Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Rhodium(III)-Catalyzed Formal Oxidative [4+1] Cycloaddition of Benzohydroxamic acids and α-Diazoesters. A Facile Synthesis of Functionalized Benzolactams

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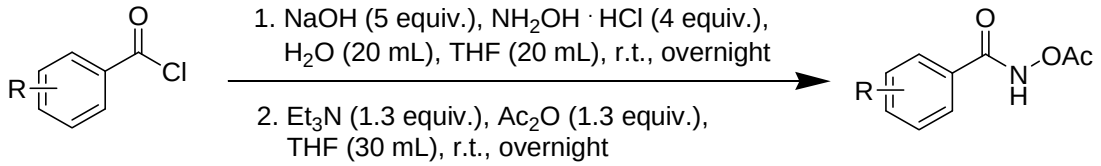
1. General Experimental Section:

All the solvents and reagents were obtained from commercial sources and used without purification. All catalytic reactions were carried out under a nitrogen atmosphere. Benzohydroxamic acids were prepared from benzoic acids and benzoyl chlorides following the literature procedures. *O*-Acetyl benzohydroxamic acids, *O*-pivaloyl benzohydroxamic acids, *O*-benzoyl benzohydroxamic acid and *O*-methoxy benzohydroxamic acid were synthesized according to the literature.[1] $[Cp^*Rh(OAc)_2]$[2a] and $[Rh(cod)Cl]_2$[2b], and diazo compounds[3] were synthesized following the literature procedures.

Thin layer chromatography was performed on silica gel plates. Silica gel (Merck, 230-400 mesh) was used for flash column chromatography. ^1H and ^{13}C NMR spectra were recorded on a Brüker (400 MHz) NMR spectrometer. The chemical shift (δ) values are given in parts per million (ppm) with multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and are referenced to residual solvent peaks. Coupling constants (J) were reported in Hertz (Hz). Melting points were measured on a Büchi Melting Point B - 545 machine. Mass spectra and high resolution mass spectra (HRMS) were obtained on a VG MICROMASS Fison VG platform, a Finnigan Model Mat 95 ST instrument, or a Brüker APEX 47e FT - ICR mass spectrometer. X-ray crystal structure was obtained by a Brüker CCD area detector diffractometer.

2. Experimental Procedures and Physical Characterizations:

2.1 General procedure A for the synthesis of benzohydroxamic acids from benzoyl chloride:

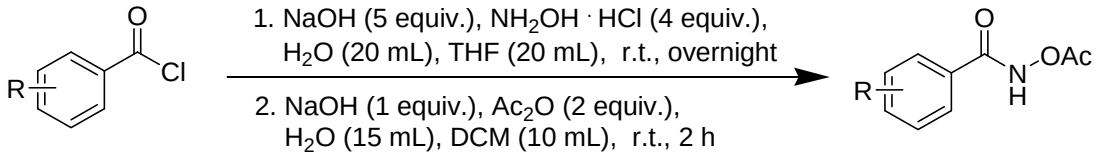


Hydroxylamine hydrochloride (2.78g, 40 mmol) and NaOH pellets (2g, 50 mmol) was dissolved in water (20 mL) and then stirred for 5 min in a 100 mL-rounded bottom flask equipped with a magnetic stirrer. Benzoyl chloride (10 mmol) THF (20 mL) was then added via a syringe. Hydrochloride solution (2 M) was added to acidify the solution to pH 1 after stirring the reaction mixture at room temperature overnight. The

organic layer was collected and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were then washed with water and brine and were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude *N*-hydroxy benzamide as a white solid.

A 100 mL-rounded bottom flask equipped with a magnetic stirrer was charged with the freshly prepared *N*-hydroxybenzamide, acetyl acetate (1.3 equiv) and THF (15 mL). Triethylamine (1.3 equiv) was then added in dropwise manner. The reaction was stirred at room temperature. Upon complete consumption of the starting materials, the organic layer was collected and washed with water and brine. The combined organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. Recrystallization of the crude residue from hexanes/EtOAc gave pure benzohydroxamic acid as a white solid.

2.2 General procedure B for the synthesis of benzohydroxamic acids from benzoyl chloride:



Hydroxylamine hydrochloride (2.78 g, 40 mmol) and NaOH pellets (2 g, 50 mmol) was dissolved in water (20 mL) and then stirred for 5 min in a 100 mL-rounded bottom flask equipped with a magnetic stirrer. Benzoyl chloride (10 mmol) THF (20 mL) was then added via a syringe. Hydrochloride solution (2 M) was added to acidify the solution to pH 1 after stirring the reaction mixture at room temperature overnight. The organic layer was collected and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were then washed with water and brine and were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude *N*-hydroxy benzamide as a white solid.

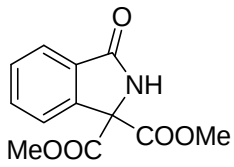
NaOH pellets (1 equiv) in water (0.5 M) and *N*-hydroxybenzamide in DCM (15 mL) were stirred for 5 minutes in a 100 mL rounded bottom flask equipped with a magnetic stirrer. Acetyl acetate in THF (5 mL) was added in dropwise manner over 30 min. Upon complete consumption of the starting material, the organic layer was collected and washed with water and brine. The combined organic extract was dried over $MgSO_4$ and concentrated under reduced pressure to afford crude

benzohydroxamic acids solid. Recrystallization of the crude residue from hexanes/EtOAc gave pure benzohydroxamic acid as a white solid

2.3 General procedure for Rh(III)-catalyzed [4+1] cycloaddition of benzohydroxamic acids with diazo compounds:

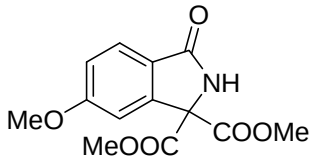
A 8 mL-vial equipped with a magnetic stirrer was charged with *O*-acetyl benzohydroxamic acid **1** (0.2 mmol) and $Cp^*Rh(OAc)_2$ (5 mol %). THF (0.5 mL) was then added via a syringe. Diazo compound **2** (0.2 mmol) in THF (1.5 mL) was added in one pot. The reaction vial was allowed to stir for 4 h at 60 °C. Upon complete reaction, the crude mixture was filtered through Celite® and concentrated under reduced pressure. The residue was then purified by flash column chromatography to give the desired product **3**.

Dimethyl 3-oxoisoindoline-1,1-dicarboxylate (3a)



Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as an off-white solid (89% isolated yield), ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86 - 7.82 (t, 2H, J = 8.0 Hz), 7.67 - 7.63 (t, 1H, J = 7.2 Hz), 7.59 - 7.55 (t, 1H, J = 7.6 Hz), 6.87 (s, 1H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.9, 167.0, 140.1, 133.1, 131.0, 130.5, 125.7, 124.3, 70.7, 54.3. HRMS (ESI): calcd. for $C_{12}H_{12}NO_5$: 250.0715 , found: 250.0712.

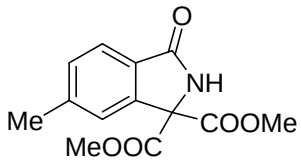
Dimethyl 6-methoxy-3-oxoisoindoline-1,1-dicarboxylate (3b)



Eluent: 40% *n*-hexane / 60% ethyl acetate. The product was obtained as a white solid (90% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.75 - 7.72(d, 1H, J = 8.8 Hz), 7.312 - 7.307 (d, 1H, J = 2.0 Hz), 7.08 - 7.06 (dd, 1H), 6.60(s, 1H), 3.91 (s, 3H), 3.83(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.7, 167.0, 163.9, 142.4, 125.7, 123.3, 117.1, 110.6, 56.35, 54.35. HRMS (ESI): calcd. for $C_{13}H_{13}NO_6Na$: 302.0641 , found:

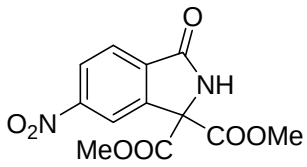
302.0630.

Dimethyl 6-methyl-3-oxoisoindoline-1,1-dicarboxylate (3c)



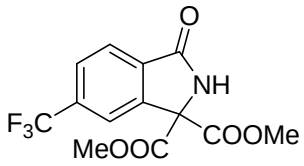
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (82% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.72-7.70 (d, 1H, J = 8 Hz), 7.63 (s, 1H), 7.37 - 7.35 (d, 1H, J = 7.6 Hz), 7.04 (s, 1H) 3.82 (s, 6H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.9, 166.9, 143.9, 140.3, 131.4, 128.2, 125.8, 123.9, 70.4, 54.1, 22.2. HRMS (ESI): calcd. for $C_{13}H_{14}NO_5$: 264.0872, found: 264.0861.

Dimethyl 6-nitro-3-oxoisoindoline-1,1-dicarboxylate (3d)



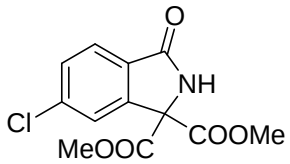
Eluent: 40% *n*-hexane / 60% ethyl acetate. The product was obtained as a white solid (93% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.692 – 8.688 (d, 1H, J = 1.6 Hz), 8.46 – 8.43 (dd, 1H), 8.008 – 7.988 (d, 1H, J = 8.0 Hz), 7.80 (s, 1H), 3.88(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.6, 165.9, 151.2, 141.2, 136.2, 126.1, 125.5, 121.7, 70.7, 54.9. HRMS (ESI): calcd. for $C_{12}H_{10}N_2O_7Na$: 317.0386, found: 317.0374.

Dimethyl 6-(trifluoromethy**l)-3-oxoisoindoline-1,1-dicarboxylate (3e)**



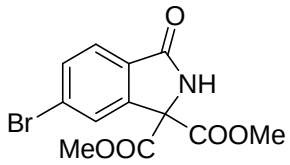
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (93% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.12 (s, 1H), 8.00 – 7.95 (d, 1H, J = 8.0 Hz), 7.85 – 7.83 (d, 1H, J = 8.0 Hz), 3.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.6, 166.2, 140.3, 134.9, 134.3, 127.9, 125.0, 123.2, 123.1, 70.8, 54.7. HRMS (ESI): calcd. for $C_{13}H_{11}NO_5F_3$: 318.0589, found: 318.0594.

Dimethyl 6-chloro-3-oxoisoindoline-1,1-dicarboxylate (3f)



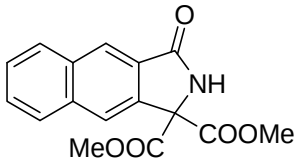
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (82% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84 - 7.83 (d, 1H, *J* = 1.6 Hz), 7.76 - 7.74 (d, 1H, *J* = 8.0 Hz), 7.55 - 7.53 (dd, 1H), 7.22(s, 1H), 3.85 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.8, 166.4, 141.6, 139.5, 131.2, 129.5, 126.2, 125.5, 70.4, 54.5. HRMS (ESI): calcd. for $C_{12}H_{11}NO_5Cl$: 284.0326, found: 284.0327. HRMS (ESI): calcd. for $C_{12}H_{11}NO_5Cl$: 284.0326, found: 284.0327.

Dimethyl 6-bromo-3-oxoisoindoline-1,1-dicarboxylate (3g)



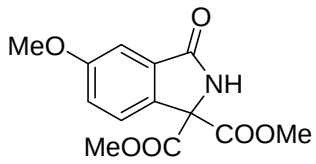
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (77% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.00 (s, 1H), 7.70 - 7.67 (dd, 2H), 7.32 (s, 1H), 3.85 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.0, 166.4, 141.7, 134.1, 130.0, 129.1, 127.8, 125.6, 70.4, 54.6. HRMS (ESI): calcd. for $C_{12}H_{11}NO_5Br$: 327.9821, found: 327.9805.

Methyl 3-oxo-1-phenyl-2,3-dihydro-1H-benzo[f]isoindole-1-carboxylate (3h)



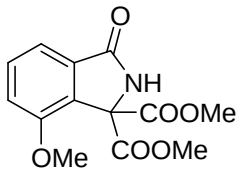
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (73% isolated yield). 1H NMR (400 MHz, $CDCl_3$): δ_H 8.34 - 8.31(d, 2H, *J* = 24.4 Hz), 8.04 - 8.00 (t, 2H, *J* = 7.6 Hz), 7.66 - 7.59 (m, 2H), 6.97 (s, 1H), 3.86(s, 6H). 13C NMR (100 MHz, $CDCl_3$): δ_C 169.6, 167.3, 139.8, 134.7, 134.1, 130.0, 129.2, 128.7, 128.0, 127.8, 125.5, 125.1, 70.5, 54.4. HRMS (ESI): calcd. for $C_{16}H_{14}N_2O_5$: 300.0872, found: 300.0870.

Dimethyl 5-methoxy-3-oxoisoindoline-1,1-dicarboxylate (3i)



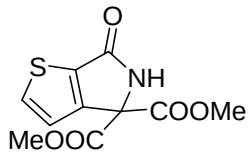
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.73 – 7.71 (d, 1H, *J* = 8.4 Hz), 7.30 – 7.29 (d, 1H, *J* = 2.4 Hz), 7.19 – 7.17 (q, 1H, *J* = 2.4 Hz), 6.82 (s, 1H), 3.87 (s, 3H), 3.82 (d, 3H). 13C NMR (100 MHz, $CDCl_3$): δ_C 169.6, 167.0, 161.7, 132.3, 132.1, 126.4, 121.0, 106.9, 70.1, 56.0 , 54.0. HRMS (ESI): calcd. for $C_{13}H_{14}NO_6$: 280.0821, found: 280.0830.

Dimethyl 7-methoxy-3-oxoisoindoline-1,1-dicarboxylate (3i')



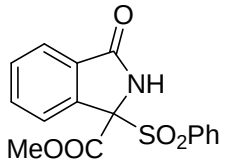
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid.^{1}H NMR (400 MHz, $CDCl_3$): 7.55 – 7.51 (t, 1H, *J* = 7.6 Hz), 7.45 – 7.43 (d, 1H, *J* = 7.6 Hz), 7.15 – 7.13 (d, 1H, *J* = 8.0 Hz), 6.91 (s, 1H), 3.92 (s, 3H), 3.79 (d, 3H). 13C NMR (100 MHz, $CDCl_3$): δ_C 170.3, 167.0, 156.3, 133.0, 132.4, 128.5, 116.5, 116.1, 70.1, 56.5, 53.9. HRMS (ESI): calcd. for $C_{13}H_{14}NO_6$: 280.0821, found: 280.0830.

Dimethyl 5, 6-dihydro-6-oxothieno[3,2-c]pyrrole-4,4-dicarboxylate (3j)



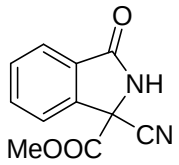
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (63% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.72 – 7.71 (q, 1H, *J* = 0.8 Hz), 7.28 – 7.27 (d, 1H, *J* = 4.8 Hz), 6.96 (s, 1H), 3.83(s, 6H). 13C NMR (100 MHz, $CDCl_3$): δ_C 166.0, 165.0, 150.6, 136.7, 135.3, 122.8, 69.7, 54.2. HRMS (ESI): calcd. for $C_{10}H_9NO_5NaS$: 278.0099, found: 278.0108.

Methyl 3-oxo-1-(phenylsulfonyl)isoindoline-1-carboxylate (3k)



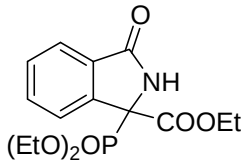
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as an off-white solid (84% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.17 - 8.15(d, 1H, J = 8 Hz), 7.71 - 7.67 (m, 1H), 7.57 - 7.48 (m, 5H), 7.35 - 7.31 (t, 2H, J = 7.6 Hz), 7.20 (s, 1H), 3.99(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.6, 163.4, 136.8, 135.3, 133.3, 132.6, 131.6, 131.4, 130.8, 129.1, 126.6, 124.3, 85.0, 54.9. HRMS (ESI): calcd. for $C_{16}H_{13}NO_5Na^+$: 354.0412, found: 354.0405.

Methyl 1-cyano-3-oxoisoindoline-1-carboxylate (3l)



Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (72% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 - 7.90 (d, 1H, J = 7.6 Hz), 7.84 - 7.83 (d, 1H, J = 7.6 Hz), 7.76 - 7.72 (td, 1H), 7.70 - 7.66 (td, 1H), 7.46 (s, 1H), 3.93(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.7, 164.7, 139.4, 134.3, 131.8, 129.9, 125.3, 123.9, 115.2, 59.7, 55.5. HRMS (ESI): calcd. for $C_{11}H_9N_2O_3$: 217.0613, found 217.0618.

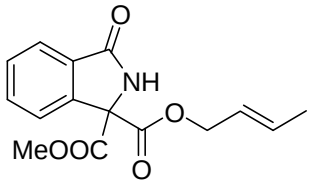
Methyl 1-(ethoxyphosphono)-3-oxoisoindoline-1-carboxylate (3m)



Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a light yellow solid (30% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.97 (d, 1H, J = 7.6 Hz), 7.86 – 7.84 (d, 1H, J = 7.2 Hz), 7.66 – 7.63 (t, 1H, J = 7.4 Hz), 7.58 – 7.54 (t, 1H, J = 7.6 Hz), 6.86 (s, 1H), 4.33 – 4.28 (q, 2H, J = 6.8 Hz), 4.15 – 4.10 (q, 2H, J = 7.2Hz), 4.08 – 3.99 (m, 1H), 3.89 – 3.79 (m, 1H), 1.34 – 1.31 (t, 3H, J = 7Hz), 1.25 – 1.21 (t, 3H, J = 7 Hz), 1.14 – 1.11 (t, 3H, 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.5, 165.8, 139.4, 139.3, 132.64, 132.62, 131.23, 131.19, 129.9, 125.62, 125.59,

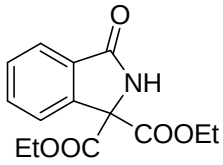
124.1, 68.4, 66.9, 65.1, 65.09, 65.02, 64.8, 64.7, 63.4, 16.47, 16.41, 16.35, 16.29, 14.12. ^{31}P NMR (100 MHz, H_3PO_4): 13.6, 13.52, 13.46, 13.42, 13.37. HRMS (ESI): calcd. for $C_{15}H_{21}NO_6P$: 342.1107, found: 342.1100.

