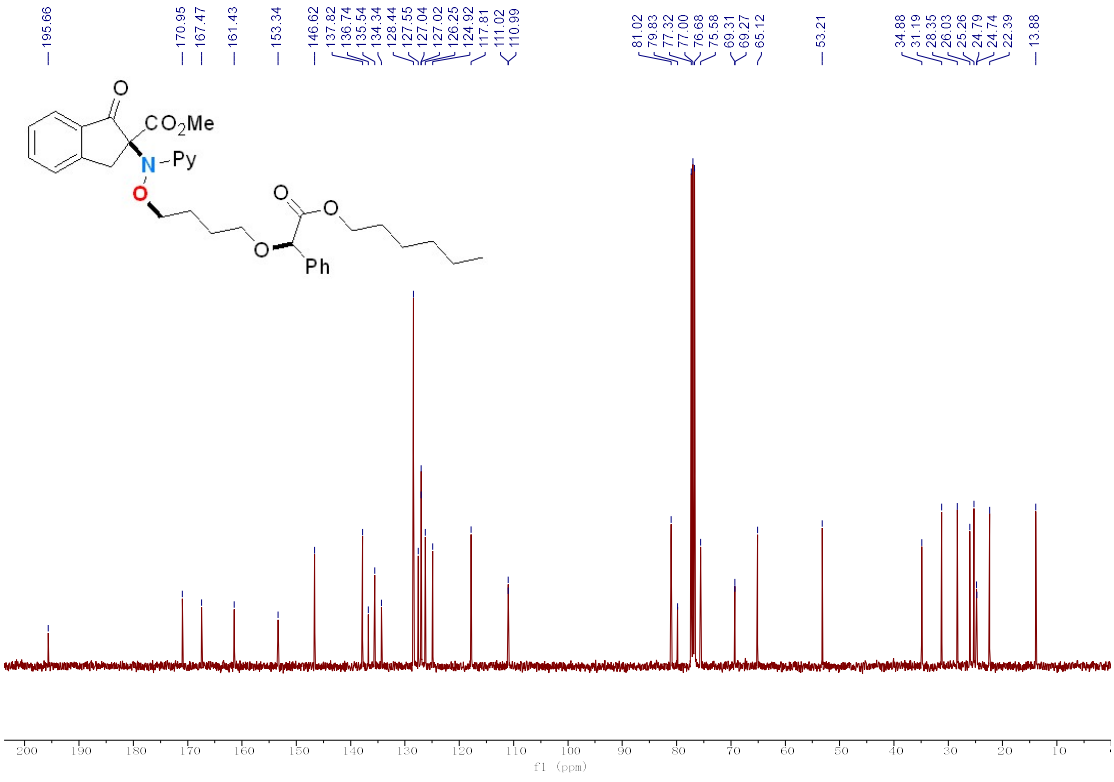
^{13}CNMR (100 MHz) Spectrum of 39 in $CDCl_3$



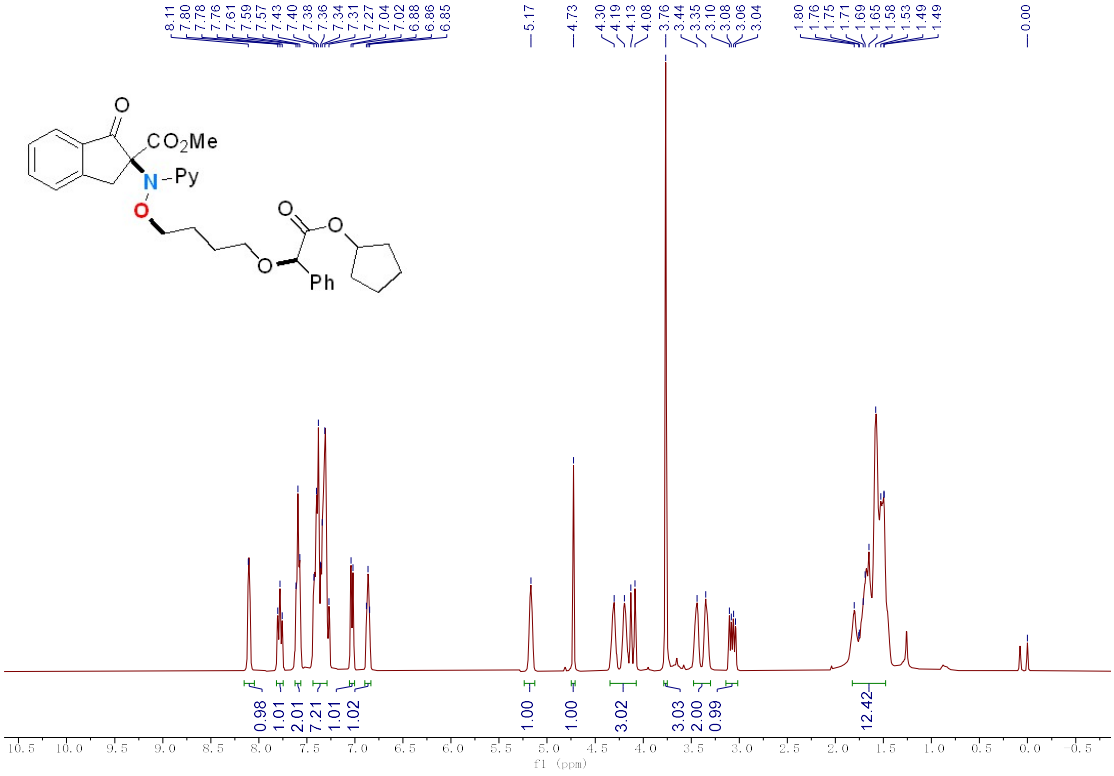
^{1}H NMR (400 MHz) Spectrum of 40 in $CDCl_3$



