Supporting Information for:

Ru-catalyzed dehydrogenative synthesis of antimalarial arylidene oxindoles

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1. General Experimental Information:

All experiments with Ru-Catalyst were carried out under an atmosphere of nitrogen. All the diaryl methanols and oxindoles derivatives were purchased from Sigma-Aldrich. Deuterated solvents were used as received. All the solvents used were dry grade and stored over 4Å molecular sieves. Column chromatographic separations performed over 100-200 Silica-gel. Visualization was accomplished with UV light and iodine. Ruthenium complex was prepared according to literature procedure[1]. ^{1}H and ^{13}C NMR spectra were Recorded on 400 and 100 MHz, respectively, using a Bruker 400 MHZ or JEOL 400 MHz spectrometers. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; td, dd doublet of triplet and double doublet; m, multiplet. High resolution mass spectra were obtained with Waters-synapt G2 using electrospray ionization (ESI). Fourier-transform infrared (FTIR) spectra were obtained with a Bruker Alpha-E Fourier transform infrared spectrometer. The quantitative analysis of molecular hydrogen gas was carried out by using gas chromatograph (GC) equipped with a TCD detector (Agilent 7890), column type - carbosieve and mesh range-100, max temp 225 ^{o}C with flow rate for other gases 14 ml/min and for hydrogen 4 ml/min. The temperature gradient of detector and oven were 200 ^{o}C, 60 ^{o}C respectively. The temperature of injector was 150 ^{o}C during experiment.

2. Biological studies (Material and methods)

SYBR Green I Drug Sensitivity Assay: The SYBR Green I assay was used for assessing the potential anti-malarial activity of the bis-arylidene oxindole compounds and assess their IC_{50} against Plasmodium falciparum, the causative pathogen of malaria. P. falciparum culture (infected RBCs in RPMI-1640 medium) at 2% parasitemia and 2% haematocrit was incubated in 96 well plates with different concentrations of the various bis-arylidene compounds. The range of concentrations tested for the 15 compounds was from 25 µM to 781 nM with a twofold serial dilution across the plate. Each concentration was tested for in duplicate for its effect on parasite viability. The parasites were cultured in presence of drug for 48 hours after which the plate was frozen at -80 ºC for one hour and subsequently thawed at room temperature to enable the lysis of parasitized RBCs.

The SYBR Green lysis buffer was added to the wells to lyse the RBCs completely and enable incorporation of the SYBR Green I fluorochrome into the released parasite DNA. Post 45 minute incubation in dark the plate was processed for SYBR Green I fluorescence readout on a Varioscan Plate Reader. The readout for SYBR Green I fluorescence was considered as representative of the viable count of parasite in a particular dosed well. The readout from the RPMI control (non-drugged) wells was considered as 100% (maximum) viability. The readout was them plotted for various dosages of the drug tested for. The IC_{50} value for each drug was calculated as the drug concentration for which the parasite viability was registered at 50% as per the curve structure. The IC_{50} was estimated using the IC_{50} estimator online tool which employs the non-linear regression method for estimation of IC_{50}.

3. Experimental procedure for hydride detection in the reaction mixture:

In a dry NMR tube charged with 2-oxindole (0.1 mmol, 13.3 mg), diphenyl methanol (0.1 mmol, 18.4 mg) Ru-NHC complex **4a** (0.02 mmol, 20 mol %), KO*t*Bu (0.1 mmol, 11.2 mg) in benzene-d_6, The NMR tube was then kept in a preheated oil bath at 80 °C for 10 min. Subsequently, sample was analyzed by ^{1}H NMR spectroscopy, dissociation of *p*-cymene ligand from metal complex was observed confirmed by NMR which shows δ 2.74 (H, *J* = 6.5 Hz, 1H), 2.16 (s, 3H), 1.16 (d, *J* = 7.9 Hz, 6H) for dissociated ligand, moreover, aromatic peak of Ru attached *p*-cymene [δ 5.35 (d, *J* = 6.1 Hz, 2H), 5.06 (d, *J* = 6.1 Hz, 2H)] were missing supports dissociation of ligand after heating. In same reaction mixture some hydride signals were detected in the range from -6 to -9 ppm. This is previously observed by Madsan's and Huynh.[8,9] Same sample was then heated at 110 ^{0}C for 1 hrs followed by NMR analysis. Apart from previous signals one more hydride signal was detected at -20.42 ppm, which support formation Ruthenium-hydrido intermediate in reaction mixture, this has been previously observed by Huynh during dehydrogenative Amidation by Ru-NHC Catalyst.[9]

4. Experimental procedure for intermediate detection in the reaction mixture:

To an oven dried 20 mL resealable pressure tube (equipped with rubber septum), Ru-NHC Complex **4a** (0. 02 mmol), KO*t*Bu (0.1 mmol), diphenylmethanol (0.1 mmol) were added in toluene under N_2 atmosphere. Then, the tube was purged with N_2 and quickly removed the septum and sealed with cap using crimper. The reaction mixture was stirred at 140 ^{o}C. After 16 hrs, crude reaction mixture was directly injected into HRMS instrument.

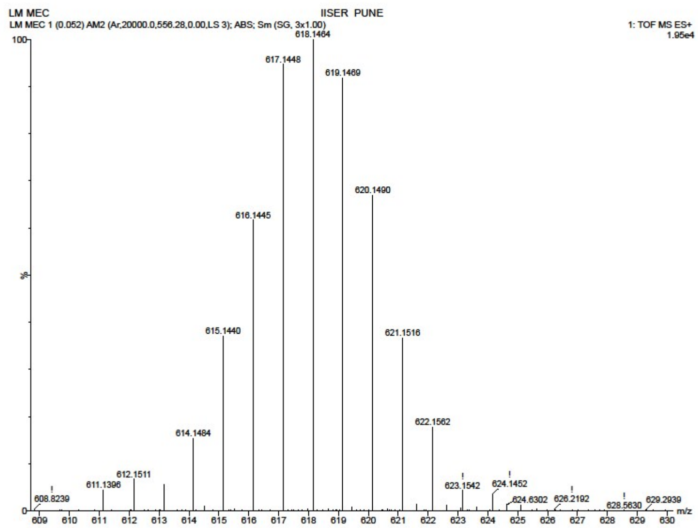


Figure 1: HRMS spectra of crude reaction mixture

5. GC Data for H_2 gas liberation:

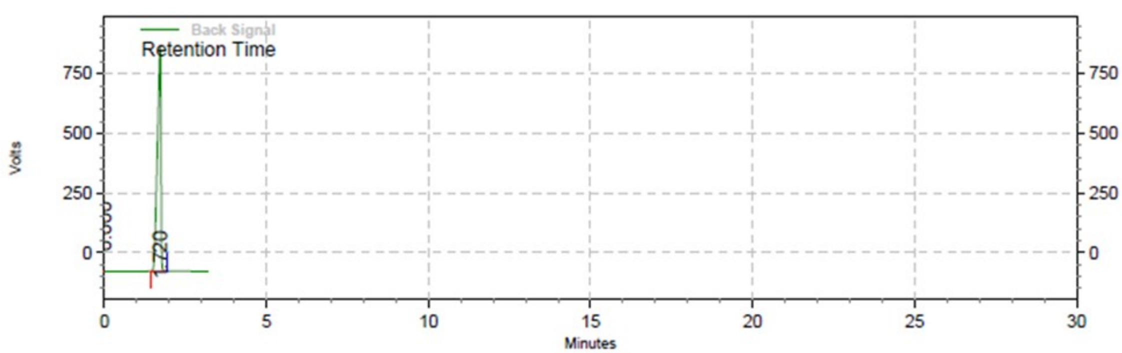


Figure 2: Detection of H_2 liberation using GC in model reaction (olefination of oxindole).

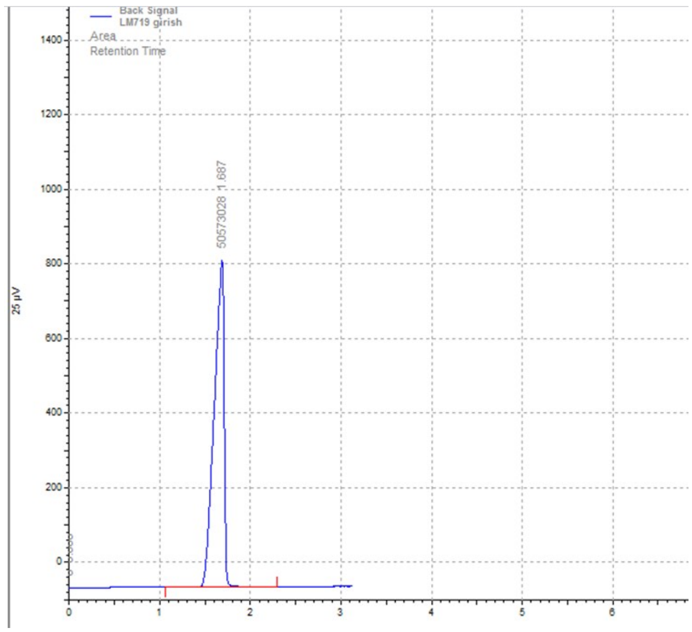
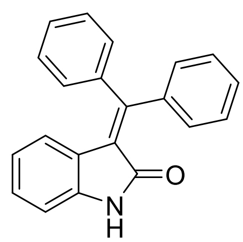


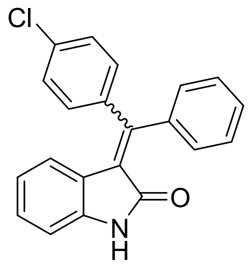
Figure 3: Detection of H_2 liberation using GC for controlled experiment in absence of oxindole.

6. Experimental details and characterization data:

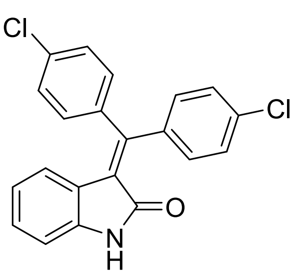


3-(diphenylmethylene)indolin-2-one (3a)[2]. Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), diphenylmethanol (46 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(diphenylmethylene)indolin-2-one **3a** (64 mg, 87 %) as a pale yellow crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.36 - 7.27 (m, 4H), 7.26 -7.19 (m, 6H), 6.94 (td, *J* = 7.6, 1.0 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 2H), 6.26 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.85, 155.02, 141.50, 140.96, 139.94, 130.52, 129.62, 129.15, 128.93, 127.87, 124.85, 124.14, 123.33, 121.27, 109.86;

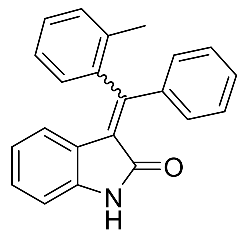
IR (neat) 1615.68, 1699.61, 3392.16 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{15}NO$ $(M+H)^{+}$: 298.1232, found: 298.1228.



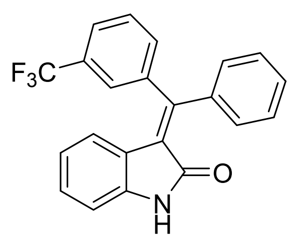
3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one (3b)[3]. Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KOtBu (84 mg, 0.75 mmol), (4-chlorophenyl)(phenyl)methanol (54 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford isomeric mixture of 3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one **3b** (57 mg, 70%) in the ratio of E/Z = (61:39)% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 8.91 (bs, 1H), 7.47–7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.31–7.25 (m, 4H), 7.07 (dt, *J* = 7.9, 4.4 Hz, 1H), 6.72 – 6.59 (m, 2H), 6.41 (dd, *J* = 47.5, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 168.81, 153.30, 141.06, 139.82, 138.27, 135.49, 132.02, 131.18, 129.55, 129.33, 129.13, 128.05, 123.89, 123.36, 121.38, 109.99; IR (neat) = 1616.75, 1696.43, 2854.44, 2924.20, 3060.78, 3216.29 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{14}ClNO$ $(M+H)^{+}$: 332.0842, found: 332.0849.



3-(bis(4-chlorophenyl)methylene)indolin-2-one (3c). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), bis(4-chlorophenyl)methanol (63 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-chlorophenyl)methylene)indolin-2-one **3c** (53 mg, 59%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.43 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 7.26 – 7.23 (m, 3H), 7.12 – 7.07 (m, 1H), 6.68 (td, *J* = 7.8, 0.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.58, 151.65, 141.10, 139.37, 137.92, 135.78, 135.64, 132.07, 131.22, 129.48, 128.27, 125.57, 123.57, 123.30, 121.56, 110.10; IR (neat) = 1452.21, 1650.08, 2831.22, 2941.86, 3321.91 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{13}Cl_2NO$ $(M+H)^+$: 366.0452, found: 366.0452.

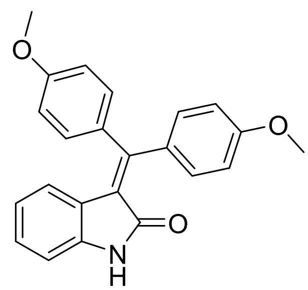


3-(phenyl(o-tolyl)methylene)indolin-2-one (3d)[6]. Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KOtBu (84 mg, 0.75 mmol), phenyl(o-tolyl)methanol (49 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford isomeric mixture of 3-(phenyl(o-tolyl)methylene)indolin-2-one **3d** (45 mg, 45%) in the ratio of E/Z = (60:40)% as a yellow crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 8.73 (s, 1H), 7.34 – 7.31 (m, 1H), 7.22–7.18 (m, 2H), 7.12 – 7.07 (m, 3H), 7.01 (dd, J = 7.8, 1.6 Hz, 2H), 6.90 (td, J = 7.7, 1.1 Hz, 1H), 6.50 – 6.43 (m, 2H), 5.78 (d, J = 7.7 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 168.44, 154.25, 141.13, 140.91, 140.18 138.32, 135.44, 131.17, 130.26, 129.27, 129.16, 128.89, 128.49, 127.75, 126.86, 125.88, 124.36, 123.39, 123.31, 121.77, 109.57, 19.69; IR (neat) = 1465.87, 1613.32, 1696.02, 3221.33 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{17}NO$ $(M+H)^+$: 312.1388, found: 312.1389.

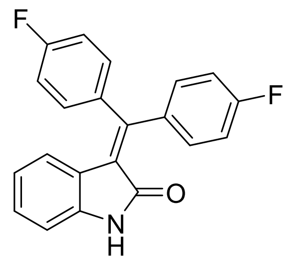


(*E*)-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one (3e). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), phenyl(3-(trifluoromethyl)phenyl)methanol (63 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford isomeric mixture of 3-(phenyl(3-

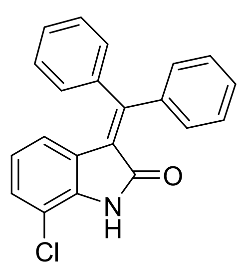
(trifluoromethyl)phenyl)methylene)indolin-2-one **3e** (34 mg, 38%) separated by preparative TLC in the ratio of E/Z = (68:32)% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) for *E* isomer δ 8.15 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.61 (s, 1H), 7.58 – 7.51 (m, 2H), 7.42 – 7.35 (m, 3H), 7.35 – 7.30 (m, 2H), 7.12 (td, *J* = 7.7, 1.1 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.66 (td, *J* = 7.7, 1.1 Hz, 1H), 6.28 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for E isomer δ 168.16, 152.52, 142.01, 140.90, 139.02, 132.91, 130.29, 129.58, 129.54, 129.35, 128.57, 128.44, 128.02, 127.05, 126.29 (q, J = 3.7 Hz), 125.90 (q, J = 3.7 Hz), 125.51, 125.23, 125.07, 123.40, 123.09, 121.47, 109.84; IR (neat) = 2831.13, 2941.51 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{14}F_3NO$ $(M+H)^+$: 366.1105, found: 366.1104.



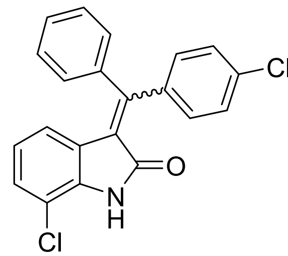
3-(bis(4-methoxyphenyl)methylene)indolin-2-one (3f)[6]. Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), Cs_2CO_3 (162 mg, 0.5 mmol), bis(4-methoxyphenyl)methanol (61 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-methoxyphenyl)methylene)indolin-2-one **3f** (34 mg, 38%) as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.34 – 7.30 (m, 2H), 7.28 (d, J = 2.5 Hz, 2H), 7.09 (td, J = 7.6, 1.1 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.91 – 6.86 (m, 2H), 6.78 (d, J = 7.7 Hz, 1H), 6.69 (td, J = 7.7, 1.0 Hz, 1H), 6.54 (d, J = 7.7 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.80, 161.20, 160.96, 155.69, 139.97, 133.89, 133.25, 132.26, 132.16, 128.05, 125.20, 122.88, 121.26, 114.26, 113.25, 109.77, 109.39, 55.52, 55.40; IR (neat) = 1606.73, 1695.63, 2831.22, 2942.25 cm^{-1}; HRMS (ESI) m/z calculated for $C_{23}H_{19}NO_3$ $(M+H)^+$: 358.1443, found: 358.1446.



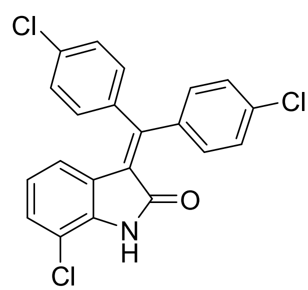
3-(bis(4-fluorophenyl)methylene)indolin-2-one (3g). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), Cs_2CO_3 (162 mg, 0.5 mmol), bis(4-fluorophenyl)methanol (55 mg, 0.25 mmol), 2-oxindole (66 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-fluorophenyl)methylene)indolin-2-one **3g** (26 mg, 31%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.35 – 7.28 (m, 4H), 7.17 – 7.13 (m, 2H), 7.11 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.69 (td, *J* = 7.7, 1.0 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.36, 163.95 (d, *J* = 24.9 Hz), 152.60, 140.64, 137.16, 135.49, 132.85 (d, *J* = 8.5 Hz), 131.91 (d, *J* = 8.2 Hz), 129.14, 124.84, 124.00, 123.26, 121.56, 116.59, 116.48, 116.35 (d, *J* = 21.7 Hz), 115.23, 115.01, 109.78; IR (neat) = 1601.09, 1699.01, 2856.08, 2926.09, 3076.40, 3241.11 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{13}F_2NO$ $(M+H)^+$: 334.1043, found: 334.1045.



7-chloro-3-(diphenylmethylene)indolin-2-one (3h). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), diphenylmethanol (46 mg, 0.25 mmol), 7-chloro-2-oxindole (83 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 7-chloro-3-(diphenylmethylene)indolin-2-one **3h** (51 mg, 62%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.50-7.42 (m, 4H), 7.38-7.36 (m, 4H), 7.34-7.29 (m, 2H), 7.09 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.60 (t, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.85, 157.14, 141.01, 139.33, 138.37, 130.54, 129.66, 129.53, 129.09, 128.60, 128.31, 127.93, 126.65, 124.44, 122.05, 121.59, 115.04; IR (neat) = 1584.58, 1696.63, 3061.19 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{14}ClNO$ $(M+H)^+$: 332.0842, found: 332.0847.

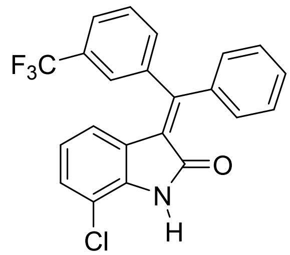


7-chloro-3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one (3i). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KOtBu (84 mg, 0.75 mmol), (4-chlorophenyl)(phenyl)methanol (54 mg, 0.25 mmol), 7-chloro-2-oxindole (83 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 7-chloro-3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one **3i** (41 mg, 46%) in the ratio of E/Z = (63:37%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.47 – 7.44 (m, 2H), 7.41 (dd, *J* = 4.1, 1.9 Hz, 2H), 7.37 (dd, *J* = 5.6, 4.0 Hz, 3H), 7.29 (t, *J* = 2.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.67 (t, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.44, 155.46, 139.36, 139.04, 135.91, 131.19, 130.58, 129.91, 129.67, 129.53, 129.45, 129.11, 128.63, 128.26, 128.07, 125.27, 122.21, 121.52, 115.18; IR (neat) = 1584.27, 1697.63, 3062.56 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{13}Cl_2NO$ $(M+H)^+$: 366.0452, found: 366.0457.

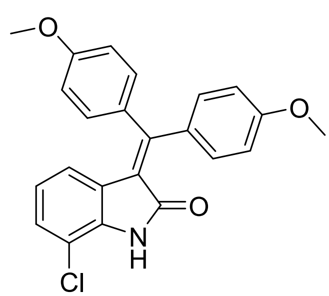


3-(bis(4-chlorophenyl)methylene)-7-chloroindolin-2-one (3j). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), bis(4-chlorophenyl)methanol (63 mg, 0.25 mmol), 7-chloro-2-oxindole (83 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-chlorophenyl)methylene)-7-chloroindolin-2-one **3j** (41 mg, 41%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.48-7.44 (m, 2H), 7.38-7.34 (m, 3H), 7.28 (dt, *J* = 6.3, 2.3 Hz, 3H), 7.15 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.41 (d, *J* =

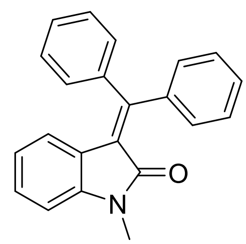
7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.31, 153.81, 138.89, 138.36, 137.30, 136.20, 132.07, 131.24, 129.59, 128.89, 128.39, 125.04, 122.36, 121.60, 115.25; IR (neat) = 1589.23, 1702.32, 2857.08, 2925.40, 3067.32, 3135.41 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{12}Cl_3NO$ $(M+H)^+$: 400.0062, found: 400.0058.



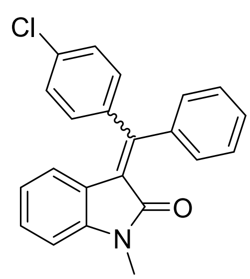
(*E*)-7-chloro-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one (3k). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), phenyl(3-(trifluoromethyl)phenyl)methanol (63 mg, 0.25 mmol), 7-chloro-2-oxindole (83 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 7-chloro-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one **3k** (44 mg, 45%) separated by preparative TLC in the ratio of E/Z = (80:20)% as a yellow solid. ^{1}H NMR for *E* isomer (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.59 (dd, J = 8.8, 6.1 Hz, 3H), 7.52 (d, J = 7.8 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.38 (t, J = 4.3 Hz, 1H), 7.35-7.34 (m, 2H), 7.12 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 8.0 Hz, 1H), 6.18 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) For *E* isomer δ 167.17, 154.63, 141.71, 138.61, 138.52, 133.04, 130.47, 130.04, 129.79, 129.43, 129.37, 128.92, 128.20, 126.43 (q, J = 4 Hz), 126.32 (q, J = 4 Hz), 122.29, 121.42, 115.28; IR (neat) = 1604.99, 1701.11, 3066.73, 3142.88 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{13}ClF_3NO$ $(M+H)^+$: 400.0716, found: 400.0715.



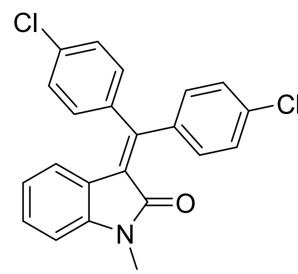
3-(bis(4-methoxyphenyl)methylene)-7-chloroindolin-2-one (3l). Ru-NHC complex **4a** (3.78 mg, 0.00625 mmol), KO*t*Bu (84 mg, 0.75 mmol), bis(4-methoxyphenyl)methanol (61 mg, 0.25 mmol), 7-chloro-2-oxindole (83 mg, 0.5 mmol) and toluene (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-methoxyphenyl)methylene)-7-chloroindolin-2-one **3l** (50 mg, 25%) as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.33 – 7.30 (m, 2H), 7.22 – 7.18 (m, 1H), 7.12 (d, J = 7.4 Hz, 1H), 7.06 (d, J = 8.3 Hz, 1H), 6.95 (t, J = 2.5 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.62 (t, J = 7.9 Hz, 1H), 6.42 (d, J = 7.8 Hz, 1H), 3.89 (s, 2H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 176.06, 133.48, 132.33, 128.02, 126.61, 123.31, 123.02, 121.00, 114.29, 113.29, 55.44, 37.09, 29.84; IR (neat) = 1563.01, 1611.25, 1698.99, 2924.97, 3435.82 cm^{-1}; HRMS (ESI) m/z calculated for $C_{23}H_{18}ClNO_3$ $(M+H)^+$: 391.0975, found: 391.0979.



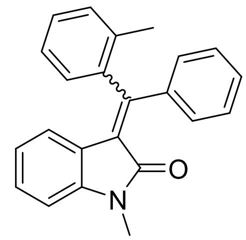
3-(diphenylmethylene)-1-methylindolin-2-one (6a)[4]. Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), diphenylmethanol (46 mg, 0.25 mmol), 1-methylindolin-2-one (73 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford 3-(diphenylmethylene)-1-methylindolin-2-one **6a** (36 mg, 46%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 3H), 7.39 – 7.35 (m, 3H), 7.35 – 7.31 (m, 4H), 7.21 – 7.13 (m, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.69 (td, *J* = 7.8, 1.0 Hz, 1H), 6.43 (d, *J* = 7.7 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.95, 154.72, 143.42, 141.41, 140.07, 130.12, 129.80, 128.63, 127.94, 124.33, 123.27, 121.51, 107.82, 25.98; IR (neat) = 1599.38, 1683.89, 3063.51, 3397.59 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{17}NO$ $(M+H)^+$: 312.1388, found: 312.1389.



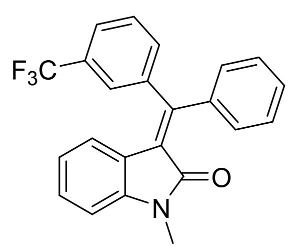
3-((4-chlorophenyl)(phenyl)methylene)-1-methylindolin-2-one (6b)[5]. Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), (4-chlorophenyl)(phenyl)methanol (54 mg, 0.25 mmol), 1-methylindolin-2-one (73 mg, 0.5 mmol) and 1,4-ioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford isomeric mixture of 3-((4-chlorophenyl)(phenyl)methylene)-1-methylindolin-2-one **6b** (36 mg, 41%) in the ratio of E/Z = (75:25)% as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 7.46 – 7.43 (m, 3H), 7.35 (d, *J* = 4.5 Hz, 7H), 6.72 – 6.65 (m, 1H), 5.82 (d, *J* = 3.4 Hz, 2H), 3.21 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) for major isomer δ 166.88, 153.04, 143.59, 142.37, 133.41, 131.66, 130.19, 129.44, 128.97, 128.73, 128.23, 128.01, 127.71, 126.66, 123.34, 121.64, 107.92, 26.01; IR (neat) = 1091.11, 1605.77, 1687.38, 3061.77 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{16}ClNO$ $(M+H)^+$: 346.0998, found: 346.1001.



