Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Eco-friendly organocatalyst- and reagent-controlled selective construction of diverse and multifunctionalized 2-hydroxybenzophenone frameworks for potent UV-A/B filters by cascade benzannulation

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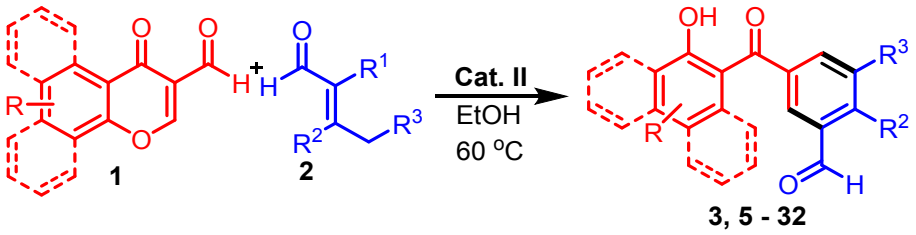
1. General remarks

All experiments were carried out under open atmosphere. All the reactions were performed in oven-dried glassware with magnetic stirring. Unless otherwise noted, toluene and DMSO were purchased from Alfa Aesar; CH_3CN from TCI and ethanol from Merck and used without further purification. All the catalysts (Cat. **I** – Cat. **VII**) were purchased from Sigma Aldrich. 3-Formylchromones **1a**, **1b**, **1f**, **1g** and **1j** were purchased from TCI; **1c**, **1i**, **1k** and **1l** from Sigma Aldrich; **1h** from Alfa Aesar while **1d**, **1e**, **1m** and **1n** were synthesized according to known method.[1] α,β-Unsaturated aldehydes **2a**, **2b**, **2d**, **2h** and **2i** were purchased from Sigma Aldrich; **2c** and **2e** from TCI; **2g** and **2f** from Alfa Aesar while **2j** was synthesized according to known method.[2] 4-Oxo-4*H*-chromene-2-d-3-carbaldehyde (**d-1a**) was synthesized according to known method.[3] Merck, pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC and were visualized with a UV lamp. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H NMR spectra were recorded on Varian VNS (600 and 150MHz) spectrometer at the core research center for natural products and medical materials of Yeungnam University. The chemical shifts were described in parts per million (δ) relative to TMS (0 ppm) as internal standard or relative to the resonance of the residual protonated solvent (^{1}H : $CDCl_3$, δ = 7.24 ppm). ^{13}C NMR spectra were referenced to the internal solvent signals (^{13}C: $CDCl_3$, δ = 77.0 ppm). IR spectra were recorded on a PerkinElmer Spectrum Two ™IR spectrometer. Melting points were measured with a Fisher Johns melting point apparatus and uncorrected. The high-resolution mass spectra (HRMS) were measured using a JEOL JMS-600 mass spectrometer (positive ion EI mode) at the Korean Basic Science Institute. GC-MS data was recorded on Shimadzu GCMS-QP2010 Ultra using SH-Rxi-1ms column.

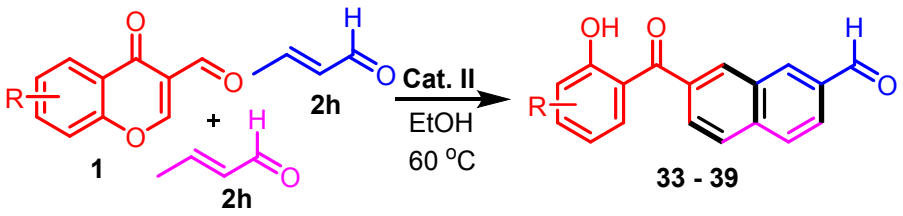
2. General procedures:

2.1 General procedure for synthesis of compounds 3, 5-32, d-3



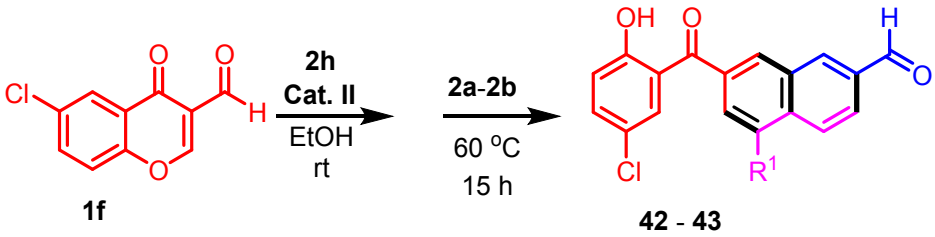
To a solution of 3-formylchromone **1** (1.0 mmol) and *α,β*-unsaturated aldehyde **2** (1.2eq.) in ethanol (5.0 mL) was added Cat. **II** (10 mol %) at room temperature. The mixture was stirred at 60 °C for 20 – 22 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

2.2 General procedure for synthesis of compounds 33-39



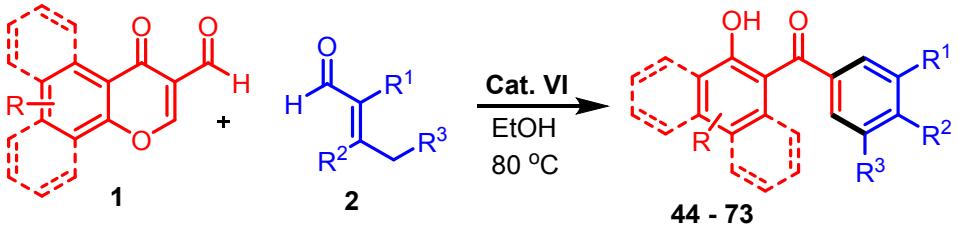
To a solution of 3-formylchromone **1** (1.0 mmol) and *α,β*-unsaturated aldehyde **2** (2.4 eq.) in ethanol (5.0 mL) was added Cat. **II** (10 mol %) at room temperature. The mixture was stirred at 60 °C for 20 – 22 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

2.3 General procedure for synthesis of compounds 42-43



To a solution of 3-formylchromone **1f** (1.0 mmol) and *α,β*-unsaturated aldehyde **2h** (1.2 eq.) in ethanol (5.0 mL) was added Cat. **II** (10 mol %) at room temperature. The mixture was kept to stir at room temperature for 10 h approx. After complete disappearance of **1f** as indicated by TLC, *α,β*-unsaturated aldehyde **2a** or **2b** were added at room temperature. The mixture was stirred at 60 °C for 10 - 15h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

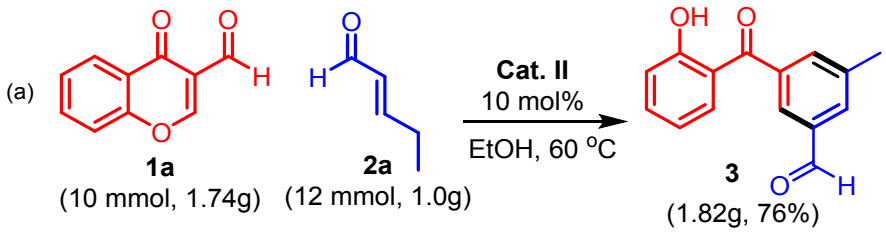
2.4 General procedure for synthesis of compounds 44-73, d-4



To a solution of 3-formylchromone **1** (1.0 mmol) and *α,β*-unsaturated aldehydes **2** (1.2 eq.) in ethanol (5.0 mL) was added Cat. **VI** (20 mol %) at room temperature. The mixture was stirred at 80 °C for 12 – 15 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

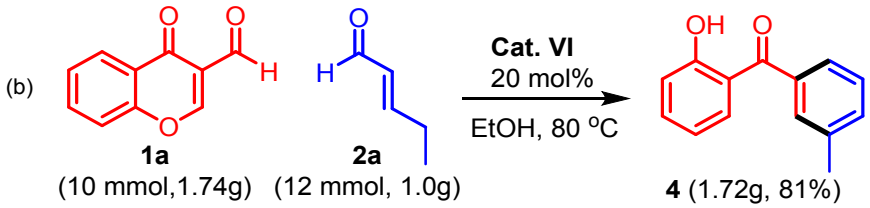
3. Gram scale synthesis:

3.1 Gram Scale synthesis of compounds 3



To a solution of 3-formylchromone **1a** (1.74g, 10 mmol) and *α,β*-unsaturated aldehyde **2a** (1.0g, 1.2 eq.) in ethanol (50 mL) was added Cat. **II** (253mg, 10 mol %) at room temperature. The mixture was stirred at 60 °C for 20 – 22 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product **3** in 76% yield.

3.2 Gram Scale synthesis of compounds 4

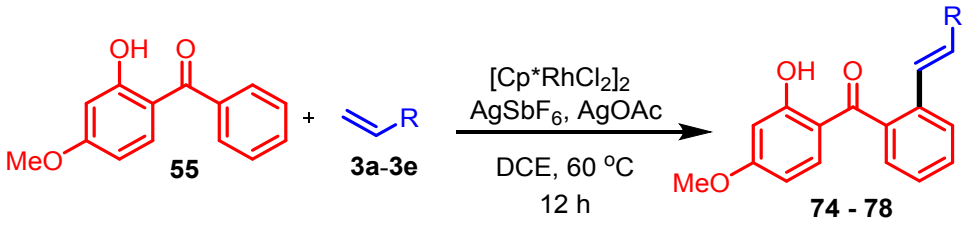


To a solution of 3-formylchromone **1a** (1.74g, 10 mmol) and *α,β*-unsaturated aldehydes **2a** (1.0g, 1.2 eq.) in ethanol (50 mL) was added Cat. **VI** (170mg, 20 mol %) at room temperature. The

mixture was stirred at 80 °C for 12 – 15 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product **4** in 81% yield.

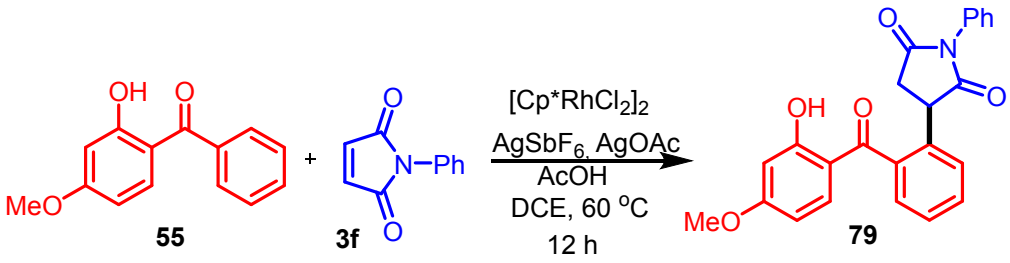
4. Synthetic transformations of 55:

4.1 General procedure for synthesis of compounds 74-78



To a solution of **55** (0.5 mmol) and **3** (1.2 eq.) in DCE (3.0 mL) were added $[Cp^*RhCl_2]_2$ (2.5 mmol), $AgSbF_6$ (10 mol %), AgOAc (30 mol %) at room temperature. The mixture was stirred 60 °C for 12 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

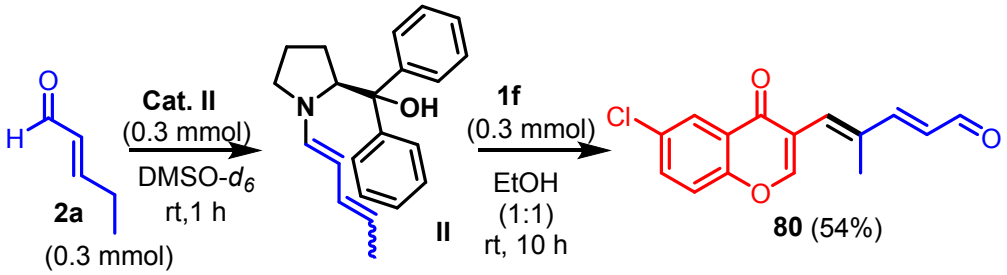
4.2 Procedure for synthesis of compound 79



To a solution of **55** (0.5 mmol) and **3f** (1.2 eq.) in DCE (3.0 mL) were added $[Cp^*RhCl_2]_2$ (2.5 mmol), $AgSbF_6$ (10 mol %), AgOAc (30 mol %) and AcOH (5.0 eq.) at room temperature. The mixture was stirred 60 °C for 12 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

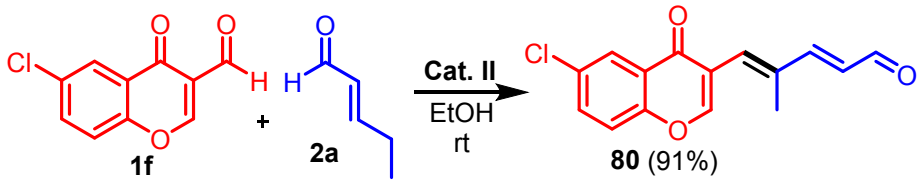
5 Control experiment:

5.1 Procedure for synthesis of compound 80 *via* intermediate II



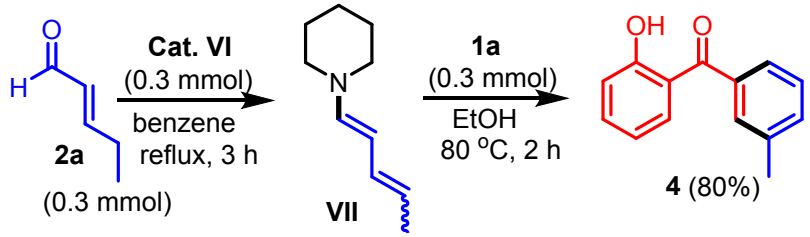
To a solution of *α,β*-unsaturated aldehyde **2a** (0.3 mmol) was added Cat. **II** (0.3 mmol) in DMSO-d_6 (2 mL) at room temperature. The mixture was stirred for 1 h and analyzed for ^{1}H NMR spectroscopy. To this crude mixture, **1f** (0.3 mmol) and ethanol (2 mL) were added. The mixture was allowed to stir at room temperature for additional 10 h and monitored by TLC. The reaction mixture was evaporated in rotary evaporator to remove ethanol. Workup by water–ethyl acetate and drying over anhydrous magnesium sulphate gave yellow residue. The residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired intermediate **80**.

5.2 Procedure for synthesis of compound 80



To a solution of 3-formylchromone **1f** (1.0 mmol) and *α,β*-unsaturated aldehyde **2a** (1.2 eq.) in ethanol (5.0 mL) was added Cat. **II** (10 mol %) at room temperature. The mixture was allowed to stir at room temperature for 12h approx. After completion of reaction as indicated by TLC, the solid precipitate obtained was filtered and washed with ethyl acetate to obtain **11** as a yellow solid.

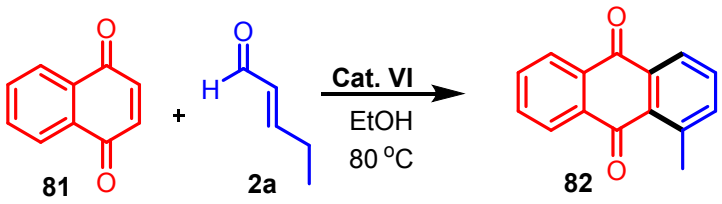
5.3 Procedure for synthesis of compound 4 *via* intermediate VII



To a solution of *α,β*-unsaturated aldehyde **2a** (0.3 mmol) in benzene (2 mL) was added piperidine (0.3 mmol) at room temperature. The mixture was stirred and heated under reflux for 3 h approx. The mixture was allowed to cool at room temperature. To this mixture of **VII** was added **1a** (0.3 mmol) and ethanol (2 mL) at room temperature. The mixture was stirred at 80 °C for 2 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary

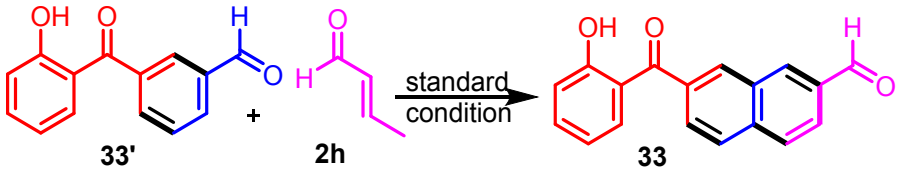
evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product **4**.

5.4 Procedure for synthesis of compound 82



To a solution of 1,4-naphthoquinone **81** (1.0 mmol) and *α,β*-unsaturated aldehyde **2a** (1.2 eq.) in ethanol (5.0 mL) was added Cat. **VI** (20 mol %) at room temperature. The mixture was stirred and heated at 80 °C for 10 h approx. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

5.5 Attempt for synthesis of compound 33



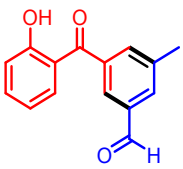
The compound **33'** was prepared according to literature report.[4] To a solution of **33'** and *α,β*-unsaturated aldehyde **2h** (1.2 eq.) in ethanol (5.0 mL) was added Cat. **II** (10 mol %) at room temperature. The mixture was stirred and heated at 60 °C for 22 h approx. The reaction was continuously monitored by TLC. Since no new spot was observed in TLC the reaction was stopped after 22 h.

References:

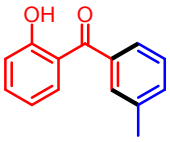
1. Ł. Albrecht, G. Dickmeiss, F. Cruz-Acosta, C. Rodríguez-Escrich, R. L. Davis and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2012, **134**, 2543.
2. H. Duckert, V. Khedkar, H. Waldmann and K. Kumar, *Chem.–Eur. J.*, 2011, **17**, 5130.
3. K. Wittstein, A. B. García, M. Schürmann and K. Kumar, *Synlett*, 2012, 227.
4. F. Weng, C. Wang and B. Xu, *Tetrahedron Lett.*, 2010, **51**, 2593.

6. Characterization data of synthesized compounds

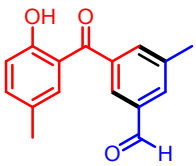
3-(2-Hydroxybenzoyl)-5-methylbenzaldehyde (3). Yield 91% (218 mg) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.86 (1H, s), 10.04 (1H, s), 7.93 (1H, s), 7.89 (1H, s), 7.73 (1H, s), 7.53 – 7.50 (2H, m), 7.08 (1H, d, J = 8.3 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.51 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 191.3, 163.3, 139.7, 138.7, 136.8, 136.3, 135.1, 133.2, 132.8, 127.7, 118.9, 118.8, 118.6, 21.2; IR (neat) 3286, 2923, 1736, 1699, 1624, 1211, 1153, 759 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{12}O_3$: 240.0786. Found: 240.0785.



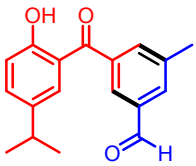
(2-Hydroxyphenyl)(m-tolyl)methanone (4). Yield 85% (181 mg) as a yellow solid: mp 53 – 55 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.04 (1H, s), 7.58 (1H, d, J = 7.8 Hz), 7.49 – 7.27 (2H, m), 7.44 (1H, d, J = 6.8 Hz), 7.38 – 7.35 (2H, m), 7.05 (1H, d, J = 8.3 Hz), 6.86 (1H, t, J = 7.6 Hz), 2.42 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.8, 163.1, 138.2, 137.8, 136.1, 133.5, 132.6, 129.5, 128.0, 126.3, 119.1, 118.5, 118.2, 21.3; IR (neat) 3042, 2923, 1727, 1624, 1482, 1444, 1248, 1205, 960, 757 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{12}O_2$: 212.0837. Found: 212.0834.



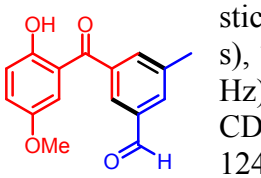
3-(2-Hydroxy-5-methylbenzoyl)-5-methylbenzaldehyde (5). Yield 81% (205 mg) as a yellow solid: mp 108 – 110 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.67 (1H, s), 10.05 (1H, s), 7.92 (1H, s), 7.90 (1H, s), 7.72 (1H, s), 7.34 (1H, d, J = 8.3 Hz,), 7.25 (1H, s), 6.99 (1H, d, J = 8.5 Hz,), 2.52 (3H, s), 2.24 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 191.4, 161.2, 139.6, 138.9, 137.9, 136.3, 135.0, 132.7, 132.6, 128.1, 127.6, 118.5, 118.4, 21.2, 20.5; IR (neat) 3458, 2922, 1738, 1696, 1631, 1482, 1340, 1189, 783, 665 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{14}O_3$: 254.0943. Found: 254.0946.



3-(2-Hydroxy-5-isopropylbenzoyl)-5-methylbenzaldehyde (6). Yield 78% (220 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.66 (1H, s), 10.04 (1H, s), 7.95 (1H, s), 7.90 (1H, s), 7.75 (1H, s), 7.41 (1H, dd, J = 8.6, 2.3 Hz), 7.31 (1H, d, J = 2.3 Hz), 7.02 (1H, d, J = 8.6 Hz), 2.80 (1H, m), 2.52 (3H, s), 1.15 (6H, d, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.3, 191.3, 161.4, 139.6, 139.2, 138.8, 136.3, 135.3, 135.2, 132.6, 130.3, 127.9, 118.4, 118.4, 33.1, 23.9, 21.21; IR (neat) 3425, 2959, 1698, 1629, 1589, 1481, 1320, 1191, 791, 663 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1253.



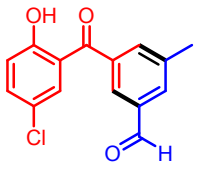
3-(2-Hydroxy-5-methoxybenzoyl)-5-methylbenzaldehyde (7). Yield 88% (237 mg) as a yellow sticky oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.41 (1H, s), 10.04 (1H, s), 7.95 (1H, s), 7.89 (1H, s), 7.74 (1H, s), 7.15 (1H, dd, J = 9.0, 3.1 Hz), 7.02 (1H, d, J = 9.1 Hz), 6.95 (1H, d, J = 3.0 Hz), 3.67 (3H, s), 2.51 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.9, 191.3, 157.6, 151.5, 139.7, 138.7, 136.3, 135.0, 132.8, 127.6, 124.5, 119.4, 118.3, 115.8, 55.9, 21.2; IR (neat) 3452, 2922, 1697, 1592, 1484, 1200, 1034, 790, 664 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{14}O_4$: 270.0892. Found: 270.0893.



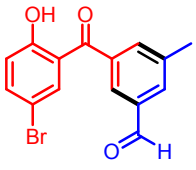
3-(2-Hydroxy-4-methoxybenzoyl)-5-methylbenzaldehyde (8). Yield 85% (230 mg) as a brown solid: mp 103 – 105 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.51 (1H, s), 10.03 (1H, s), 7.89 (1H, s), 7.86 (1H, s), 7.68 (1H, s), 7.41 (1H, d, J = 8.9 Hz),

6.51 (1H, d, J = 2.5 Hz), 6.41 (1H, dd, J = 9.0, 2.5 Hz), 3.85 (3H, s), 2.50 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 191.4, 166.5, 166.4, 139.6, 139.1, 136.2, 134.9, 134.8, 132.3, 127.5, 112.8, 107.8, 101.2, 55.6, 21.2; IR (neat) 3438, 2922, 1690, 1587, 1349, 1237, 802, 608 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{14}O_4$: 270.0892. Found: 270.0893.

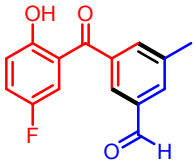
3-(5-Chloro-2-hydroxybenzoyl)-5-methylbenzaldehyde (9). Yield 79% (217 mg) as a yellow solid: mp 108 – 110 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.73 (1H, s), 10.05 (1H, s), 7.92 (2H, s), 7.71 (1H, s), 7.48 – 7.44 (2H, m), 7.04 (1H, d, J = 8.8 Hz), 2.53 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 191.2, 161.7, 139.9, 138.1, 136.70, 136.4, 134.8, 133.1, 131.9, 127.5, 123.6, 120.3, 119.4, 21.2; IR (neat) 3448, 2921, 2852, 1699, 1595, 1466, 1337, 1197, 790, 698 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{11}ClO_3$: 274.0397. Found: 274.0397.



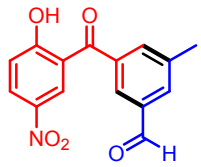
3-(5-Bromo-2-hydroxybenzoyl)-5-methylbenzaldehyde (10). Yield 82% (261 mg) as a brown solid: mp 111 – 113 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.74 (1H, s), 10.05 (1H, s), 7.92 (1H, s), 7.91 (1H, s), 7.70 (1H, s), 7.59 (2H, d, J = 7.5 Hz), 6.99 (1H, d, J = 9.5 Hz), 2.53 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.5, 191.1, 162.1, 139.9, 139.4, 138.1, 136.5, 134.9, 134.8, 133.1, 127.5, 120.6, 120.1, 110.5, 21.2; IR (neat) 3482, 3005, 1739, 1700, 1594, 1467, 1337, 1200, 785 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{11}BrO_3$: 317.9892. Found: 317.9889.



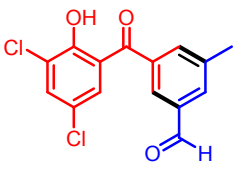
3-(5-Fluoro-2-hydroxybenzoyl)-5-methylbenzaldehyde (11). Yield 76% (195 mg) as a brown solid: mp 133 – 135 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.58 (1H, s), 10.05 (1H, s), 7.93 (1H, s), 7.92 (1H, s), 7.72 (1H, s), 7.27 (1H, m), 7.18 (1H, dd, J = 8.7, 3.1 Hz), 7.05 (1H, dd, J = 9.1, 4.5 Hz), 2.52 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.5, 191.1, 159.4, 155.4, 153.8, 139.9, 138.2, 136.4, 134.9, 133.1, 127.5, 124.5, 124.3, 120.0, 120.0, 117.9, 117.7, 21.2; IR (neat) 3468, 2924, 1739, 1614, 1479, 1344, 1202, 782 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{11}FO_3$: 258.0692. Found: 258.0690.



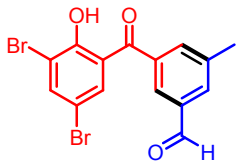
3-(2-Hydroxy-5-nitrobenzoyl)-5-methylbenzaldehyde (12). Yield 85% (243 mg) as a yellow solid: mp 137 – 139 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.44 (1H, s), 10.06 (1H, s), 8.49 (1H, d, J = 2.8 Hz), 8.40 (1H, dd, J = 9.2, 2.8 Hz), 7.98 (1H, s), 7.96 (1H, s), 7.75 (1H, s), 7.20 (1H, d, J = 9.2 Hz), 2.55 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 190.9, 167.8, 140.3, 139.6, 137.3, 136.7, 134.8, 134.0, 131.2, 129.2, 127.4, 119.7, 117.7, 21.2; IR (neat) 3485, 2970, 1737, 1632, 1470, 1377, 1230, 701 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{11}NO_5$: 285.0637. Found: 285.0640.



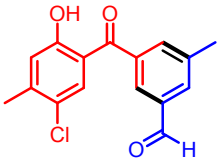
3-(3,5-Dichloro-2-hydroxybenzoyl)-5-methylbenzaldehyde (13). Yield 76% (235 mg) as a brown solid: mp 140 – 142 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.20 (1H, s), 10.05 (1H, s), 7.94 (1H, s), 7.92 (1H, s), 7.71 (1H, s), 7.62 (1H, d, J = 2.5 Hz), 7.40 (1H, d, J = 2.5 Hz), 2.53 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.3, 191.0, 157.5, 140.1, 137.6, 136.5, 136.2, 134.8, 133.6, 130.5, 127.5, 124.3, 123.5, 120.0, 21.2; IR (neat) 3482, 2924, 1702, 1629, 1428, 1215, 747 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}Cl_2O_3$: 308.0007. Found: 308.0007.



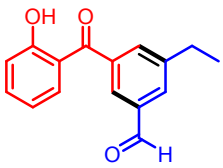
3-(3,5-Dibromo-2-hydroxybenzoyl)-5-methylbenzaldehyde (14). Yield 83% (330 mg) as a yellow solid: mp 173 – 175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.33 (1H, s), 10.04 (1H, s), 7.93 (1H, s), 7.90 (1H, s), 7.89 (1H, d, J = 2.3 Hz), 7.70 (1H, s), 7.57 (1H, d, J = 2.3 Hz), 2.53 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.1, 190.9, 158.7, 141.7, 140.1, 137.5, 136.5, 134.8, 134.2, 133.5, 127.5, 120.4, 113.4, 110.4, 21.2; IR (neat) 3465, 2969, 1738, 1692, 1427, 1215, 785 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}Br_2O_3$: 395.8997. Found: 395.8994.



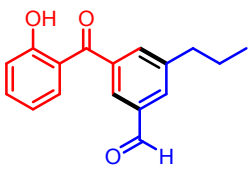
3-(5-Chloro-2-hydroxy-4-methylbenzoyl)-5-methylbenzaldehyde (15). Yield 77% (222 mg) as a yellow solid: mp 125 – 127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.73 (1H, s), 10.04 (1H, s), 7.90 (2H, s), 7.69 (1H, s), 7.43 (1H, s), 6.97 (1H, s), 2.52 (3H, s), 2.39 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.1, 191.2, 161.6, 146.2, 139.8, 138.3, 136.4, 134.8, 132.9, 132.3, 127.5, 124.3, 120.6, 117.7, 21.2, 20.8; IR (neat) 3436, 3038, 2917, 1774, 1699, 1513, 1233, 1085, 755 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{13}ClO_3$: 288.0553. Found: 288.0550.



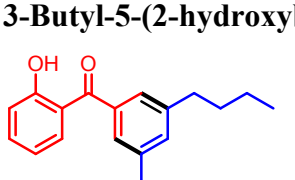
3-Ethyl-5-(2-hydroxybenzoyl)benzaldehyde (16). Yield 75% (191 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (1H, s), 10.05 (1H, s), 7.95 (1H, s), 7.92 (1H, s), 7.75 (1H, s), 7.52 (2H, m), 7.08 (1H, d, J = 8.3 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.81 (2H, q, J = 7.6 Hz), 1.31 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 191.4, 163.3, 145.9, 138.8, 136.7, 136.4, 134.1, 133.2, 131.6, 128.0, 118.9, 118.8, 118.6, 28.5, 15.1; IR (neat) 3465, 3073, 2966, 1698, 1624, 1592, 1482, 1208, 757, 656 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{14}O_3$: 254.0943. Found: 254.0940.



3-(2-Hydroxybenzoyl)-5-propylbenzaldehyde (17). Yield 84% (225 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (1H, s), 10.05 (1H, s), 7.95 (1H, s), 7.90 (1H, s), 7.73 (1H, s), 7.53 – 7.50 (2H, m), 7.07 (1H, d, J = 8.2 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.74 (2H, t J = 7.2 Hz), 1.73 – 1.67 (2H, m), 0.96 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 191.4, 163.3, 144.4, 138.7, 136.7, 136.3, 134.6, 133.1, 132.1, 128.1, 118.9, 118.8, 118.6, 37.5, 24.2, 13.6; IR (neat) 3463, 2969, 2929, 1732, 1698, 1592, 1338, 1209, 755 cm^{-1}; HRMS m/z (M^+) calcd for $C_{17}H_{16}O_3$: 268.1099. Found: 268.1097.



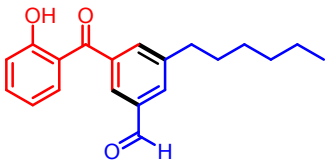
3-Butyl-5-(2-hydroxybenzoyl)benzaldehyde (18). Yield 81% (229 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (1H, s), 10.05 (1H, s), 7.95 (1H, s), 7.90 (1H, s), 7.73 (1H, s), 7.53 – 7.50 (2H, m), 7.07 (1H, d, J = 8.2 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.76 (2H, t, J = 7.8 Hz), 1.68 – 1.63 (2H, m), 1.40 – 1.33 (2H, m), 0.93 (3H, t, J = 7.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 191.4, 163.3, 144.6, 138.7, 136.7, 136.3, 134.6, 133.1, 132.1, 128.0, 118.9, 118.8, 118.6, 35.2, 33.2, 22.2, 13.8; IR (neat) 3463, 3073, 2928, 1700, 1625, 1340, 1209, 757, 656 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1258.



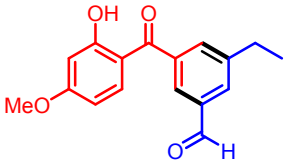
3-(2-Hydroxybenzoyl)-5-pentylbenzaldehyde (19). Yield 86% (254 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (1H, s), 10.05 (1H, s), 7.95 (1H, s), 7.90 (1H, s), 7.73 (1H, s), 7.52 (2H, t, J = 8.8 Hz), 7.08 (1H, d, J = 8.3 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.75 (2H, t, J = 7.8 Hz), 1.68 (2H, m), 1.35

– 1.31 (4H, m), 0.89 (3H, t, J = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 191.4, 163.3, 144.6, 138.73, 136.7, 136.3, 134.6, 133.1, 132.1, 128.0, 118.9, 118.8, 118.6, 35.5, 31.3, 30.7, 22.4, 13.9; IR (neat) 3468, 2927, 2856, 1701, 1625, 1445, 1209, 757, 656 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1414.

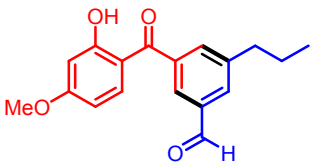
3-Hexyl-5-(2-hydroxybenzoyl)benzaldehyde (20). Yield 81% (251 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (1H, s), 10.05 (1H, s), 7.95 (1H, s), 7.90 (1H, s), 7.73 (1H, s), 7.53 – 7.50 (2H, m), 7.08 (1H, d, J = 8.2 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.77 – 2.73 (2H, m), 1.69 – 1.64 (2H, m), 1.35 – 1.32 (2H, m), 1.31 – 1.27 (4H, m), 0.89 – 0.85 (3H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 191.4, 163.3, 144.7, 138.7, 136.7, 136.3, 134.6, 133.2, 132.1, 128.0, 118.9, 118.8, 118.6, 35.5, 31.5, 31.0, 28.8, 22.5, 14.0; IR (neat) 3456, 2926, 2855, 1701, 1625, 1445, 1209, 757, 657 cm^{-1}; HRMS m/z (M^+) calcd for $C_{20}H_{22}O_3$: 310.1569. Found: 310.1570.



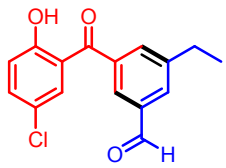
3-Ethyl-5-(2-hydroxy-4-methoxybenzoyl)benzaldehyde (21). Yield 72% (205 mg) as a brown solid: mp 66 – 68 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.53 (1H, s), 10.04 (1H, s), 7.91 (1H, s), 7.89 (1H, s), 7.71 (1H, s), 7.42 (1H, d, J = 8.9 Hz), 6.52 (1H, d, J = 2.5 Hz), 6.42 (1H, dd, J = 9.0, 2.5 Hz), 3.86 (3H, s), 2.80 (2H, q, J = 7.6 Hz), 1.30 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.7, 191.5, 166.5, 166.4, 145.8, 139.1, 136.3, 134.8, 133.9, 131.2, 127.8, 112.8, 107.8, 101.2, 55.7, 28.5, 15.2; IR (neat) 3454, 2965, 2848, 1695, 1590, 1353, 1231, 957, 801, 612 cm^{-1}; HRMS m/z (M^+) calcd for $C_{17}H_{16}O_4$: 284.1049. Found: 284.1049.



3-(2-Hydroxy-4-methoxybenzoyl)-5-propylbenzaldehyde (22). Yield 79% (236 mg) as a brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.51 (1H, s), 10.04 (1H, s), 7.91 (1H, s), 7.87 (1H, s), 7.68 (1H, s), 7.41 (1H, d, J = 8.9 Hz), 6.51 (1H, d, J = 2.5 Hz), 6.41 (1H, dd, J = 9.0, 2.5 Hz), 3.85 (3H, s), 2.73 (2H, t, J = 7.7 Hz), 1.73 – 1.67 (2H, m), 0.96 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.7, 191.5, 166.5, 166.4, 144.3, 139.0, 136.3, 134.8, 134.4, 131.7, 127.8, 112.8, 107.7, 101.2, 55.6, 37.5, 24.2, 13.6; IR (neat) 3468, 2959, 2869, 1700, 1611, 1350, 1231, 957, 778 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{18}O_4$: 298.1205. Found: 298.1205.



3-(5-Chloro-2-hydroxybenzoyl)-5-ethylbenzaldehyde (23). Yield 75% (215 mg) as a light yellow solid; mp 51 – 53 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.75 (1H, s), 10.06 (1H, s), 7.95 (1H, s), 7.93 (1H, s), 7.73 (1H, s), 7.47 – 7.45 (2H, m), 7.04 (1H, d, J = 9.6 Hz), 2.82 (2H, q, J = 7.6 Hz), 1.32 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 191.2, 161.7, 146.1, 138.1, 136.6, 136.5, 133.9, 132.0, 132.0, 127.8, 123.6, 120.3, 119.4, 28.5, 15.2; IR (neat) 3452, 3070, 2969, 1699, 1627, 1466, 1193, 986, 735 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{13}ClO_3$: 288.0553. Found: 288.0557.



3-(5-Chloro-2-hydroxybenzoyl)-5-propylbenzaldehyde (24). Yield 68% (206 mg) as a light yellow solid; mp 75 – 77 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.73 (1H, s), 10.06 (1H, s), 7.94 (1H, s), 7.93 (1H, s), 7.70 (1H, s), 7.46 – 7.44 (2H, m), 7.03 (1H, d, J = 9.6 Hz), 2.75 (2H,t, J = 7.8 Hz), 1.74 – 1.68 (2H, m) 0.97 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.5, 191.2, 161.7, 144.6, 138.0, 136.6, 136.5, 134.4, 132.5, 132.0, 127.9, 123.6, 120.2, 119.4, 37.5, 24.2, 13.6; IR (neat) 3465, 3063, 2960, 1700, 1634, 1463, 1322, 1179, 985, 728 cm^{-1}; HRMS m/z (M^+) calcd for $C_{17}H_{15}ClO_3$: 302.0710. Found: 302.0711.

5-(2-Hydroxybenzoyl)-[1,1'-biphenyl]-3-carbaldehyde (25). Yield 72% (218 mg) as a yellow sticky liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (1H, s), 10.14 (1H, s), 8.30 (1H, s), 8.13 (1H, s), 8.11 (1H, s), 7.65 (2H, d, J = 7.6 Hz), 7.57 – 7.53 (2H, m), 7.49 (2H, t, J = 7.5 Hz), 7.43 (1H, t, J = 7.4 Hz), 7.10 (1H, d, J = 8.4 Hz), 6.90 (1H t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.2, 191.2, 163.4, 142.7, 139.3, 138.5, 137.0, 136.9, 133.2, 133.0, 130.7, 129.2, 129.0, 128.6, 127.2, 119.1, 118.8, 118.7; IR (neat) 3429, 3061, 2929, 1671, 1626, 1344, 1239, 1156, 760 cm^{-1}; HRMS m/z (M^+) calcd for $C_{20}H_{14}O_3$: 302.0943. Found: 302.0945.

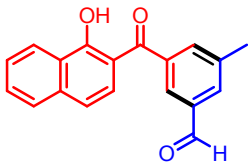
3-(2-Hydroxy-1-naphthoyl)-5-methylbenzaldehyde (27). Yield 65% (189 mg) as a brown solid: mp 118 – 120 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.22 (1H, s), 9.92 (1H, s), 7.97 (1H, d, J = 9.0 Hz), 7.89 (1H, s), 7.85 (1H, s), 7.77 (1H, d, J = 8.0 Hz), 7.73 (1H, s), 7.28 (1H, t, J = 7.4 Hz), 7.25 (2H, dd, J = 9.2, 4.0 Hz), 7.15 (1H, t, J = 7.7 Hz), 2.44 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.1, 191.3, 161.8, 141.2, 139.8, 136.8, 136.6, 135.3, 132.9, 132.0, 128.8, 128.6, 128.5, 126.9, 125.9, 123.9, 119.2, 113.9, 21.1; IR (neat) 3266, 3073, 2922, 1698, 1625, 1591, 1262, 1192, 943, 819, 744 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{14}O_3$: 290.0943. Found: 290.0940.

3-Ethyl-5-(2-hydroxy-1-naphthoyl)benzaldehyde (28). Yield 69% (211 mg) as a brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.29 (1H, s), 9.94 (1H, s), 7.96 (1H, d, J = 9.0 Hz), 7.90 (2H, s), 7.76 (1H, d, J = 7.9 Hz), 7.70 (1H, s), 7.28 – 7.24 (2H, m), 7.23 (1H, d, J = 9.4 Hz), 7.14 (1H, t, J = 7.8 Hz), 2.70 (2H, q, J = 7.6 Hz), 1.20 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.0, 191.4, 161.9, 145.9, 141.1, 136.8, 136.7, 134.6, 132.0, 131.7, 128.9, 128.8, 128.4, 126.9, 125.9, 123.9, 119.2, 113.8, 28.4, 15.1; IR (neat) 3286, 2966, 2927, 1740, 1697, 1622, 1587, 1189, 818, 748 cm^{-1}; HRMS m/z (M^+) calcd for $C_{20}H_{16}O_3$: 304.1099. Found: 304.1098.

3-(2-Hydroxy-1-naphthoyl)-5-propylbenzaldehyde (29). Yield 75% (238 mg) as a brown solid: mp 114 – 116 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.23 (1H, s), 9.89 (1H, s), 7.89 (1H, d, J = 9.0 Hz), 7.87 (1H, s), 7.82 (1H, s), 7.70 (1H, d, J = 8.1 Hz), 7.59 (1H, s), 7.22 – 7.18 (2H, m), 7.17 (1H, d, J = 8.5 Hz), 7.07 (1H, t, J = 7.8 Hz), 2.56 (2H, t, J = 7.6 Hz), 1.55 – 1.49 (2H, m), 0.82 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.1, 191.4, 161.9, 144.3, 141.1, 136.8, 136.7, 135.1 132.34,

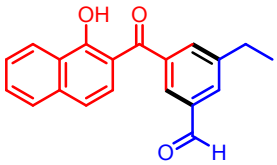
132.0, 128.8 128.82, 128.4, 126.9, 125.9, 123.9, 119.2, 113.8, 37.3, 24.1, 13.5; IR (neat) 3324, 3018, 2968, 1740, 1701, 1645, 1373, 1215, 950, 821, 755 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{18}O_3$: 318.1256. Found: 318.1256.

3-(1-Hydroxy-2-naphthoyl)-5-methylbenzaldehyde (30). Yield 78% (226 mg) as a brown solid:



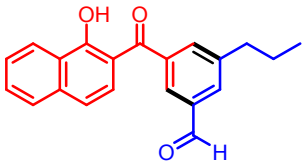
mp 102 – 104 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 13.80 (1H, s), 10.06 (1H, s), 8.51 (1H, d, J = 8.3 Hz), 7.98 (1H, s), 7.90 (1H, s), 7.76 (2H, d, J = 9.0 Hz), 7.66 (1H, t, J = 7.5 Hz), 7.56 (1H, t, J = 7.6 Hz), 7.45 (1H, d, J = 8.9 Hz), 7.23 (1H, d, J = 9.7 Hz), 2.53 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 191.4, 164.1, 139.6, 139.0, 137.4, 136.3 135.1, 132.4, 130.6, 127.8, 127.4, 126.7, 126.1, 125.2, 124.5 118.3, 112.2 21.2; IR (neat) 3466, 3063, 2920, 1699, 1593, 1294, 1230, 803, 761 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{14}O_3$: 290.0943. Found: 290.0945.

3-Ethyl-5-(1-hydroxy-2-naphthoyl)benzaldehyde (31). Yield 72% (219 mg) as a yellow solid:



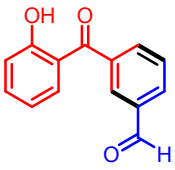
mp 93 – 95 °C; ^1H NMR (600 MHz, $CDCl_3$)) δ 13.81 (1H, s), 10.07 (1H, s), 8.52 (1H, d, J = 8.3 Hz), 8.00 (1H, s), 7.93 (1H, s), 7.80 (1H, s), 7.76 (1H, d, J = 8.1 Hz), 7.66 (1H, t, J = 7.5 Hz), 7.56 (1H, t, J = 7.6 Hz), 7.45 (1H, d, J = 8.8 Hz), 7.23 (1H, d, J = 8.8 Hz), 2.83 (2H, q, J = 7.6 Hz), 1.32 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.2, 191.5, 164.1, 145.8, 139.0, 137.4, 136.4, 134.1, 131.2, 130.6, 128.1, 127.4, 126.7, 126.1, 125.2, 124.5, 118.3, 112.3, 28.5, 15.2; IR (neat) 3457, 3025, 2969, 1739, 1626, 1353, 1230, 818, 764 cm^{-1}; HRMS m/z (M^+) calcd for $C_{20}H_{16}O_3$: 304.1099. Found: 304.1102.

3-(1-Hydroxy-2-naphthoyl)-5-propylbenzaldehyde (32). Yield 83% (264 mg) as a brown oil: ^1H



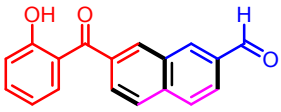
NMR (600 MHz, $CDCl_3$) δ 13.81 (1H, s), 10.06 (1H, s), 8.51 (1H, d, J = 8.3 Hz), 8.00 (1H, s), 7.91 (1H, s), 7.77 – 7.75 (2H, m), 7.66 (1H, t, J = 7.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.45 (1H, d, J = 8.9 Hz), 7.23 (1H, d, J = 8.9 Hz), 2.75(2H, t, J = 7.8 Hz), 1.75 – 1.69 (2H, m), 0.98 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 191.5, 164.1, 144.3, 139.0, 137.4, 136.3, 134.6, 131.8, 130.6, 128.1, 127.4, 126.6, 126.1, 125.2, 124.5, 118.2, 112.3, 37.5, 24.2, 13.6; IR (neat) 3458, 3063, 2958, 1743, 1594, 1459, 1230, 763 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{18}O_3$: 318.1256. Found: 318.1255.

3-(2-Hydroxybenzoyl)benzaldehyde (33'). Yield 57% (129 mg) as a yellow solid: mp 65 – 67 °C;

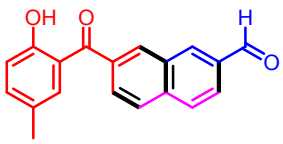


^1H NMR (600 MHz, $CDCl_3$) δ 11.83 (1H, s), 10.07 (1H, s), 8.14 (1H, s), 8.08 (1H, d, J = 7.6 Hz), 7.91 (1H, d, J = 7.4 Hz), 7.68 (1H, t, J = 7.7 Hz), 7.52 – 7.48 (2H, m), 7.06 (1H, d, J = 8.4 Hz), 6.87 (1H, t, J = 7.5 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 191.1 163.2, 138.6, 136.8, 136.2, 134.4 133.1, 132.3, 130.2, 129.2 118.9, 118.6, 118.6; IR (neat) 3428, 3051, 2835, 1698, 1623, 1598, 1191, 972, 757, 646 cm^{-1} ; HRMS m/z (M^+) calcd for $C_{14}H_{10}O_3$: 226.0630. Found: 226.0628.

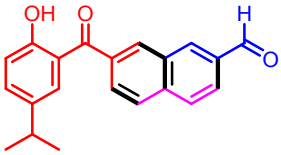
3-(2-Hydroxybenzoyl)-1-naphthaldehyde (33). Yield 75% (206 mg) as a white solid: mp 125 – 127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.93 (1H, s), 10.17 (1H, s), 8.42 (1H, s), 8.31 (1H, s), 8.07 (1H, d, J = 8.4 Hz), 8.02 (2H, t, J = 7.2 Hz), 7.91 (1H, d, J = 8.5 Hz), 7.62 (1H, d, J = 8.0 Hz), 7.54 (1H, t, J = 7.8 Hz), 7.10 (1H, d, J = 8.4 Hz), 6.89 (1H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.6, 191.6, 163.3, 137.6, 136.6, 136.3, 135.1, 134.9, 133.3, 131.5, 131.4, 129.0, 128.5, 128.4, 125.0, 119.0, 118.8, 118.6; IR (neat) 3463, 3060, 2922, 1691, 1623, 1216, 852, 758 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{12}O_3$: 276.0786. Found: 276.0784.



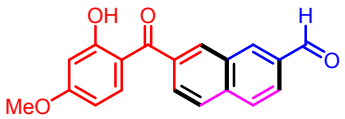
3-(2-Hydroxy-5-methylbenzoyl)-1-naphthaldehyde (34). Yield 68% (197 mg) as a yellow solid: mp 172 – 174 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.74 (1H, s), 10.19 (1H, s), 8.44 (1H, s), 8.30 (1H, s), 8.08 (1H, d, J = 8.5 Hz), 8.03 – 8.01 (2H, m), 7.91 (1H, d, J = 8.4 Hz), 7.37 – 7.34 (2H, m), 7.01 (1H, d, J = 8.4 Hz), 2.24 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.6, 191.7, 161.2, 137.7, 137.6, 136.5, 135.1, 134.9, 132.9, 131.6, 131.2, 129.1, 128.5, 128.4, 128.0, 125.0, 118.8, 118.4, 20.5; IR (neat) 3468, 2922, 2853, 1736, 1684, 1481, 1203, 806, 785 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{14}O_3$: 290.0943. Found: 290.0941.



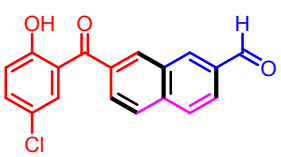
3-(2-Hydroxy-5-isopropylbenzoyl)-1-naphthaldehyde (35). Yield 73% (233 mg) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.75 (1H, s), 10.18 (1H, s), 8.42 (1H, s), 8.32 (1H, s), 8.08 (1H, d, J = 8.6 Hz), 8.03 – 8.01 (2H, m), 7.92 (1H, d, J = 8.4 Hz), 7.43 – 7.42 (2H, m), 7.04 (1H, d, J = 8.9 Hz), 2.82 – 2.78 (1H, m), 1.16 (6H, d, J = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 191.6, 161.4, 139.2, 137.6, 136.5, 135.1, 135.0, 134.9, 131.6, 131.4 130.5, 129.1, 128.5, 128.4, 125.0, 118.7, 118.4, 33.1, 23.9; IR (neat) 3466, 3020, 2958, 1738, 1693, 1627, 1207, 830 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{18}O_3$: 318.1256. Found: 318.1253.



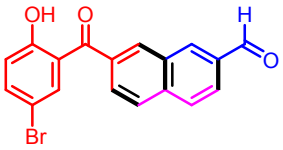
3-(2-Hydroxy-4-methoxybenzoyl)-1-naphthaldehyde (36). Yield 72% (219 mg) as a yellow solid: mp 137 – 139 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.60 (1H, s), 10.18 (1H, s), 8.41 (1H, s), 8.26 (1H, s), 8.06 (1H, d, J = 8.6 Hz), 8.01 – 7.99 (2H, m), 7.87 (1H, d, J = 8.3 Hz), 7.52 (1H, d, J = 9.0 Hz), 6.55 (1H, d, J = 2.5 Hz), 6.43 (1H, dd, J = 9.0, 2.5 Hz), 3.87 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.9, 191.7, 166.5, 137.4, 136.7, 135.0, 135.0, 134.9, 131.6, 130.8, 129.0, 128.5, 128.4, 125.9 124.8, 113.1, 107.7, 101.2, 55.7; IR (neat) 3466, 3012, 2970, 1738, 1688, 1368, 1207, 844, 794 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{14}O_4$: 306.0892. Found: 306.0893.



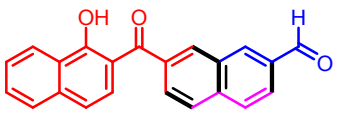
3-(5-Chloro-2-hydroxybenzoyl)-1-naphthaldehyde (37). Yield 69% (215 mg) as a white solid: mp 172 – 174 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.81 (1H, s), 10.19 (1H, s), 8.46 (1H, s), 8.31 (1H, s), 8.10 (1H, d, J = 8.6 Hz), 8.05 – 8.02 (2H, m), 7.90 (1H, d, J = 8.3 Hz), 7.58 (1H, d, J = 2.6 Hz), 7.48 (1H, dd, J = 8.9, 2.6 Hz), 7.07 (1H, d, J = 8.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.7, 191.6,



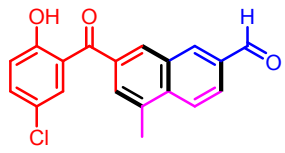
161.7, 137.8, 136.5, 135.6, 135.1, 135.1, 132.1, 131.6, 131.5, 129.1, 128.8, 128.1, 125.3, 123.6, 120.3, 119.7; IR (neat) 3460, 3025, 2970, 1739, 1684, 1621, 1207, 865 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{11}ClO_3$: 310.0397. Found: 310.0398.

3-(5-Bromo-2-hydroxybenzoyl)-1-naphthaldehyde (38). Yield 85% (301 mg) as a yellow solid: 

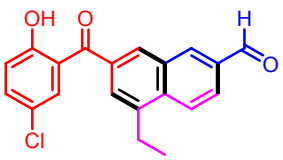
mp 179 – 181 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 11.82 (1H, s), 10.20 (1H, s), 8.46 (1H, s), 8.31 (1H, s), 8.10 (1H, d, J = 8.5 Hz), 8.06 – 8.02 (2H, m), 7.90 (1H, d, J = 8.5 Hz), 7.72 (1H, d, J = 2.3 Hz), 7.61 (1H, dd, J = 9.1, 2.4 Hz), 7.02 (1H, d, J = 8.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 191.6, 162.2, 139.2, 137.8, 135.6, 135.1, 135.1, 131.6, 131.5, 129.1, 128.8, 128.1, 125.3, 120.7, 120.3, 110.5; IR (neat) 3482, 3073, 2923, 1743, 1684, 1619, 1465, 1205, 905, 826 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{11}BrO_3$: 353.9892. Found: 353.9887.

