Borane catalyzed transesterification of *tert*-butyl esters using α-aryl α-diazoesters

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Supporting Information

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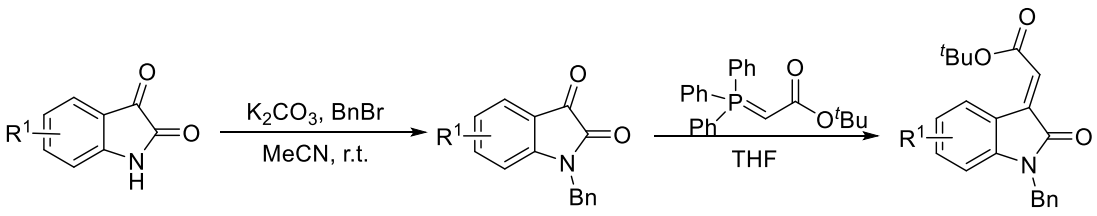
General information

All preparative procedures were performed in an inert atmosphere of dry, deoxygenated (O_2 < 0.5 ppm) argon, using glovebox techniques or standard Schlenk techniques unless otherwise specified. Solvents were stored over activated 3Å molecular sieves following drying procedures. Dichloromethane (DCM) and hexane were purchased from Tedia Company, Inc. Toluene and ethyl ether (Et_2O) were purchased from Tedia Company, Inc. 1,2-Dichloroethane (DCE) was purchased from Adamas-beta. Deuterated solvent ($CDCl_3$) was purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. Methyl phenylacetate was obtained from Energy Chemical. *p*-Tolyacetic acid, *p*-fluorophenylacetic acid, *p*-chlorophenylacetic acid, *p*-bromophenylacetic acid, *p*-*tert*-butylphenlacetic acid, *m*-methylphenylacetic acid, 2-(naphthalen-2-yl)acetic acid, *o*-tolylacetic acid, 2-bromophenylacetic acid and 3,4-dimethylphenylacetic acid were obtained from Aladdin. *p*-Iodophenylacetic acid, *p*-cyanophenylacetic acid, 3-bromophenylacetic acid, 4-methoxyphenylacetic acid, 3,4-(methylenedioxy)phenylacetic acid and *p*-toluenesulfonyl azide were obtained from Adamas-beta. *p*-(Trifluoromethyl)phenylacetic acid was obtained from Innochem. Thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F254 aluminum plates or EMD basic Aluminium Oxide 60 F254 plastic plates. Silicycle Silia-P Flash Silica Gel was used for all column chromatography.

All NMR spectra were collected at 298 K on Bruker 500 spectrometers in 5 mm diameter NMR tubes. ^1H chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 7.26 ppm). Data are reported as: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets), coupling constants (Hz), integration and assignment. $^{13}C\{^1H\}$ chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 77.00 ppm). ^{19}F NMR spectra were measured at 376 MHz and $CFCl_3$ (-63.2 ppm) was used as an external standard. Departmental facilities were used for mass spectrometry (FTMS ESI)

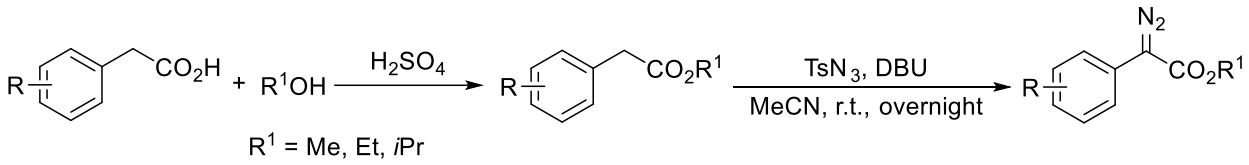
Preparation of 3-alkenyl-oxindoles[1]



Step 1: To an MeCN solution (0.10 M) of isation (1.0 equiv.) was added K_2CO_3 (3.0 equiv.) and benzyl bromide (1.5 equiv.) at room temperature. The mixture was heat at reflux overnight. The mixture was cooled, filtered and concentrated. The residue was purified by recrystallization.

Step 2: To a stirred solution of *tert*-butyl 2-(triphenylphosphoranylidene) acetate (11 mmol, 1.1 equiv.) in anhydrous THF (10 mL), the *N*-benzylindoline-2,3-dione (10 mmol, 10 mmol) was added at 0 °C. The mixture was stirred at the same temperature until the reaction was completed monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (ethyl acetate/ petroleum ether = 1:5~1:2). 3-Alkenyl-oxindoles were obtained as a red or orange solid.

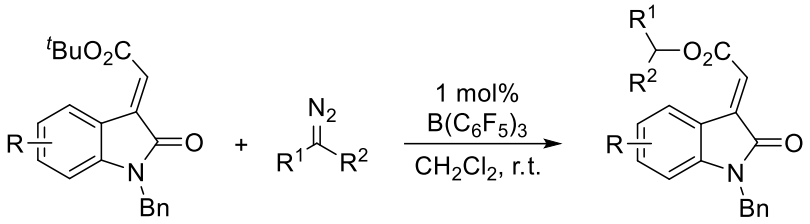
Preparation of α-diazo compounds[2]



Phenylacetic acid derivatives (53.0 mmol) was dissolved in alcohols (80 mL) and concentrated sulfuric acid (0.5 mL) was added. The mixture was refluxed for 15 hours with stirring. Upon cooling the mixture and evaporating the excess alcohols, the mixture was subjected to column chromatography (ethyl acetate/petroleum ether = 1:50), and ester was obtained as a colorless oil.

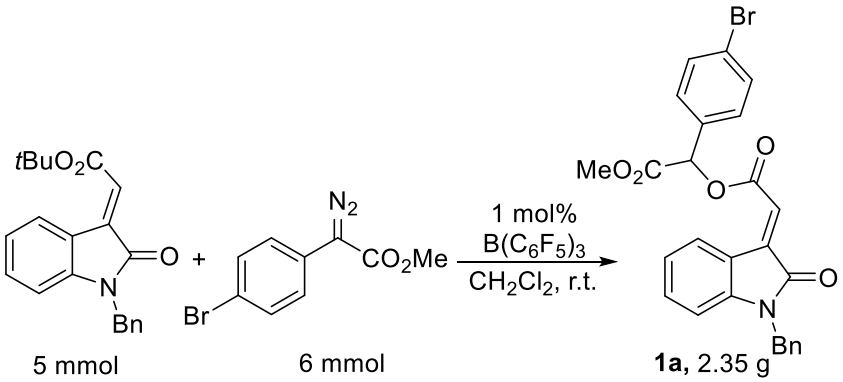
DBU (15.0 mmol) was added to ester (10.0 mmol) and *p*-toluenesulfonyl azide (2.960 g, 15.0 mmol) in MeCN (15 mL). The reaction mixture was stirred overnight. TLC was used to confirm the consumption of the starting materials, and upon so doing, the reaction mixture was quenched with a saturated solution of NH_4Cl (5 mL). An extraction with DCM (3 x 30 mL), washing with brine (3 x 10 mL), drying over $MgSO_4$ was performed, before the mixture was concentrated under pressure to the crude product. Purification by column chromatography (ethyl acetate/petroleum ether = 1:100) gave the α-diazoester as a dark orange oil.

General procedure for catalytic selective carbonate functionality transfer reaction

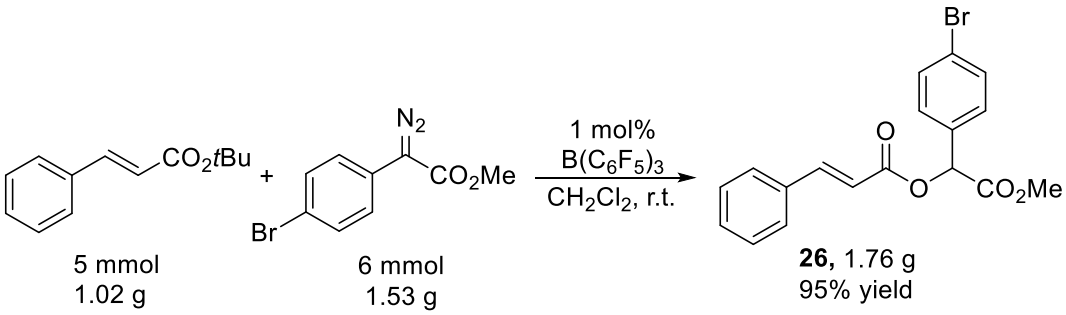


In an inert atmosphere glovebox, to a solution of 3-alkenyl-oxindoles (0.20 mmol, 1 equiv.) and diazomethanes (0.24 mmol, 1.2 equiv.) in CH_2Cl_2 (1.2 mL) was added a solution of $B(C_6F_5)_3$ (1.0 mg, 0.002 mmol, 1 mol%) in CH_2Cl_2 (0.8 mL). The reaction was stirred for the specified time at room temperature. The residue was purified by flash chromatography (eluent: ethyl acetate/ petroleum ether = 1:20~1:6) on silica gel to afford the desired products.

Typical procedure for gram-scale version of selective carbonate functionality transfer reaction



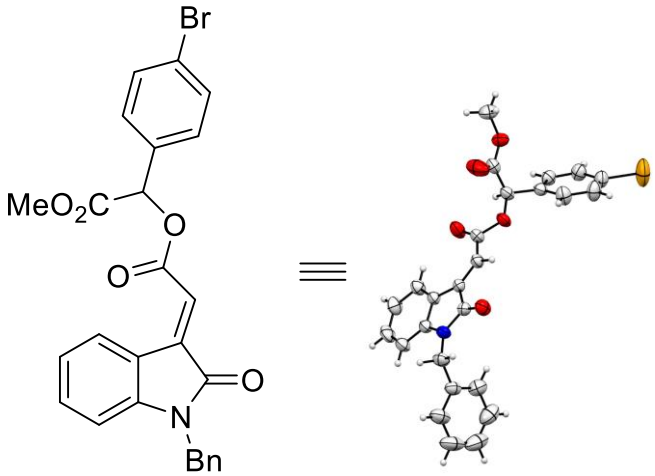
In an inert atmosphere glovebox, a Schlenk flask (100 mL) was charged with *tert*-butyl (*E*)-2-(1-benzyl-2-oxoindolin-3-ylidene)acetate (1.68 g, 5.0 mmol). Next, methyl 4-bromophenyldiazoacetate (1.53 g, 6.0 mmol) and DCM (40 mL) were added. Then, a solution of $B(C_6F_5)_3$ (0.025 g, 0.05 mmol) in DCM (10 mL) was added to the mixture under stirring. The reaction mixture was stirred at room temperature for 24 hours. The residue was purified by flash chromatography (eluent: ethyl acetate/petroleum ether = 1:20~1:6) on silica gel to afford the carbonate functionality transfer product **1a** as an orange solid (2.35 g, 93% yield).

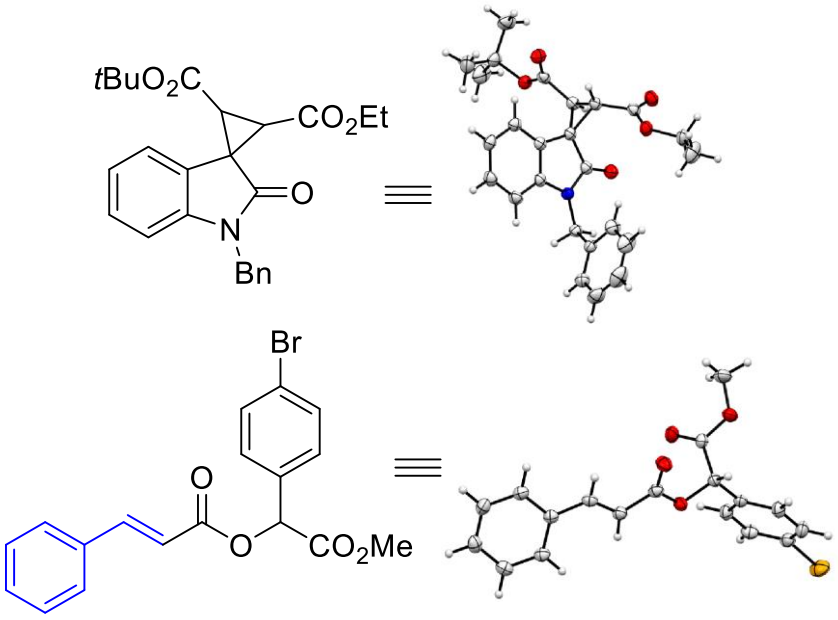


In an inert atmosphere glovebox, a Schlenk flask (100 mL) was charged with *tert*-butyl cinnamate (1.02 g, 5.0 mmol). Next, methyl 4-bromophenyldiazoacetate (1.530 g, 6.0 mmol) and DCM (40 mL) were added. Then, a solution of $B(C_6F_5)_3$ (0.025 g, 0.05 mmol) in DCM (10 mL) was added to the mixture under stirring. The reaction mixture was stirred at room temperature for 24 hours. The residue was purified by flash chromatography (eluent: ethyl acetate/petroleum ether = 1:50~1:20) on silica gel to afford the carbonate functionality transfer product **26** as a white solid (1.76 g, 95% yield).

Single crystal X-ray crystallography

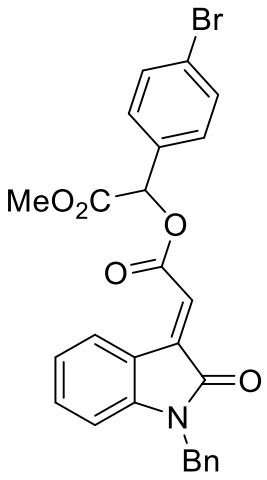
X-ray crystallographic data were collected on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, μKα = 12.894 mm^{-1}) micro-focus X-ray sources at 161 K. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS and SHELXL[3] within OLEX2.[4]





Characterization data

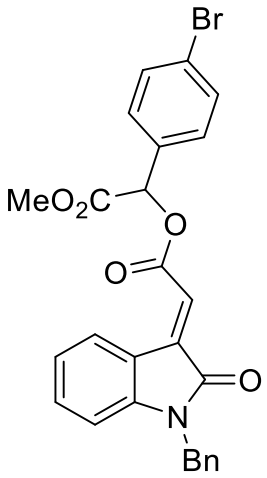
Methyl(*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl)acetate 1



Prepared according to the general procedure (24 h). The title compound **1** was obtained as an orange solid in 99% yield (100.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.56 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 6H), 7.12 (s, 1H), 7.02 (td, *J* = 8.5 Hz, 1.0 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.09 (s, 1H), 4.95 (s, 2H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.43, 167.29, 164.59, 145.36, 139.39, 135.23, 132.89, 132.35, 132.03, 129.17, 129.06, 128.80, 127.73, 127.17, 123.63, 122.88, 120.61, 119.70, 109.22, 74.33, 52.89,

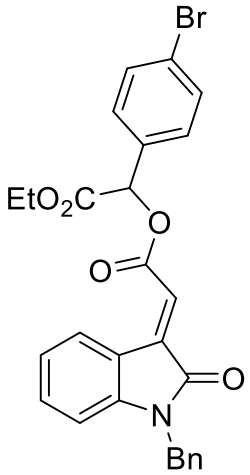
43.82. HRMS (ESI, m/z): Calcd. for $C_{26}H_{21}Br^{78.9183}NO_5^+$, ([M+H]$^+$): 506.0598; Found: 506.0601; $C_{26}H_{21}Br^{80.9163}NO_5^+$, ([M+H]$^+$): 508.0578; Found: 508.0579.

Gram-scale methyl(*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 1



^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.56 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.25 (m, 6H), 7.13 (s, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 3.0 Hz, 1H), 6.09 (s, 1H), 4.95 (d, *J* = 2.0 Hz, 2H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.42, 167.25, 164.57, 145.31, 139.37, 135.19, 132.88, 132.30, 132.00, 129.15, 129.03, 128.77, 127.71, 127.15, 123.61, 122.87, 120.58, 119.66, 109.20, 74.30, 52.89, 43.77.

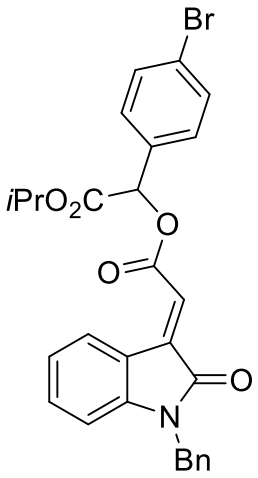
Ethyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl)acetate 2



Prepared according to the general procedure (24 h). The title compound **2** was obtained as an orange solid in 96% yield (98.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.47 (d, *J* = 8.0 Hz, 1H), 7.48

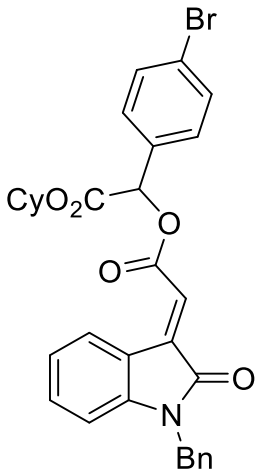
(d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 6H), 7.04 (s, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 5.98 (s, 1H), 4.86 (s, 2H), 4.22 – 4.10 (m, 2H), 1.71 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 167.94, 167.34, 164.62, 145.34, 139.28, 135.25, 132.85, 132.51, 131.99, 129.15, 129.04, 128.81, 127.74, 127.18, 123.55, 122.89, 120.76, 119.74, 109.22, 74.50, 62.08, 43.84, 13.96. HRMS (ESI, m/z): Calcd. for $C_{27}H_{23}Br^{78.9183}NO_5^+$, ($[M+H]^+$): 520.0754; Found: 520.0758; $C_{27}H_{23}Br^{80.9163}NO_5^+$, ($[M+H]^+$): 522.0734; Found: 522.0736.

Isopropyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl)acetate 3



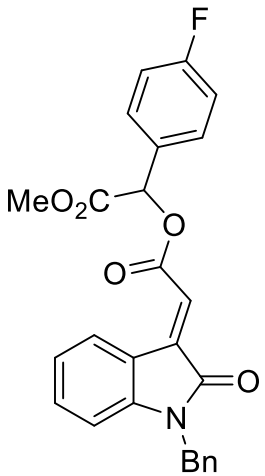
Prepared according to the general procedure (24 h). The title compound **3** was obtained as an orange solid in 96% yield (103.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.35 – 7.27 (m, 6H), 7.12 (s, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 5.12 – 5.06 (m, 1H), 4.95 (s, 2H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 167.45, 167.38, 164.63, 145.34, 139.18, 135.27, 132.82, 132.64, 131.96, 129.10, 129.03, 128.82, 127.75, 127.20, 123.46, 122.90, 120.87, 119.76, 109.22, 74.70, 69.94, 43.85, 21.61, 21.38. HRMS (ESI, m/z): Calcd. for $C_{28}H_{25}Br^{78.9183}NO_5^+$, ($[M+H]^+$): 534.0911; Found: 534.0914; $C_{28}H_{25}Br^{80.9163}NO_5^+$, ($[M+H]^+$): 536.0890; Found: 536.0893.

Cyclohexyl (E)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl)acetate 4



Prepared according to the general procedure (24 h). The title compound **4** was obtained as an orange solid in 98% yield (113.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.47 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.16 (m, 6H), 7.04 (s, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 4.86 (s, 2H), 4.81 – 4.75 (m, 1H), 1.82 – 1.76 (m, 1H), 1.67 – 1.62 (m, 1H), 1.51 – 1.46 (m, 1H), 1.45 – 1.38 (m, 2H), 1.33 – 1.13 (m, 5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.35, 167.33, 164.60, 145.30, 139.15, 135.25, 132.80, 132.75, 131.91, 129.08, 129.03, 128.79, 127.73, 127.18, 123.41, 122.88, 120.85, 119.73, 109.19, 74.67, 74.51, 43.83, 31.22, 30.97, 25.12, 23.37, 23.24. HRMS (ESI, m/z): Calcd. for $C_{31}H_{29}Br^{78.9183}NO_5^+$, ($[M+H]^+$):574.1224; Found: 574.1225; $C_{31}H_{29}Br^{80.9163}NO_5^+$, ($[M+H]^+$): 576.1203; Found: 576.1204.

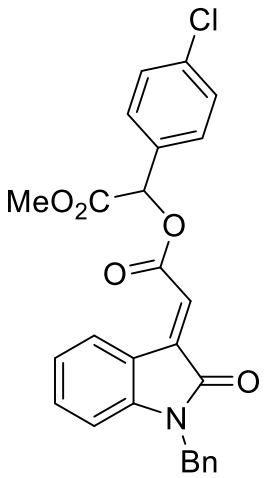
Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-fluorophenyl)acetate 5



Prepared according to the general procedure (24 h). The title compound **5** was obtained as an orange solid in 91% yield (81.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.67 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.47 – 7.37 (m, 6H), 7.25 – 7.22 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5

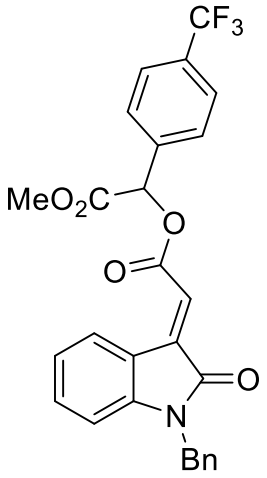
Hz, 1H), 6.22 (s, 1H), 5.07 (s, 2H), 3.90 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.75, 167.36, 164.70, 163.27 (d, J_{C-F} = 249.2 Hz), 145.37, 139.32, 135.27, 132.87, 129.56 (d, J_{C-F} =8.6 Hz), 129.27 (d, J_{C-F} = 3.3 Hz), 129.08, 128.83, 127.76, 127.20, 122.91, 120.80, 119.76, 115.92 (d, J_{C-F} = 21.8 Hz), 109.24, 74.36, 52.86, 43.85. $^{19}F\{^{1}H\}$ NMR (471 MHz, CDCl3), δ: -111.61. HRMS (ESI, m/z): Calcd. for $C_{26}H_{21}FNO_5^+$, ($[M+H]^+$):446.1398; Found: 446.1397

Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-chlorophenyl)acetate 6



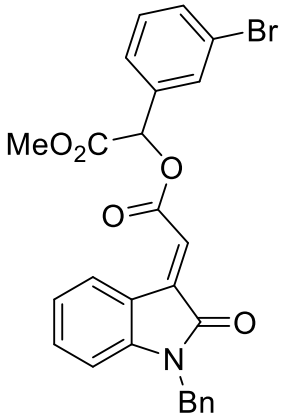
Prepared according to the general procedure (24 h). The title compound **6** was obtained as an orange solid in 96% yield (89.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.27 (m, 6H), 7.12 (s, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.10 (s, 1H), 4.95 (s, 2H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.56, 167.37, 164.67, 145.41, 139.43, 135.49, 135.27, 132.92, 131.87, 129.12, 128.95, 128.85, 127.78, 127.21, 122.94, 120.72, 119.77, 109.26, 74.33, 52.93, 43.88. HRMS (ESI, m/z): Calcd. for $C_{26}H_{21}ClNO_5^+$, ($[M+H]^+$):462.1103; Found: 462.1104.

Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-(trifluoromethyl)phenyl) acetate 7



Prepared according to the general procedure (24 h). The title compound **7** was obtained as an orange solid in 90% yield (89.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.48 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 4H), 7.27 – 7.17 (m, 6H), 7.06 (s, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.12 (s, 1H), 4.86 (s, 2H), 3.71 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.20, 167.25, 164.50, 145.40, 139.60, 137.17, 135.21, 132.97, 131.45 (q, $J_{C\text{-}F}$ = 32.6 H), 129.06, 128.79, 127.84, 127.74, 127.17, 125.79 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.74 (q, $J_{C\text{-}F}$ = 272.8 Hz), 122.89, 120.37, 119.67, 109.25, 74.25, 52.98, 43.81. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ: -62.75. HRMS (ESI, m/z): Calcd. for $C_{27}H_{21}F_3NO_5^+$, ([M+H]$^+$):496.1366; Found: 496.1364.

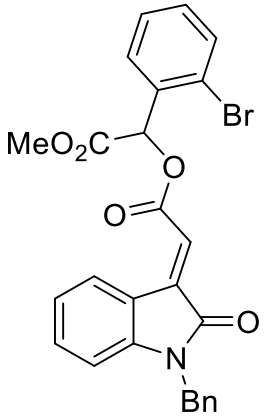
Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(3-bromophenyl)acetate 8



Prepared according to the general procedure (24 h). The title compound **8** was obtained as an orange solid in 99% yield (100.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (d, *J* = 7.5 Hz, 1H), 7.72 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.26 (m, 7H), 7.13 (s, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.09 (s, 1H), 4.95 (s, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.34, 167.30, 164.55, 145.38, 139.47, 135.41, 135.24, 132.92, 132.50,

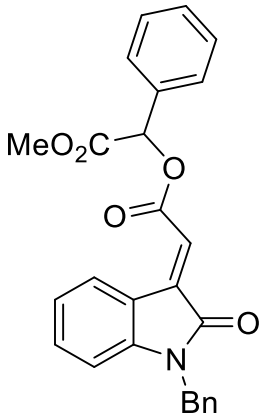
130.53, 130.37, 129.08, 128.81, 127.74, 127.18, 126.13, 122.91, 122.81, 120.57, 119.72, 109.24, 74.17, 52.96, 43.84. HRMS (ESI, m/z): Calcd. for $C_{26}H_{21}Br^{78.9183}NO_5^+$, ([M+H]$^+$): 506.0598; Found: 506.0601; $C_{26}H_{21}Br^{80.9163}NO_5^+$, ([M+H]$^+$): 508.0578; Found: 508.0579.

Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(2-bromophenyl)acetate 9



Prepared according to the general procedure (24 h). The title compound **9** was obtained as an orange solid in 89% yield (89.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.51 (d, *J* = 7.5 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.17 (m, 7H), 7.03 (s, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 4.86 (s, 2H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.42, 167.32, 164.45, 145.30, 139.29, 135.25, 133.37, 133.25, 132.81, 130.90, 129.55, 129.13, 128.78, 127.93, 127.70, 127.15, 124.15, 122.89, 120.77, 119.74, 109.17, 73.80, 52.88, 43.79. HRMS (ESI, m/z): Calcd. for $C_{26}H_{21}Br^{78.9183}NO_5^+$, ([M+H]$^+$): 506.0598; Found: 506.0602; $C_{26}H_{21}Br^{80.9163}NO_5^+$, ([M+H]$^+$): 508.0578; Found: 508.0580.

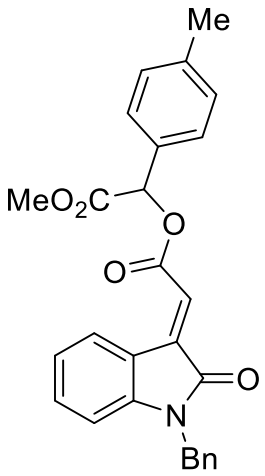
Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-phenylacetate 10



Prepared according to the general procedure (24 h). The title compound **10** was obtained as an orange solid in 93% yield (86.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (d, *J* = 7.5 Hz, 1H), 7.56

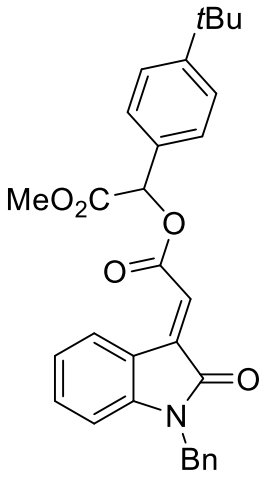
– 7.53 (m, 2H), 7.45 – 7.41 (m, 3H), 7.34 – 7.24 (m, 6H), 7.13 (s, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.12 (s, 1H), 4.94 (s, 2H), 3.77 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.89, 167.40, 164.81, 145.33, 139.14, 135.29, 133.32, 132.78, 129.42, 129.09, 128.87, 128.82, 127.74, 127.63, 127.19, 122.90, 121.04, 119.80, 109.20, 75.11, 52.79, 43.84. HRMS (ESI, m/z): Calcd. for $C_{26}H_{22}NO_5^+$, ($[M+H]^+$):428.1492; Found: 428.1496.

Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(*p*-tolyl)acetate 11



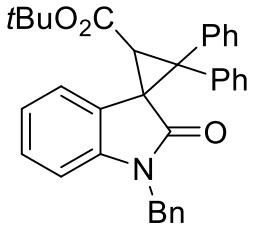
Prepared according to the general procedure (24 h). The title compound **11** was obtained as an orange solid in 90% yield (79.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.22 (m, 8H), 7.12 (s, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 1H), 4.94 (s, 2H), 3.77 (s, 3H), 2.38 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 169.03, 167.41, 164.85, 145.29, 139.47, 139.02, 135.30, 132.73, 130.37, 129.55, 129.08, 128.81, 127.73, 127.62, 127.19, 122.88, 121.18, 119.81, 109.18, 75.01, 52.73, 43.83, 21.23. HRMS (ESI, m/z): Calcd. for $C_{27}H_{24}NO_5^+$, ($[M+H]^+$):442.1649; Found: 442.1650.

Methyl (*E*)-2-(2-(1-benzyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-(*tert*-butyl)phenyl)acetate 12



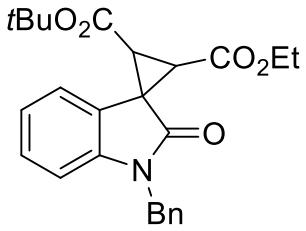
Prepared according to the general procedure (24 h). The title compound **12** was obtained as an orange solid in 87% yield (84.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.56 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.34 – 7.23 (m, 6H), 7.12 (s, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.10 (s, 1H), 4.94 (d, *J* = 3.0 Hz, 2H), 3.77 (s, 3H), 1.34(s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 169.03, 167.40, 164.87, 152.58, 145.30, 139.00, 135.30, 132.72, 130.26, 129.08, 128.81, 127.72, 127.41, 127.18, 125.84, 122.87, 121.18, 119.81, 109.17, 74.98, 52.72, 43.82, 34.68, 31.21. HRMS (ESI, m/z): Calcd. for $C_{30}H_{30}NO_5^+$, ([M+H]$^+$):484.2118; Found: 484.2121.

***tert*-Butyl 1'-benzyl-2'-oxo-2,2-diphenylspiro[cyclopropane-1,3'-indoline]-3-carboxylate 13**



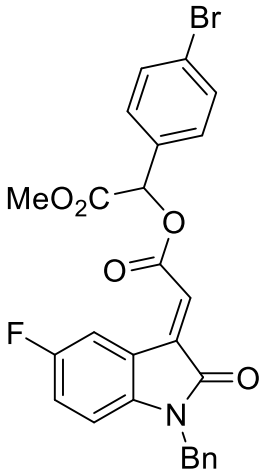
Prepared according to the general procedure (24 h). The title compound **13** was obtained as a white solid in 52% yield (54.5 mg, >19:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.38 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.26 (m, 7H), 7.22 – 7.15 (m, 7H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 15.5 Hz, 1H), 4.78 (d, *J* = 15.5 Hz, 1H), 3.66 (s, 1H), 1.51 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 172.89, 167.00, 143.32, 141.72, 136.56, 136.32, 130.47, 128.91, 128.67, 128.43, 128.32, 127.94, 127.59, 127.56, 127.36, 127.25, 127.01, 123.55, 120.71, 108.33, 81.90, 51.92, 44.16, 42.12, 41.85, 28.15. HRMS (ESI, m/z): Calcd. for $C_{34}H_{32}NO_3^+$, ([M+H]$^+$):502.2377; Found: 502.2379.

2-(*tert*-Butyl) 3-ethyl 1'-benzyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate 14



Prepared according to the general procedure (24 h). The title compound **14** was obtained as a white solid in 49% yield (42.0 mg, >19:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.33 – 7.21 (m, 6H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 15.5 Hz, 1H), 4.79 (d, *J* = 15.5 Hz, 1H), 4.24 – 4.13 (m, 2H), 3.25 (s, 2H), 1.37 (s, 9H), 1.22 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 172.01, 166.06, 166.03, 143.33, 135.55, 128.71, 128.13, 127.59, 127.14, 124.54, 122.48, 122.27, 109.12, 82.51, 61.61, 44.10, 37.15, 36.34, 35.29, 27.99, 14.06. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}NO_5^+$, ([M+H]$^+$): 422.1962; Found: 422.1959.

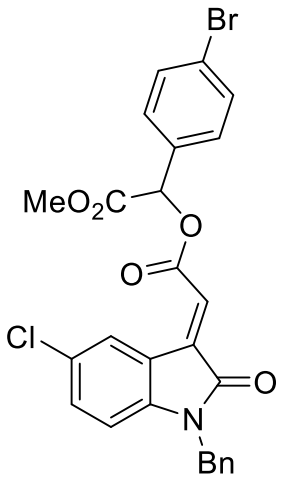
Methyl (*E*)-2-(2-(1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 15



Prepared according to the general procedure (24 h). The title compound **15** was obtained as an orange solid in 96% yield (100.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.33 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 – 7.24 (m, 5H), 7.12 (s, 1H), 6.95 (td, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.58 (dd, *J* = 8.5 Hz, 4.0 Hz, 1H), 6.06 (s, 1H), 4.90 (d, *J* = 3.0 Hz, 2H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.33, 167.04, 164.36, 158.86 (d, $J_{C\text{-}F}$ = 240.4 Hz), 141.43 (d, $J_{C\text{-}F}$ = 2.1 Hz), 138.97 (d, $J_{C\text{-}F}$ = 2.9 Hz), 134.93, 132.20, 132.08, 129.21, 128.88, 127.87, 127.14, 123.74, 122.02, 120.58 (d, $J_{C\text{-}F}$ = 9.7 Hz), 119.16 (d, $J_{C\text{-}F}$ = 24.2 Hz), 116.62 (d, $J_{C\text{-}F}$ = 27.0 Hz), 109.69 (d, $J_{C\text{-}F}$ = 7.9 Hz), 74.48, 52.96, 43.96. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ:

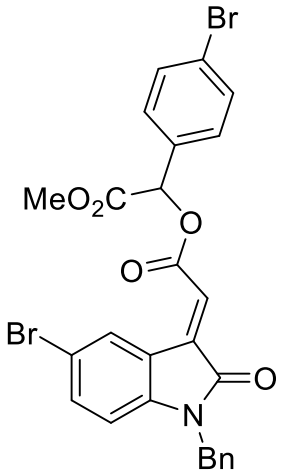
-119.78. HRMS (ESI, m/z): Calcd. for $C_{26}H_{20}Br^{78.9183}FNO_5^+$, ([M+H]$^+$): 524.0503; Found: 524.0505; $C_{26}H_{20}Br^{80.9163}FNO_5^+$, ([M+H]$^+$): 526.0483; Found: 526.0483

Methyl (*E*)-2-(2-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 16



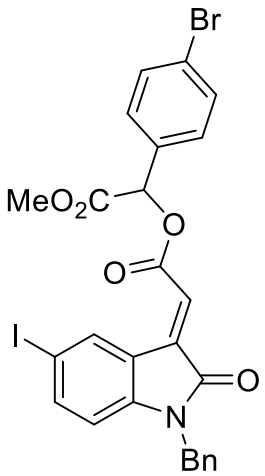
Prepared according to the general procedure (24 h). The title compound **16** was obtained as an orange solid in 94% yield (101.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.48 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.15 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.06 (s, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 6.01 (s, 1H), 4.85 (d, *J* = 3.0 Hz, 2H), 3.71 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.32, 166.85, 164.30, 143.74, 138.31, 134.79, 132.46, 132.17, 132.10, 129.25, 129.00, 128.90, 128.35, 127.91, 127.13, 123.76, 122.20, 120.85, 110.16, 74.50, 52.98, 43.94. HRMS (ESI, m/z): Calcd. for $C_{26}H_{20}Br^{78.9183}Cl^{34.9689}NO_5^+$, ([M+H]$^+$): 540.0208; Found: 540.0208; $C_{26}H_{20}Br^{80.9163}Cl^{34.9689}NO_5^+$, ([M+H]$^+$): 542.0188; Found: 542.0184.

Methyl (*E*)-2-(2-(1-benzyl-5-bromo-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 17



Prepared according to the general procedure (24 h). The title compound **17** was obtained as an orange solid in 94% yield (110.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.65 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.35 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.22 (m, 3H), 7.10 (s, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 1H), 4.89 (d, *J* = 2.0 Hz, 2H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.26, 166.63, 164.21, 144.12, 138.04, 135.27, 134.72, 132.11, 132.04, 131.61, 129.20, 128.84, 127.85, 127.08, 123.70, 122.14, 121.17, 115.55, 110.60, 74.44, 52.93, 43.84. HRMS (ESI, m/z): Calcd. for $C_{26}H_{20}Br^{78.9183}{}_2NO_5^+$, ([M+H]$^+$): 583.9703; Found: 583.9705; $C_{26}H_{20}Br^{78.9183}Br^{80.9163}NO_5^+$, ([M+H]$^+$): 585.9683; Found: 585.9683; $C_{26}H_{20}Br^{80.9163}{}_2NO_5^+$, ([M+H]$^+$): 587.9662; Found: 587.9661.

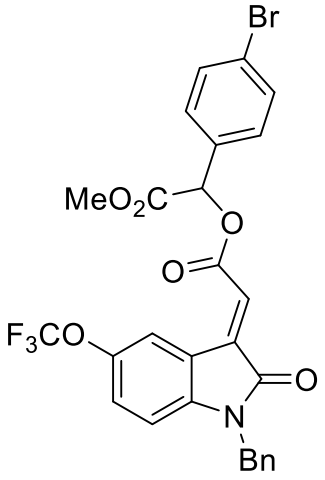
Methyl (*E*)-2-(2-(1-benzyl-5-iodo-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 18



Prepared according to the general procedure (24 h). The title compound **18** was obtained as an orange solid in 93% yield (118.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.83 (d, *J* = 2.0 Hz, 1H), 7.56

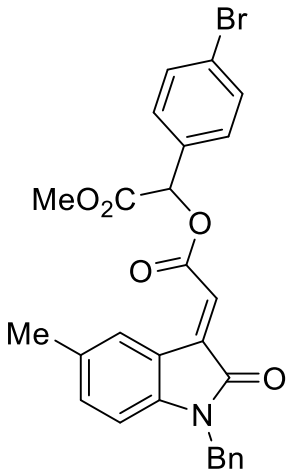
(d, *J* = 8.5 Hz, 3H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.24 (m, 5H), 7.11 (s, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.10 (s, 1H), 4.91 (d, *J* = 3.0 Hz, 2H), 3.79 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.30, 166.52, 164.27, 144.78, 141.24, 137.81, 137.21, 134.74, 132.17, 132.10, 129.25, 128.89, 127.90, 127.11, 123.76, 122.12, 121.62, 111.21, 85.50, 74.45, 52.99, 43.85. HRMS (ESI, m/z): Calcd. for $C_{26}H_{20}Br^{78.9183}INO_5^+$, ($[M+H]^+$): 631.9564; Found: 631.9564; $C_{26}H_{20}Br^{80.9163}INO_5^+$, ($[M+H]^+$): 633.9544; Found: 633.9541.

Methyl (*E*)-2-(2-(1-benzyl-2-oxo-5-(trifluoromethoxy)indolin-3-ylidene)acetoxy)-2-(4-bromophenyl)acetate 19



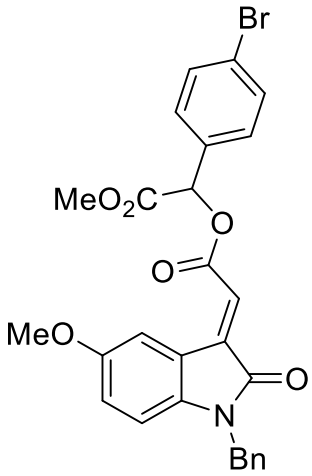
Prepared according to the general procedure (24 h). The title compound **19** was obtained as an orange solid in 97% yield (114.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.50 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 7.17 (s, 1H), 7.14 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.10 (s, 1H), 4.94 (d, *J* = 3.0 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$), δ: 168.29, 167.05, 164.28, 144.62 (q, J_{C-F} = 2.1 Hz), 143.85, 138.37, 134.74, 132.16, 132.10, 129.24, 128.95, 127.98, 127.18, 125.72, 123.77, 122.81, 122.58, 120.56, 120.47 (q, J_{C-F} = 257.54 Hz), 109.64, 74.51, 52.95, 44.02. $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), δ: -58.29. HRMS (ESI, m/z): Calcd. for $C_{27}H_{20}Br^{78.9183}F_3NO_6^+$, ($[M+H]^+$): 590.0421; Found:590.0422; $C_{27}H_{20}Br^{80.9163}F_3NO_6^+$, ($[M+H]^+$): 592.0400; Found: 592.0403.

Methyl (*E*)-2-(2-(1-benzyl-5-methyl-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 20



Prepared according to the general procedure (24 h). The title compound **20** was obtained as a dark orange solid in 90% yield (93.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.27 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.02 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 1H), 4.85 (s, 2H), 3.71 (s, 3H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.45, 167.32, 164.64, 143.14, 139.56, 135.34, 133.29, 132.38, 132.36, 132.03, 129.55, 129.18, 128.76, 127.67, 127.14, 123.63, 120.29, 119.69, 108.97, 74.27, 52.89, 43.81, 20.98. HRMS (ESI, m/z): Calcd. for $C_{27}H_{23}Br^{78.9183}NO_5^+$, ([M+H]$^+$): 520.0754; Found: 520.0754; $C_{27}H_{23}Br^{80.9163}NO_5^+$, ([M+H]$^+$): 522.0734; Found: 522.0732.

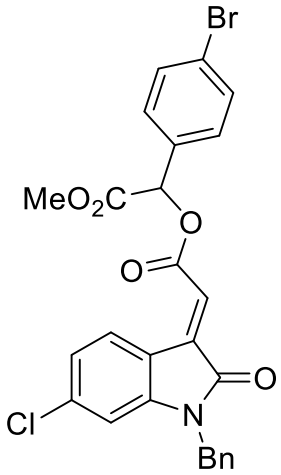
Methyl (*E*)-2-(2-(1-benzyl-5-methoxy-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 21



Prepared according to the general procedure (24 h). The title compound **21** was obtained as a dark red solid in 93% yield (93.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.15 (d, *J* = 2.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.03 (s, 1H), 6.75 (dd, *J* = 8.5

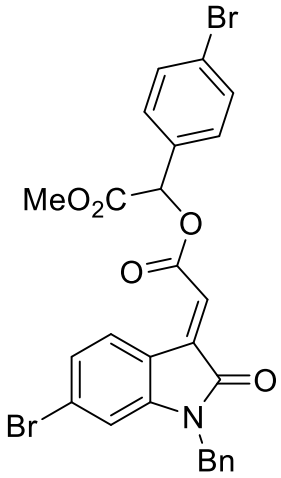
Hz, 2.5 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 4.83 (d, *J* = 1.0 Hz, 2H), 3.70 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.45, 167.18, 164.56, 155.79, 139.83, 139.17, 135.33, 132.37, 132.05, 129.19, 128.80, 127.72, 127.17, 123.65, 120.88, 120.40, 118.55, 114.97, 109.68, 74.30, 55.83, 52.90, 43.90. HRMS (ESI, m/z): Calcd. for $C_{27}H_{23}Br^{78.9183}NO_6^+$, ($[M+H]^+$): 536.0704; Found: 536.0703; $C_{27}H_{23}Br^{80.9163}NO_6^+$, ($[M+H]^+$): 538.0683; Found: 538.0681.