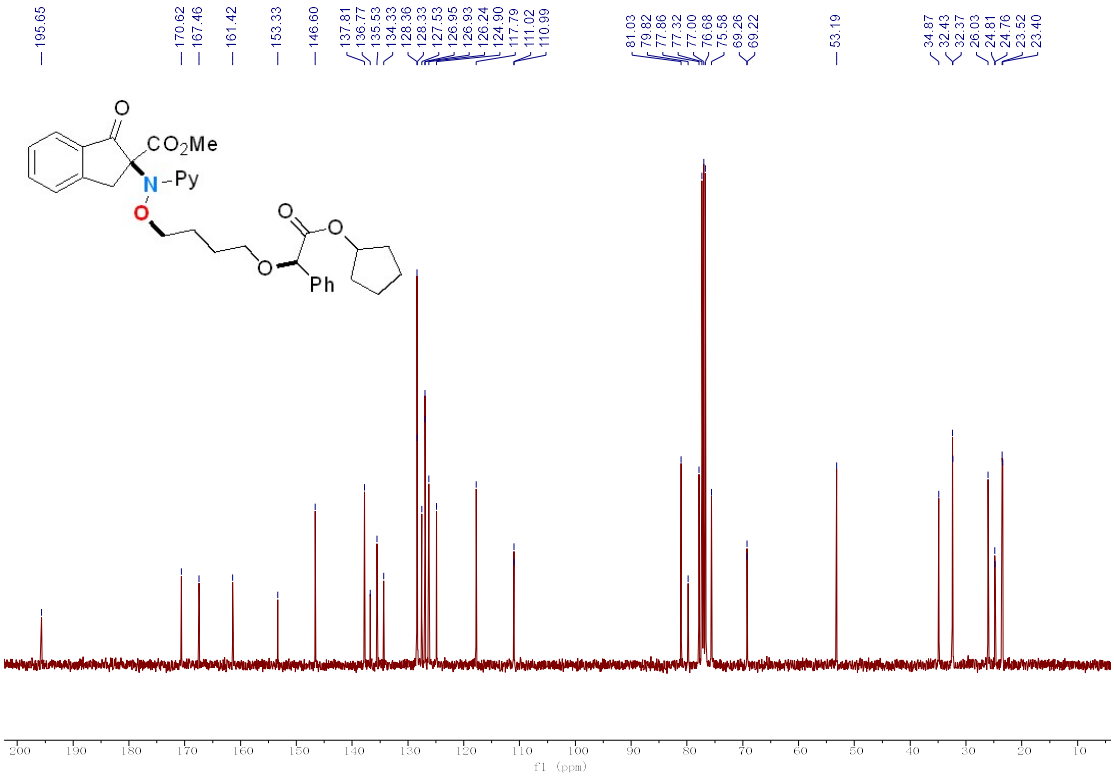
^{13}CNMR (100 MHz) Spectrum of 40 in $CDCl_3$



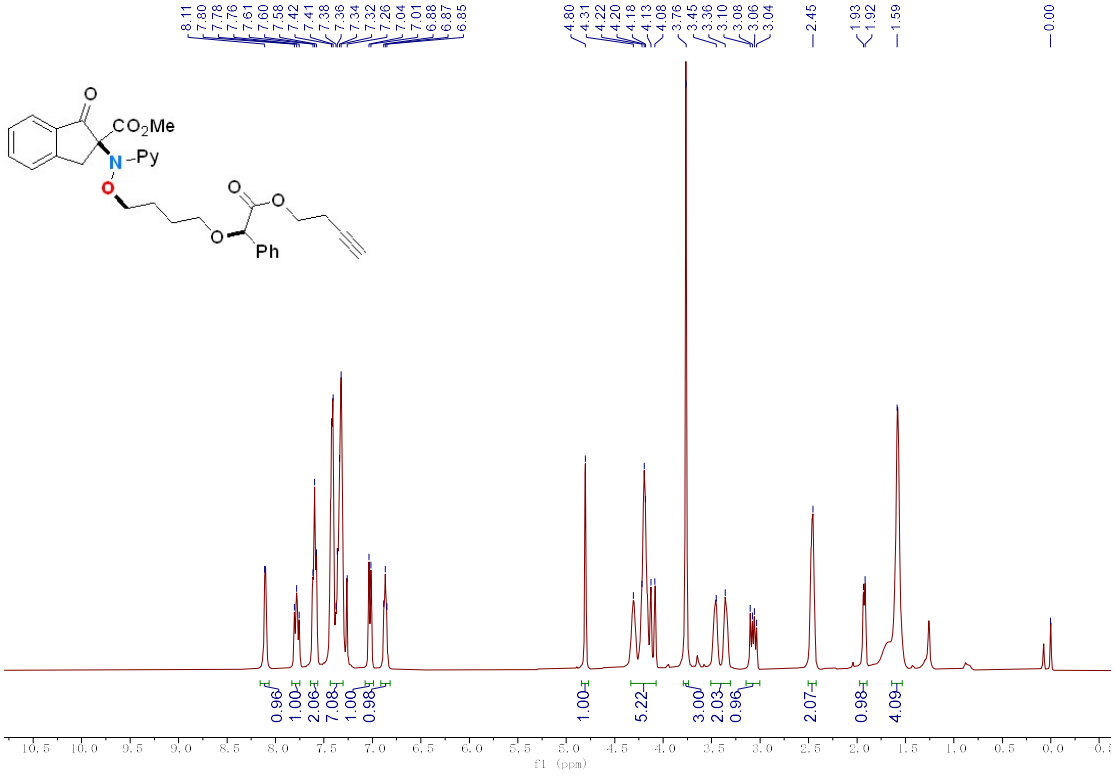
^{1}H NMR (400 MHz) Spectrum of 41 in $CDCl_3$



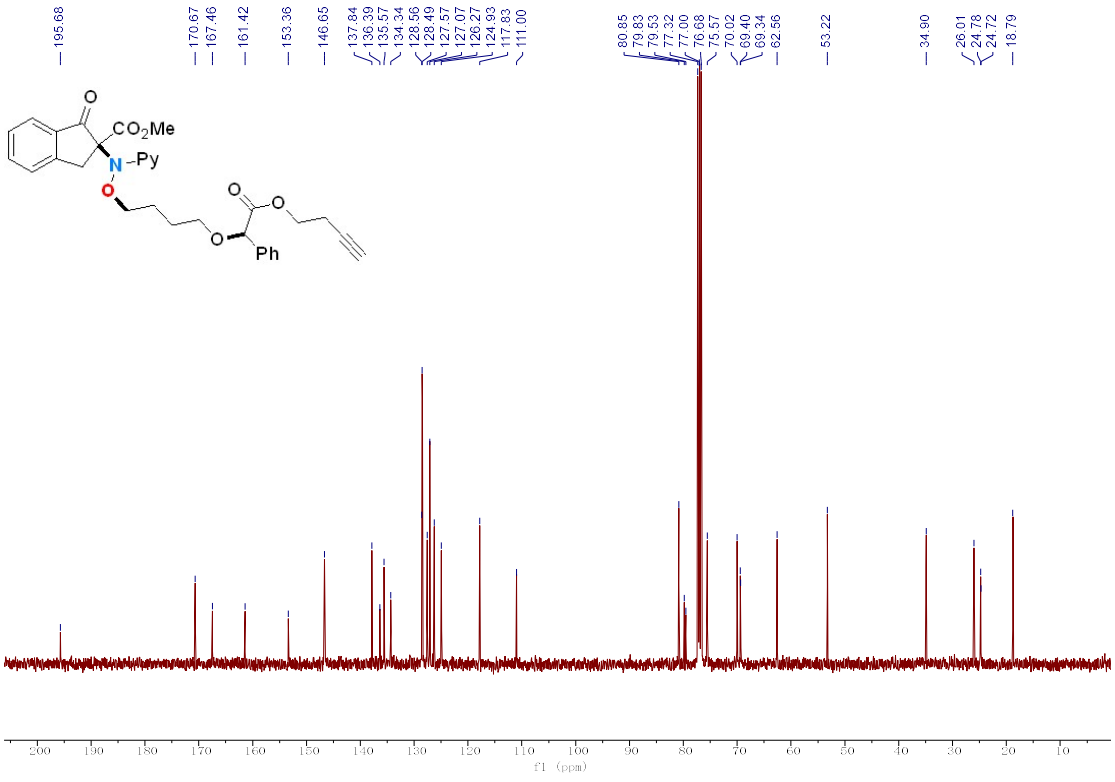
^{13}CNMR (100 MHz) Spectrum of 41 in $CDCl_3$