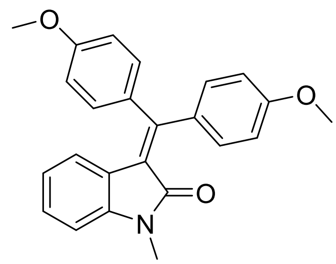
3-(bis(4-chlorophenyl)methylene)-1-methylindolin-2-one (6c)[5]. Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), bis(4-chlorophenyl)methanol (63 mg, 0.25 mmol), 1-methylindolin-2-one (73 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford 3-(bis(4-chlorophenyl)methylene)-1-methylindolin-2-one **6c** (43 mg, 46%) as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.38 – 7.35 (m, 3H), 7.33 (d, *J* = 4.3 Hz, 4H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.77 (td, *J* = 7.7, 1.0 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 151.37, 143.56, 142.01, 139.31, 138.01, 135.74, 135.60, 133.70, 131.72, 131.17, 129.49, 129.44, 128.88, 128.34, 127.99, 126.65, 125.07, 123.23, 122.84, 121.75, 108.10, 26.04; IR (neat) = 1600.82, 1692.24, 3058.71, 3407.79 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{15}Cl_2NO$ $(M+H)^+$: 380.0609, found: 380.0609.



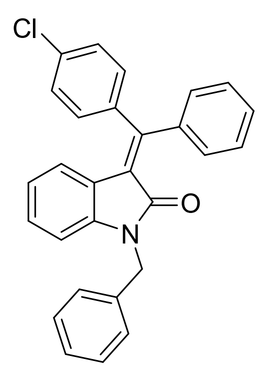
1-methyl-3-(phenyl(o-tolyl)methylene)indolin-2-one (6d)[3]. Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), phenyl(o-tolyl)methanol (49 mg, 0.25 mmol), 1-methylindolin-2-one (73 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford isomeric mixture of 1-methyl-3-(phenyl(o-tolyl)methylene)indolin-2-one **6d** (35 mg, 43%) in the ratio of E/Z = (69:31)% as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 7.48 – 7.47 (m, 1H), 7.39 – 7.35 (m, 4H), 7.31 (s, 2H), 7.19 – 7.14 (m, 2H), 6.83 – 6.75 (m, 3H), 6.01 (d, *J* = 7.7, 0.6 Hz, 1H), 3.24 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 166.65, 153.83, 140.85, 138.44, 131.13, 129.95, 129.14, 128.85, 128.40, 127.73, 126.83, 125.92, 123.09, 121.90, 107.67, 53.56, 25.94; IR (neat) = 1702.28, 1607.04, 2927.85, 3058.71 cm^{-1}; HRMS (ESI) m/z calculated for $C_{23}H_{19}NO$ $(M+H)^+$: 326.1545, found: 326.1549.



(*E*)-1-methyl-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one (6e). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), phenyl(3-(trifluoromethyl)phenyl)methanol (63 mg, 0.25 mmol), 1-methyl-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford isomeric mixture of 1-methyl-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one **6e** (30 mg, 31%) separated by preparative TLC in the ratio of E/Z = (79:21)% as a blood red semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) for *E* isomer δ 7.63-7.56 (m, 2H), 7.53 (s, 1H), 7.51 – 7.42 (m, 4H), 7.34 – 7.29 (m, 2H), 7.19 (dd, *J* = 11.2, 4.2 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* = 7.7 Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for *E* isomer δ 166.69, 152.14, 143.70, 140.27, 140.63, 133.49, 129.62, 129.43, 129.35, 129.29, 128.31, 126.76 (q, J = 4 Hz), 125.70 (q, J = 4 Hz), 125.42, 123.50, 122.88, 121.70, 107.98, 26.05; IR (neat) = 1609.08, 1704.64, 2931.52, 3489.66 cm^{-1}; HRMS (ESI) m/z calculated for $C_{23}H_{16}F_3NO$ $(M+H)^+$: 380.1262, found: 380.1263.

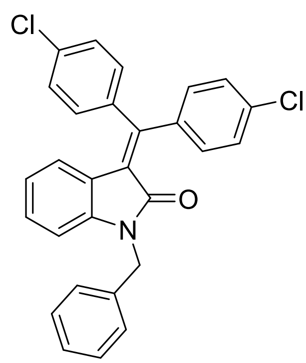


3-(bis(4-methoxyphenyl)methylene)-1-methylindolin-2-one (6f)[2]. Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), bis(4-methoxyphenyl)methanol (61 mg, 0.25 mmol), 1-methylindolin-2-one (73 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford 3-(bis(4-methoxyphenyl)methylene)-1-methylindolin-2-one **6f** (30 mg, 32%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 3H), 7.16 (dd, J = 7.7, 1.1 Hz, 1H), 6.92 – 6.86 (m, 4H), 6.80 (d, J = 7.7 Hz, 1H), 6.73 – 6.69 (m, 2H), 6.60 (d, J = 7.7 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.26, 167.26, 160.81, 158.24, 155.09, 142.79, 132.92, 132.08, 129.53, 128.02, 125.11, 124.23, 122.63, 121.27, 114.17, 113.17, 107.66, 55.36, 25.99; IR (neat) = 1605.11, 1696.61, 2850.40, 2925.61, 3056.93 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H2_1NO_3$ $(M+H)^+$: 372.1599, found: 372.1598.

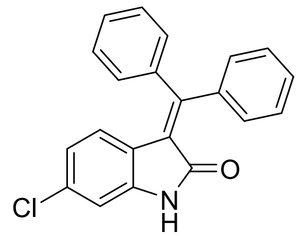


(*E*)-1-benzyl-3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one (6g)[2]. Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), (4-chlorophenyl)(phenyl)methanol (54 mg, 0.25 mmol), 1-benzylindolin-2-one (111 mg, 0.5

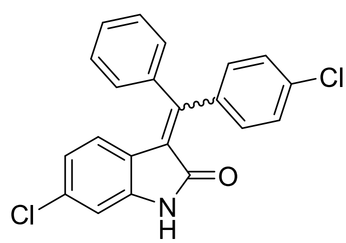
mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford (*E*)-1-benzyl-3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one **6g** (36 mg, 35 %) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.6, 3.5 Hz, 3H), 7.43 – 7.39 (m, 3H), 7.35 (dd, *J* = 13.1, 7.4 Hz, 7H), 7.10 (dd, *J* = 14.3, 7.6 Hz, 2H), 6.71 (dt, *J* = 15.4, 6.6 Hz, 2H), 6.52 (dd, *J* = 44.5, 7.9 Hz, 1H), 4.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 153.38, 142.56, 140.98, 139.76, 136.29, 135.42, 131.79, 131.10, 130.34, 129.17, 128.76, 128.76, 128.20, 127.77, 123.28, 121.62, 43.58; IR (neat) = 1608.26, 1703.91, 2853.41, 2920.46, 3057.09 cm^{-1}; HRMS (ESI) m/z calculated for $C_{28}H_{20}ClNO$ $(M+H)^+$: 422.1311, found: 422.1318.



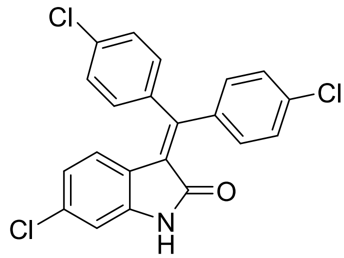
1-benzyl-3-(bis(4-chlorophenyl)methylene)indolin-2-one (6h). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), K_3PO_4 (159 mg, 0.75 mmol), bis(4-chlorophenyl)methanol (63 mg, 0.25 mmol), 1-benzylindolin-2-one (111 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method B to afford 1-benzyl-3-(bis(4-chlorophenyl)methylene)indolin-2-one **6h** (40 mg, 35%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.37 – 7.34 (m, 2H), 7.33 – 7.30 (m, 4H), 7.30 (t, *J* = 2.0 Hz, 3H), 7.27 (d, *J* = 2.2 Hz, 2H), 7.09 (td, *J* = 7.7, 1.0 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.52 (dd, *J* = 8.0, 0.9 Hz, 1H), 4.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.69, 151.79, 142.72, 139.37, 137.95, 136.23, 135.80, 135.73, 131.89, 131.19, 129.52, 129.36, 128.85, 128.39, 127.68, 127.59, 124.84, 123.28, 122.97, 121.79, 109.06, 43.69; IR (neat) = 1453.28, 1649.97, 2942.96, 3328.01 cm^{-1}; HRMS (ESI) m/z calculated for $C_{28}H_{19}Cl_2NO$ $(M+H)^+$: 456.0922, found: 456.0923.



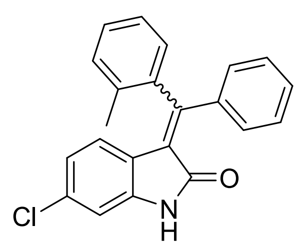
6-chloro-3-(diphenylmethylene)indolin-2-one (6i). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), KO*t*Bu (84 mg, 0.75 mmol), diphenylmethanol (46 mg, 0.25 mmol), 6-chloro-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 6-chloro-3-(diphenylmethylene)indolin-2-one **6i** (49 mg, 60%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.47 – 7.44 (m, 3H), 7.37 (t, *J* = 4.4 Hz, 4H), 7.30 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.66 (dd, *J* = 8.0, 6.0 Hz, 2H), 6.26 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.82, 155.79, 141.84, 141.45, 141.21, 139.60, 134.31, 130.55, 129.63, 129.53, 129.12, 128.86, 127.95, 124.14, 122.66, 121.37, 110.25; IR (neat) = 1510.28, 1694.70, 1707.95, 2925.21 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{14}ClNO$ $(M+H)^+$: 332.0842, found: 332.0849.



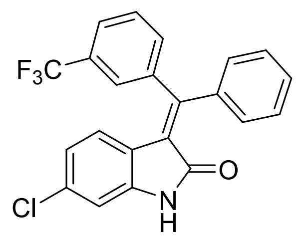
(6-chloro-3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one (6j). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), KOtBu (84 mg, 0.75 mmol), (4-chlorophenyl)(phenyl)methanol (54 mg, 0.25 mmol), 6-chloro-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford isomeric mixture of 6-chloro-3-((4-chlorophenyl)(phenyl)methylene)indolin-2-one **6j** (52 mg, 57%) in the ratio of E/Z = 64:36% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 8.55 (s, 1H), 7.45 (dd, *J* = 4.5, 2.1 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.35-7.33 (m, 2H) 7.31 (t, *J* = 1.9 Hz, 2H), 7.25 (d, *J* = 1.1 Hz, 1H), 6.72 – 6.63 (m, 2H), 6.25 (dd, *J* = 8.3, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 167.78, 155.45, 140.57, 139.34, 138.47, 137.65, 135.89, 132.01, 131.19, 130.59, 129.89, 129.57, 129.44, 129.22, 128.64 128.23, 128.05, 125.36, 125.23, 124.76, 122.19, 121.49, 115.23; IR (neat) = 1657.87, 1703.40, 2853.47, 2922.39, 3066.31, 3221.70 cm^{-1}; HRMS (ESI) m/z calculated for $C_{21}H_{13}Cl_2NO$ $(M+H)^+$: 366.0452, found: 366.0449.



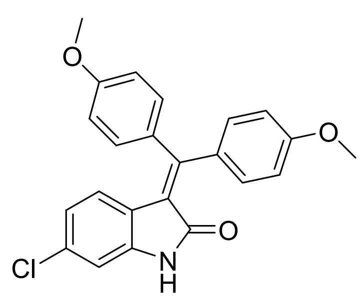
3-(bis(4-chlorophenyl)methylene)-6-chloroindolin-2-one (6k). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), KOtBu (84 mg, 0.75 mmol), bis(4-chlorophenyl)methanol (63 mg, 0.25 mmol), 6-chloro-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-chlorophenyl)methylene)-6-chloroindolin-2-one **6k** (43 mg, 43%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.44 (d, J = 2.3 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.32 – 7.29 (m, 3H), 7.25 (t, J = 2.0 Hz, 1H), 6.67 – 6.62 (m, 2H), 6.24 (dd, J = 8.3, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 168.79, 156.01, 154.28, 141.66, 141.16, 139.57, 139.26, 135.86, 134.31, 132.05, 130.55, 129.87, 129.66, 129.54, 129.13, 128.27, 127.98, 124.25, 121.57, 110.41; IR (neat) = 1611.66, 1705.61, 2855.80, 2925.15, 3243.24 cm-1; HRMS (ESI) m/z calculated for $C_{21}H_{12}Cl_3NO$ $(M+H)^+$: 400.0062, found: 400.0061.



6-chloro-3-(phenyl(o-tolyl)methylene)indolin-2-one (6l). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), KOtBu (84 mg, 0.75 mmol), phenyl(o-tolyl)methanol (49 mg, 0.25 mmol), 6-chloro-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford isomeric mixture of 6-chloro-3-(phenyl(o-tolyl)methylene)indolin-2-one **6l** (44 mg, 51%) in the ratio of E/Z = 54:46% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 8.24 (bs, 1H), 7.43 (dd, J = 10.1, 5.6Hz, 4H), 7.29 (dd, J = 6.8, 4.5 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.70 (dd, J = 15.3, 7.3 Hz, 2H), 6.63 (s, 1H), 5.81 (d, J = 8.4 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 168.19, 155.04, 141.92, 140.63, 137.98, 135.38, 134.44, 131.28, 130.25, 129.63, 129.14, 128.53, 127.84, 125.95, 124.17, 121.88, 121.46, 109.93, 19.66; IR (neat) = 1608.83, 1703.94, 2856.77, 2926.52, 3067.37, 3231.30 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{16}ClNO$ $(M+H)^+$: 346.0998, found: 346.0994.

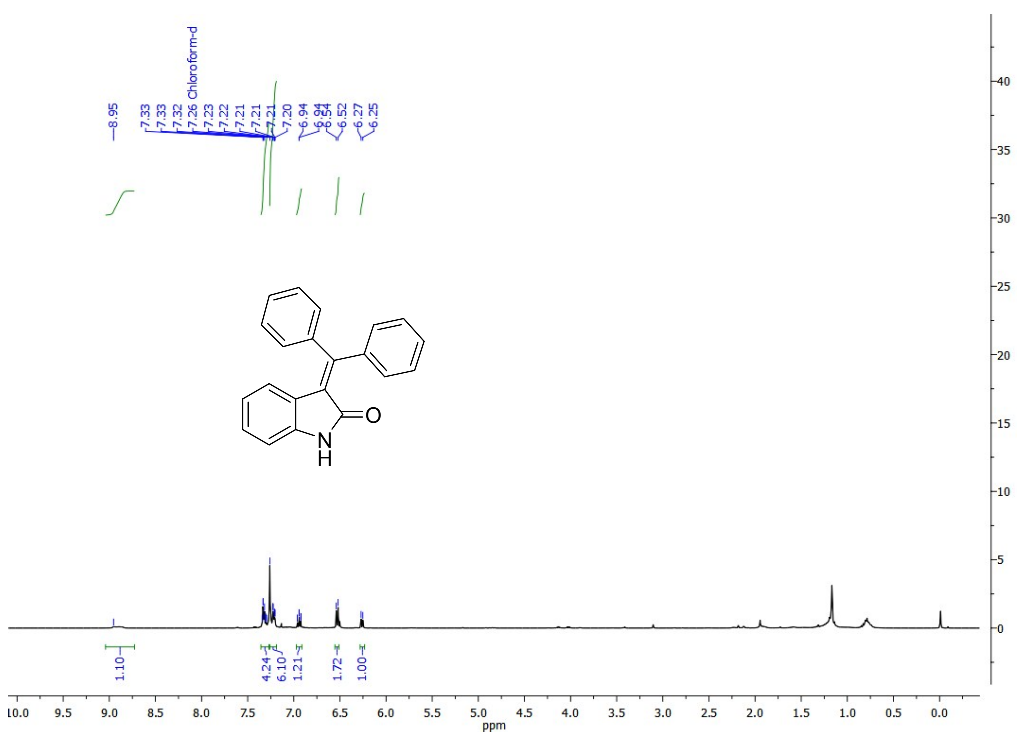


(*E*)-6-chloro-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one (6m). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), KO*t*Bu (84 mg, 0.75 mmol), phenyl(3-(trifluoromethyl)phenyl)methanol (63 mg, 0.25 mmol), 6-chloro-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford isomeric mixture of 6-chloro-3-(phenyl(3-(trifluoromethyl)phenyl)methylene)indolin-2-one **6m** (40 mg, 40%) separated by preparative TLC in the ratio of E/Z = (58:42)% as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) for *E* isomer δ 7.95 (s, 1H), 7.76 – 7.71 (m, 1H), 7.61 – 7.56 (m, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 6.79 (d, J = 1.9 Hz, 1H), 6.64 (dd, J = 8.4, 1.9 Hz, 1H), 6.18 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for *E* isomer δ 168.48, 153.35, 141.88, 140.38, 140.10, 135.00, 133.63, 130.51, 129.97, 129.41, 128.48, 128.22, 127.36 (q, J = 4 Hz), 126.12 (q, J = 4 Hz), 124.80, 124.50, 124.97, 122.16, 121.81, 110.31; IR (neat) = 1692.83, 2831.20, 2942.43 cm^{-1}; HRMS (ESI) m/z calculated for $C_{22}H_{14}ClF_3NO$ $(M+H)^+$: 400.0761, found: 400.0716.

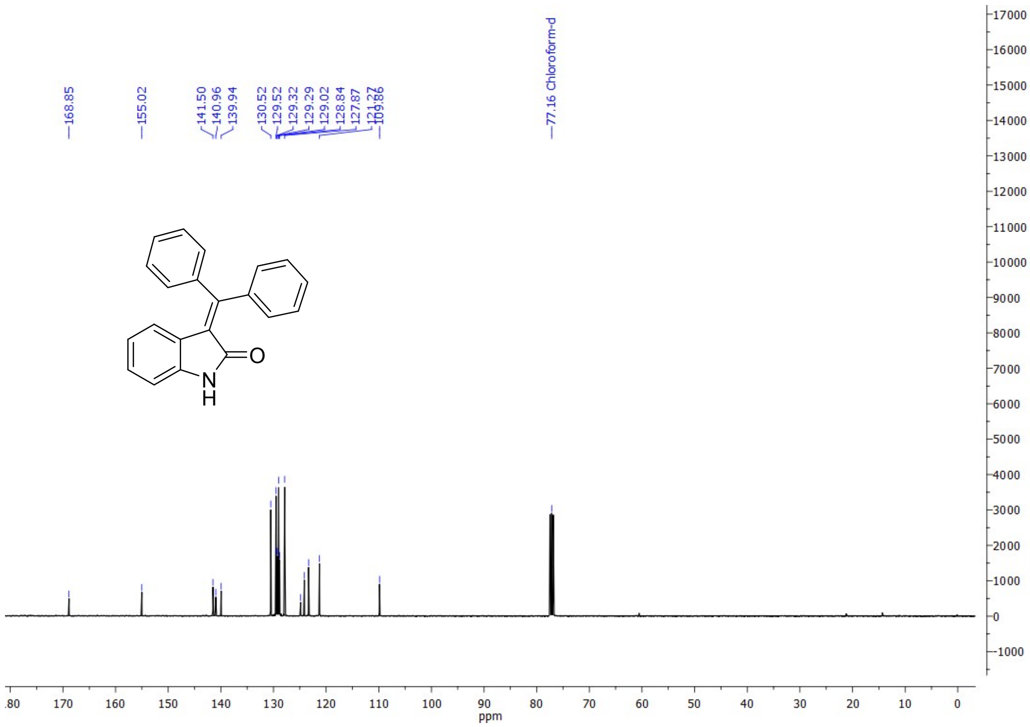


3-(bis(4-methoxyphenyl)methylene)-6-chloroindolin-2-one (6n). Ru-NHC complex **4a** (6.05 mg, 0.01 mmol), KO*t*Bu (84 mg, 0.75 mmol), bis(4-methoxyphenyl)methanol (63 mg, 0.25 mmol), 6-chloro-2-oxindole (83 mg, 0.5 mmol) and 1,4-dioxane (2 ml) were allowed to react in 20 mL resealable pressure tube according to method A to afford 3-(bis(4-methoxyphenyl)methylene)-6-chloroindolin-2-one **6n** (50 mg, 60%) as a yellow semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.90 – 6.85 (m, 2H), 6.71 (dd, J = 3.1, 1.6 Hz, 1H), 6.62 (dd, J = 8.4, 2.0 Hz, 1H), 6.40 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.11, 161.42, 161.10, 156.39, 141.04, 133.43, 133.30, 132.27, 123.66, 123.48, 121.15, 114.27, 113.25, 110.00, 55.51, 55.41; IR (neat) = 1507.61, 1612.10, 1705.99, 3212.99 cm-1; HRMS (ESI) m/z calculated for $C_{23}H_{18}ClNO_3$ $(M+H)^+$: 392.1052, found: 392.1050.

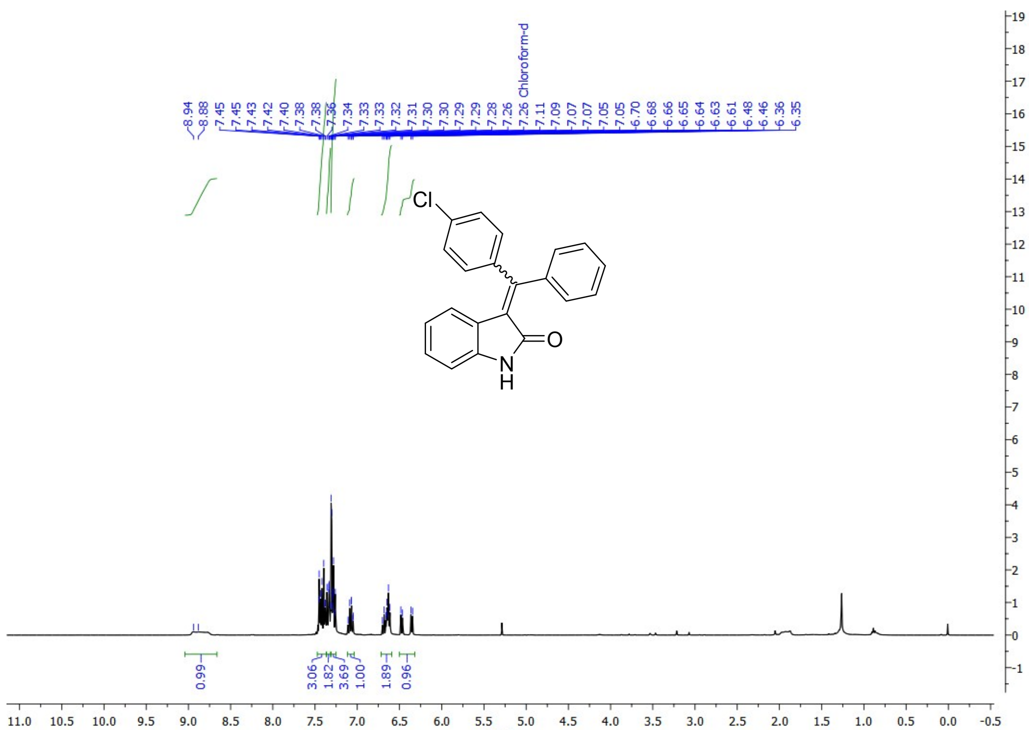
7. Copies of NMR spectra:



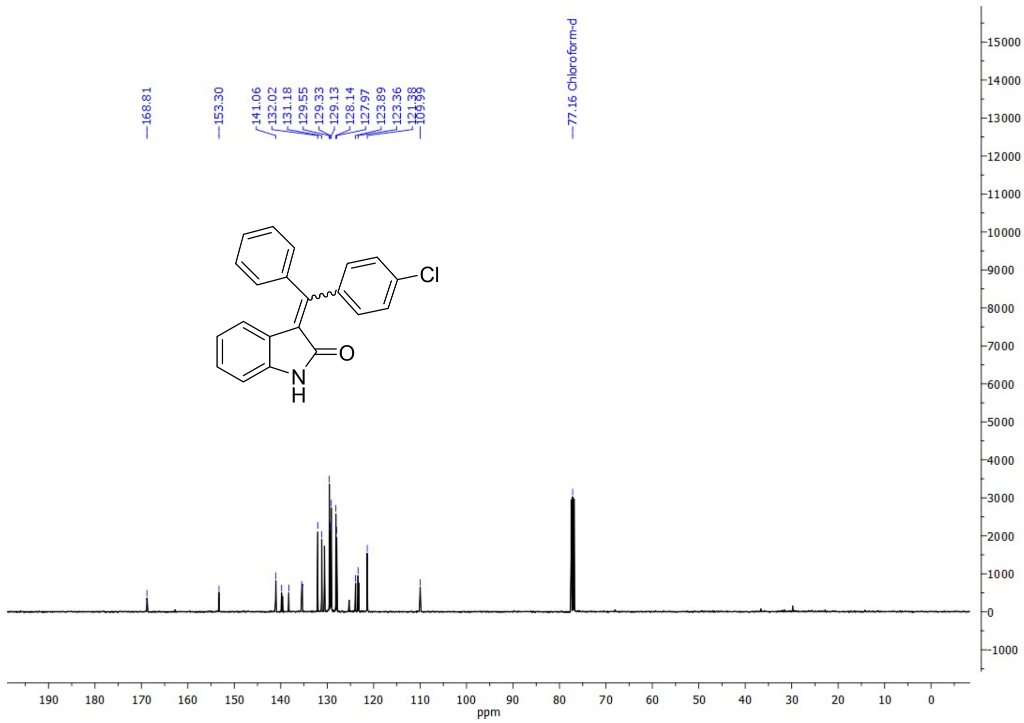
^{1}H NMR of Compound 3a



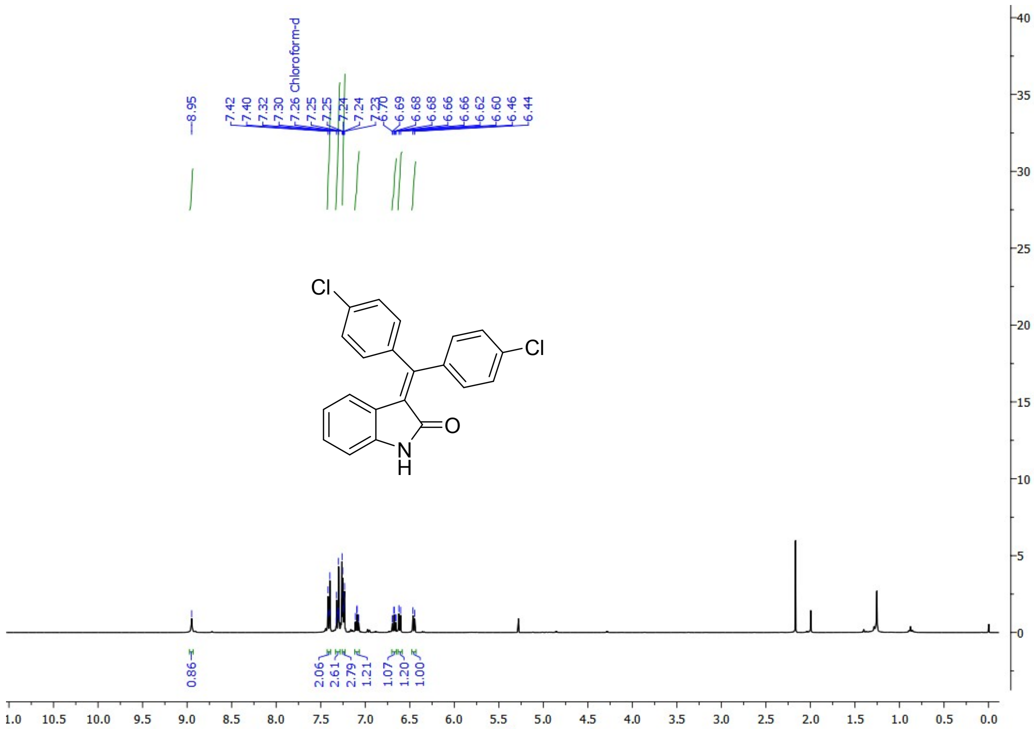
^{13}C NMR of Compound 3a



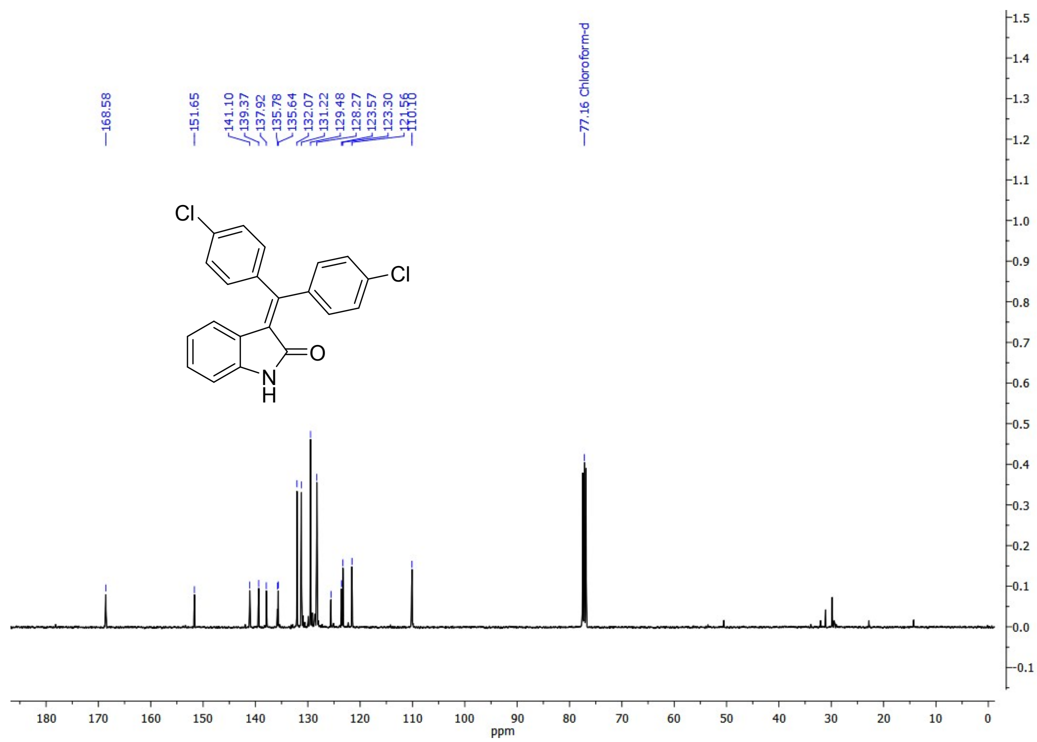
^{1}H NMR of Compound 3b (*E:Z* mixture)



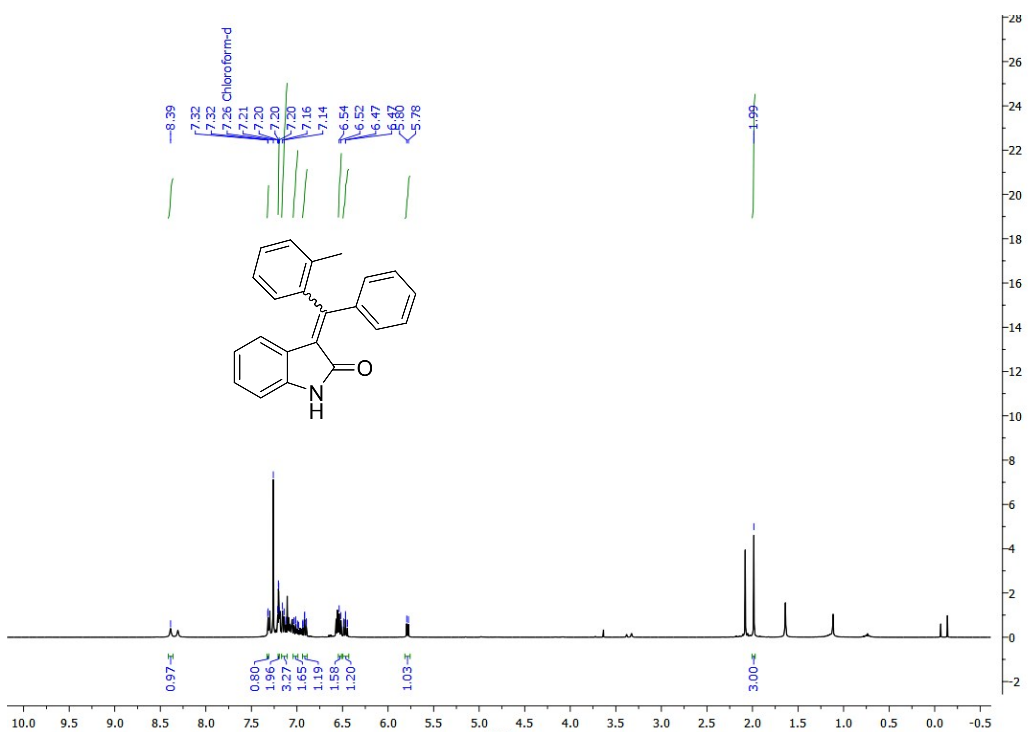
^{13}C NMR of Compound 3b (*E*:*Z* mixture)



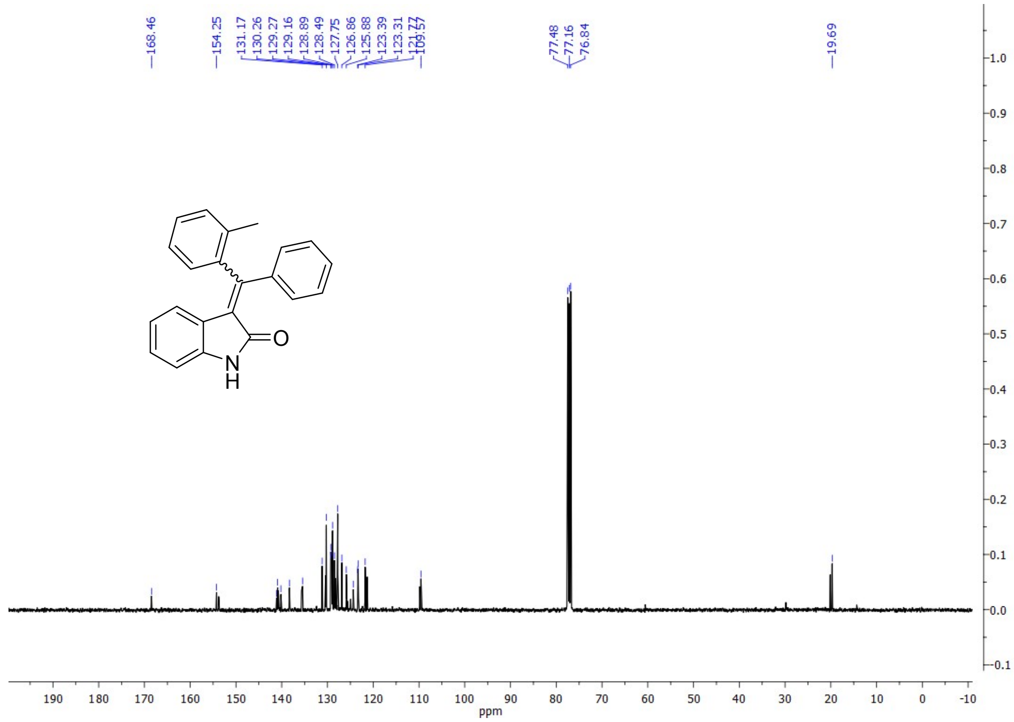
^{1}H NMR of Compound 3c



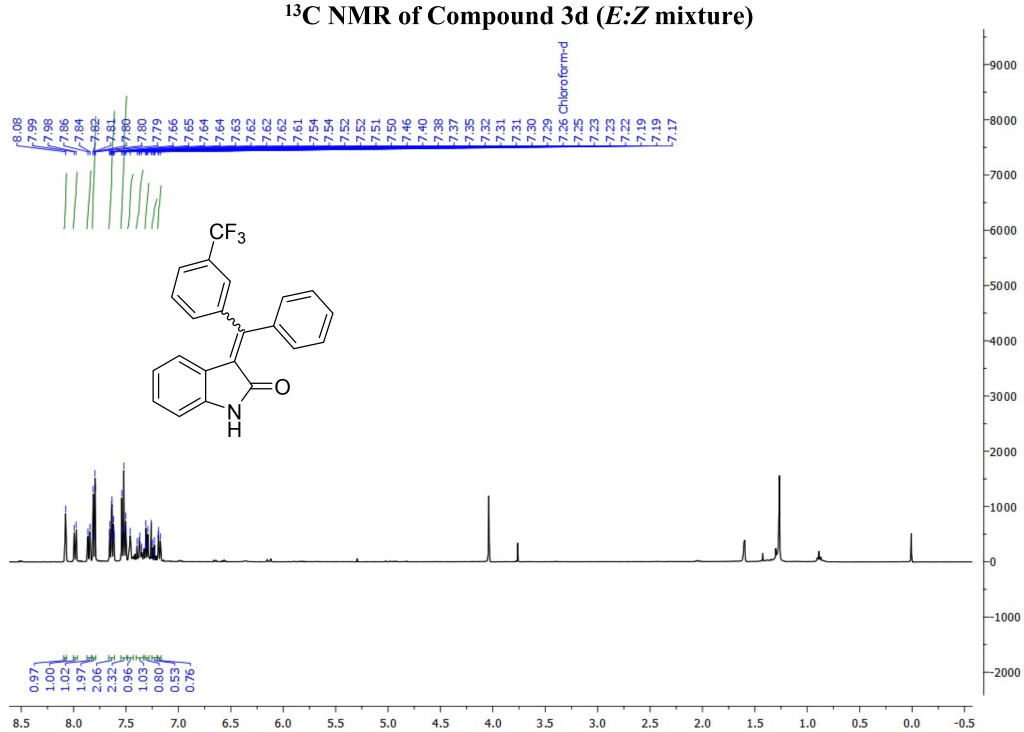
^{13}C NMR of Compound 3c



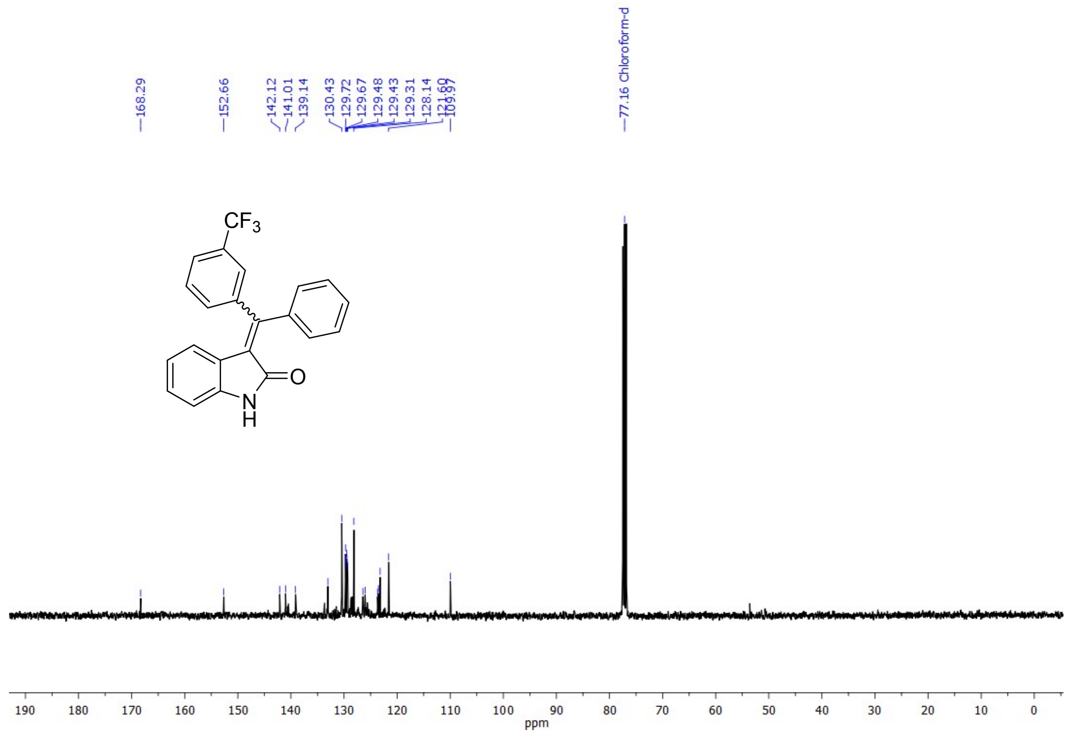
^{1}H NMR of Compound 3d (*E:Z* mixture)



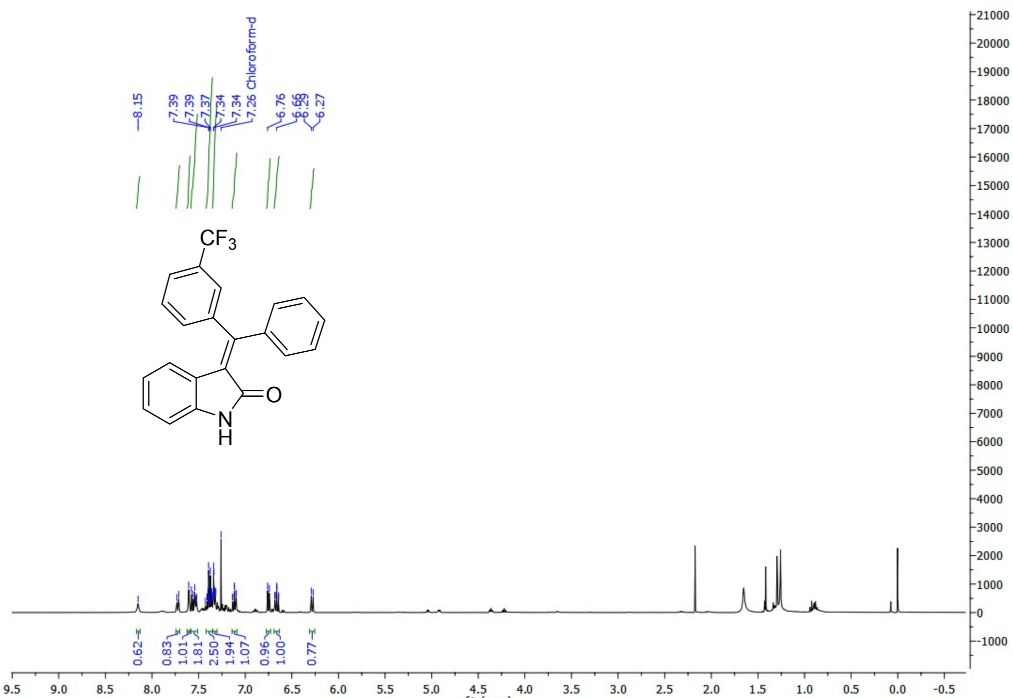
^{13}C NMR of Compound 3d (*E:Z* mixture)



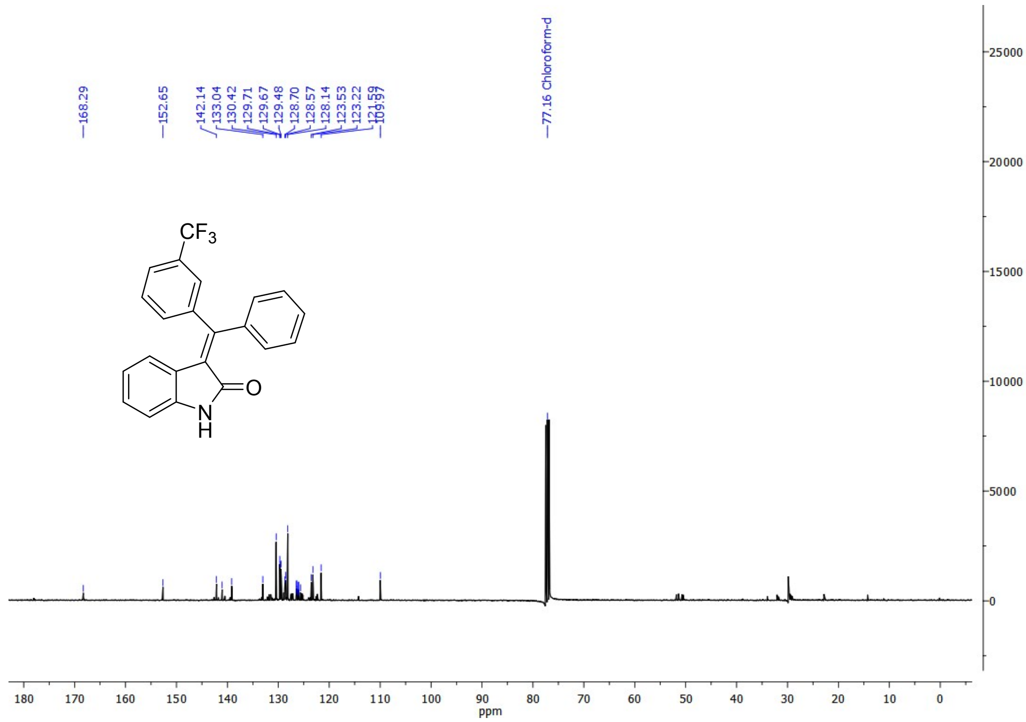
^{1}H NMR of Compound 3e (*E:Z* mixture)



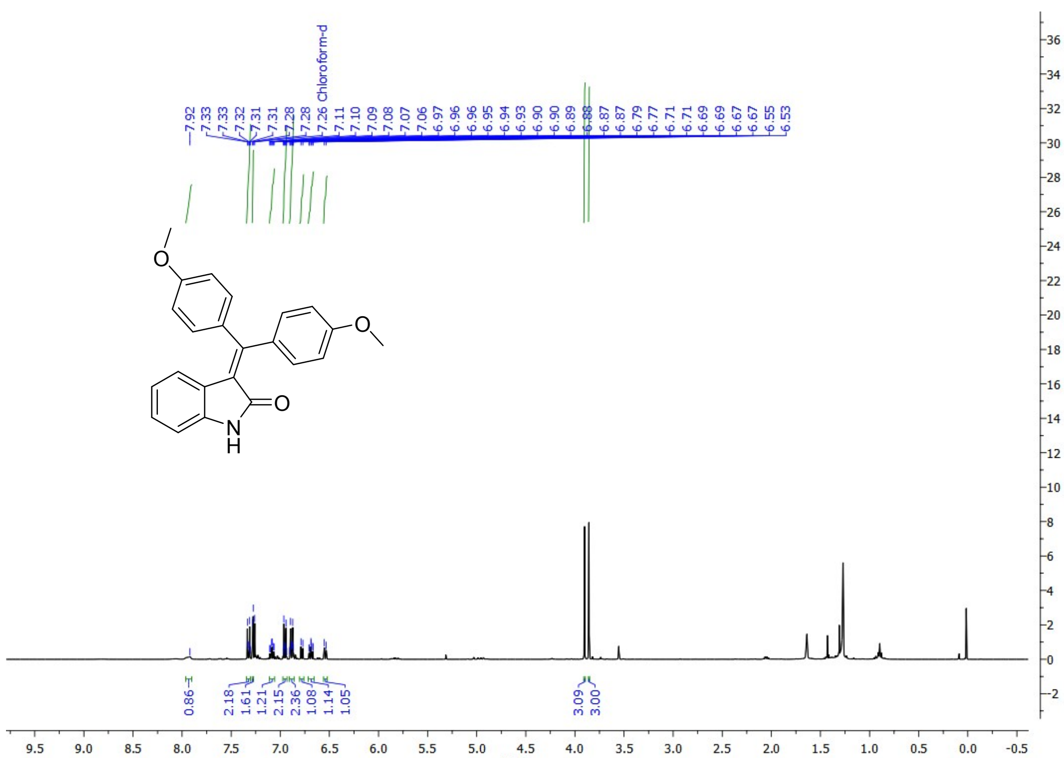
^{13}C NMR of Compound 3e (*E:Z* mixture)