1-methyl 1-(E)-pent-3-enyl 3-oxoisoindoline-1,1-dicarboxylate (3n)



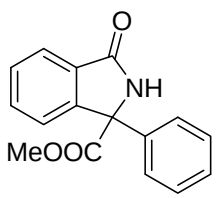
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (86% isolated yield), ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 – 7.84 (d, 1H, J = 7.6 Hz), 7.84 – 7.82 (d, 1H, J = 7.6 Hz), 7.67 – 7.63 (m, 1H), 7.58 – 7.55 (m, 1H), 6.85 (s, 1H), 5.85 – 5.76 (m, 1H), 5.57 – 5.50 (m, 1H), 4.64 – 4.62 (m, 2H), 3.83 (s, 1H), 1.72-1.70 (d, 3H, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.6, 166.8, 166.0, 140.0, 133.3, 132.8, 130.8, 130.3, 125.6, 124.1, 123.7, 70.6, 68.0, 54.0, 17.9. HRMS (ESI): calcd. for $C_{15}H_{15}NO_5Na$: 312.0848, found: 312.0838.

Diethyl 3-oxoisoindoline-1,1-dicarboxylate (3o)



Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (80% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 - 7.81(t, 2H, J = 8.0 Hz), 7.65 - 7.61 (t, 1H, J = 7.6 Hz), 7.57 - 7.53 (t, 1H, J = 7.6 Hz), 7.23 (s, 1H), 4.30 - 4.25 (dd, 4H, J = 7.2 Hz), 1.30 - 1.26 (t, 6H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.1, 166.5, 140.3, 133.0, 131.1, 130.4, 125.7, 124.3, 70.9, 63.6, 14.3. HRMS (ESI): calcd. for $C_{14}H_{16}NO_5$: 278.1028, found: 278.1021.

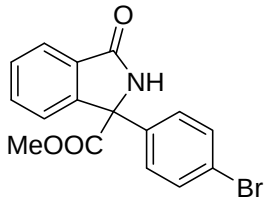
Methyl 3-oxo-1-phenylisoindoline-1-carboxylate (3p)



Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid

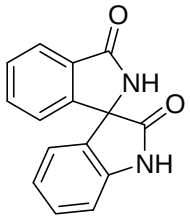
(83% isolated yield), mp 168 – 169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86 - 7.84 (d, 1H, *J* = 7.2 Hz), 7.71 - 7.69 (d, 1H, *J* = 7.6 Hz), 7.61 - 7.57 (td, 1H), 7.54 - 7.50 (t, 1H, *J* = 7.6 Hz), 7.37 - 7.33 (m, 5H), 7.02 (s, 1H), 3.84(s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.4, 170.2, 145.6, 138.7, 132.9, 131.0, 129.7, 129.5, 129.1, 125.8, 125.7, 124.2, 71.1, 53.8 . HRMS (ESI): calcd. for $C_{16}H_{14}NO_3$: 268.0974, found: 268.0971.

Methyl 1-(4-bromophenyl)-3-oxoisoindoline-1-carboxylate (3q)



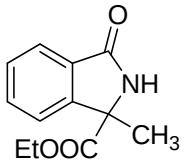
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as an off-white solid (90% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.06 (s, 1H), 7.85 - 7.83 (d, 1H, *J* = 7.6 Hz), 7.70 - 7.68 (d, 1H, *J* = 7.6 Hz), 7.61 - 7.57 (t, 1H, *J* = 7.2 Hz), 7.54 - 7.50 (t, 1H, *J* = 7.6 Hz), 7.47 - 7.44 (d, 2H, *J* = 8.6 Hz), 7.30 - 7.28 (d, 2H, *J* = 8.8 Hz), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.95, 169.87, 145.3, 137.8, 133.1, 132.6, 130.7, 129.9, 127.6, 125.5, 124.4, 123.4, 70.5, 53.9. HRMS (ESI): calcd. for $C_{16}H_{13}NO_3Br$: 346.0079, found: 346.0085.

Spiro[indoline-3,1'-isoindoline]-2,3'-dione (3r)



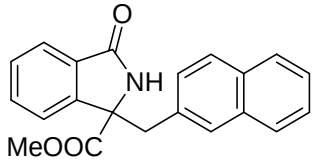
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (75% isolated yield). ^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.9 (s, 1H), 9.03 (s, 1H), 7.75 - 7.73 (m, 1H), 7.55 – 7.49 (m, 2H), 7.33 - 7.29 (m, 1H), 7.02 - 6.90 (m, 4H). ^{13}C NMR (100 MHz, d_6-DMSO): δ_C 175.8, 170.9, 146.2, 143.2, 133.2, 132.3, 130.7, 129.7, 128.5, 124.7, 123.9, 123.2, 111.1, 67.7. HRMS (ESI): calcd. for C15H10N2O2Na : 273.0640, found: 273.0627.

Ethyl 1-methyl-3-oxoisoindoline-1-carboxylate (3s)



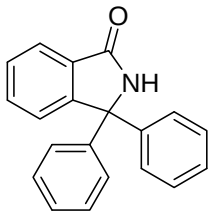
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as an orange solid (32% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.82 - 7.80(d, 1H, *J* = 7.2 Hz), 7.68 - 7.66 (d, 1H, *J* = 7.6 Hz),7.61 - 7.57 (t, 1H, *J* = 7.6 Hz), 7.52 - 7.48 (t, 1H, *J* = 7.6 Hz), 7.03 (s, 1H), 4.21 - 4.16 (q, 2H), 1.80 (s, 3H), 1.26 - 1.23 (t, 3H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δC 13C NMR (100 MHz, $CDCl_3$): δ_C 170.5, 170.2, 136.8, 135.3, 133.3, 132.6, 131.6, 131.4, 64.9, 62.7, 25.7, 14.3. HRMS (ESI): calcd. for $C_{12}H_{14}NO_3$: 220.0974, found: 220.0967.

Methyl 1-((naphthalen-2-yl)methyl)-3-oxoisoindoline-1-carboxylate (3t)



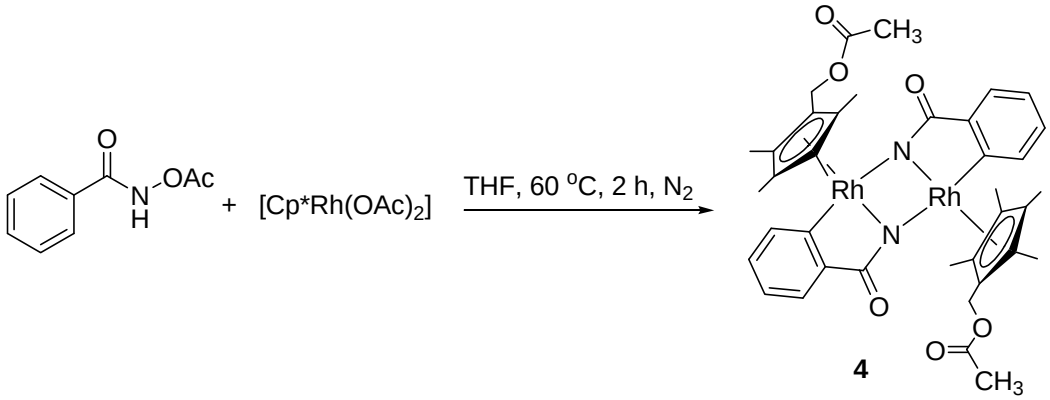
Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (62% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 – 7.87 (m, 1H), 7.78 – 7.76 (m, 4H), 7.69 - 7.64 (m, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.46 (m, 2H), 7.27 - 7.25 (m, 1H), 6.42 (s, 1H), 3.97 – 3.93 (d, 1H, *J* = 13.6 Hz), 3.69 (s, 3H), 3.10 – 3.06 (d, 1H, *J* = 13.2 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.8, 169.6, 145.2, 133.5, 132.9, 132.7, 132.3, 131.0, 129.7, 129.0, 128.6, 127.9, 127.8, 127.6, 126.4, 126.3, 124.2, 123.5, 69.0, 53.2, 45.5. HRMS (ESI): calcd. for $C_{21}H_{18}NO_3$: 332.1287, found: 332.1284.

3,3-diphenylisoindolin-1-one (3u)



Eluent: 50% *n*-hexane / 50% ethyl acetate. The product was obtained as a white solid (82% isolated yield), mp 216 – 217 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7. 89 - 7.87(d, 1H, *J* = 7.6 Hz), 7.58 - 7.54(td, 1H), 7.50 - 7.43 (m, 2H), 7.32 - 7.26 (m, 10H), 7.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.3, 150.5, 143.1, 132.6, 131.1, 129.0, 128.8, 128.3, 127.5, 124.9, 124.7, 71.4. HRMS (ESI): calcd. for $C_{20}H_{16}NO$: 286.1232, found: 286.1226.

2.4 Synthesis of Rhodacyclic Complex 4:



A 10 mL-Schlenk flask was charged with [Cp*Rh(OAc)$_2$] (0.1 mmol) and sealed with a rubber septum. The flask was evacuated and refilled with N_2. THF (2 mL) was then added to dissolve the Rh complex. *O*-Acetyl benzohydroxamic acid **1a** in THF (1 mL) was then added via a syringe and the septum was replaced with a glass stopper. The reaction mixture was stirred at 60 ^{o}C for 2 h under a N_2 atmosphere. The solution was then concentrated under vacuum and the resulting residue was purified through a short pad of alumina gel using CH_2Cl_2 as eluent. An orange band was collected and the organic collection was concentrated to yield the complex **4** as a orange-red solid. To obtain the single crystal for X-ray crystallography, complex **4** was dissolved in a minimum amount of CH_2Cl_2 and then layered with diethyl ether. The solution was left standing for 3 days to obtain a quality single crystal for X-ray diffraction study.

2.5 Kinetic Isotope Effect Study:

A 8 mL-vial equipped with a magnetic stirrer was charged with [Cp*Rh(OAc)$_2$] (5 mol%) substrate (**1a** or **1a**-d_5, 0.2 mmol) and THF (0.5 mL). A solution of **2a** (0.2 mmol) in THF (1.5 mL) was then added in one-pot and the mixture was stirred and heated at 40 °C for 20 min. The reaction was then cooled down quickly in ice bath. The solvent was removed under reduced pressure. The residue was then purified by flash column chromatography to give the product. The KIE experiment was repeated three times and the average value (k_H/k_D = 1.03) was obtained based on the product formation.

	%yield of **3a**	%yield of **3a**-d_5	KIE value
run 1	13	13	1.00
run 2	11	10	1.10
run 3	11	11	1.00
		Average	1.03

3. X-ray Crystallographic Data of 4

Figure S1. Molecular Structure of **4**

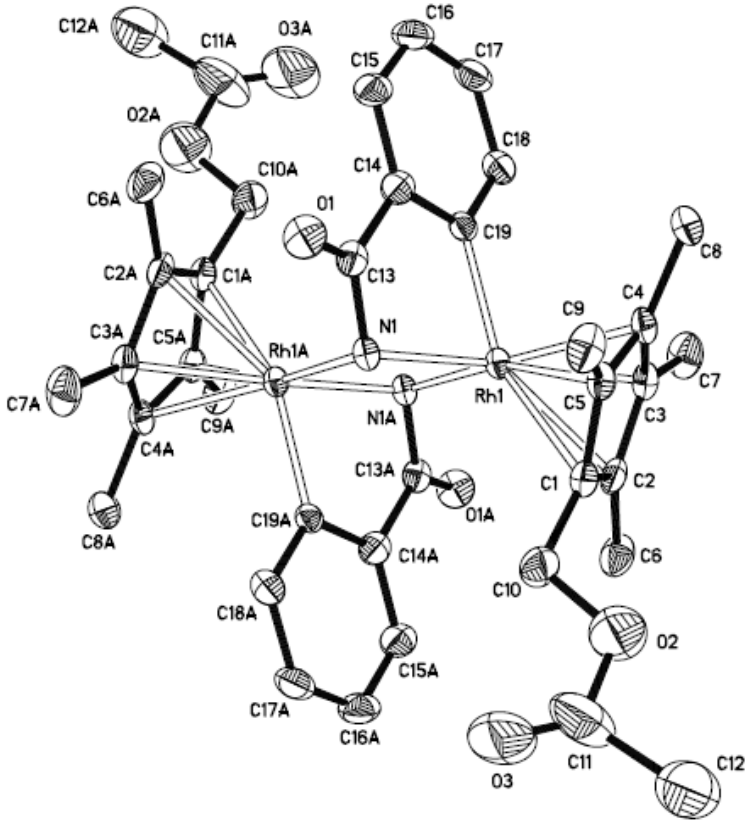


Table S1. Crystal data and structure refinement for **4**.

Identification code	lhw16
Empirical formula	$[Rh(C_{19}H_{21}NO_3)]_2$
Formula weight	828.56
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	R-3
Unit cell dimensions	a = 34.5934(6) Å = 90°.
	b = 34.5934(6) Å = 90°.
	c = 8.2566(3) Å = 120°.
Volume	8556.9(4) $Å^3$
Z	9
Density (calculated)	1.447 Mg/m^3
Absorption coefficient	0.913 mm^{-1}
F(000)	3798

Crystal size	0.42 x 0.24 x 0.24 mm^3
Theta range for data collection	2.04 to 27.48°.
Index ranges	-44<=h<=44, -44<=k<=44, -10<=l<=10
Reflections collected	30007
Independent reflections	4313 [R(int) = 0.0472]
Completeness to theta = 27.48°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6128
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4313 / 3 / 212
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0649, wR2 = 0.1959
R indices (all data)	R1 = 0.0885, wR2 = 0.2312
Extinction coefficient	0.00012(4)
Largest diff. peak and hole	1.250 and -1.203 e.$Å^{-3}$

Table S2. Bond length [Å] and angles [°] for **4**.

Rh(1)-C(19)	2.024(3)
Rh(1)-N(1)	2.111(3)
Rh(1)-C(5)	2.142(4)
Rh(1)-N(1)#1	2.169(3)
Rh(1)-C(4)	2.176(4)
Rh(1)-C(3)	2.190(4)
Rh(1)-C(1)	2.251(4)
Rh(1)-C(2)	2.297(4)
O(1)-C(13)	1.224(5)
O(2)-C(11)	1.337(6)
O(2)-C(10)	1.397(8)
N(1)-C(13)	1.383(4)
N(1)-Rh(1)#1	2.169(3)
C(1)-C(2)	1.416(6)
C(1)-C(5)	1.447(5)
C(1)-C(10)	1.503(7)
C(2)-C(3)	1.451(5)
C(2)-C(6)	1.493(6)
C(3)-C(4)	1.416(6)
C(3)-C(7)	1.491(6)

C(4)-C(5)	1.408(6)
C(4)-C(8)	1.496(6)
C(5)-C(9)	1.519(6)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(13)-C(14)	1.490(6)
C(14)-C(19)	1.385(6)
C(14)-C(15)	1.395(5)
C(15)-C(16)	1.381(8)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.381(9)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.386(6)
C(17)-H(17A)	0.9300
C(18)-C(19)	1.405(6)
C(18)-H(18A)	0.9300
O(3)-C(11)	1.113(7)
C(11)-C(12)	1.632(8)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600

C(19)-Rh(1)-N(1)	78.11(13)
C(19)-Rh(1)-C(5)	111.52(15)
N(1)-Rh(1)-C(5)	100.26(15)
C(19)-Rh(1)-N(1)#1	85.48(13)

N(1)-Rh(1)-N(1)#1	81.24(13)
C(5)-Rh(1)-N(1)#1	162.93(11)
C(19)-Rh(1)-C(4)	92.05(14)
N(1)-Rh(1)-C(4)	129.57(15)
C(5)-Rh(1)-C(4)	38.06(16)
N(1)#1-Rh(1)-C(4)	147.90(14)
C(19)-Rh(1)-C(3)	108.40(15)
N(1)-Rh(1)-C(3)	164.07(15)
C(5)-Rh(1)-C(3)	63.90(16)
N(1)#1-Rh(1)-C(3)	113.32(14)
C(4)-Rh(1)-C(3)	37.85(16)
C(19)-Rh(1)-C(1)	149.88(16)
N(1)-Rh(1)-C(1)	104.00(14)
C(5)-Rh(1)-C(1)	38.37(14)
N(1)#1-Rh(1)-C(1)	124.63(12)
C(4)-Rh(1)-C(1)	63.04(14)
C(3)-Rh(1)-C(1)	62.90(15)
C(19)-Rh(1)-C(2)	145.94(16)
N(1)-Rh(1)-C(2)	135.11(13)
C(5)-Rh(1)-C(2)	62.49(15)
N(1)#1-Rh(1)-C(2)	104.41(14)
C(4)-Rh(1)-C(2)	62.20(14)
C(3)-Rh(1)-C(2)	37.65(14)
C(1)-Rh(1)-C(2)	36.26(16)
C(11)-O(2)-C(10)	110.7(6)
C(13)-N(1)-Rh(1)	110.4(2)
C(13)-N(1)-Rh(1)#1	111.4(3)
Rh(1)-N(1)-Rh(1)#1	98.76(13)
C(2)-C(1)-C(5)	107.3(3)
C(2)-C(1)-C(10)	126.6(4)
C(5)-C(1)-C(10)	126.0(4)
C(2)-C(1)-Rh(1)	73.6(2)
C(5)-C(1)-Rh(1)	66.7(2)
C(10)-C(1)-Rh(1)	124.3(3)
C(1)-C(2)-C(3)	107.9(3)
C(1)-C(2)-C(6)	126.6(4)
C(3)-C(2)-C(6)	125.5(4)
C(1)-C(2)-Rh(1)	70.1(2)

C(3)-C(2)-Rh(1)	67.2(2)
C(6)-C(2)-Rh(1)	131.0(4)
C(4)-C(3)-C(2)	107.5(4)
C(4)-C(3)-C(7)	127.5(4)
C(2)-C(3)-C(7)	124.1(4)
C(4)-C(3)-Rh(1)	70.5(2)
C(2)-C(3)-Rh(1)	75.2(2)
C(7)-C(3)-Rh(1)	128.1(4)
C(5)-C(4)-C(3)	108.5(3)
C(5)-C(4)-C(8)	126.1(4)
C(3)-C(4)-C(8)	125.3(4)
C(5)-C(4)-Rh(1)	69.7(3)
C(3)-C(4)-Rh(1)	71.6(2)
C(8)-C(4)-Rh(1)	127.7(3)
C(4)-C(5)-C(1)	108.3(3)
C(4)-C(5)-C(9)	126.1(4)
C(1)-C(5)-C(9)	125.1(4)
C(4)-C(5)-Rh(1)	72.3(3)
C(1)-C(5)-Rh(1)	74.9(3)
C(9)-C(5)-Rh(1)	124.7(3)
C(2)-C(6)-H(6A)	109.5
C(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(3)-C(7)-H(7A)	109.5
C(3)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(3)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(4)-C(8)-H(8A)	109.5
C(4)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(4)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