3-(1-Hydroxy-2-naphthoyl)-1-naphthaldehyde (39). Yield 81% (265 mg) as a yellow solid: mp 

173 – 175 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 13.86 (1H, s), 10.18 (1H, s), 8.53 (1H, d, J = 8.4 Hz), 8.43 (1H, s), 8.34 (1H, s), 8.07 (1H, d, J = 8.6 Hz), 8.04 – 8.00 (2H, m), 7.95 (1H, d, J = 8.5 Hz), 7.77 (1H, d, J = 8.2 Hz), 7.66 (1H, t, J = 7.6 Hz), 7.56 (2H, t, J = 8.8 Hz), 7.23 (1H, d, J = 4.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.3, 191.7, 164.1 137.5, 137.3, 136.6, 135.1, 134.9, 131.6, 131.2, 130.6, 129.1, 128.5, 127.4, 126.9, 126.1, 125.3, 124.9, 124.5, 118.2, 112.5; IR (neat) 3452, 3064, 2925, 1742, 1695, 1623, 1203, 835, 636 cm^{-1}; HRMS m/z (M^+) calcd for $C_{22}H_{14}O_3$: 326.0943. Found: 326.0941.

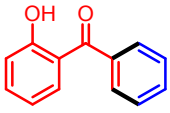
3-(5-Chloro-2-hydroxybenzoyl)-5-methyl-1-naphthaldehyde (42). Yield 68% (221 mg) as a 

yellow solid: mp 38 – 140 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 11.82 (1H, s), 10.20 (1H, s), 8.44 (1H, s), 8.18 (1H, d, J = 8.7 Hz), 8.14 – 8.11 (2H, m), 7.74 (1H, s), 7.60 (1H, d, J = 2.6 Hz), 7.48 (1H, dd, J = 9.0, 2.6 Hz), 7.07 (1H, d, J = 8.9 Hz), 2.80 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.9, 191.6, 161.7, 137.2, 136.4, 136.2, 135.6, 135.3, 134.7, 132.2, 131.7, 129.9, 128.4, 125.5, 125.2, 123.6, 120.2, 119.8, 19.5; IR (neat) 3428, 3073, 2925, 1737, 1694, 1203, 818, 732 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{13}ClO_3$: 324.0553. Found: 324.0550.

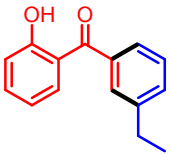
3-(5-Chloro-2-hydroxybenzoyl)-5-ethyl-1-naphthaldehyde (43). Yield 73% (246 mg) as a 

yellow solid: mp 112 – 114 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 11.83 (1H, s), 10.19 (1H, s), 8.44 (1H, s), 8.22 (1H, d, J = 8.8 Hz), 8.14 (1H, s), 8.11 (1H, d, J = 8.7 Hz), 7.75 (1H, s), 7.60 (1H, d, J = 2.6 Hz), 7.47 (1H, dd, J = 9.0, 2.4 Hz), 7.06 (1H, d, J = 9.0 Hz), 3.20 (2H, q, J = 7.6 Hz), 1.42 (3H, t, J = 7.5 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.0, 191.6, 161.7, 142.0, 136.4, 136.4, 135.9, 135.3, 134.5, 132.2, 132.0, 129.9, 126.8, 125.1, 125.0, 123.5, 120.2, 119.7, 25.9, 14.7; IR (neat) 3426, 2921, 2852, 1694, 1619, 1461, 1186, 817, 794 cm^{-1}; HRMS m/z (M^+) calcd for $C_{20}H_{15}ClO_3$: 338.0710. Found: 338.0712.

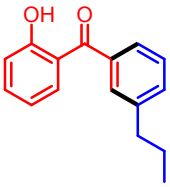
(2-Hydroxyphenyl)(phenyl)methanone (44). Yield 74% (147 mg) as a yellow solid: mp 37 – 39 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.01 (1H, s), 7.66 (2H, d, J = 7.6 Hz), 7.59 – 7.56 (2H, m), 7.49 (3H, t, J = 7.5 Hz), 7.06 (1H, d, J = 8.3 Hz), 6.86 (1H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.6, 163.2, 137.9, 136.3, 133.5, 131.8, 129.1, 128.3, 119.1, 118.6, 118.4; IR (neat) 3466, 2921, 2852, 1738, 1456, 1216, 804 cm^{-1}; HRMS m/z (M^+) calcd for $C_{13}H_{10}O_2$: 198.0681. Found: 198.0679.



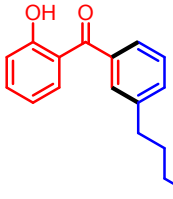
(3-Ethylphenyl)(2-hydroxyphenyl)methanone (45). Yield 83% (188 mg) as a light yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$ δ 12.05 (1H, s), 7.59 (1H, dd, J = 8.1, 1.6 Hz), 7.50 (1H, s), 7.48 – 7.45 (2H, m), 7.41 – 7.37 (2H, m), 7.06 (1H, d, J = 8.3 Hz), 6.86 (1H, t, J = 7.6 Hz), 2.72 (2H, q, J = 7.6 Hz), 1.27 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.9, 163.1, 144.5, 137.9, 136.1, 133.6, 131.5, 128.4, 128.17, 126.5, 119.2, 118.5, 118.3, 28.7, 15.4; IR (neat) 3452, 2965, 2930, 1738, 1624, 1598, 1482, 1443, 1334, 1305, 1245, 1202, 1157 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{14}O_2$: 226.0994. Found: 226.0993.



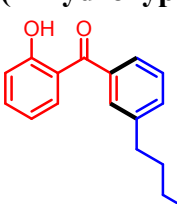
(2-Hydroxyphenyl)(3-propylphenyl)methanone (46). Yield 86% (207 mg) as a light yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.06 (1H, s), 7.59 (1H, d, J = 7.9 Hz), 7.49 – 7.46 (3H, m), 7.39 – 7.38 (2H, m), 7.06 (1H, d, J = 8.4 Hz), 6.86 (1H, t, J = 7.5 Hz), 2.66 (2H, t, J = 7.6 Hz), 1.67 (2H, m), 0.96 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.8, 163.1 142.9, 137.8, 136.1, 133.5, 132.0, 129.0, 128.0, 126.5, 119.1, 118.5, 118.2, 37.7, 24.3, 13.6; IR (neat) 3361, 3043, 2959, 1740, 1624, 1482, 1245, 949, 756, 649 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1151.



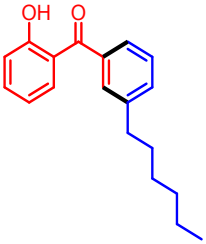
(3-Butylphenyl)(2-hydroxyphenyl)methanone (57). Yield 82% (209 mg) as a light yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.07 (1H, s), 7.59 (1H, d, J = 7.9 Hz), 7.49 – 7.44 (3H, m), 7.39 – 7.37 (2H, m), 7.06 (1H, d, J = 8.3 Hz), 6.86 (1H, t, J = 7.6 Hz), 2.68 (2H, t, J = 7.7 Hz), 1.65 – 1.60 (2H, m), 1.40 – 1.33 (2H, m), 0.93 (3H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.8, 163.1, 143.2, 137.8, 136.1, 133.5, 132.0, 128.9, 128.0, 126.5, 119.1, 118.5, 118.2, 35.4, 33.4, 22.2, 13.8; IR (neat) 3396, 2956, 2928, 1740, 1625, 1482, 1443, 1244, 962, 756 cm^{-1}; HRMS m/z (M^+) calcd for $C_{17}H_{18}O_2$: 254.1307. Found: 254.1303.



(2-Hydroxyphenyl)(3-pentylphenyl)methanone (48). Yield 86% (231 mg) as a light yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.05 (1H, s), 7.59 (1H, d, J = 7.9 Hz), 7.49 – 7.45 (3H, m), 7.39 – 7.38 (2H, m), 7.06 (1H, d, J = 8.4 Hz), 6.86 (1H, t, J = 7.6 Hz), 2.67 (2H, t, J = 7.8 Hz), 1.66 – 1.61 (2H, m), 1.35 – 1.31 (4H, m), 0.89 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.9, 163.1, 143.2 137.8 136.1, 133.6, 132.0, 129.0, 128.1, 126.5, 119.2, 118.5, 118.3, 35.7, 31.3, 30.9, 22.4, 13.9; IR (neat) 3433, 2927, 1740, 1625, 1482, 1245, 963, 756, 650 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{20}O_2$: 268.1463. Found: 268.1464.

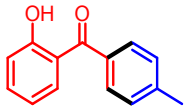


(3-Hexylphenyl)(2-hydroxyphenyl)methanone (49). Yield 89% (251 mg) as a light yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.05 (1H, s), 7.59 (1H, d, J = 8.2 Hz),

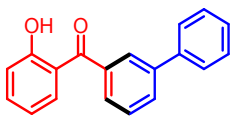


7.49 – 7.45 (3H, m), 7.39 – 7.38 (2H, m), 7.06 (1H, d, J = 8.3 Hz), 6.86 (1H, t, J = 7.5 Hz), 2.67 (2H, t, J = 7.8 Hz), 1.65 – 1.60 (2H, m), 1.36 – 1.26 (6H, m), 0.87 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.9, 163.1, 143.2, 137.8, 136.1, 133.6, 132.0, 129.0, 128.1, 126.5, 119.2, 118.5, 118.3, 35.7, 31.6, 31.2, 28.8, 22.5, 14.0; IR (neat) 3385, 2926, 1739, 1625, 1483, 1245, 756, 650 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{22}O_2$: 282.1620. Found: 282.1621.

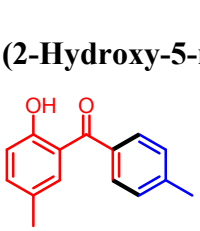
(2-Hydroxyphenyl)(p-tolyl)methanone (50). Yield 91% (194 mg) as a yellow solid: mp 38 – 40 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.01 (1H, s), 7.60 – 7.58 (3H, m), 7.48 (1H, t, J = 7.8 Hz), 7.29 (2H, d, J = 7.8 Hz), 7.05 (1H, d, J = 8.4 Hz), 6.85 (1H, t, J = 7.6 Hz), 2.44 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.3, 163.0, 142.7, 136.0, 135.1, 133.5, 129.4, 128.9, 119.2, 118.5, 118.3, 21.6; IR (neat) 3036, 2920, 1739, 1623, 1482, 1242, 934, 757 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{12}O_2$: 212.0837. Found: 212.0838.



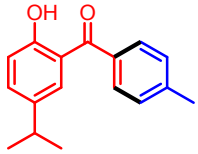
[1,1'-Biphenyl]-3-yl(2-hydroxyphenyl)methanone (51). Yield 82% (225 mg) as a brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.02 (1H, s), 7.87 (1H, s), 7.80 (1H, d, J = 7.4 Hz), 7.63 (2H, d, J = 7.7 Hz), 7.60 (2H, d, J = 7.4 Hz), 7.56 (1H, t, J = 7.6 Hz), 7.51 (1H, t, J = 7.8 Hz), 7.45 (2H, t, J = 7.7 Hz), 7.37 (1H, t, J = 7.5 Hz), 7.08 (1H, d, J = 8.4 Hz), 6.87 (1H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.6, 163.2, 141.4, 139.9, 138.4, 136.4, 133.5, 130.5, 128.9, 128.8, 127.9, 127.8, 127.7, 127.1, 119.1, 118.7, 118.4; IR (neat) 3385, 2923, 1736, 1624, 1479, 1217, 950, 752, 695 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{14}O_2$: 274.0994. Found: 274.0991.



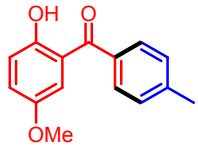
(2-Hydroxy-5-methylphenyl)(*p*-tolyl)methanone (52). Yield 72% (163 mg) as a brown solid: mp 85 – 89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.84 (1H, s), 7.58 (2H, d, J = 7.6 Hz), 7.37 (1H, s), 7.29 (3H, d, J = 7.9 Hz), 6.96 (1H, d, J = 8.5 Hz), 2.44 (3H, s), 2.24 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.2, 160.9, 142.5, 137.0, 135.2, 133.1, 129.3, 128.9, 127.6, 118.9, 118.0, 21.5, 20.43; IR (neat) 3368, 3015, 2921, 1739, 1600, 1478, 1224, 950, 758 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{14}O_2$: 226.0994. Found: 226.0995.



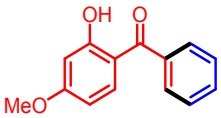
(2-Hydroxy-5-isopropylphenyl)(*p*-tolyl)methanone (53). Yield 70% (155 mg) as a light yellow liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.85 (1H, s), 7.60 (2H, d, J = 8.1 Hz), 7.44 (1H, d, J = 2.3 Hz), 7.37 (1H, dd, J = 8.5, 2.4 Hz), 7.30 (2H, d, J = 7.8 Hz), 6.99 (1H, d, J = 8.5 Hz), 2.85 – 2.78 (1H, m), 2.44 (3H, s), 1.18 (6H, d, J = 6.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.1, 161.1, 142.5, 138.7, 135.2, 134.4, 130.7, 129.4, 128.9, 118.8, 118.0, 33.1, 23.9, 21.5; IR (neat) 3386, 2958, 1737, 1628, 1479, 1223, 962, 779 cm^{-1}; HRMS m/z (M^+) calcd for $C_{17}H_{18}O_2$: 254.1307. Found: 254.1305.



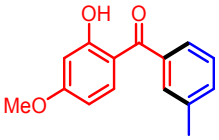
(2-Hydroxy-5-methoxyphenyl)(*p*-tolyl)methanone (54). Yield 81% (197 mg) as a yellow solid: mp 82 – 84 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.56 (1H, s), 7.60 (2H, d, J = 8.0 Hz), 7.28 (2H, d, J = 7.8 Hz), 7.11 (1H, dd, J = 9.1, 3.1 Hz), 7.07 (1H, d, J = 3.1 Hz), 6.98 (1H, d, J = 9.1 Hz), 3.68 (3H, s), 2.43 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.7, 157.2, 151.3, 142.7, 135.0, 129.3, 128.9, 123.7, 119.0,



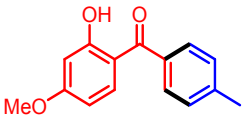
118.7, 116.2, 55.8, 21.5; IR (neat) 3426, 3004, 2919, 1736, 1598, 1482, 1229, 775 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{14}O_3$: 242.0943. Found: 242.0940.

(2-Hydroxy-4-methoxyphenyl)(phenyl)methanone (55). Yield 82% (186 mg) as a white solid: 

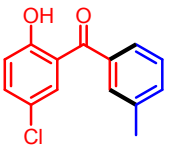
mp 57 – 59 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.68 (1H, s), 7.61 (2H, d, J = 7.5 Hz), 7.54 (1H, t, J = 7.4 Hz), 7.49 – 7.45 (3H, m), 6.50 (1H, d, J = 2.6 Hz), 6.39 (1H, dd, J = 8.9, 2.5 Hz), 3.84 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.9, 166.2, 166.1, 138.2, 135.2, 131.4, 128.8, 128.2, 113.0, 107.3, 101.0, 55.6; IR (neat) 3433, 3068, 1738, 1626, 1434, 1252, 912, 813, 706 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{12}O_3$: 228.0786. Found: 228.0785.

(2-Hydroxy-4-methoxyphenyl)(*m*-tolyl)methanone (56). Yield 88% (212 mg) as a light yellow liquid; 

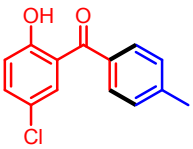
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.70 (1H, s), 7.49 (1H, d, J = 8.9 Hz), 7.42 (1H, s), 7.39 – 7.38 (1H, m), 7.34 – 7.33 (2H, m), 6.49 (1H, d, J = 2.5 Hz), 6.39 (1H, dd, J = 9.0, 2.5 Hz), 3.83 (3H, s), 2.40 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 166.2, 166.0, 138.2, 138.1, 135.2, 132.1, 129.2, 128.0, 125.9, 113.1, 107.2, 100.9, 55.5, 21.3; IR (neat) 3369, 2921, 1727, 1619, 1440, 1260, 947, 789 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{14}O_3$: 242.0943. Found: 242.0940.

(2-Hydroxy-4-methoxyphenyl)(*p*-tolyl)methanone (57). Yield 89% (216 mg) as a white solid: 

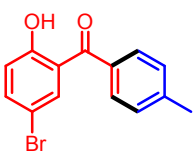
mp 93 – 95 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.70 (1H, s), 7.53 – 7.50 (3H, m), 7.27 (2H, d, J = 7.8 Hz), 6.49 (1H, d, J = 2.5 Hz), 6.39 (1H, dd, J = 8.9, 2.5 Hz), 3.84 (3H, s), 2.42 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.7, 166.1, 165.9, 142.0, 135.4, 135.1, 129.0, 128.9, 113.1, 107.1, 101.0, 55.5, 21.5; IR (neat) 3425, 2920, 1727, 1629, 1442, 1256, 915, 792 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{14}O_3$: 242.0943. Found: 242.0940.

(5-Chloro-2-hydroxyphenyl)(*m*-tolyl)methanone (58). Yield 69% (170 mg) as a yellow solid: 

mp 85 – 87 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.90 (1H, s), 7.54 (1H, d, J = 2.6 Hz), 7.46 (1H, s), 7.43 – 7.37 (4H, m), 7.01 (1H, d, J = 8.8 Hz), 2.43 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.8, 161.6, 138.6, 137.2, 136.0, 133.1, 132.4, 129.4, 128.3, 126.3, 123.3, 119.9, 119.8, 21.3; IR (neat) 3379, 3068, 2923, 1739, 1621, 1467, 1248, 954, 770 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{11}ClO_2$: 246.0448. Found: 246.0448.

(5-Chloro-2-hydroxyphenyl)(*p*-tolyl)methanone (59). Yield 85% (209 mg) as a yellow solid: mp 

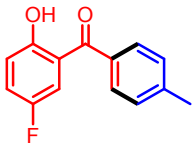
85 – 87 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.89 (1H, s), 7.58 – 7.56 (3H, m), 7.42 (1H, d, J = 9.0 Hz), 7.31 (2H, d, J = 7.8 Hz), 7.00 (1H, d, J = 8.9 Hz), 2.44 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 161.5, 143.2, 135.8, 134.4, 132.3, 129.3, 129.2, 123.2, 119.9, 119.8, 21.62; IR (neat) 3365, 3047, 2969, 1743, 1661, 1467, 1284, 1215, 819 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{11}ClO_2$: 246.0448. Found: 246.0449.

(5-Bromo-2-hydroxyphenyl)(*p*-tolyl)methanone (60). Yield 76% (220 mg) as a white solid: mp 

103 – 105 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.90 (1H, s), 7.70 (1H, d, J = 2.8 Hz), 7.57 (2H, d, J = 7.8 Hz), 7.54 (1H, dd, J = 8.9, 2.4 Hz), 7.31 (2H, d, J = 7.8 Hz), 6.95 (1H, d, J = 8.8 Hz), 2.44 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.0, 161.9, 143.2, 138.6, 135.2, 134.4, 129.3, 129.2, 120.4, 120.3, 110.1, 21.6; IR

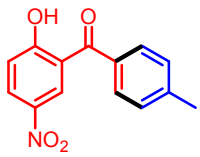
(neat) 3392, 3061, 1739, 1622, 1463, 1223, 943, 828, 699 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{11}BrO_2$: 289.9942. Found: 289.9943.

(5-Fluoro-2-hydroxyphenyl)(*p*-tolyl)methanone (61). Yield 90% (207 mg) as a yellow solid: mp



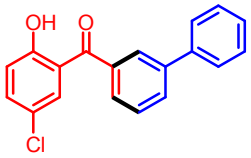
73 – 75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.72 (1H s), 7.58 (2H, d, J = 7.9 Hz), 7.29 – 7.26 (3H, m), 7.20 (1H, td, J = 8.4, 3.2 Hz), 7.00 (1H, dd, J = 9.1, 4.5 Hz), 2.43 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 200.1, 159.1, 155.2, 153.6, 143.1, 134.5, 129.3, 129.1, 123.5, 123.3, 119.5, 119.4, 118.7, 118.7, 118.2, 118.0, 21.5; IR (neat) 3348, 2969, 1739, 1600, 1474, 1223, 825, 780 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{11}FO_2$: 230.0743. Found: 230.0741.

(2-Hydroxy-5-nitrophenyl)(*p*-tolyl)methanone (62). Yield 83% (214 mg) as an off-white solid:



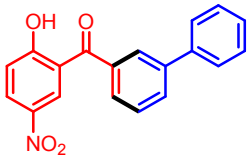
mp 104 – 106 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.66 (1H, s), 8.59 (1H, d, J = 2.7 Hz), 8.35 (1H, dd, J = 9.2, 2.8 Hz), 7.61 (2H, d, J = 8.0 Hz), 7.36 (2H, d, J = 7.9 Hz), 7.15 (1H, d, J = 9.2 Hz), 2.47 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 167.9, 144.2 , 139.3, 133.6, 130.6, 129.5, 129.5, 129.5, 119.4, 118.1, 21.7; IR (neat) 3415, 3029, 1737, 1626, 1467, 1201, 958, 766 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{11}NO_4$: 257.0688.Found:257.0686.

[1,1'-Biphenyl]-3-yl(5-chloro-2-hydroxyphenyl)methanone (63). Yield 73% (225 mg) as a



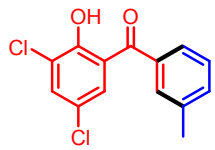
brown solid: mp 72 – 74 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.93 (1H, s), 7.88 (1H, s), 7.83 (1H, d, J = 7.2 Hz), 7.62 – 7.60 (4H, m), 7.58 (1H, t, J = 7.6 Hz), 7.48 – 7.44 (3H, m), 7.39 (1H, t, J = 7.5 Hz), 7.05 (1H, d, J = 8.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 161.6, 141.7, 139.7, 137.7, 136.2, 132.3, 130.9, 128.9, 128.8, 127.9, 127.8, 127.5, 127.1, 123.4, 120.0, 119.7; IR (neat) 3379, 2924, 1740, 1628, 1462, 1209, 960, 752 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{13}ClO_2$: 308.0604. Found: 308.0605.

[1,1'-Biphenyl]-3-yl(2-hydroxy-5-nitrophenyl)methanone (64). Yield 75% (239 mg) as a light

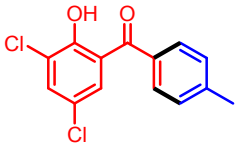


brown solid: mp 182 – 184 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.65 (1H, s), 8.67 (1H, d, J = 2.8 Hz), 8.38 (1H, dd, J = 9.3, 2.7 Hz), 7.90 (1H, d, J = 1.9 Hz), 7.88 (1H, d, J = 7.4 Hz), 7.66 (1H, d, J = 7.5 Hz), 7.64 (1H, d, J = 7.5 Hz), 7.61 – 7.59 (2H, m), 7.46 (2H, t, J = 7.6 Hz), 7.39 (1H, t, J = 7.4 Hz), 7.18 (1H, d, J = 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 167.9, 142.2, 139.5, 139.4, 136.8, 131.8, 130.9, 129.6, 129.2, 129.0, 128.1, 127.9, 127.9, 127.2, 119.5, 117.9; IR (neat) 3371, 2921, 1740, 1613, 1468, 1215, 964, 754, 699 cm^{-1} HRMS m/z (M^+) calcd for $C_{19}H_{13}NO_4$: 319.0845. Found: 319.0844.

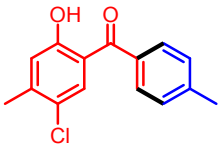
(3,5-Dichloro-2-hydroxyphenyl)(*m*-tolyl)methanone (65). Yield 73% (205 mg) as a yellow



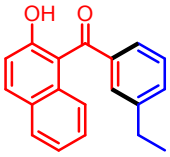
solid: mp 143 – 145 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.41 (1H, s), 7.57 (1H, d, J = 2.6 Hz), 7.49 (1H, d, J = 2.5 Hz), 7.46 (1H, s), 7.43 – 7.38 (3H, m), 2.43 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 157.4, 138.7, 136.7, 135.6, 133.5, 131.0, 129.5, 128.4, 126.4, 123.9 123.13, 120.3, 21.3; IR (neat) , 3422, 3066, 2976, 1738, 1624, 1583, 1425, 1210, 880, 753 cm^{-1} HRMS m/z (M^+) calcd for $C_{14}H_{10}Cl_2O_2$: 280.0058. Found: 280.0054.

(3,5-Dichloro-2-hydroxyphenyl)(*p*-tolyl)methanone (66). Yield 88% (247 mg) as a yellow solid: 

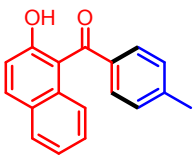
mp 92 – 94 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.38 (1H, s), 7.56 (2H, d, J = 7.9 Hz), 7.53 (1H, d, J = 2.5 Hz), 7.49 (1H, d, J = 2.5 Hz), 7.30 (2H, d, J = 7.8 Hz), 2.44 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 157.2, 143.7 135.3, 133.8, 130.8, 129.4, 129.2, 123.7, 122.9, 120.3, 21.5; IR (neat) 3361, 3075, 2924, 1740, 1625, 1425, 1233, 975, 754 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{10}Cl_2O_2$: 280.0058. Found: 280.0060.

(5-Chloro-2-hydroxy-4-methylphenyl)(*p*-tolyl)methanone (67). Yield 82% (213 mg) as an off-white solid: 

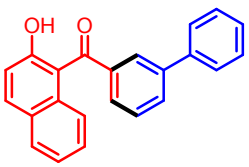
mp 89 – 91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.91 (1H, s), 7.56 – 7.54 (3H, m), 7.30 (2H, d, J = 7.8 Hz), 6.93 (1H, s), 2.43 (3H, s), 2.37 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.8, 161.4, 145.2, 142.9, 134.6, 132.6, 129.2, 129.1, 123.8, 120.3, 118.1, 21.5, 20.7; IR (neat) 3398, 3032, 2922, 1737, 1634, 1473, 1245, 1228, 915, 778 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{13}ClO_2$: 260.0604. Found: 260.0603.

(3-Ethylphenyl)(2-hydroxynaphthalen-1-yl)methanone (68). Yield 91% (251 mg) as a yellow solid: 

mp 40 – 42 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.10 (1H, s), 7.78 (1H, d, J = 8.9 Hz), 7.60 (1H, d, J = 8.0 Hz), 7.39 (1H, s), 7.29 (1H, d, J = 7.7 Hz), 7.25 (1H, d, J = 7.6 Hz), 7.20 (1H, d, J = 8.6 Hz), 7.16 – 7.10 (3H, m), 7.01 (1H, t, J = 7.8 Hz), 2.50 (2H, q, J = 7.6 Hz), 1.05 (3H, t, J = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 161.0, 144.6, 140.1, 136.0, 132.3, 132.2, 128.6, 128.4, 128.3, 128.3, 126.9, 126.5, 126.2, 123.5, 119.0, 114.5, 28.5, 15.3; IR (neat) 3349, 3057, 2965, 1743, 1596, 1461, 1203, 755 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{16}O_2$: 276.1150. Found: 276.1153.

(2-Hydroxynaphthalen-1-yl)(*p*-tolyl)methanone (69). Yield 75% (197 mg) as a yellow solid: mp 

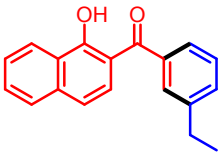
120 – 122 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.83 (1H, s), 7.78 (1H, d, J = 8.9 Hz), 7.62 (1H, d, J = 8.0 Hz), 7.43 (2H, d, J = 7.7 Hz), 7.25 (1H, d, J = 8.5 Hz), 7.14 (1H, t, J = 7.5 Hz), 7.11 (1H, d, J = 9.2 Hz), 7.06 – 7.03 (3H, m), 2.28 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.8, 160.5, 143.6, 137.3, 135.7, 132.3, 129.6, 129.1, 128.4, 128.3, 126.5, 126.1, 123.5, 118.9, 114.7 21.6; IR (neat) 3382, 3054, 2926, 1734, 1600, 1457, 1202, 915, 827, 767 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{14}O_2$: 262.0994. Found: 262.0992.

[1,1'-Biphenyl]-3-yl(2-hydroxynaphthalen-1-yl)methanone (70). Yield 87% (281 mg) as a yellow solid: 

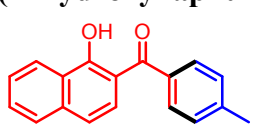
mp 65 – 67 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.87 (1H, s), 8.44 (1H, d, J = 8.3 Hz), 7.83 (1H, s), 7.71 (1H, d, J = 7.4 Hz), 7.66 (1H, d, J = 8.1 Hz,), 7.58 (1H, d, J = 7.7 Hz), 7.55 – 7.52 (3H, m), 7.49 (2H, d, J = 8.3 Hz,), 7.47 – 7.43 (1H, m), 7.36 (2H, t, J = 7.6 Hz), 7.28 (1H, t, J = 7.4 Hz), 7.12 (1H, d, J = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.3, 163.9, 141.4, 140.0, 138.7, 137.3, 130.3, 130.2, 128.9, 128.7, 127.8, 127.6, 127.4, 127.2, 127.1, 125.9, 125.2,

124.4, 117.9, 112.5; IR (neat) 3465, 3057, 2923, 1753, 1628, 1461, 1203, 993, 748 cm^{-1}; HRMS m/z (M^+) calcd for $C_{23}H_{16}O_2$: 324.1150. Found: 324.1149.

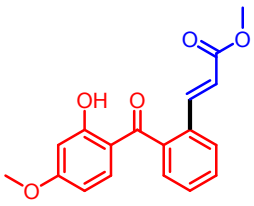
(3-Ethylphenyl)(1-hydroxynaphthalen-2-yl)methanone (71). Yield 93% (257 mg) as a yellow solid: mp 64 – 66 °C; ^1H NMR (600 MHz, $CDCl_3$)) δ 13.98 (1H, s), 8.52 (1H, d, J = 8.4 Hz), 7.75 (1H, d, J = 8.1 Hz), 7.64 – 7.62 (1H, m), 7.55 – 7.53 (3H, m), 7.51 – 7.50 (1H, m), 7.43 – 7.41 (2H, m), 7.21 (1H, d, J = 8.9 Hz), 2.74 (2H, q, J = 7.6 Hz), 1.29 (3H, t, J = 7.5 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.7, 163.8, 144.5, 138.2, 137.2, 131.2, 130.2, 128.4, 128.1, 127.4, 127.3, 126.5, 125.8, 125.2, 124.4, 117.7, 112.6, 28.7, 15.4; IR (neat) 3246, 2969, 1745, 1638, 1433, 1240, 968, 814 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{16}O_2$: 276.1150. Found: 276.1153.



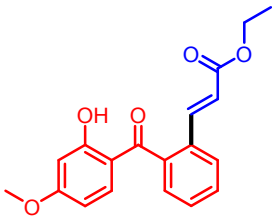
(1-Hydroxynaphthalen-2-yl)(*p*-tolyl)methanone (72). Yield 85% (224 mg) as a yellow solid: mp 67 – 69 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.53 (1H, d, J = 8.3 Hz), 7.74 (1H, d, J = 8.1 Hz), 7.64 – 7.61 (3H, m), 7.57 (1H, d, J = 8.8 Hz), 7.54 (1H, t, J = 7.6 Hz), 7.31 (2H, d, J = 7.8 Hz), 7.20 (1H, d, J = 8.8 Hz), 2.45 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.9, 163.6, 142.2, 137.1, 135.3, 130.0, 129.2, 128.8, 127.3, 127.2, 125.7, 125.2, 124.3, 117.6, 112.5, 21.5; IR (neat) 3281, 3034, 2916, 1743, 1594, 1459, 1255, 990, 757 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{14}O_2$: 262.0994. Found: 262.0993.



[1,1'-Biphenyl]-3-yl(1-hydroxynaphthalen-2-yl)methanone (73). Yield 84% (271 mg) as a grey semi-solid paste: ^1H NMR (600 MHz, $CDCl_3$) δ 11.29 (1H, s), 7.94 (1H, d, J = 9.0 Hz), 7.89 (1H, s), 7.77 (2H, t, J = 8.2 Hz), 7.57 (1H, d, J = 7.7 Hz), 7.49 (2H, d, J = 7.7 Hz), 7.45 (1H, t, J = 7.7 Hz), 7.42 – 7.38 (3H, m), 7.34 (1H, t, J = 7.3 Hz), 7.28 (1H, t, J = 7.4 Hz), 7.25 (1H, d, J = 9.0 Hz), 7.18 (1H, t, J = 7.7 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 161.5, 141.6, 140.7, 139.9, 136.4, 132.3, 131.2, 128.9, 128.8, 128.6, 128.4, 128.3, 127.9, 127.7, 127.0, 126.7, 126.2, 123.7, 119.1, 114.3; IR (neat) 3326, 3058, 1739, 1620, 1457, 1205, 931, 744, 695 cm^{-1}; HRMS m/z (M^+) calcd for $C_{23}H_{16}O_2$: 324.1150. Found: 324.1146.



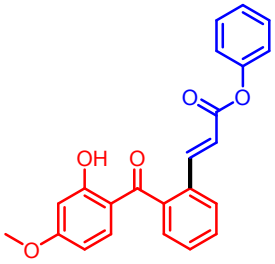
Methyl (*E*)-3-(2-(2-hydroxy-4-methoxybenzoyl)phenyl)acrylate (74). Yield 82% (256 mg) as a white solid: mp 69 – 71 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 12.59 (1H, s), 7.70 (1H, d, J = 7.9 Hz), 7.66 (1H, d, J = 15.9 Hz), 7.48 (1H, t, J = 7.6 Hz), 7.42 (1H, t, J = 7.5 Hz), 7.32 (1H, d, J = 7.5 Hz), 7.10 (1H, d, J = 8.9 Hz), 6.47 (1H, d, J = 2.4 Hz), 6.38 (1H, d, J = 15.9 Hz), 6.30 (1H, dd, J = 9.0, 2.4 Hz,), 3.81 (3H, s), 3.70 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.3, 166.7, 166.5, 166.3, 141.1, 138.6, 135.1, 132.5, 130.2, 129.2, 128.2, 126.8, 120.4, 113.9, 107.8, 100.8, 55.5, 51.6; IR (neat) 3395, 2933, 1705, 1597, 1344, 1258, 1197, 921, 807, 767 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{16}O_5$: 312.0998. Found: 312.0998.



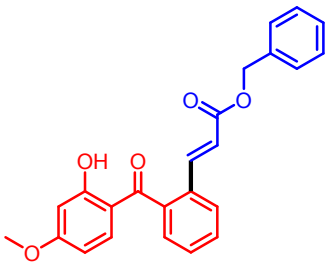
Ethyl (*E*)-3-(2-(2-hydroxy-4-methoxybenzoyl)phenyl)acrylate (75). Yield 71% (231 mg) as a colorless liquid; ^1H NMR (600 MHz, $CDCl_3$) δ 12.60 (1H, s), 7.72 (1H, d, J

= 7.9 Hz), 7.66 (1H, d, *J* = 15.9 Hz), 7.50 – 7.47 (1H, m), 7.43 (1H, t, *J* = 7.5 Hz), 7.34 (1H, dd, *J* = 7.5, 1.4 Hz), 7.11 (1H, d, *J* = 9.0 Hz), 6.49 (1H, d, *J* = 2.5 Hz), 6.38 (1H, d, *J* = 15.9 Hz), 6.31 (1H, dd, *J* = 9.0, 2.5 Hz), 4.18 (2H, q, *J* = 7.1 Hz), 3.83 (3H, s), 1.25 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 166.8, 166.4, 166.2, 141.0, 138.6, 135.2, 132.7, 130.3, 129.2, 128.3, 126.9, 120.9, 114.0, 107.9, 100.9, 60.5, 55.6, 14.1; IR (neat) 3344, 3073, 1704, 1598, 1259, 1179, 920, 811, 764 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{18}O_5$: 326.1154. Found: 326.1156.

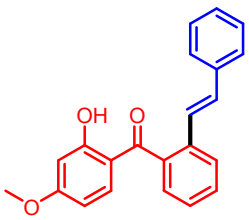
Phenyl (*E*)-3-(2-(2-hydroxy-4-methoxybenzoyl)phenyl)acrylate (76). Yield 79% (295 mg) as a white solid: mp 125 – 127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.59 (1H, s), 7.87 (1H, d, *J* = 15.8 Hz), 7.81 (1H, d, *J* = 7.9 Hz), 7.55 (1H, t, *J* = 7.7 Hz), 7.49 (1H, t, *J* = 7.5 Hz), 7.40 – 7.33 (3H, m), 7.21 (1H, t, *J* = 7.5 Hz), 7.15 (1H, d, *J* = 9.0 Hz), 7.10 (2H, d, *J* = 7.9 Hz), 6.59 (1H, d, *J* = 15.8 Hz), 6.49 (1H, s), 6.34 (1H, dd, *J* = 9.0, 2.3 Hz), 3.84 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.2, 166.9, 166.5, 164.6, 150.6, 143.0, 138.9, 135.2, 132.5, 130.4, 129.7, 129.3, 128.5, 127.1, 125.7, 121.5, 120.0, 114.0, 108.11, 100.9, 55.7; IR (neat) 3395, 2844, 1731, 1634, 1590, 1265, 1136, 970, 763 cm^{-1}; HRMS m/z (M^+) calcd for $C_{23}H_{18}O_5$: 374.1154. Found: 374.1152.



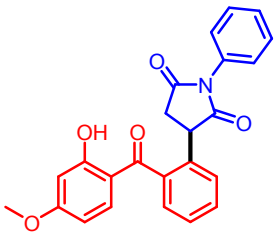
Benzyl (*E*)-3-(2-(2-hydroxy-4-methoxybenzoyl)phenyl)acrylate (77). Yield 85% (331 mg) as a yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.62 (1H, s), 7.77 – 7.71 (2H, m), 7.50 (1H, t, *J* = 7.6 Hz), 7.44 (1H, t, *J* = 7.5 Hz), 7.37 – 7.28 (6H, m), 7.12 (1H, d, *J* = 8.9 Hz), 6.50 (1H, d, *J* = 2.5 Hz), 6.45 (1H, d, *J* = 15.8 Hz), 6.32 (1H, dd, *J* = 8.9, 2.5 Hz), 5.18 (2H, s), 3.83 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.3, 166.8, 166.3, 165.9, 141.6, 138.7, 135.8, 135.2, 132.5, 130.3, 129.4, 128.4, 128.3, 128.1, 128.0, 126.8, 120.4, 114.0, 107.9, 100.9, 66.2, 55.6; IR (neat) 3428, 2938, 1711, 1620, 1256, 1205, 1159, 968, 764 cm^{-1}; HRMS m/z (M^+) calcd for $C_{24}H_{20}O_5$: 388.1311. Found: 388.1312.



(*E*)-(2-Hydroxy-4-methoxyphenyl)(2-styrylphenyl)methanone (78). Yield 92% (304 mg) as a white solid: mp 84 – 86 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.86 (1H, s), 7.83 (1H, d, *J* = 7.9 Hz), 7.52 (1H, t, *J* = 7.5 Hz), 7.40 (2H, d, *J* = 7.7 Hz), 7.38 – 7.34 (2H, m), 7.32 (2H, t, *J* = 7.6 Hz), 7.26 – 7.23 (2H, m), 7.17 – 7.09 (2H, m), 6.54 (1H, d, *J* = 2.4 Hz), 6.36 (1H, dd, *J* = 9.1, 2.5 Hz), 3.85 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.7, 166.5, 166.1, 137.2, 136.8, 135.4, 135.2, 131.2, 130.1, 128.5, 127.9, 127.9, 126.8, 126.6, 125.6, 125.2, 114.2, 107.7, 100.8, 55.5; IR (neat) 3469, 3018, 1738, 1597, 1501, 1255, 1201, 961, 758, 687 cm^{-1}; HRMS m/z (M^+) calcd for $C_{22}H_{18}O_3$: 330.1256. Found: 330.1252.

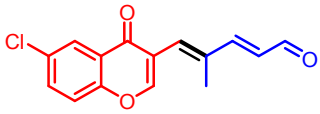


(*R*)-3-(2-(2-Hydroxy-4-methoxybenzoyl)phenyl)-1-phenylpyrrolidine-2,5-dione (79). Yield 58% (234 mg) as a white solid: mp 71 – 73 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ

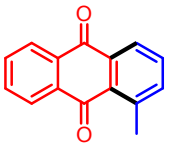


12.43 (1H, s), 7.55 – 7.52 (1H, m), 7.44 (2H, t, J = 7.6 Hz), 7.41 – 7.39 (2H, m), 7.38 – 7.35 (3H, m), 7.26 (2H, d, J = 7.8 Hz), 6.47 (1H, d, J = 2.4 Hz), 6.38 (1H, dd, J = 9.0, 2.4 Hz), 4.36 (1H, dd, J = 9.9, 6.0 Hz), 3.84 (3H, s), 3.34 (1H, dd, J = 18.5, 9.8 Hz), 3.07 (1H, dd, J = 19.0, 5.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.0, 176.5, 174.8, 166.8, 166.5, 137.2, 136.2, 135.6, 131.9, 131.2, 129.9, 129.1, 128.6, 127.2, 126.5, 113.6, 107.9, 101.0, 55.7, 44.8, 38.4; IR (neat) 3489, 2923, 1710, 1597, 1497, 1257, 1201, 758, 691 cm^{-1}; HRMS m/z (M^+) calcd for $C_{24}H_{19}NO_5$: 401.1263. Found: 401.1264.

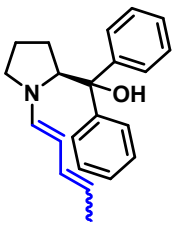
(2*E*,4*E*)-5-(6-Chloro-4-oxo-4*H*-chromen-3-yl)-4-methylpenta-2,4-dienal (80). Yield 91% (237 mg) as a yellow solid: mp 208 – 210 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (1H, d, J = 7.7 Hz), 8.20 (1H, s), 8.01 (1H, s), 7.62 (1H, d, J = 8.9 Hz), 7.44 (1H, d, J = 8.9 Hz), 7.31 (1H, d, J = 15.6 Hz), 6.88 (1H, s), 6.24 (1H, dd, J = 15.7, 7.8 Hz), 2.03 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 175.2, 156.1, 154.5, 154.3, 136.2, 134.2, 131.6, 129.3, 129.1, 125.5, 124.7, 121.1, 119.9, 14.3; IR (neat) 3083, 2970, 1740, 1695, 1643, 1465, 1216, 1130, 969, 817, 664 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{11}ClO_3$: 274.0397. Found: 274.0393.



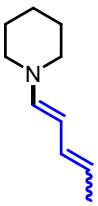
1- Methylanthracene-9,10-dione (82). Yield 76% (169 mg) as a yellow solid: mp 171 – 173 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.18 (3H, m), 7.75 – 7.70 (2H, m), 7.59 (1H, t, J = 7.7 Hz), 7.53 (1H, d, J = 7.6 Hz), 2.81 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.9, 183.5, 141.9, 138.1, 134.9, 134.7, 134.0, 133.4, 133.0, 132.7, 131.1, 127.1, 126.6, 126.0, 23.3; IR (neat) 2822, 1665, 1580, 1454, 1317, 1273, 1159, 968, 807, 702 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}O_2$: 222.0681. Found: 222.0683.



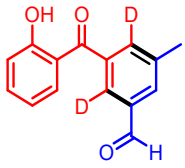
((*S*)-1-((1*E*,3*E*)-penta-1,3-dien-1-yl)pyrrolidin-2-yl)diphenylmethanol/ ((*S*)-1-((1*E*,3*Z*)-penta-1,3-dien-1-yl)pyrrolidin-2-yl)diphenylmethanol (II). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.74 – 7.08 (Ar-H), 5.77 – 4.47 (olefinic-H), 1.55 – 1.51 (Methyl-H); HRMS (FAB) m/z $(M+H)^+$ calcd for $C_{22}H_{26}NO$: 320.2014. Found: 320.2011.



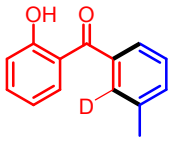
1-((1*E*, 3*E*)-Penta-1,3-dien-1-yl)piperidine/1-((1*E*, 3*Z*)-Penta-1,3-dien-1-yl)piperidine (VII, 1:1) ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.16 (1H, d, J = 13.5 Hz), 6.05 (1H, d, J = 13.6 Hz), 5.89 – 5.82 (2H, m), 5.19 (dd, J = 13.4, 10.9 Hz, 1H), 5.15 – 5.11 (1H, m), 5.02 (dd, J = 13.6, 10.3 Hz, 1H), 4.89 – 4.83 (1H, m), 2.90 – 2.89 (4H, m), 2.82 – 2.81 (4H, m), 1.64 (3H, dd, J = 6.6, 1.6 Hz), 1.60 (3H, dd, J = 6.9, 1.7 Hz), 1.48 – 1.46 (12H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 143.4, 141.7, 131.4, 129.6, 116.7, 113.7, 100.5, 95.8, 48.9, 48.8, 24.7, 24.7, 23.8, 17.9, 12.9; IR (neat) 2930, 2852, 1686, 1640, 1448, 1386, 1193, 1115, 968, 858, 710 cm^{-1}; HRMS m/z (M^+) calcd for $C_{10}H_{17}N$: 151.1361. Found: 151.1359.



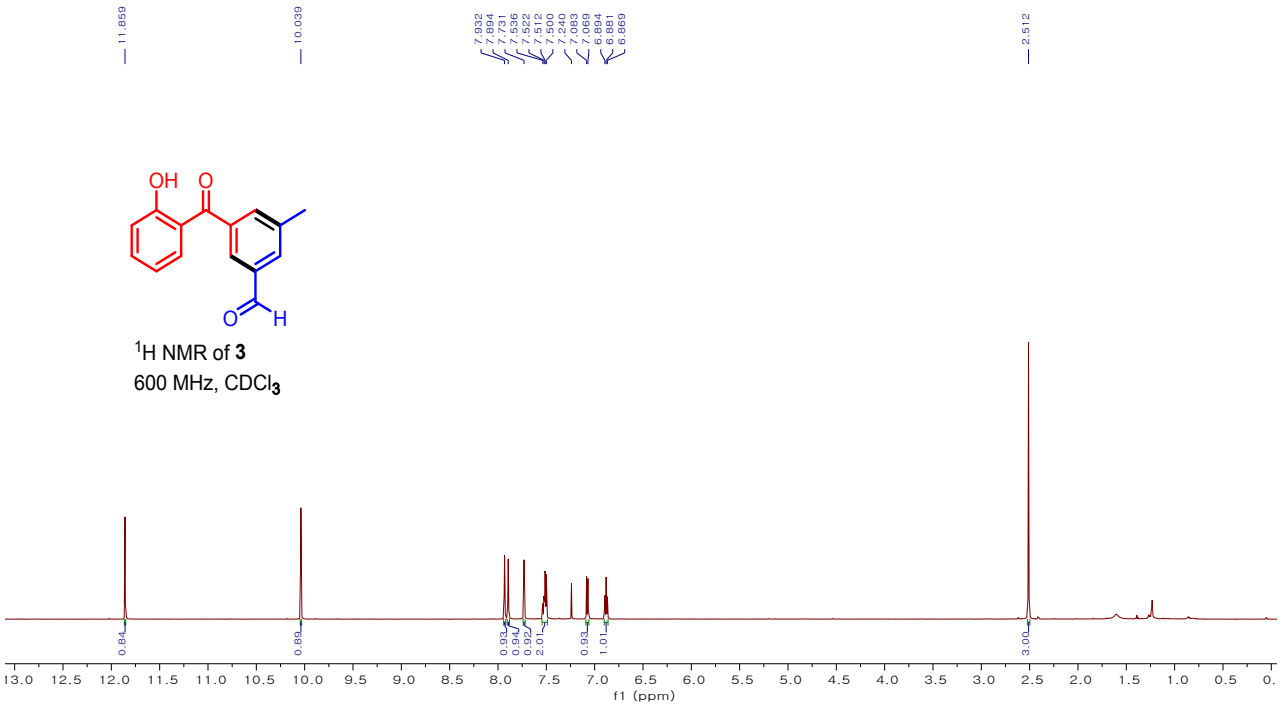
3-(2-Hydroxybenzoyl)-5-methylbenzaldehyde-2,4-d2 (d-3). Yield 90% (216 mg) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.86 (1H, s), 10.04 (1H, s), 7.89 (1H, s), 7.53 – 7.49 (2H, m), 7.07 (1H, d, J = 8.3 Hz), 6.88 (1H, t, J = 7.6 Hz), 2.51 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 191.3, 163.2, 139.6, 138.5, 136.7, 136.2, 134.9 (t, J = 24.1 Hz), 133.1, 132.8, 127.5 (t, J = 24.7 Hz), 118.9, 118.8, 118.6, 21.1; IR (neat) 2826, 1698, 1623, 1483, 1205, 1154, 758, 654 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}D_2O_3$: 242.0912. Found: 242.0910.



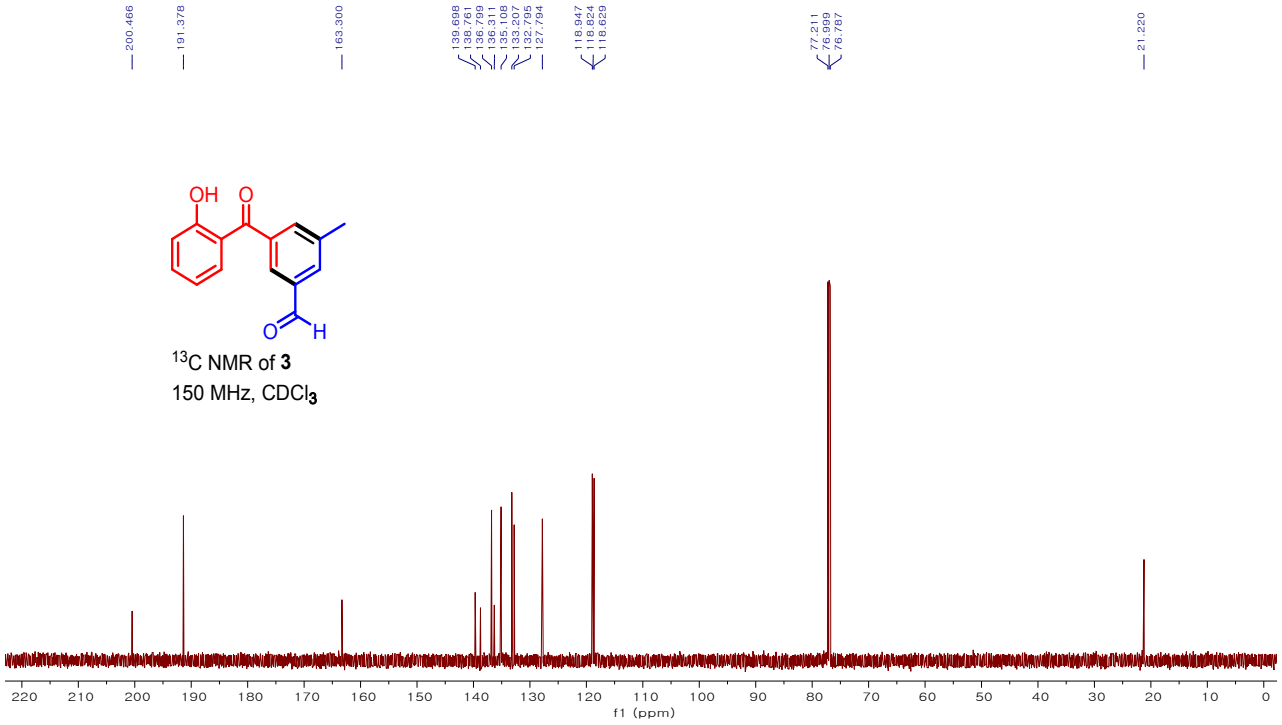
(2-Hydroxyphenyl)(3-methylphenyl-2-d)methanone (d-4). Yield 86% (182 mg) as a yellow liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.04 (1H, s), 7.58 (1H, d, J = 8.0 Hz), 7.49 (1H, t, J = 7.8 Hz), 7.44 (1H, dd, J = 6.6, 2.2 Hz), 7.39 – 7.35 (2H, m), 7.05 (1H, d, J = 8.3 Hz), 6.86 (1H, t, J = 7.5 Hz), 2.42 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.8, 163.1, 138.1, 137.8, 136.2, 133.6, 132.6, 129.2 (t, J = 24.6 Hz), 128.1, 126.3, 119.1, 118.5, 118.3, 21.3; IR (neat) 3049, 1623, 1482, 1330, 1243, 1149, 1033, 755 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{11}DO_2$: 213.0900. Found: 213.0898.