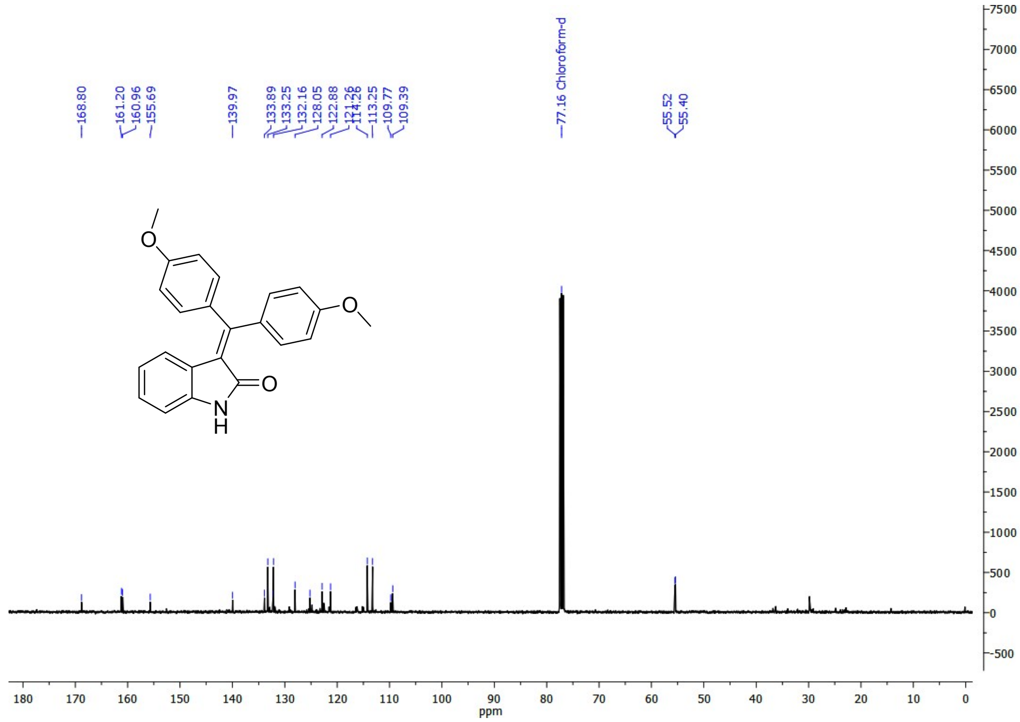
^{1}H NMR of *E* isomer of Compound 3e



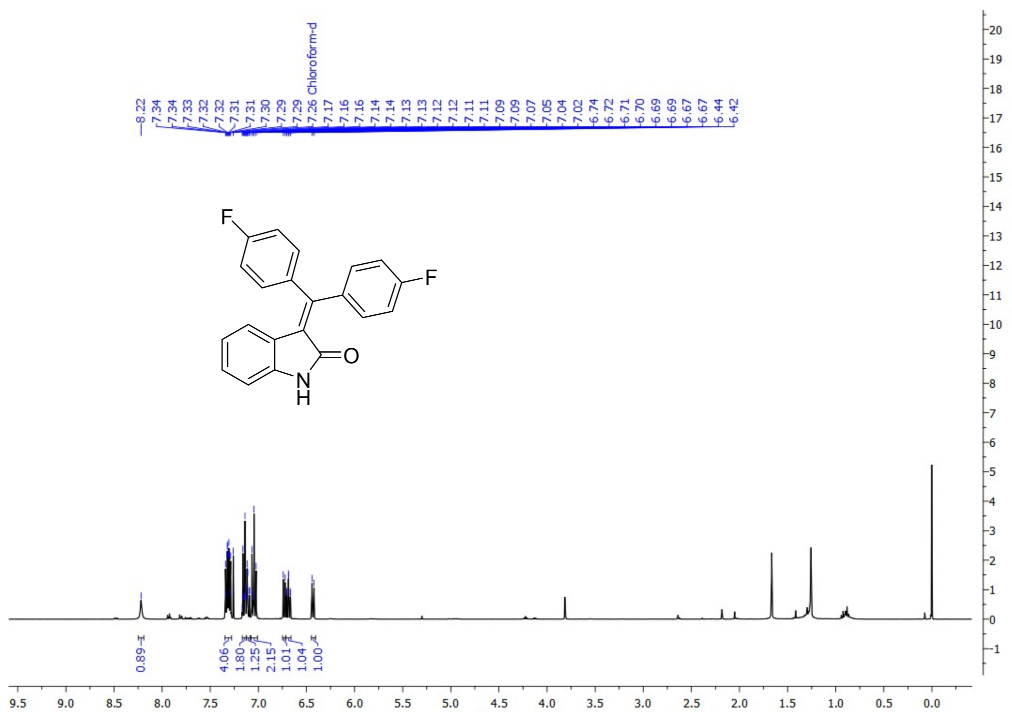
^{13}C NMR of *E* isomer of Compound 3e



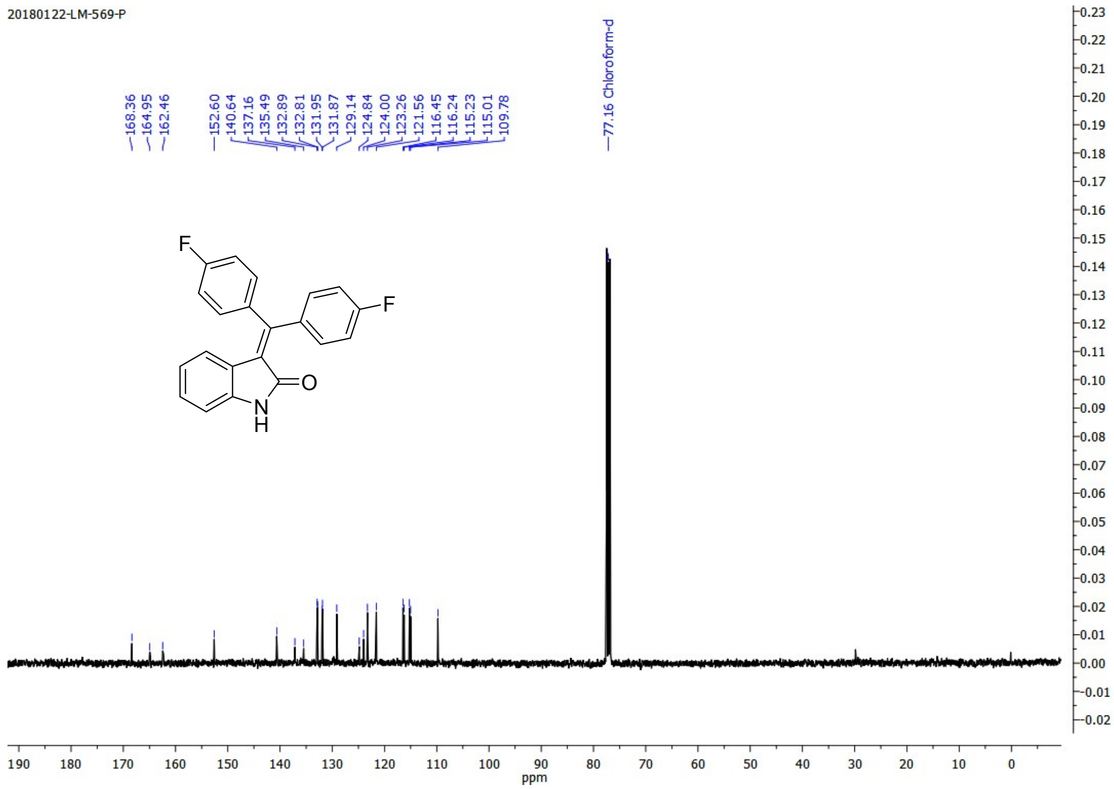
^{1}H NMR of Compound 3f



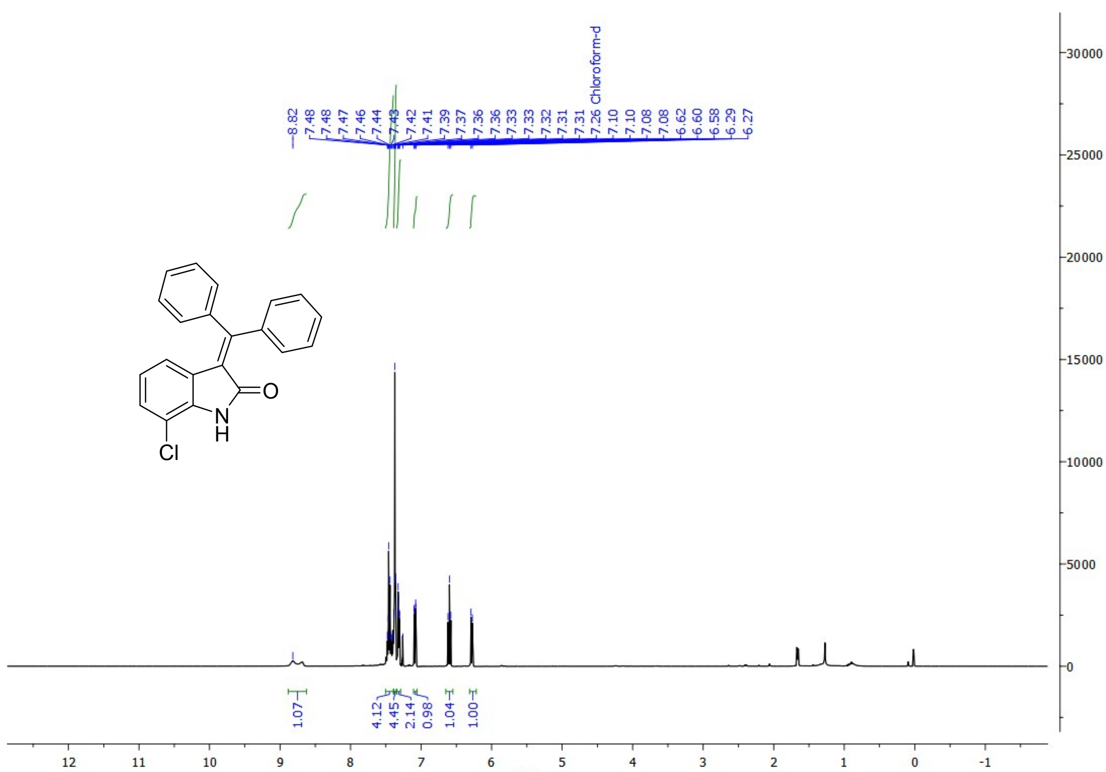
^{13}C NMR of Compound 3f



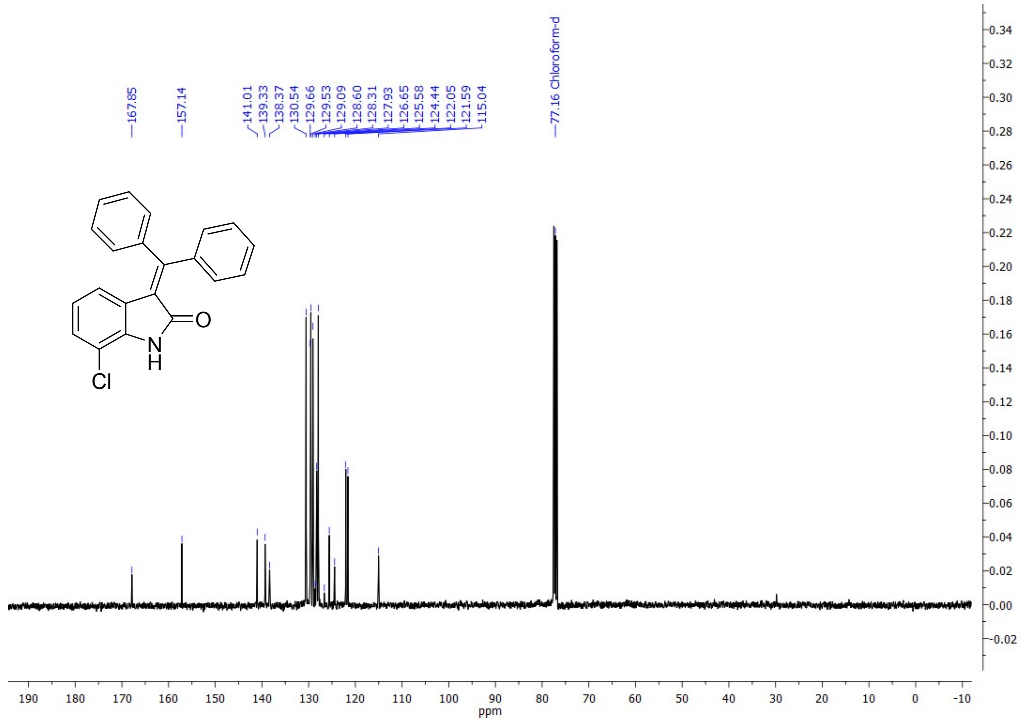
^{1}H NMR of Compound 3g



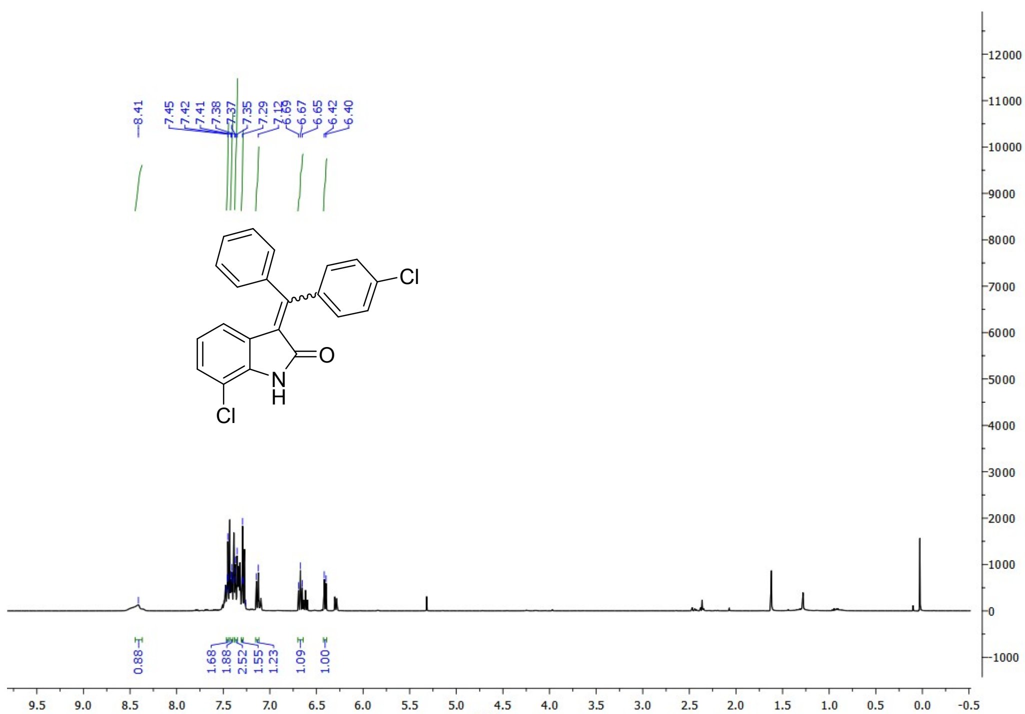
^{13}C NMR of Compound 3g



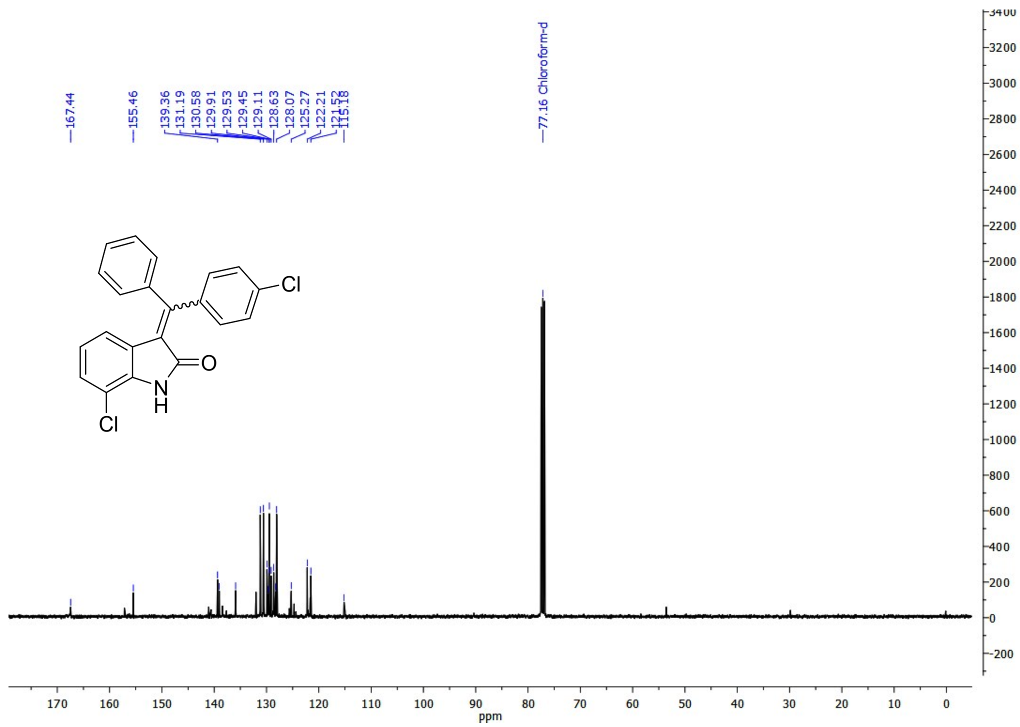
^{1}H NMR of Compound 3h



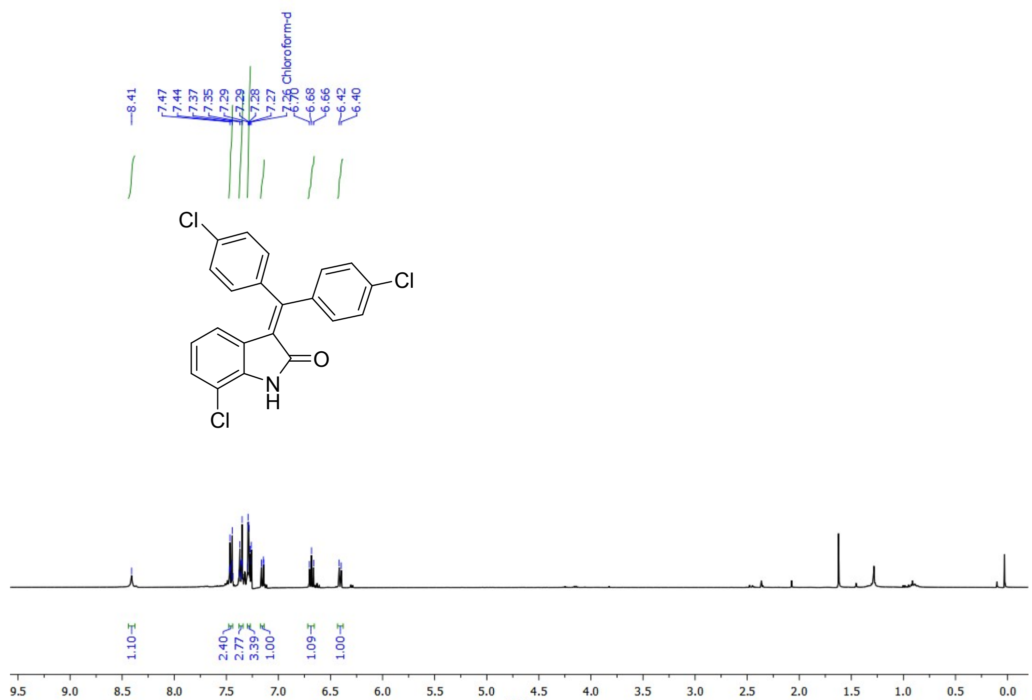
^{13}C NMR of Compound 3h



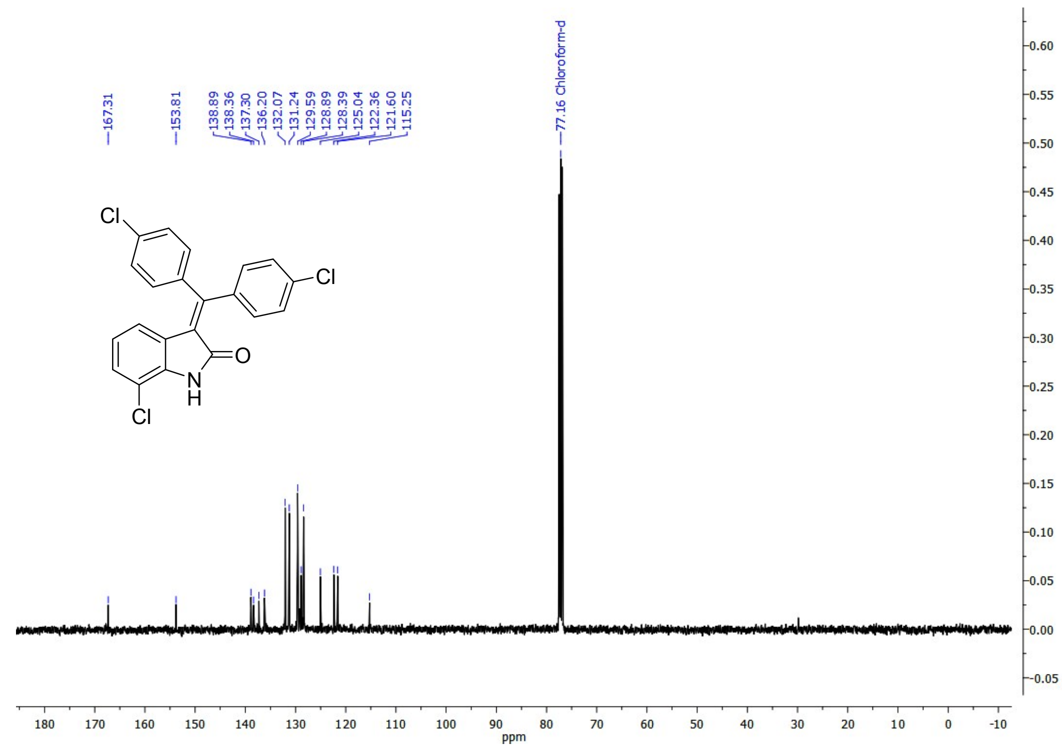
^{1}H NMR of Compound 3i (*E:Z* mixture)



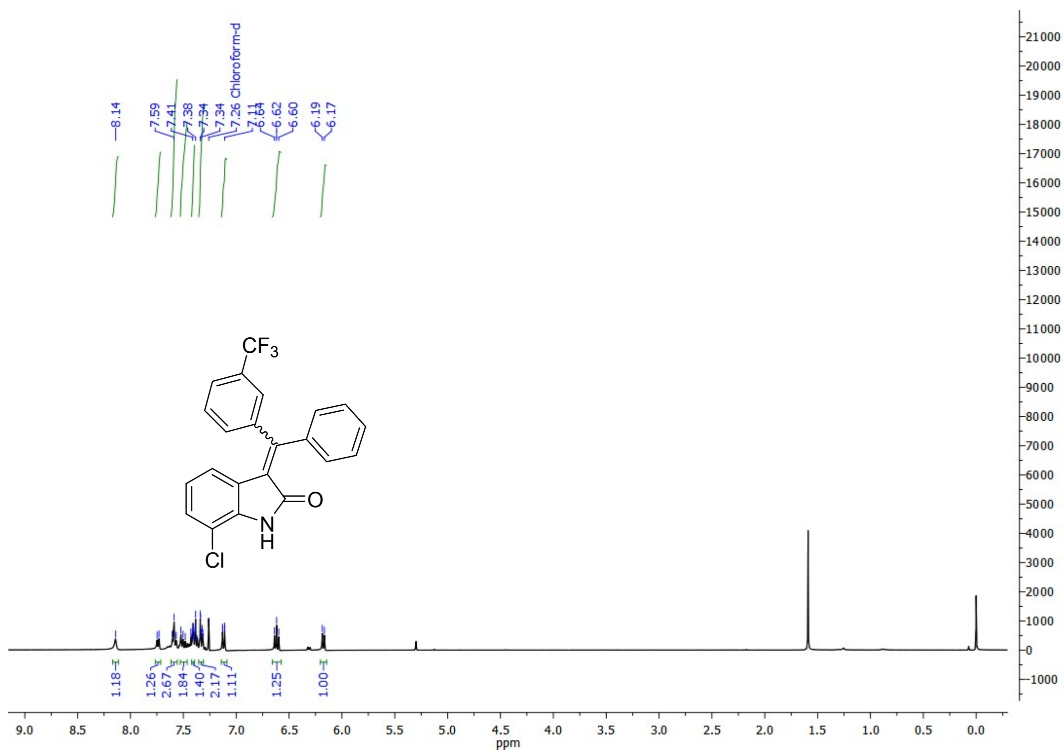
^{13}C NMR of Compound 3i (*E:Z* mixture)



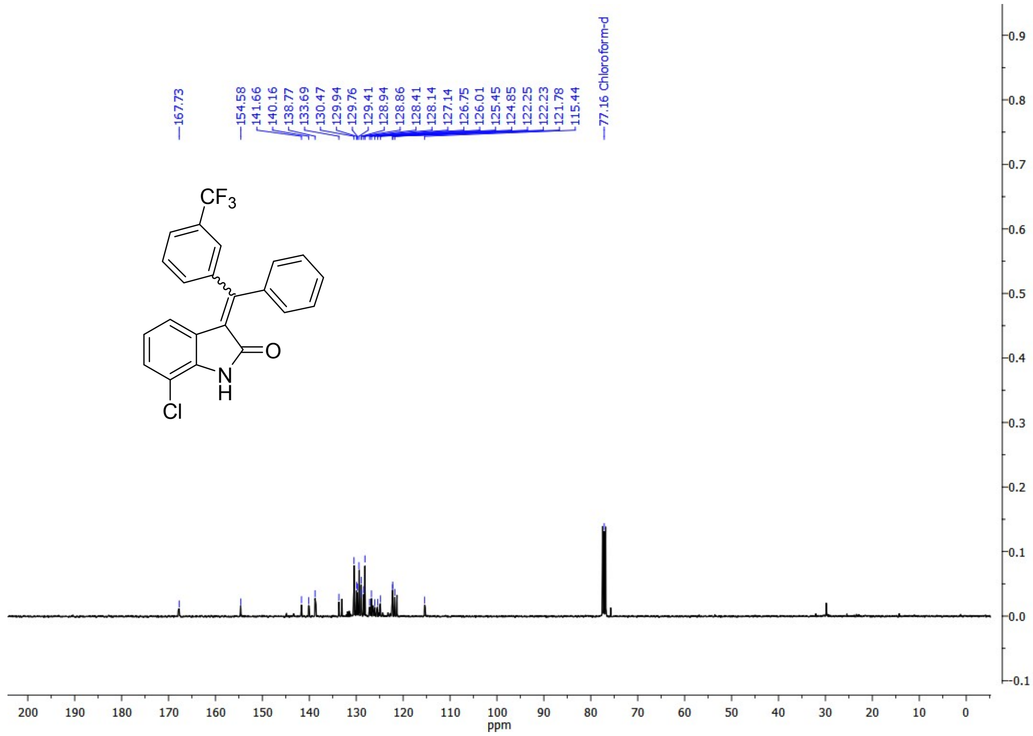
^{1}H NMR of Compound 3j



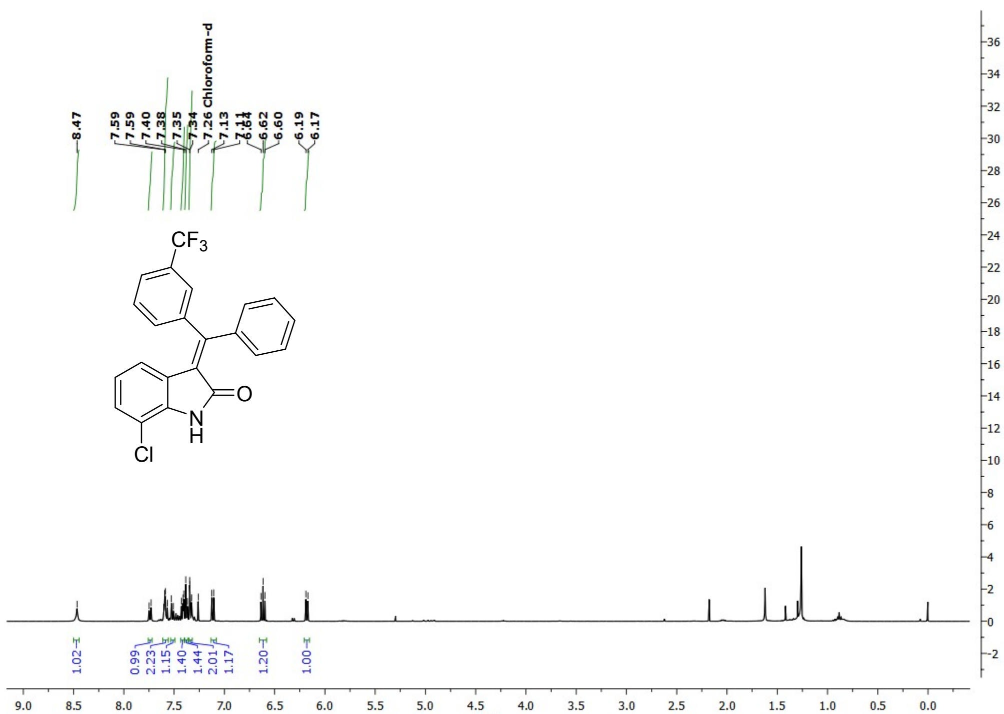
^{13}C NMR of Compound 3j



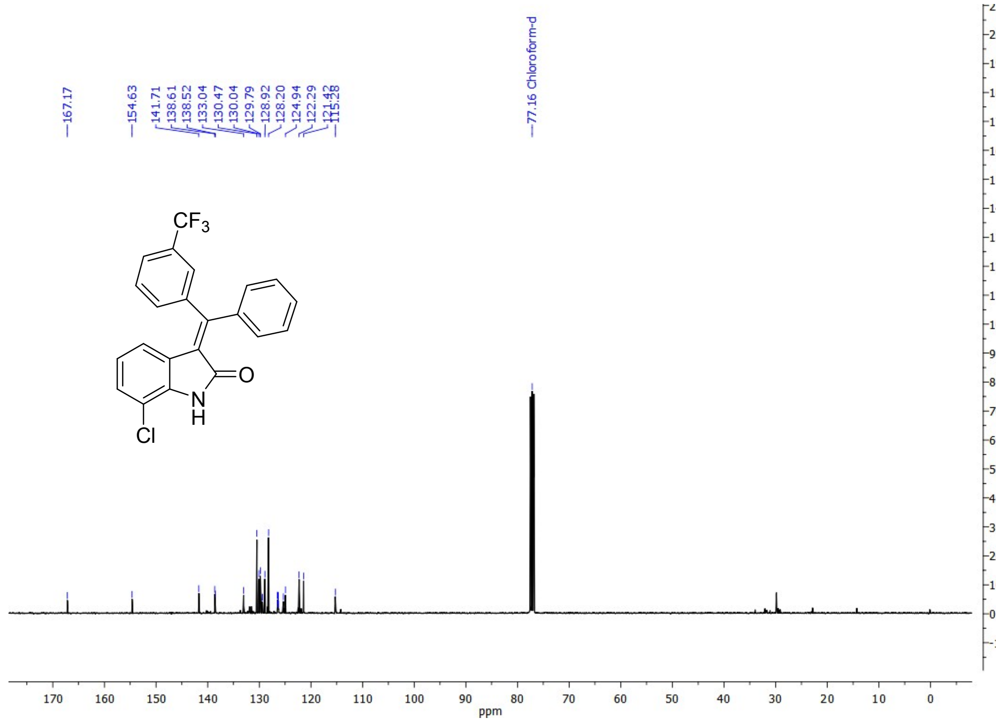
^{1}H NMR of Compound 3k (*E:Z* mixture)