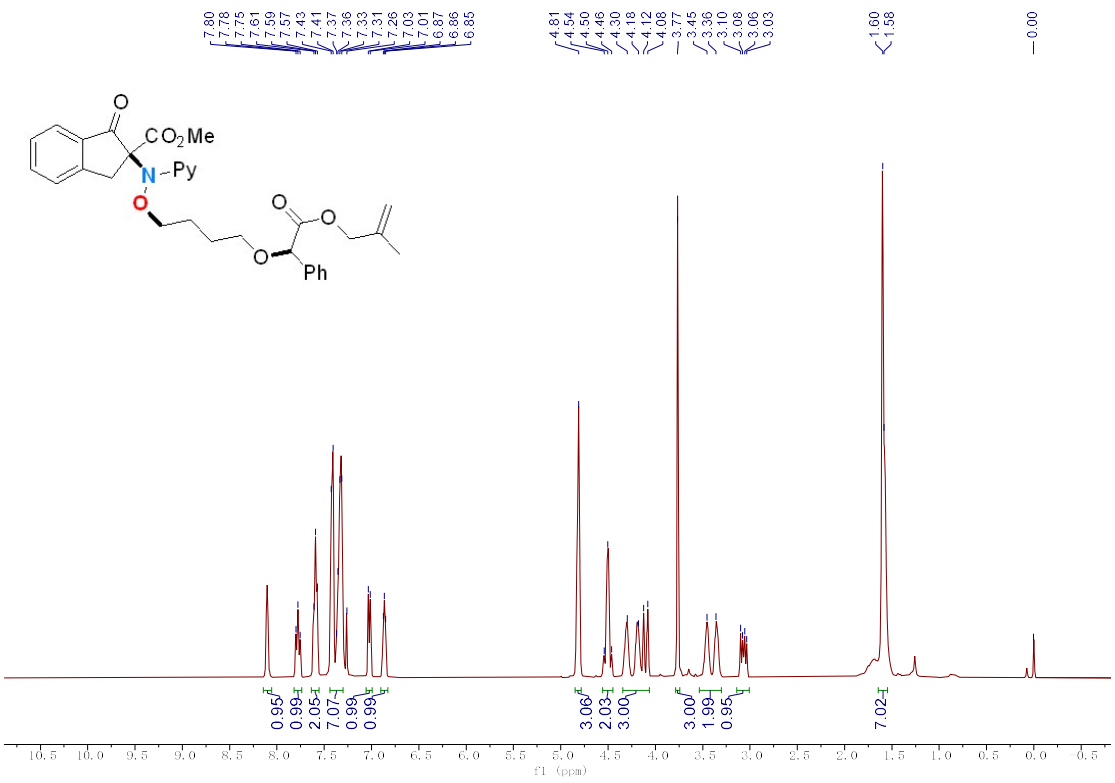
^{1}H NMR (400 MHz) Spectrum of 42 in $CDCl_3$



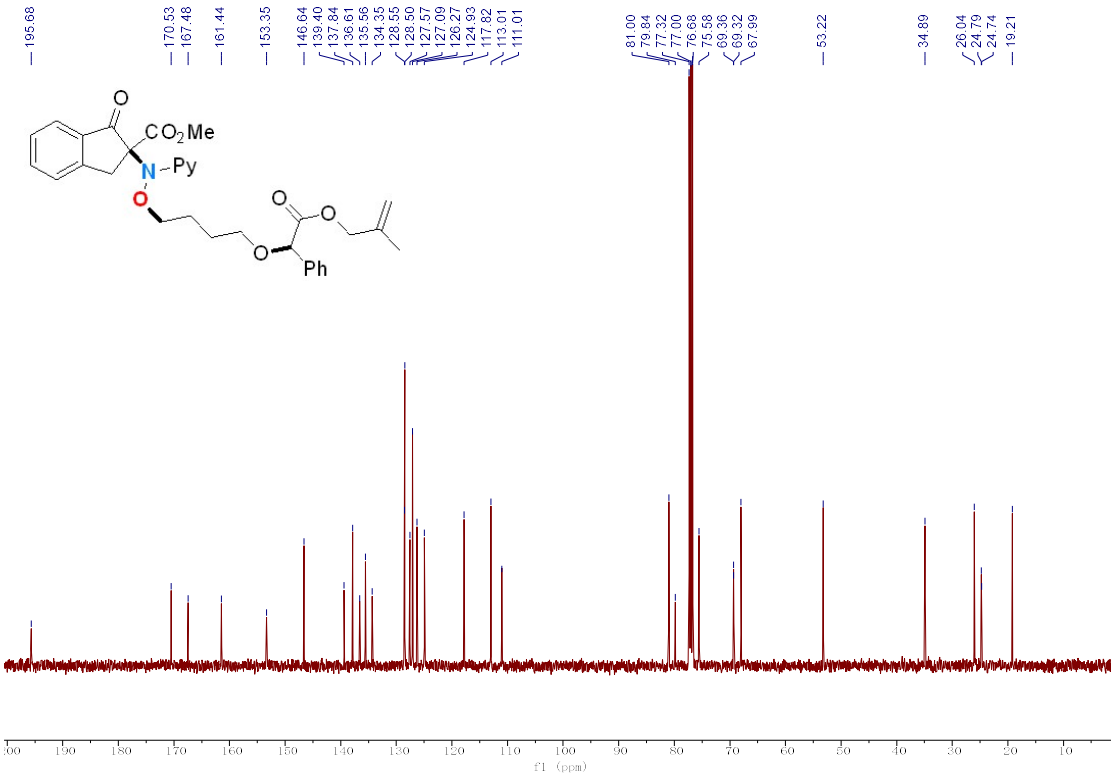
^{13}CNMR (100 MHz) Spectrum of 42 in $CDCl_3$