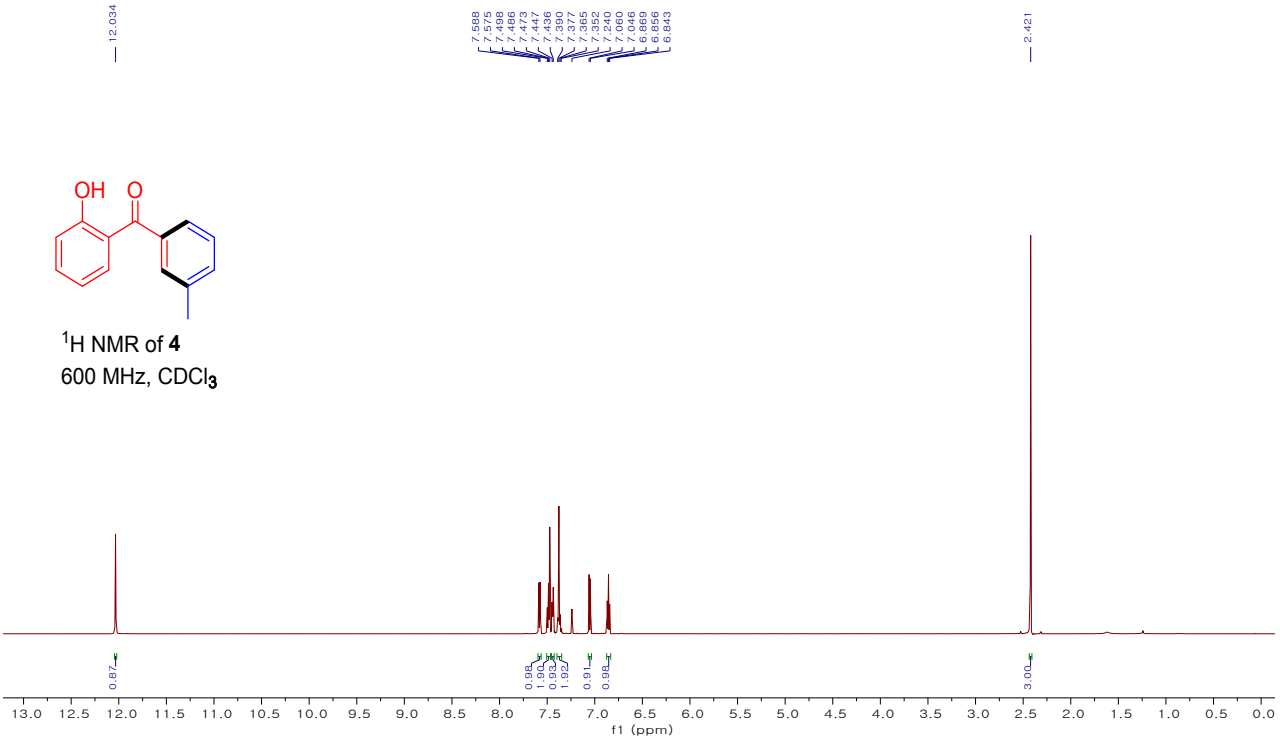
7. ^{1}H NMR and ^{13}C NMR spectra of synthesized compounds