Methyl (*E*)-2-(2-(1-benzyl-6-chloro-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 22



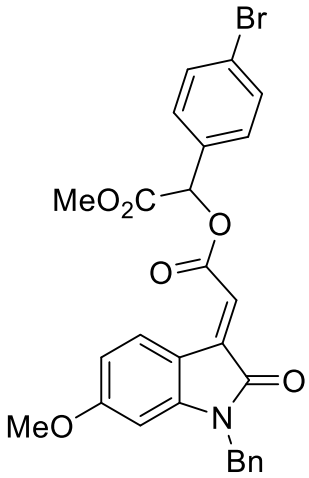
Prepared according to the general procedure (24 h). The title compound **22** was obtained as an orange solid in 86% yield (92.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.40 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.01 (s, 1H), 6.88 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 5.97 (s, 1H), 4.81 (d, *J* = 2.0 Hz, 2H), 3.68 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.34, 167.27, 164.50, 146.43, 138.82, 138.25, 134.71, 132.22, 132.04, 130.06, 129.16, 128.92, 127.94, 127.13, 123.69, 122.88, 120.95, 118.14, 109.78, 74.40, 52.91, 43.91. HRMS (ESI, m/z): Calcd. for $C_{26}H_{20}Br^{78.9183}Cl^{34.9689}NO_5^+$, ($[M+H]^+$): 540.0208; Found: 540.0208; $C_{26}H_{20}Br^{80.9163}Cl^{34.9689}NO_5^+$, ($[M+H]^+$): 542.0188; Found: 542.0184.

Methyl (*E*)-2-(2-(1-benzyl-6-bromo-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 23



Prepared according to the general procedure (24 h). The title compound **23** was obtained as an orange solid in 94% yield (109.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.42 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.15 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.12 (s, 1H), 6.85 (d, *J* = 1.5 Hz, 1H), 6.05 (s, 1H), 4.90 (d, *J* = 1.5 Hz, 2H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.37, 167.19, 164.56, 146.39, 138.39, 134.70, 132.21, 132.08, 130.22, 129.19, 128.97, 127.98, 127.30, 127.14, 125.95, 123.74, 121.25, 118.59, 112.61, 74.45, 52.97, 43.94. HRMS (ESI, m/z): Calcd. for $C_{26}H_{20}Br^{78.9183}{}_2NO_5^+$, ([M+H]$^+$): 583.9703; Found: 583.9702; $C_{26}H_{20}Br^{78.9183}Br^{80.9163}NO_5^+$, ([M+H]$^+$): 585.9683; Found: 585.9681; $C_{26}H_{20}Br^{80.9163}{}_2NO_5^+$, ([M+H]$^+$): 587.9662; Found: 587.9659.

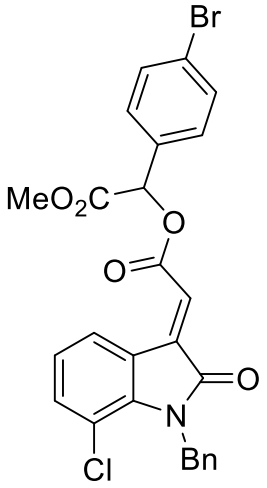
Methyl (*E*)-2-(2-(1-benzyl-6-methoxy-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 24



Prepared according to the general procedure (24 h). The title compound **24** was obtained as an orange solid in 93% yield (99.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.52 (d, *J* = 8.5 Hz, 1H), 7.54

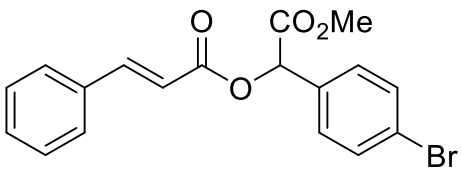
(d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.23 (m, 5H), 6.92 (s, 1H), 6.45 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.21 (d, *J* = 2.5 Hz, 1H), 6.04 (s, 1H), 4.88 (d, *J* = 0.5 Hz, 2H), 3.75 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.59, 168.17, 165.04, 163.75, 147.48, 139.07, 135.28, 132.54, 131.97, 131.06, 129.14, 128.79, 127.72, 127.17, 123.52, 116.92, 112.95, 106.50, 97.09, 74.12, 55.50, 52.83, 43.80. HRMS (ESI, m/z): Calcd. for $C_{27}H_{23}Br^{78.9183}NO_6^+$, ($[M+H]^+$): 536.0703; Found: 536.0706; $C_{27}H_{23}Br^{80.9163}NO_6^+$, ($[M+H]^+$): 538.0683; Found: 538.0685.

Methyl (*E*)-2-(2-(1-benzyl-7-chloro-2-oxoindolin-3-ylidene)acetoxy)-2-(4-bromophenyl) acetate 25



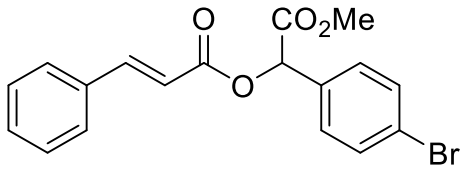
Prepared according to the general procedure (24 h). The title compound **25** was obtained as a yellow solid in 95% yield (102.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.57 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.22 (m, 4H), 7.16 (s, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 5.40 (s, 2H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.28, 167.88, 164.32, 141.05, 137.72, 136.88, 135.20, 132.15, 132.03, 129.14, 128.54, 127.59, 127.23, 126.33, 123.73, 123.69, 122.44, 121.97, 115.60, 74.45, 52.91, 45.15. HRMS(ESI,m/z): Calcd. For $C_{26}H_{20}Br^{78.9183}Cl^{34.9689}NO_5^+$, ($[M+H]^+$): 540.0208; Found:540.0212; $C_{26}H_{20}Br^{80.9163}Cl^{34.9689}NO_5^+$, ($[M+H]^{+)}$: 542.0188; Found:542.0189.

(*E*)-1-(4-bromophenyl)-2-methoxy-2-oxoethyl cinnamate 26



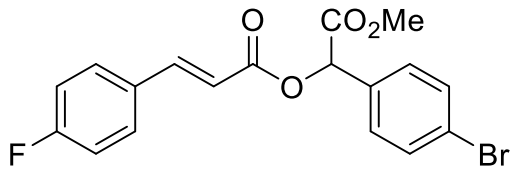
Prepared according to the general procedure (24 h). The title compound **26** was obtained as colorless oil in 87% yield (70.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.79 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.53 (m, 4H), 7.44 – 7.37 (m, 5H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.05 (s, 1H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.88, 165.85, 146.53, 133.96, 132.91, 131.94, 130.63, 129.22, 128.86, 128.21, 123.42, 116.55, 73.70, 52.71. HRMS (ESI, m/z): Calcd. for $C_{18}H_{16}Br^{78.9183}O_4^+$, ([M+H]$^+$): 375.0226; Found: 375.0230; $C_{18}H_{16}Br^{80.9163}O_4^+$, ([M+H]$^+$): 377.0206; Found: 377.0209.

Gram-scale (*E*)-1-(4-bromophenyl)-2-methoxy-2-oxoethyl cinnamate 26



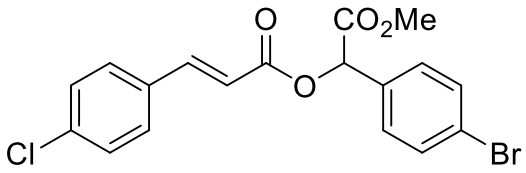
^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.78 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.53 (m, 4H), 7.43 – 7.39 (m, 5H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.04 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$), δ: 168.89, 165.87, 146.54, 133.95, 132.89, 131.95, 130.64, 129.23, 128.87, 128.22, 123.43, 116.52, 73.70, 52.73. HRMS (ESI, m/z): Calcd. for $C_{18}H_{16}Br^{78.9183}O_4^+$, ([M+H]$^+$): 375.0226; Found: 375.0230; $C_{18}H_{16}Br^{80.9163}O_4^+$, ([M+H]$^+$): 377.0206; Found: 377.0209.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(4-fluorophenyl)acrylate 27



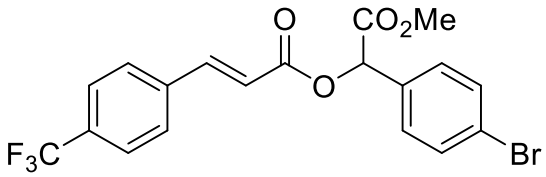
Prepared according to the general procedure (24 h). The title compound **27** was obtained as colorless oil in 99% yield (78.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.72 (d, *J* = 16.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.03 (s, 1H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.87, 165.74, 164.06 (d, $J_{C\text{-}F}$ = 252.4 Hz), 145.19, 132.88, 131.97, 130.26 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.16 (d, $J_{C\text{-}F}$ = 8.7 Hz), 129.23, 123.47, 116.33 (d, $J_{C\text{-}F}$ = 2.4 Hz), 116.07 (d, $J_{C\text{-}F}$ = 22.1 Hz), 73.74, 52.74. ^{19}F{^{1}H} NMR (471 MHz, CDCl3) δ -108.71. HRMS (ESI, m/z): Calcd. for $C_{18}H_{15}Br^{78.9183}FNO_4^+$, ([M+H]$^+$): 393.0132; Found: 393.0132.; $C_{18}H_{15}Br^{80.9163}FNO_4^+$, ([M+H]$^+$): 395.0112; Found: 395.0110.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(4-chlorophenyl)acrylate 28



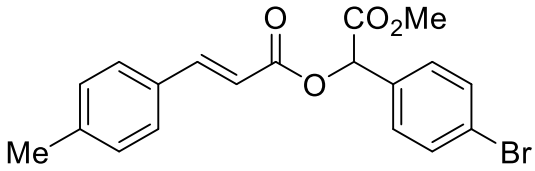
Prepared according to the general procedure (24 h). The title compound **28** was obtained as colorless oil in 97% yield (79.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.72 (d, *J* = 16.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.03 (s, 1H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.84, 165.63, 145.05, 136.60, 132.83, 132.48, 131.99, 129.39, 129.24, 129.20, 123.51, 117.17, 73.80, 52.77. HRMS (ESI, m/z): Calcd. for $C_{18}H_{15}Br^{78.9183}Cl^{34.9689}O_4^+$, ([M+H]$^+$): 408.9837; Found: 408.9836.; $C_{18}H_{15}Br^{80.9163}Cl^{34.9689}O_4^+$, ([M+H]$^+$): 410.9816; Found: 410.9812.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(4-trifluoromethylphenyl)acrylate 29



Prepared according to the general procedure (24 h). The title compound **29** was obtained as colorless oil in 92% yield (81.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.79 (d, *J* = 16.0 Hz, 1H), 7.64 (t, *J* = 9.5 Hz, 4H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz ,2H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.05 (s, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.76, 165.34, 144.58, 137.34 (d, $J_{C\text{-}F}$ = 1.0 Hz), 132.73, 132.07 (q, *J* = 32.9 Hz), 132.04, 129.27, 128.35, 125.87 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.71 (q, $J_{C\text{-}F}$ = 272.7 Hz), 123.60, 119.22, 73.95, 52.81. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ: -62.90. HRMS (ESI, m/z): Calcd. for $C_{19}H_{15}Br^{78.9183}O_4^+$, ([M+H]$^+$): 443.0100; Found: 443.0102.; $C_{19}H_{15}Br^{80.9163}O_4^+$, ([M+H]$^+$):445.0080; Found: 445.0079.

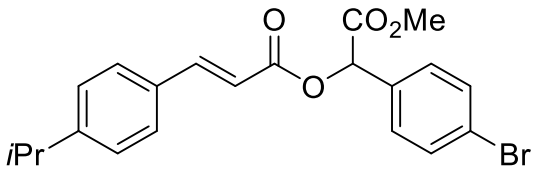
1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(*p*-tolyl)acrylate 30



Prepared according to the general procedure (24 h). The title compound **30** was obtained as colorless oil in 98% yield (76.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.77 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.40 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.04

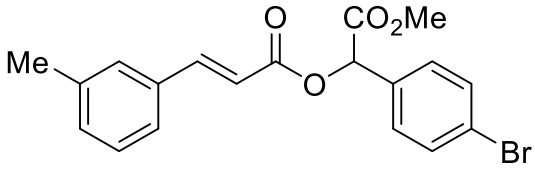
(s, 1H), 3.75 (s, 3H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.96, 166.06, 146.57, 141.16, 133.00, 131.94, 131.28, 129.61, 129.23, 128.25, 123.40, 115.41, 73.65, 52.70, 21.43. HRMS (ESI, m/z): Calcd. for $C_{19}H_{18}Br^{78.9183}O_4^+$, ($[M+H]^+$): 389.0383; Found: 389.0380.; $C_{19}H_{18}Br^{80.9163}O_4^+$, ($[M+H]^+$): 391.0363; Found: 391.0357.

1-(4-bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(4-isopropylphenyl)acrylate 31



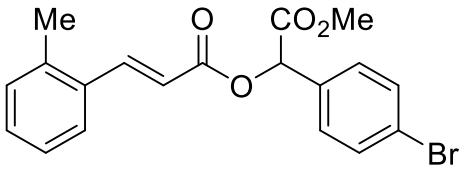
Prepared according to the general procedure (24 h). The title compound **31** was obtained as colorless oil in 85% yield (71.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.77 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 15.5 Hz, 1H), 6.03 (s, 1H), 3.75 (s, 3H), 2.97 – 2.88 (m, 1H), 1.26 (d, *J* = 6.5 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.99, 166.12, 152.06, 146.63, 133.03, 131.97, 131.68, 129.26, 128.40, 127.03, 123.43, 115.49, 73.68, 52.74, 34.07, 23.69. HRMS (ESI, m/z): Calcd. for $C_{21}H_{22}Br^{78.9183}O_4^+$, ($[M+H]^+$): 417.0696; Found: 417.0694; $C_{21}H_{22}Br^{80.9163}O_4^+$, ($[M+H]^+$): 419.0676; Found: 419.0671.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(*m*-tolyl)acrylate 32



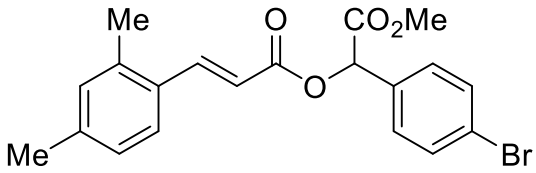
Prepared according to the general procedure (24 h). The title compound **32** was obtained as colorless oil in 83% yield (64.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.76 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.04 (s, 1H), 3.75 (s, 3H), 2.37 (s, 3H).$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.93, 165.95, 146.76, 138.55, 133.95, 132.98, 131.96, 131.50, 129.23, 128.90, 128.77, 125.45, 123.43, 116.32, 73.70, 52.73, 21.24. HRMS (ESI, m/z): Calcd. for $C_{19}H_{18}Br^{78.9183}O_4^+$, ($[M+H]^+$): 389.0383; Found:389.0381.; $C_{19}H_{18}Br^{80.9163}O_4^+$, ($[M+H]^+$): 391.0363; Found: 391.0360.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(*o*-tolyl)acrylate 33



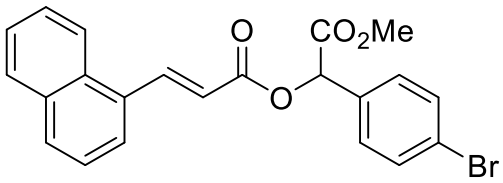
Prepared according to the general procedure (24 h). The title compound **33** was obtained as colorless oil in 92% yield (71.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.01 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.15(m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.99 (s, 1H), 3.71 (s, 3H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.98, 166.07, 144.30, 137.94, 132.99, 132.95, 132.01, 130.86, 130.44, 129.25, 126.54, 126.38, 123.49, 117.46, 73.78, 52.78, 19.74. HRMS (ESI, m/z): Calcd. for $C_{19}H_{18}Br^{78.9183}O_4^+$, ([M+H]$^+$): 389.0383; Found:389.0380.; $C_{19}H_{18}Br^{80.9163}O_4^+$, ([M+H]$^+$): 391.0363; Found: 391.0356.

1-(4-bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(2,4-dimethylphenyl)acrylate 34



Prepared according to the general procedure (24 h). The title compound **34** was obtained as colorless oil in 92% yield (74.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.07 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 2H), 6.47 (d, *J* = 15.5 Hz, 1H), 6.04 (s, 1H), 3.76 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.99, 166.23, 144.18, 140.83, 137.90, 133.03, 131.95, 131.61, 130.07, 129.22, 127.18, 126.50, 123.40, 116.18, 73.68, 52.72, 21.28, 19.61. HRMS (ESI, m/z): Calcd. for $C_{20}H_{20}Br^{78.9183}O_4^+$, ([M+H]$^+$): 403.0540; Found: 403.0535; $C_{20}H_{20}Br^{80.9163}O_4^+$, ([M+H]$^+$): 405.0520; Found: 405.0513.

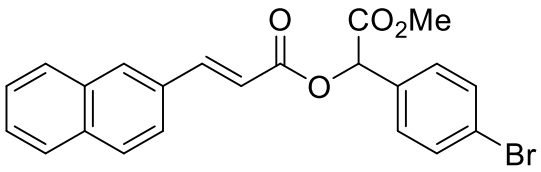
1-(4-bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(naphthalen-1-yl)acrylate 35



Prepared according to the general procedure (24 h). The title compound **35** was obtained as colorless oil in 94% yield (79.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.65 (d, *J* = 16.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.79 (d, *J* = 7.0Hz, 1H), 7.60 – 7.45 (m, 7H), 6.68 (d, *J* =

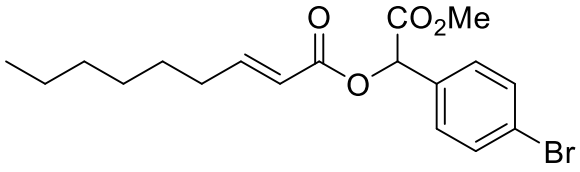
16.0 Hz, 1H), 6.11 (s, 1H), 3.79 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.92, 165.81, 143.51, 133.59, 132.93, 131.99, 131.30, 131.22, 130.92, 129.26, 128.70, 126.95, 126.23, 125.36, 125.25, 123.48, 123.16, 119.01, 73.82, 52.76. HRMS (ESI, m/z): Calcd. for $C_{22}H_{18}Br^{78.9183}O_4^+$, ($[M+H]^+$): 425.0383; Found: 425.0379; $C_{22}H_{18}Br^{80.9163}O_4^+$, ($[M+H]^+$): 427.0363; Found: 427.0358.

1-(4-bromophenyl)-2-methoxy-2-oxoethyl (*E*)-3-(naphthalen-2-yl)acrylate 36



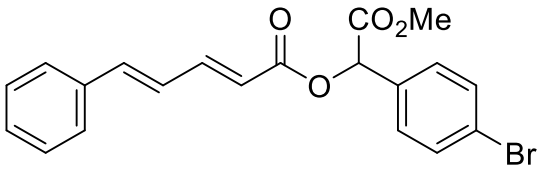
Prepared according to the general procedure (24 h). The title compound **36** was obtained as colorless oil in 99% yield (84.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.97 – 7.94 (m, 2H), 7.87 – 7.82 (m, 3H), 7.68 – 7.66(m, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.50 (m,2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.08 (s, 1H), 3.77 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.95, 165.95, 146.59, 134.35, 133.16, 132.98, 131.99, 131.50, 130.40, 129.26, 128.73, 128.60, 127.74, 127.42, 126.74, 123.46, 123.39, 116.68, 73.76, 52.76. HRMS (ESI, m/z): Calcd. for $C_{22}H_{18}Br^{78.9183}O_4^+$, ($[M+H]^+$): 425.0383; Found: 425.0377; $C_{22}H_{18}Br^{80.9163}O_4^+$, ($[M+H]^+$): 427.0363; Found: 427.0356.

1-(4-bromophenyl)-2-methoxy-2-oxoethyl (*E*)-non-2-enoate 37



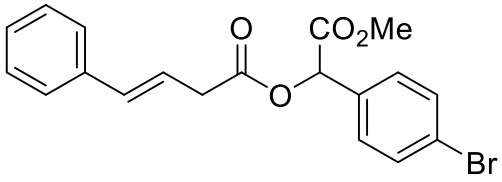
Prepared according to the general procedure (24 h). The title compound **37** was obtained as colorless oil in 83% yield (65.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.52 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.07 (m, 1H), 5.96 – 5.92 (m, 2H), 3.72 (s, 3H), 2.25 – 2.20 (m, 2H), 1.49 – 1.43 (m, 2H), 1.34 – 1.25 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.98, 165.57, 151.96, 133.02, 131.92, 129.19, 123.36, 119.78, 73.46, 52.67, 32.34, 31.51, 28.78, 27.73, 22.46, 13.99. HRMS (ESI, m/z): Calcd. for $C_{18}H_{24}Br^{78.9183}O_4^+$, ($[M+H]^+$): 383.0853; Found: 383.0848; $C_{18}H_{24}Br^{80.9163}O_4^+$, ($[M+H]^+$): 385.0833; Found: 385.0827.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate 38



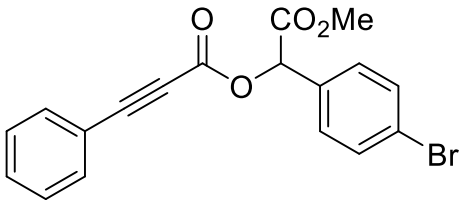
Prepared according to the general procedure (24 h). The title compound **38** was obtained as colorless oil in 95% yield (76.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.58 – 7.53(m, 3H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.31(m, 3H), 6.97 – 6.87(m, 2H), 6.11 (d, *J* = 15.5 Hz, 1H), 6.01 (s, 1H), 3.75 (s, 3H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.92, 165.86, 146.41, 141.53, 135.70, 132.96, 131.90, 129.23, 129.20, 128.76, 127.25, 125.83, 123.36, 119.42, 73.57, 52.68. HRMS (ESI, m/z): Calcd. for $C_{20}H_{18}Br^{78.9183}O_4^+$, ([M+H]$^+$): 401.0383; Found: 401.0378.; $C_{20}H_{18}Br^{80.9163}O_4^+$, ([M+H]$^+$): 403.0363; Found: 403.0356.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl (*E*)-5-phenylpent-4-enoate 39



Prepared according to the general procedure (24 h). The title compound **39** was obtained as colorless oil in 97% yield (75.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.55 (d, *J* = 8.5 Hz, 2H), 7.40 – 7.38 (m, 4H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.36 – 6.30 (m, 1H), 5.96 (s, 1H), 3.75 (s, 3H), 3.48 – 3.38 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 170.72, 168.70, 136.60, 134.01, 132.61, 131.96, 129.19, 128.49, 127.62, 126.27, 123.50, 120.62, 73.84, 52.76, 37.77. HRMS (ESI, m/z): Calcd. for $C_{19}H_{18}Br^{78.9183}O_4^+$, ([M+H]$^+$): 389.0383; Found: 389.0380.; $C_{19}H_{18}Br^{80.9163}O_4^+$, ([M+H]$^+$): 391.0363; Found: 391.0359.

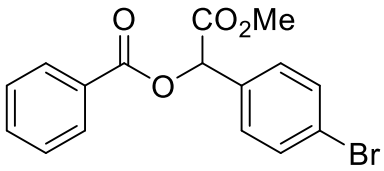
1-(4-Bromophenyl)-2-methoxy-2-oxoethyl 3-phenylpropiolate 40



Prepared according to the general procedure (24 h). The title compound **40** was obtained as colorless oil in 94% yield (70.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.62 – 7.60 (m, 2H), 7.55 (d, *J* = 9.0 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.41 – 7.37 (m, 4H), 6.02 (s, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR

(126 MHz, $CDCl_3$), δ: 168.11, 152.89, 133.11, 132.05, 130.97, 129.33, 128.58, 123.77, 119.13, 88.39, 79.75, 74.70, 52.94. HRMS (ESI, m/z): Calcd. for $C_{18}H_{14}Br^{78.9183}O_4^+$, ($[M+H]^+$): 373.0070; Found: 373.0067; $C_{18}H_{14}Br^{80.9163}O_4^+$, ($[M+H]^+$): 375.0050; Found: 375.0045.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl benzoate 41



Prepared according to the general procedure (24 h). The title compound **41** was obtained as colorless oil in 96% yield (67.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.12 (d, *J* = 7.0 Hz, 2H), 7.61-7.55 (m, 3H), 7.48 – 7.45 (m, 4H), 6.13 (s, 1H), 3.76 (s, 3H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.82, 165.65, 133.59, 132.96, 132.03, 129.92, 129.21, 128.95, 128.47, 123.50, 74.10, 52.78. HRMS (ESI, m/z): Calcd. for $C_{16}H_{14}Br^{78.9183}O_4^+$, ($[M+H]^+$): 349.0070; Found: 349.0074; $C_{16}H_{14}Br^{80.9163}O_4^+$, ($[M+H]^+$): 351.0050; Found: 351.0049.

References

1 a) G. Wille, W. Steglich, *Synthesis*, **2001**, 759; b) B. Tan, N. R. Candeias, C. F. Barbas III, *J. Am. Chem. Soc.*, **2011**, 133, 4672; c) A. Noole, N. S. Sucman, M. A. Kabeshov, T. Kanger, F. Z. Macaev, A. V. Malkov, *Chem. Eur. J.*, 2012, **18**, 14929.

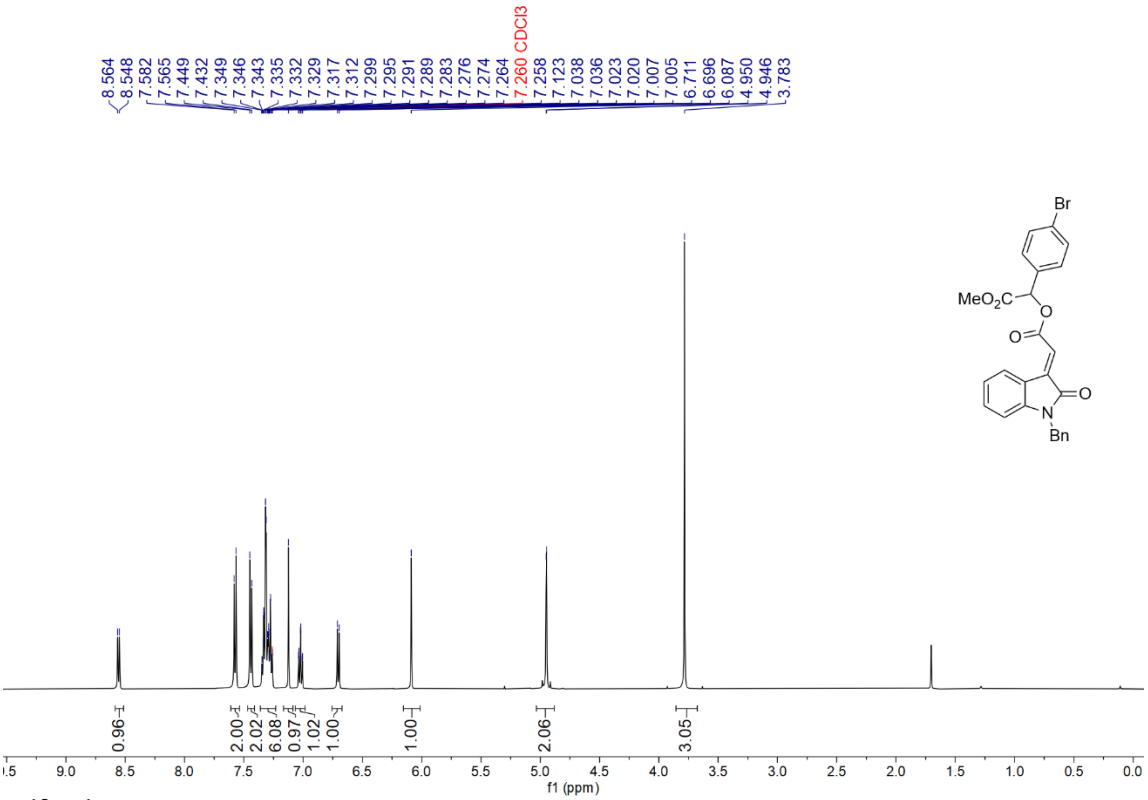
2 S. Lee, G.-S. Hwang and D. H. Ryu, *J. Am. Chem. Soc.*, 2013, **135**, 7126.

3 G. M. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112.

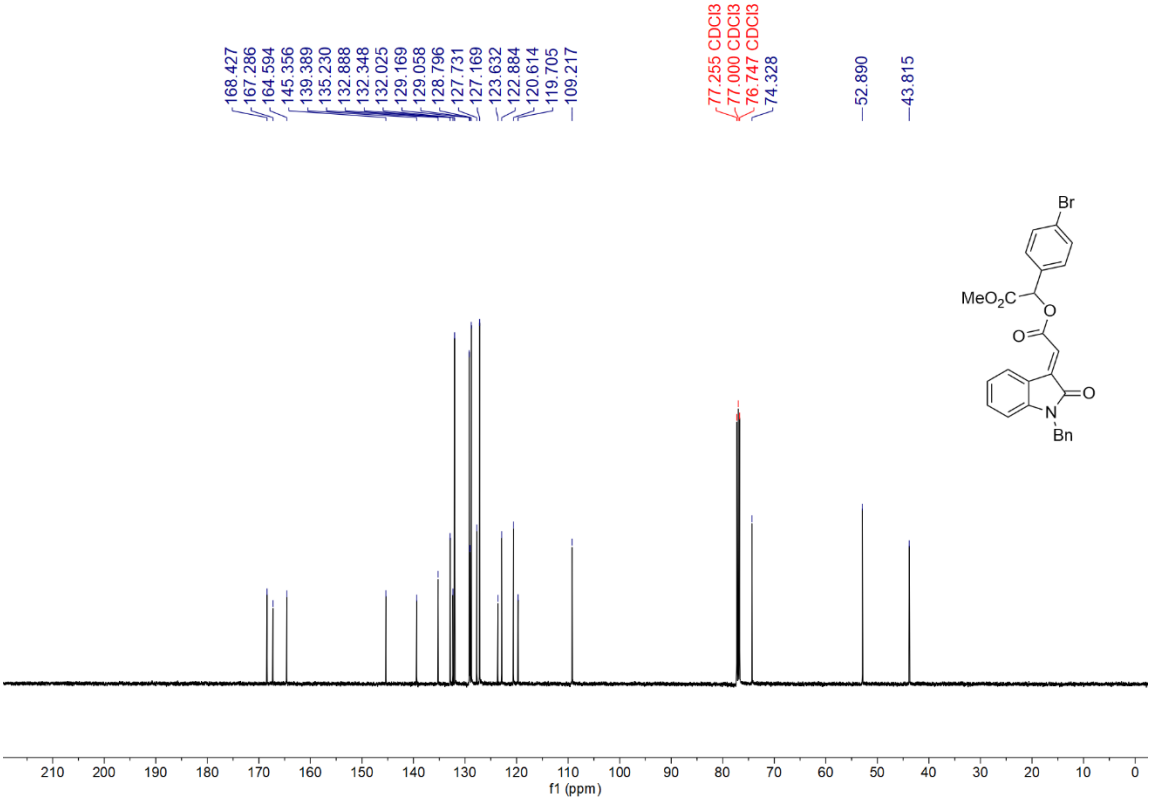
4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

NMR spectra of isolated compounds

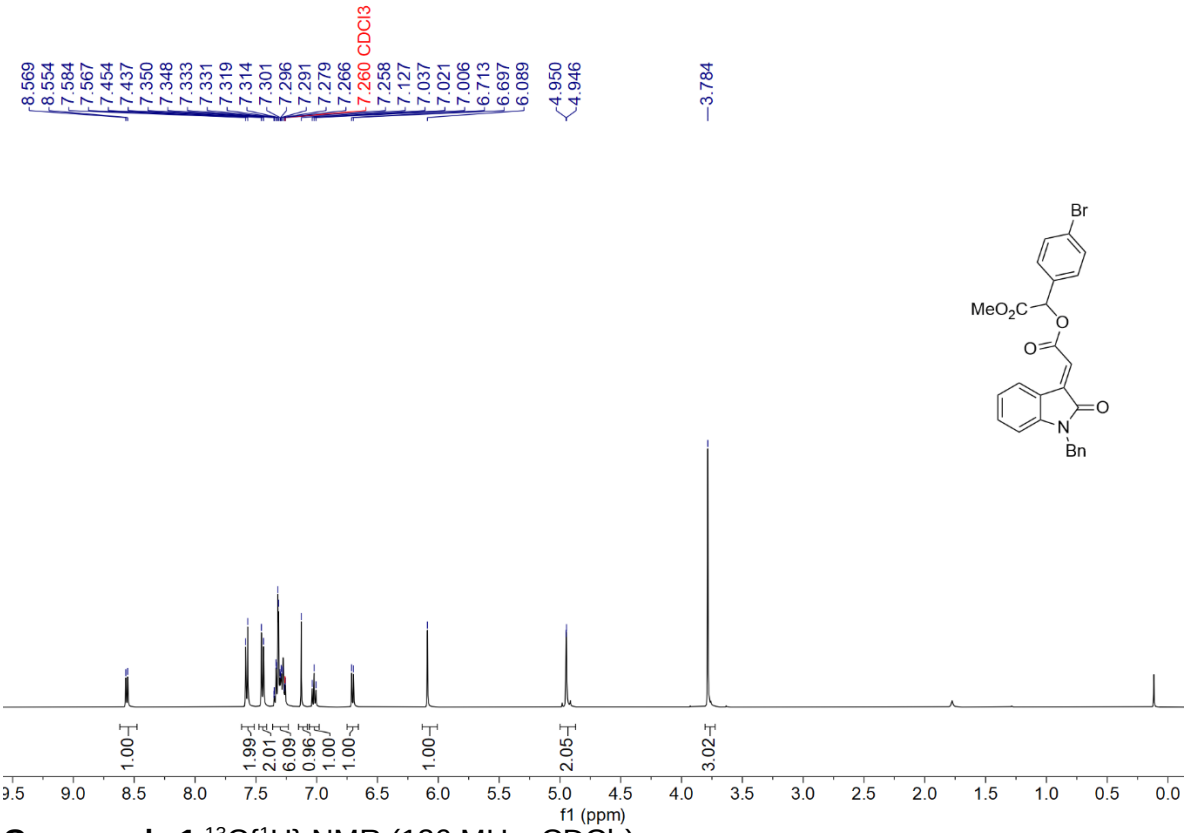
1 ^{1}H NMR (500 MHz, $CDCl_3$)



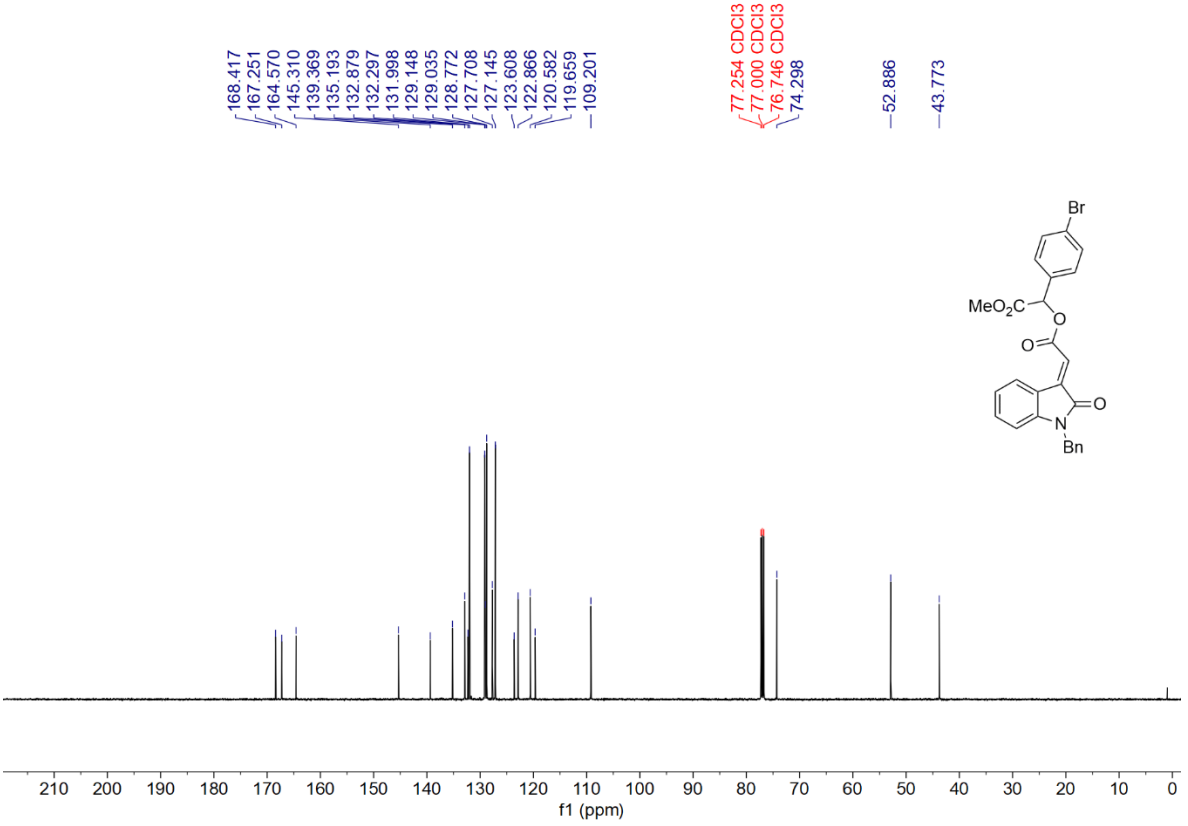
1 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



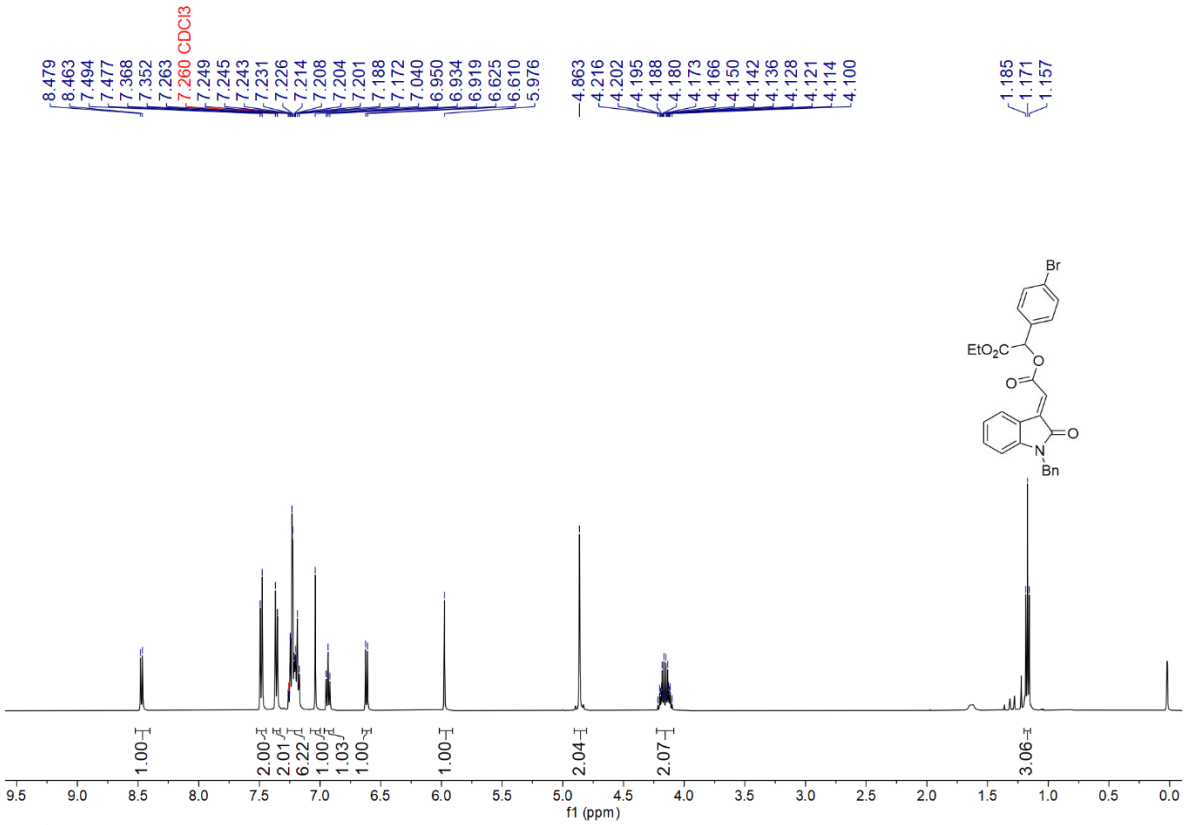
Gram-scale 1 ^{1}H NMR (500 MHz, $CDCl_3$)



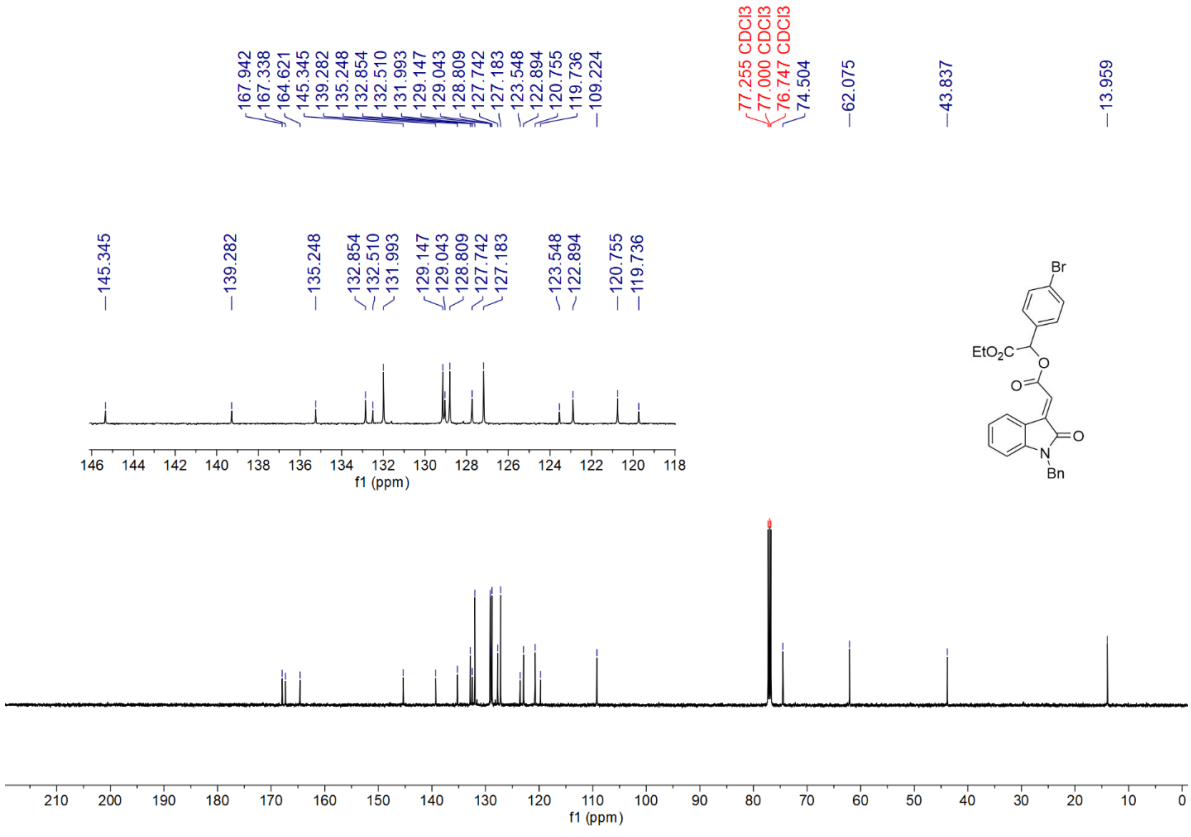
Gram-scale 1 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



