Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting Information

MeOTf- catalyzed Friedel-Crafts alkylation of benzoxazolones, benzothiazolones, indolinones and benzimidazolones with activated secondary alcohols

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A. General considerations:

^{1}H and ^{13}C NMR spectra were recorded with a 300, 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ ($\delta = 7.28$ ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals includes: s = singlet, d = doublet, t = triplet, q =quadrate, m = multiplet, dd = doublet of doublets, dq =doublet of quadrate, ddd = doublet of doublet of doublets, td = triplet of doublet, and brs. = broad singlet. ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, *δ*) and are referenced to $CDCl_3$ (δ =77.16 ppm) as an internal standard. The molecular fragments in High Resolution Mass Spectra (HRMS) are quoted as the relation between mass and charge (m/z). The routine monitoring of reactions was performed with silica gel GF_{254} pre-coated Al plate, which was analysed with iodine and/or UV light. All reactions were executed with oven-dried glassware under nitrogen atmosphere.

B. List of heterocycles and alcohols used in this study:

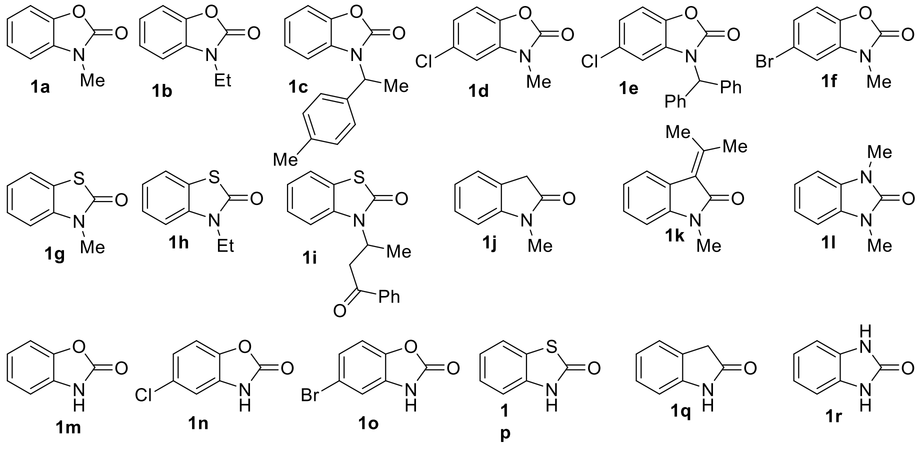


Figure S1: List of heterocycles used

Compound **1a**,[1] **1b**,[1] **1d**,[2] **1f**,[2] **1g**,[3] and **1h**[3] were prepared by following a reported protocol.[1a] Reactant (3 mmol, 1 equiv.) and K_2CO_3 (4.5 mmol, 1.5 equiv.) was dissolved in 30 mL acetone. After 10 min, MeI or EtI (6 mmol, 2 equiv.) was added and stirred the reaction mixture for 12 h at room temperature. After completion of reaction, acetone was evaporated at reduced pressure, diluted with saturated $Na_2S_2O_3$ and the organic product was separated using EtOAc. The product was purified by silica gel column chromatography using EtOAc/hexane as eluent. The NMR data was matched and found to be identical with the reported one.[1–3]

Compound **1c**,[4] **1e**,[4] and **1i**[4] were prepared by our previously reported method.[4] Catalyst MeOTf (10 mol%), nucleophile (0.5 mmol, 1equiv.), alcohol (0.7 mmol, 1.2 equiv.) and 1.5 mL toluene were taken in a 5 mL screw capped vial. The vial was capped and allowed to heat at 90 °C for 24 h with continuous stirring. After completion of the reaction (monitored by TLC), toluene was evaporated under reduced pressure and the crude reaction mixture was directly separated by silica gel column chromatography using ethyl acetate / hexane solution to obtain the desired product. The NMR data was matched and found to be identical with the reported one.[4]

Compound **1j**[5] was prepared by the following reported method. Heterocycle (3 mmol, 1 equiv.) and NaH (3.6 mmol, 1.2 equiv.) was taken in 15 mL dry THF under argon atmosphere and allowed to cool at 0 °C in ice. After 15 min, MeI (6 mmol, 2 equiv.) was added and allowed to come at room temperature and stirred for 12 h. After completion of reaction, THF was evaporated at reduced pressure, diluted with saturated $Na_2S_2O_3$ and the organic product was separated using EtOAc. The product was purified by silica gel column chromatography using EtOAc/hexane as eluent. The NMR data was matched and found to be identical with the reported one.[5]

Compound **1k**[5] was prepared by the following reported method. *p*-TSA·H_2O (1.1 mmol, 1.1 equiv.), **1j** (1 mmol, 1equiv.), acetone (2 mmol, 2 equiv.) and 4 mL toluene were taken in a 25 mL RB flask equipped with a condenser. The mixture was allowed to heat at 90 °C for 24 h with continuous stirring. After completion of the reaction (monitored by TLC), toluene was evaporated under reduced pressure and the crude reaction mixture was directly separated by silica gel column chromatography using ethyl acetate / hexane solution to obtain the desired product. The NMR data was matched and found to be identical with the reported one.[5]

Compound **1l**[6] was prepared by the following way. Heterocycle (3 mmol, 1 equiv.) and NaH (7.2 mmol, 2.4 equiv.) was taken in 15 mL dry THF under argon atmosphere and allowed to cool at 0 °C in ice. After 15 min, MeI (12 mmol, 4 equiv.) was added and allowed to come at room temperature and stirred for 12 h. After completion of reaction, THF was evaporated at reduced pressure, diluted with saturated $Na_2S_2O_3$ and the organic product was separated using EtOAc. The product was purified by silica gel column chromatography using EtOAc/hexane as eluent. The NMR data was matched and found to be identical with the reported one.[6]

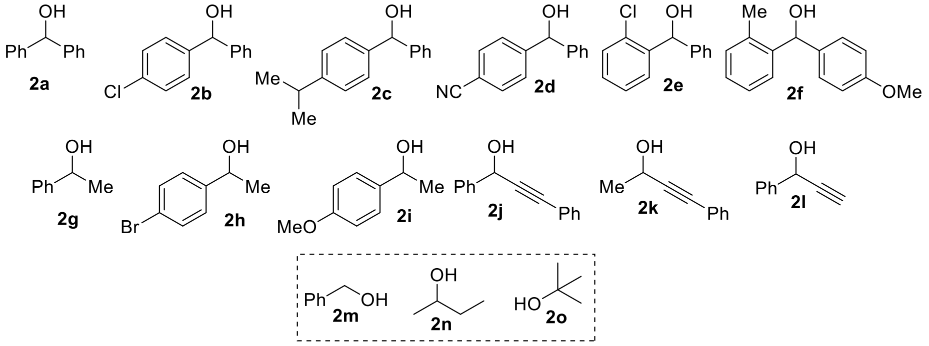
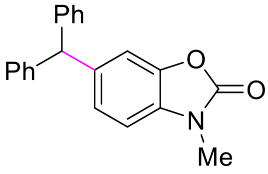


Figure S2: List of alcohols used

C. General synthetic method A and characterisation data of compounds 3aa–3lg:

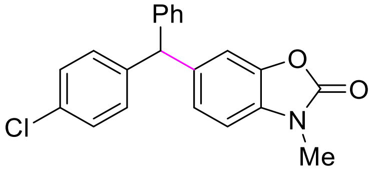
Unless otherwise noted *N*-alkylated heterocycle **1** (0.2 mmol, 1 equiv.), alcohol **2** (0.24 mmol, 1.2 equiv.) Catalyst MeOTf (3.3 mg, 0.02 mmol, 10 mol%), and 0.6 mL CH_3NO_2 were taken in a 5 mL screw capped reaction vial under nitrogen atmosphere. The vial was capped and allowed to heat at 80 °C for 10 h with continuous stirring. After completion of the reaction (monitored by TLC), CH_3NO_2 was evaporated under reduced pressure and the crude reaction mixture was used directly to isolate the product by silica gel (230–400 mess) column chromatography (flash) using ethyl acetate / hexane solution to obtain the desired product **3**.

6-Benzhydryl-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3aa):



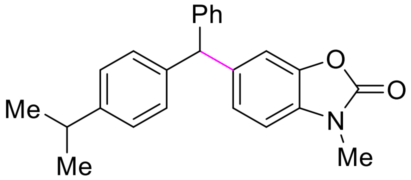
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3aa**, which was purified by silica gel flash column chromatography (using 3-6% ethyl acetate/hexane as eluent) to give the titled compound as a white crystalline solid (61.9 mg, 0.19 mmol, 98%). Melting point 118–120 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.36 – 7.24 (m, 6H), 7.14 (dd, *J* = 6.8, 1.9 Hz, 4H), 7.03 – 7.00 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 1H), 5.62 (s, 1H), 3.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.96, 143.51, 142.83, 139.23, 130.18, 129.34, 128.50, 126.61, 124.95, 111.17, 107.72, 56.61, 28.17 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{17}ClNO_2$ 350.0942; found 350.0929.

6-((4-Chlorophenyl)(phenyl)methyl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3ab):



Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and (4-chlorophenyl)(phenyl)methanol **2b** (52.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ab**, which was purified by silica gel flash column chromatography (using 5-8% ethyl acetate/hexane as eluent) to give the titled compound as a colourless oil (65.0 mg, 0.18 mmol, 93%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.36 – 7.24 (m, 5H), 7.13 – 7.05 (m, 4H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 7.4 Hz, 1H), 5.58 (s, 1H), 3.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.88, 143.01, 142.87, 142.12, 138.63, 132.43, 130.69, 130.36, 129.24, 128.63, 126.83, 124.87, 111.03, 107.86, 55.94, 28.20 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{18}NO_2$ 316.1332; found 316.1327.

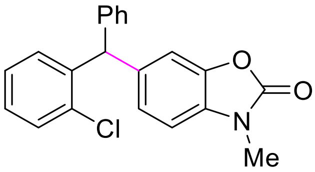
6-((4-Isopropylphenyl)(phenyl)methyl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3ac):



Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and (4-isopropylphenyl)(phenyl)methanol **2c** (54.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ac**, which was purified by silica gel flash column chromatography (using 3-6% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (54.3 mg, 0.15 mmol, 76%). Melting point 126–128 °C.

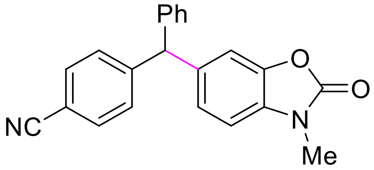
Following the same method, reaction between **1a** (149.1 mg, 1mmol) and **2c** (271.6 mg, 1.2 mmol) afforded the product **3ac** in 74% (264.3 mg, 0.74 mmol) yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.12 (m, 4H), 7.02 (d, *J* = 4.5 Hz, 1H), 7.00 (s, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 5.57 (s, 1H), 3.40 (s, 3H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 147.10, 143.76, 142.79, 140.75, 139.53, 129.32, 129.17, 128.44, 126.51, 124.91, 123.88, 122.53, 111.17, 109.98, 108.10, 107.66, 56.28, 33.67, 28.16, 24.02 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{24}NO_2$ 358.1802; found 358.1794.

6-((2-Chlorophenyl)(phenyl)methyl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3ae):



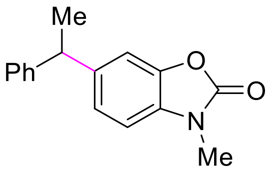
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and (2-chlorophenyl)(phenyl)methanol **2e** (52.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ae**, which was purified by silica gel flash column chromatography (using 5-10% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (60.2 mg, 0.17 mmol, 86%). Melting point 148–150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43 – 7.41 (m, 1H), 7.33 (dd, *J* = 8.1, 6.3 Hz, 2H), 7.29 (dd, *J* = 6.5, 2.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.11 – 7.08 (m, 2H), 6.99 – 6.94 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 1H), 3.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 154.92, 142.86, 142.25, 141.20, 137.73, 134.50, 130.97, 130.33, 129.87, 129.45, 128.56, 128.11, 126.81, 126.78, 125.06, 111.21, 107.84, 53.22, 28.19 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{17}ClNO_2$ 350.0942; found 350.0938.

4-((3-Methyl-2-oxo-2,3-dihydrobenzo[*d*]oxazol-6-yl)(phenyl)methyl)benzonitrile (3ad):



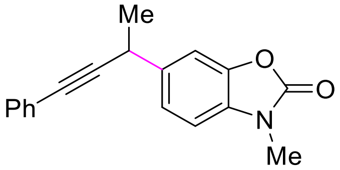
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and 4-(hydroxy(phenyl)methyl)benzonitrile **2d** (41.9 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ad**, which was purified by silica gel flash column chromatography (using 10-20% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (30.6 mg, 0.09 mmol, 45%). Melting point 188–190 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.61(d, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.96 – 6.90 (m, 3H), 5.64 (s, 1H), 3.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.79, 149.07, 142.94, 142.01, 137.57, 132.31, 130.63, 130.10, 129.20, 128.81, 127.17, 124.86, 118.79, 111.02, 110.57, 107.98, 56.54, 28.22 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{17}N_2O_2$ 341.1285; found 341.1279.

3-Methyl-6-(1-phenylethyl)benzo[*d*]oxazol-2(3*H*)-one (3ag):



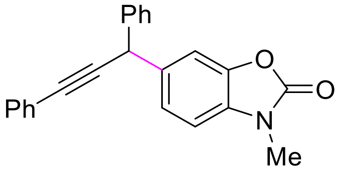
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and 1-phenylethan-1-ol **2g** (29.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ag**, which was purified by silica gel flash column chromatography (using 3-5% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (38.0 mg, 0.15 mmol, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 – 7.28 (m, 2H), 7.24 – 7.20 (m, 3H), 7.10 – 7.07 (m, 2H), 6.91 – 6.86 (d, *J* = 7.3 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 1H), 3.40 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 155.00, 145.94, 142.85, 141.72, 129.88, 128.53, 127.46, 126.31, 123.03, 109.33, 107.73, 44.65, 28.13, 22.03 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{16}NO_2$ 254.1176; found 254.1191.

3-Methyl-6-(4-phenylbut-3-yn-2-yl)benzo[*d*]oxazol-2(3*H*)-one (3ak):



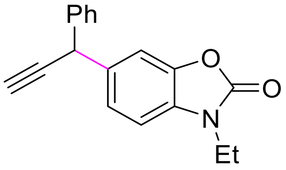
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and 4-phenyl-3-butyn-2-ol **2k** (35.1 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **3ak**, which was purified by silica gel flash column chromatography (using 4-6% ethyl acetate/hexane as eluent) to give the titled compound as a yellow liquid (16.6 mg, 0.06 mmol, 30%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.48 – 7.45 (m, 2H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.35 – 7.29 (m, 4H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.42 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 155.45, 142.85, 138.57, 131.62, 130.44, 128.28, 127.97, 123.40, 122.36, 108.83, 107.86, 92.00, 82.87, 32.45, 28.19, 24.80 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{16}NO_2$ 278.1176; found 278.1165.

6-(1,3-Diphenylprop-2-yn-1-yl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3aj):



Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and 1,3-diphenyl-2-propyn-1-ol **2j** (50.0 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **3aj**, which was purified by silica gel flash column chromatography (using 5-10% ethyl acetate/hexane as eluent) to give the titled compound as a yellow liquid (40.8 mg, 0.12 mmol, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.52 – 7.49 (m, 2H), 7.47 – 7.44 (m, 2H), 7.39 – 7.32 (m, 7H), 7.30 – 7.29 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H), 3.40 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.86, 142.83, 142.40, 137.03, 131.70, 130.68, 128.73, 128.27, 128.18, 127.79, 127.19, 123.41, 123.08, 109.65, 107.77, 89.47, 85.40, 43.53, 28.27 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{23}H_{18}NO_2$ 340.1332; found 340.1327.

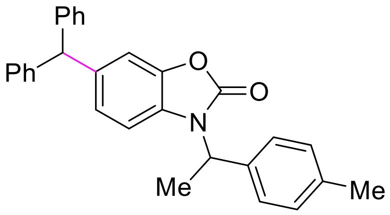
3-Ethyl-6-(1-phenylprop-2-yn-1-yl)benzo[*d*]oxazol-2(3*H*)-one (3bl):



Following the general synthetic method A, reaction between 3-ethylbenzo[*d*]oxazol-2(3*H*)-one **1b** (32.6 mg, 0.2 mmol, 1 equiv.) and 1-phenylprop-2-yn-1-ol **2l** (31.7 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **3bl**, which was purified by silica gel flash column chromatography (using 5-7% ethyl acetate/hexane as eluent) to give the titled compound as a yellow liquid (25.0 mg, 0.09 mmol, 45%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.42 – 7.32 (m, 5H), 7.30 – 7.22 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 2.6 Hz, 1H), 3.88 (q, *J* = 7.3 Hz, 2H), 2.56 (d, *J* =

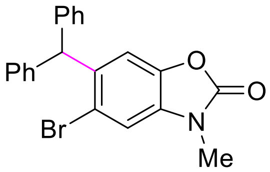
2.6 Hz, 1H), 1.37 (t, *J* = 7.3 Hz, 4H) ppm. **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) δ = 154.41, 142.95, 140.77, 136.17, 129.85, 128.81, 127.68, 127.28, 123.22, 109.78, 108.00, 84.17, 73.44, 42.73, 37.24, 13.05 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{16}NO_2$ 278.1176; found 278.1170.

6-Benzhydryl-3-(1-(*p*-tolyl)ethyl)benzo[*d*]oxazol-2(3*H*)-one (3ca):



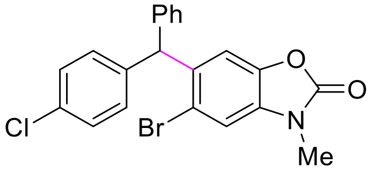
Following the general synthetic method A, reaction between 3-(1-(*p*-tolyl)ethyl)benzo[*d*]oxazol-2(3*H*)-one **1c** (26.6 mg, 0.1 mmol, 1 equiv.) and diphenylmethanol **2a** (22.1 mg, 0.12 mmol, 1.2 equiv.) afforded the corresponding product **3ca**, which was purified by silica gel flash column chromatography (using 2-5% ethyl acetate/hexane as eluent) to give the titled compound as a colourless liquid (31.5 mg, 0.08 mmol, 75%). **^1H NMR** (400 MHz, $CDCl_3$) δ = 7.22 – 7.19 (m, 7H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 4H), 6.87 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 5.54 (q, *J* = 7.3 Hz, 1H), 5.43 (s, 1H), 2.26 (s, 3H), 1.78 (d, *J* = 7.1 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ = 154.60, 143.45, 142.88, 138.68, 137.90, 136.98, 135.34, 129.49, 129.31, 128.80, 128.45, 128.43, 126.82, 126.55, 124.56, 111.09, 109.72, 56.55, 52.23, 21.10, 17.00 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{29}H_{26}NO_2$ 420.1958; found 420.1949.

6-Benzhydryl-5-bromo-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3fa):



Following the general synthetic method A, reaction between 5-bromo-3-methylbenzo[*d*]oxazol-2(3*H*)-one **1f** (45.6 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3fa**, which was purified by silica gel flash column chromatography (using 5-8% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (63.9 mg, 0.16 mmol, 81%). Melting point 175–177 °C. **^1H NMR** (400 MHz, $CDCl_3$) δ = 7.36 – 7.32 (m, 4H), 7.30 – 7.26 (m, 2H), 7.23 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 4H), 6.84 (s, 1H), 5.99 (s, 1H), 3.39 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ = 154.47, 142.26, 141.97, 137.89, 131.36, 129.48, 129.40, 128.57, 126.79, 119.23, 112.74, 112.35, 56.02, 28.33 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{17}BrNO_2$ 394.0437; found 394.0440.

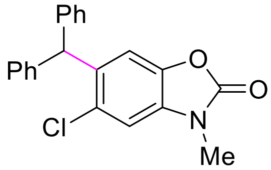
5-Bromo-6-((4-chlorophenyl)(phenyl)methyl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3fb):



Following the general synthetic method A, reaction between 5-bromo-3-methylbenzo[*d*]oxazol-2(3*H*)-one **1f** (45.6 mg, 0.2 mmol, 1 equiv.) and (4-chlorophenyl)(phenyl)methanol **2b** (52.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3fb**, which was purified by silica gel flash column chromatography (using 5-8% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (65.2 mg, 0.15 mmol, 76%). Melting point 186–188 °C.

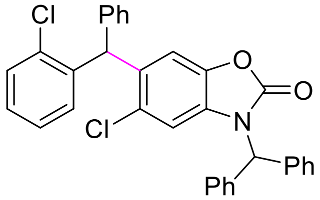
Following the same method, reaction between **1f** (228.1 mg, 1mmol.) and **2b** (262.4 mg, 1.2 mmol) afforded the product **3fb** in 72% (307.4 mg, 0.72 mmol) yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.27 (m, 5H), 7.23 (s, 1H), 7.07 – 7.00 (m, 4H), 6.80 (s, 1H), 5.94 (s, 1H), 3.40 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.40, 142.00, 141.82, 140.76, 137.31, 132.63, 131.53, 130.79, 129.39, 128.72, 128.71, 127.02, 119.17, 112.55, 112.44, 55.40, 28.34 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{16}BrClNO_2$ 428.0047; found 428.0032.

6-Benzhydryl-5-chloro-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3da):



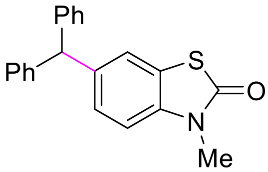
Following the general synthetic method A, reaction between 5-chloro-3-methylbenzo[*d*]oxazol-2(3*H*)-one **1d** (36.9 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3da**, which was purified by silica gel flash column chromatography (using 3-5% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (69.3 mg, 0.20 mmol, 99%). Melting point 160–162 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.25 (m, 6H), 7.11 – 7.08 (m, 4H), 7.05 (s, 1H), 6.83 (s, 1H), 6.00 (s, 1H), 3.39 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.59, 142.21, 141.31, 136.36, 131.10, 129.45, 129.41, 128.58, 126.81, 112.48, 109.31, 53.42, 28.34 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{17}ClNO_2$ 350.0942; found 350.0940.

3-Benzhydryl-5-chloro-6-((2-chlorophenyl)(phenyl)methyl)benzo[*d*]oxazol-2(3*H*)-one (3de):



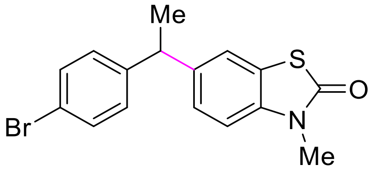
Following the general synthetic method A, reaction between 3-benzhydryl-5-chlorobenzo[*d*]oxazol-2(3*H*)-one **1e** (33.5 mg, 0.1 mmol, 1 equiv.) and (2-chlorophenyl)(phenyl)methanol **2e** (26.3 mg, 0.12 mmol, 1.2 equiv.) afforded the corresponding product **3de**, which was purified by silica gel flash column chromatography (using 2-3% ethyl acetate/hexane as eluent) to give the titled compound as a yellowish gummy liquid (35.9 mg, 0.07 mmol, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.43 – 7.39 (m, 7H), 7.34 (s, 1H), 7.33 – 7.30 (m, 4H), 7.27 – 7.21 (m, 4H), 7.06 – 7.03 (m, 2H), 6.89 – 6.82 (m, 1H), 6.79 (s, 1H), 6.72 (s, 1H), 6.43 (s, 1H), 6.19 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 154.36, 141.29, 140.53, 139.96, 136.49, 136.47, 135.03, 134.67, 130.52, 129.94, 129.75, 129.52, 129.49, 129.35, 128.99, 128.97, 128.68, 128.61, 128.39, 128.35, 128.26, 127.04, 126.76, 112.17, 111.98, 61.60, 50.74 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{33}H_{24}Cl_2NO_2$ 536.1179; found 536.1169.

6-Benzhydryl-3-methylbenzo[*d*]thiazol-2(3*H*)-one (3ga):



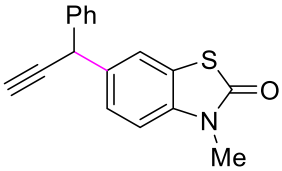
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]thiazol-2(3*H*)-one **1g** (33.0 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ga**, which was purified by silica gel flash column chromatography (using 3-4% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (64.9 mg, 0.19 mmol, 98%). Melting point 125–126 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.32 (m, 4H), 7.31 – 7.25 (m, 2H), 7.19 – 7.13 (m, 6H), 6.99 (d, *J* = 8.3 Hz, 1H), 5.62 (s, 1H), 3.46 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 170.13, 143.49, 139.56, 136.25, 129.39, 128.53, 127.76, 126.91, 126.63, 123.33, 122.73, 110.27, 56.41, 29.07 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{18}NOS$ 332.1104; found 332.1097.

6-(1-(4-Bromophenyl)ethyl)-3-methylbenzo[*d*]thiazol-2(3*H*)-one (3gh):



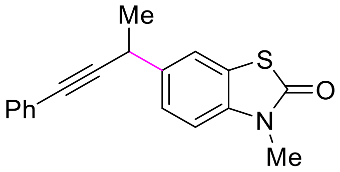
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]thiazol-2(3*H*)-one **1g** (33.0 mg, 0.2 mmol, 1 equiv.) and 1-(4-bromophenyl)ethan-1-ol **2h** (48.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3gh**, which was purified by silica gel flash column chromatography (using 3-4% ethyl acetate/hexane as eluent) to give the titled compound as a colourless oil (59.2 mg, 0.17 mmol, 85%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.44 – 7.41 (m, 2H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.17 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.10 (d, *J* = 7.8, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 1H), 3.44 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 170.04, 144.95, 141.26, 136.17, 131.59, 129.31, 125.84, 122.83, 121.44, 120.11, 110.39, 43.88, 29.06, 21.88 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{15}BrNOS$ 348.0052; found 348.0050.

3-Methyl-6-(1-phenylprop-2-yn-1-yl)benzo[*d*]thiazol-2(3*H*)-one (3gl):



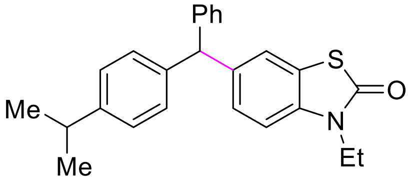
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]thiazol-2(3*H*)-one **1g** (33.0 mg, 0.2 mmol, 1 equiv.) and 1-phenylprop-2-yn-1-ol **2l** (31.7 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **3gl**, which was purified by silica gel flash column chromatography (using 5-9% ethyl acetate/hexane as eluent) to give the titled compound as a yellow oil (27.9 mg, 0.10 mmol, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 1.8 Hz, 1H), 7.41 – 7.33 (m, 5H), 7.29 (dd, *J* = 6.7, 2.0 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.06 (s, 1H), 3.45 (s, 3H), 2.56 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 170.06, 140.74, 136.75, 136.64, 128.82, 127.73, 127.29, 126.10, 123.02, 121.84, 110.45, 84.16, 73.48, 42.51, 29.09 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{17}H_{14}NOS$ 280.0791; found 280.0776.

3-Methyl-6-(4-phenylbut-3-yn-2-yl)benzo[*d*]thiazol-2(3*H*)-one (3gk):



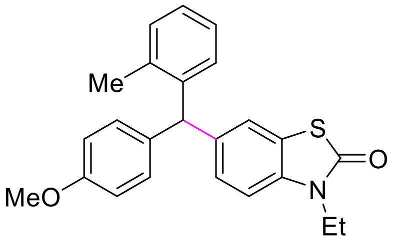
Following the general synthetic method A, reaction between 3-methylbenzo[*d*]thiazol-2(3*H*)-one **1g** (33.0 mg, 0.2 mmol, 1 equiv.) and 4-phenylbut-3-yn-2-ol **2k** (35.1 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **3gk**, which was purified by silica gel flash column chromatography (using 5% ethyl acetate/hexane as eluent) to give the titled compound as a yellow oil (21.1 mg, 0.07 mmol, 36%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 1.8 Hz, 1H), 7.47 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.34 – 7.32 (m, 3H), 7.03 (d, *J* = 8.3 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.48 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 170.15, 138.82, 136.52, 131.64, 128.29, 127.99, 125.22, 123.40, 122.86, 121.00, 110.42, 91.99, 82.88, 32.19, 29.09, 24.71 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{16}NOS$ 294.0947; found 294.0940.

3-Ethyl-6-((4-isopropylphenyl)(phenyl)methyl)benzo[*d*]thiazol-2(3*H*)-one (3hc):



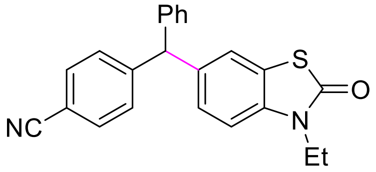
Following the general synthetic method A, reaction between 3-ethylbenzo[*d*]thiazol-2(3*H*)-one **1h** (35.8 mg, 0.2 mmol, 1 equiv.) and (4-isopropylphenyl)(phenyl)methanol **2c** (54.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3hc**, which was purified by silica gel flash column chromatography (using 4-6% ethyl acetate/hexane as eluent) to give the titled compound as a yellow sticky liquid (60.5 mg, 0.16 mmol, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.36 – 7.26 (m, 3H), 7.21 – 7.11 (m, 6H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.57 (s, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 2.92 (p, *J* = 6.9 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.28 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 169.76, 147.09, 143.77, 140.74, 139.57, 135.25, 129.37, 129.22, 128.46, 127.67, 126.53, 126.51, 123.47, 122.99, 110.20, 56.09, 37.74, 33.68, 24.03, 12.94 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{26}NOS$ 388.1730; found 388.1720.

3-Ethyl-6-((4-methoxyphenyl)(o-tolyl)methyl)benzo[*d*]thiazol-2(3*H*)-one (3hf):



Following the general synthetic method A, reaction between 3-ethylbenzo[*d*]thiazol-2(3*H*)-one **1h** (35.8 mg, 0.2 mmol, 1 equiv.) and (4-methoxyphenyl)(*o*-tolyl)methanol **2f** (54.9 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3hf**, which was purified by silica gel flash column chromatography (using 3-5% ethyl acetate/hexane as eluent) to give the titled compound as a yellow oil (22.6 mg, 0.06 mmol, 29%). **^{1}H NMR** (300 MHz, CDCl$_3$) δ = 7.20 – 7.10 (m, 4H), 7.05 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.00 – 6.97 (m, 3H), 6.98 – 6.80 (m, 3H), 5.65 (s, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 2.24 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) δ = 169.76, 158.16, 142.20, 139.15, 136.51, 135.23, 135.06, 130.56, 130.44, 129.22, 127.70, 126.57, 125.88, 123.49, 123.00, 113.83, 110.19, 55.26, 52.25, 37.75, 19.88, 12.93 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{24}H_{24}NO_2S$ 390.1522; found 390.1517.

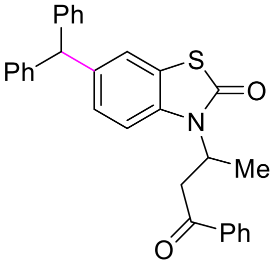
4-((3-Ethyl-2-oxo-2,3-dihydrobenzo[*d*]thiazol-6-yl)(phenyl)methyl)benzonitrile (3hd):



Following the general synthetic method A, reaction between 3-ethylbenzo[*d*]thiazol-2(3*H*)-one **1h** (35.8 mg, 0.2 mmol, 1 equiv.) and 4-(hydroxy(phenyl)methyl)benzonitrile **2d** (41.9 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3hd**, which was purified by silica gel flash column chromatography (using 10-15% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (37.8 mg, 0.10 mmol, 51%). Melting point 198–200 °C.

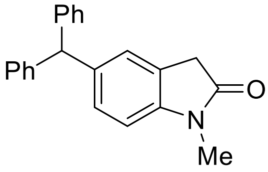
Following the same method, reaction between **1h** (179.2 mg, 1mmol.) and **2d** (251.1 mg, 1.2 mmol) afforded the product **3hd** in 50% (185.1 mg, 0.50 mmol) yield. **^{1}H NMR** (300 MHz, CDCl$_3$) δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.24 (m, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.00 (m, 5H), 5.63 (s, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) δ = 169.56, 149.08, 142.01, 137.66, 135.72, 132.32, 130.14, 129.25, 128.82, 127.51, 127.16, 126.71, 123.45, 123.37, 118.81, 110.46, 56.34, 37.82, 12.91 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{23}H_{19}N_2OS$ 371.1213; found 371.1210.

6-Benzhydryl-3-(4-oxo-4-phenylbutan-2-yl)benzo[*d*]thiazol-2(3*H*)-one (3ia):



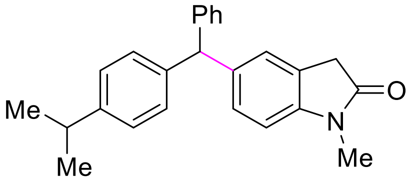
Following the general synthetic method A, reaction between 3-(4-oxo-4-phenylbutan-2-yl)benzo[*d*]thiazol-2(3*H*)-one **1i** (29.7 mg, 0.1 mmol, 1 equiv.) and diphenylmethanol **2a** (22.1 mg, 0.12 mmol, 1.2 equiv.) afforded the corresponding product **3ia**, which was purified by silica gel flash column chromatography (using 5-9% ethyl acetate/hexane as eluent) to give the titled compound as a yellow oil (38.5 mg, 0.08 mmol, 83%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ = 7.88 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 4H), 7.19 – 7.17 (m, 3H), 7.04 (d, *J* = 7.7 Hz, 6H), 5.48 (s, 1H), 5.04 – 4.99 (m, 1H), 4.00 (dd, *J* = 17.9, 6.9 Hz, 1H), 3.48 (dd, *J* = 17.9, 6.2 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) δ = 197.64, 170.11, 143.47, 143.46, 138.95, 136.46, 135.59, 133.52, 129.47, 129.39, 128.70, 128.56, 128.47, 128.42, 128.17, 127.62, 126.56, 123.30, 123.04, 111.09, 56.33, 48.12, 41.85, 17.87 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{30}H_{26}NO_2S$ 464.1679; found 464.1675.

5-Benzhydryl-1-methylindolin-2-one (3ja):



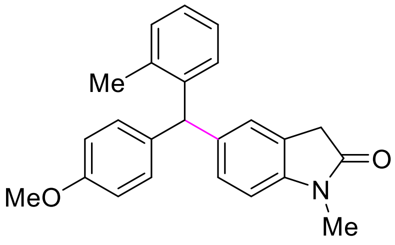
Following the general synthetic method A, reaction between 1-methylindolin-2-one **1j** (29.5 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ja**, which was purified by silica gel flash column chromatography (using 5-8% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (62.2 mg, 0.20 mmol, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 (dd, J = 8.2, 6.6 Hz, 4H), 7.28 – 7.24 (m, 2H), 7.18 – 7.15 (m, 4H), 7.09 – 7.05 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 5.58 (s, 1H), 3.49 (s, 2H), 3.23 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 175.20, 143.97, 143.65, 138.43, 129.39, 128.90, 128.43, 126.44, 125.54, 124.68, 107.84, 56.51, 35.88, 26.25 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{20}NO$ 314.1539; found 314.1528.

5-((4-Isopropylphenyl)(phenyl)methyl)-1-methylindolin-2-one (3jc):



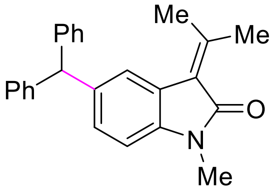
Following the general synthetic method A, reaction between 1-methylindolin-2-one **1j** (29.5 mg, 0.2 mmol, 1 equiv.) and (4-isopropylphenyl)(phenyl)methanol **2c** (54.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3jc**, which was purified by silica gel flash column chromatography (using 3-5% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (67.5 mg, 0.19 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 (dd, J = 8.2, 6.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.23 – 7.17 (m, 4H), 7.11 – 7.07 (m, 4H), 6.78 (d, J = 8.0 Hz, 1H), 5.55 (s, 1H), 3.49 (s, 2H), 3.23 (s, 3H), 2.94 (hept, J = 6.9 Hz, 1H), 1.30 (d, J = 6.9 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 175.20, 146.90, 144.25, 143.58, 141.24, 138.71, 129.39, 129.24, 128.88, 128.40, 126.47, 126.36, 125.55, 124.63, 107.81, 56.20, 35.90, 33.70, 26.25, 24.08 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{26}NO$ 356.2009; found 356.1998.

5-((4-Methoxyphenyl)(*o*-tolyl)methyl)-1-methylindolin-2-one (3jf):



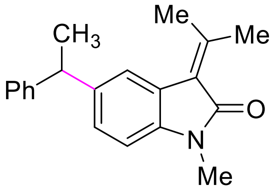
Following the general synthetic method A, reaction between 1-methylindolin-2-one **1j** (29.5 mg, 0.2 mmol, 1 equiv.) and (4-methoxyphenyl)(*o*-tolyl)methanol **2f** (54.9 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3jf**, which was purified by silica gel flash column chromatography (using 10-15% ethyl acetate/hexane as eluent) to give the titled compound as a yellowish sticky liquid (66.5 mg, 0.18 mmol, 93%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.20 – 7.14 (m, 3H), 7.01 (d, J = 8.5 Hz, 4H), 6.89 – 6.84 (m, 3H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.64 (s, 1H), 3.82 (s, 3H), 3.49 (s, 2H), 3.23 (s, 3H), 2.26 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 175.24, 158.08, 143.54, 142.67, 138.24, 136.53, 135.58, 130.51, 130.45, 129.24, 128.91, 126.43, 125.82, 125.61, 124.62, 113.78, 107.82, 55.25, 52.37, 35.90, 26.25, 19.90 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{24}NO_2$ 358.1802; found 358.1799.

5-Benzhydryl-1-methyl-3-(propan-2-ylidene)indolin-2-one (3ka):



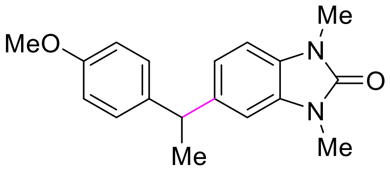
Following the general synthetic method A, reaction between 1-methyl-3-(propan-2-ylidene)indolin-2-one **1k** (37.4 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3ka**, which was purified by silica gel flash column chromatography (using 2% ethyl acetate/hexane as eluent) to give the titled compound as a yellow solid (70.7 mg, 0.20 mmol, 100%). Melting point 145–147 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.35 – 7.28 (m, 5H), 7.27 – 7.22 (m, 2H), 7.16 (dd, *J* = 7.1, 1.6 Hz, 4H), 7.02 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.59 (s, 1H), 3.24 (s, 3H), 2.61 (s, 3H), 2.21 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 168.00, 154.88, 144.19, 140.52, 137.29, 129.38, 128.56, 128.34, 126.35, 124.74, 123.67, 122.74, 107.21, 56.69, 25.68, 25.15, 23.16 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{24}NO$ 354.1852; found 354.1850.

1-Methyl-5-(1-phenylethyl)-3-(propan-2-ylidene)indolin-2-one (3kg):



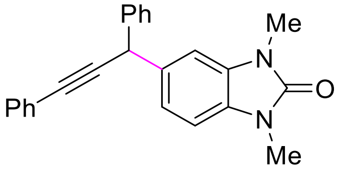
Following the general synthetic method A, reaction between 1-methyl-3-(propan-2-ylidene)indolin-2-one **1k** (37.4 mg, 0.2 mmol, 1 equiv.) and 1-phenylethan-1-ol **2g** (29.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3kg**, which was purified by silica gel flash column chromatography (using 2-3% ethyl acetate/hexane as eluent) to give the titled compound as a yellow oil (46.0 mg, 0.16 mmol, 79%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.41 (s, 1H), 7.35 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 7.14 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 1H), 3.24 (s, 3H), 2.63 (s, 3H), 2.34 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 168.00, 154.56, 146.57, 140.36, 139.84, 128.42, 127.48, 126.53, 126.06, 123.72, 123.04, 122.86, 107.28, 44.69, 25.66, 25.26, 23.15, 22.21 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{22}NO$ 292.1696; found 292.1692.

5-(1-(4-Methoxyphenyl)ethyl)-1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3li):



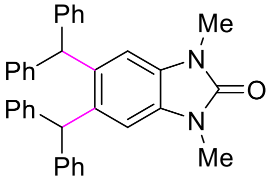
Following the general synthetic method A, reaction between 1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1l** (32.4 mg, 0.2 mmol, 1 equiv.) and 1-(4-methoxyphenyl)ethan-1-ol **2i** (36.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3li**, which was purified by silica gel flash column chromatography (using 20-32% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (53.3 mg, 0.18 mmol, 90%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 8.5 Hz, 2H), 7.00 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.91 (s, 1H), 6.89 – 6.82 (m, 3H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.40 (d, *J* = 4.4 Hz, 6H), 1.67 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 157.86, 154.87, 140.51, 138.76, 130.15, 128.39, 128.31, 120.43, 113.78, 113.72, 107.11, 106.61, 55.27, 43.98, 27.19, 27.17, 22.47 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{21}N_2O_2$ 297.1598; found 297.1610.

5-(1,3-Diphenylprop-2-yn-1-yl)-1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3lj):



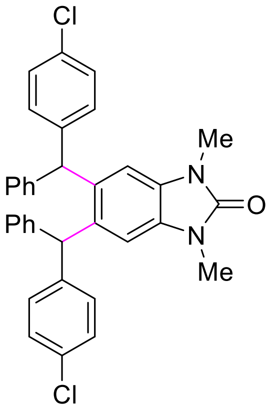
Following the general synthetic method A, reaction between 1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1l** (32.4 mg, 0.2 mmol, 1 equiv.) and 1,3-diphenylprop-2-yn-1-ol **2j** (50.0 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **3lj**, which was purified by silica gel flash column chromatography (using 20-32% ethyl acetate/hexane as eluent) to give the titled compound as a white gummy liquid (52.1 mg, 0.15 mmol, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.55 – 7.48 (m, 4H), 7.39 – 7.30 (m, 5H), 7.29 – 7.25 (m, 1H), 7.21 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.07 (d, *J* = 1.6 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.30 (s, 1H), 3.42 (s, 3H) 3.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 154.86, 141.99, 135.39, 131.69, 130.34, 129.07, 128.70, 128.31, 128.12, 127.78, 126.99, 123.43, 121.02, 107.28, 107.00, 90.34, 85.07, 43.76, 27.26, 27.24 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{21}N_2O$ 353.1648; found 353.1638.

5,6-Dibenzhydryl-1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3la):



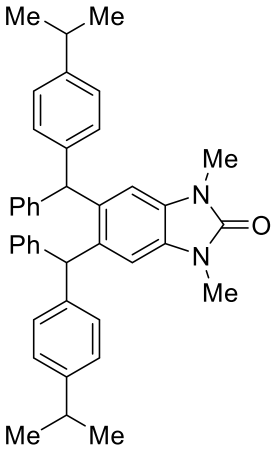
Following the general synthetic method A, reaction between 1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1l** (32.4 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3la**, which was purified by silica gel flash column chromatography (using 15-20% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (48.5 mg, 0.10 mmol, 49%) and 94% (0.19 mmol, 92.9 mg) **3la** was obtained by using 0.5 mmol **2a** (92 mg, 2.5 equiv.). Melting point 220–222 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 – 7.25 (m, 12H), 6.99 – 6.97 (m, 8H), 6.48 (s, 2H), 5.71 (s, 2H), 3.26 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 154.90, 143.73, 136.06, 129.48, 128.45, 128.42, 126.53, 109.35, 52.49, 27.14 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{35}H_{31}N_2O$ 495.2431; found 495.2436.

5,6-Bis((4-chlorophenyl)(phenyl)methyl)-1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3lb):



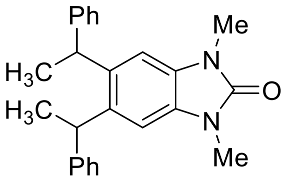
Following the general synthetic method A, reaction between 1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1l** (32.4 mg, 0.2 mmol, 1 equiv.) and (4-chlorophenyl)(phenyl)methanol **2b** (52.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3lb** (dr = 1:1), which was purified by silica gel flash column chromatography (using 18% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (48.5 mg, 0.08 mmol, 43%) and 82% (0.16 mmol, 92.4 mg) **3lb** was obtained by using 0.5 mmol **2a** (109.4 mg, 2.5 equiv.). Melting point 258–260 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 10H), 6.97 – 6.92 (m, 3H), 6.90 (s, 2H), 6.88 – 6.84 (m, 3H), 6.43 (s, 2H), 5.61 (s, 2H), 3.27 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.84, 143.15, 143.03, 142.22, 142.10, 135.35, 132.43, 132.37, 130.74, 129.33, 128.64, 128.60, 126.85, 126.82, 109.26, 51.90, 27.20 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{35}H_{29}Cl_2N_2O$ 563.1651; found 563.1642.

5,6-Bis((4-isopropylphenyl)(phenyl)methyl)-1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3lc):



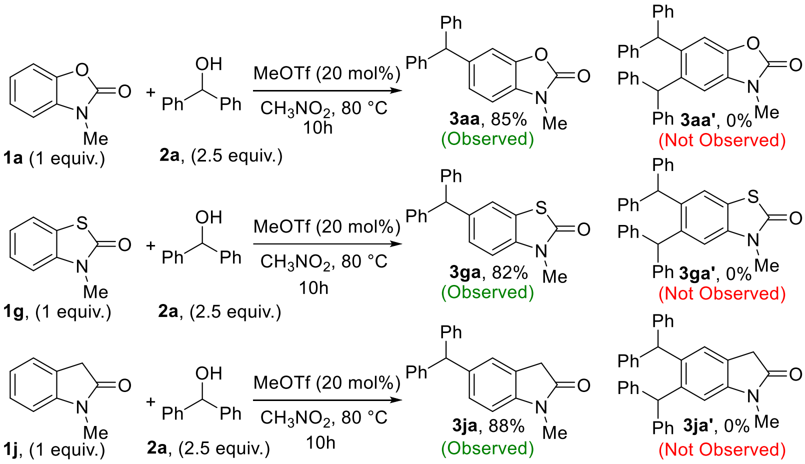
Following the general synthetic method A, reaction between 1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1l** (32.4 mg, 0.2 mmol, 1 equiv.) and (4-isopropylphenyl)(phenyl)methanol **2c** (113.1 mg, 0.5 mmol, 2.5 equiv.) afforded the corresponding product **3lc** (dr = 1:1), which was purified by silica gel flash column chromatography (using 10-20% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (102.0 mg, 0.18 mmol, 88%). Melting point 243–245 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 6H), 7.17 (d, J = 8.0 Hz, 4H), 6.99 (t, J = 6.1 Hz, 4H), 6.89 (dd, J = 7.9, 3.8 Hz, 4H), 6.51 (s, 2H), 5.71 (s, 2H), 3.27 (s, 6H), 2.94 (hept, J = 6.8 Hz, 2H), 1.30 (d, J = 1.9 Hz, 6H), 1.28 (d, J = 1.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.92, 146.98, 146.95, 144.01, 143.97, 141.11, 141.05, 136.31, 129.49, 129.39, 129.38, 128.37, 128.35, 126.42, 126.39, 109.25, 52.04, 33.71, 27.14, 24.09, 24.06 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{41}H_{43}N_2O$ 579.3370; found 579.3368.

1,3-Dimethyl-5,6-bis(1-phenylethyl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3lg):



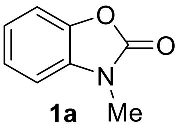
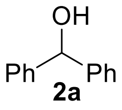
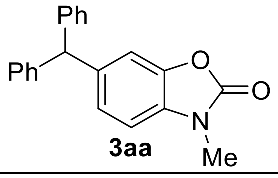
Following the general synthetic method A, reaction between 1,3-dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1l** (32.4 mg, 0.2 mmol, 1 equiv.) and 1-phenylethan-1-ol **2g** (61.0 mg, 0.5 mmol, 2.5 equiv.) afforded the corresponding product **3lg** (dr = 1:1), which was purified by silica gel flash column chromatography (using 20-30% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (62.2 mg, 0.17 mmol, 84%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.33 (dd, *J* = 8.3, 6.3 Hz, 2H), 7.26 – 7.18 (m, 6H), 7.06 – 7.03 (m, 2H), 6.92 (s, 1H), 6.78 (s, 1H), 4.64 (q, *J* = 7.1 Hz, 1H), 4.51 (q, *J* = 7.1 Hz, 1H), 3.43 (s, 3H), 3.37 (s, 3H), 1.72 (d, *J* = 7.1 Hz, 3H), 1.52 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 154.99, 154.96, 146.98, 146.52, 137.47, 137.08, 128.58, 128.56, 128.50, 128.39, 127.66, 127.45, 125.99, 106.56, 106.44, 39.92, 39.73, 27.22, 27.17, 22.85, 22.75 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{27}N_2O$ 371.2118; found 371.2114.

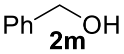
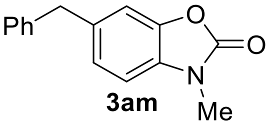
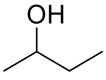
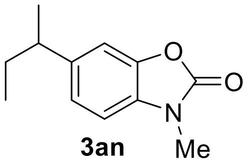
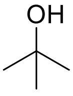
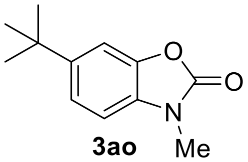
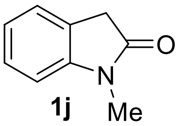
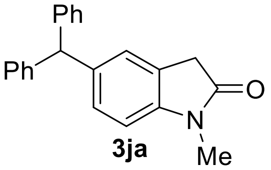
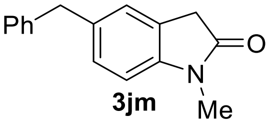
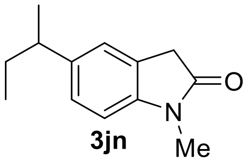
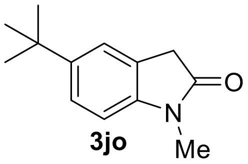
Scheme S1: Test for C-5 and C-6 dialkylation of *N*-methylatedheterocycles with benzhydrol:



The possibility of the formation of C-5 and C-6 dialkylated products with excess amount of alcohols were tested. In presence of excess amount of alcohols (2.5 equiv.) under MeOTf catalyst, *N*-methylbenzoxazolone and *N*-methylbenzothiazolone provided only C-6 alkylate products, whereas, *N*-methyloxindole provided C-5 alkylated products. In every case, no dialkylation (at C-5 and C-6 position) was observed.

Table S1: The catalytic superiority of MeOTf over TfOH towards nucleophilic substitution of alcohols:

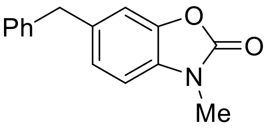
Entry	Nucleophile	Alcohol	Product	% of yield (MeOTf catalyst)	% of yield (TfOH catalyst)
1	 **1a**	 **2a**	 **3aa**	98	85

2	**1a**	 **2m**	 **3am**	29	22
3	**1a**	 **2n**	 **3an**	0	0
4	**1a**	 **2o**	 **3ao**	0	0
5	 **1j**	**2a**	 **3ja**	99	82
6	**1j**	**2m**	 **3jm**	30	26
7	**1j**	**2n**	 **3jn**	0	0
8	**1j**	**2o**	 **3jo**	0	0

A comparative study of Friedel-Crafts alkylation was performed by using MeOTf and TfOH as catalyst by using benzhydrol (**2a**), benzyl alcohol (**2m**), iso-butanol (**2n**) and tert-butanol (**2o**) as electrophiles and N-methylbenzoxazolone (**1a**) and N-methylindolinone (**1j**) as nucleophile (Table S1). The catalytic superiority of MeOTf over TfOH was observed towards regioselective Friedel-Crafts alkylation using benzylic alcohols. Whereas, both MeOTf and TfOH was unable to provide alkylation in presence of aliphatic alcohols (isobutanol and tert-butanol).

Characterisation data of 3am and 3jm:

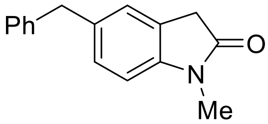
6-Benzyl-3-methylbenzo[*d*]oxazol-2(3*H*)-one (3am):



Following the general synthetic method A, reaction between 3-methylbenzo[*d*]oxazol-2(3*H*)-one **1a** (30.0 mg, 0.2 mmol, 1 equiv.) and benzyl alcohol (26.0 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3am**, which was purified by silica gel flash column chromatography (using 3-6% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (14.0 mg, 0.06 mmol, 29%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.35 – 7.29 (m, 2H), 7.26 – 7.24 (m, 1H), 7.21 – 7.18 (m, 2H), 7.09 – 7.04 (m, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.03 (s, 2H), 3.40 (s, 3H) ppm. **^{13}C{^{1}H}**

NMR (75 MHz, $CDCl_3$) δ = 154.94, 142.90, 140.77, 136.22, 128.80, 128.63, 128.60, 126.36, 124.25, 110.59, 107.83, 41.79, 28.14 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}NO_2$ 240.1019; found 240.1008.

5-Benzyl-1-methylindolin-2-one (3jm):

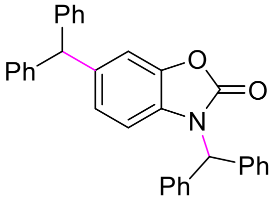


Following the general synthetic method A, reaction between 1-methylindolin-2-one **1j** (29.5 mg, 0.2 mmol, 1 equiv.) and benzyl alcohol (26.0 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **3jm**, which was purified by silica gel flash column chromatography (using 5-7% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (15.0 mg, 0.06 mmol, 30%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.30 (m, 2H), 7.25 – 7.19 (m, 4H), 7.13 – 7.12 (m, 1H), 6.76 (d, J = 8.0 Hz, 1H), 53.98 (s, 2H), 3.50 (s, 2H), 3.21 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 175.15, 143.47, 141.31, 135.47, 129.08, 128.80, 128.56, 128.20, 126.18, 125.07, 107.93, 41.59, 35.82, 26.22 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{16}NO$ 238.1226; found 238.1221.

D. General synthetic method B and characterisation data of compounds (4a–4e):

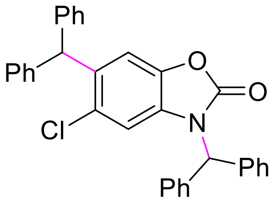
Unless otherwise noted heterocycle **1** (0.2 mmol, 1 equiv.), alcohol **2** (0.48 mmol, 2.4 equiv.) Catalyst MeOTf (6.6 mg, 0.04 mmol, 20 mol%), and 0.6 mL CH_3NO_2 were taken in a 5 mL screw capped reaction vial under nitrogen atmosphere. The vial was capped and allowed to heat at 80 °C for 24 h with continuous stirring. After completion of the reaction (monitored by TLC), CH_3NO_2 was evaporated under reduced pressure and the crude reaction mixture was directly separated by silica gel (230–400 mess) column chromatography (flash) using ethyl acetate / hexane solution to obtain the desired product **4**.

3,6-Dibenzhydrylbenzo[*d*]oxazol-2(3*H*)-one (4a):



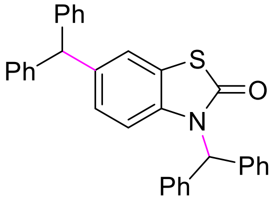
Following the general synthetic method B, reaction between benzo[*d*]oxazol-2(3*H*)-one **1m** (27.0 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (88.4 mg, 0.48 mmol, 2.4 equiv.) afforded the corresponding product **4a**, which was purified by silica gel flash column chromatography (using 2% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (67.3 mg, 0.14 mmol, 72%). Melting point 140–142 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.36 (m, 5H), 7.35 – 7.23 (m, 11H), 7.14 – 7.11 (m, 4H), 7.02 (s, 1H), 6.84 (s, 1H), 6.73 – 6.71 (m, 1H), 6.33 (d, J = 8.2 Hz, 1H), 5.54 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 154.81, 143.40, 142.82, 138.83, 137.00, 129.35, 129.16, 128.82, 128.70, 128.63, 128.48, 128.36, 126.61, 124.64, 111.17, 110.68, 61.32, 56.58 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{33}H_{26}NO_2$ 468.1958; found 468.1950.

3,6-Dibenzhydryl-5-chlorobenzo[*d*]oxazol-2(3*H*)-one (4b):



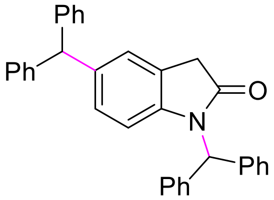
Following the general synthetic method B, reaction between 5-chlorobenzo[*d*]oxazol-2(3*H*)-one **1n** (34.0 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (88.4 mg, 0.48 mmol, 2.4 equiv.) afforded the corresponding product **4b**, which was purified by silica gel flash column chromatography (using 2% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (70.3 mg, 0.14 mmol, 70%). Melting point 175–177 °C. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ = 7.44 – 7.41 (m, 6H), 7.39 – 7.29 (m, 10H), 7.14 – 7.11 (m, 4H), 6.88 (s, 1H), 6.84 (s, 1H), 6.46 (s, 1H), 5.95 (s, 1H) ppm. ^{13}**C{**^{1}**H} NMR** (75 MHz, $CDCl_3$) δ = 154.43, 142.10, 141.38, 136.54, 136.27, 129.62, 129.45, 129.10, 129.01, 128.63, 128.60, 128.43, 126.84, 112.49, 111.90, 61.57, 53.40 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{33}H_{25}ClNO_2$ 502.1568; found 502.1562.

3,6-Dibenzhydrylbenzo[*d*]thiazol-2(3*H*)-one (4c):



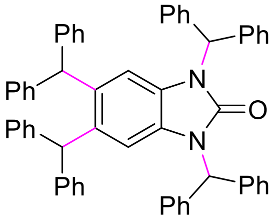
Following the general synthetic method B, reaction between benzo[*d*]thiazol-2(3*H*)-one **1p** (30.2 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (88.4 mg, 0.48 mmol, 2.4 equiv.) afforded the corresponding product **4c**, which was purified by silica gel flash column chromatography (using 5-8% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (77.4 mg, 0.16 mmol, 80%). Melting point 144–146 °C. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.25 (m, 13H), 7.12 – 7.05 (m, 9H), 6.70 (s, 1H), 5.69 (s, 1H), 5.50 (s, 1H) ppm. ^{13}**C{**^{1}**H} NMR** (100 MHz, $CDCl_3$) δ = 172.43, 143.58, 141.25, 139.11, 132.33, 129.31, 129.30, 129.27, 128.67, 128.41, 127.68, 127.02, 126.49, 124.37, 121.47, 56.36, 52.41 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{33}H_{26}NOS$ 484.1730; found 484.1719.

1,5-Dibenzhydrylindolin-2-one (4d):



Following the general synthetic method B, reaction between indolin-2-one **1q** (26.6 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (88.4 mg, 0.48 mmol, 2.4 equiv.) afforded the corresponding product **4d**, which was purified by silica gel flash column chromatography (using 5% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (60.5 mg, 0.13 mmol, 65%). Melting point 141–142 °C. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ = 7.39 – 7.27 (m, 14H), 7.26 – 7.20 (m, 2H), 7.13 (d, *J* = 6.9 Hz, 4H), 7.05 (s, 1H), 7.03 (s, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 5.47 (s, 1H), 3.61 (s, 2H) ppm. ^{13}**C{**^{1}**H} NMR** (75 MHz, $CDCl_3$) δ = 175.35, 143.87, 142.17, 137.85, 137.84, 129.39, 128.57, 128.38, 128.30, 127.74, 126.40, 125.37, 124.60, 111.51, 58.24, 56.46, 35.75 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{34}H_{28}NO$ 466.2165; found 466.2150.