C(5)-C(9)-H(9A)	109.5
C(5)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(5)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(2)-C(10)-C(1)	108.3(5)
O(2)-C(10)-H(10A)	110.0
C(1)-C(10)-H(10A)	110.0
O(2)-C(10)-H(10B)	110.0
C(1)-C(10)-H(10B)	110.0
H(10A)-C(10)-H(10B)	108.4
O(1)-C(13)-N(1)	123.9(4)
O(1)-C(13)-C(14)	124.8(3)
N(1)-C(13)-C(14)	111.4(3)
C(19)-C(14)-C(15)	122.1(4)
C(19)-C(14)-C(13)	115.0(3)
C(15)-C(14)-C(13)	122.9(4)
C(16)-C(15)-C(14)	119.2(5)
C(16)-C(15)-H(15A)	120.4
C(14)-C(15)-H(15A)	120.4
C(15)-C(16)-C(17)	120.0(4)
C(15)-C(16)-H(16A)	120.0
C(17)-C(16)-H(16A)	120.0
C(16)-C(17)-C(18)	120.4(5)
C(16)-C(17)-H(17A)	119.8
C(18)-C(17)-H(17A)	119.8
C(17)-C(18)-C(19)	120.9(4)
C(17)-C(18)-H(18A)	119.6
C(19)-C(18)-H(18A)	119.6
C(14)-C(19)-C(18)	117.3(3)
C(14)-C(19)-Rh(1)	114.3(3)
C(18)-C(19)-Rh(1)	128.2(3)
O(3)-C(11)-O(2)	130.5(7)
O(3)-C(11)-C(12)	127.5(7)
O(2)-C(11)-C(12)	101.4(6)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5

H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

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4. References

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2. a) P. M. Boyer, C. P. Roy, J. M. Bielski, J. S. Merola, *Inorganica Chimica Acta*, **1996**, *245*, 7; b) M. L. Cooke, K. Xu, B. Breit, *Angew. Chem. Int. Ed.* **2012**, *51*, 10876.
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5. ^{1}H and ^{13}C NMR Spectra:

Figure S1. ^{1}H NMR spectrum of **3a**

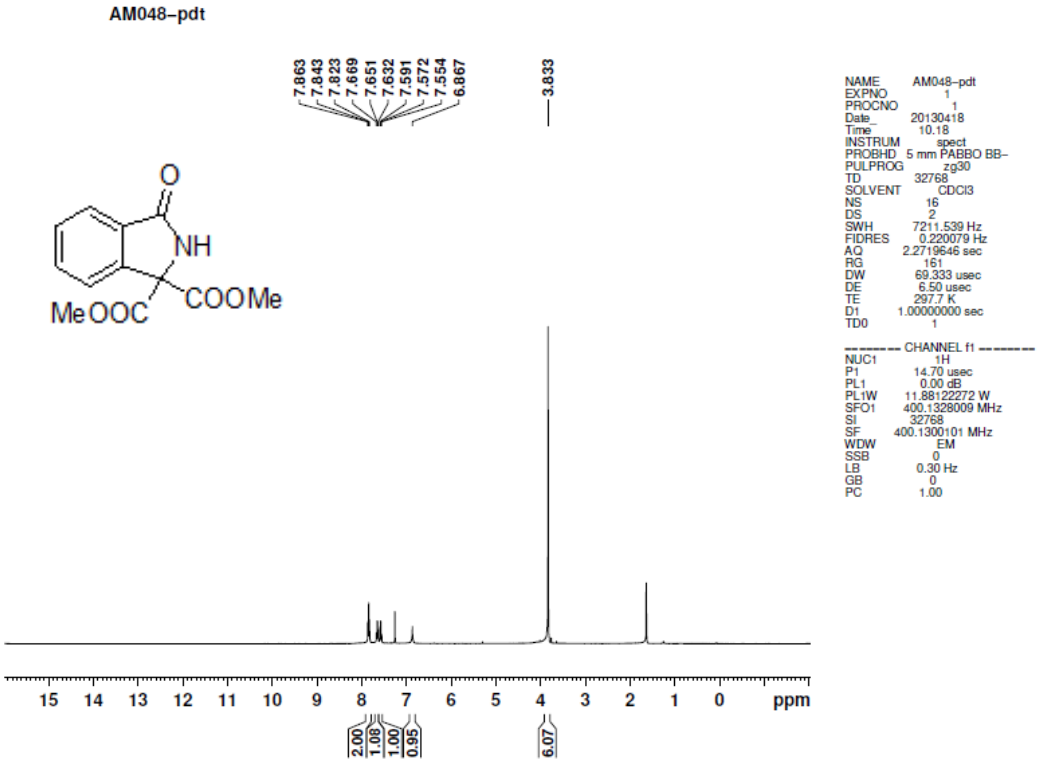

Figure S2. ^{13}C NMR spectrum of **3a**

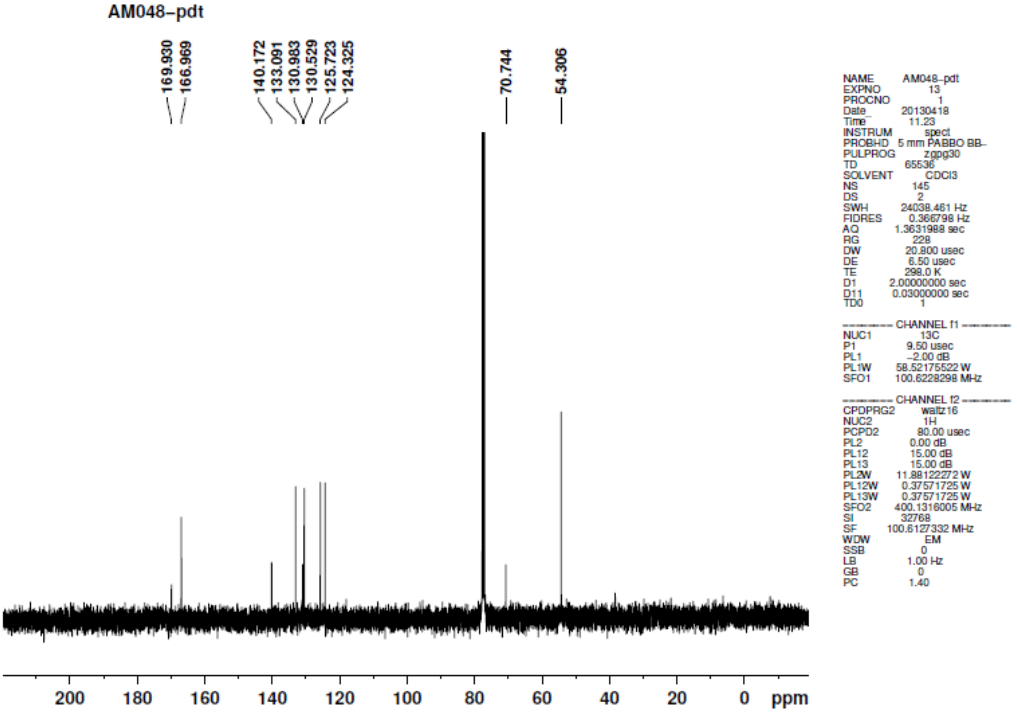

Figure S3. ^{1}H NMR spectrum of **3b**

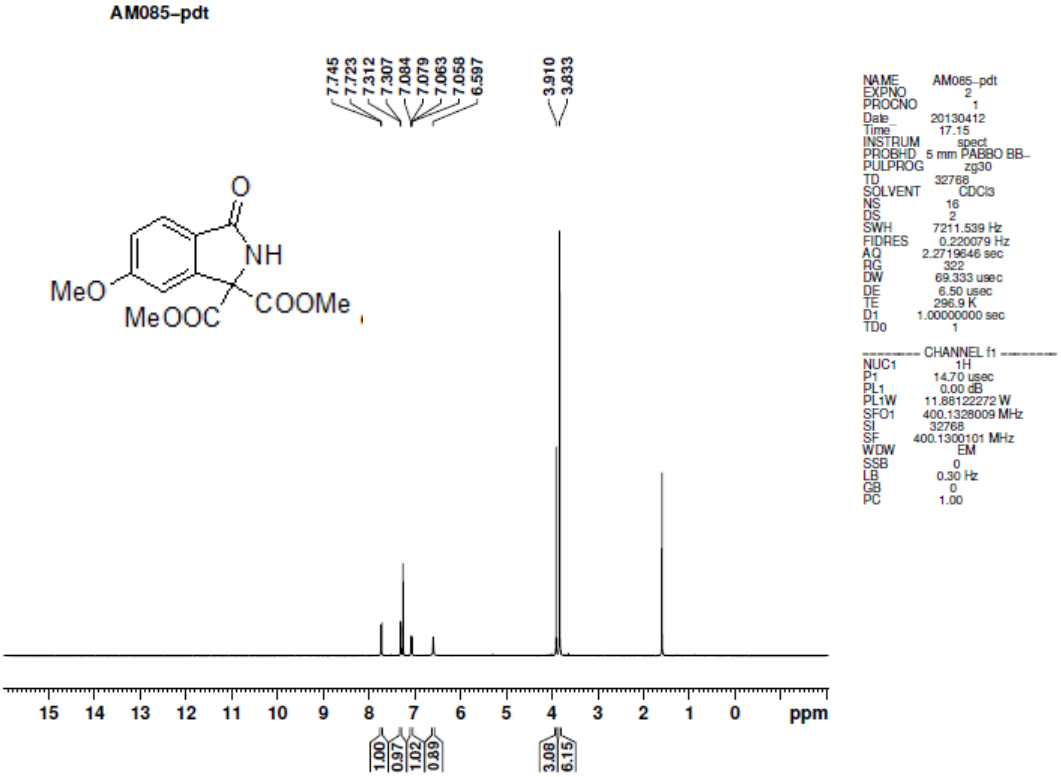

Figure S4. ^{13}C NMR spectrum of **3b**

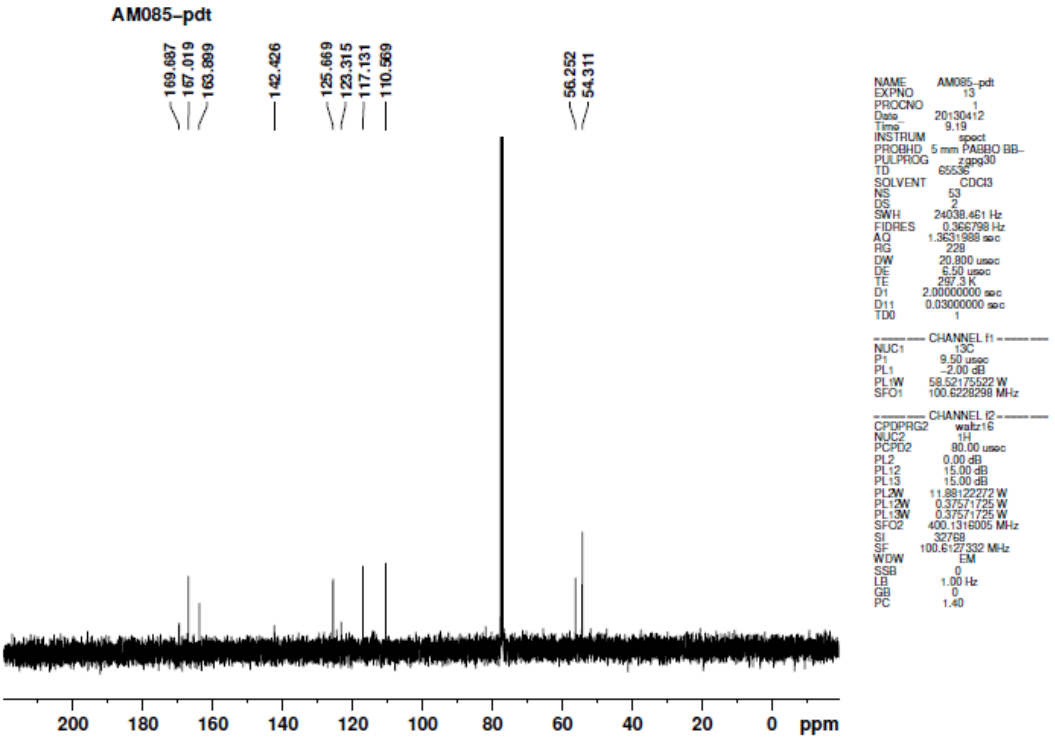

Figure S5. ^{1}H NMR spectrum of **3c**

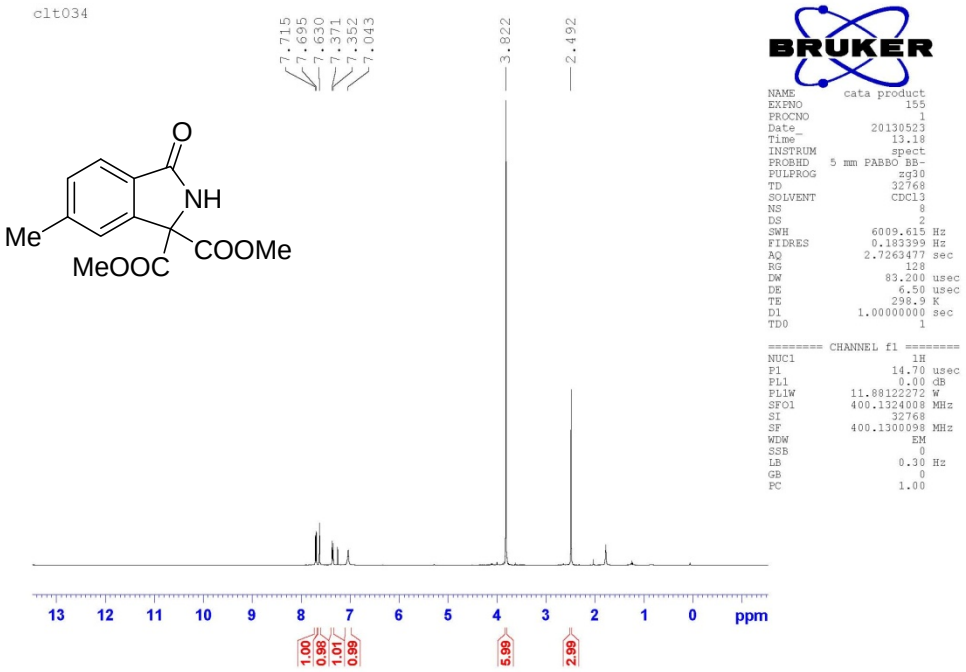

Figure S6. ^{13}C NMR spectrum of **3c**

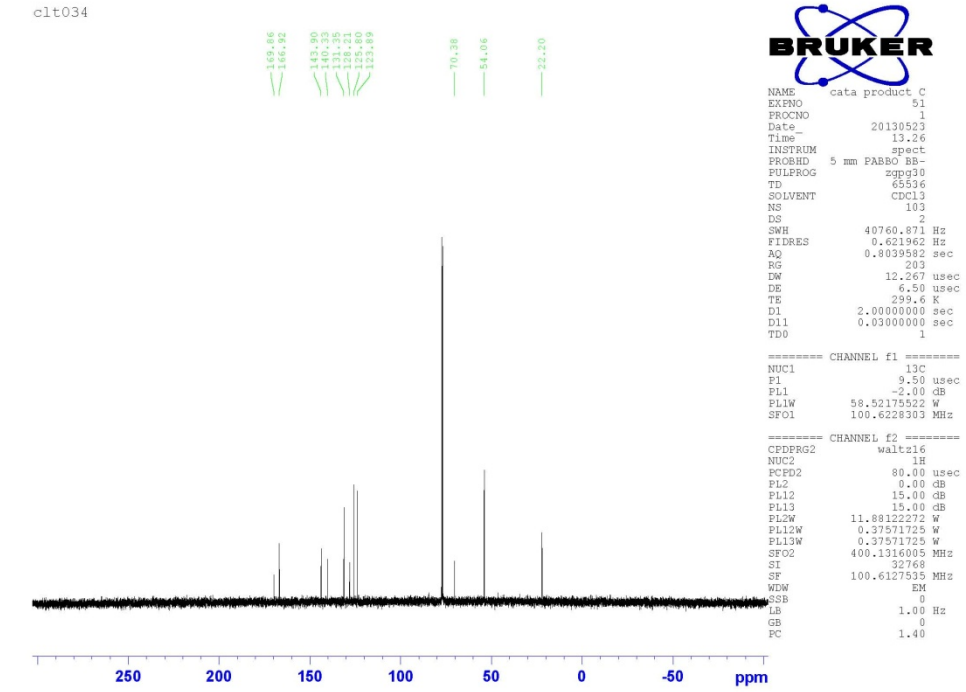

Figure S7. ^{1}H NMR spectrum of **3d**

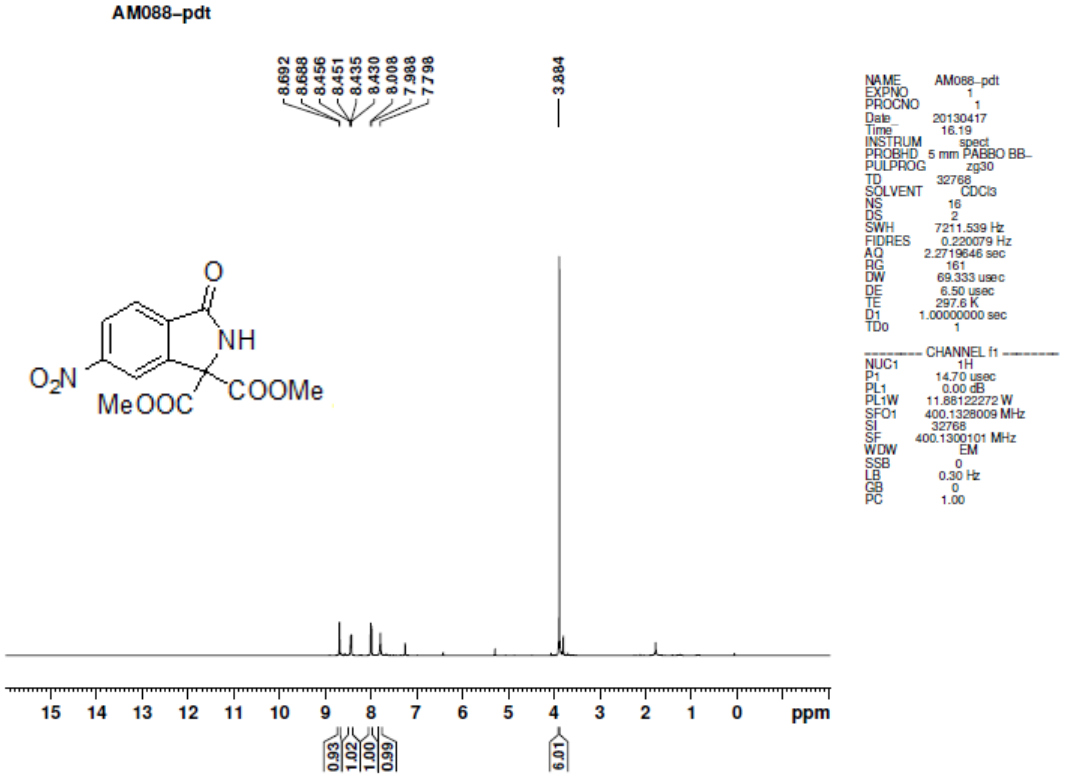

Figure S8. ^{13}C NMR spectrum of **3d**

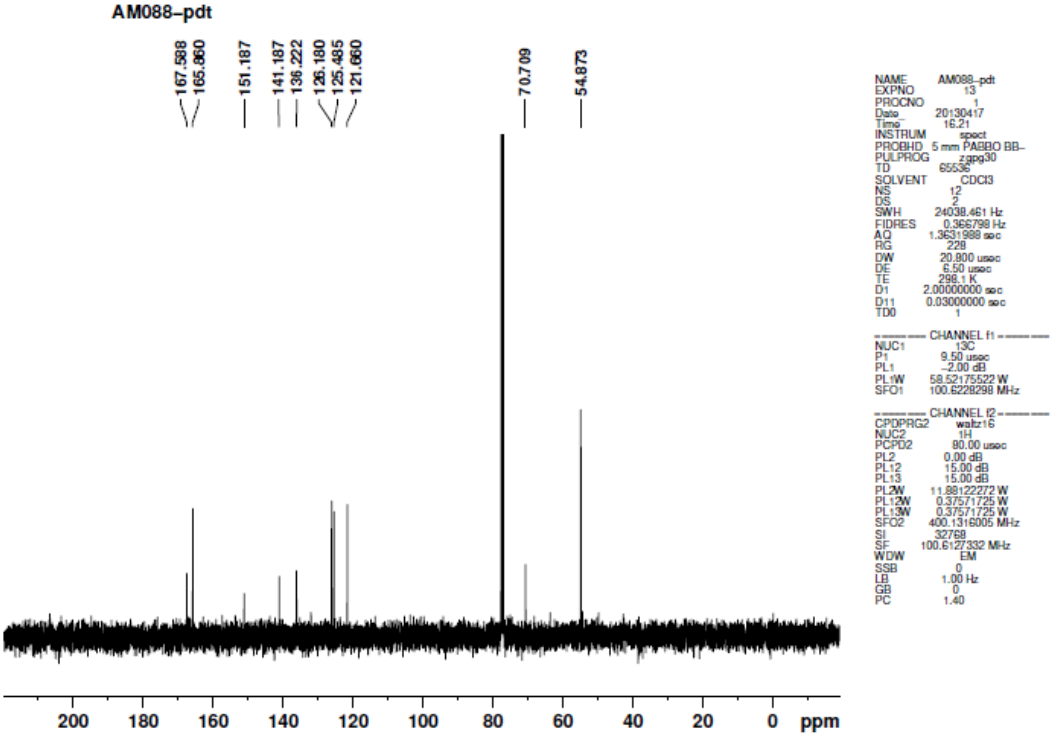

Figure S9. ^{1}H NMR spectrum of **3e**

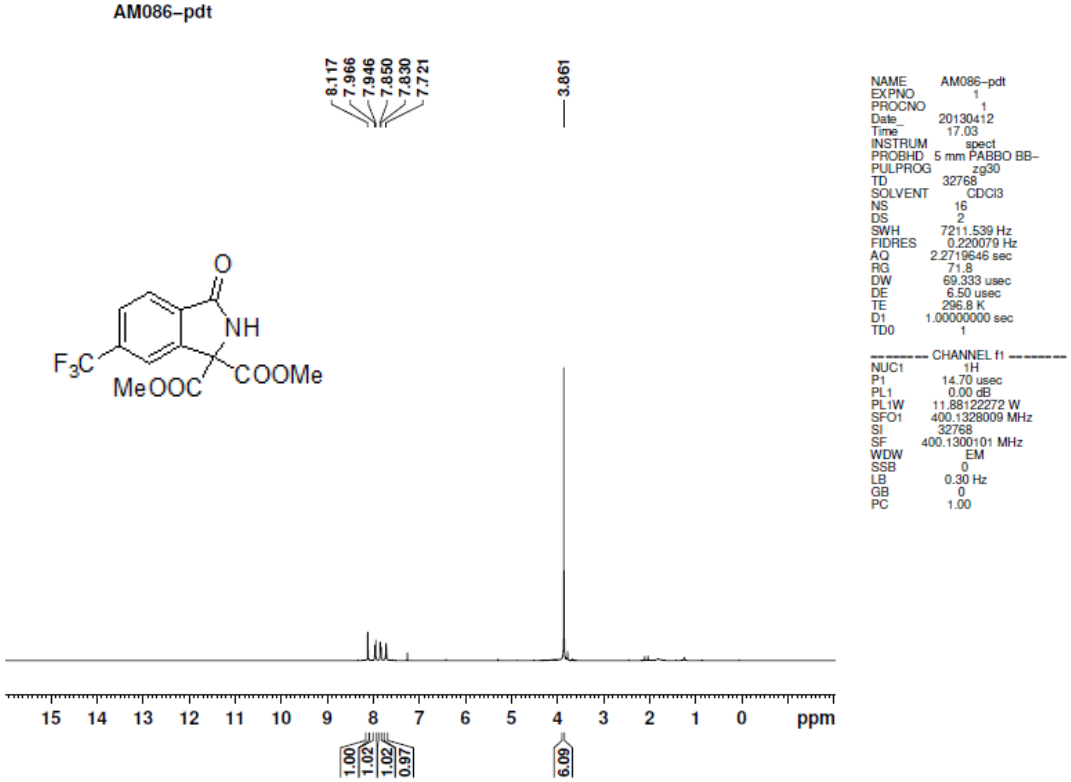