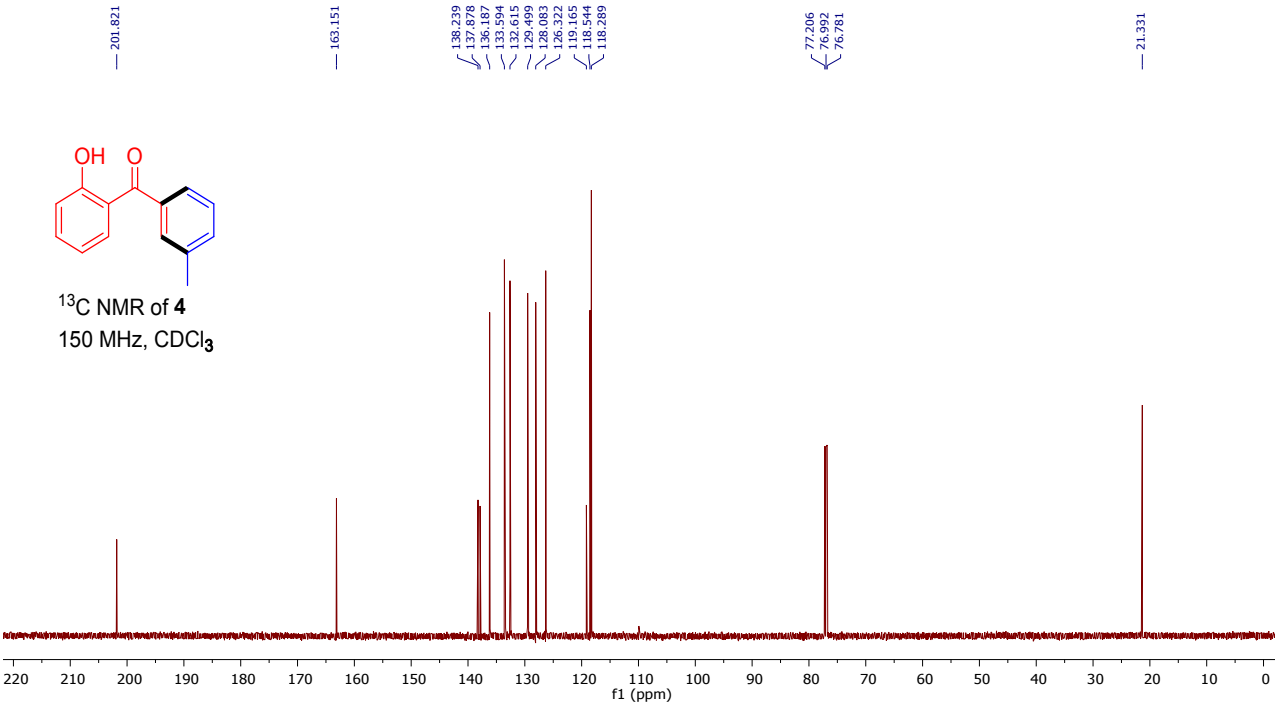
^{1}H NMR of **3**
600 MHz, $CDCl_3$



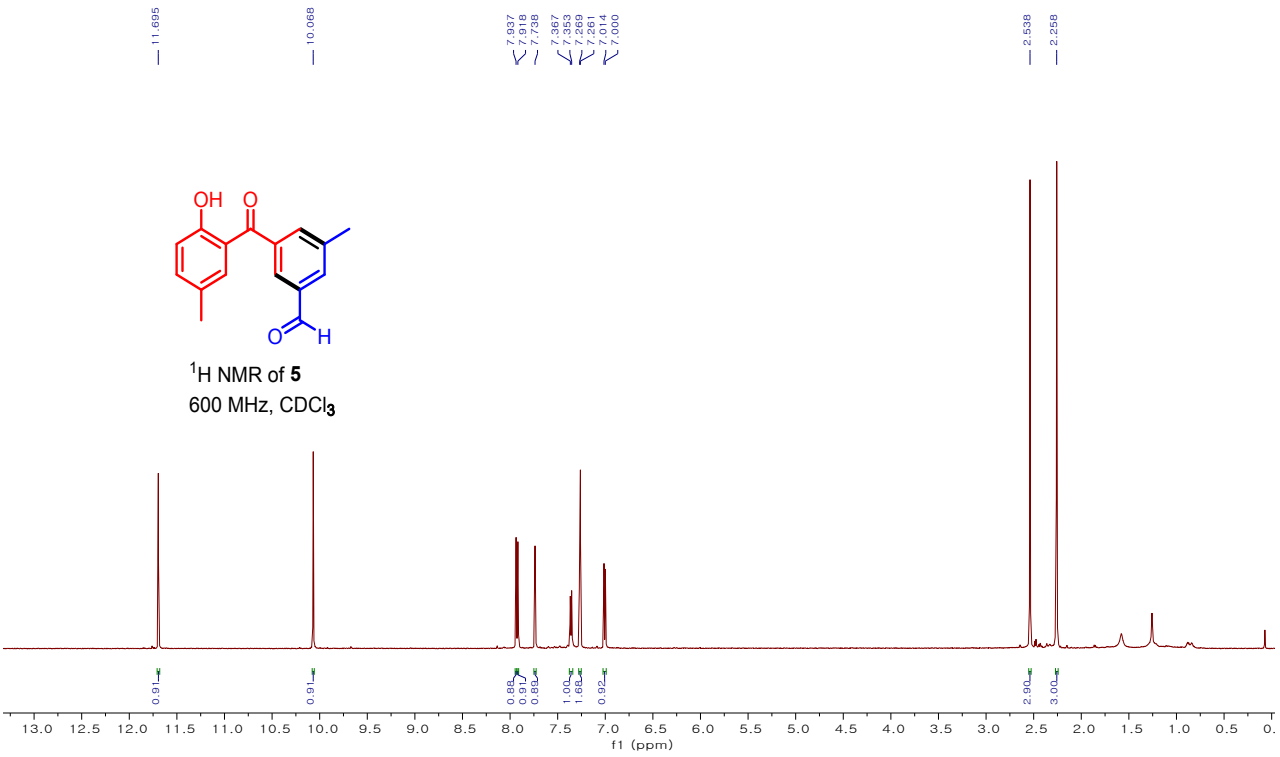
^{13}C NMR of **3**
150 MHz, $CDCl_3$



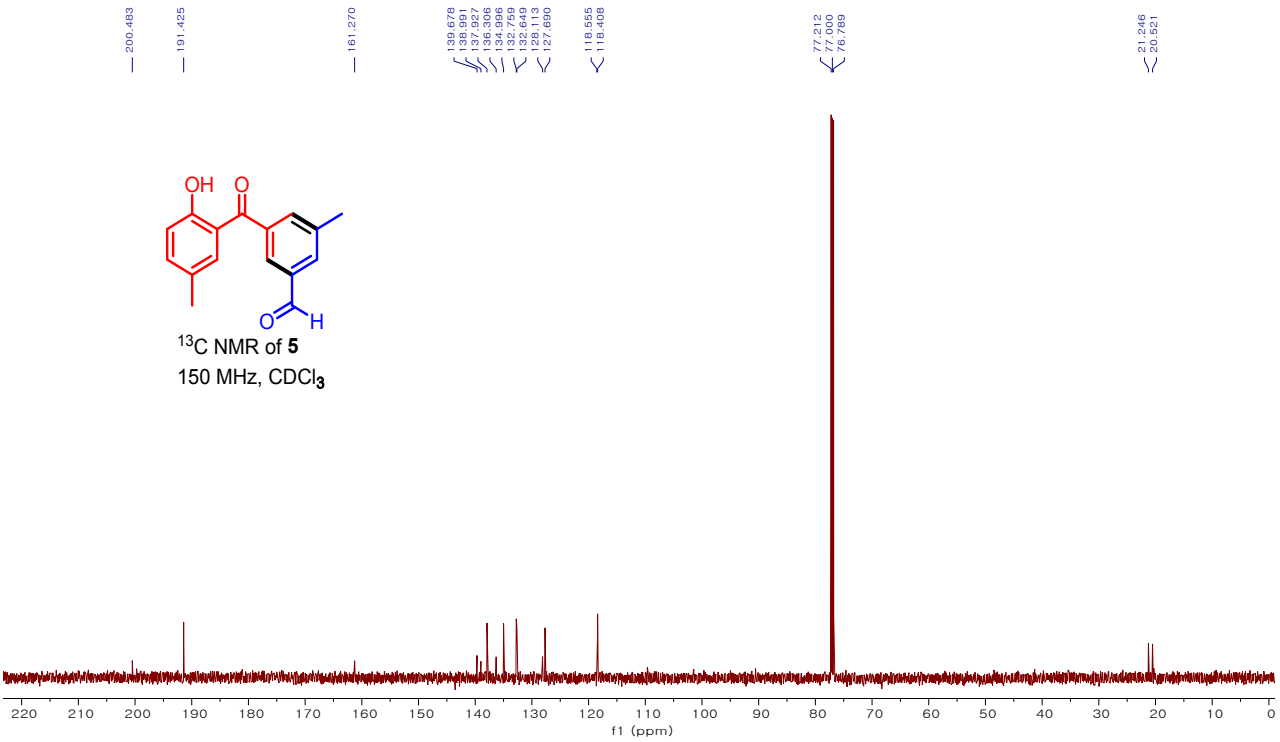
^{1}H NMR of **4**
600 MHz, $CDCl_3$



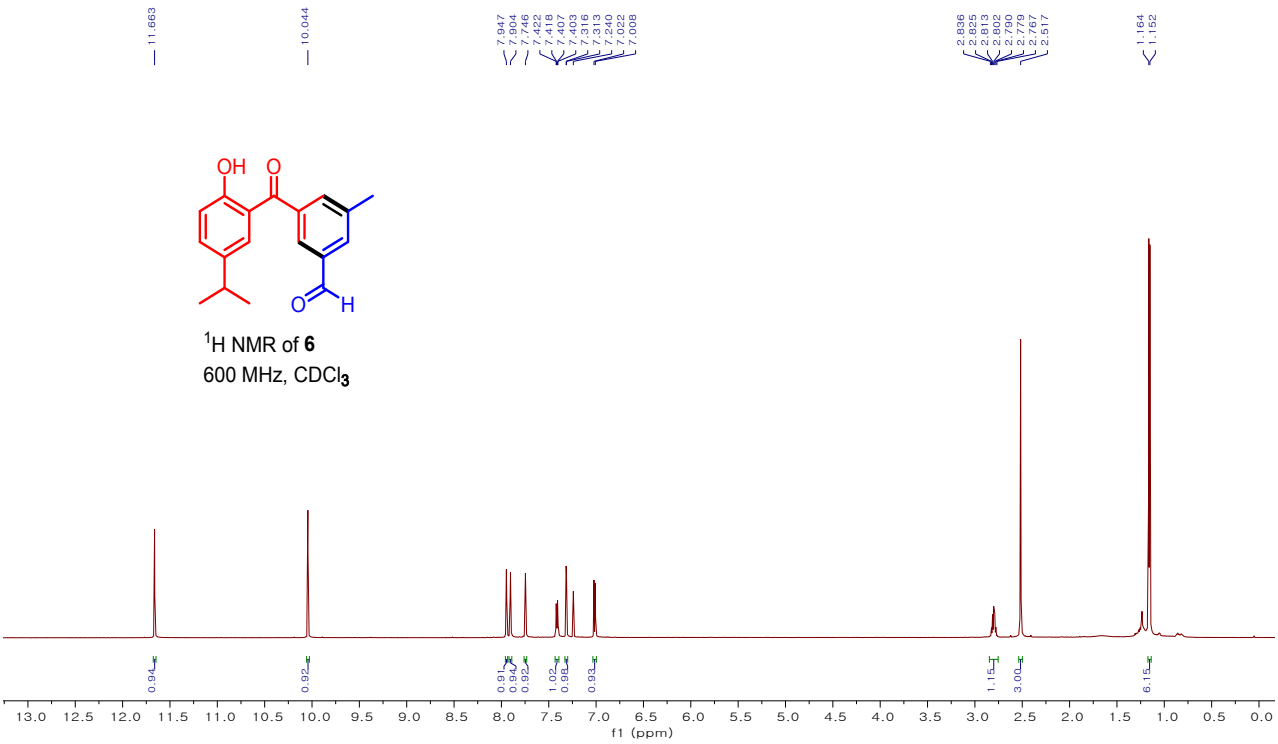
^{13}C NMR of **4**
150 MHz, $CDCl_3$



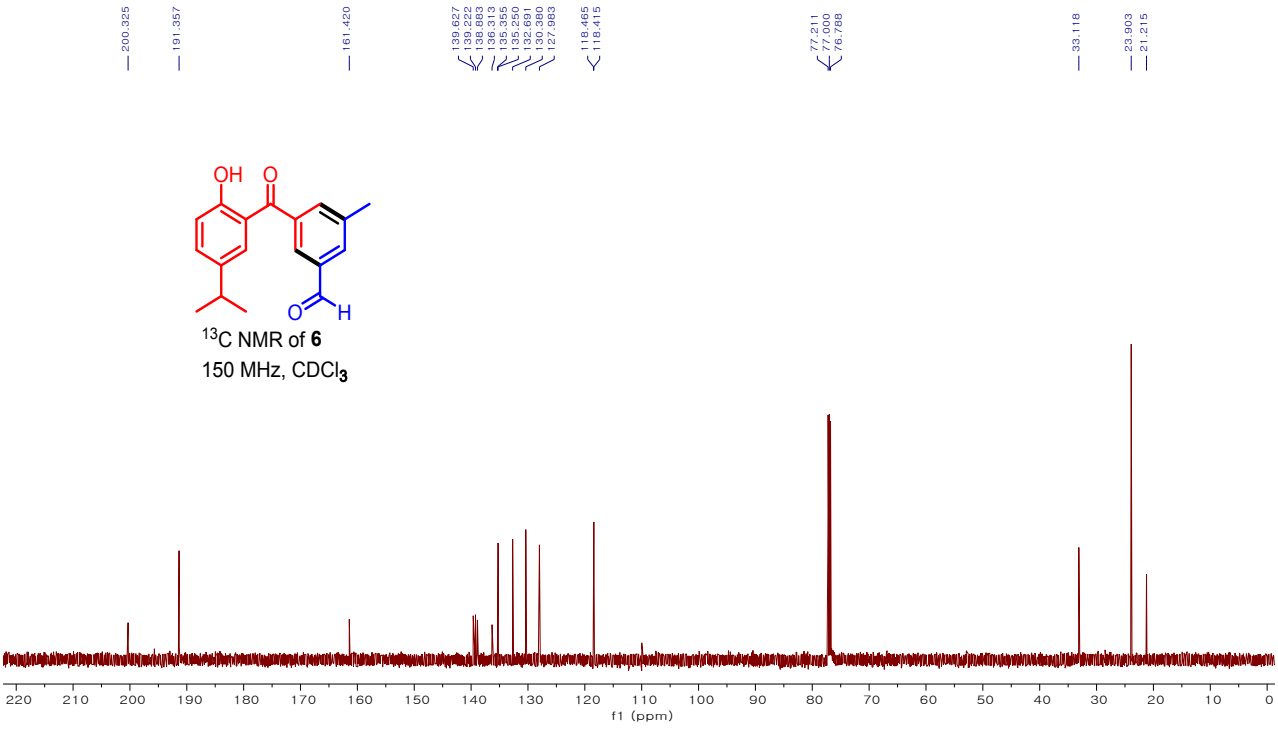
^{1}H NMR of **5**
600 MHz, $CDCl_3$



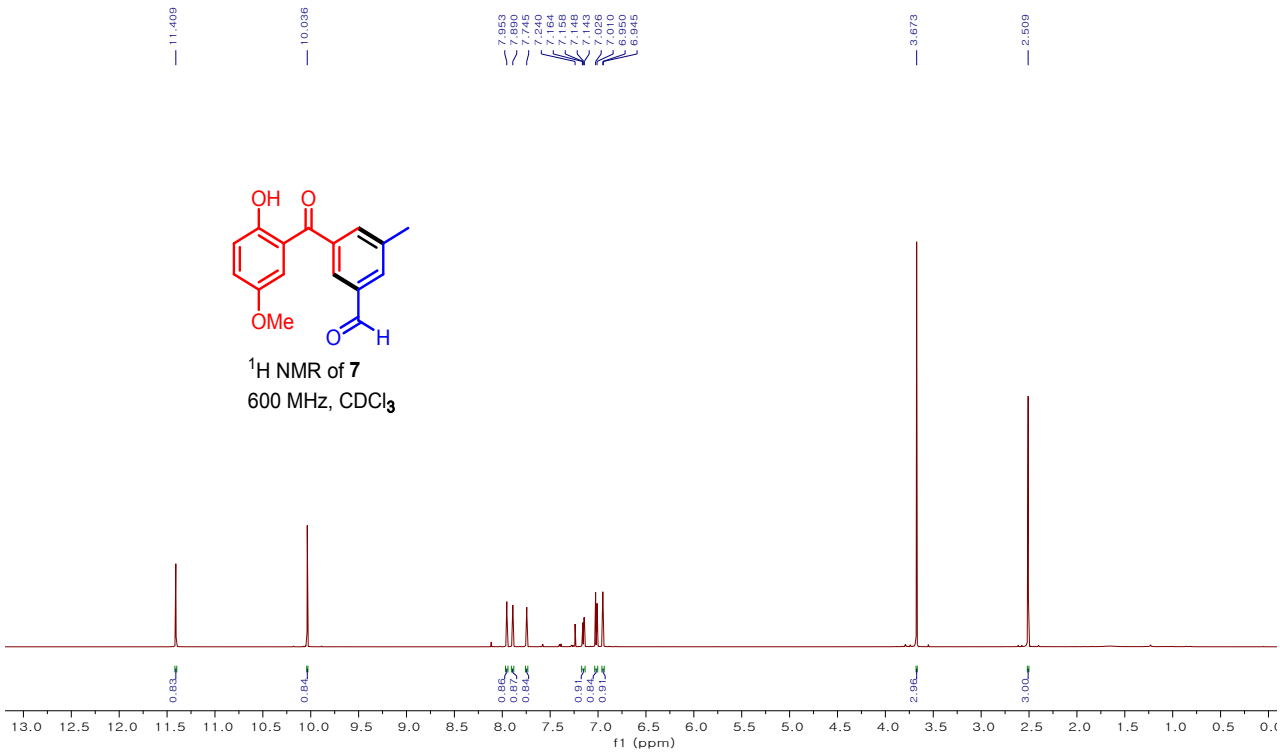
^{13}C NMR of **5**
150 MHz, $CDCl_3$



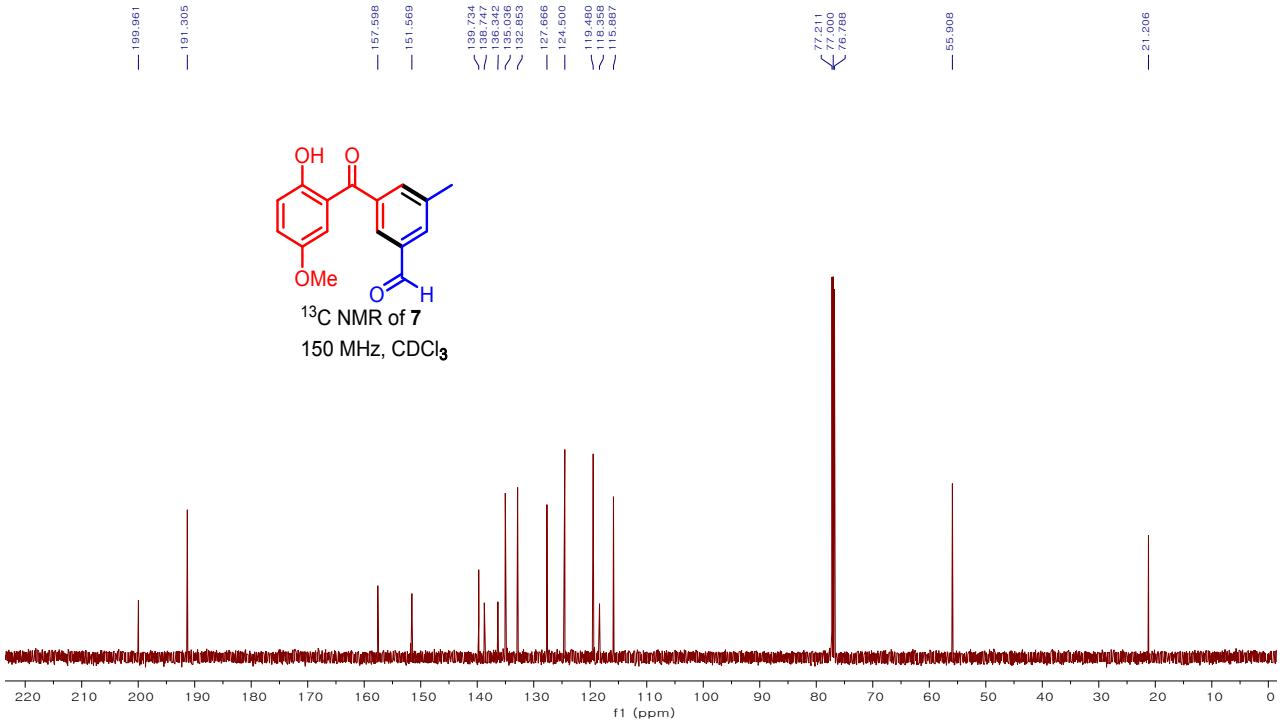
^{1}H NMR of **6**
600 MHz, $CDCl_3$



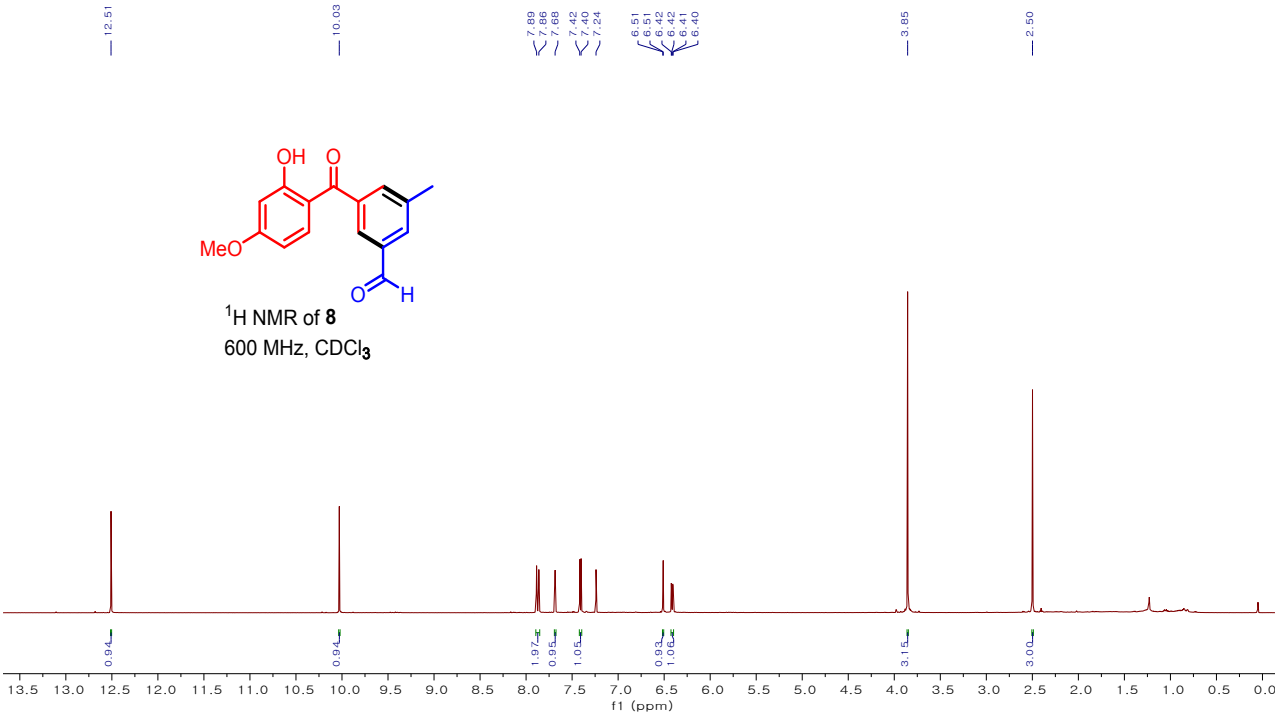
^{13}C NMR of **6**
150 MHz, $CDCl_3$



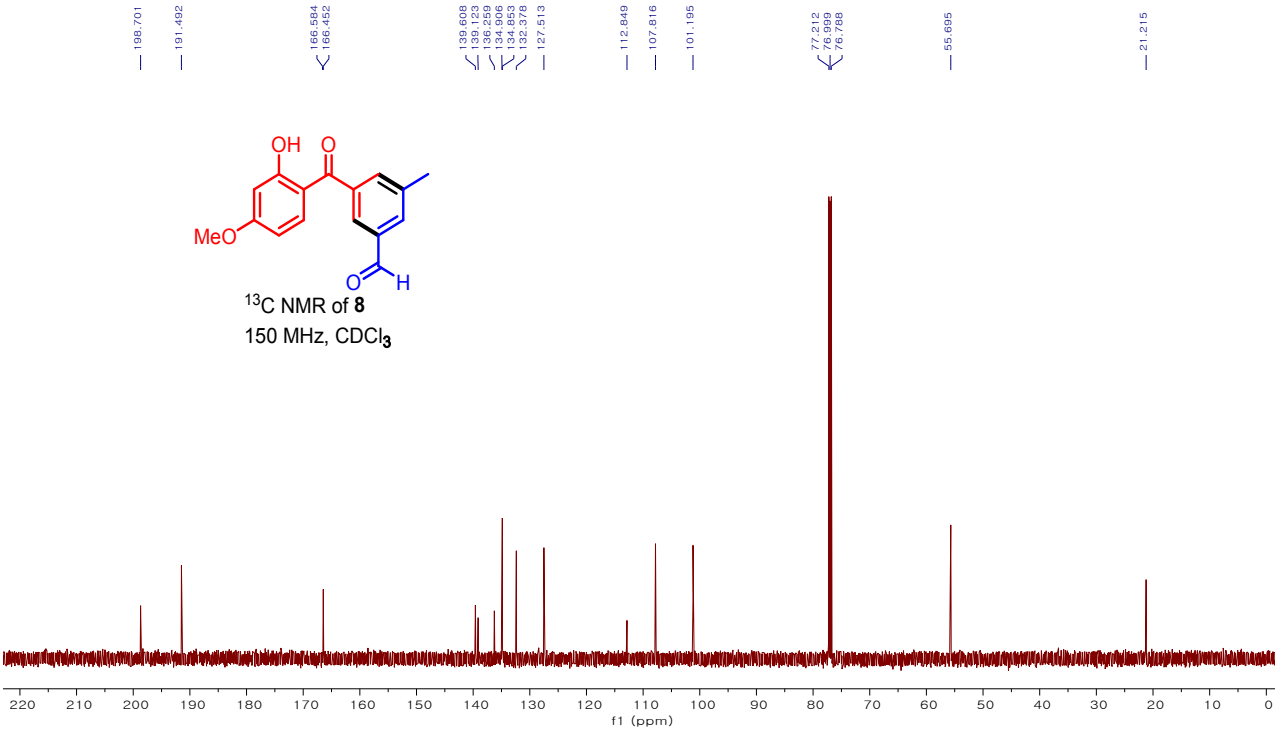
^{1}H NMR of **7**
600 MHz, $CDCl_3$



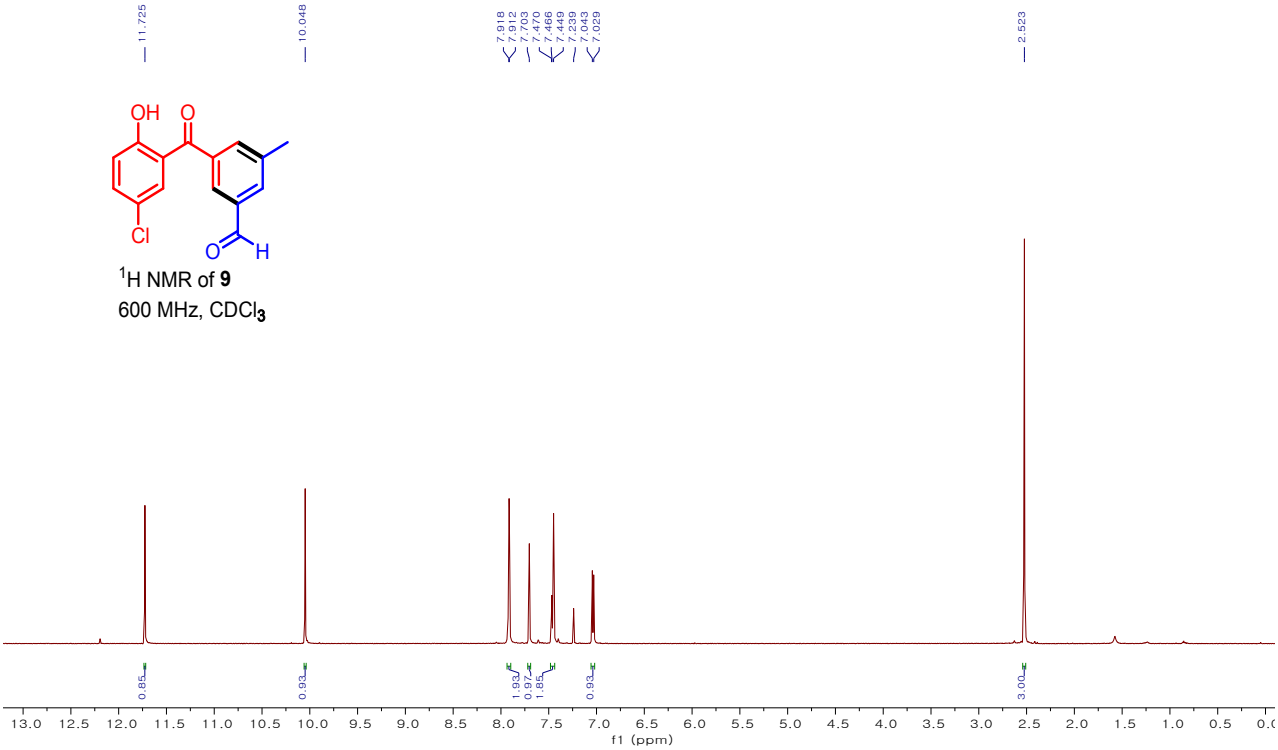
^{13}C NMR of **7**
150 MHz, $CDCl_3$



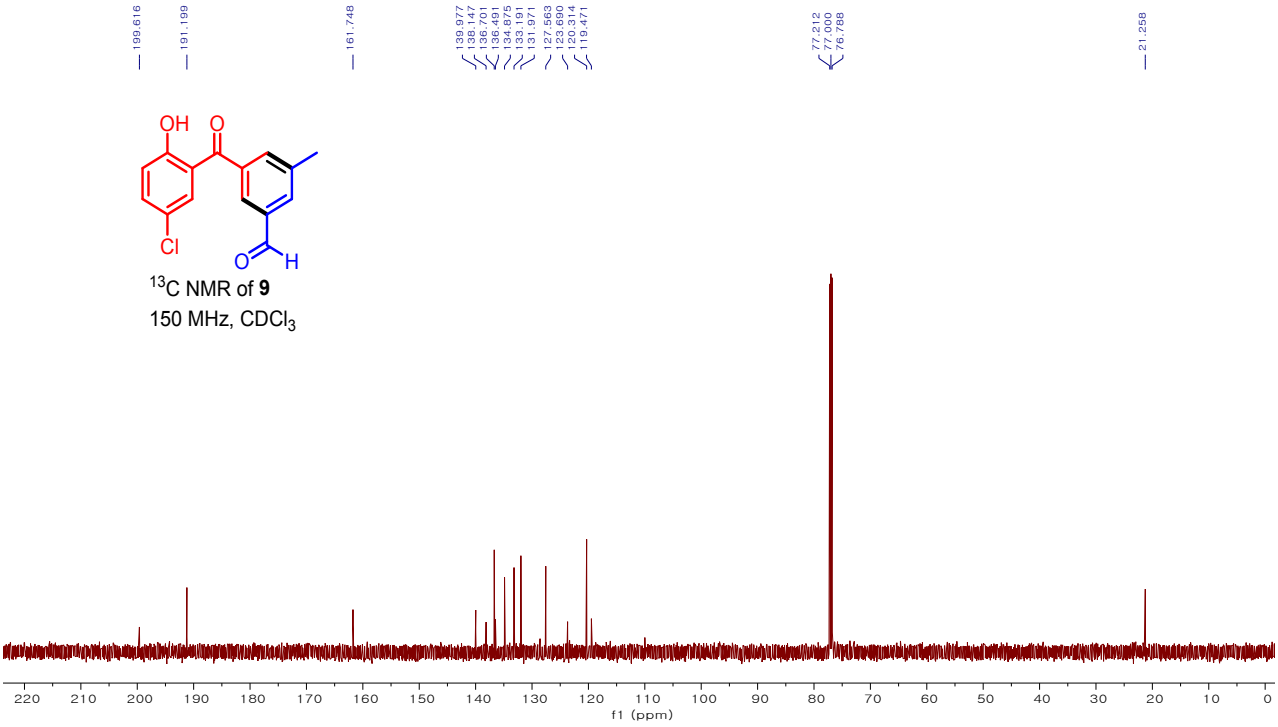
^{1}H NMR of **8**
600 MHz, $CDCl_3$



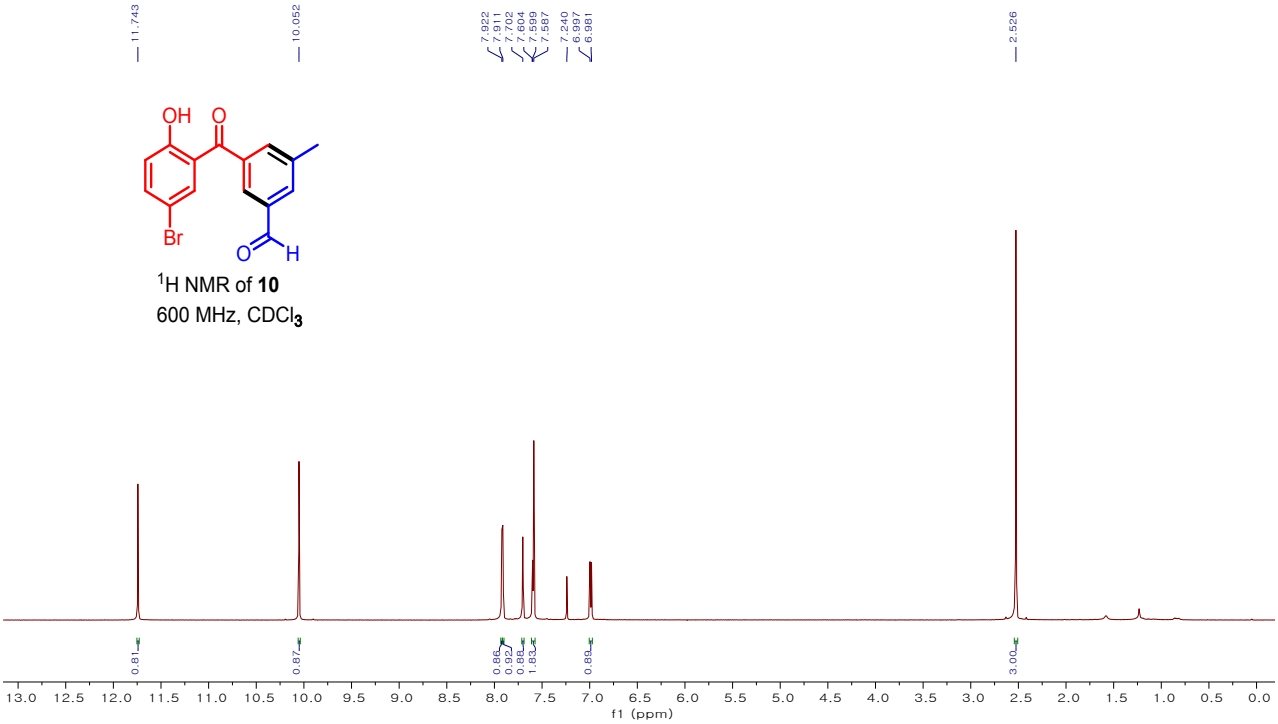
^{13}C NMR of **8**
150 MHz, $CDCl_3$



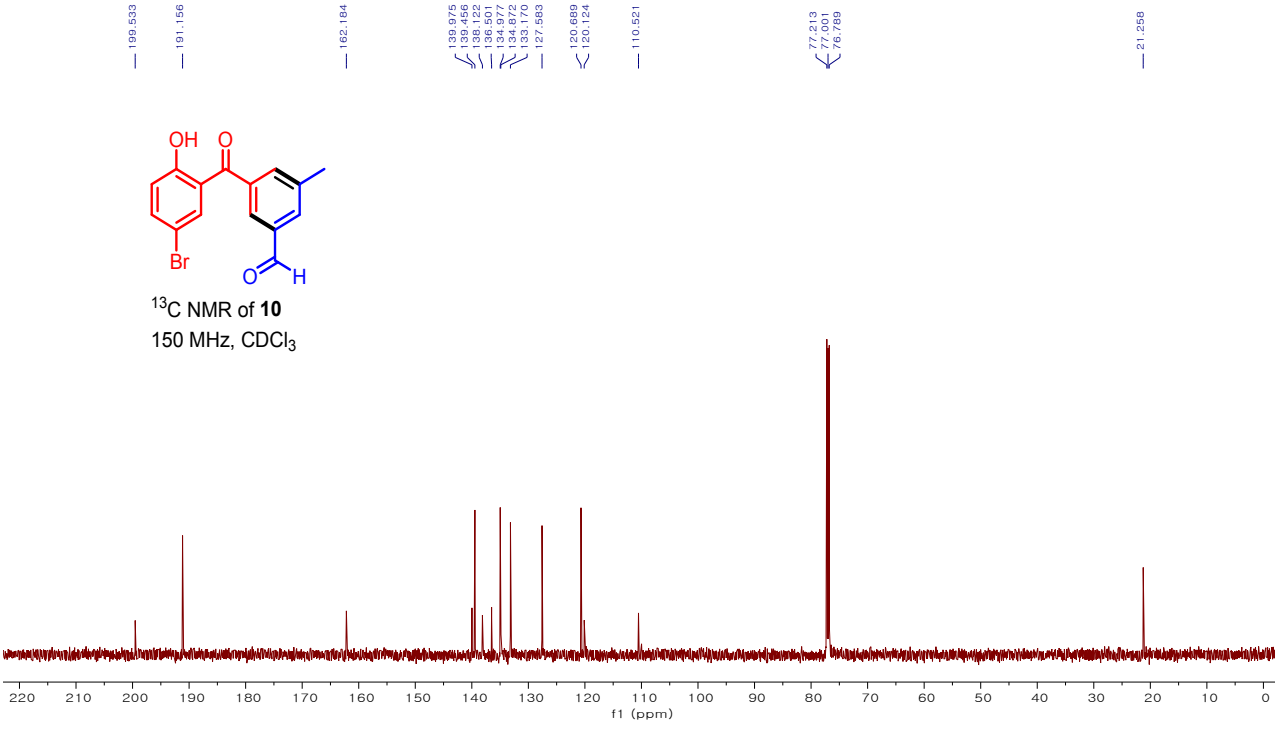
^{1}H NMR of **9**
600 MHz, $CDCl_3$



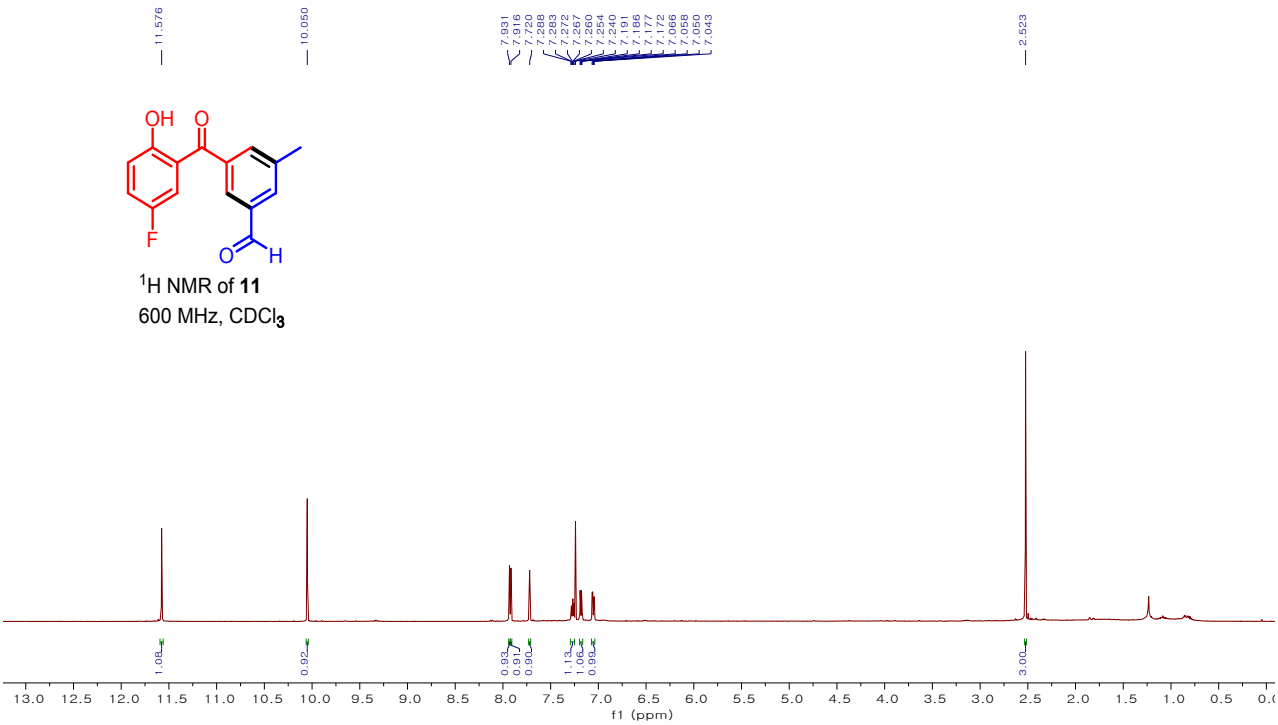
^{13}C NMR of **9**
150 MHz, $CDCl_3$



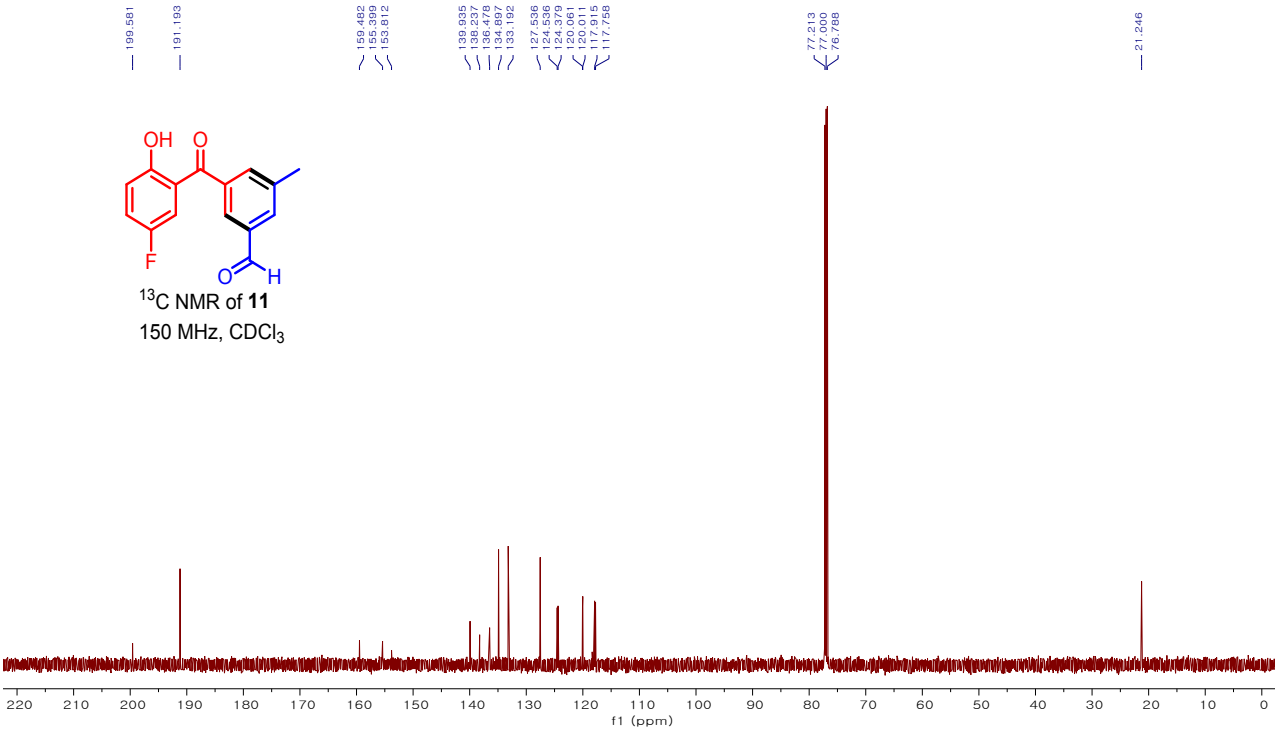
^{1}H NMR of **10**
600 MHz, $CDCl_3$



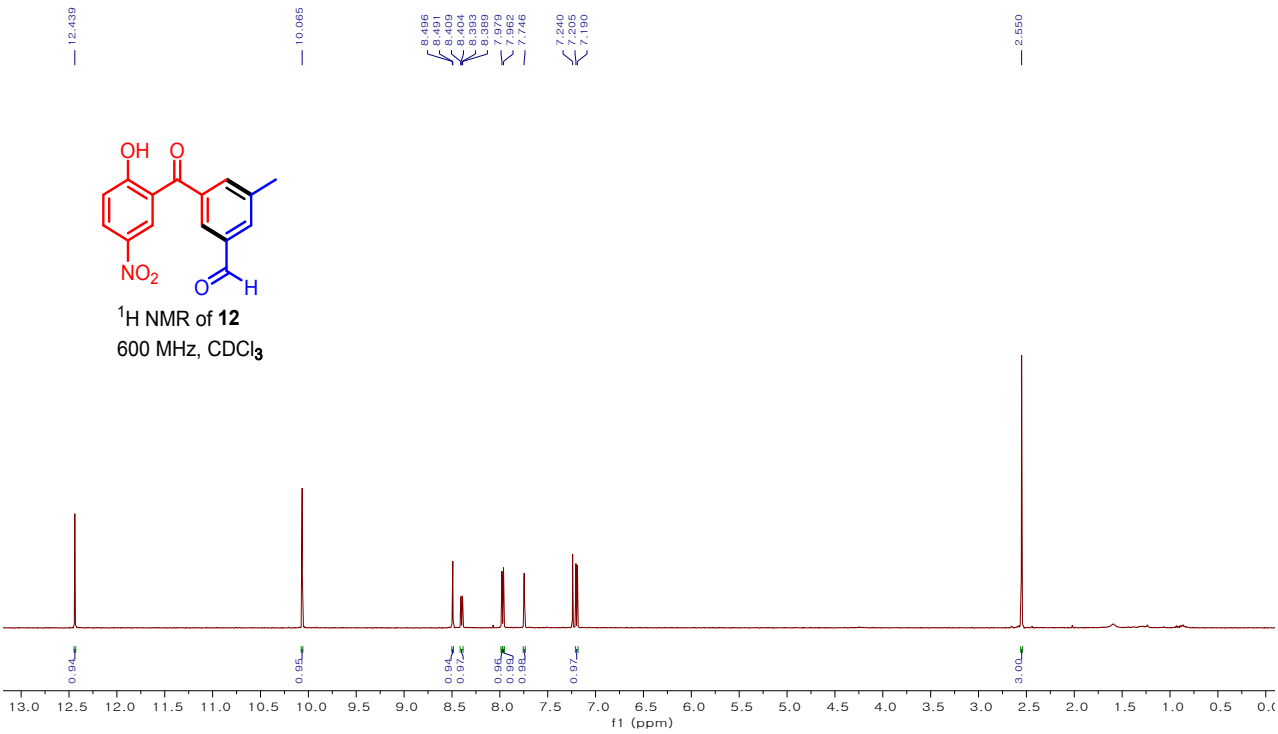
^{13}C NMR of **10**
150 MHz, $CDCl_3$



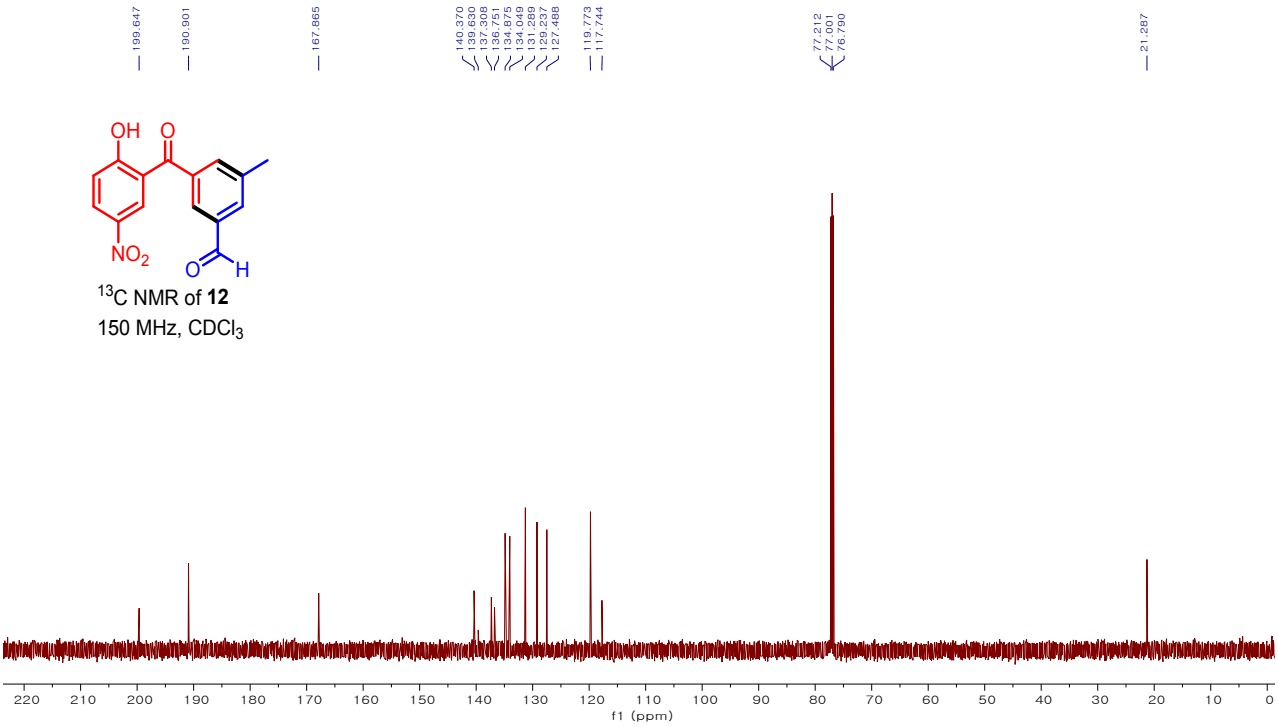
^{1}H NMR of **11**
600 MHz, $CDCl_3$



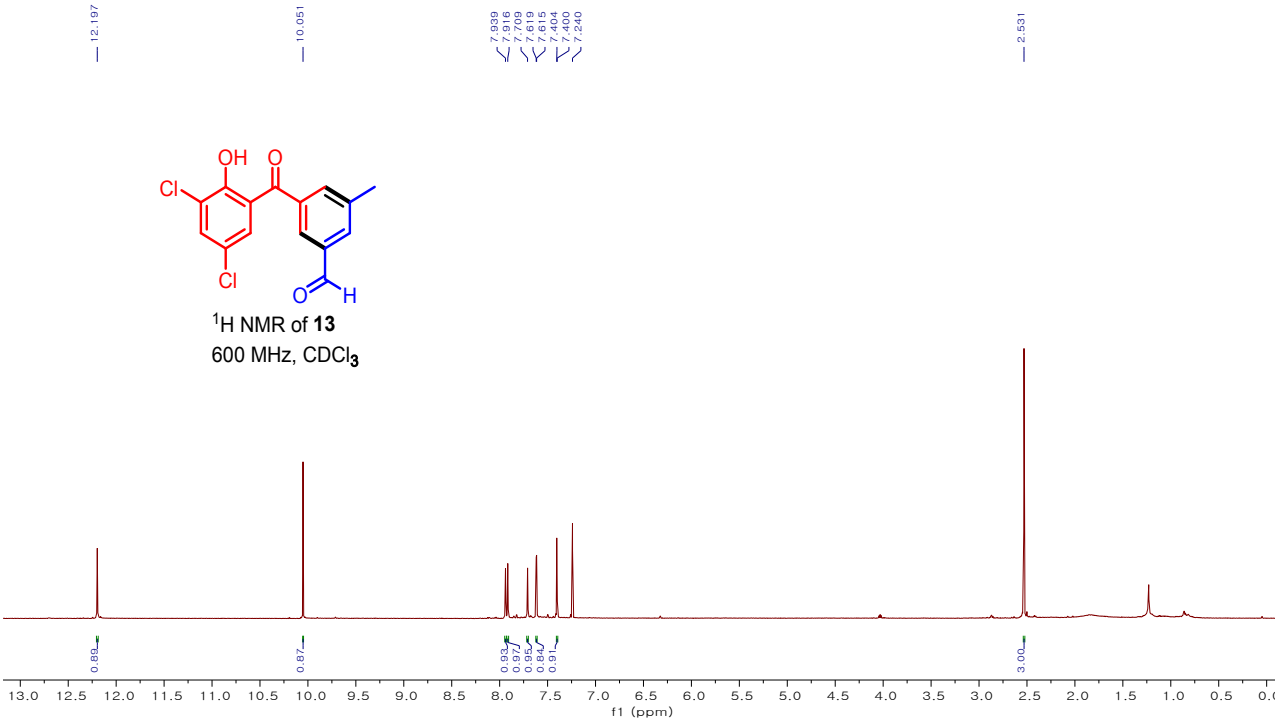
^{13}C NMR of **11**
150 MHz, $CDCl_3$



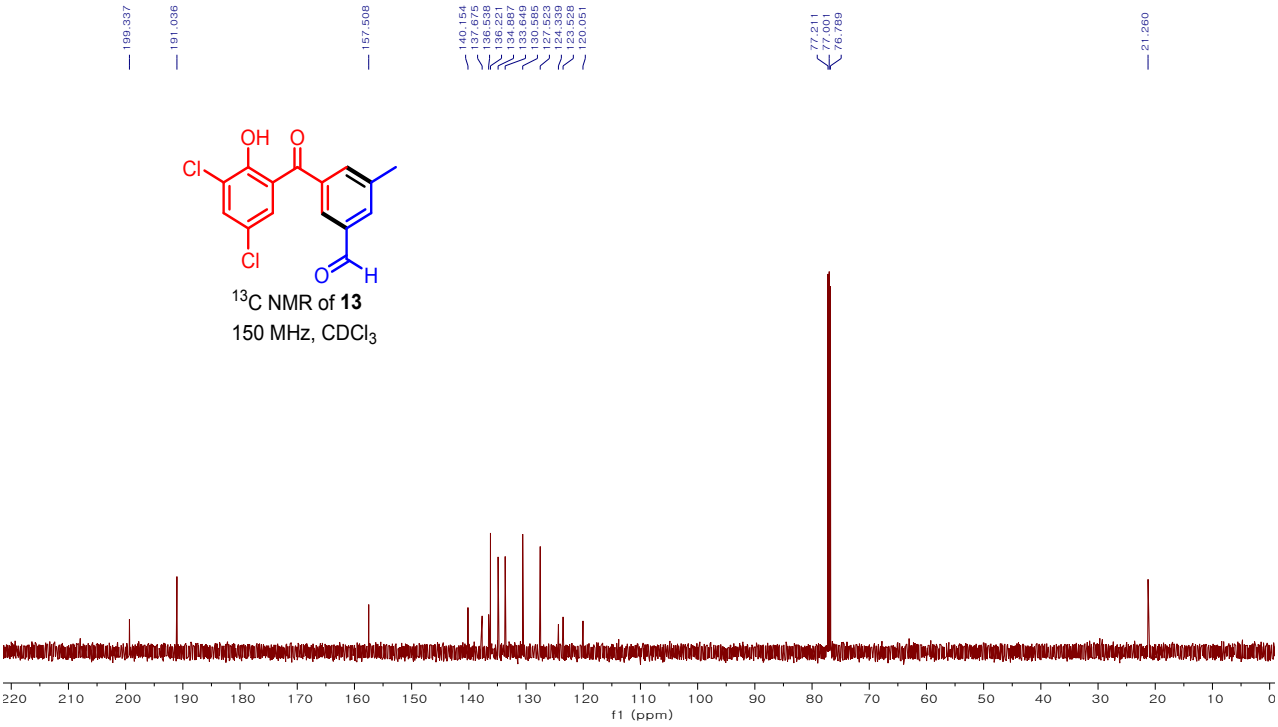
^{1}H NMR of **12**
600 MHz, $CDCl_3$



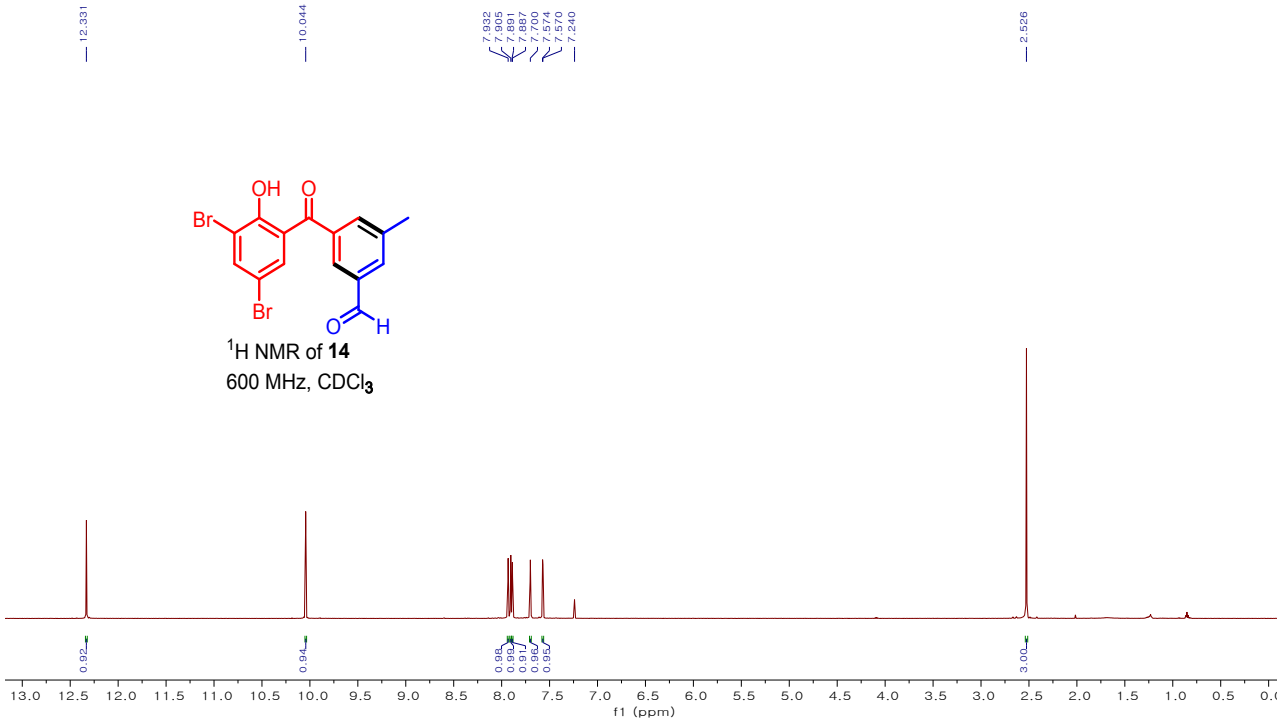
^{13}C NMR of **12**
150 MHz, $CDCl_3$



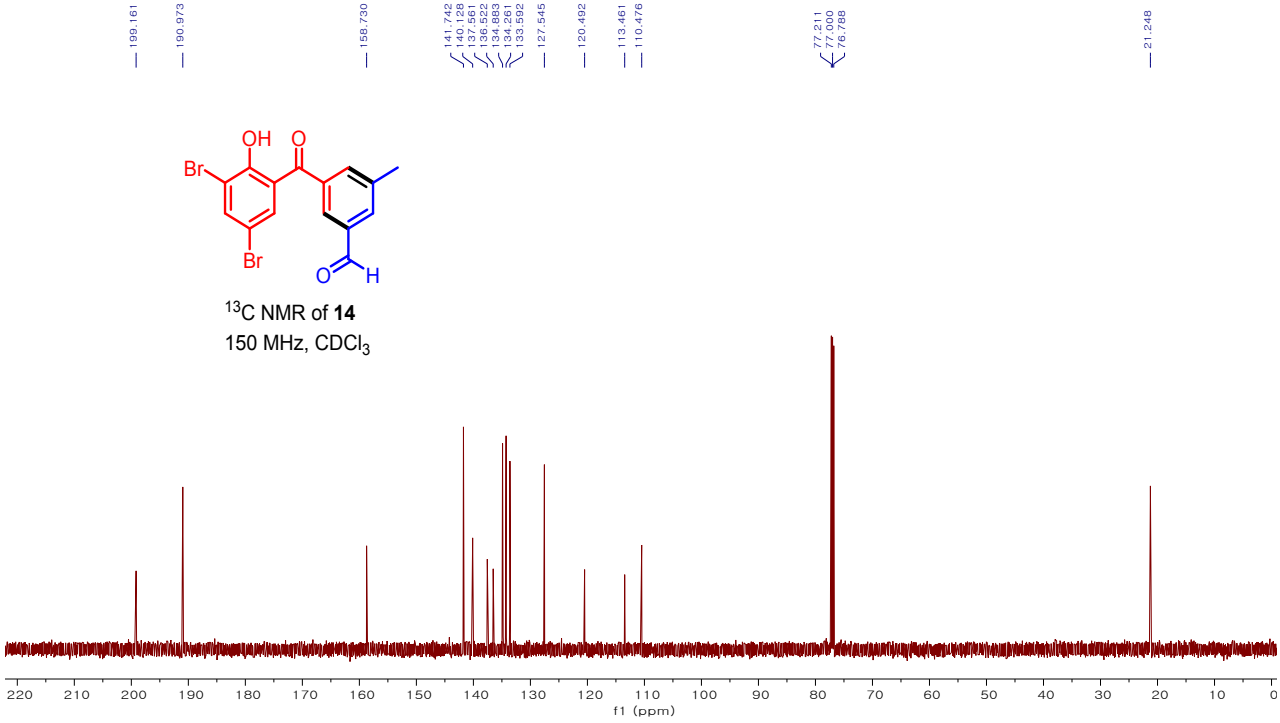
^{1}H NMR of **13**
600 MHz, $CDCl_3$



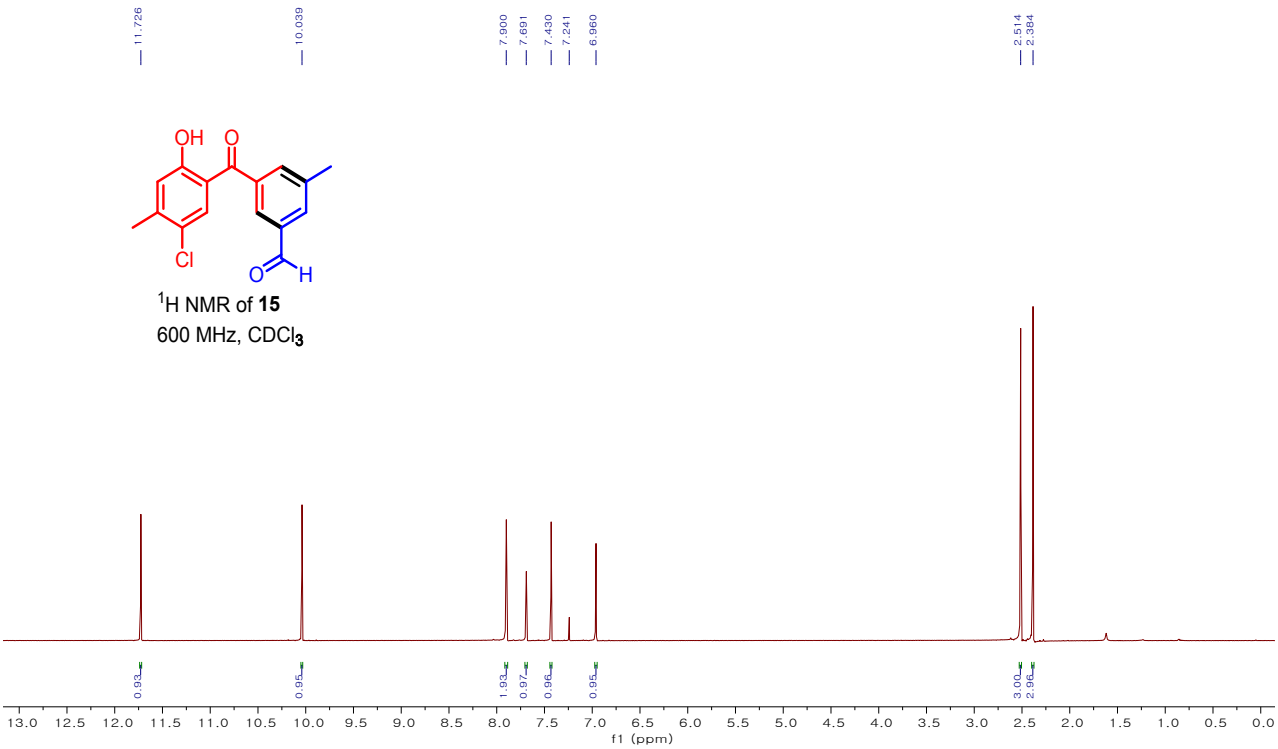
^{13}C NMR of **13**
150 MHz, $CDCl_3$



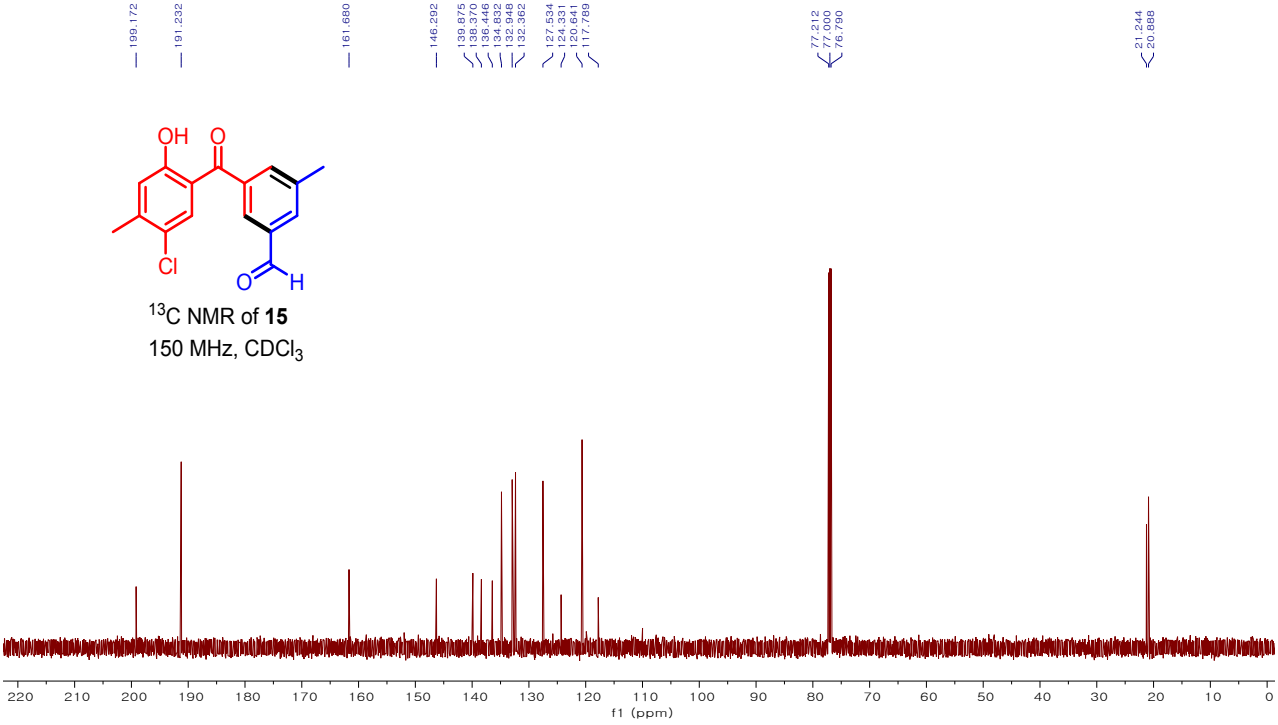
^{1}H NMR of **14**