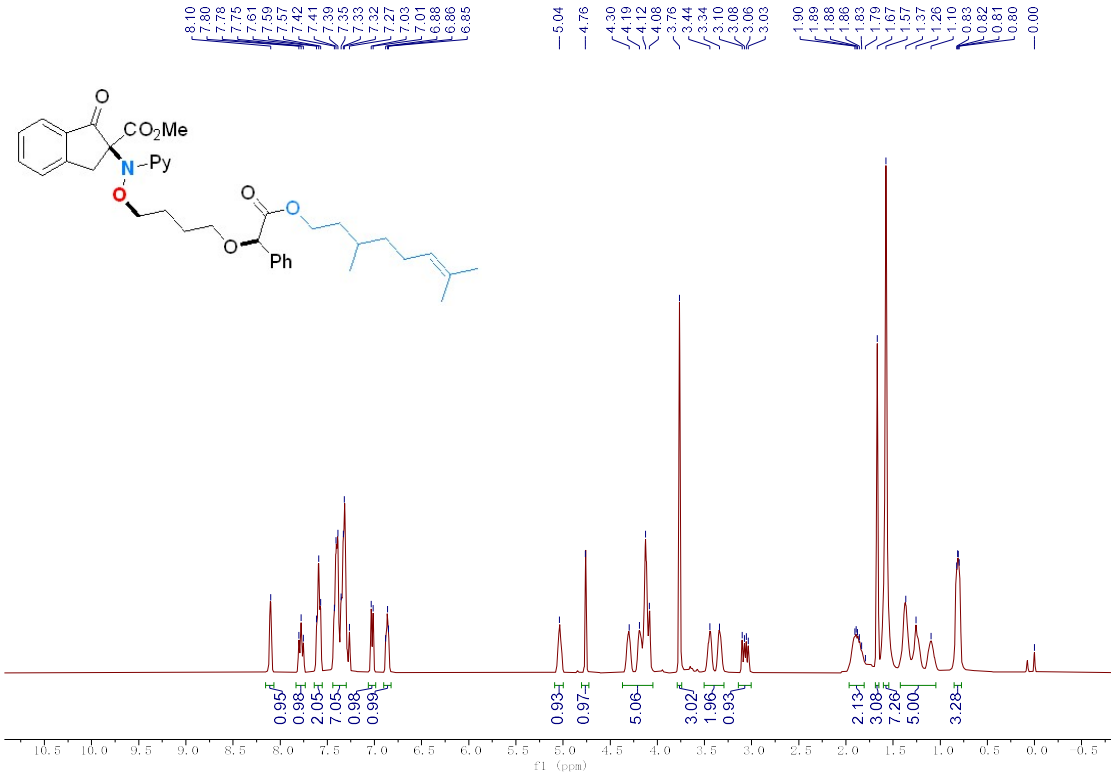
^{1}H NMR (400 MHz) Spectrum of 43 in $CDCl_3$



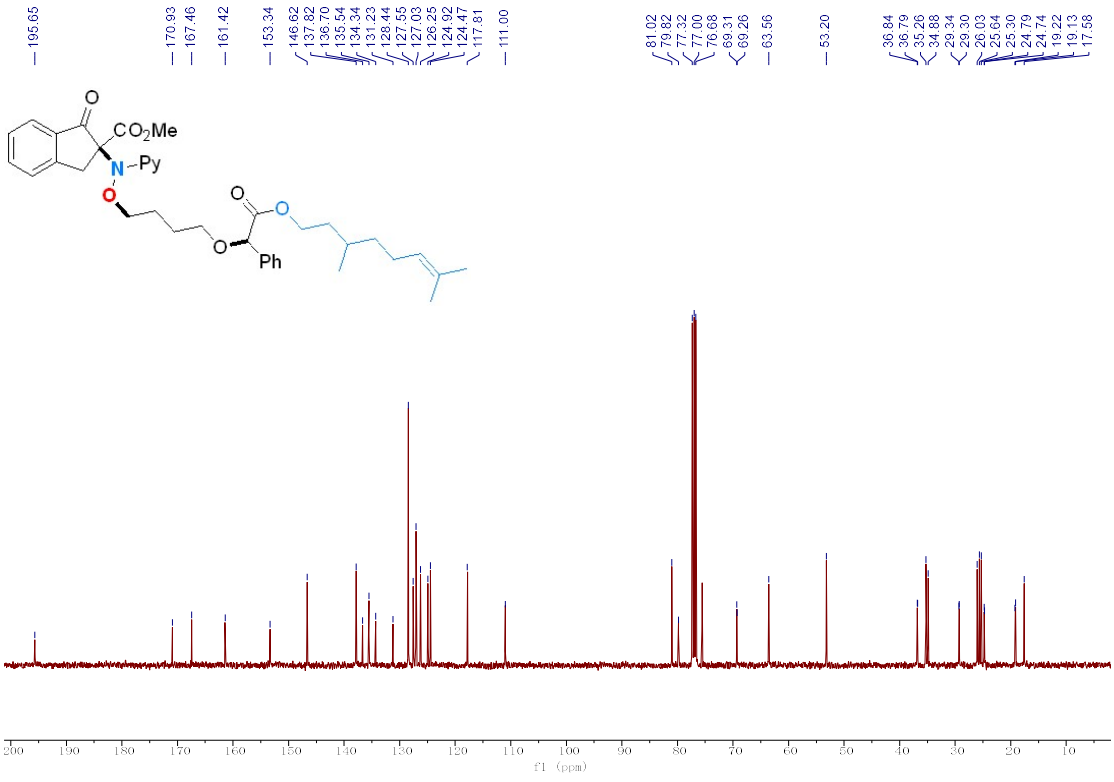
^{13}CNMR (100 MHz) Spectrum of 43 in $CDCl_3$