Figure S10. ^{13}C NMR spectrum of **3e**

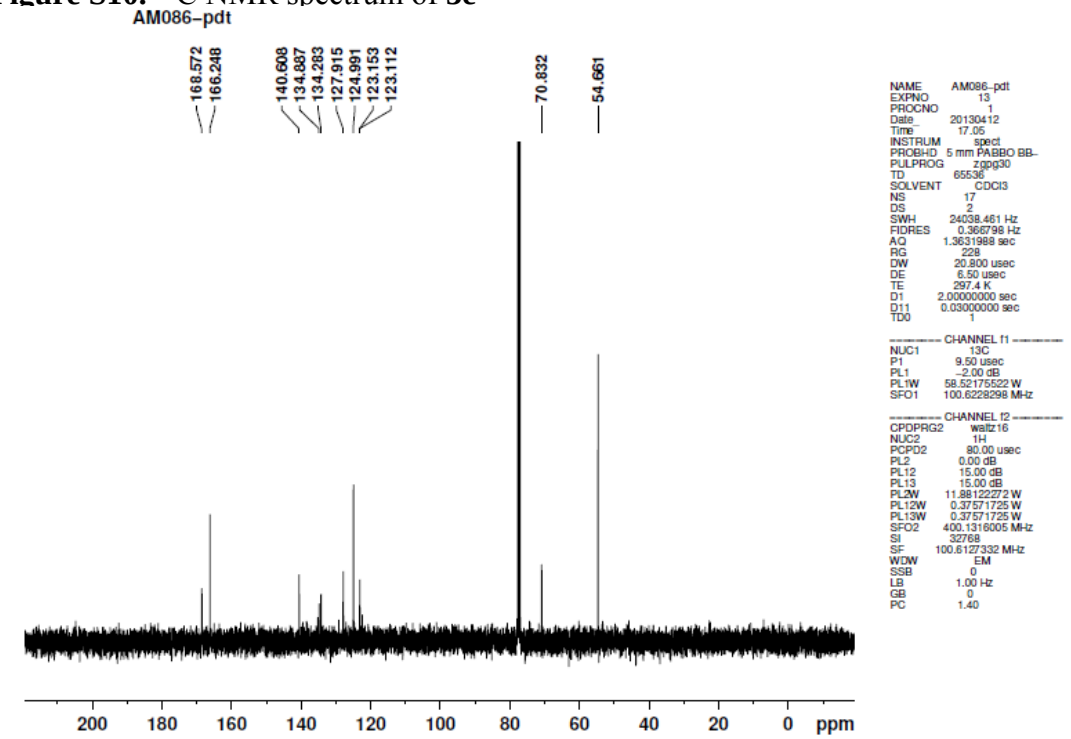

Figure S11. ^{1}H NMR spectrum of **3f**

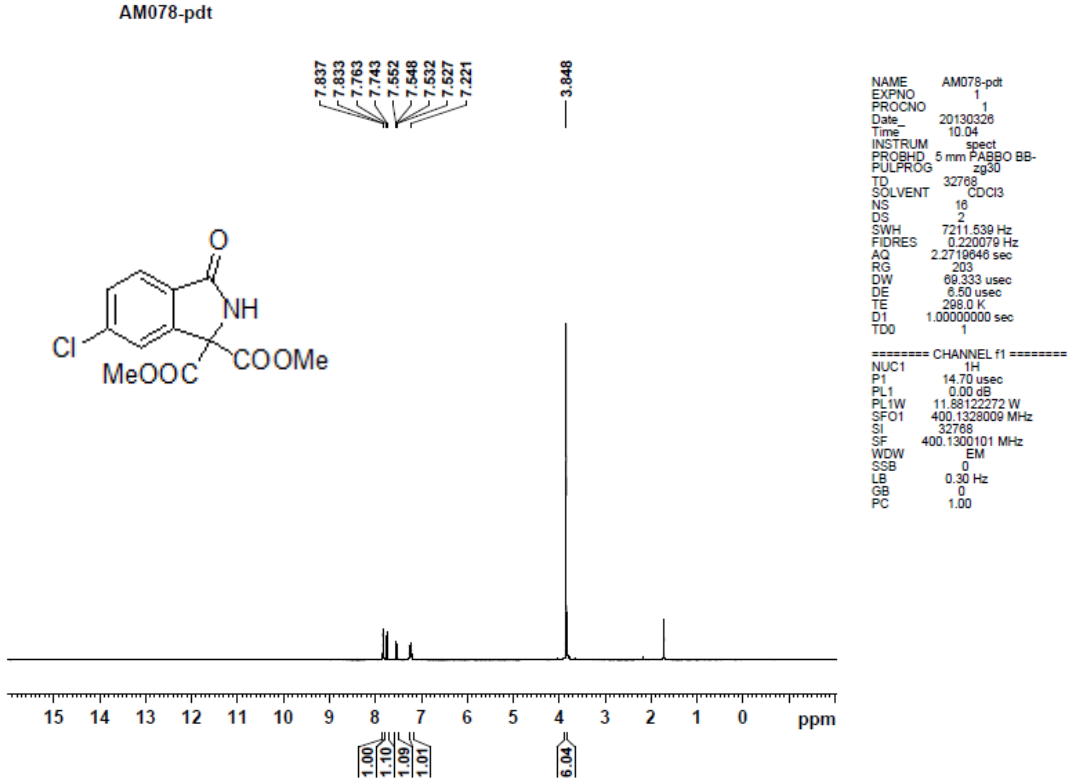

Figure S12. ^{13}C NMR spectrum of **3f**

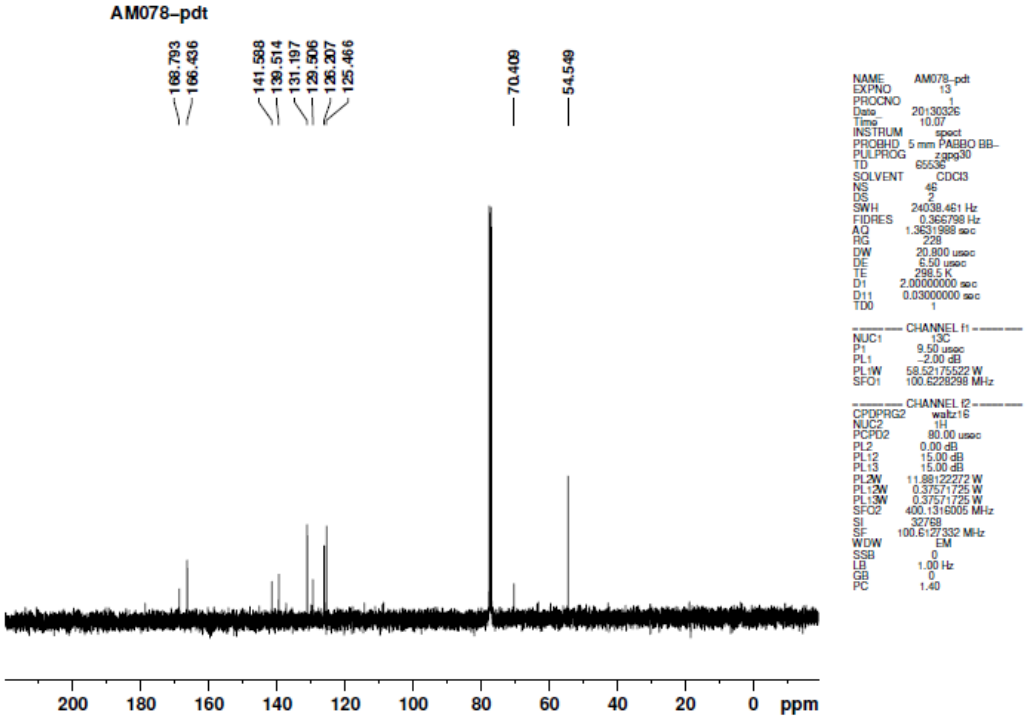

Figure S13. ^{1}H NMR spectrum of **3g**

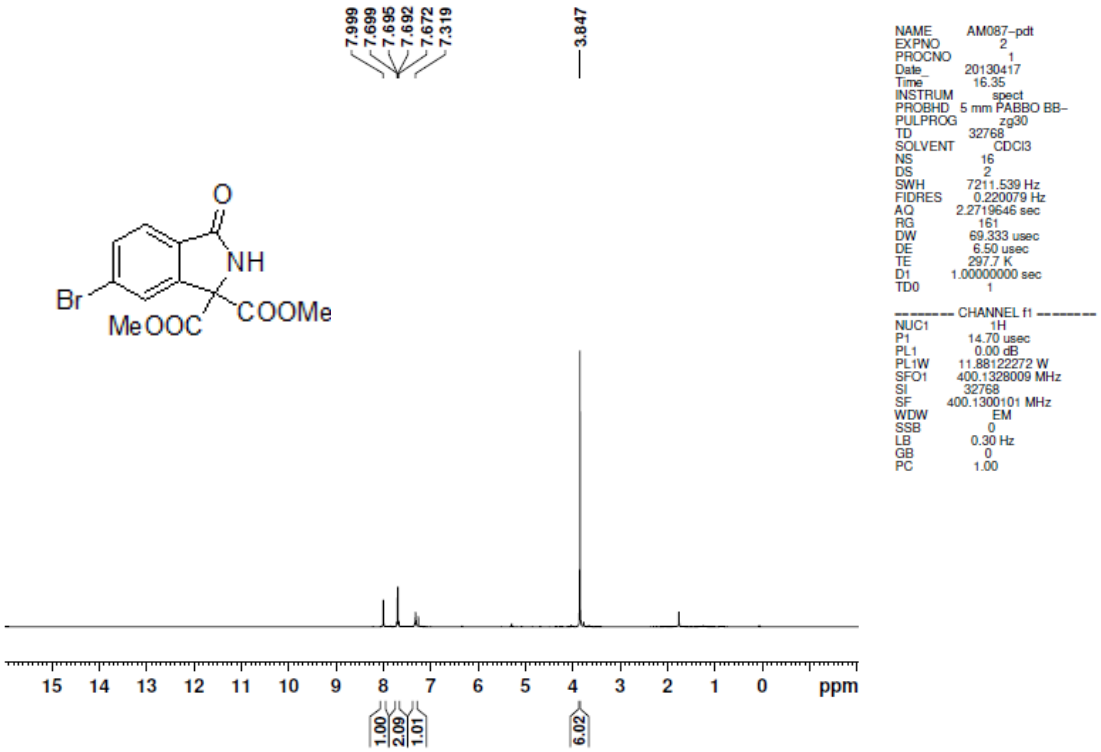

Figure S14. ^{13}C NMR spectrum of **3g**

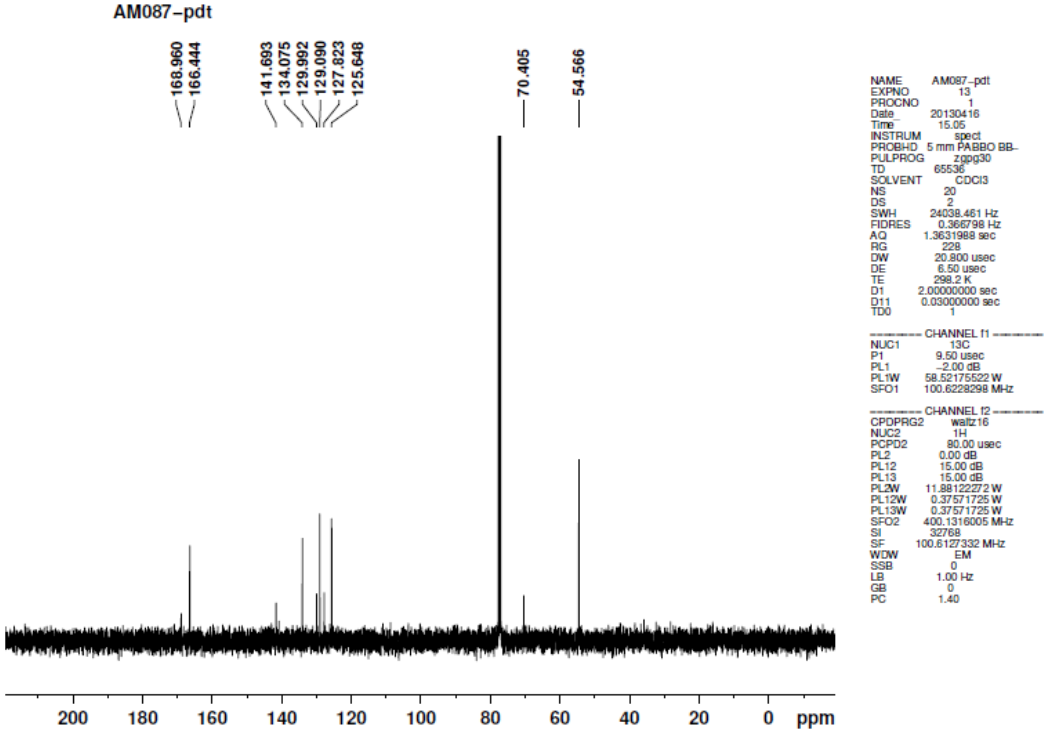

Figure S15. ^{1}H NMR spectrum of **3h**

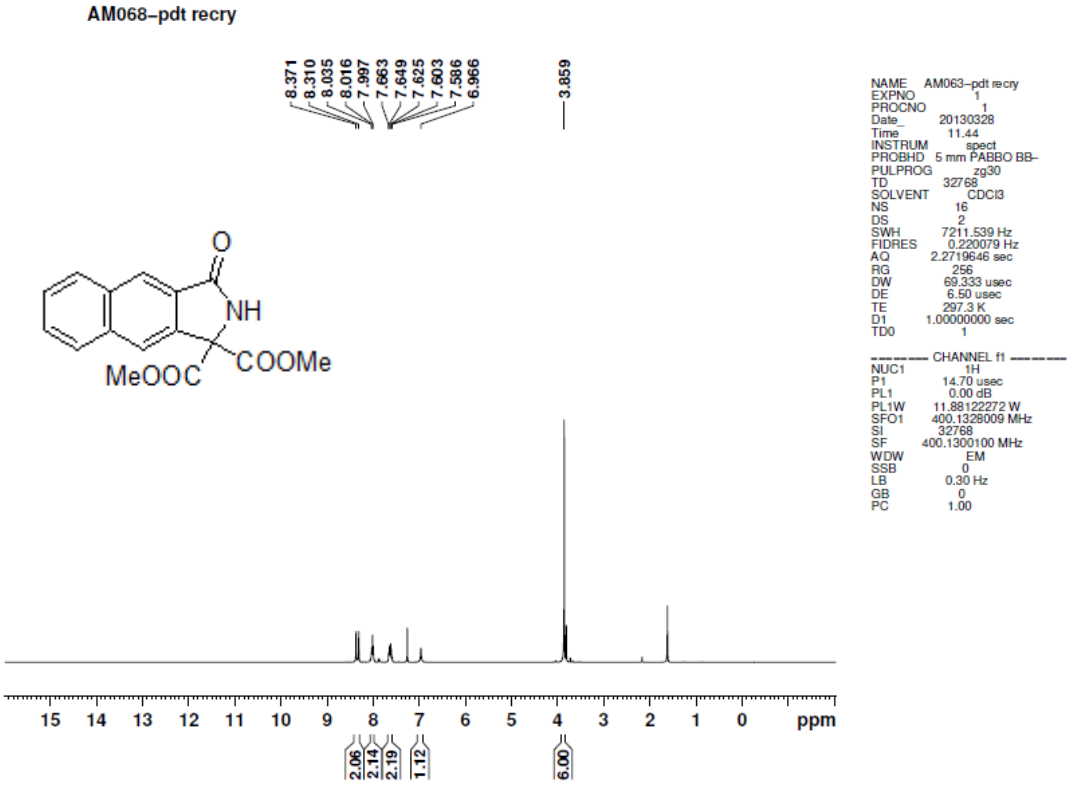

Figure S16. ^{13}C NMR spectrum of **3h**

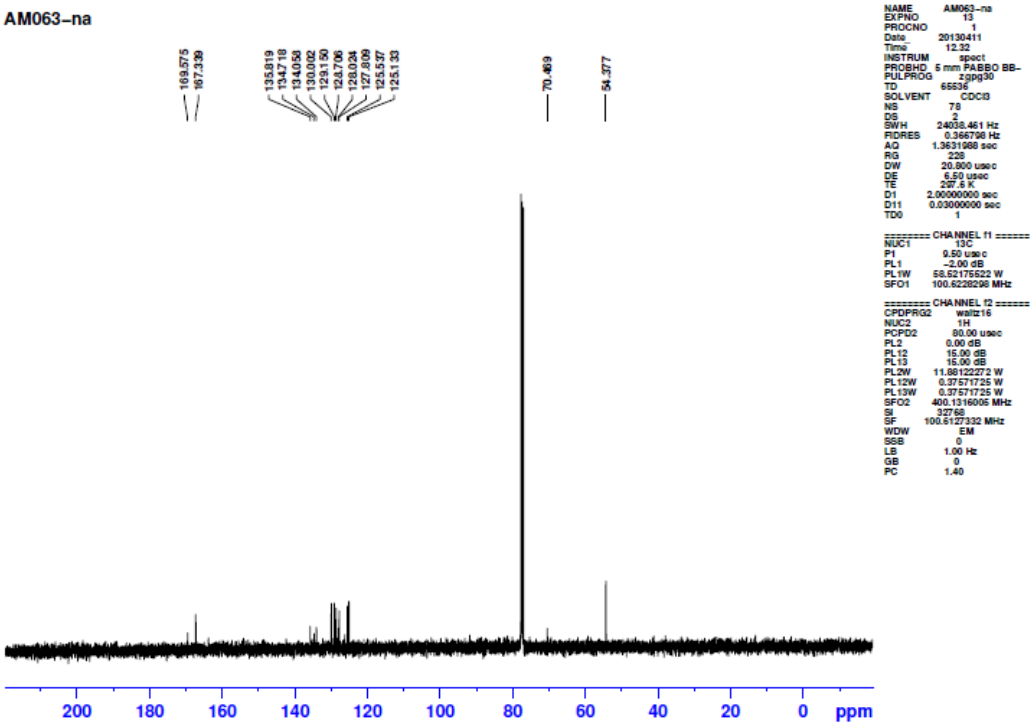

Figure S17. ^{1}H NMR spectrum of **3i**

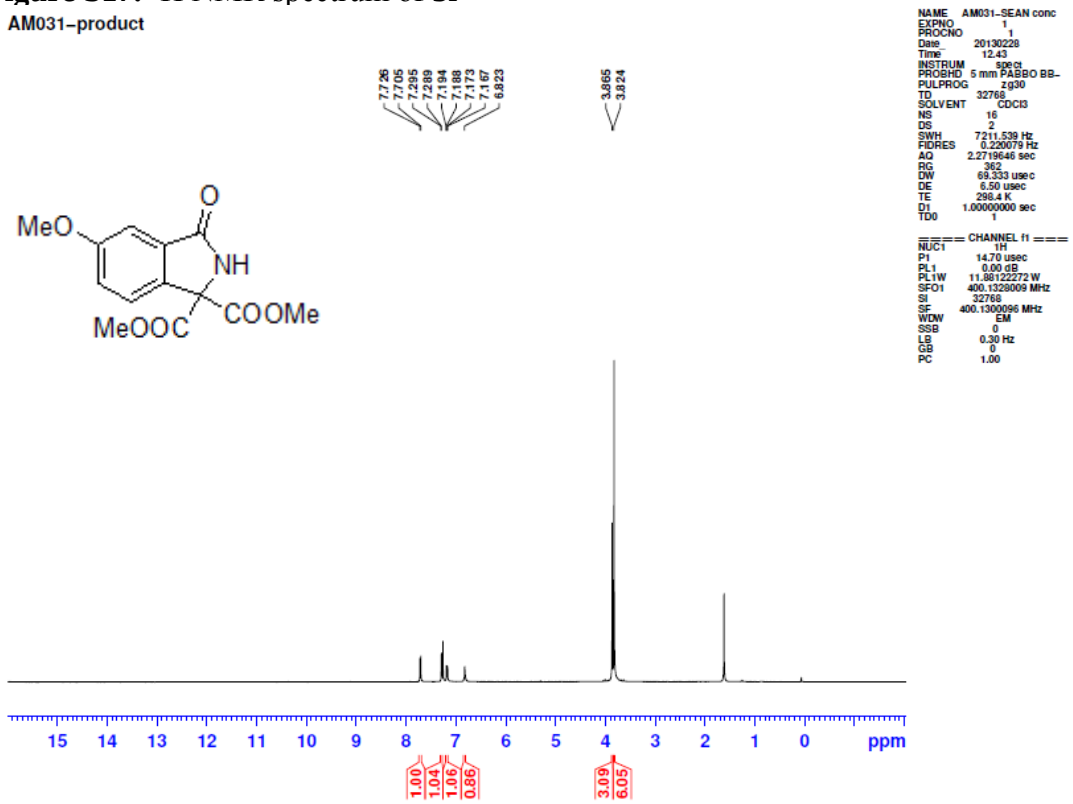

Figure S18. ^{13}C NMR spectrum of **3i**

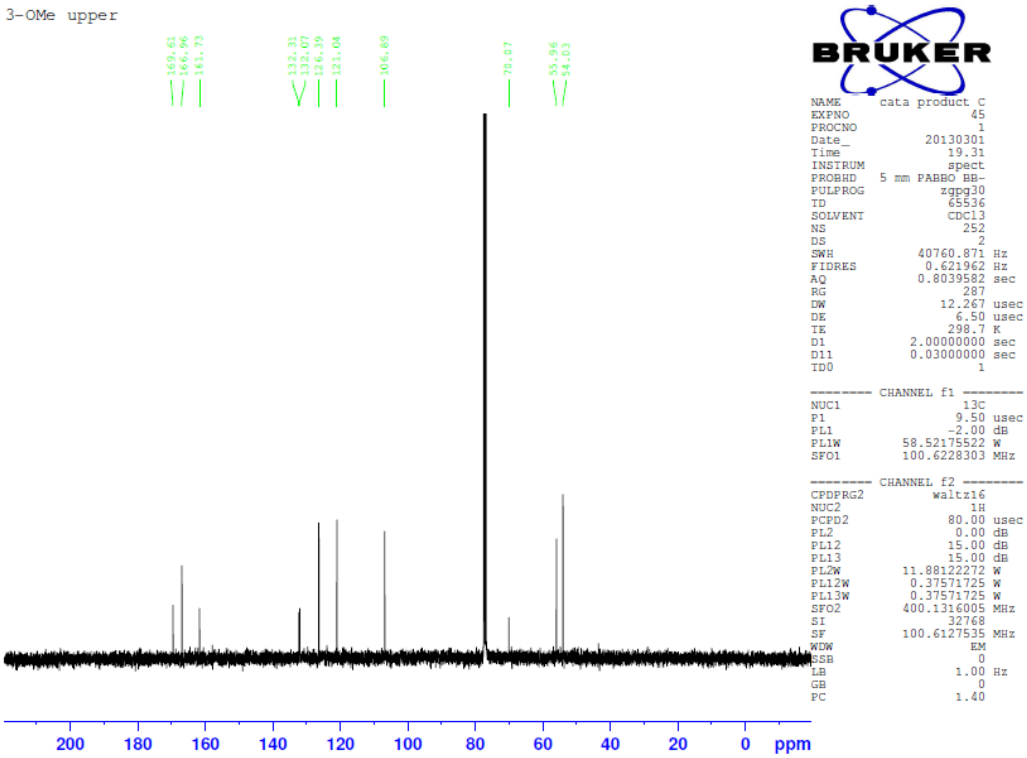