600 MHz, $CDCl_3$



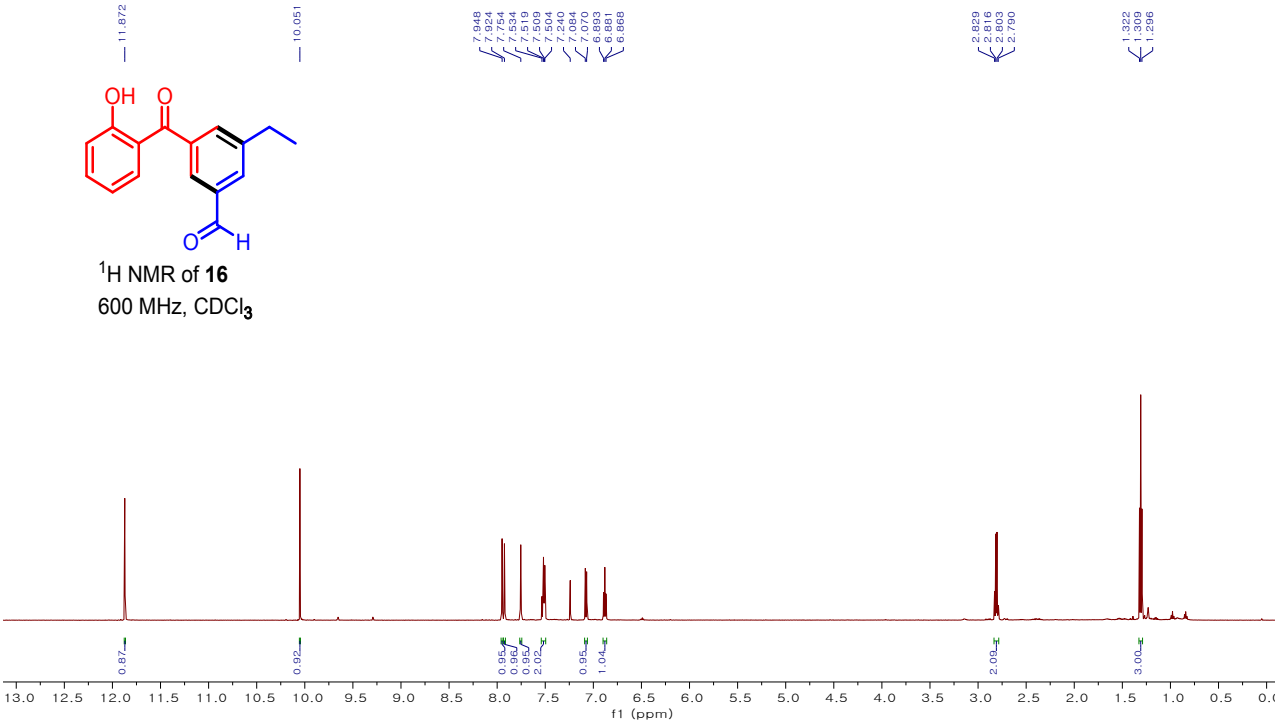
^{13}C NMR of **14**
150 MHz, $CDCl_3$



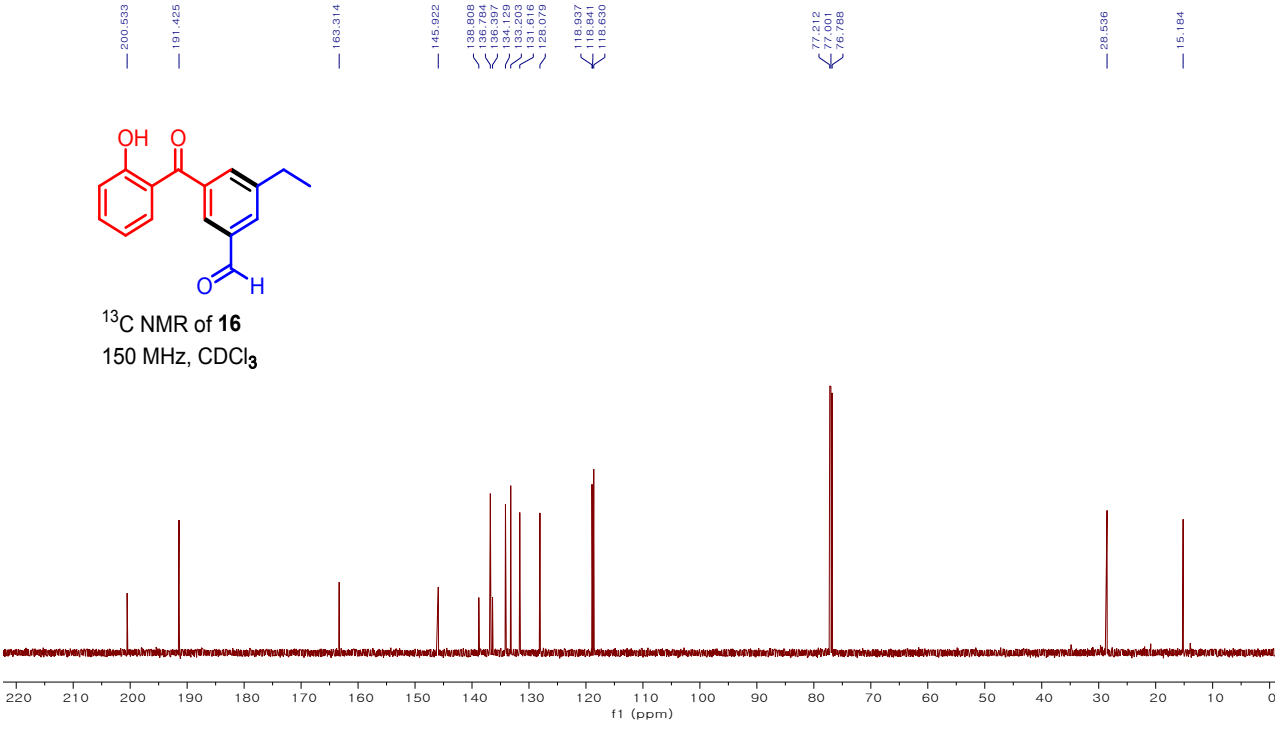
^{1}H NMR of **15**
600 MHz, $CDCl_3$



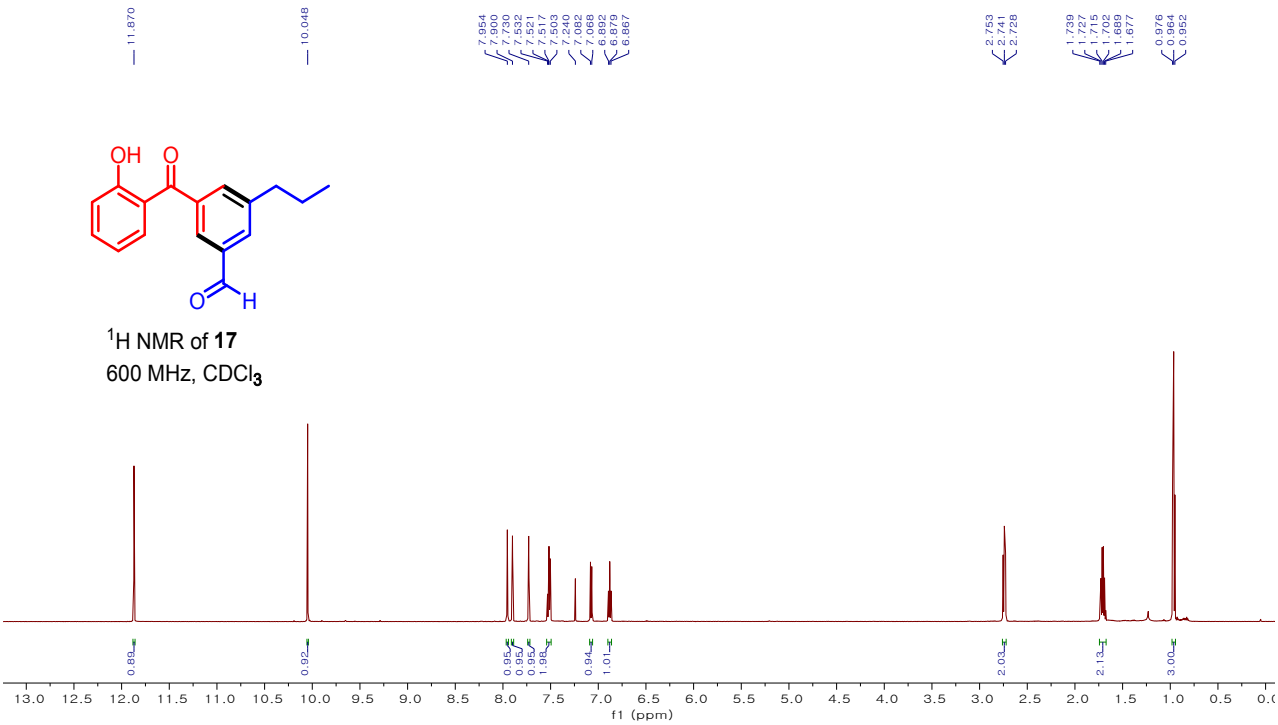
^{13}C NMR of **15**
150 MHz, $CDCl_3$



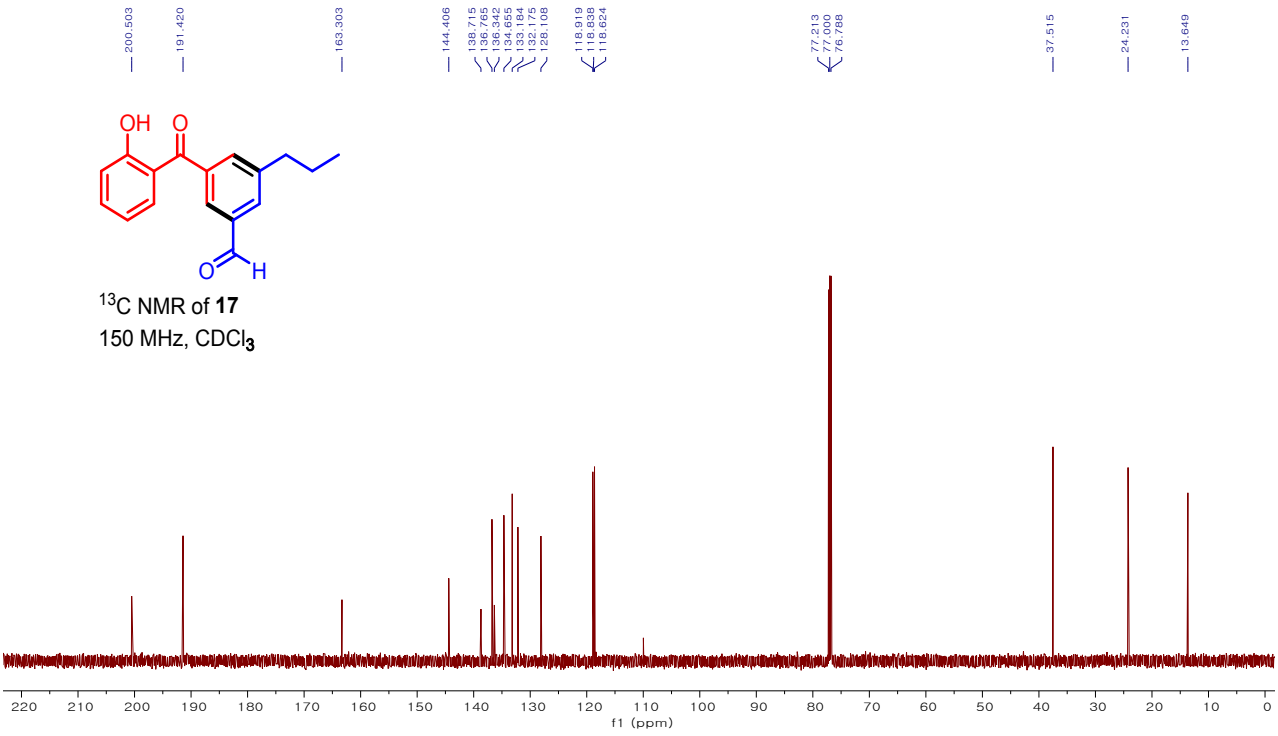
^{1}H NMR of **16**
600 MHz, $CDCl_3$



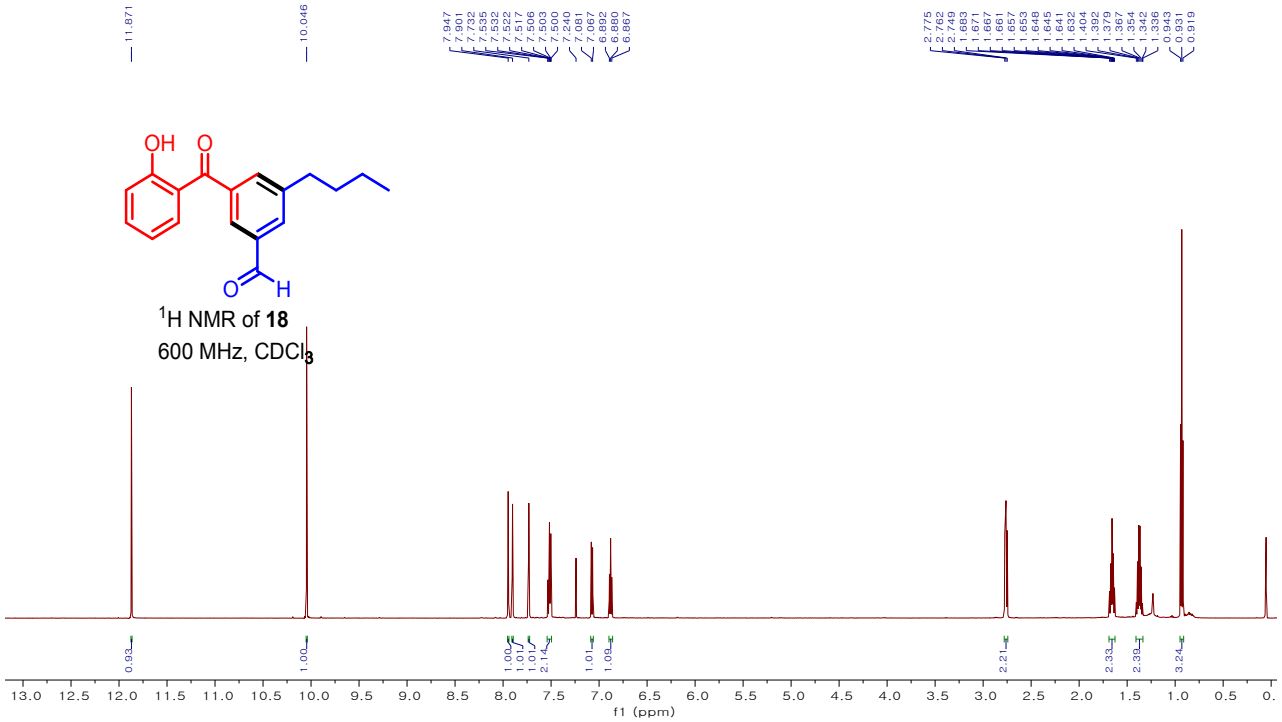
^{13}C NMR of **16**
150 MHz, $CDCl_3$



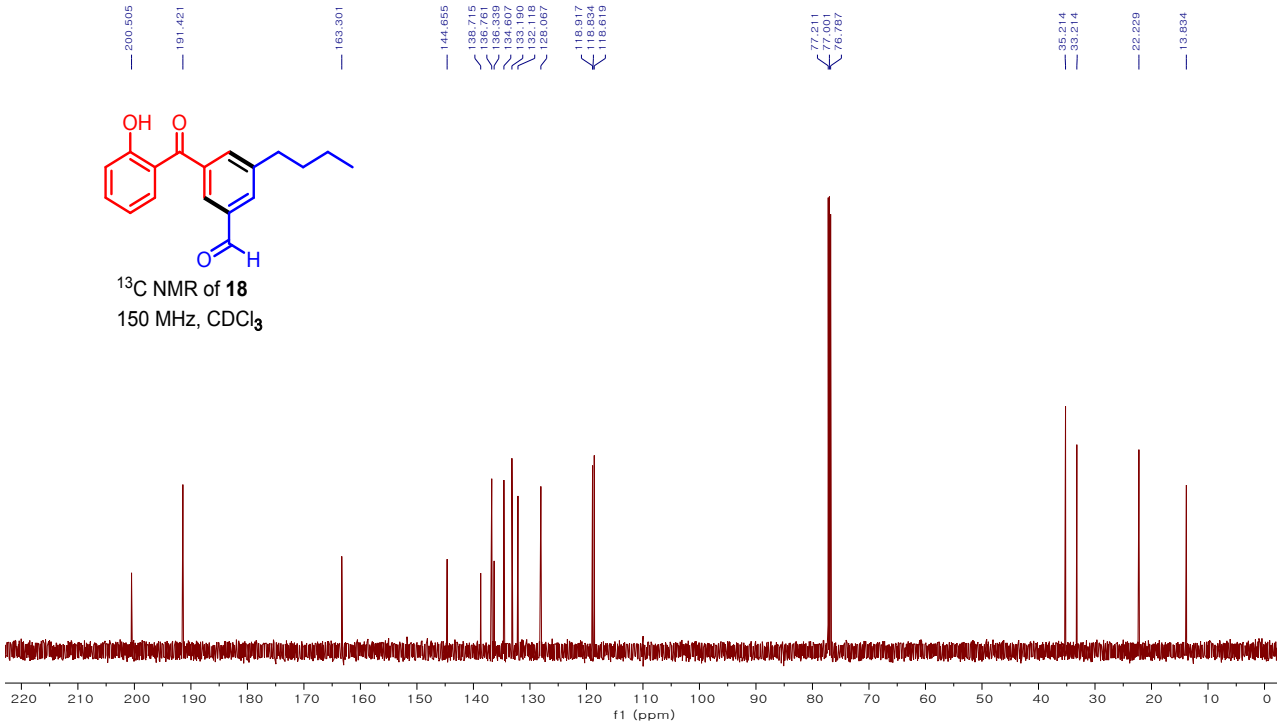
^{1}H NMR of **17**
600 MHz, $CDCl_3$



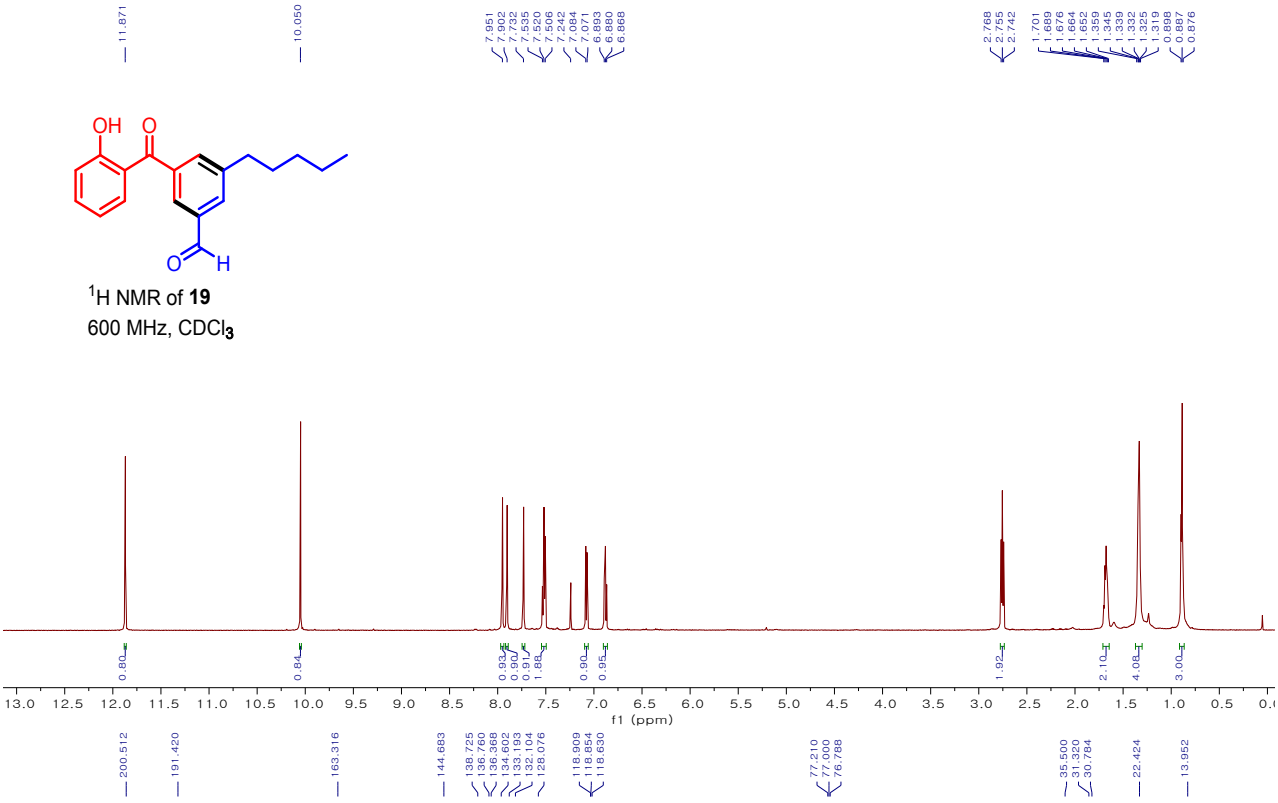
^{13}C NMR of **17**
150 MHz, $CDCl_3$



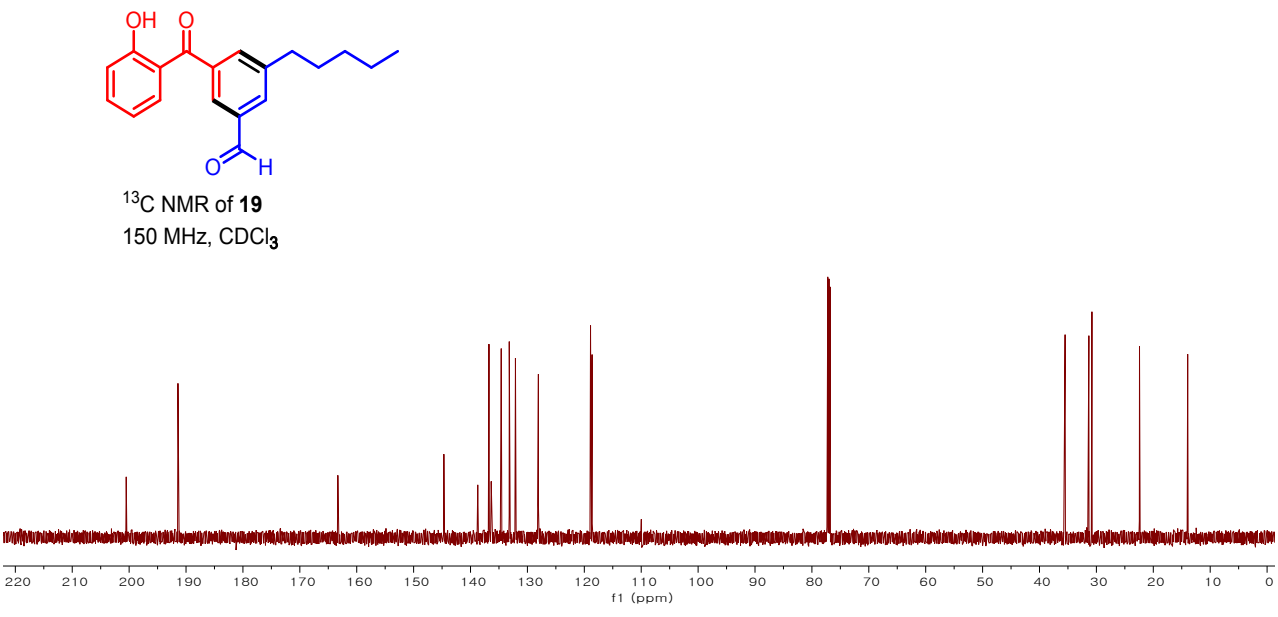
^{1}H NMR of **18**
600 MHz, $CDCl_3$



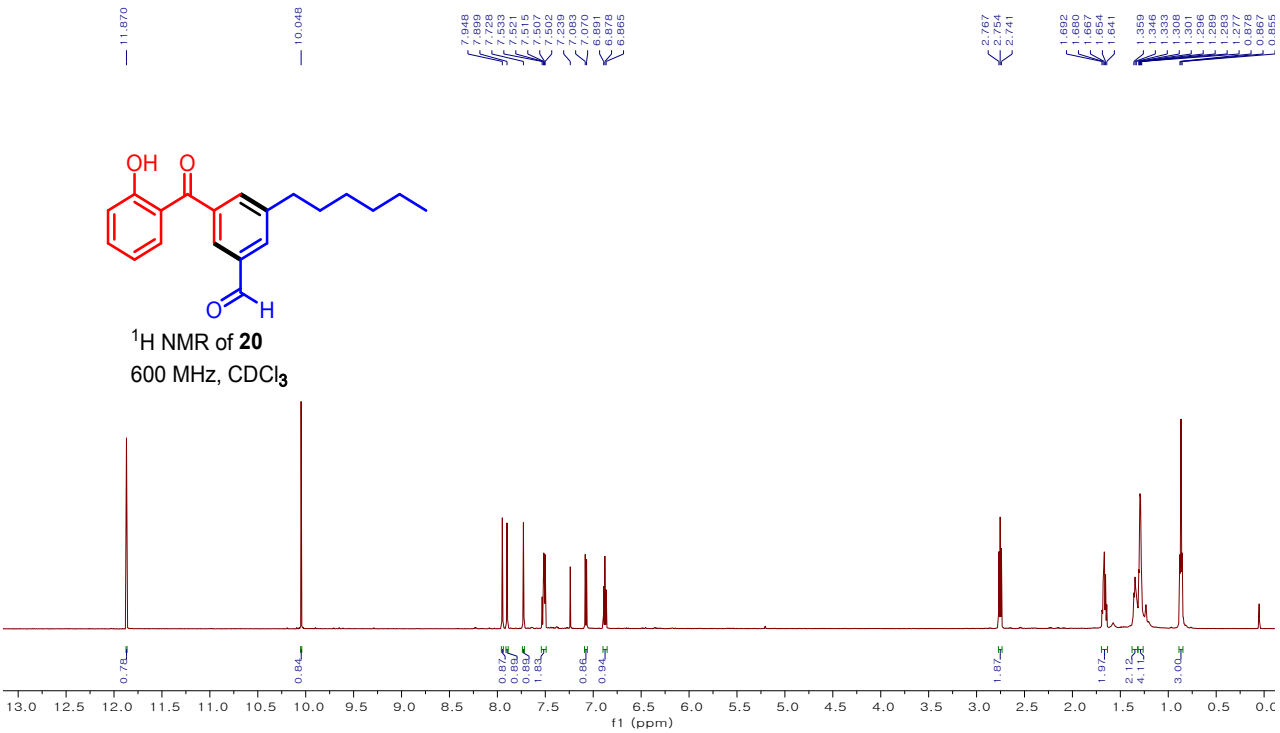
^{13}C NMR of **18**
150 MHz, $CDCl_3$



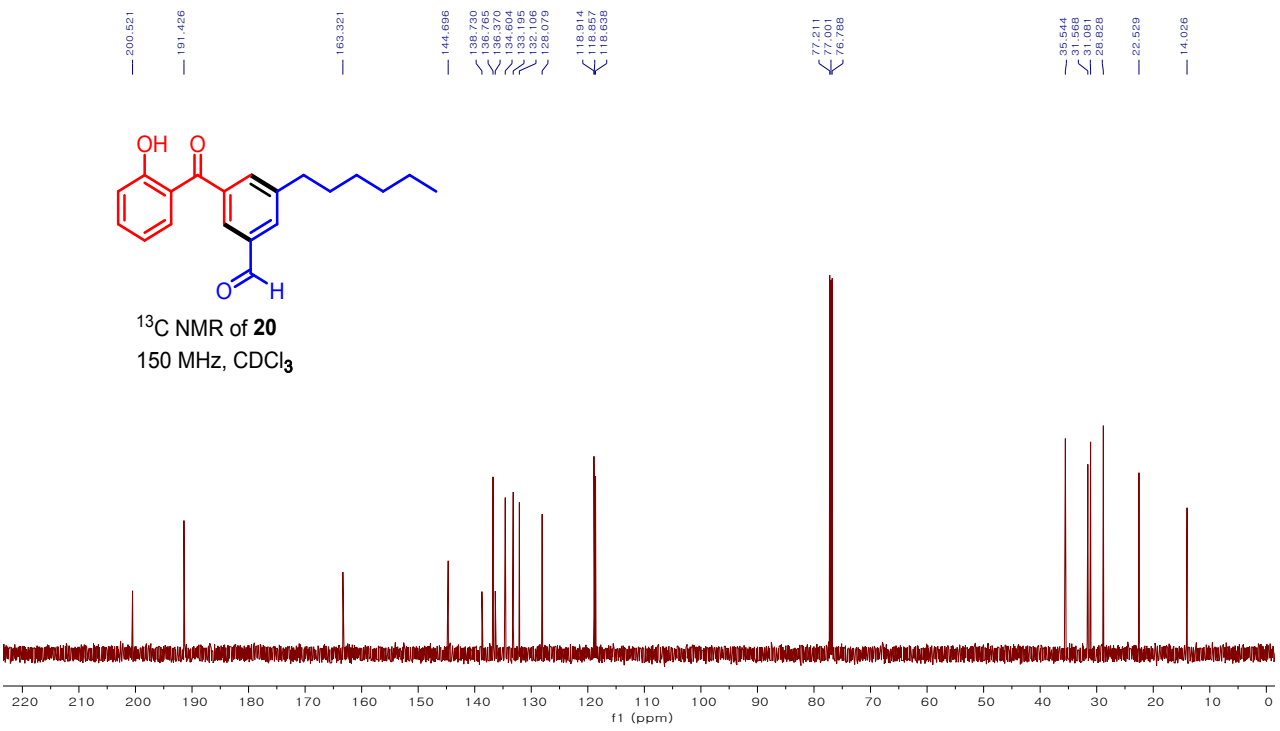
^{1}H NMR of **19**
600 MHz, $CDCl_3$



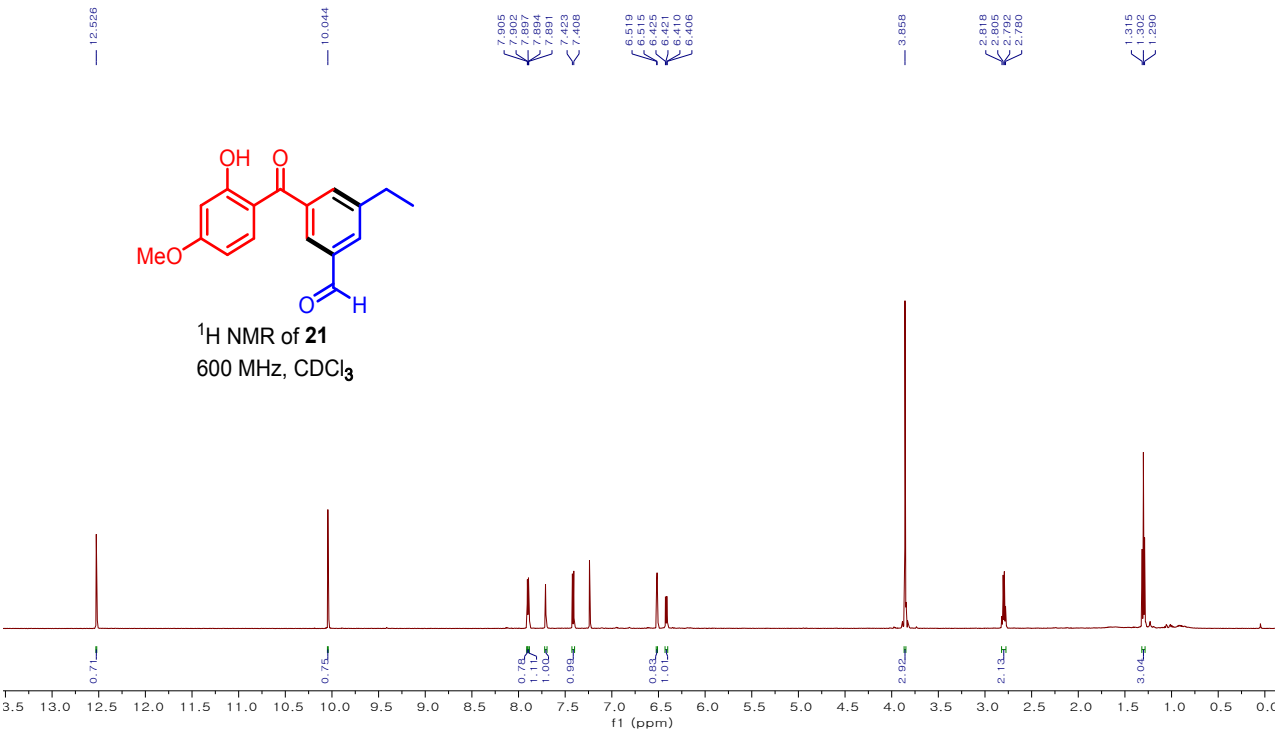
^{13}C NMR of **19**
150 MHz, $CDCl_3$



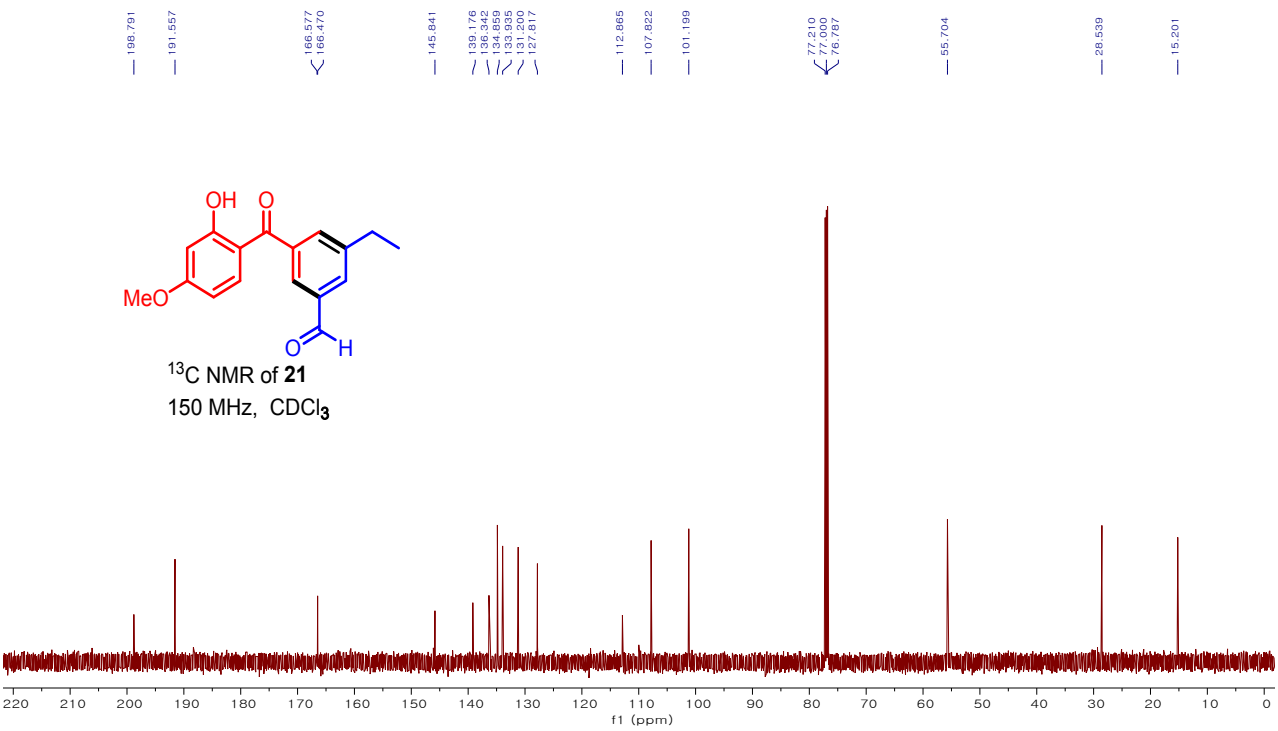
^{1}H NMR of **20**
600 MHz, $CDCl_3$



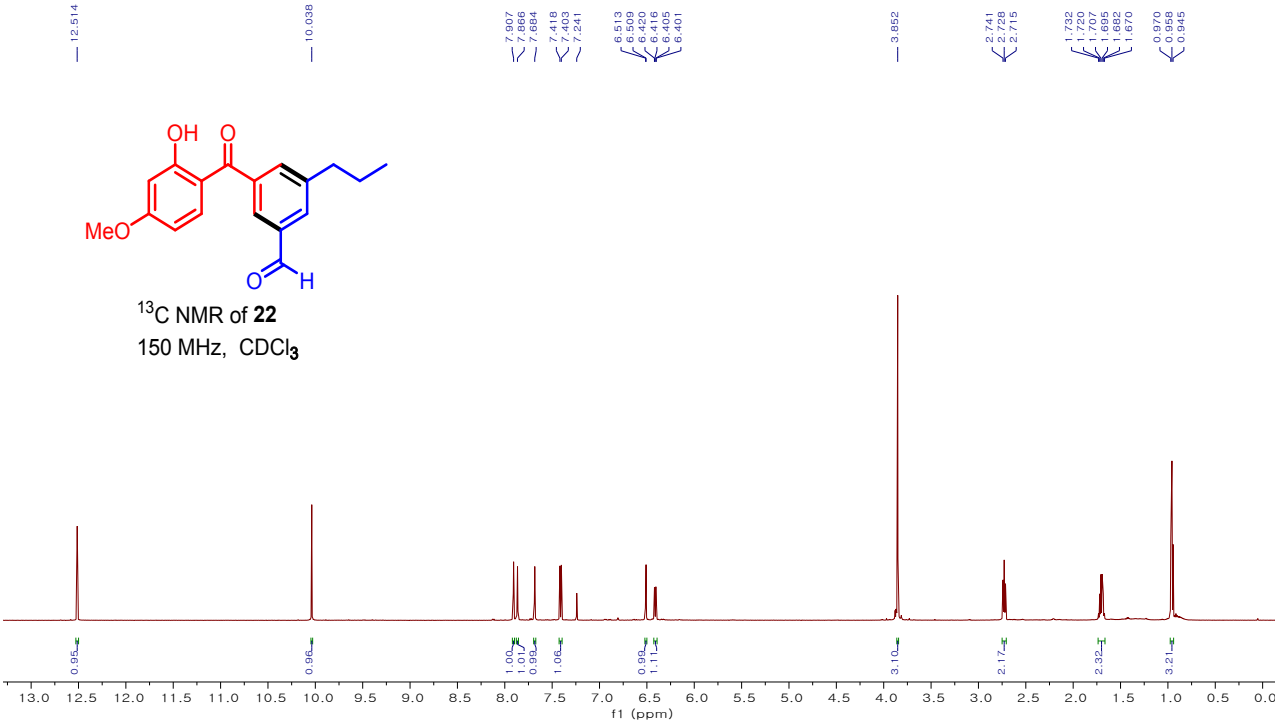
^{13}C NMR of **20**
150 MHz, $CDCl_3$



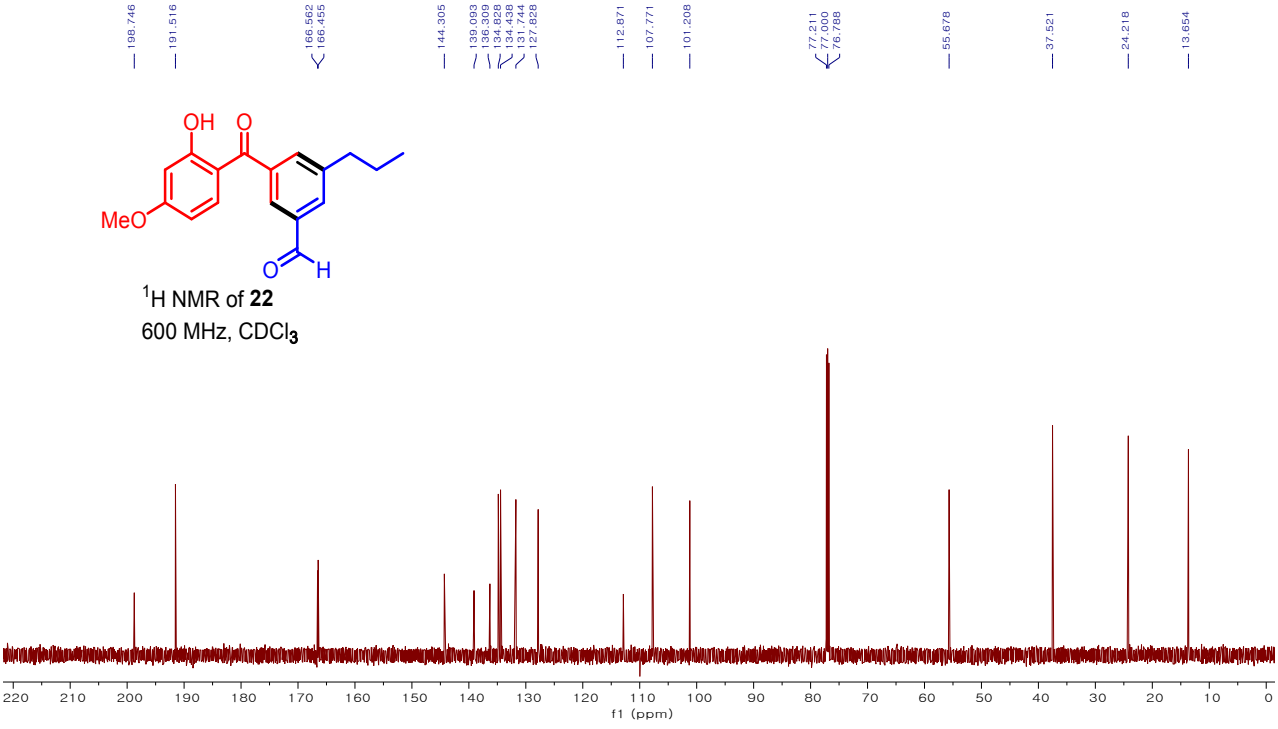
^{1}H NMR of **21**
600 MHz, $CDCl_3$



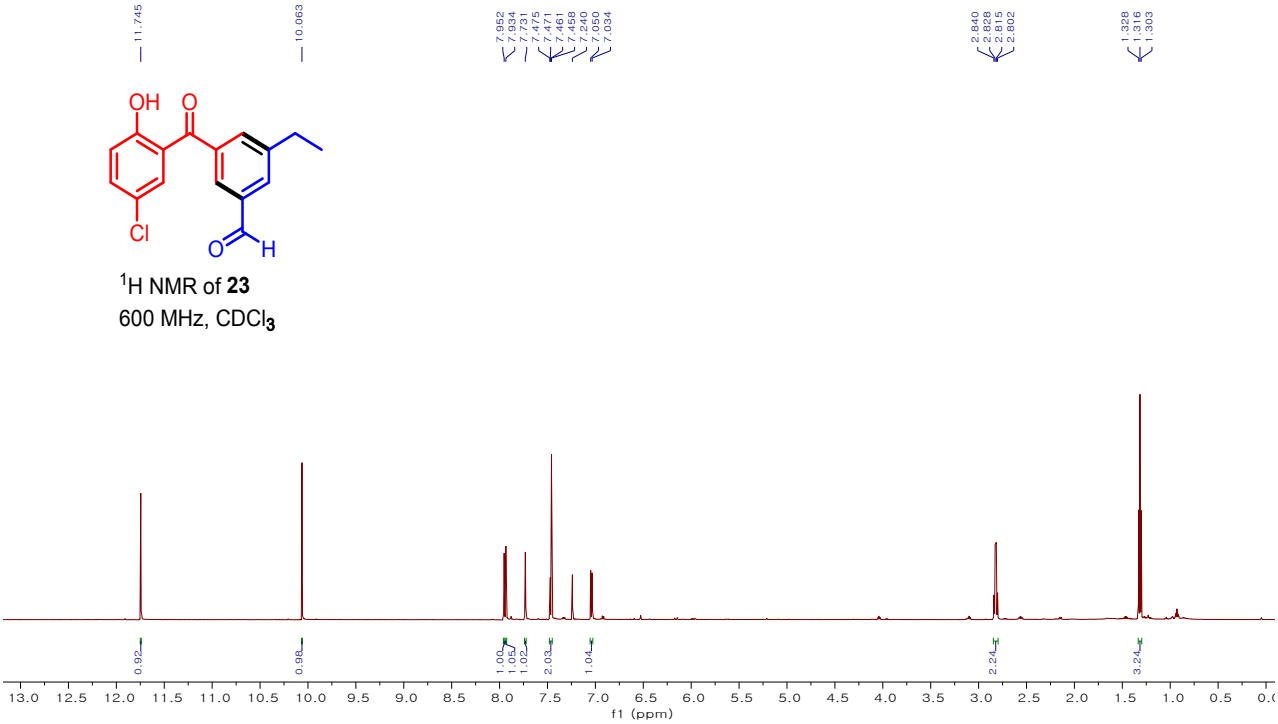
^{13}C NMR of **21**
150 MHz, $CDCl_3$



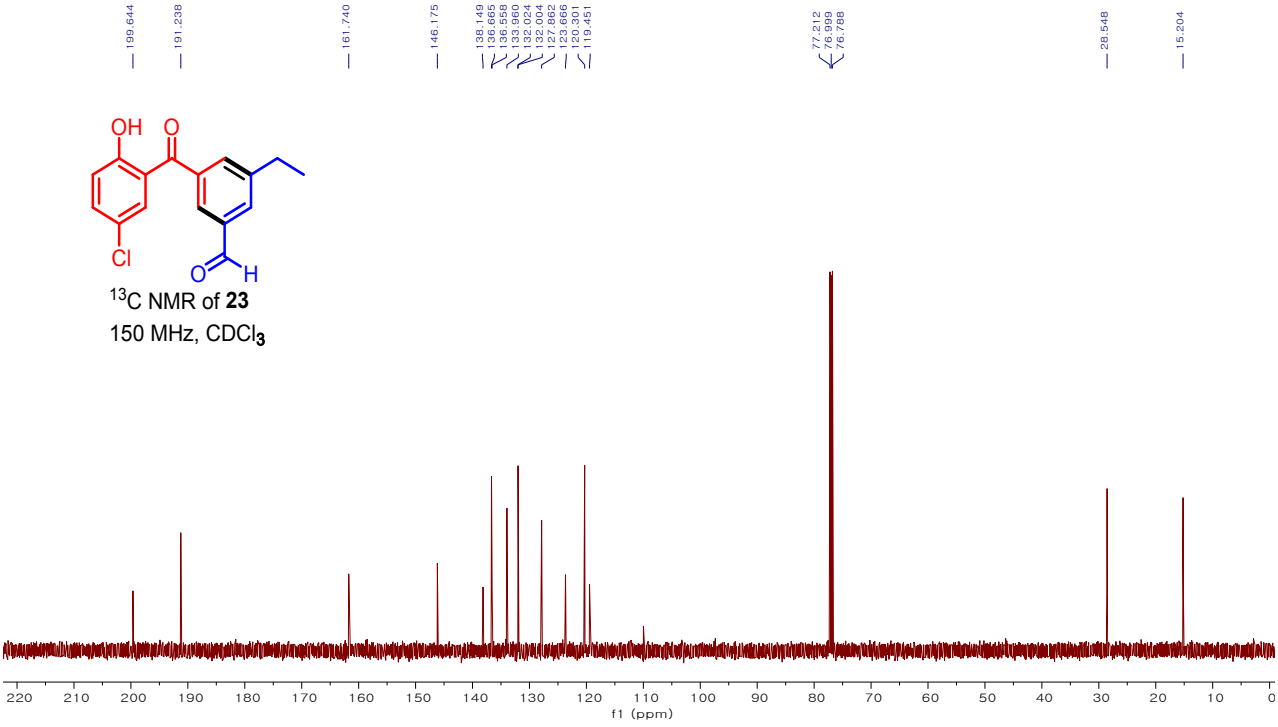
^{13}C NMR of **22**
150 MHz, $CDCl_3$



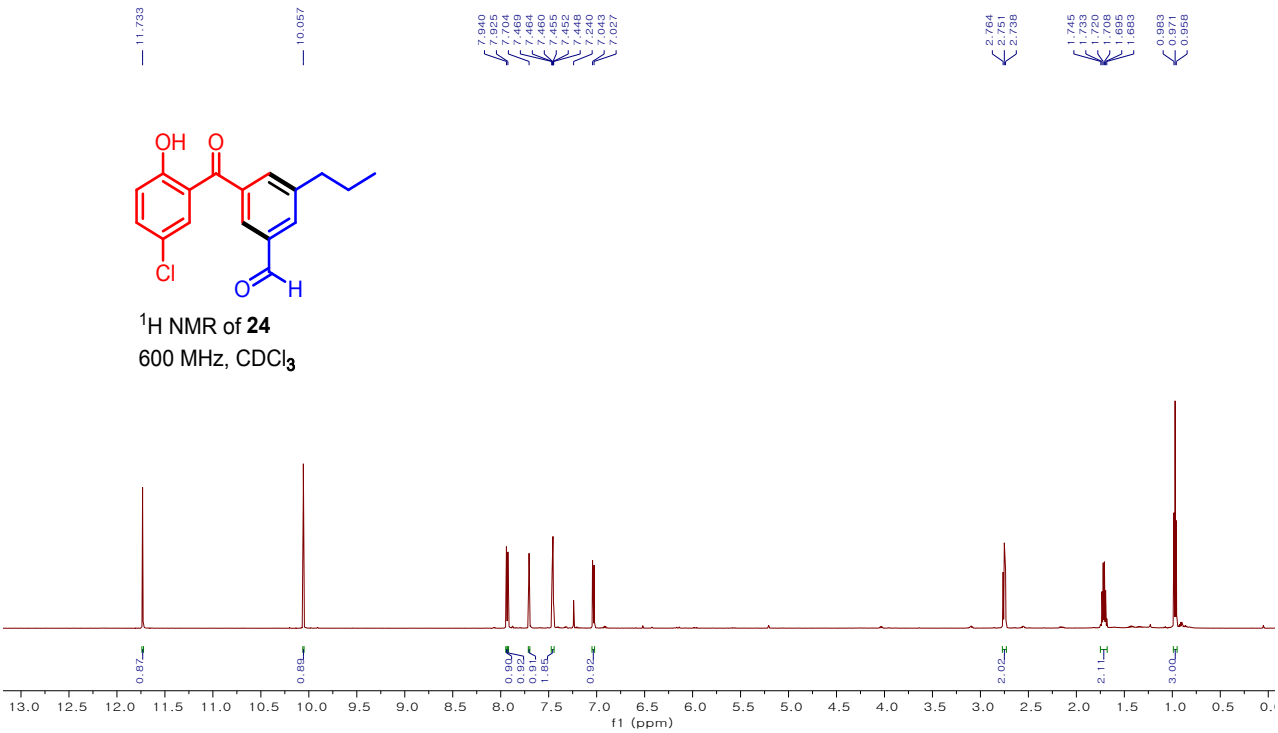
^{1}H NMR of **22**
600 MHz, $CDCl_3$



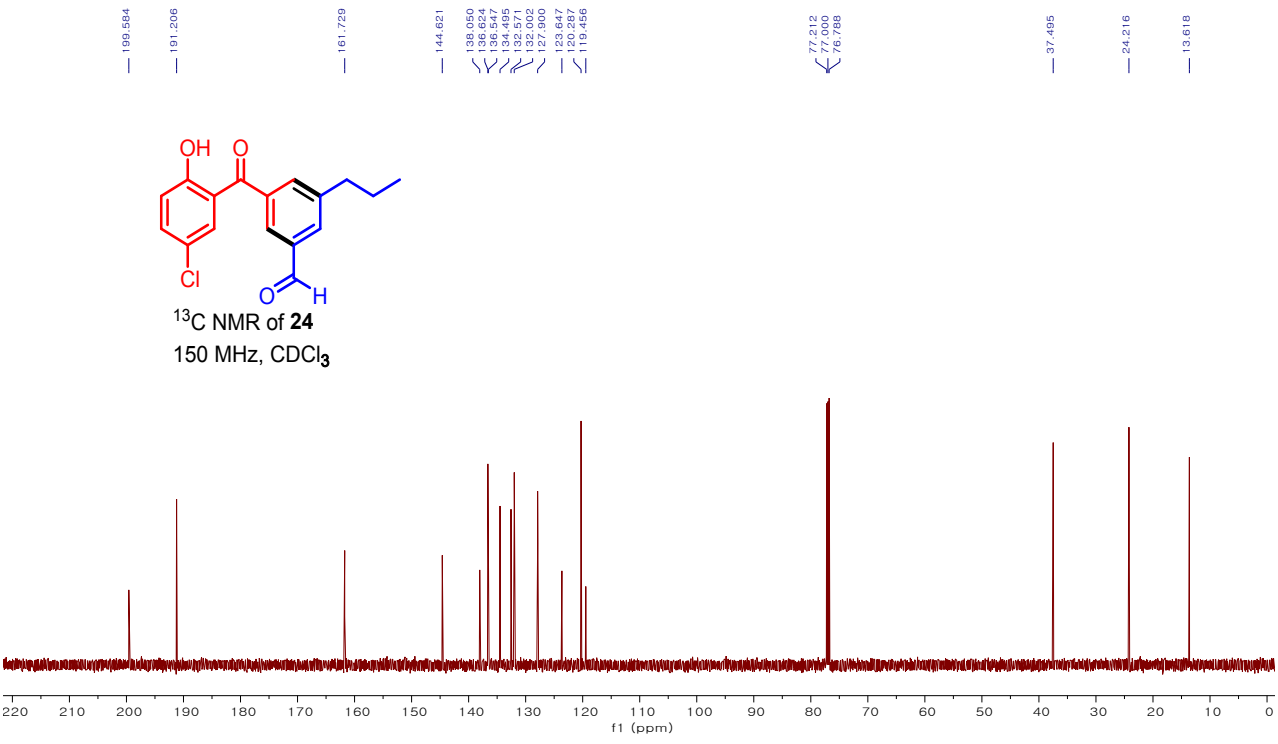
^{1}H NMR of **23**
600 MHz, $CDCl_3$



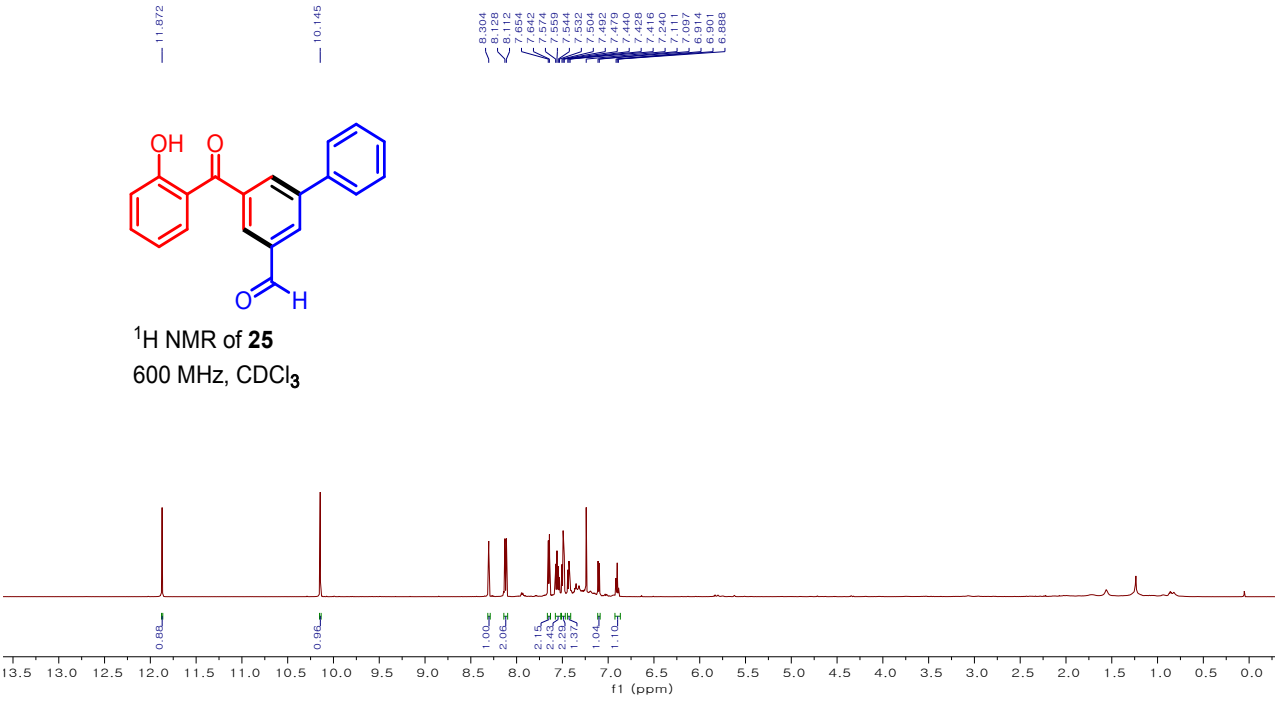
^{13}C NMR of **23**
150 MHz, $CDCl_3$



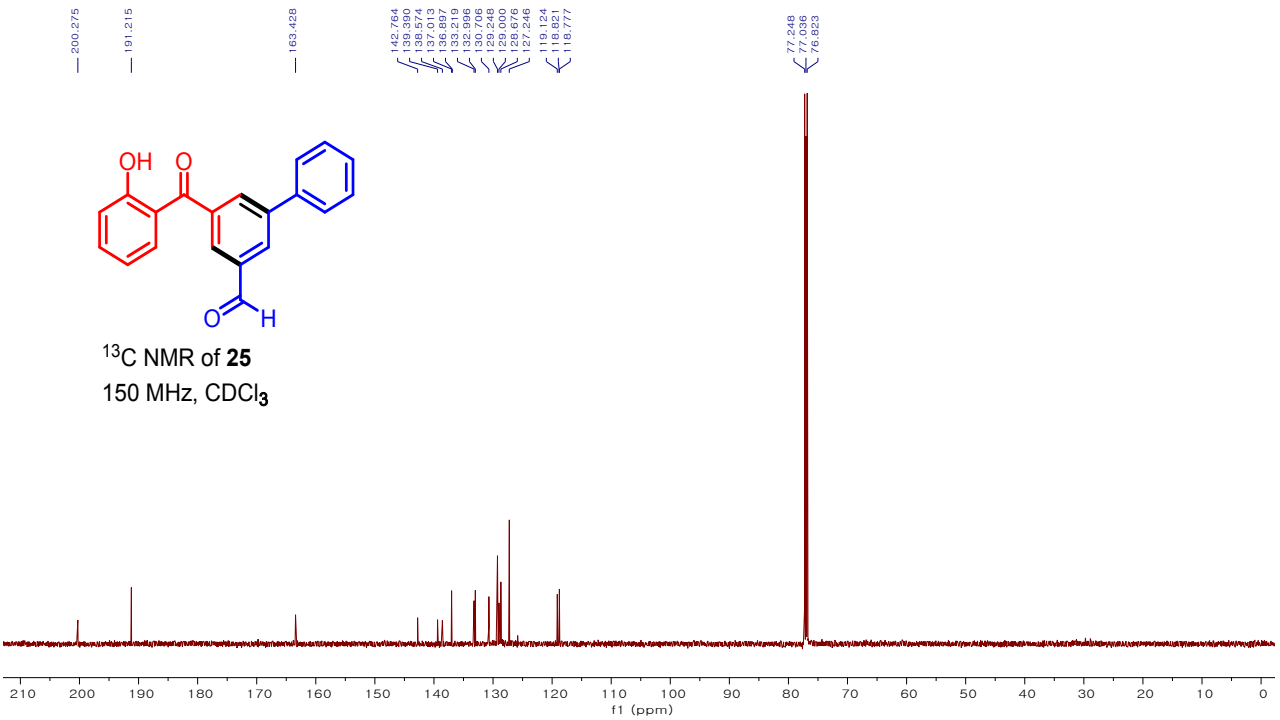
^{1}H NMR of **24**
600 MHz, $CDCl_3$



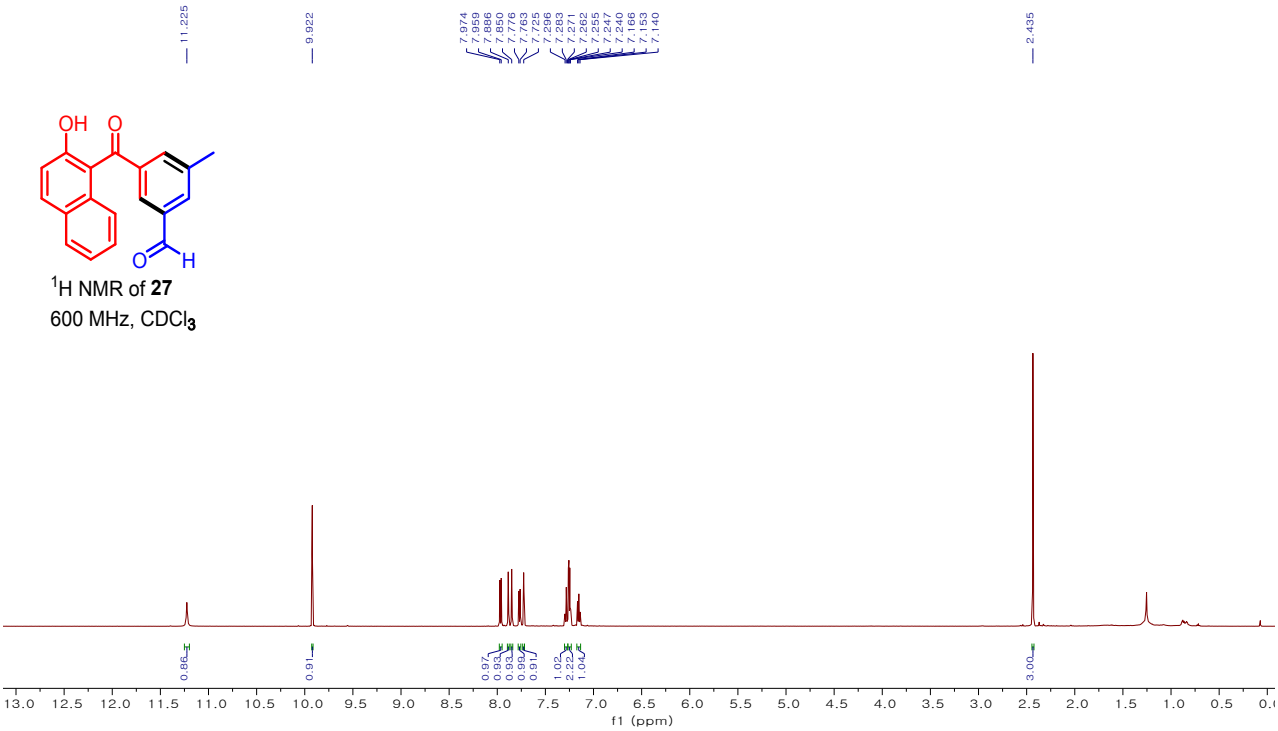
^{13}C NMR of **24**
150 MHz, $CDCl_3$



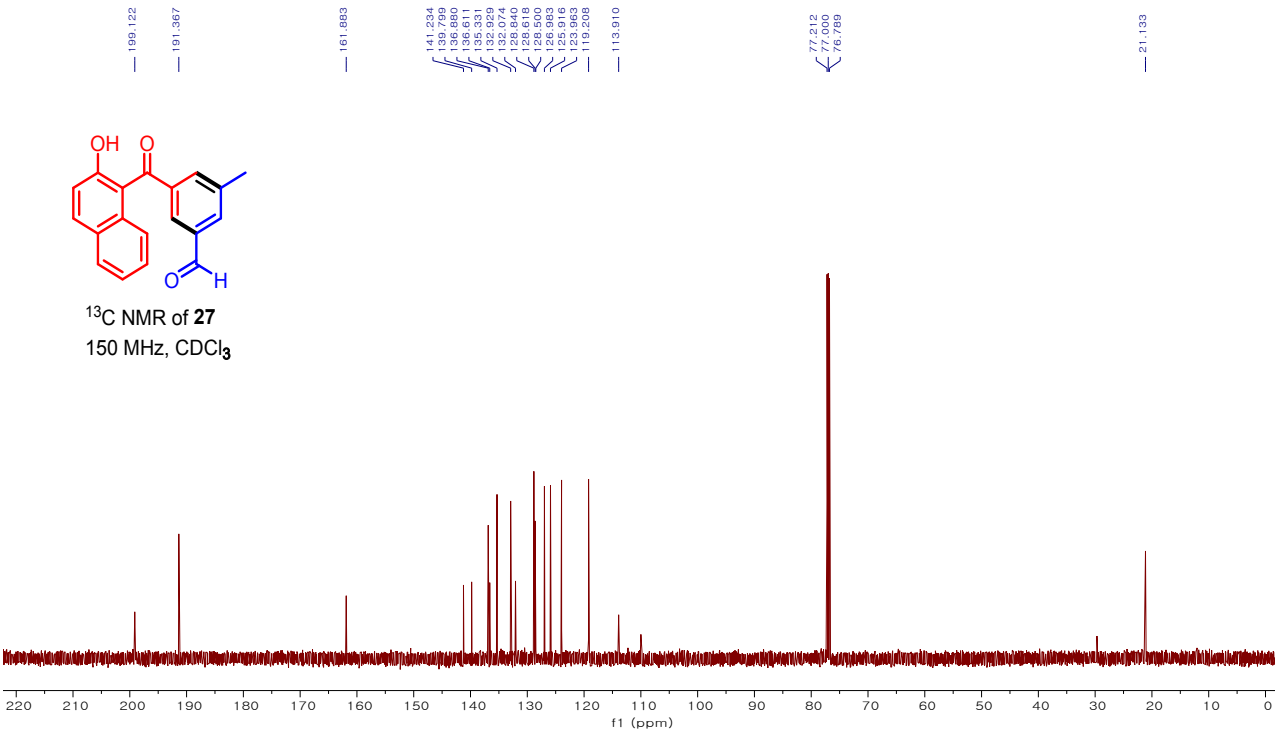
^{1}H NMR of **25**
600 MHz, $CDCl_3$



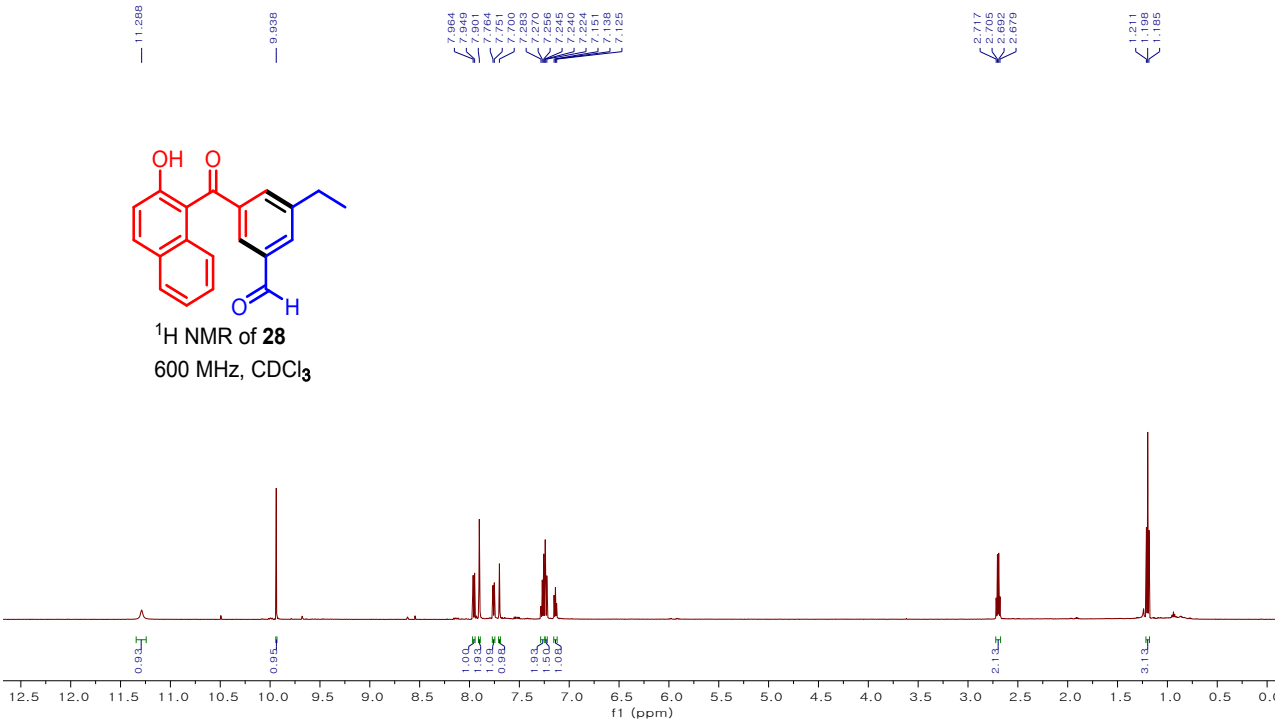