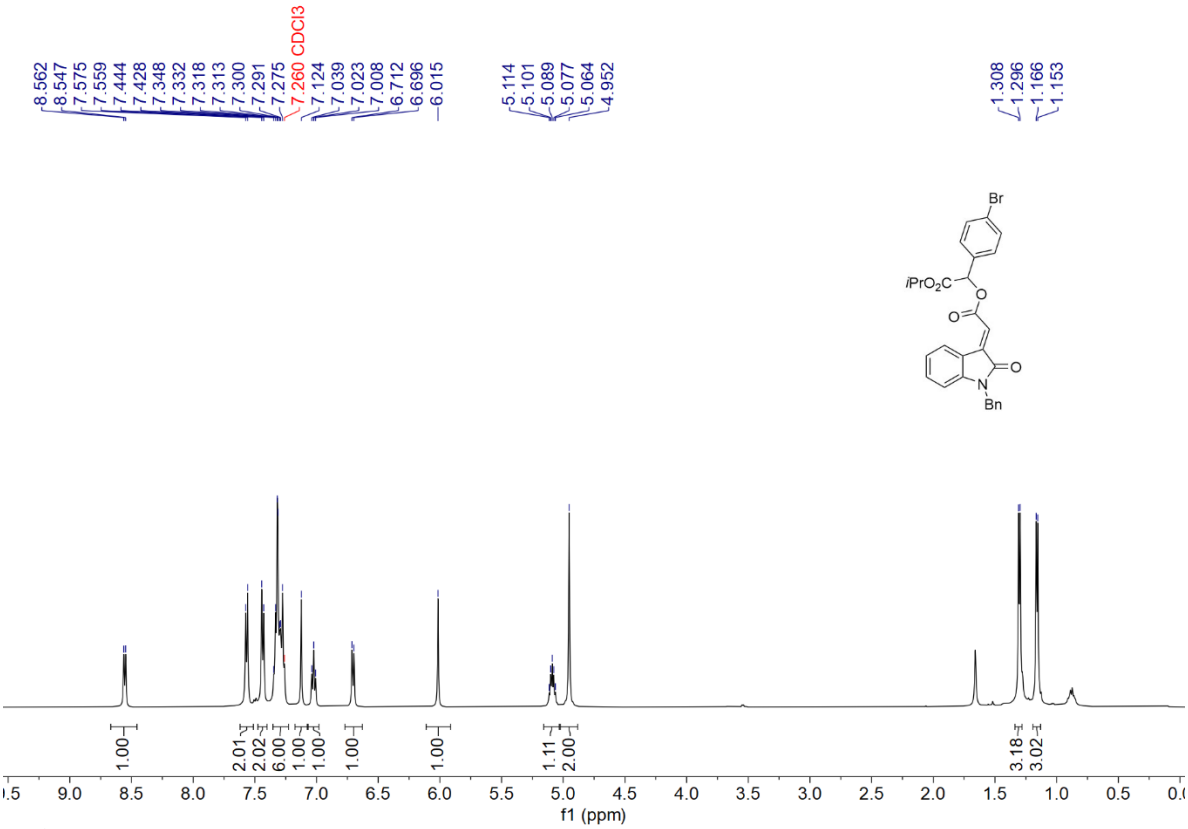
2 ^{1}H NMR (500 MHz, $CDCl_3$)



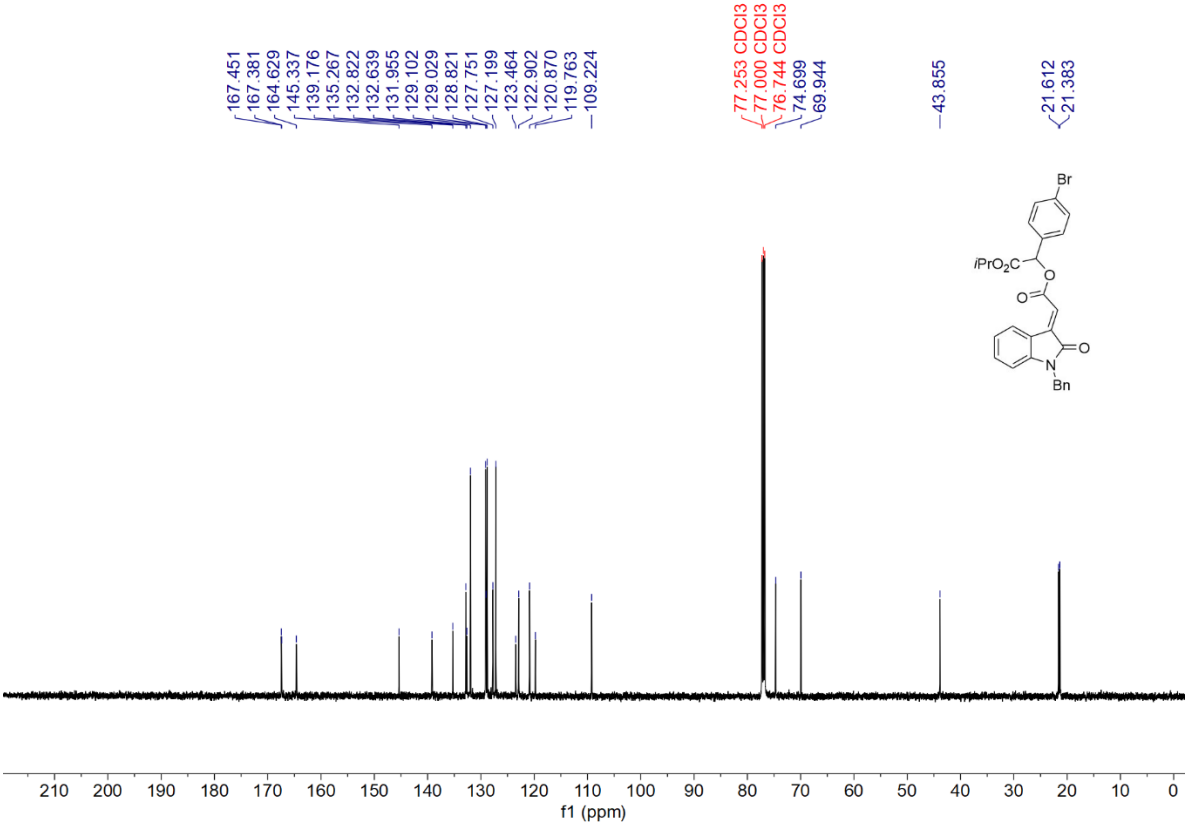
2 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



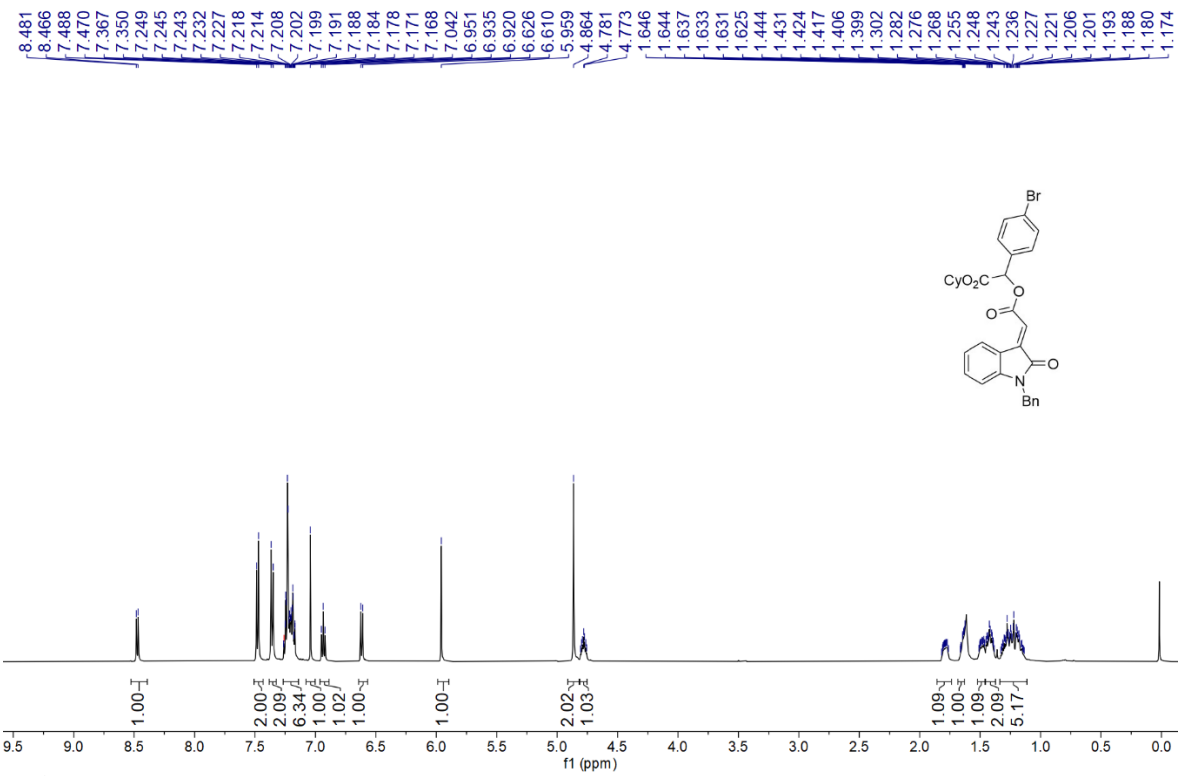
3 ^{1}H NMR (500 MHz, $CDCl_3$)



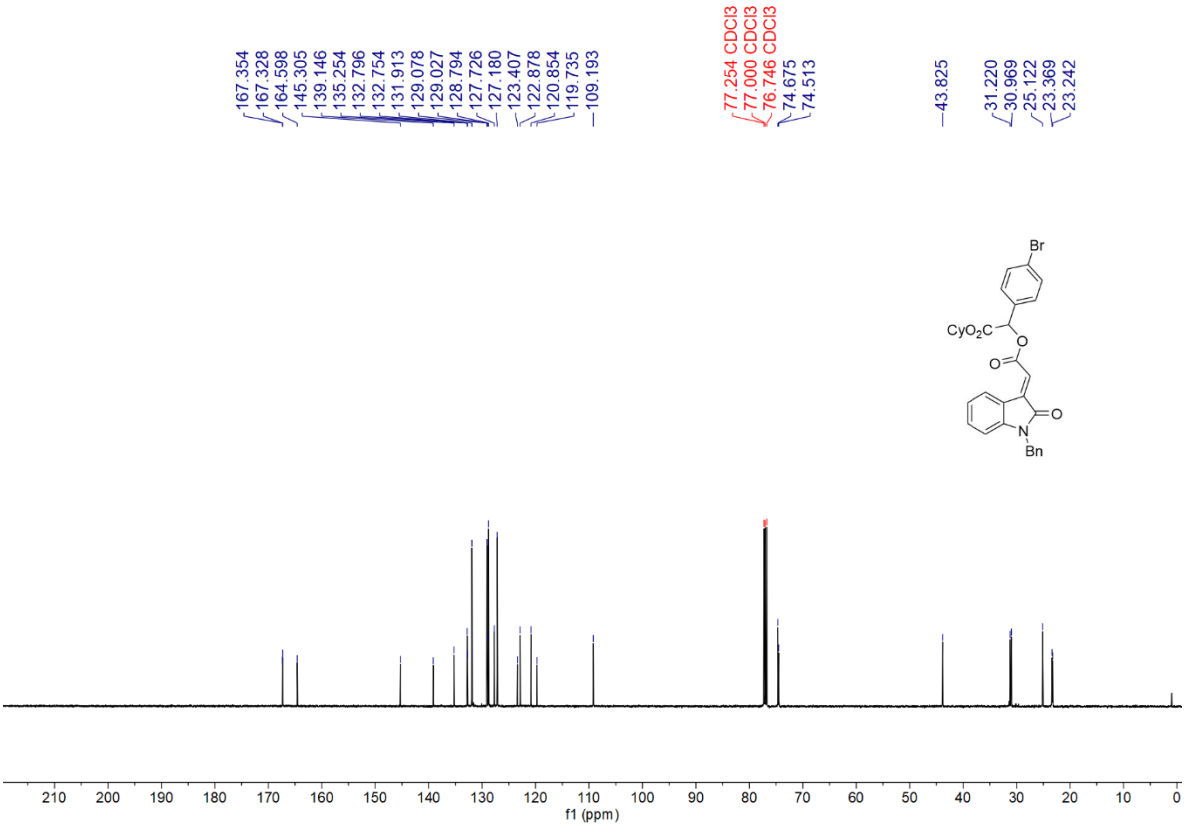
3 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



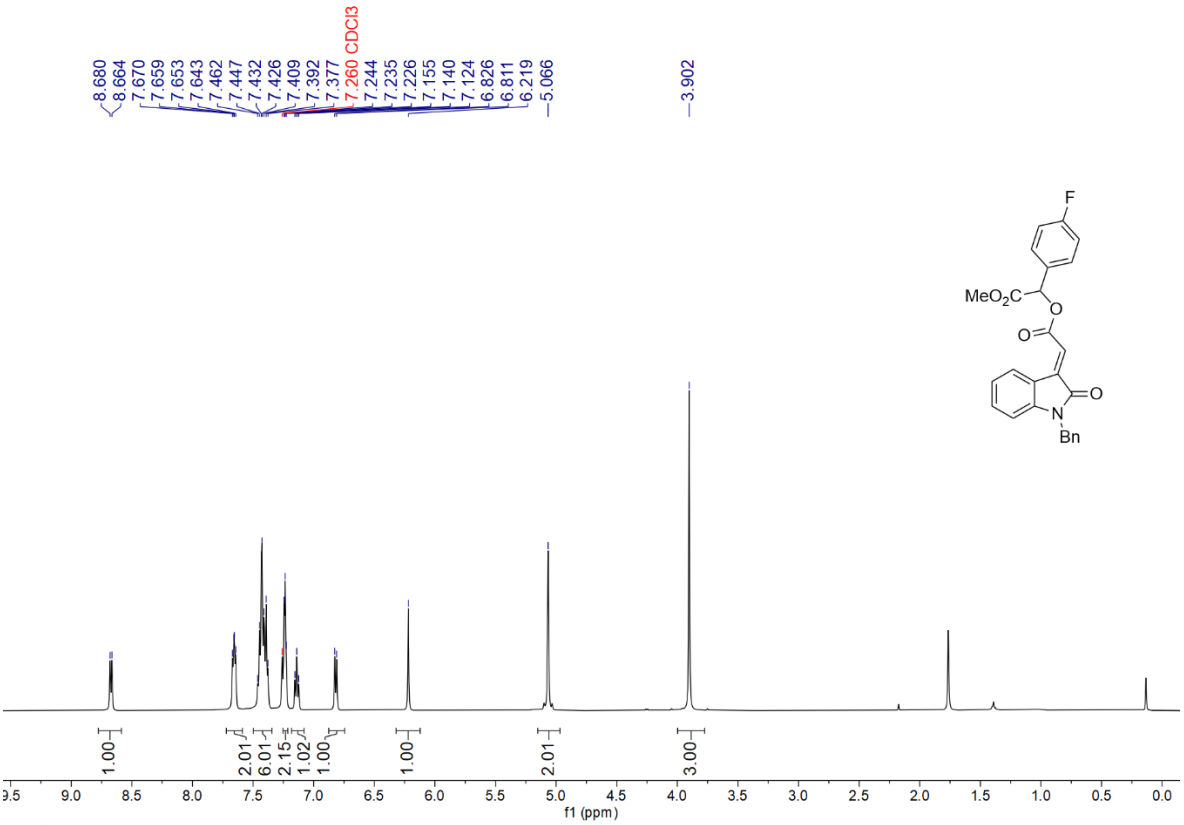
4 ^{1}H NMR (500 MHz, $CDCl_3$)



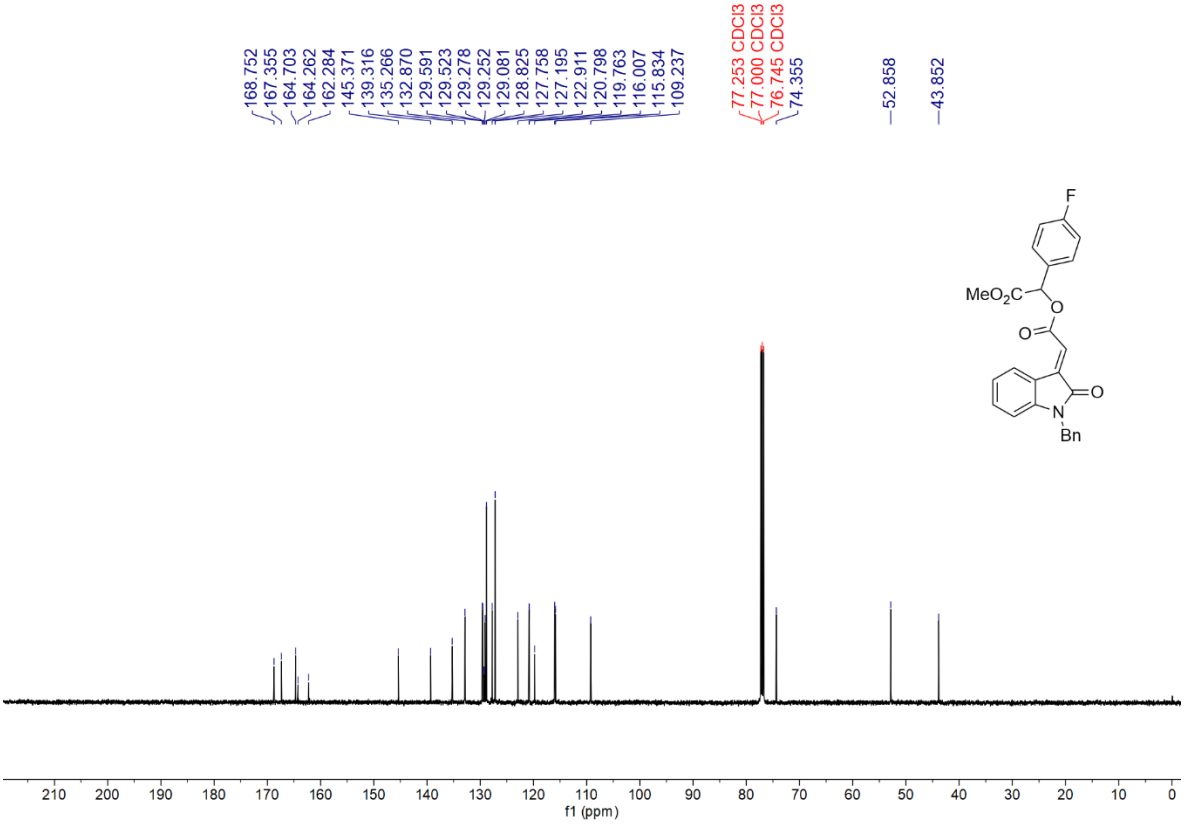
4 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



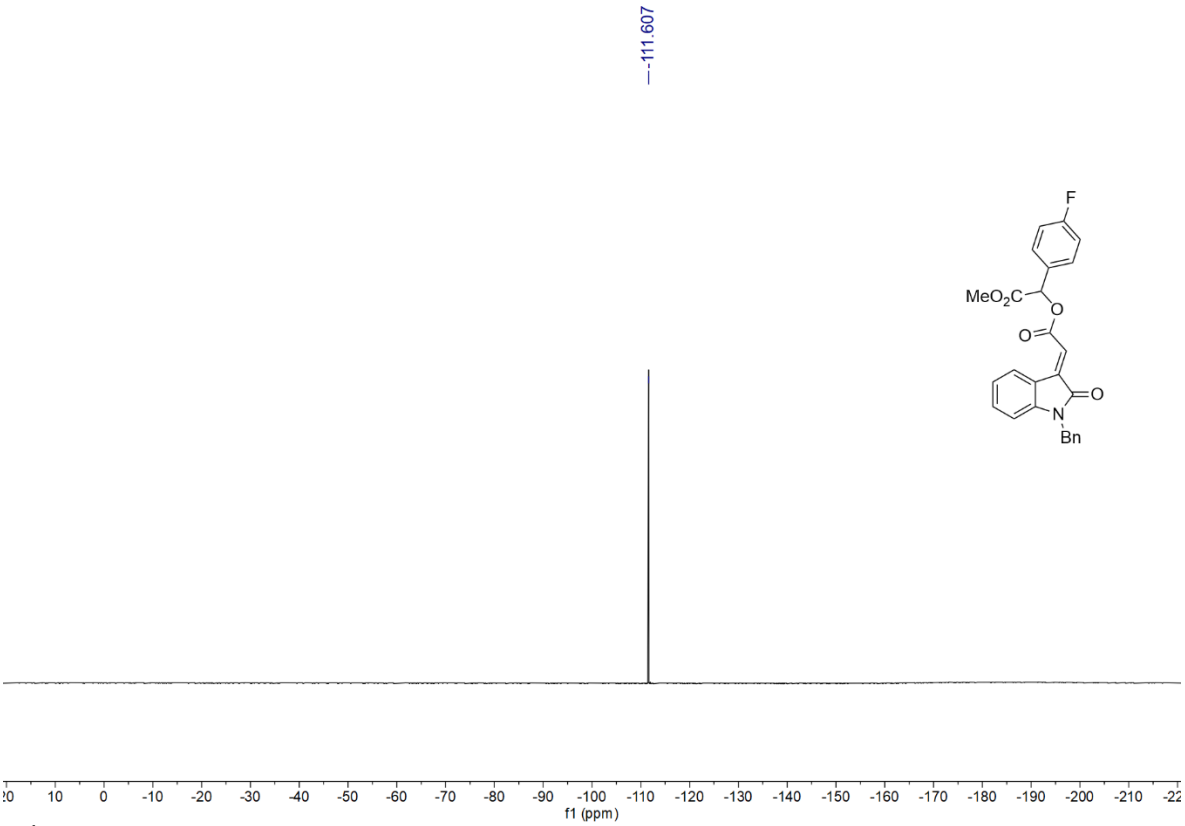
5 ^{1}H NMR (500 MHz, $CDCl_3$)



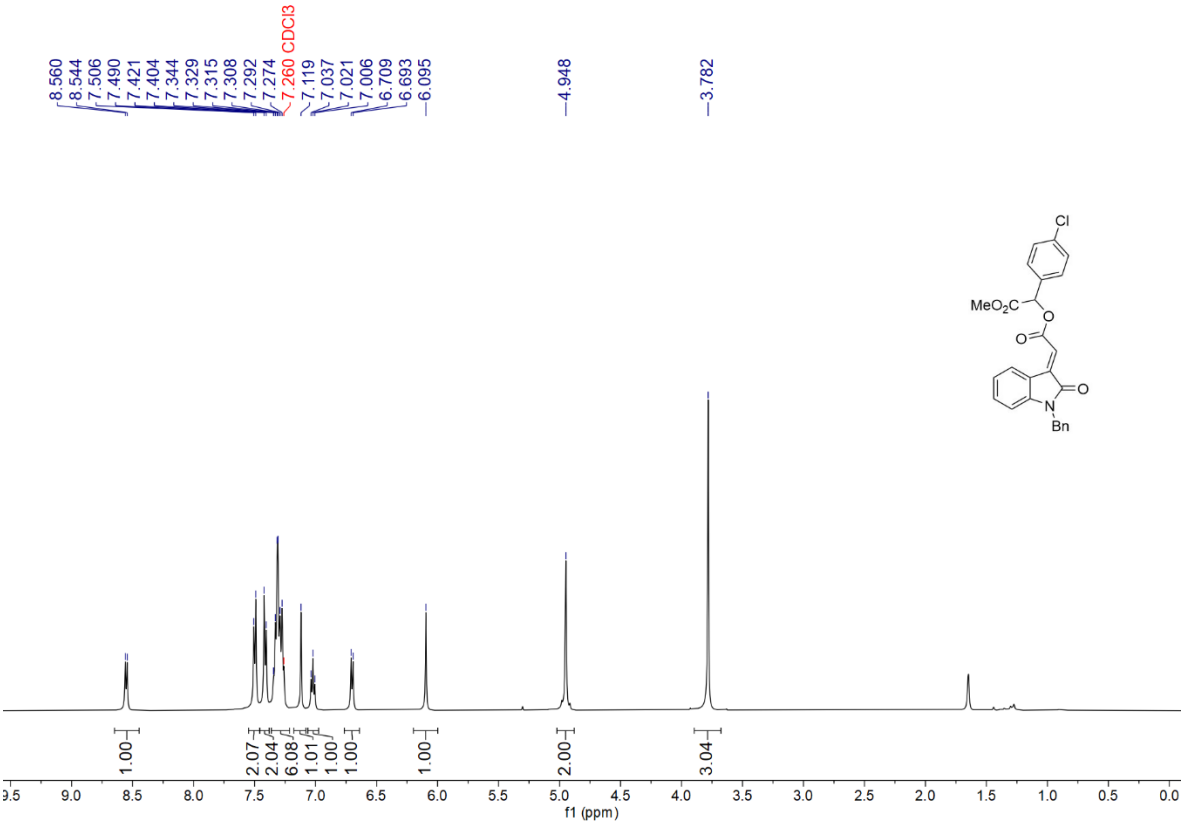
5 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



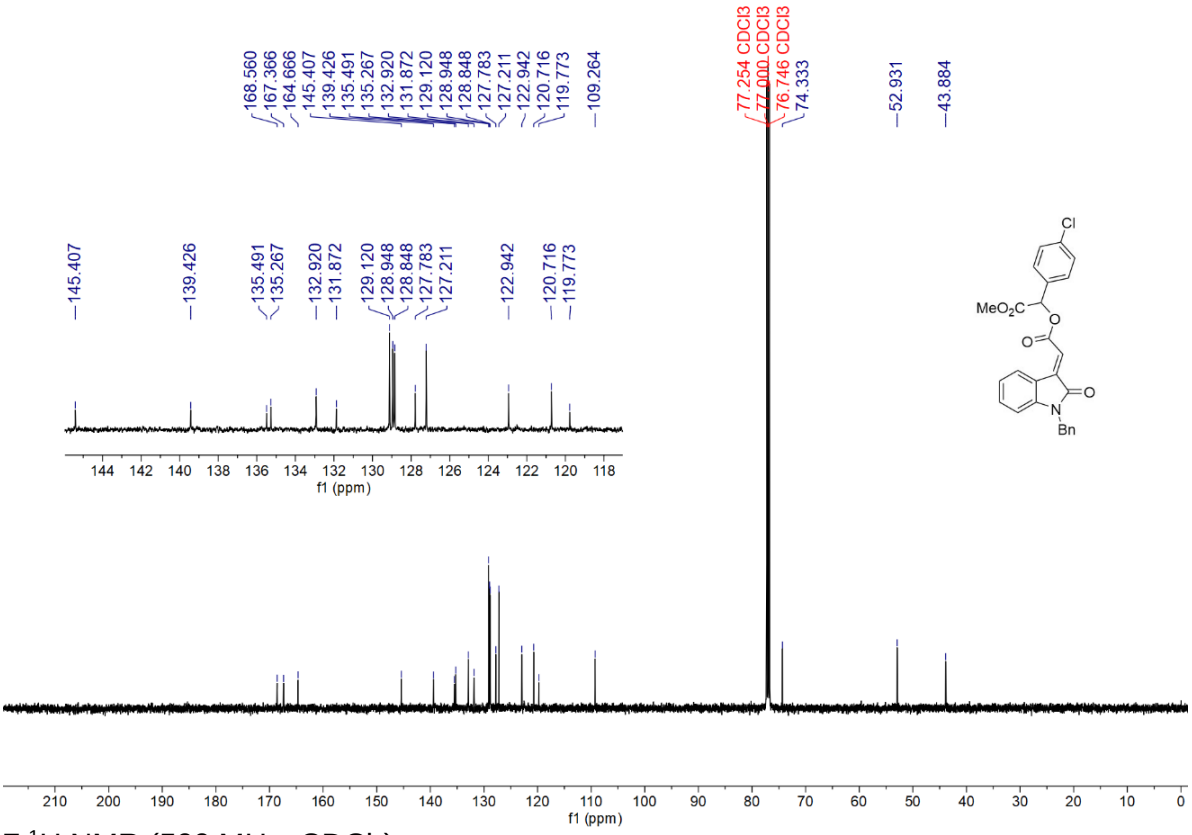
5 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



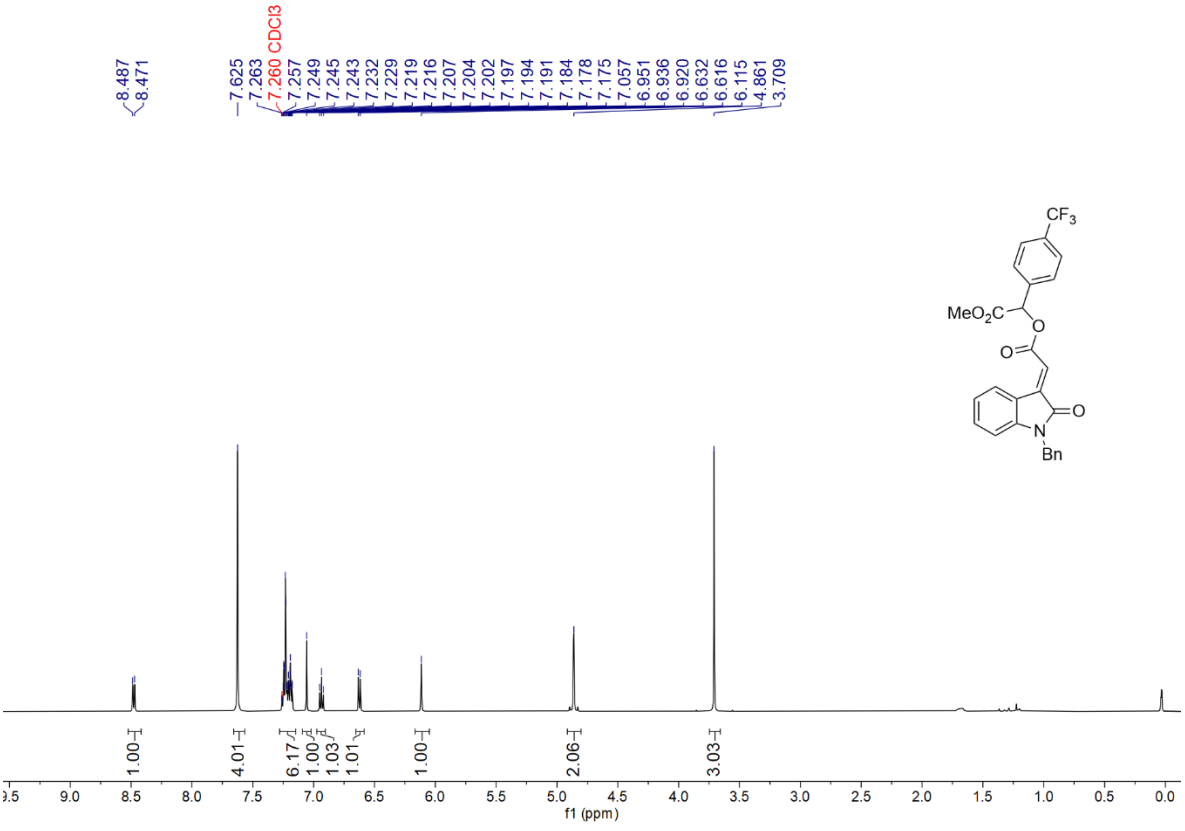
6 ^{1}H NMR (500 MHz, $CDCl_3$)



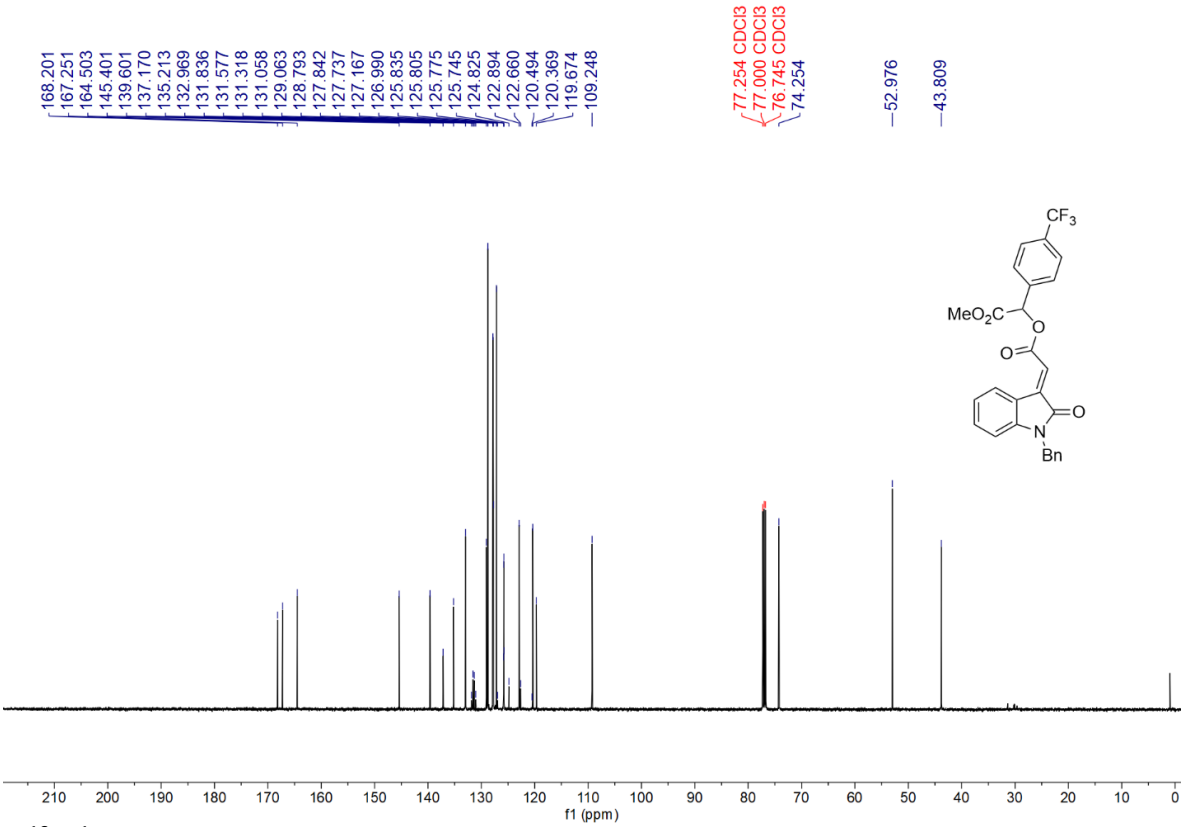
6 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



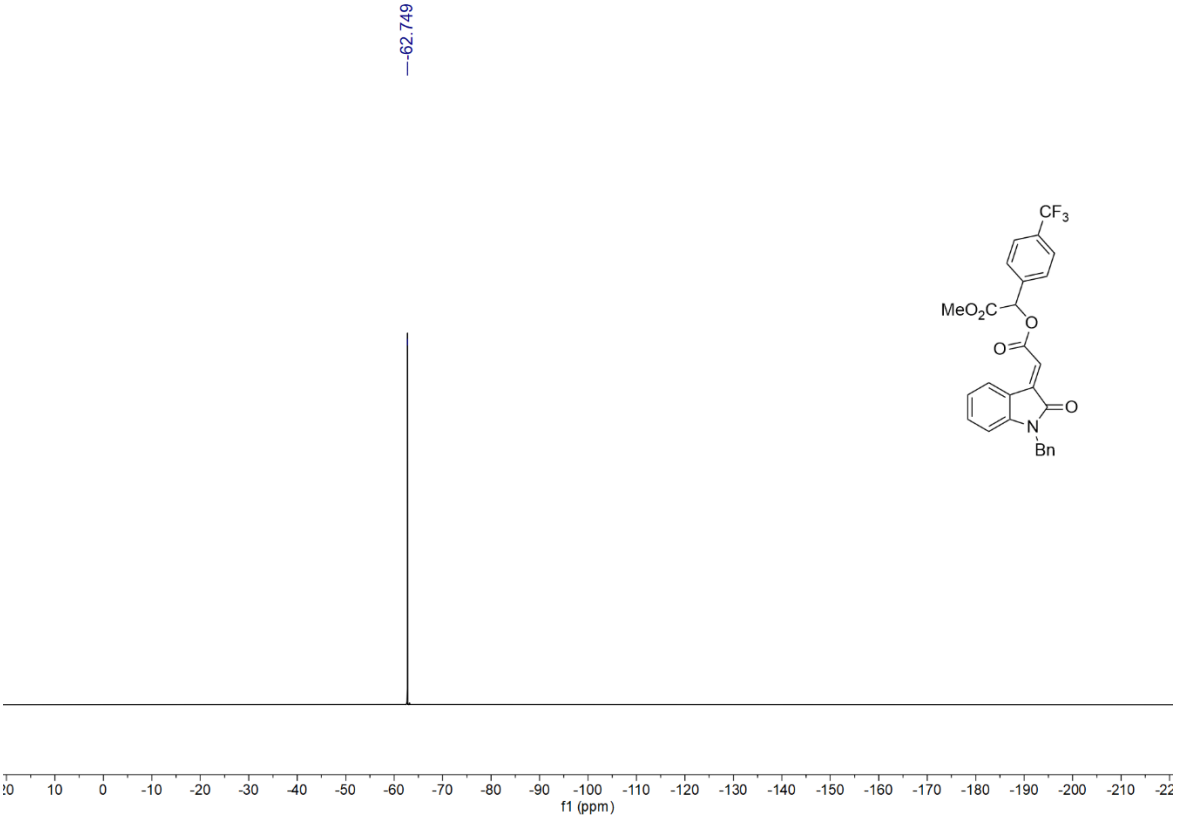
7 ^{1}H NMR (500 MHz, $CDCl_3$)



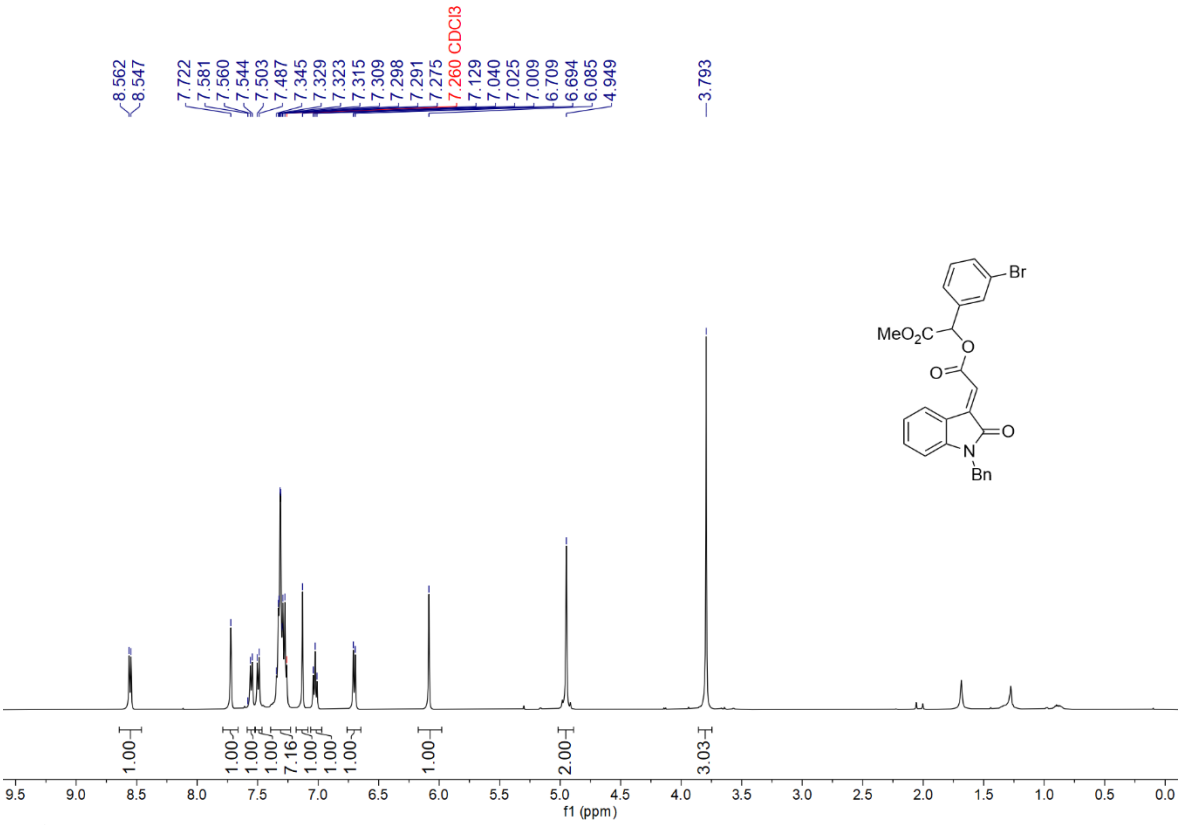
7 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



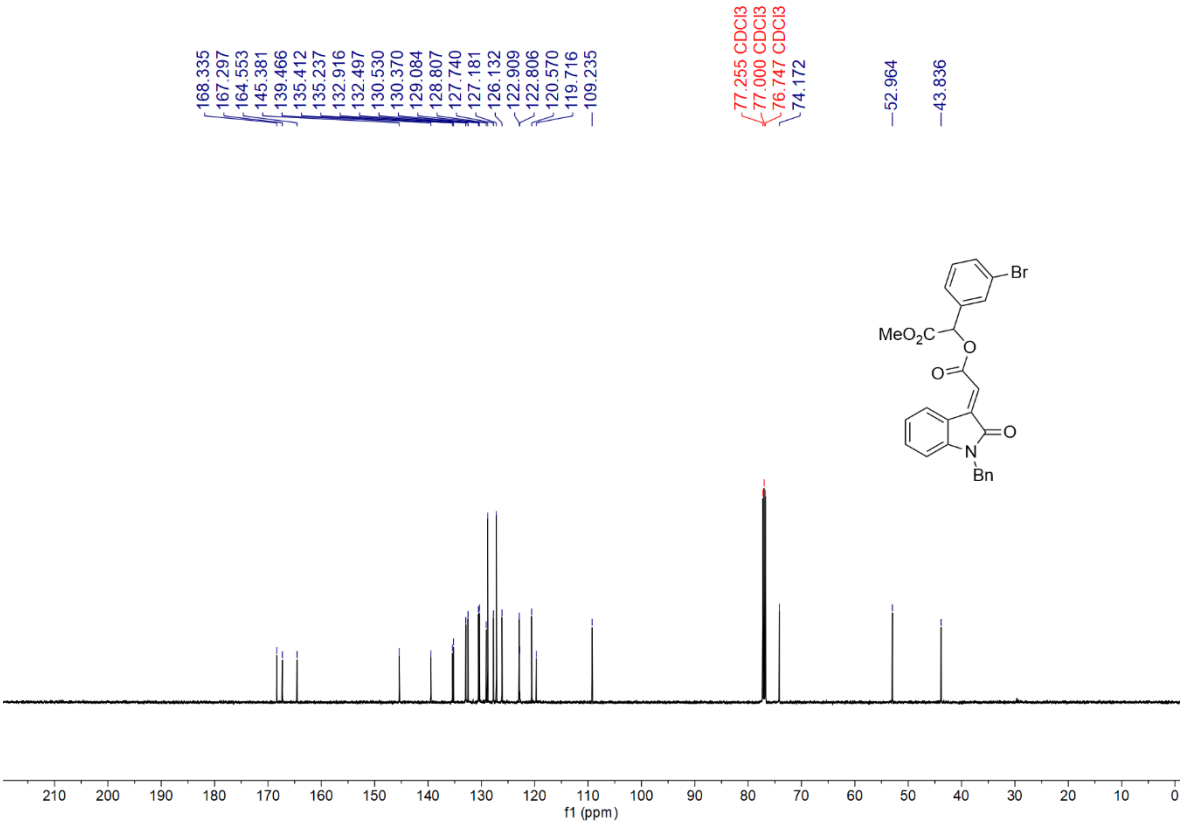
7 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