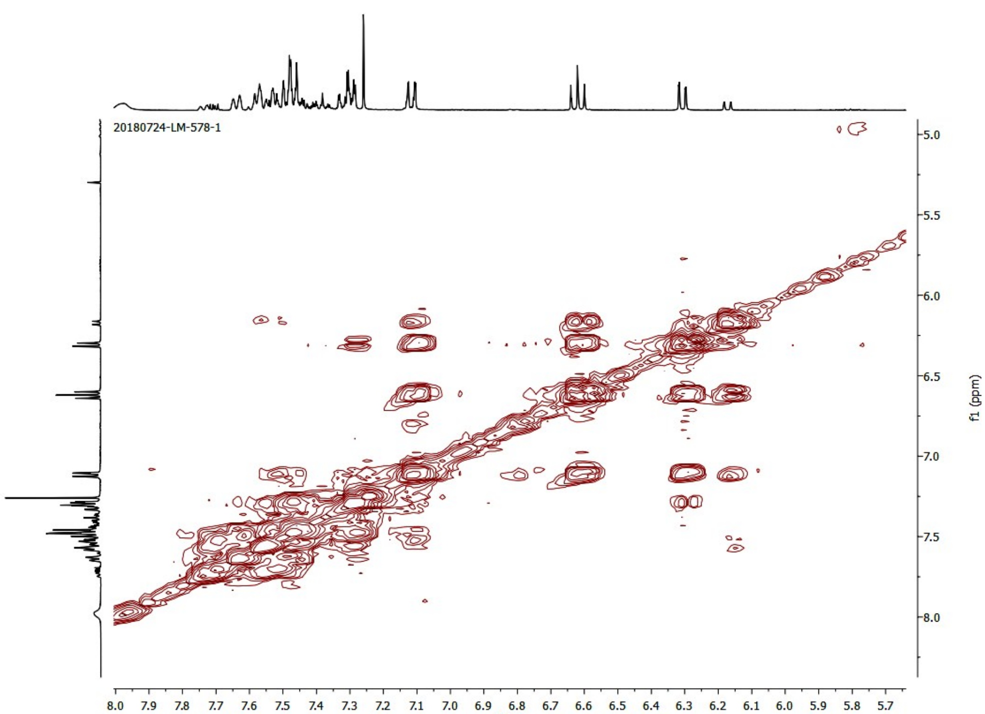
[13]C NMR of Compound 3k (*E:Z* mixture)



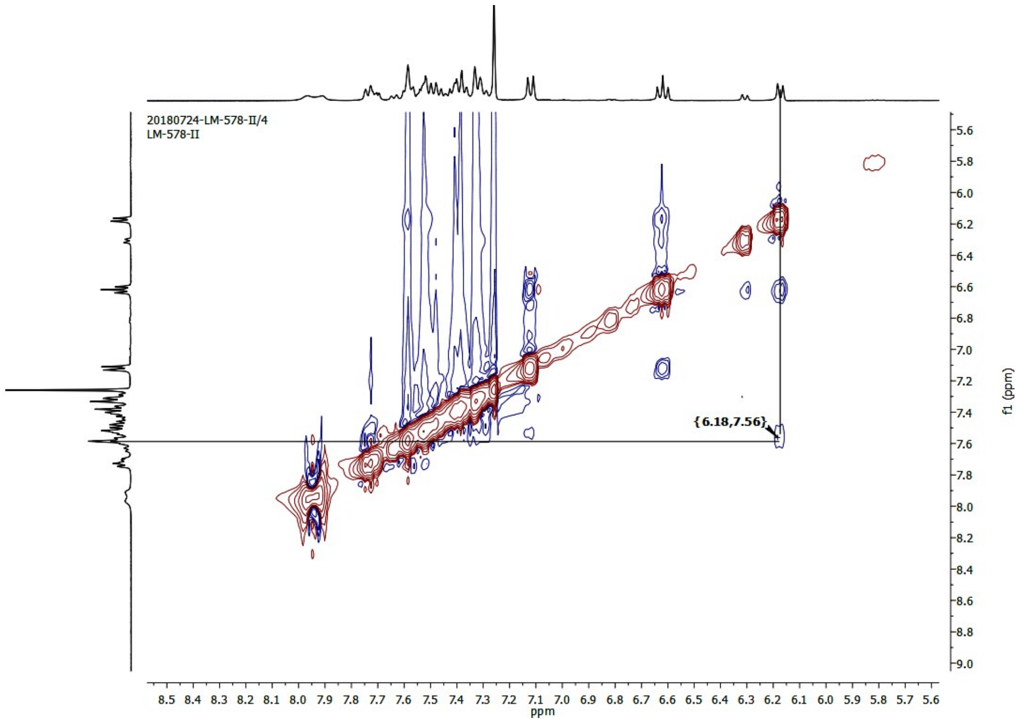
[1]H NMR of *E* isomer of compound 3k



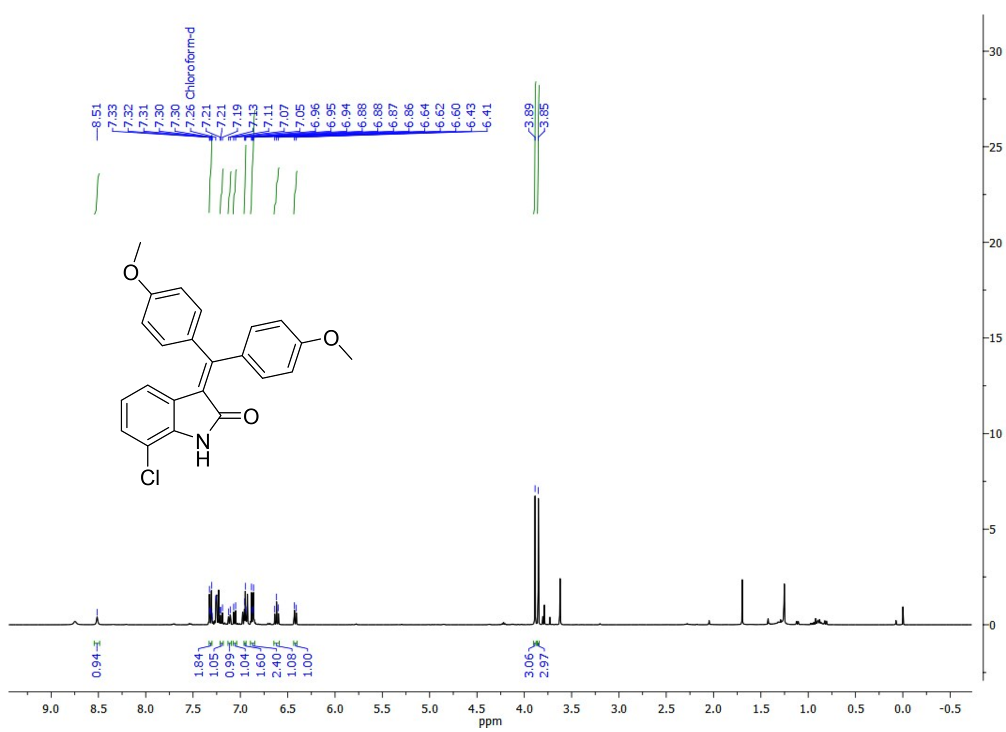
^{13}C NMR of *E* isomer of Compound 3k



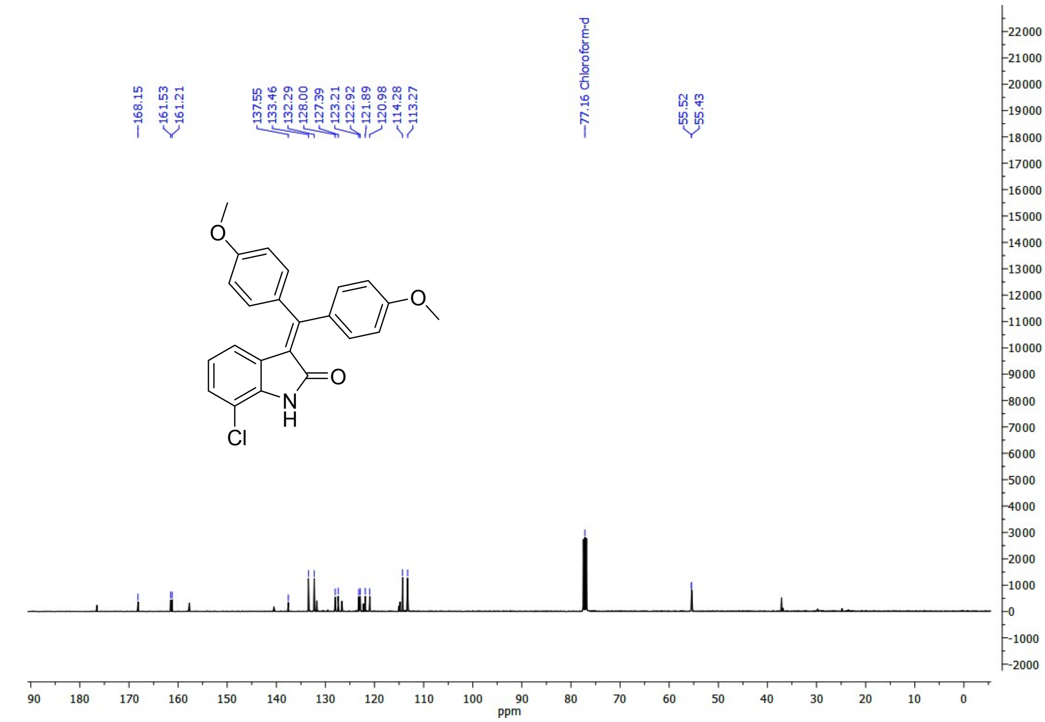
NOESY NMR of *Z* isomer of Compound 3k



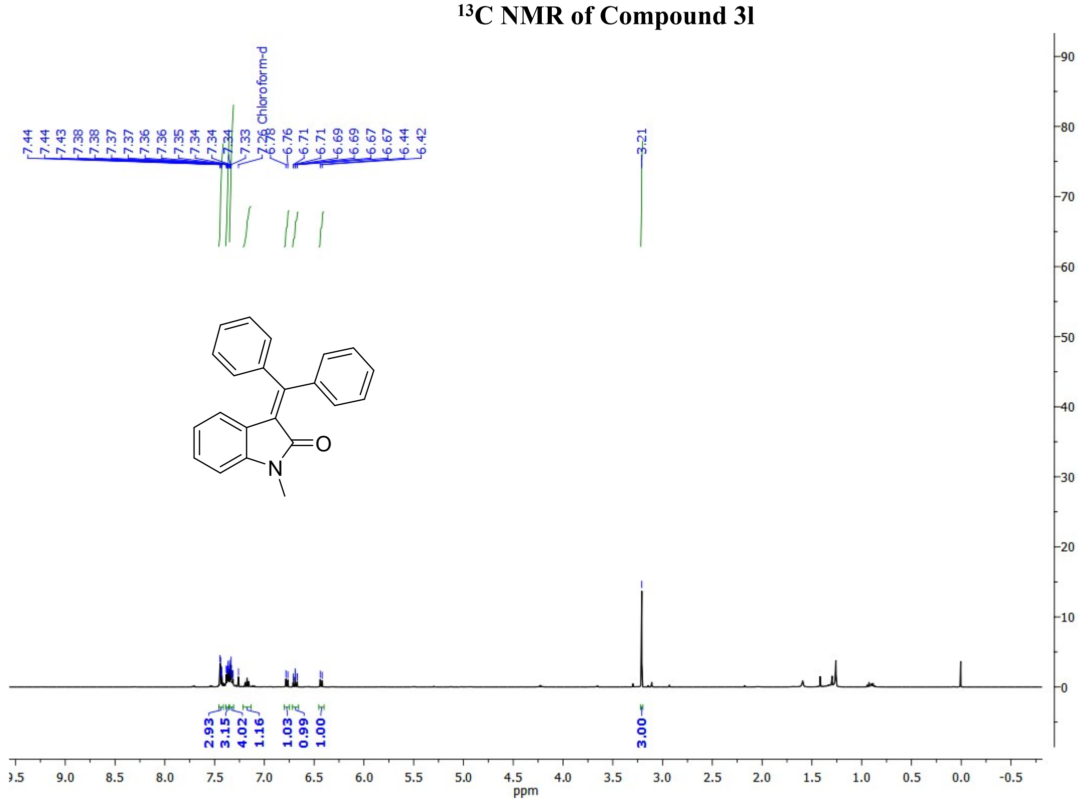
NOESY NMR of *E* isomer of Compound 3k



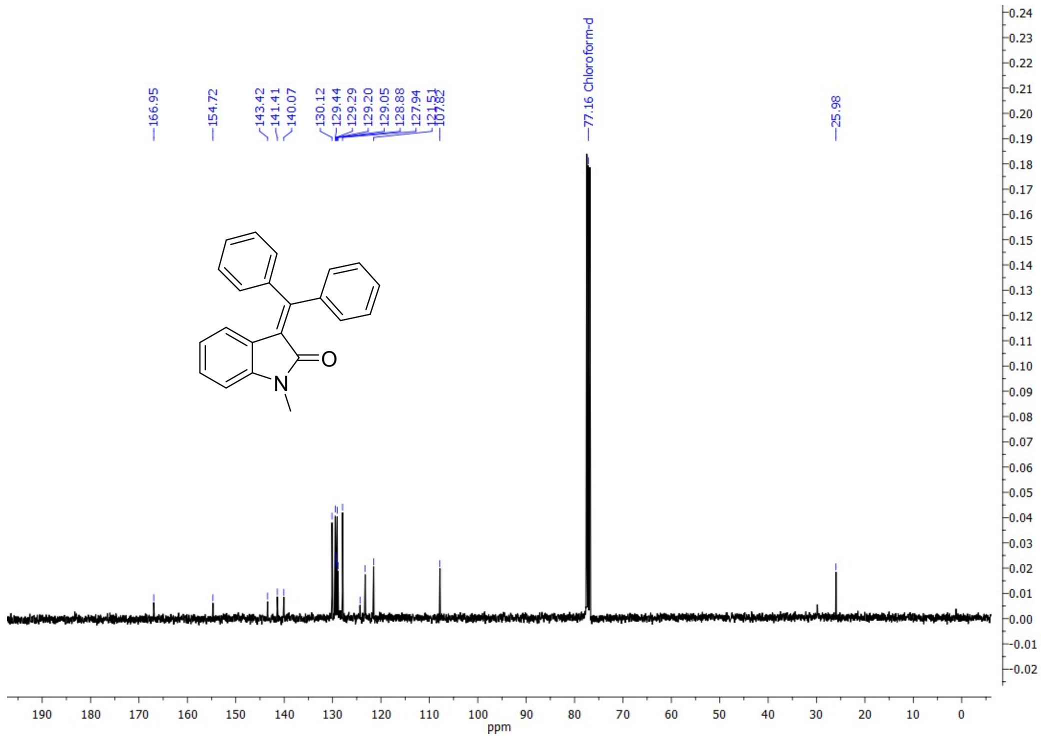
[1]H NMR of Compound 3l



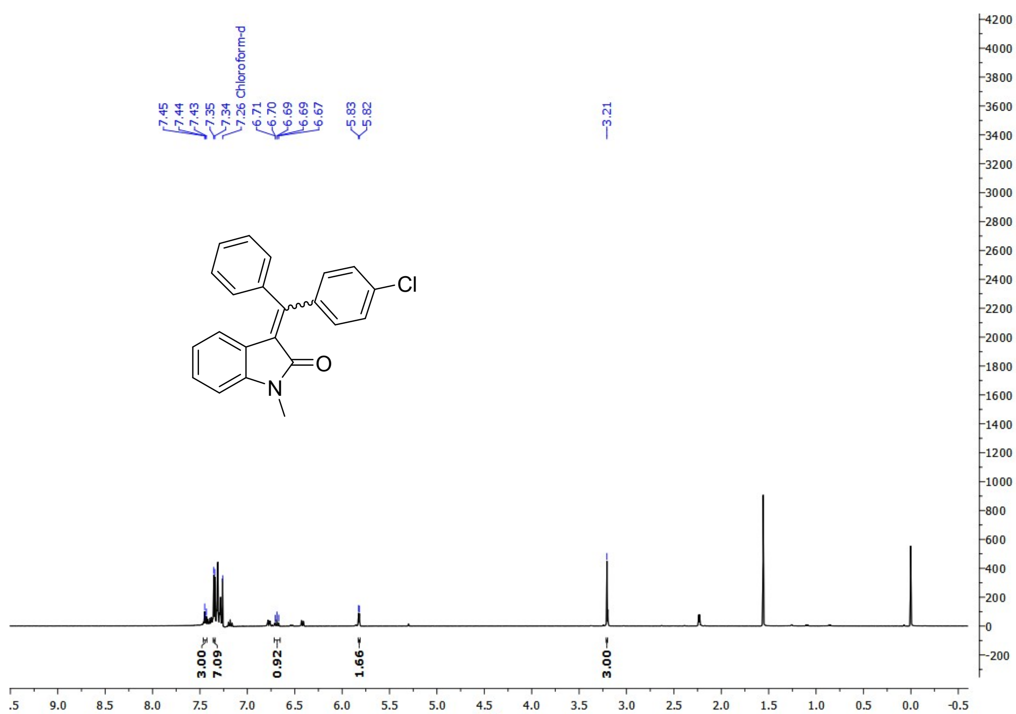
^{13}C NMR of Compound 3l



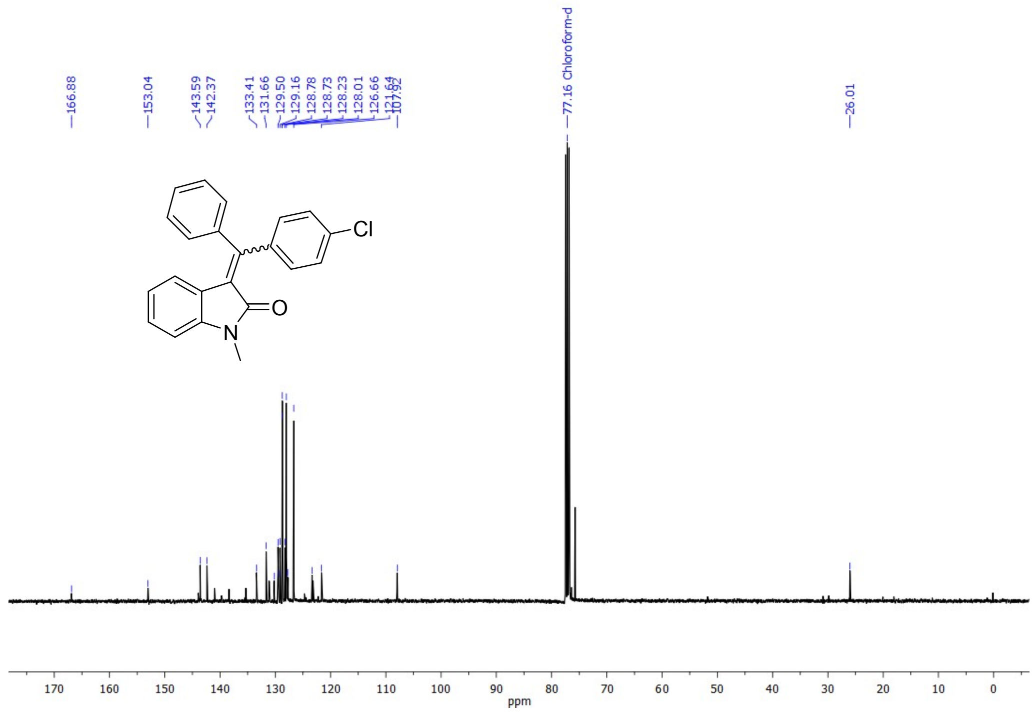
^{1}H NMR of Compound 6a



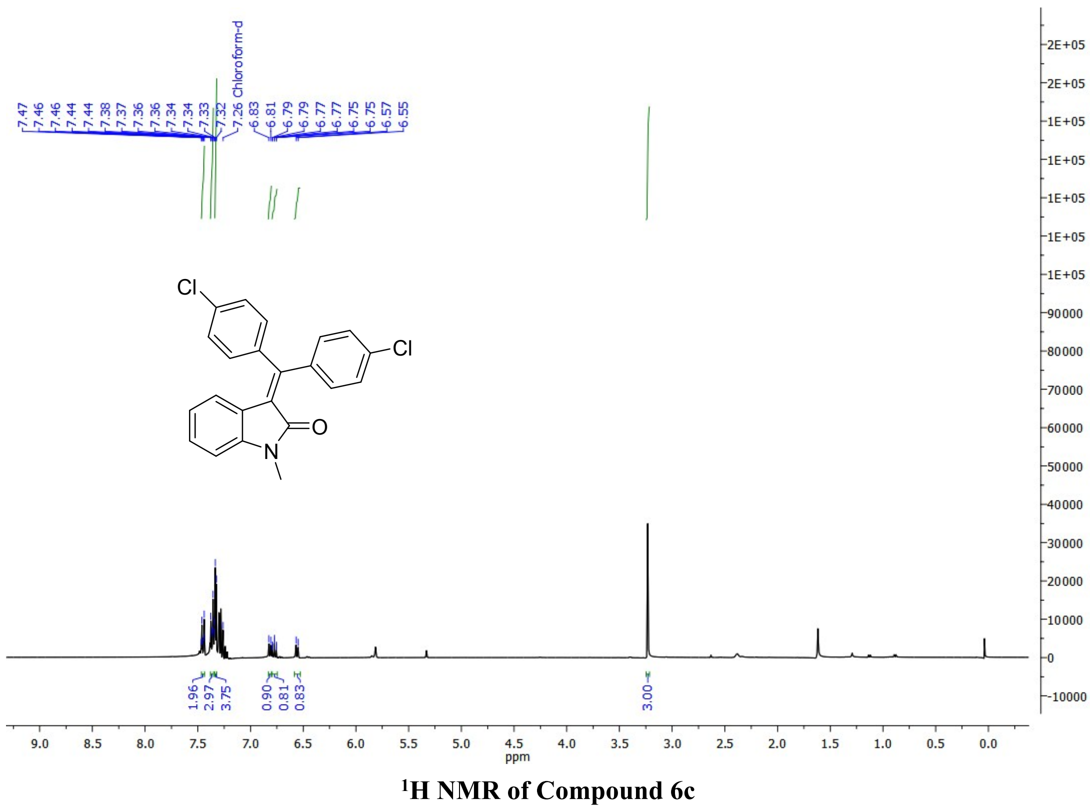
^{13}C NMR of Compound 6a



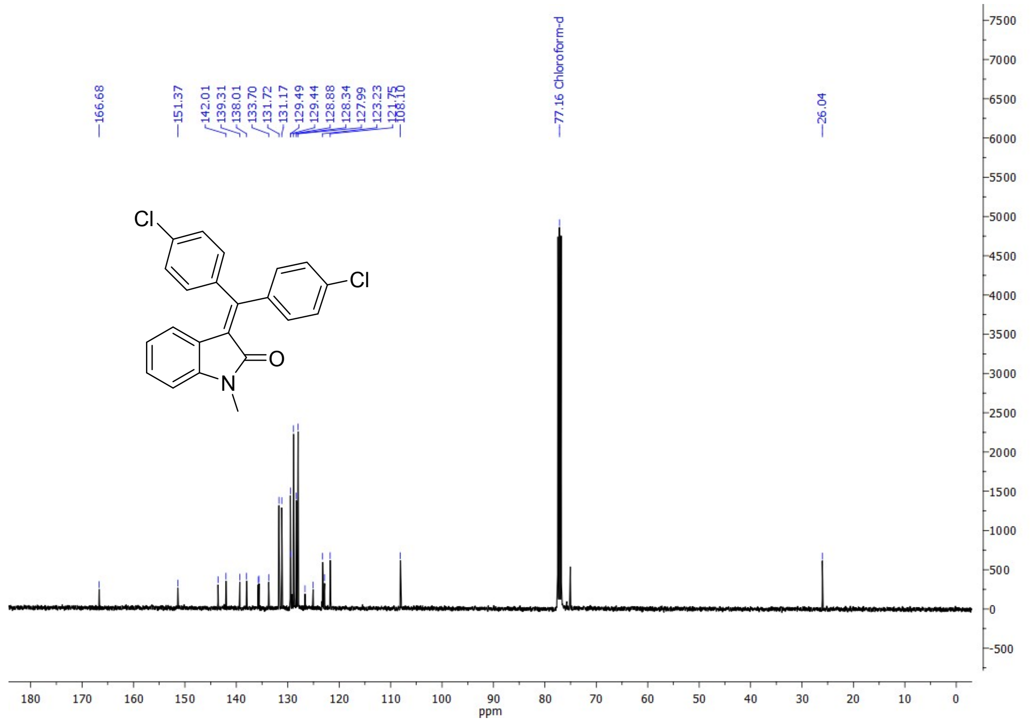
^{1}H NMR of Compound 6b (*E:Z* mixture)



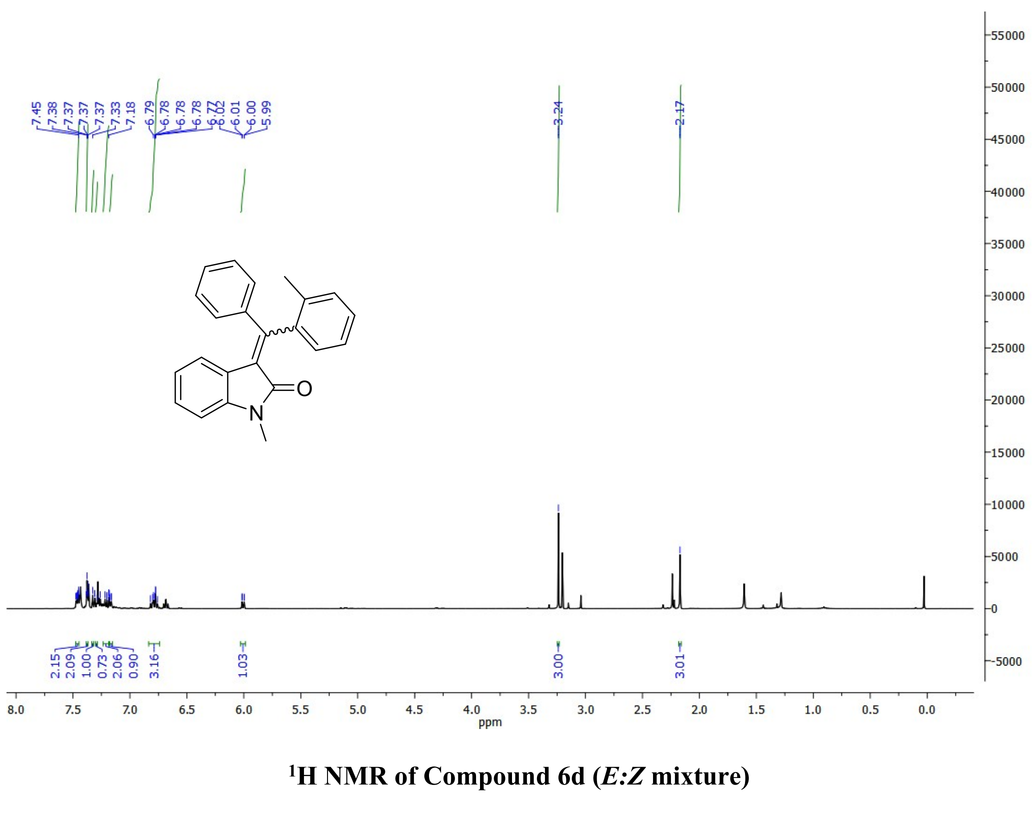
^{13}C NMR of Compound 6b (*E:Z* mixture)