^{13}C NMR of **25**
150 MHz, $CDCl_3$



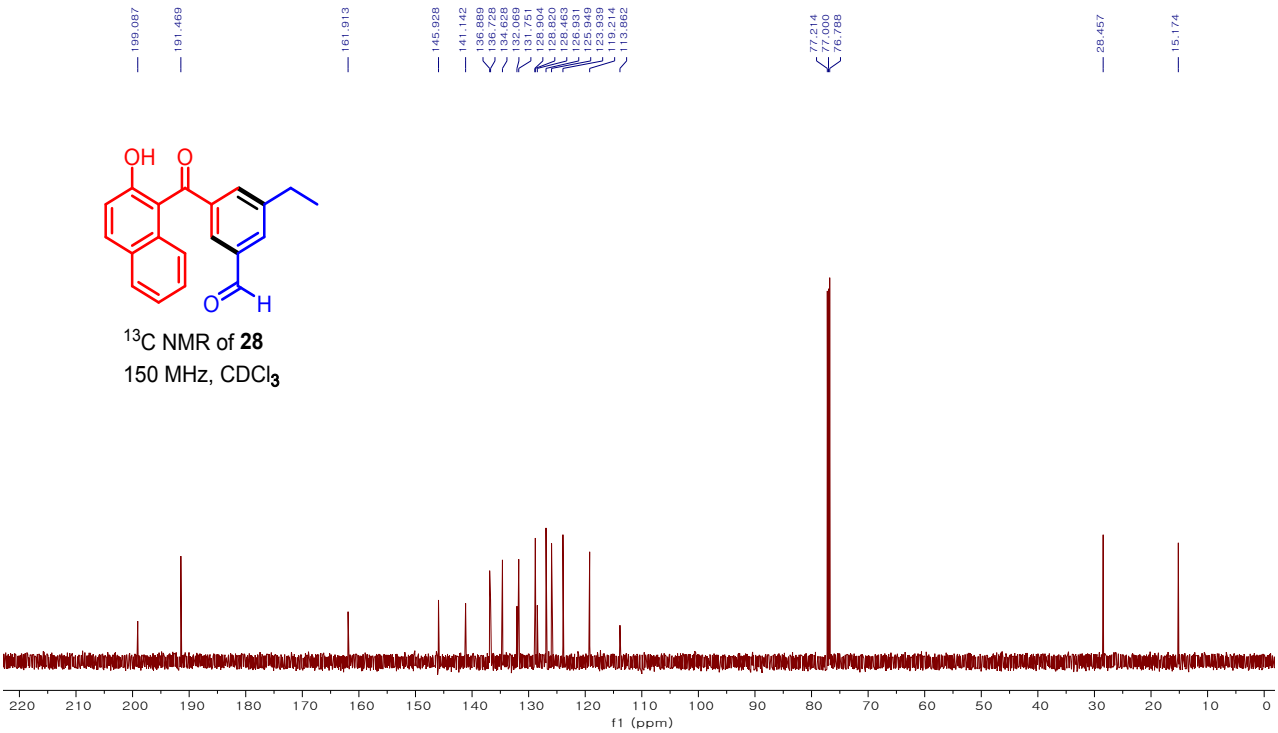
^{1}H NMR of **27**
600 MHz, $CDCl_3$



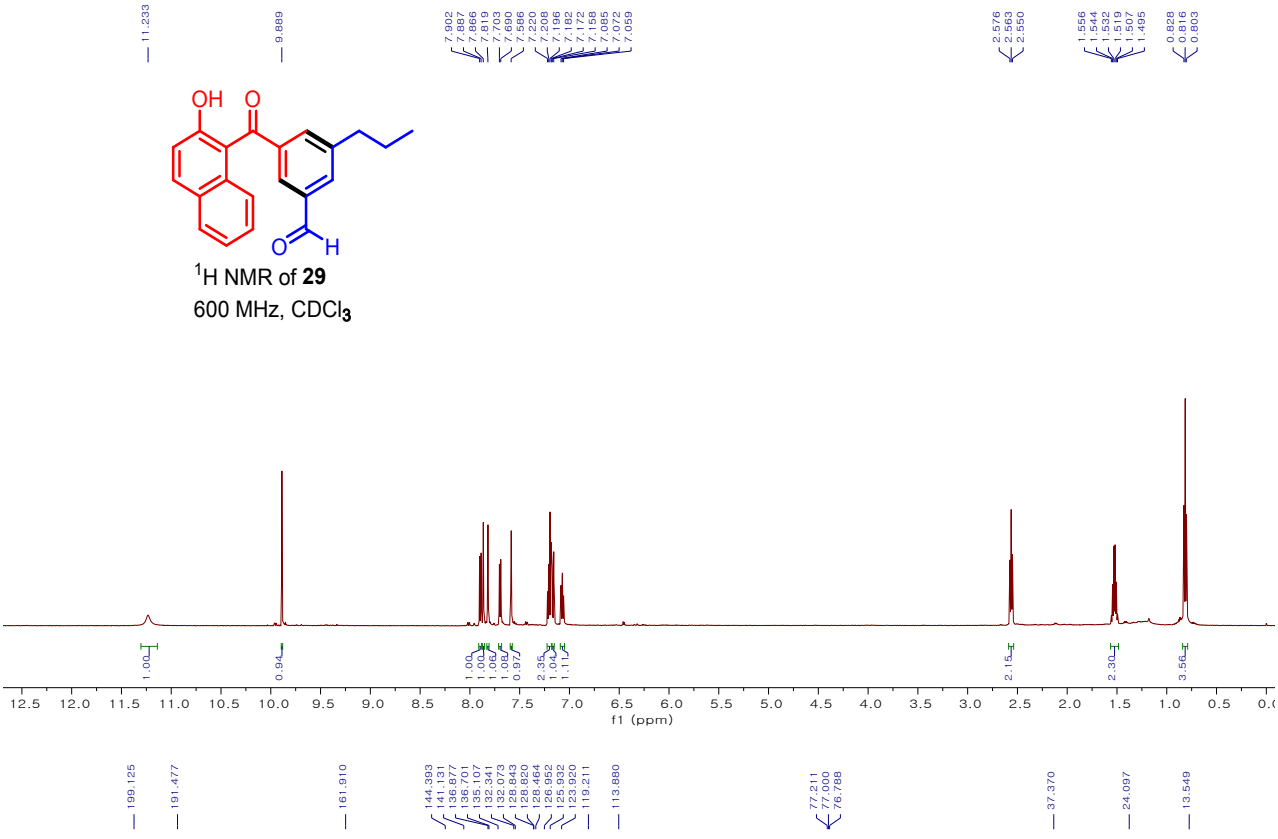
^{13}C NMR of **27**
150 MHz, $CDCl_3$



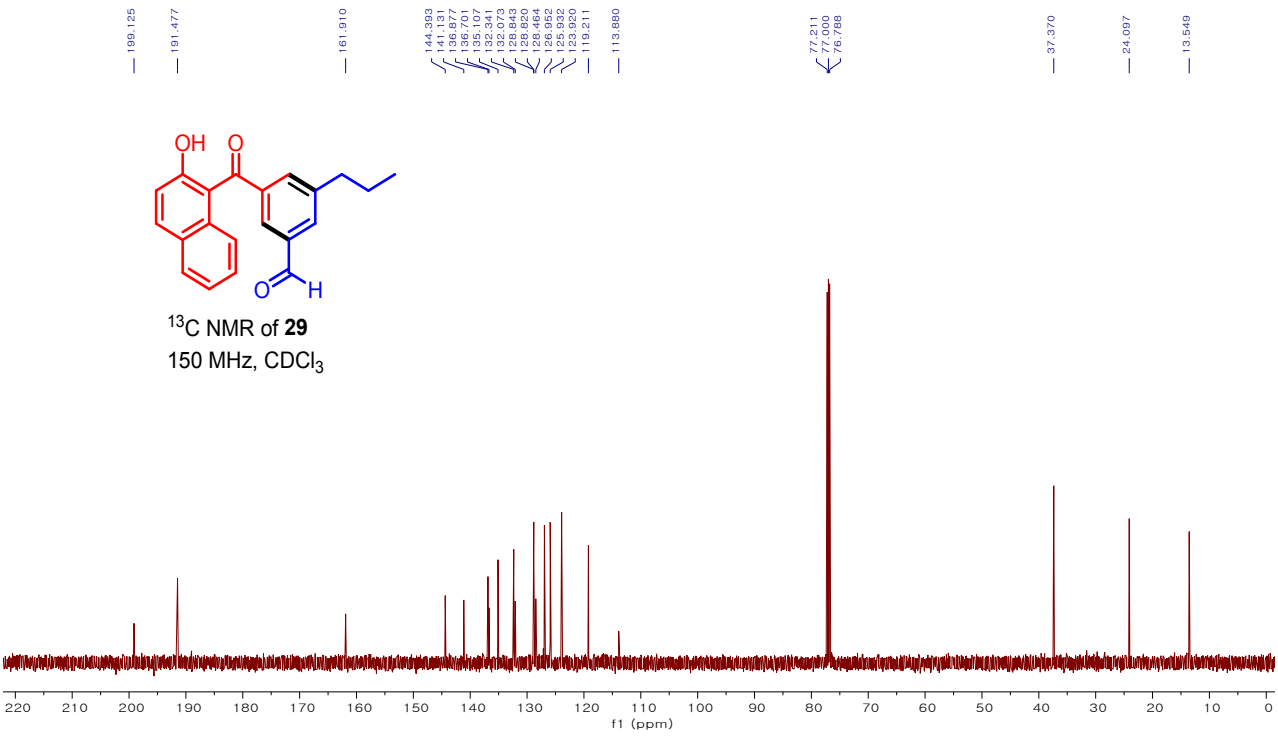
^{1}H NMR of **28**
600 MHz, $CDCl_3$



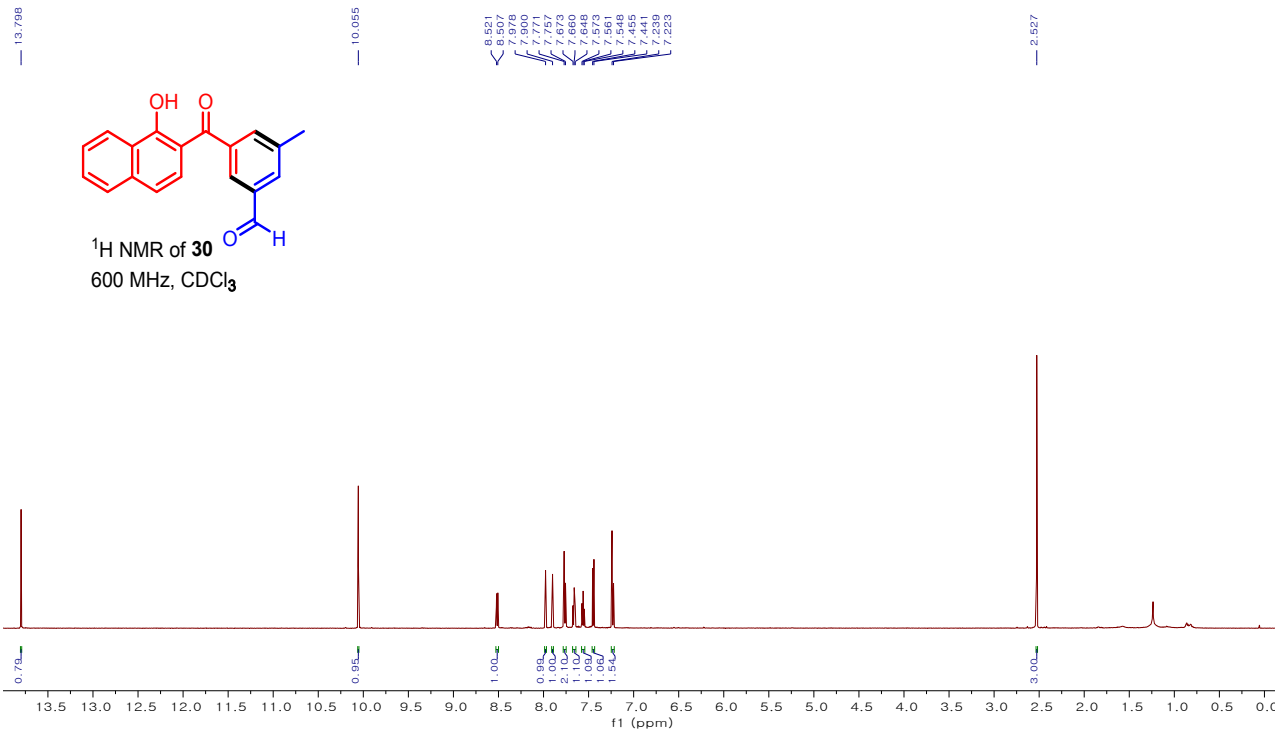
^{13}C NMR of **28**
150 MHz, $CDCl_3$



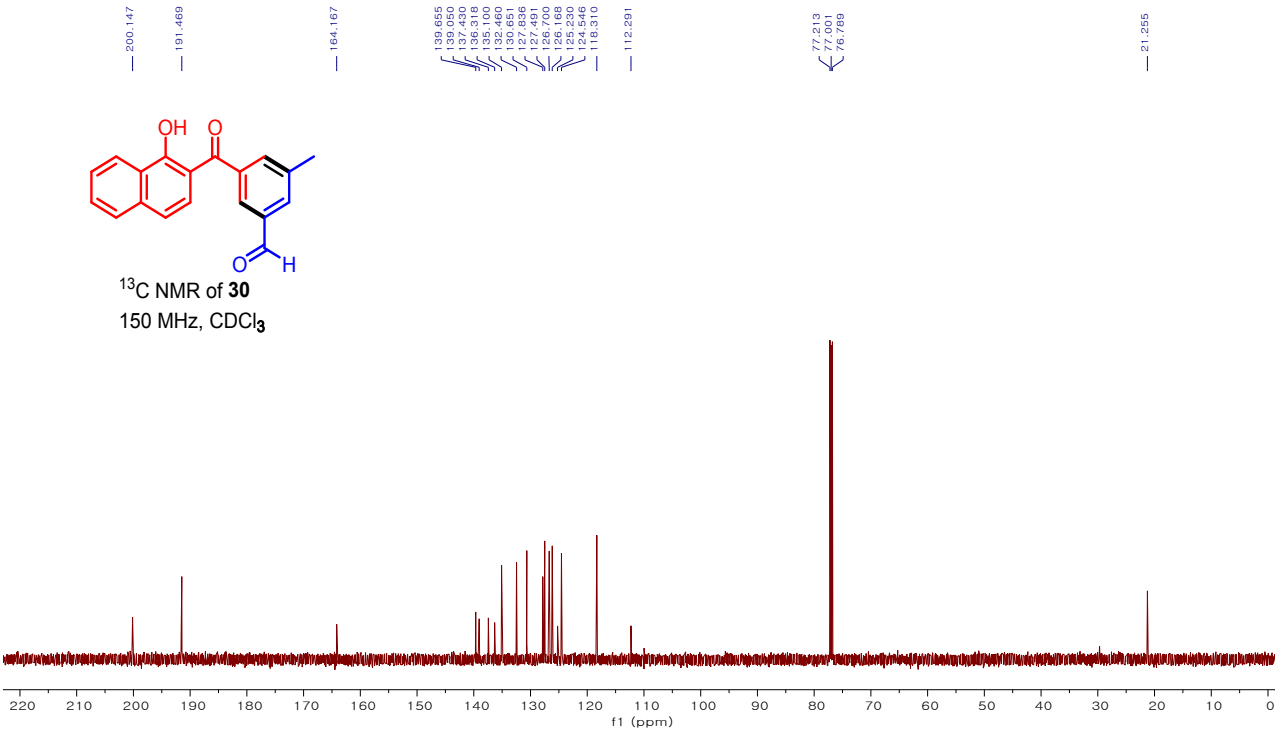
^{1}H NMR of **29**
600 MHz, $CDCl_3$



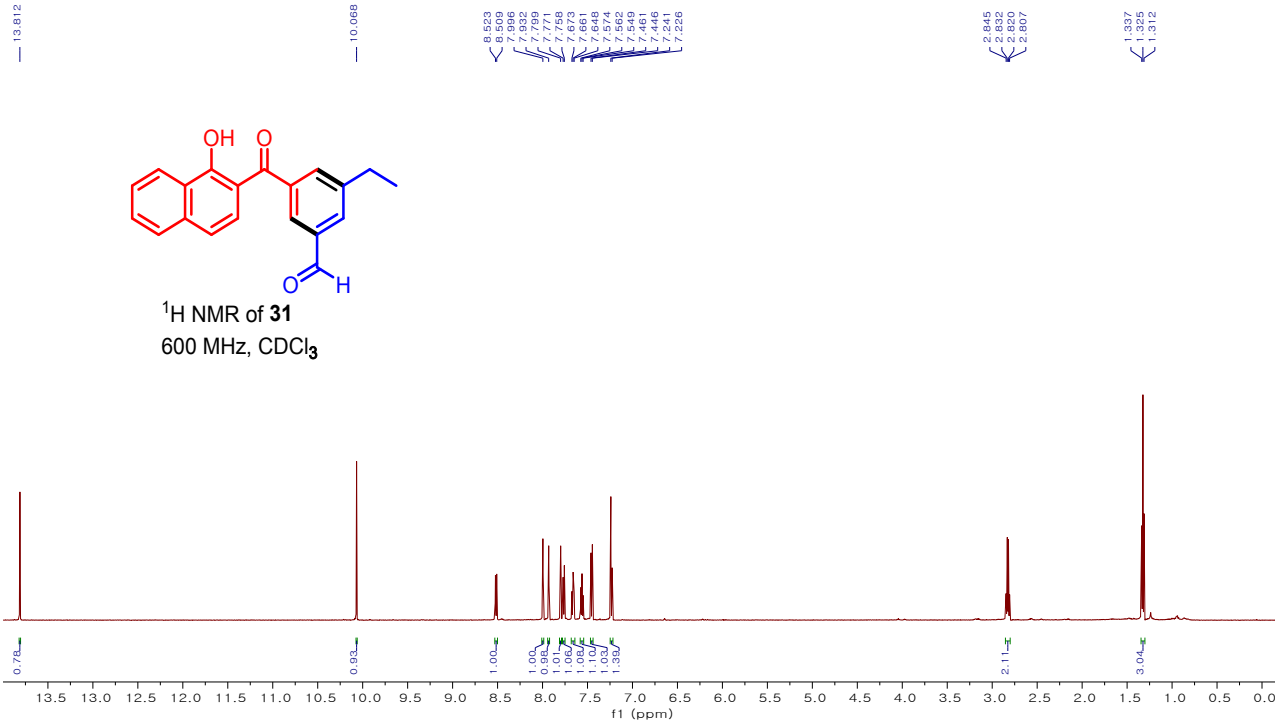
^{13}C NMR of **29**
150 MHz, $CDCl_3$



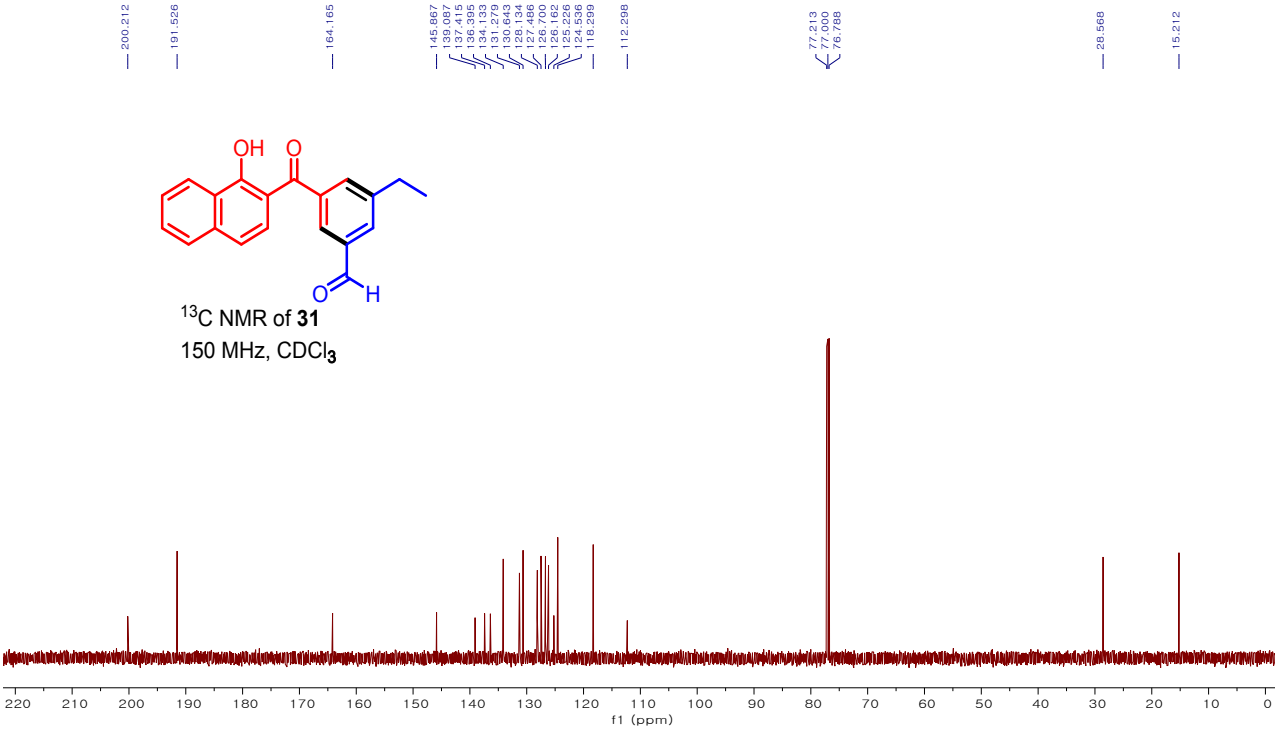
^{1}H NMR of **30**
600 MHz, $CDCl_3$



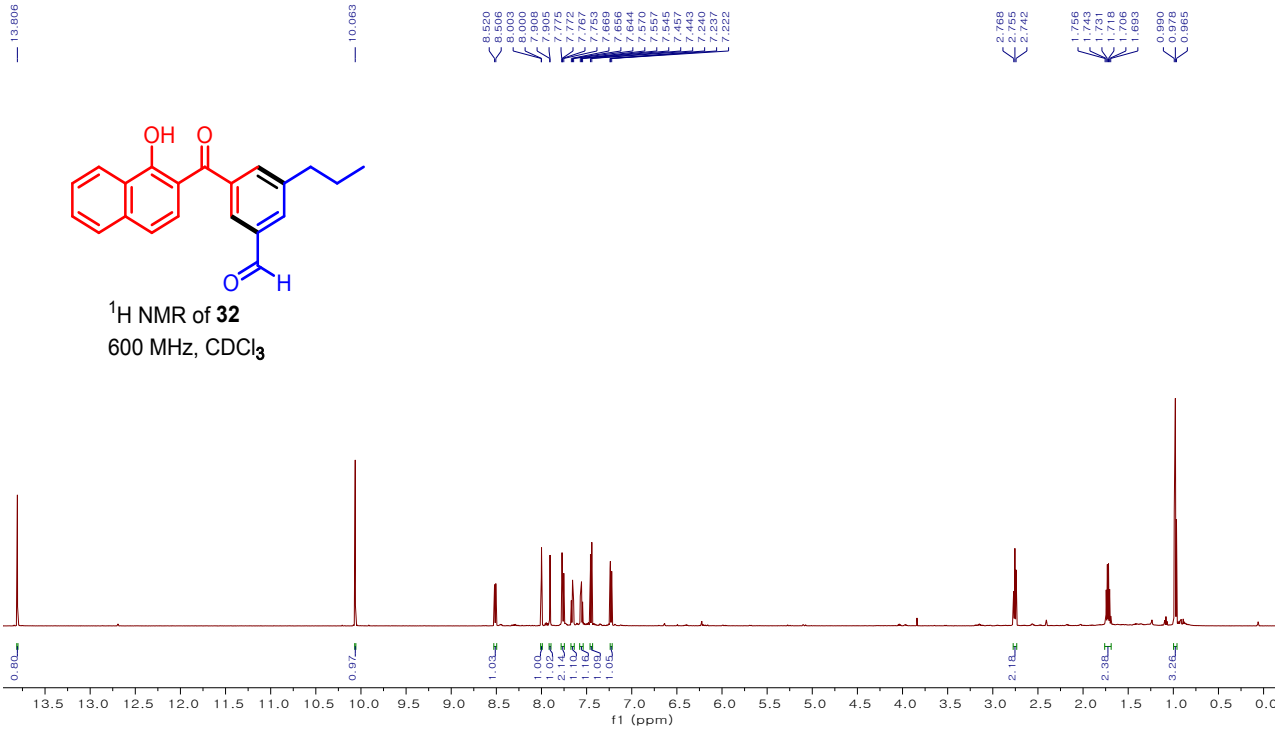
^{13}C NMR of **30**
150 MHz, $CDCl_3$



^{1}H NMR of **31**
600 MHz, $CDCl_3$

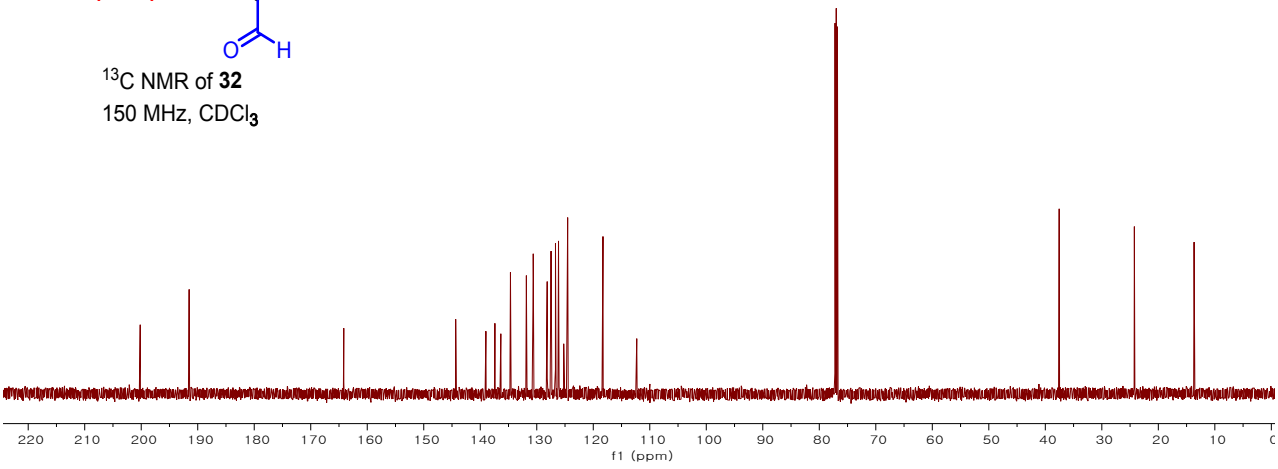


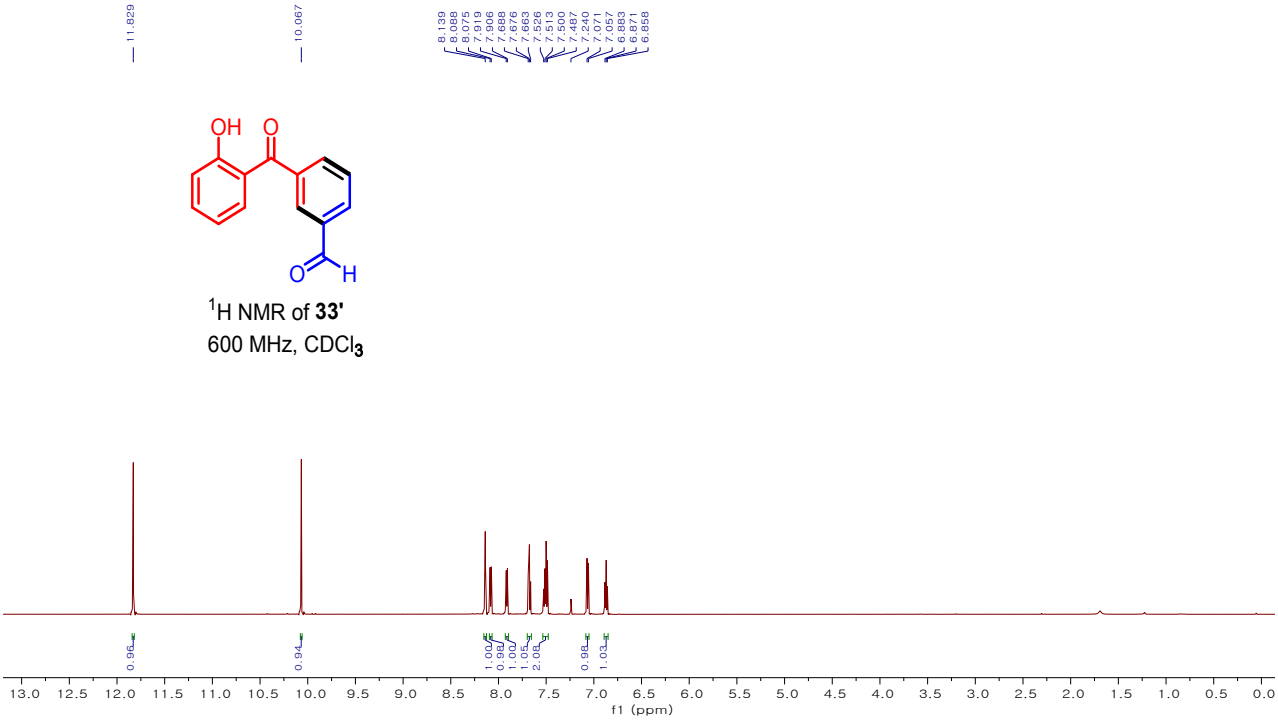
^{13}C NMR of **31**
150 MHz, $CDCl_3$



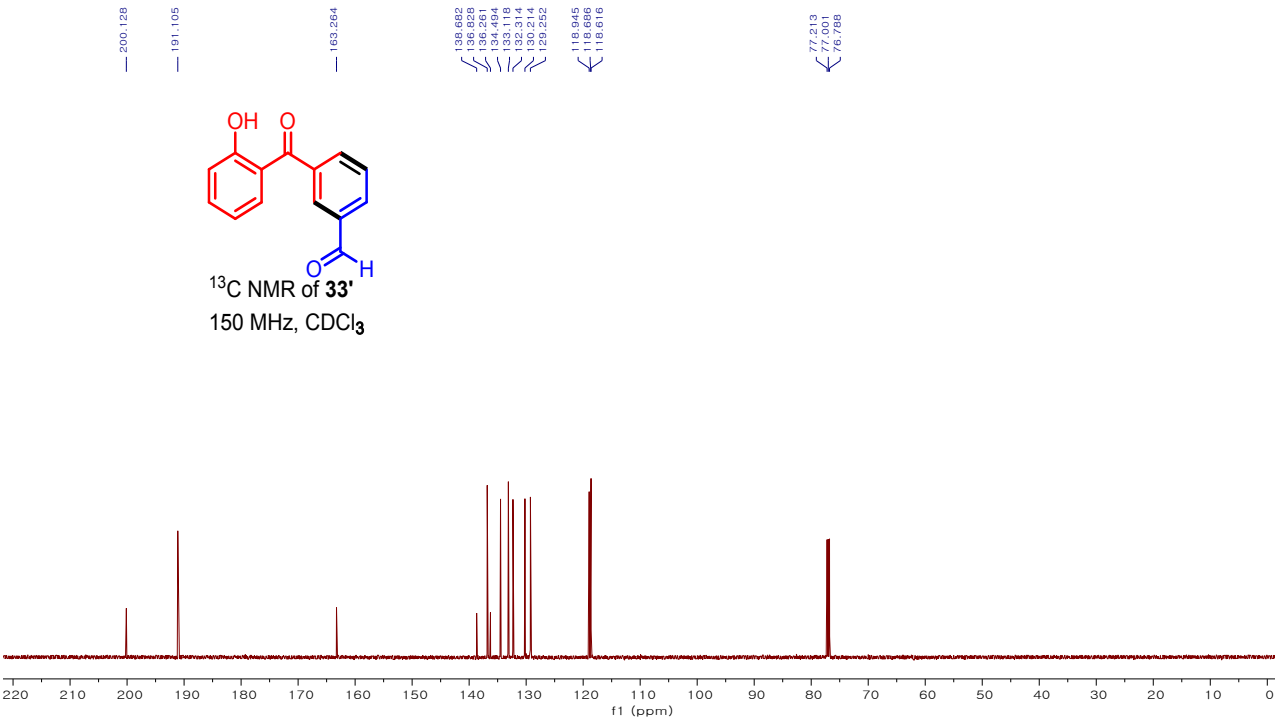
^{1}H NMR of **32**
600 MHz, $CDCl_3$

^{13}C NMR of **32**
150 MHz, $CDCl_3$

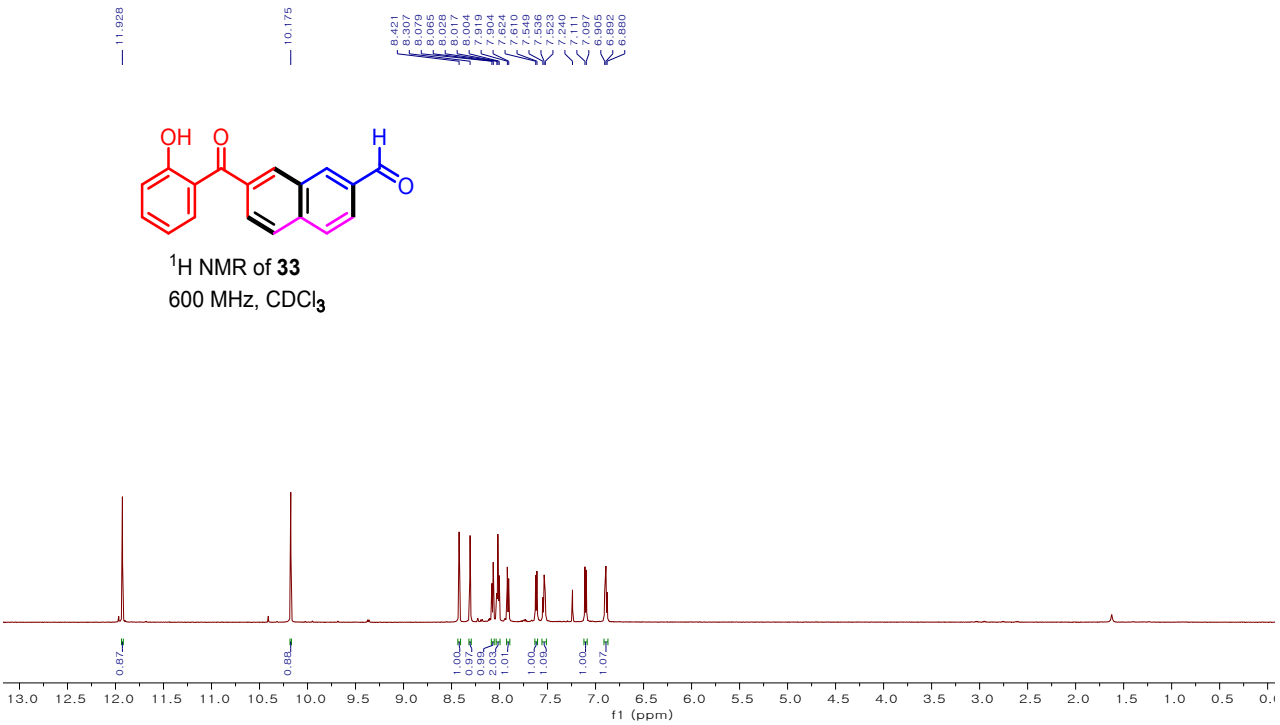




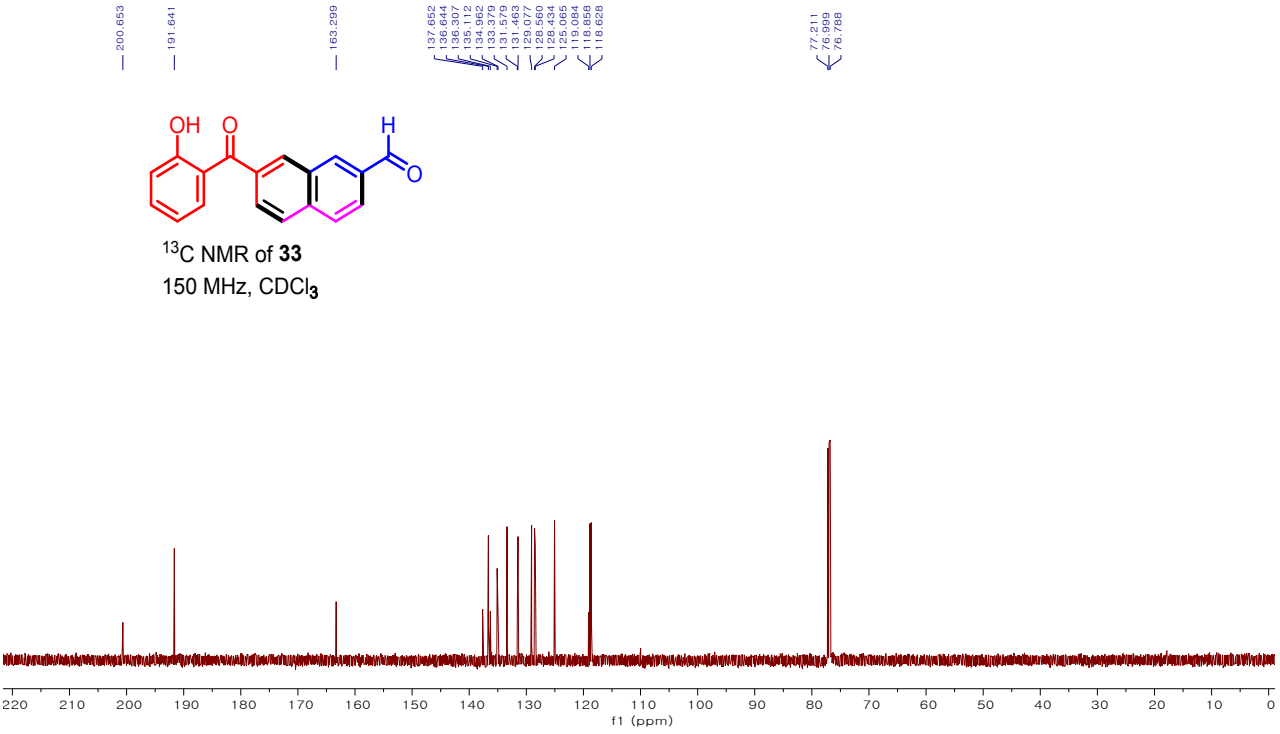
^{1}H NMR of **33'**
600 MHz, $CDCl_3$



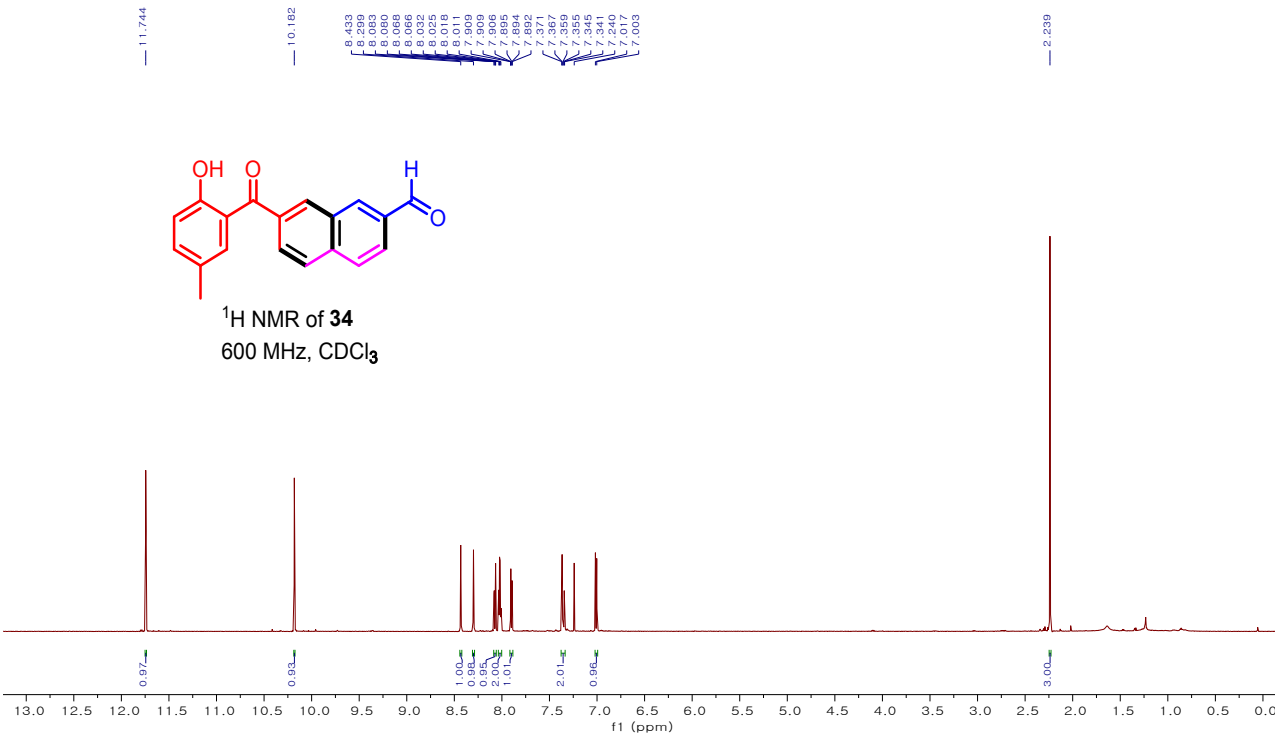
^{13}C NMR of **33'**
150 MHz, $CDCl_3$



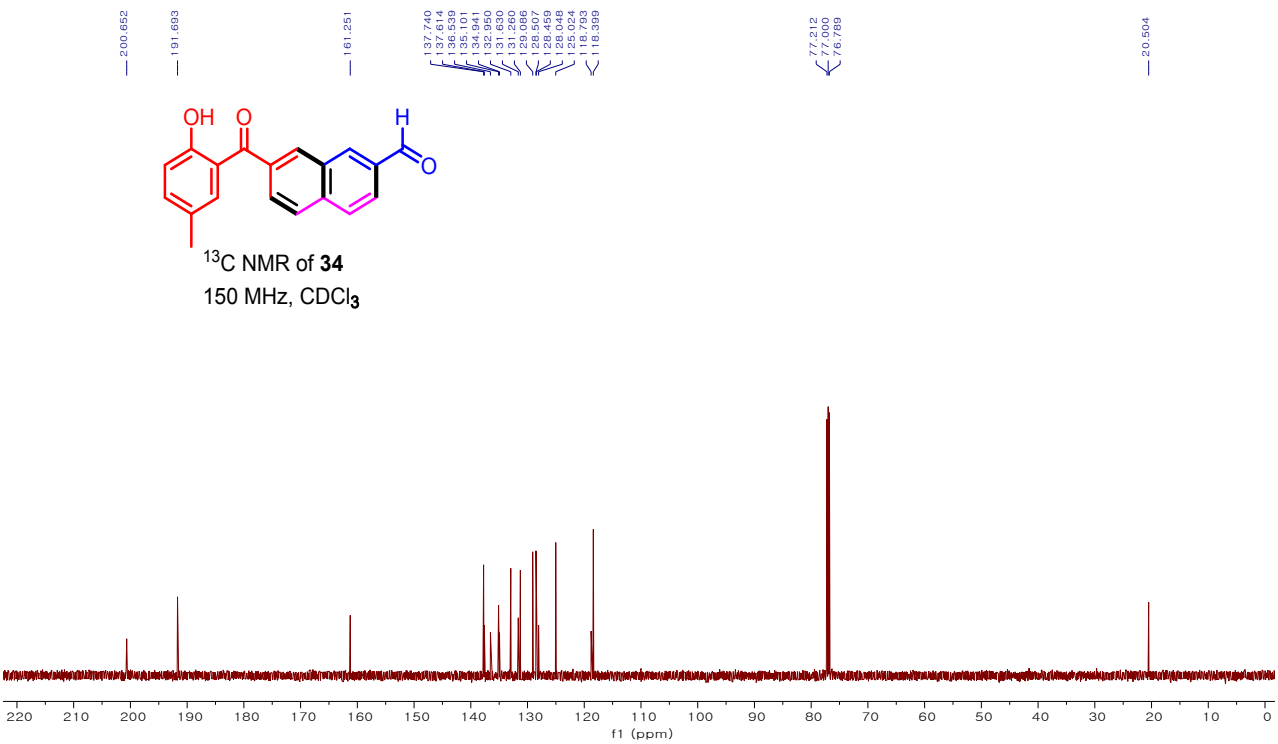
^{1}H NMR of **33**
600 MHz, $CDCl_3$



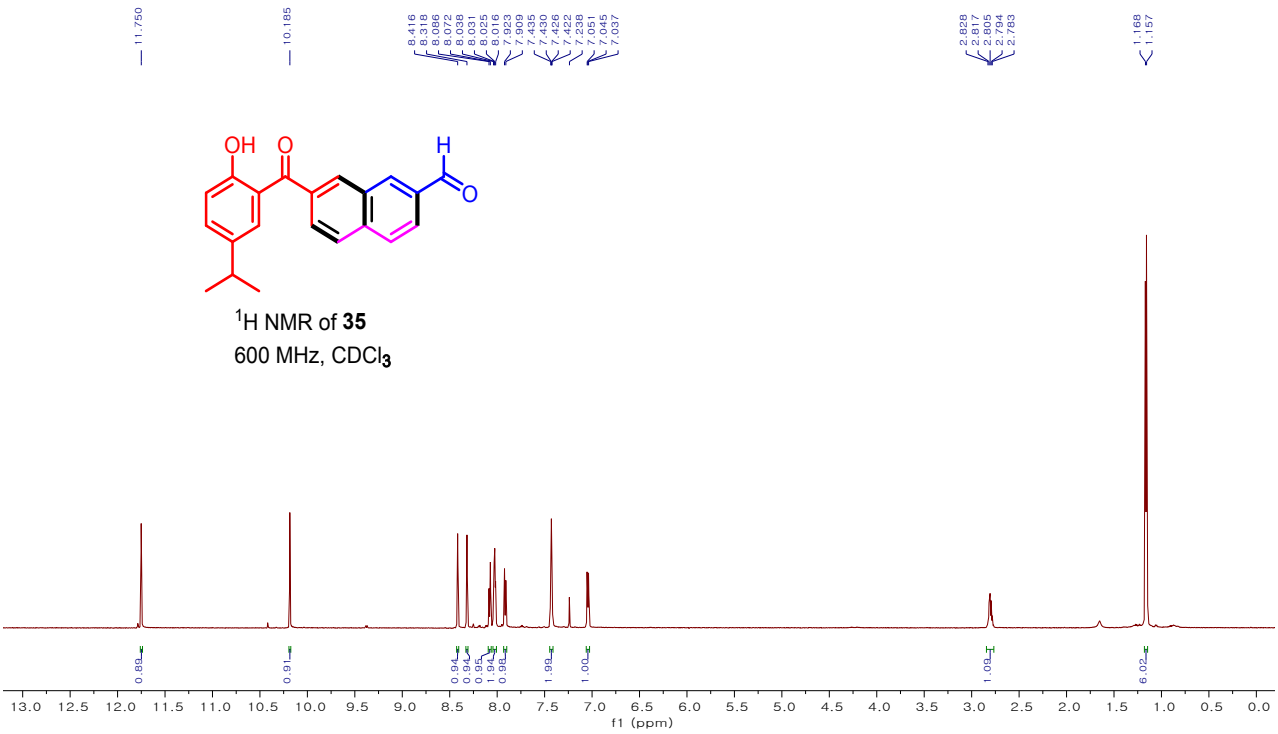
^{13}C NMR of **33**
150 MHz, $CDCl_3$



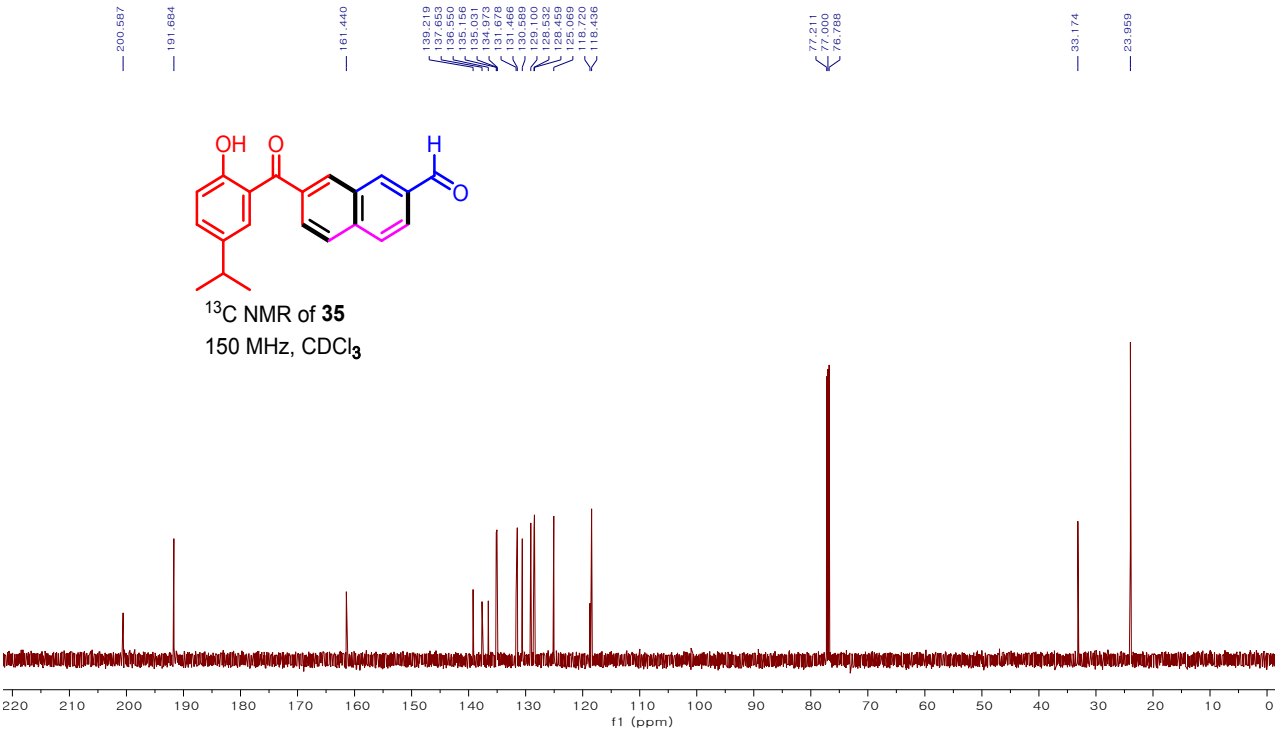
^{1}H NMR of **34**
600 MHz, $CDCl_3$



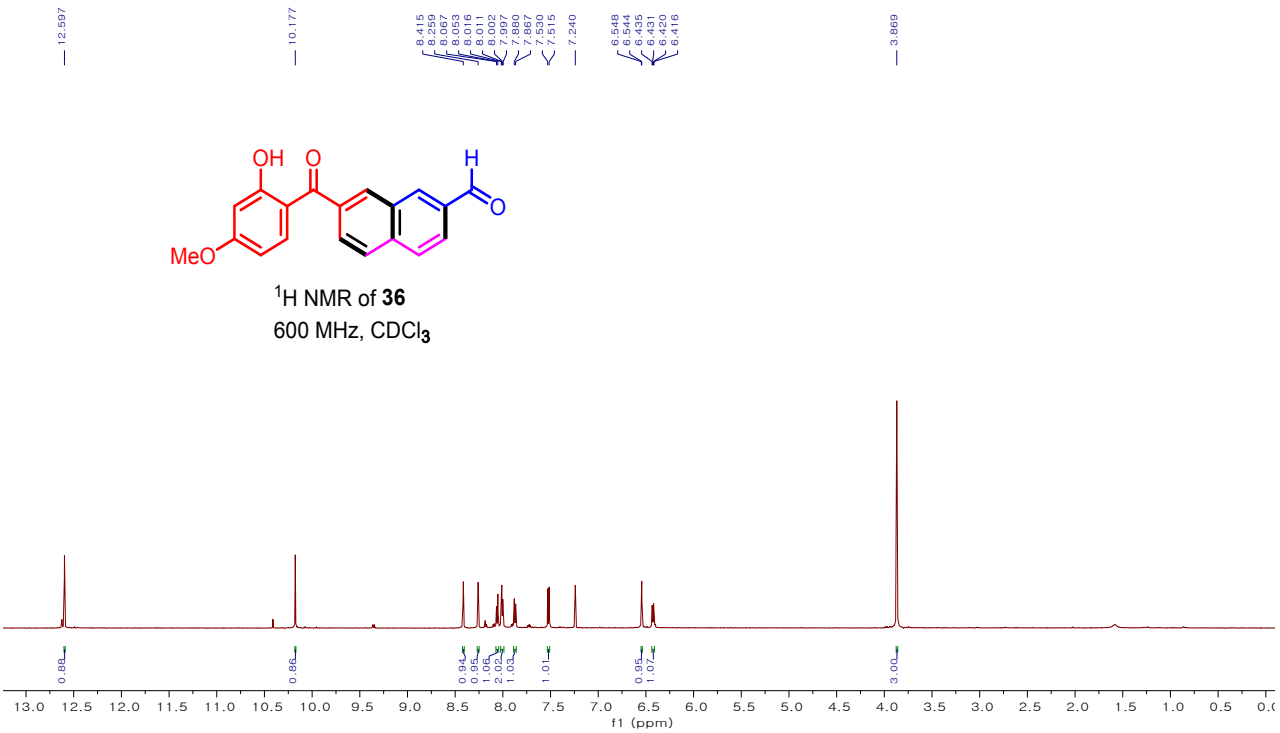
^{13}C NMR of **34**
150 MHz, $CDCl_3$



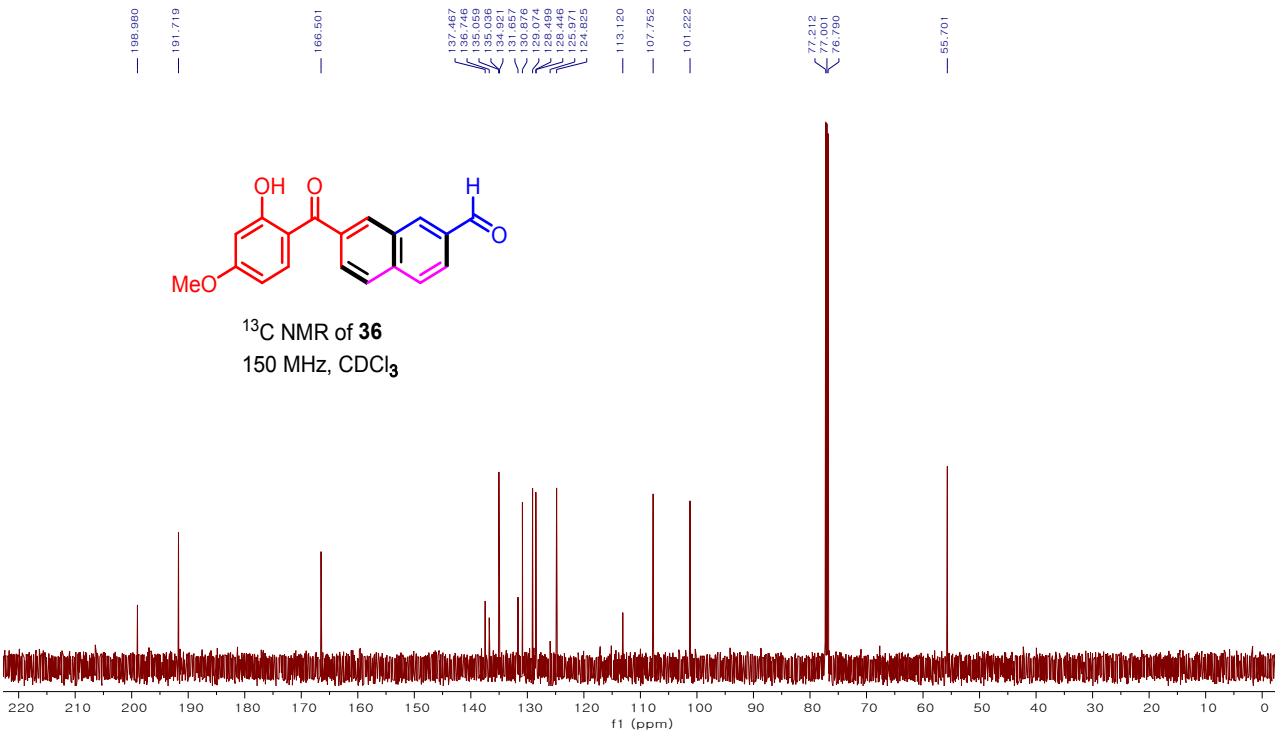
^{1}H NMR of **35**
600 MHz, $CDCl_3$



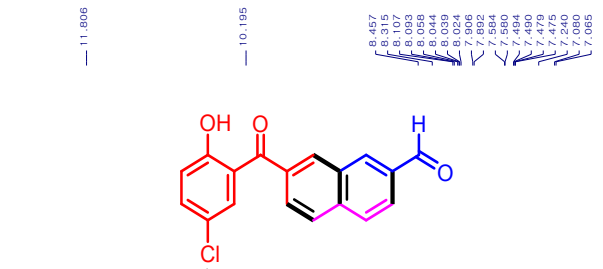
^{13}C NMR of **35**
150 MHz, $CDCl_3$



^{1}H NMR of **36**
600 MHz, $CDCl_3$

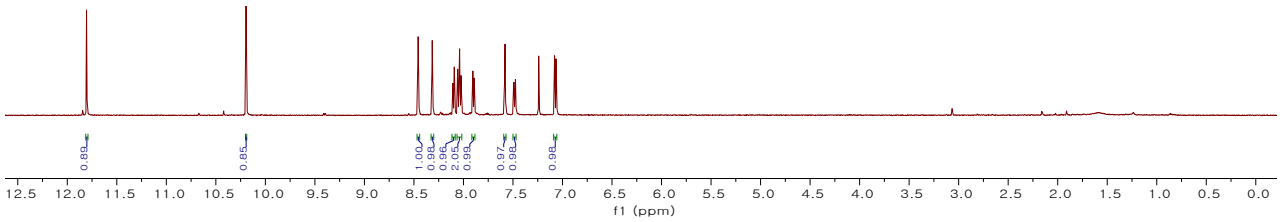


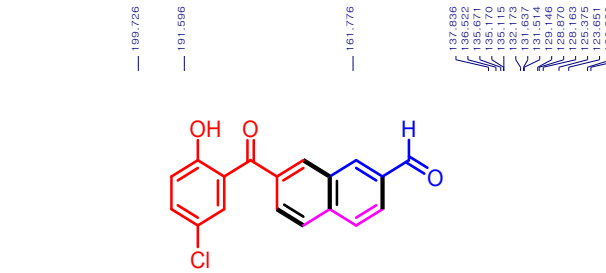
^{13}C NMR of **36**
150 MHz, $CDCl_3$