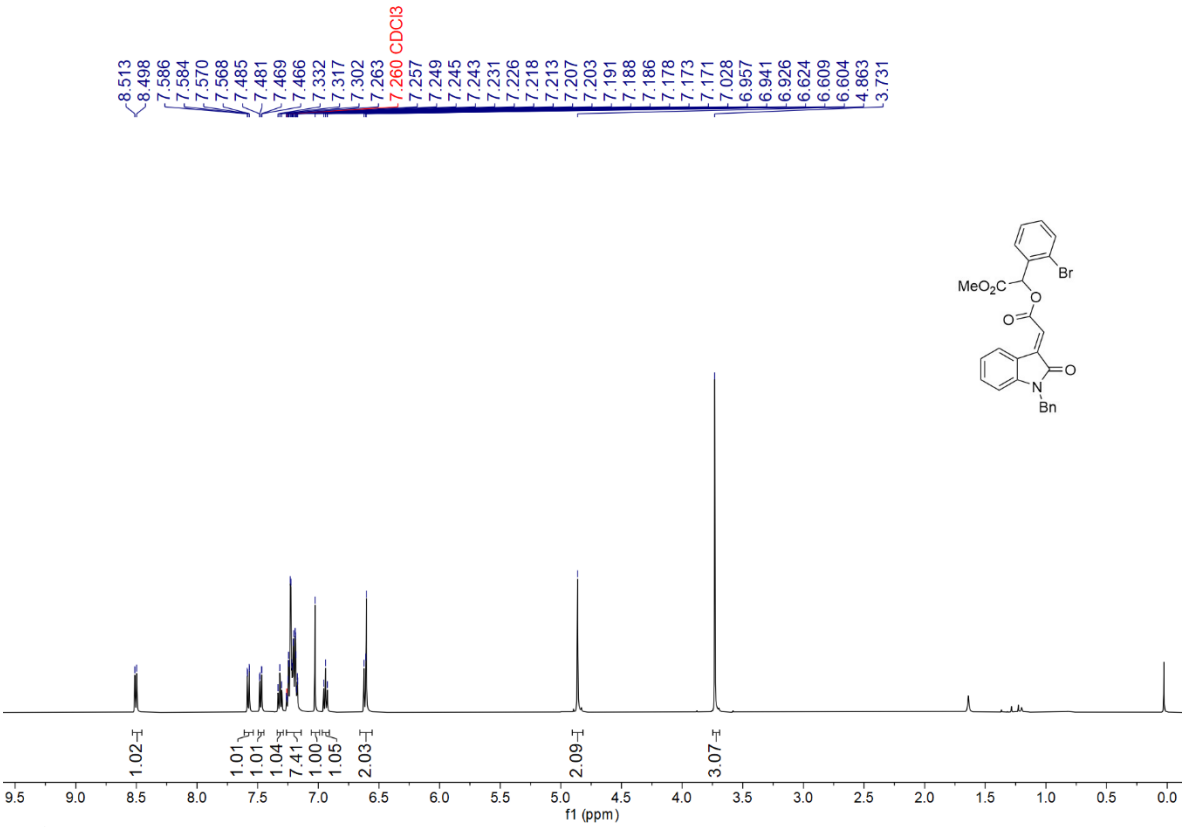
8 ^{1}H NMR (500 MHz, $CDCl_3$)



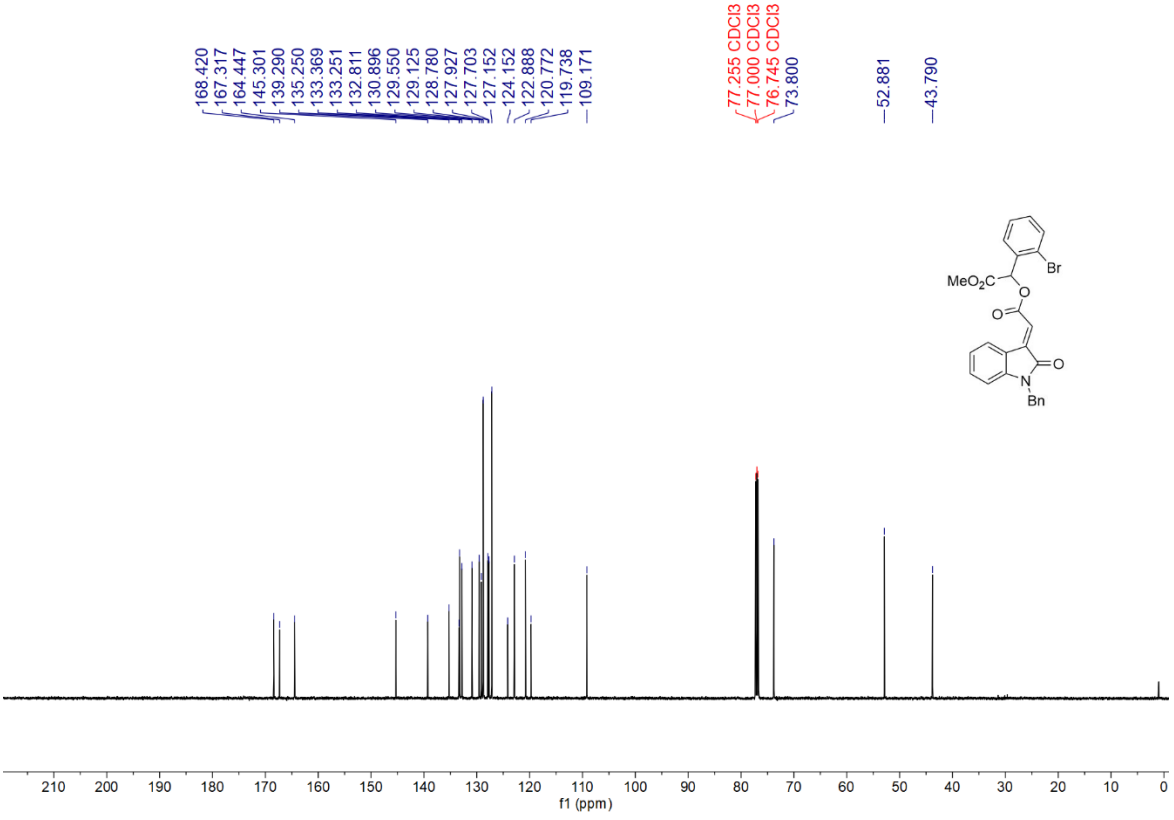
8 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



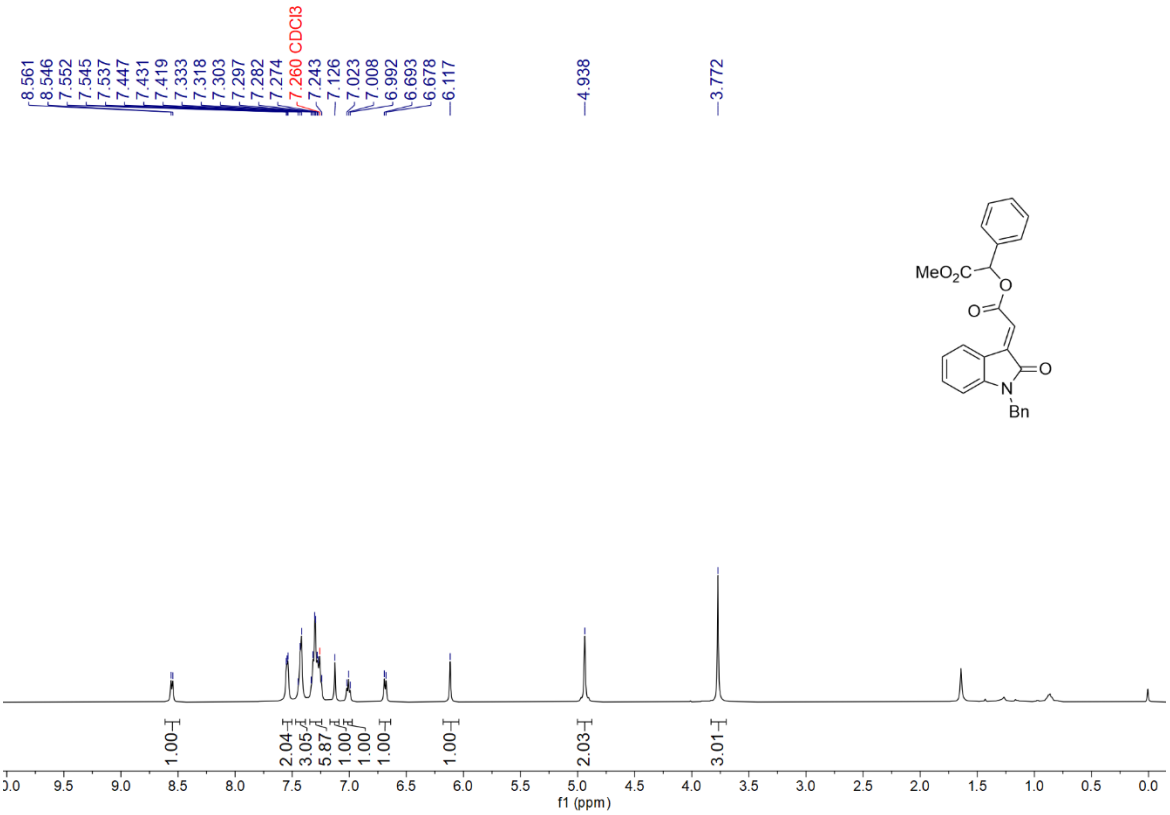
9 ^{1}H NMR (500 MHz, $CDCl_3$)



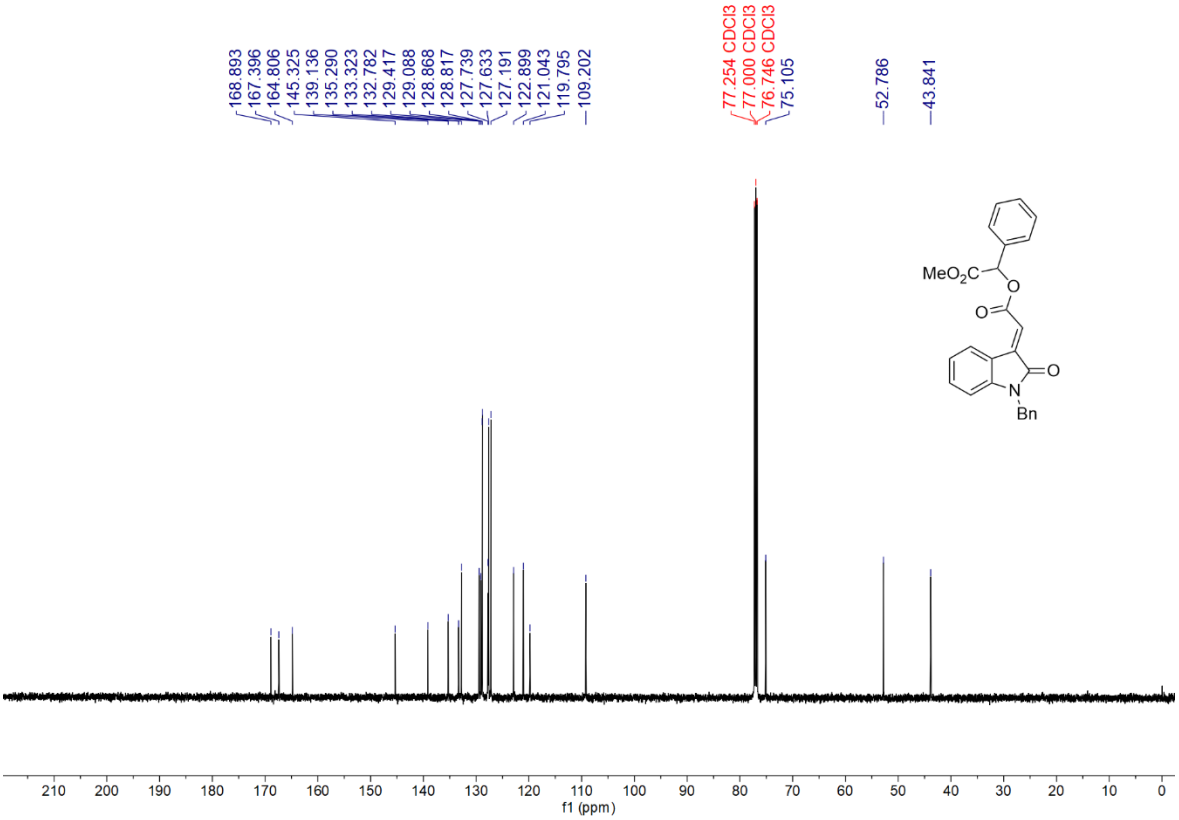
9 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



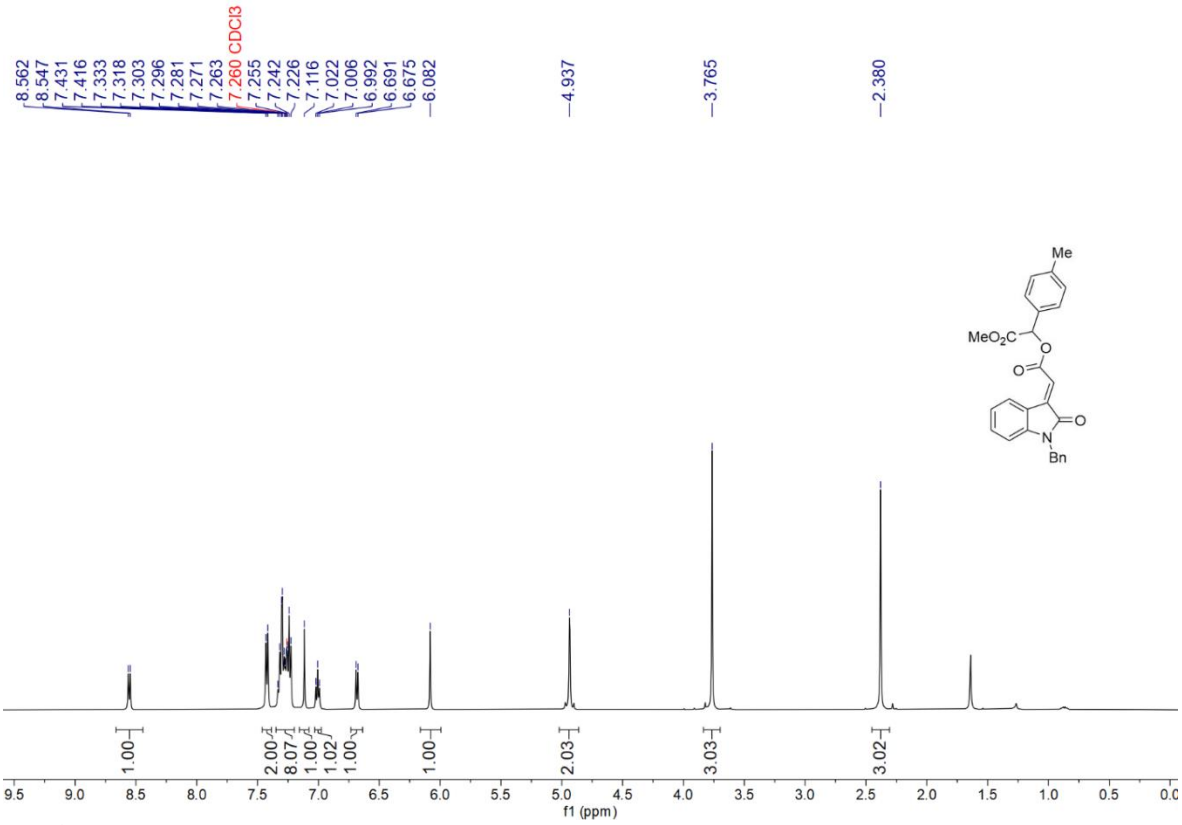
10 ^{1}H NMR (500 MHz, $CDCl_3$)



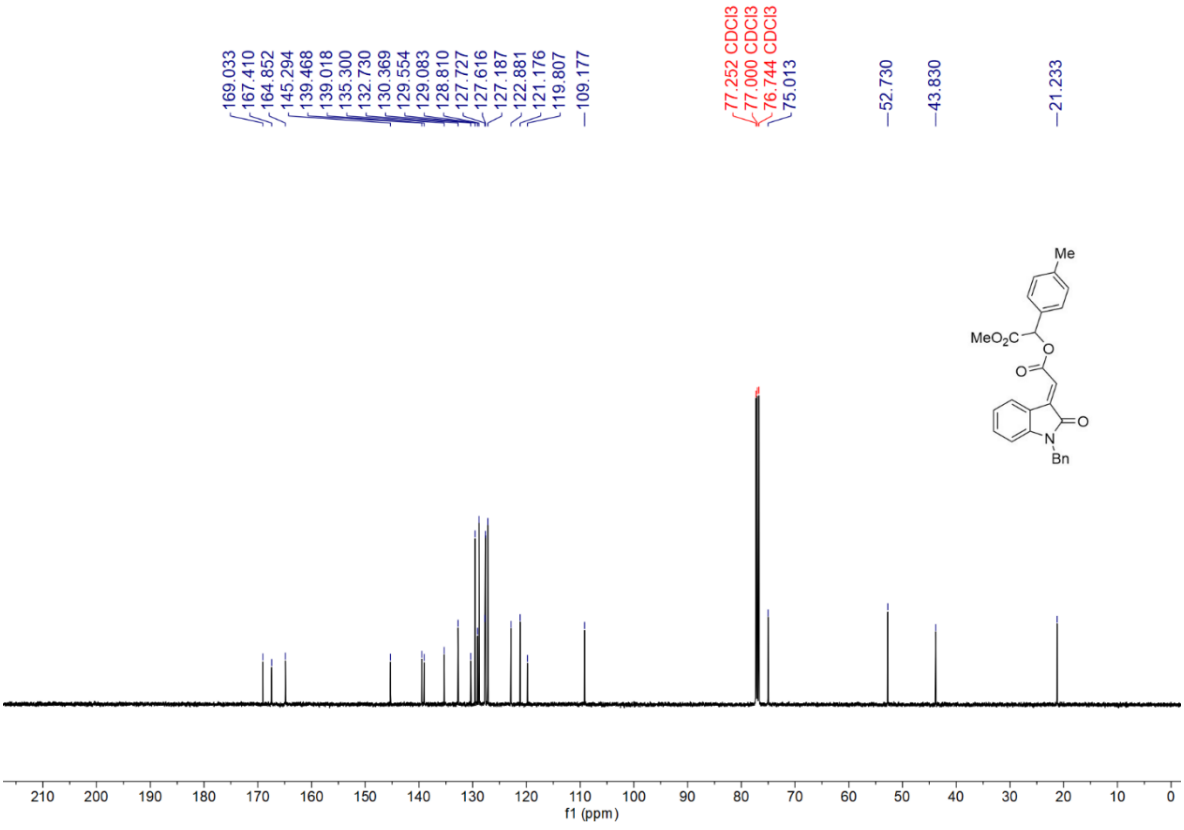
10 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



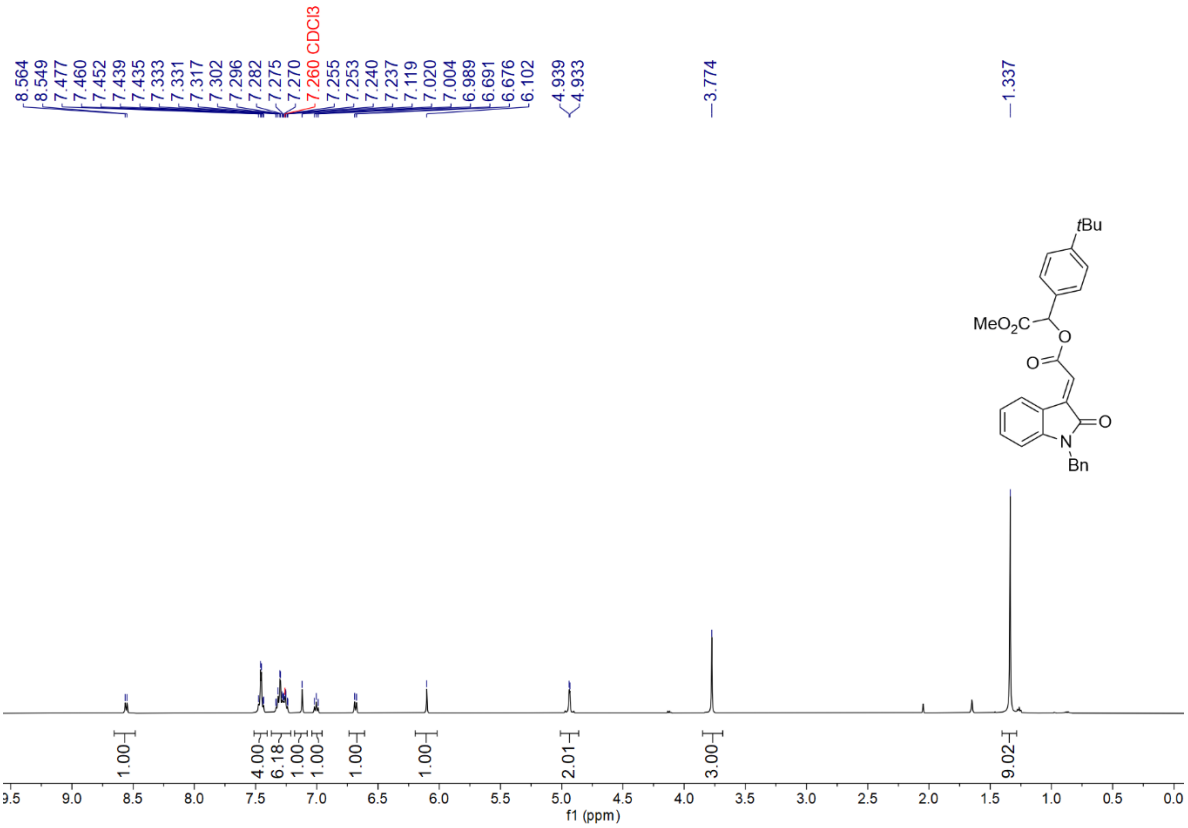
11 ^{1}H NMR (500 MHz, $CDCl_3$)



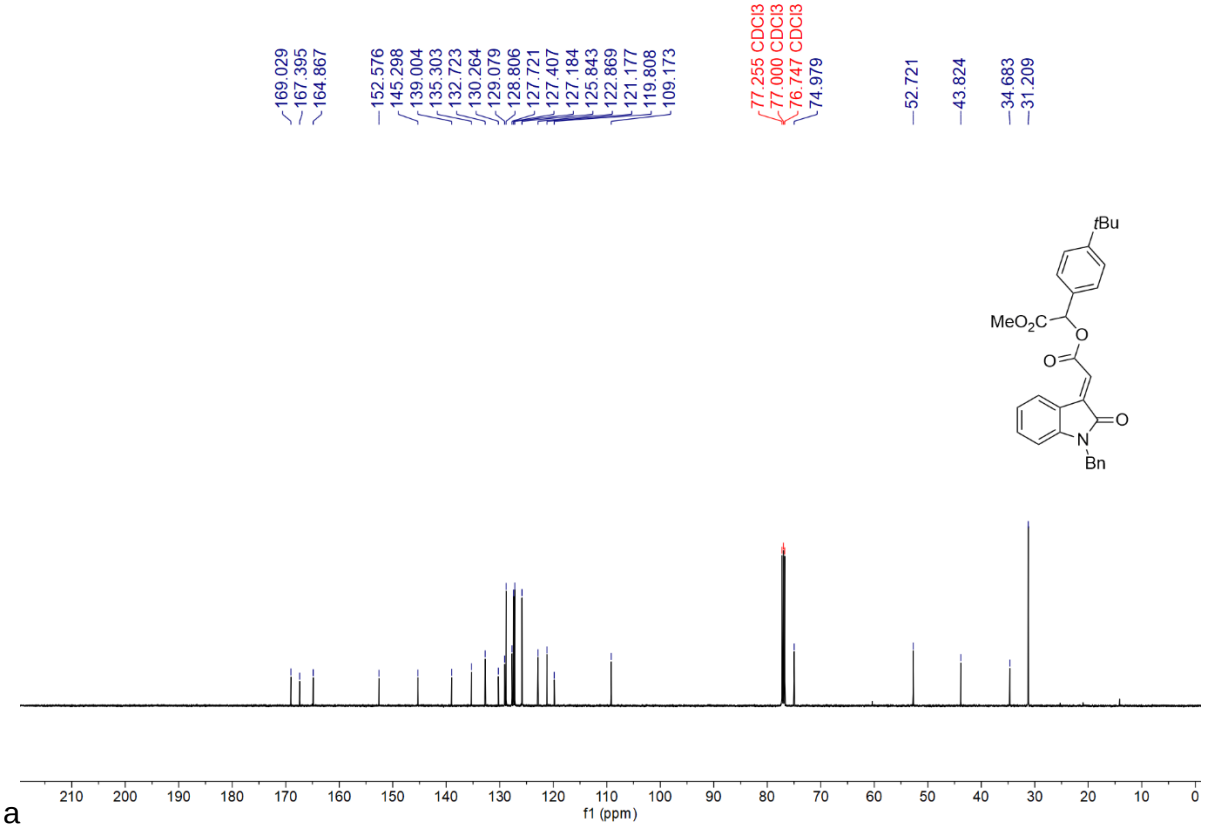
11 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



12 ^{1}H NMR (500 MHz, $CDCl_3$)

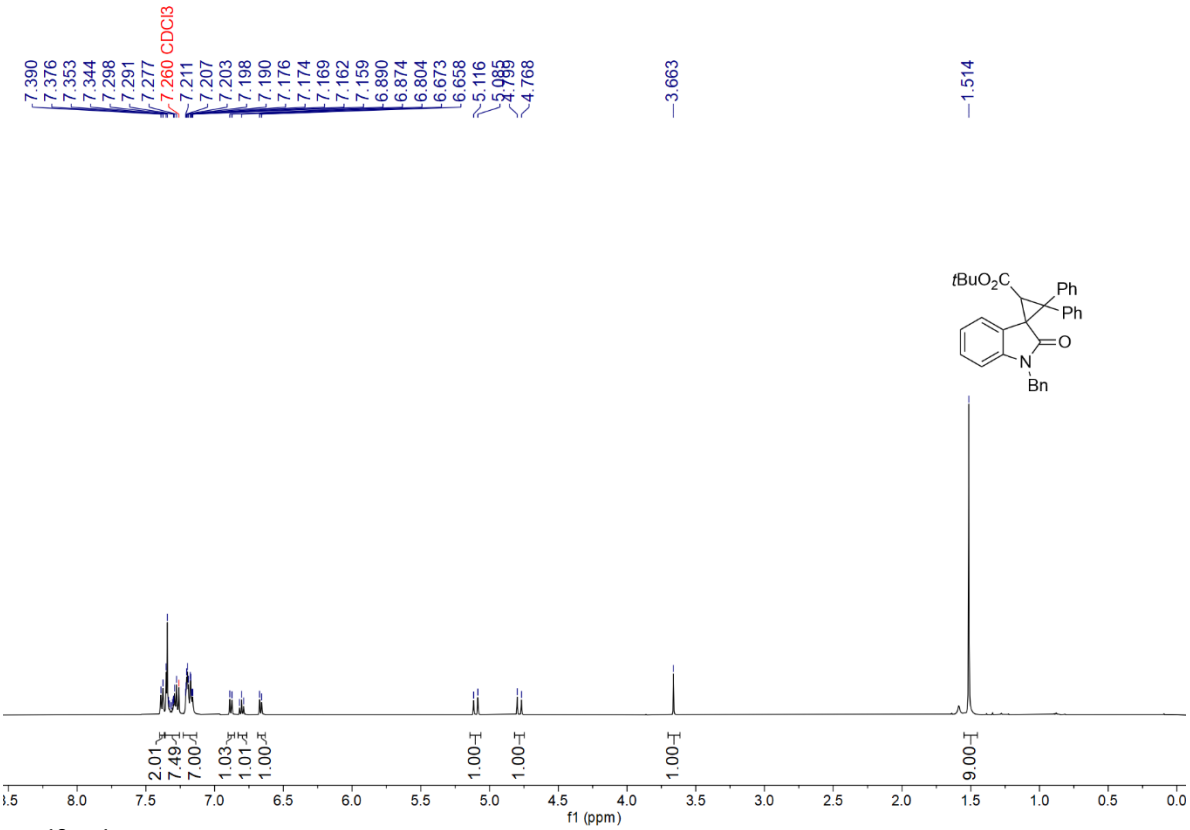


12 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

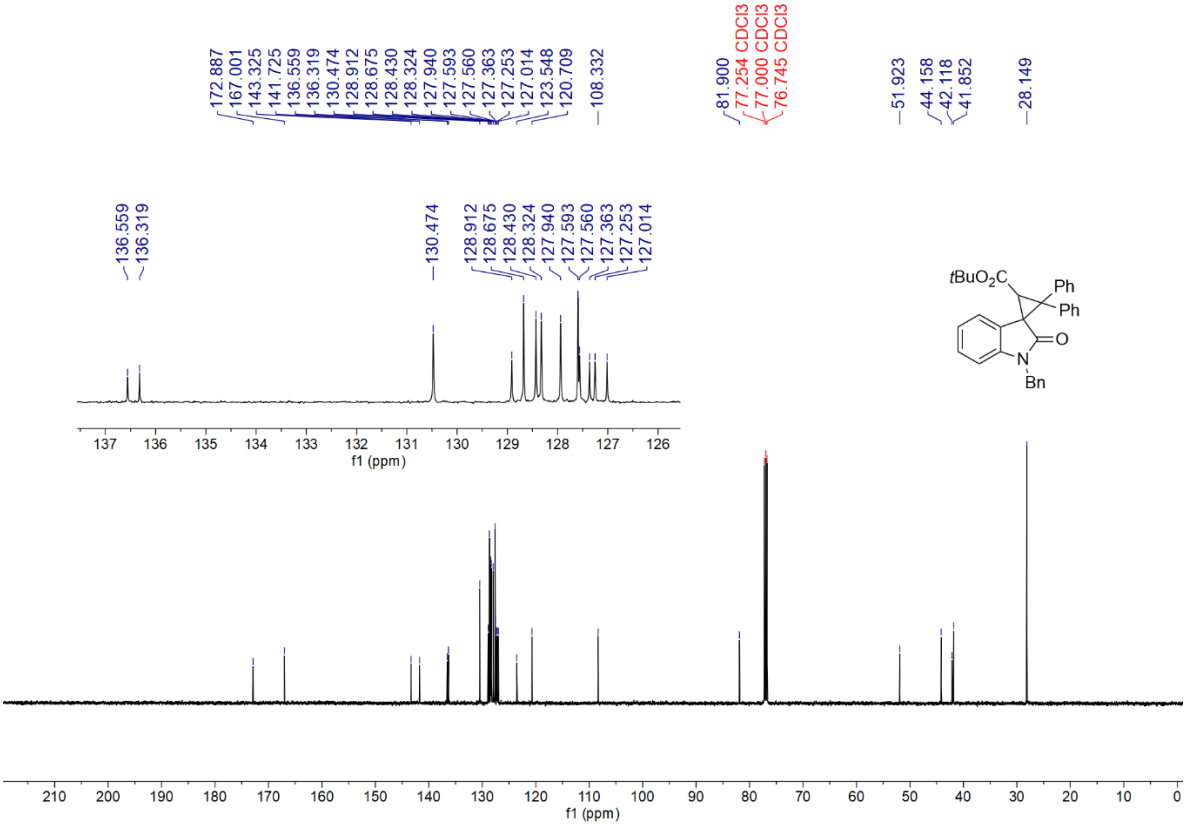


a

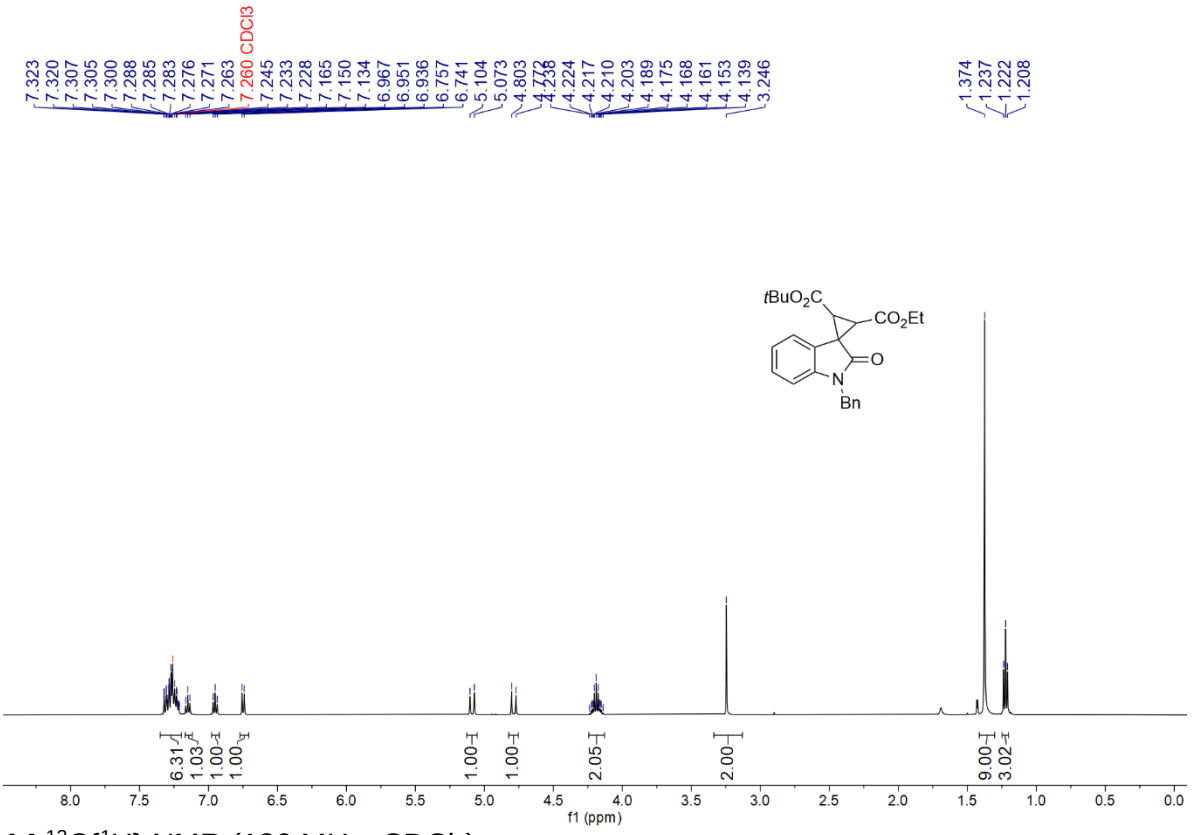
13 ^{1}H NMR (500 MHz, $CDCl_3$)



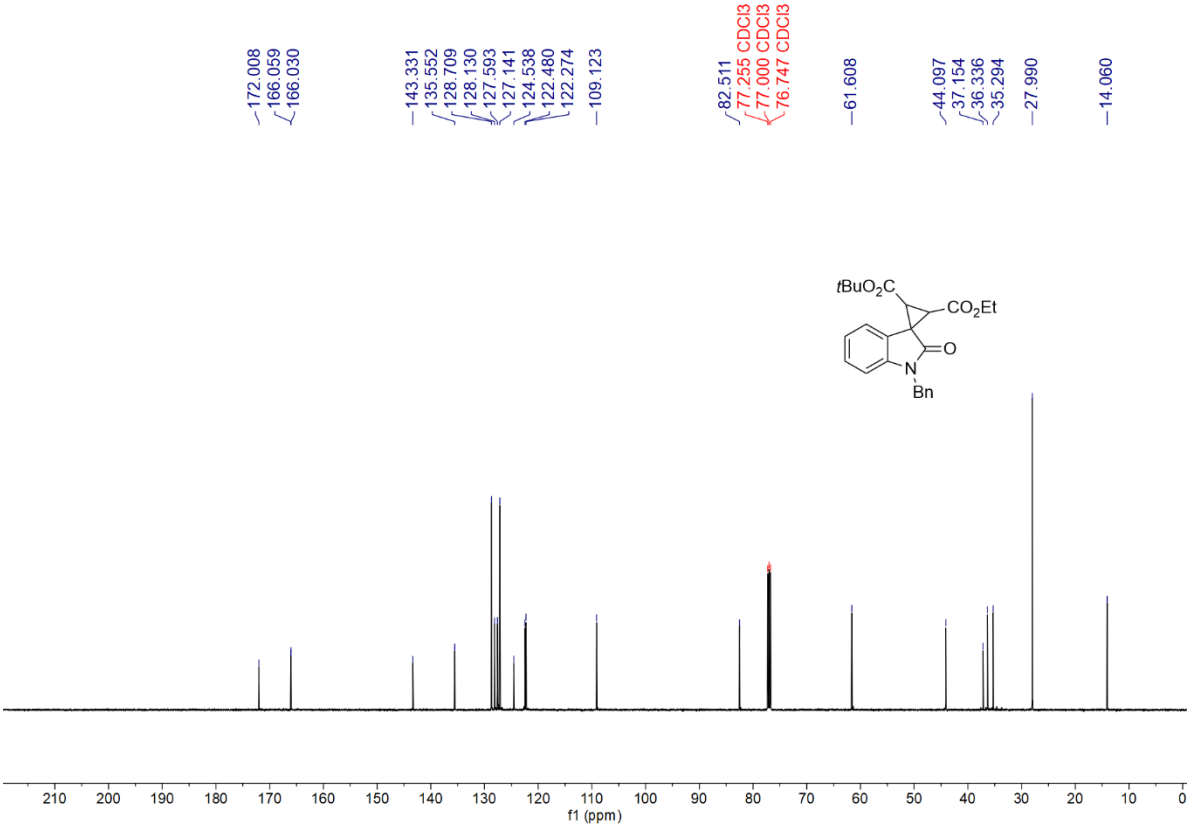
13 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



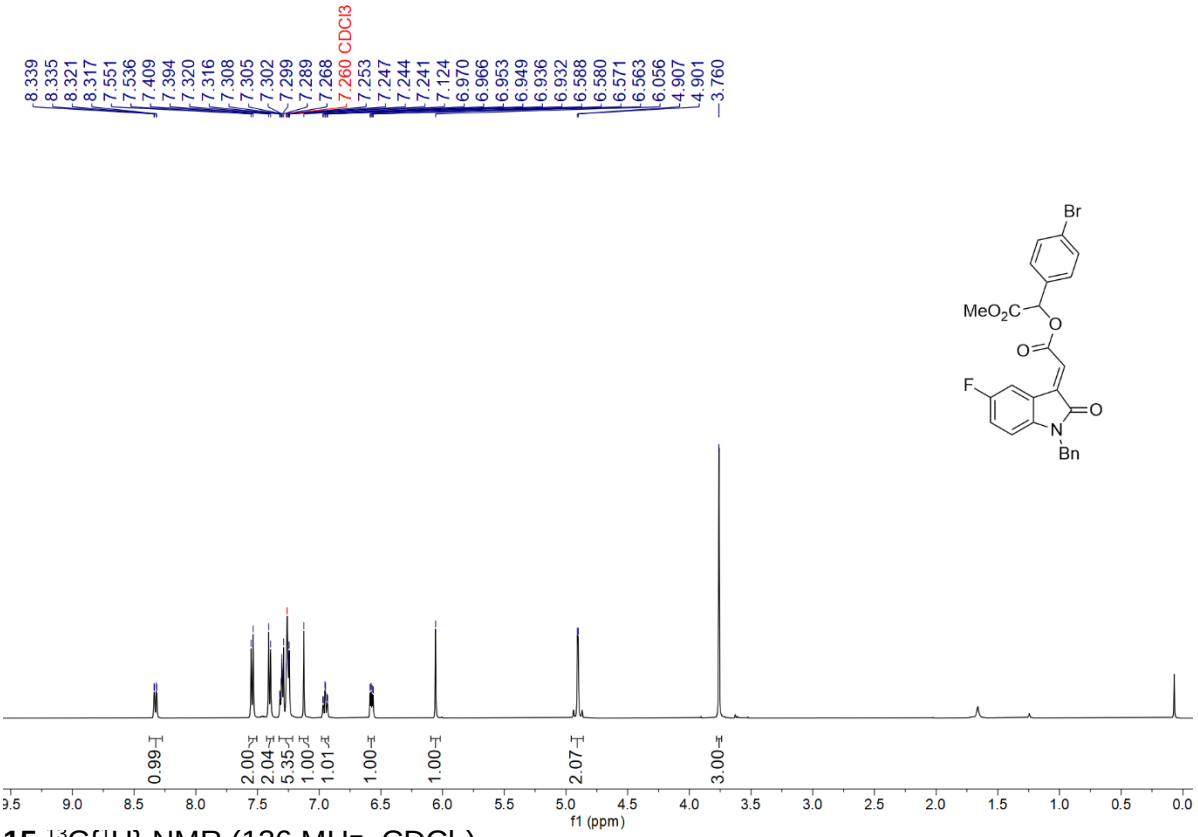
14 ^{1}H NMR (500 MHz, $CDCl_3$)



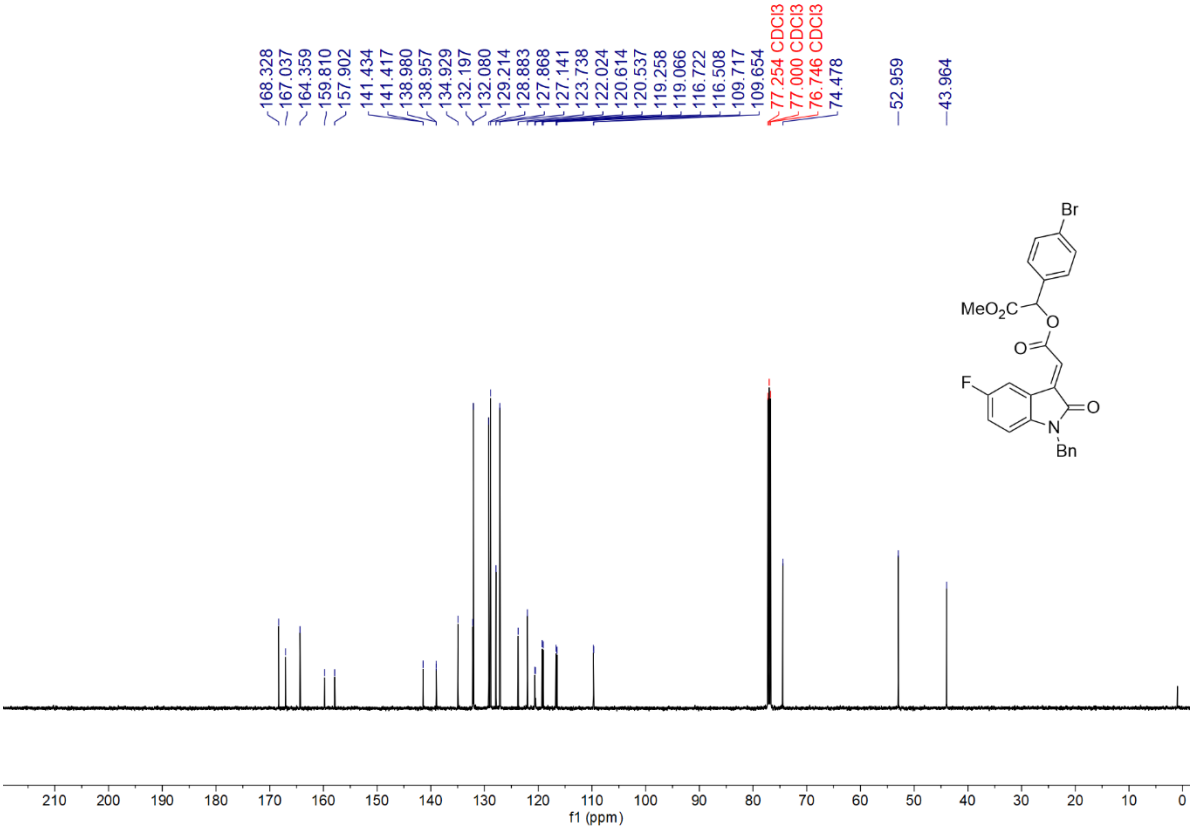
14 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