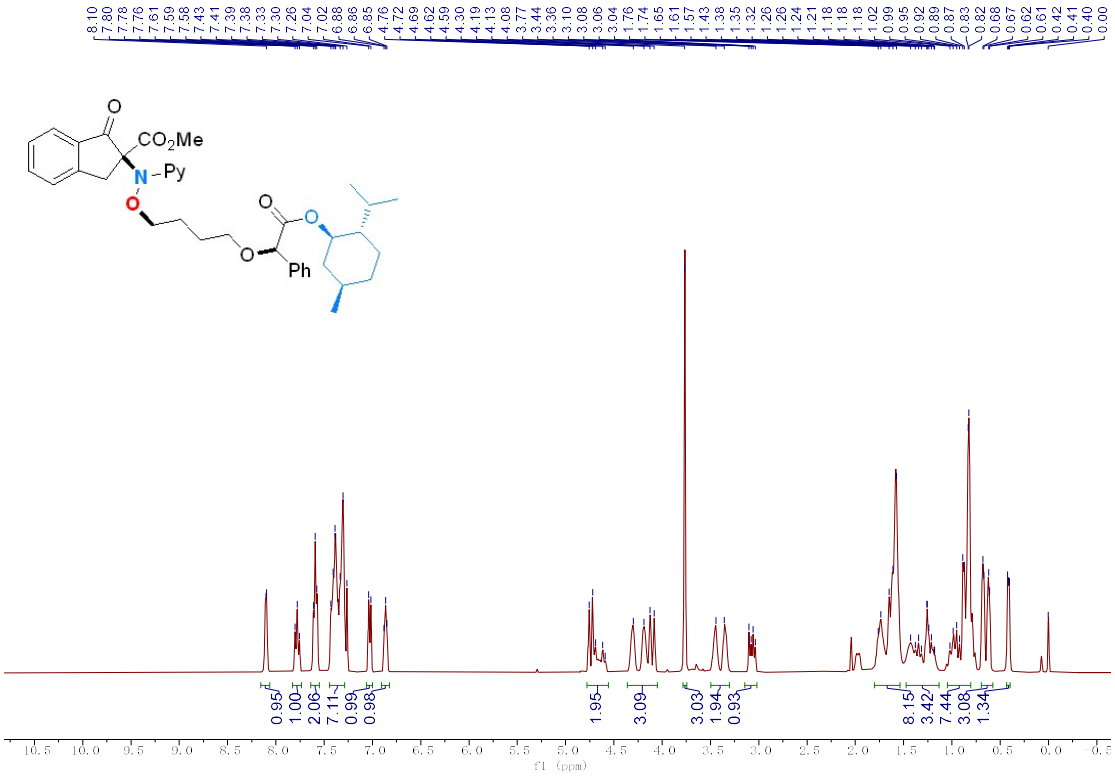
^{1}H NMR (400 MHz) Spectrum of 44 in $CDCl_3$



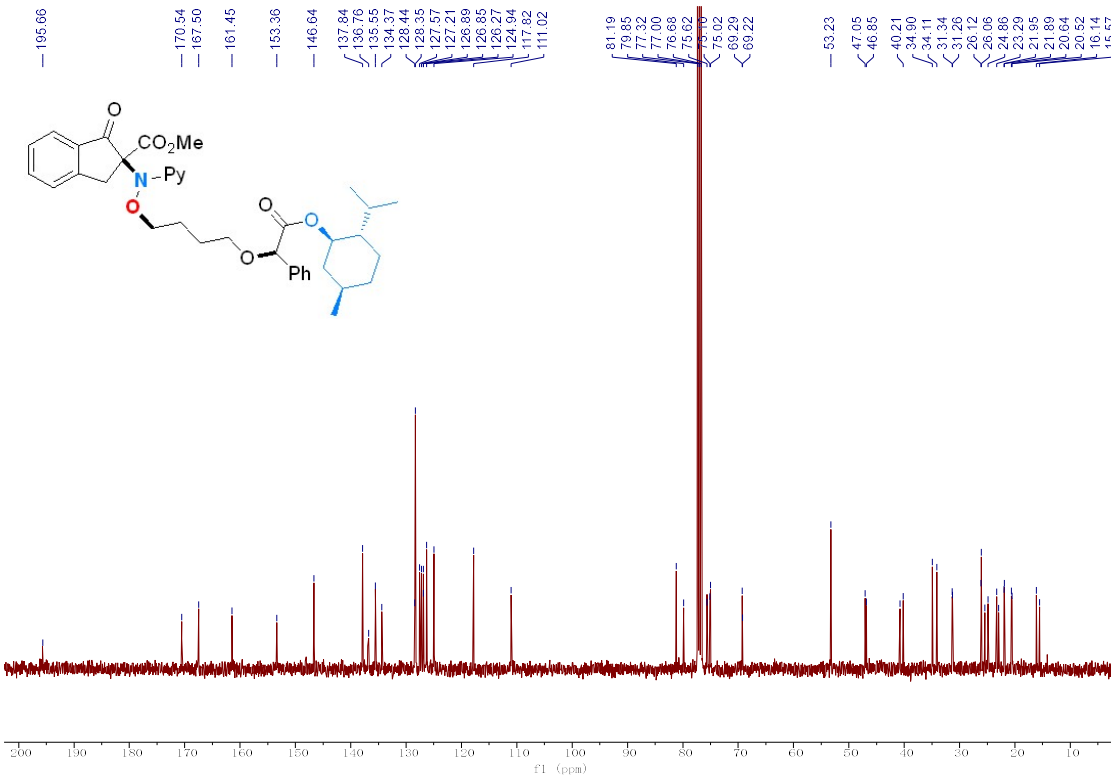
^{13}CNMR (100 MHz) Spectrum of 44 in $CDCl_3$