^{1}H NMR of **37**

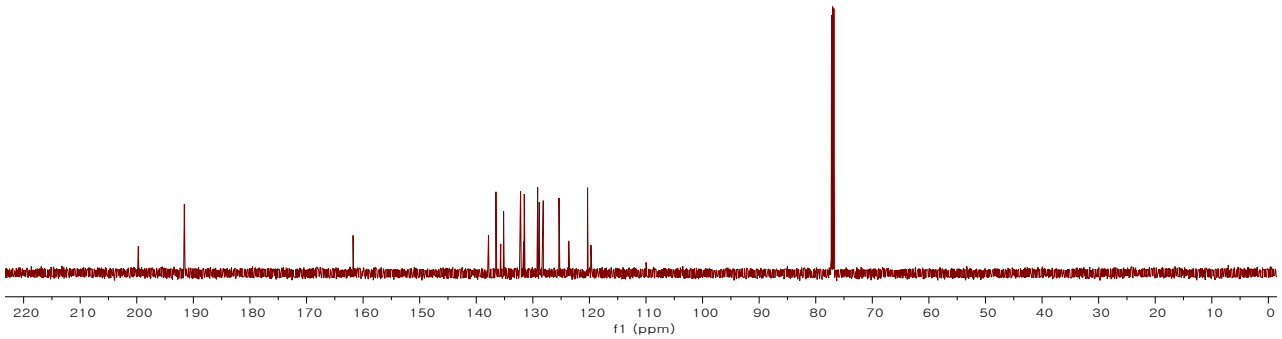
600 MHz, $CDCl_3$

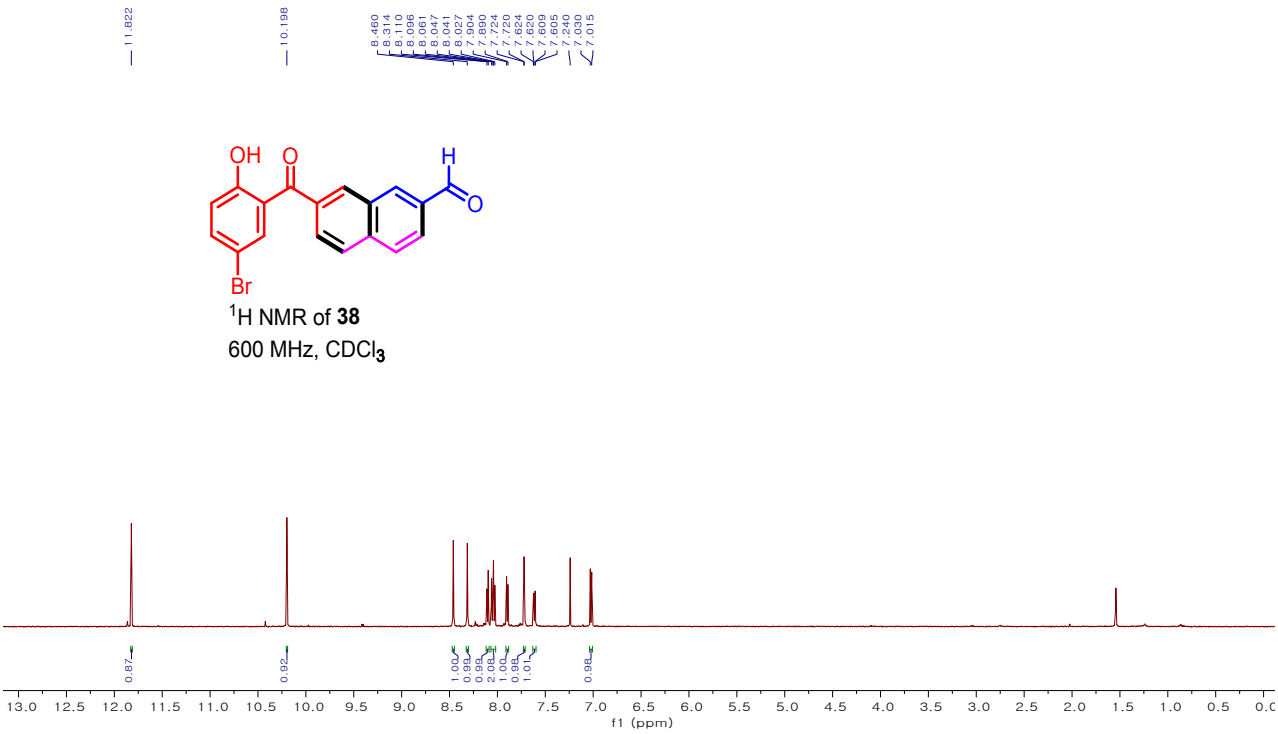




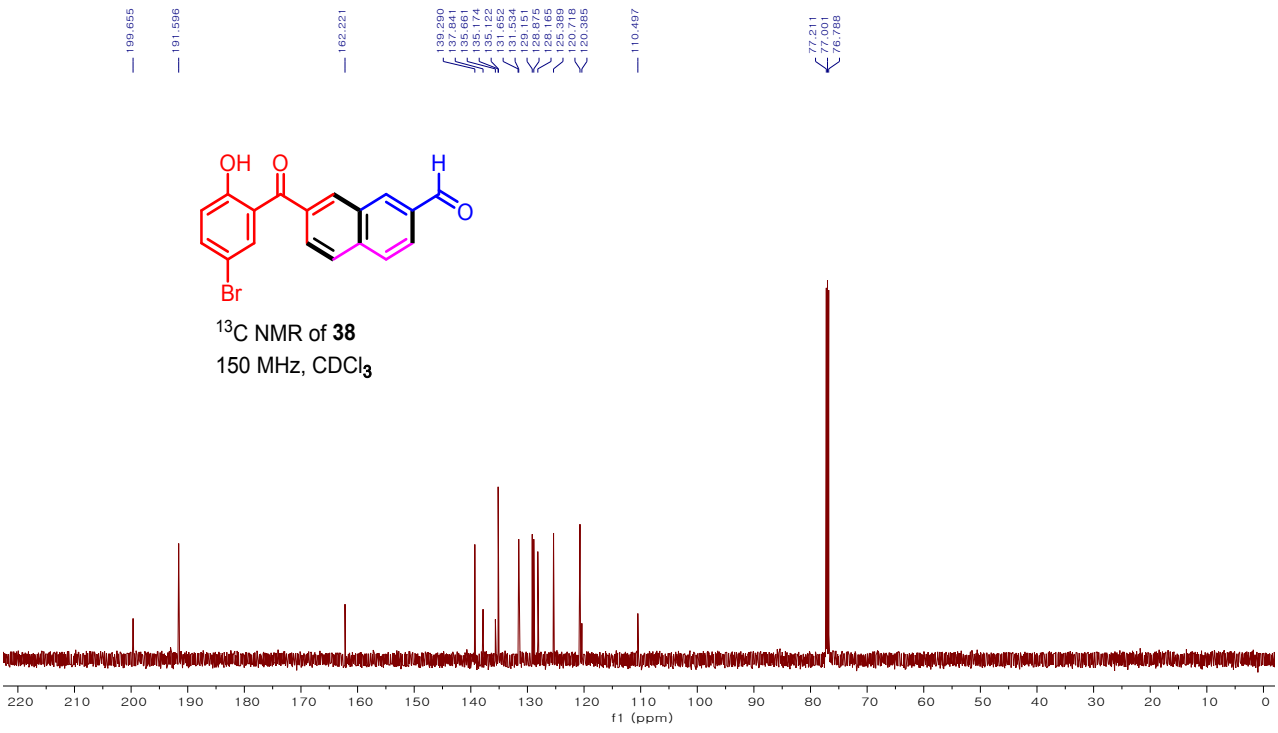
^{13}C NMR of **37**

150 MHz, $CDCl_3$

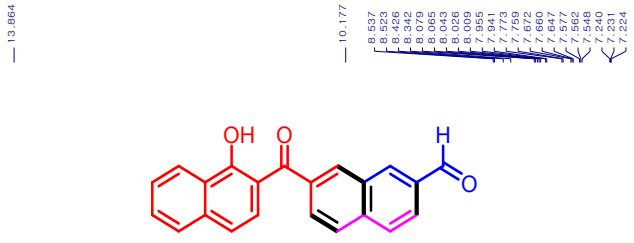




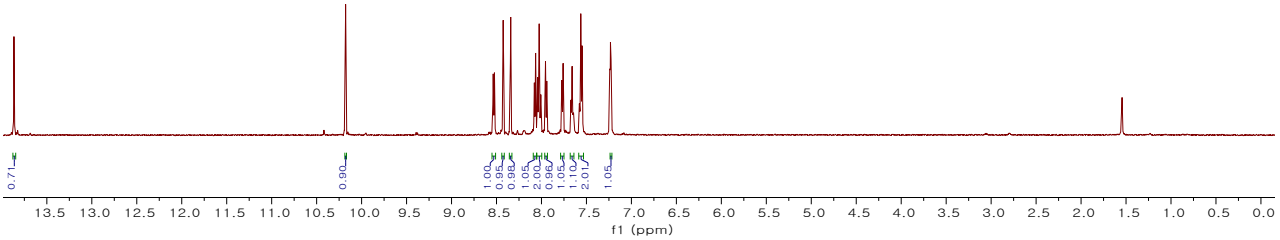
^{1}H NMR of **38**
600 MHz, $CDCl_3$

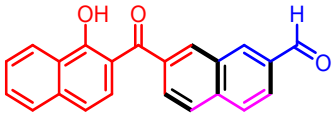


^{13}C NMR of **38**
150 MHz, $CDCl_3$

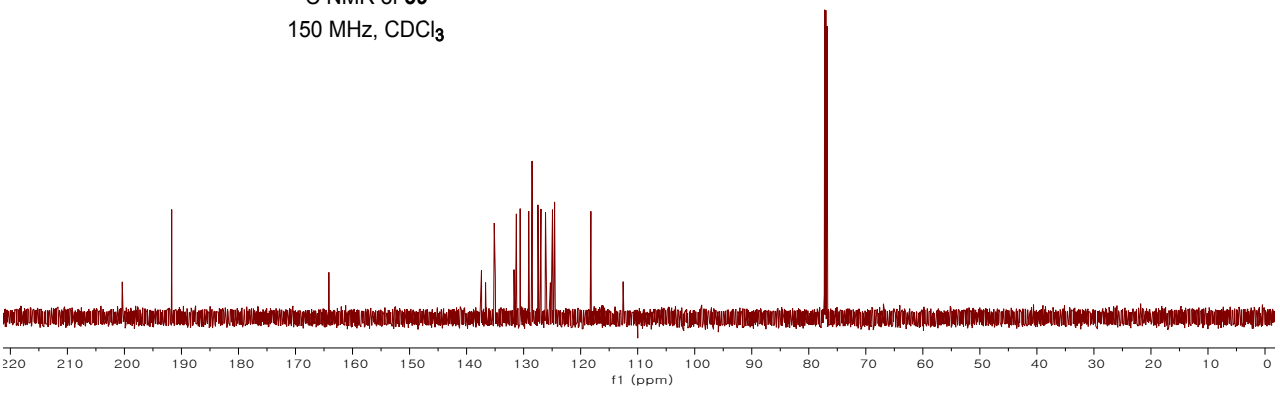


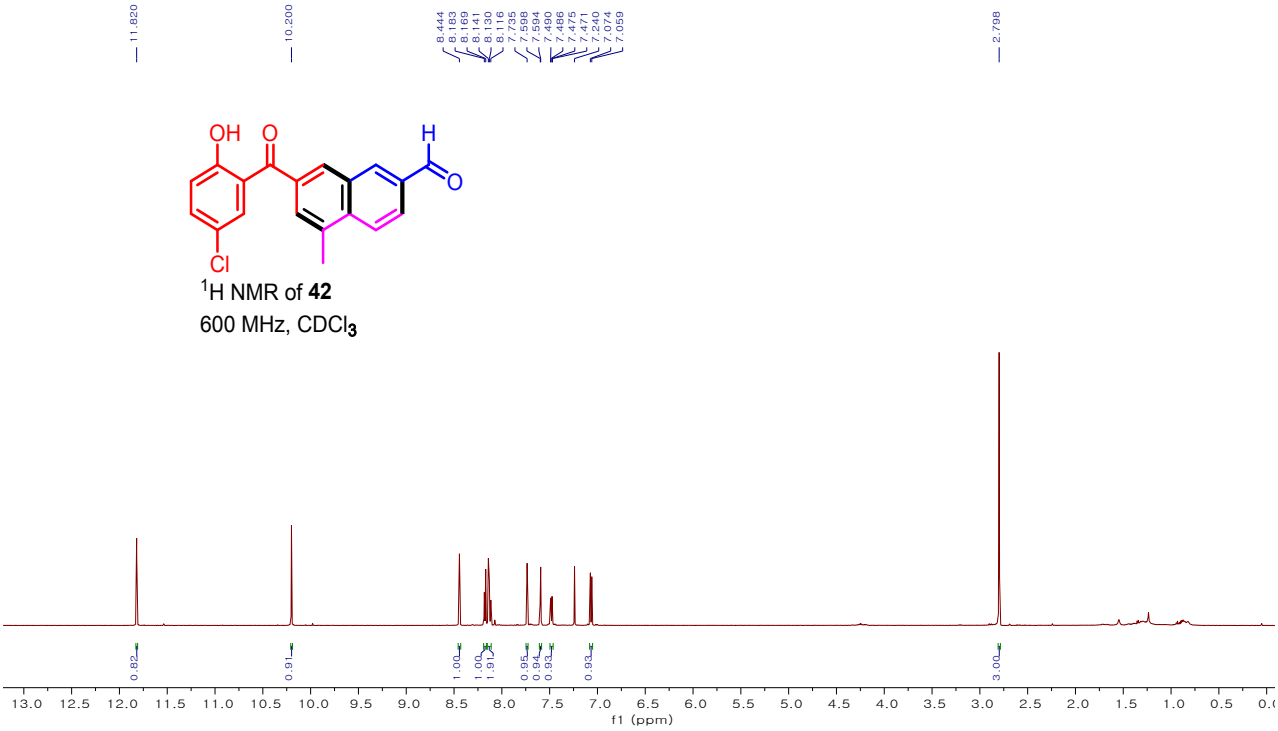
^{1}H NMR of **39**
600 MHz, $CDCl_3$



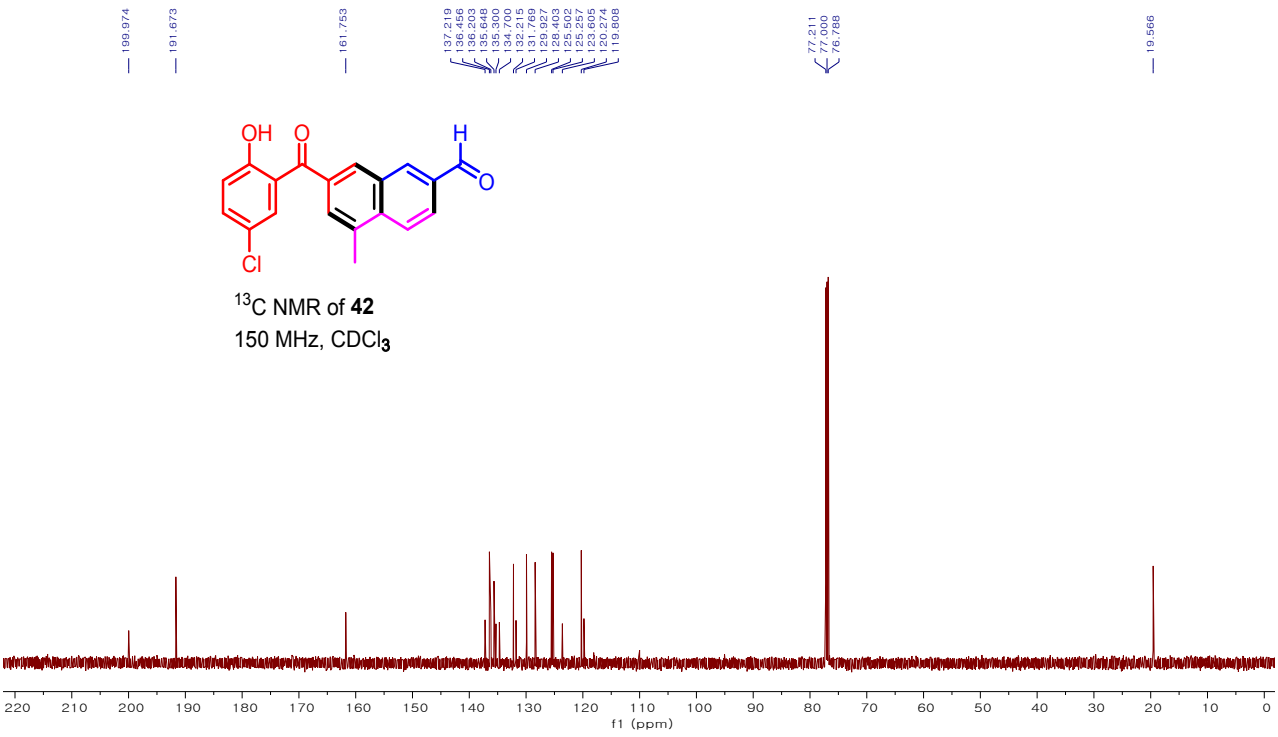


^{13}C NMR of **39**
150 MHz, $CDCl_3$

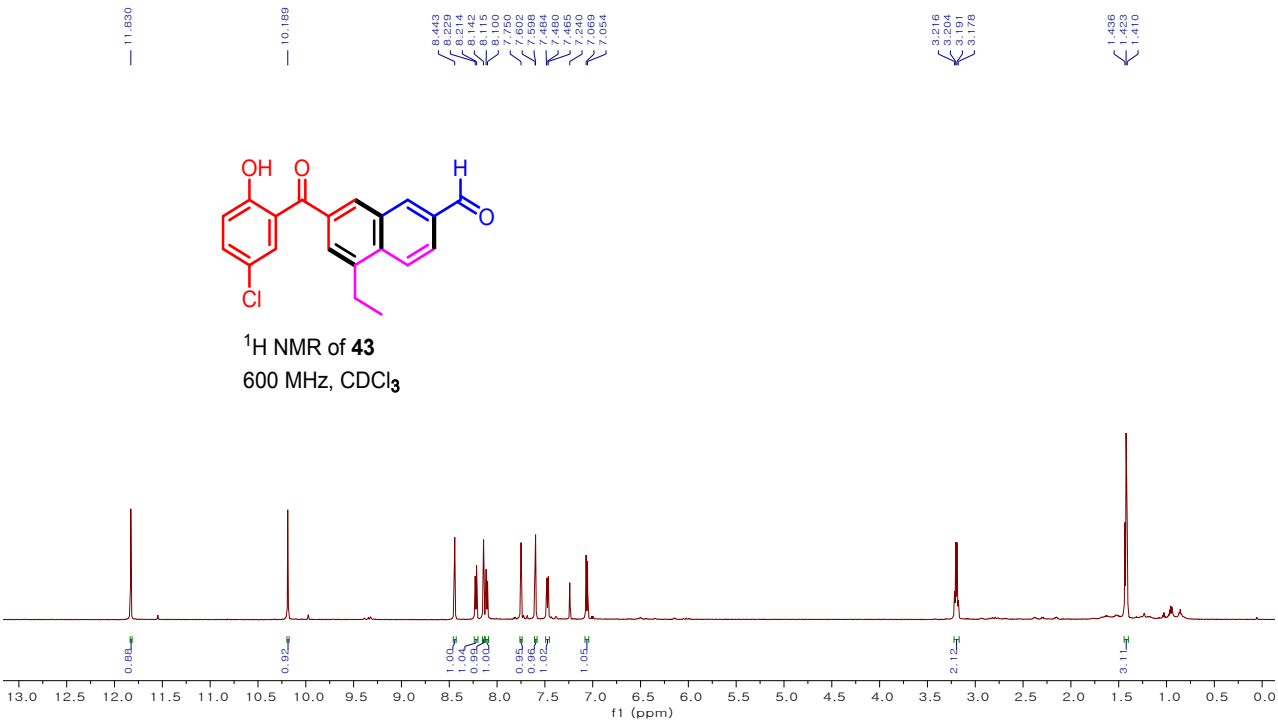




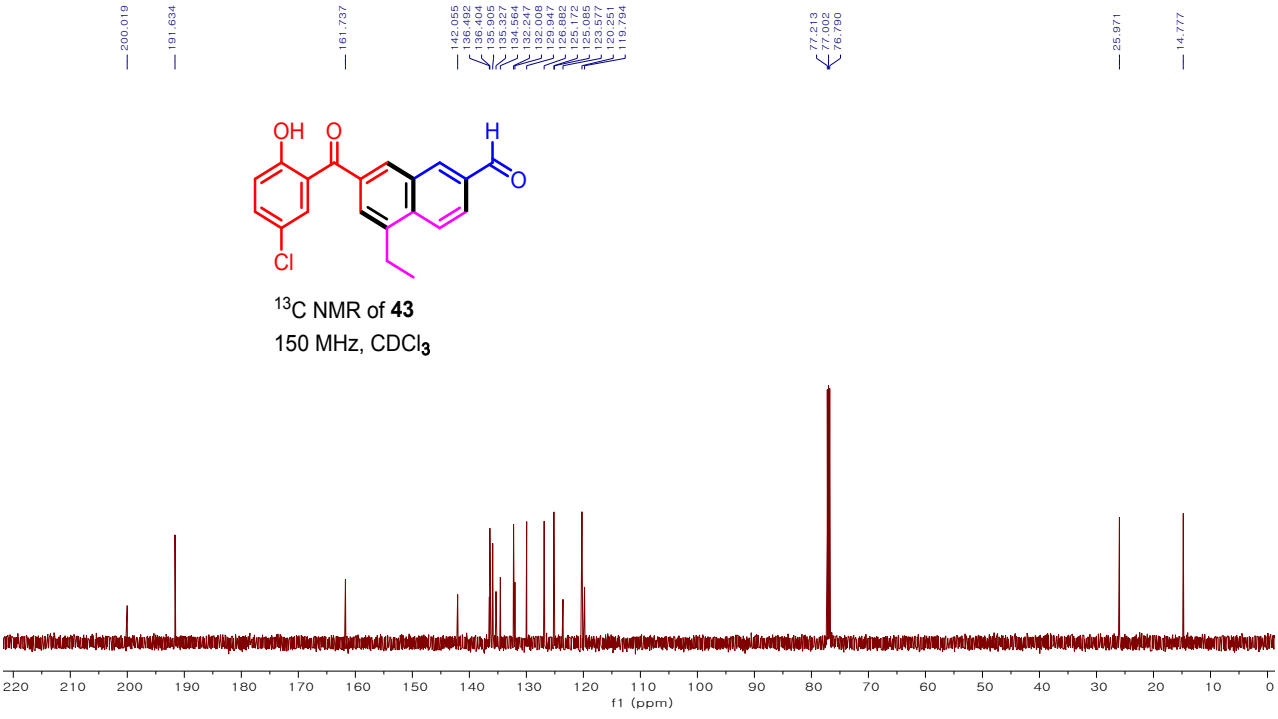
^{1}H NMR of **42**
600 MHz, $CDCl_3$



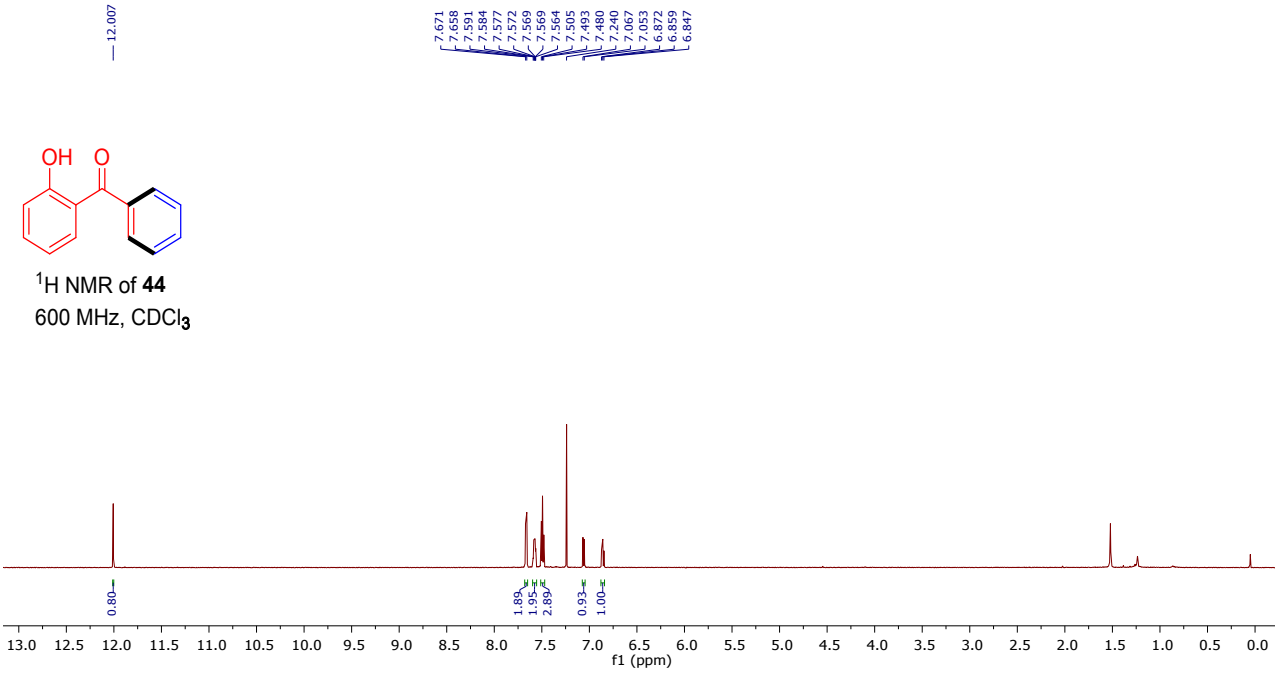
^{13}C NMR of **42**
150 MHz, $CDCl_3$



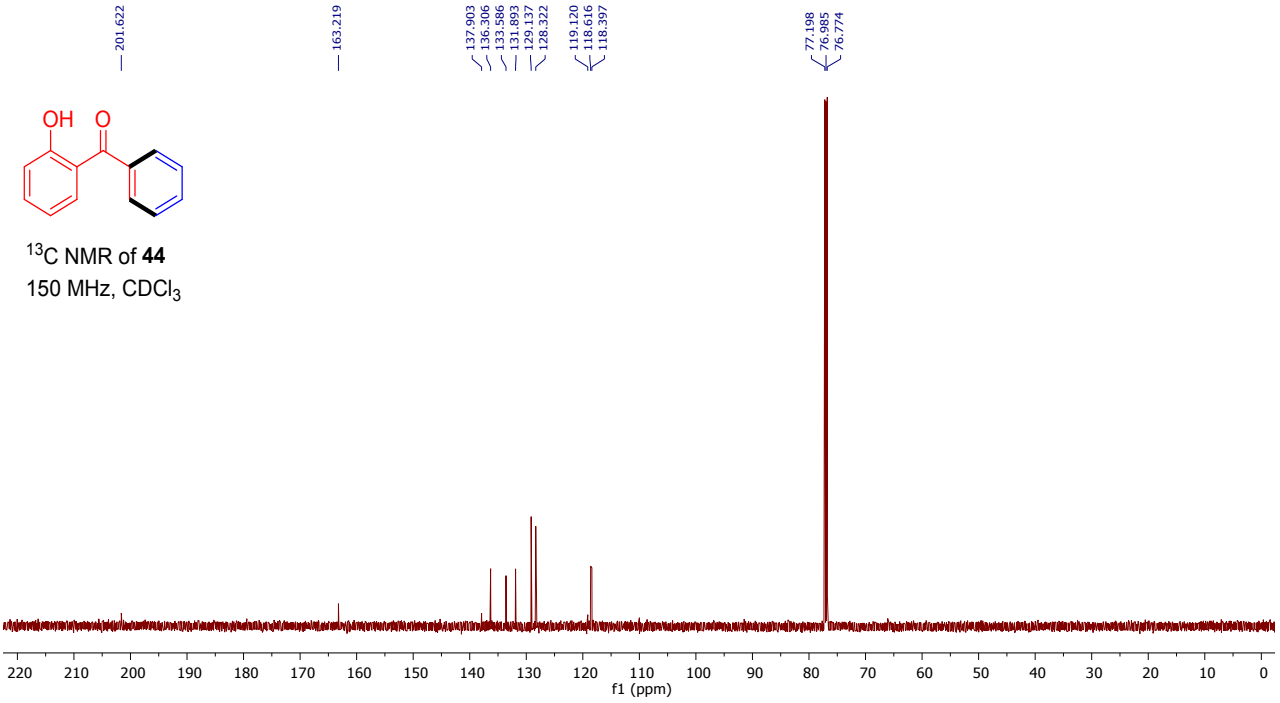
^{1}H NMR of **43**
600 MHz, $CDCl_3$



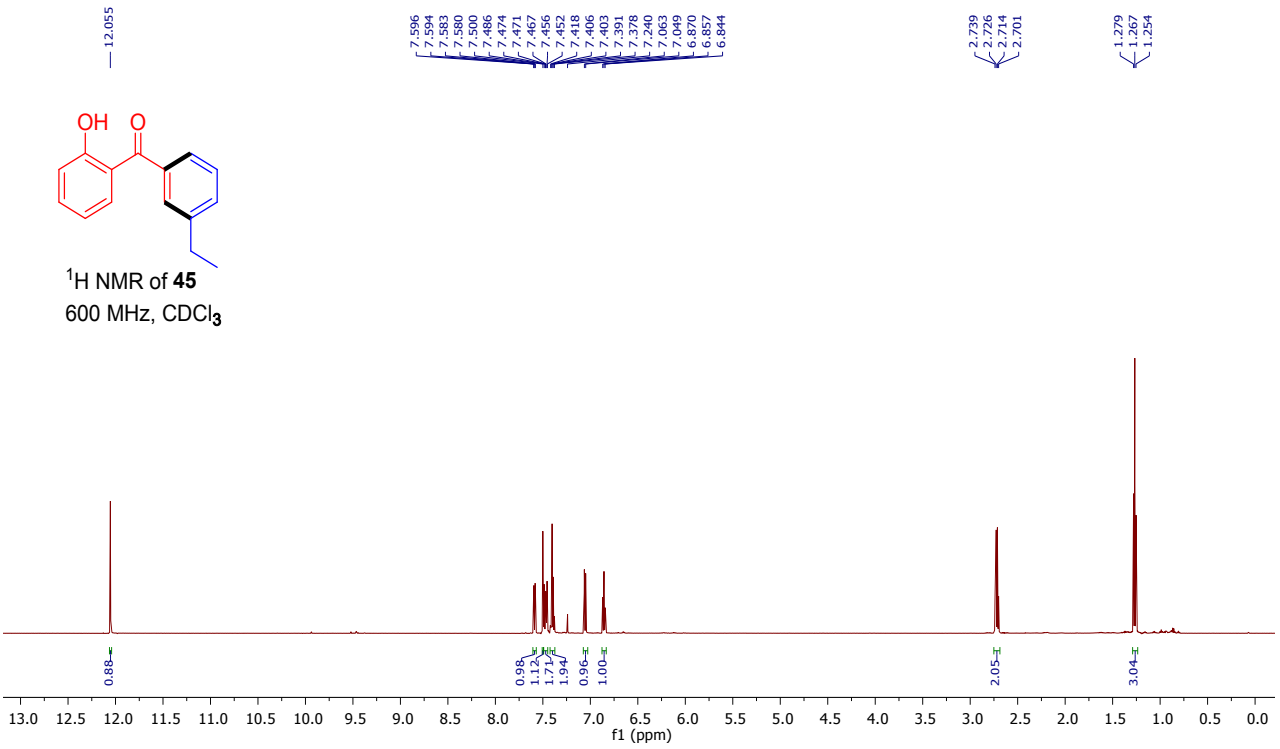
^{13}C NMR of **43**
150 MHz, $CDCl_3$



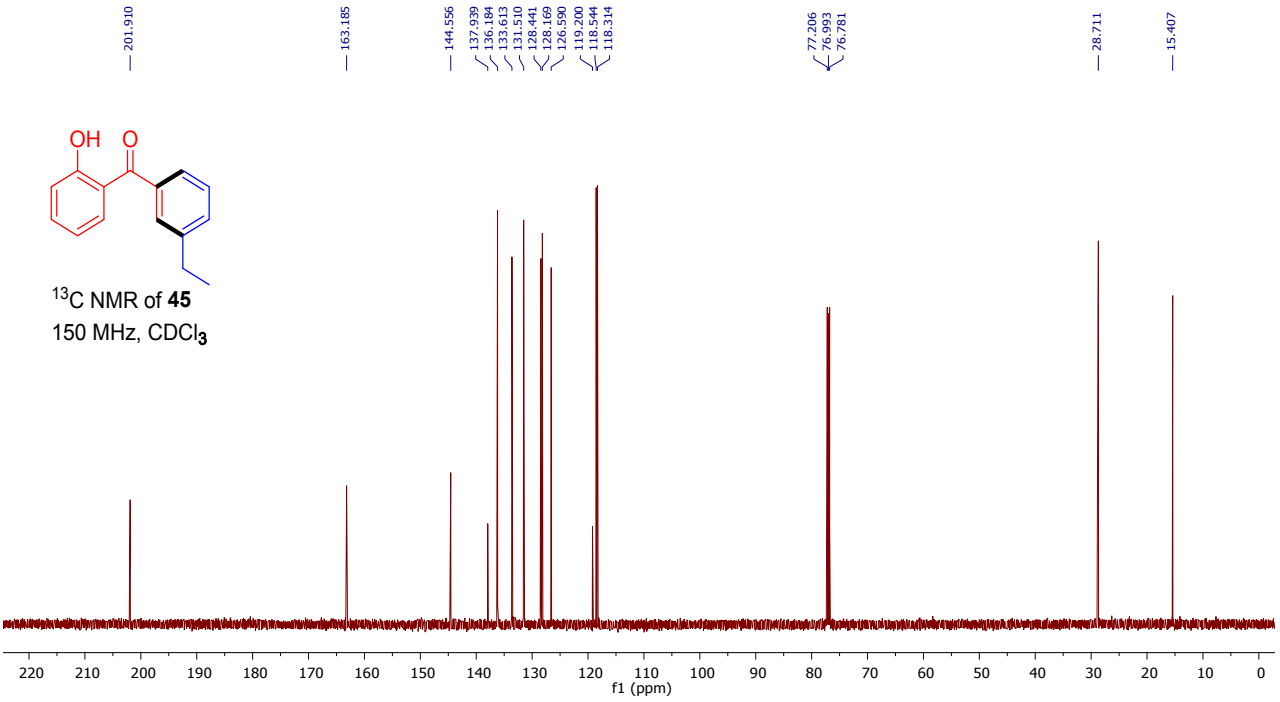
^{1}H NMR of **44**
600 MHz, $CDCl_3$



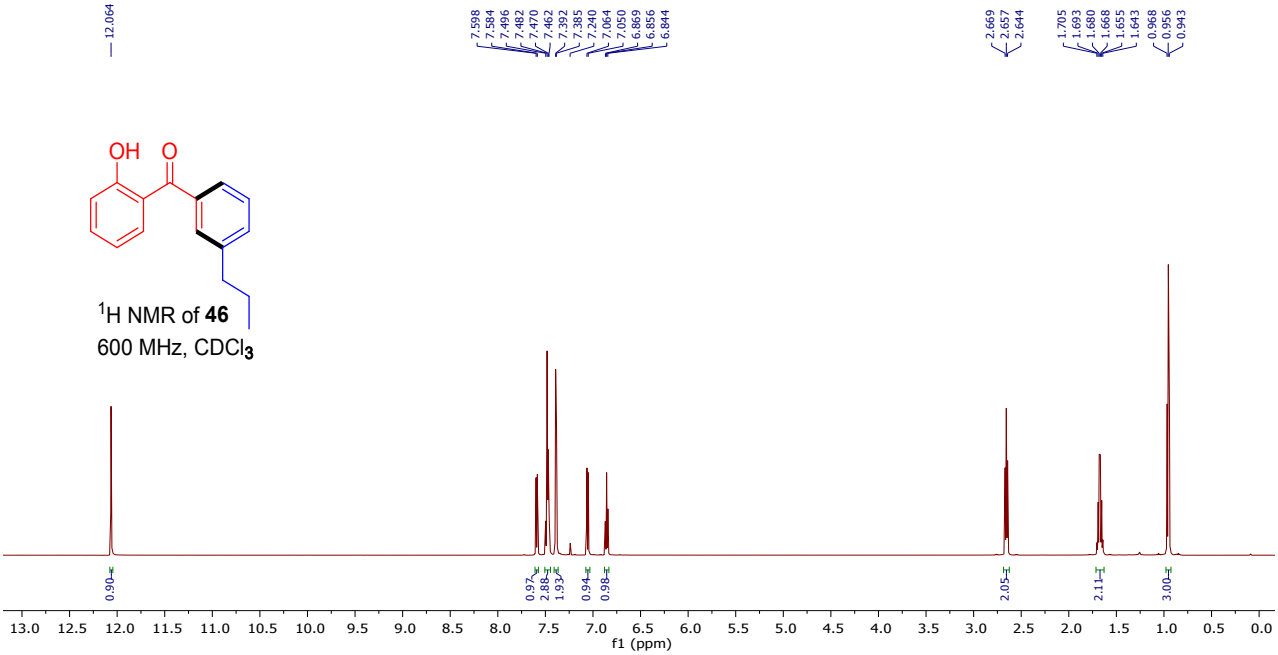
^{13}C NMR of **44**
150 MHz, $CDCl_3$



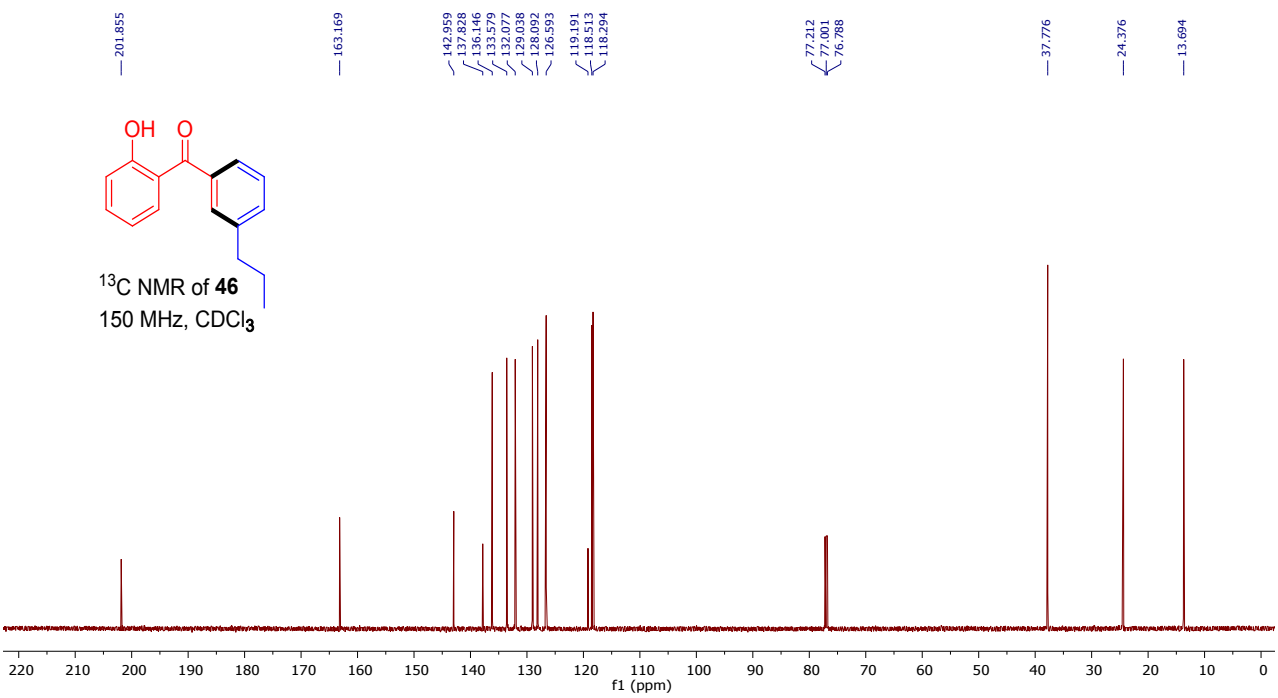
^{1}H NMR of **45**
600 MHz, $CDCl_3$



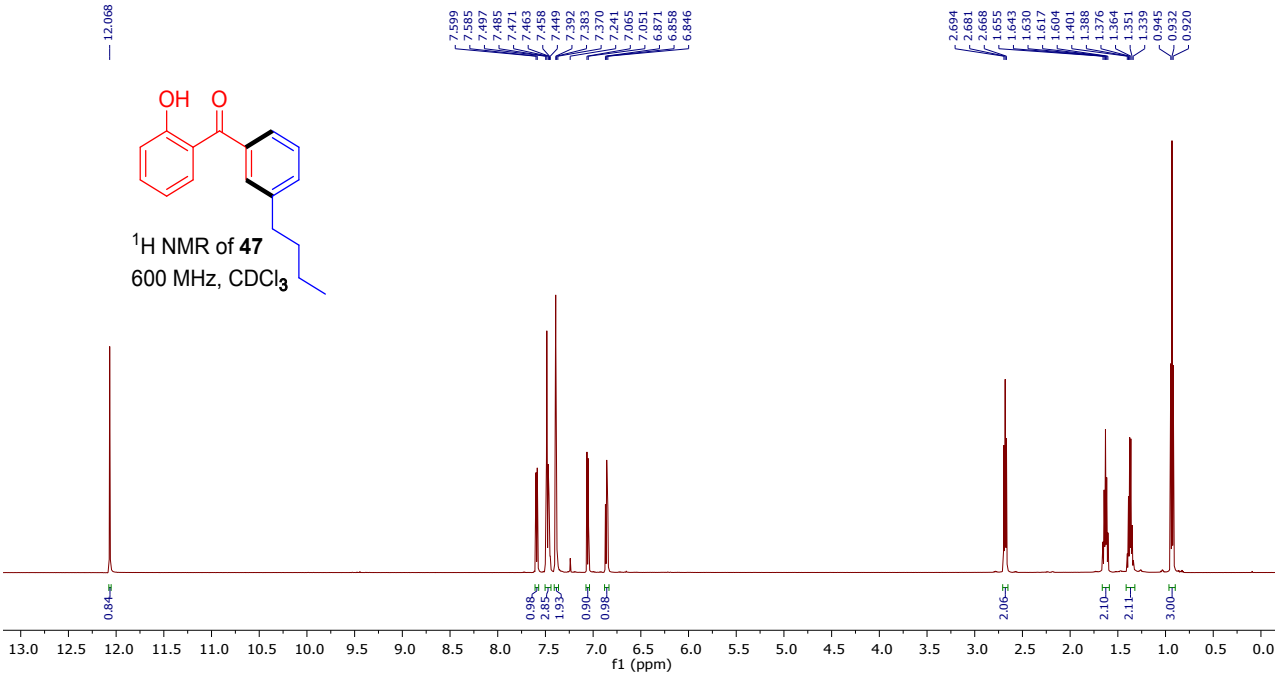
^{13}C NMR of **45**
150 MHz, $CDCl_3$

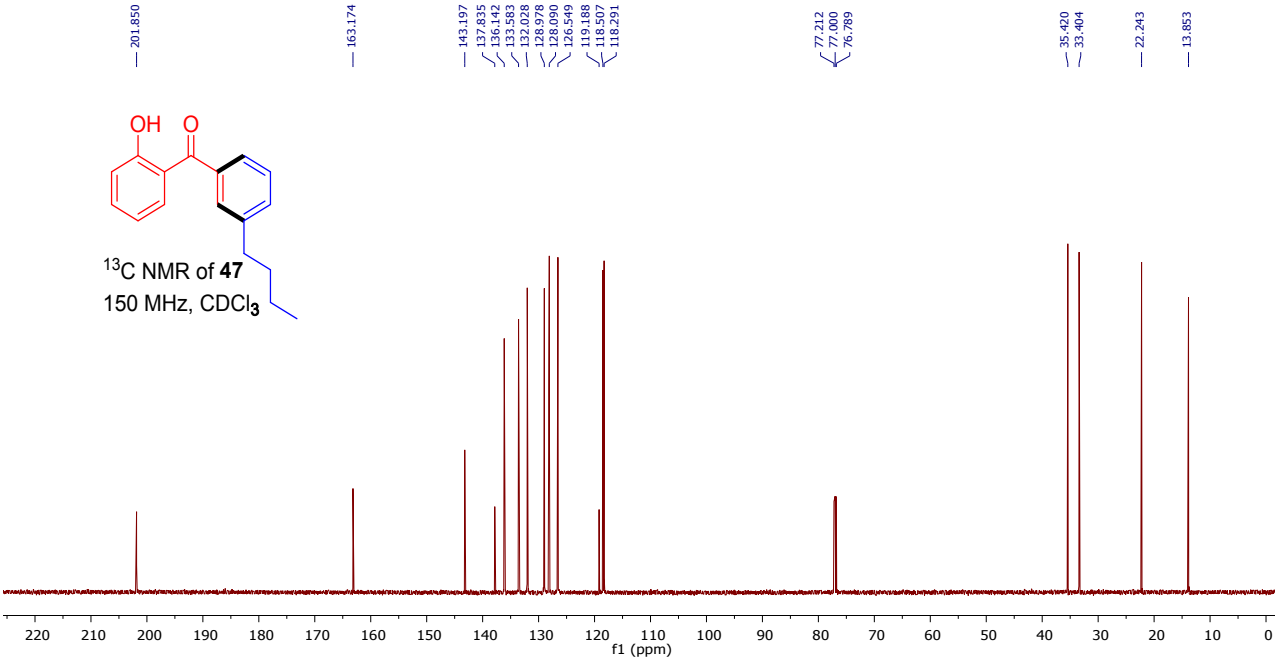


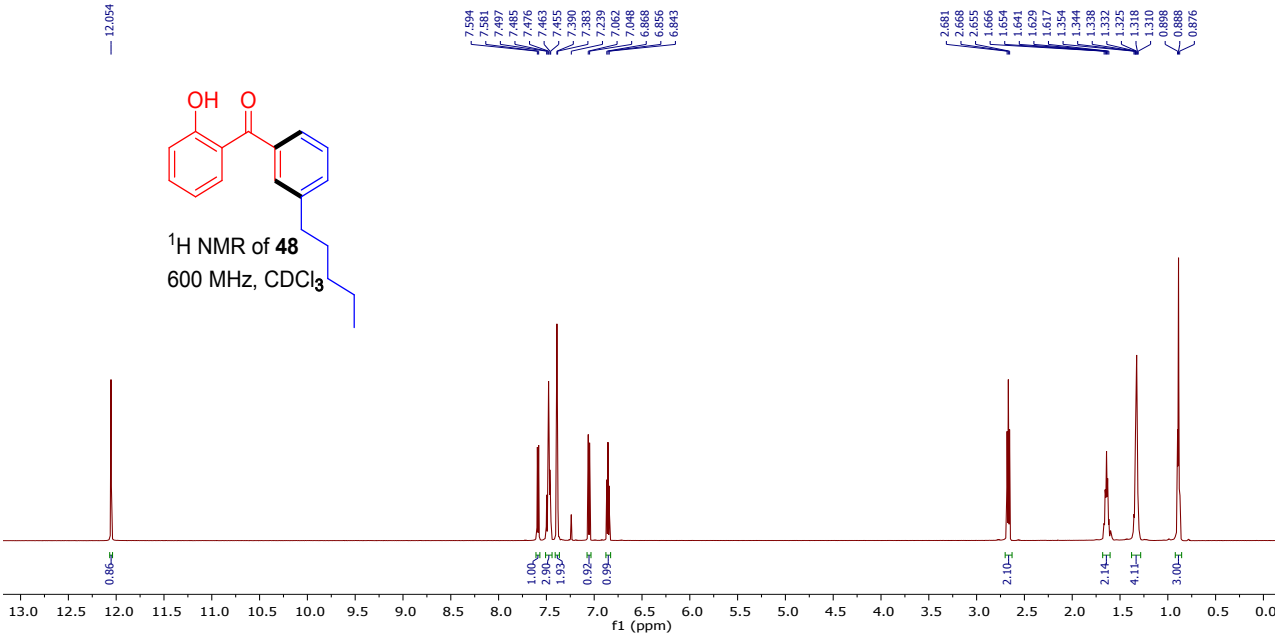
^{1}H NMR of **46**
600 MHz, $CDCl_3$

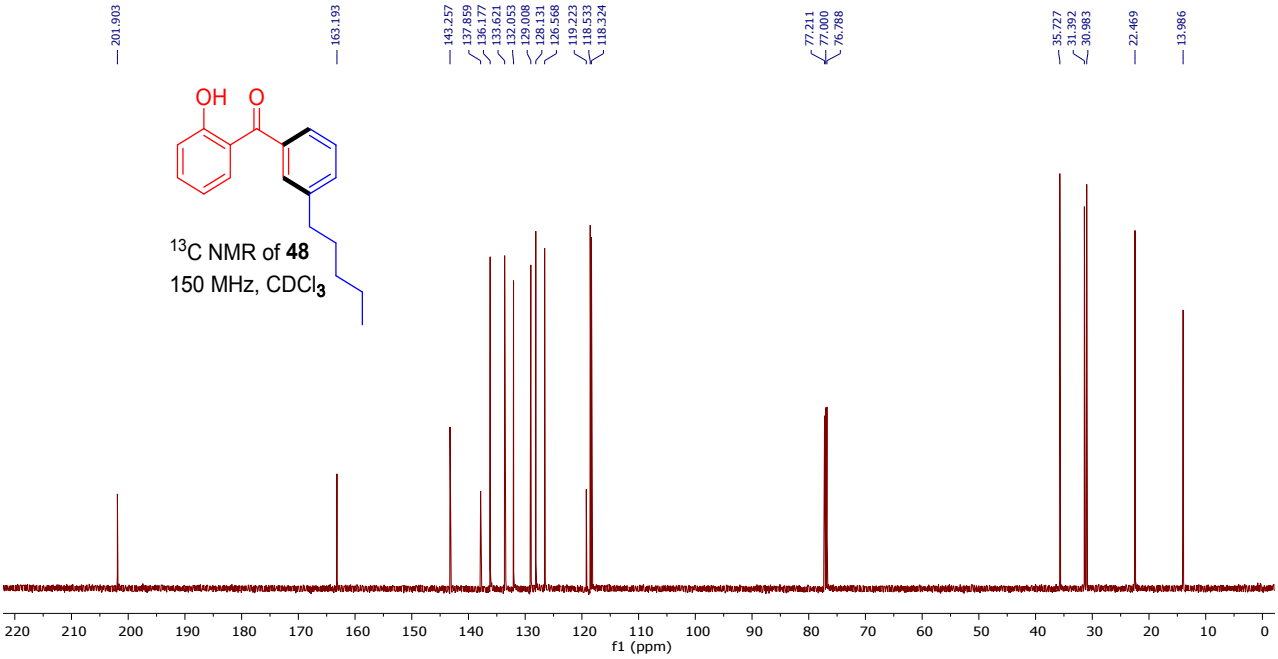


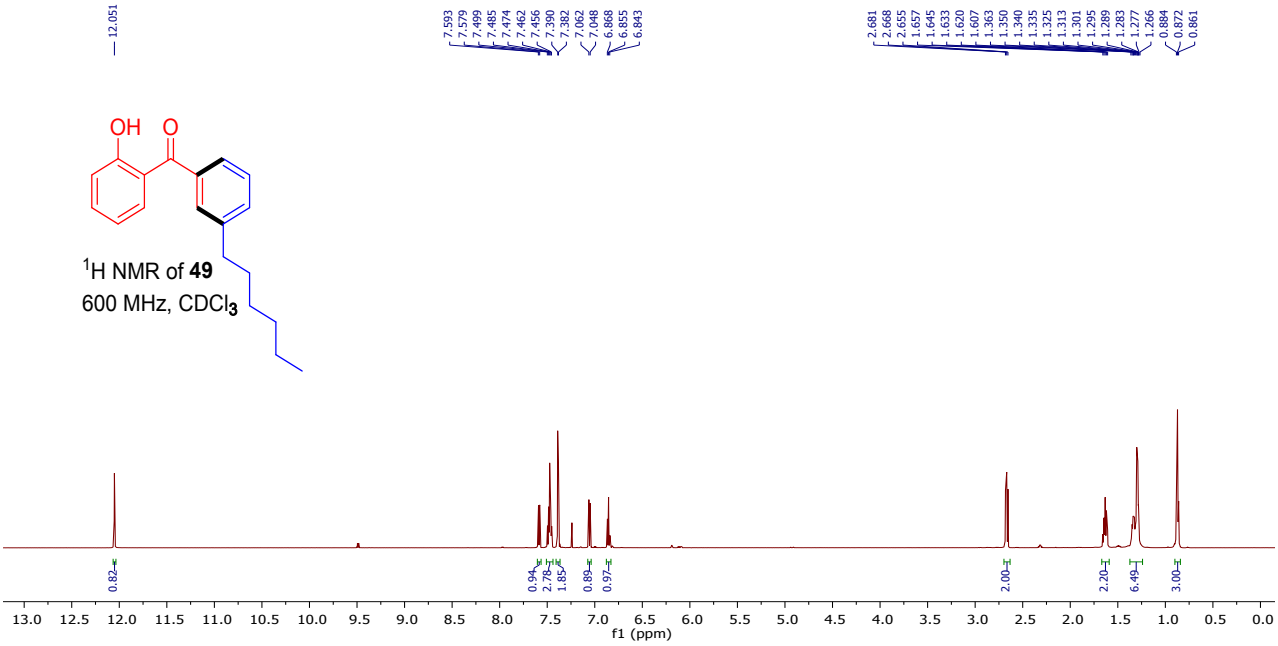
^{13}C NMR of **46**
150 MHz, $CDCl_3$


OH
O
^{1}H NMR of **47**
600 MHz, $CDCl_3$
f1 (ppm)

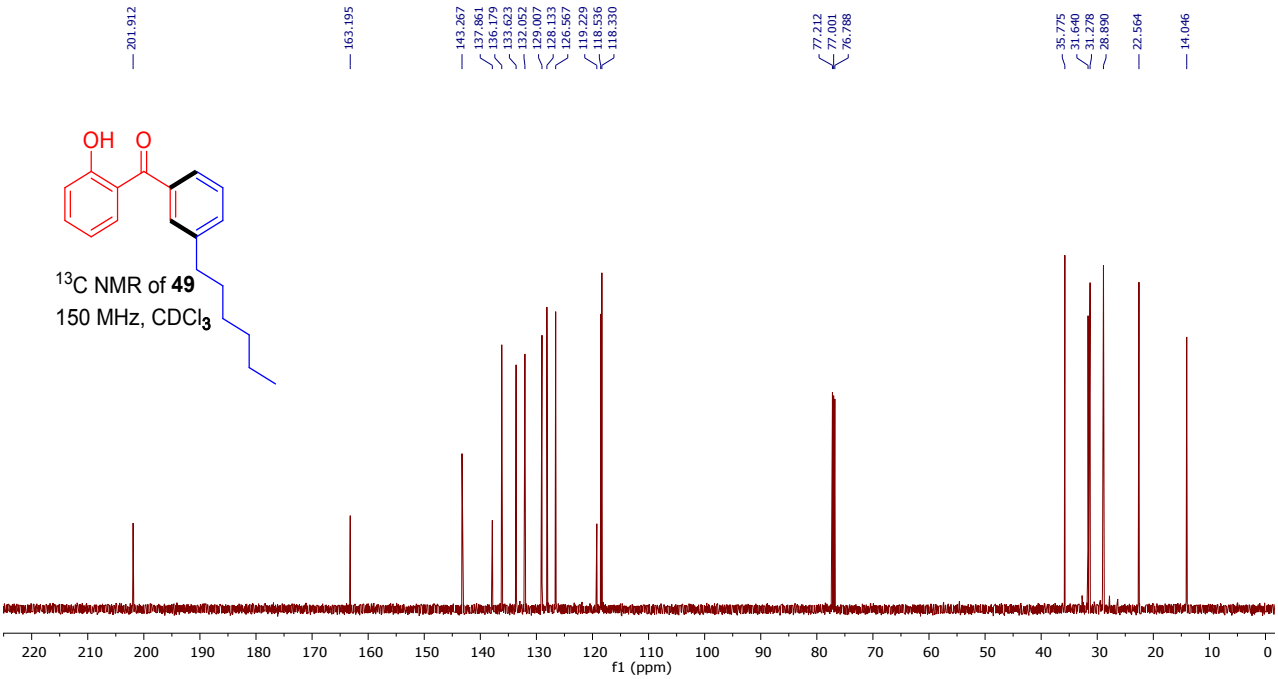

OH
O
^{13}C NMR of **47**
150 MHz, $CDCl_3$
f1 (ppm)


OH
O
^{1}H NMR of **48**
600 MHz, $CDCl_3$
f1 (ppm)

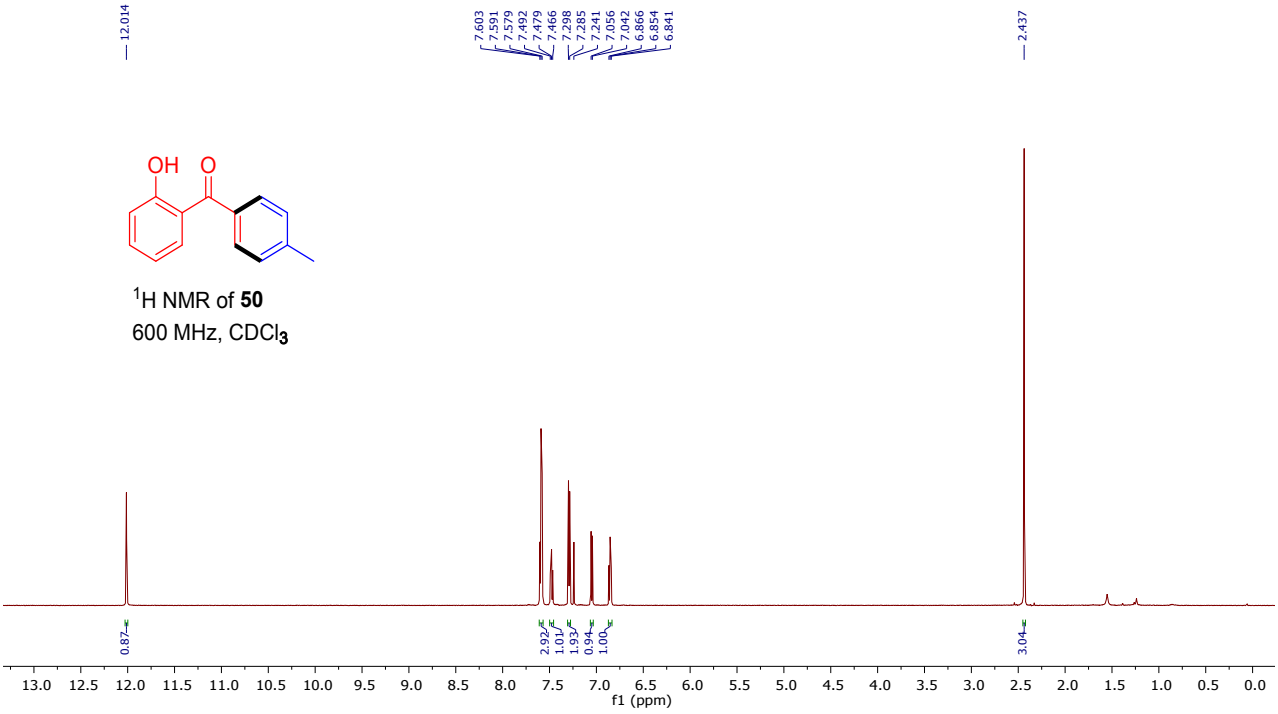

OH
O
^{13}C NMR of **48**
150 MHz, $CDCl_3$
f1 (ppm)