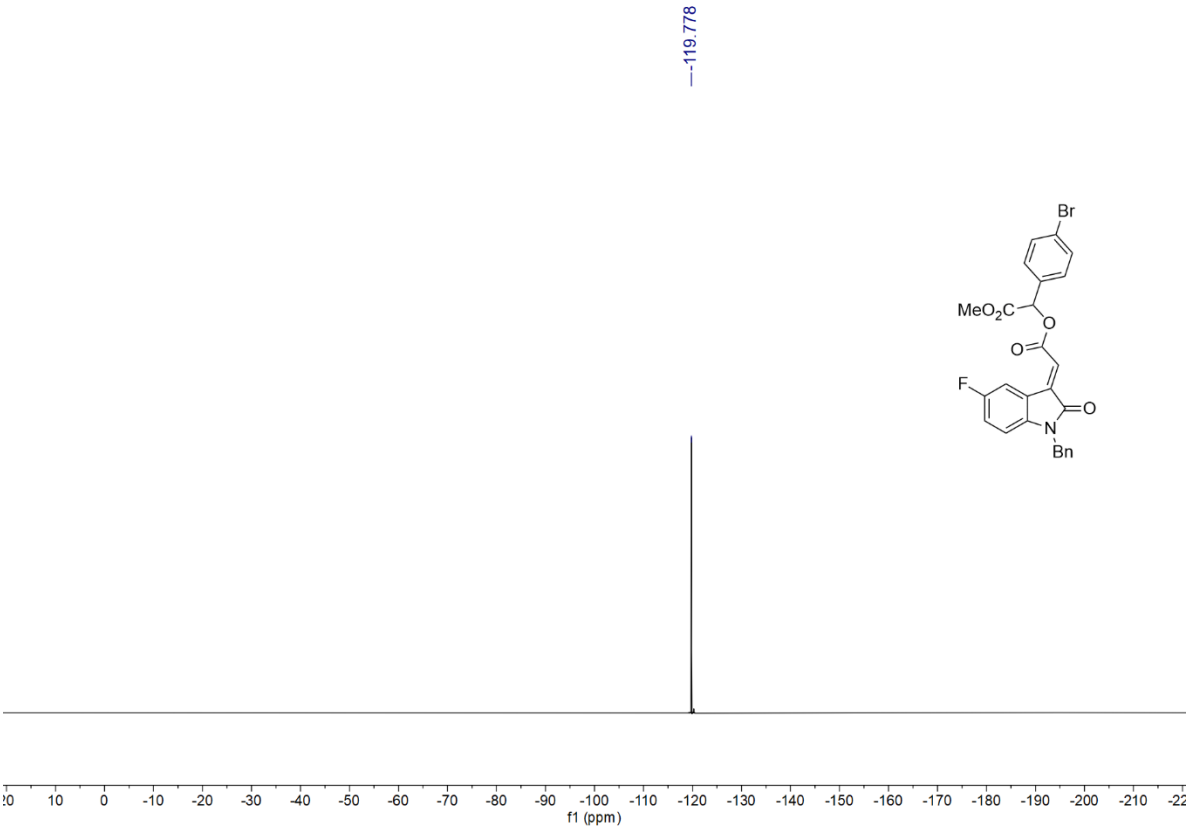
15 ^{1}H NMR (500 MHz, $CDCl_3$)



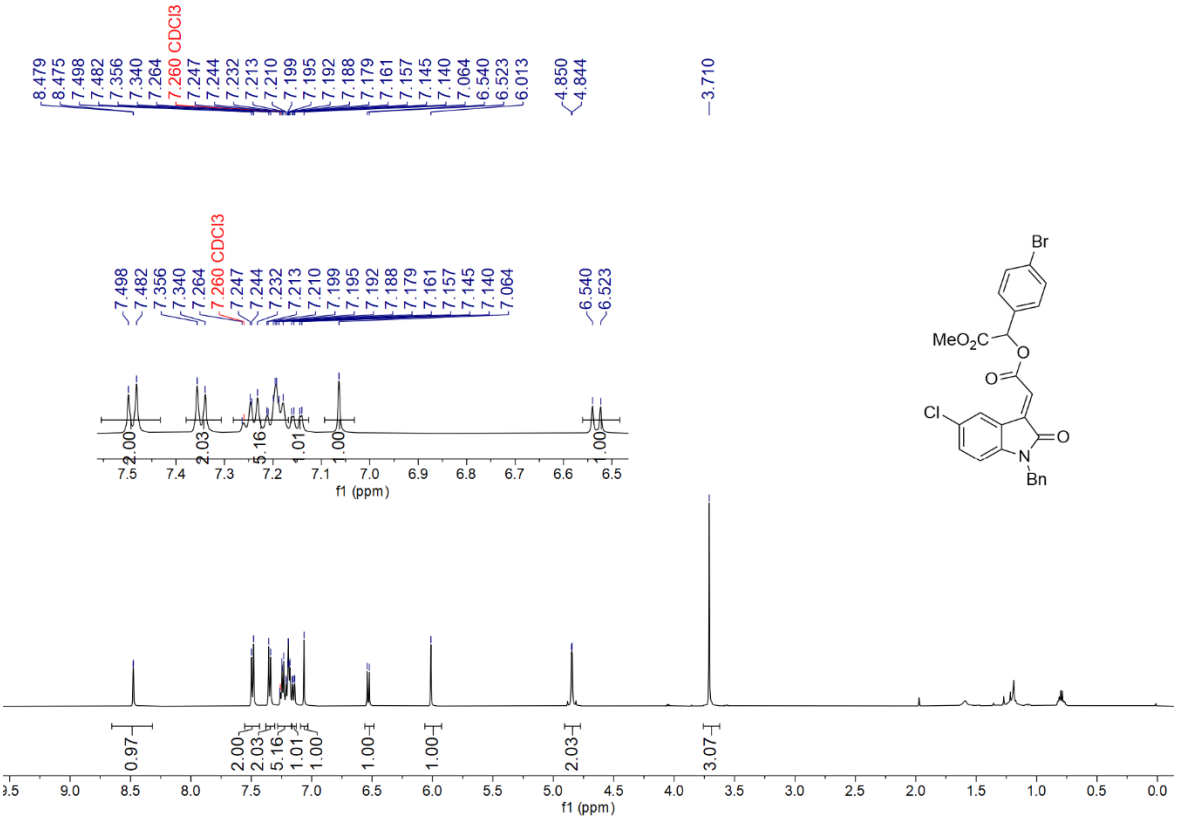
15 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



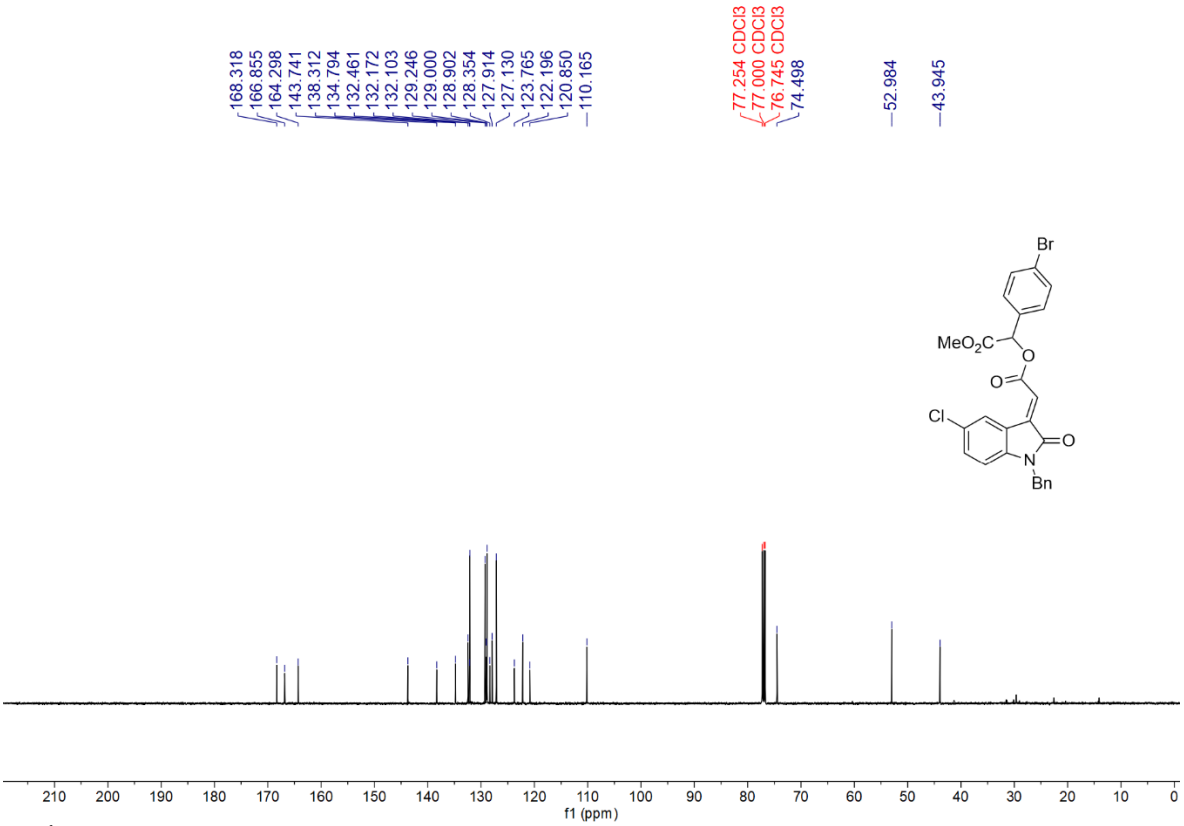
15 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



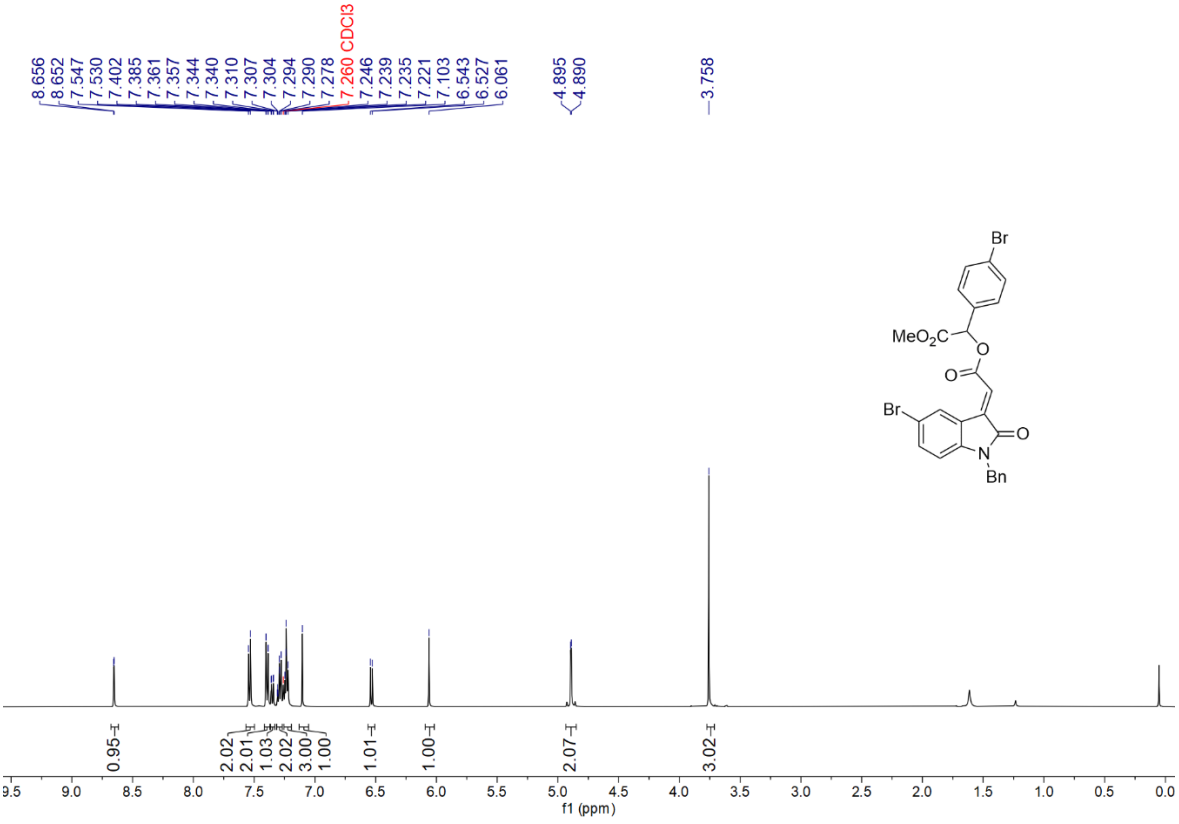
16 ^{1}H NMR (500 MHz, $CDCl_3$)



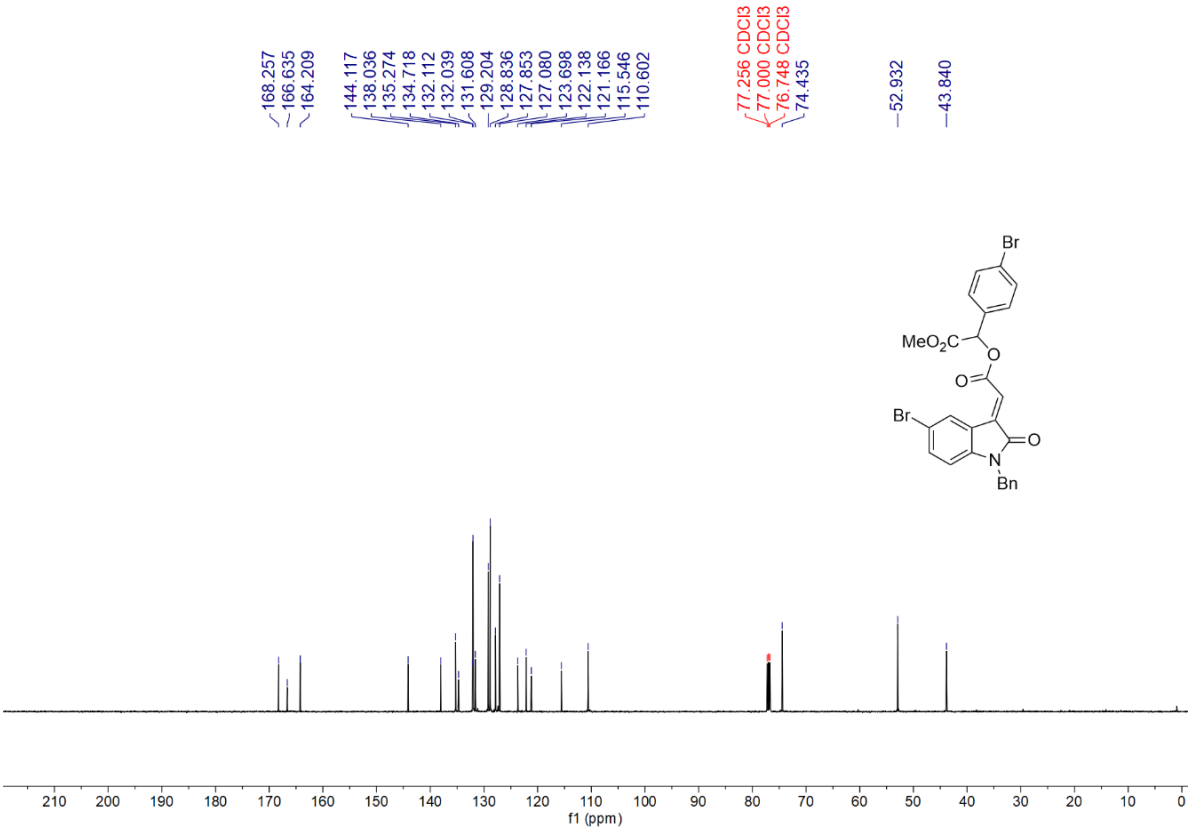
16 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



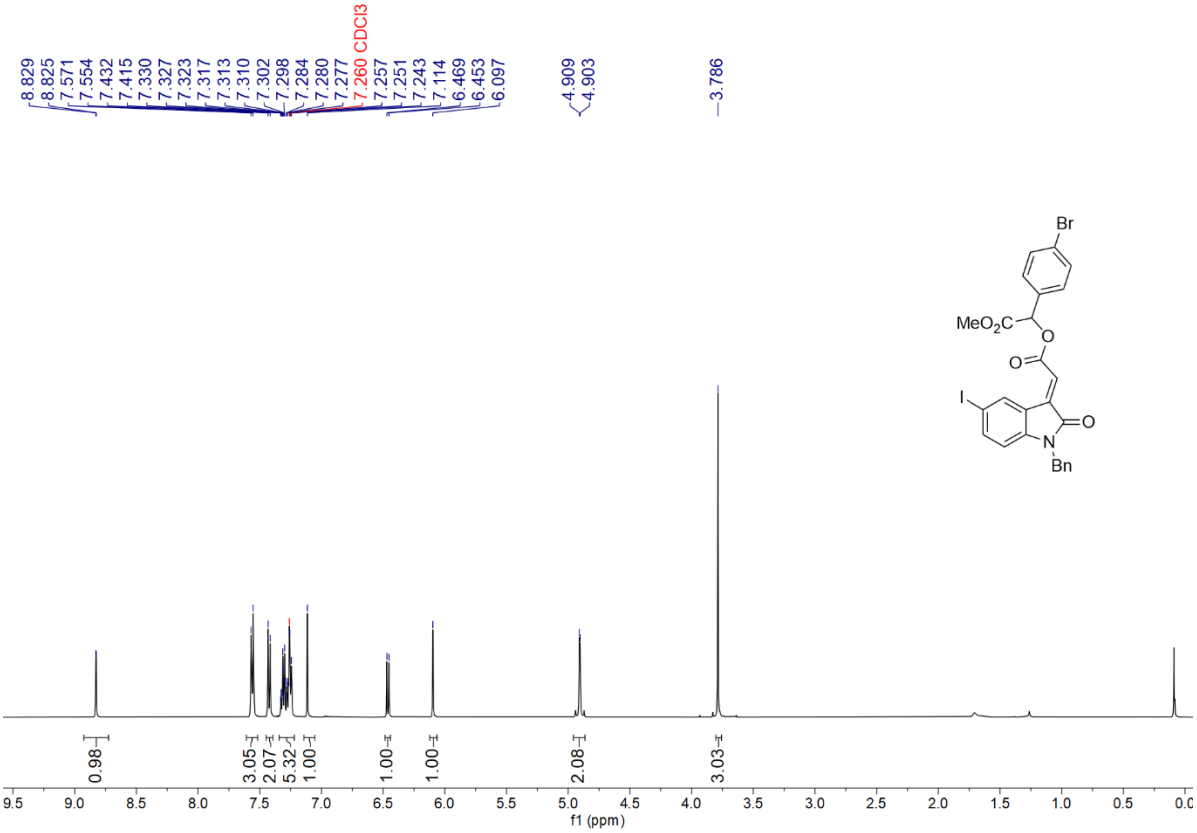
17 ^{1}H NMR (500 MHz, $CDCl_3$)



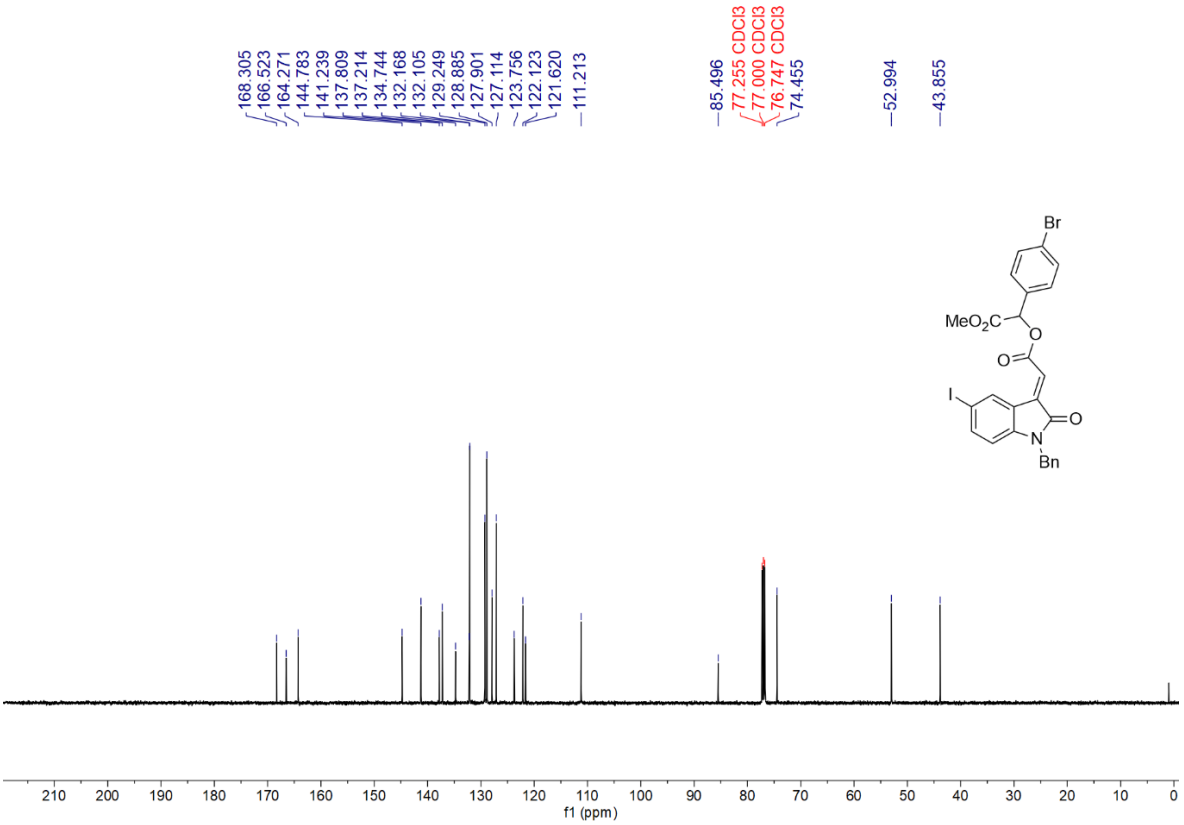
17 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



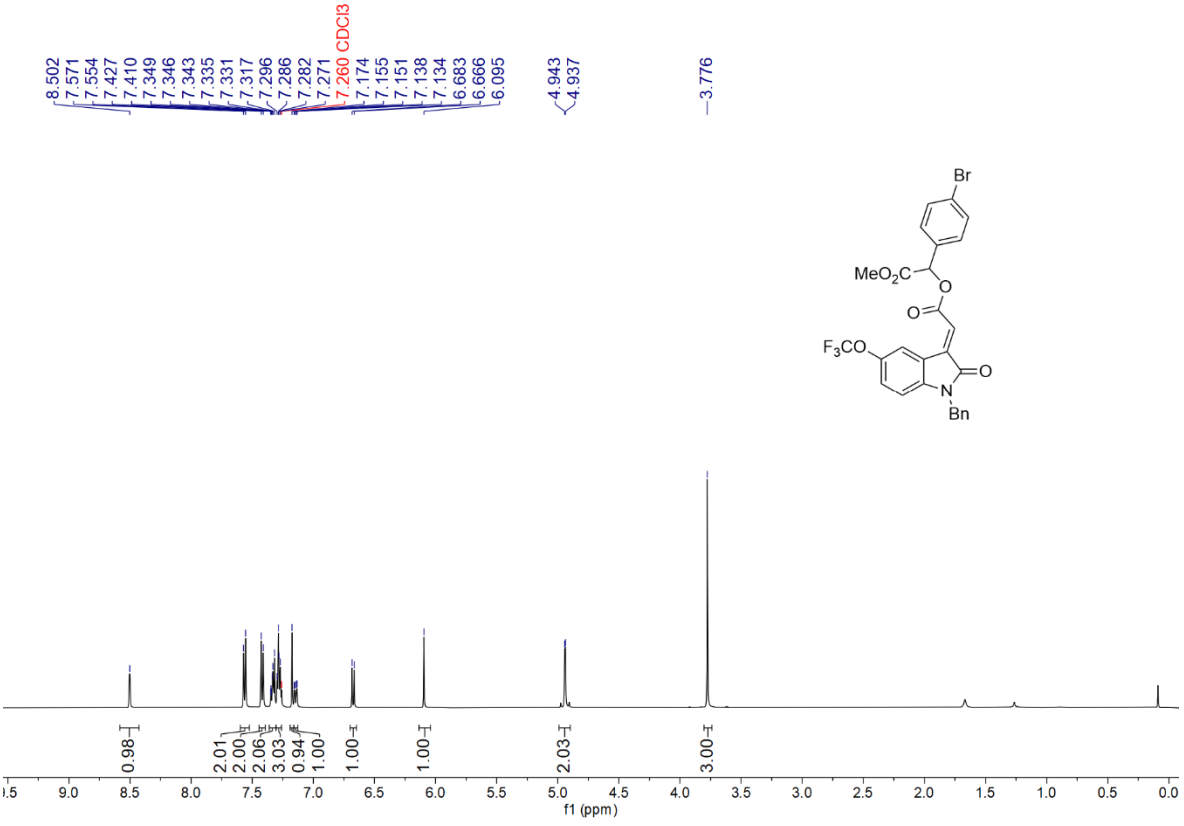
18 ^{1}H NMR (500 MHz, $CDCl_3$)



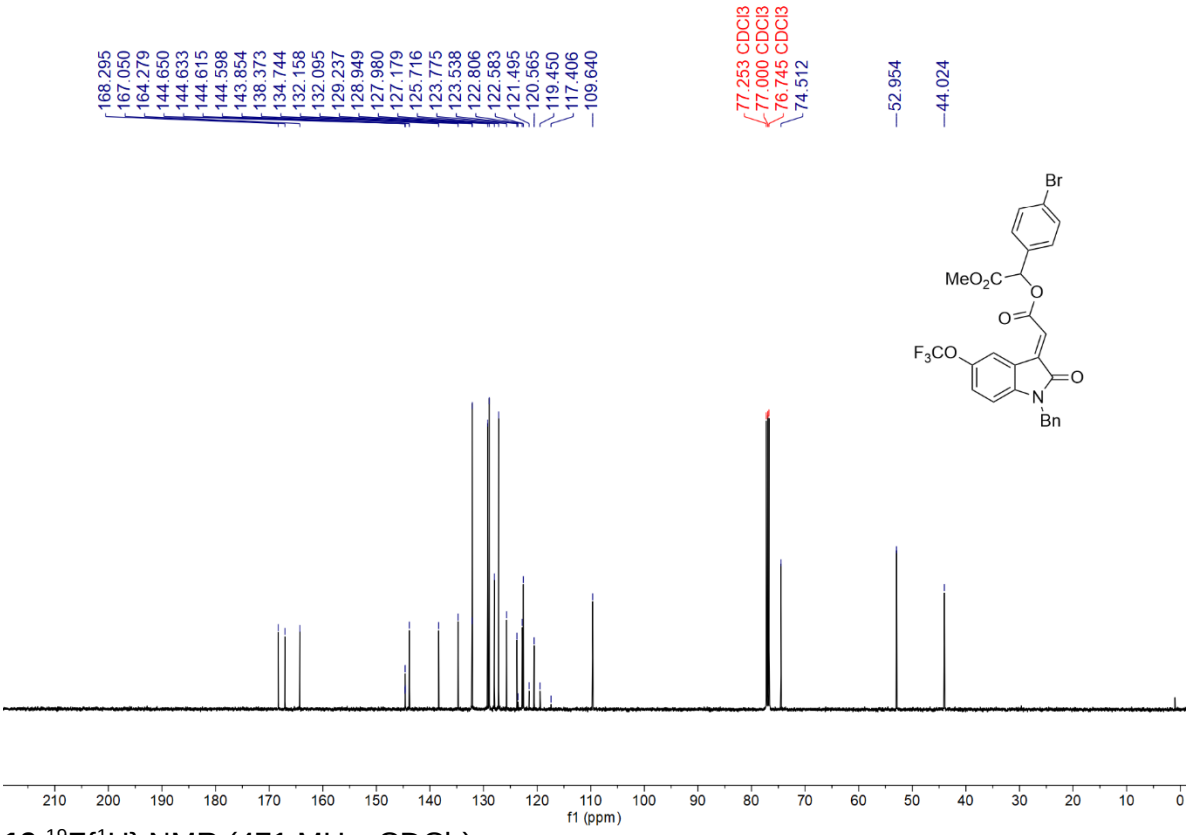
18 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



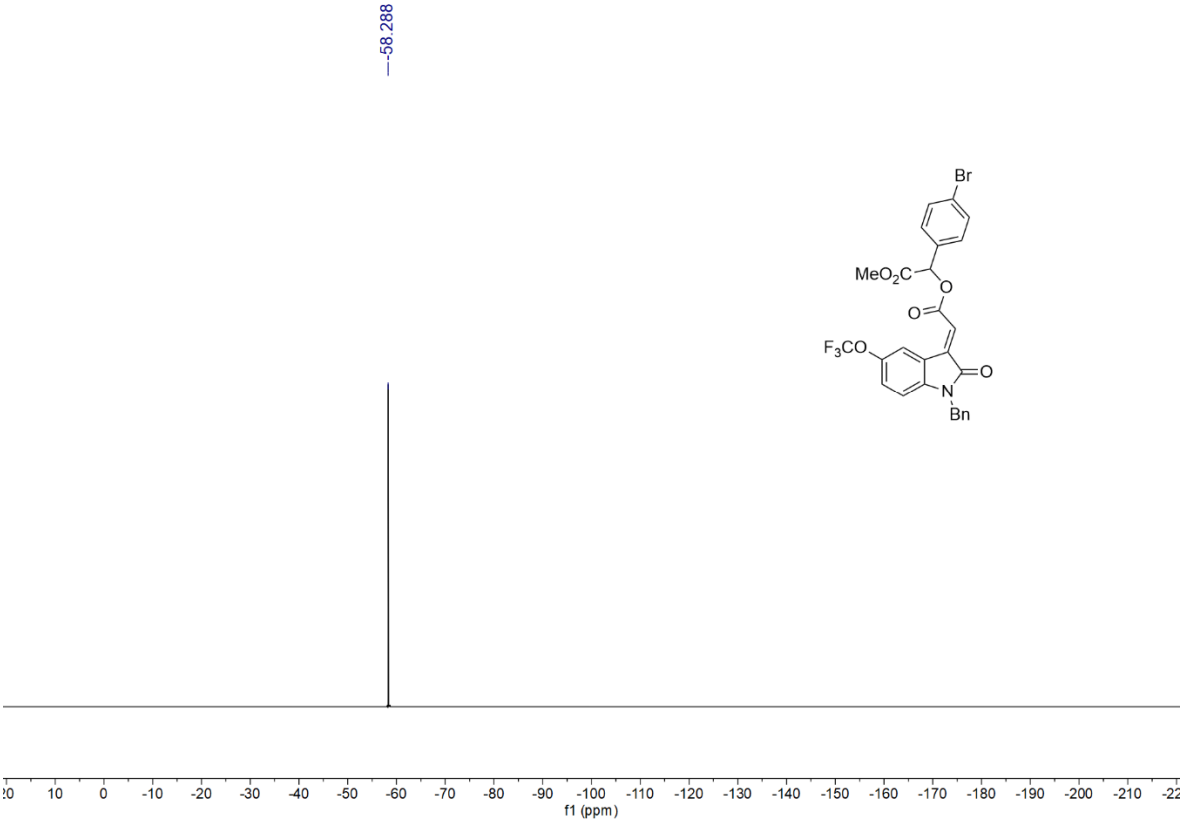
19 ^{1}H NMR (500 MHz, $CDCl_3$)



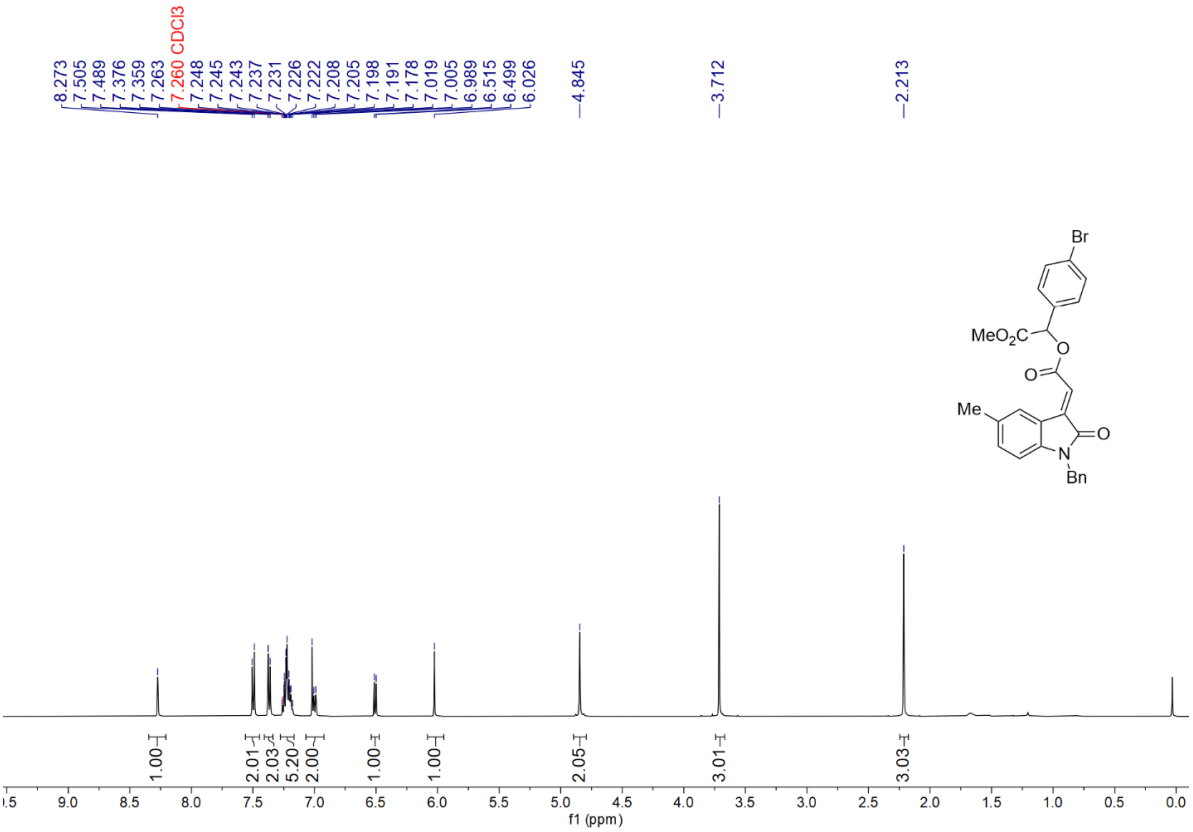
19 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



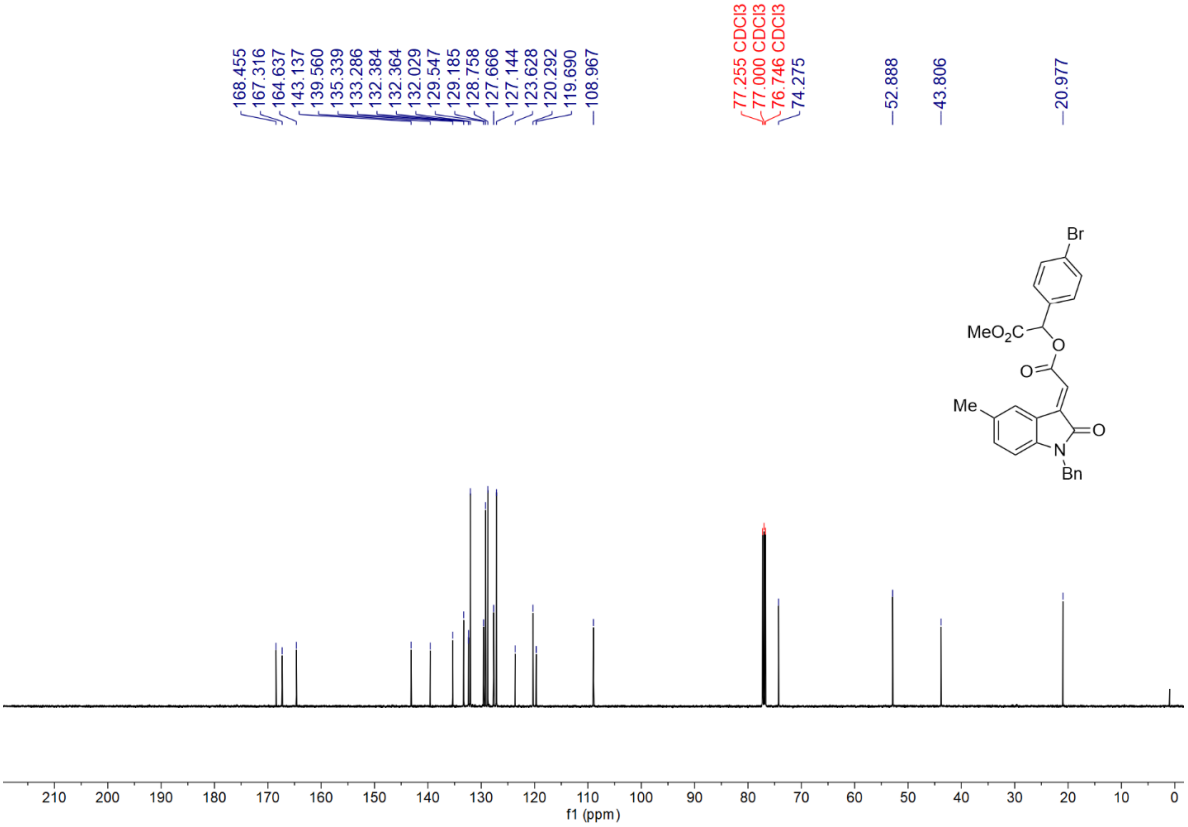
19 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



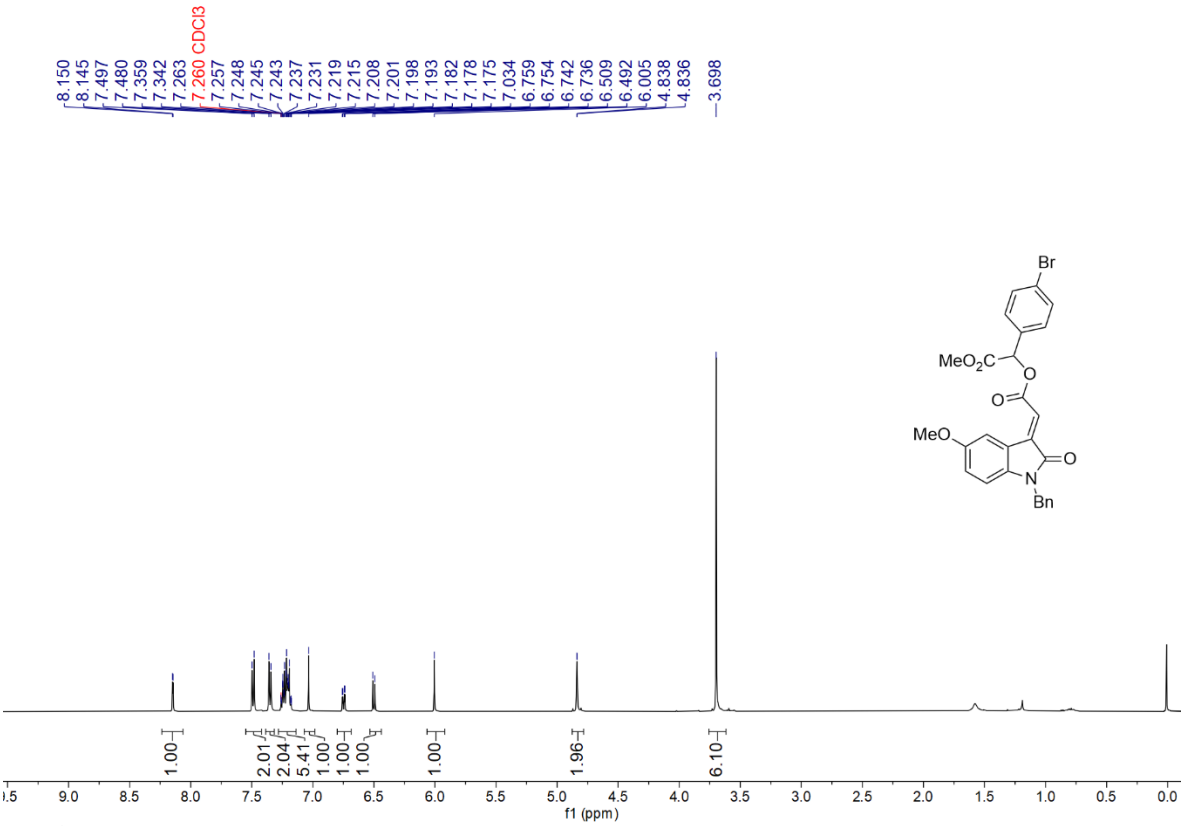
20 ^{1}H NMR (500 MHz, $CDCl_3$)



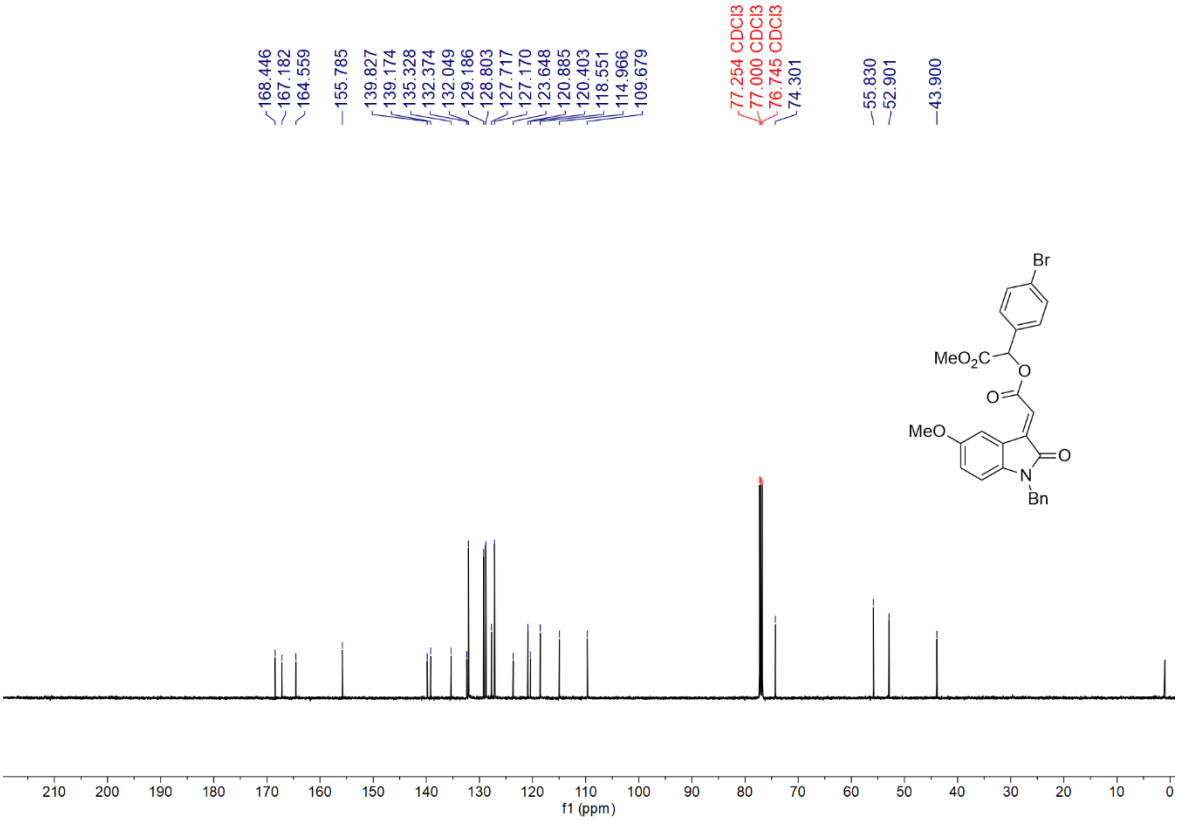
20 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