Figure S19. ^{1}H NMR spectrum of **3i'**

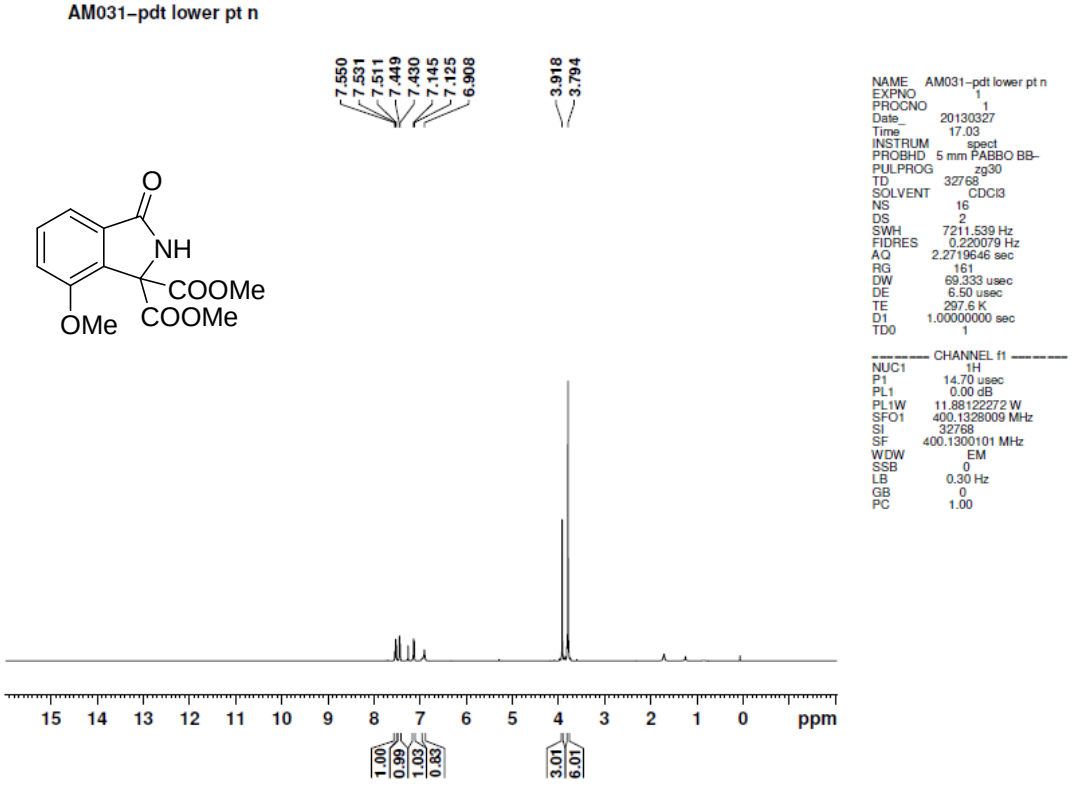

Figure S20. ^{13}C NMR spectrum of **3i'**

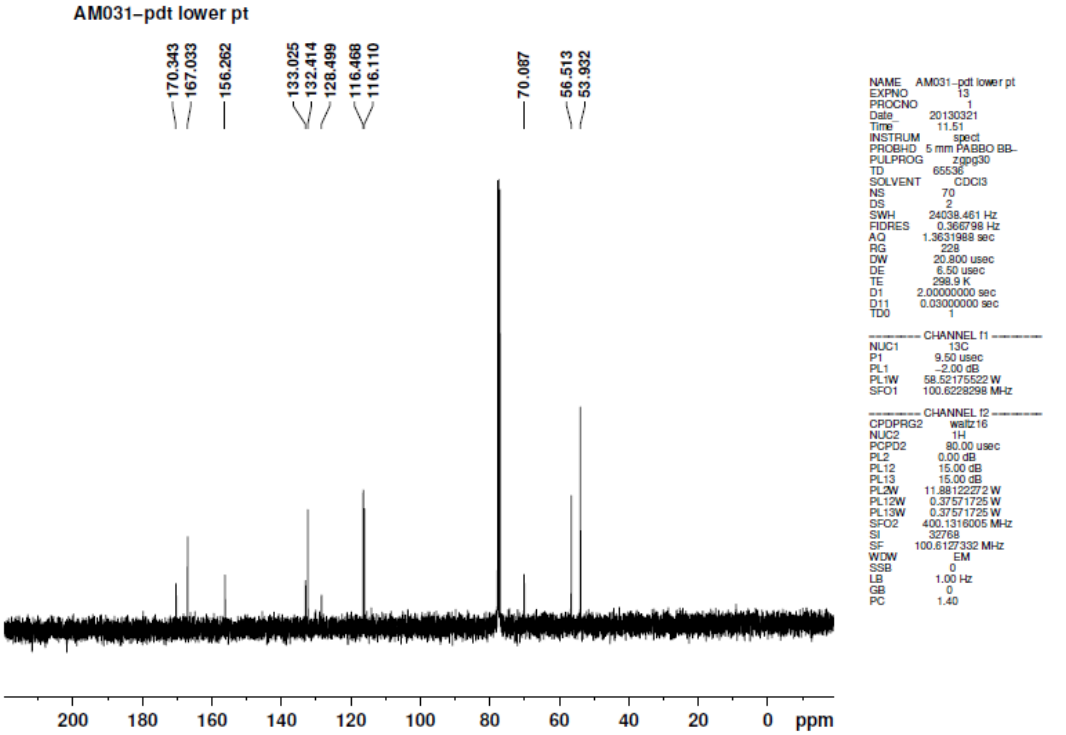

Figure S21. ^{1}H NMR spectrum of **3j**

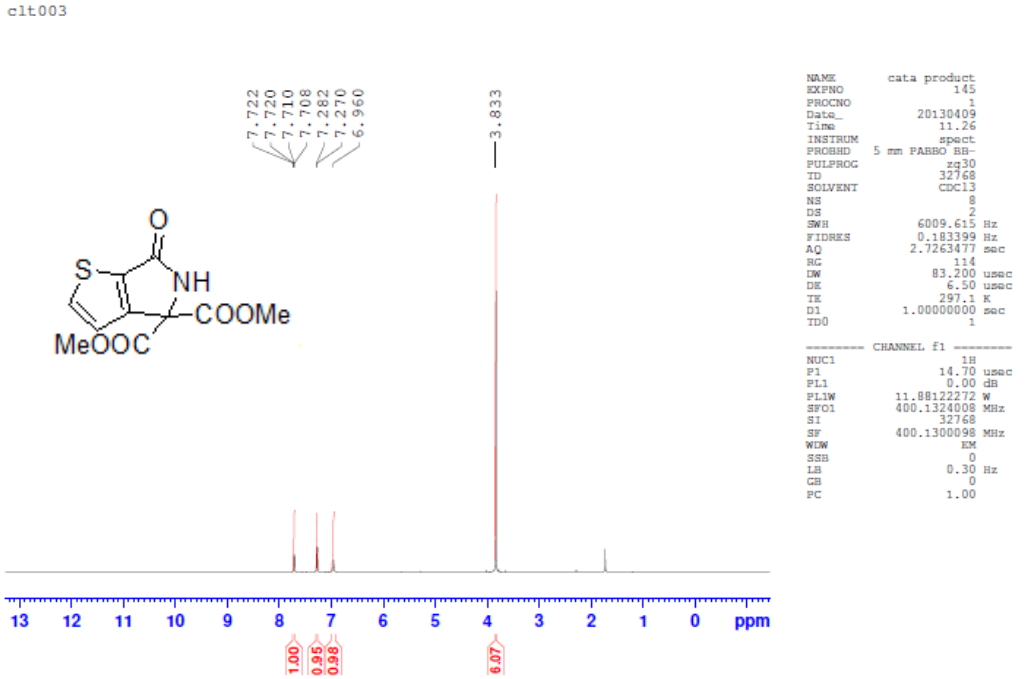

Figure S22. ^{13}C NMR spectrum of **3j**

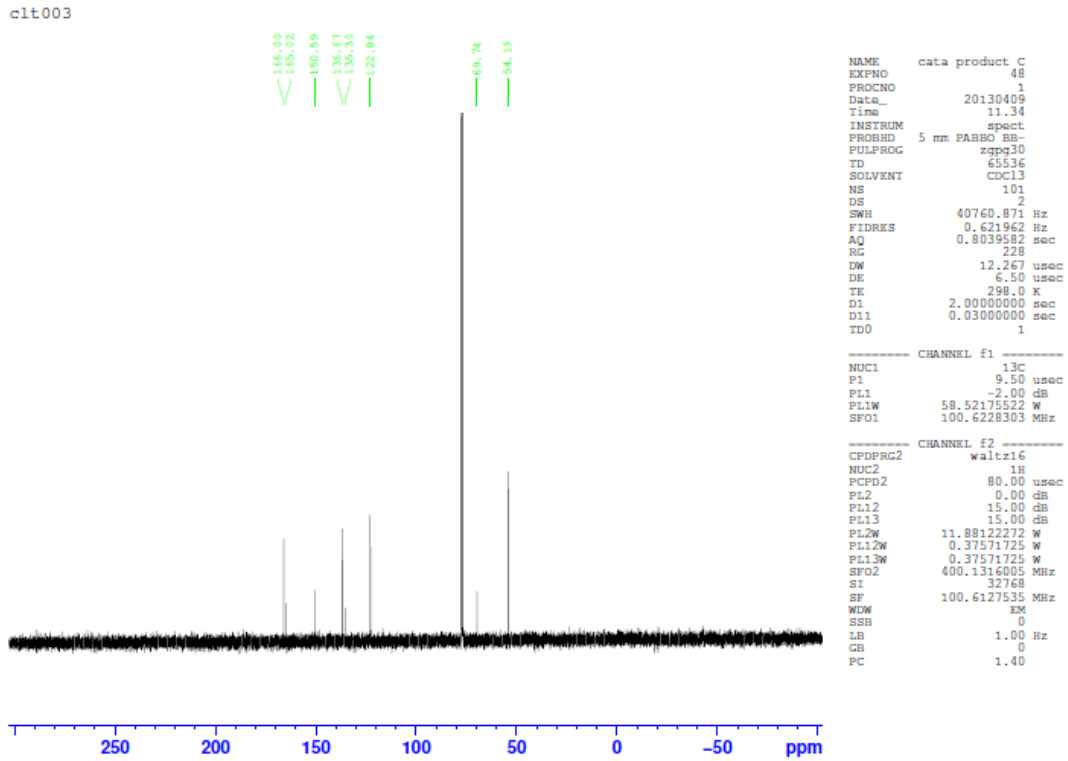

Figure S23. ^{1}H NMR spectrum of **3k**

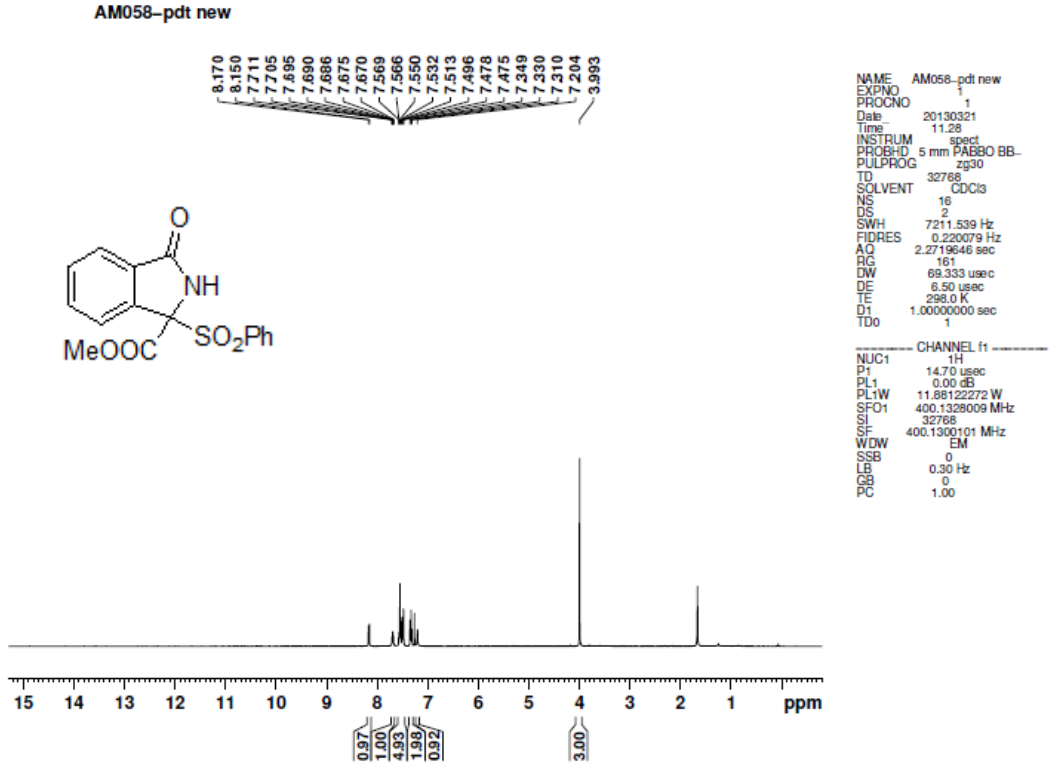

Figure S24. ^{13}C NMR spectrum of **3k**

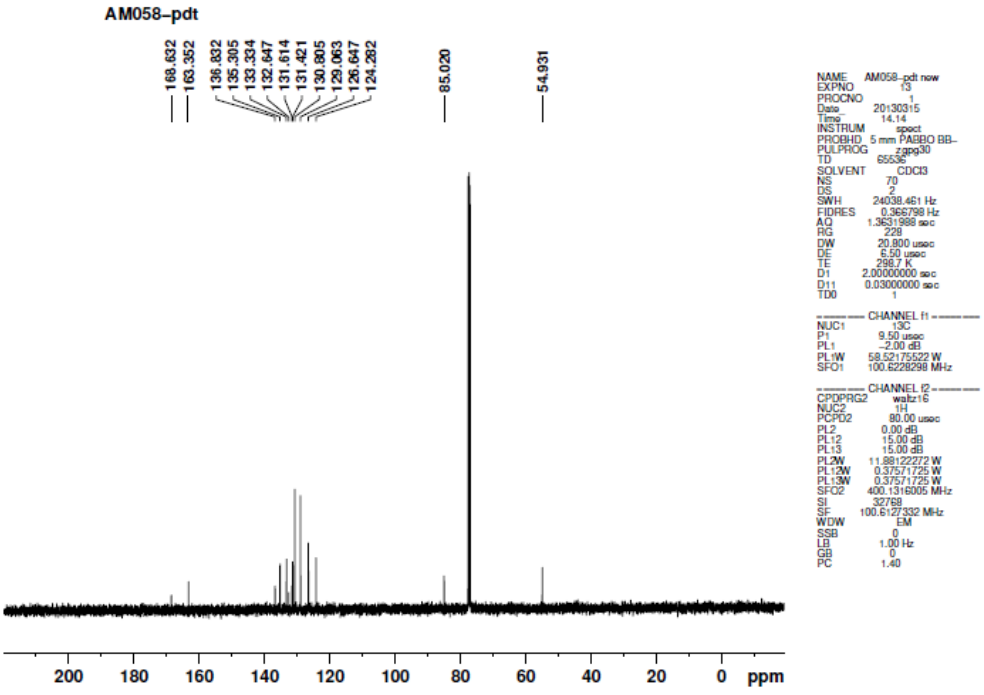

Figure S25. ^{1}H NMR spectrum of **3l**

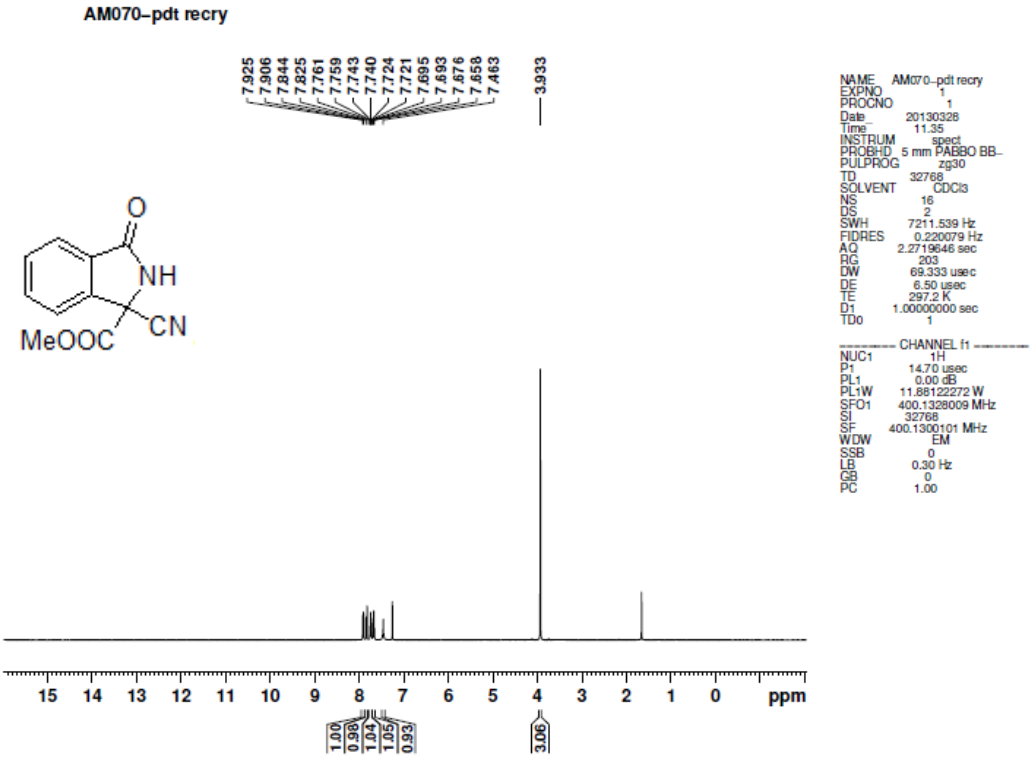

Figure S26. ^{13}C NMR spectrum of **3l**

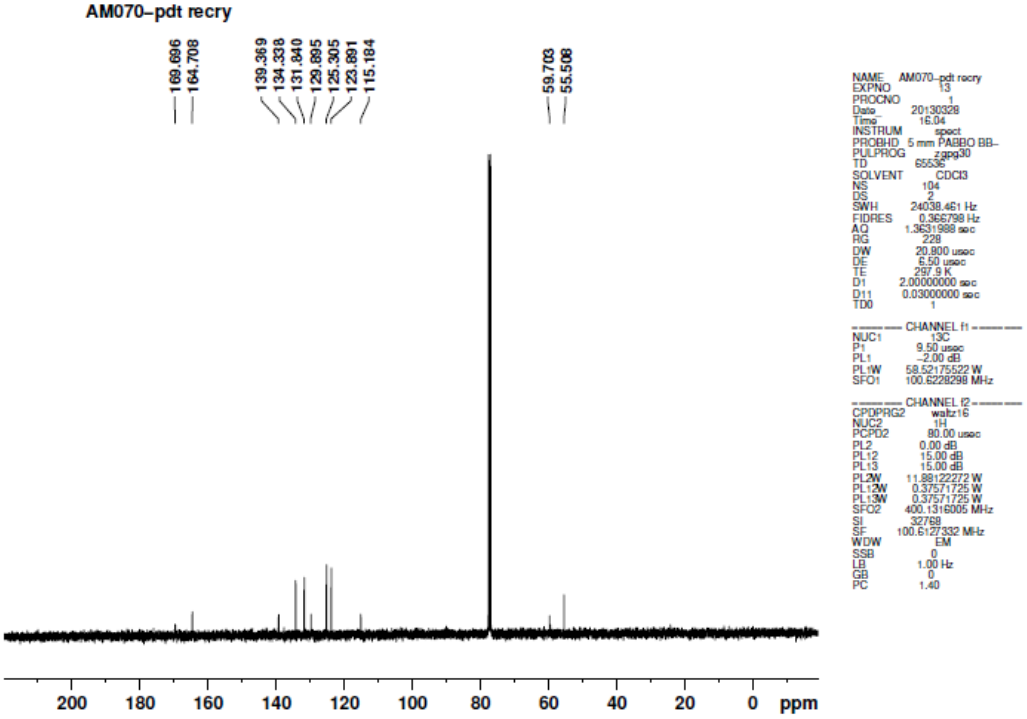

Figure S27. ^{1}H NMR spectrum of **3m**