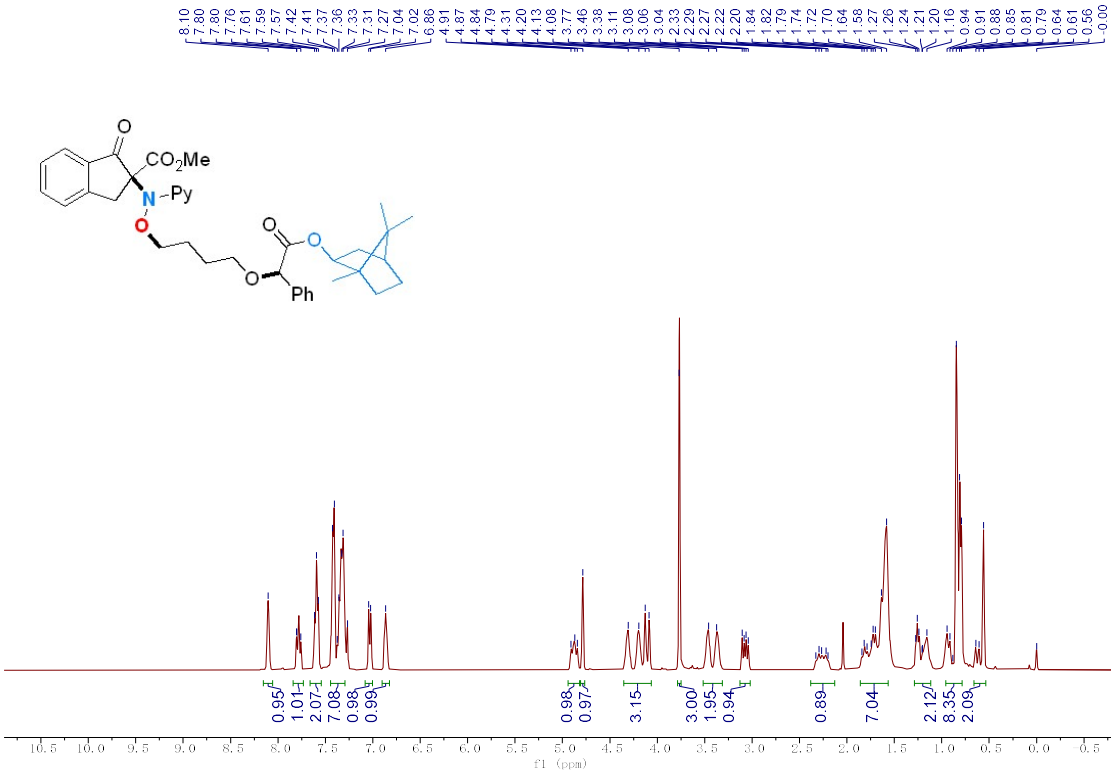
^{1}H NMR (400 MHz) Spectrum of 45 in $CDCl_3$



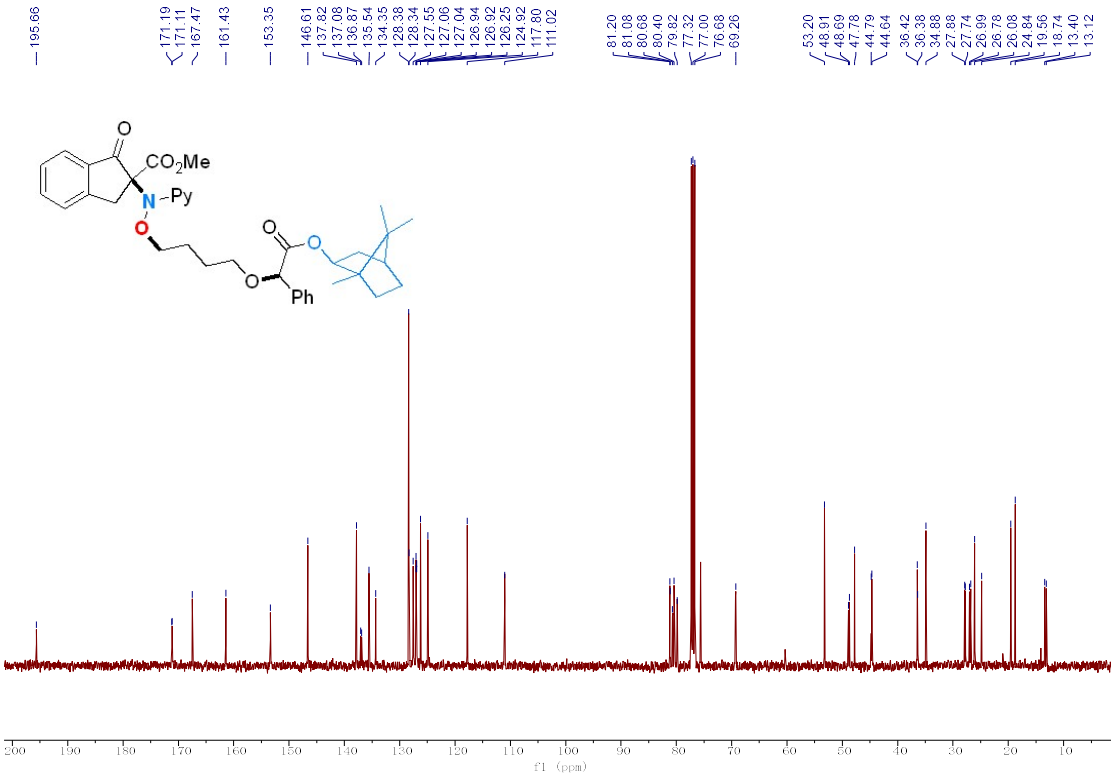
^{13}CNMR (100 MHz) Spectrum of 45 in $CDCl_3$



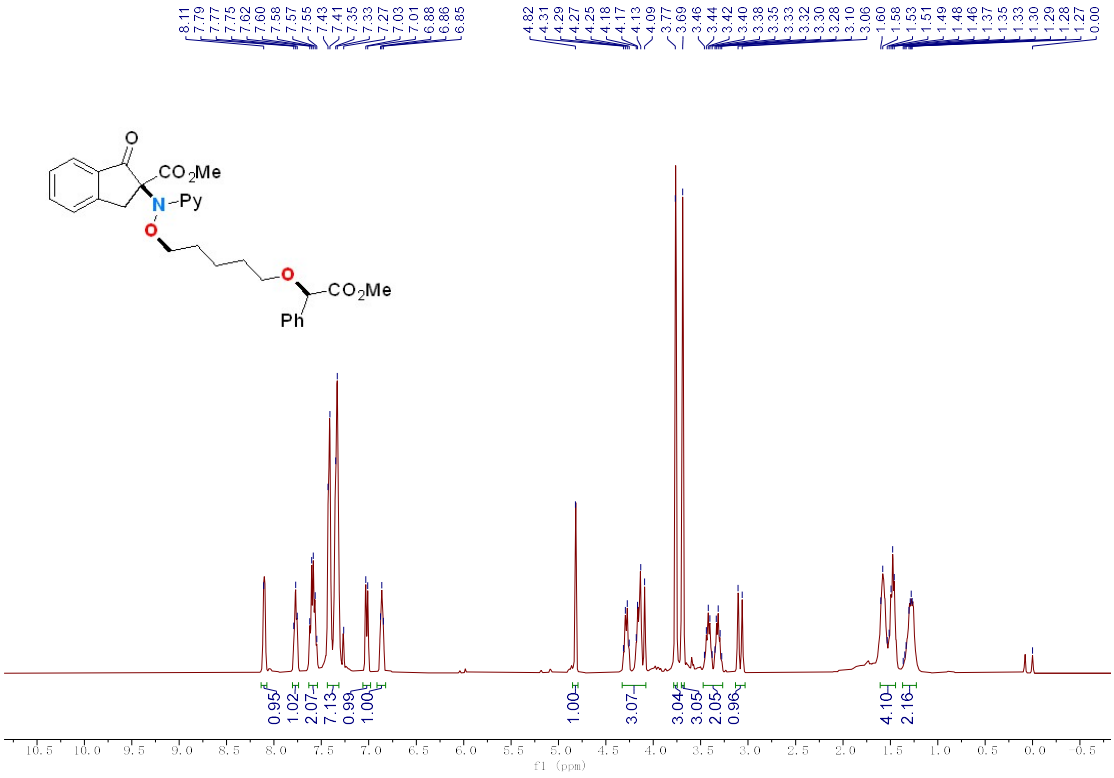
^{1}H NMR (400 MHz) Spectrum of 46 in $CDCl_3$