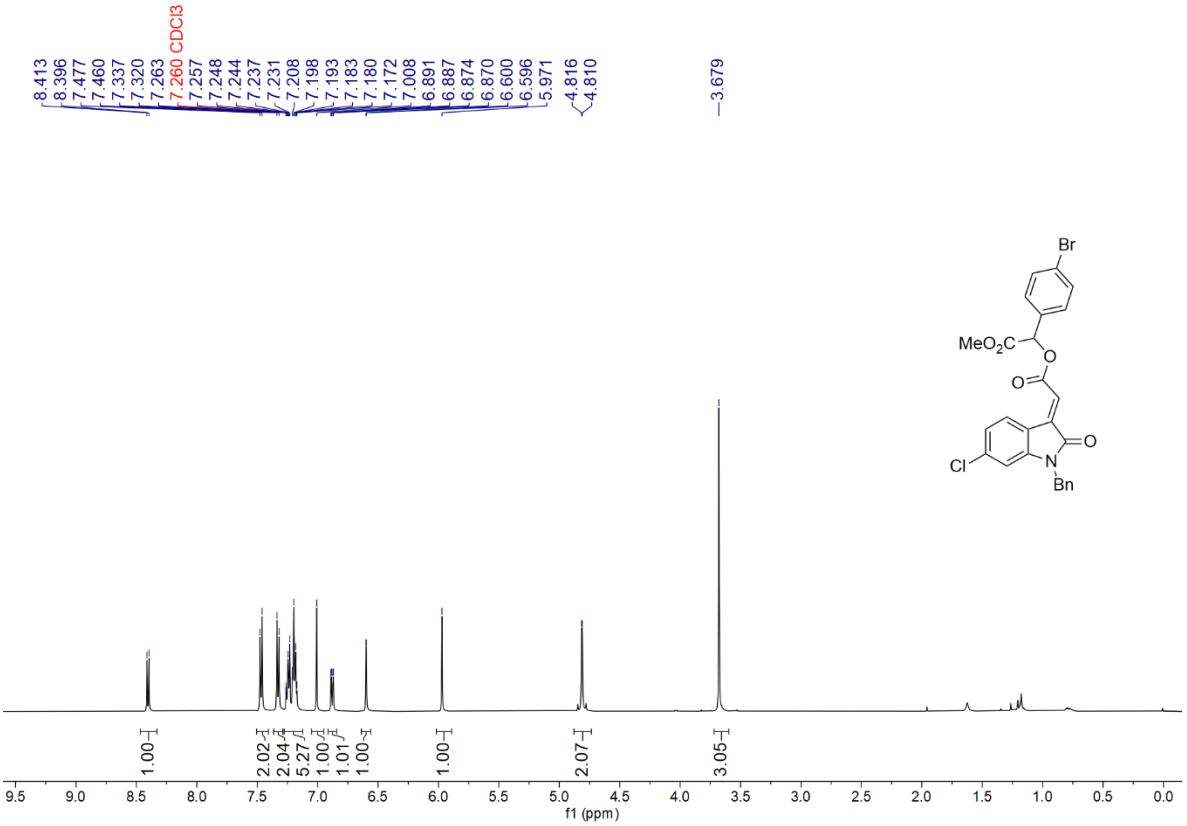
21 ^{1}H NMR (500 MHz, $CDCl_3$)



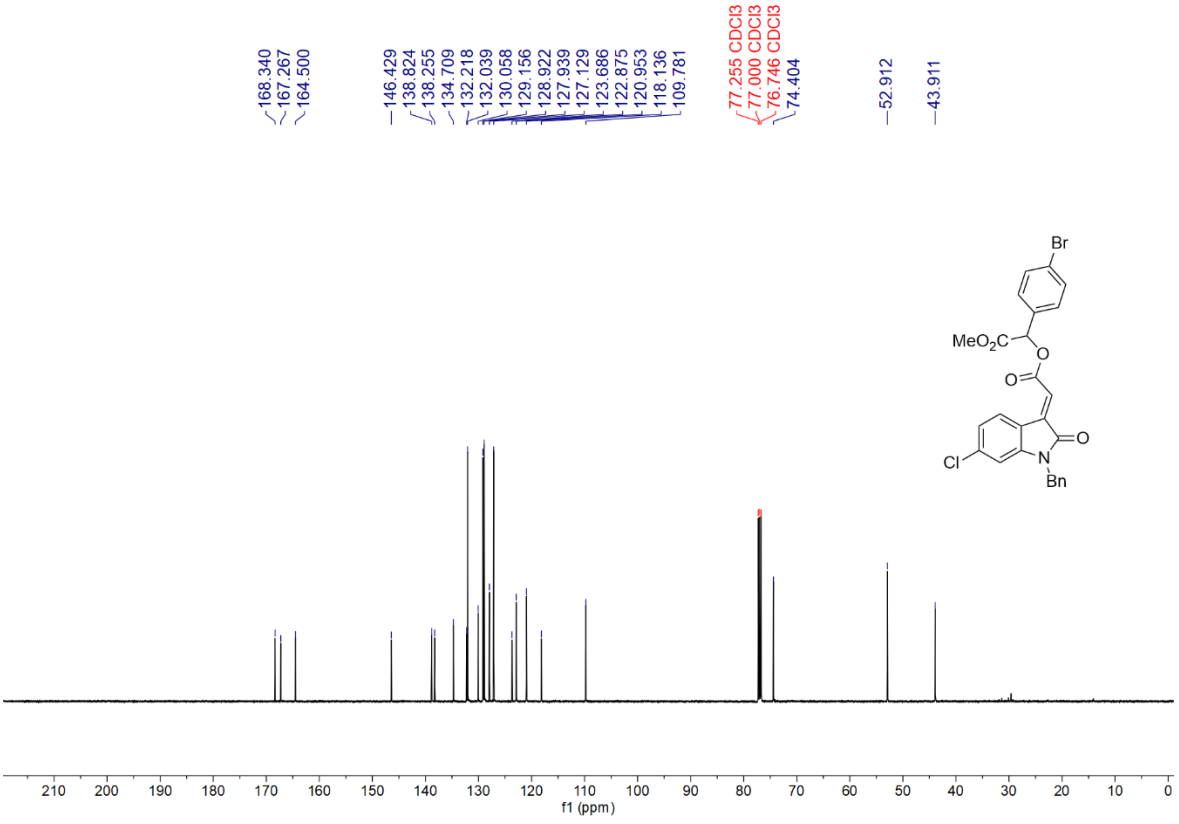
21 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



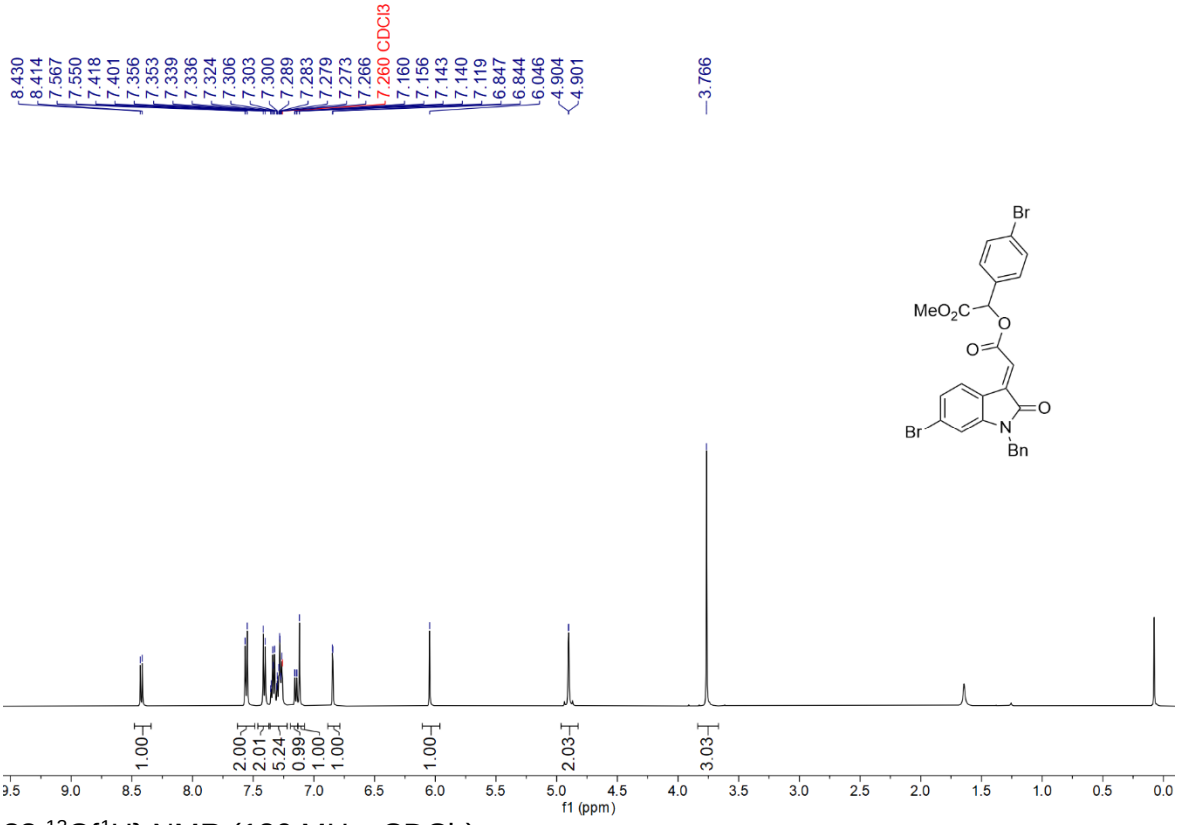
22 ^{1}H NMR (500 MHz, $CDCl_3$)



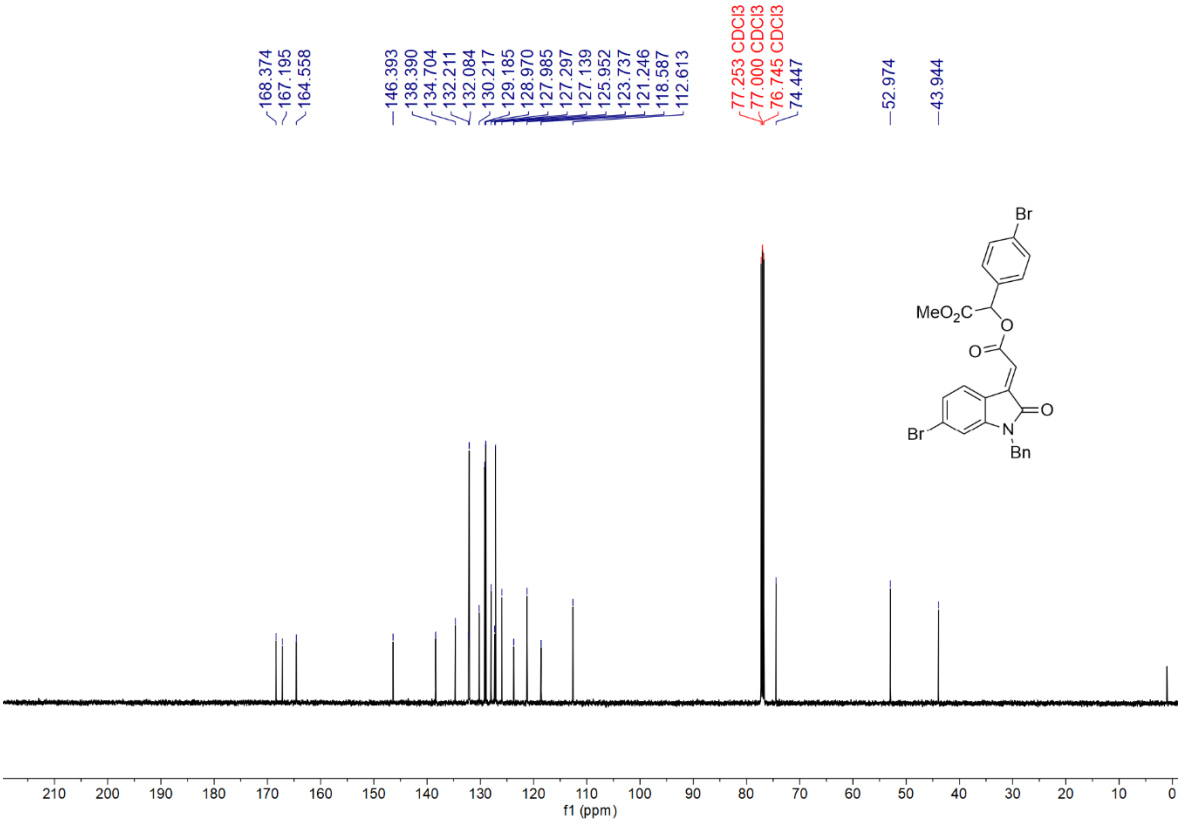
22 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



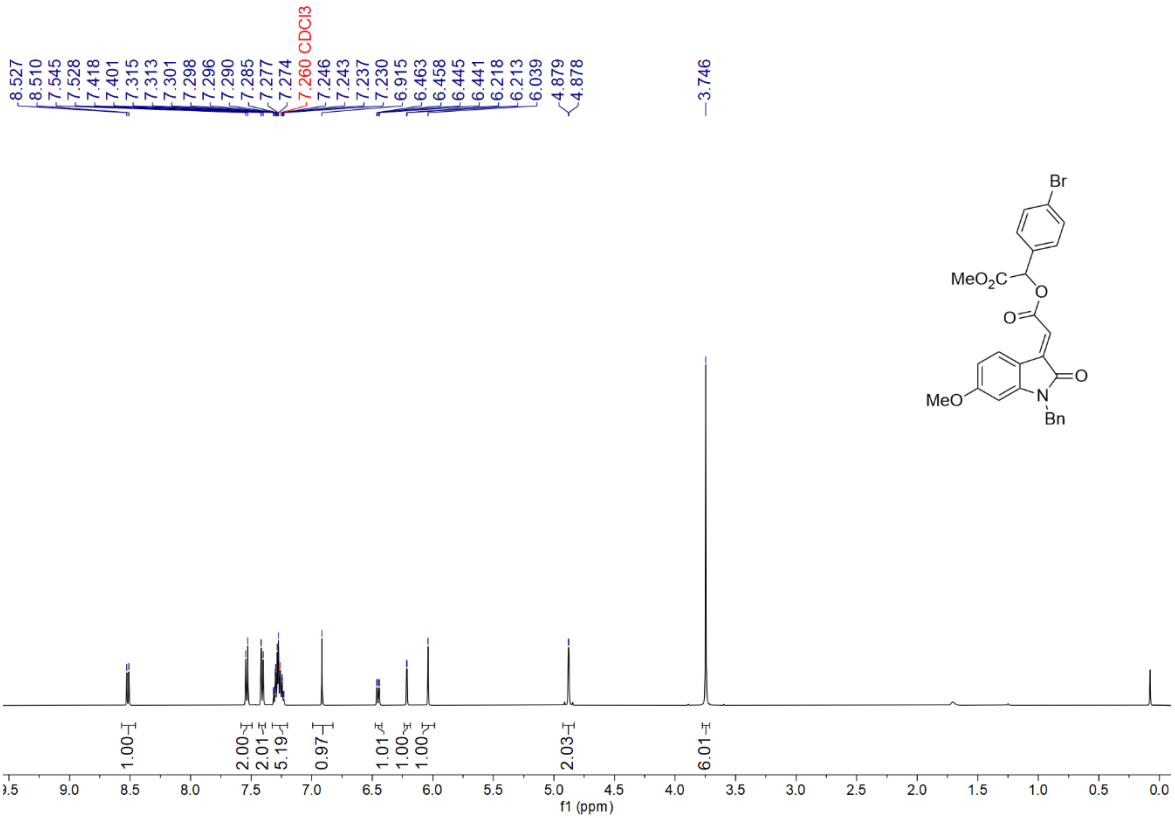
23 ^{1}H NMR (500 MHz, $CDCl_3$)



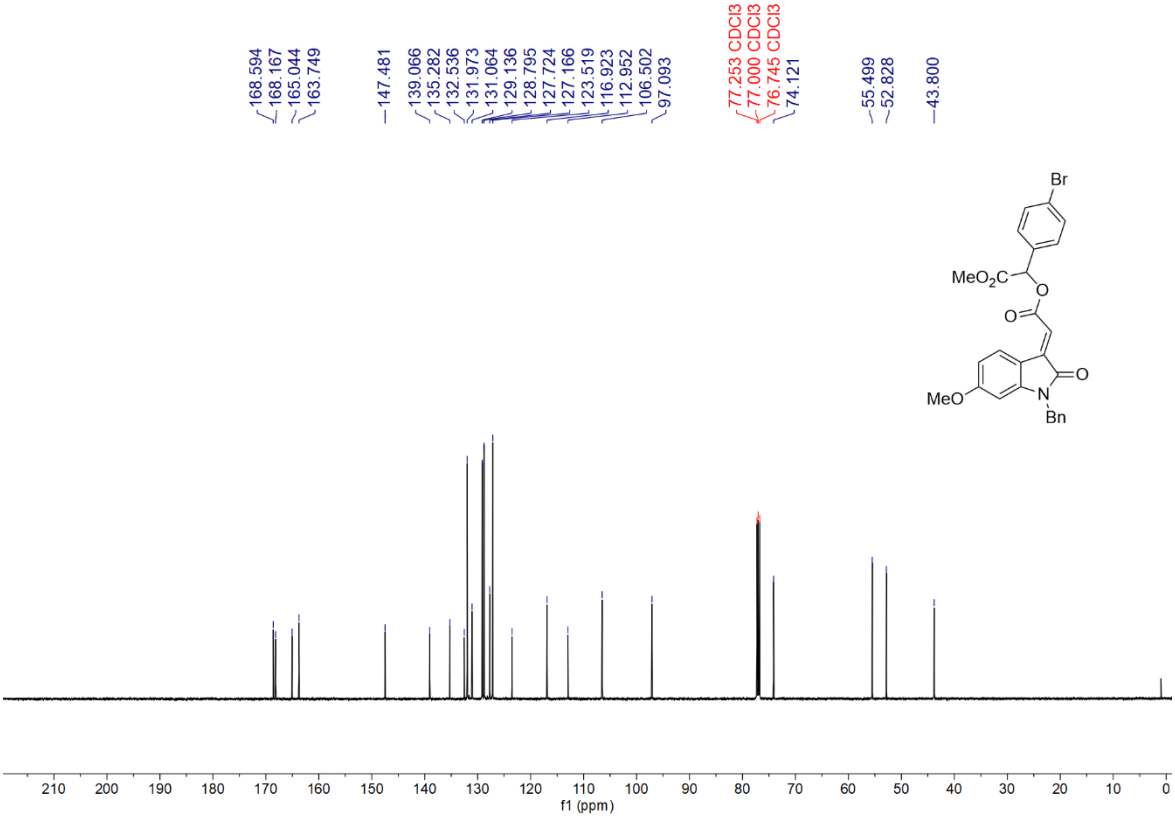
23 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



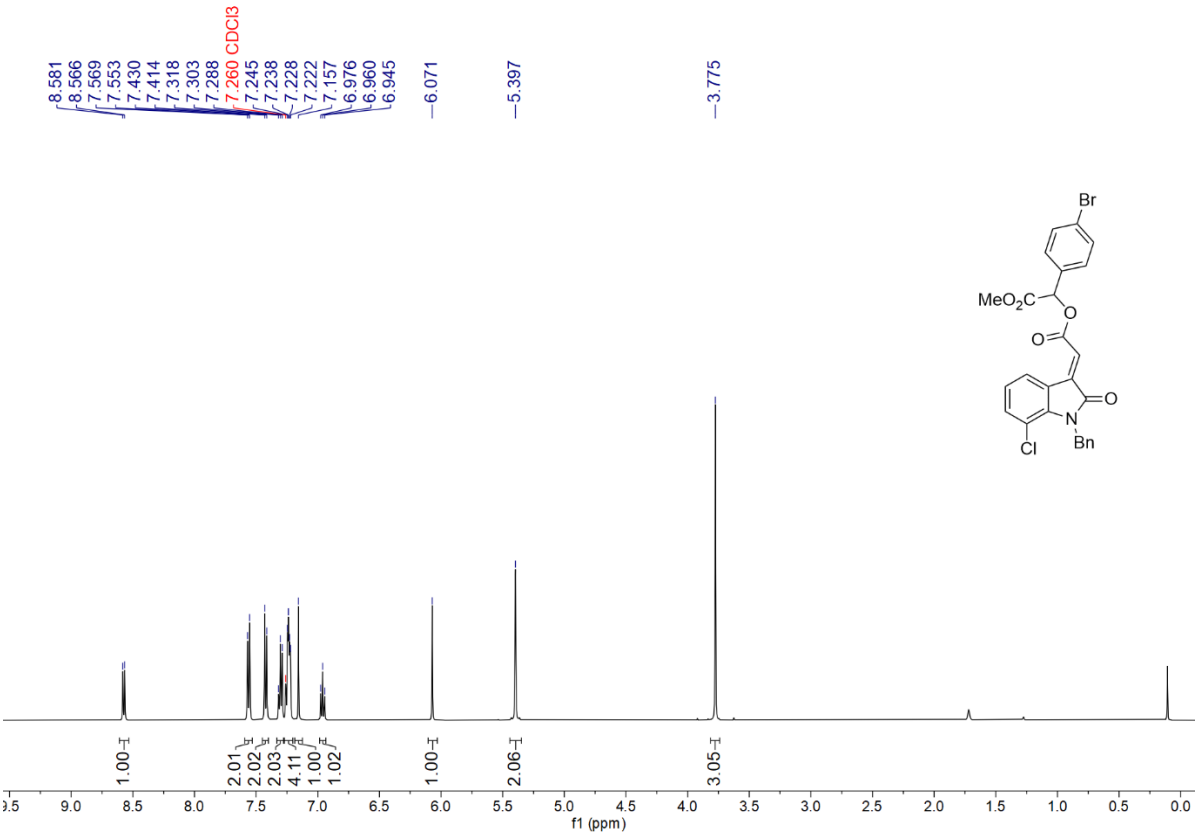
24 ^{1}H NMR (500 MHz, $CDCl_3$)



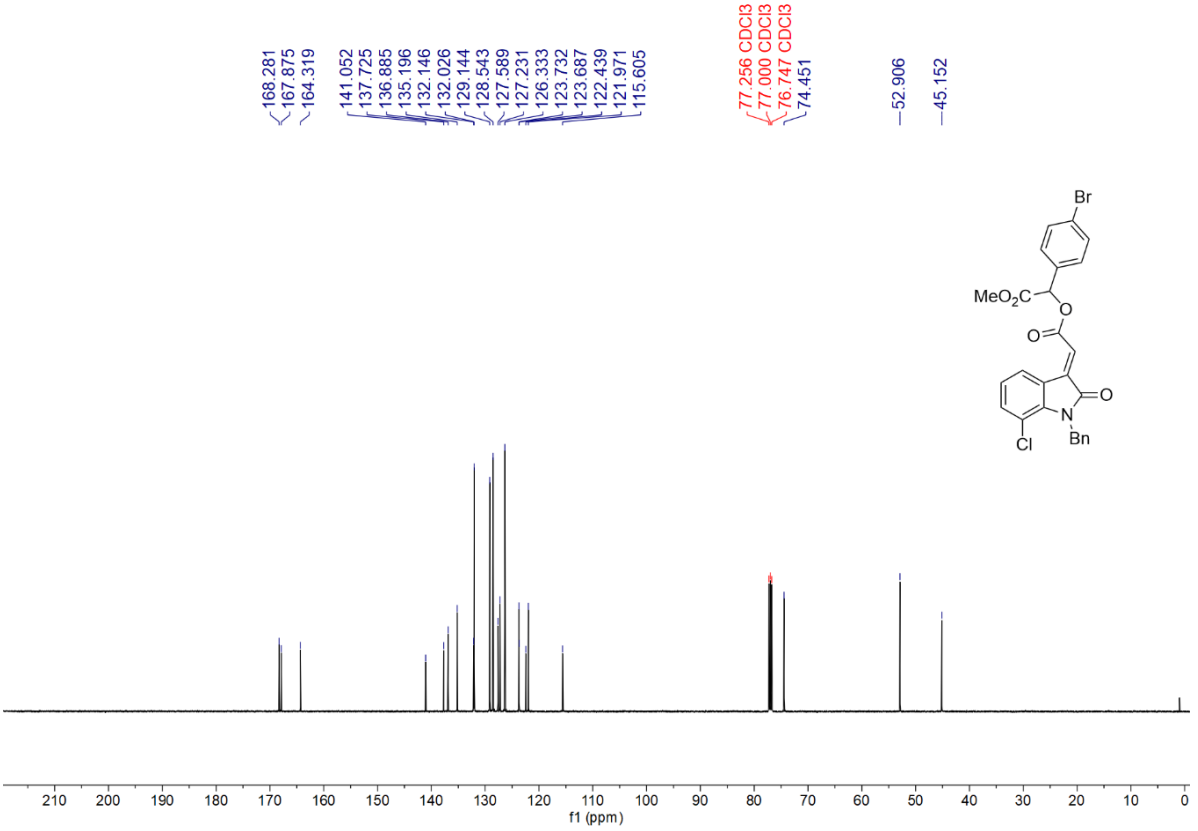
24 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



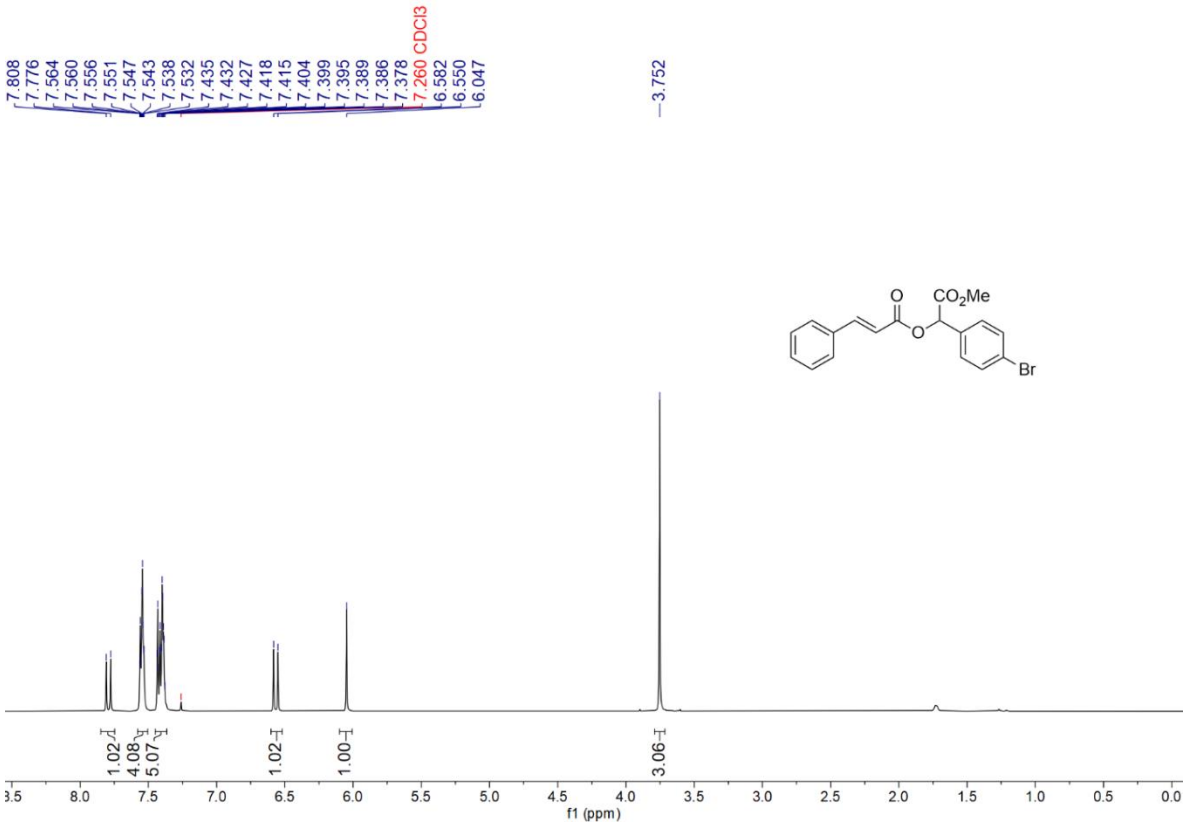
25 ^{1}H NMR (500 MHz, $CDCl_3$)



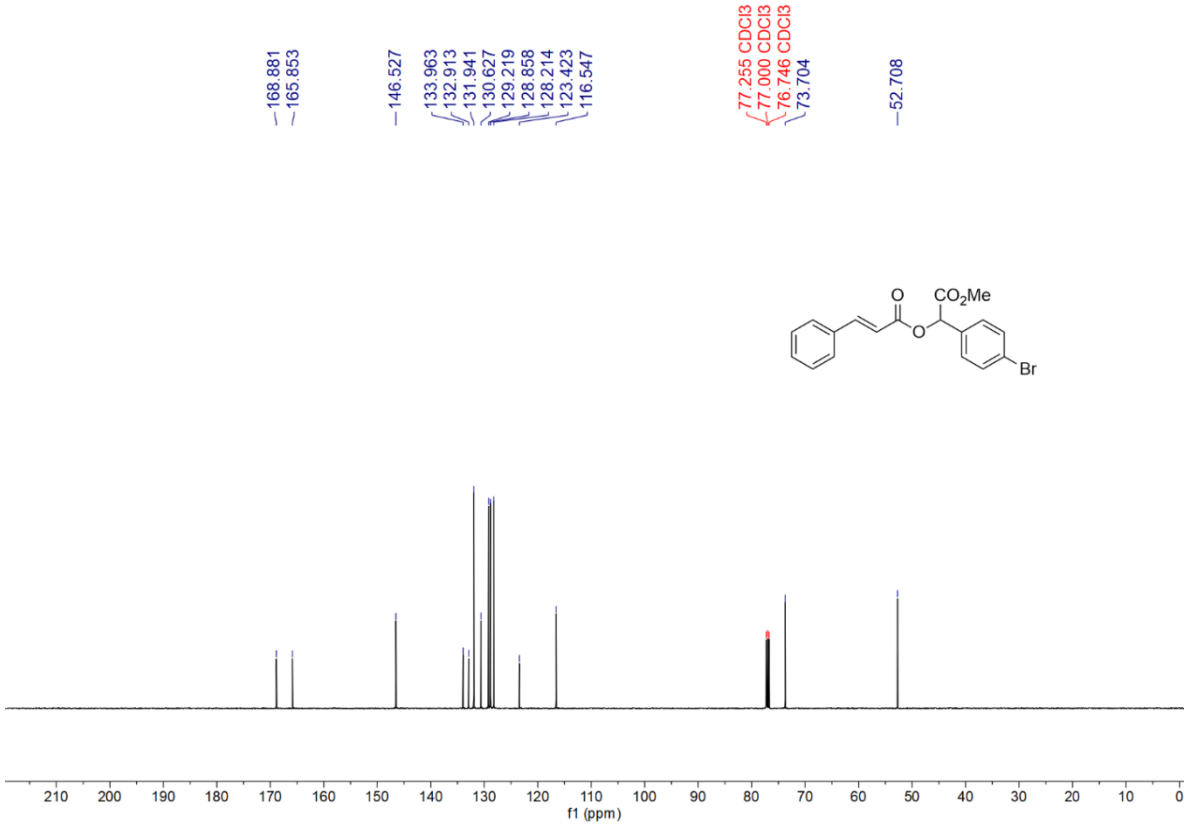
25 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



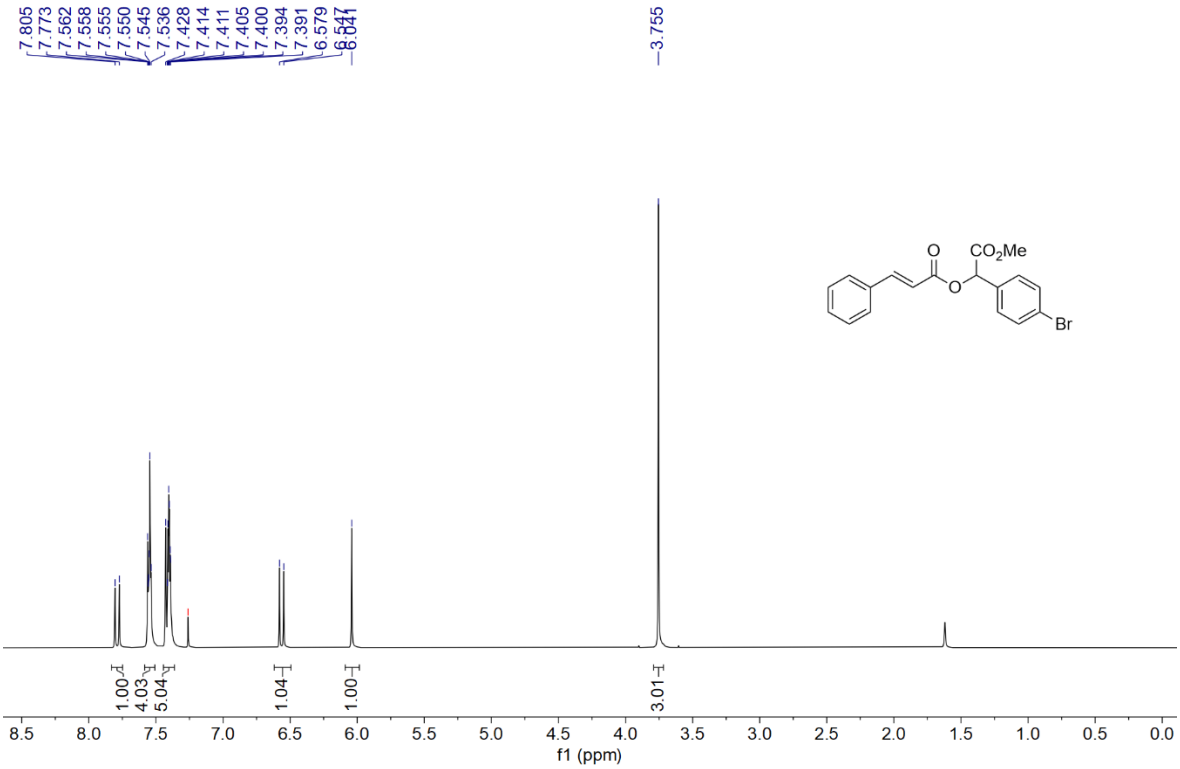
26 ^{1}H NMR (500 MHz, $CDCl_3$)



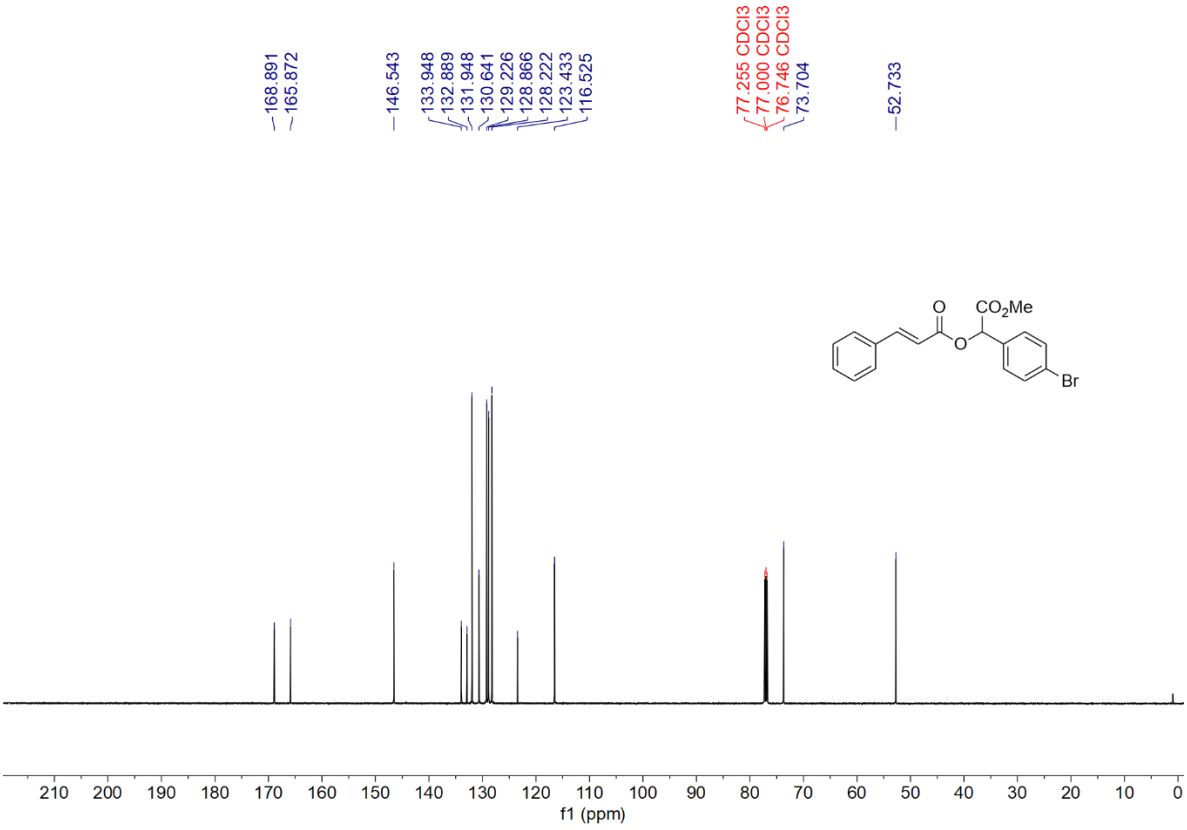
26 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



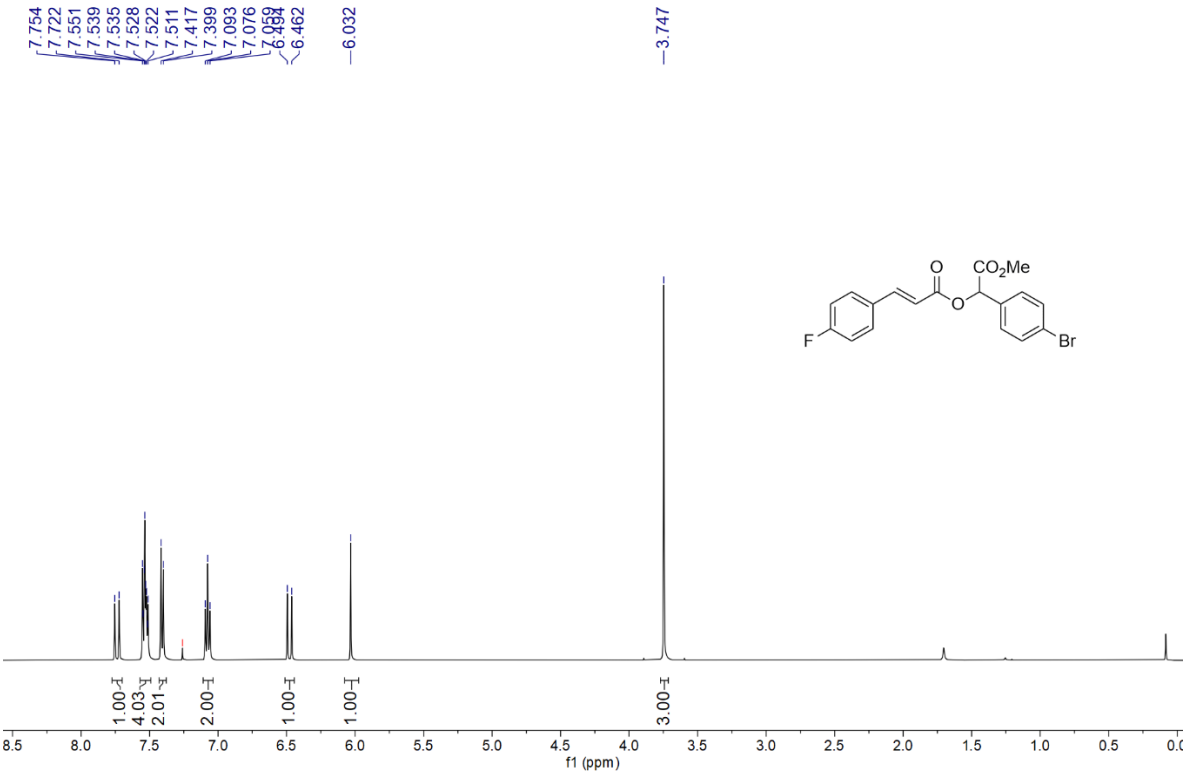
Gram-scale 26 ^{1}H NMR (500 MHz, $CDCl_3$)



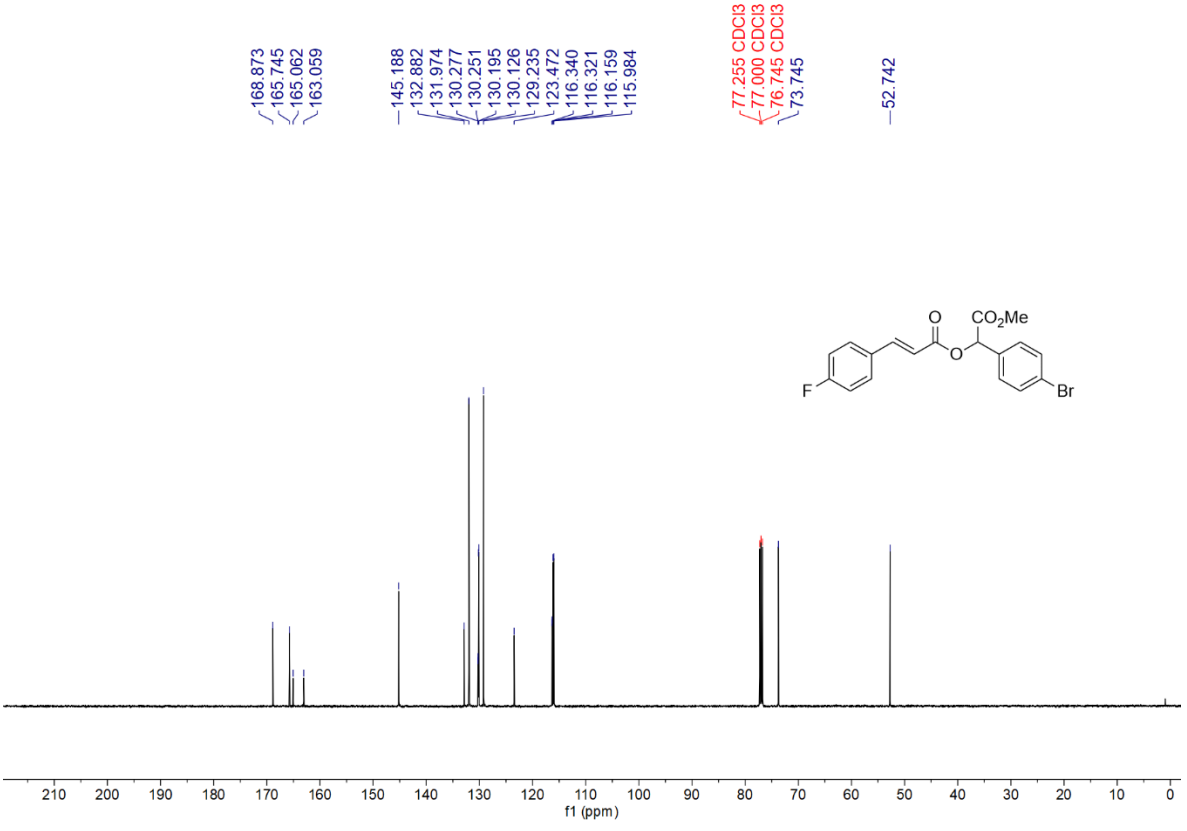
Gram-scale 26 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