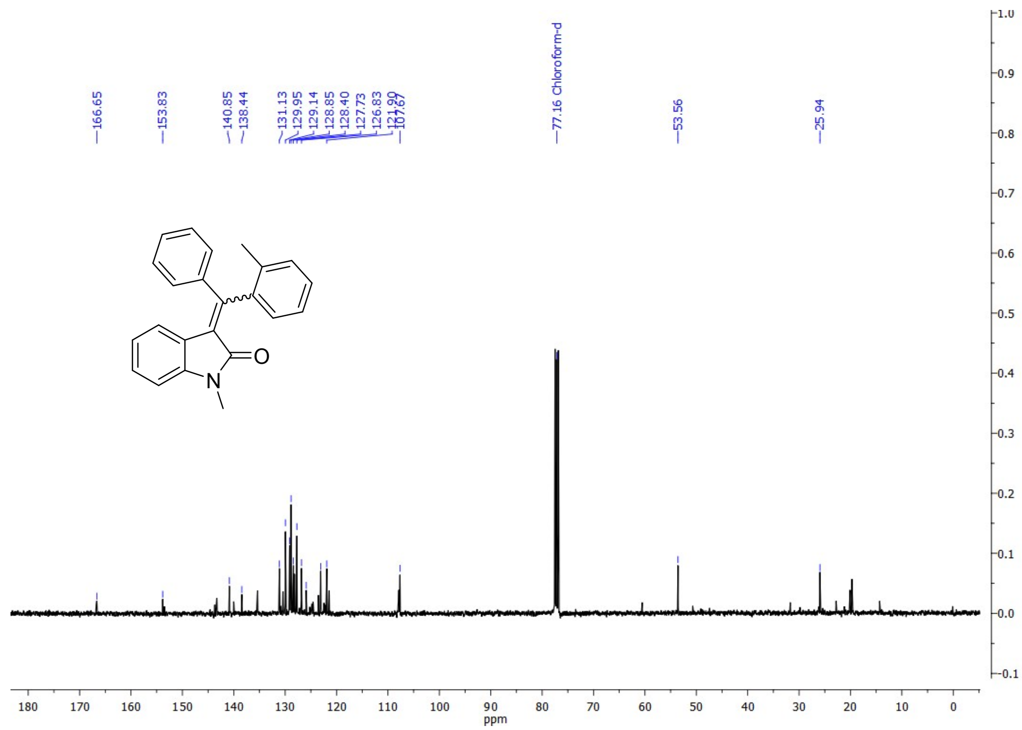
^{1}H NMR of Compound 6c



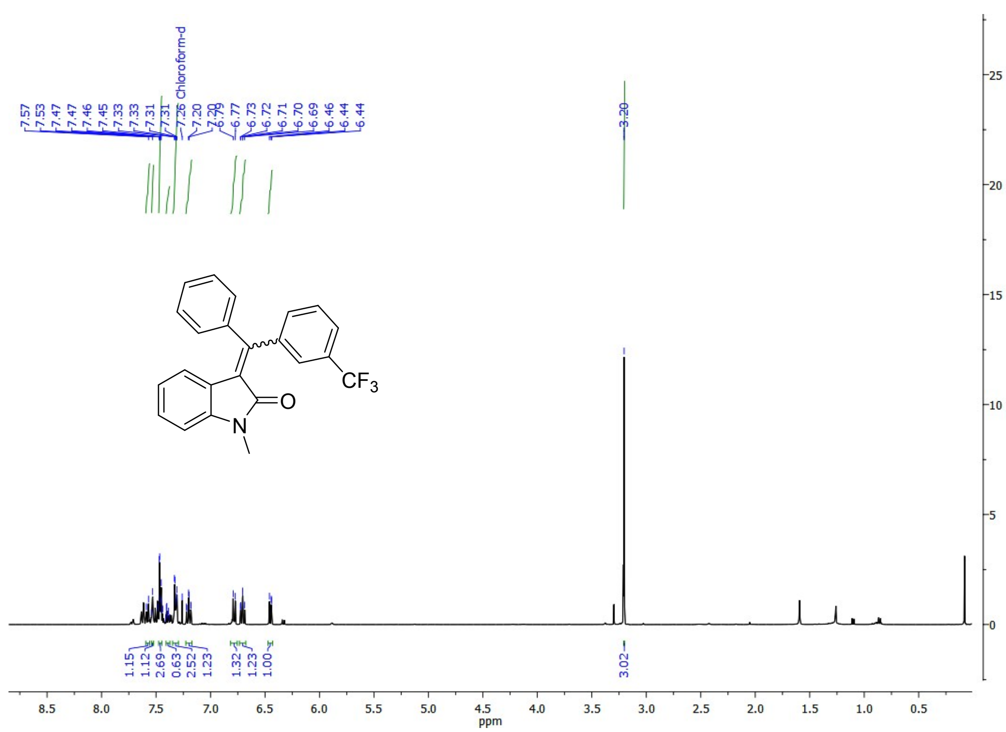
^{13}C NMR of Compound 6c



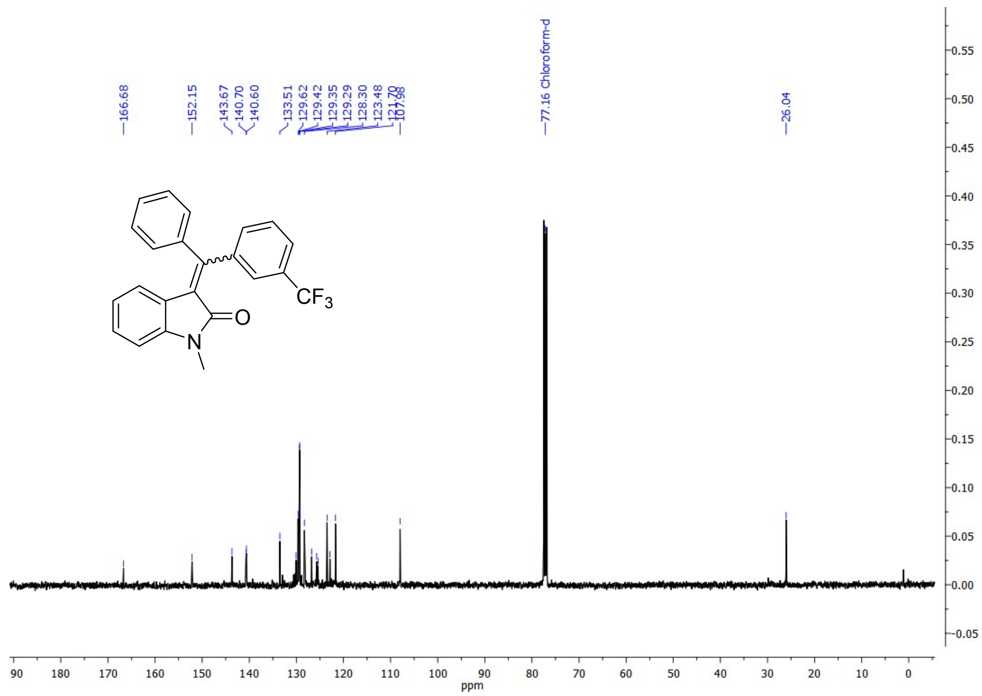
^{1}H NMR of Compound 6d (*E:Z* mixture)



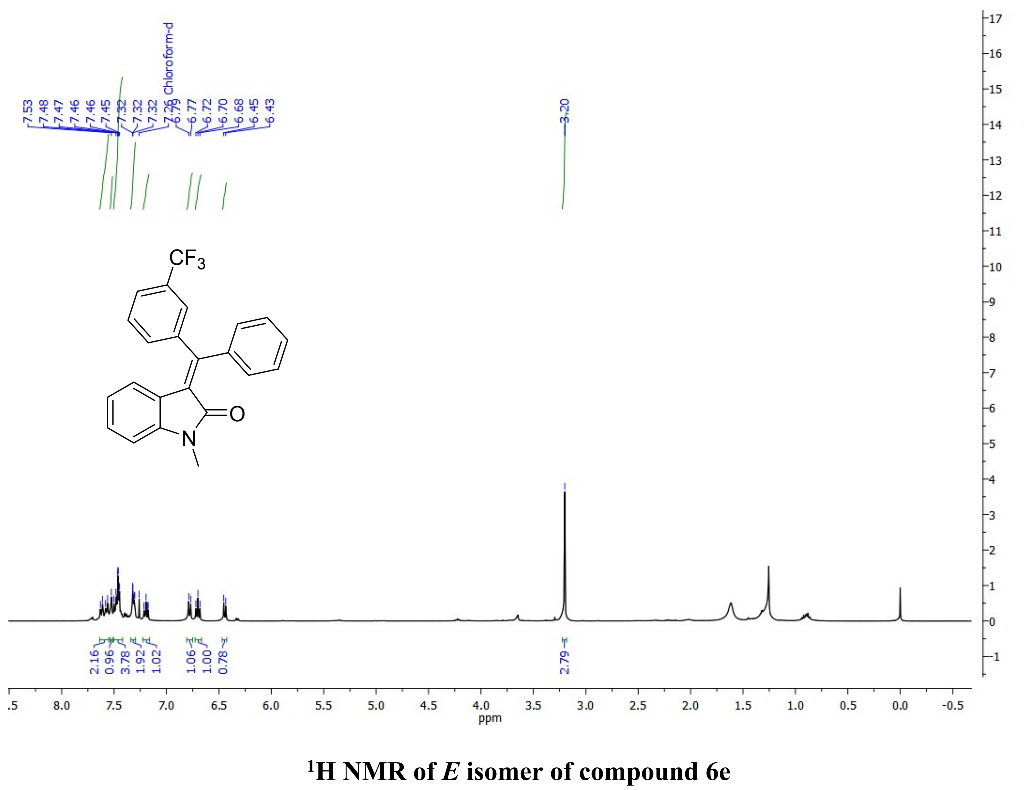
^{13}C NMR of Compound 6d (*E:Z* mixture)



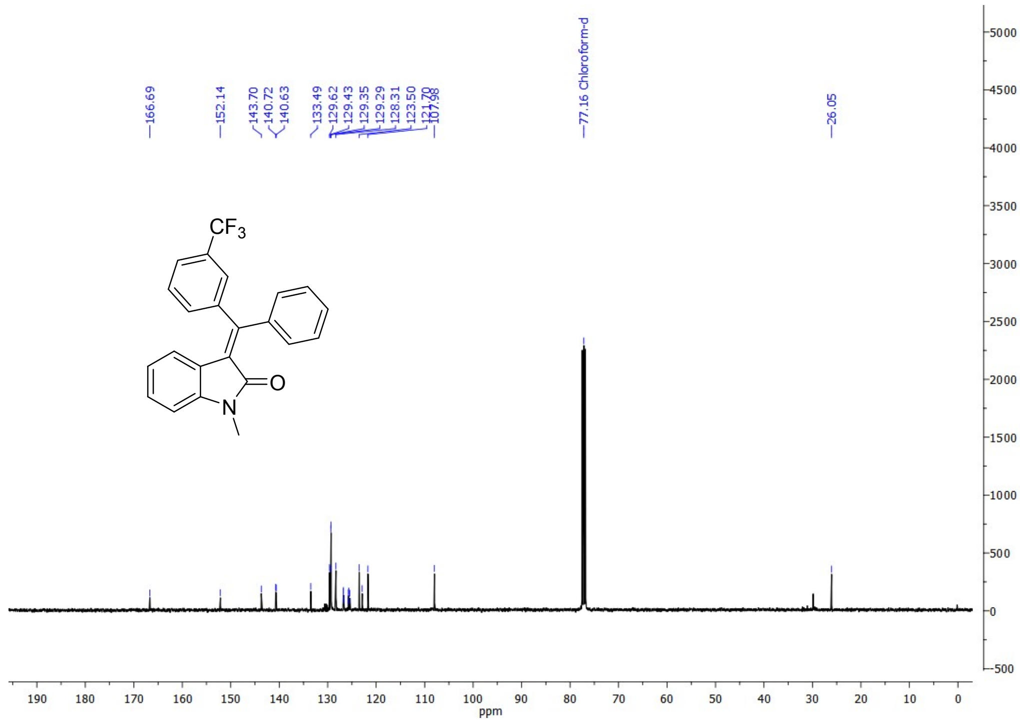
^{1}H NMR of Compound 6e (*E:Z* mixture)



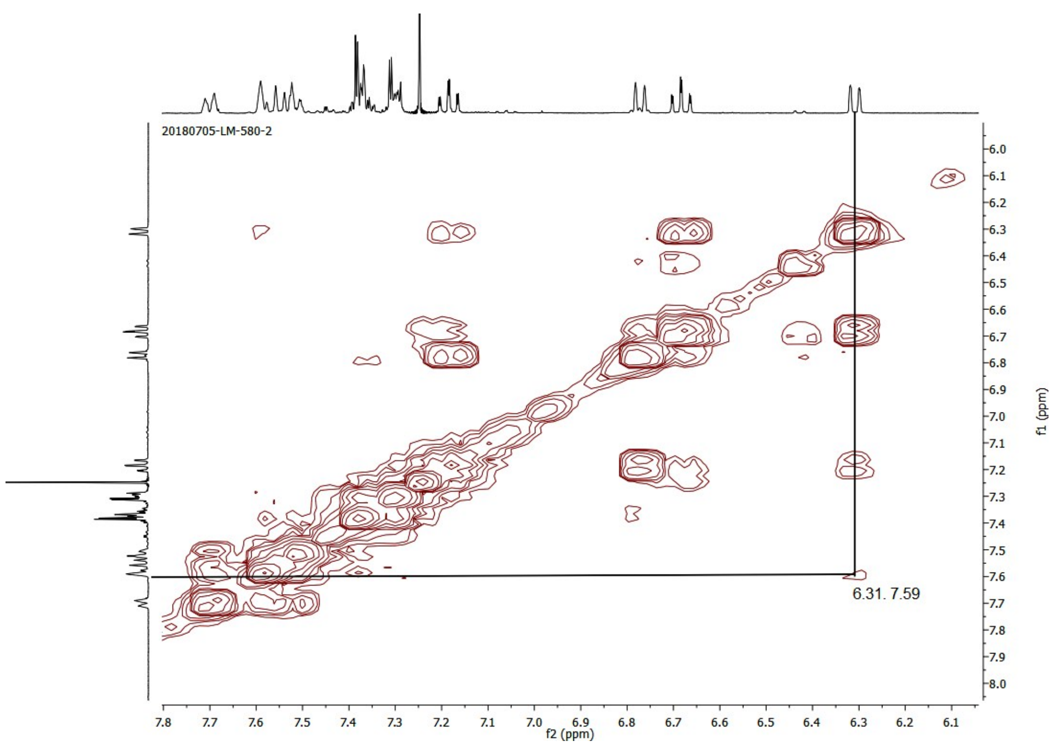
^{13}C NMR of Compound 6e (*E:Z* mixture)