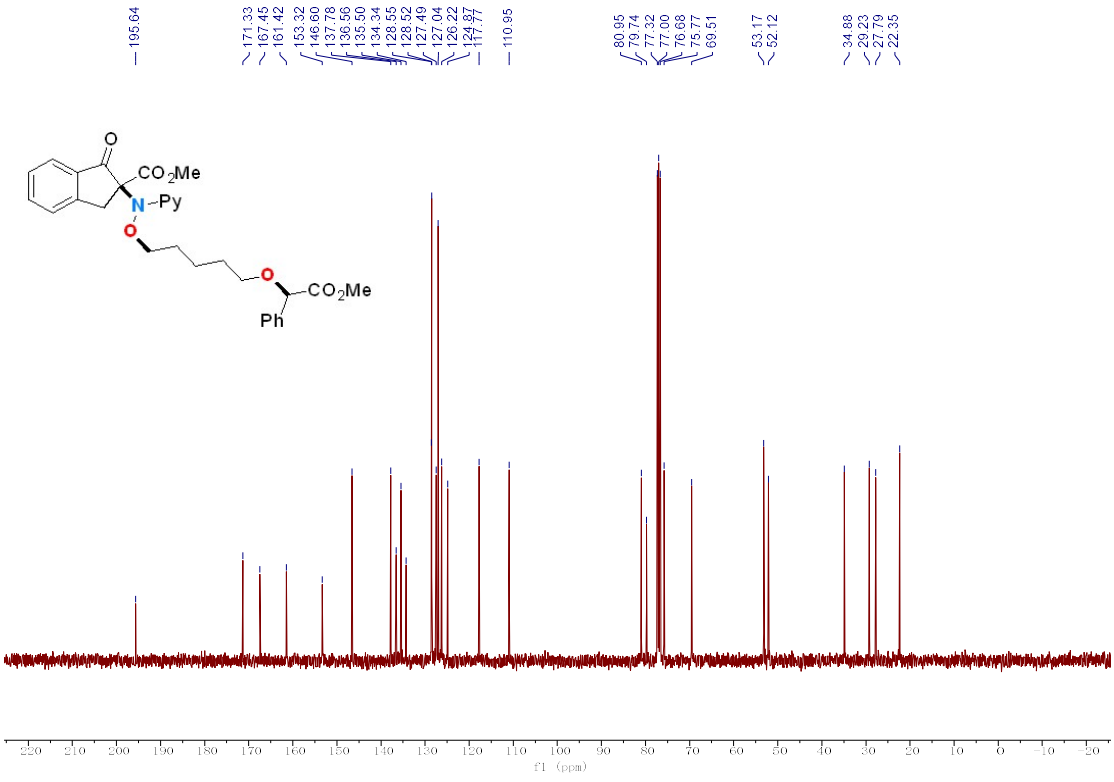
^{13}CNMR (100 MHz) Spectrum of 46 in $CDCl_3$



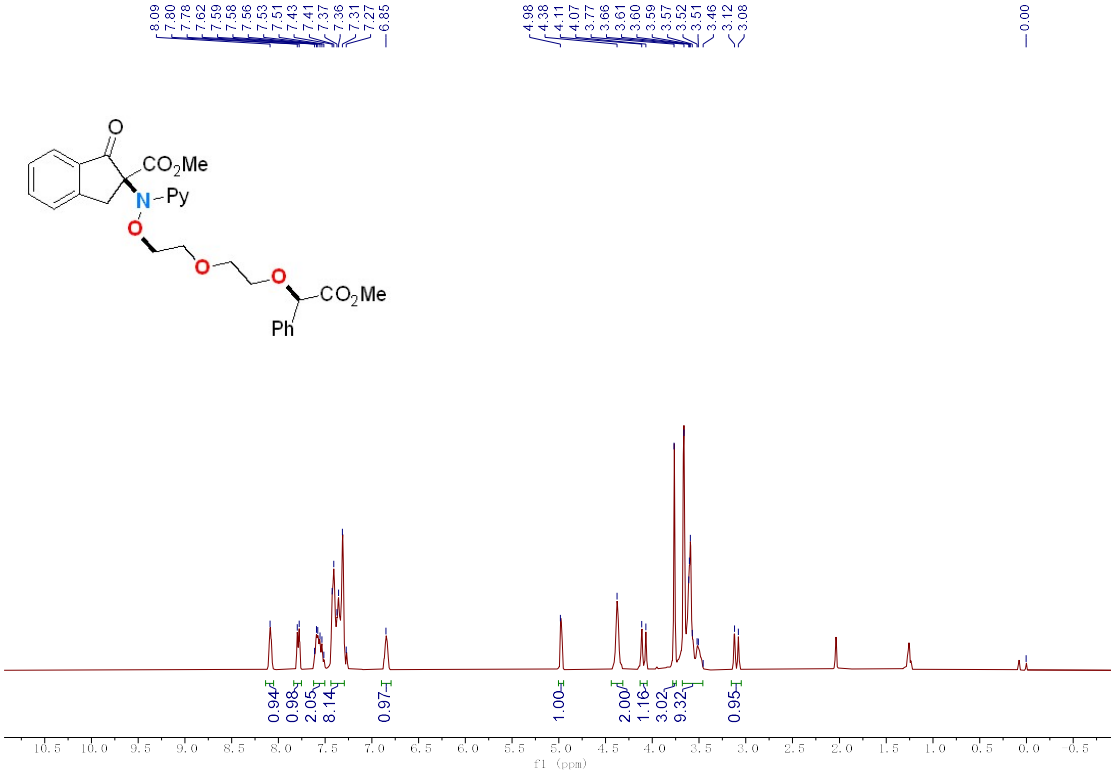
^{1}H NMR (400 MHz) Spectrum of 47 in $CDCl_3$