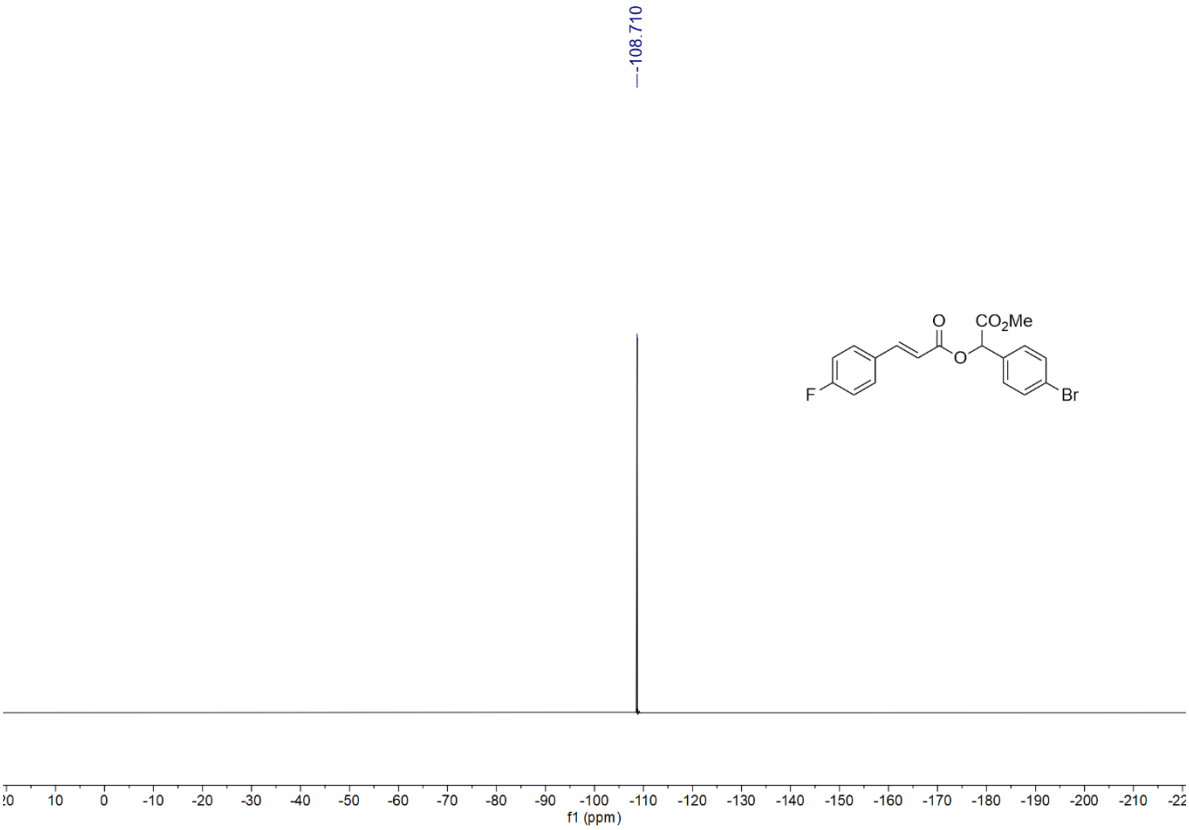
27 ^{1}H NMR (500 MHz, $CDCl_3$)



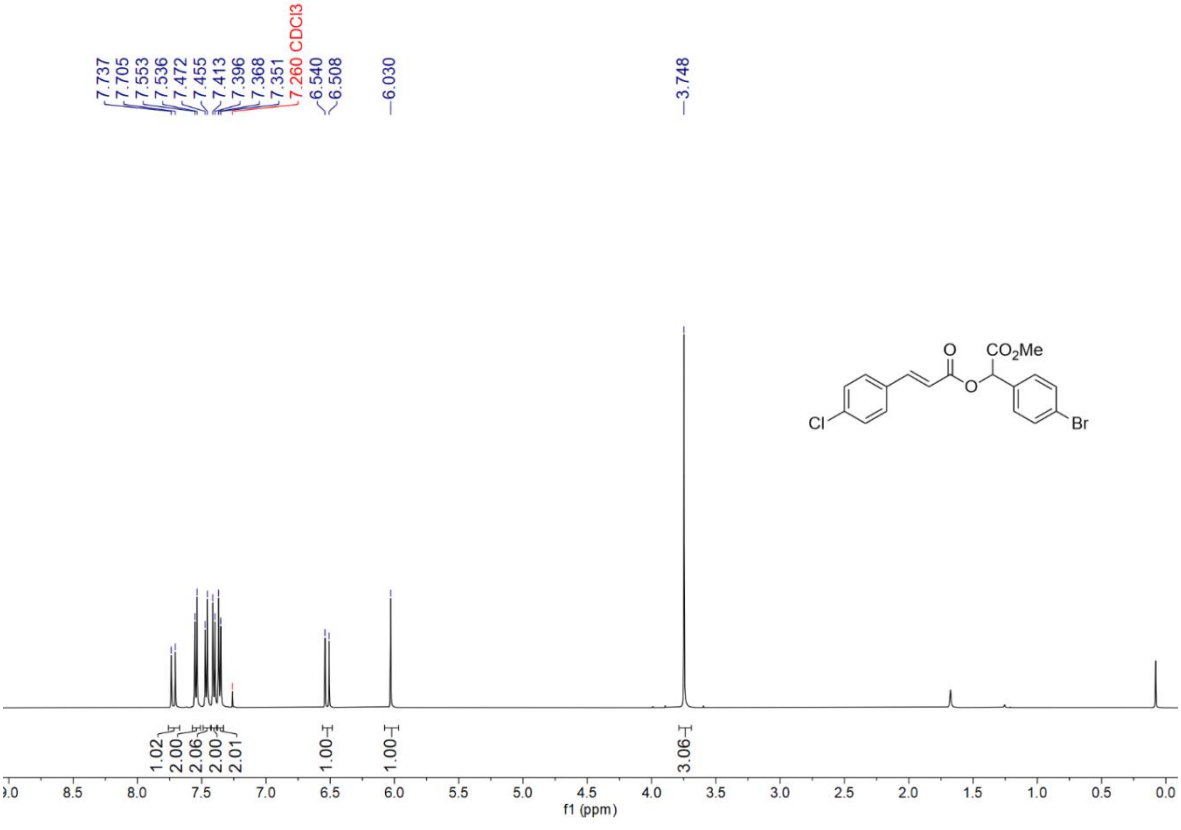
27 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



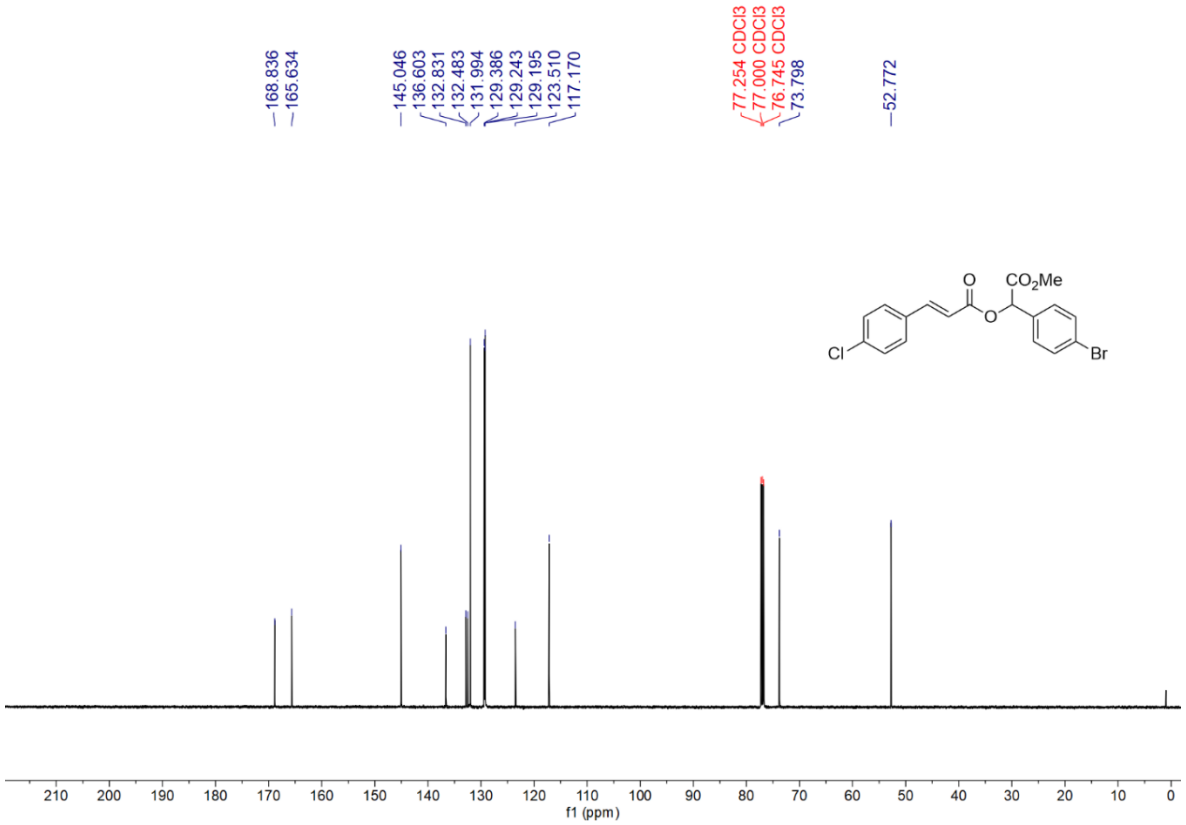
27 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



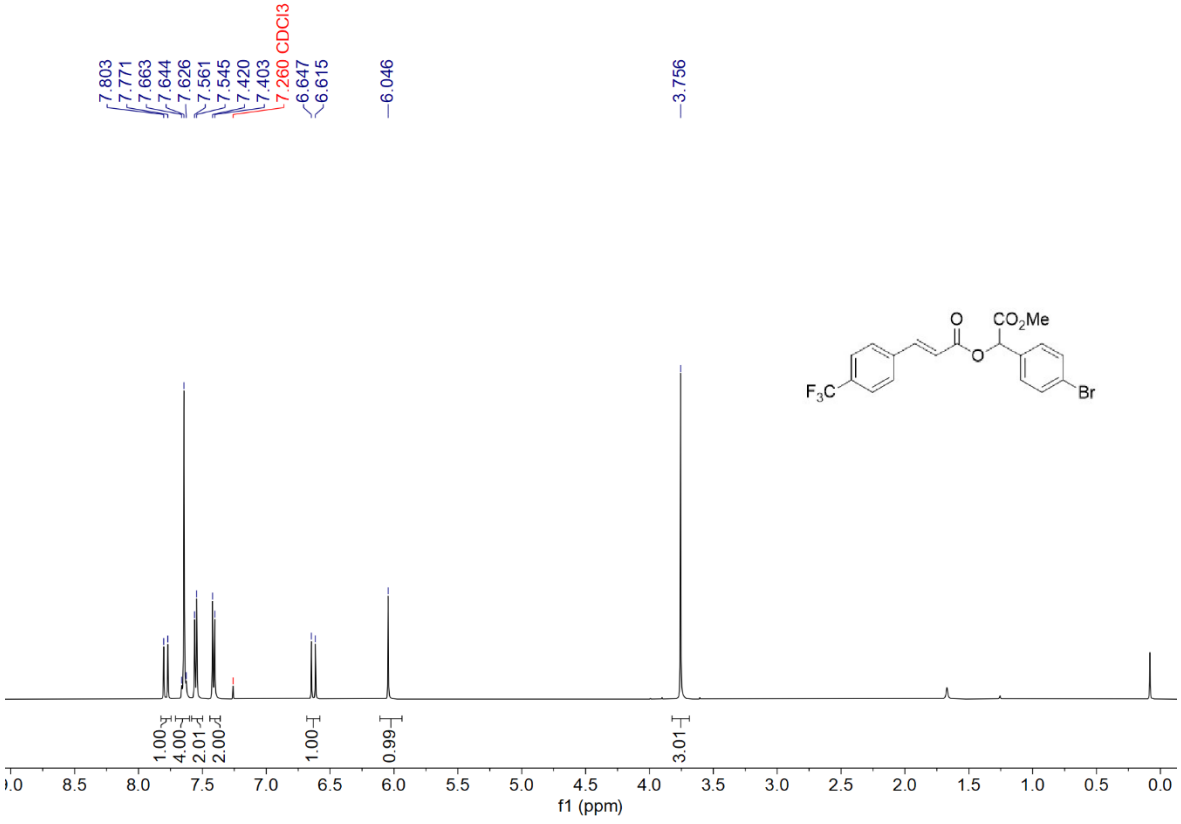
28 ^{1}H NMR (500 MHz, $CDCl_3$)



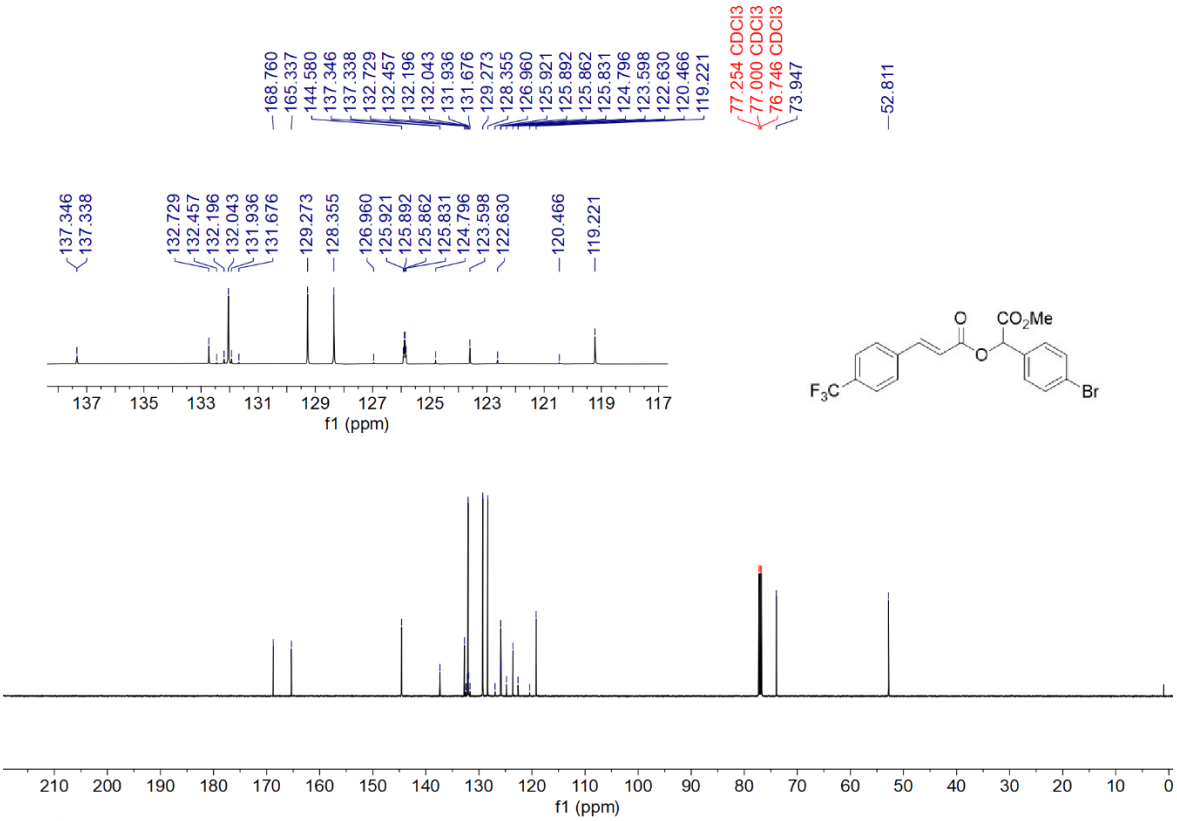
28 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



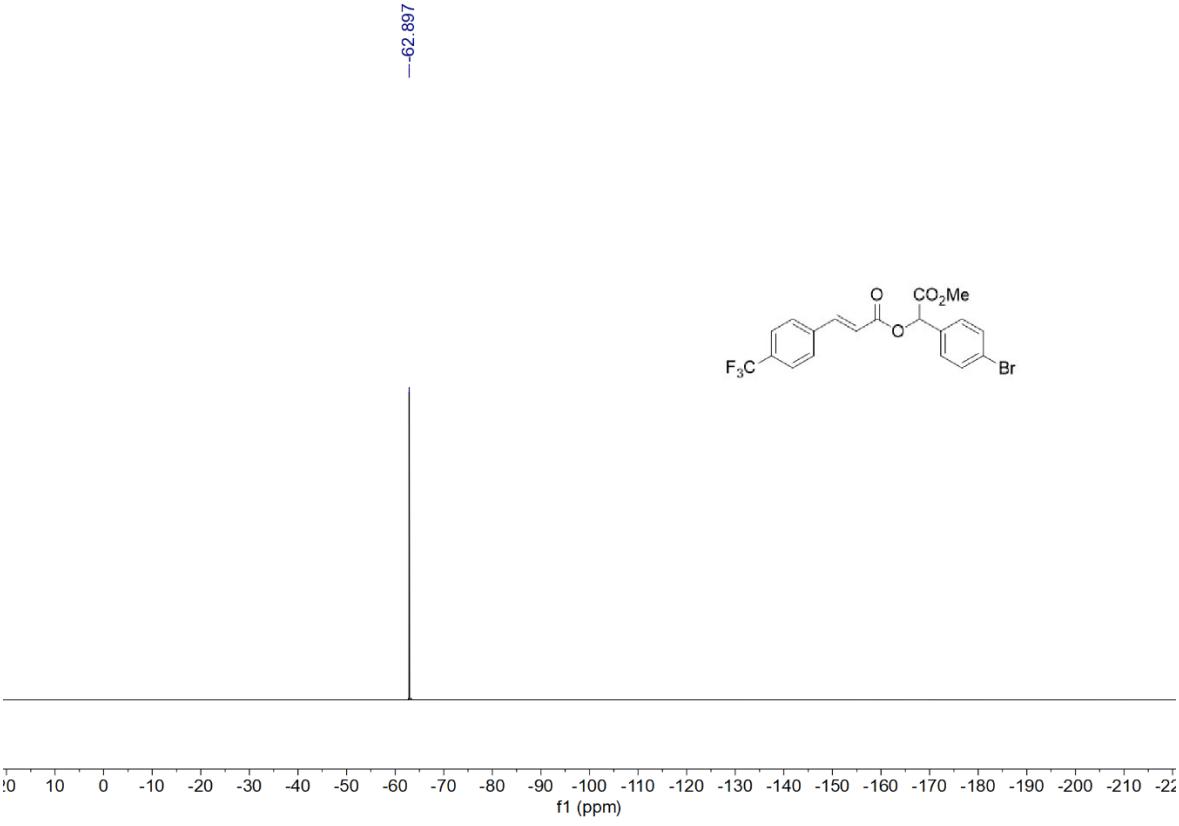
29 ^{1}H NMR (500 MHz, $CDCl_3$)



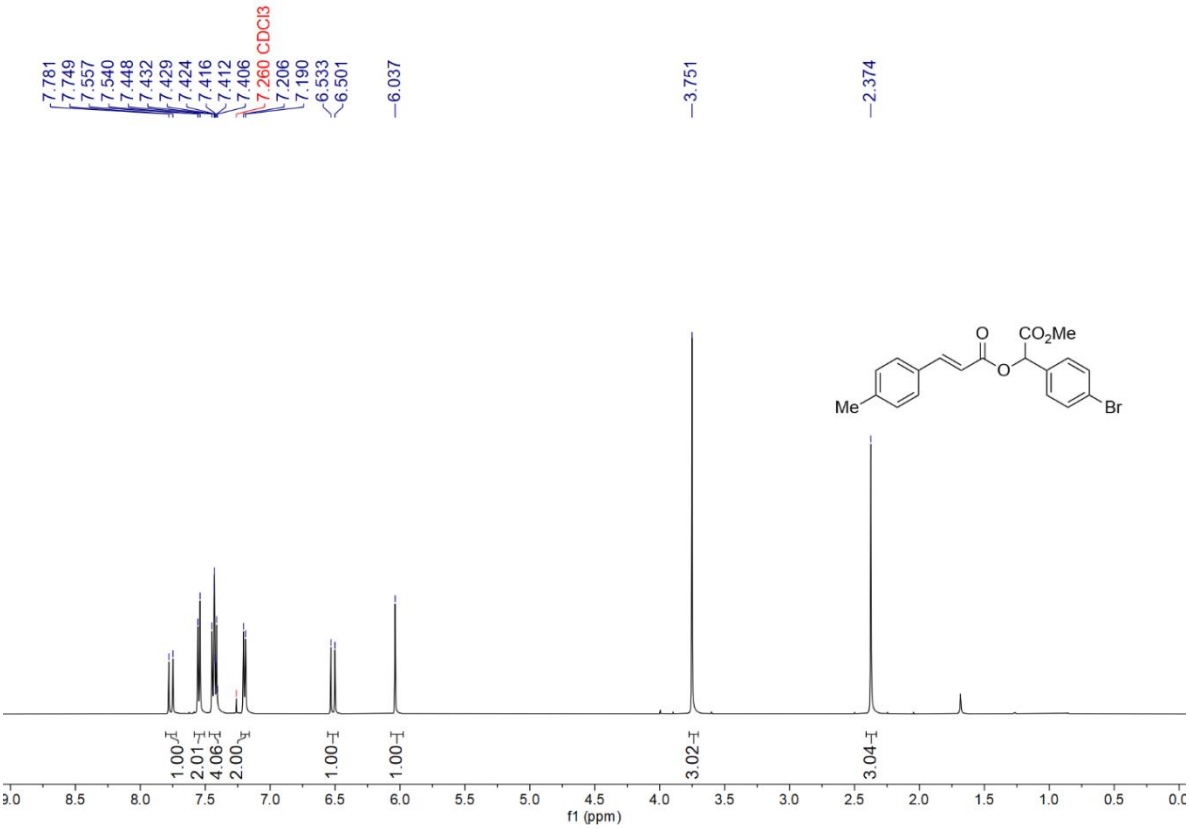
29 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



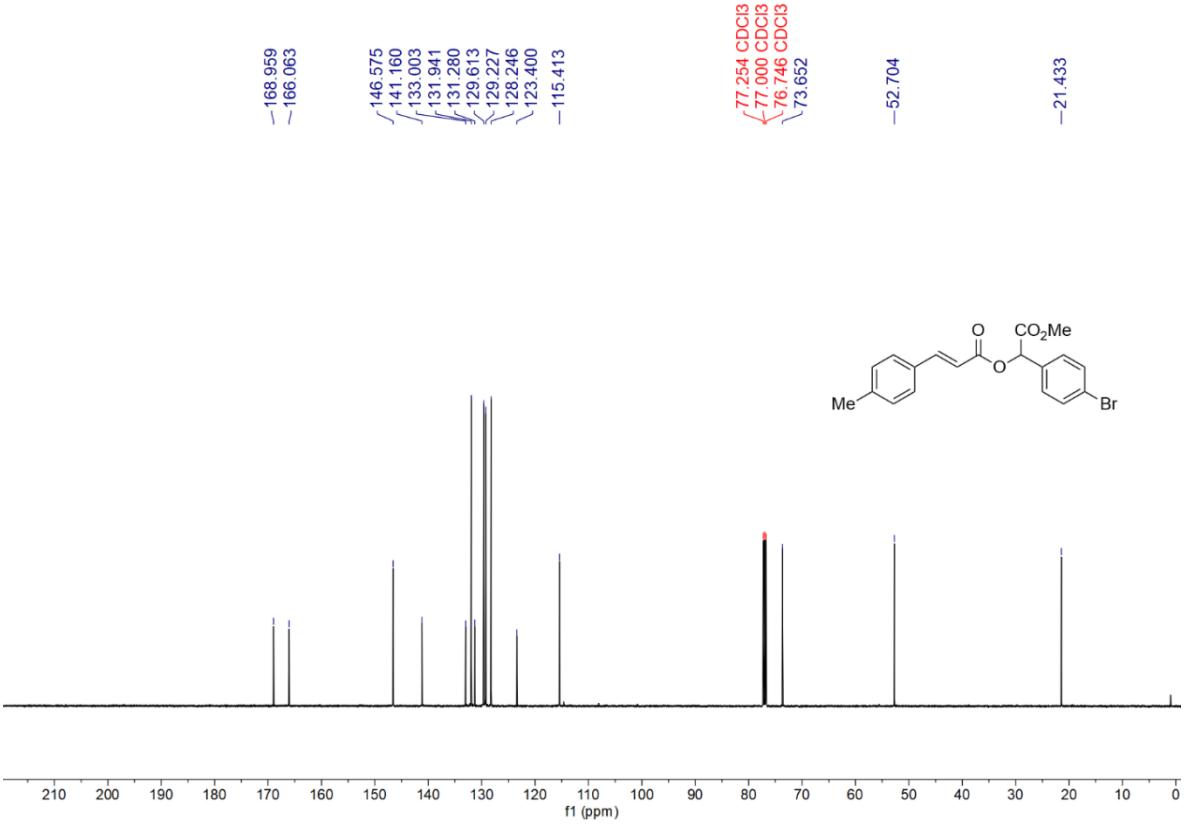
29 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



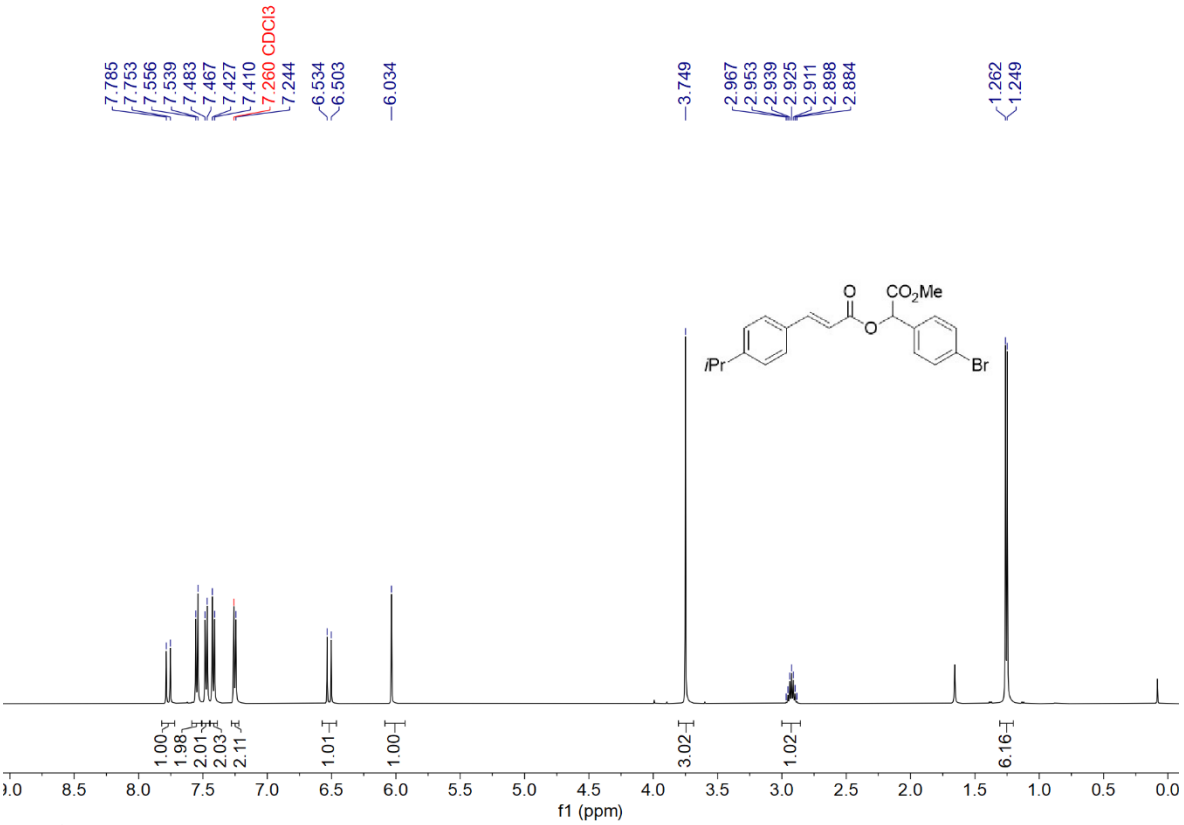
30 ^{1}H NMR (500 MHz, $CDCl_3$)



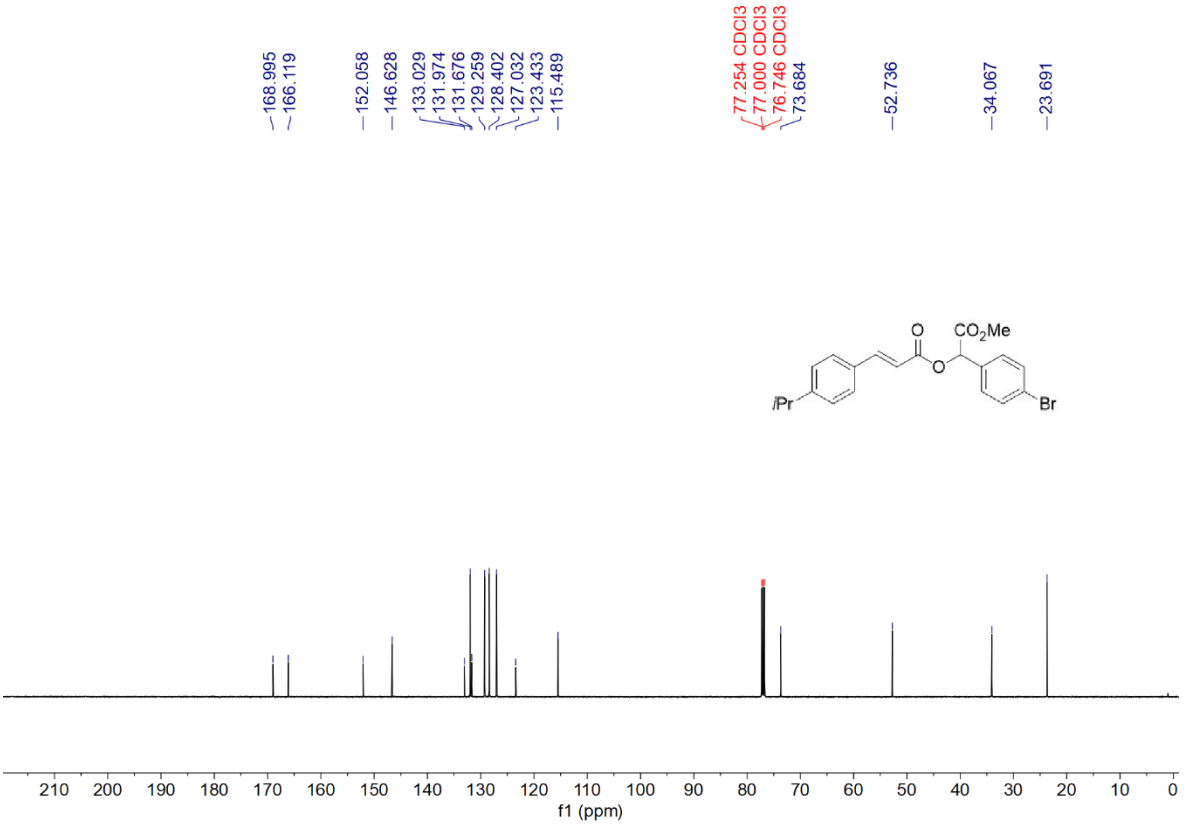
30 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



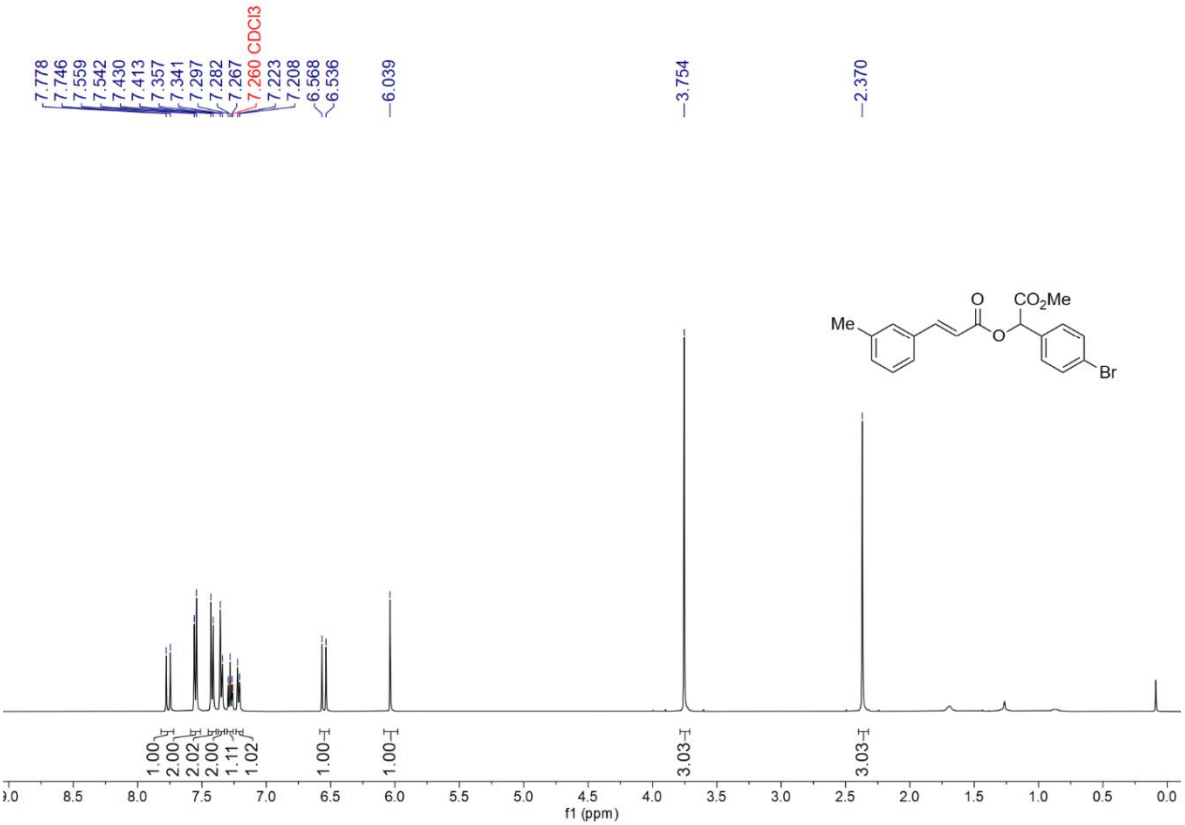
31 ^{1}H NMR (500 MHz, $CDCl_3$)



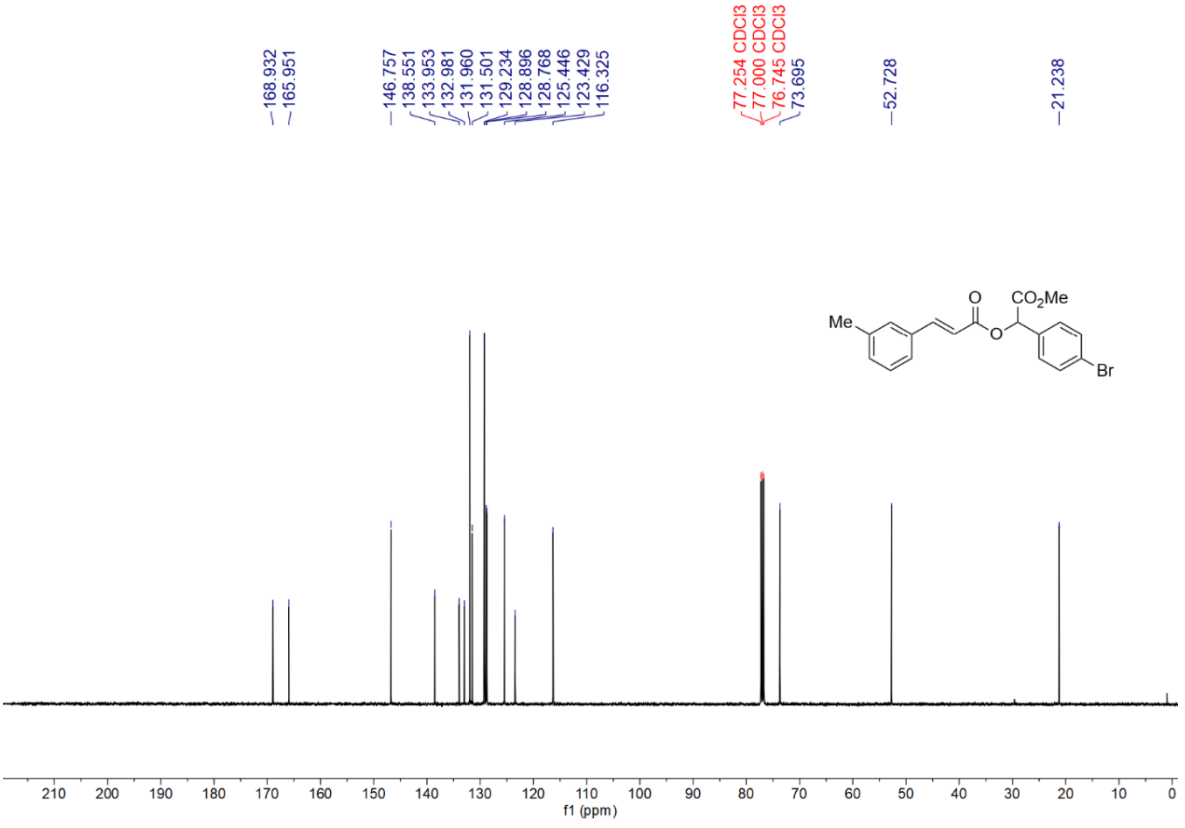
31 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



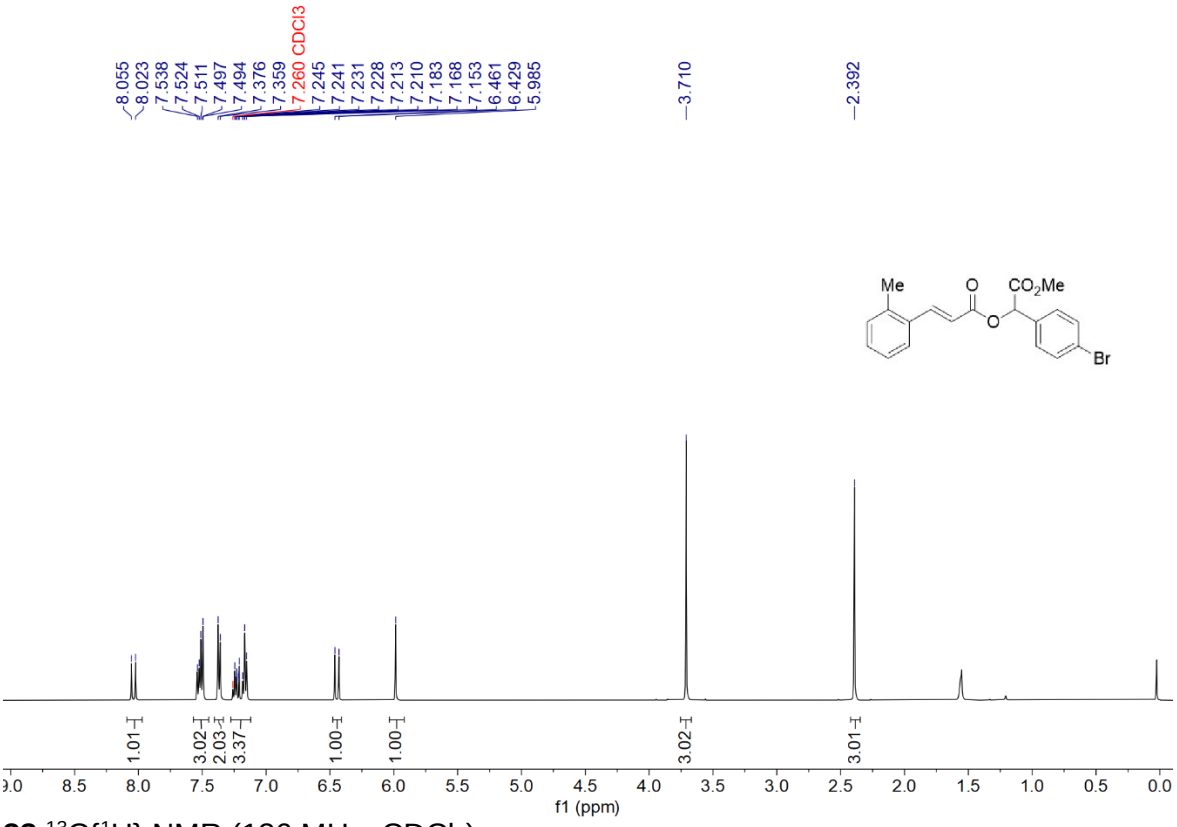
32 ^{1}H NMR (500 MHz, $CDCl_3$)



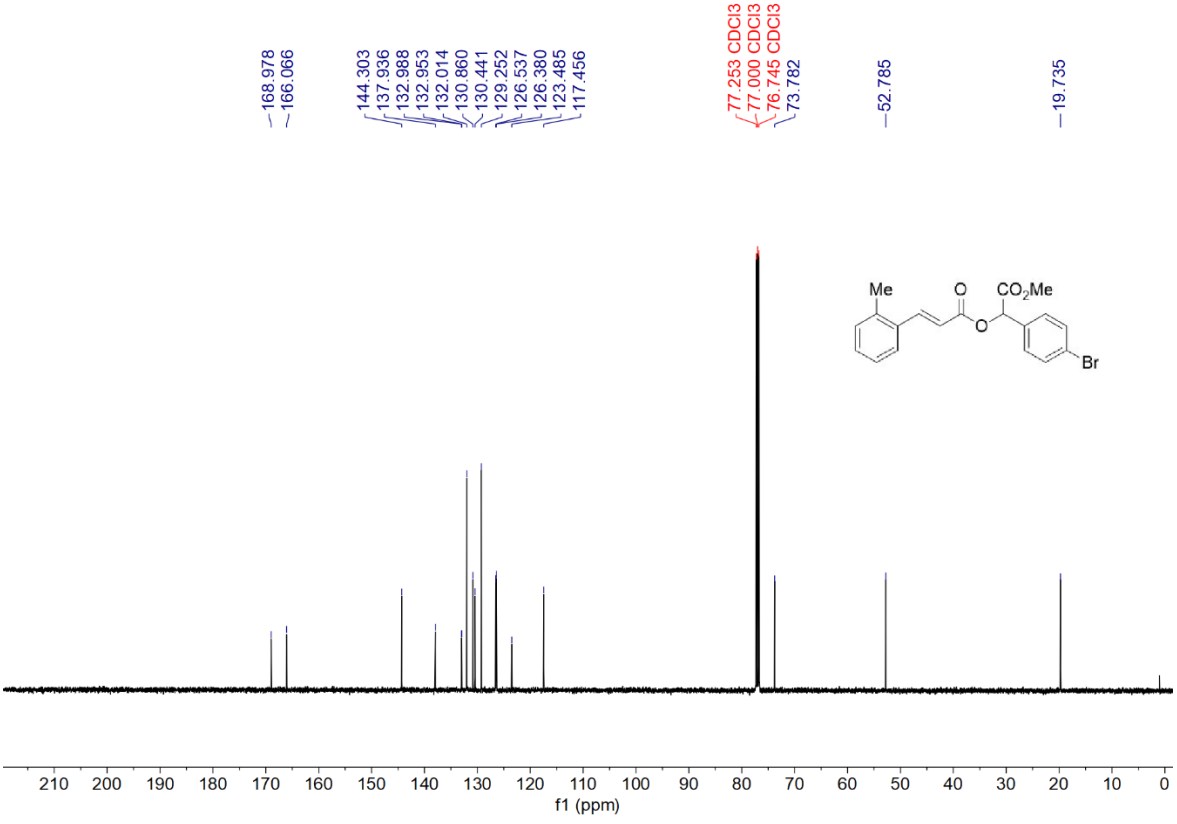
32 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