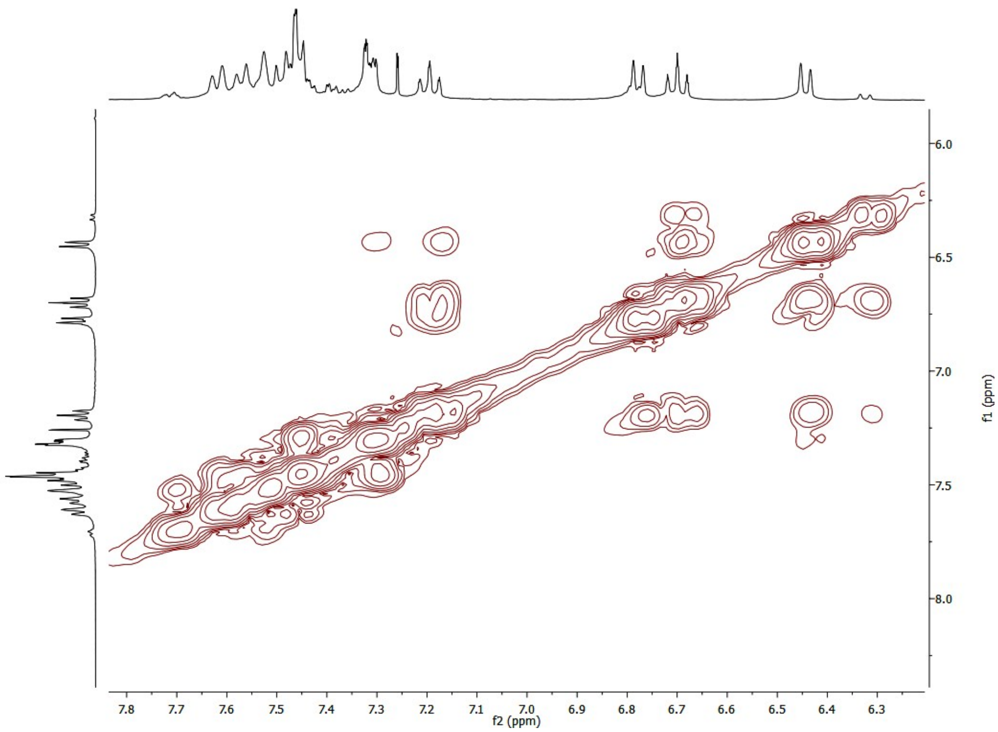
^{1}H NMR of *E* isomer of compound 6e



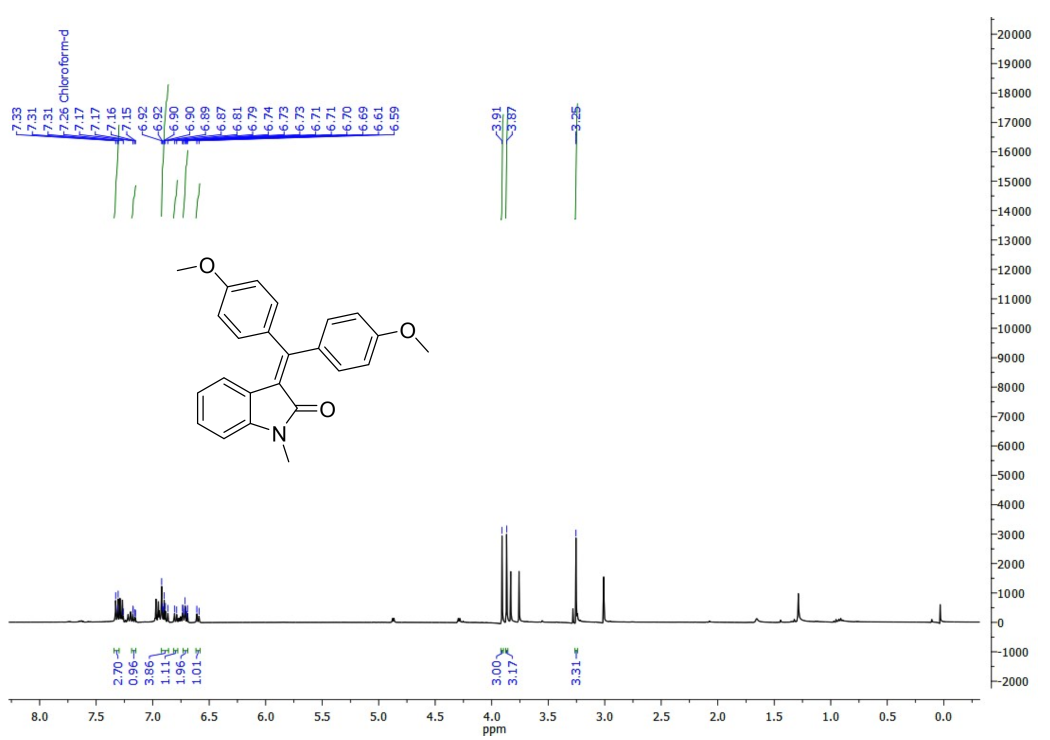
^{13}C NMR of *E* isomer of Compound 6e



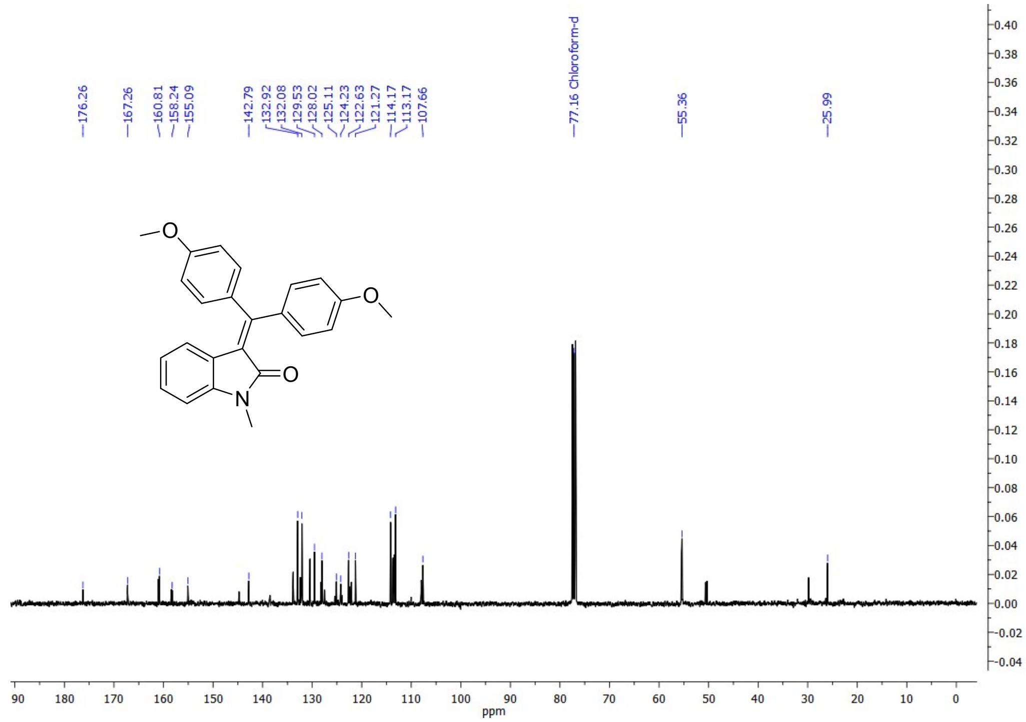
NOESY NMR of *E* isomer of Compound 6e



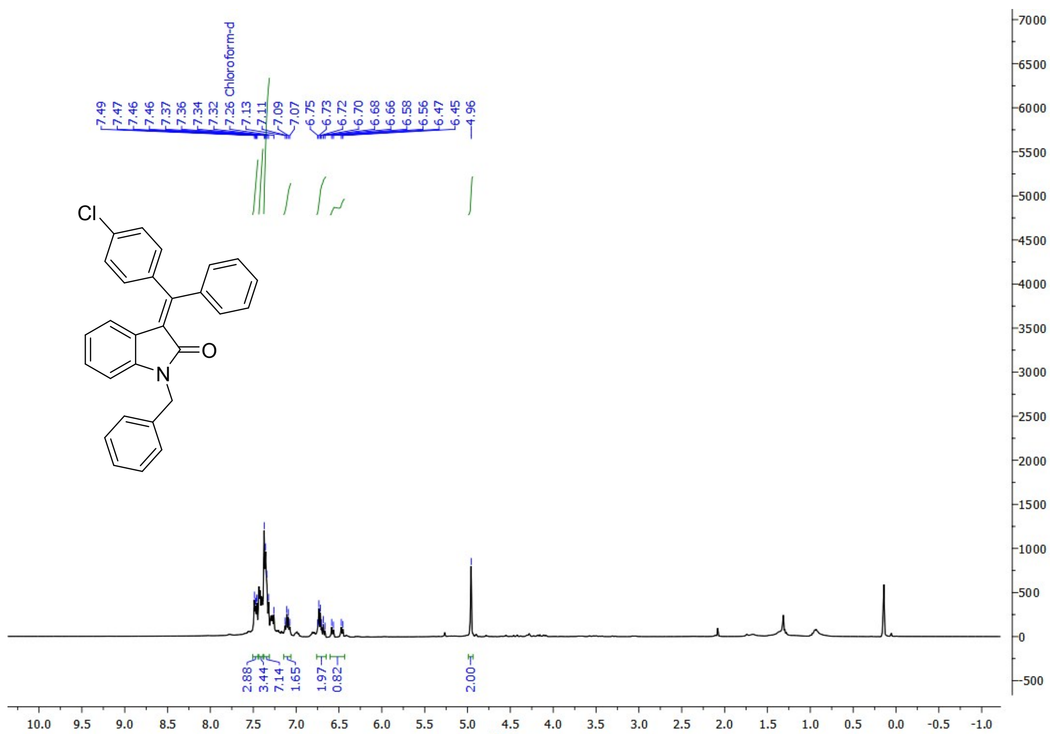
NOESY NMR of *Z* isomer of Compound 6e



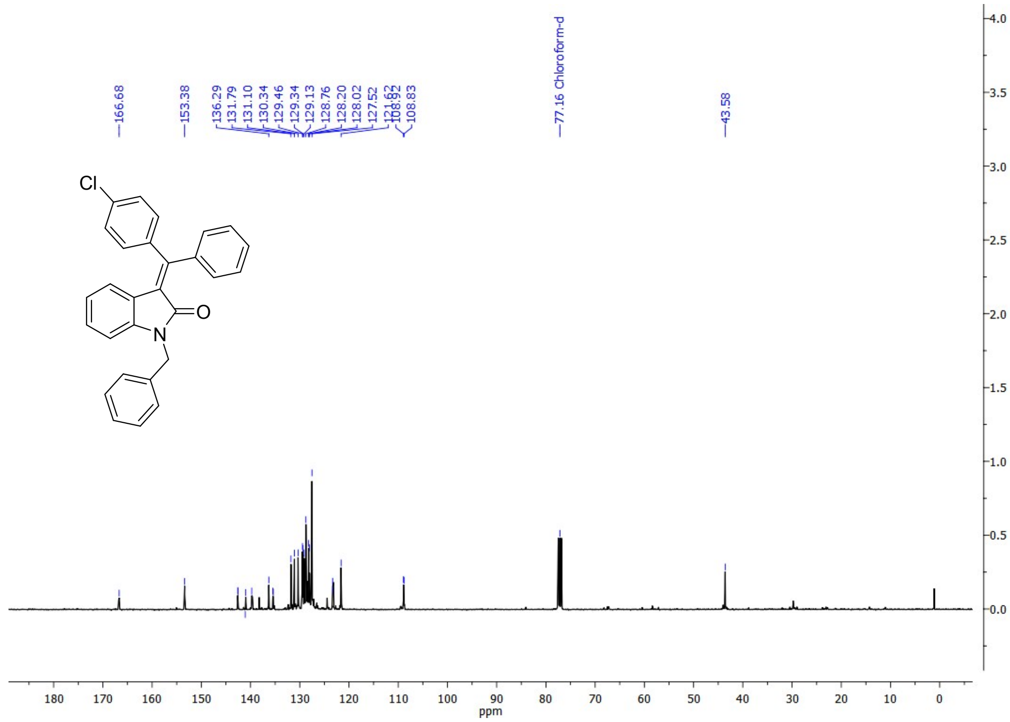
^{1}H NMR of Compound 6f



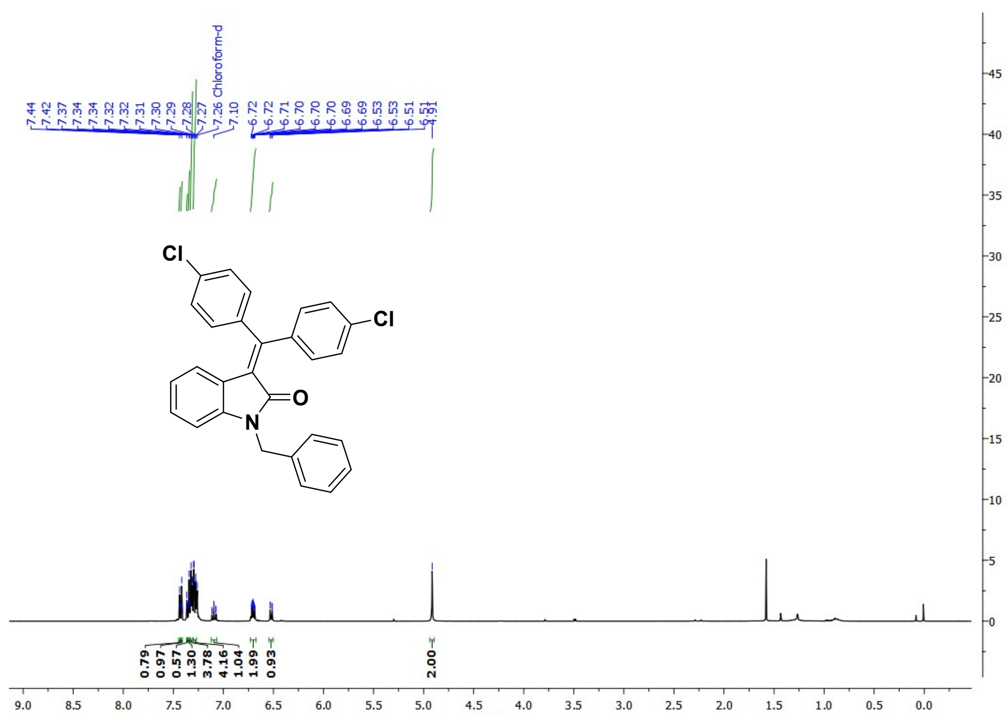
^{13}C NMR of Compound 6f



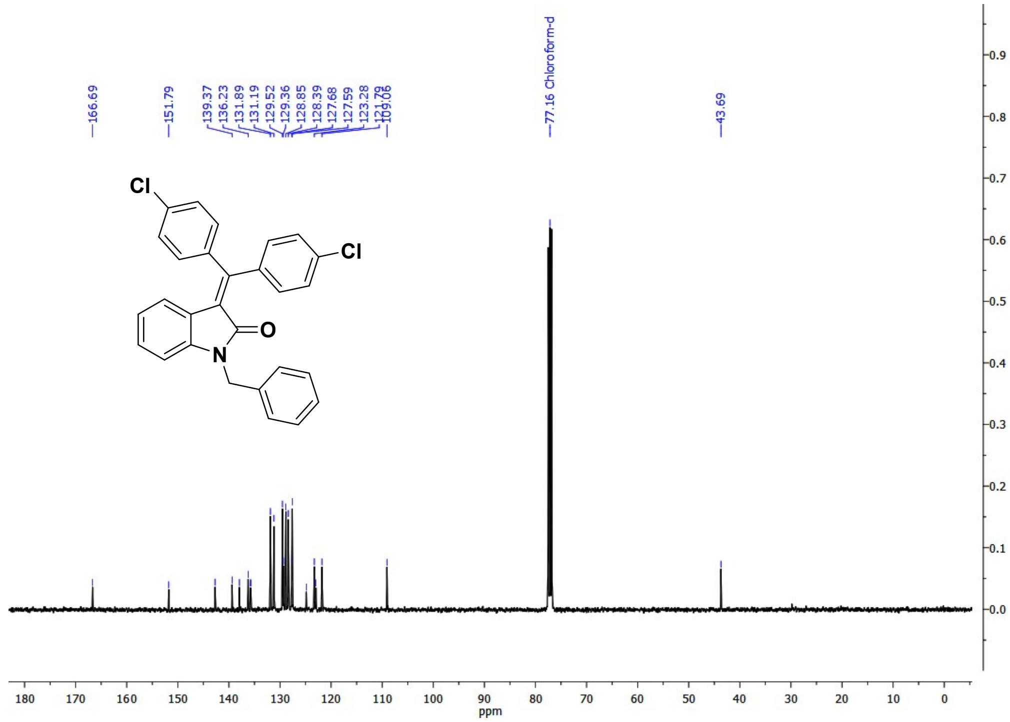
^{1}H NMR of *E* isomer of Compound 6g



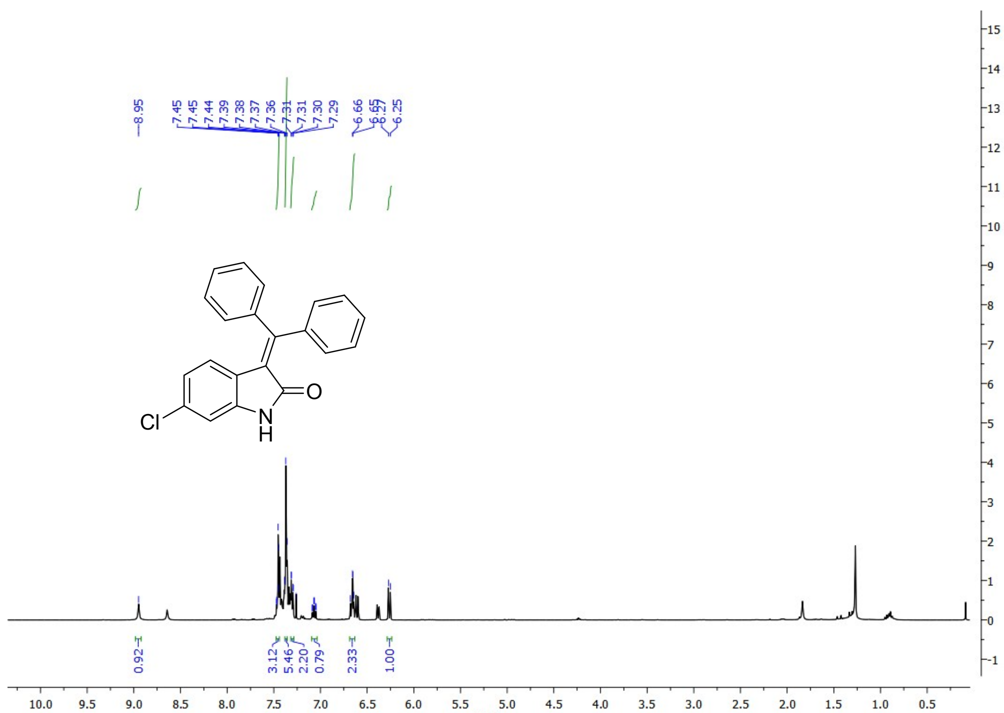
^{13}C NMR of *E* isomer of Compound 6g



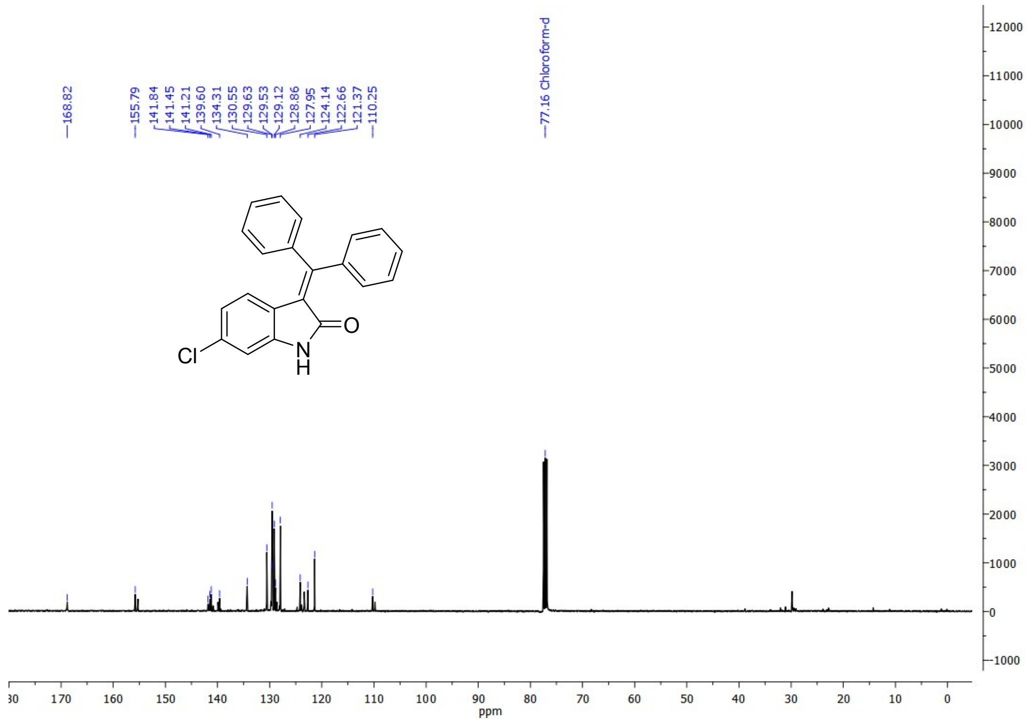
^{1}H NMR of Compound 6h



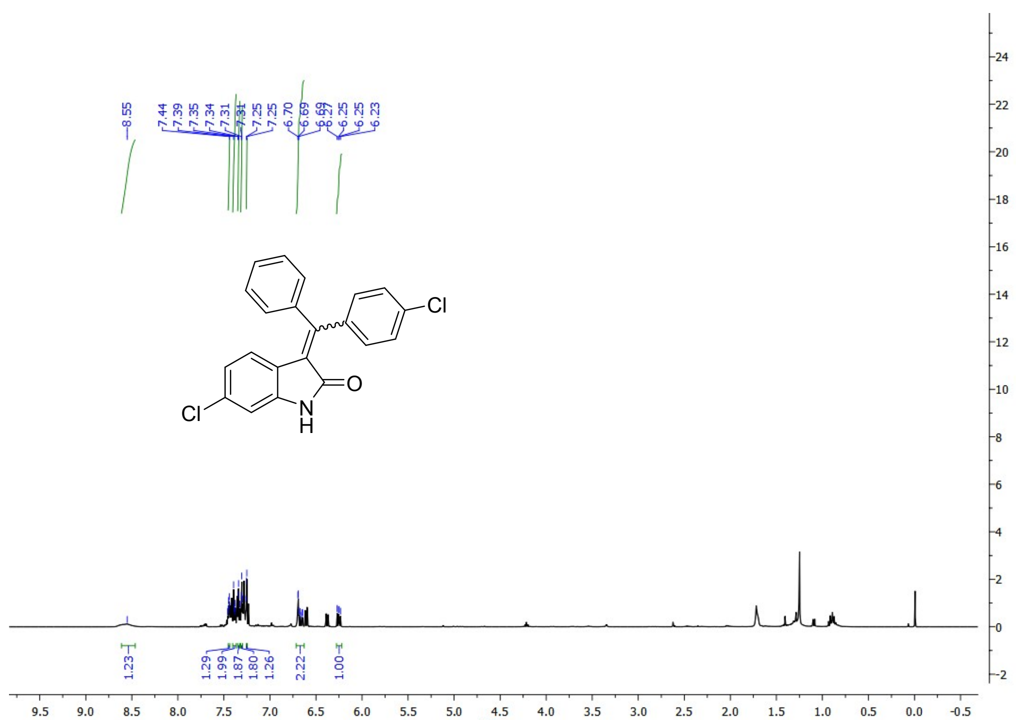
^{13}C NMR of Compound 6h



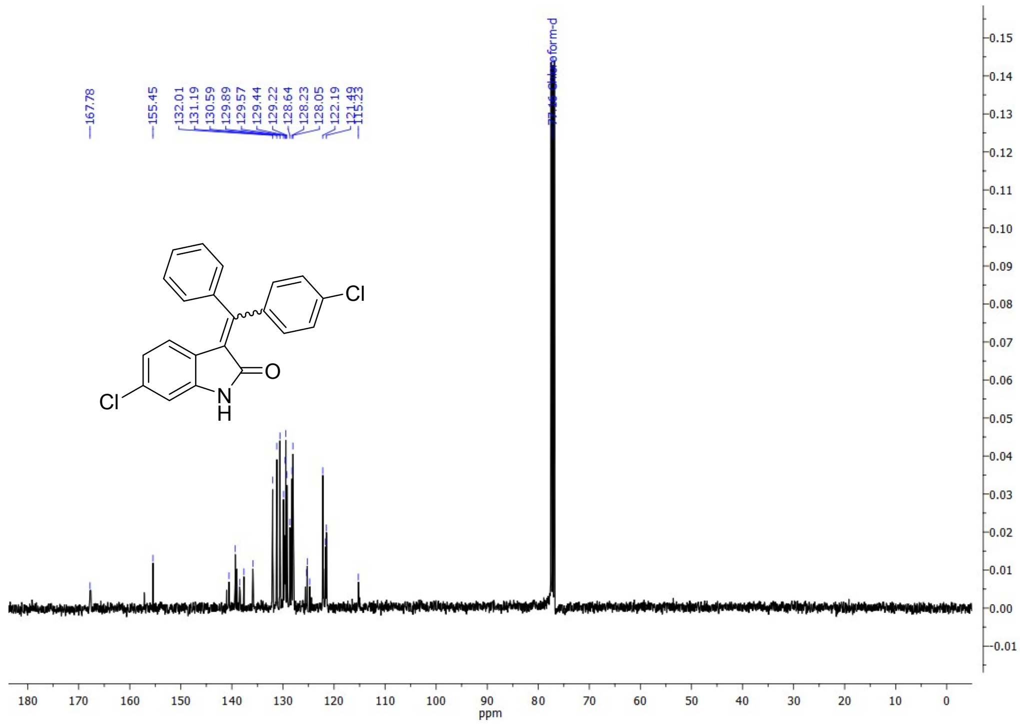
^{1}H NMR of compound 6i



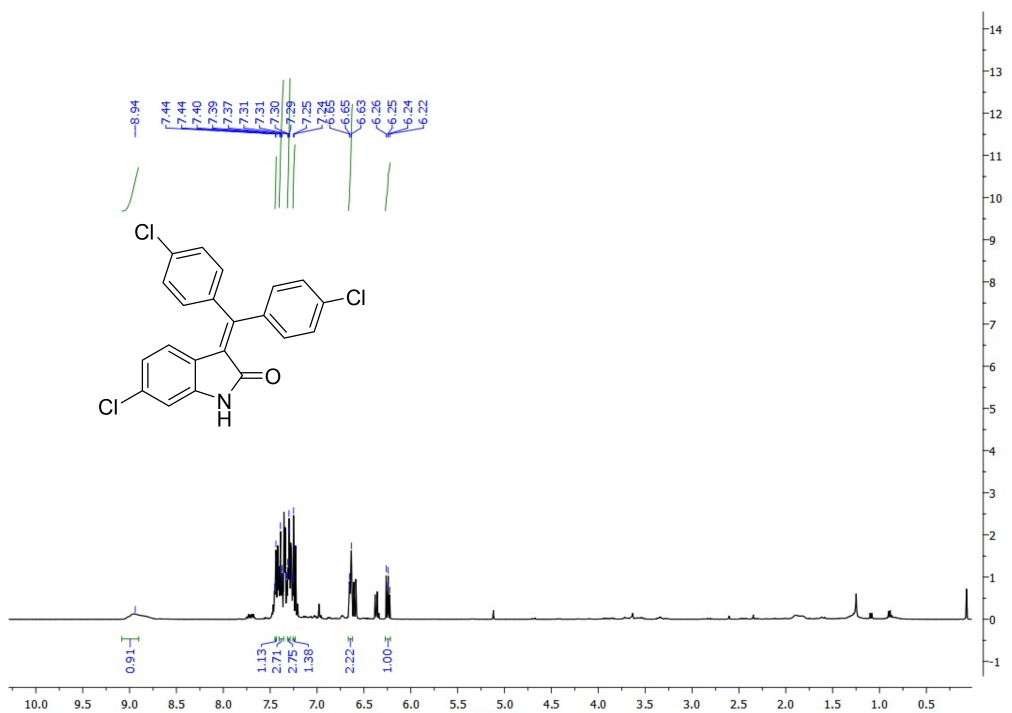
^{13}C NMR of Compound 6i



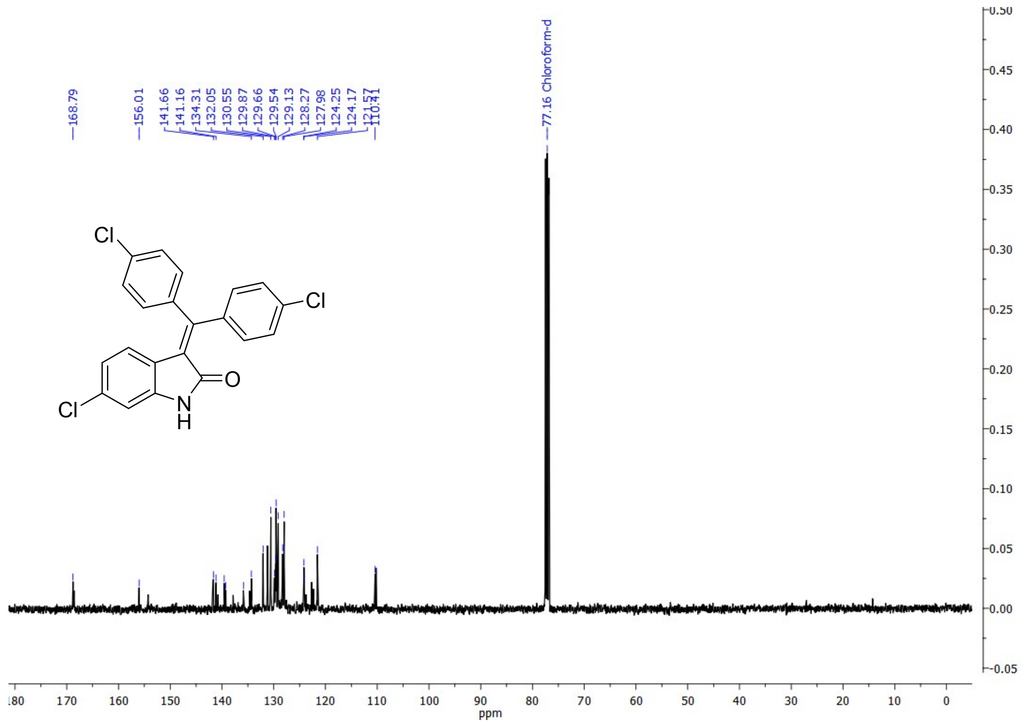
^{1}H NMR of Compound 6j (*E:Z* mixture)



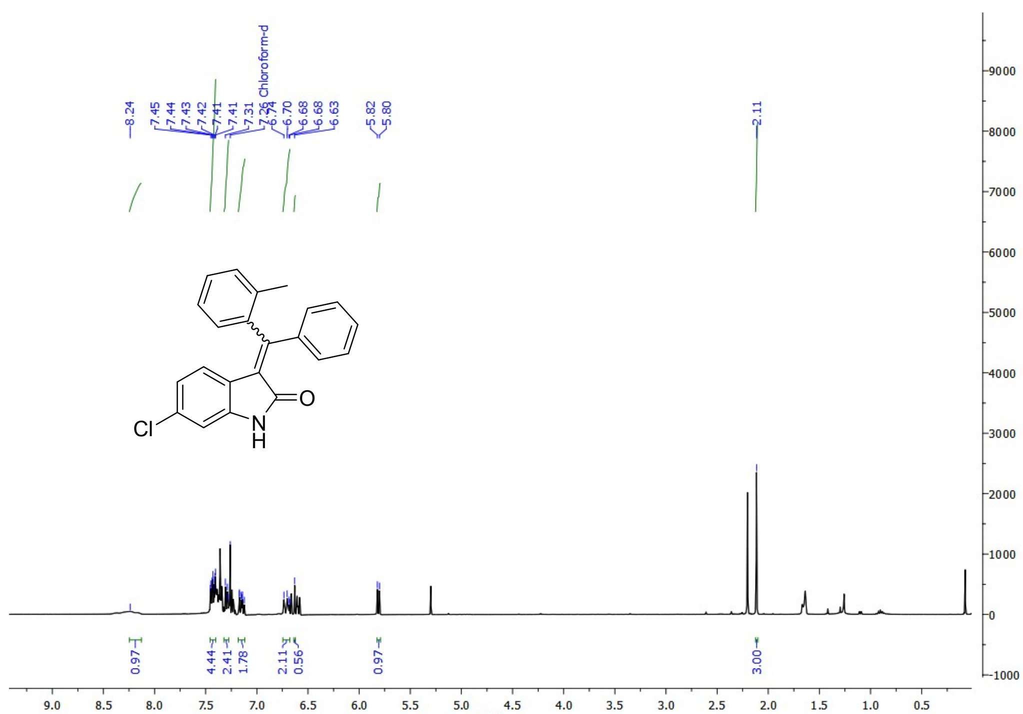
^{13}C NMR of Compound 6j (*E:Z* mixture)



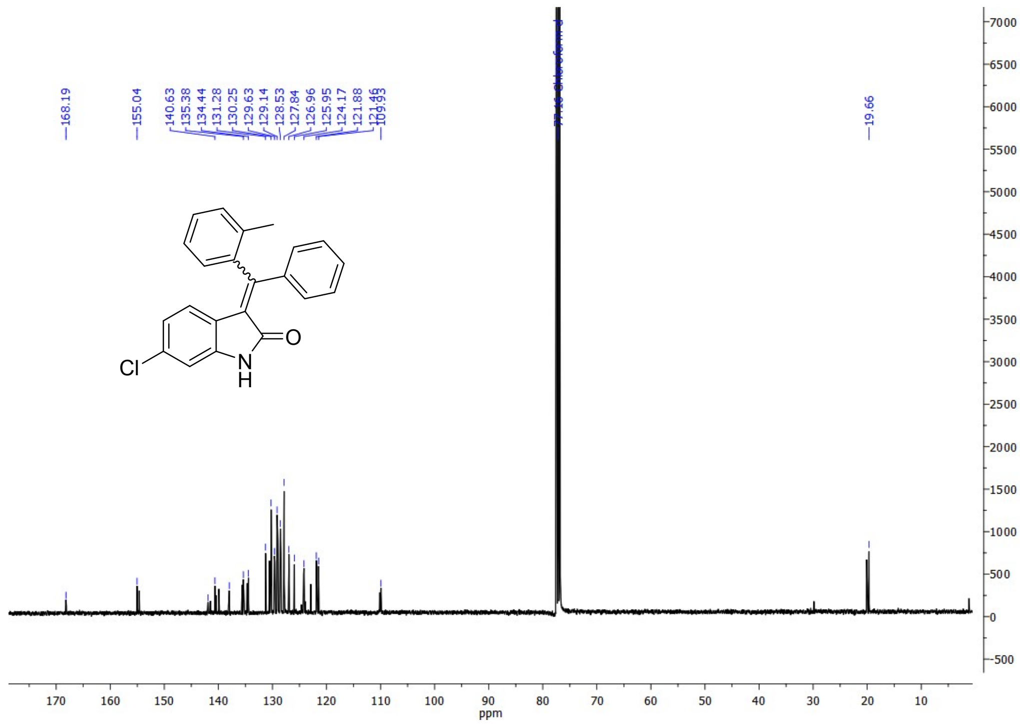
^{1}H NMR of Compound 6k



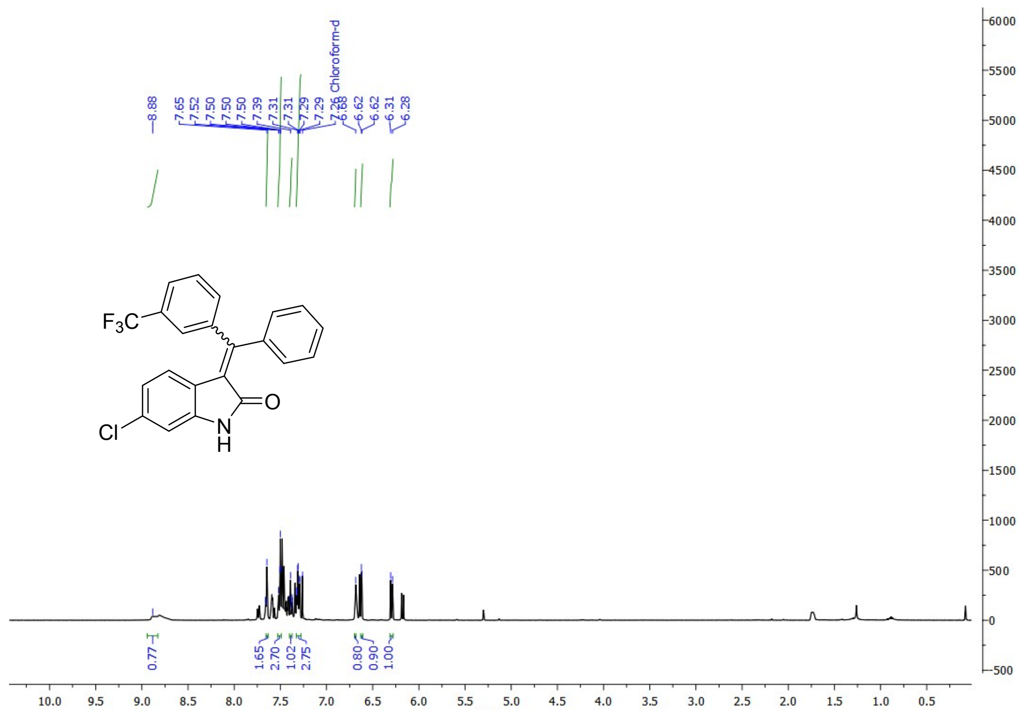
^{13}C NMR of Compound 6k



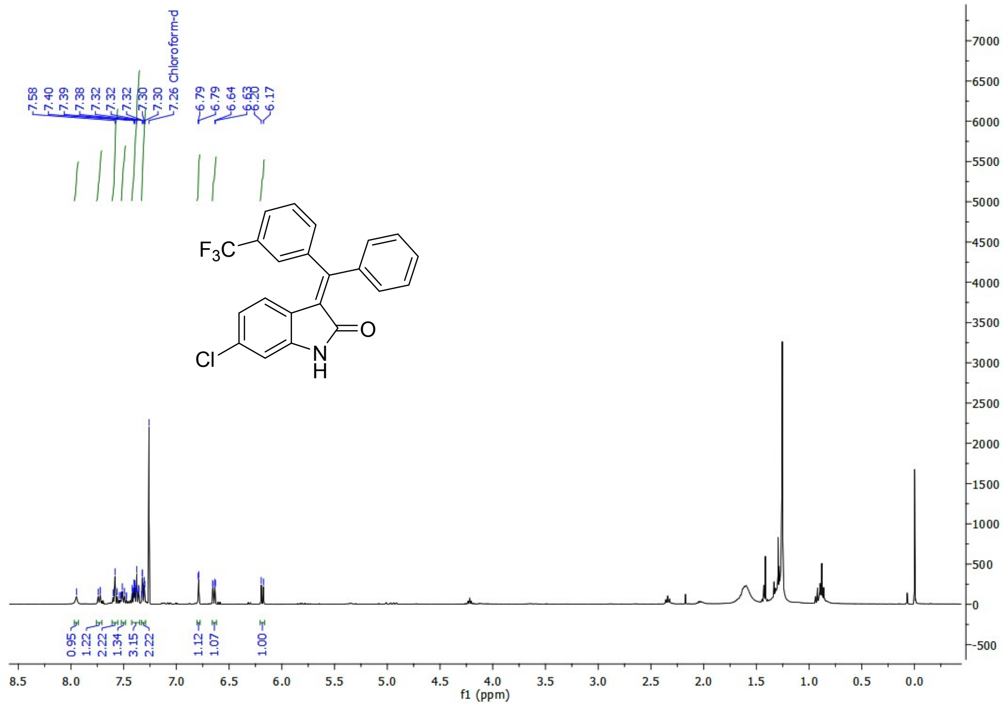
^{1}H NMR of Compound 6l (*E:Z* mixture)