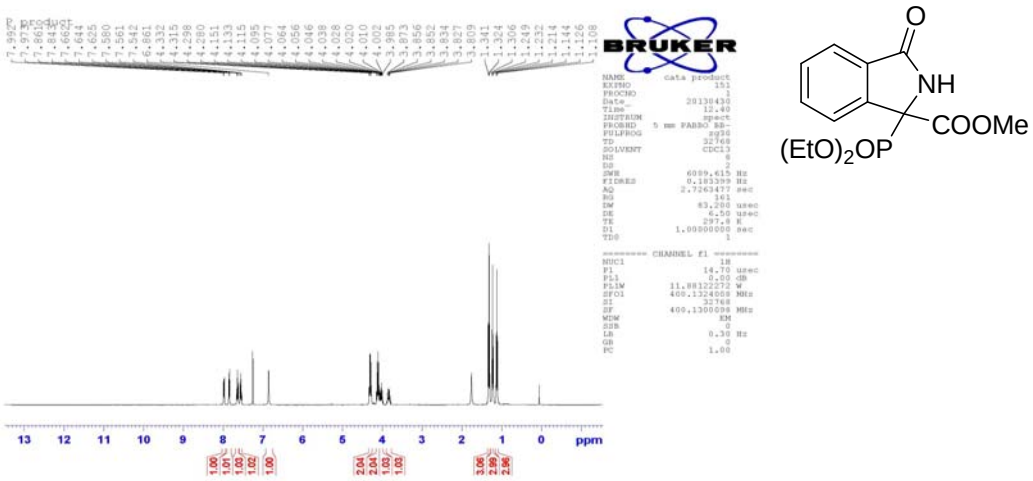

Figure S28. ^{13}C NMR spectrum of **3m**

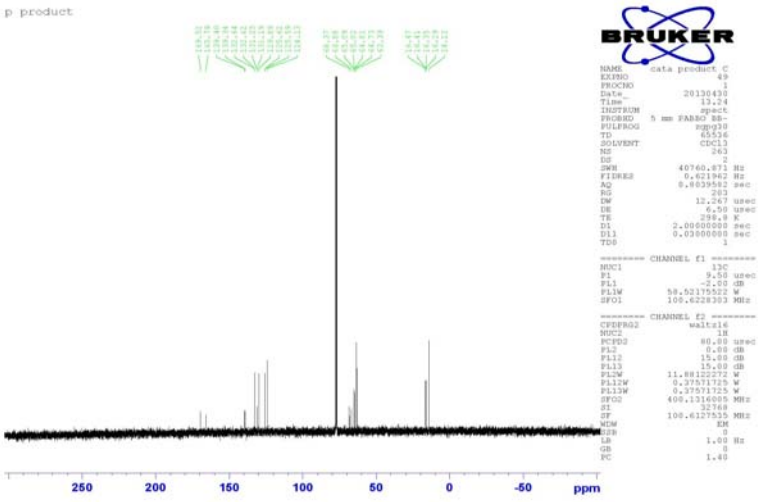

Figure S29. ^{19}F NMR spectrum of **3m**

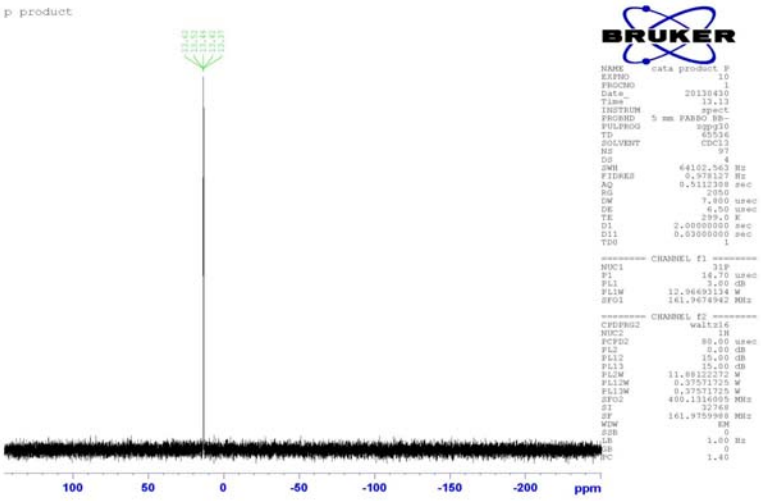

Figure S30. ^{1}H NMR spectrum of **3n**

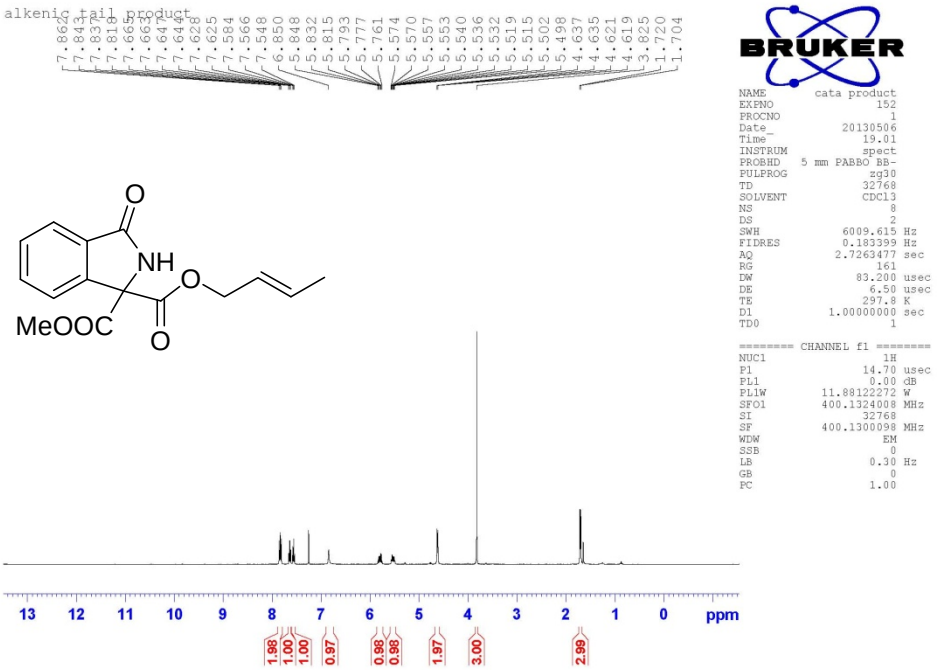

Figure S31. ^{13}C NMR spectrum of **3n**

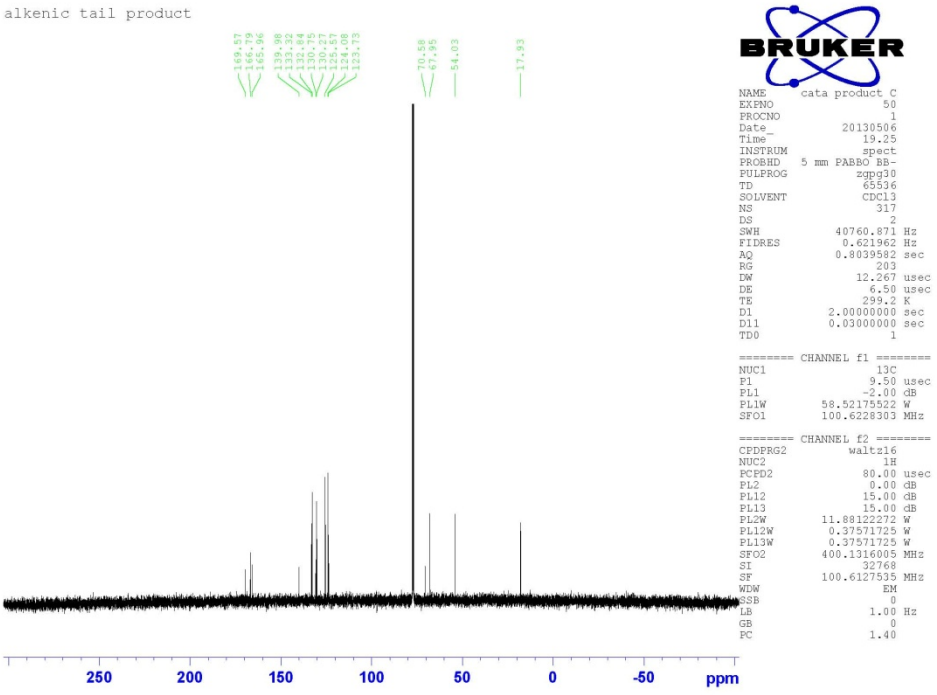

Figure S32. ^{1}H NMR spectrum of **3o**

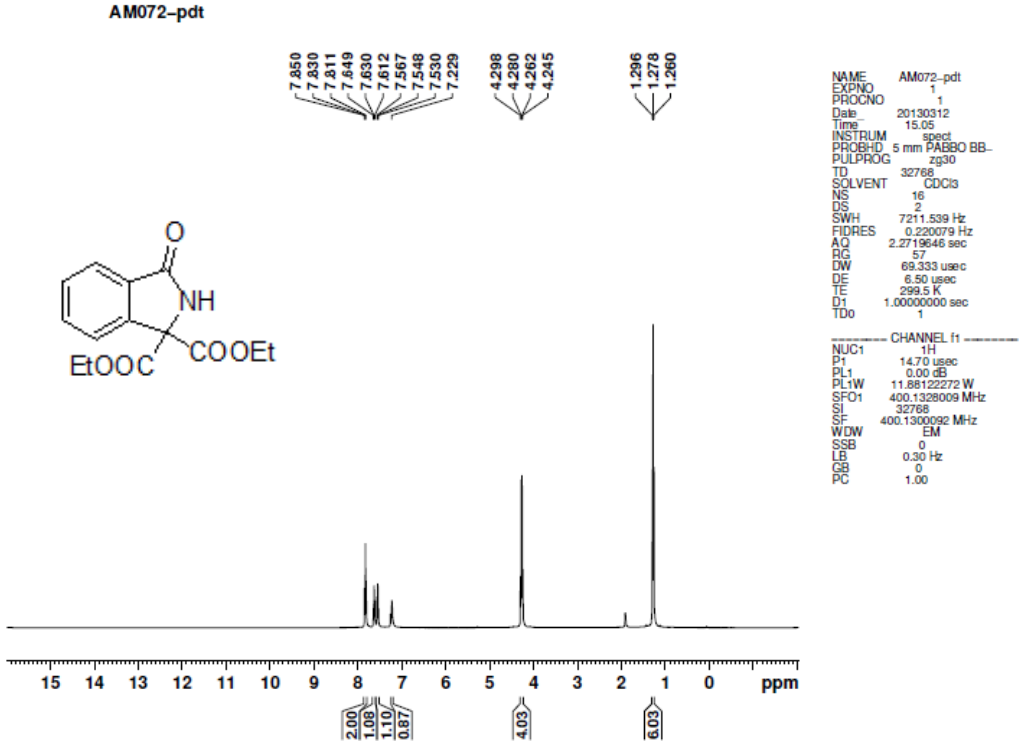

Figure S33. ^{13}C NMR spectrum of **3o**

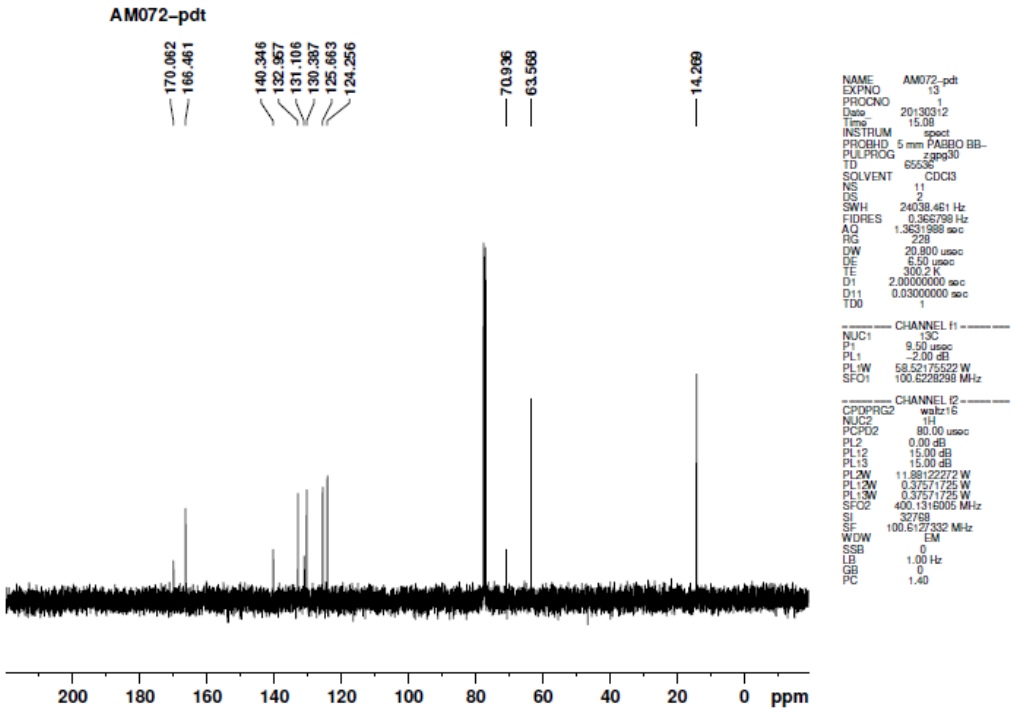

Figure S34. ^{1}H NMR spectrum of **3p**

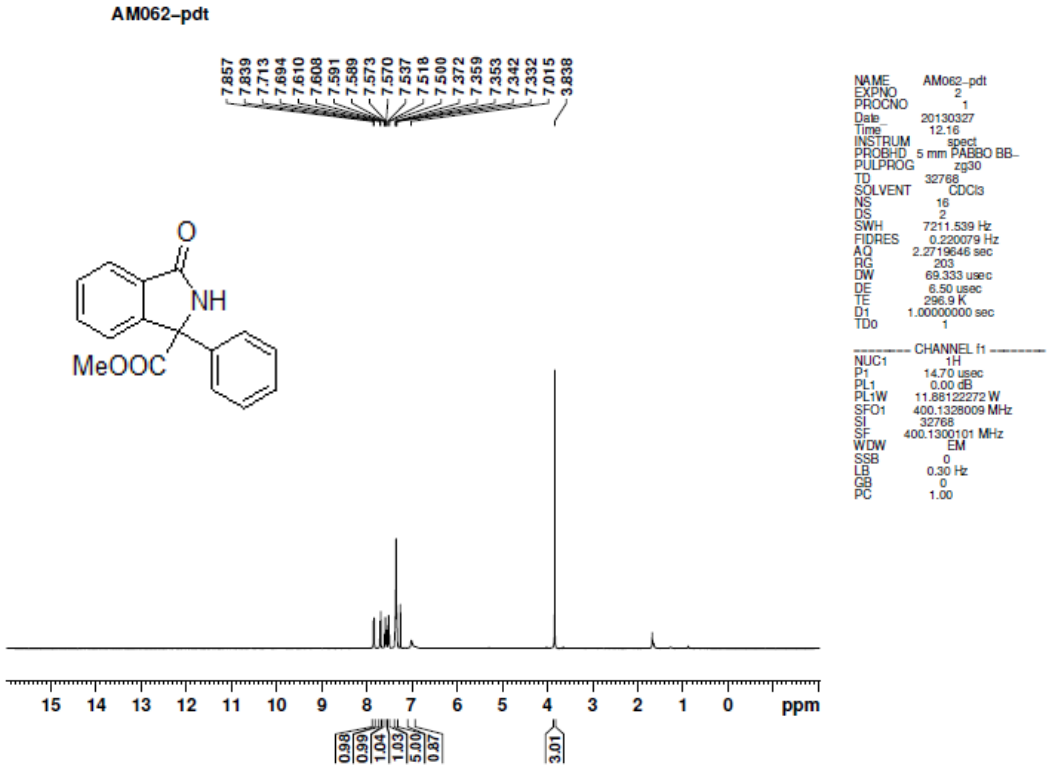

Figure S35. ^{13}C NMR spectrum of **3p**

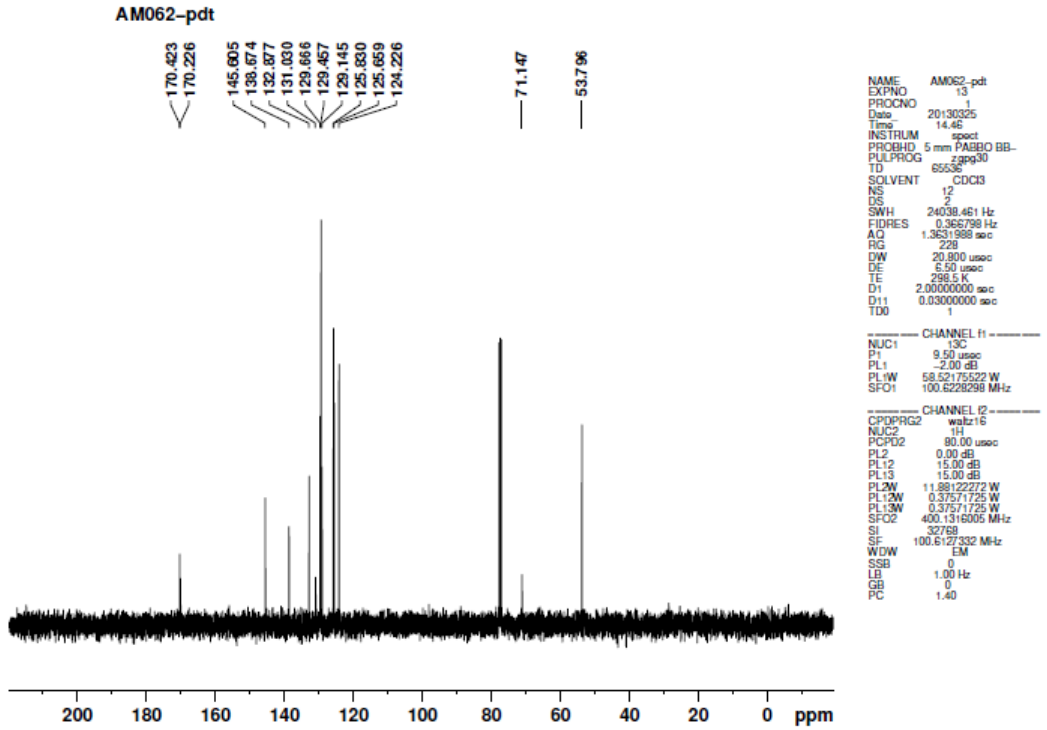

Figure S36. ^{1}H NMR spectrum of **3q**