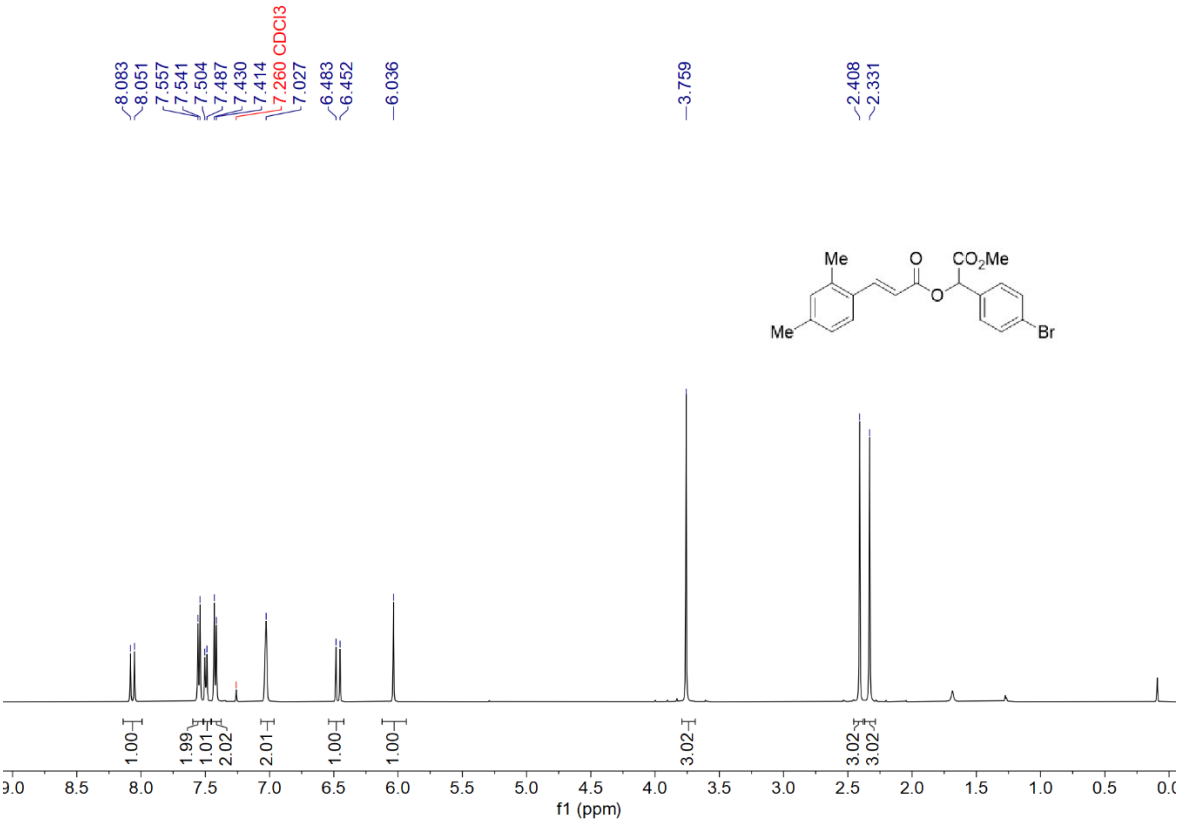
33 ^{1}H NMR (500 MHz, $CDCl_3$)



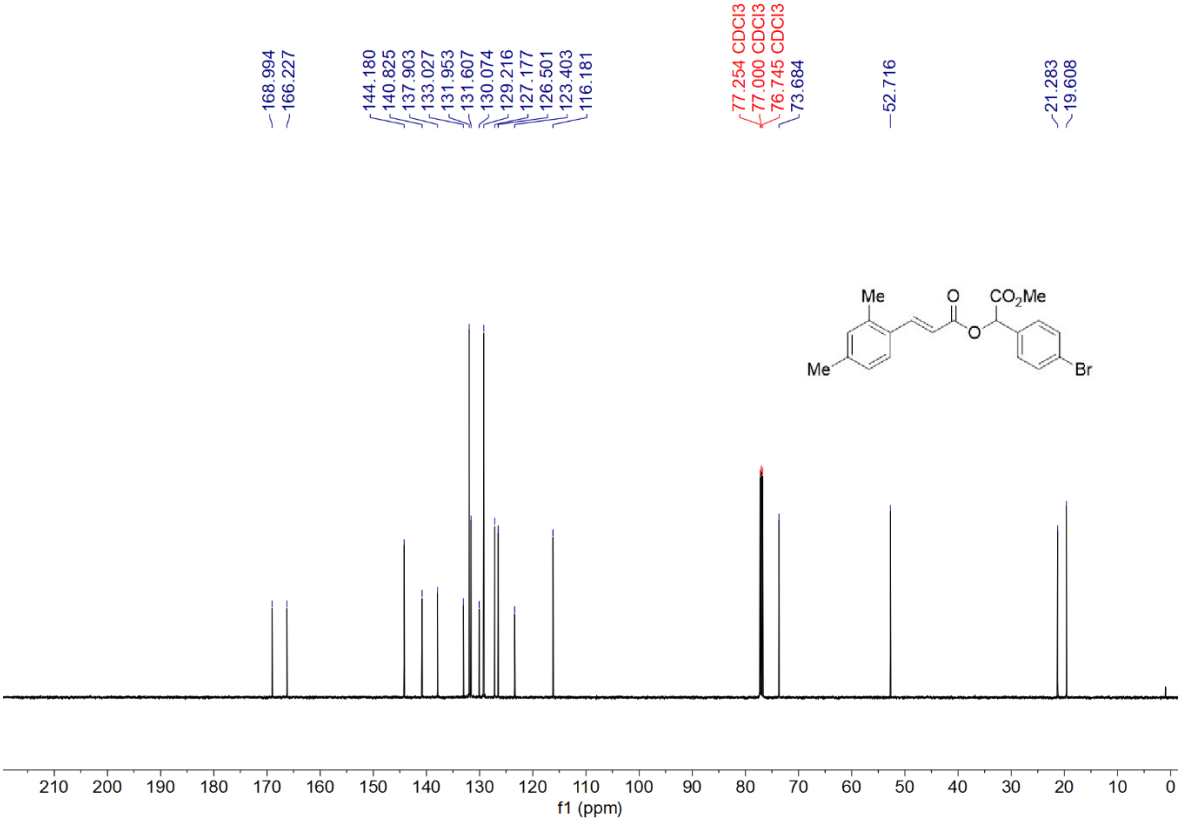
33 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



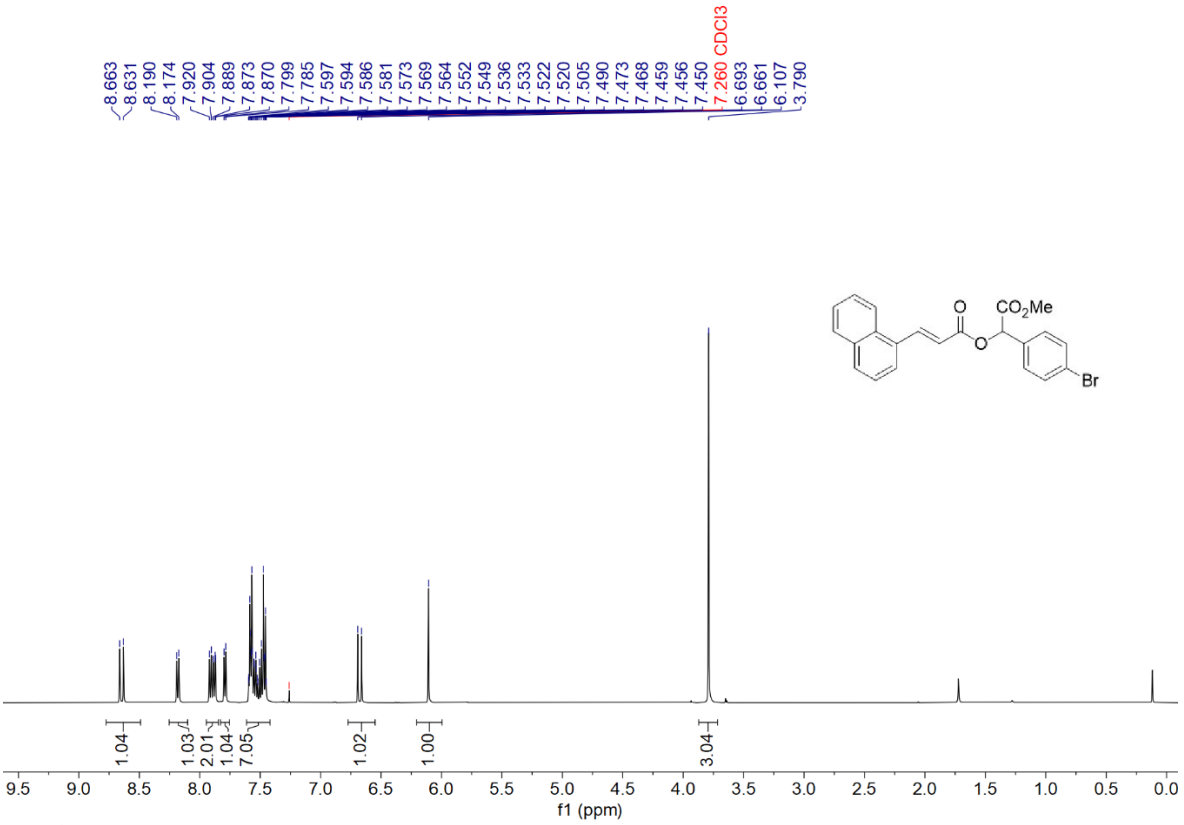
34 ^{1}H NMR (500 MHz, $CDCl_3$)



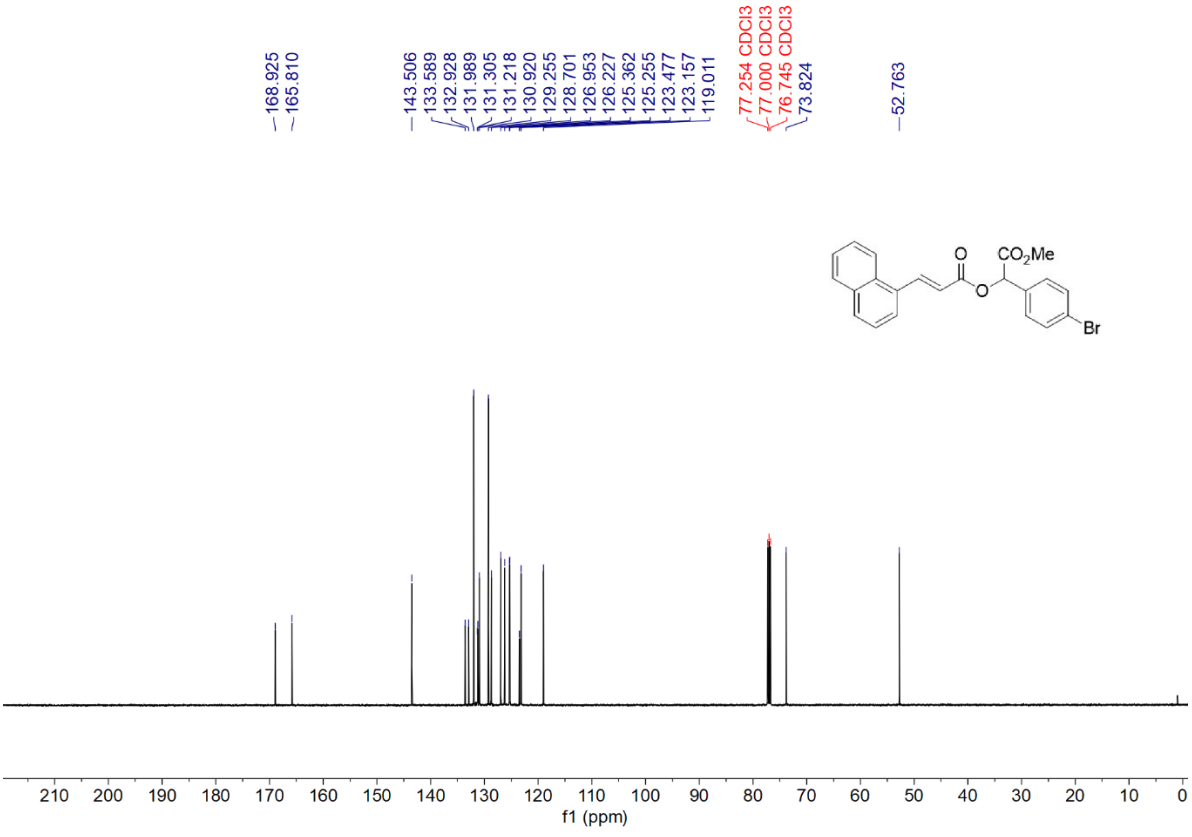
34 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



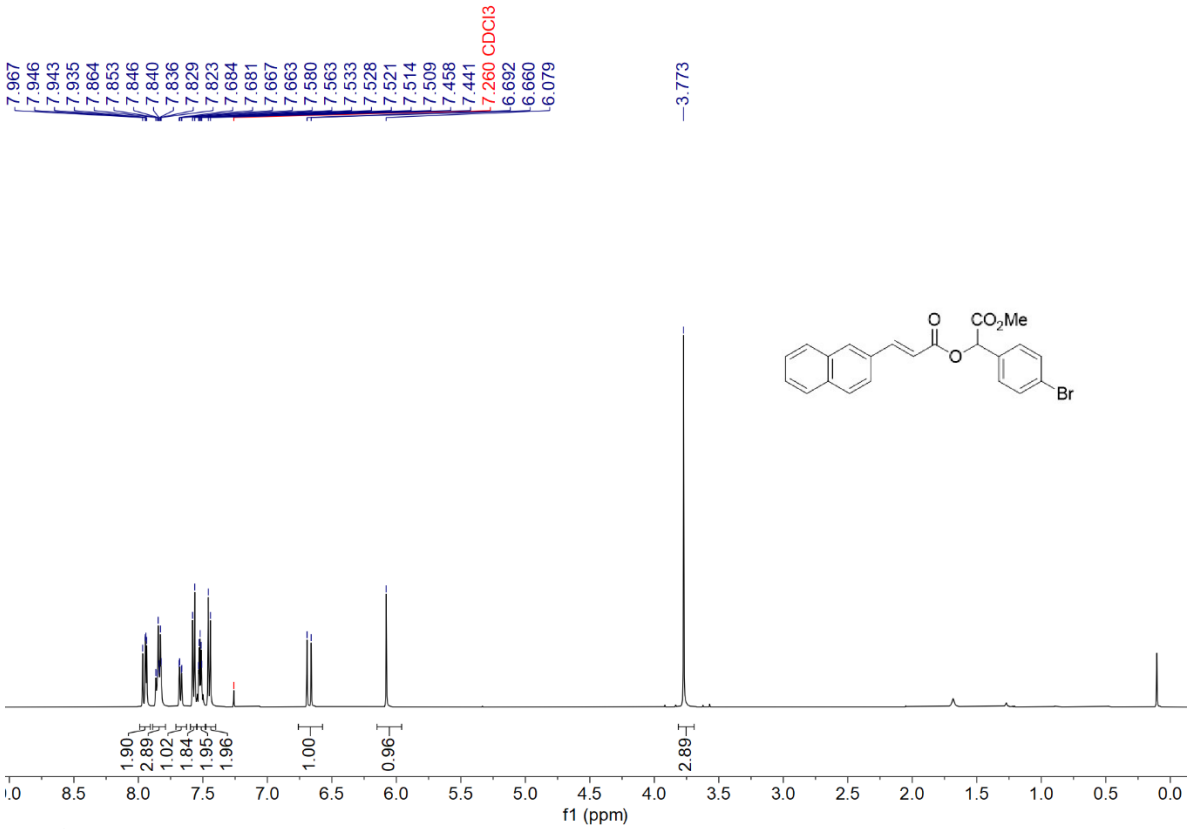
35 ^{1}H NMR (500 MHz, $CDCl_3$)



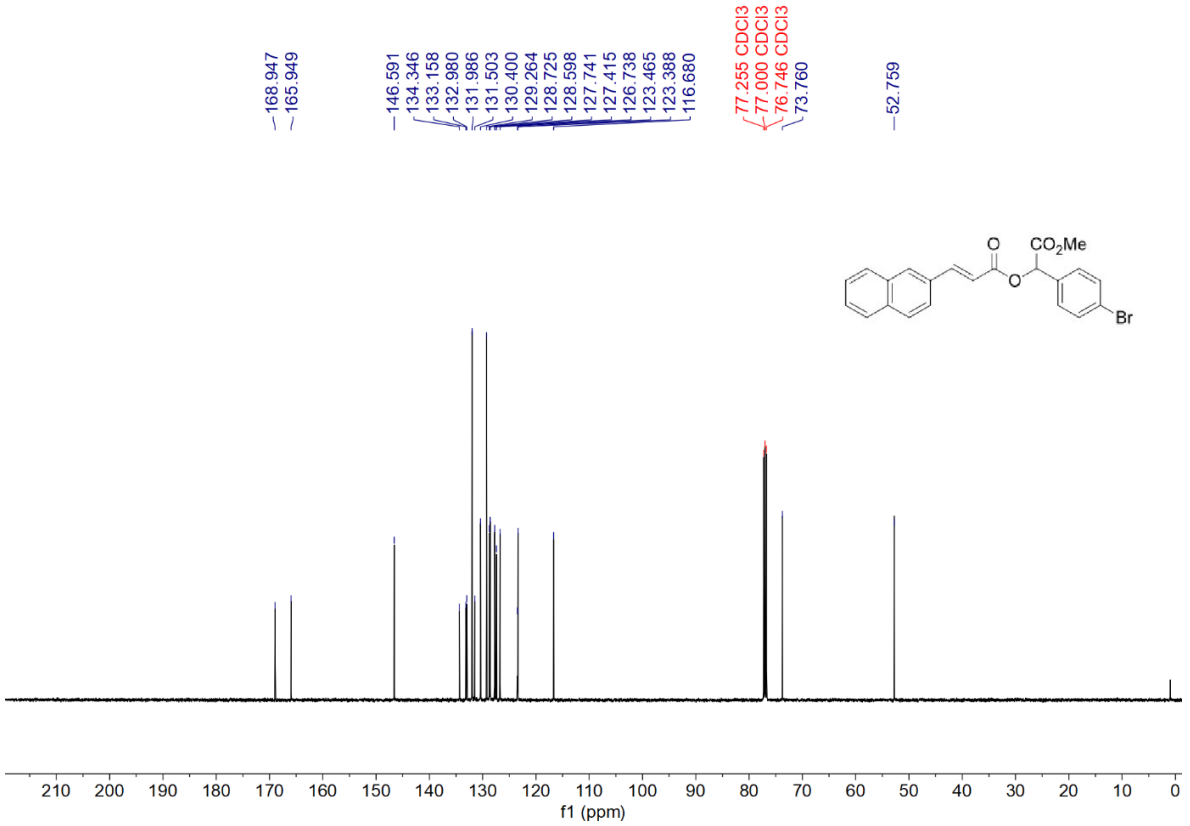
35 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



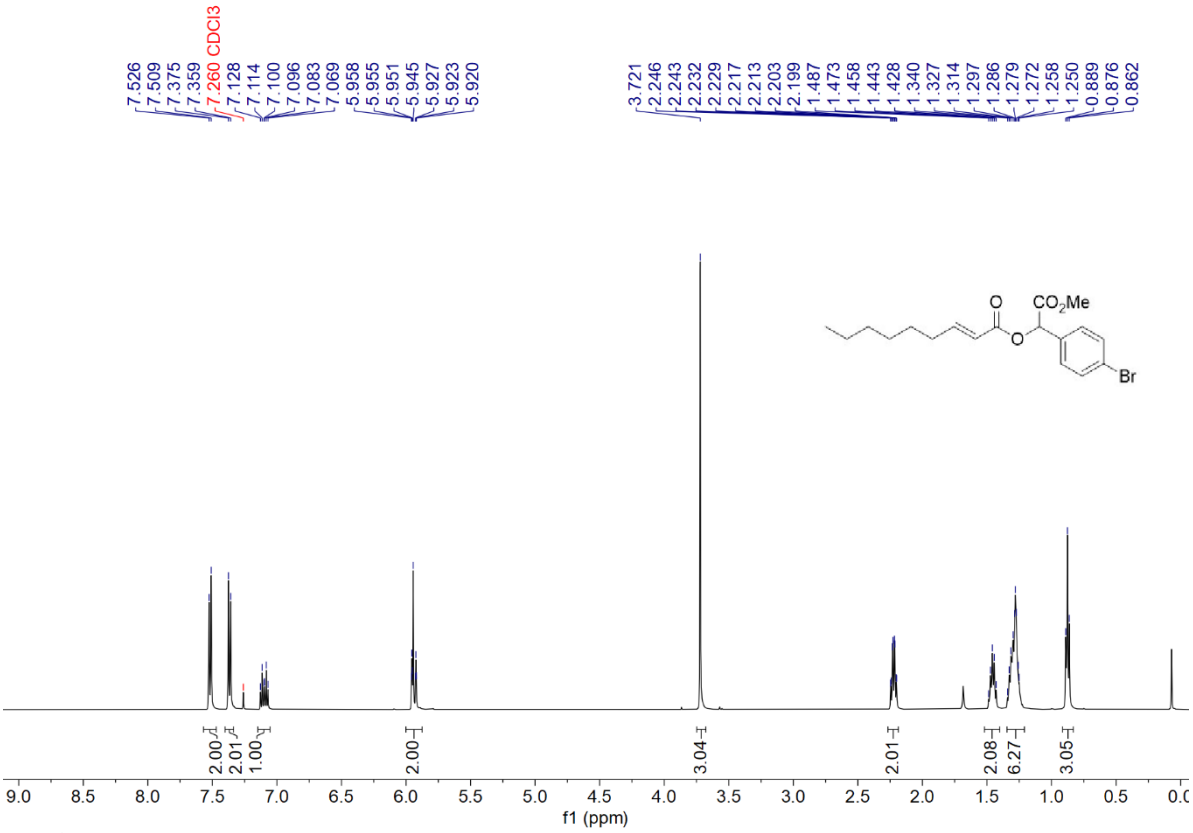
36 ^{1}H NMR (500 MHz, $CDCl_3$)



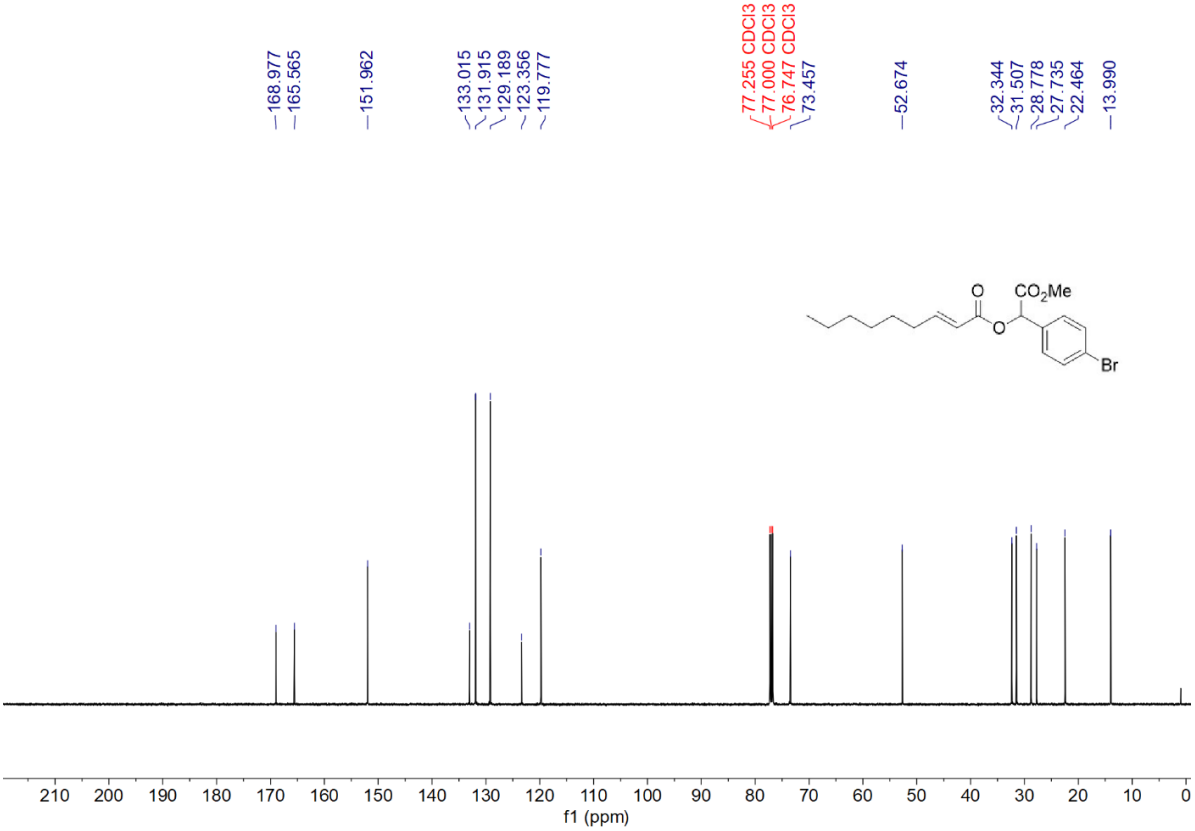
36 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



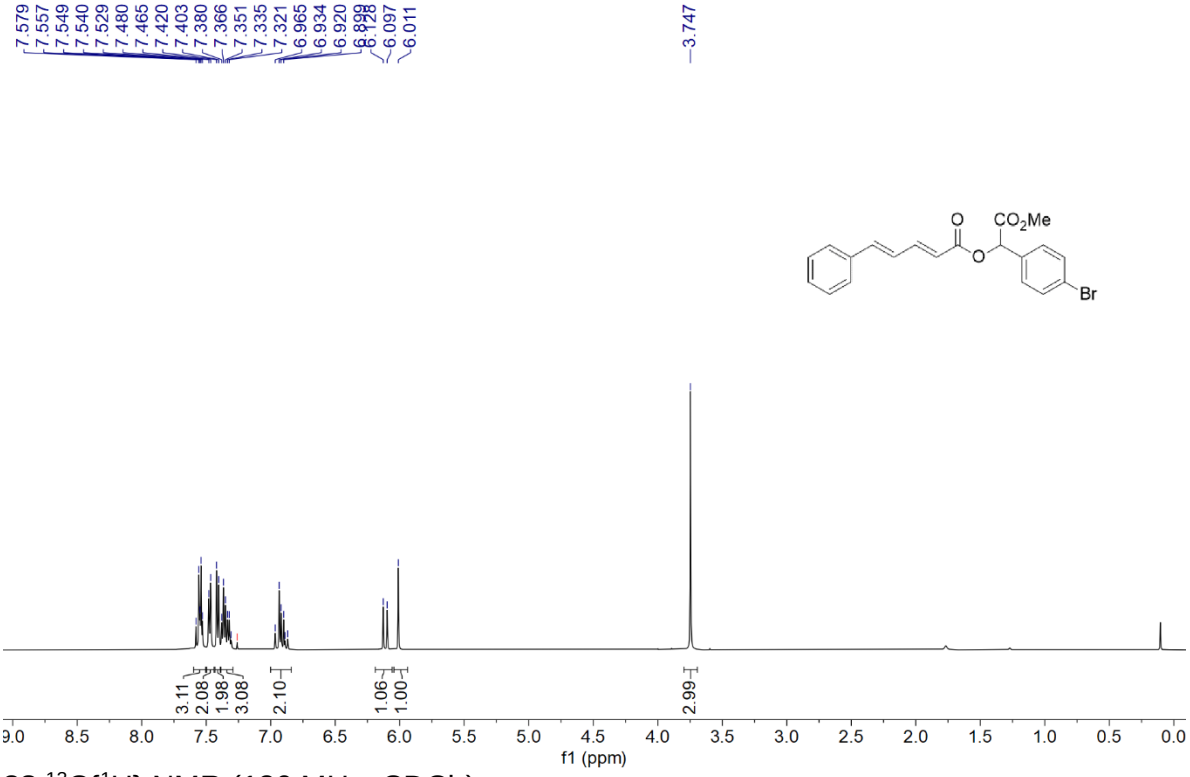
37 ^{1}H NMR (500 MHz, $CDCl_3$)



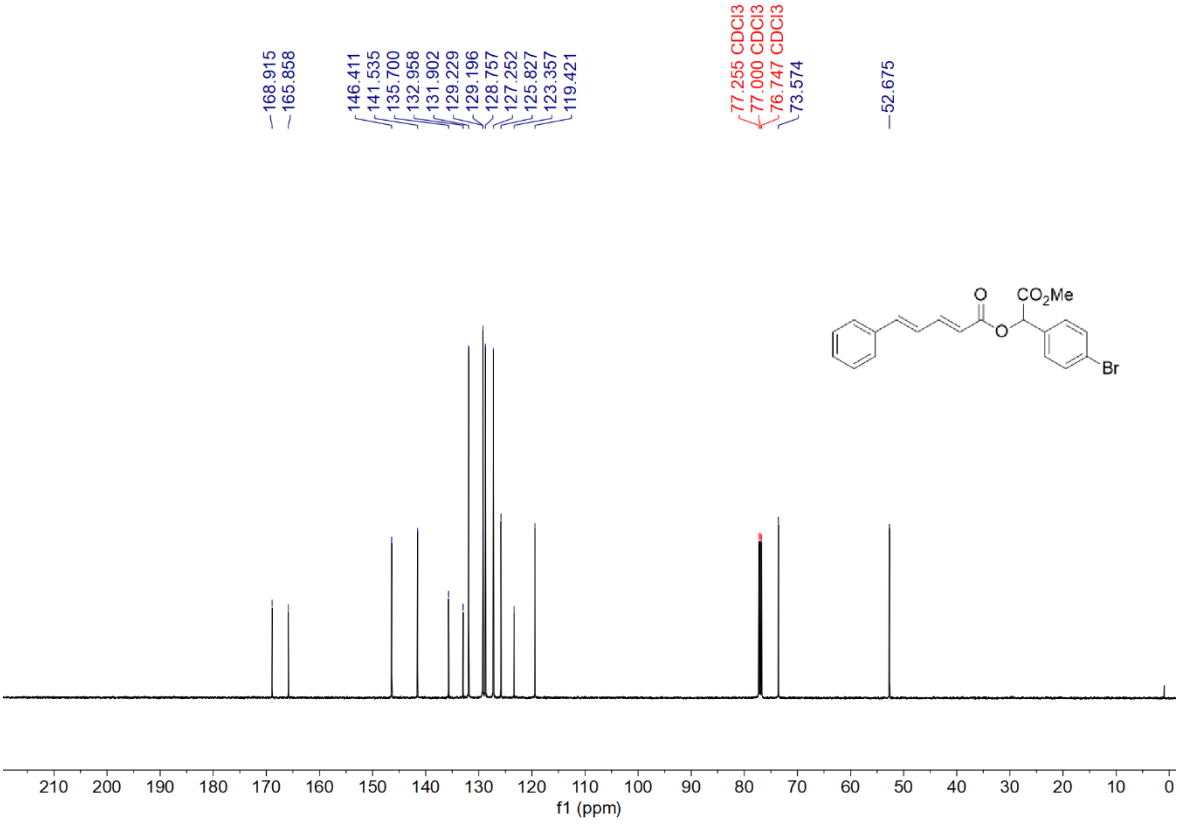
37 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



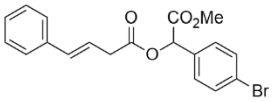
38 ^{1}H NMR (500 MHz, $CDCl_3$)

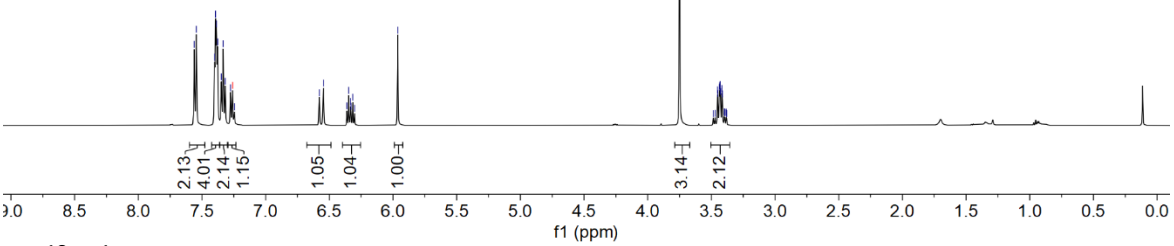


38 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

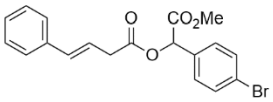


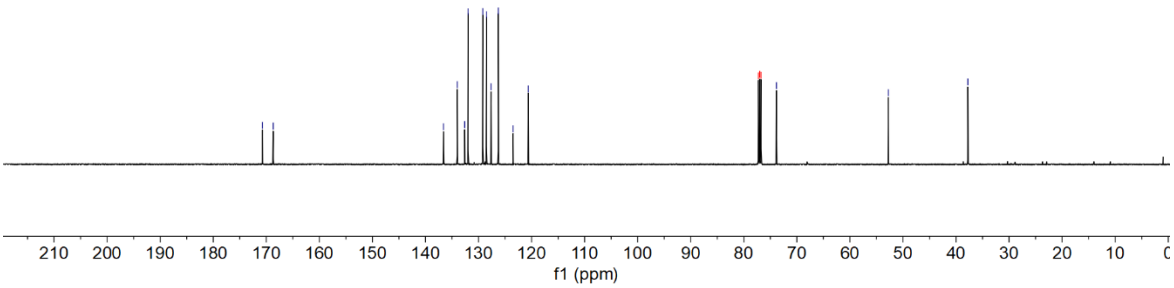
39 ^{1}H NMR (500 MHz, $CDCl_3$)



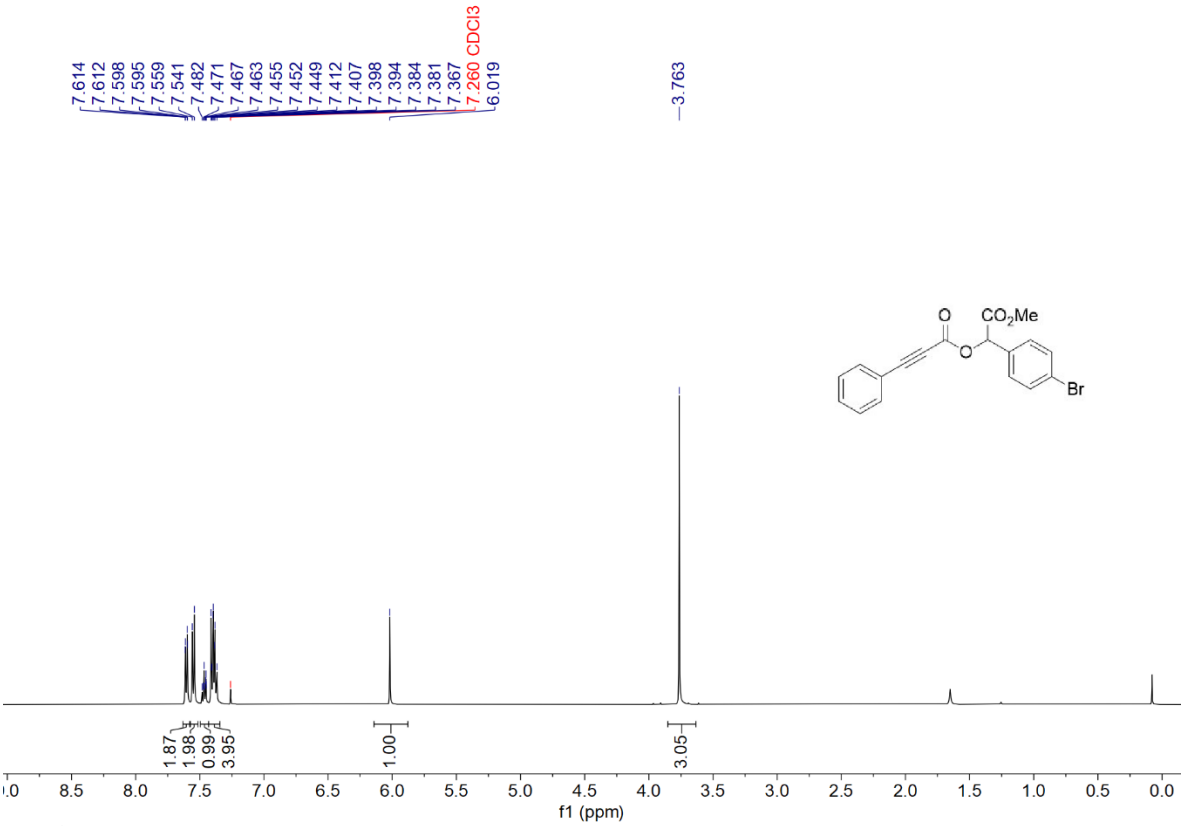


39 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

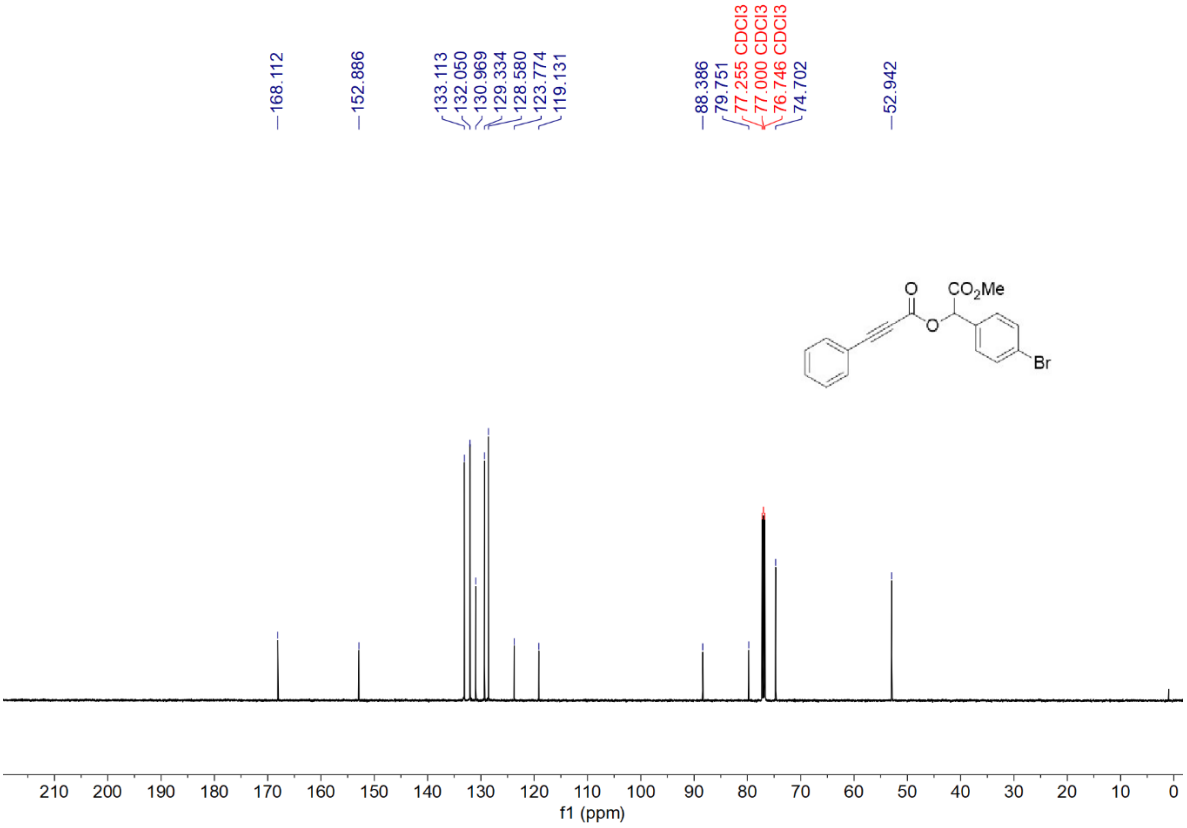




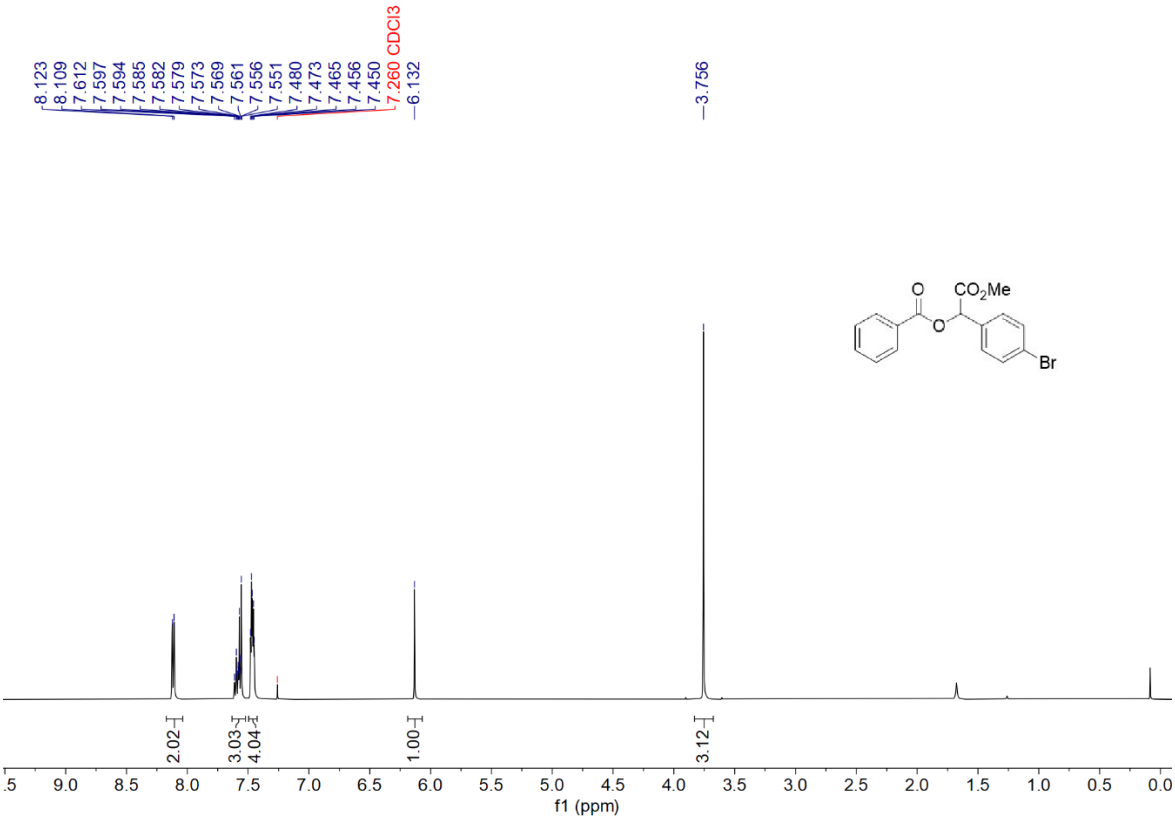
40 ^{1}H NMR (500 MHz, $CDCl_3$)



40 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



41 ^{1}H NMR (500 MHz, $CDCl_3$)



41 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)