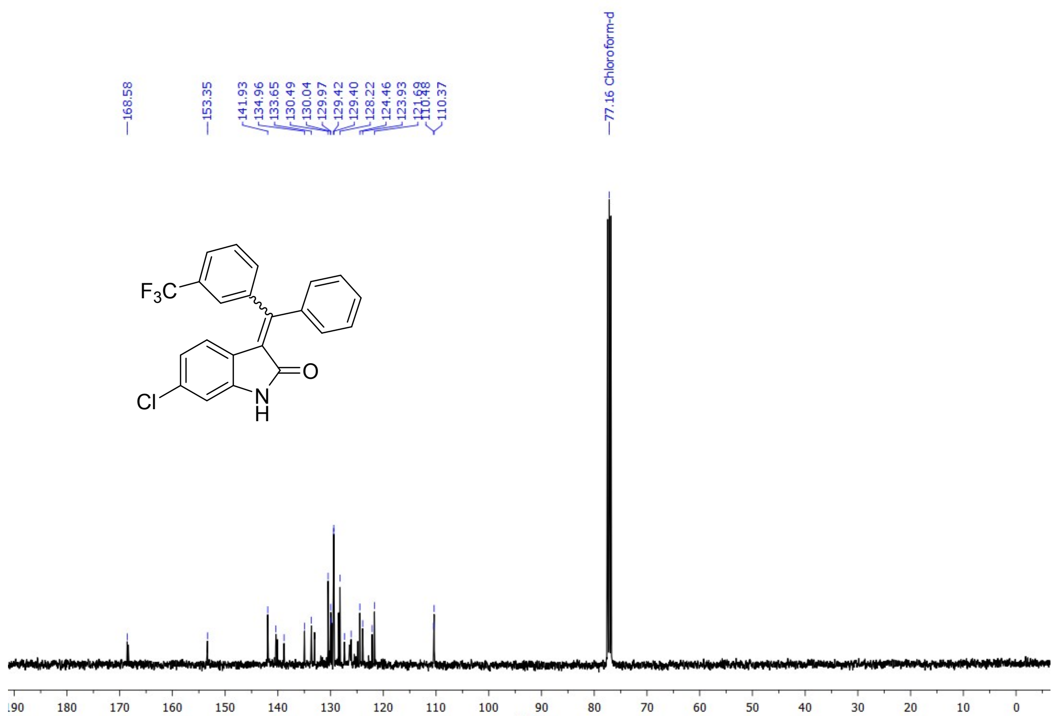
^{13}C NMR of Compound 6l (*E:Z* mixture)



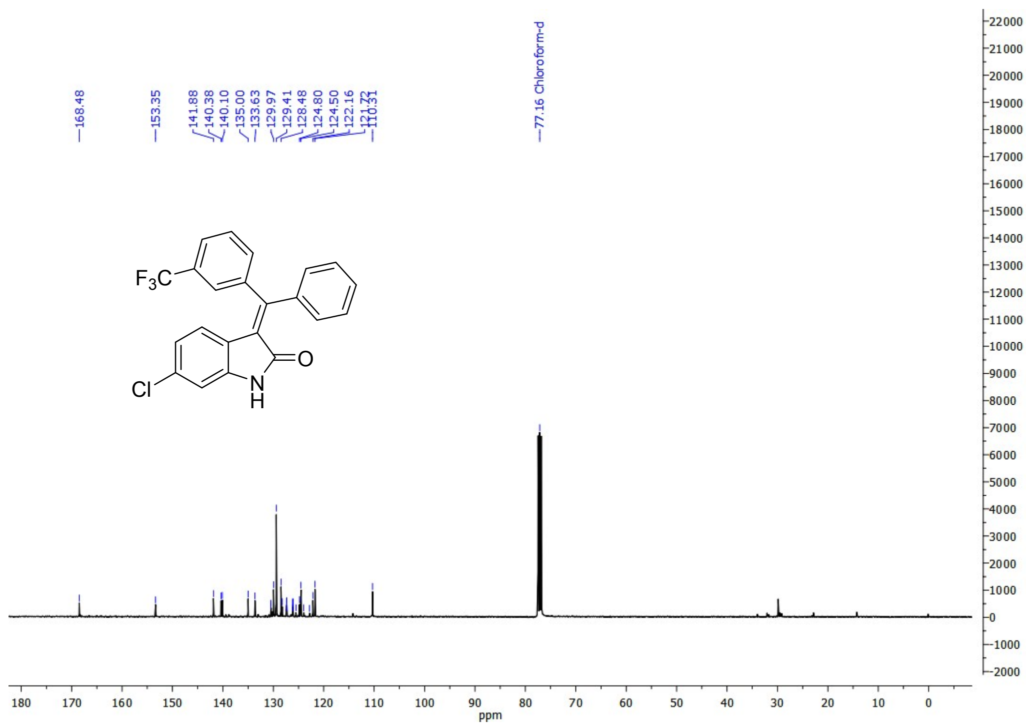
^{1}H NMR of Compound 6m (*E:Z* mixture)



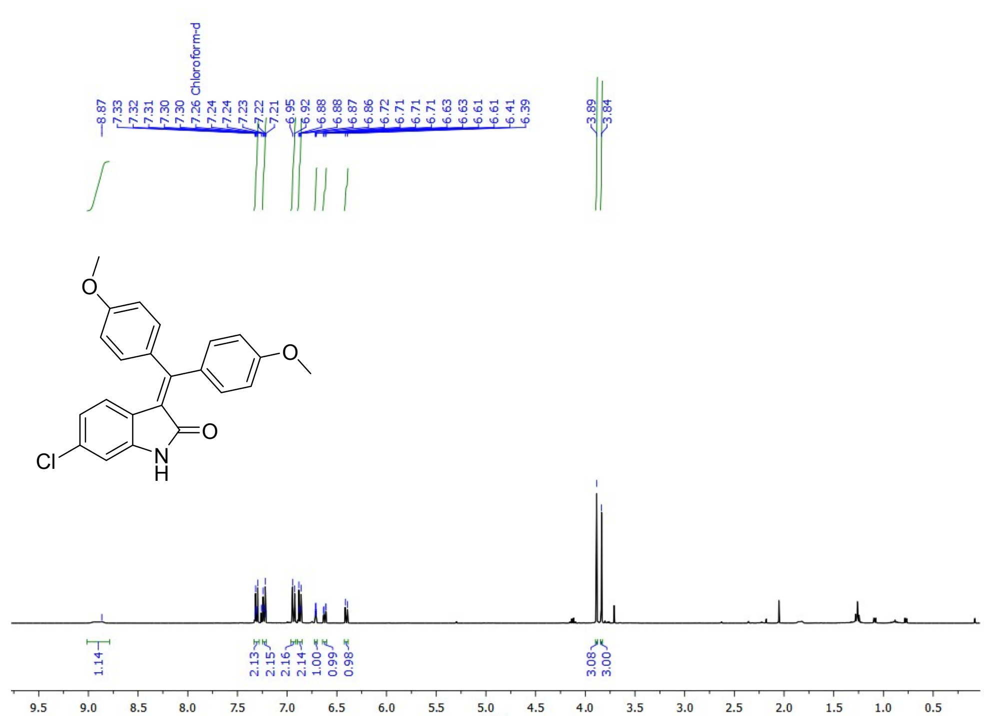
^{1}H NMR of *E* isomer of Compound 6m



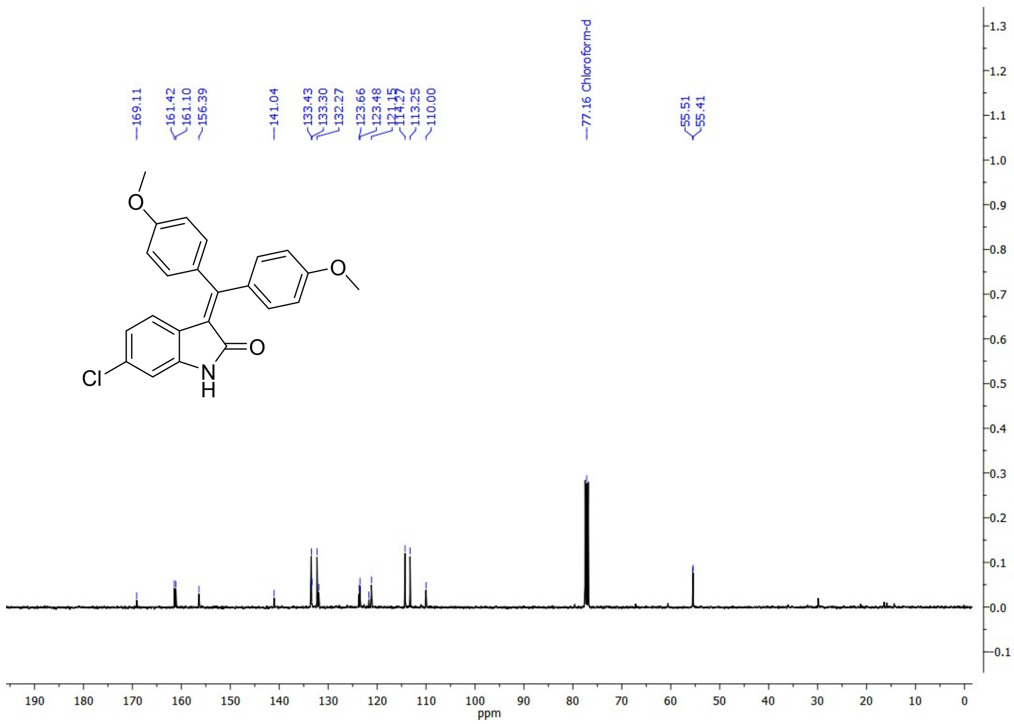
^{13}C NMR of Compound 6m (*E:Z* mixture)



^{13}C NMR of *E* isomer of Compound 6m

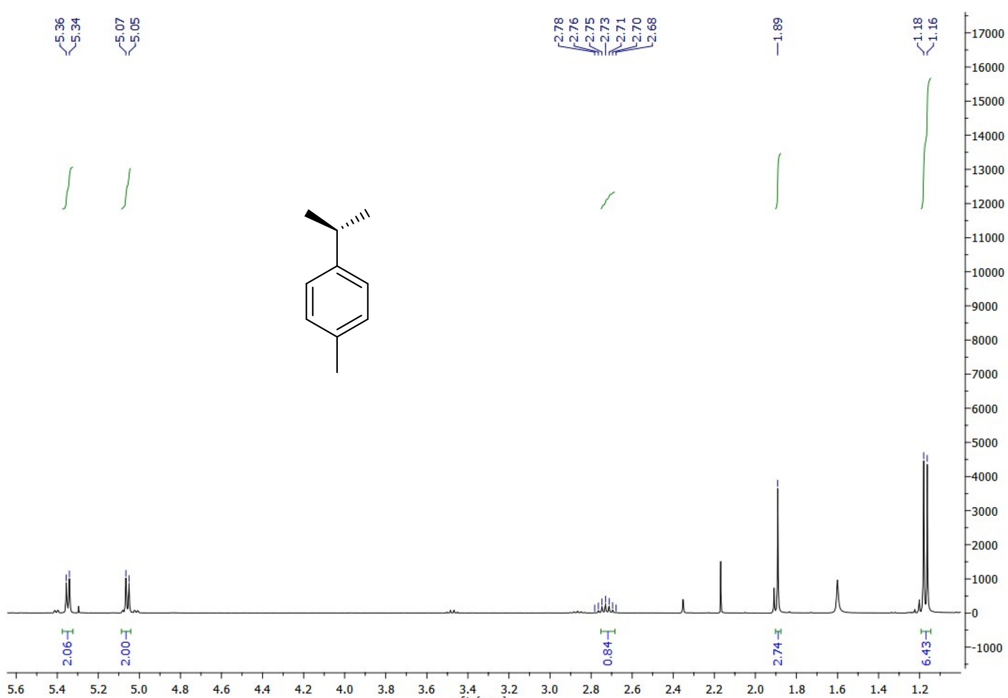


^{1}H NMR of Compound 6n

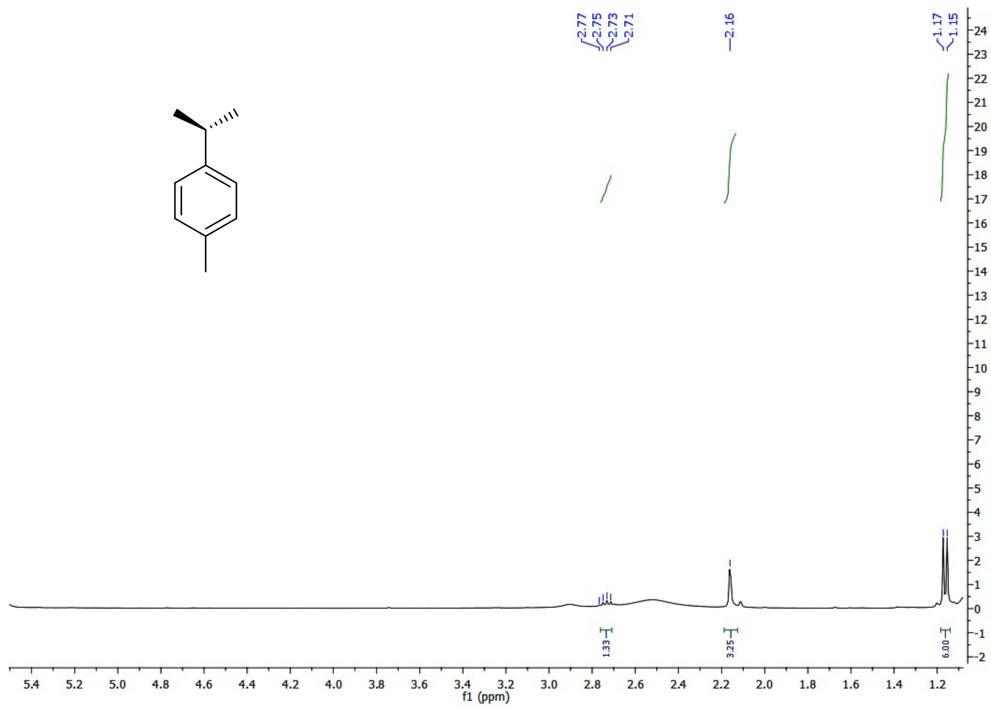


^{13}C NMR of Compound 6n

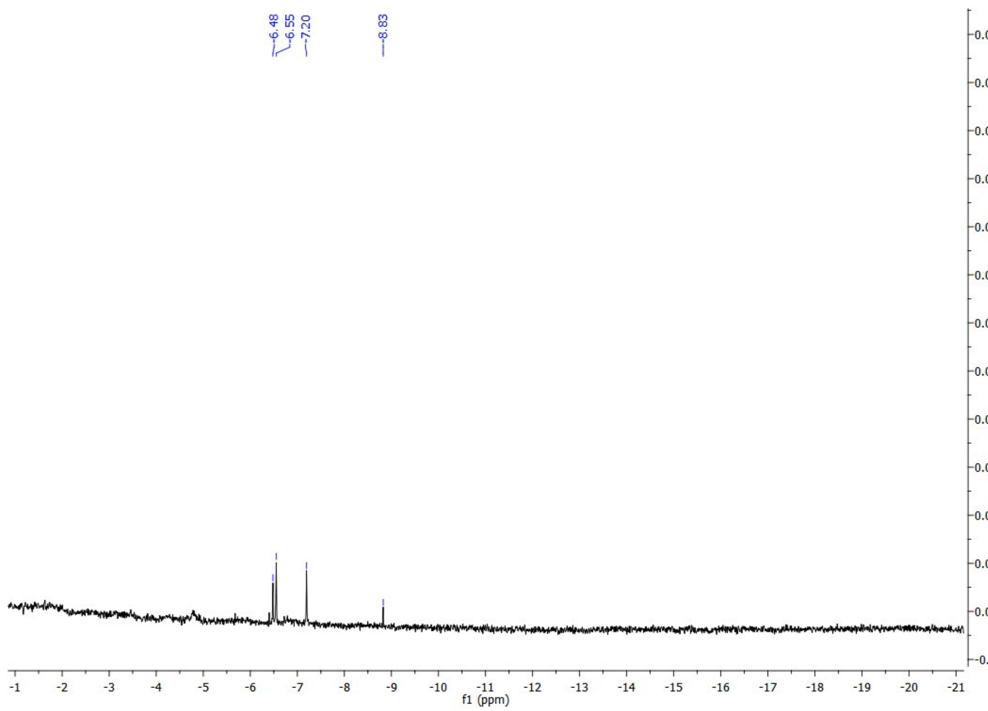
8. Copies of NMR spectra for the mechanistic studies:



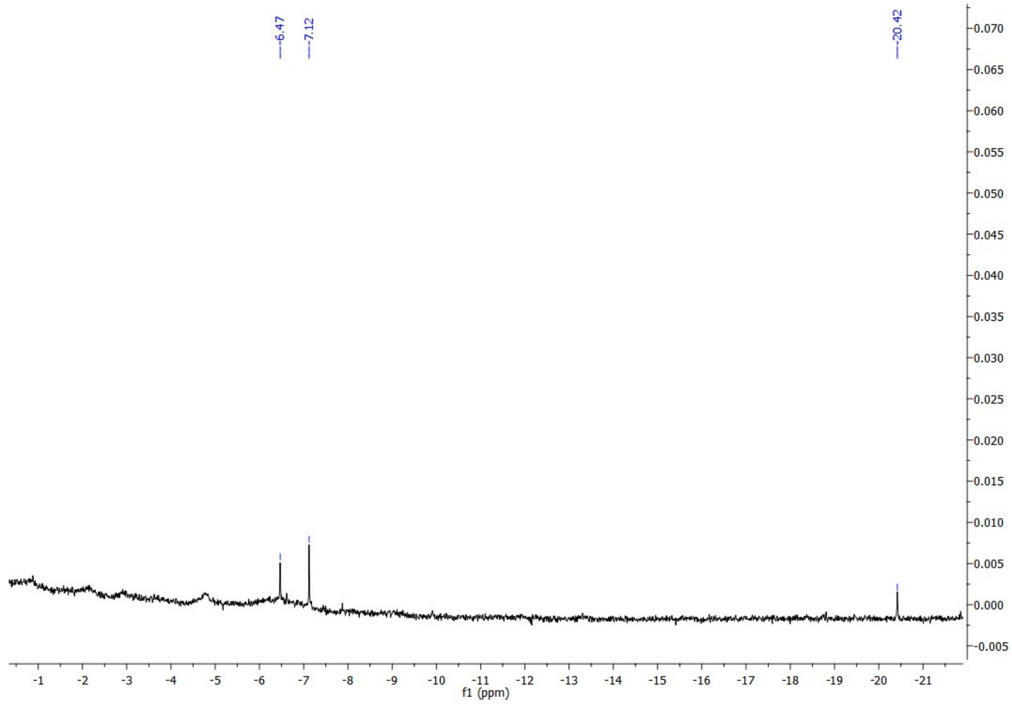
^1H NMR spectra of *p*-cymene in Ru-NHC complex 4a in $CDCl_3$ before reaction



^{1}H NMR spectra of *p*-cymene in Ru-NHC complex 4a in benzene-d$_6$ after reaction (Absence of aromatic protons of *p*-cymene after dissociation from Ru-complex)

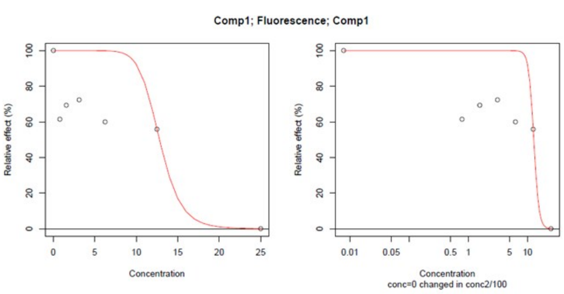


Detection of Ru-H by ^{1}H NMR (in benzene-d$_6$) of Ru-NHC complex 4a after the reaction at 80 ^{o}C (^{1}H NMR spectrum of hydride region of reaction mixture for olefination)



Detection of Ru-H by ^{1}H NMR (in benzene-d_6) of Ru-NHC complex 4a after the reaction at 110 ^{o}C (^{1}H NMR spectrum of hydride region of reaction mixture for olefination)

9. IC_n Estimation plot

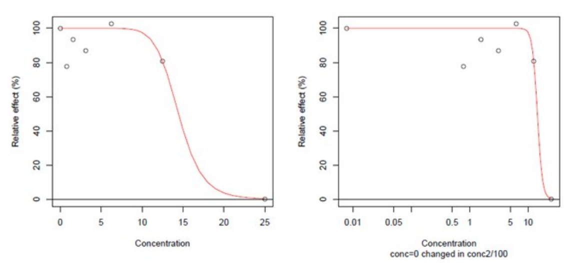


ICn Estimations

	Estimation	Standard error	Lower CI95%	Upper CI95%	Ratio CI
IC50	12.8	1.46	9.23	16.37	1.77
IC90	15.95	1.82	11.49	20.4	1.77
IC99	20.27	2.31	14.61	25.93	1.77
Gamma	10	–	–	–	–

Remember that gamma was fixed to 10

IC_n values of compound **3b**

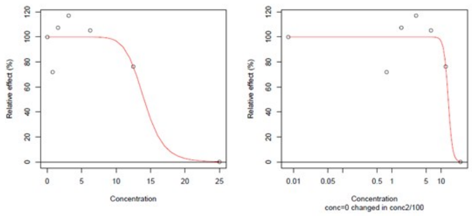


ICn Estimations

	Estimation	Standard error	Lower CI95%	Upper CI95%	Ratio CI
IC50	14.44	1.02	11.95	16.93	1.42
IC90	17.99	1.27	14.89	21.09	1.42
IC99	22.86	1.61	18.92	26.8	1.42
Gamma	10	–	–	–	–

Remember that gamma was fixed to 10

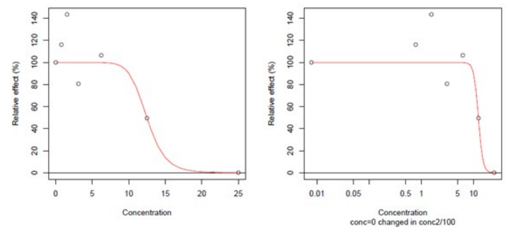
IC_n values of compound **3c**



ICn Estimations

	Estimation	Standard error	Lower CI95%	Upper CI95%	Ratio CI
IC50	14.05	1.08	11.41	16.7	1.46
IC90	17.51	1.35	14.21	20.8	1.46
IC99	22.25	1.71	18.06	26.44	1.46
Gamma	10	-	-	-	-

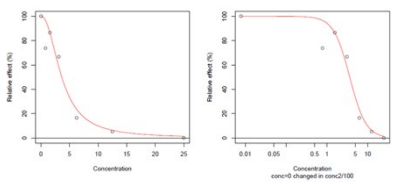
IC_n values of compound **3e**



ICn Estimations

	Estimation	Standard error	Lower CI95%	Upper CI95%	Ratio CI
IC50	12.48	1.03	9.95	15	1.51
IC90	15.54	1.28	12.4	18.69	1.51
IC99	19.75	1.63	15.76	23.75	1.51
Gamma	10	-	-	-	-

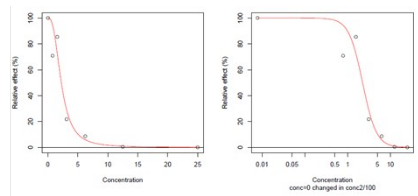
IC_n values of compound **3j**



ICn Estimations

	Estimation	Standard error	Lower CI95%	Upper CI95%	Ratio CI
IC50	3.64	0.57	2.19	5.09	2.33
IC90	9.98	0.7	8.26	11.71	1.42
IC99	30.03	0.9	27.84	32.22	1.16
Gamma	2.18	0.65	0.5	3.86	-

IC_n values of compound **6g**



ICn Estimations

	Estimation	Standard error	Lower CI95%	Upper CI95%	Ratio CI
IC50	2.24	0.35	1.34	3.14	2.35
IC90	5.07	0.44	4	6.14	1.54
IC99	12.37	0.56	11	13.73	1.25
Gamma	2.69	0.98	0.18	5.2	-

IC_n values of compound **6h**

10. References

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