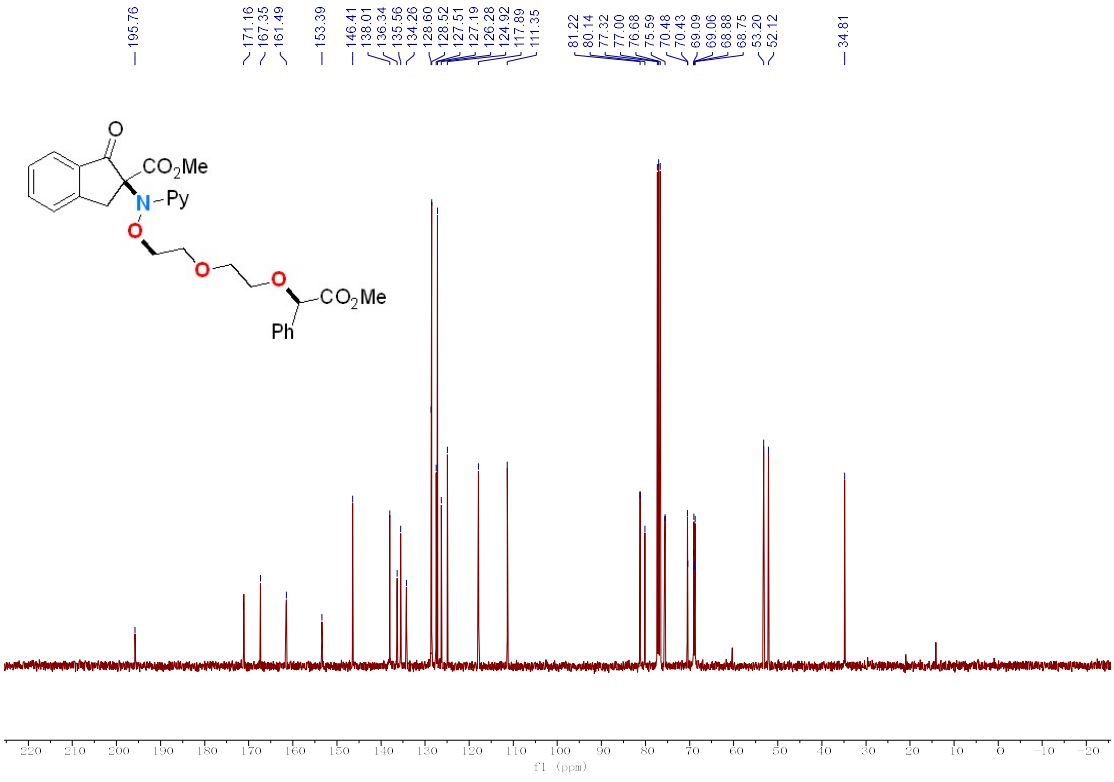
^{13}CNMR (100 MHz) Spectrum of 47 in $CDCl_3$



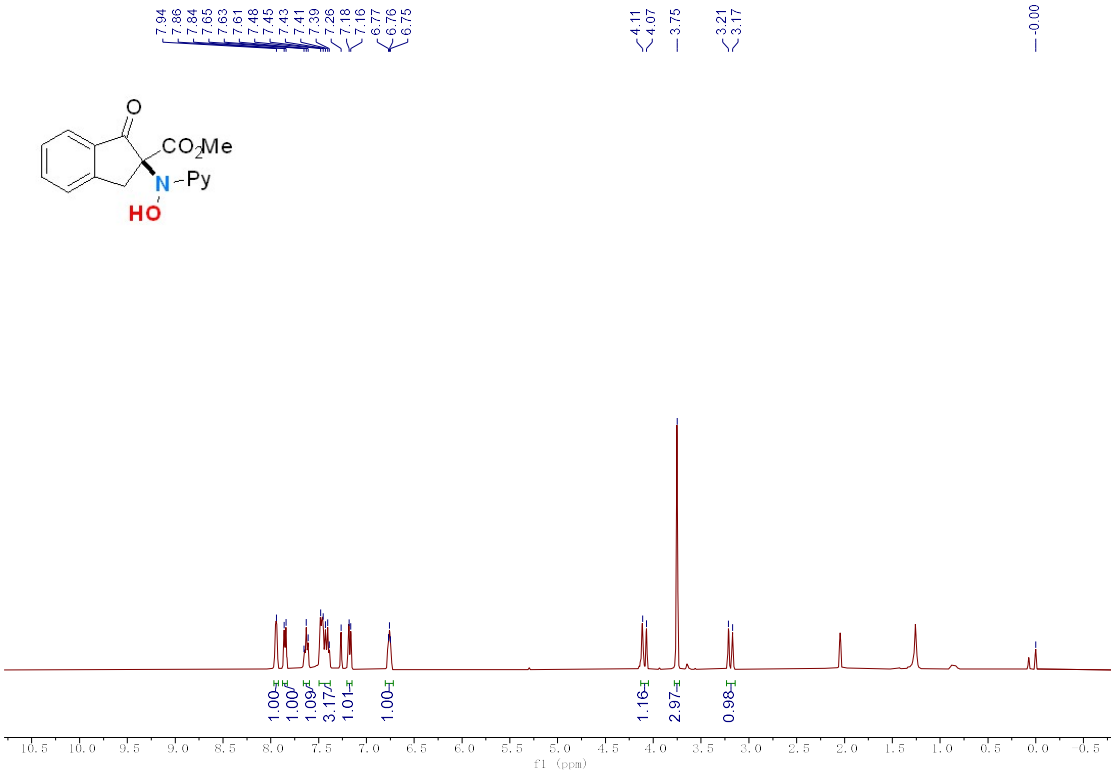
^{1}H NMR (400 MHz) Spectrum of 48 in $CDCl_3$



^{13}CNMR (100 MHz) Spectrum of 48 in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of 49 in $CDCl_3$



^{13}CNMR (100 MHz) Spectrum of 49 in $CDCl_3$