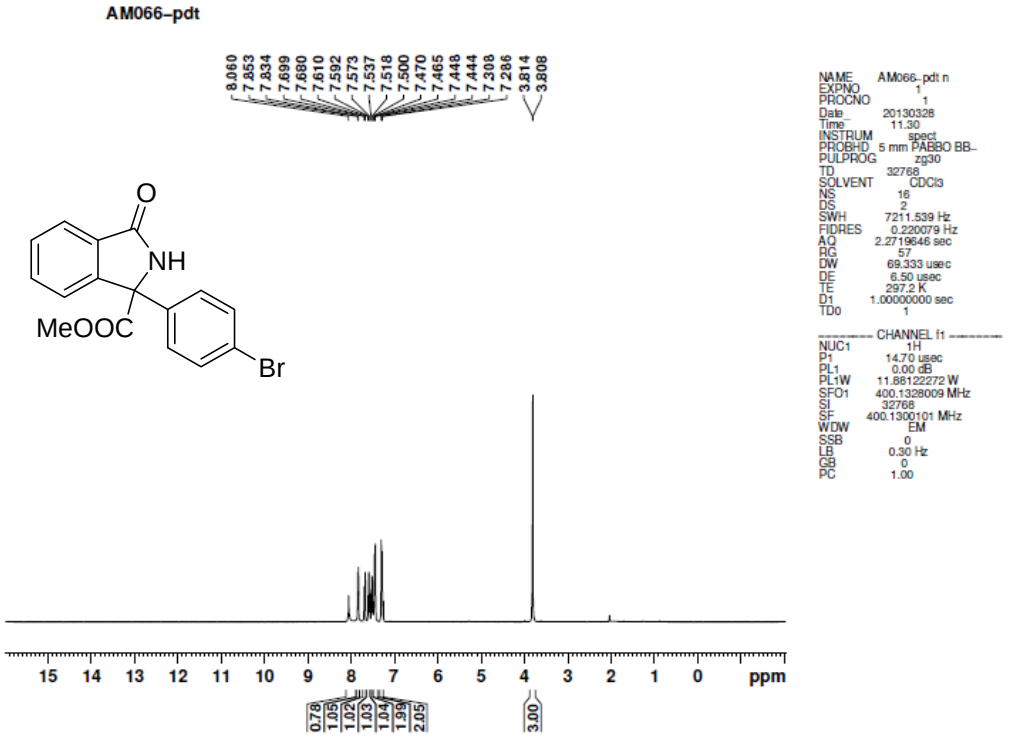

Figure S37. ^{13}C NMR spectrum of **3q**

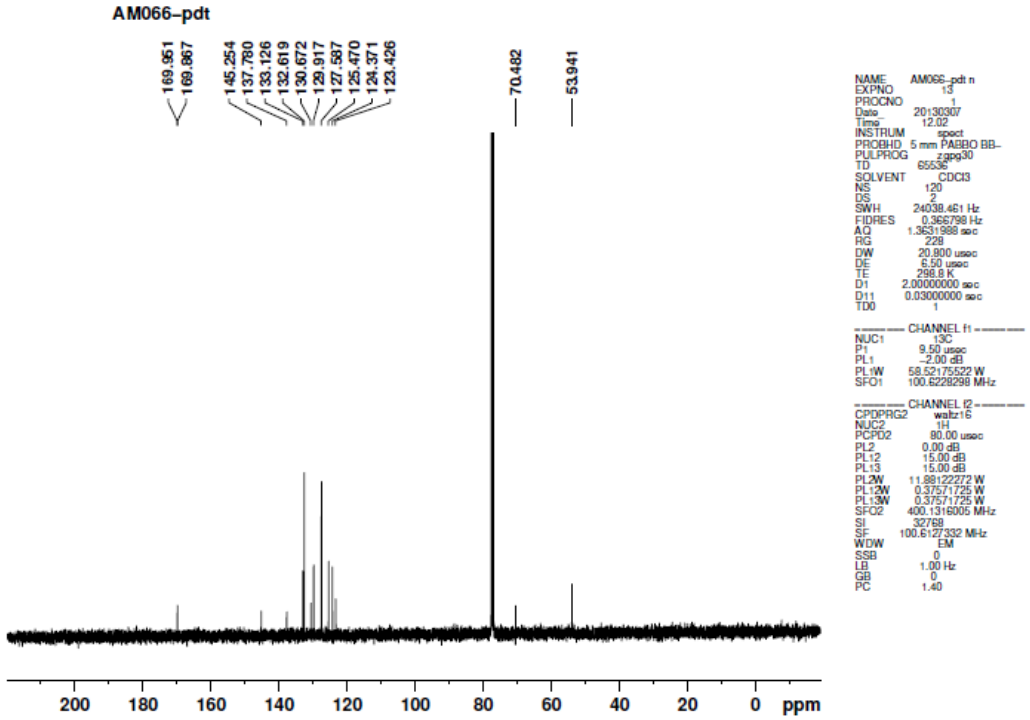

Figure S38. ^{1}H NMR spectrum of **3r**

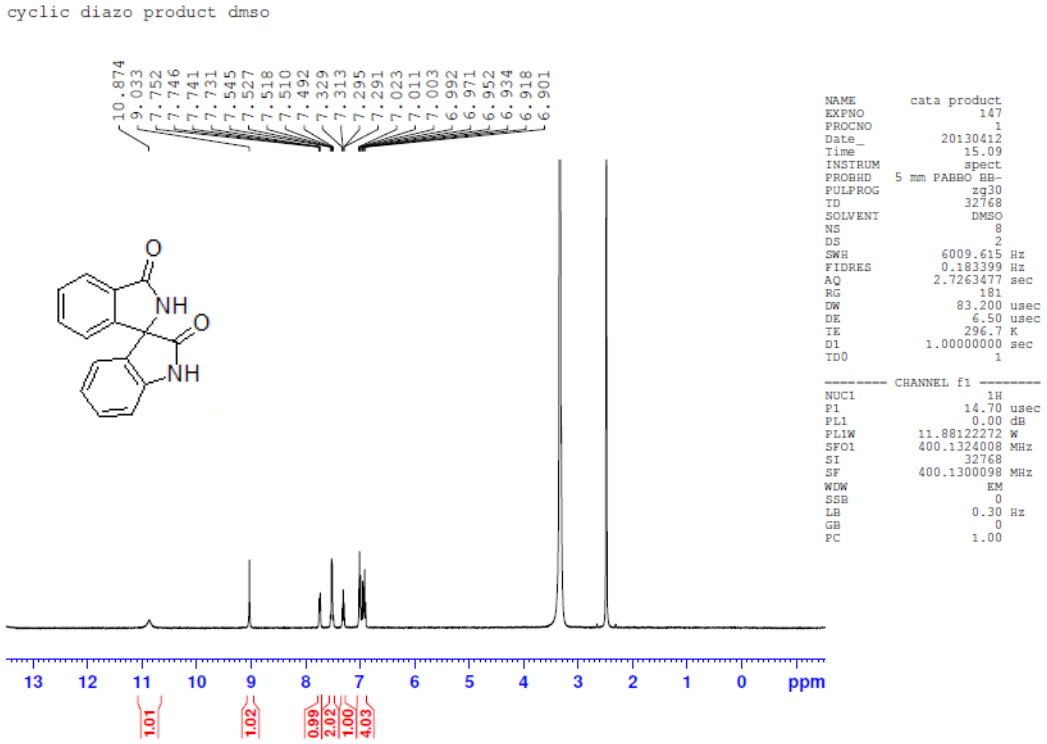

Figure S39. ^{13}C NMR spectrum of **3r**

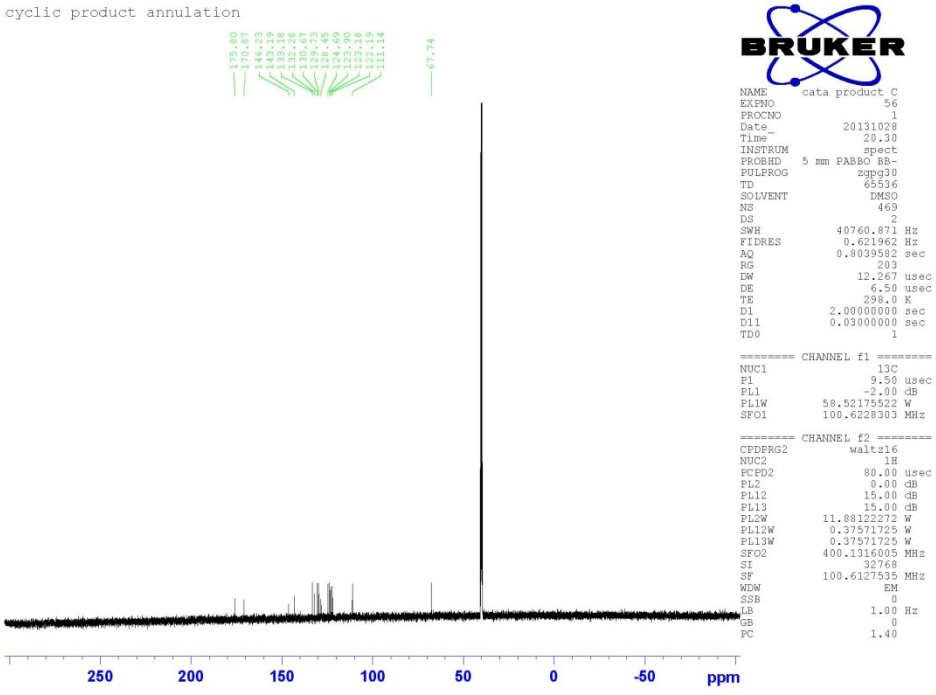

Figure S40. ^{1}H NMR spectrum of **3s**

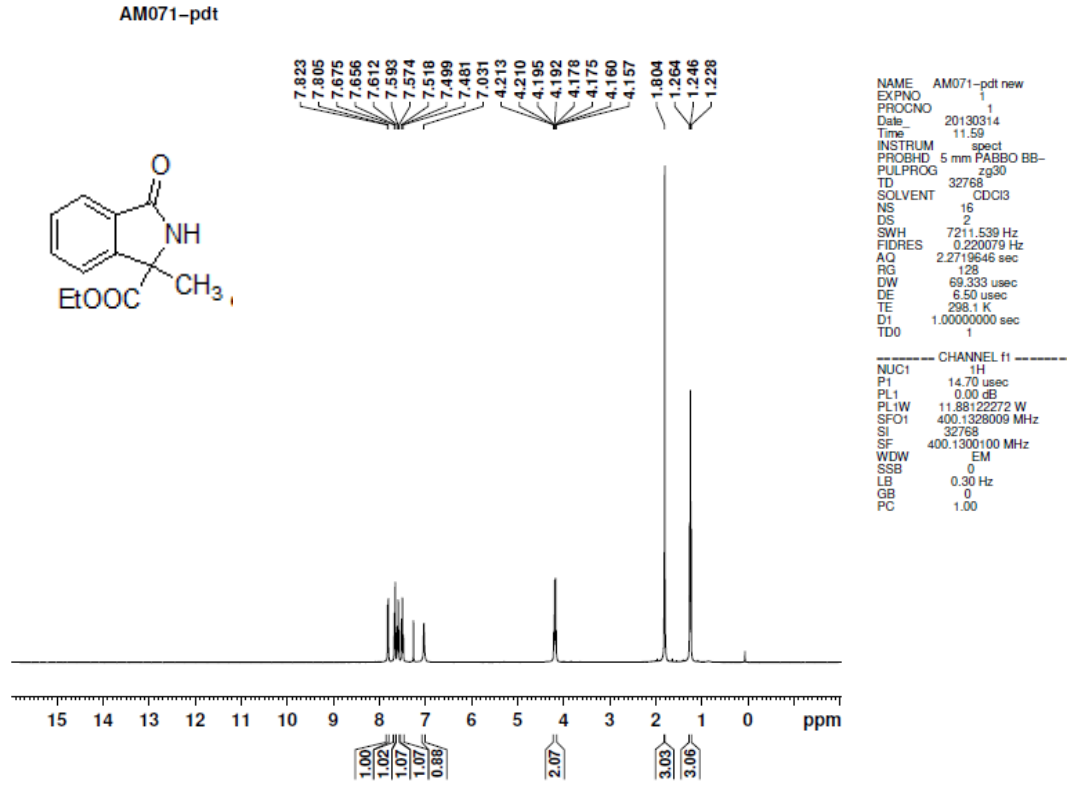

Figure S41. ^{13}C NMR spectrum of **3s**

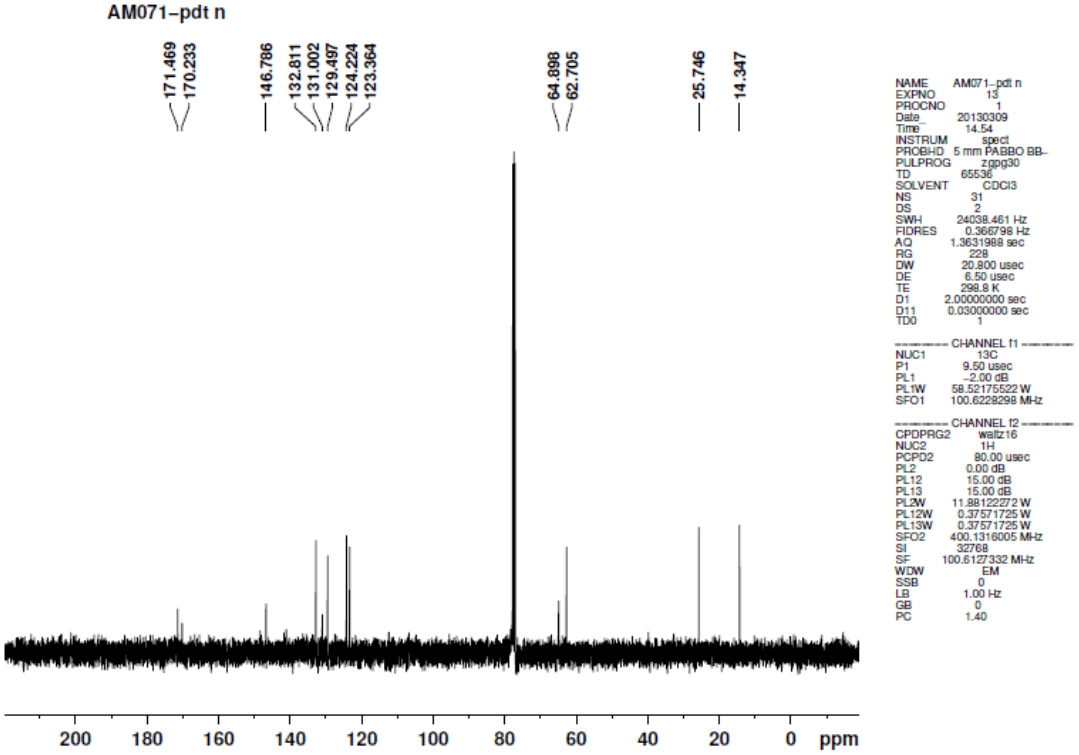

Figure S42. ^{1}H NMR spectrum of **3t**

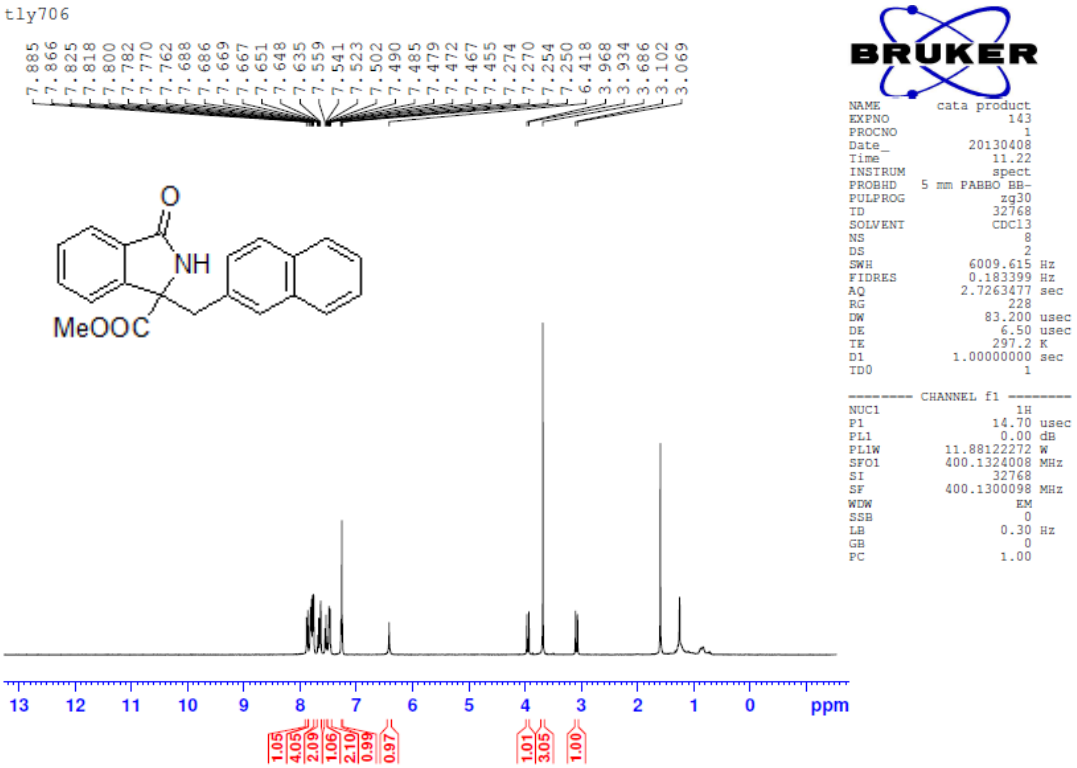

Figure S43. ^{13}C NMR spectrum of **3t**

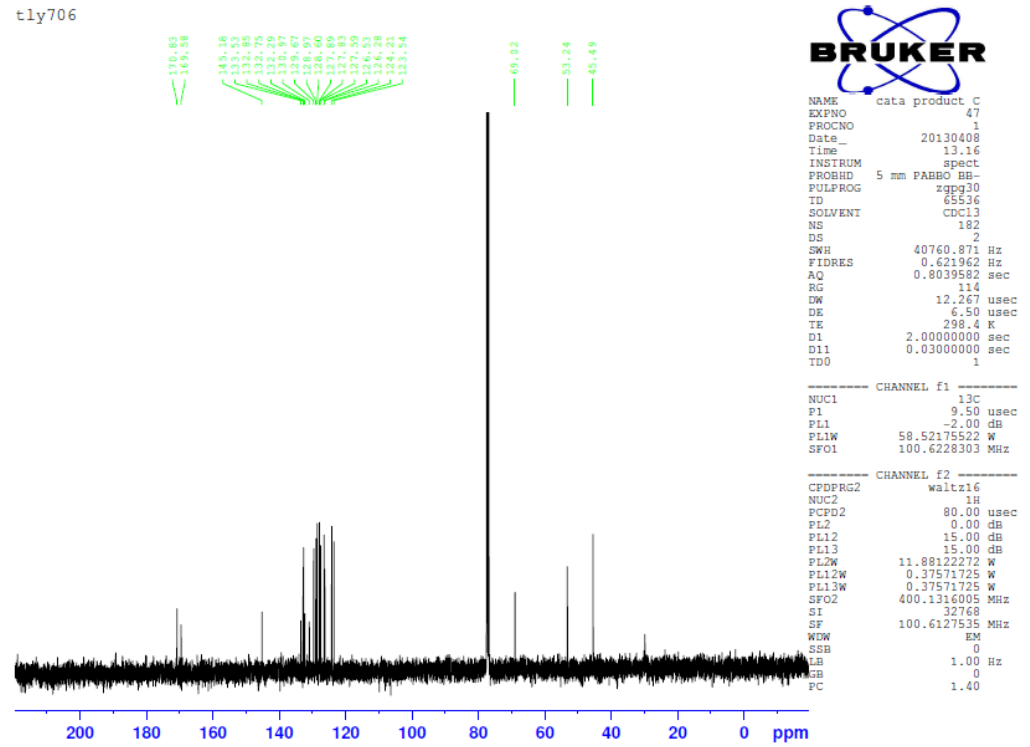

Figure S44. ^{1}H NMR spectrum of **3u**

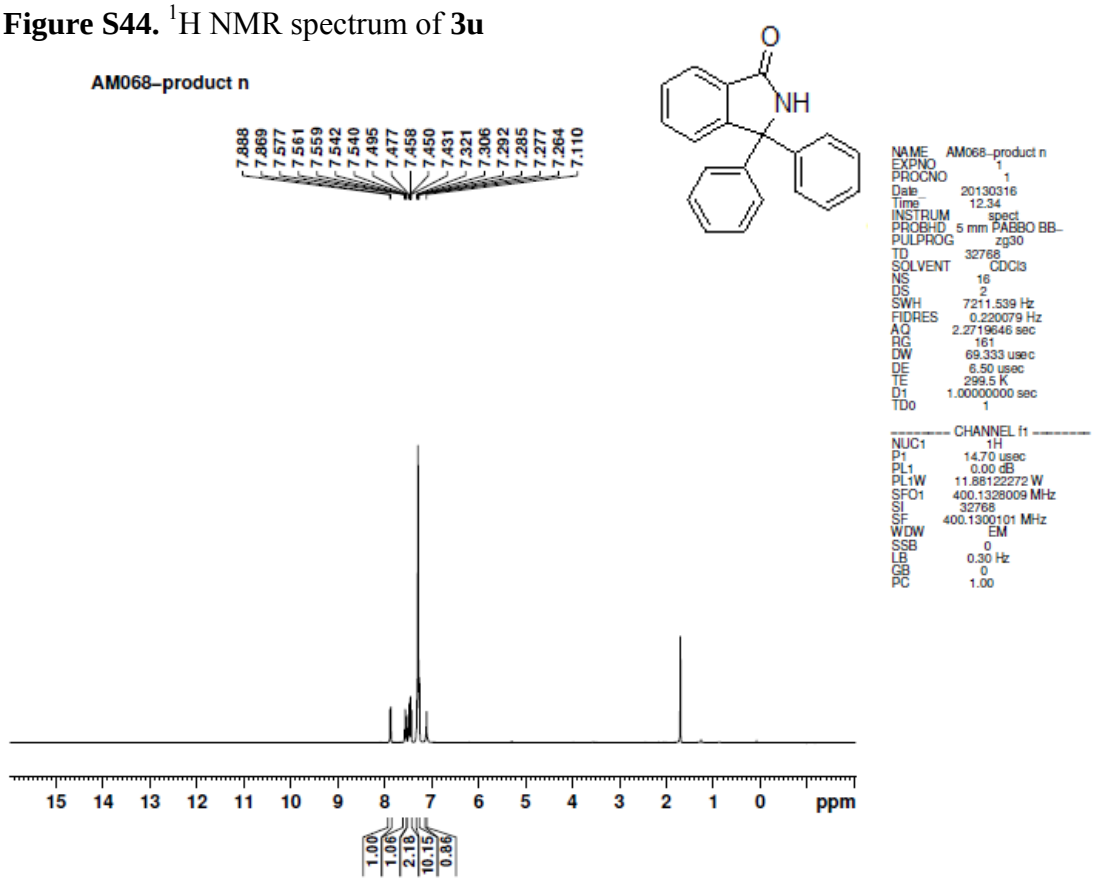

Figure S45. ^{13}C NMR spectrum of **3u**