1,3,5,6-Tetrabenzhydryl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (4e):

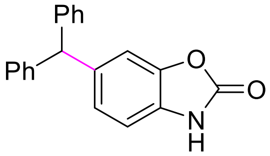


Following the general synthetic method B, reaction between 1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1r** (26.8 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (165.8 mg, 0.9 mmol, 4.5 equiv.) by using MeOTf (0.06mmol, 10 mg, 30 mol%) afforded the corresponding product **4e**, which was purified by silica gel flash column chromatography (using 10% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (126.2 mg, 0.16 mmol, 79%). Melting point 249–251 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.34 – 7.27 (m, 12H), 7.25 – 7.23 (m, 12H), 7.12 – 7.09 (m, 8H), 7.03 (s, 2H), 6.75 – 6.72 (m, 8H), 6.17 (s, 2H), 5.53 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 154.94, 143.43, 138.20, 135.21, 129.33, 128.59, 128.48, 128.24, 127.60, 126.65, 126.26, 113.69, 60.02, 52.18 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{59}H_{47}N_2O$ 799.3683; found 799.3672.

E. General synthetic method C and characterisation data of compounds (5a–5o):

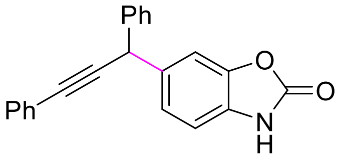
Unless otherwise noted heterocycle **1** (0.2 mmol, 1 equiv.), uric acid (8.4 mg, 0.05 mmol, 25 mol%) and 0.6 mL CH_3NO_2 were taken in a 5 mL screw capped reaction vial under nitrogen atmosphere and stirred the mixture for 1h. Then alcohol **2** (0.24 mmol, 1.2 equiv.) and catalyst MeOTf (3.3 mg, 0.02 mmol, 10 mol%) was added into the reaction mixture and the vial was capped and allowed to heat at 80 °C for 10 h with continuous stirring. After completion of the reaction (monitored by TLC), CH_3NO_2 was evaporated under reduced pressure and the crude reaction mixture was directly separated by silica gel (230–400 mess) column chromatography (flash) using ethyl acetate / hexane solution to obtain the desired product **5**.

6-Benzhydrylbenzo[*d*]oxazol-2(3*H*)-one (5a):



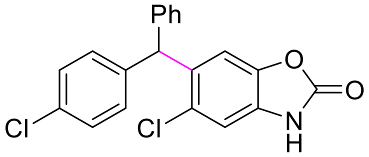
Following the general synthetic method C, reaction between benzo[*d*]oxazol-2(3*H*)-one **1m** (27.0 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5a**, which was purified by silica gel flash column chromatography (using 10-15% ethyl acetate/hexane as eluent) to give the titled compound as a white sticky liquid (44.6 mg, 0.15 mmol, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.49 (d, *J* = 52.4 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.28 – 7.24 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 4H), 7.04 – 6.96 (m, 3H), 5.61 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 156.16, 144.11, 143.44, 139.46, 129.35, 128.49, 127.69, 127.67, 126.61, 125.32, 111.34, 109.70, 56.59 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{16}NO_2$ 302.1176; found 302.1170.

6-(1,3-Diphenylprop-2-yn-1-yl)benzo[*d*]oxazol-2(3*H*)-one (5b):



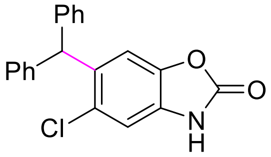
Following the general synthetic method C, reaction between benzo[*d*]oxazol-2(3*H*)-one **1m** (27.0 mg, 0.2 mmol, 1 equiv.) and 1,3-diphenylprop-2-yn-1-ol **2j** (50.0 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **5b**, which was purified by silica gel flash column chromatography (using 5-18% ethyl acetate/hexane as eluent) to give the titled compound as a yellowish sticky liquid (29.3 mg, 0.09 mmol, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.21 (s, 1H), 7.52 – 7.50 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.33 (m, 6H), 7.30 (s, 1H), 7.27 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 155.87, 144.13, 141.38, 137.29, 131.70, 128.81, 128.32, 128.23, 128.14, 127.81, 127.21, 123.75, 123.15, 109.96, 109.83, 89.57, 85.43, 43.57 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{16}NO_2$ 326.1176; found 326.1173.

5-Chloro-6-((4-chlorophenyl)(phenyl)methyl)benzo[*d*]oxazol-2(3*H*)-one (5c):



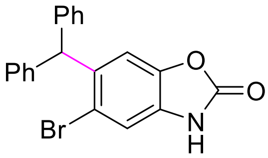
Following the general synthetic method C, reaction between 5-chlorobenzo[*d*]oxazol-2(3*H*)-one **1n** (34.0 mg, 0.2 mmol, 1 equiv.) and (4-chlorophenyl)(phenyl)methanol **2b** (52.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5c**, which was purified by silica gel flash column chromatography (using 10-13% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (48.1 mg, 0.13 mmol, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.70 (s, 1H), 7.36 – 7.27 (m, 5H), 7.19 (s, 1H), 7.07 – 7.00 (m, 4H), 6.79 (s, 1H), 5.94 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 155.82, 142.63, 141.68, 140.66, 136.22, 132.66, 130.69, 129.74, 129.32, 128.79, 128.73, 128.71, 127.04, 112.48, 111.36, 52.82 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{14}Cl_2NO_2$ 370.0396; found 370.0390.

6-Benzhydryl-5-chlorobenzo[*d*]oxazol-2(3*H*)-one (5d):



Following the general synthetic method C, reaction between 5-chlorobenzo[*d*]oxazol-2(3*H*)-one **1n** (34.0 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5d**, which was purified by silica gel flash column chromatography (using 10-20% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (52.4 mg, 0.15 mmol, 78%). Melting point 155–157 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.86 (s, 1H), 7.36 – 7.28 (m, 6H), 7.20 (s, 1H), 7.13 – 7.08 (m, 4H), 6.84 (s, 1H), 5.99 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 156.09, 142.61, 142.17, 136.77, 129.81, 129.42, 128.69, 128.58, 126.81, 122.79, 112.64, 111.37, 110.99, 110.79, 53.44 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{15}ClNO_2$ 336.0786; found 336.0783.

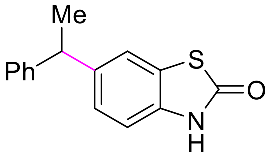
6-Benzhydryl-5-bromobenzo[*d*]oxazol-2(3*H*)-one (5e):



Following the general synthetic method C, reaction between 5-bromobenzo[*d*]oxazol-2(3*H*)-one **1o** (42.8 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5e**, which was purified by silica gel flash column chromatography (using 8-13% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (44.9 mg, 0.12 mmol, 59%).

Following the same method, reaction between **1o** (214.0 mg, 1mmol.) and **2a** (220.8 mg, 1.2 mmol.) afforded the product **3c** in 61% (228.3 mg, 0.61 mmol.) yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.64 (s, 1H), 7.36 – 7.25 (m, 7H), 7.10 – 7.07 (m, 4H), 6.85 (s, 1H), 5.97 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 155.74, 143.26, 142.22, 138.28, 129.49, 128.91, 128.57, 126.79, 119.59, 114.32, 112.92, 56.03 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{15}BrNO_2$ 380.0281; found 380.0279.

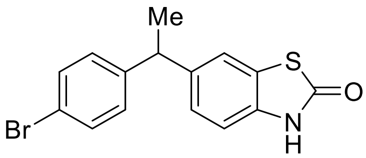
6-(1-Phenylethyl)benzo[*d*]thiazol-2(3*H*)-one (5f):



Following the general synthetic method C, reaction between benzo[*d*]thiazol-2(3*H*)-one **1p** (30.2 mg, 0.2 mmol, 1 equiv.) and 1-phenylethan-1-ol **2g** (29.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5f**, which was purified by silica gel flash column chromatography (using 8-13% ethyl acetate/hexane as eluent) to give the titled compound as a white crystalline solid (39.3 mg, 0.15 mmol, 77%). Melting point 106–108 °C.

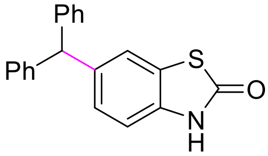
Following the same method, reaction between **1p** (151.2 mg, 1mmol.) and **2g** (146.6 mg, 1.2 mmol.) afforded the product **3c** in 75% (191.3 mg, 0.75 mmol.) yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.01 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 173.12, 145.89, 141.99, 133.53, 128.53, 127.55, 126.31, 126.17, 124.06, 121.42, 111.63, 44.47, 21.99. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}NOS$ 256.0791; found 256.0789.

6-(1-(4-Bromophenyl)ethyl)benzo[*d*]thiazol-2(3*H*)-one (5g):



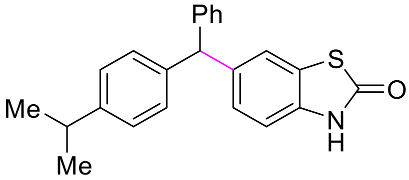
Following the general synthetic method C, reaction between benzo[*d*]thiazol-2(3*H*)-one **1p** (30.2 mg, 0.2 mmol, 1 equiv.) and 1-(4-bromophenyl)ethan-1-ol **2h** (48.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5g**, which was purified by silica gel flash column chromatography (using 8-12% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (46.0 mg, 0.14 mmol, 69%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 10.10 (d, *J* = 19.8 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.23 (s, 1H), 7.15 – 7.05 (m, 4H), 4.14 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 173.14, 144.91, 141.30, 133.73, 131.59, 129.31, 126.09, 124.20, 121.33, 120.12, 111.74, 43.93, 21.86 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{13}BrNOS$ 333.9896; found 333.9891.

6-Benzhydrylbenzo[*d*]thiazol-2(3*H*)-one (5h):



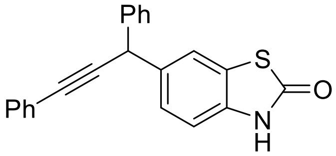
Following the general synthetic method C, reaction between benzo[*d*]thiazol-2(3*H*)-one **1p** (30.2 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5h**, which was purified by silica gel flash column chromatography (using 12% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (54.6 mg, 0.17 mmol, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.20 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 4H), 7.28 – 7.25 (m, 2H), 7.15 – 7.13 (m, 5H), 7.10 – 7.07 (m, 2H), 5.60 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 173.30, 143.46, 139.57, 133.82, 129.39, 128.51, 127.99, 126.60, 124.10, 123.22, 111.65, 56.44 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{16}NOS$ 318.0947; found 318.0943.

6-((4-Isopropylphenyl)(phenyl)methyl)benzo[*d*]thiazol-2(3*H*)-one (5i):



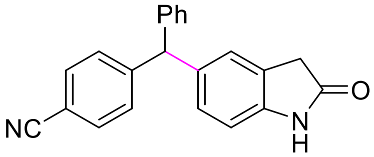
Following the general synthetic method C, reaction between benzo[*d*]thiazol-2(3*H*)-one **1p** (30.2 mg, 0.2 mmol, 1 equiv.) and (4-isopropylphenyl)(phenyl)methanol **2c** (54.3 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5i**, which was purified by silica gel flash column chromatography (using 8-15% ethyl acetate/hexane as eluent) to give the titled compound as a yellowish sticky liquid (58.9 mg, 0.16 mmol, 82%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.71 (s, 1H), 7.34 – 7.30 (m, 2H), 7.27 – 7.25 (m, 1H), 7.19 – 7.12 (m, 5H), 7.08 – 7.02 (m, 4H), 5.54 (s, 1H), 2.91 (hept, *J* = 7.0 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 172.77, 147.09, 143.71, 140.67, 139.86, 133.54, 129.36, 129.20, 128.44, 127.95, 126.51, 124.02, 123.29, 123.26, 122.60, 111.64, 111.40, 56.11, 33.66, 24.00 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{23}H_{22}NOS$ 360.1417; found 360.1412.

6-(1,3-Diphenylprop-2-yn-1-yl)benzo[*d*]thiazol-2(3*H*)-one (5j):



Following the general synthetic method C, reaction between benzo[*d*]thiazol-2(3*H*)-one **1p** (30.2 mg, 0.2 mmol, 1 equiv.) and 1,3-diphenyl-2-propyn-1-ol **2j** (50.0 mg, 0.24 mmol, 1.2 equiv.) in DCE solvent rather than CH_3NO_2 afforded the corresponding product **5j**, which was purified by silica gel flash column chromatography (using 7-11% ethyl acetate/hexane as eluent) to give the titled compound as a yellowish liquid (33.5 mg, 0.10 mmol, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.92 (s, 1H), 7.52 – 7.50 (m, 3H), 7.47 – 7.45 (m, 2H), 7.39 – 7.37 (m, 2H), 7.36 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 5.25 (s, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 172.93, 141.38, 137.35, 134.21, 131.72, 128.80, 128.32, 128.22, 127.86, 127.19, 126.44, 124.35, 123.19, 121.86, 111.77, 89.64, 85.42, 43.40 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{16}NOS$ 342.0947; found 342.0941.

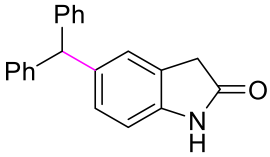
4-((2-Oxoindolin-5-yl)(phenyl)methyl)benzonitrile (5k):



Following the general synthetic method C, reaction between indolin-2-one **1q** (26.6 mg, 0.2 mmol, 1 equiv.) and 4-(hydroxy(phenyl)methyl)benzonitrile **2d** (41.9 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5k**, which was purified by silica gel flash column chromatography (using 20-30% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (40.9 mg, 0.12 mmol, 63%). Melting point 190–192 °C.

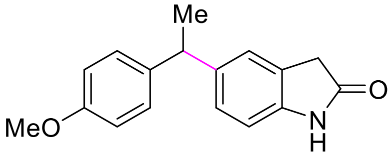
Following the same method, reaction between **1q** (133.1 mg, 1mmol.) and **2d** (251.0 mg, 1.2 mmol.) afforded the product **5k** in 62% (201.0 mg, 0.62 mmol.) yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.92 (s, 1H), 7.61 – 7.59 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 7.25 – 7.23 (m, 2H), 7.10 – 7.08 (m, 2H), 6.96 – 6.94 (m, 2H), 6.87 – 6.84 (m, 1H), 5.57 (s, 1H), 3.51 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 177.82, 149.55, 142.44, 141.36, 136.77, 132.24, 130.13, 129.25, 128.96, 128.72, 126.98, 125.80, 125.60, 118.90, 110.35, 109.76, 56.46, 36.32 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{27}N_2O$ 325.1335; found 325.1333.

5-Benzhydrylindolin-2-one (5l):



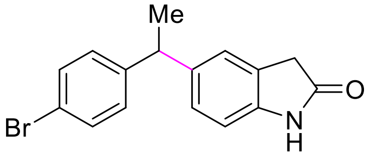
Following the general synthetic method C, reaction between indolin-2-one **1q** (26.6 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5l**, which was purified by silica gel flash column chromatography (using 10-25% ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (44.1 mg, 0.15 mmol, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.14 (s, 1H), 7.35 – 7.28 (m, 4H), 7.25 – 7.22 (m, 2H), 7.15 – 7.12 (m, 4H), 7.07 – 7.01 (m, 2H), 6.84 (d, J = 8.6 Hz, 1H), 5.54 (s, 1H), 3.51 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 178.29, 143.94, 138.33, 129.38, 128.99, 128.40, 127.95, 125.70, 124.61, 122.35, 109.57, 56.49, 36.31 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{18}NO$ 300.1383; found 300.1381.

5-(1-(4-Methoxyphenyl)ethyl)indolin-2-one (5m):



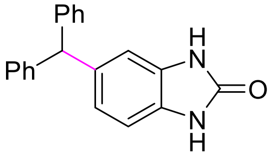
Following the general synthetic method C, reaction between indolin-2-one **1q** (26.6 mg, 0.2 mmol, 1 equiv.) and 1-(4-methoxyphenyl)ethan-1-ol **2i** (36.5 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5m**, which was purified by silica gel flash column chromatography (using 18-25% ethyl acetate/hexane as eluent) to give the titled compound as a white amorphous liquid (41.7 mg, 0.15 mmol, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.86 (s, 1H), 7.18 – 7.14 (m, 2H), 7.11 – 7.07 (m, 2H), 6.88 – 6.81 (m, 3H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.51 (s, 2H), 1.62 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 178.02, 157.88, 141.25, 140.54, 138.57, 128.41, 126.84, 125.49, 123.95, 113.80, 109.49, 55.27, 43.61, 36.38, 22.25 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{17}H_{18}NO_2$ 268.1332; found 268.1328.

5-(1-(4-Bromophenyl)ethyl)indolin-2-one (5n):



Following the general synthetic method C, reaction between indolin-2-one **1q** (26.6 mg, 0.2 mmol, 1 equiv.) and 1-(4-bromophenyl)ethan-1-ol **2h** (48.2 mg, 0.24 mmol, 1.2 equiv.) afforded the corresponding product **5n**, which was purified by silica gel flash column chromatography (using 10-20% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (44.2 mg, 0.14 mmol, 70%). Melting point 151–153 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.02 (d, *J* = 6.0 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.05 (m, 4H), 6.84 (d, *J* = 7.9 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.51 (s, 2H), 1.61 (d, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 178.02, 145.44, 140.84, 140.13, 131.49, 129.29, 126.91, 125.63, 123.93, 119.90, 109.62, 43.91, 36.36, 21.91 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{15}BrNO$ 316.0332; found 316.0327.

5-Benzhydryl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (5o):

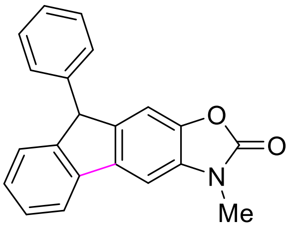


Following the general synthetic method C, reaction between 1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1r** (26.8 mg, 0.2 mmol, 1 equiv.) and diphenylmethanol **2a** (44.2 mg, 0.24 mmol, 1.2 equiv.) by using 20 mol% (6.7 mg) MeOTf instead of 10 mol% MeOTf and performing the reaction for 30 h instead of 10 h afforded the corresponding product **5o**, which was purified by silica gel flash column chromatography (using 30-50% ethyl acetate/hexane as eluent) to give the titled compound as a white semi-solid (16.8 mg, 0.06 mmol, 28%). **^{1}H NMR** (300 MHz, DMSO-*d*$_6$) δ = 10.57 (s, 1H), 10.48 (s, 1H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.15 – 7.06 (m, 4H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.69 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.62 (s, 1H), 5.59 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-*d*$_6$) δ = 155.90, 144.72, 136.81, 130.19, 129.49, 128.77, 128.48, 126.63, 121.91, 109.65, 108.75, 56.09 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{17}N_2O$ 301.1335; found 301.1332.

F. General synthetic method D and characterisation data of compounds (6a, 6b and 6b'):

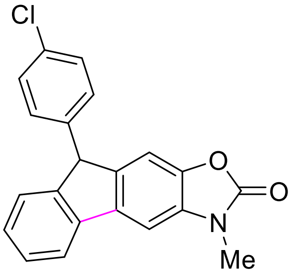
Unless otherwise noted heterocycle **3fa** and **3fb** (0.2 mmol, 1 equiv.), K_2CO_3 (55.2 mg, 0.4 mmol, 2 equiv.), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 10 mol%), $Pd(OAc)_2$ (2.2mg, 0.01 mmol, 5 mol%) and 2.0 mL DMF were taken in a 5 mL screw capped reaction vial under nitrogen atmosphere. The reaction mixture was degassed for 1h by using nitrogen. Then the reaction vial was capped and allowed to heat at 120 °C for 20 h with continuous stirring. After completion of the reaction (monitored by TLC), the reaction mixture was poured into cold water (10 mL) and extracted by using EtOAc (10 mL * 3). The entire EtOAc was further washed with cold water (3 times) followed by brine solution and then dried over Na_2SO_4. Then it was evaporated under reduced pressure and separated by silica gel (230–400 mess) column chromatography (flash) using ethyl acetate / hexane solution to obtain the desired product **6**.

3-Methyl-9-phenyl-3,9-dihydro-2*H*-fluoreno[3,2-*d*]oxazol-2-one (6a):



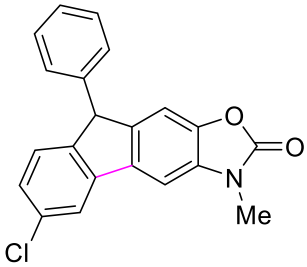
Following the general synthetic method D, coupling reaction of 6-benzhydryl-5-bromo-3-methylbenzo[*d*]oxazol-2(3*H*)-one **3fa** (78.8 mg, 0.2 mmol) afforded the corresponding product **6a**, which was purified by silica gel flash column chromatography (using 10% ethyl acetate/hexane as eluent) to give the titled compound as a grey liquid (44.5 mg, 0.14 mmol, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 7.6 Hz, 1H), 7.43 (td, *J* = 7.2, 1.7 Hz, 1H), 7.37 (s, 1H), 7.34 – 7.26 (m, 5H), 7.15 (s, 1H), 7.10 – 7.07 (m, 2H), 5.06 (s, 1H), 3.51 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ = 155.07, 147.96, 142.86, 142.44, 141.05, 140.29, 136.94, 131.53, 128.89, 128.20, 127.53, 127.24, 127.17, 125.36, 119.37, 107.64, 99.58, 54.42, 28.31 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{16}NO_2$ 314.1176; found 314.1180.

9-(4-Chlorophenyl)-3-methyl-3,9-dihydro-2*H*-fluoreno[3,2-*d*]oxazol-2-one (6b):



Following the general synthetic method D, coupling reaction of 5-bromo-6-((4-chlorophenyl)(phenyl)methyl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one **3fb** (85.6 mg, 0.2 mmol) afforded one of the corresponding product **6b**, which was purified by silica gel flash column chromatography (using 2-5% ethyl acetate/hexane as eluent) to give the titled compound as a light pink liquid (32.0 mg, 0.09 mmol, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.34 – 7.30 (m, 2H), 7.27 (d, *J* = 2.9 Hz, 1H), 7.11 – 7.06 (m, 3H), 7.03 (s, 1H), 6.98 – 6.94 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.57 (s, 1H), 3.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 154.88, 142.97, 142.88, 142.05, 138.64, 132.46, 130.64, 130.35, 129.21, 128.62, 126.82, 124.82, 111.06, 107.77, 55.94, 28.18 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{15}ClNO_2$ 348.0786; found 348.0772.

6-Chloro-3-methyl-9-phenyl-3,9-dihydro-2*H*-fluoreno[3,2-*d*]oxazol-2-one (6b'):



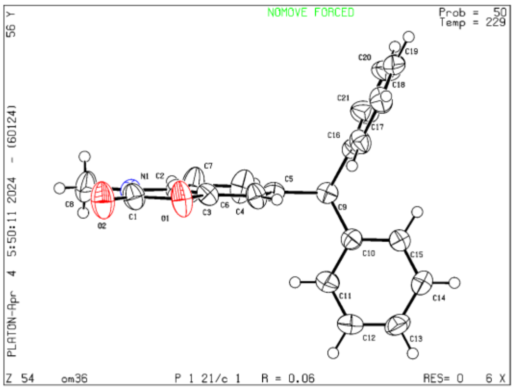
Following the general synthetic method D, coupling reaction of 5-bromo-6-((4-chlorophenyl)(phenyl)methyl)-3-methylbenzo[*d*]oxazol-2(3*H*)-one **3fb** (85.6 mg, 0.2 mmol) afforded one of the corresponding product **6b’**, which was purified by silica gel flash column chromatography (using 2-5% ethyl acetate/hexane as eluent) to give the titled compound as a white solid (20.2 mg, 0.06 mmol, 29%). Melting point 225–227 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 (s, 1H), 7.30 – 7.28 (m, 3H), 7.26 (s, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.02 (s, 1H), 3.51 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 155.00, 147.50, 142.47, 142.31, 140.25, 139.63, 136.94, 132.95, 131.71, 129.55, 129.05, 127.74, 127.36, 125.25, 119.47, 107.52, 99.67, 53.69, 28.34 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{15}ClNO_2$ 348.0786; found 348.0775.

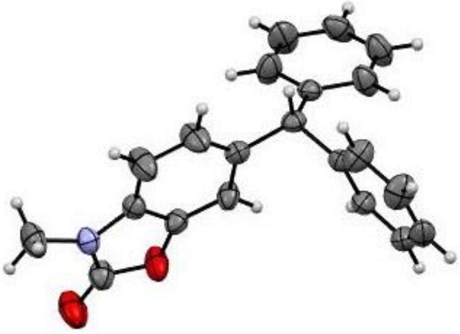
G. X-ray Crystallography:

Single-crystal X-ray data of compound **3aa** and **5f** were collected on a Bruker SMART Apex-II CCD diffractometer in the presence of graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 229.24 K and 180 K temperature respectively. The Bruker Apex-II suite program was used to perform data processing, structure solution, and refinement. Reflections available in $2\Theta_{max}$ range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus. [8] Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS. [9] The structures were solved using direct methods and refined by means of full-matrix least-squares techniques based on F^2 with with SHELX2017/1 software package. [10] Non-hydrogen atoms present in the structures were refined with anisotropic thermal parameters. C−H hydrogen atoms were introduced at geometrical positions with $U_{iso} = 1/2U_{eq}$ to those of the atoms to which they are attached.

Crystallisation process of compound 3aa:

60 mg compound of **3aa** was taken in a 10 mL conical flask. Then the compound was dissolved in 0.5 mL DCM solvent. The conical flask was kept at 5-7 °C temperature inside a fridge. The slow evaporation (1 week) of DCM at that temperature grows clear white crystals in block shaped.





ORTEP view of **3aa**

(Ellipsoids are drawn at 50% probability)

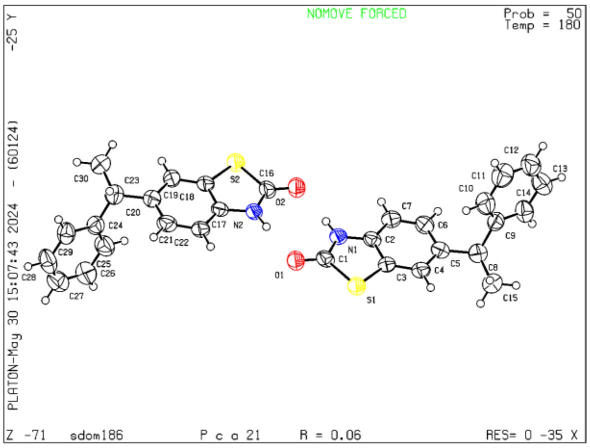
Table S1: Crystal data and structure refinement for 3aa:

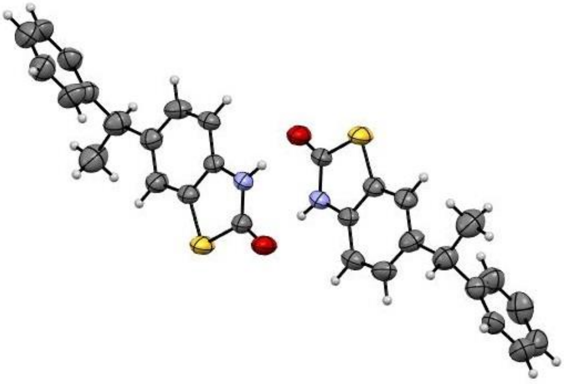
Identification code	**3aa**
Empirical formula	$C_{21}H_{17}NO_2$
Formula weight	315.36
Temperature/K	229.24
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.0708(12)
b/Å	12.580(2)
c/Å	21.139(4)
α/°	90
β/°	91.779(7)
γ/°	90
Volume/Å^3	1613.5(5)
Z	4

ρ_{calc}g/cm^3	1.298
μ/mm^{-1}	0.083
F(000)	664.0
Crystal size/mm^3	0.25 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.478 to 54.01
Index ranges	$-7 \leq h \leq 7$, $-16 \leq k \leq 15$, $-26 \leq l \leq 26$
Reflections collected	16013
Independent reflections	3487 [R_{int} = 0.0823, R_{sigma} = 0.0655]
Data/restraints/parameters	3487/0/219
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0626, wR_2 = 0.1658
Final R indexes [all data]	R_1 = 0.0773, wR_2 = 0.1824
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21
CCDC number	2366440

Crystallisation process of compound 5f:

50 mg compound of **5f** was taken in a 10 mL conical flask. Then the compound was dissolved in minimum amount (0.4 mL) DCM solvent and then 0.5 mL MeOH was added. The conical flask was kept at room temperature for slow evaporation. The slow evaporation (3-4 days) of the solvents at that temperature grows clear white crystals in block shaped.





ORTEP view of **5f**

(Ellipsoids are drawn at 50% probability)

Table S2: Crystal data and structure refinement for 5f:

Identification code	**5f**
Empirical formula	$C_{15}H_{13}NOS$
Formula weight	255.32
Temperature/K	180.00
Crystal system	orthorhombic
Space group	$Pca2_1$

a/Å	13.3265(16)
b/Å	6.1652(8)
c/Å	31.478(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2586.2(6)
Z	8
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.237
F(000)	1072.0
Crystal size/mm^3	0.2 × 0.15 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.176 to 55.12
Index ranges	$-17 \le h \le 13$, $-8 \le k \le 8$, $-40 \le l \le 40$
Reflections collected	30386
Independent reflections	5878 [R_{int} = 0.1034, R_{sigma} = 0.0813]
Data/restraints/parameters	5878/1/328
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1283
Final R indexes [all data]	R_1 = 0.1179, wR_2 = 0.1687
Largest diff. peak/hole / e Å^{-3}	0.36/-0.22
Flack parameter	0.40(10)
CCDC number	2366659

H. References:

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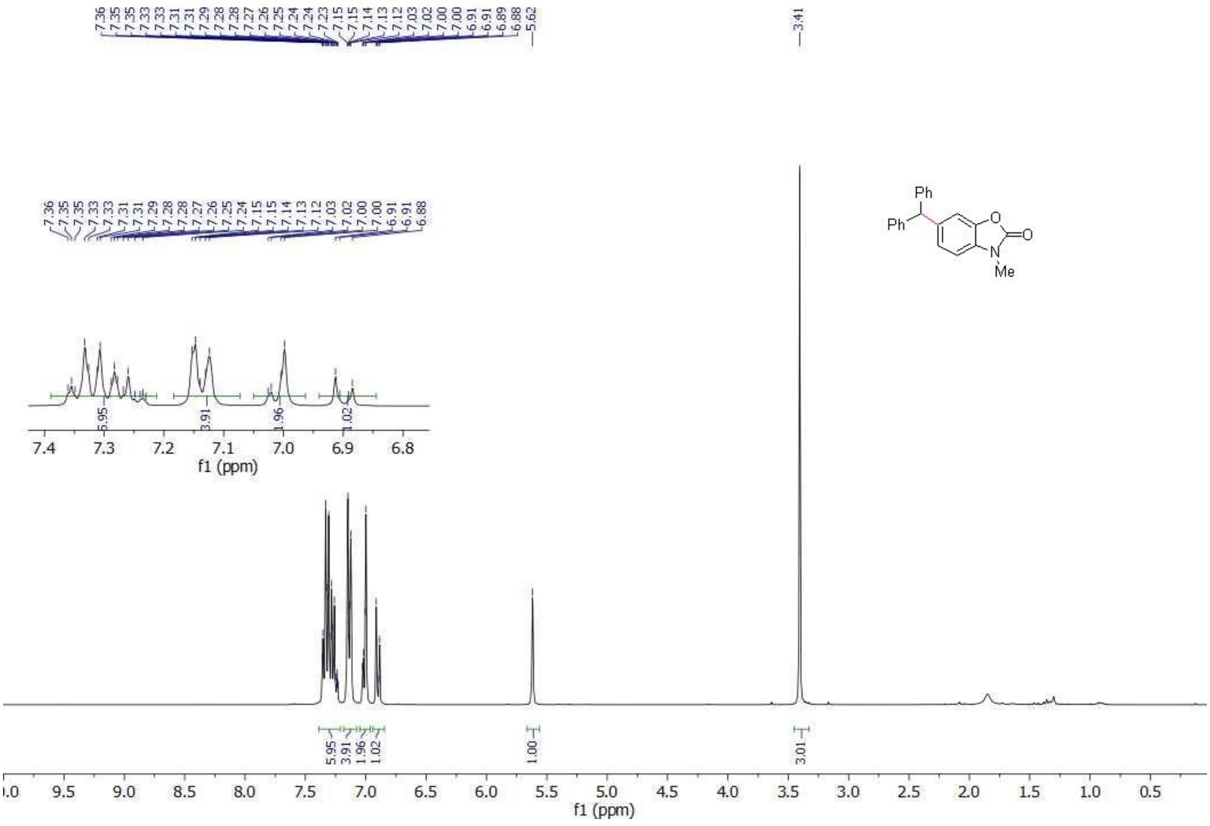
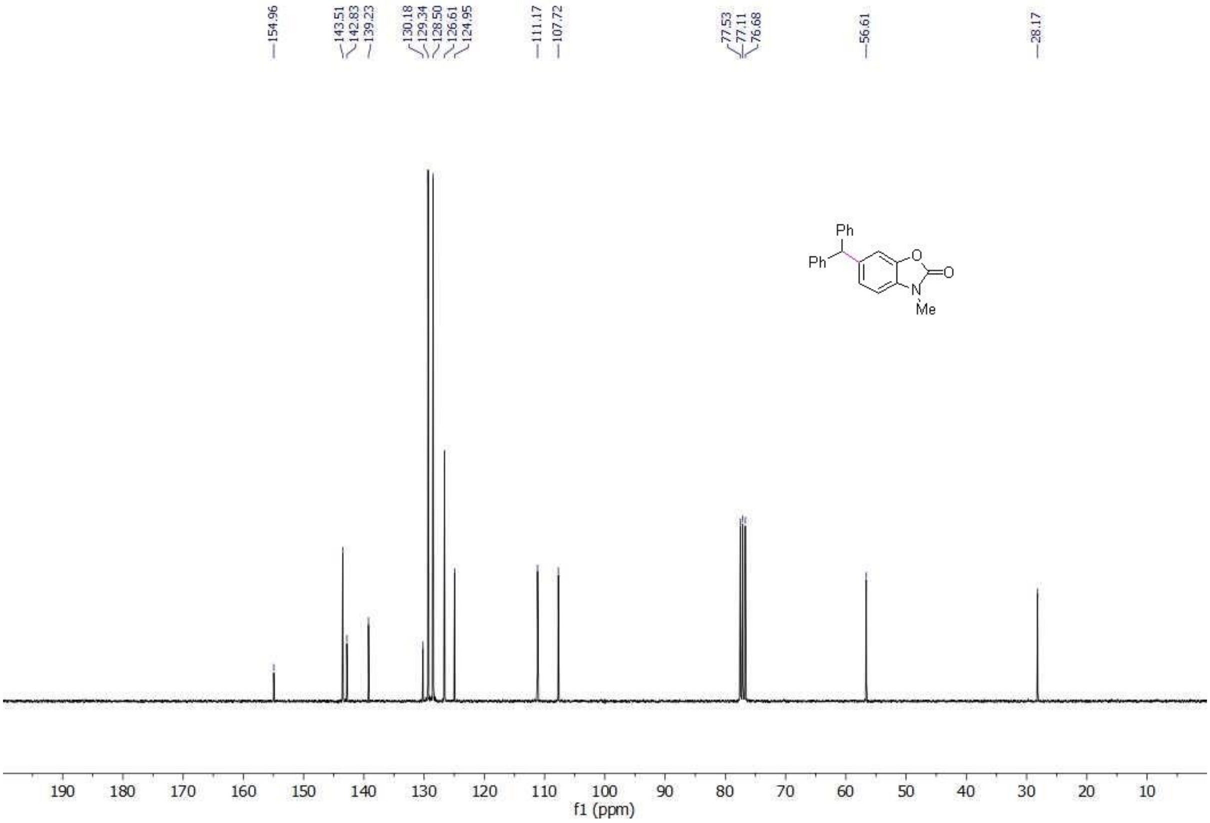
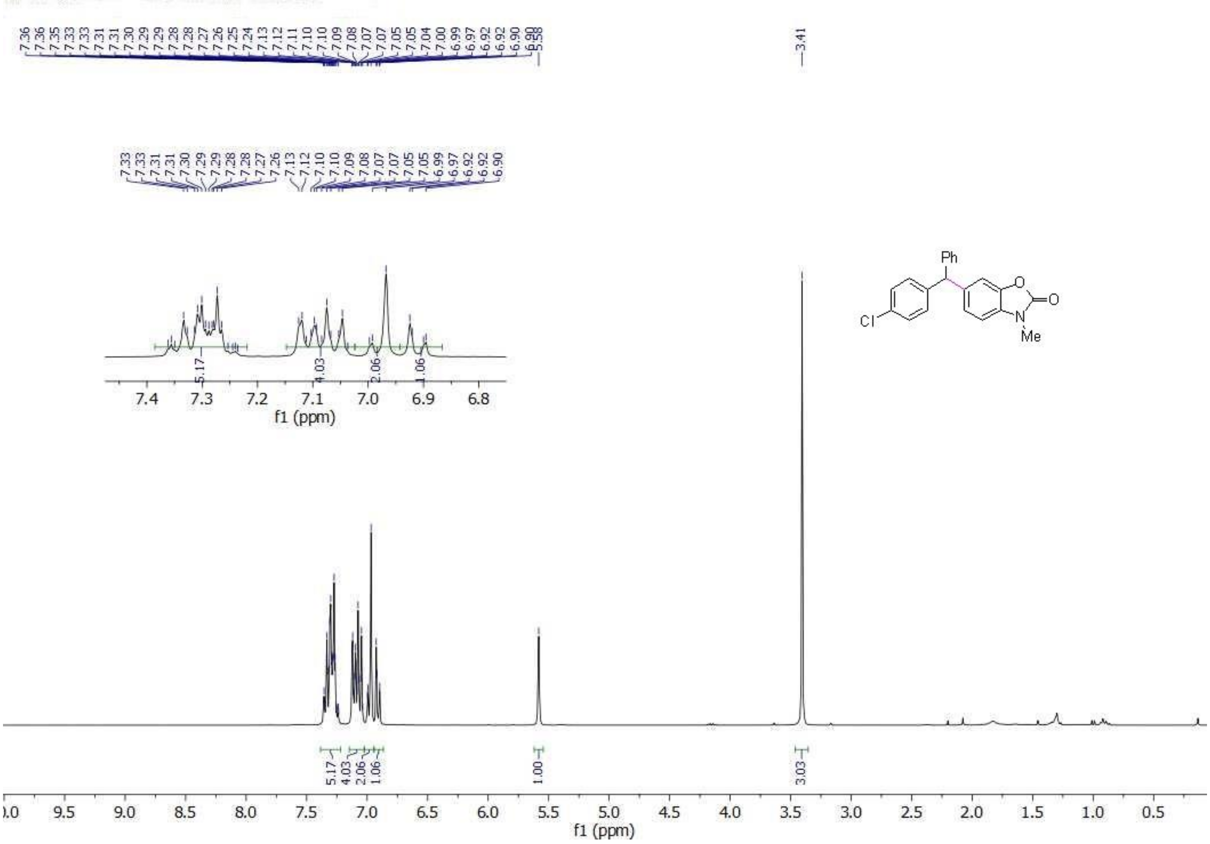
I. Copies of ^{1}H and ^{13}C{^{1}H} NMR spectra of all products:

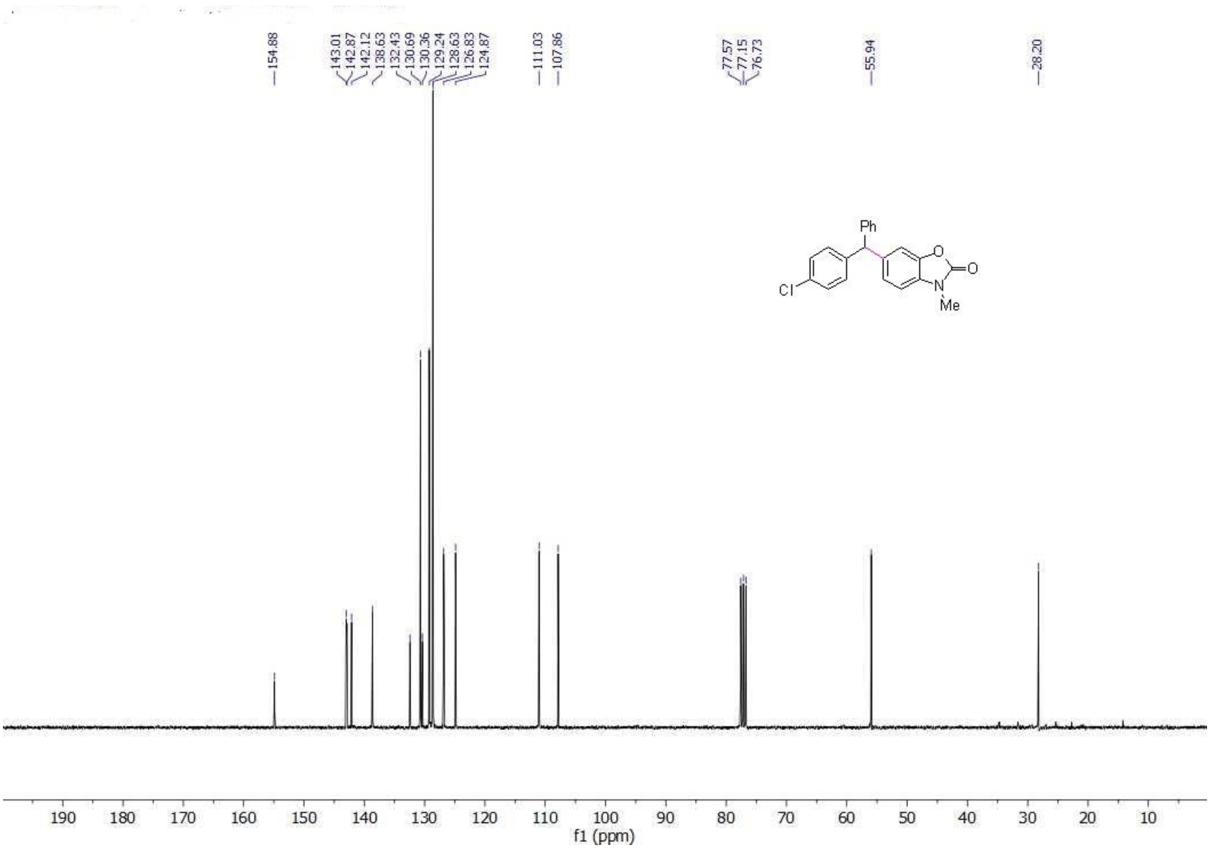
^{1}H NMR (300 MHz, $CDCl_3$) and **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **3aa**:



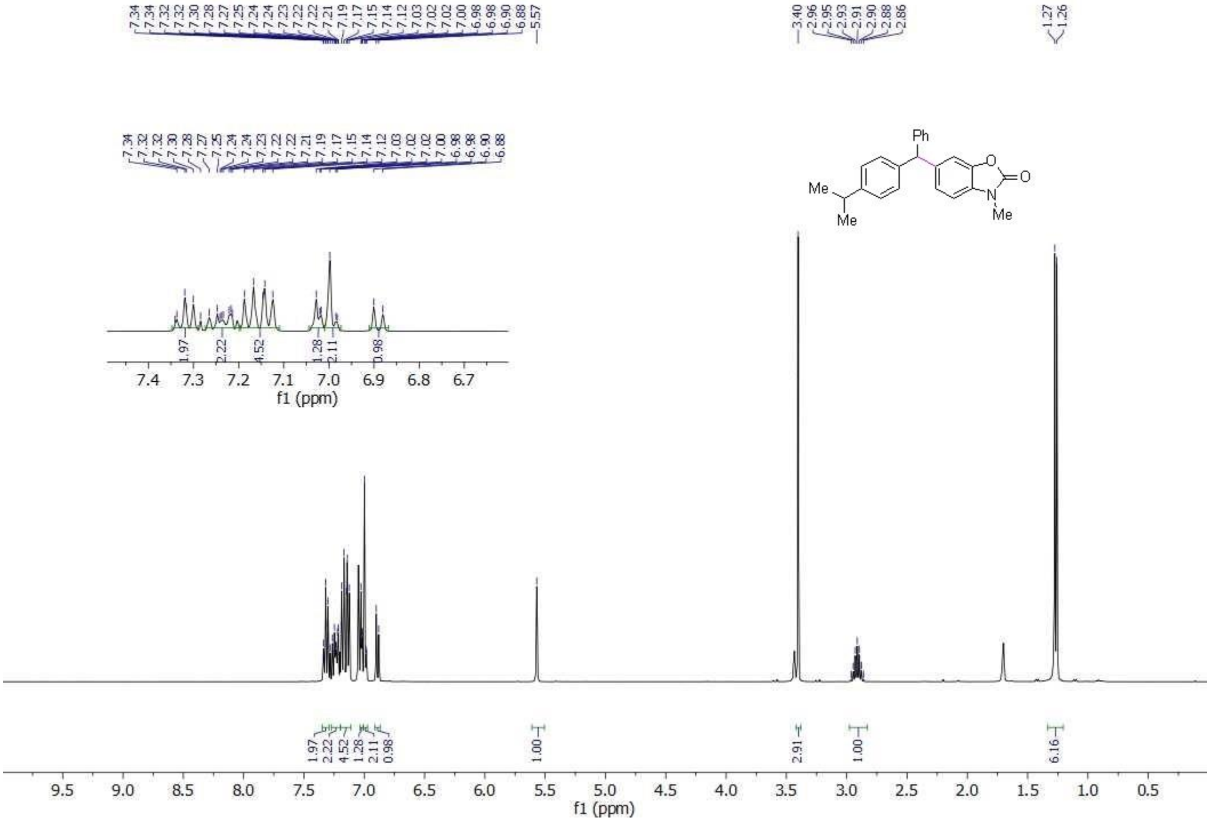


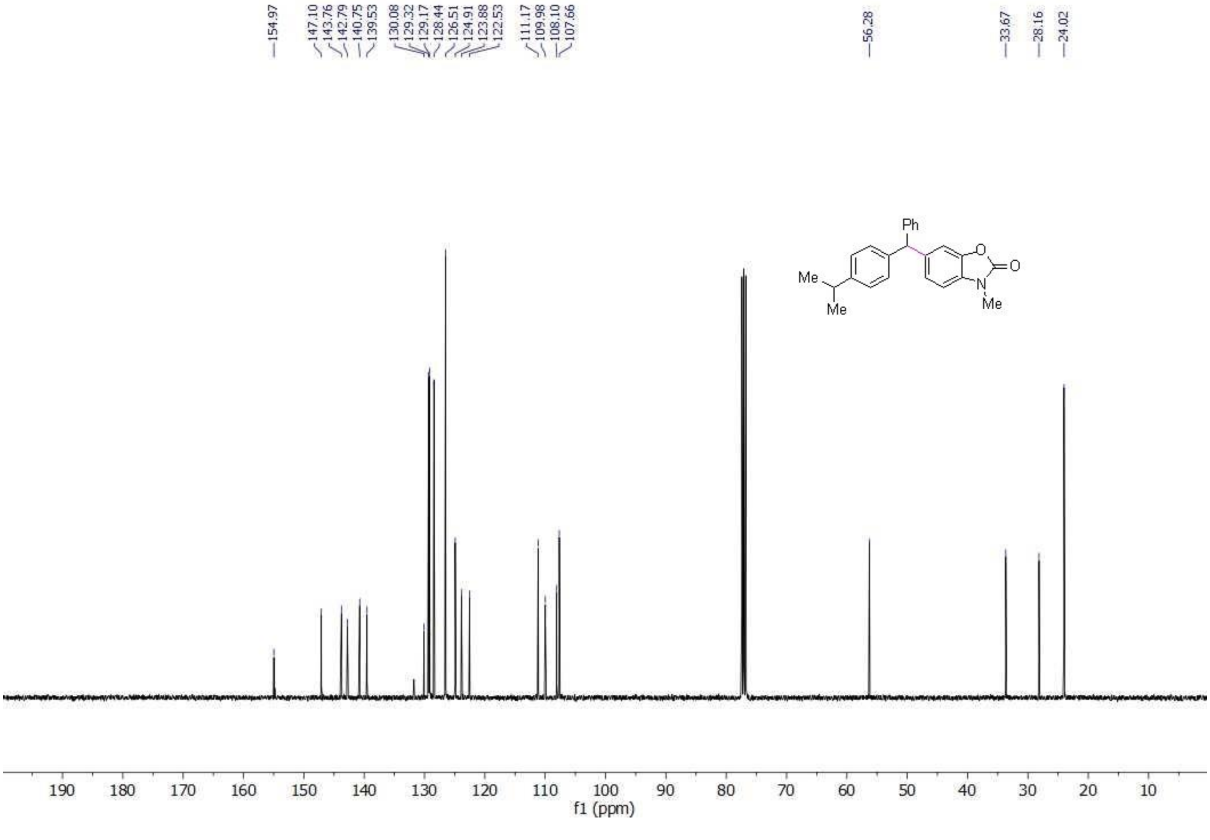
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3ab**:



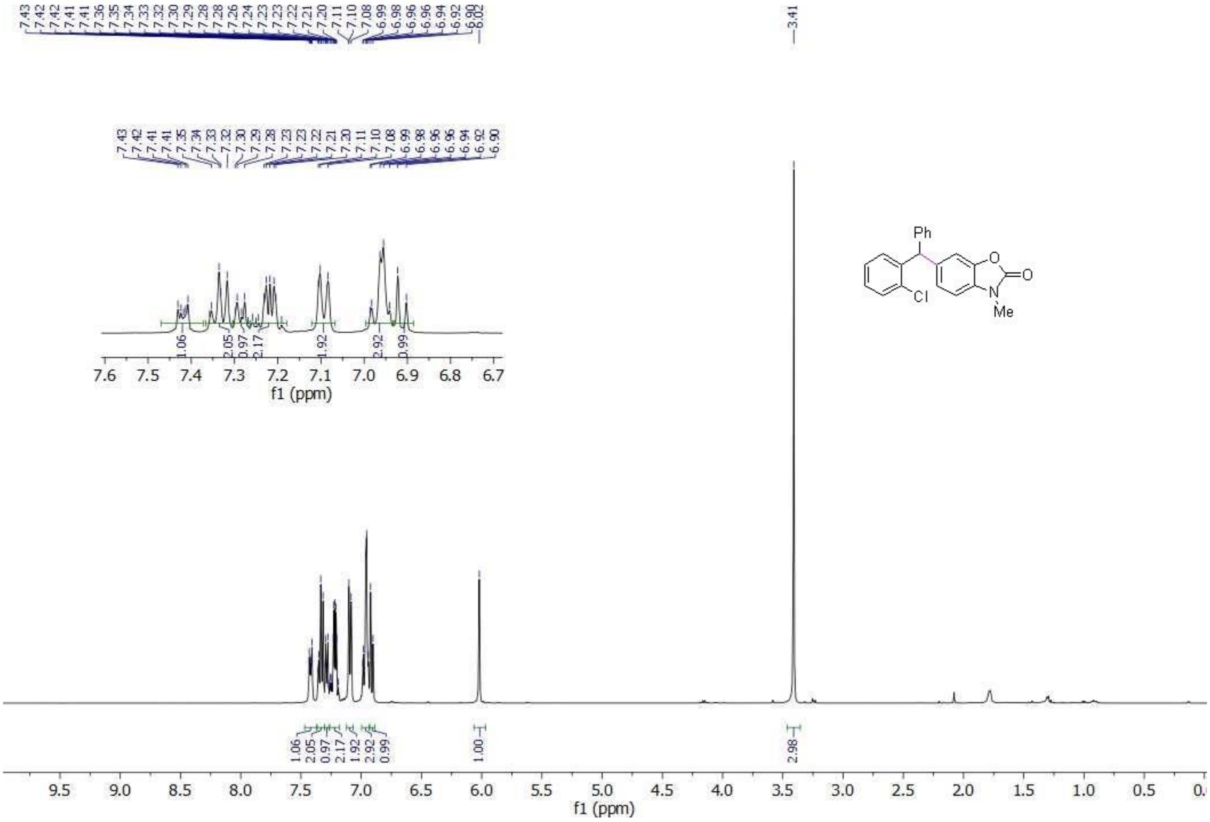


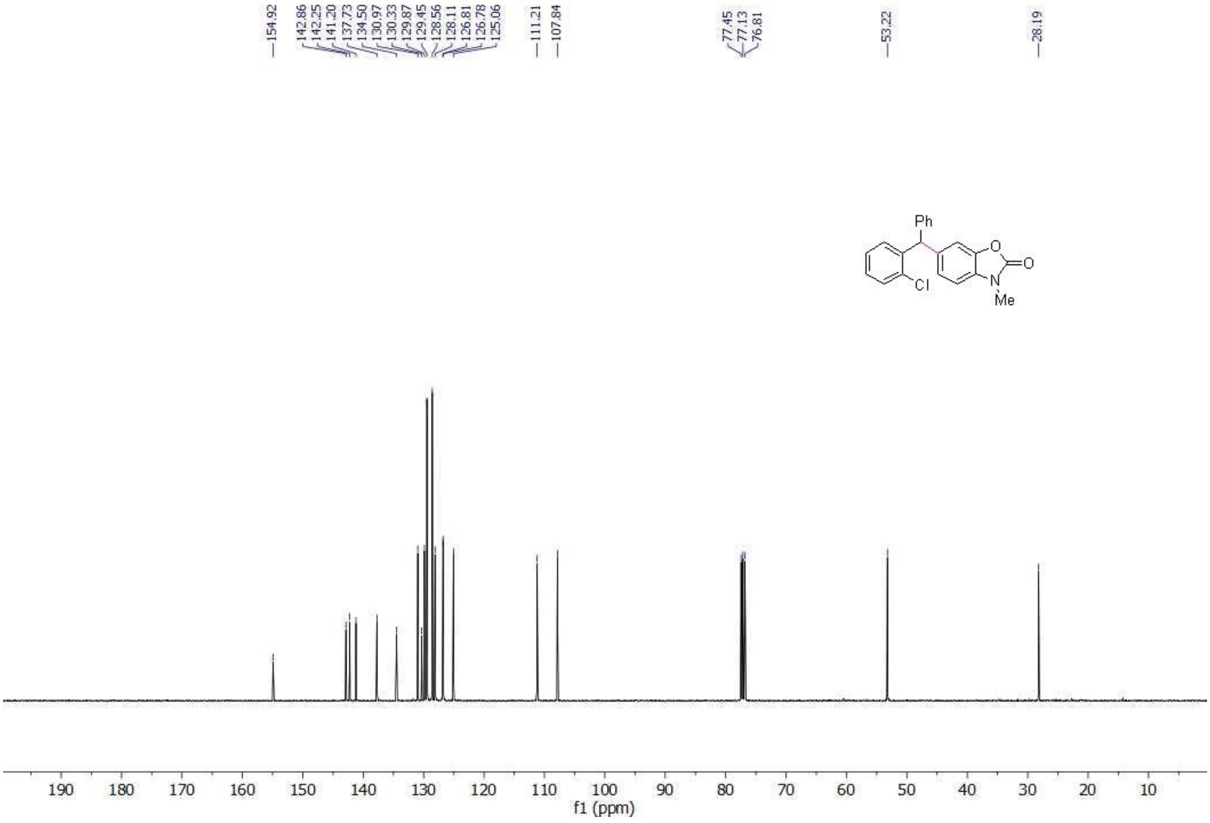
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3ac**:



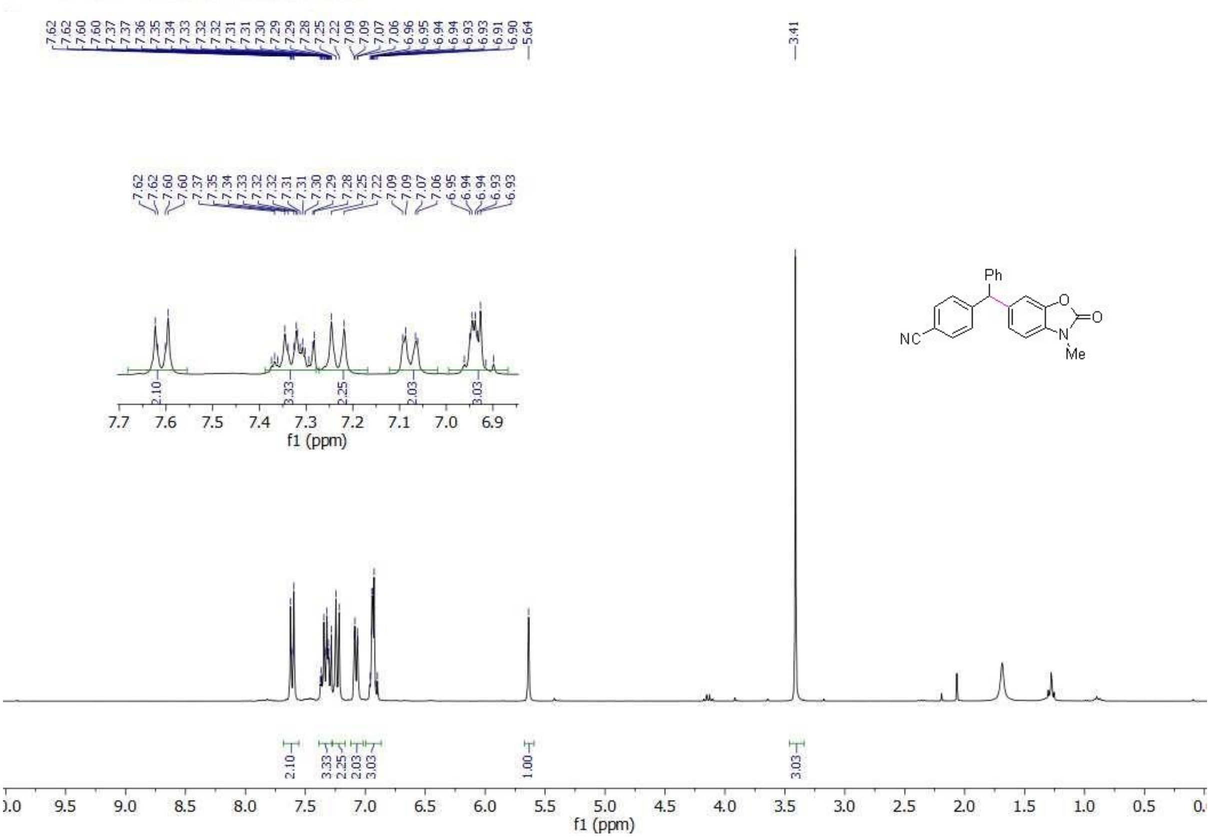


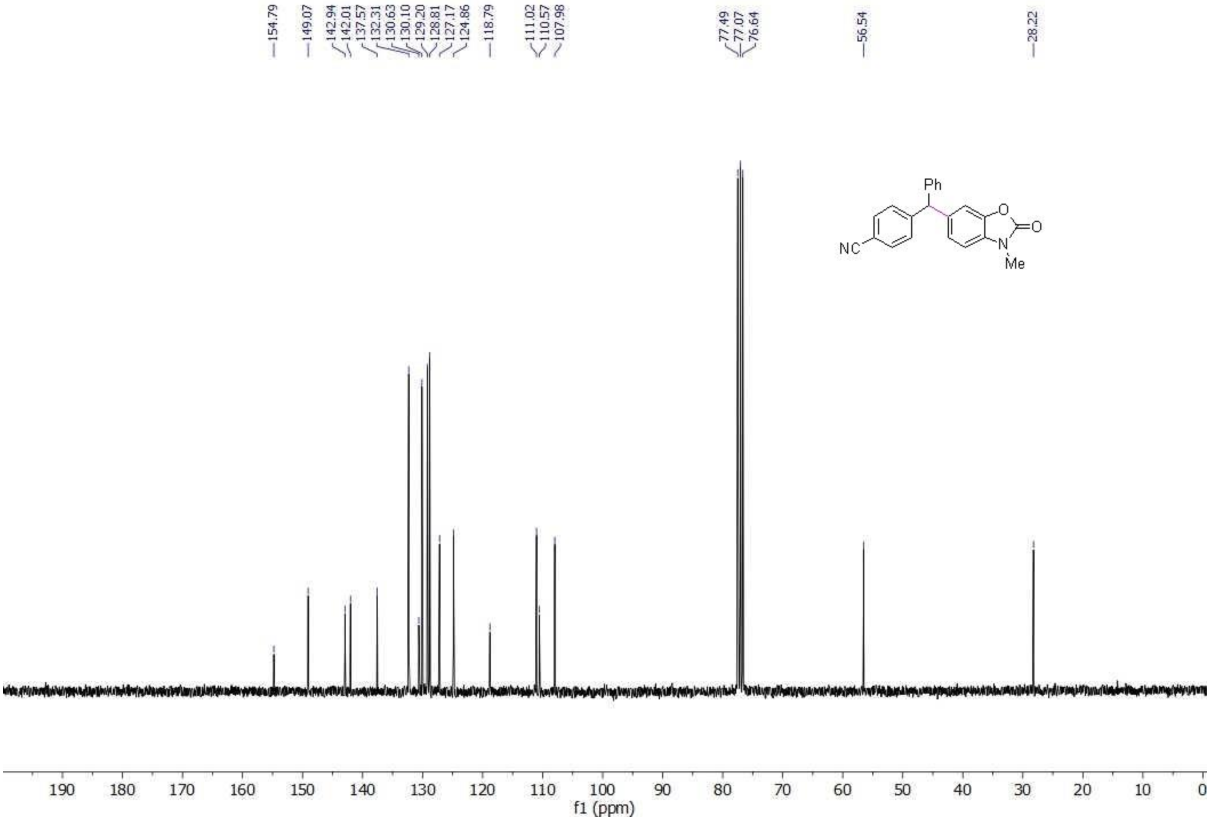
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3ae**:



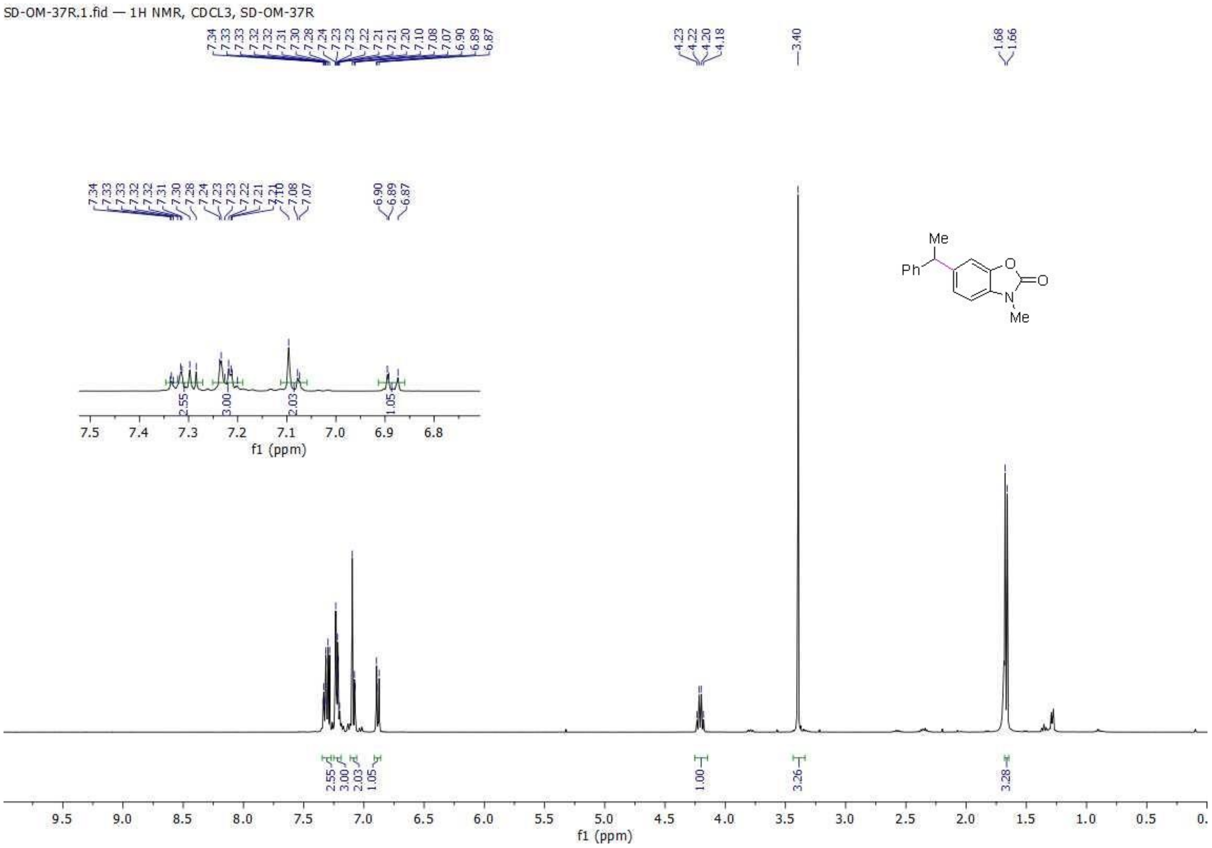


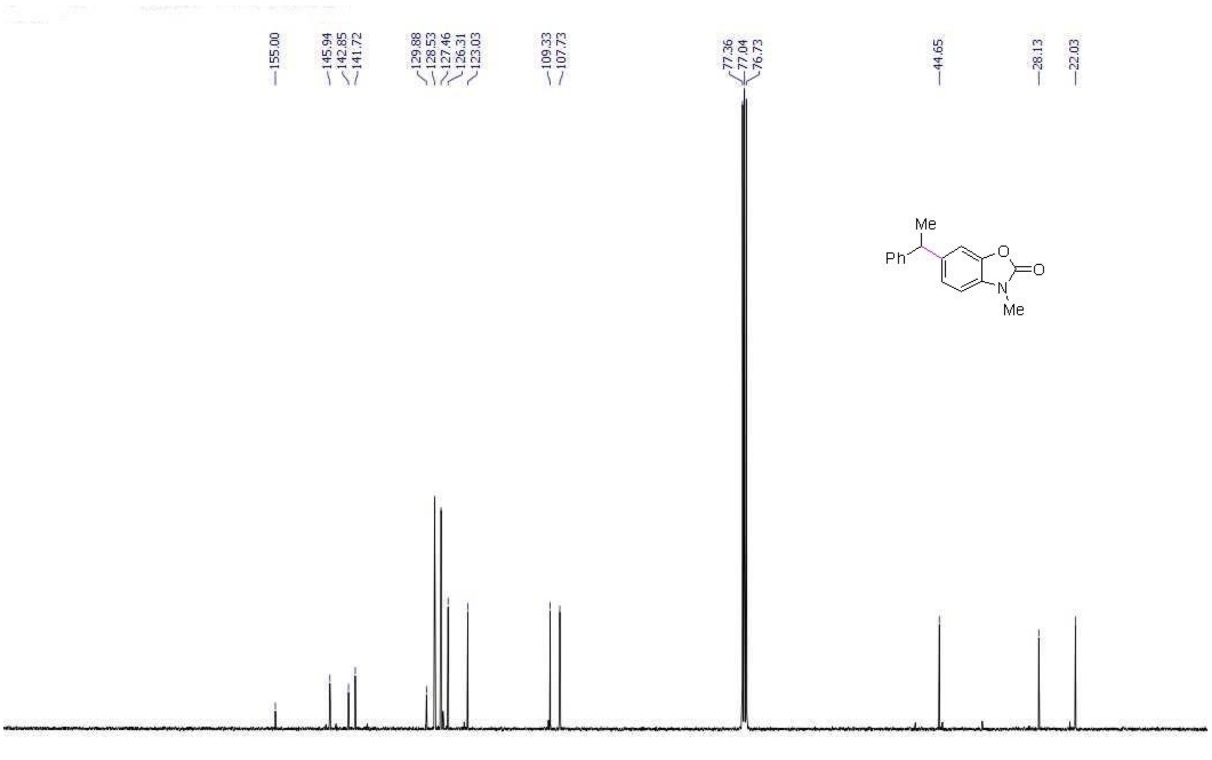
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **3ad**:



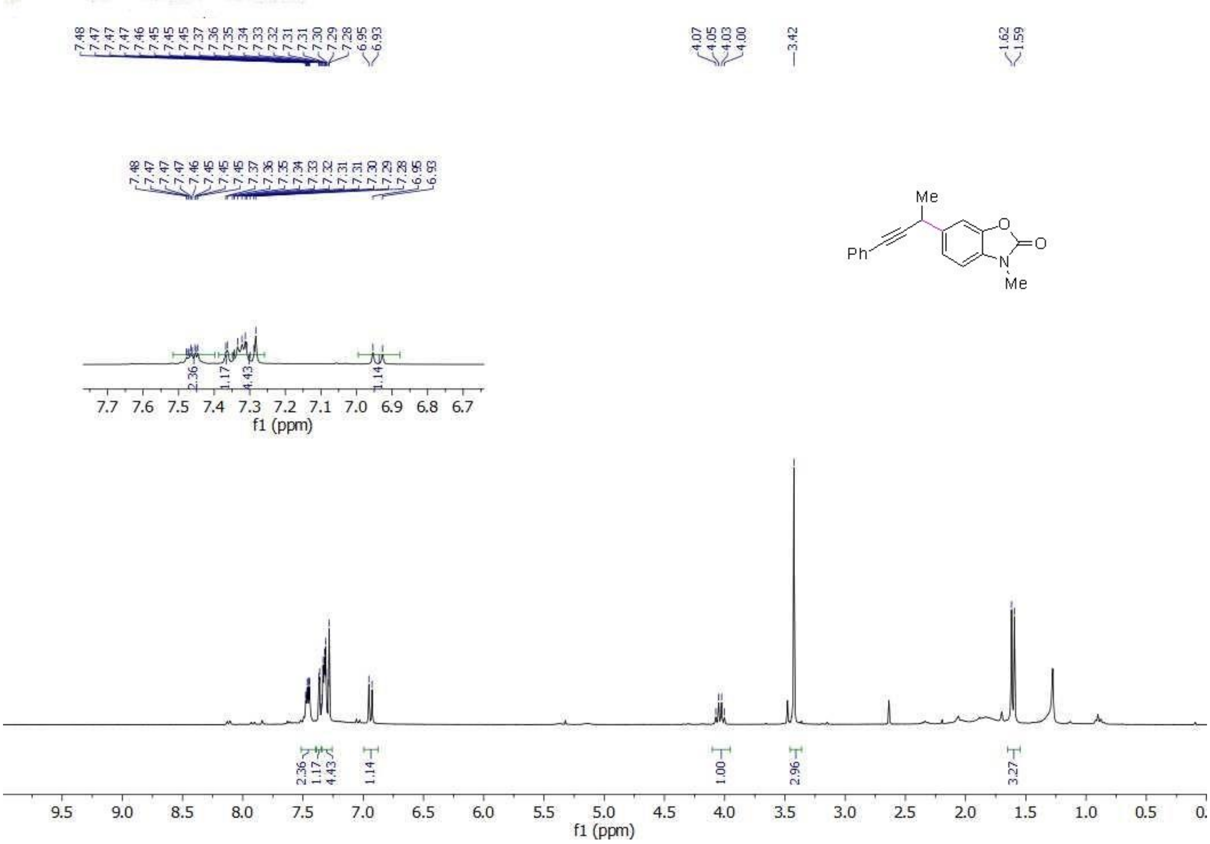


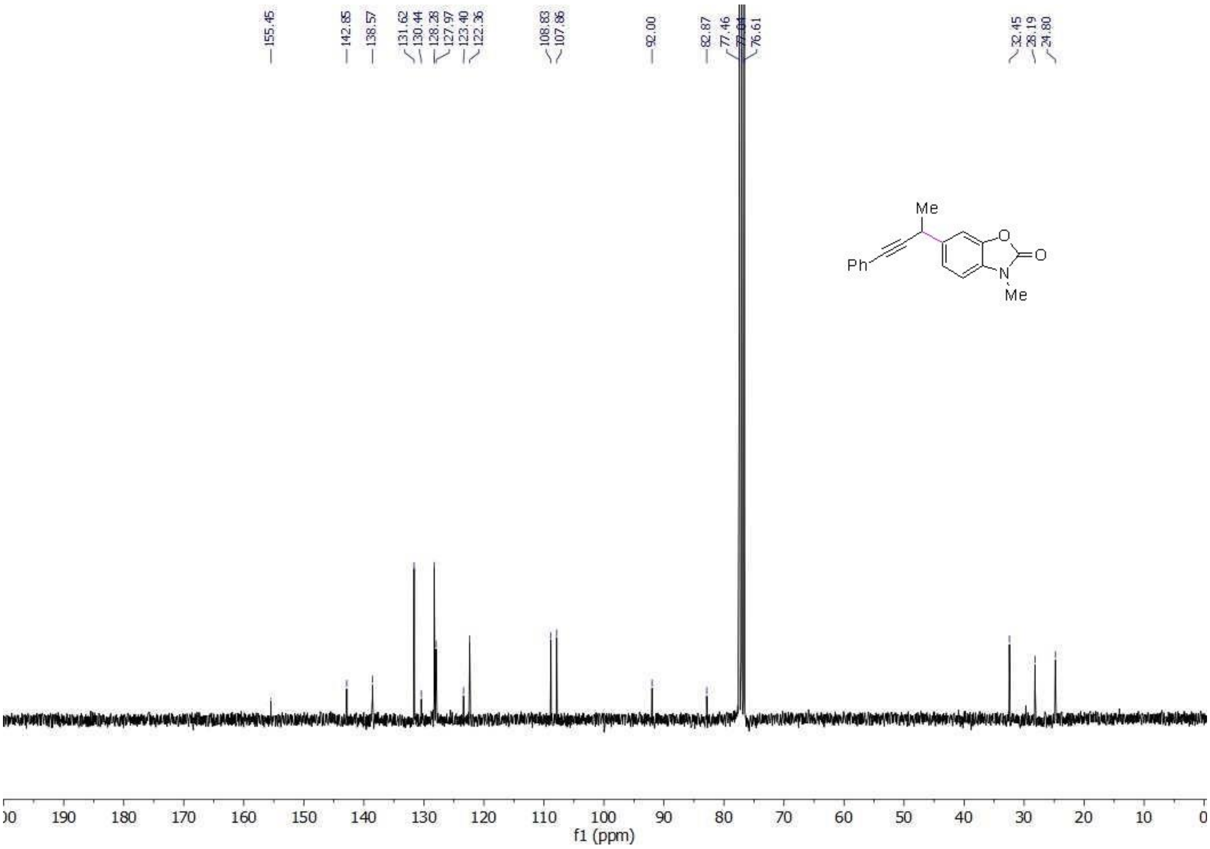
^{1}**H NMR** (400 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3ag**:



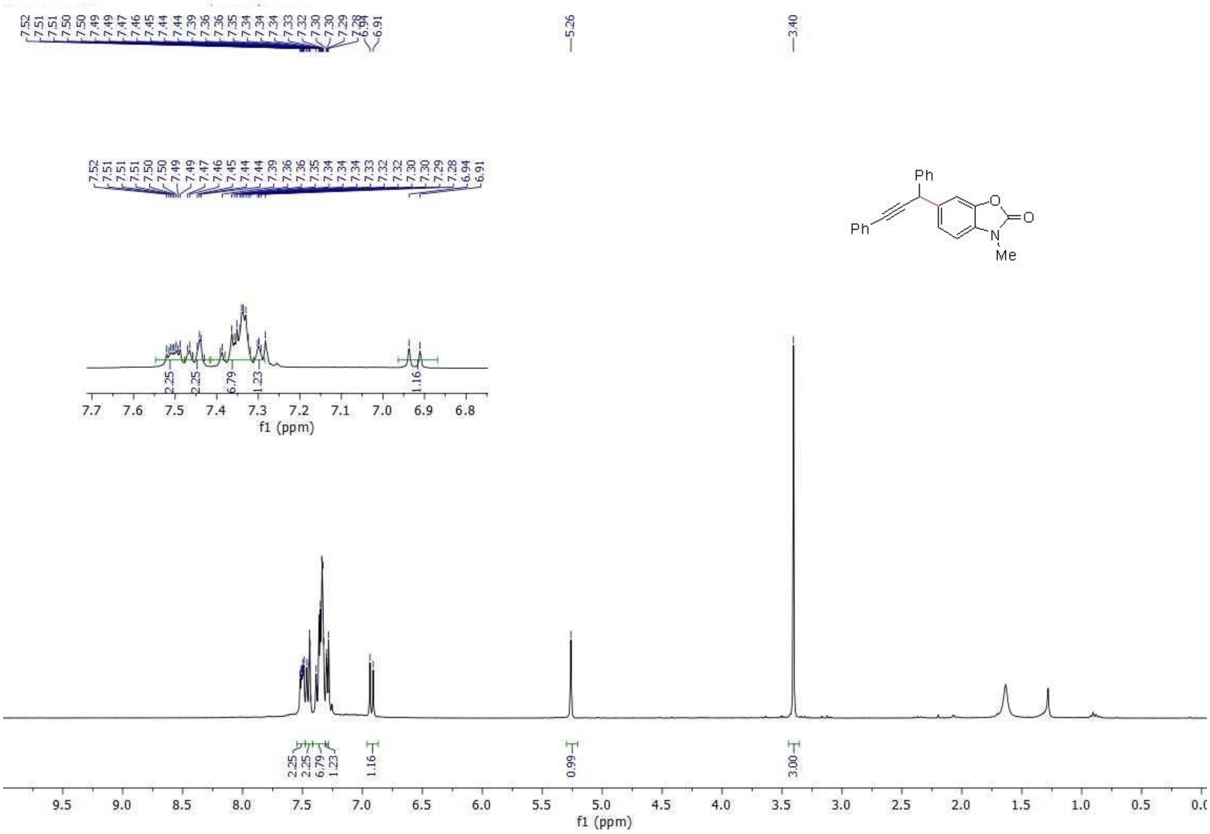


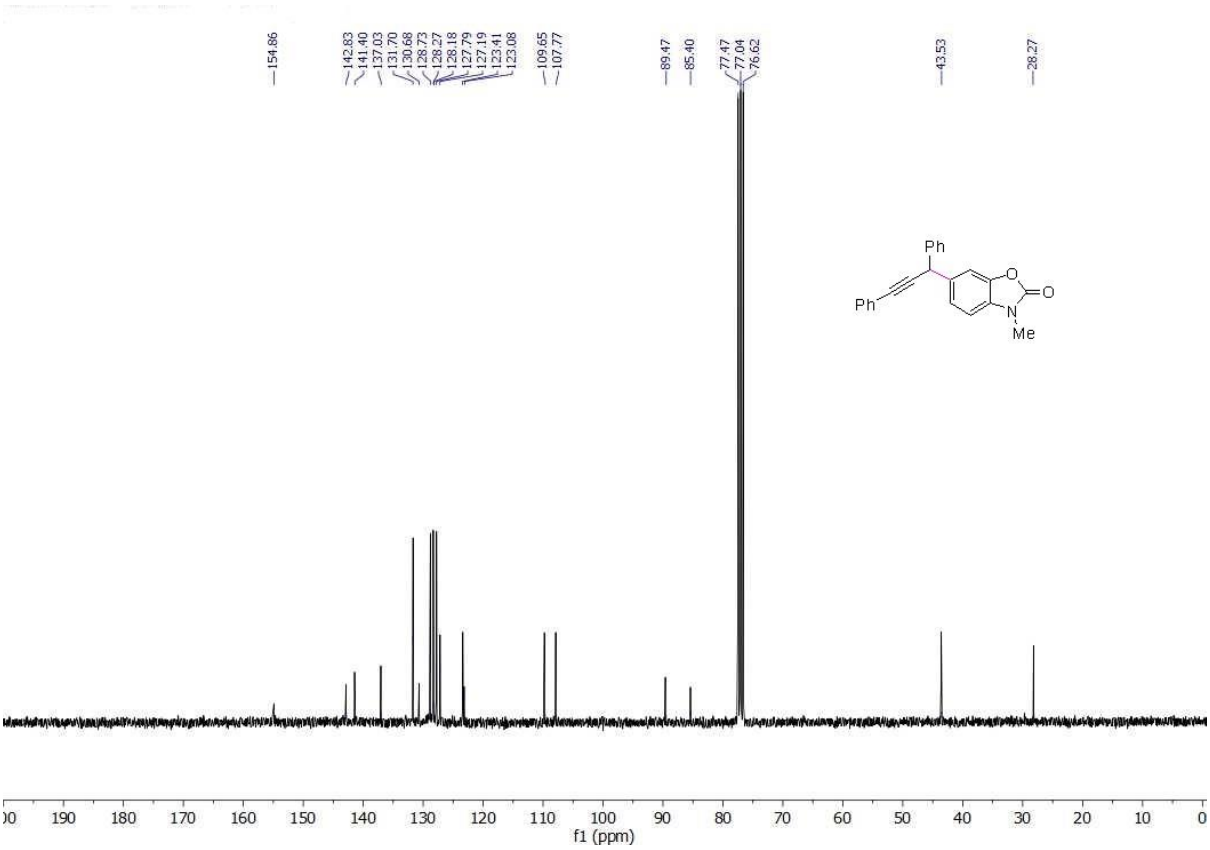
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3ak**:



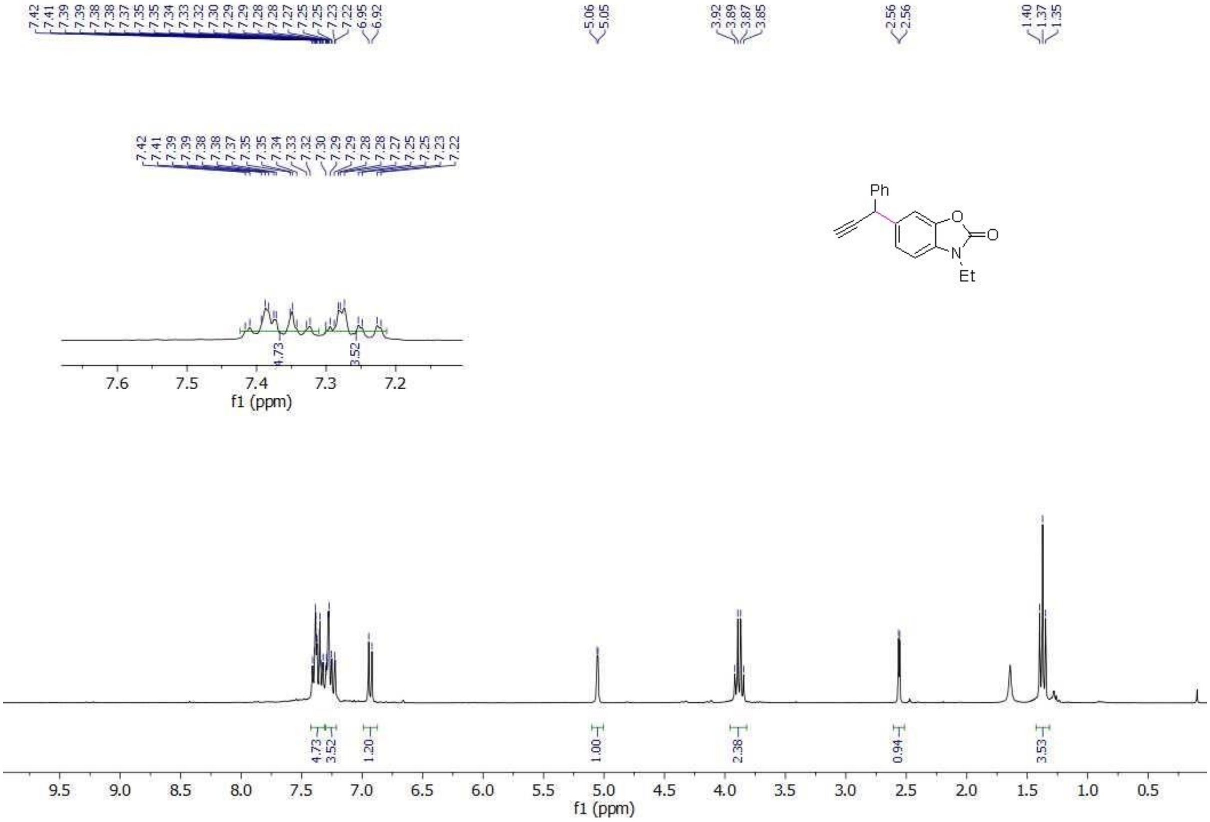


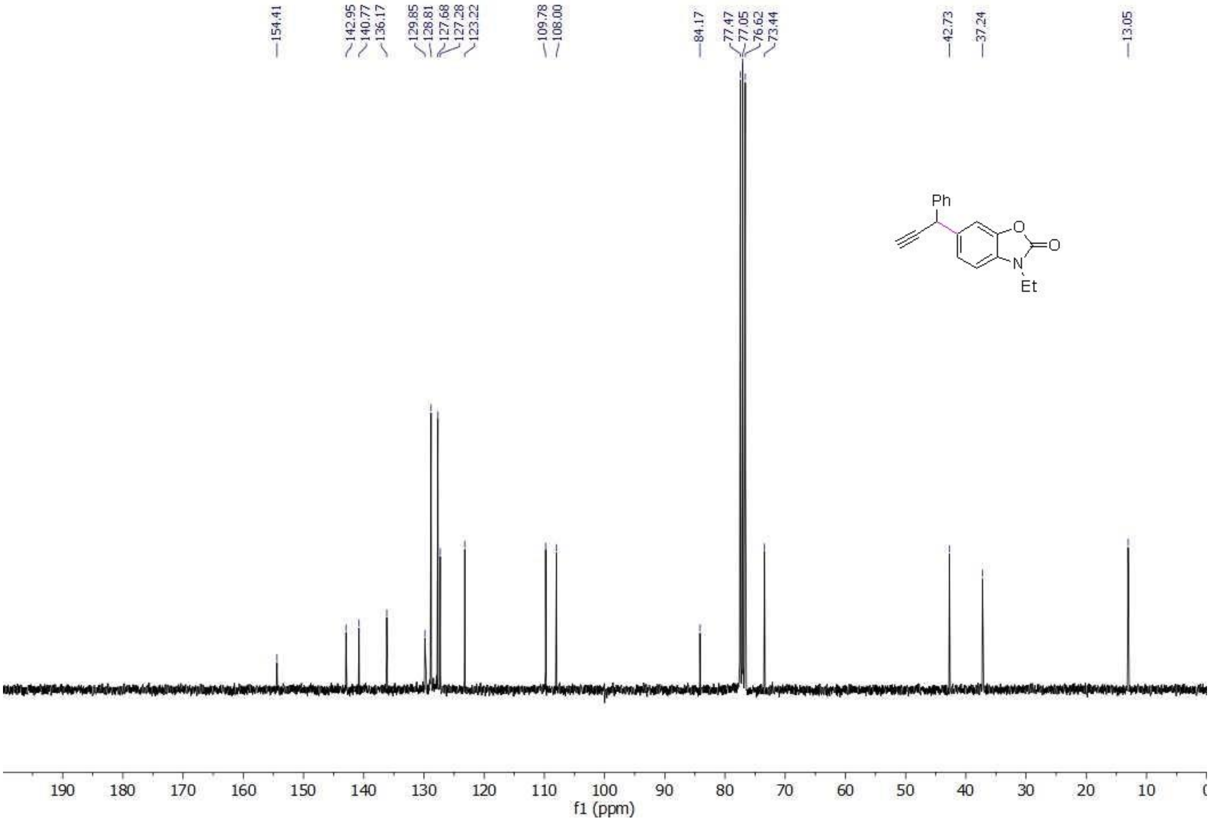
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3aj**:



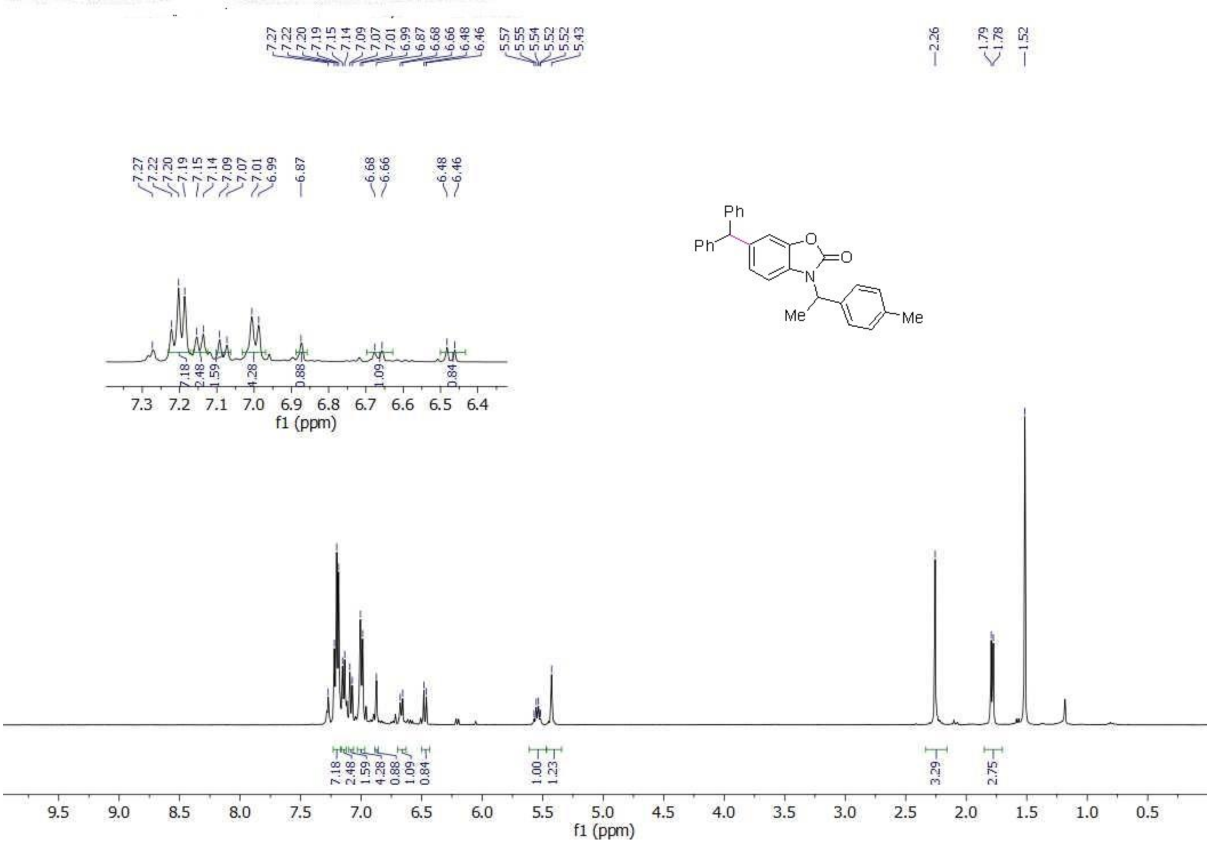


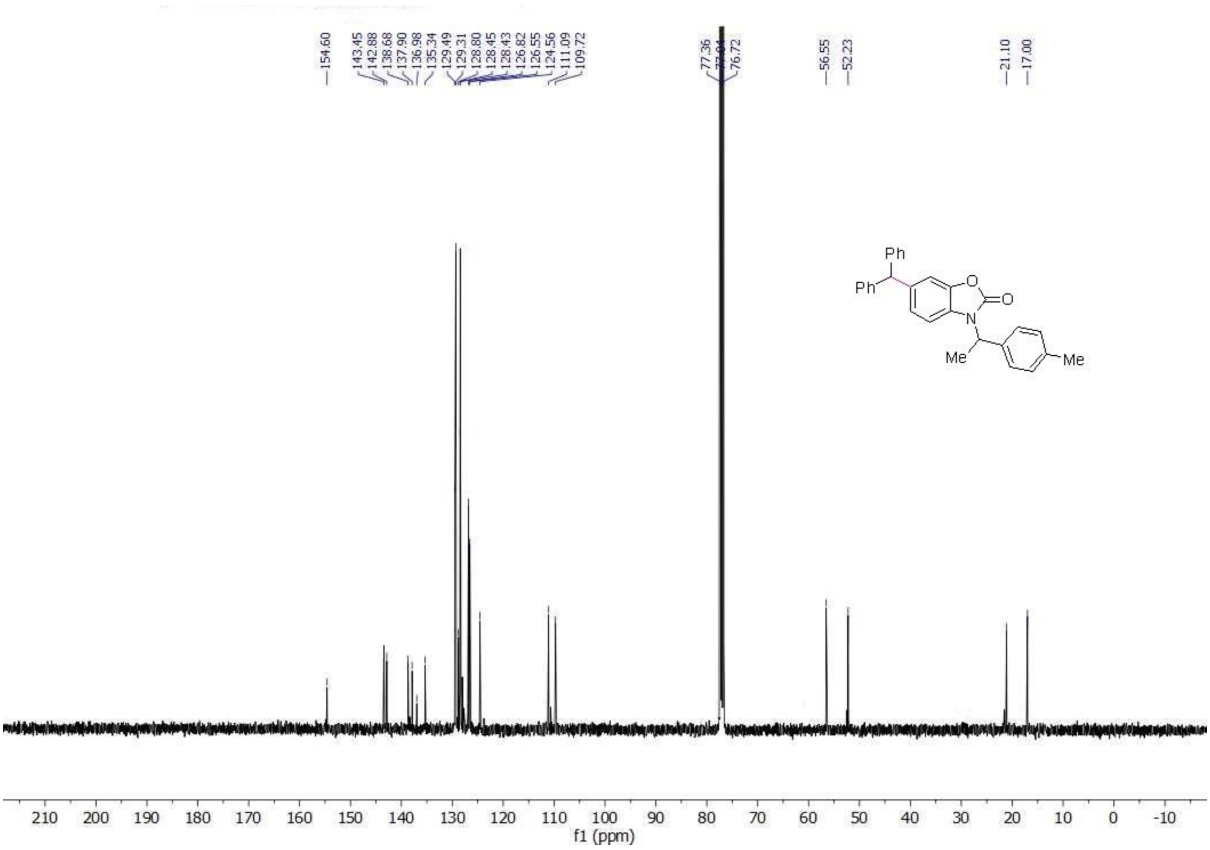
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3bl**:



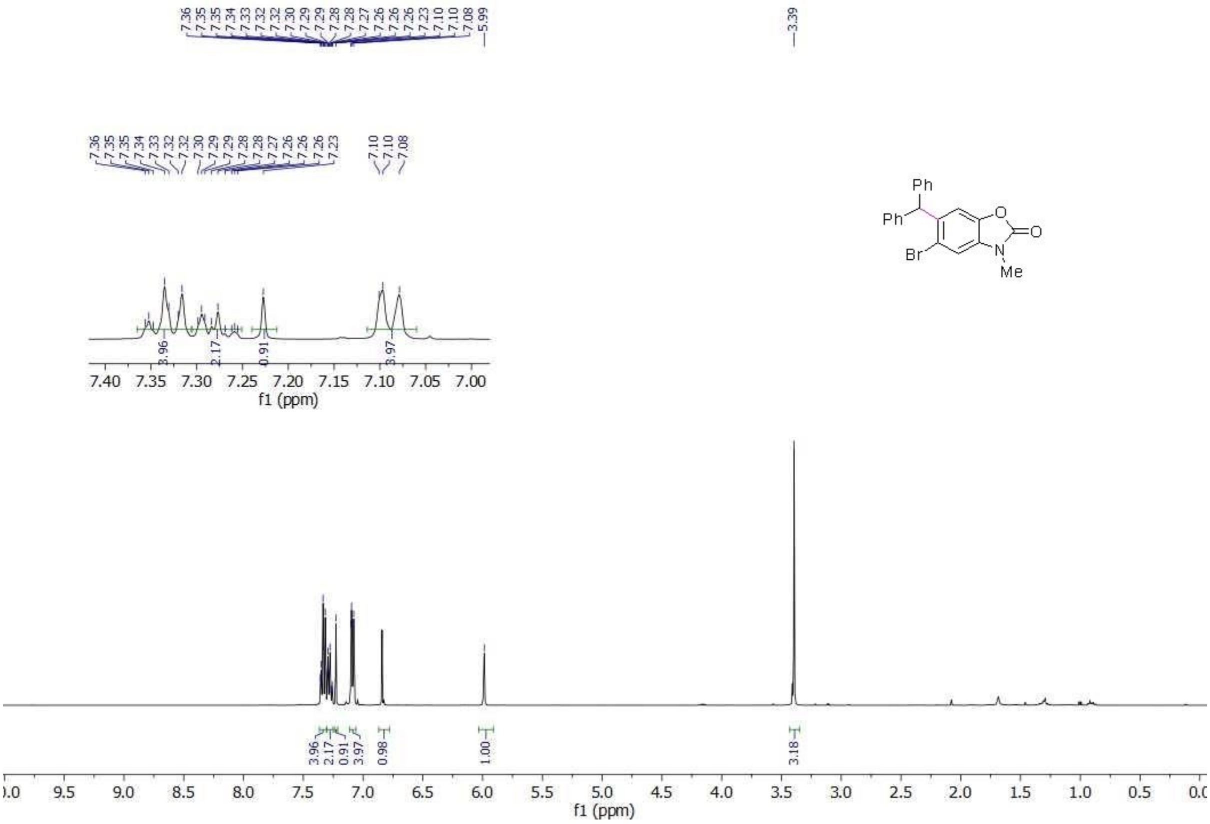


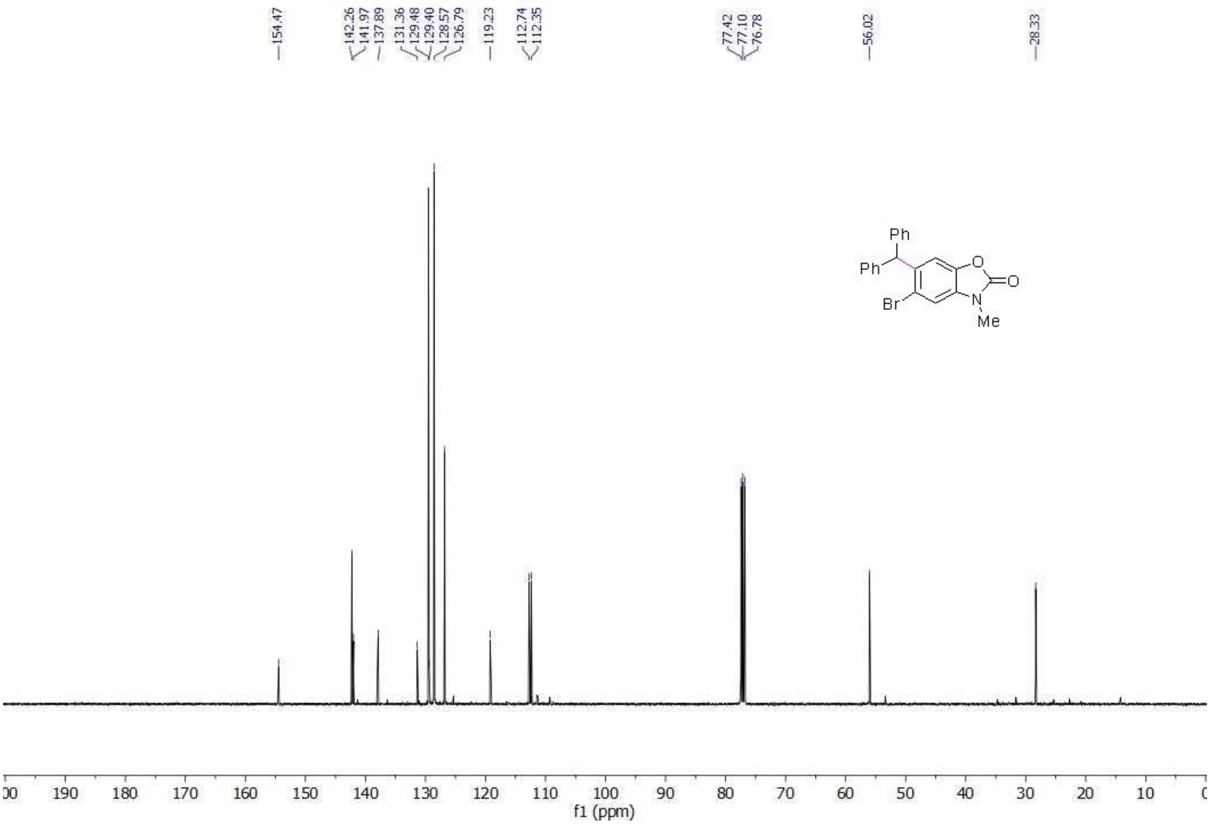
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **3ca**:



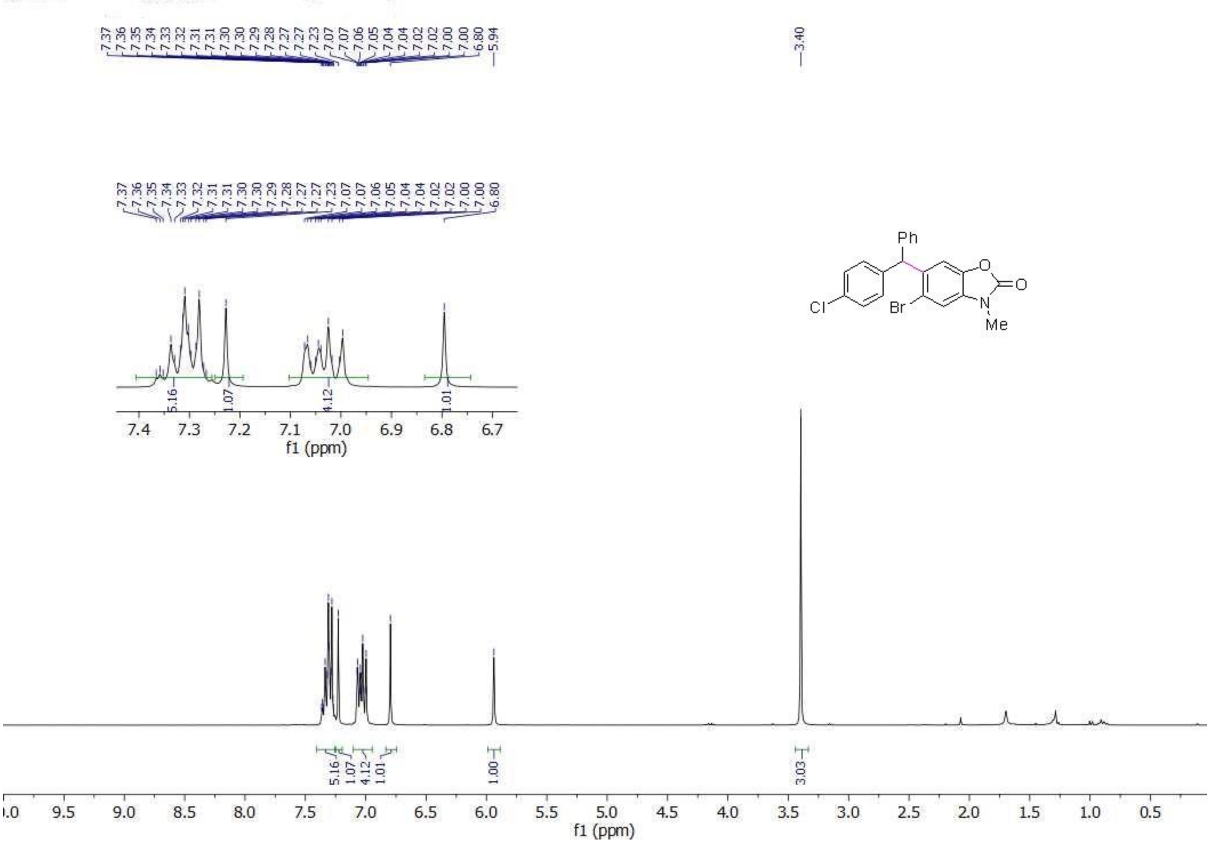


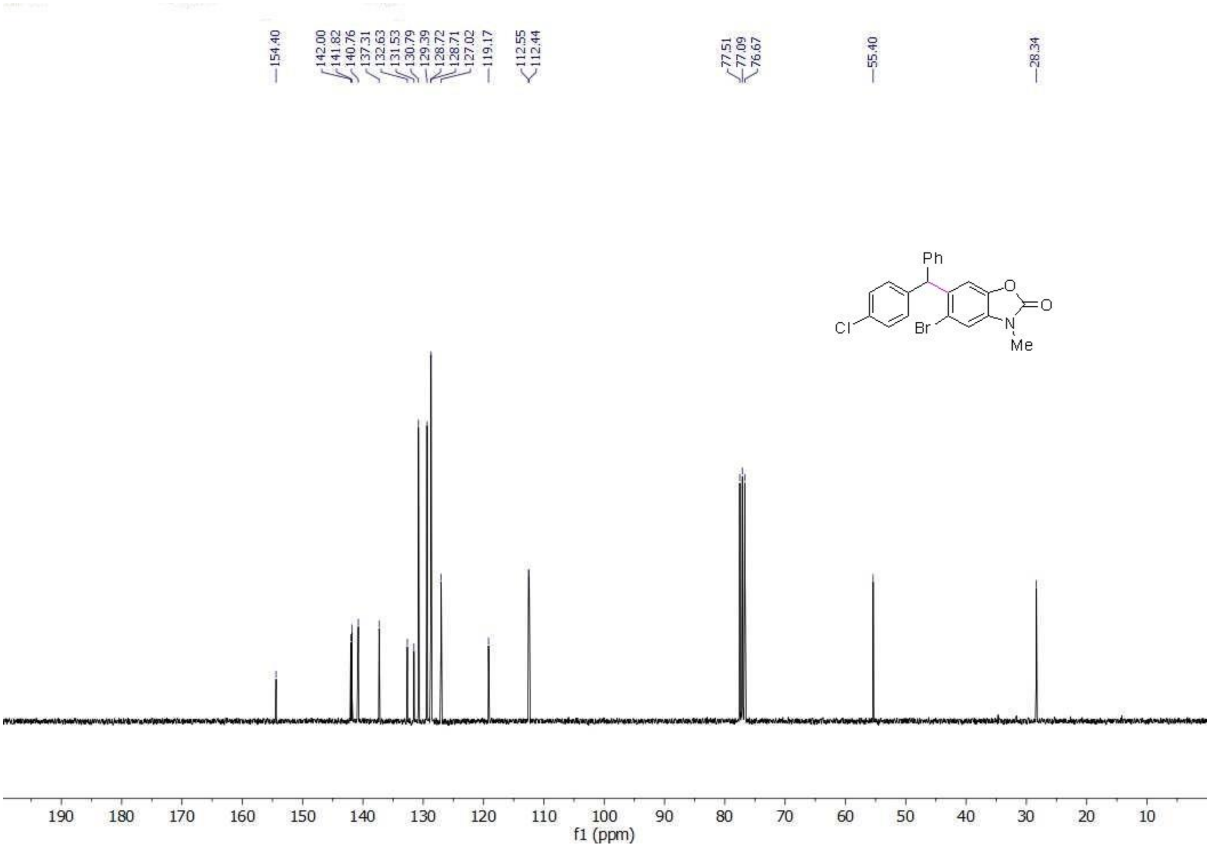
^{1}**H NMR** (400 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3fa**:



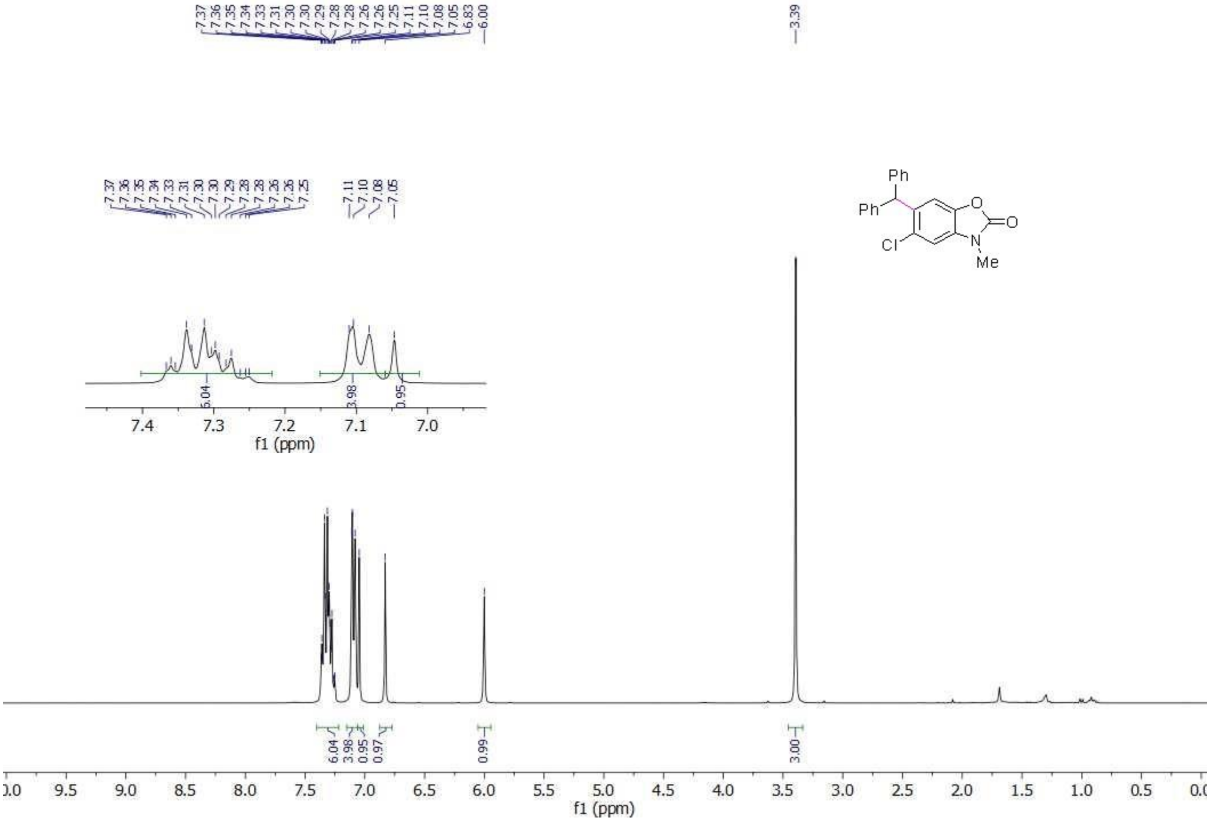


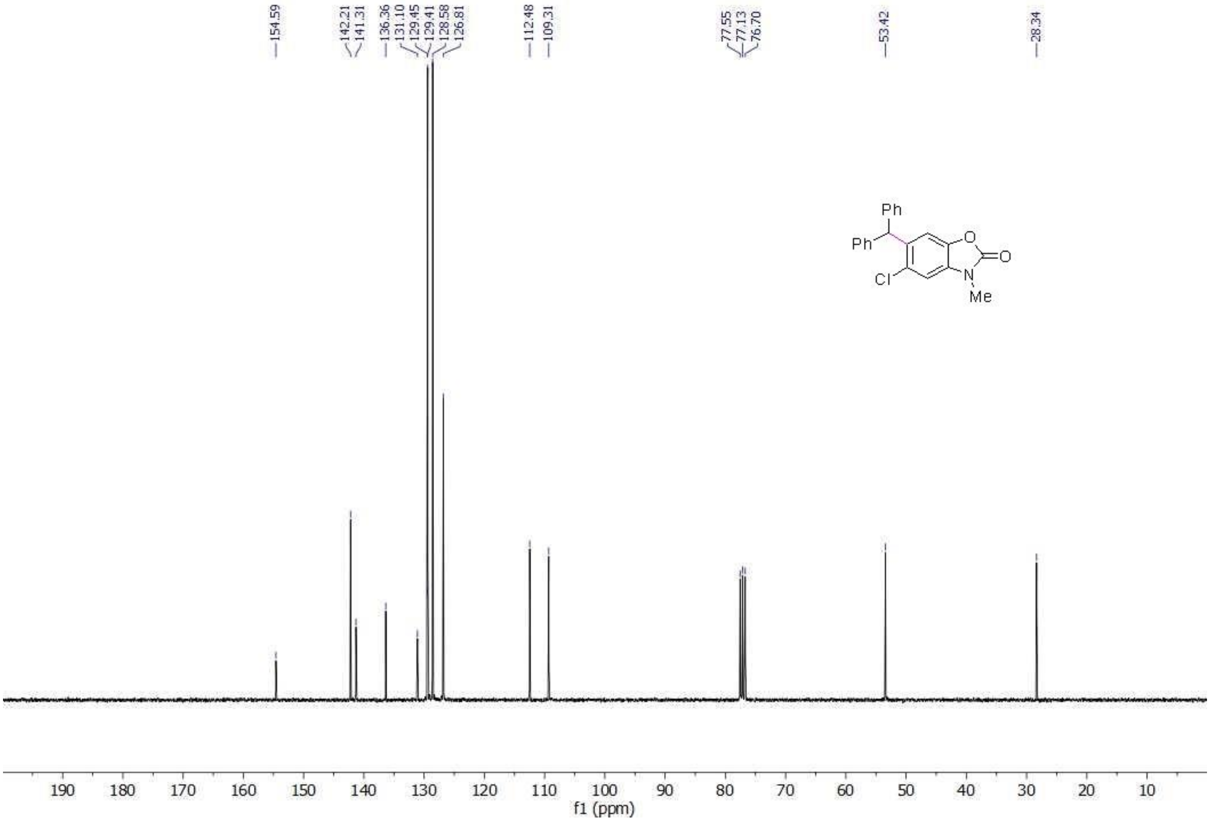
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3fb**:



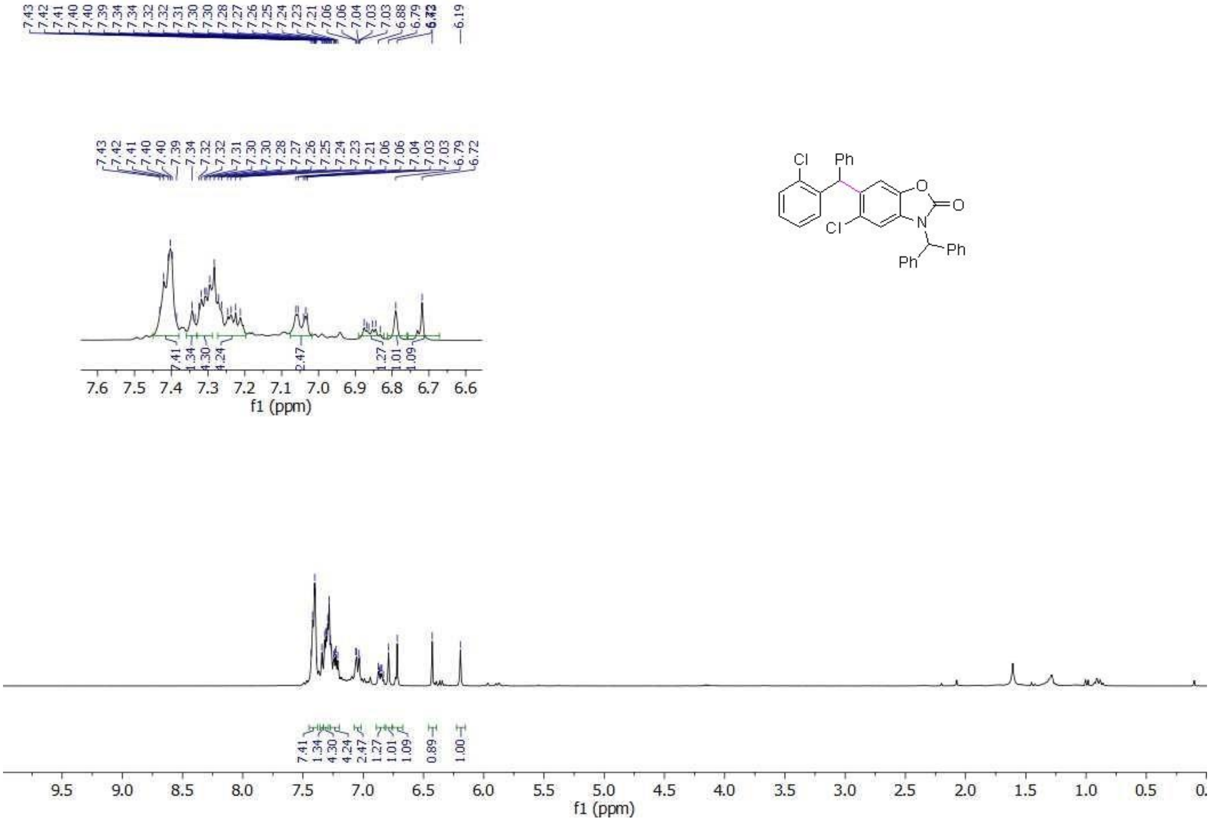


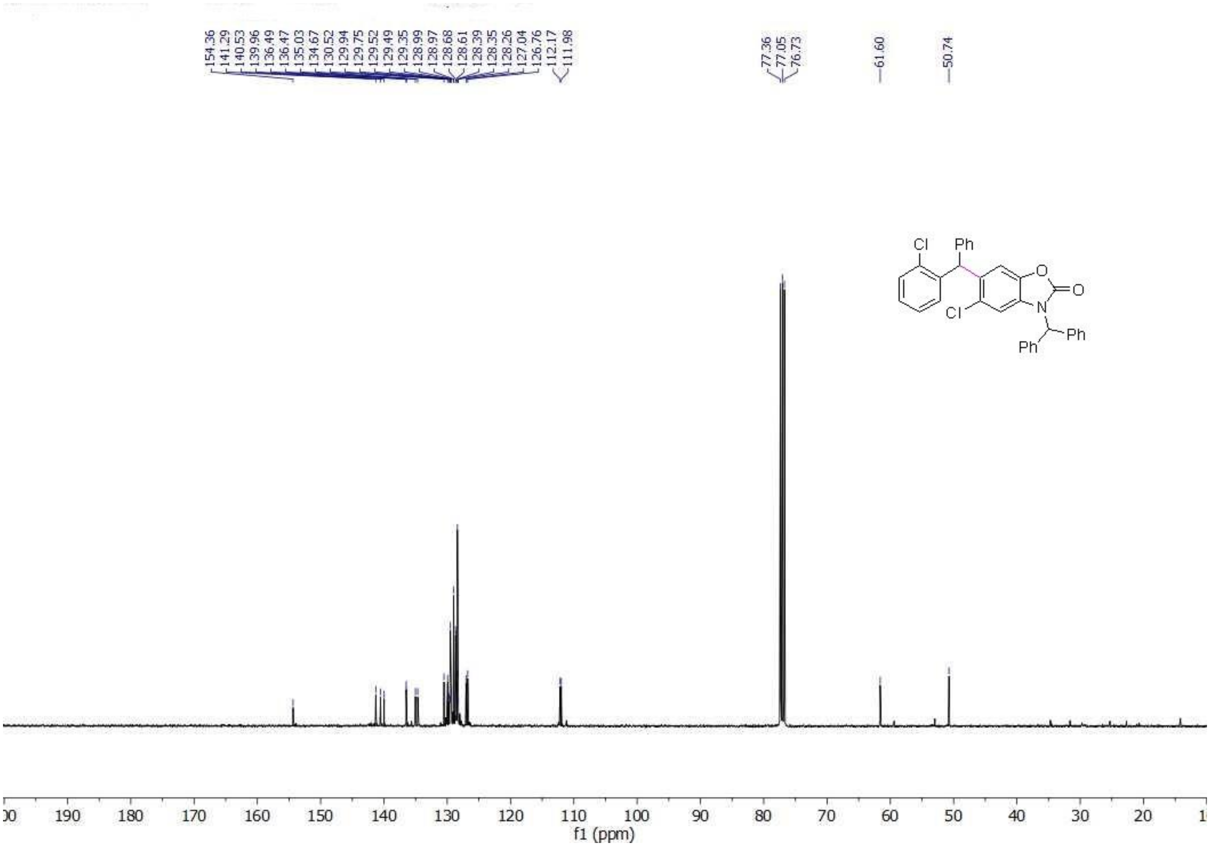
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3da**:



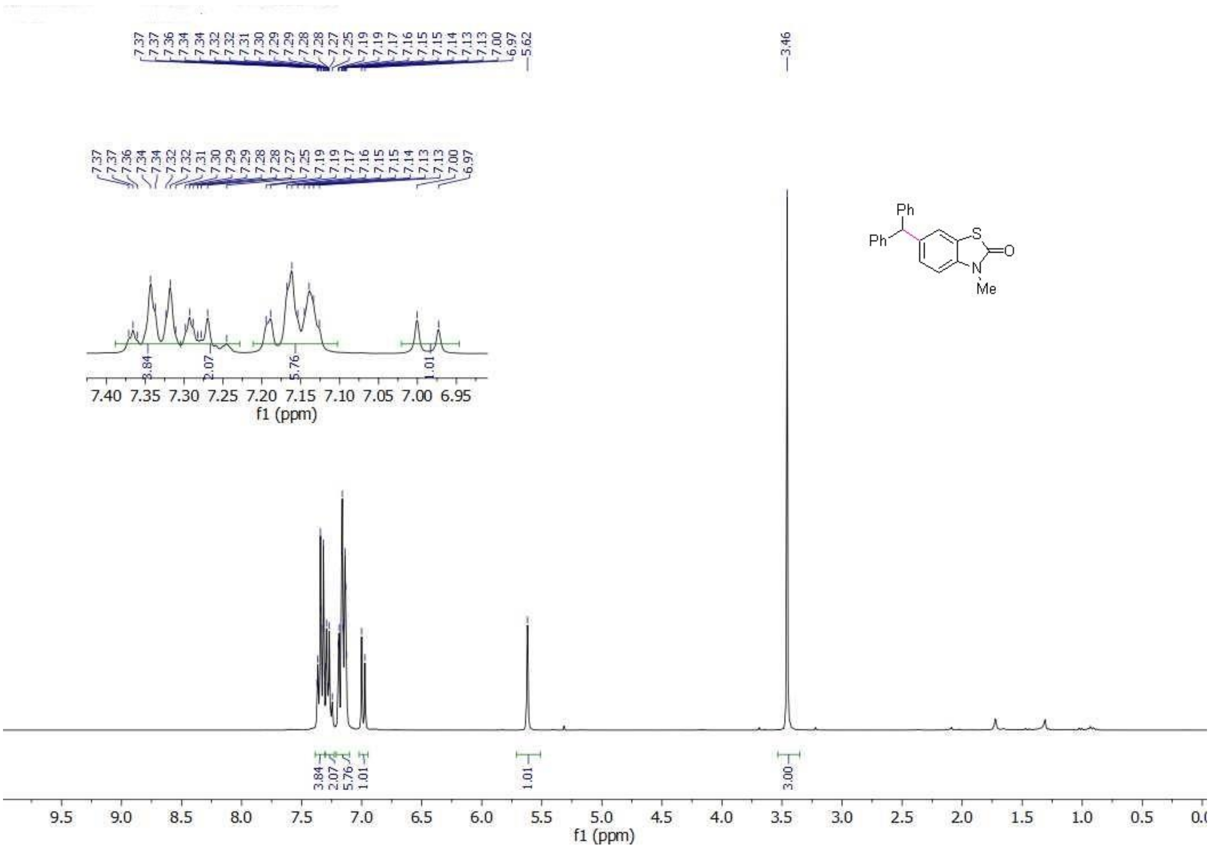


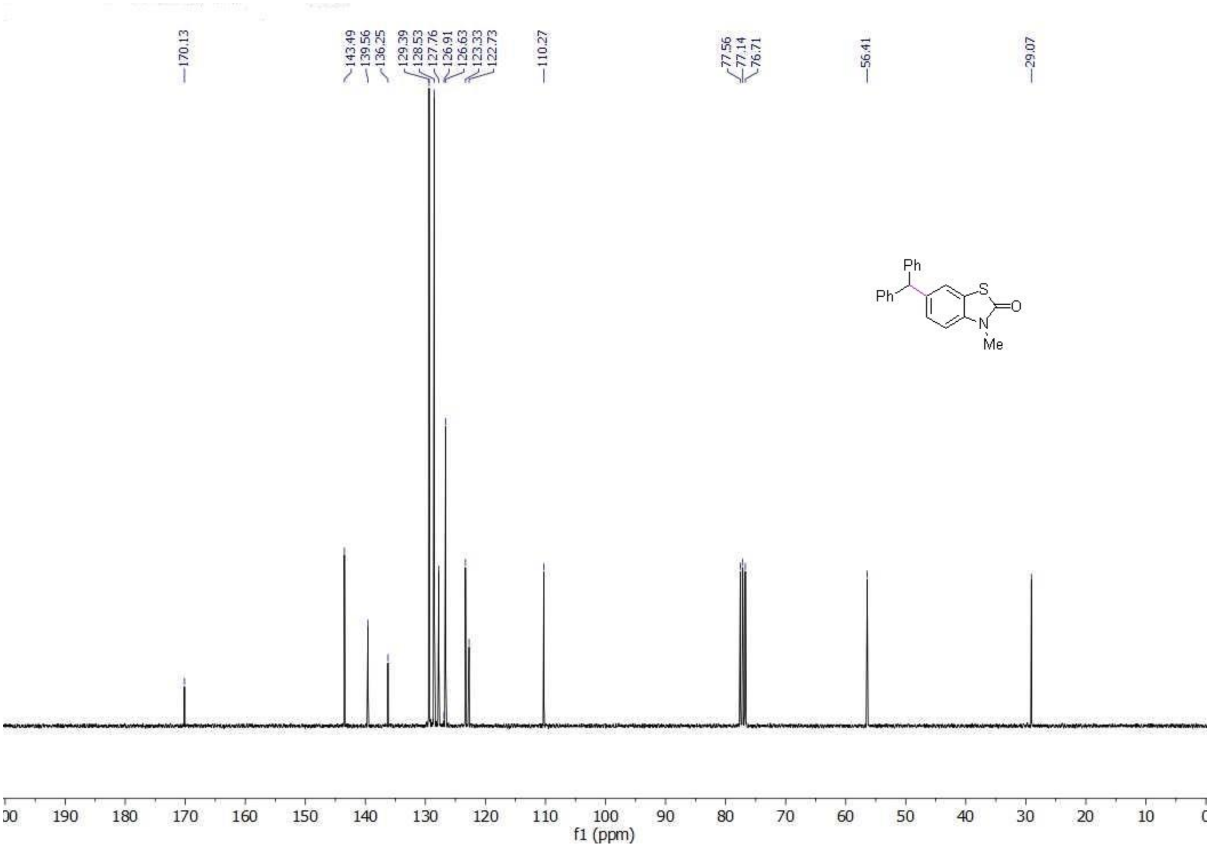
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3de**:



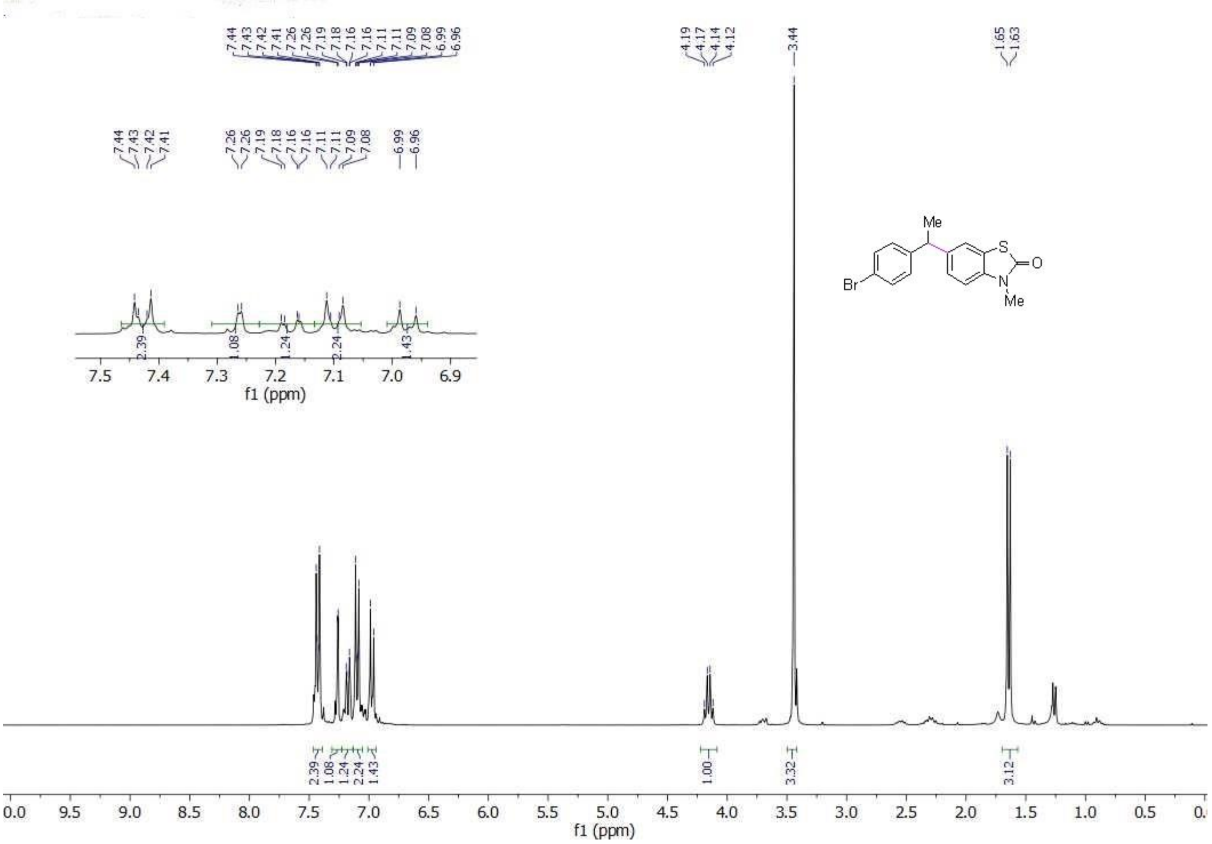


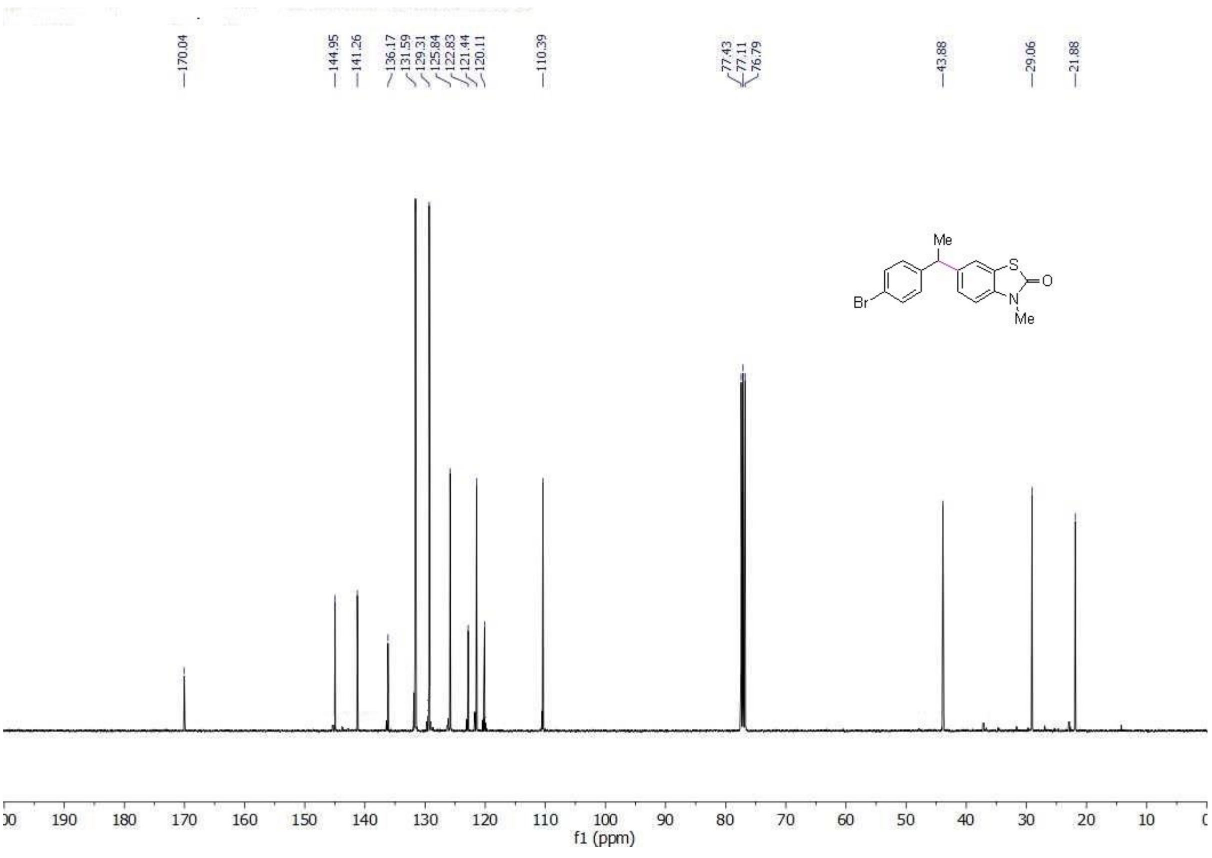
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3ga**:



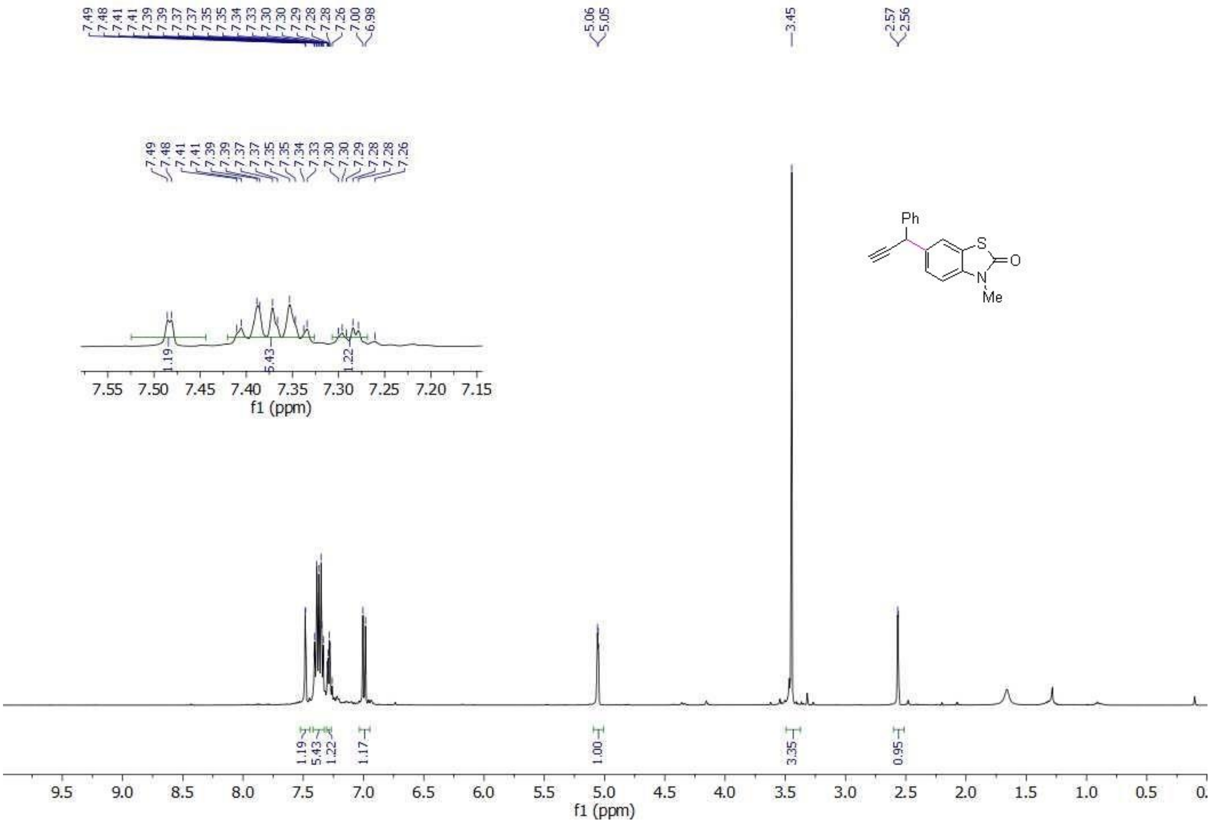


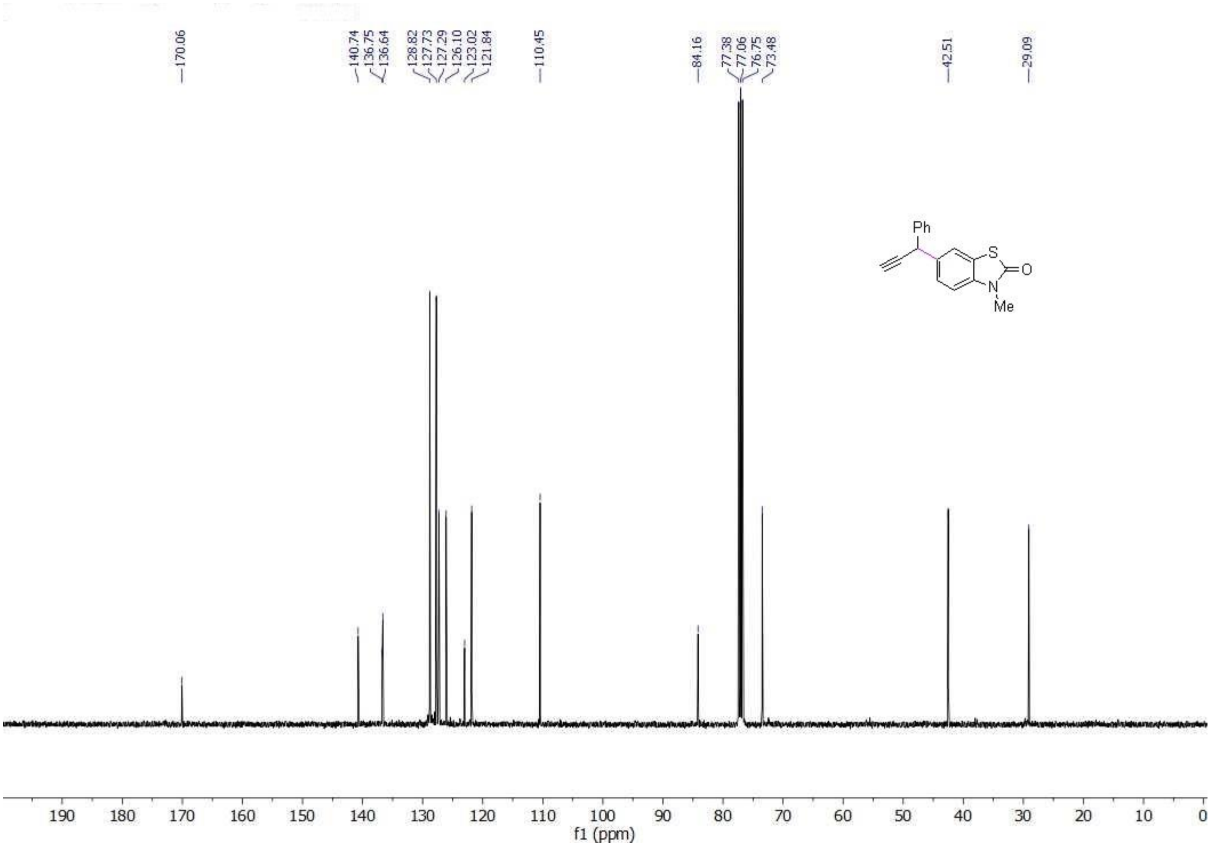
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3gh**:



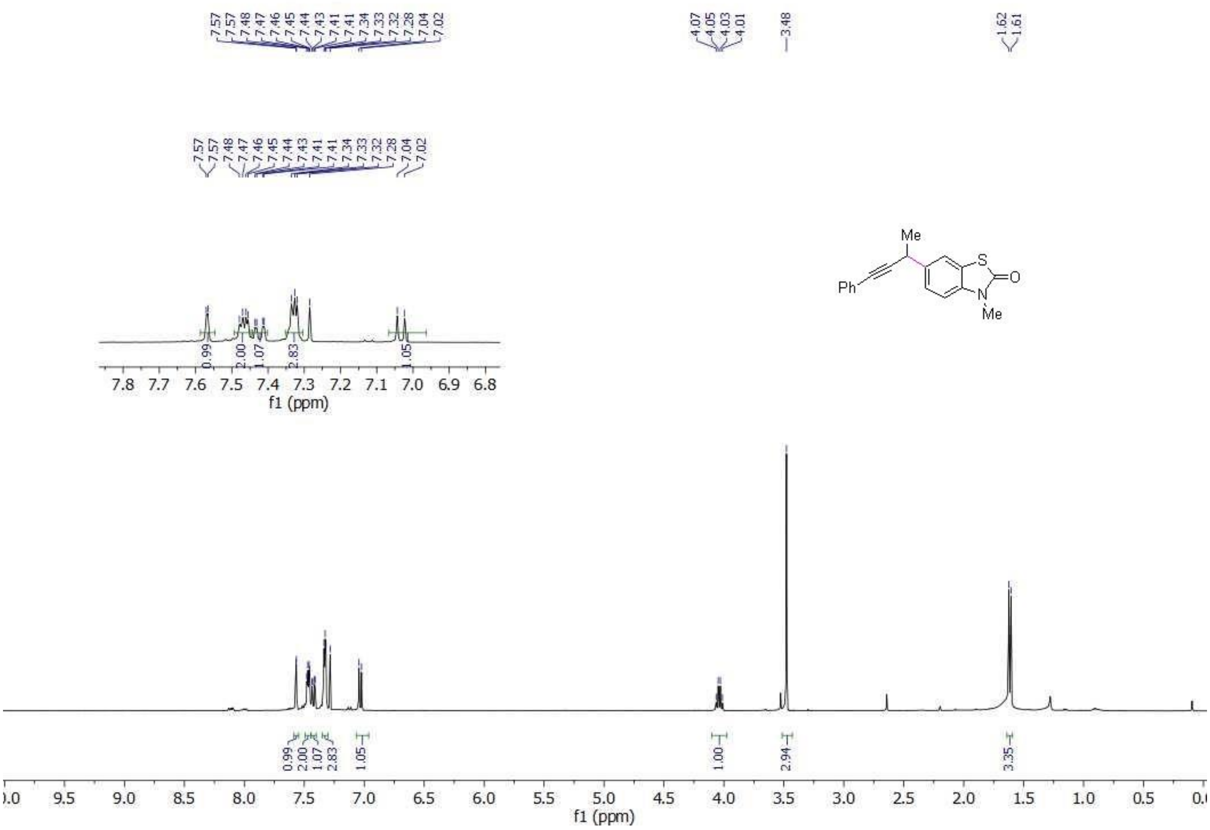


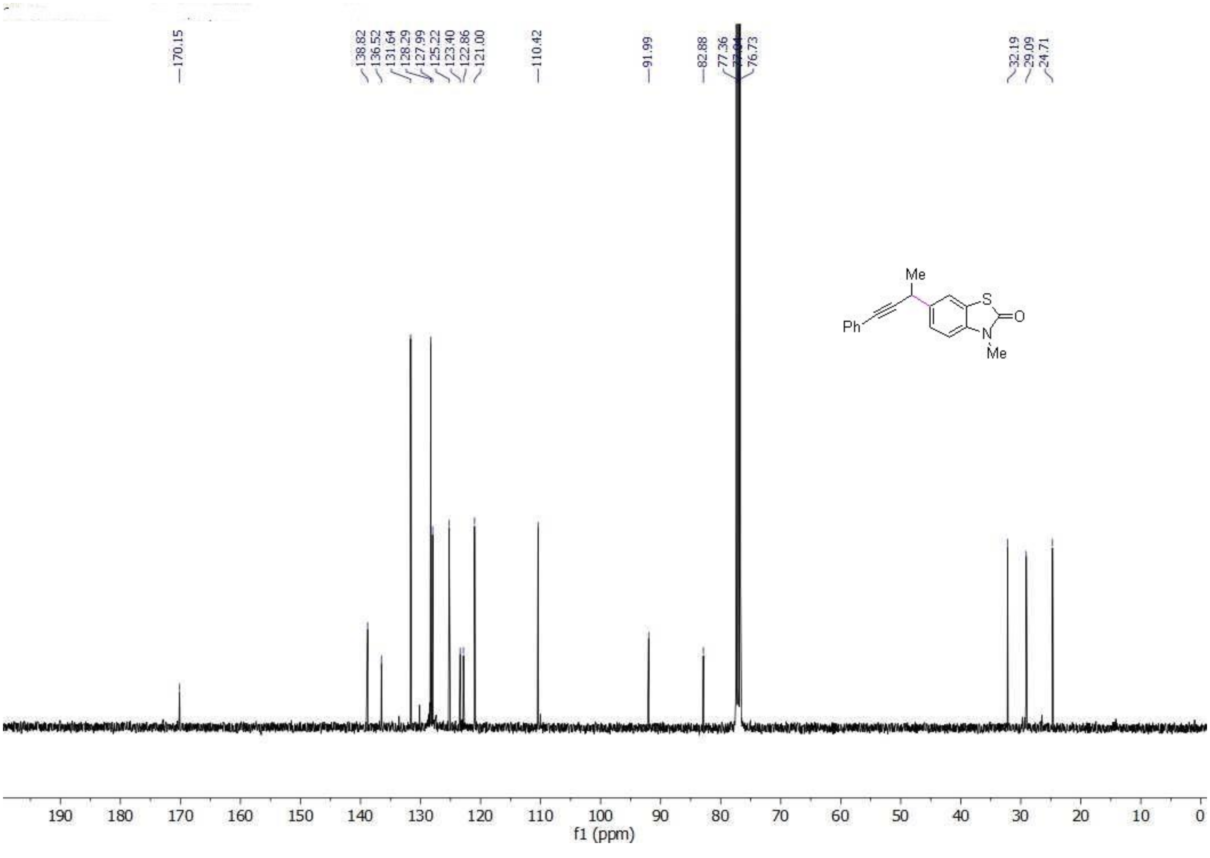
^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **3gl**:



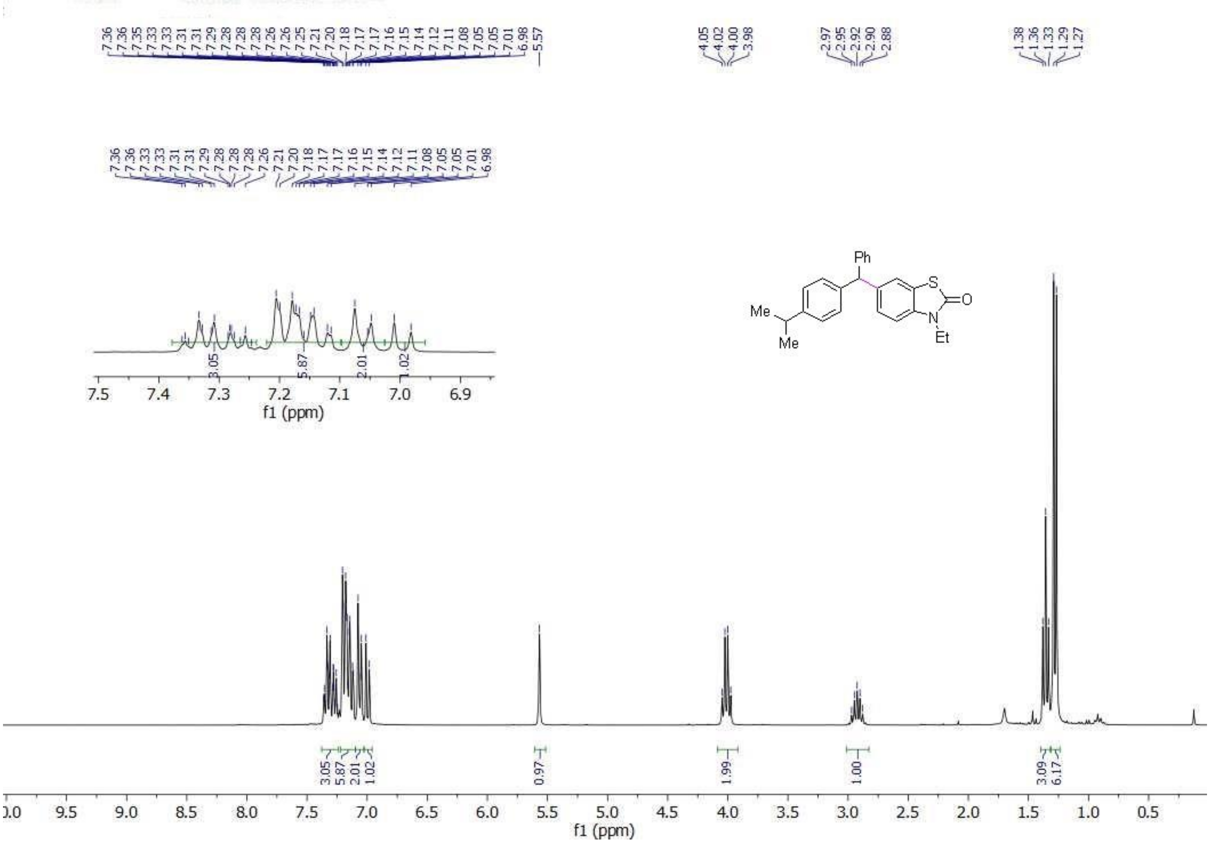


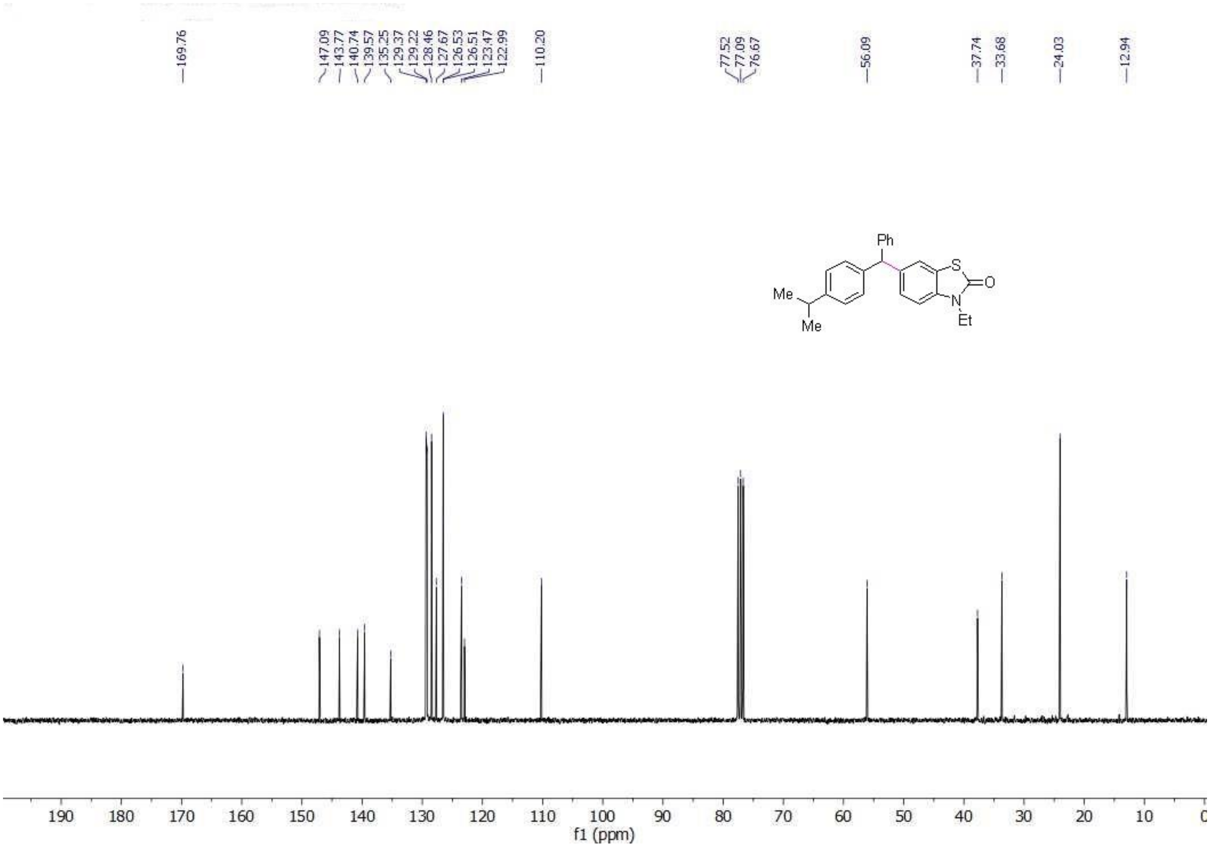
^{1}**H NMR** (400 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3gk**:



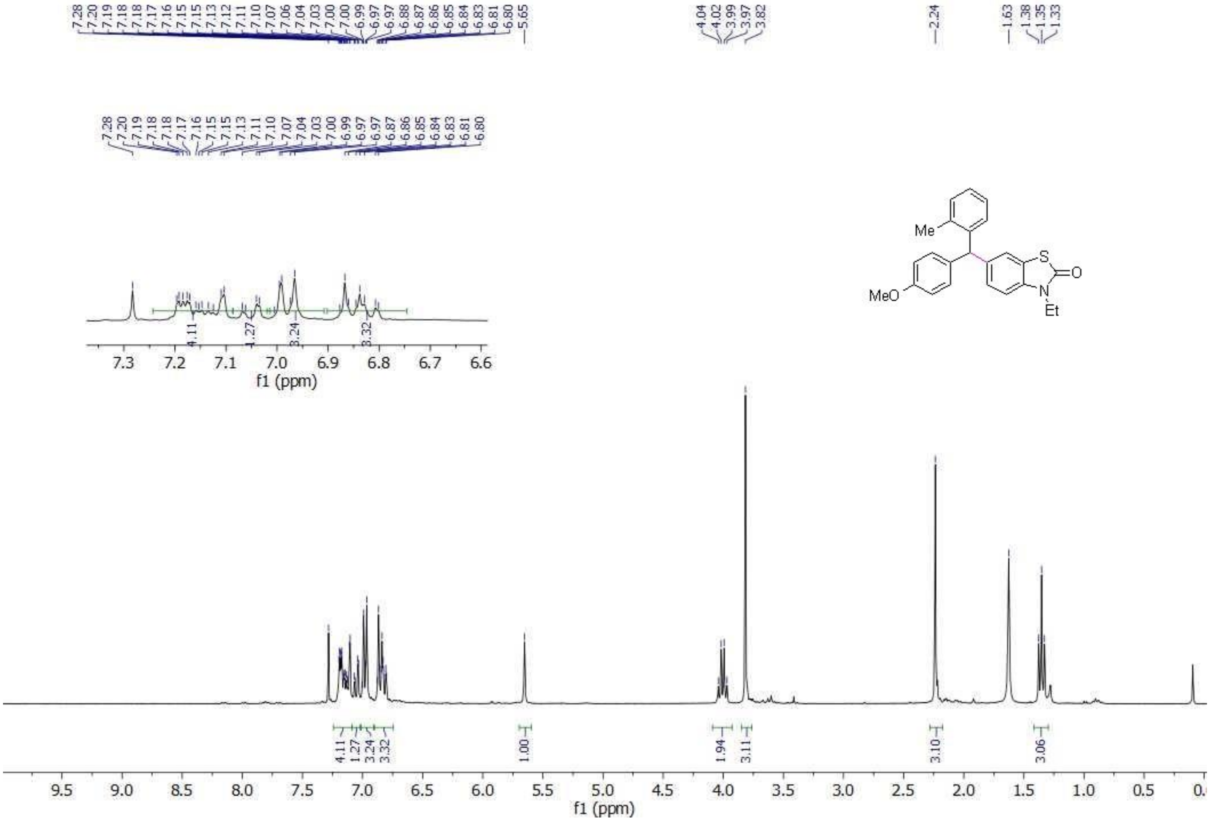


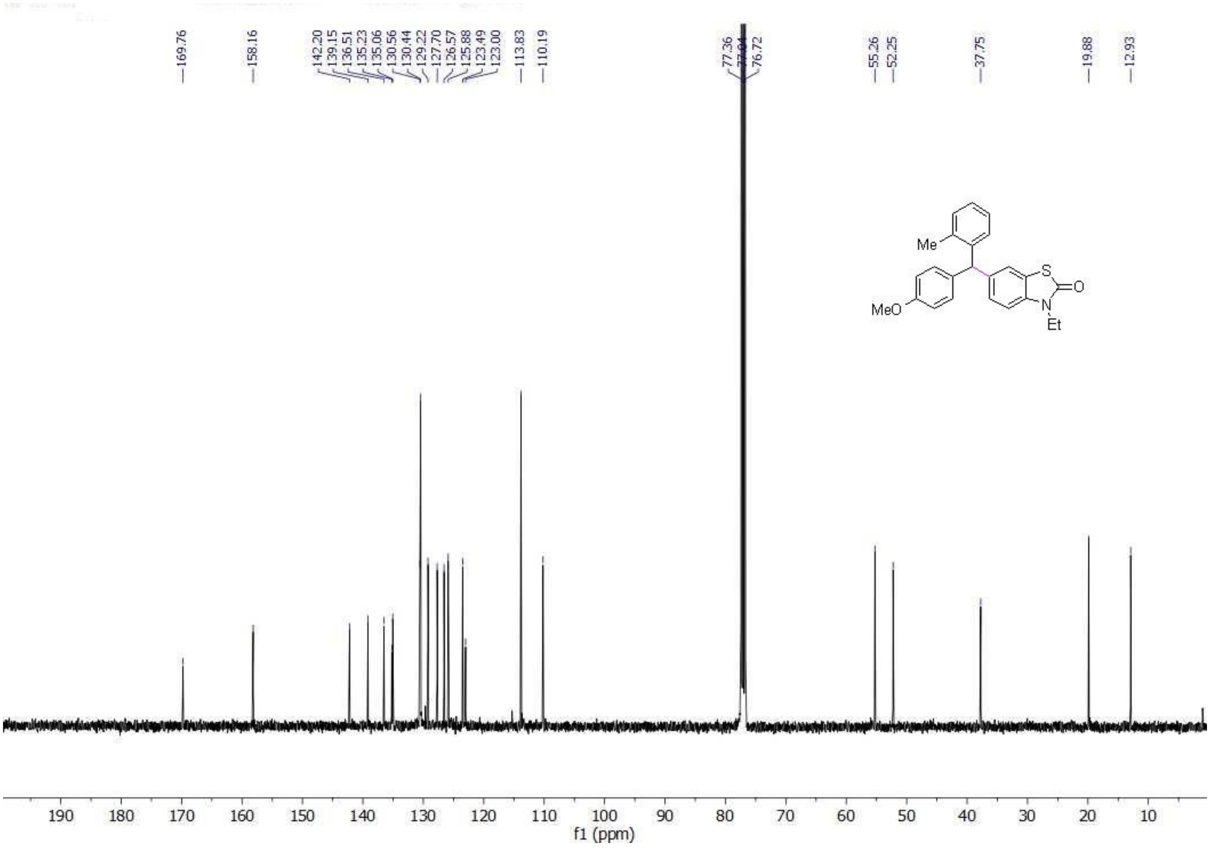
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3hc**:



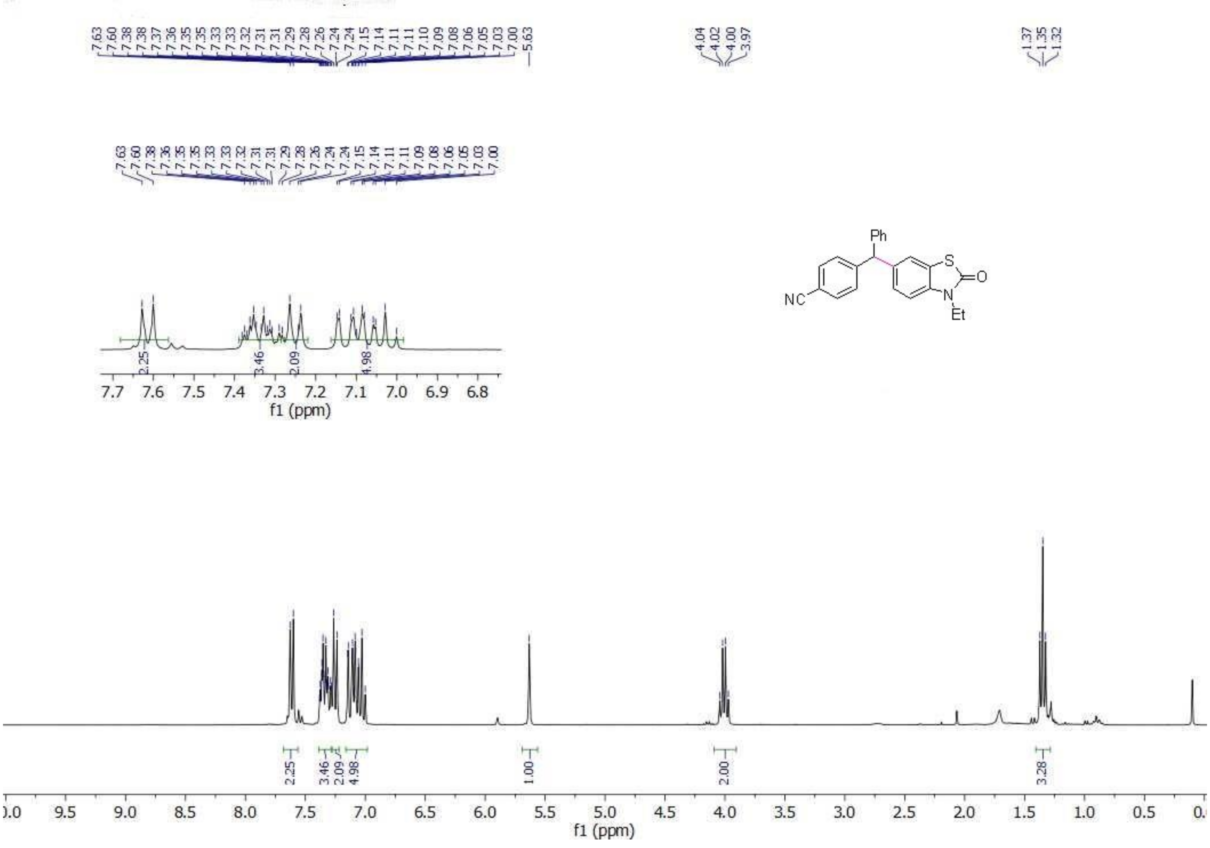


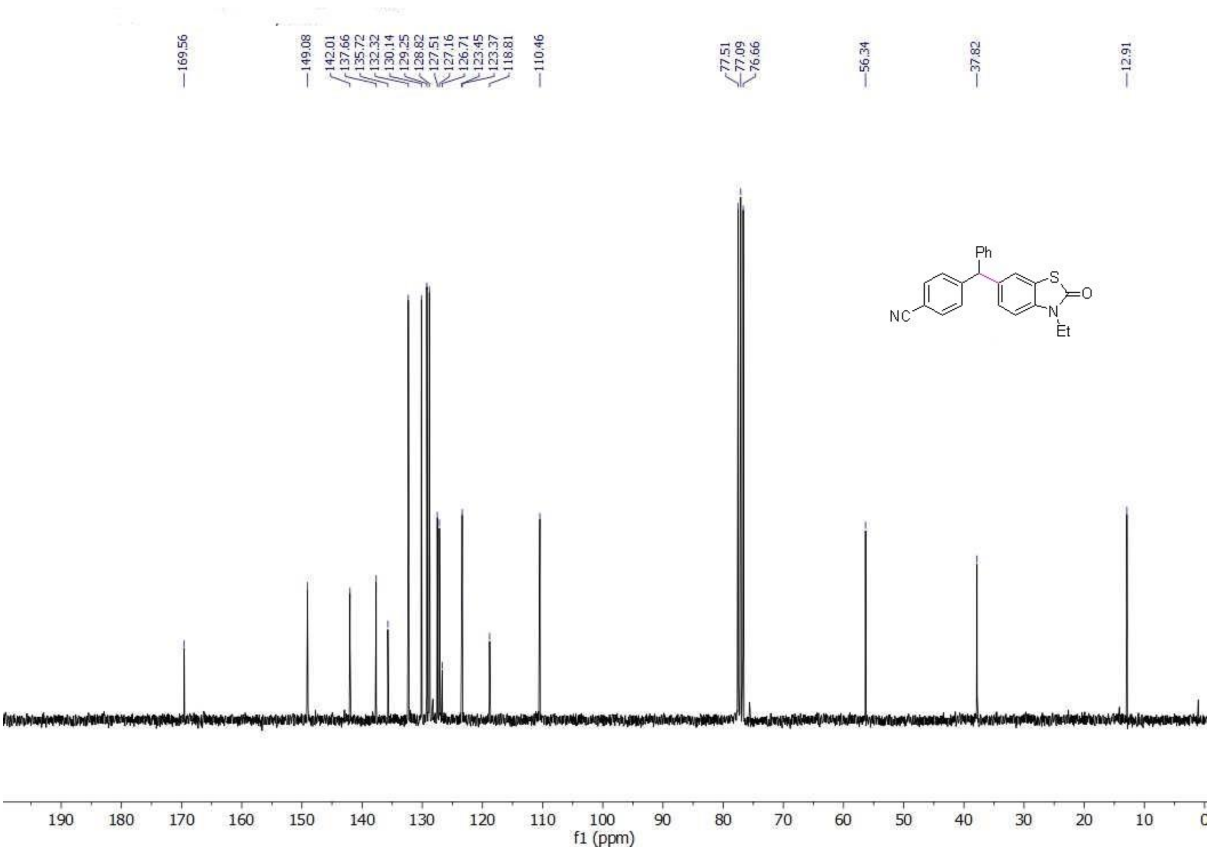
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3hf**:



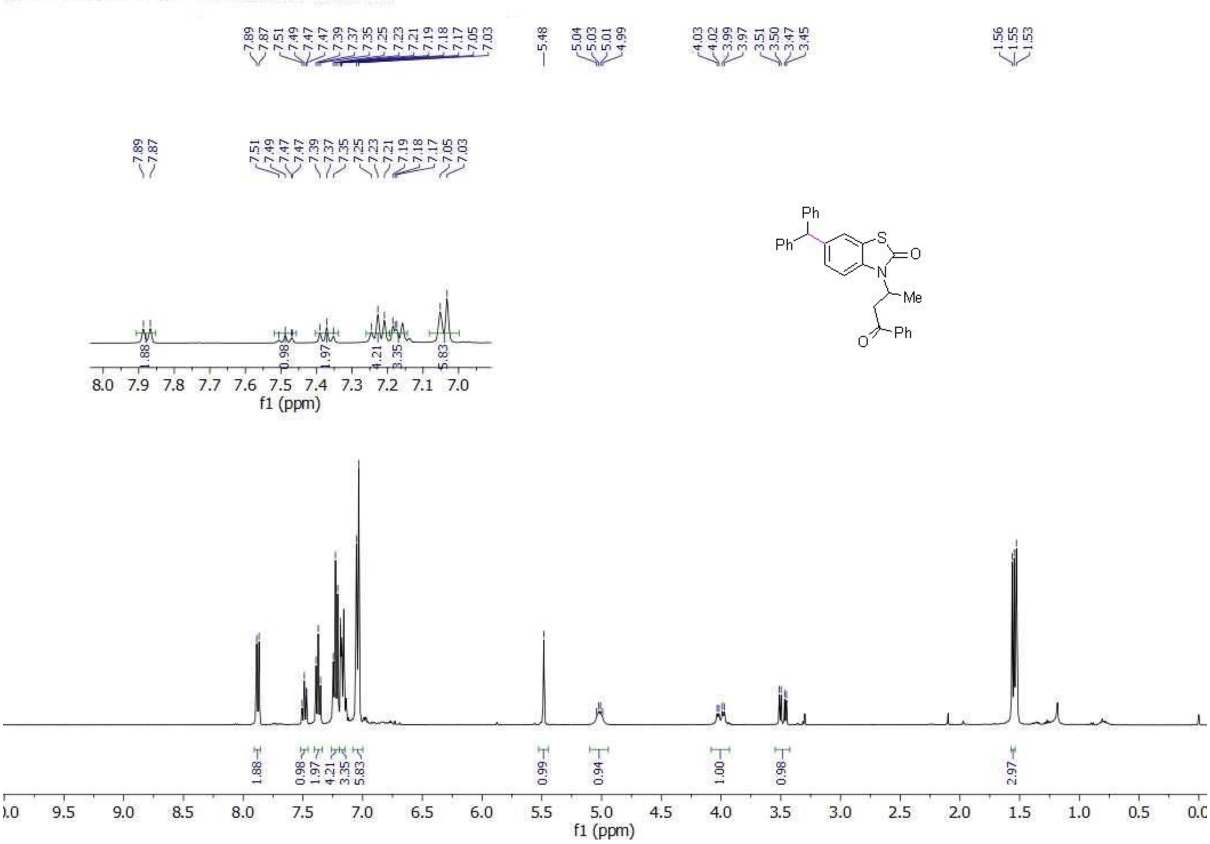


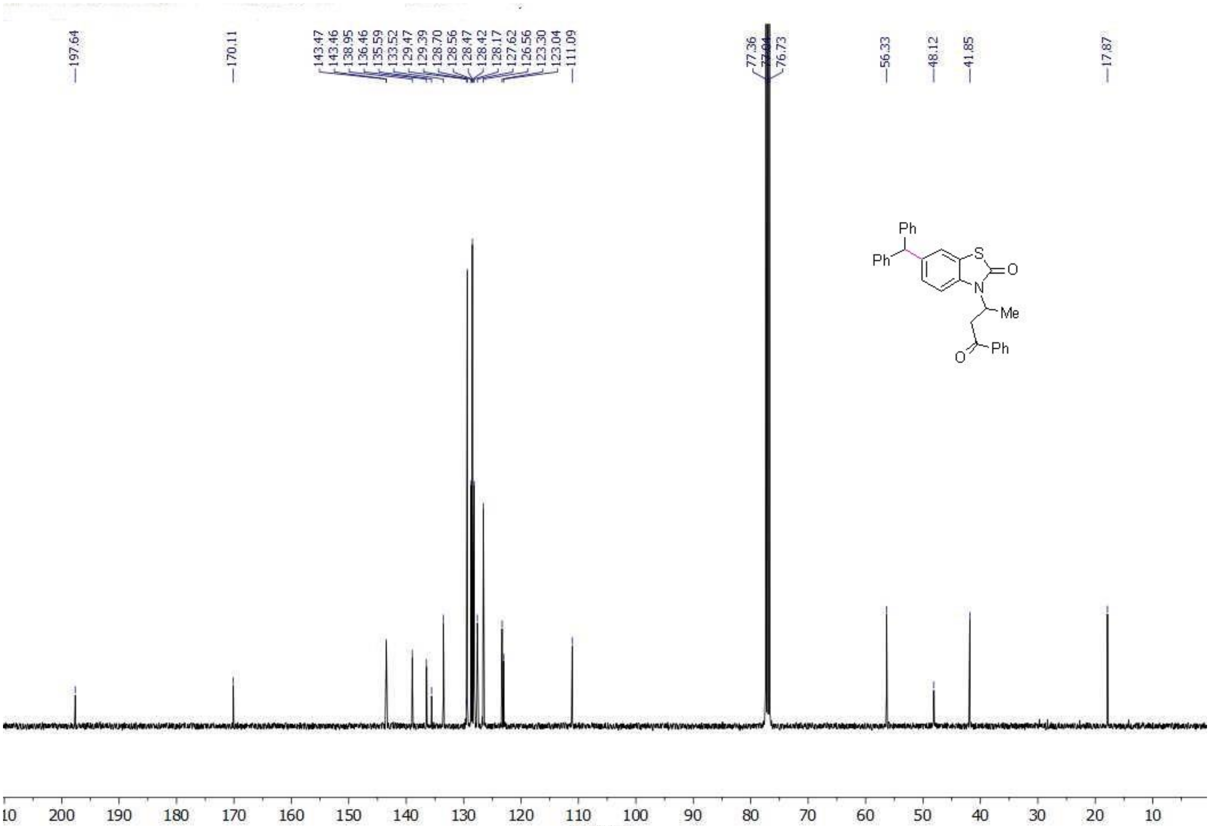
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3hd**:



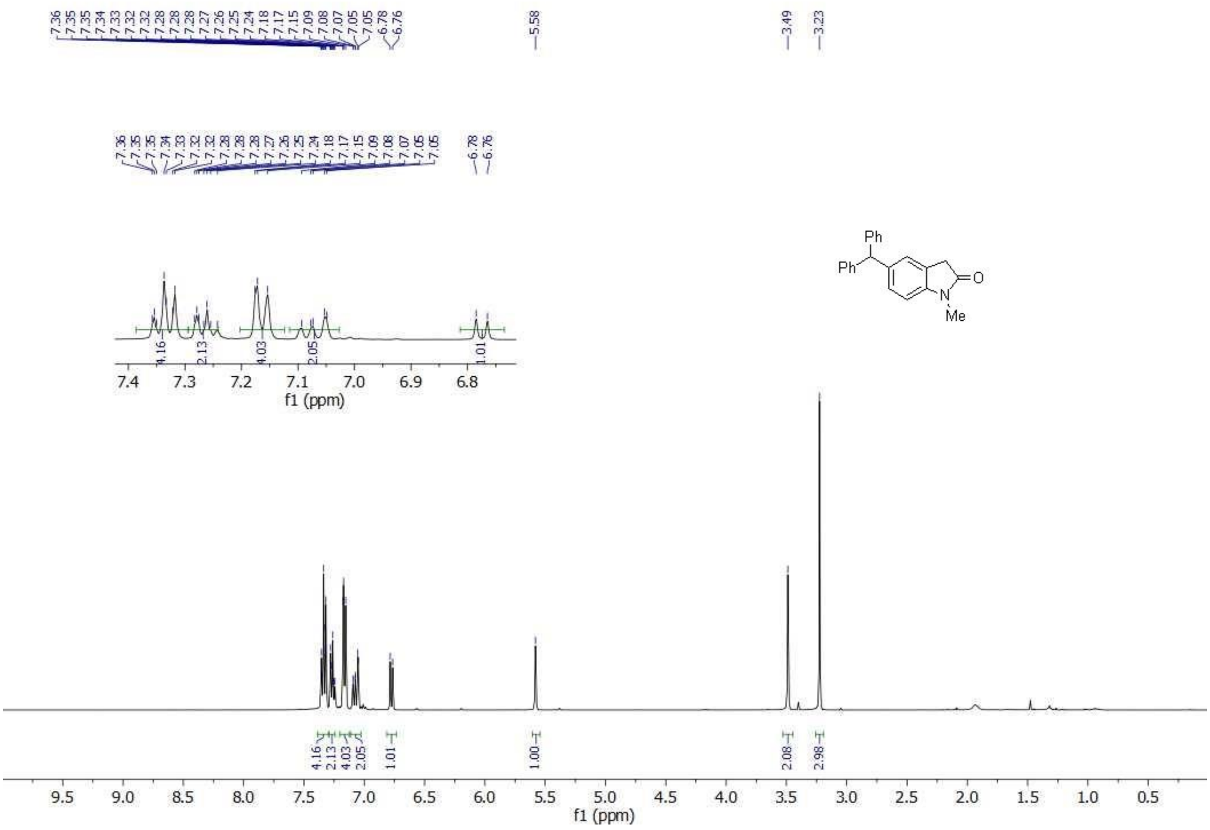


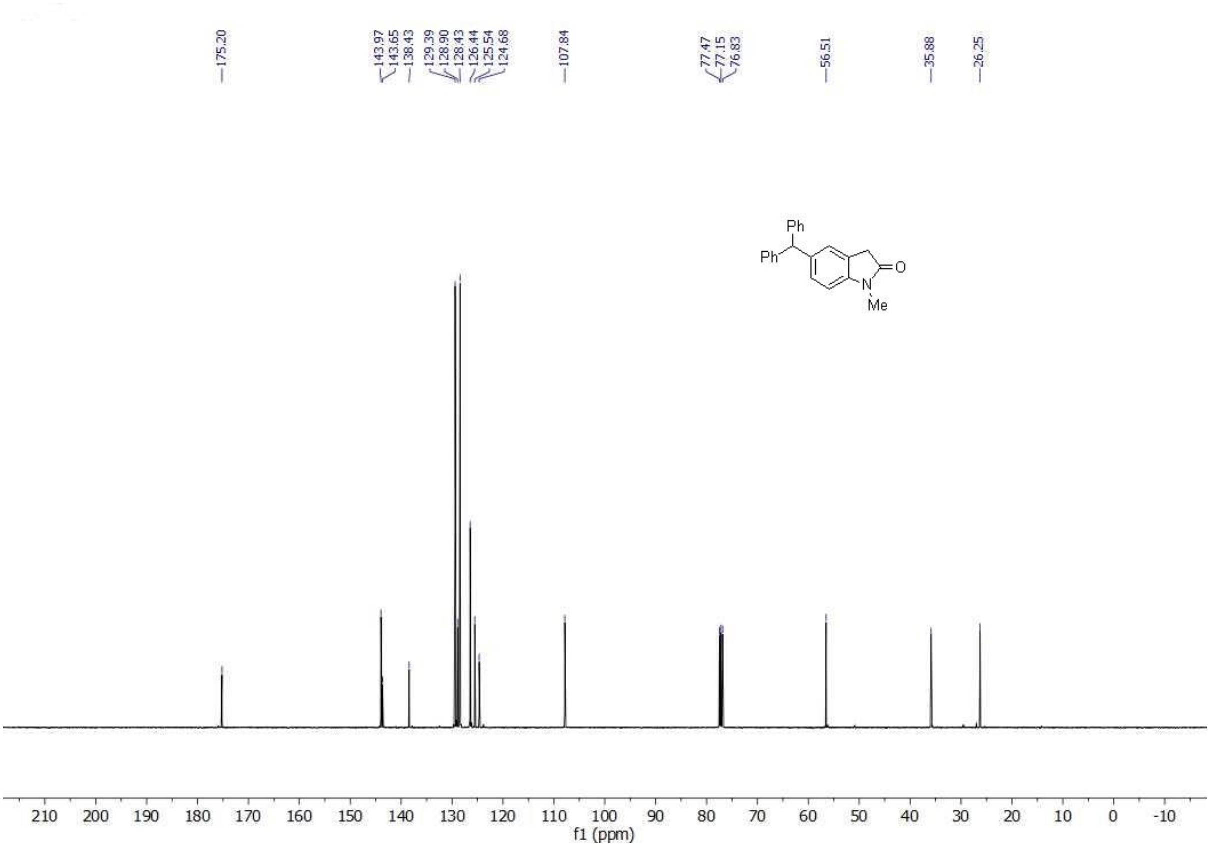
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3ia**:



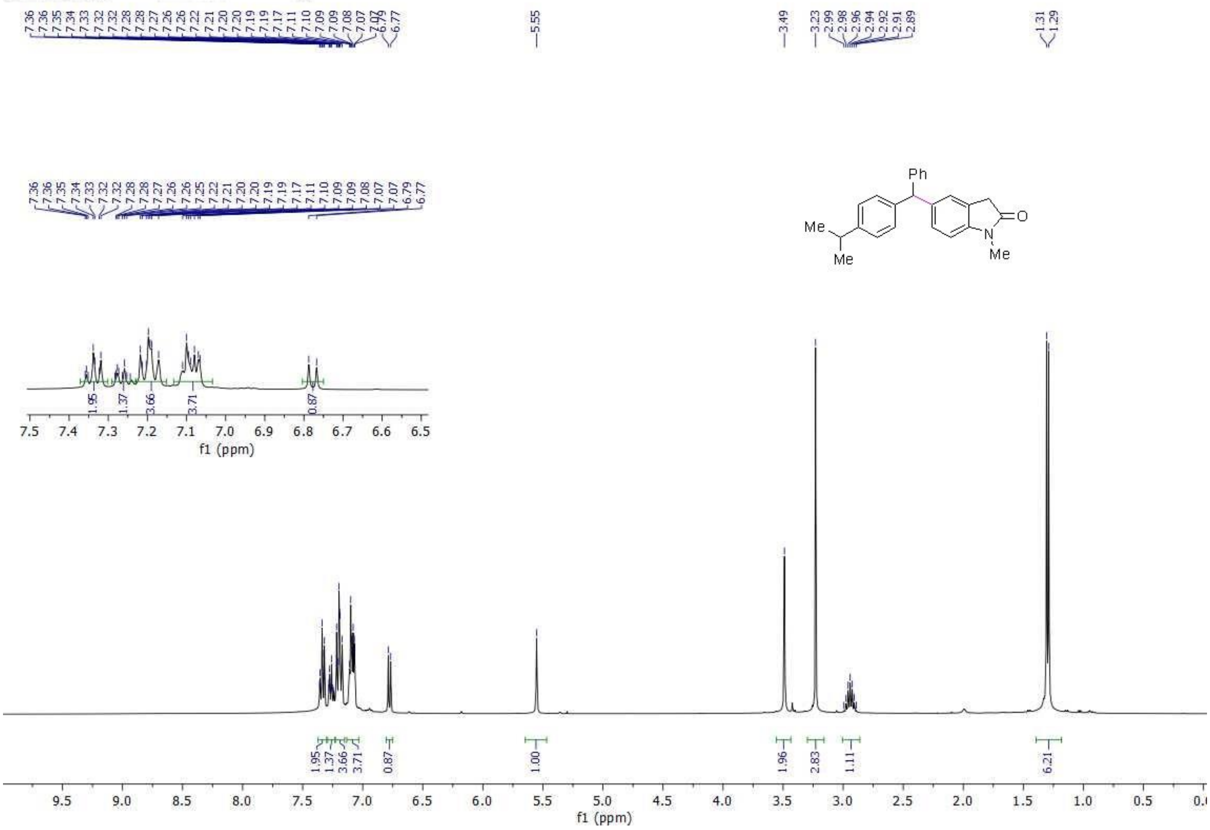


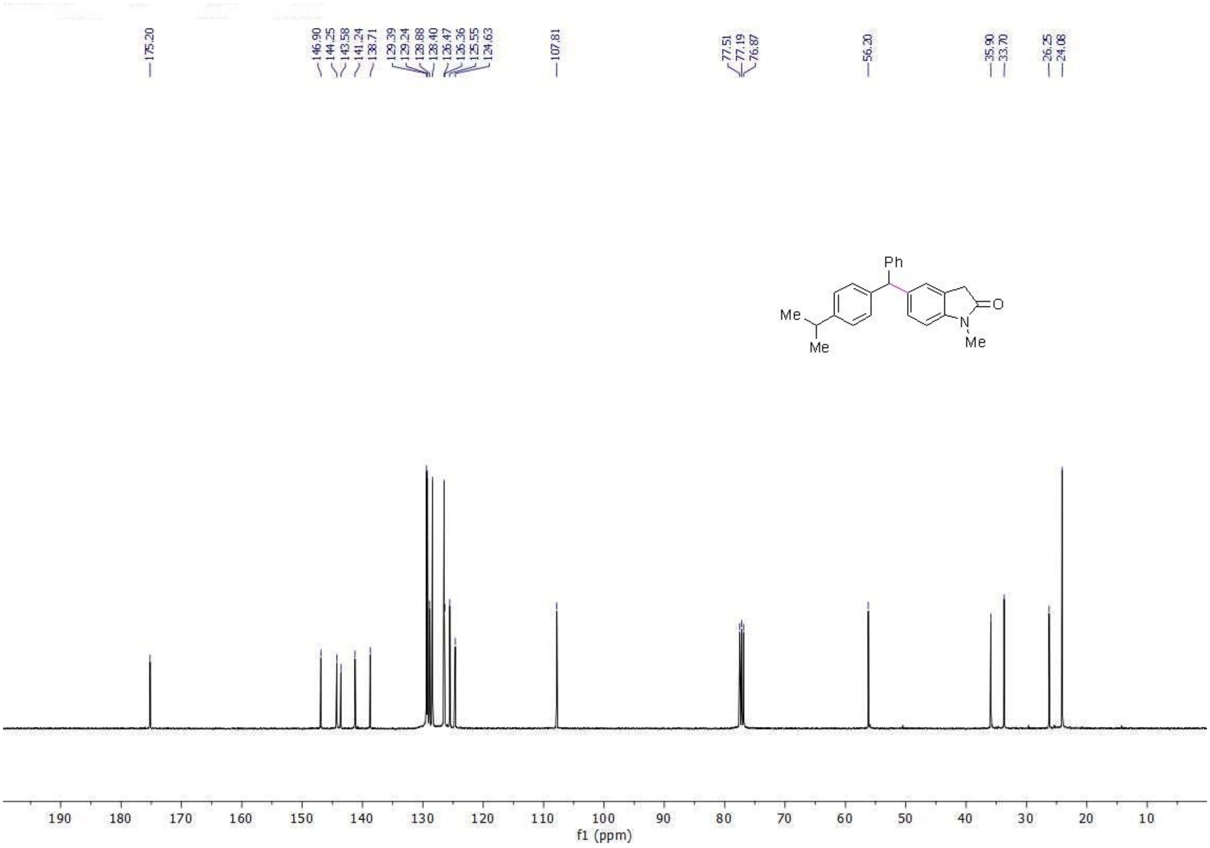
^{1}**H NMR** (400 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3ja**:



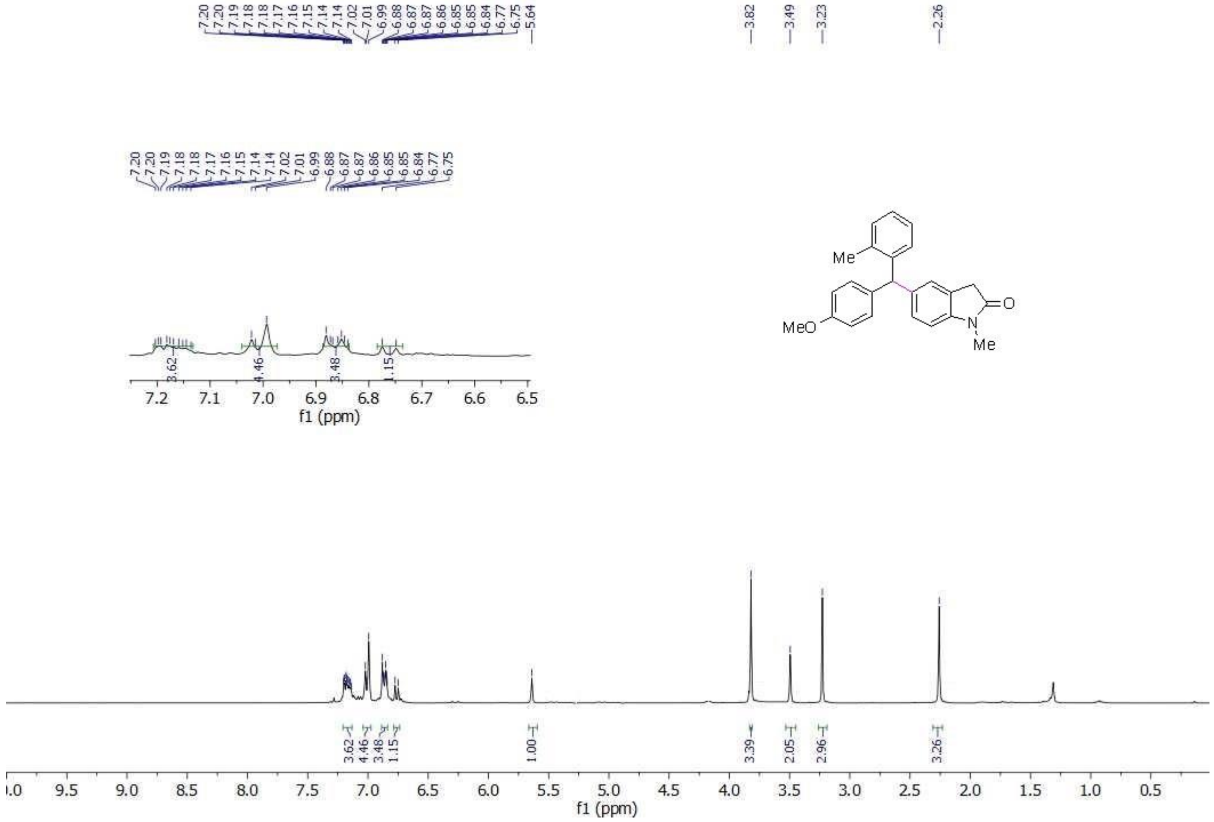


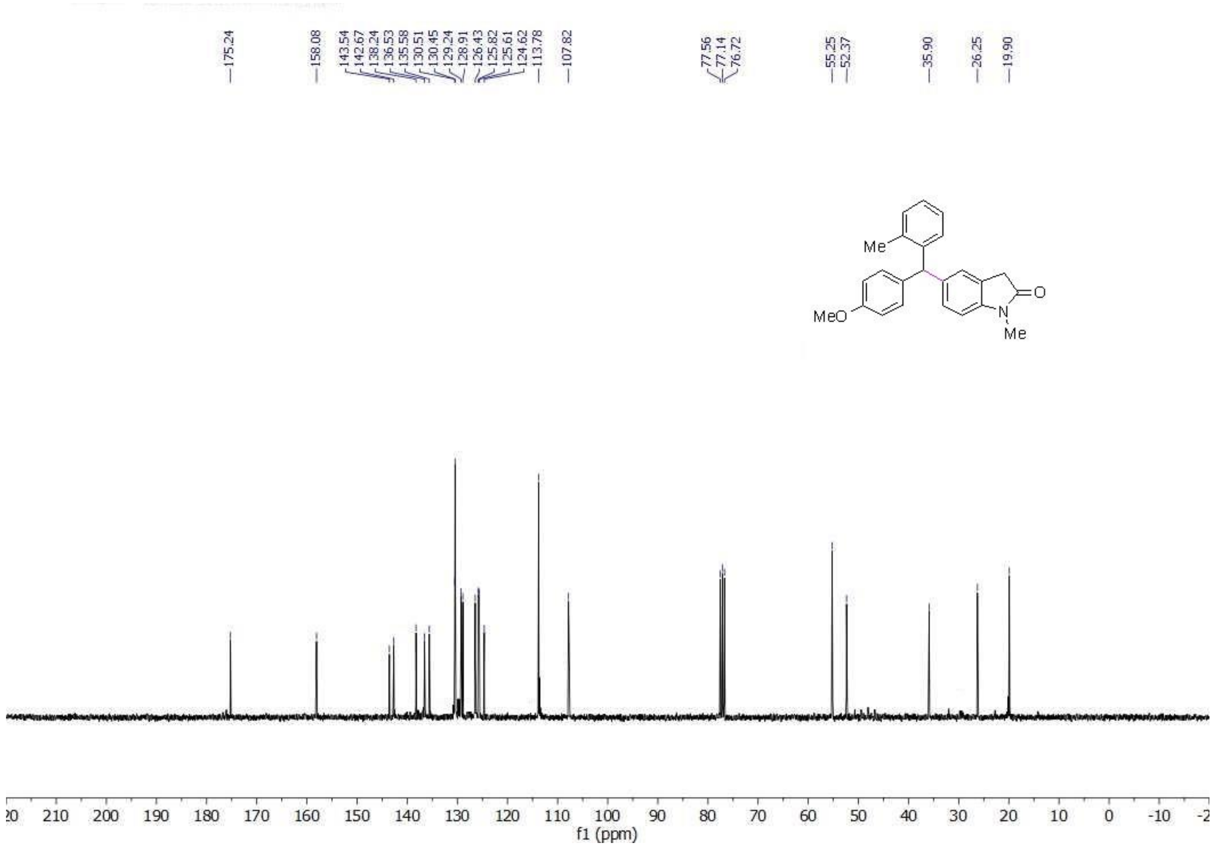
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3jc**:



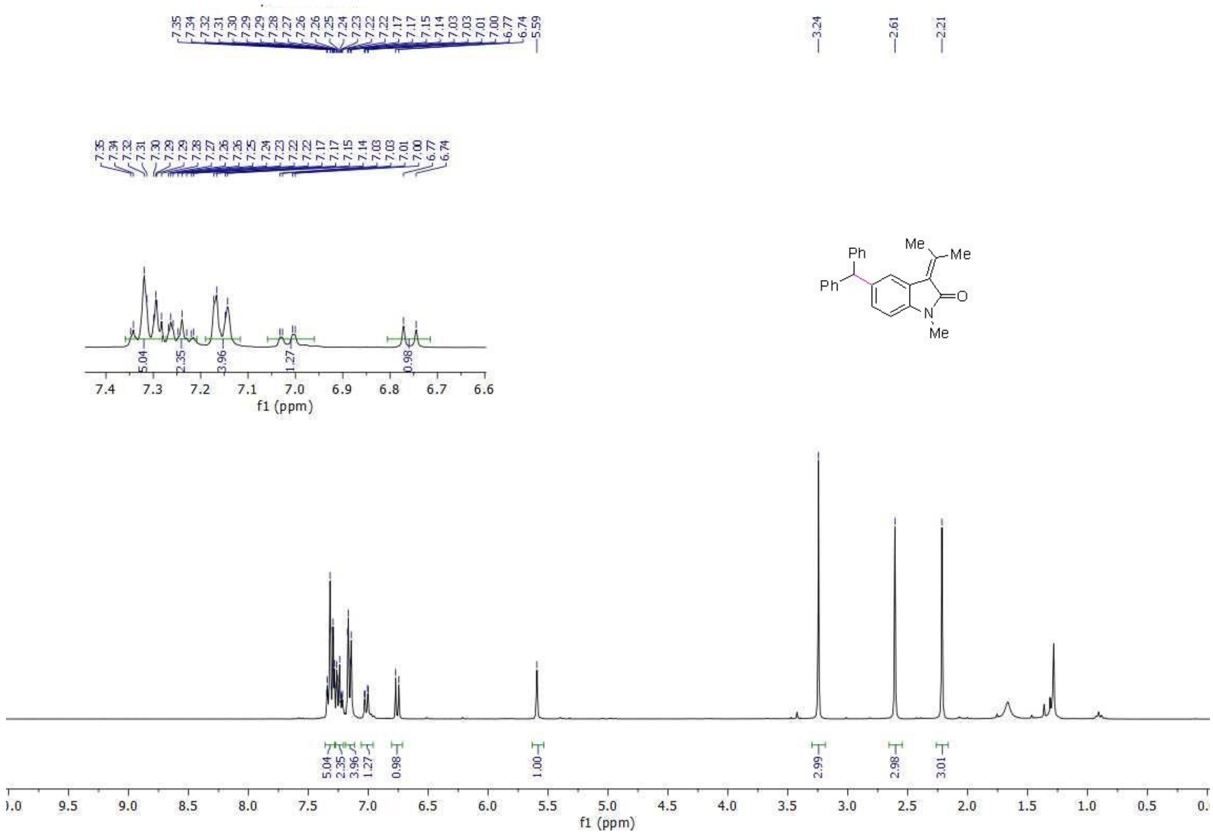


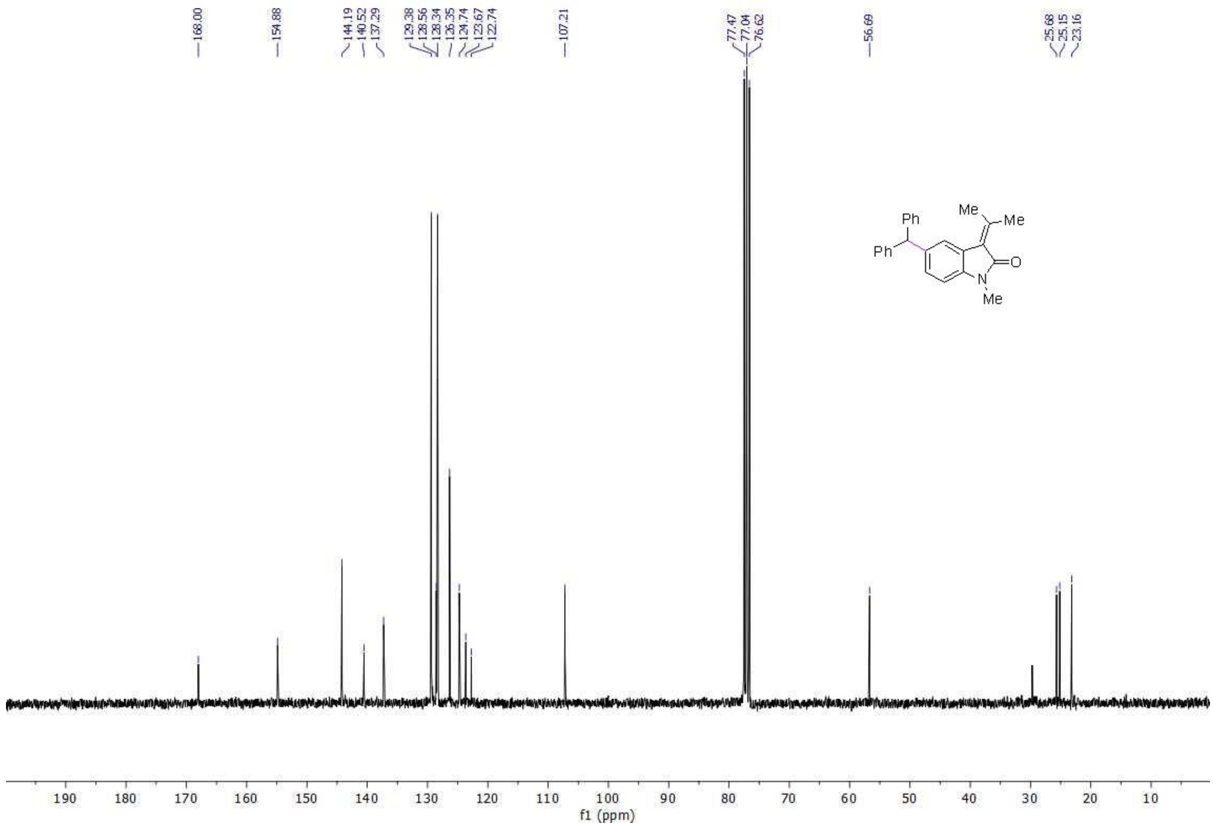
^{1}H NMR (300 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) spectra of **3jf**:



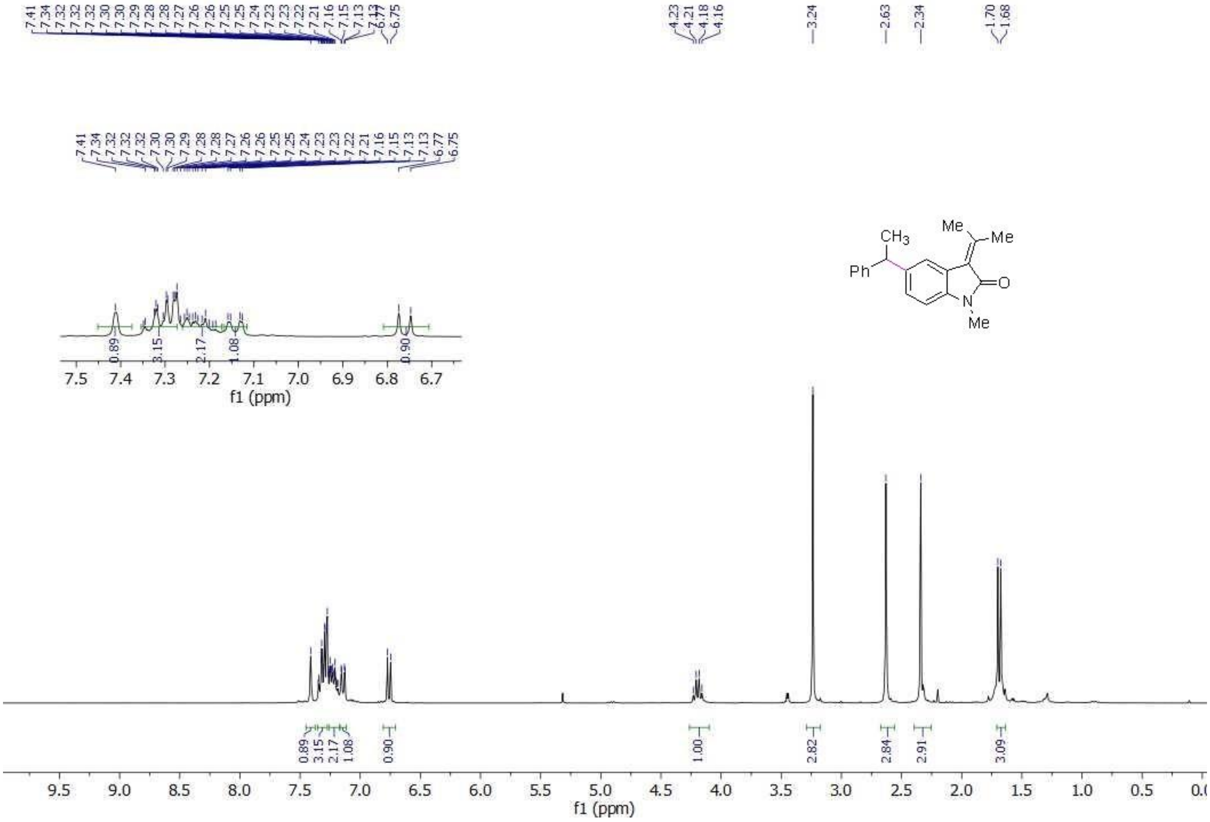


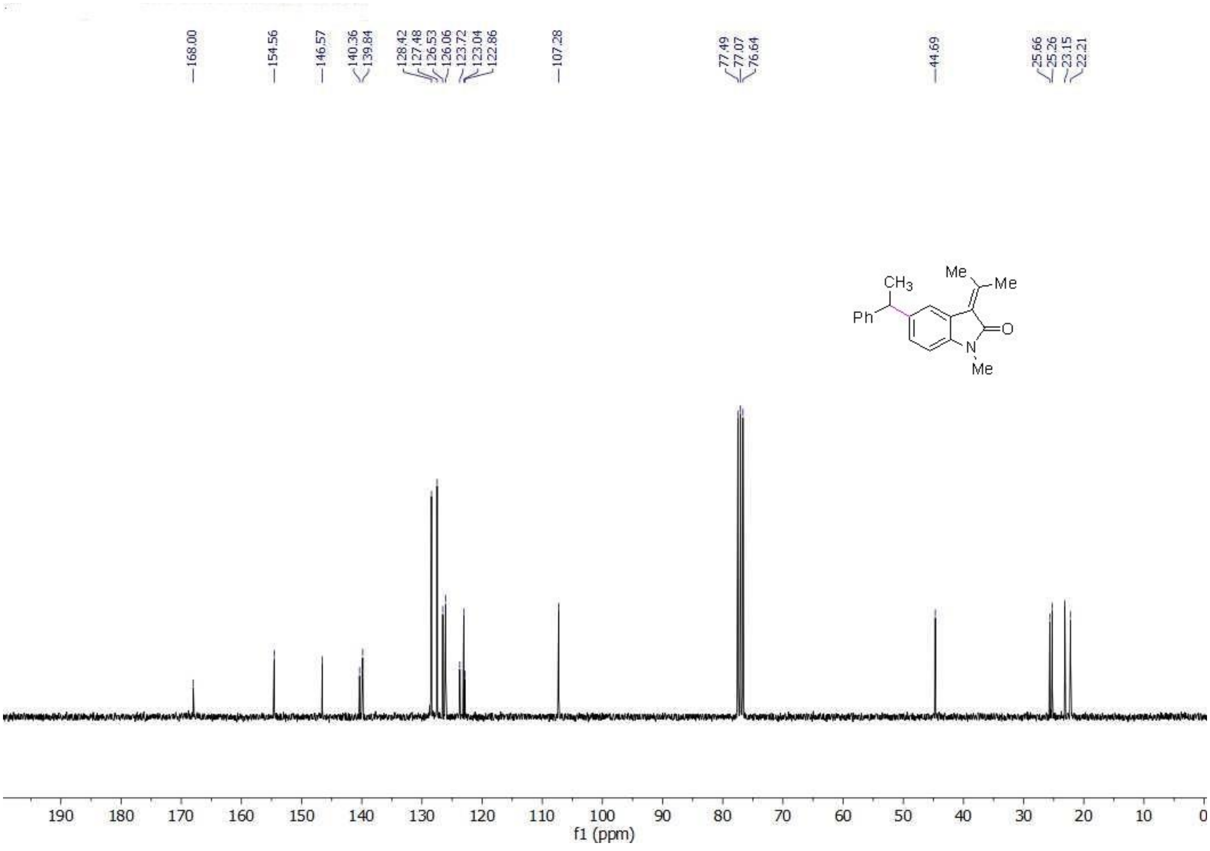
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **3ka**:



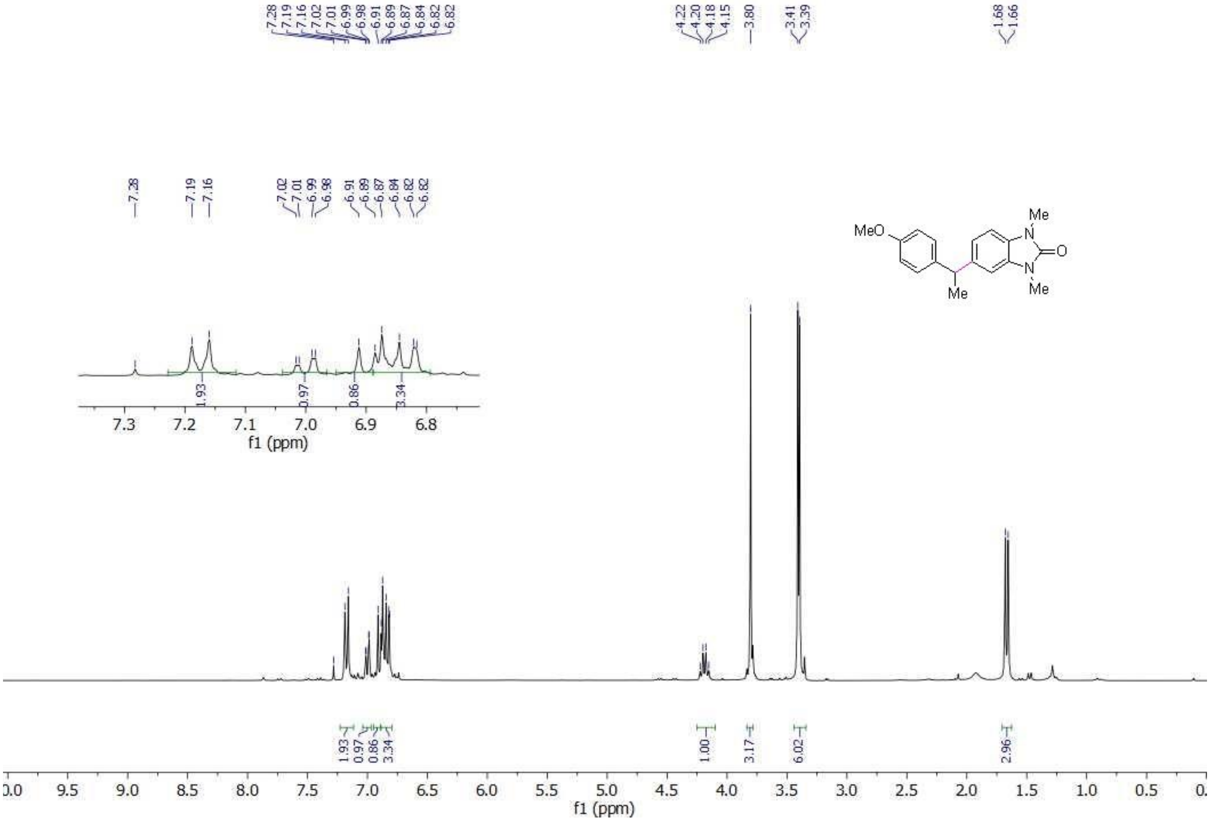


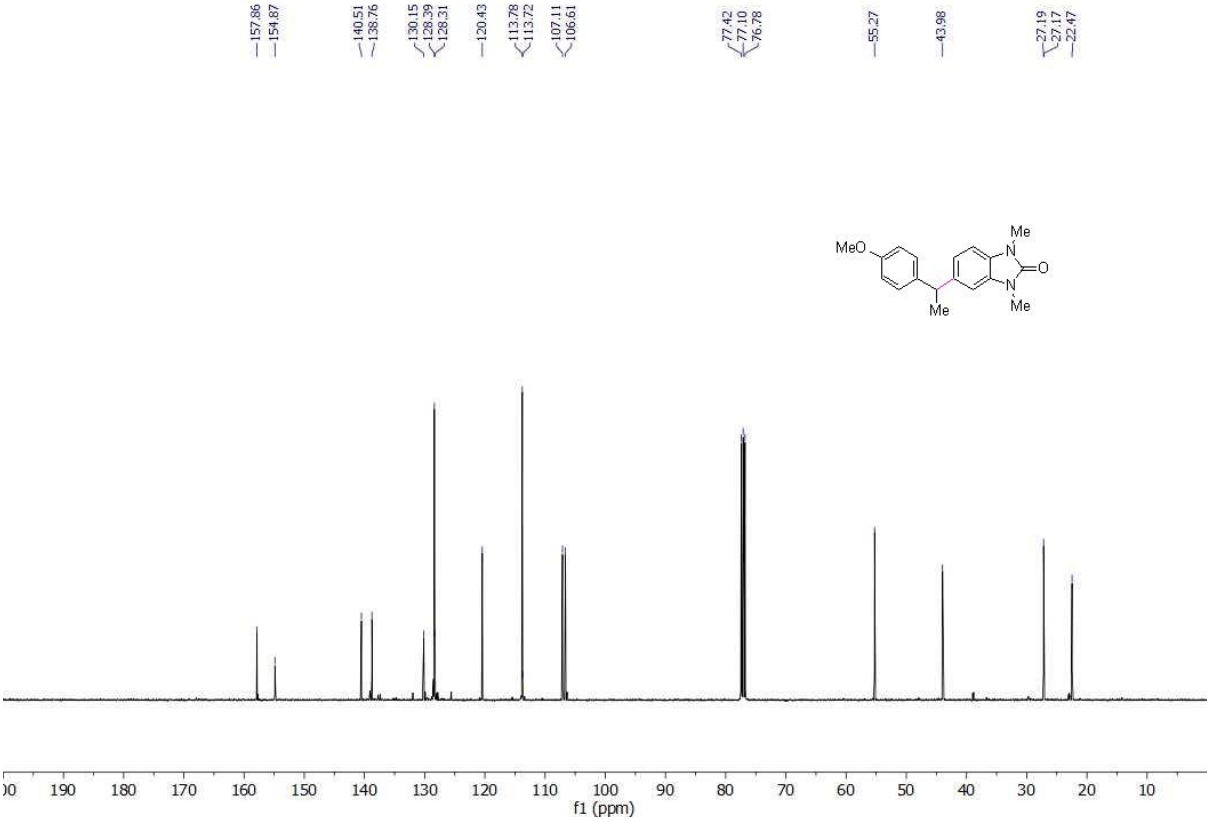
^{1}H NMR (300 MHz, $CDCl_3$) and **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **3kg**:



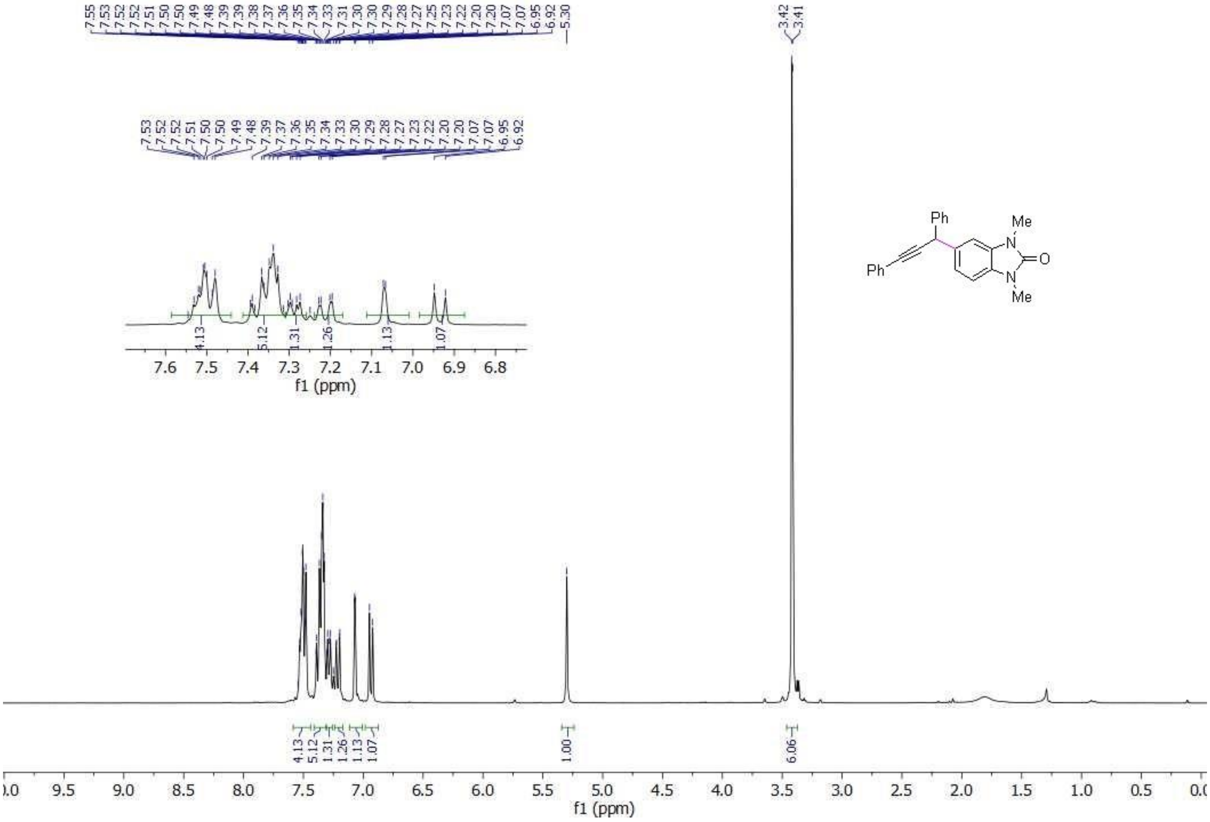


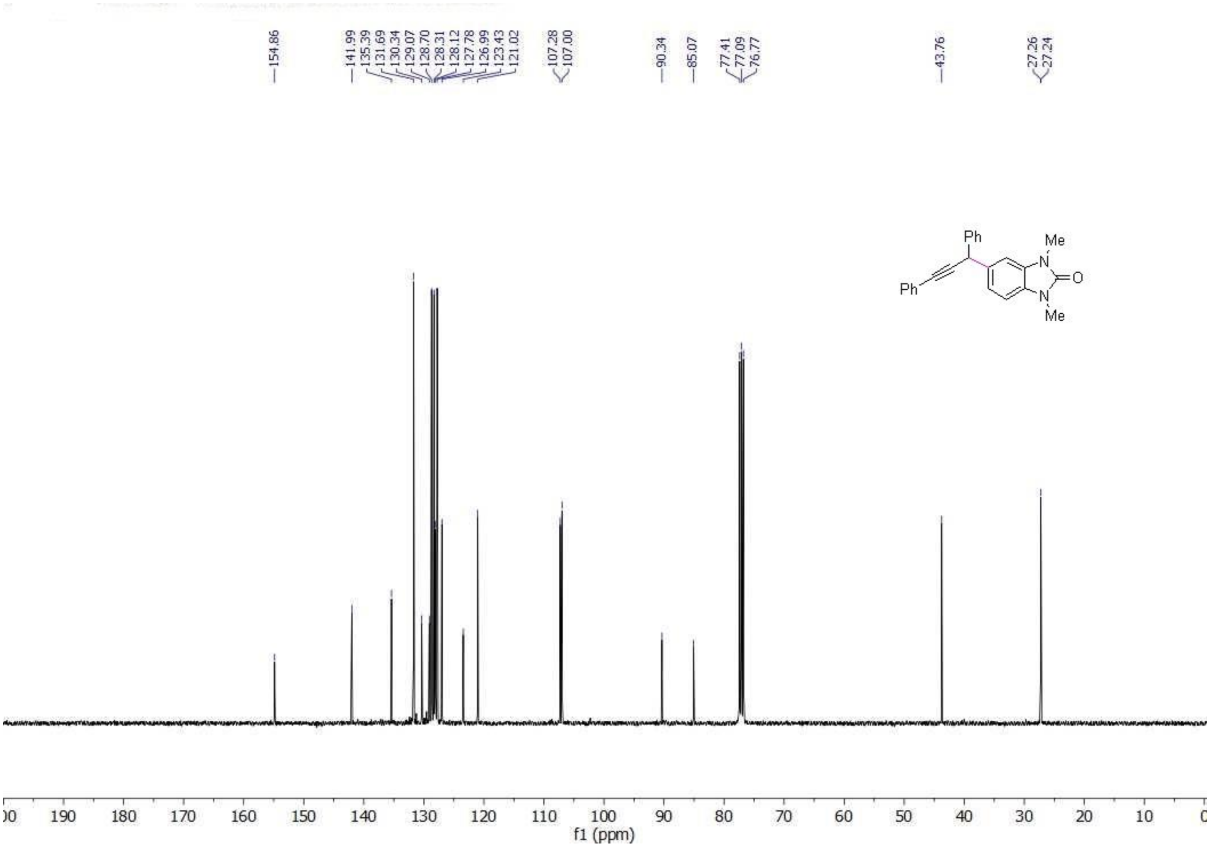
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3li**:



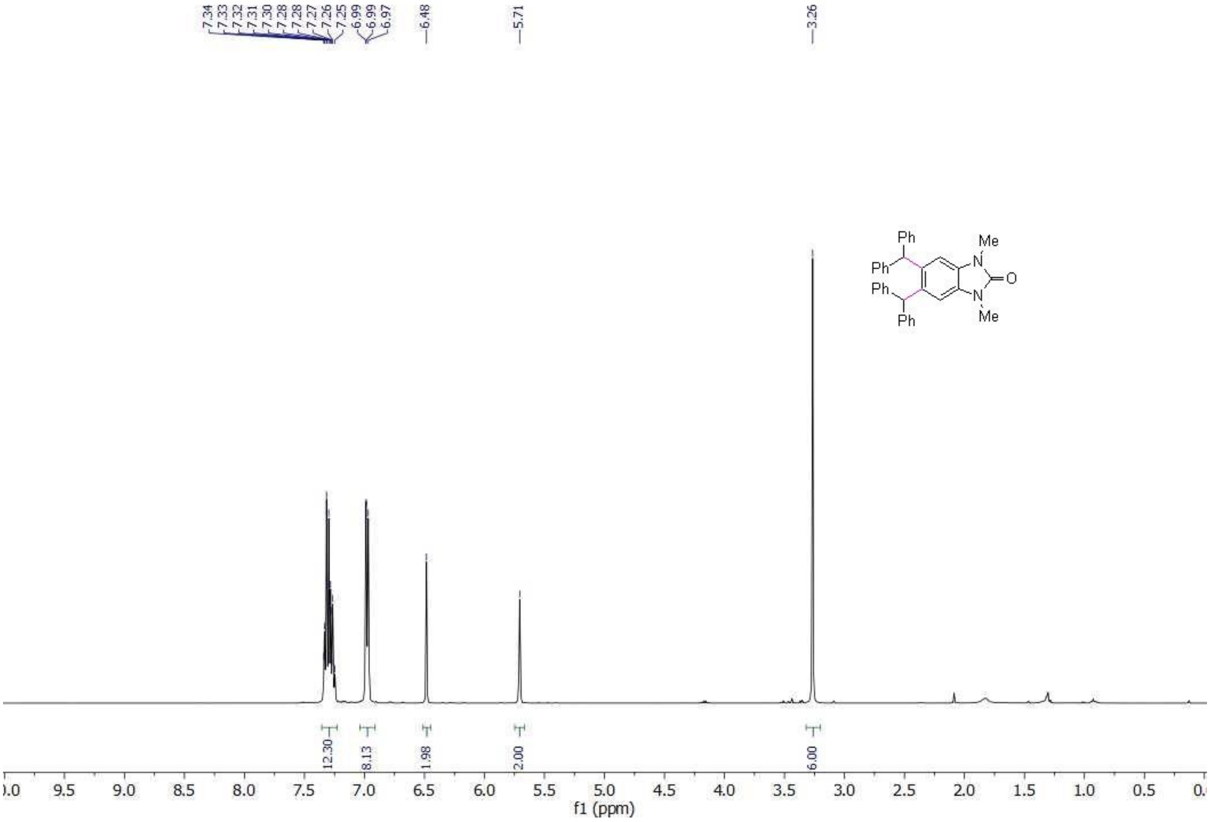


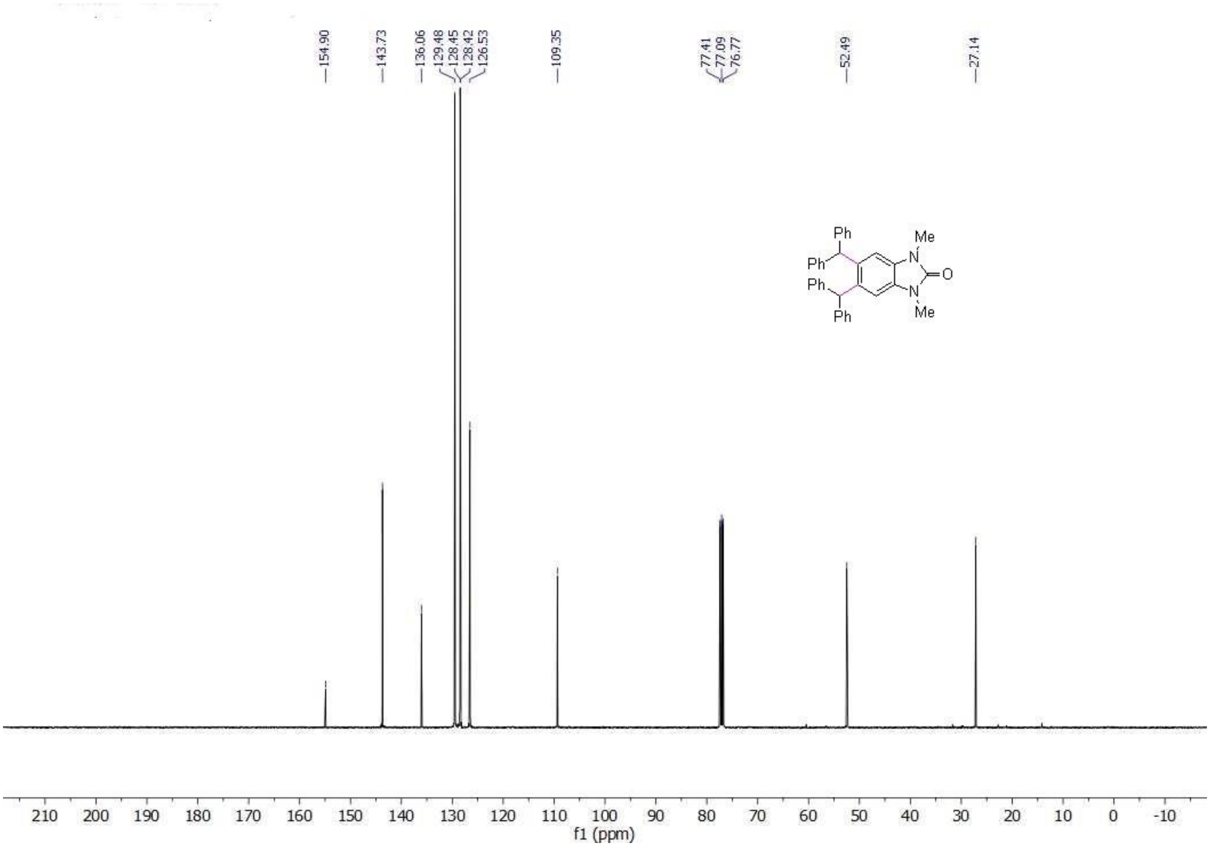
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **3lj**:



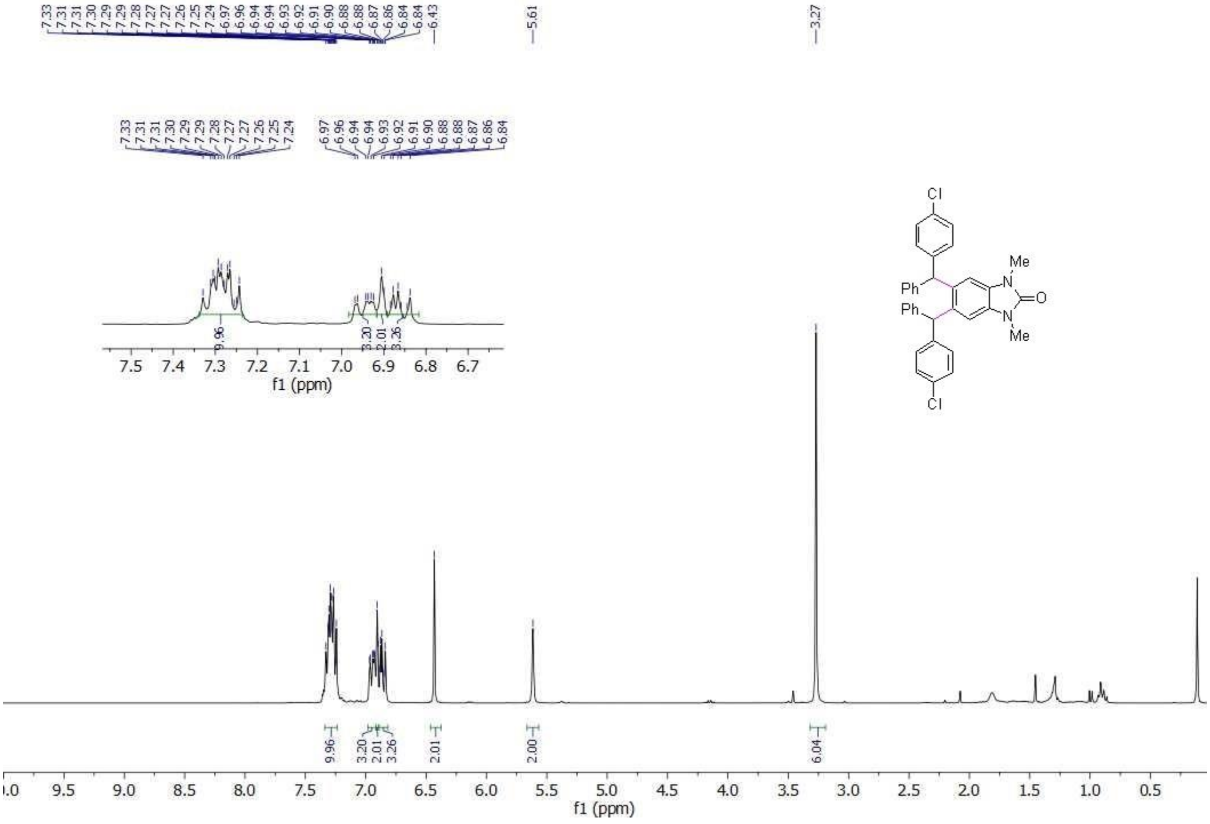


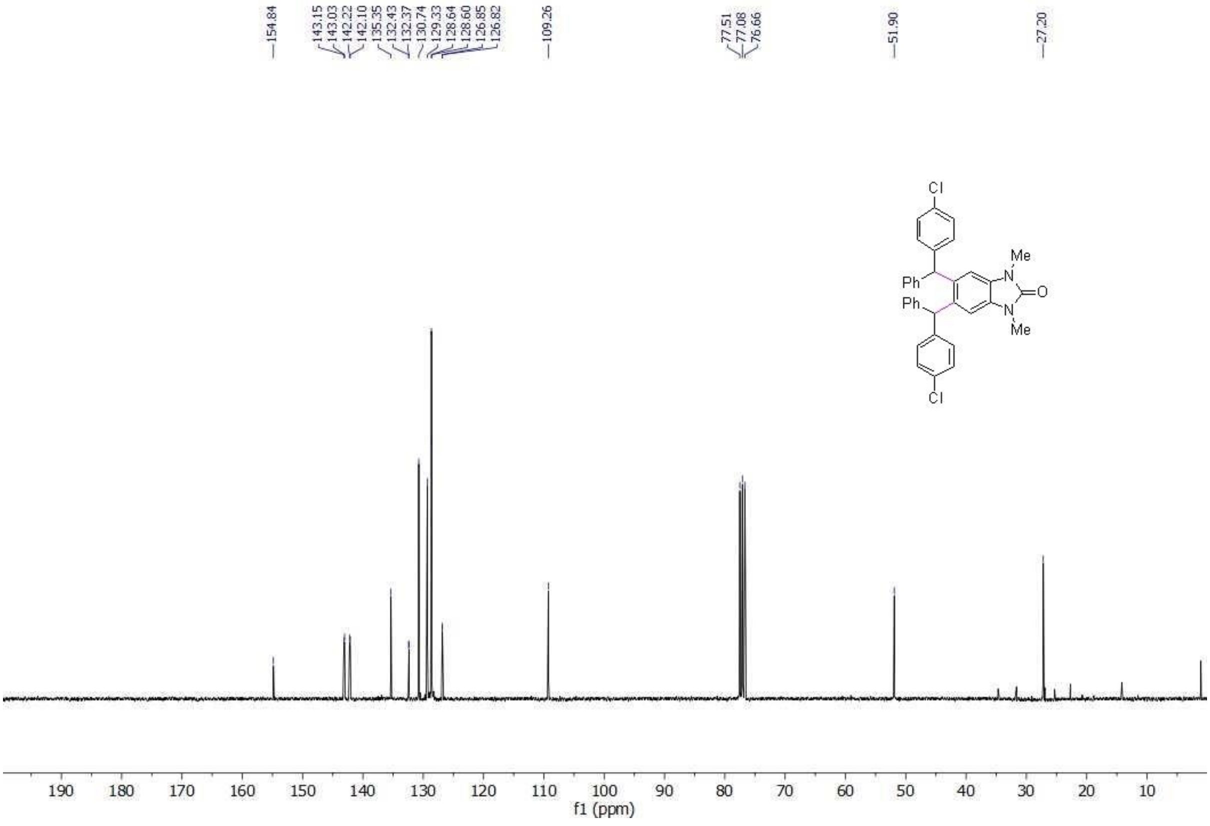
^{1}**H NMR** (400 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3la**:



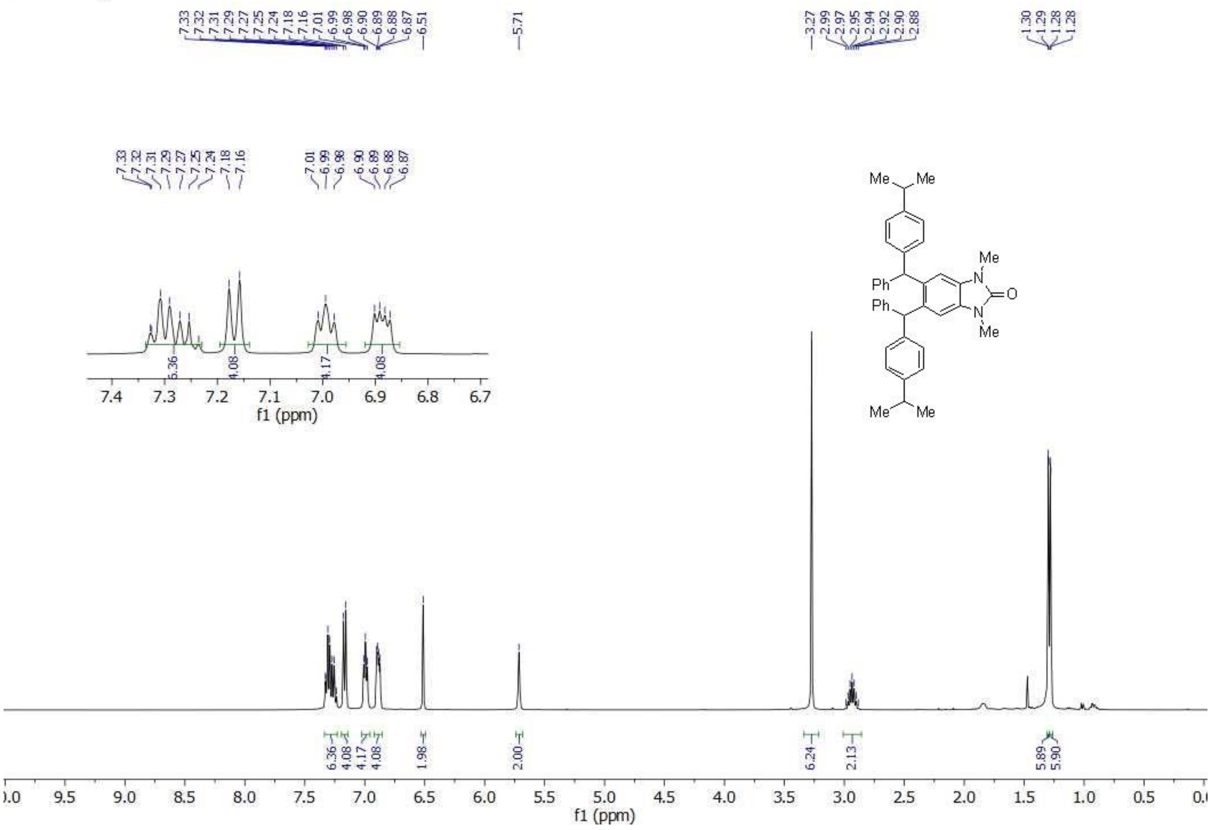


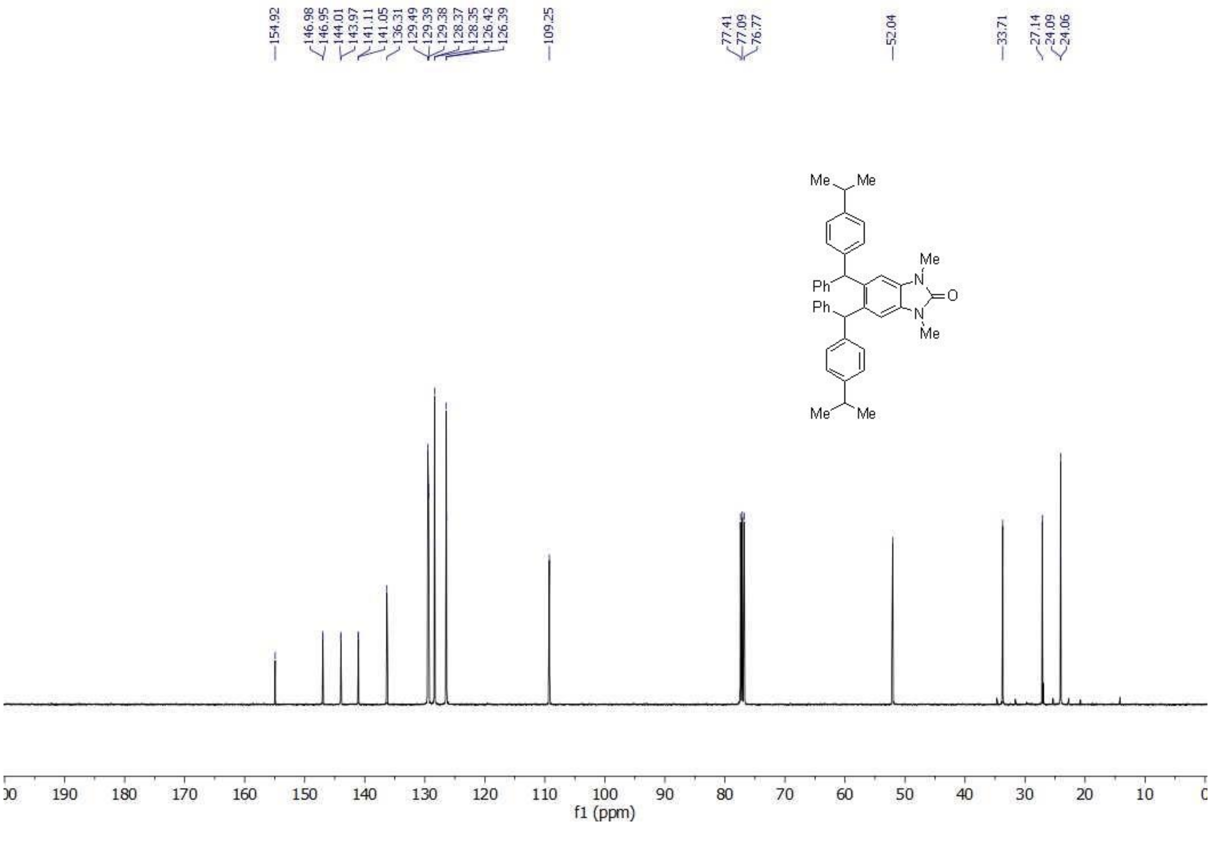
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **3lb**:



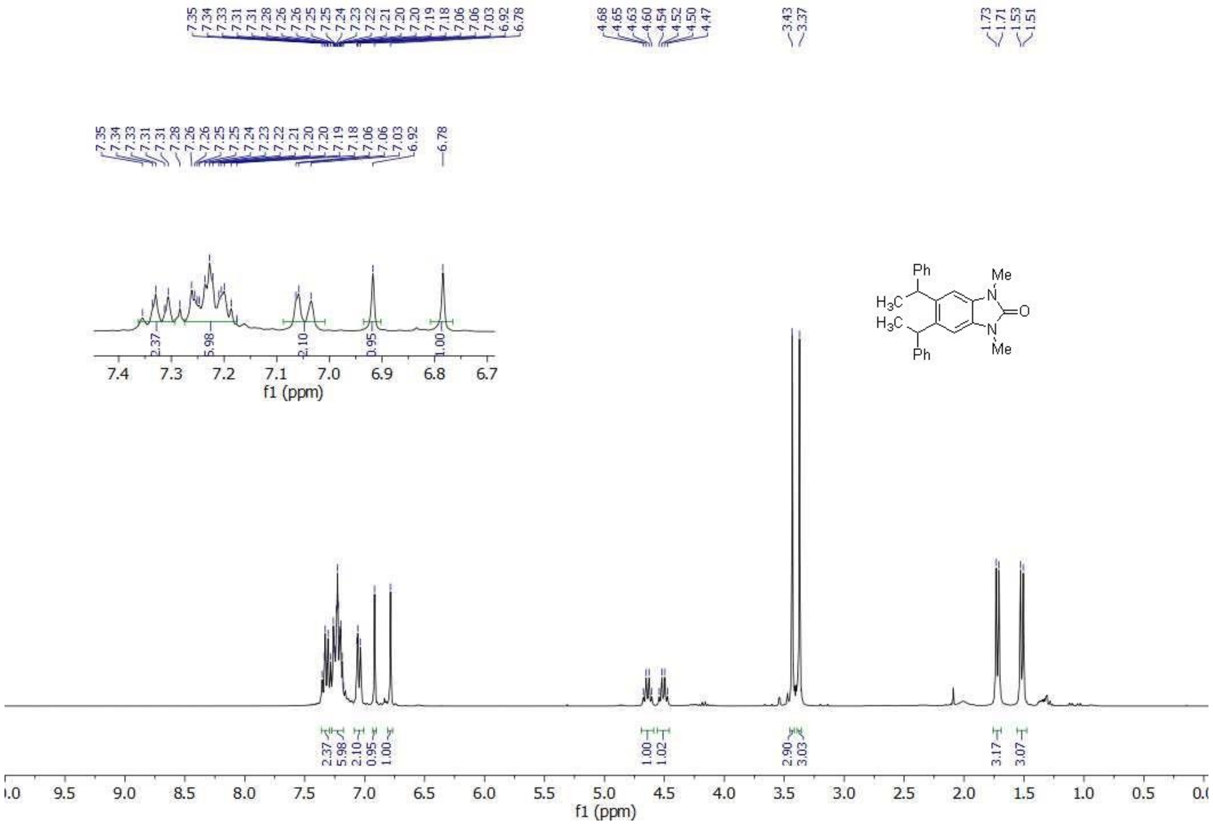


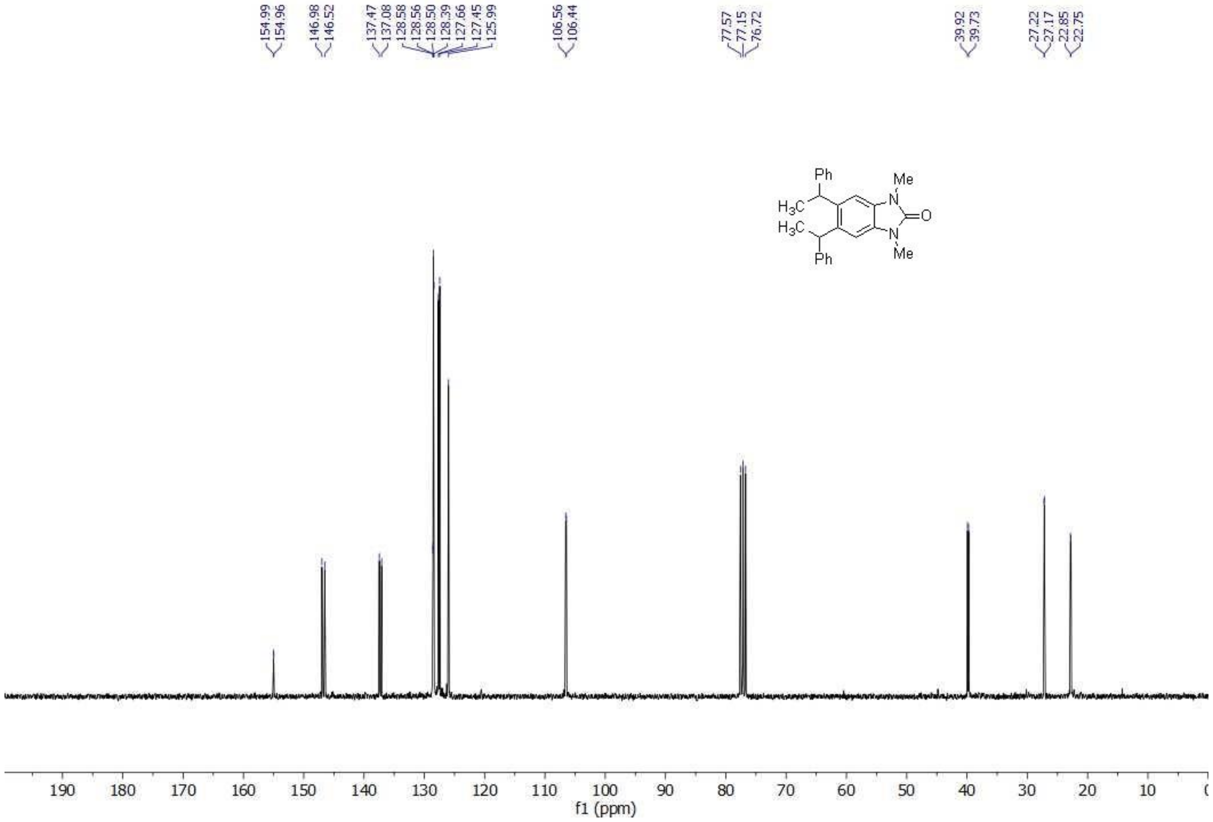
^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **3lc**:



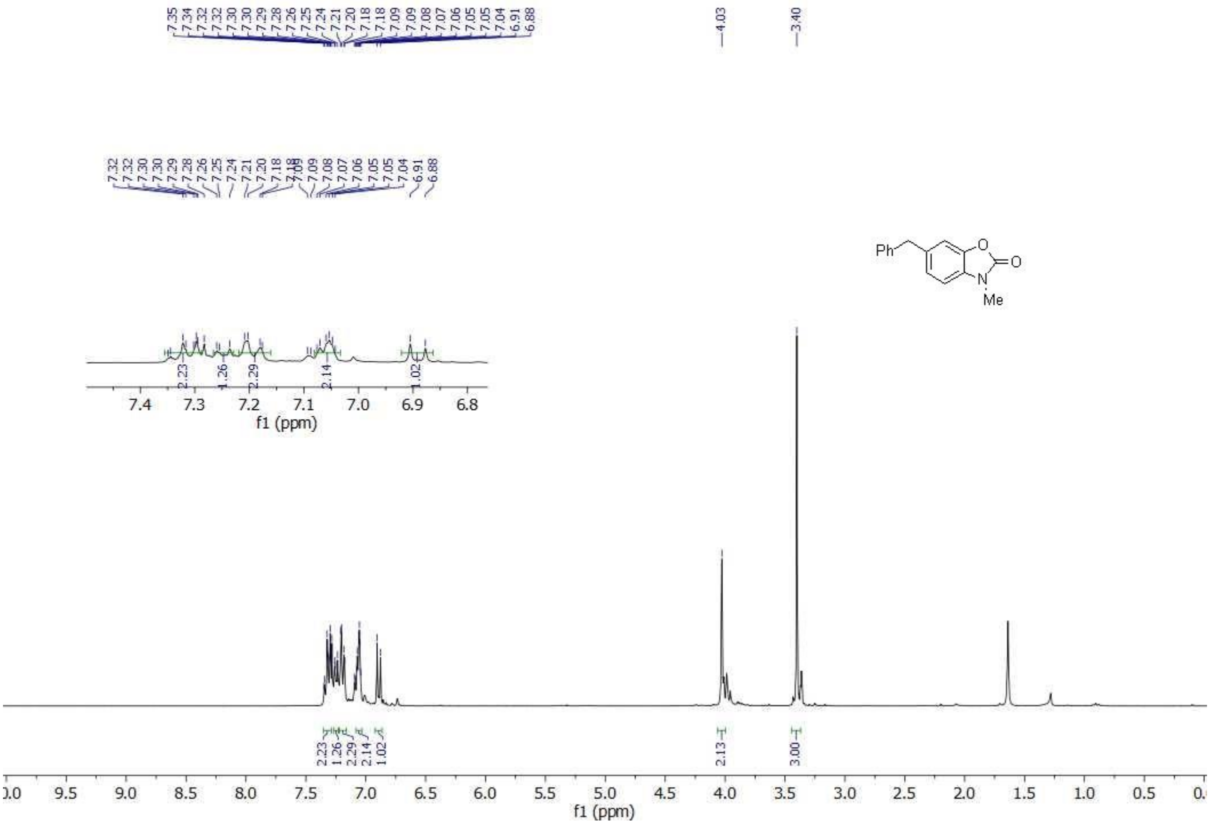


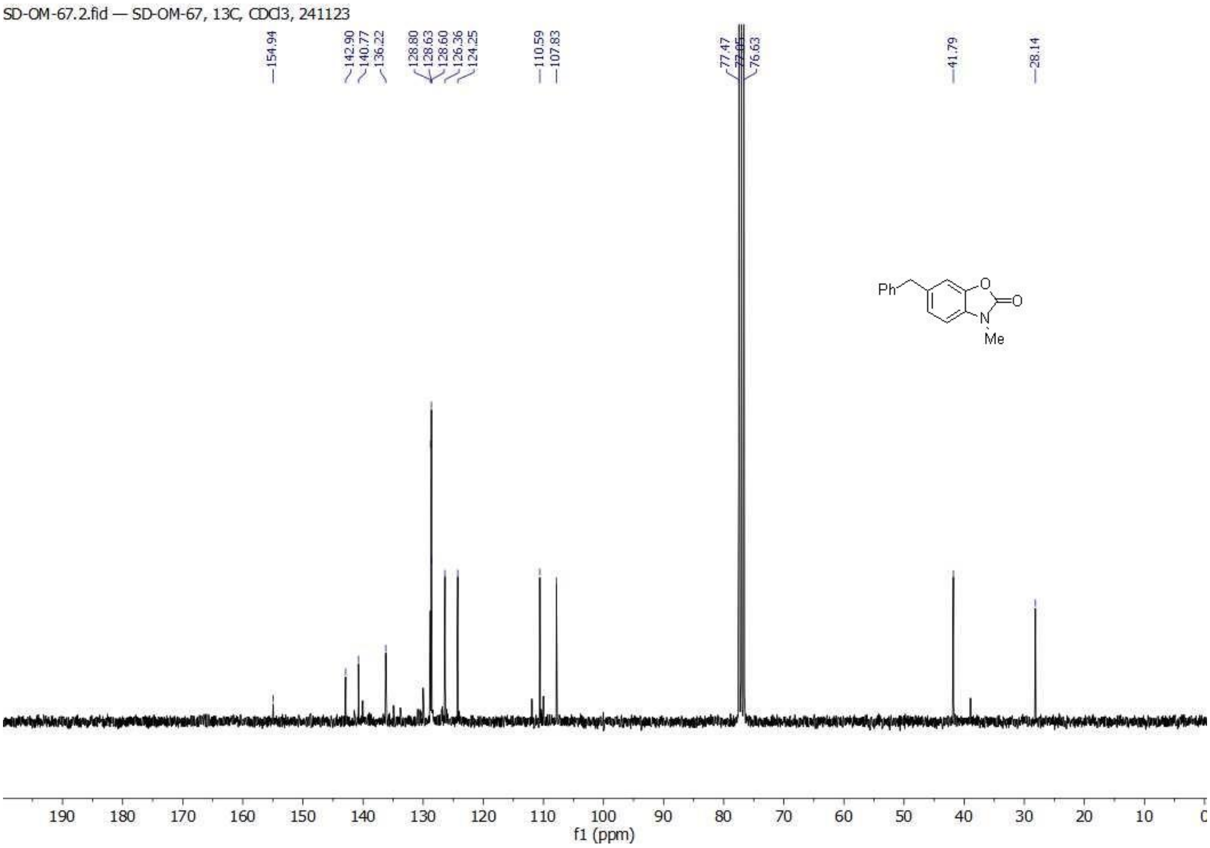
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **3lg**:



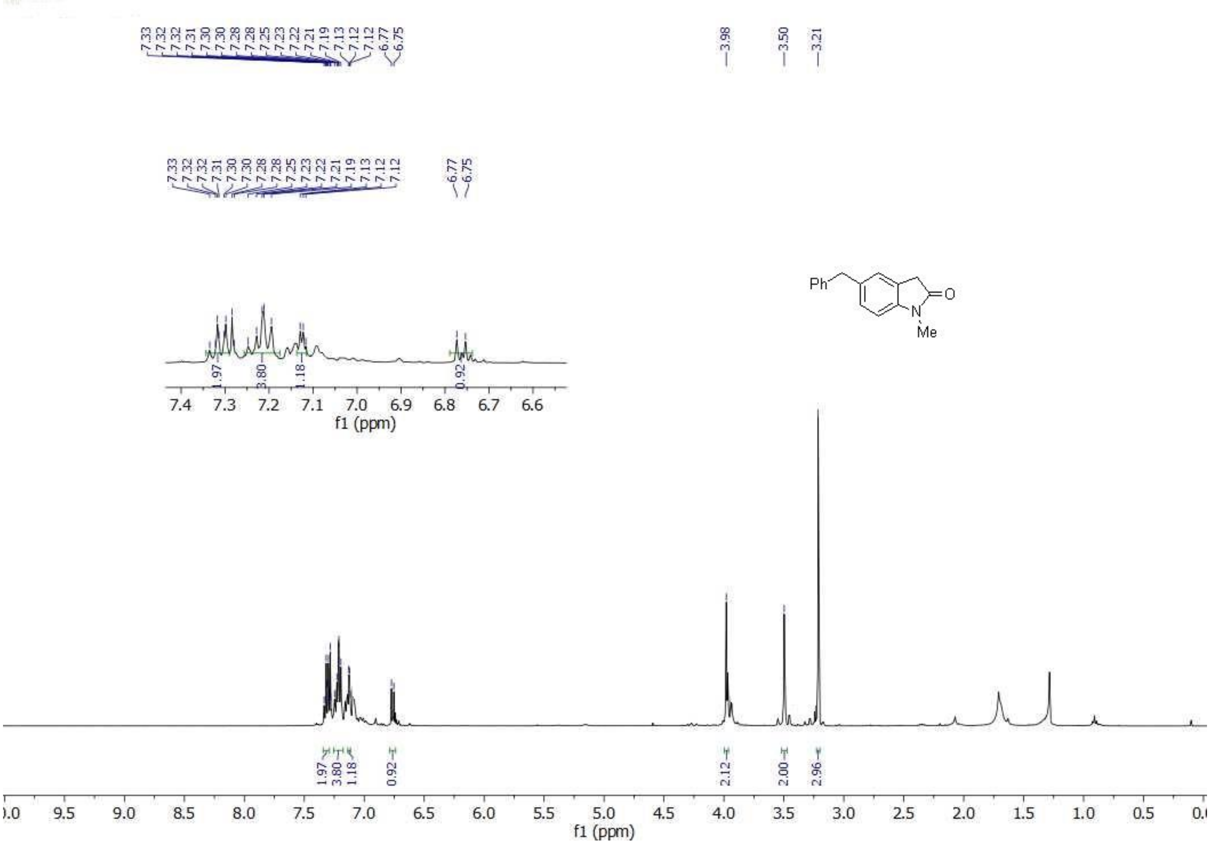


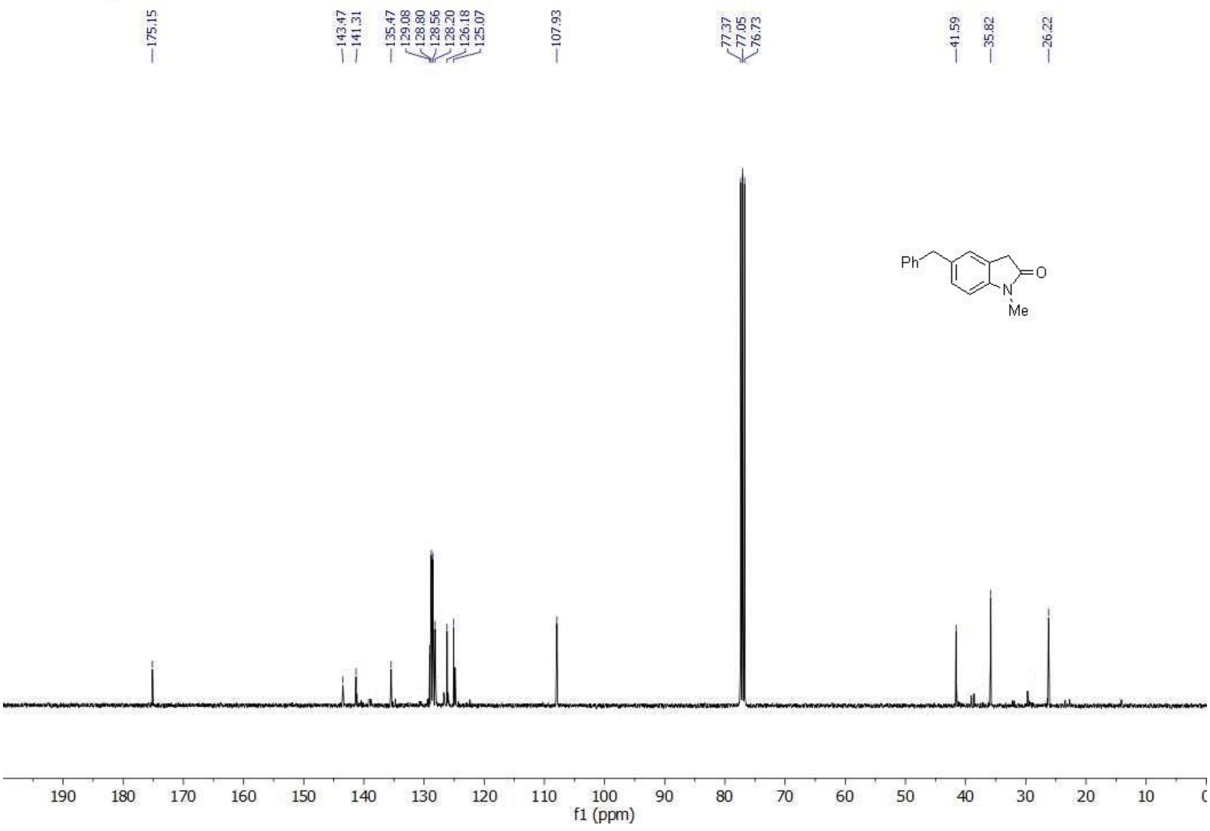
^{1}H NMR (300 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) spectra of **3am**:



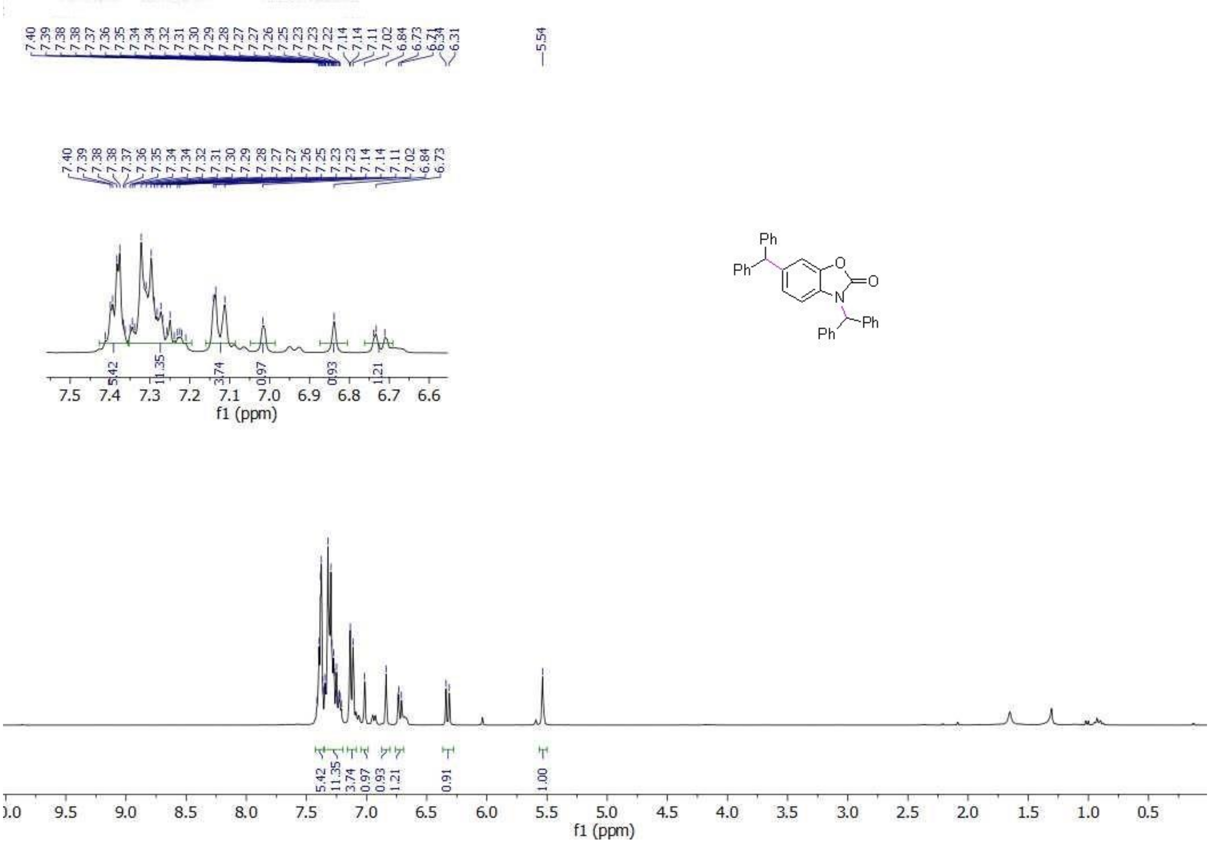


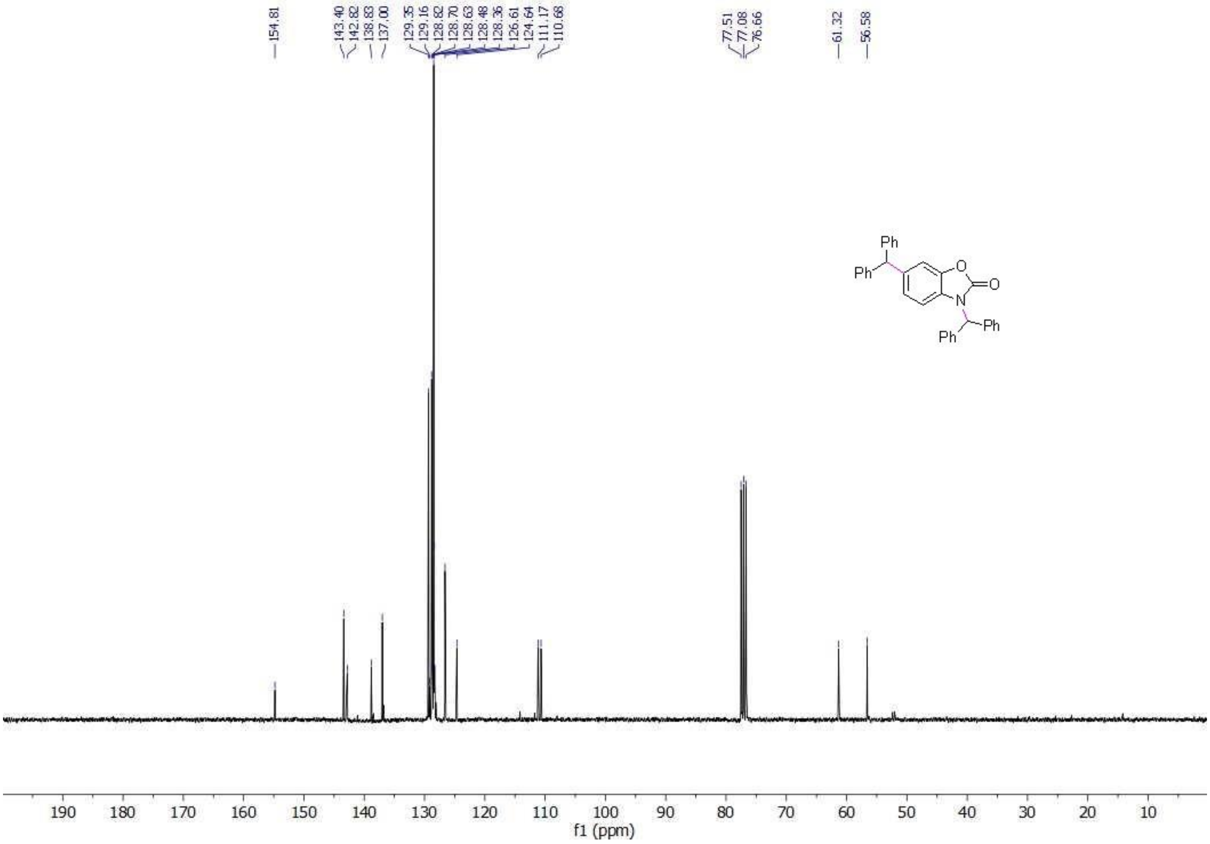
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **3jm**:



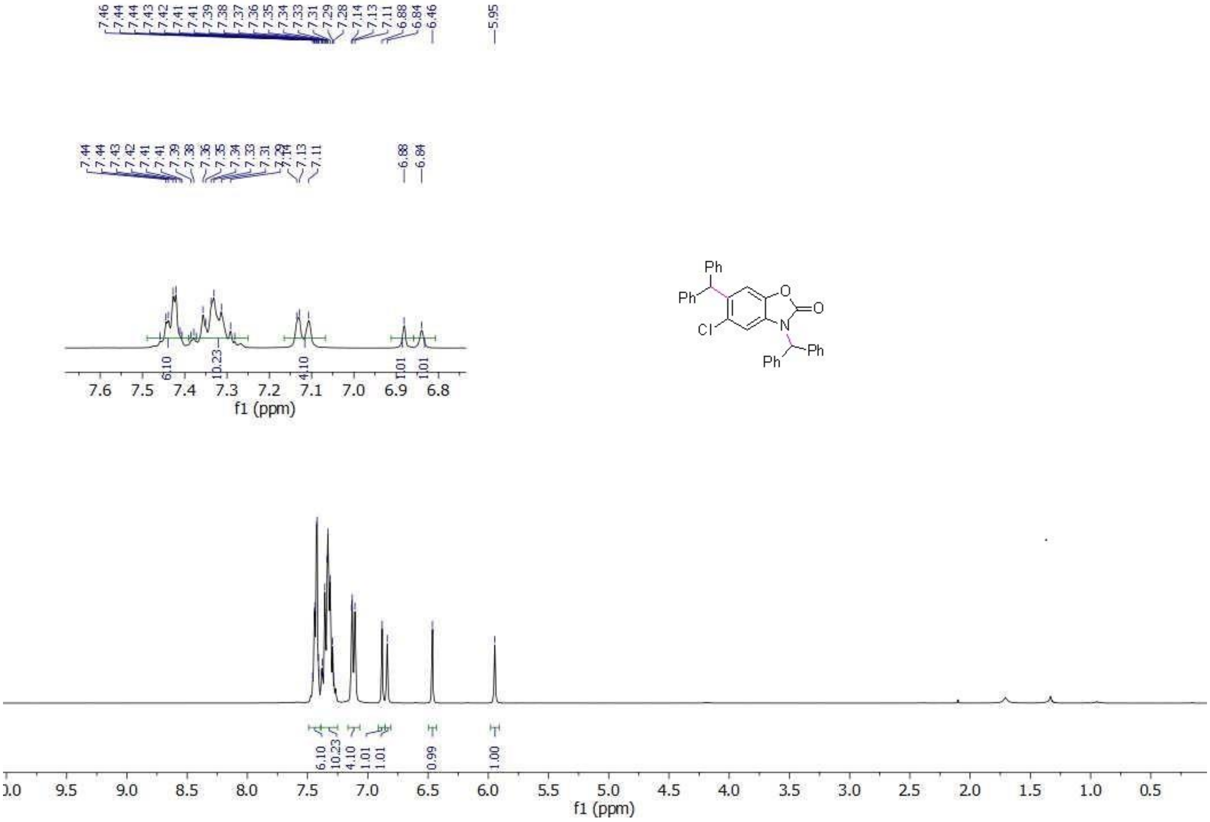


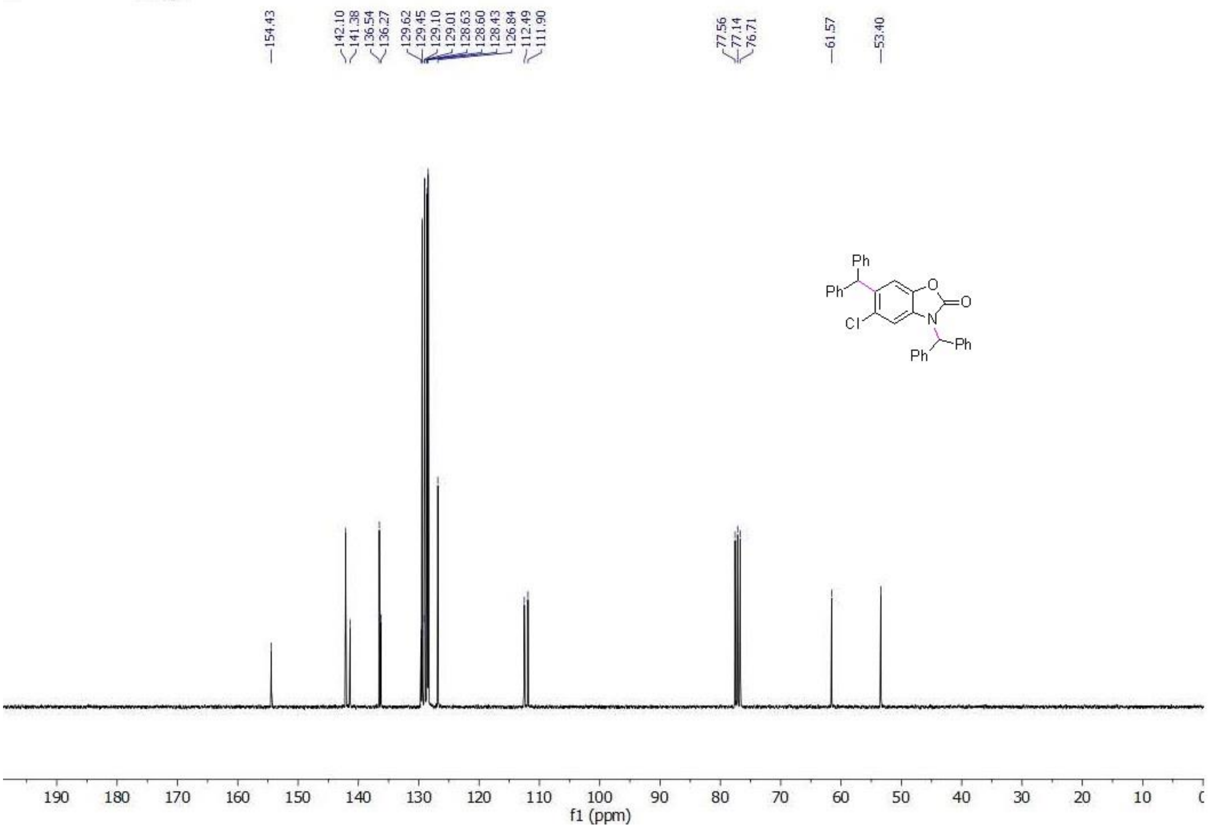
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **4a**:



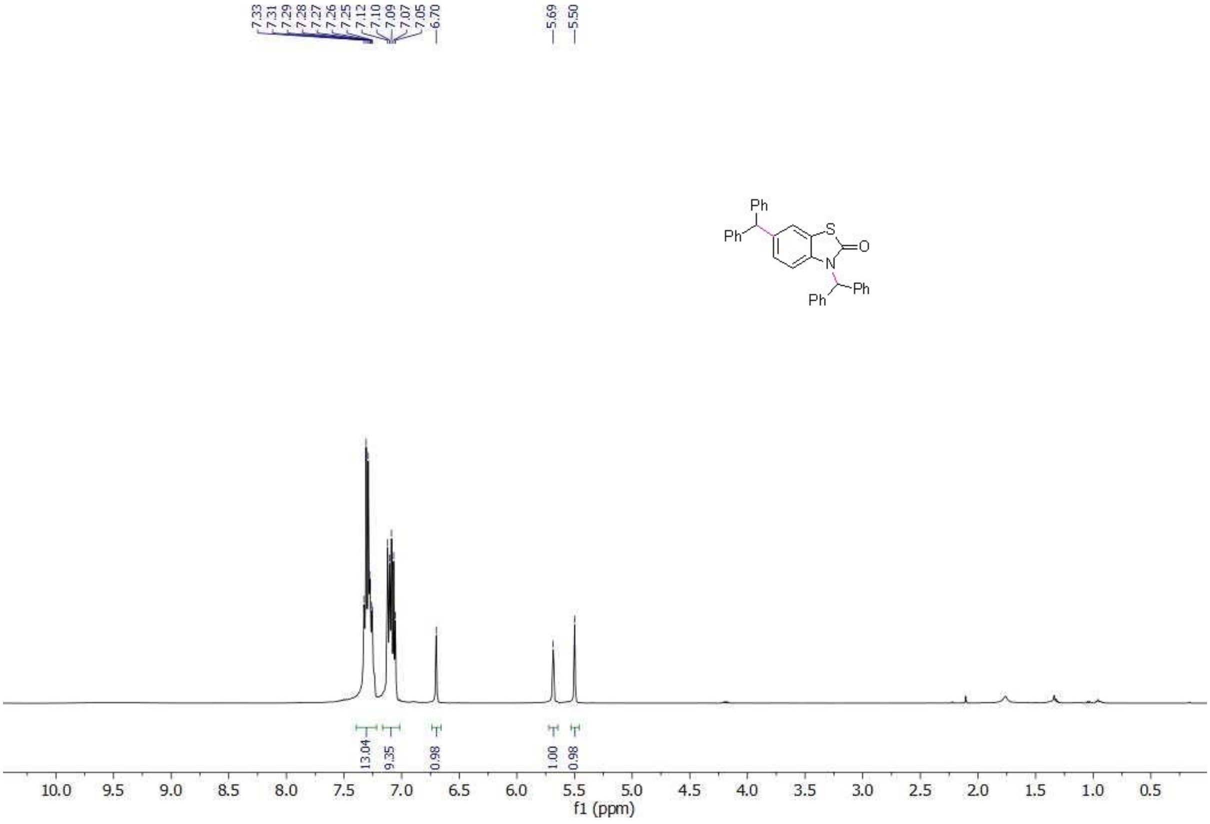


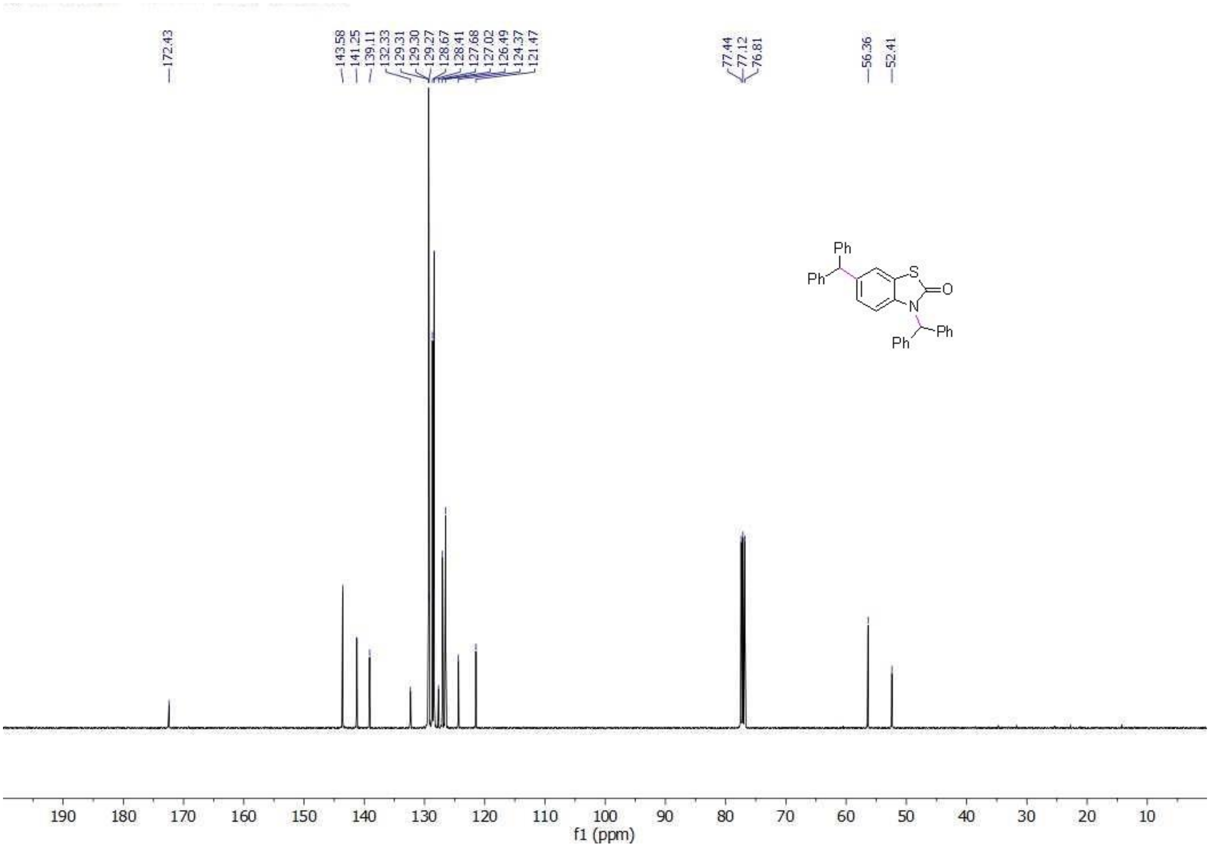
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **4b**:



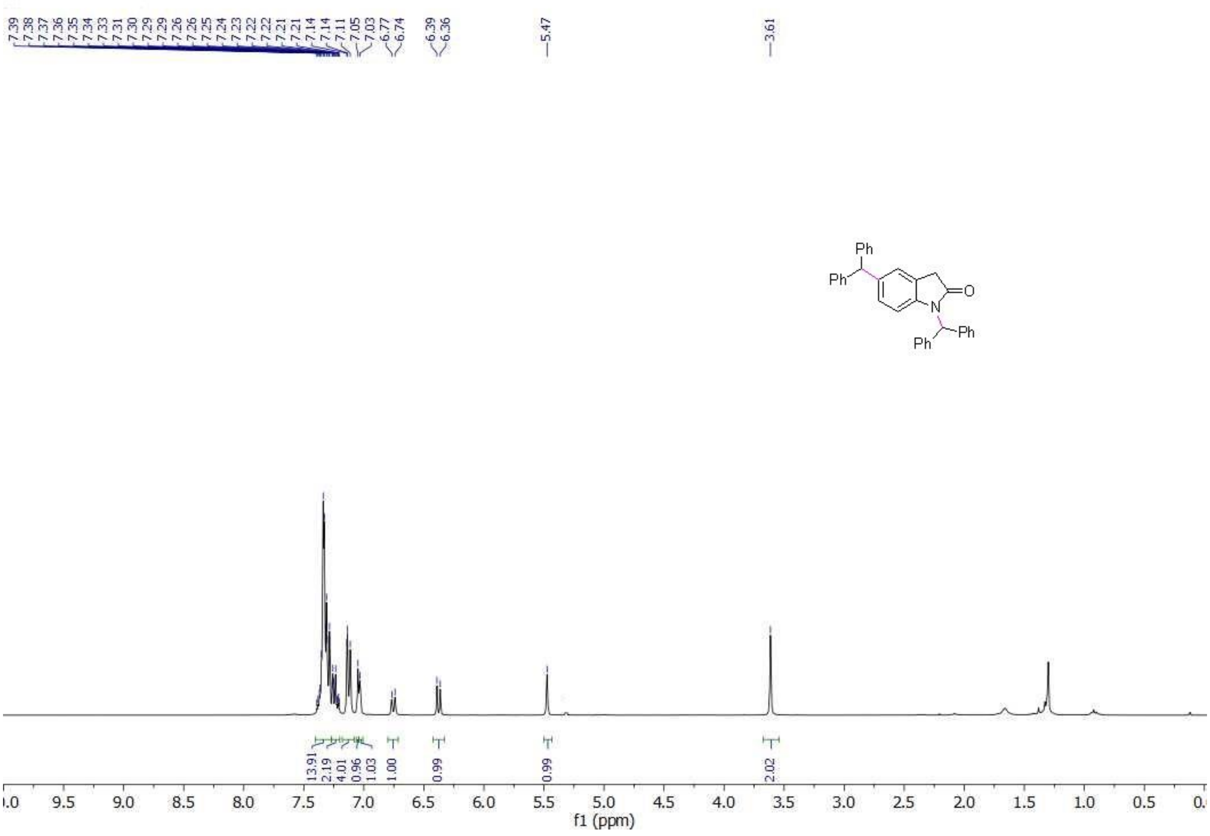


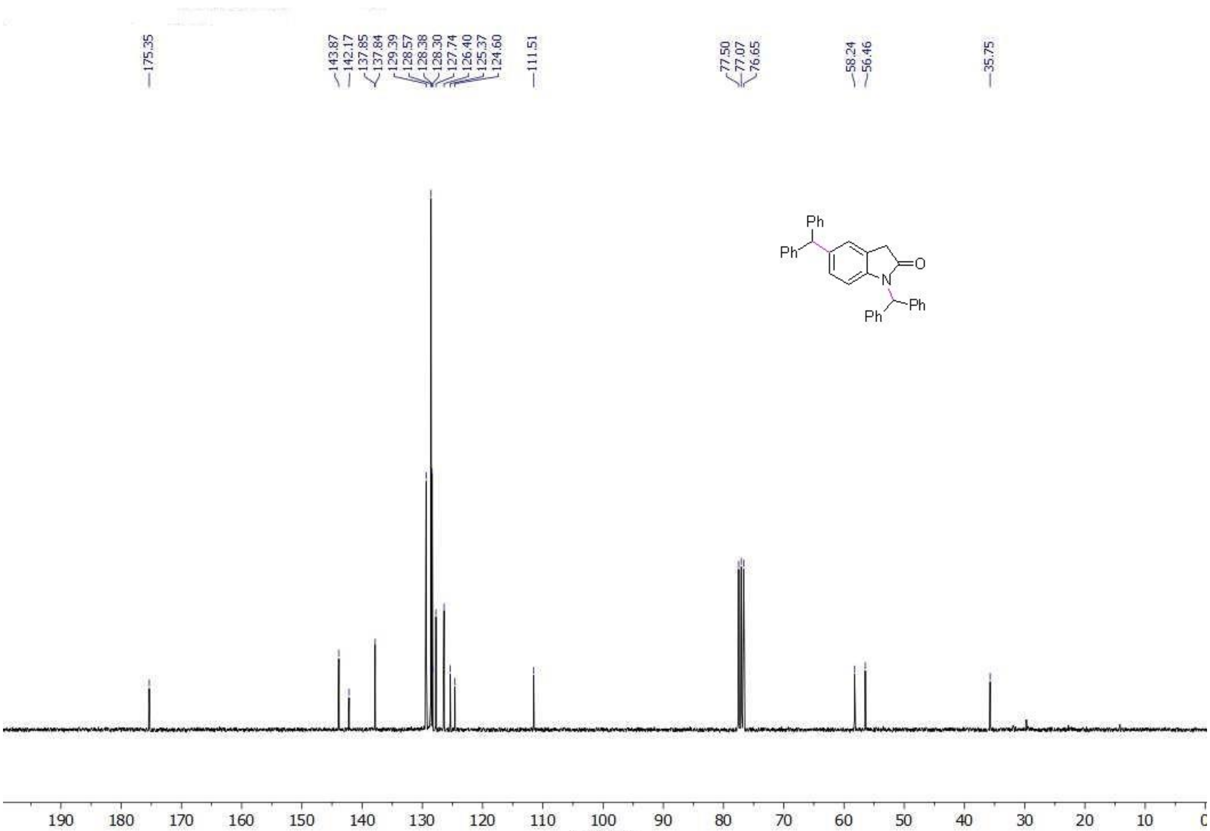
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **4c**:



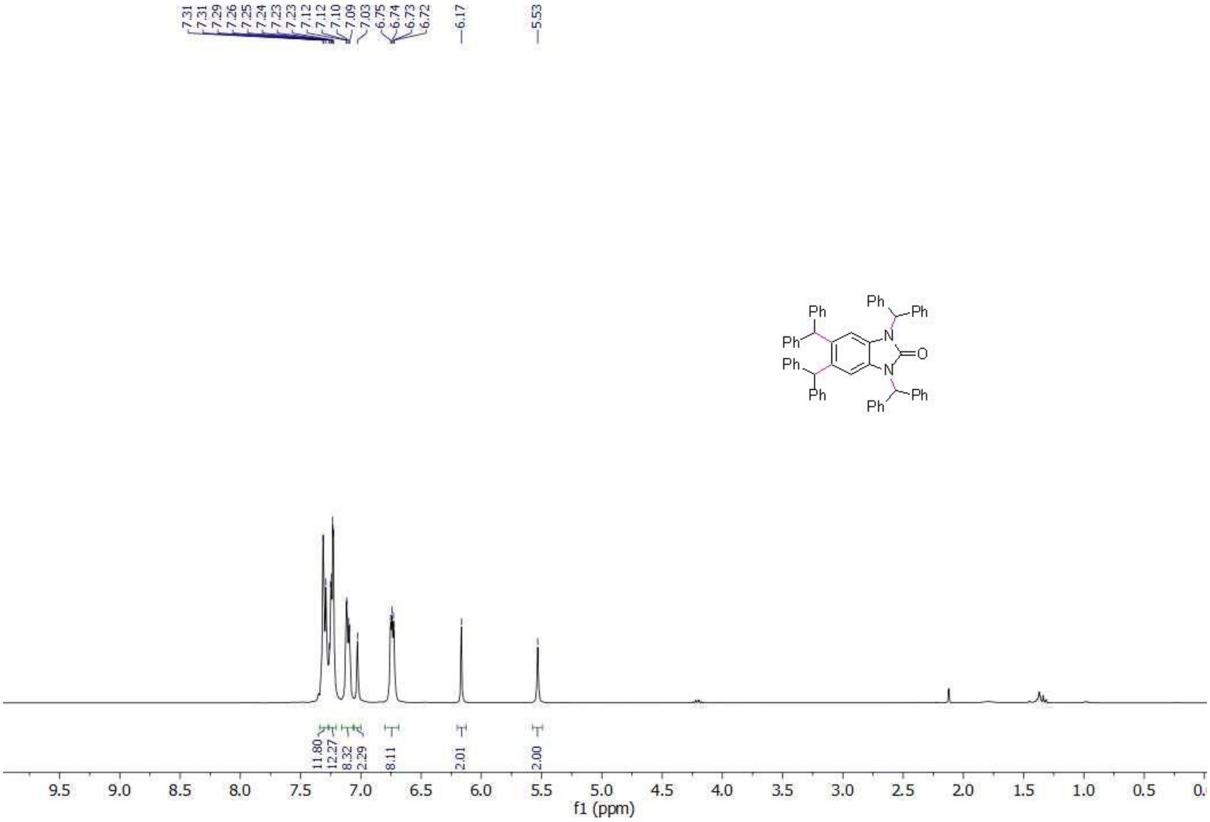


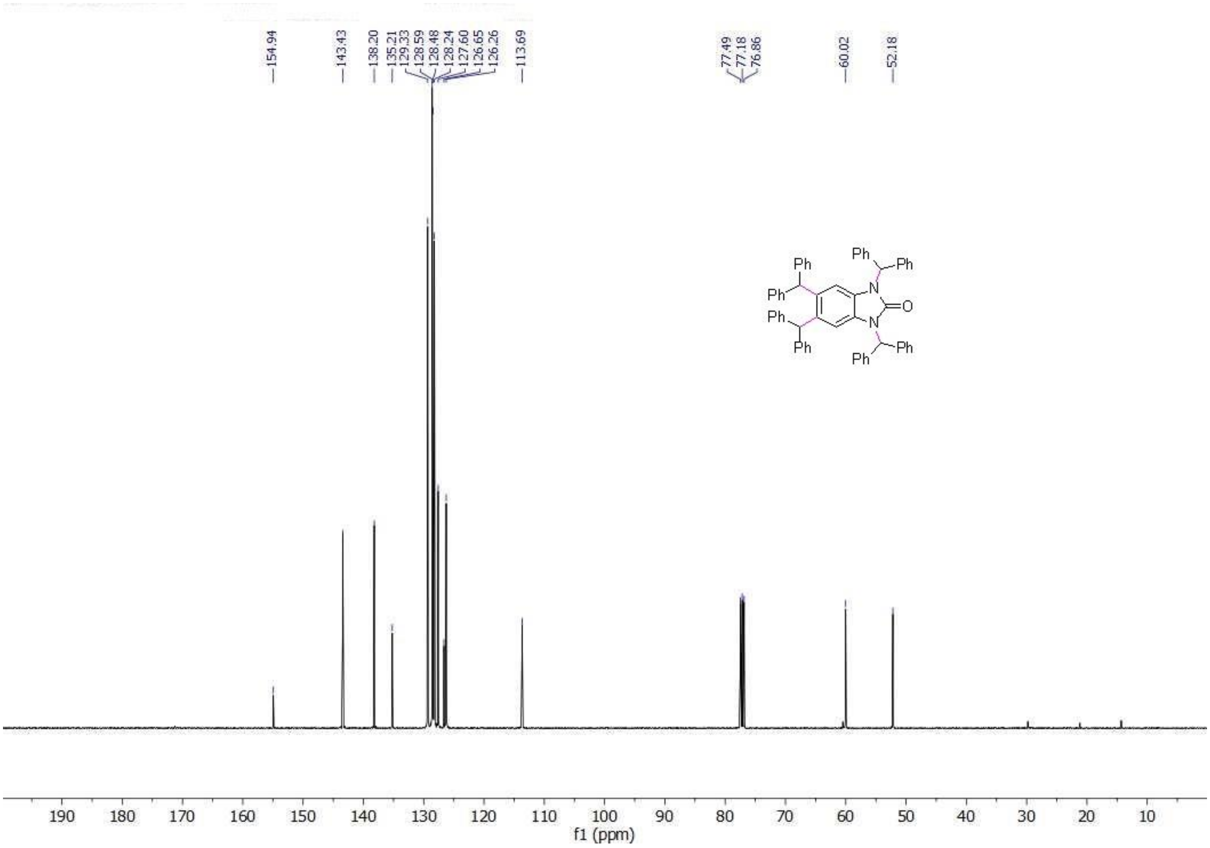
^{1}H NMR (300 MHz, $CDCl_3$) and **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **4d**:



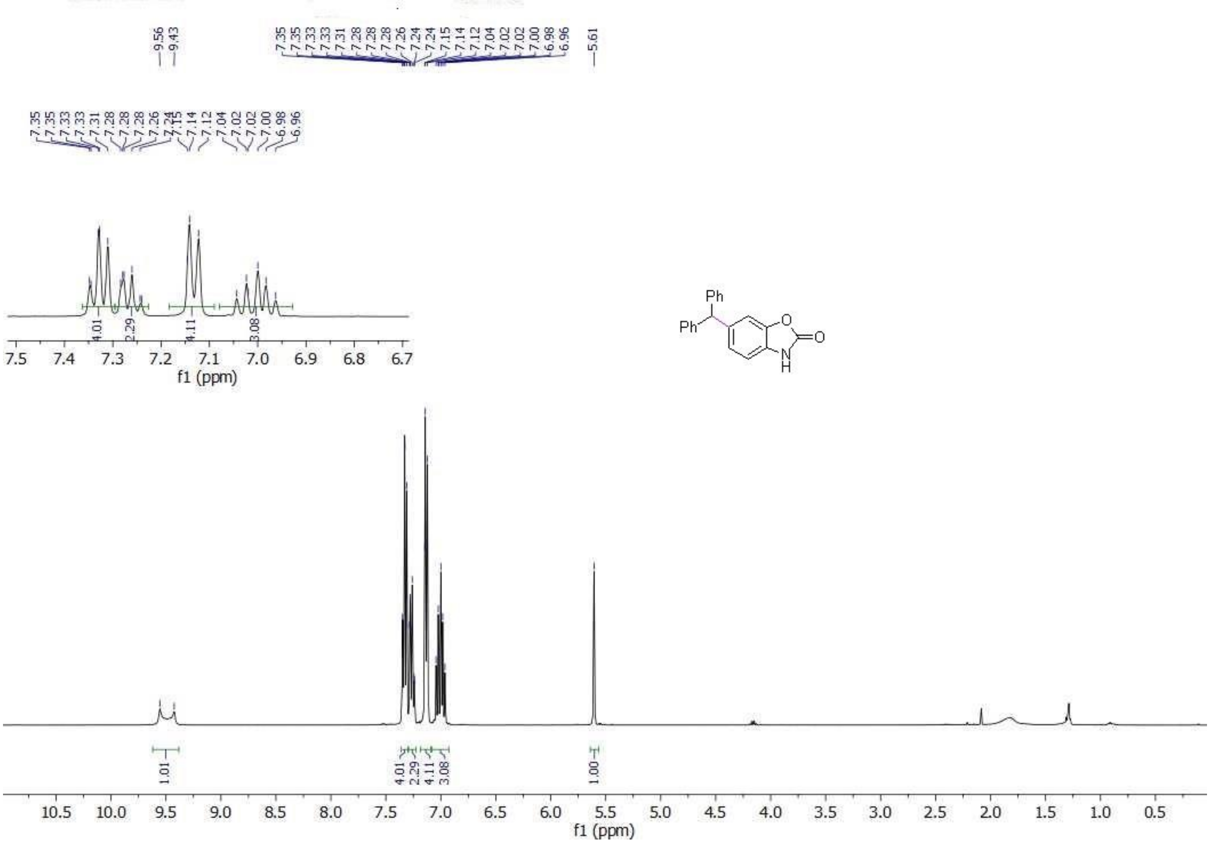


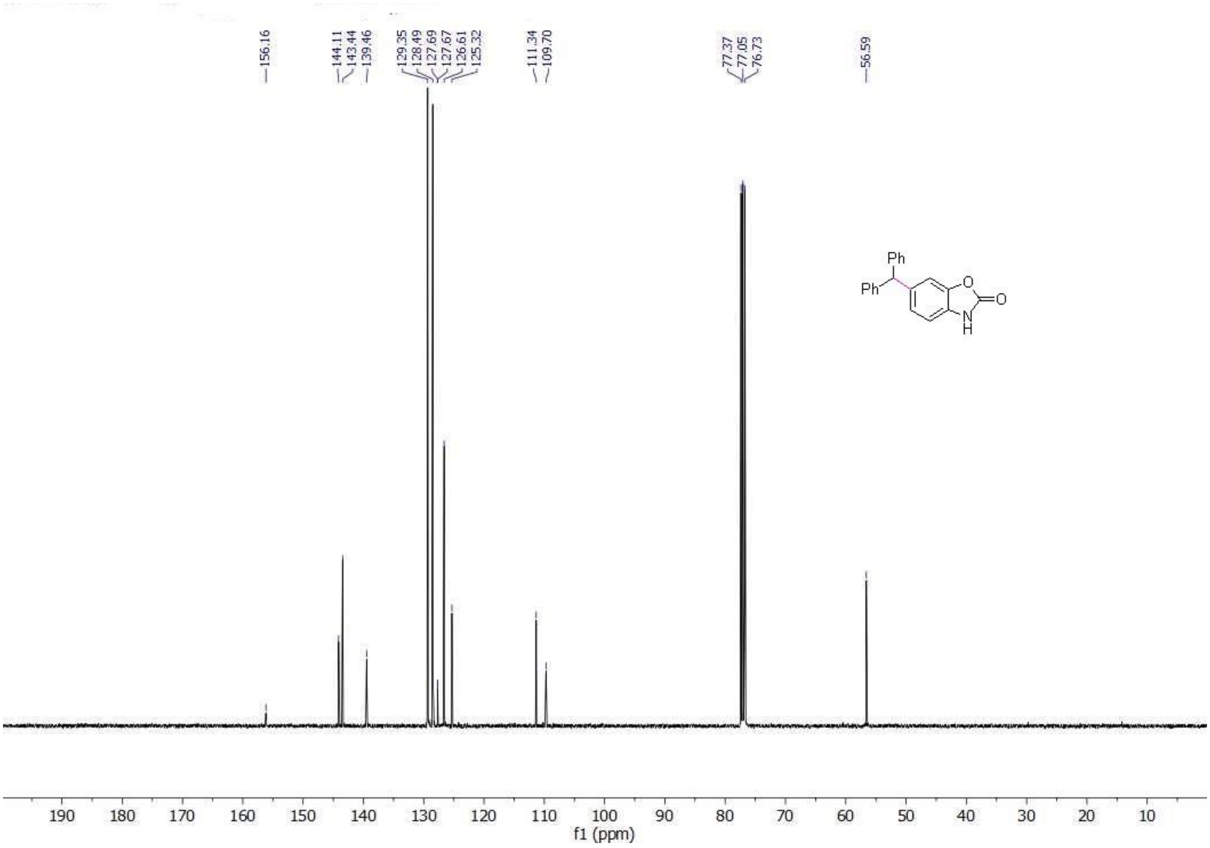
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **4e**:



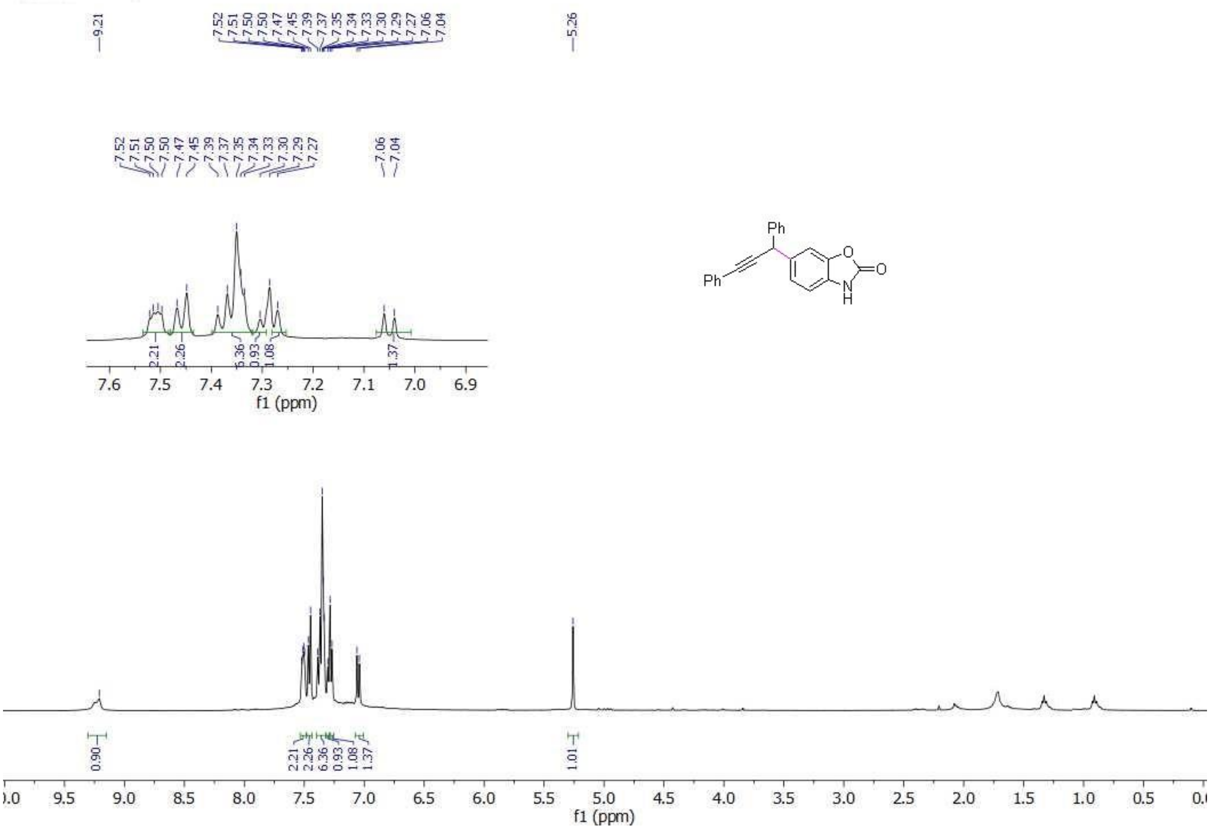


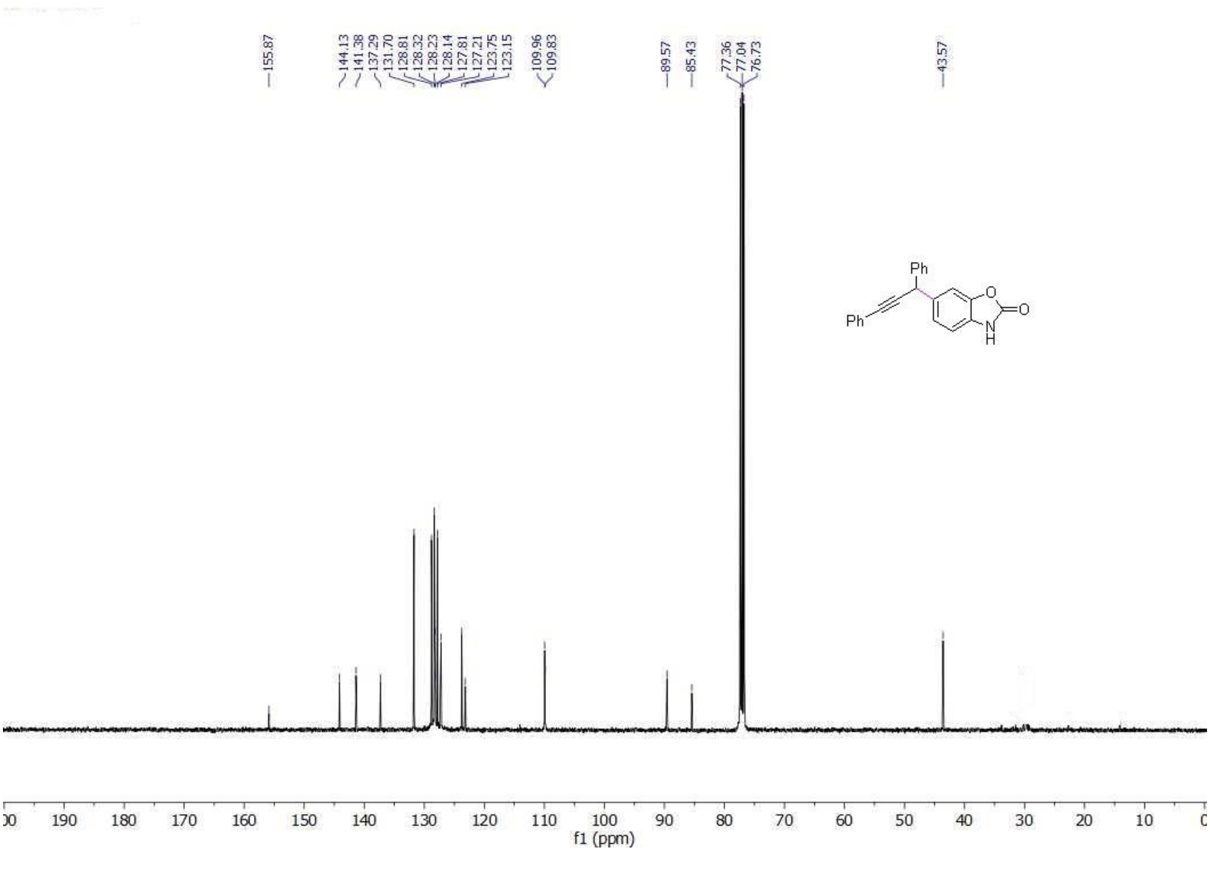
^{1}H NMR (400 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) spectra of **5a**:



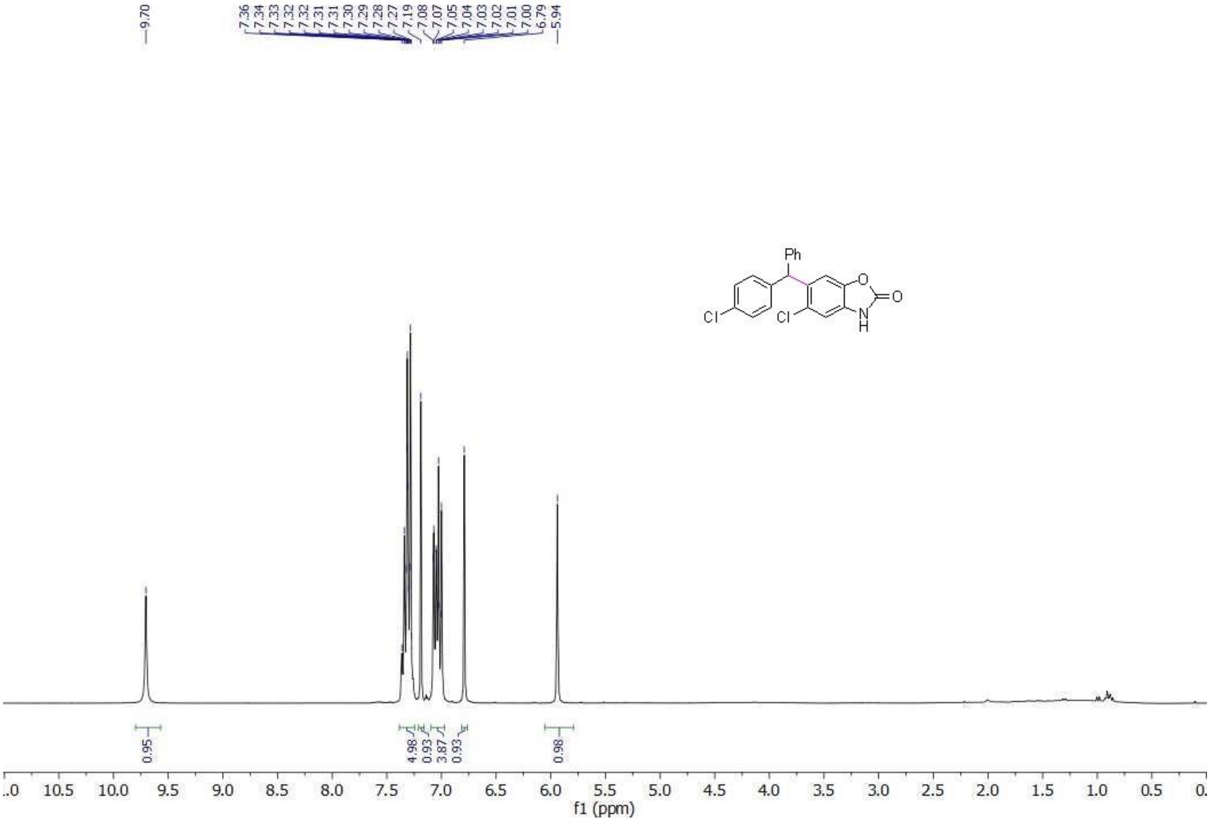


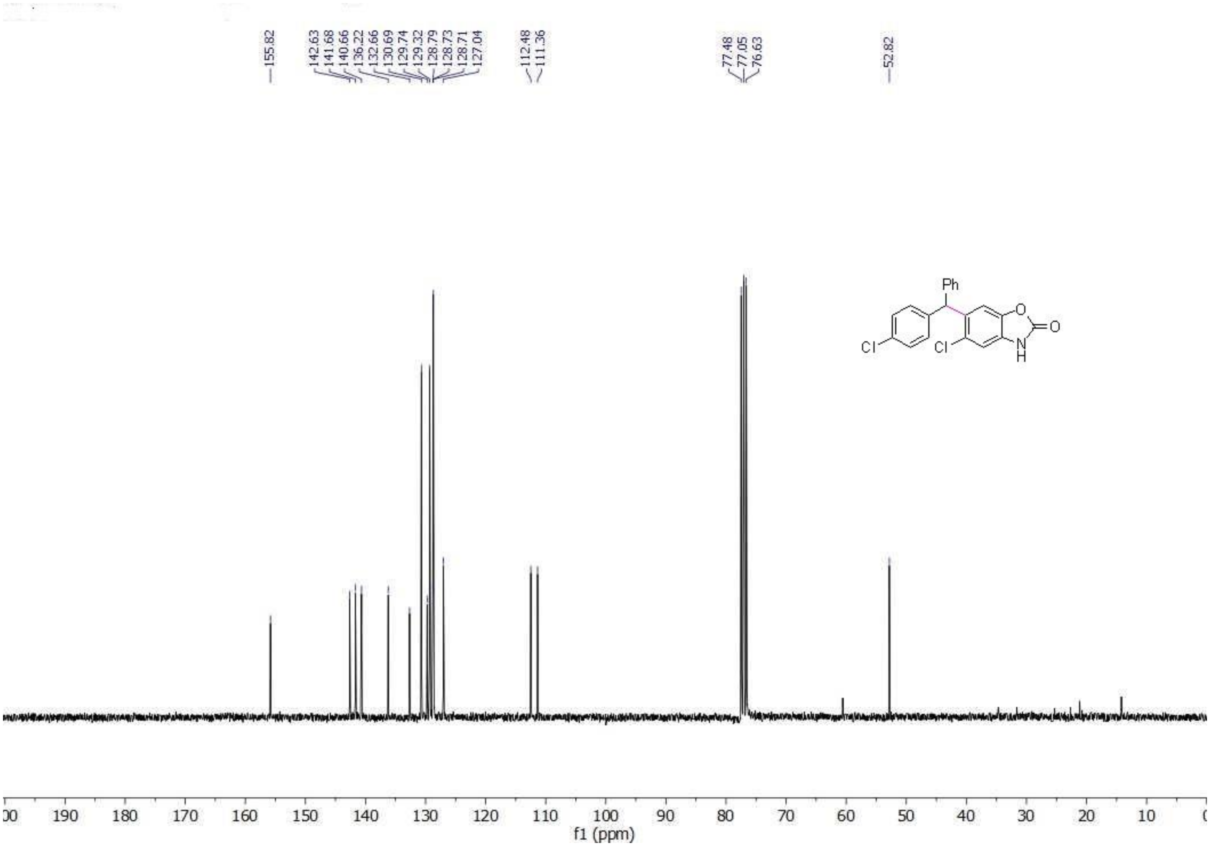
^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **5b**:



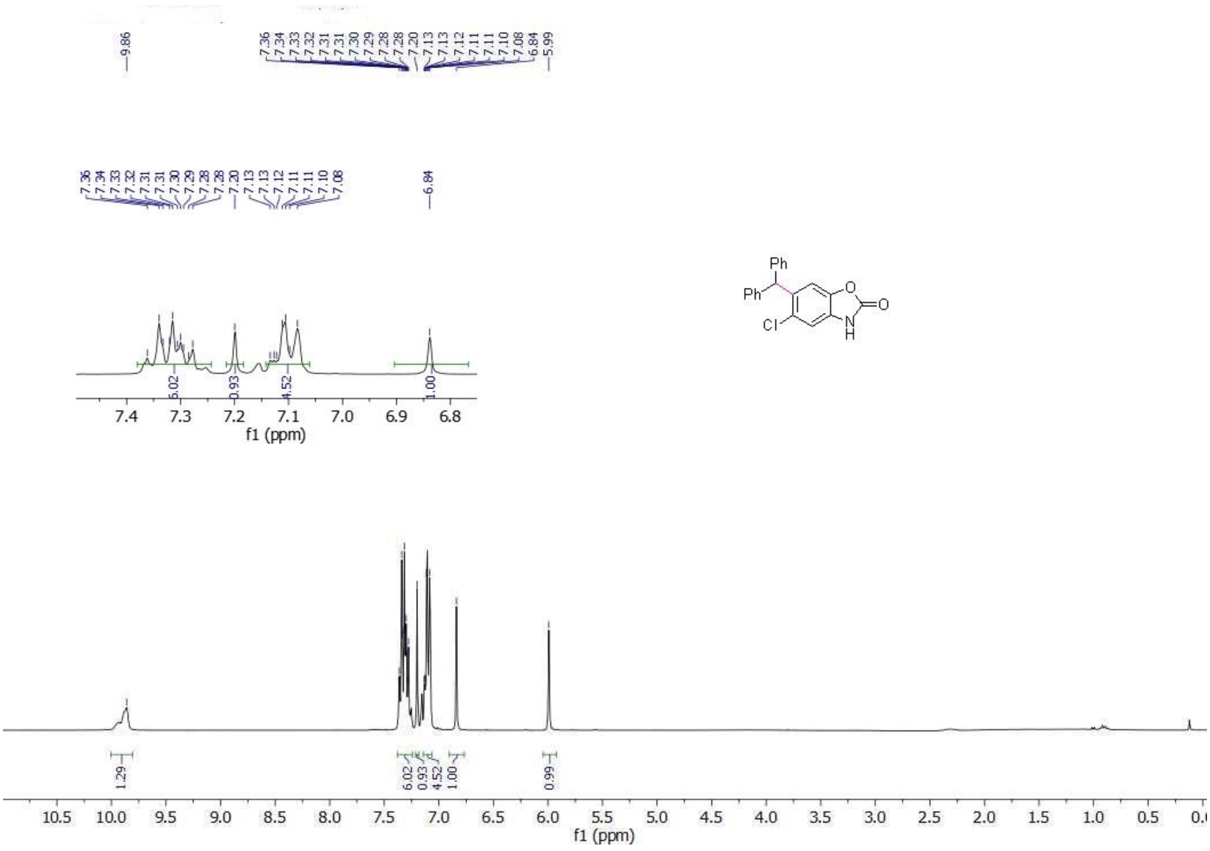


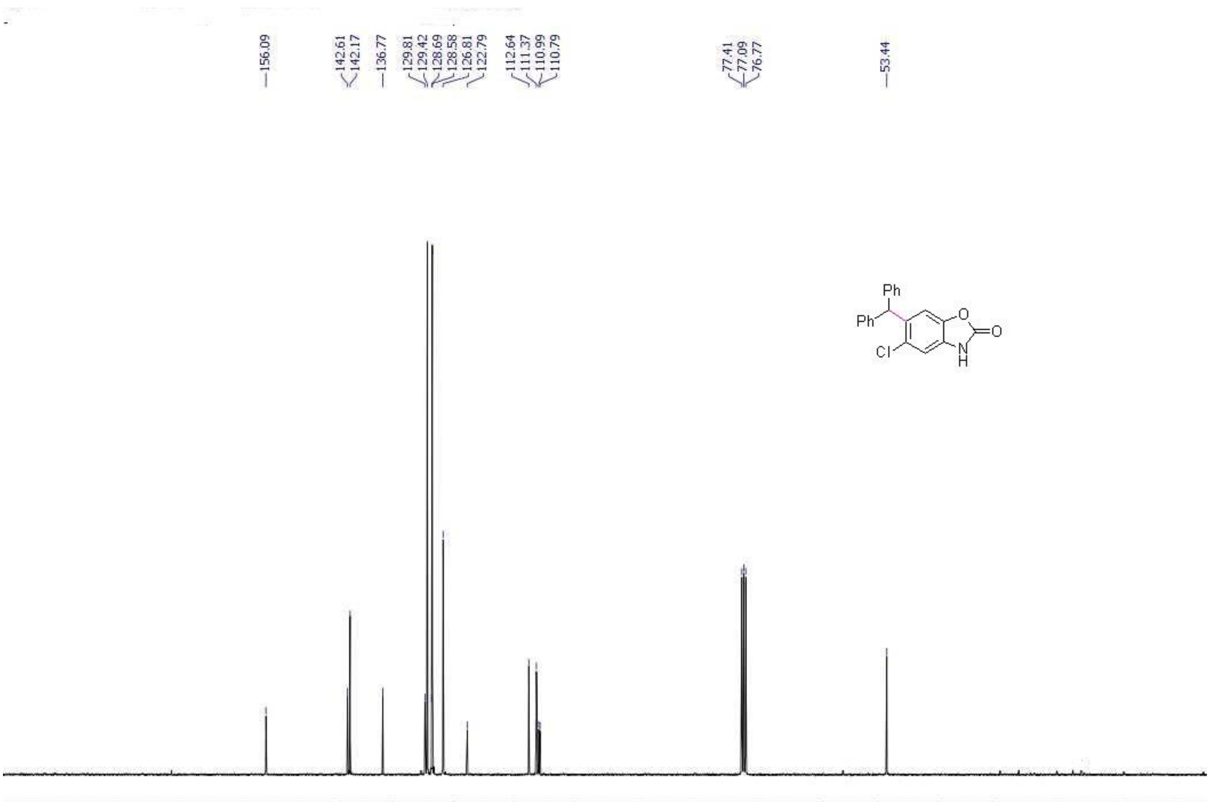
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **5c**:



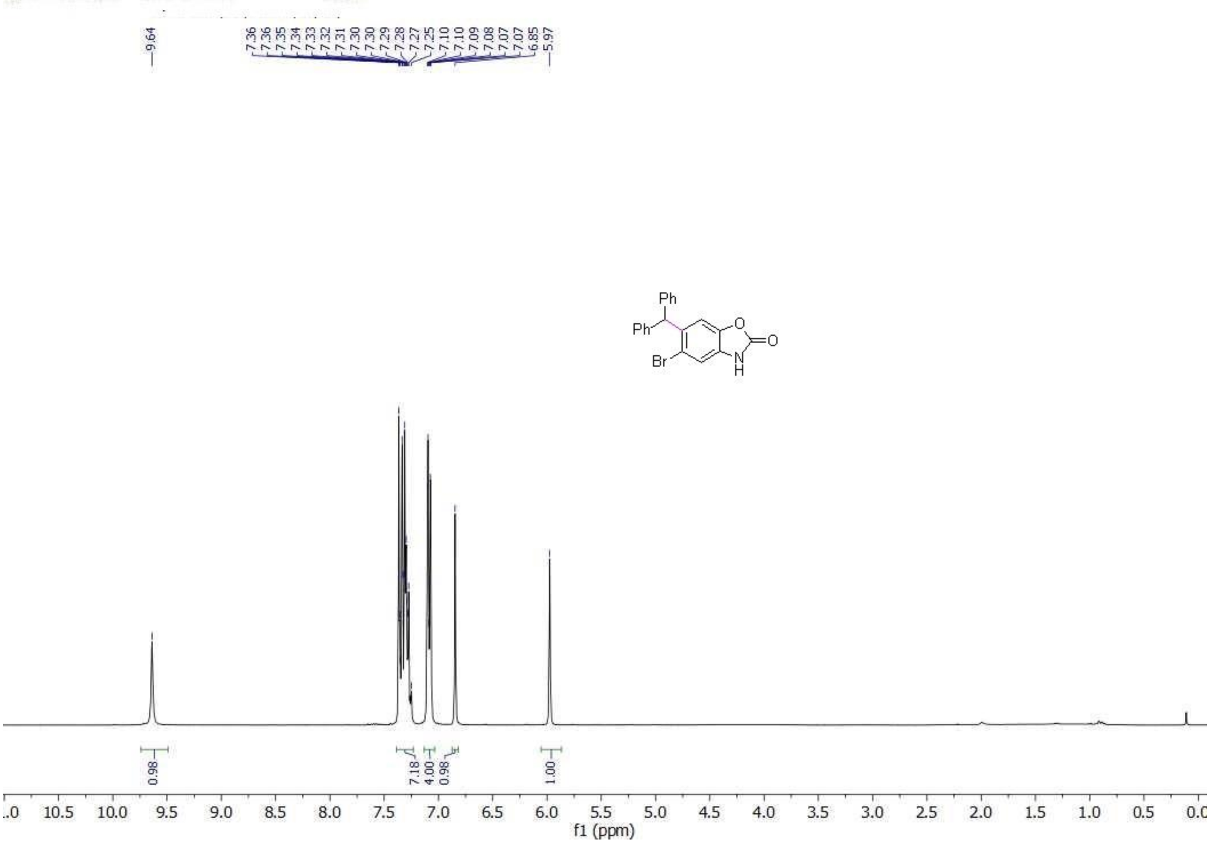


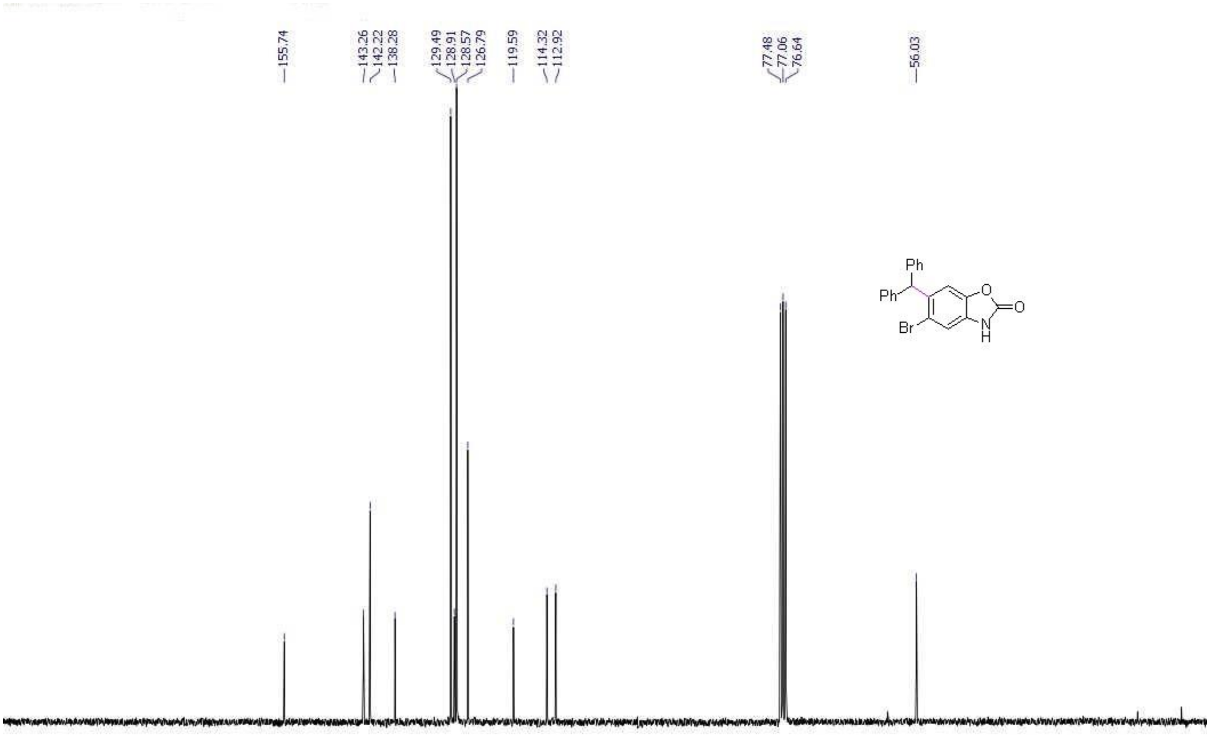
^{1}H NMR (300 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **5d**:



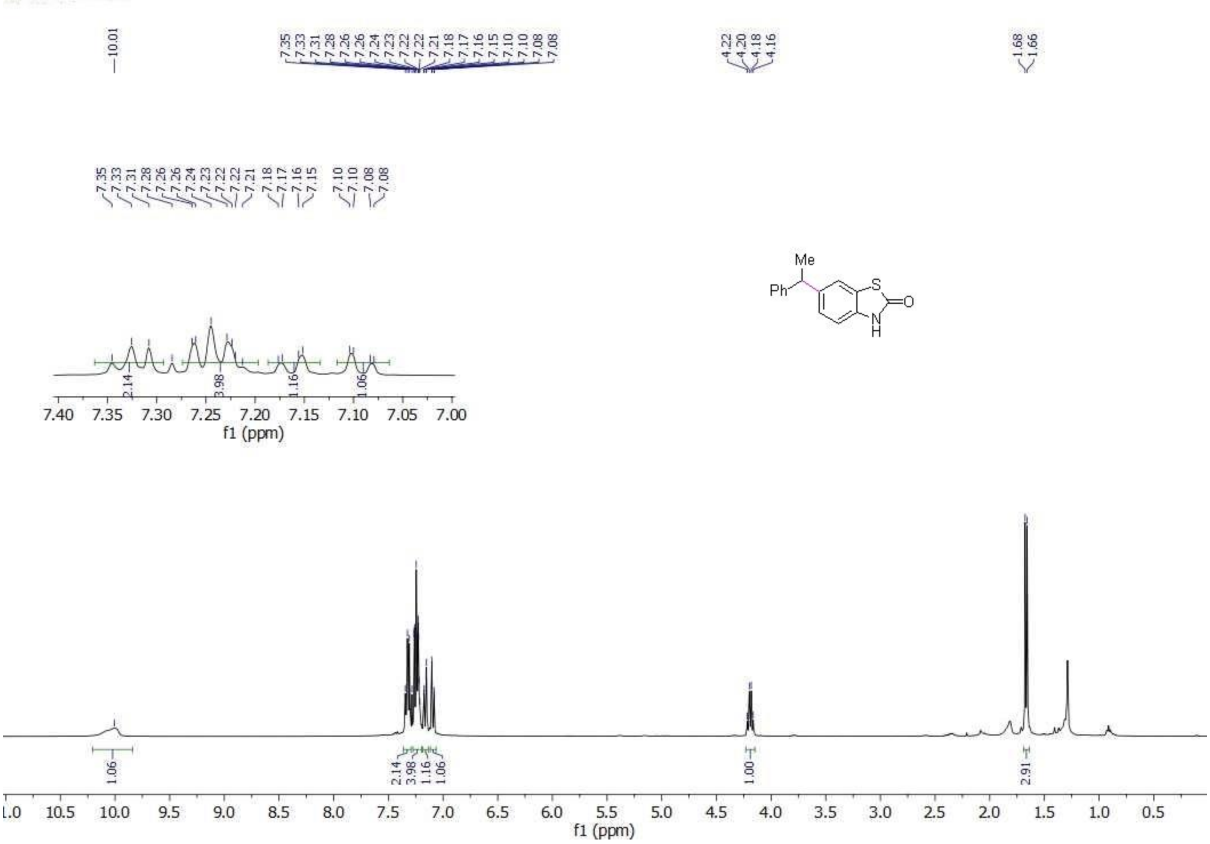


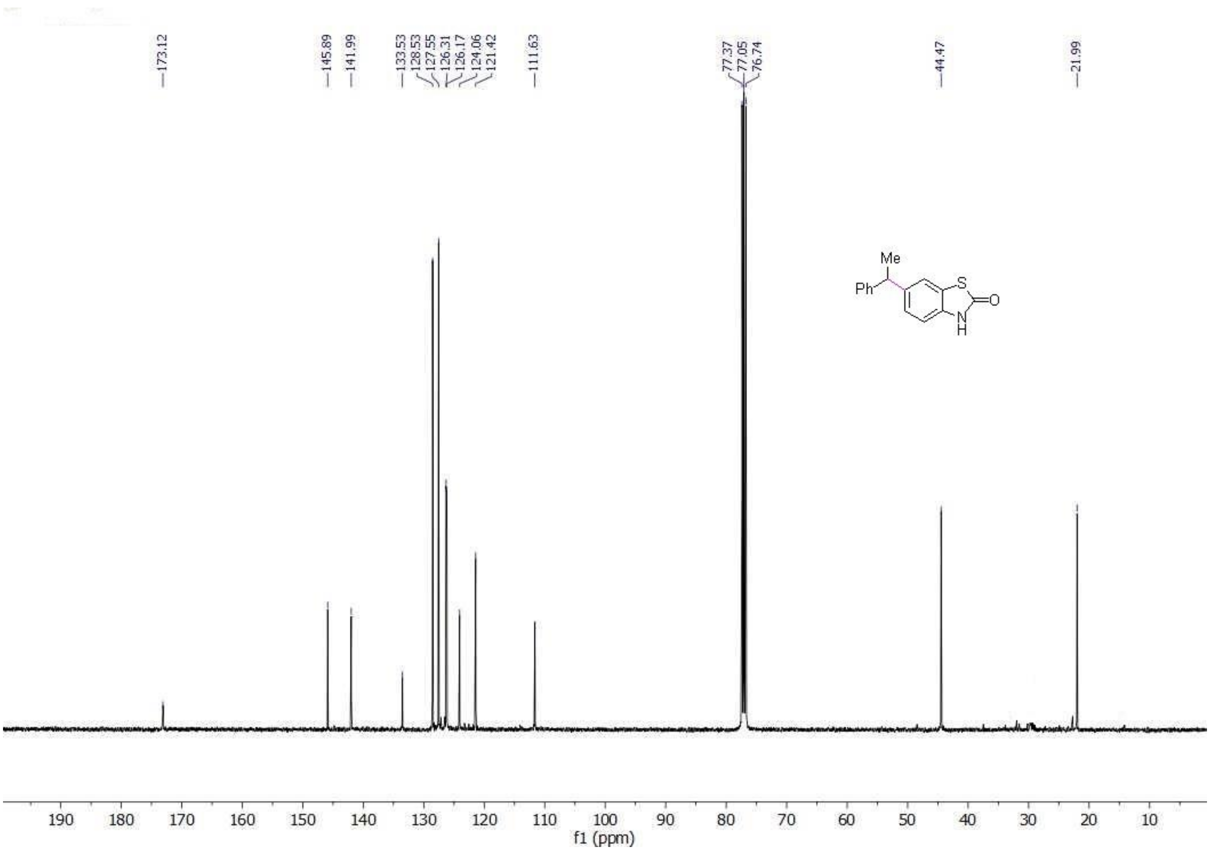
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **5e**:



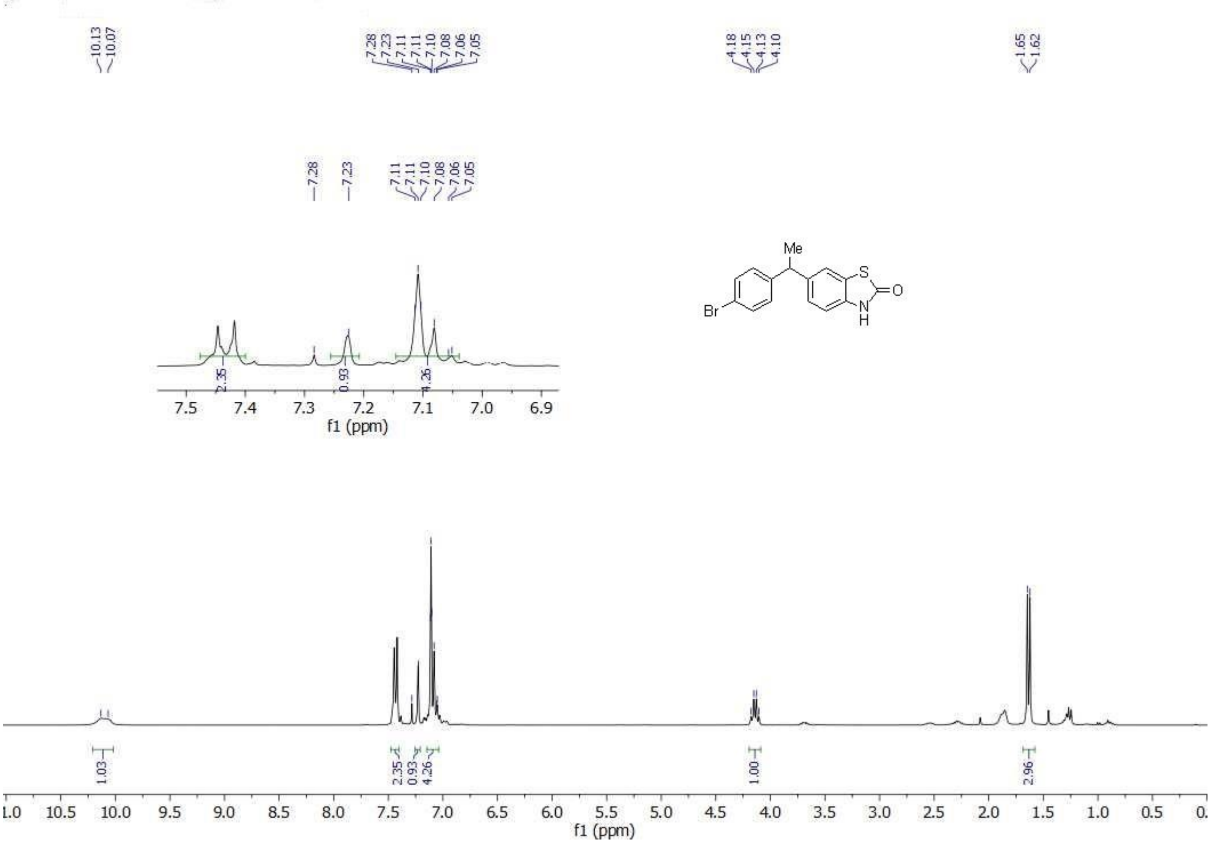


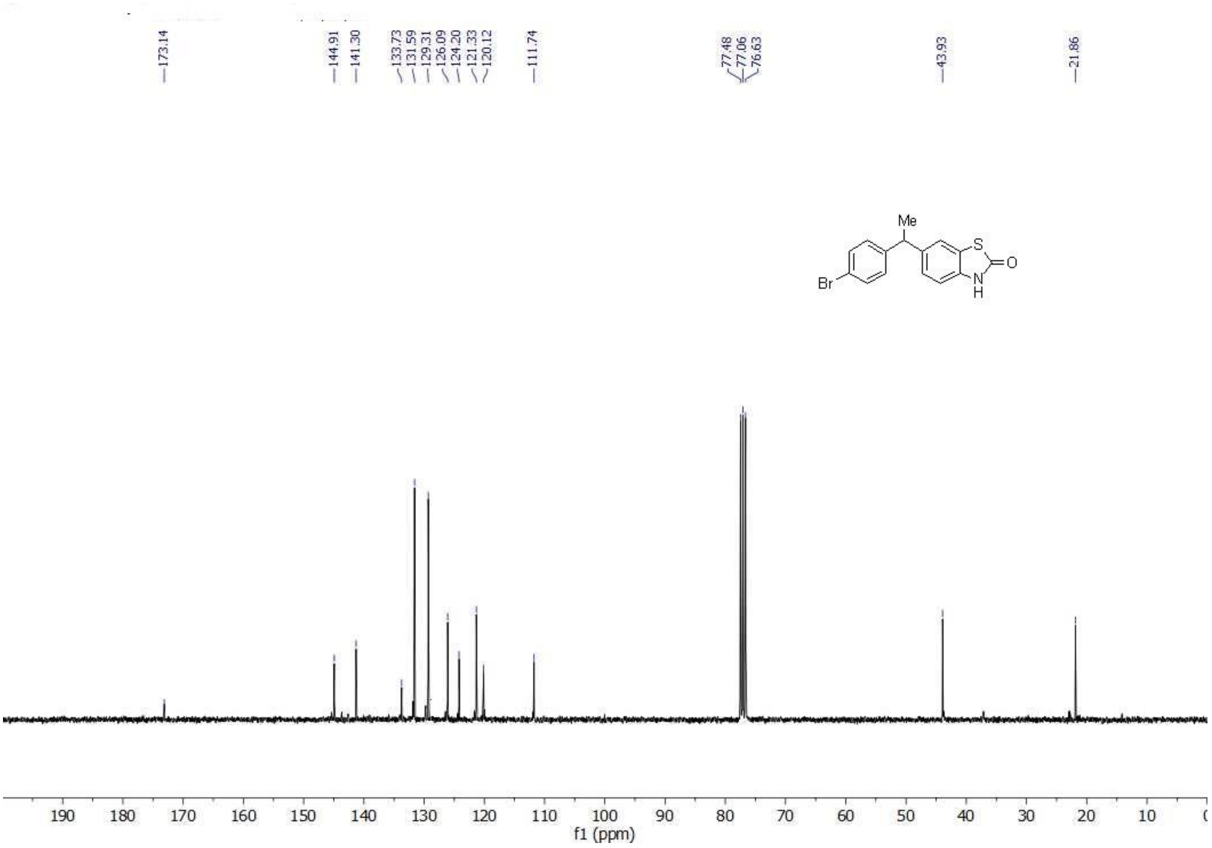
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **5f**:



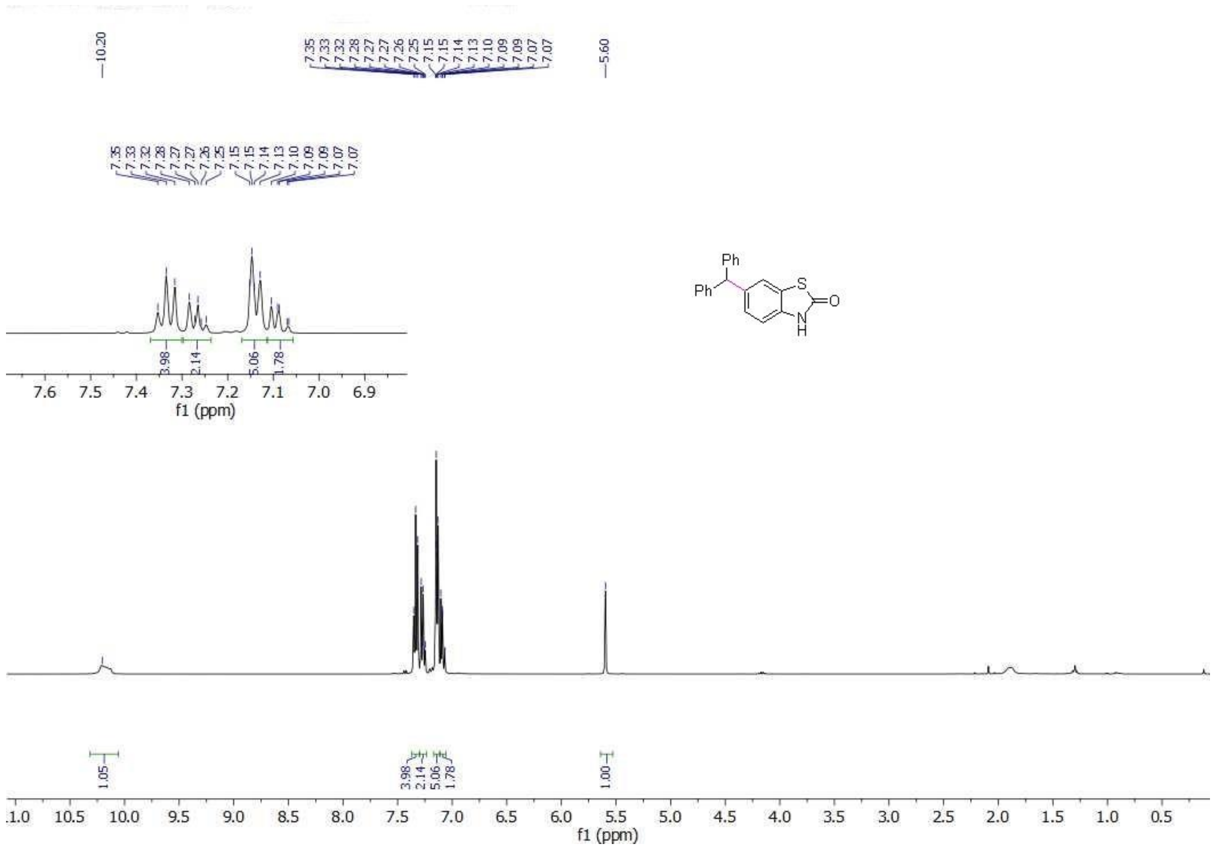


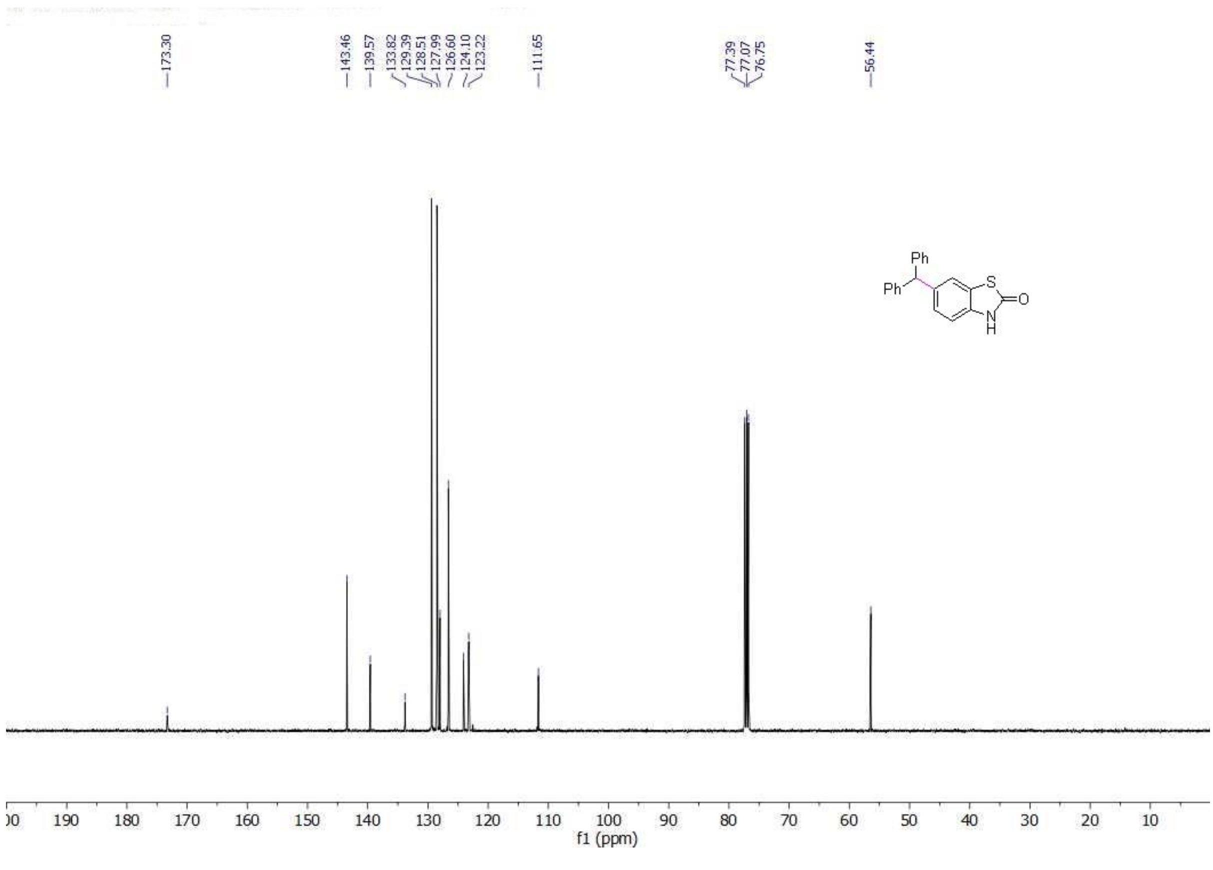
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, $CDCl_3$) spectra of **5g**:



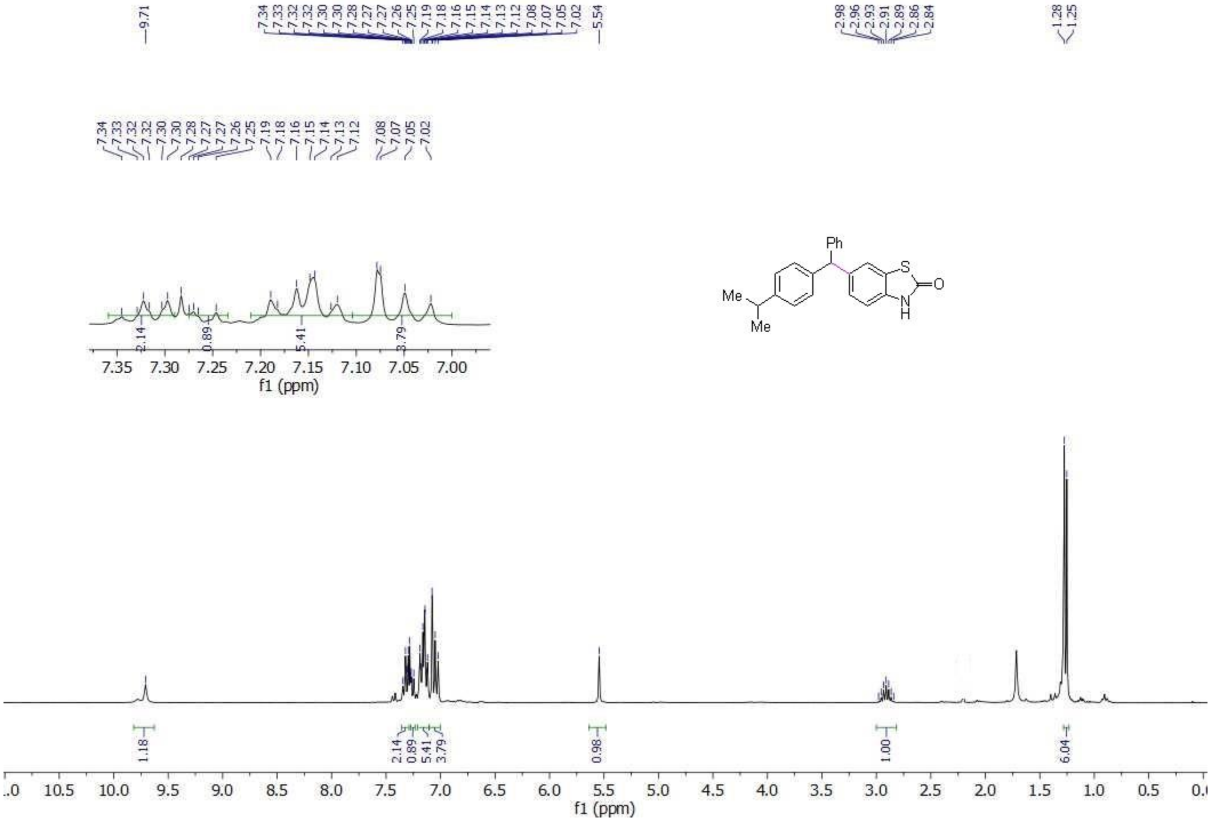


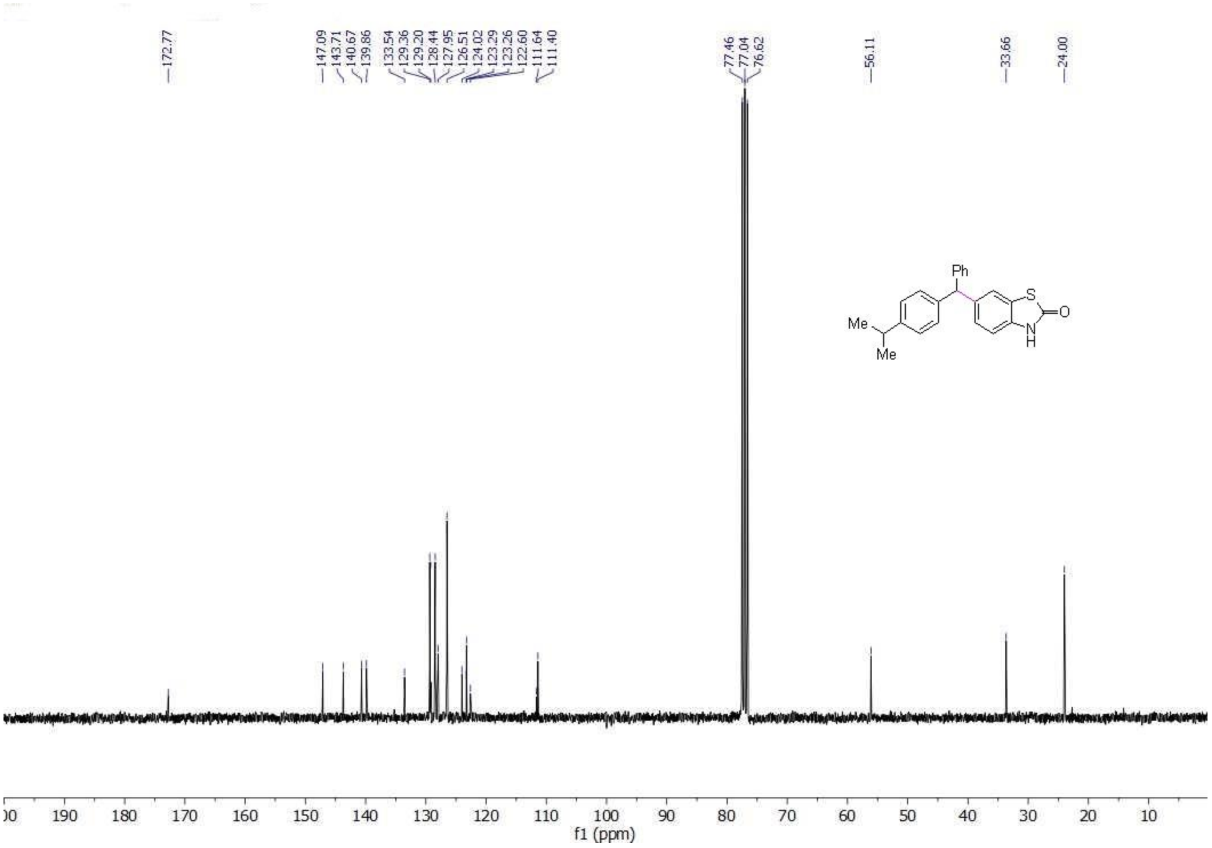
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **5h**:



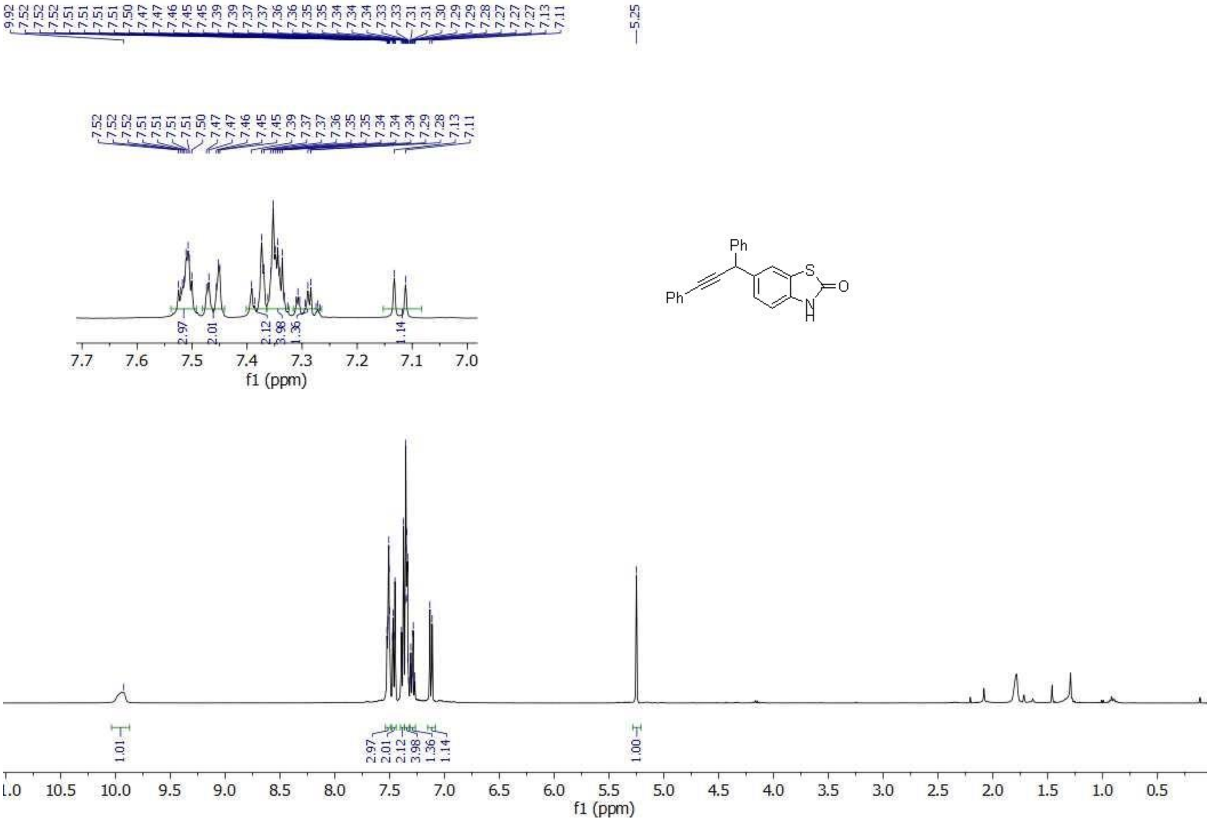


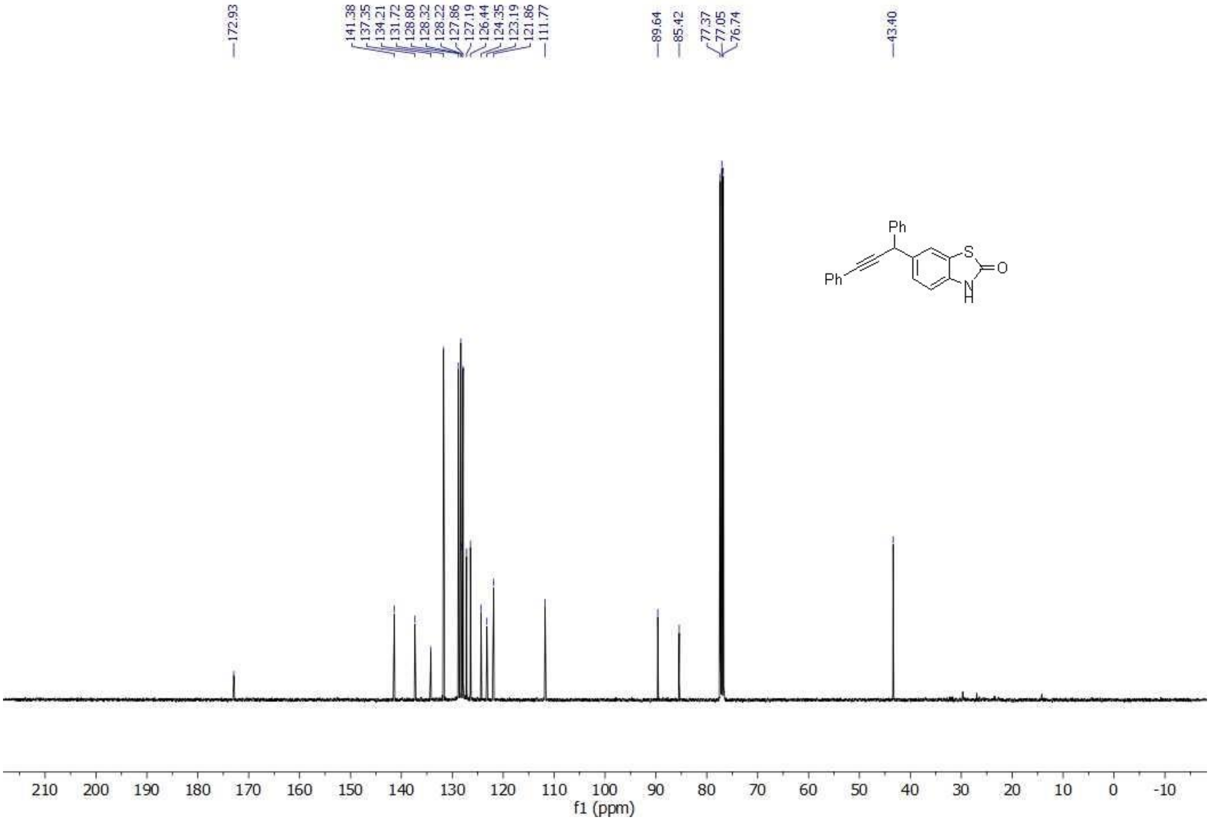
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **5i**:



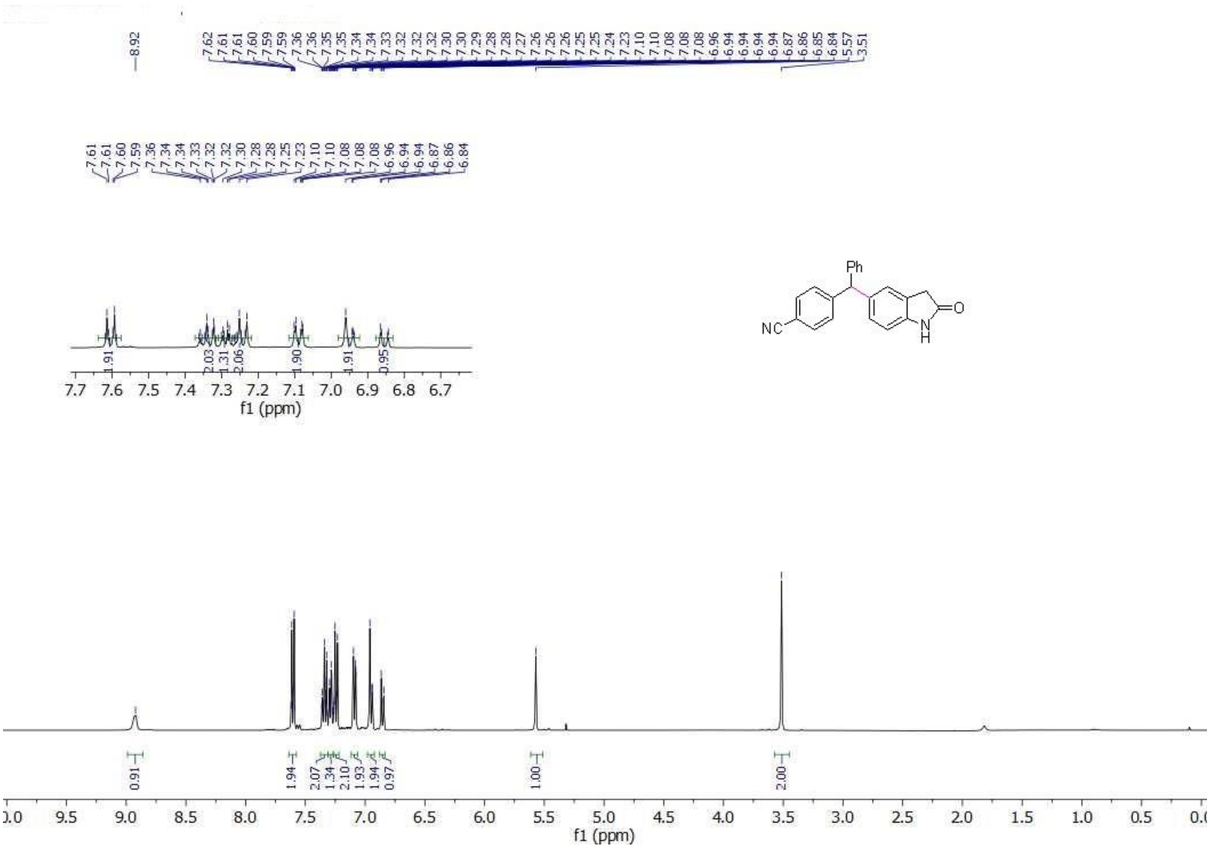


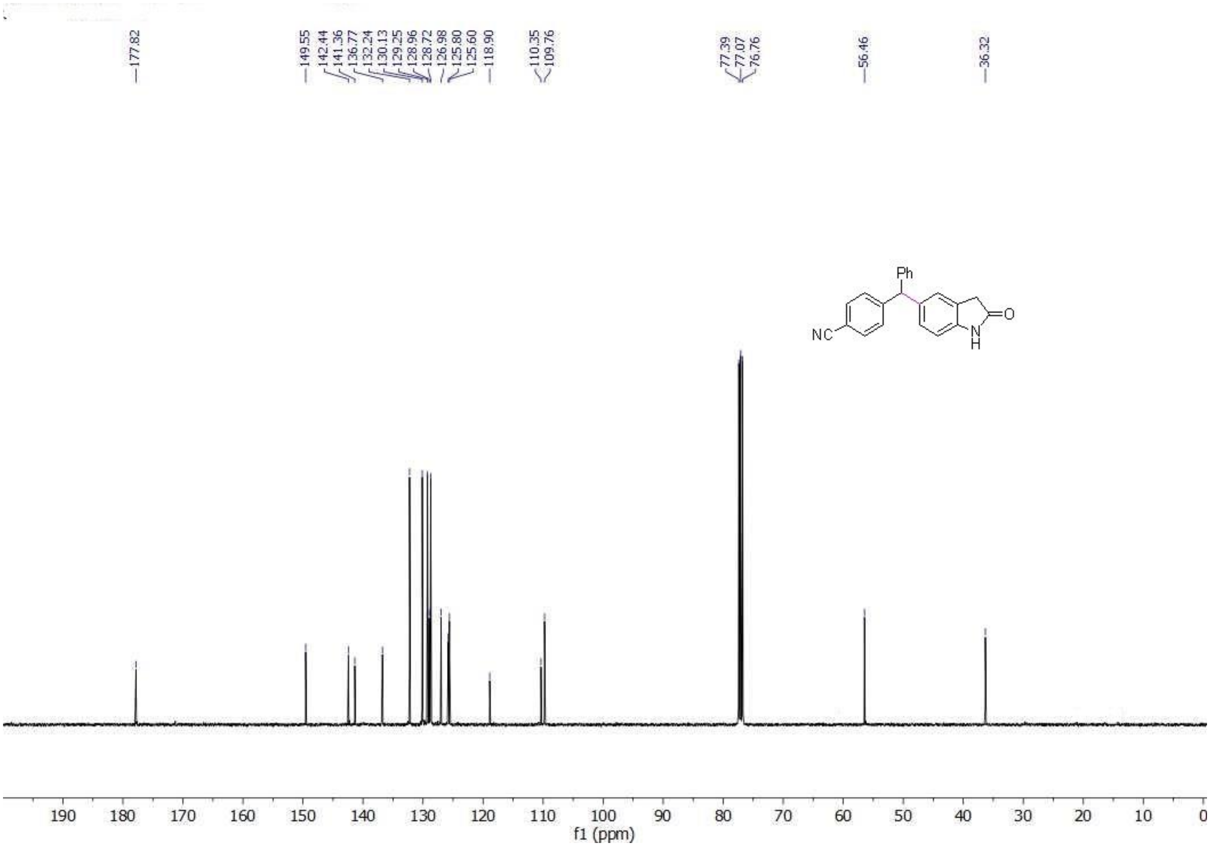
^{1}H NMR (400 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) spectra of **5j**:



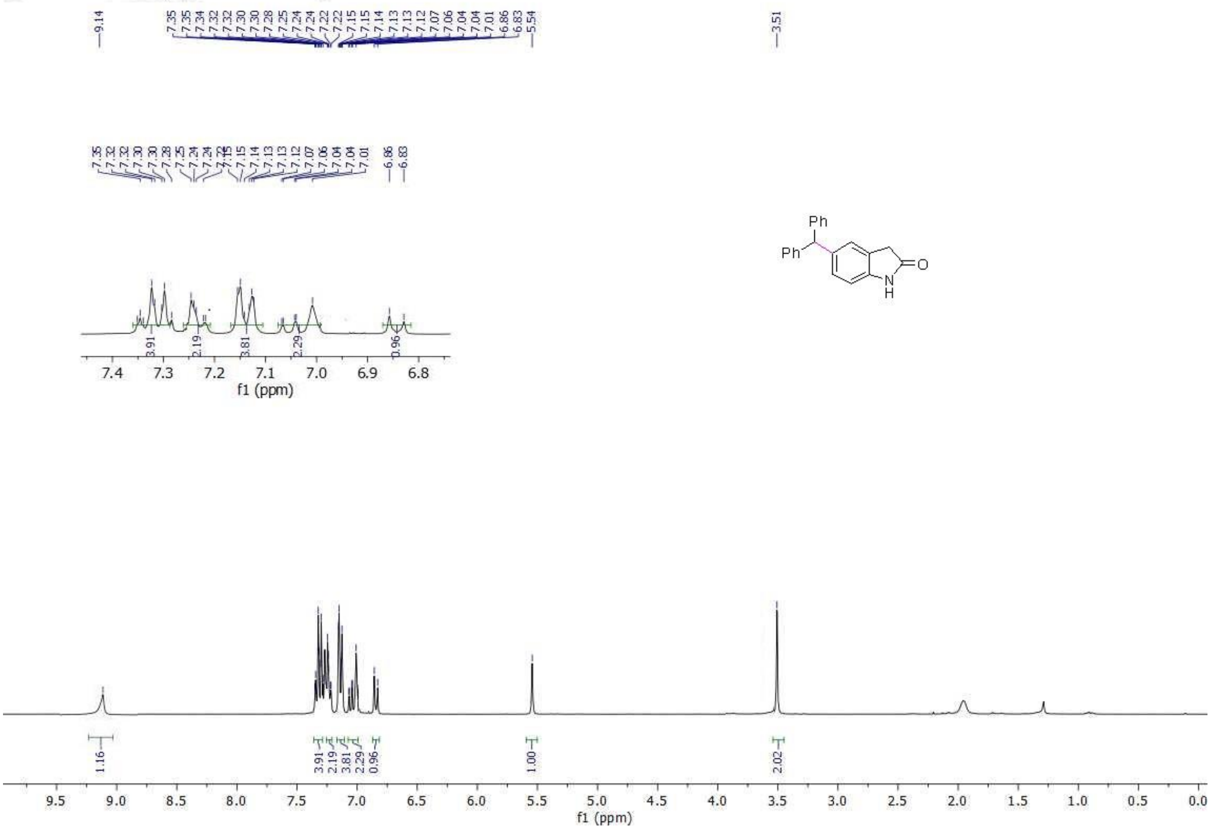


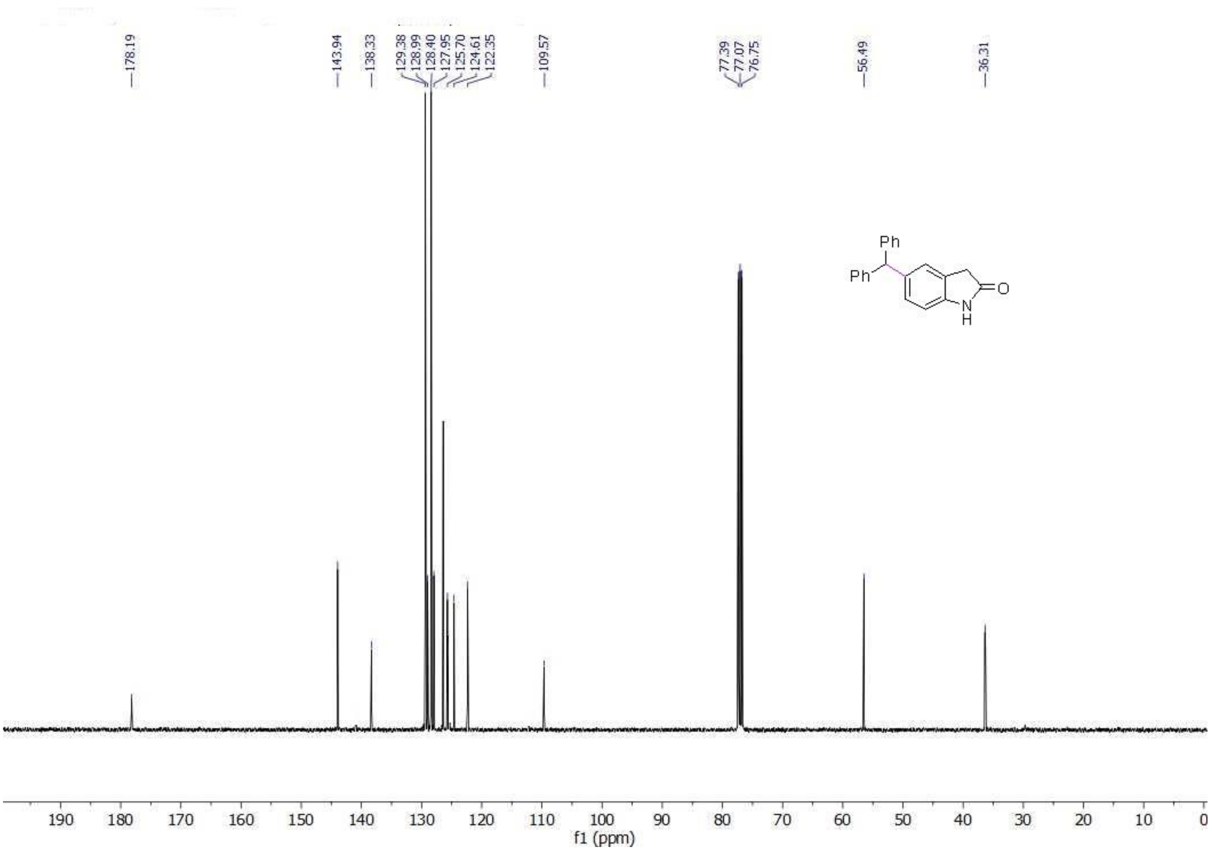
^{1}H NMR (400 MHz, CDCl$_3$) and **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **5k**:



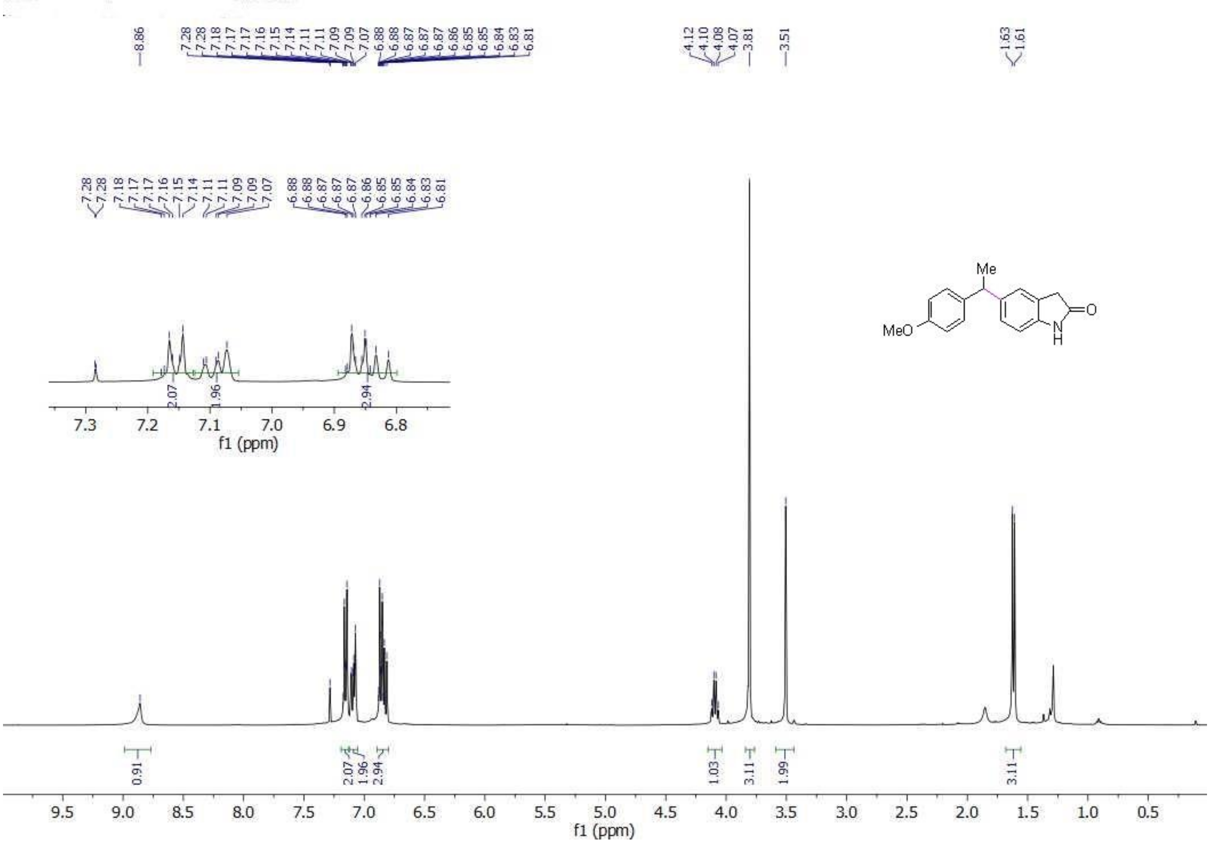


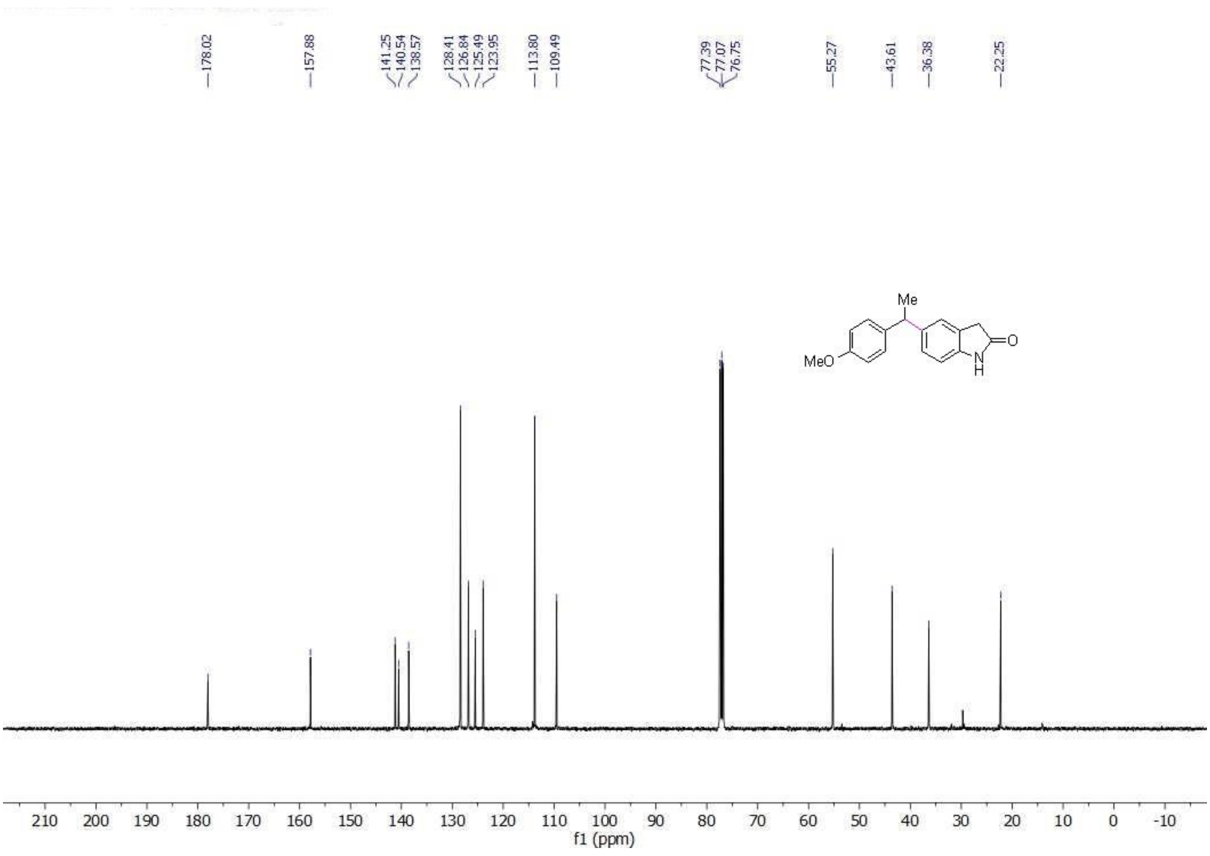
^{1}**H NMR** (300 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **5l**:



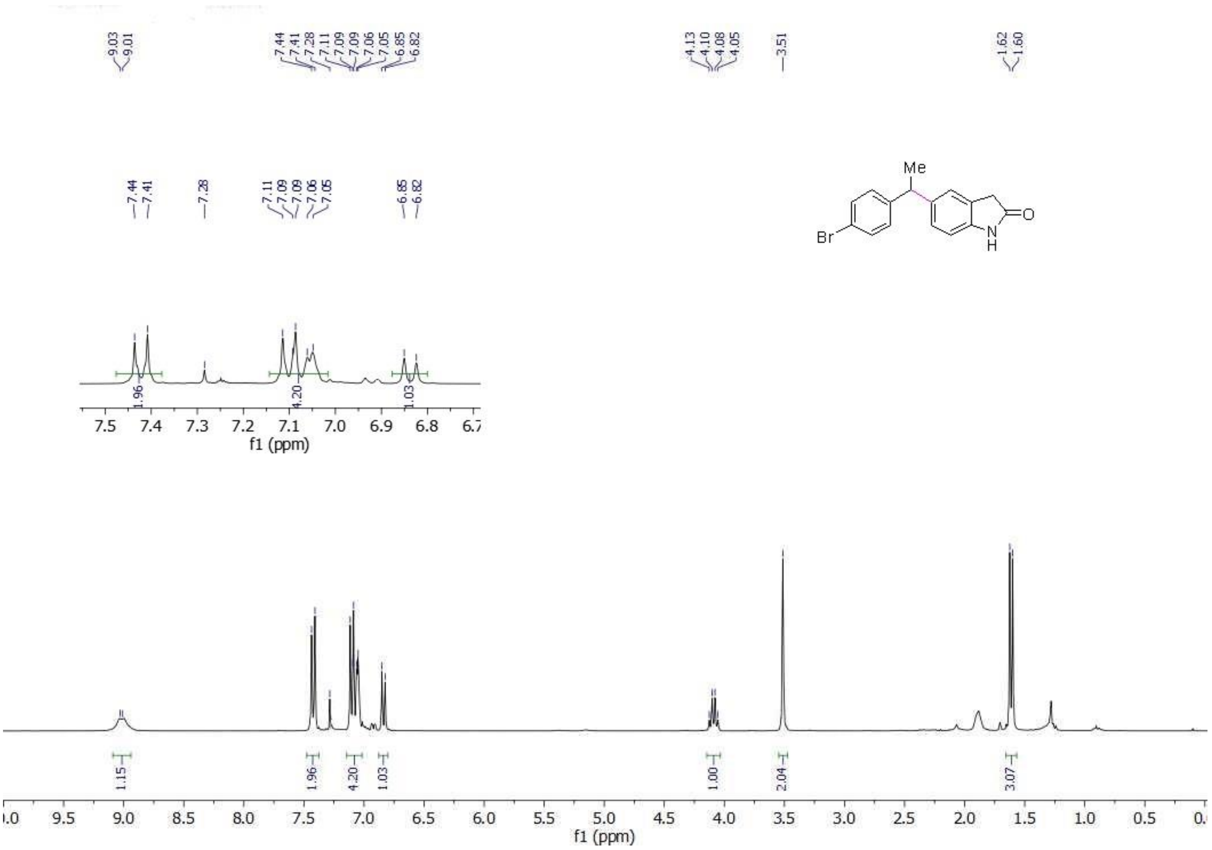


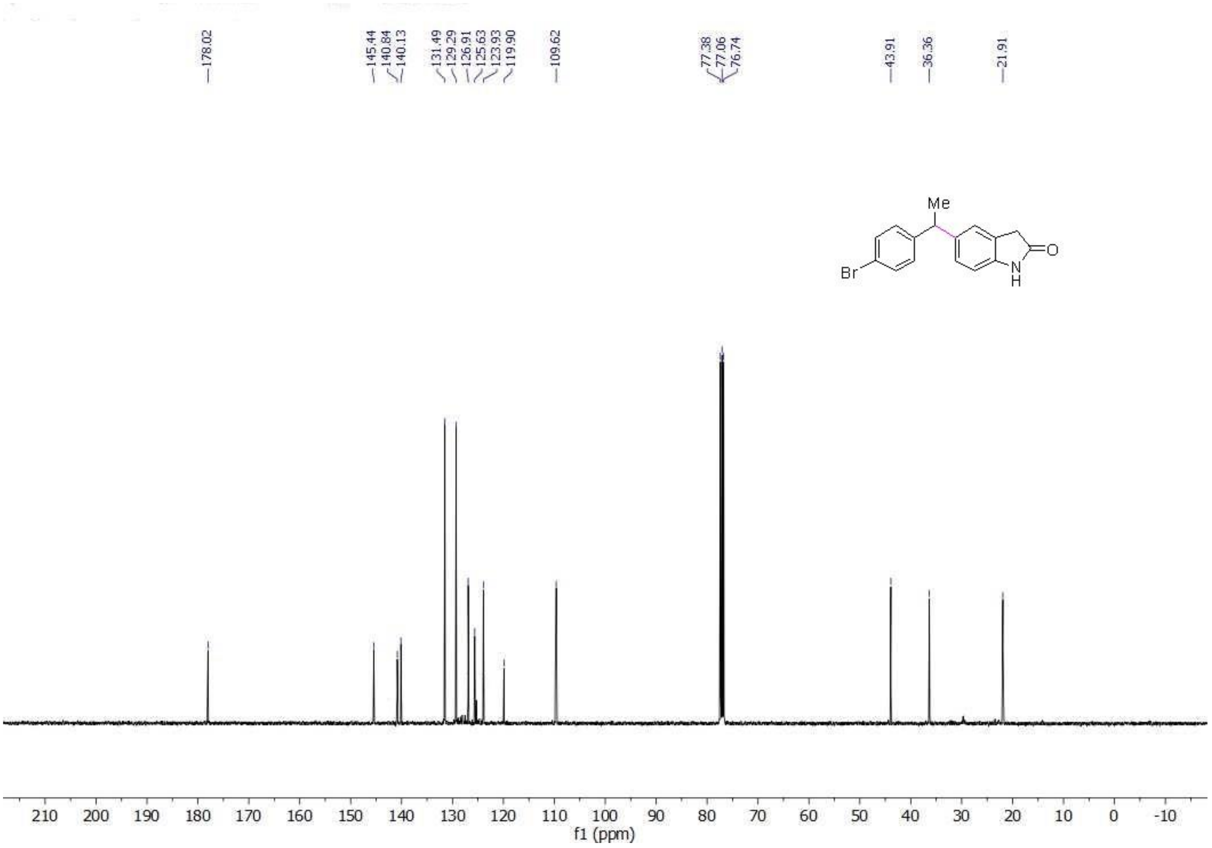
^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$) spectra of **5m**:



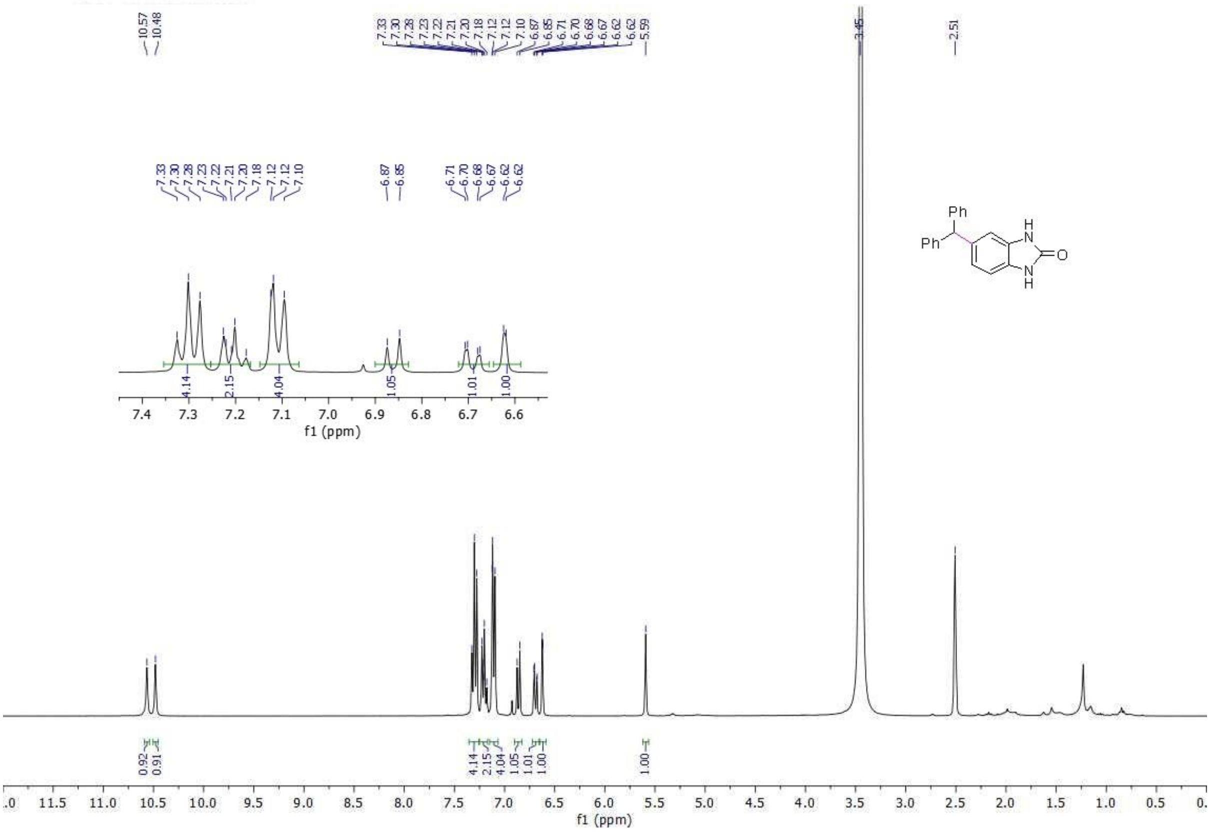


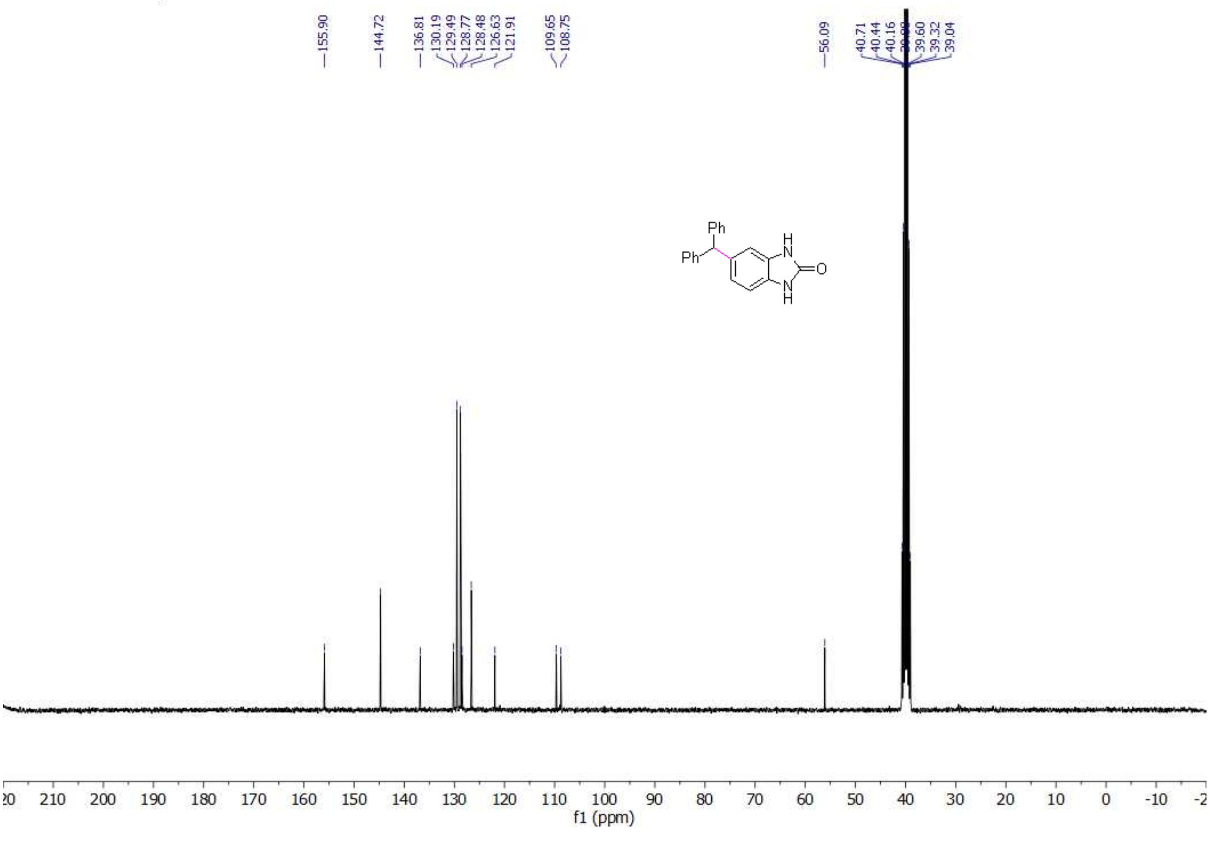
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{**^{1}**H} NMR** (100 MHz, CDCl$_3$) spectra of **5n**:



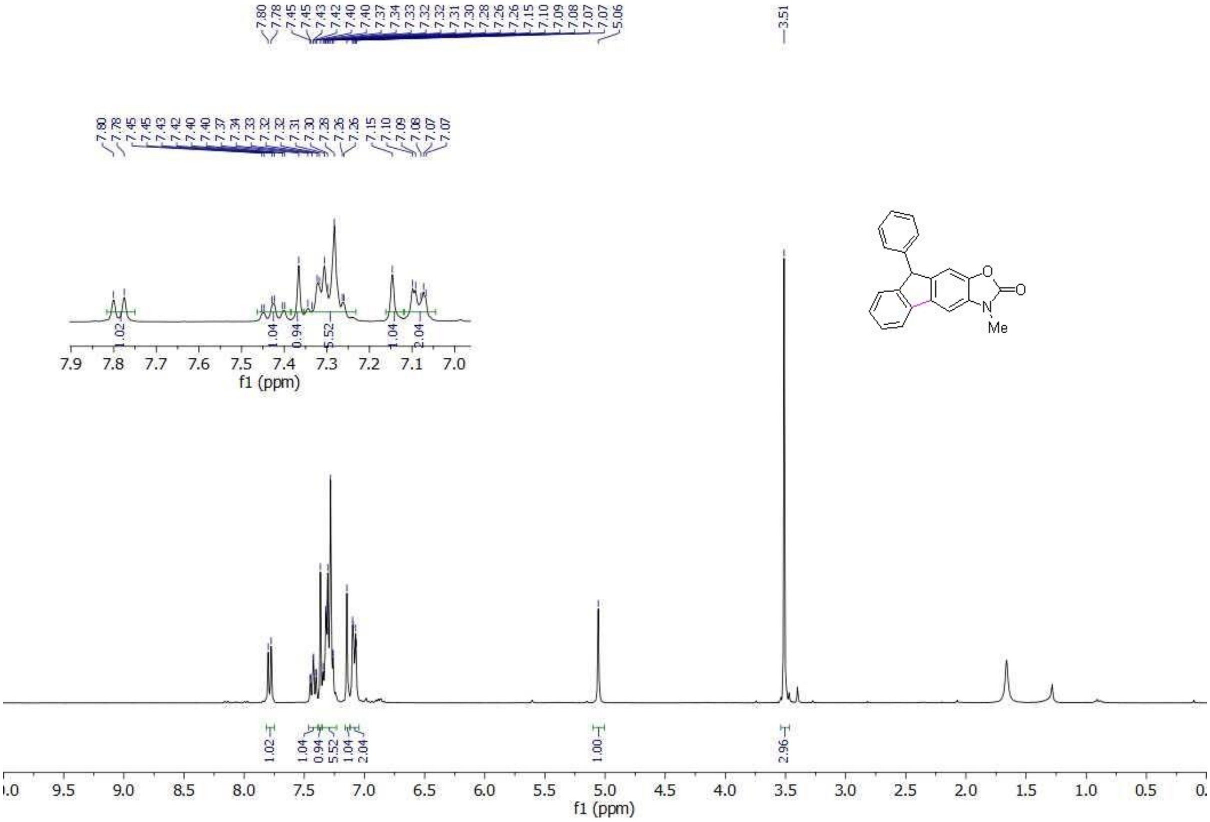


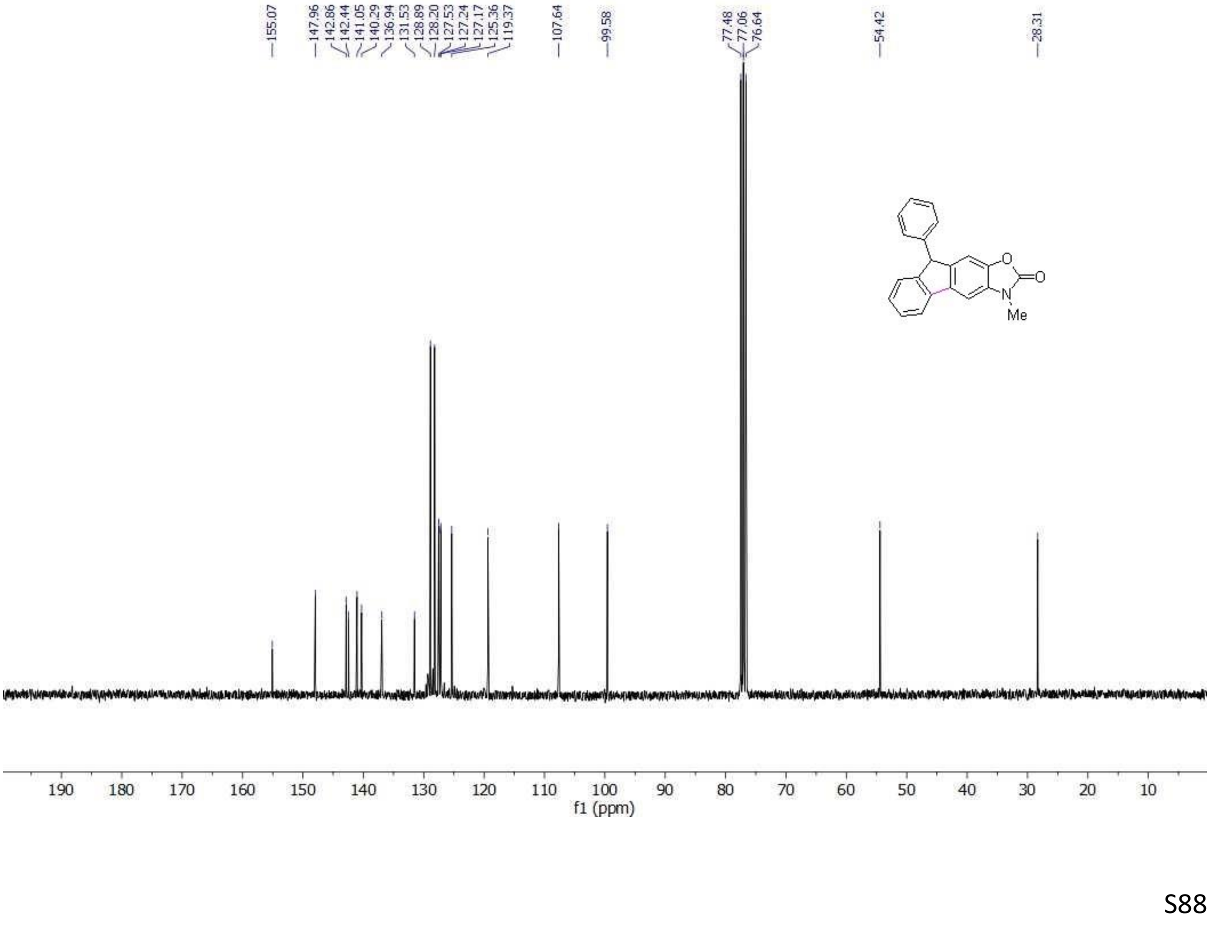
^{1}**H NMR** (300 MHz, DMSO-d6) and ^{13}**C{^{1}H} NMR** (75 MHz, DMSO-d6) spectra of **5o**:



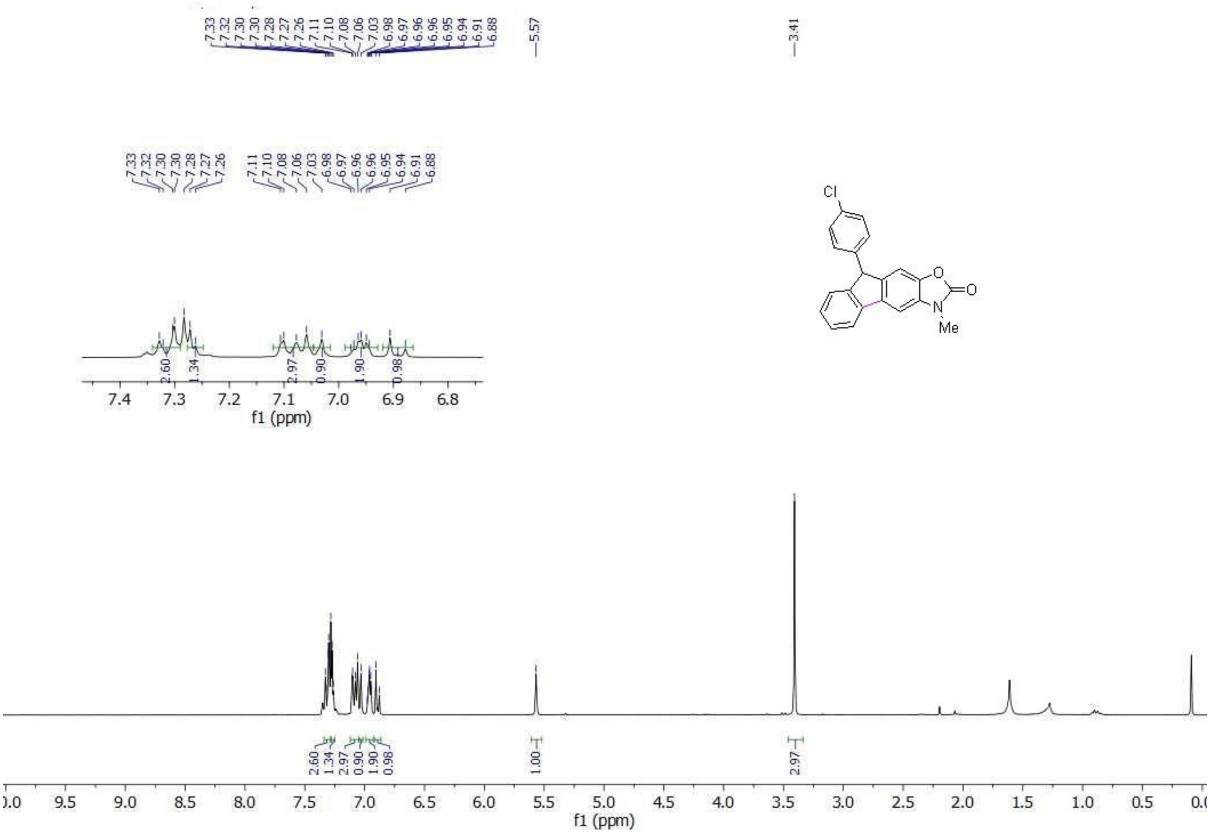


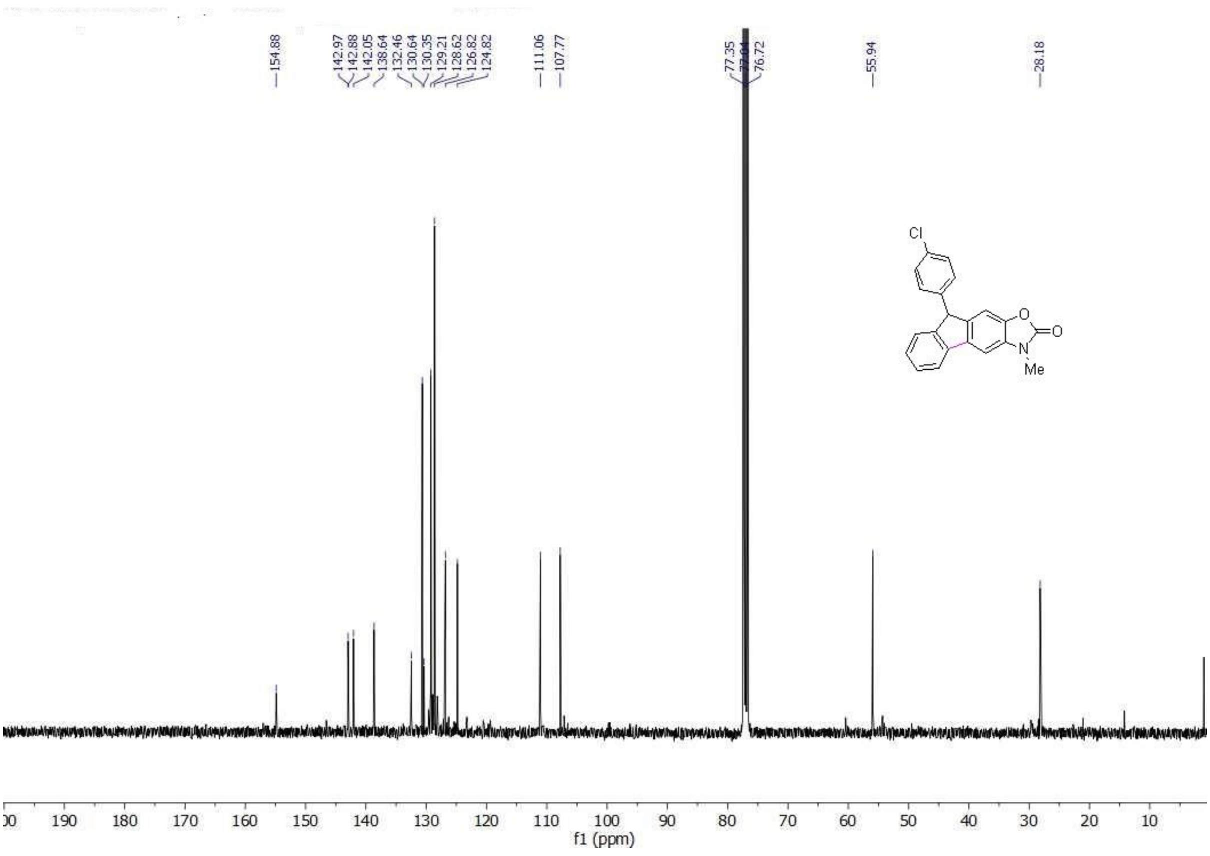
^{1}H NMR (300 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) spectra of **6a**:



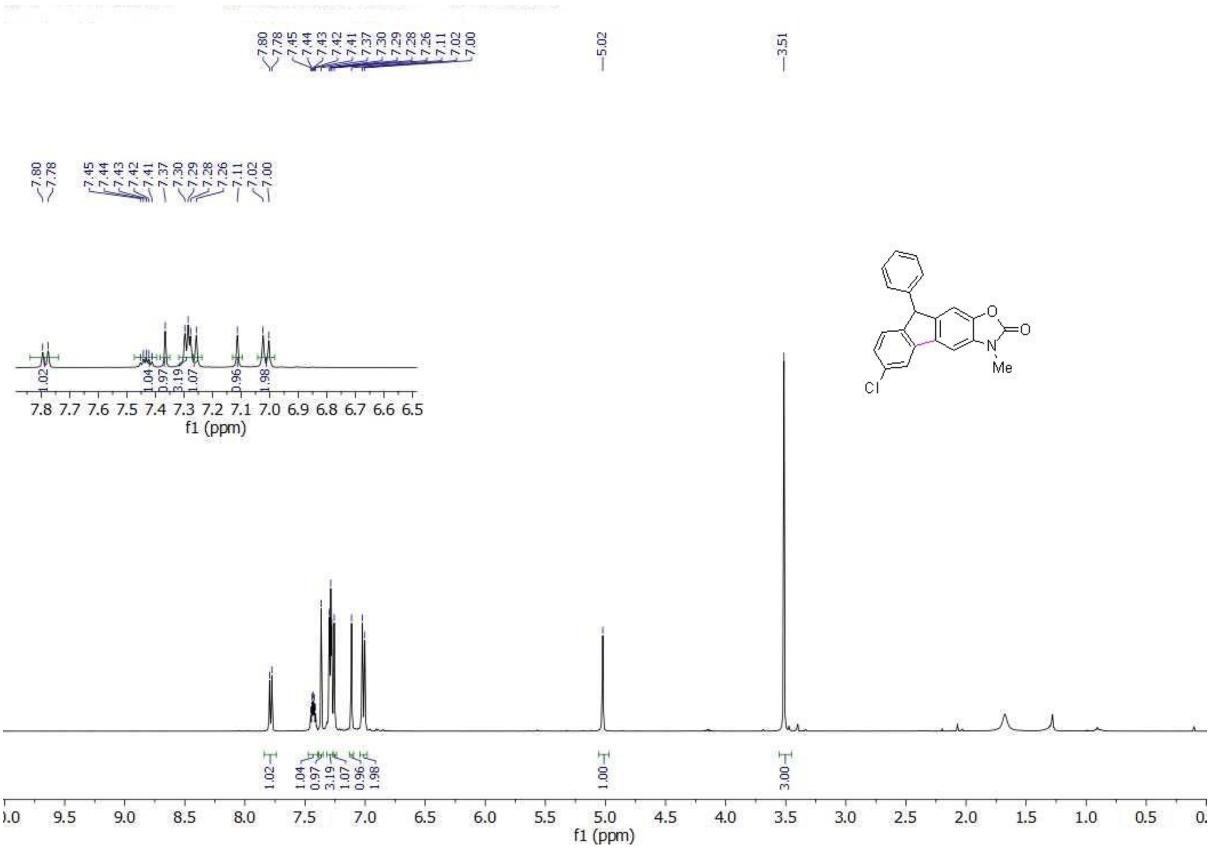


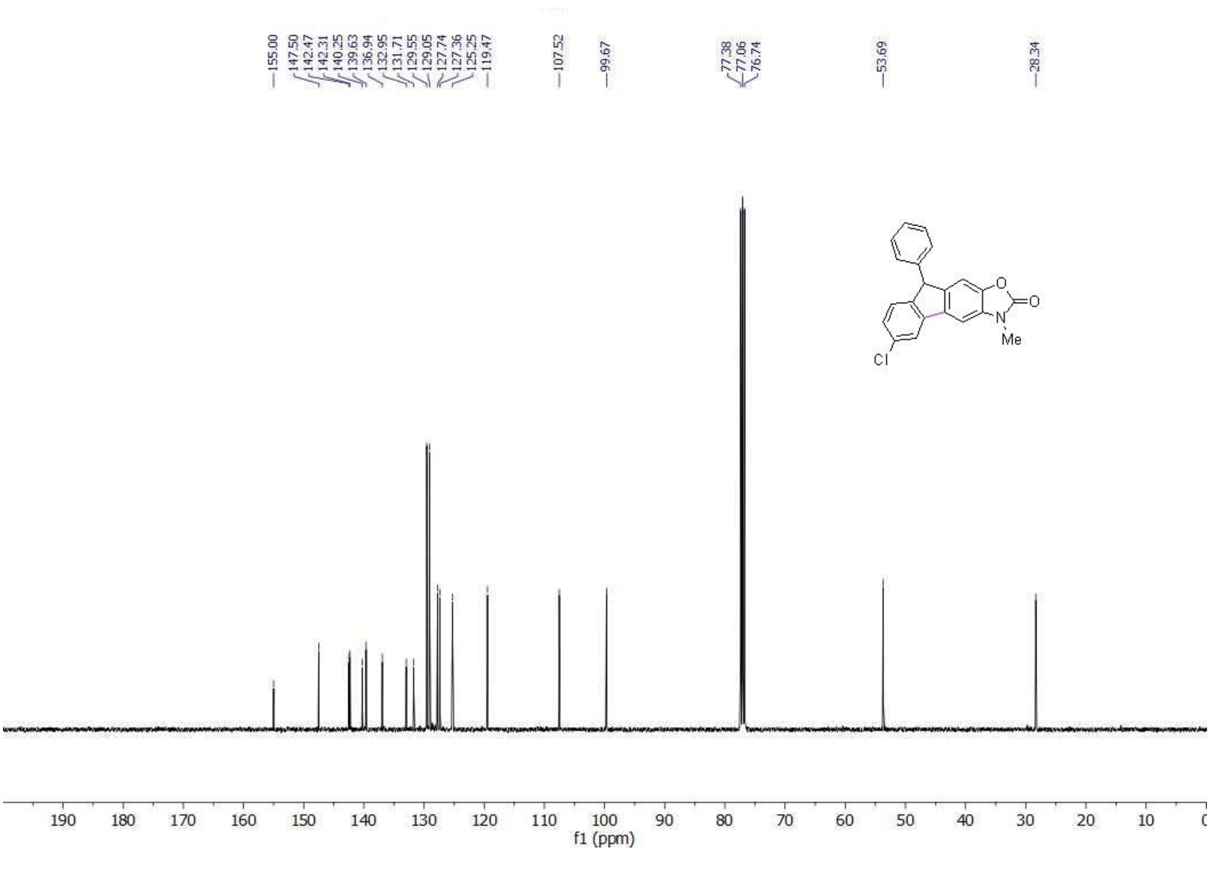
^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **6b**:



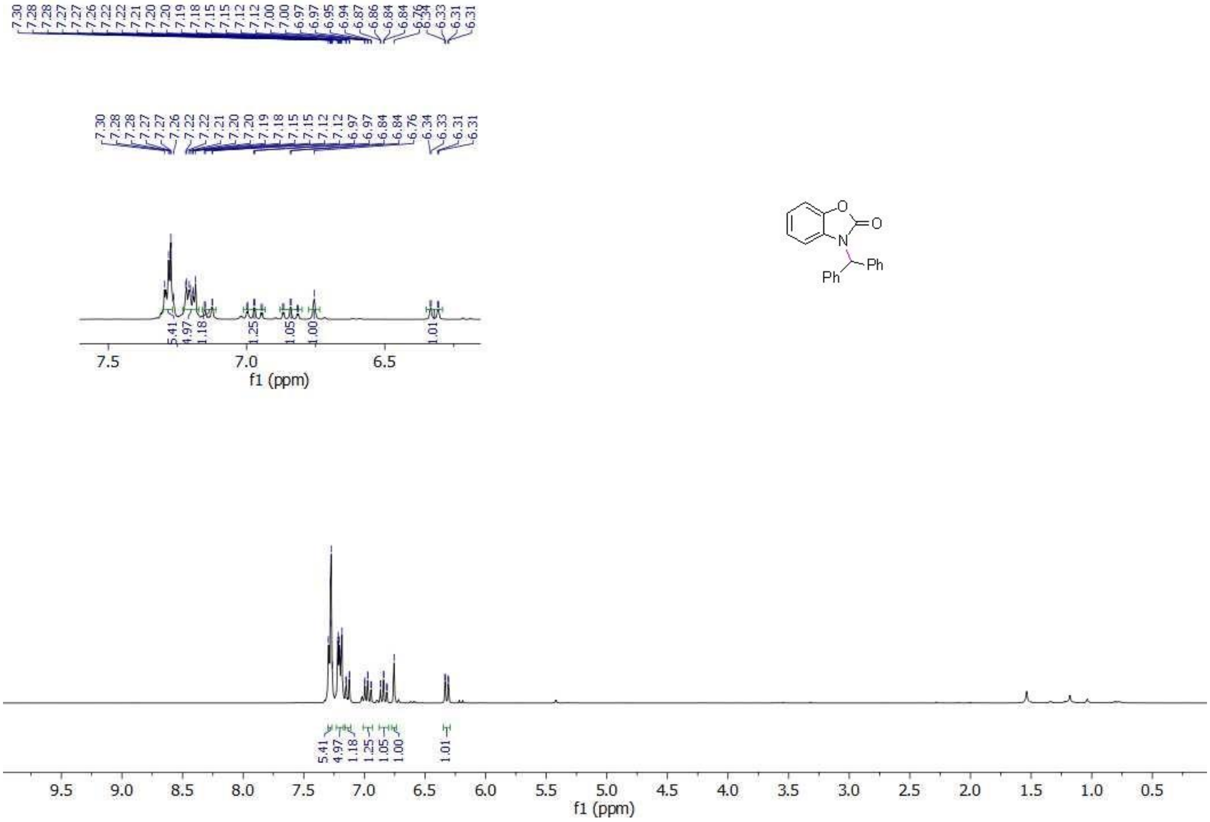


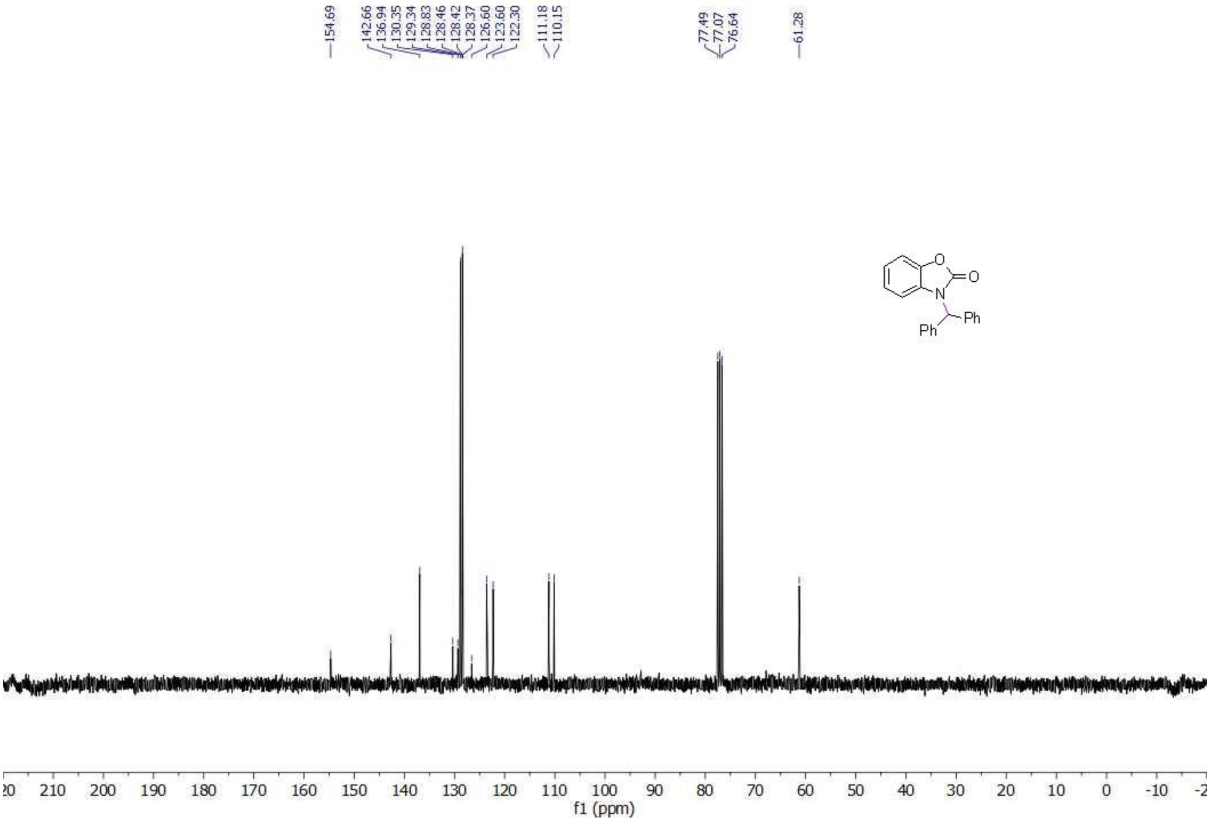
^{1}**H NMR** (400 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (100 MHz, CDCl$_3$) spectra of **6b'**:



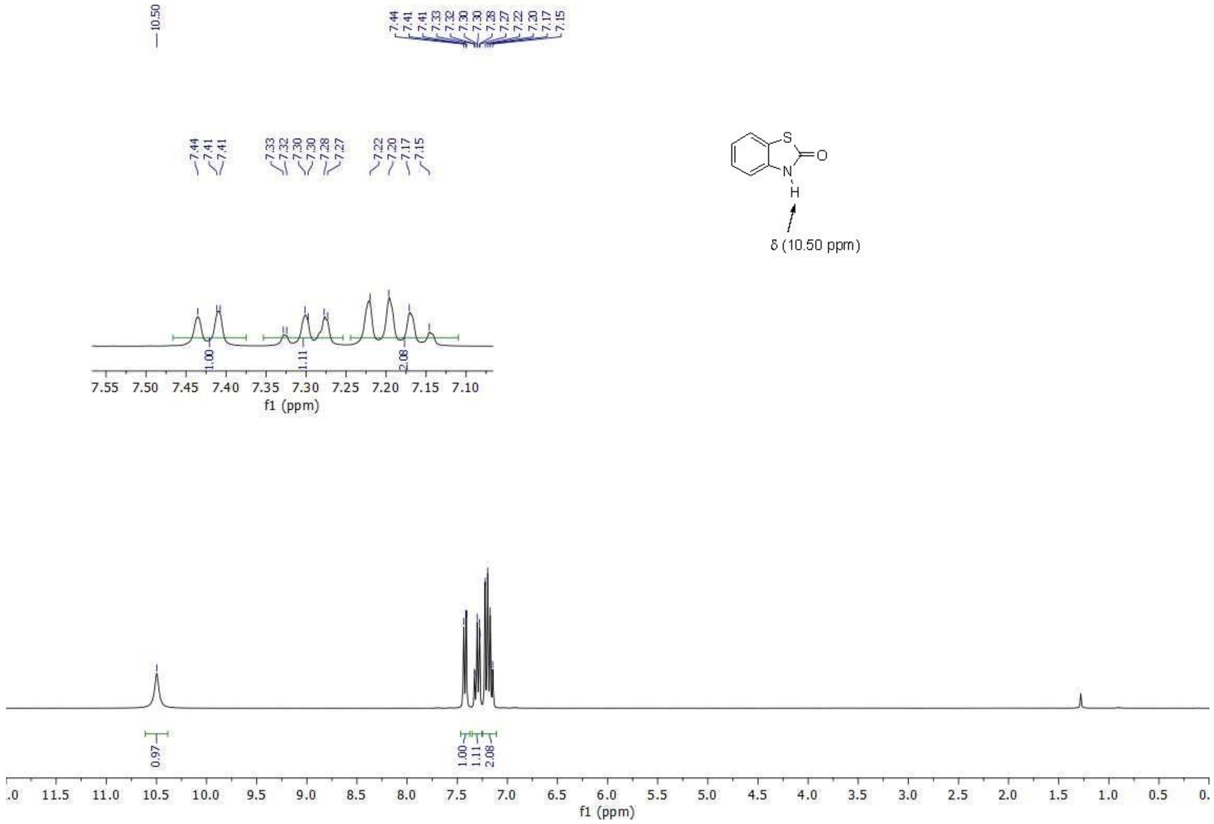


^{1}**H NMR** (300 MHz, CDCl$_3$) and ^{13}**C{^{1}H} NMR** (75 MHz, CDCl$_3$) spectra of **5a'**:





^{1}**H NMR** (300 MHz, $CDCl_3$) of commercially available Benzothiazolone (**1p**):



Crude ^{1}**H NMR** (300 MHz, $CDCl_3$) of Benzothiazolone in presence of Uric acid to show H-bonding (**1p-U**):