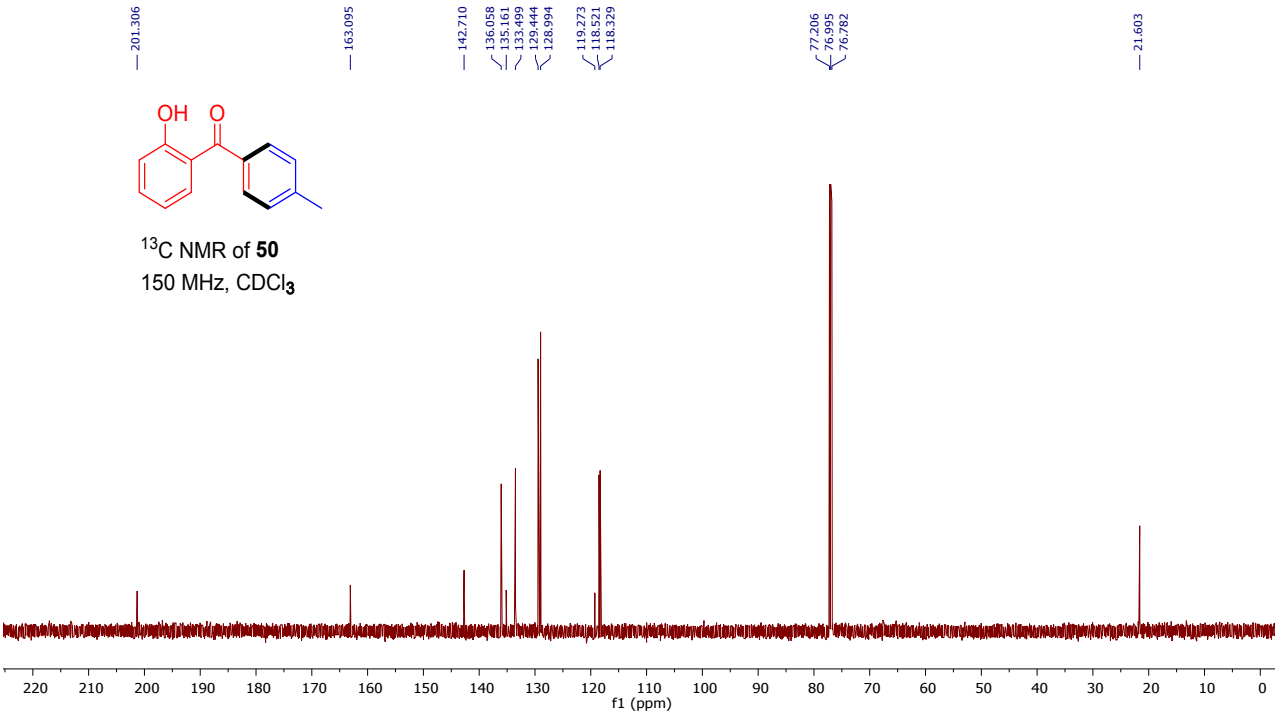
^{1}H NMR of **49**
600 MHz, $CDCl_3$



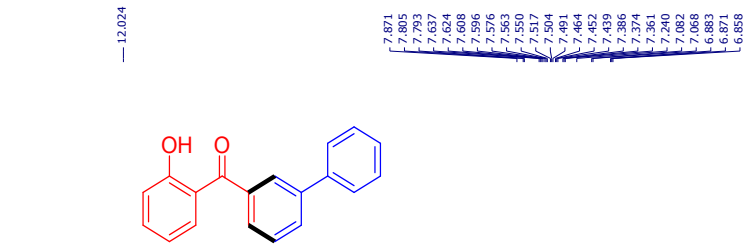
^{13}C NMR of **49**
150 MHz, $CDCl_3$



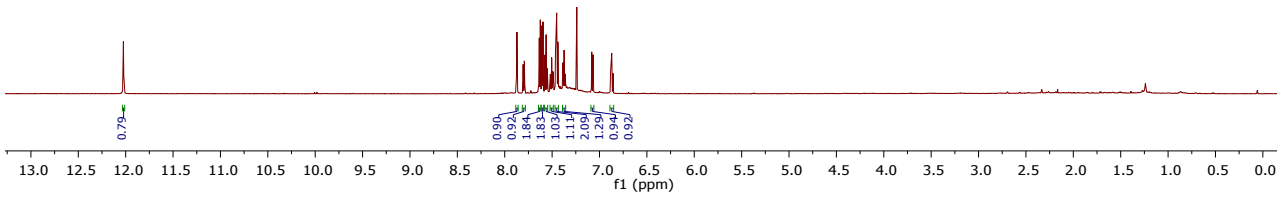
^{1}H NMR of **50**
600 MHz, $CDCl_3$

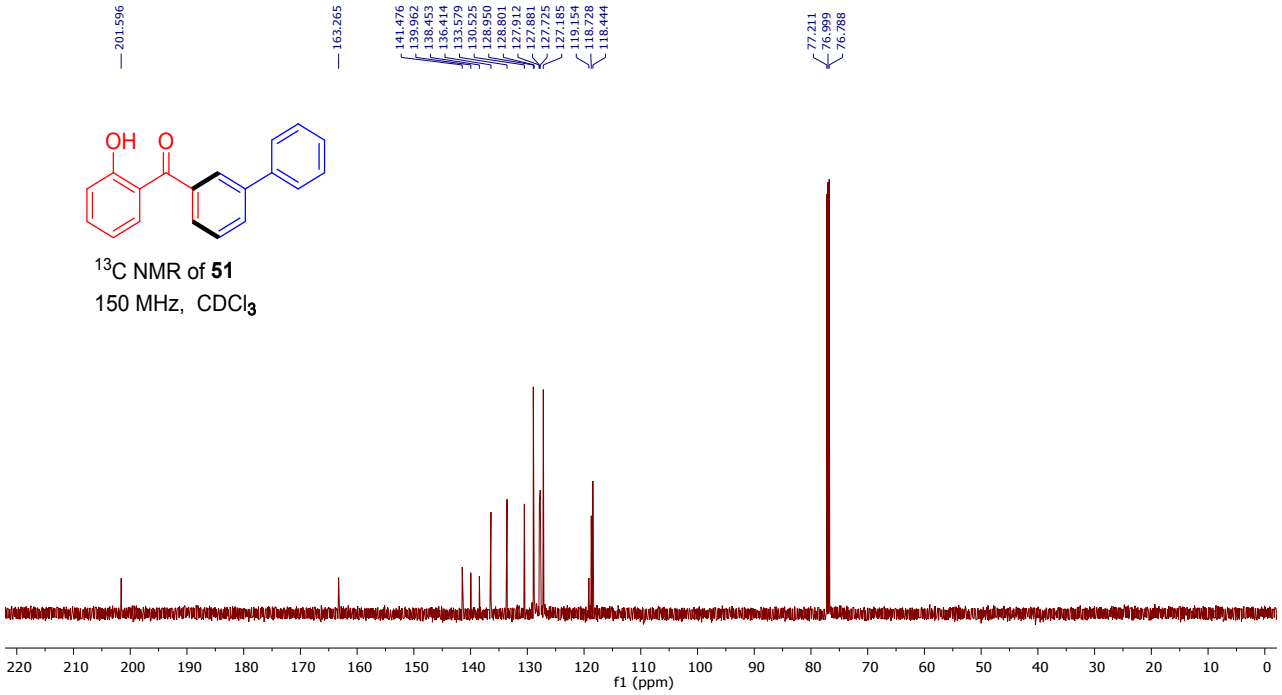


^{13}C NMR of **50**
150 MHz, $CDCl_3$

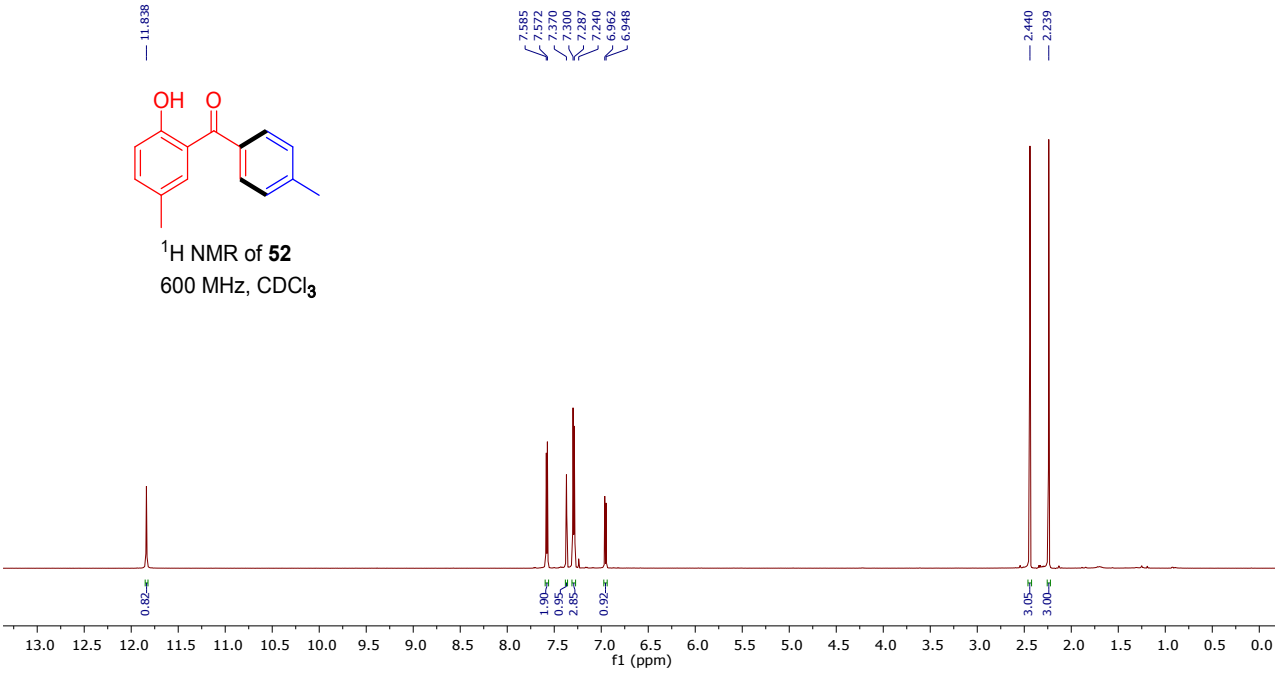


^{1}H NMR of **51**
600 MHz, $CDCl_3$

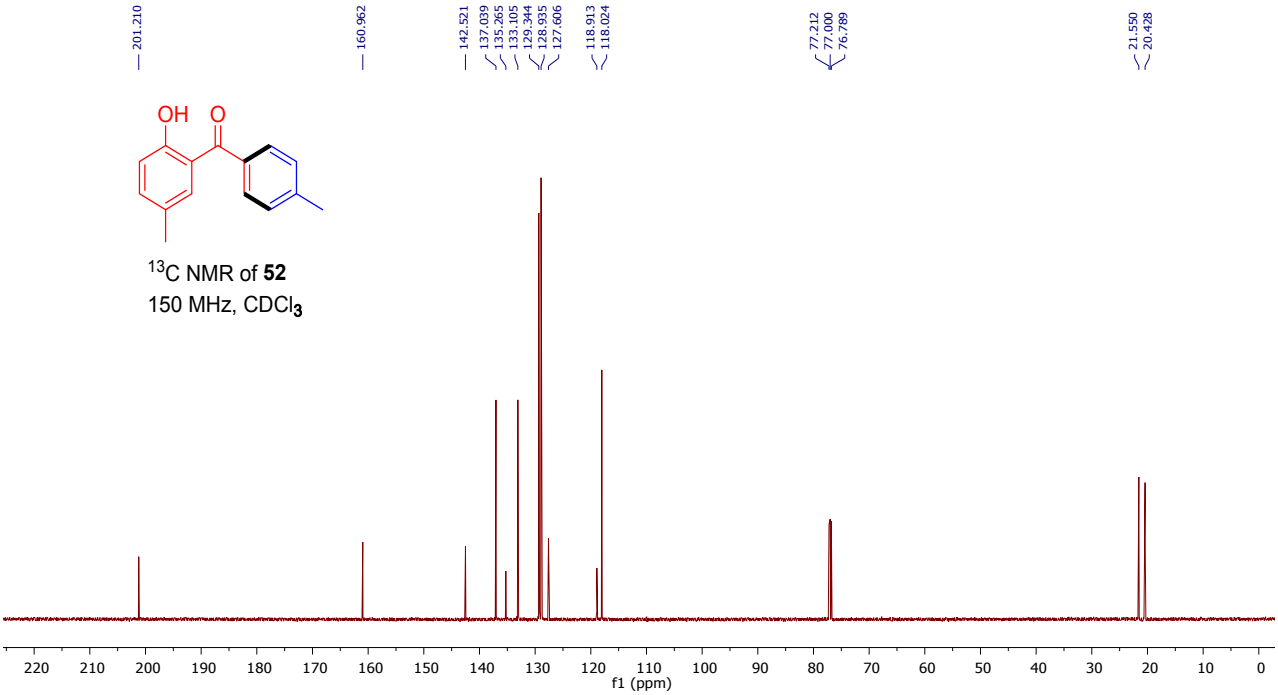




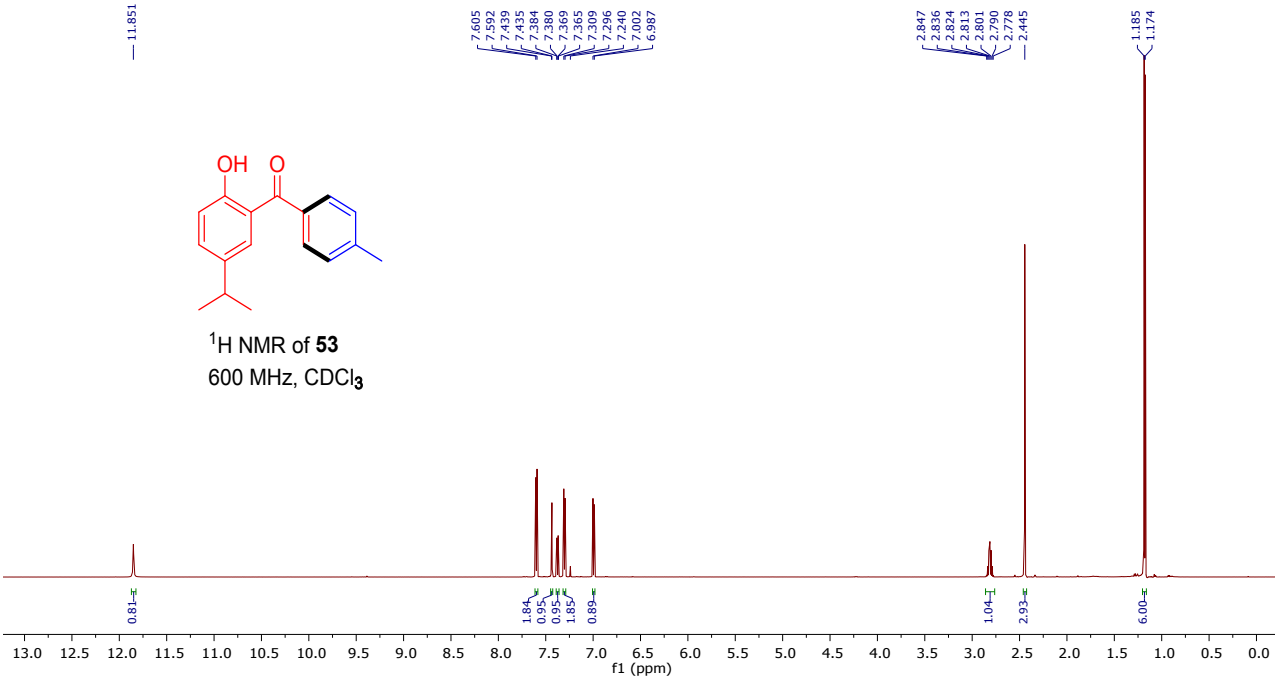
^{13}C NMR of **51**
150 MHz, $CDCl_3$



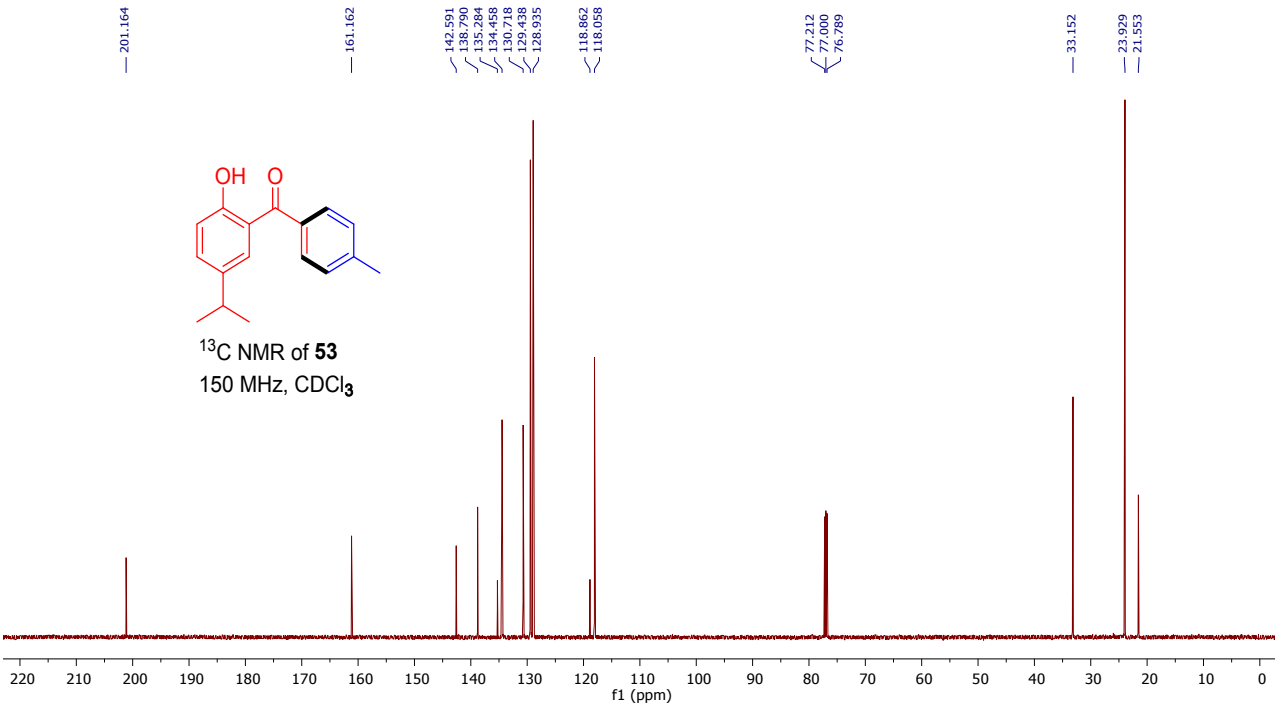
^{1}H NMR of **52**
600 MHz, $CDCl_3$



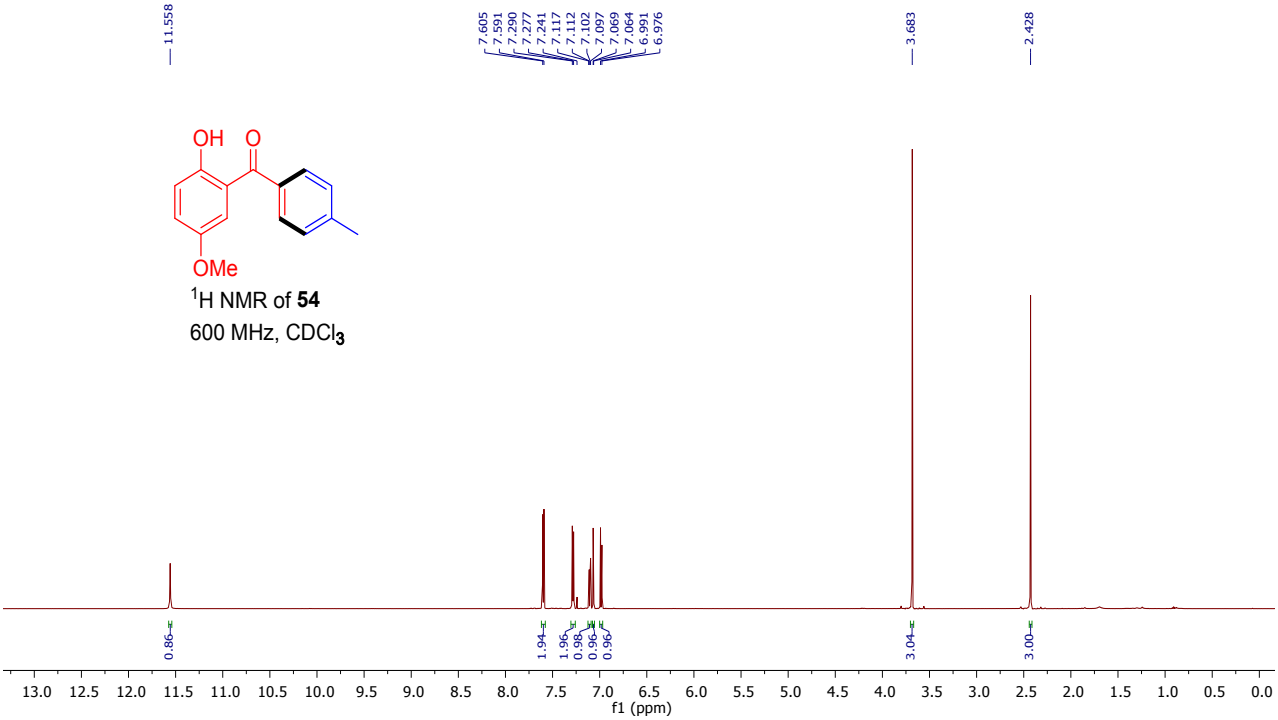
^{13}C NMR of **52**
150 MHz, $CDCl_3$



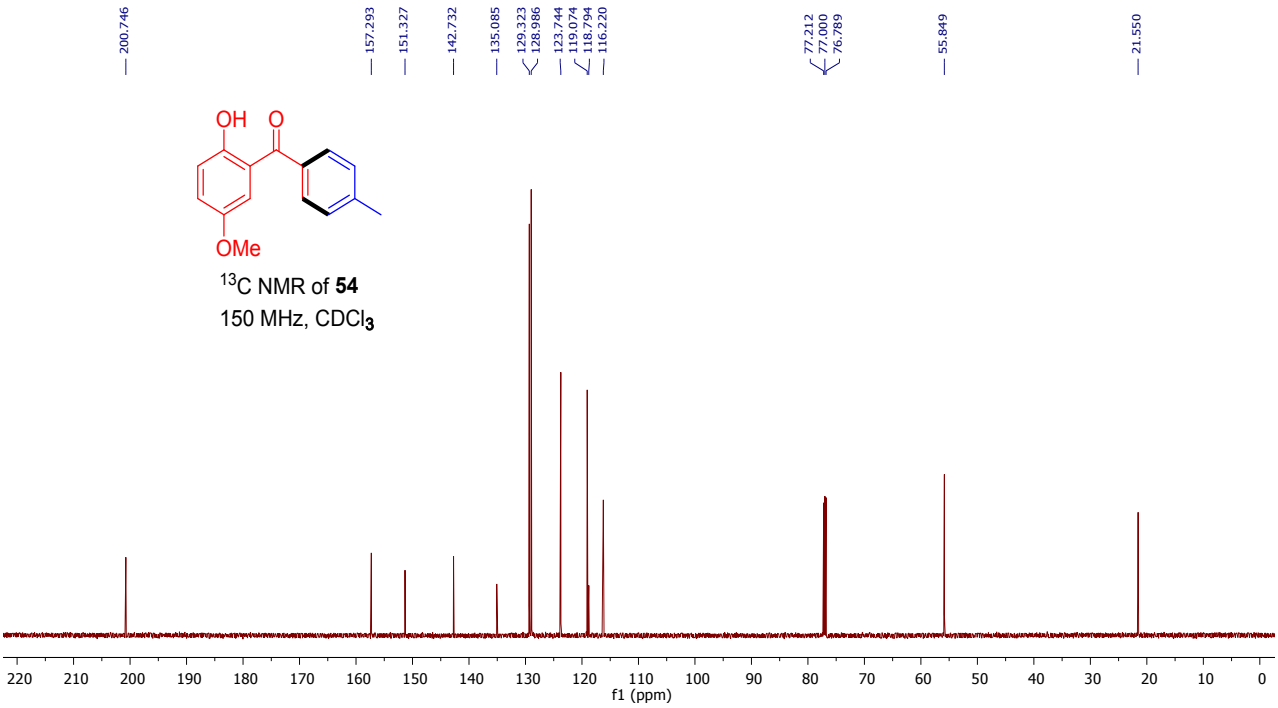
^{1}H NMR of **53**
600 MHz, $CDCl_3$



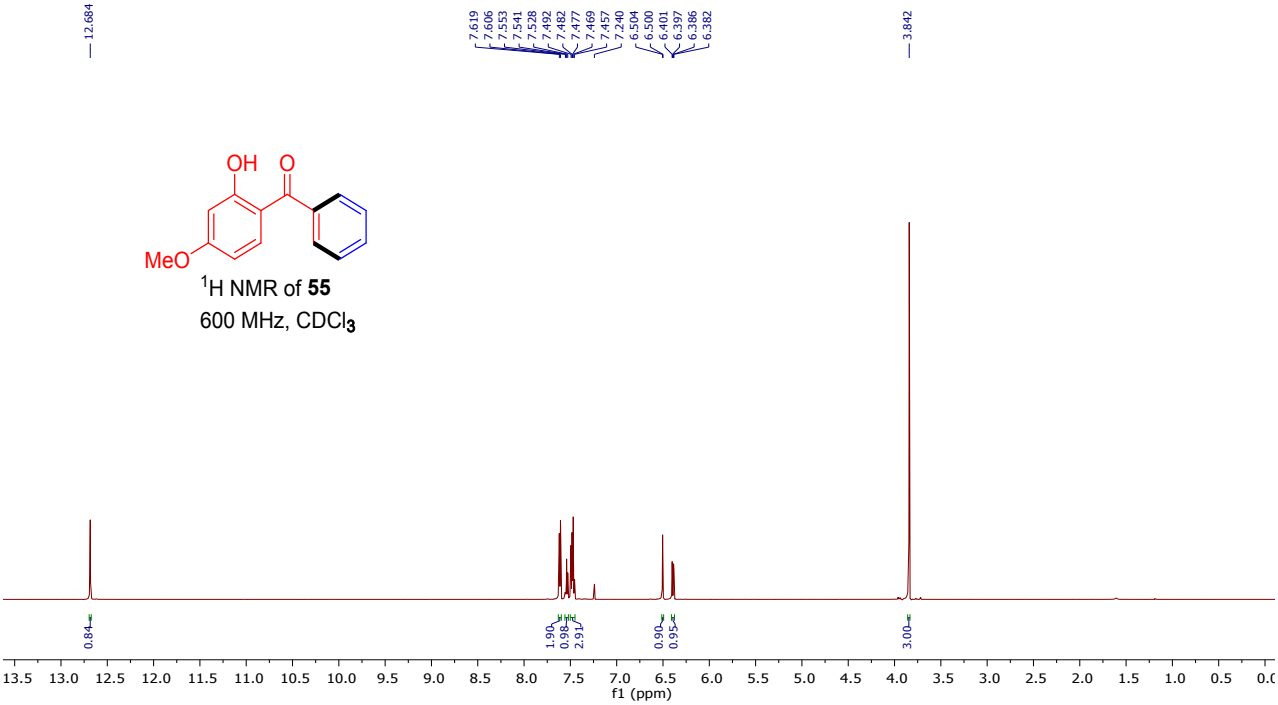
^{13}C NMR of **53**
150 MHz, $CDCl_3$



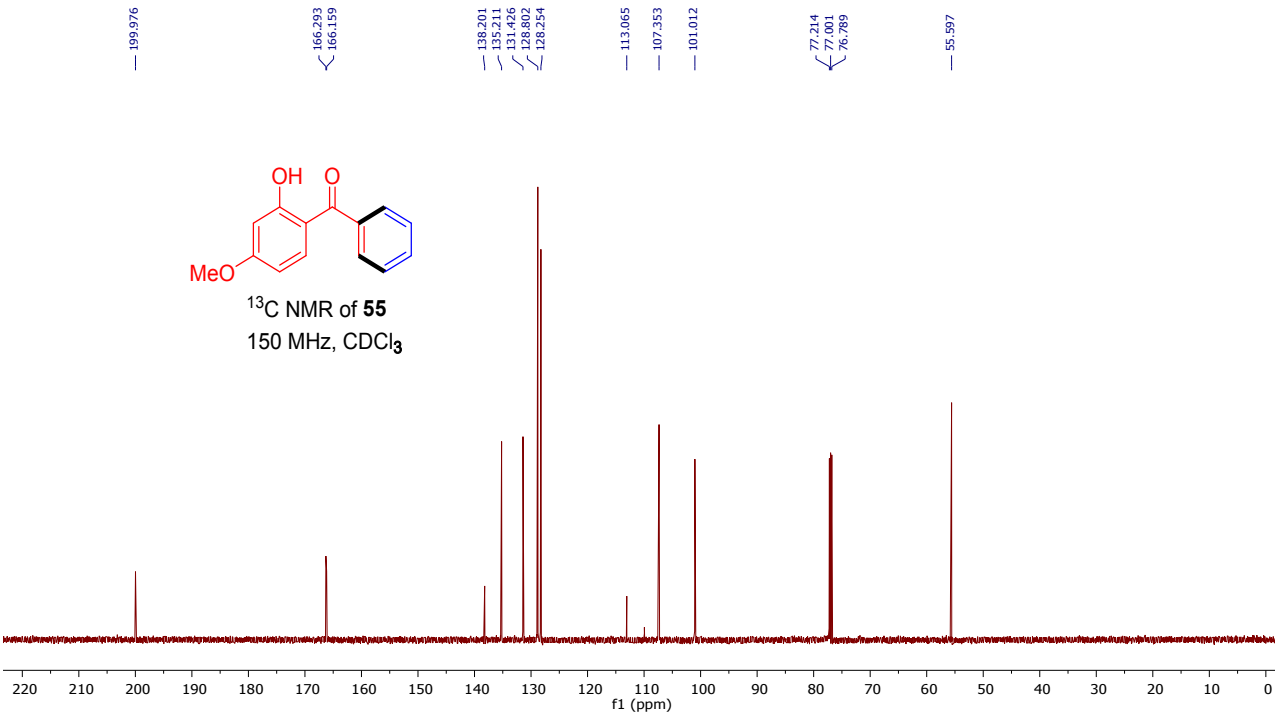
^{1}H NMR of **54**
600 MHz, $CDCl_3$



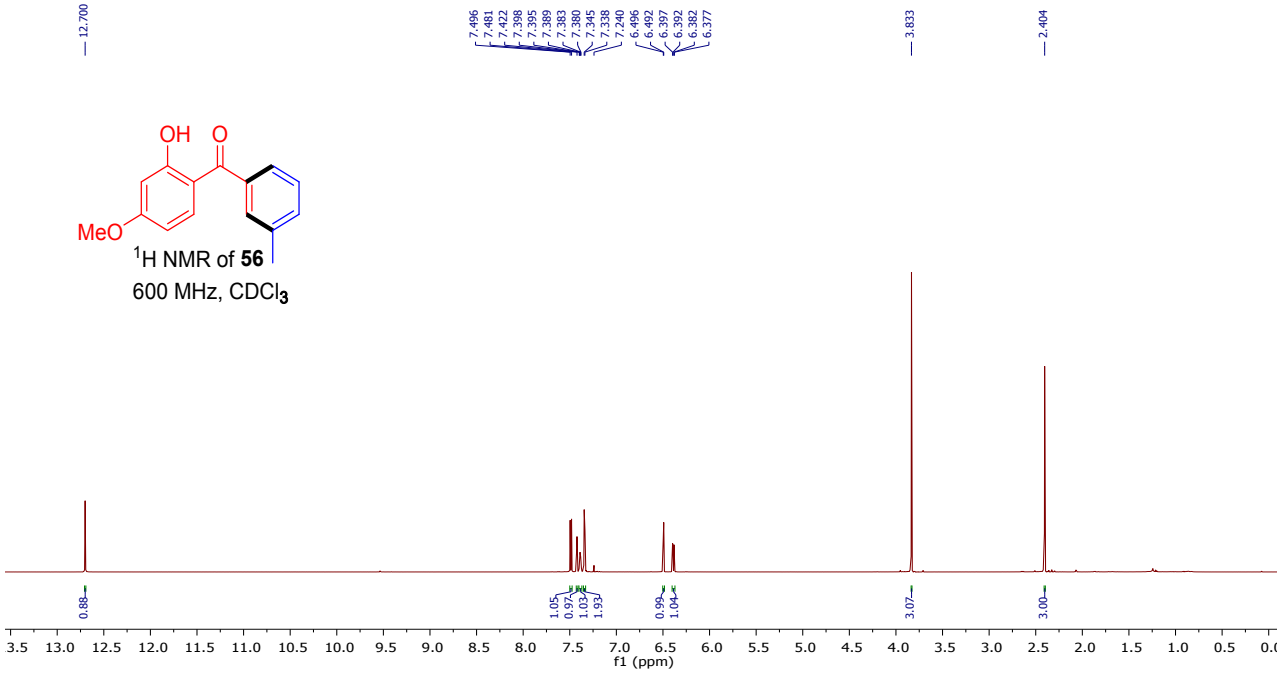
^{13}C NMR of **54**
150 MHz, $CDCl_3$



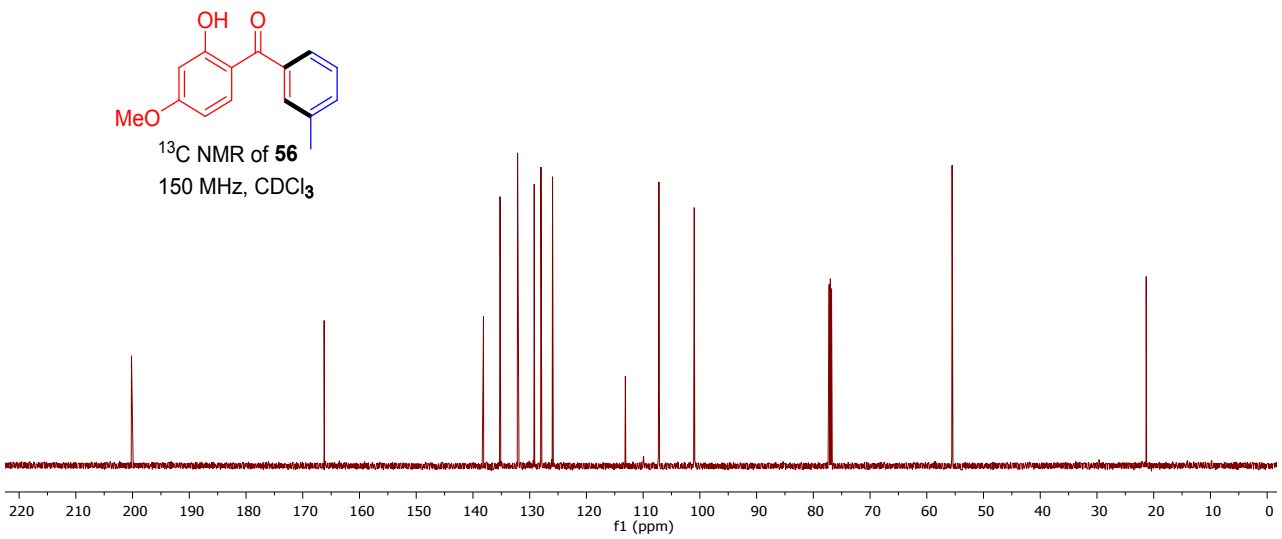
^{1}H NMR of **55**
600 MHz, $CDCl_3$



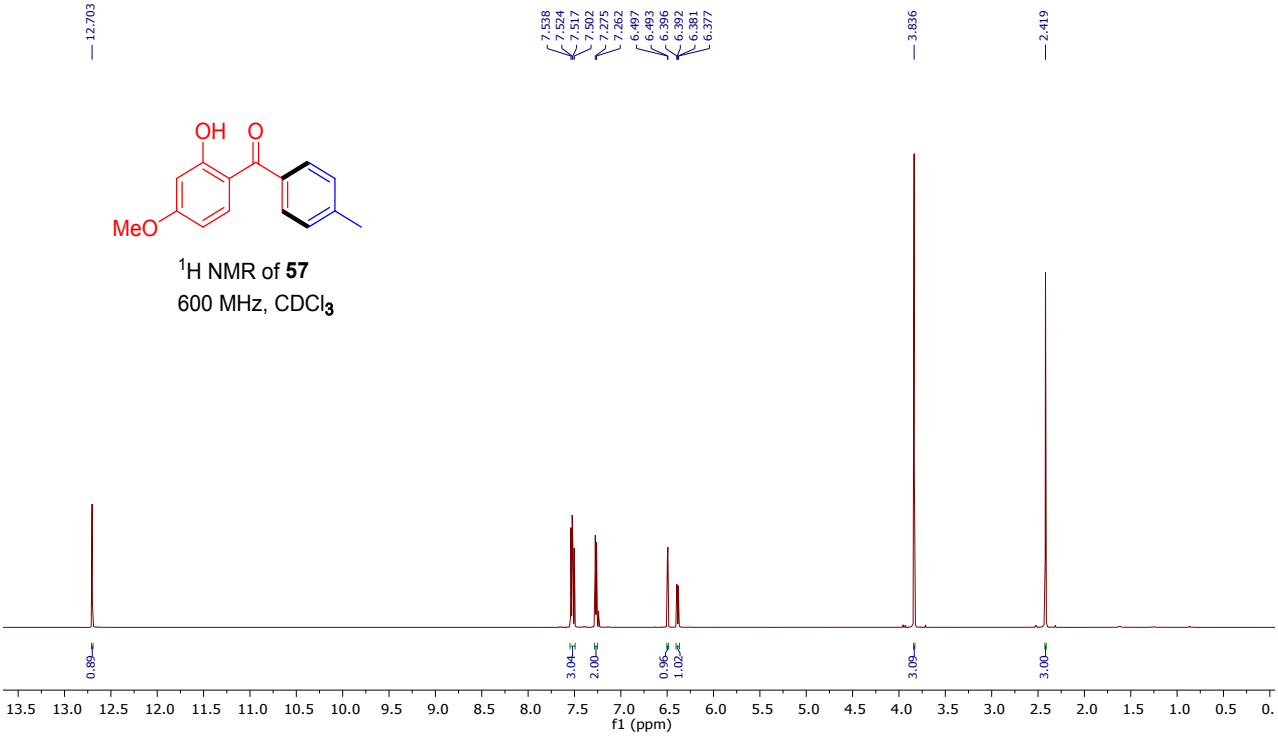
^{13}C NMR of **55**
150 MHz, $CDCl_3$



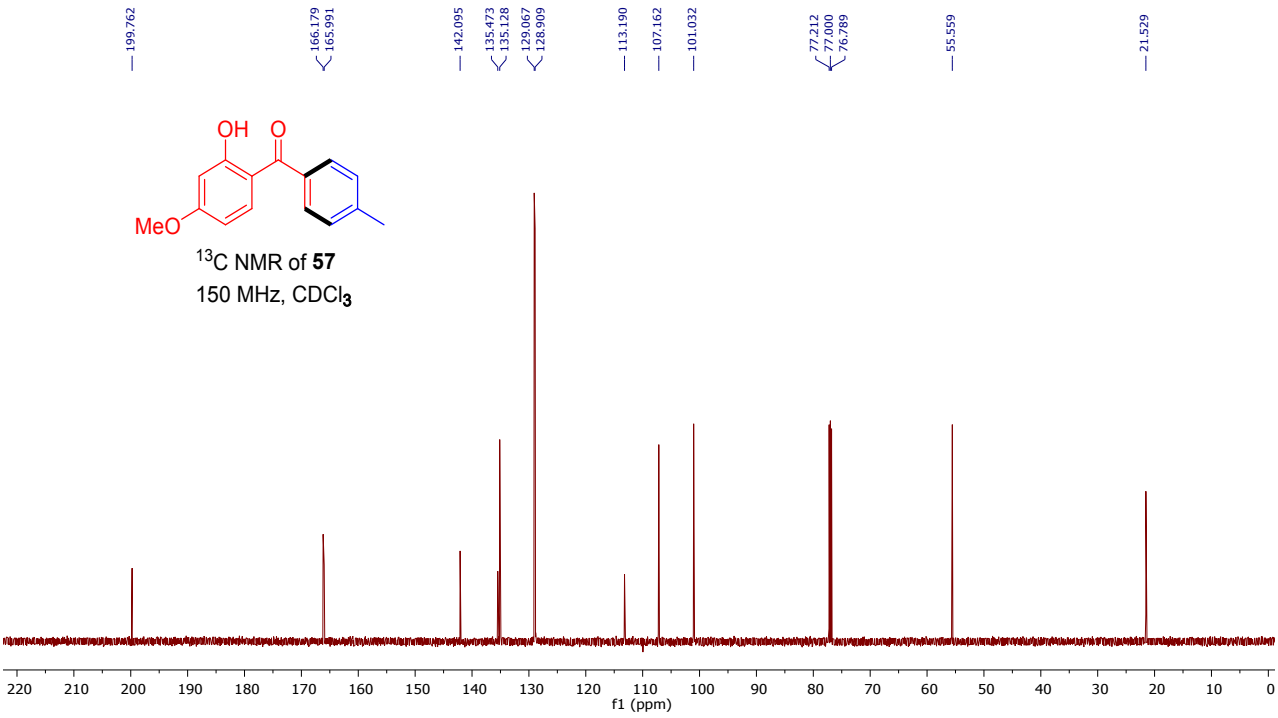
^{1}H NMR of **56**
600 MHz, $CDCl_3$



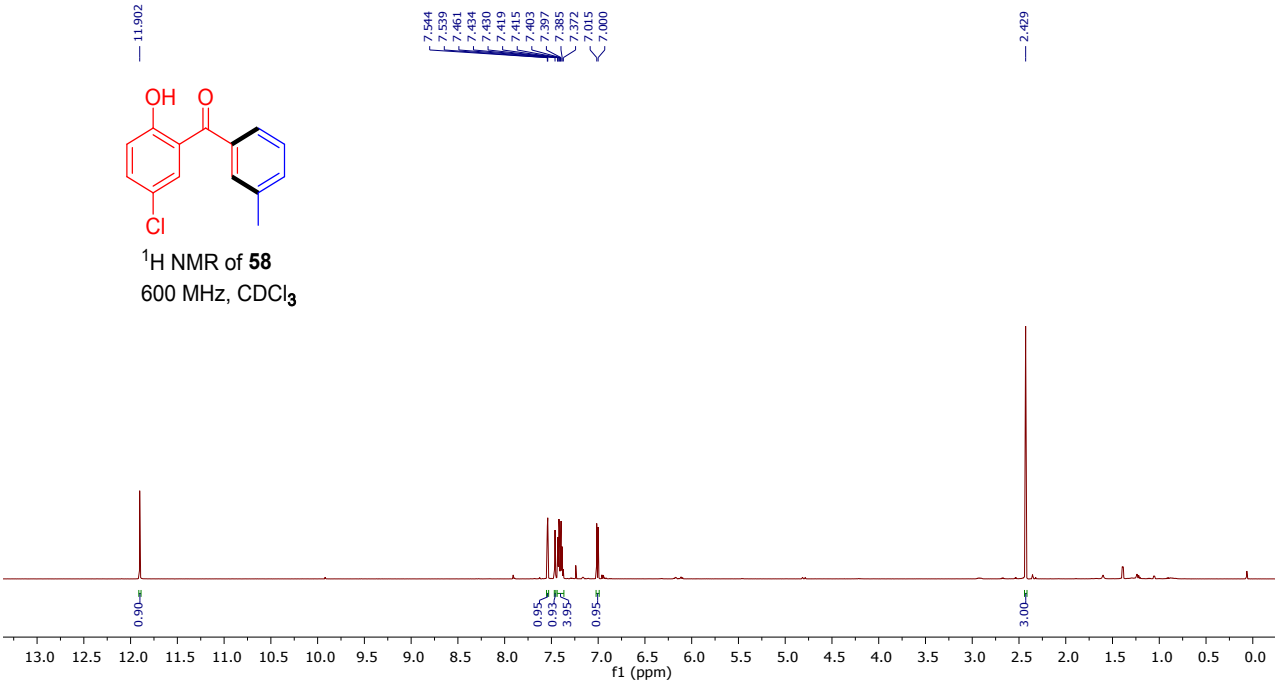
^{13}C NMR of **56**
150 MHz, $CDCl_3$



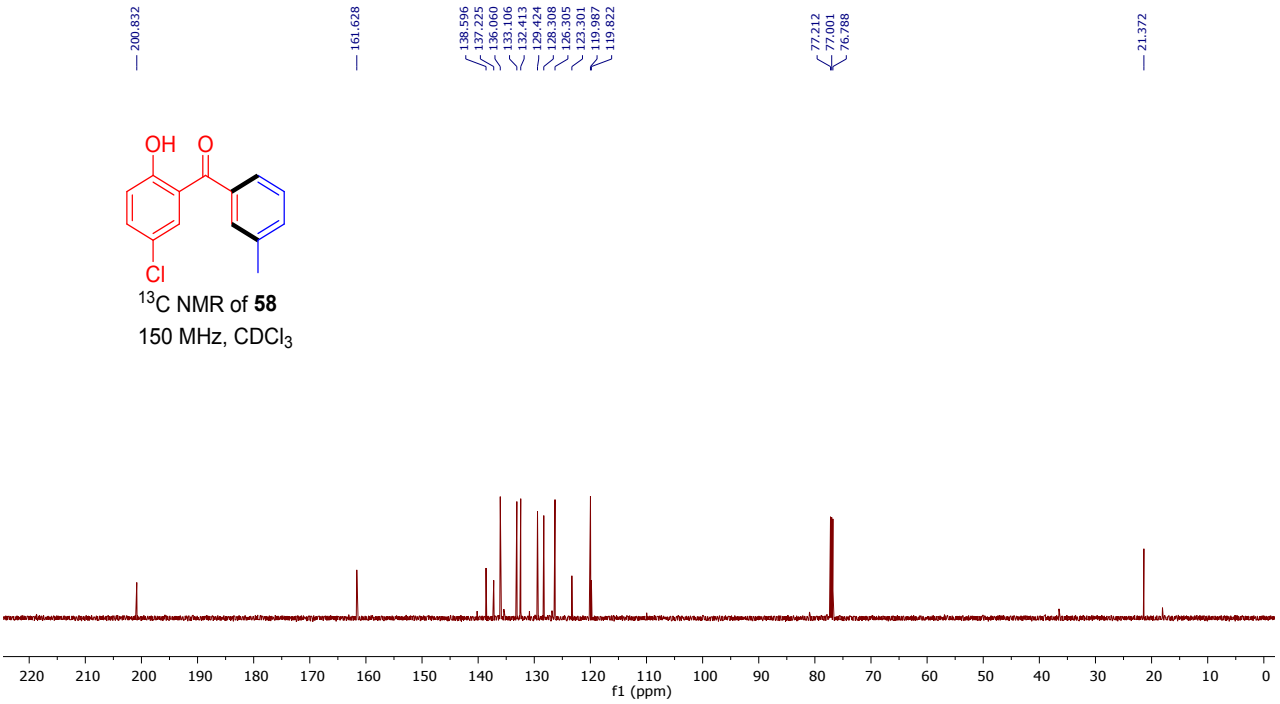
^{1}H NMR of **57**
600 MHz, $CDCl_3$



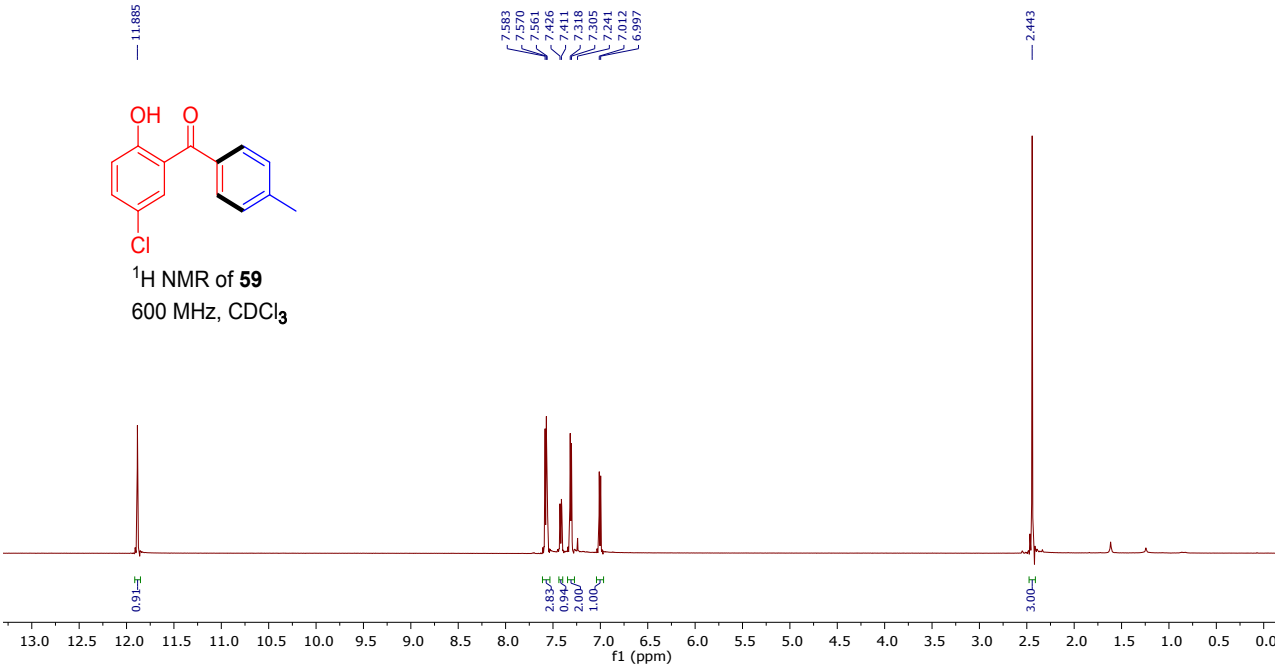
^{13}C NMR of **57**
150 MHz, $CDCl_3$



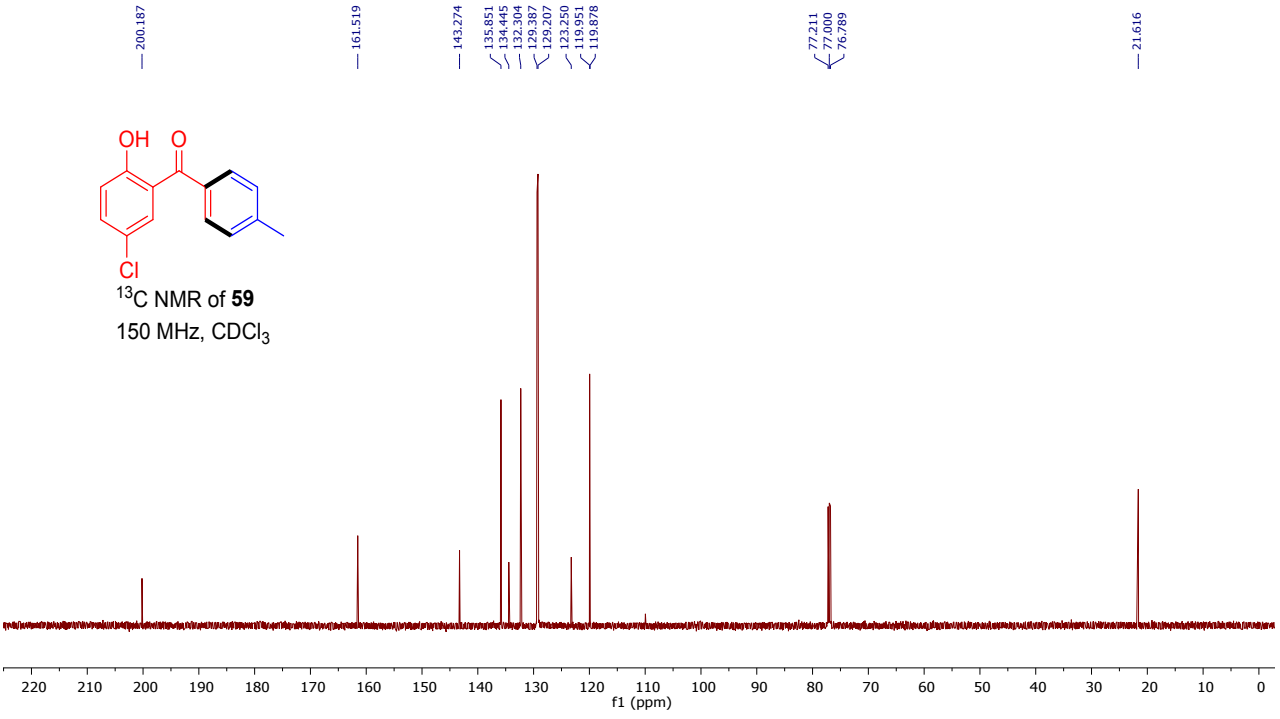
^{1}H NMR of **58**
600 MHz, $CDCl_3$



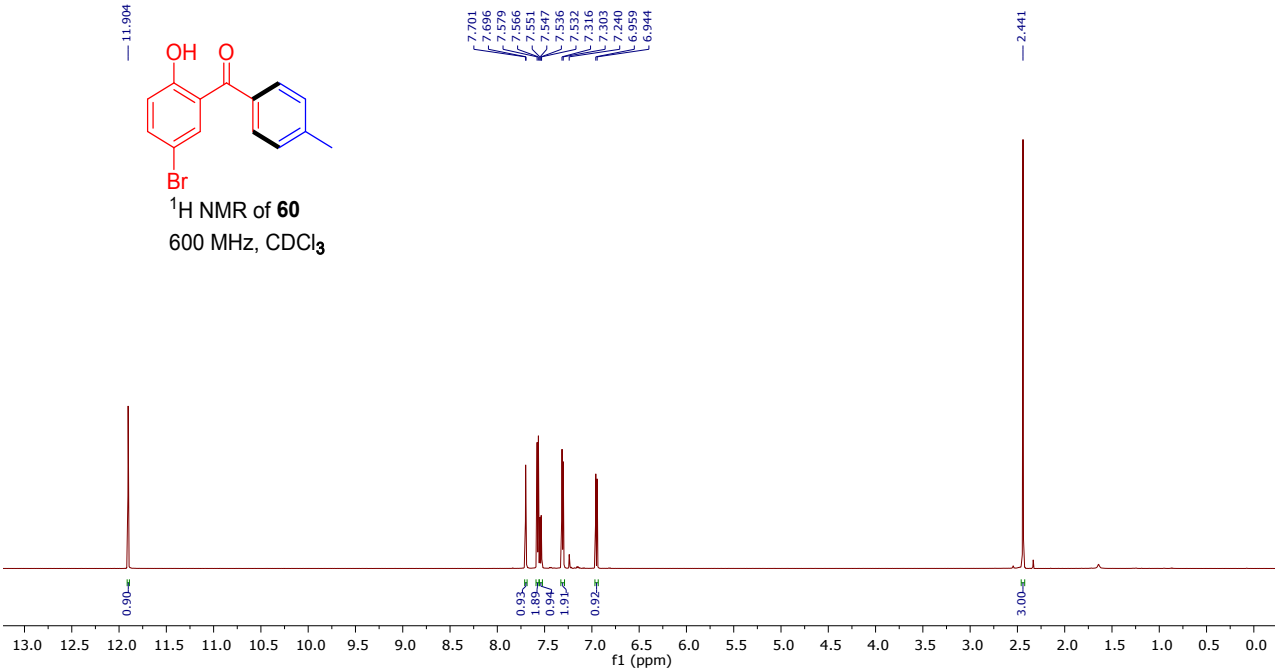
^{13}C NMR of **58**
150 MHz, $CDCl_3$



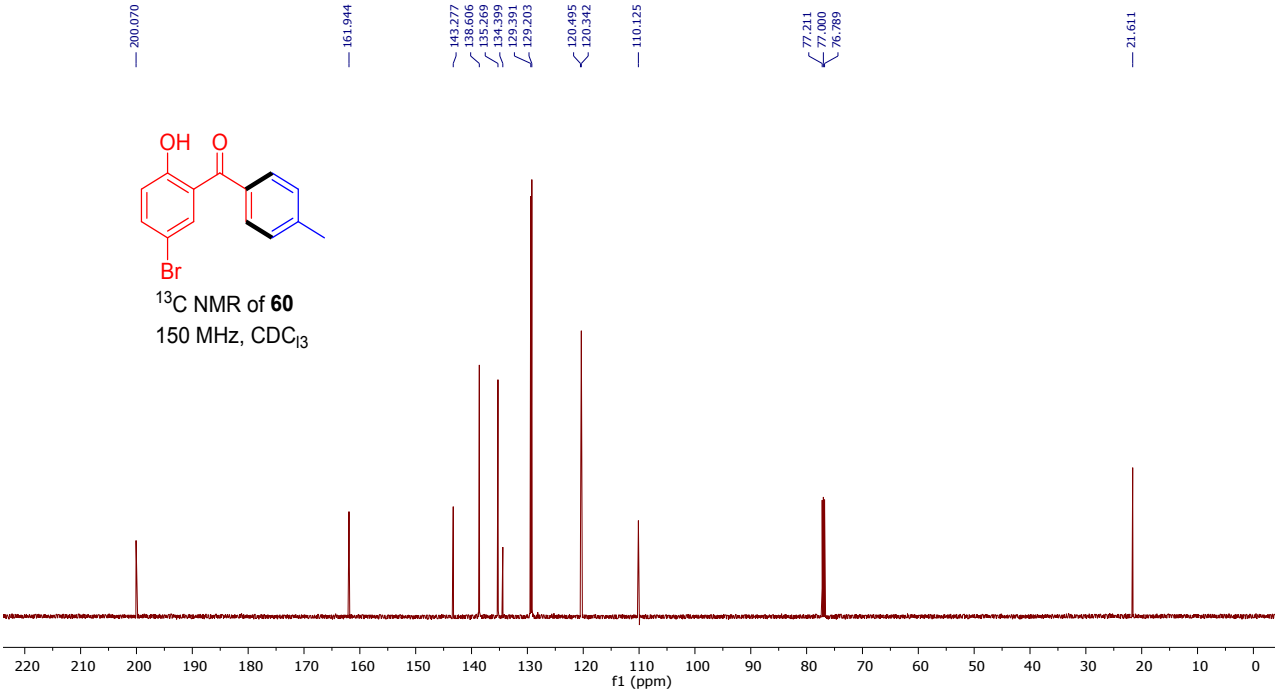
^{1}H NMR of **59**
600 MHz, $CDCl_3$



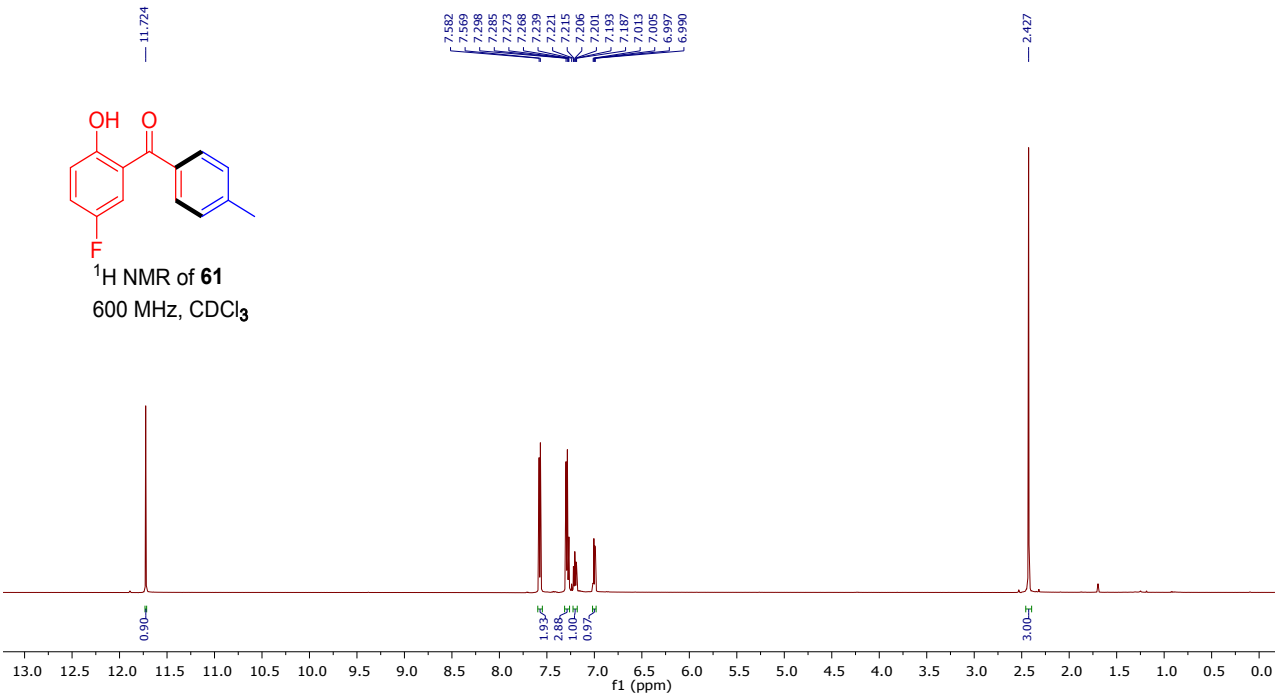
^{13}C NMR of **59**
150 MHz, $CDCl_3$



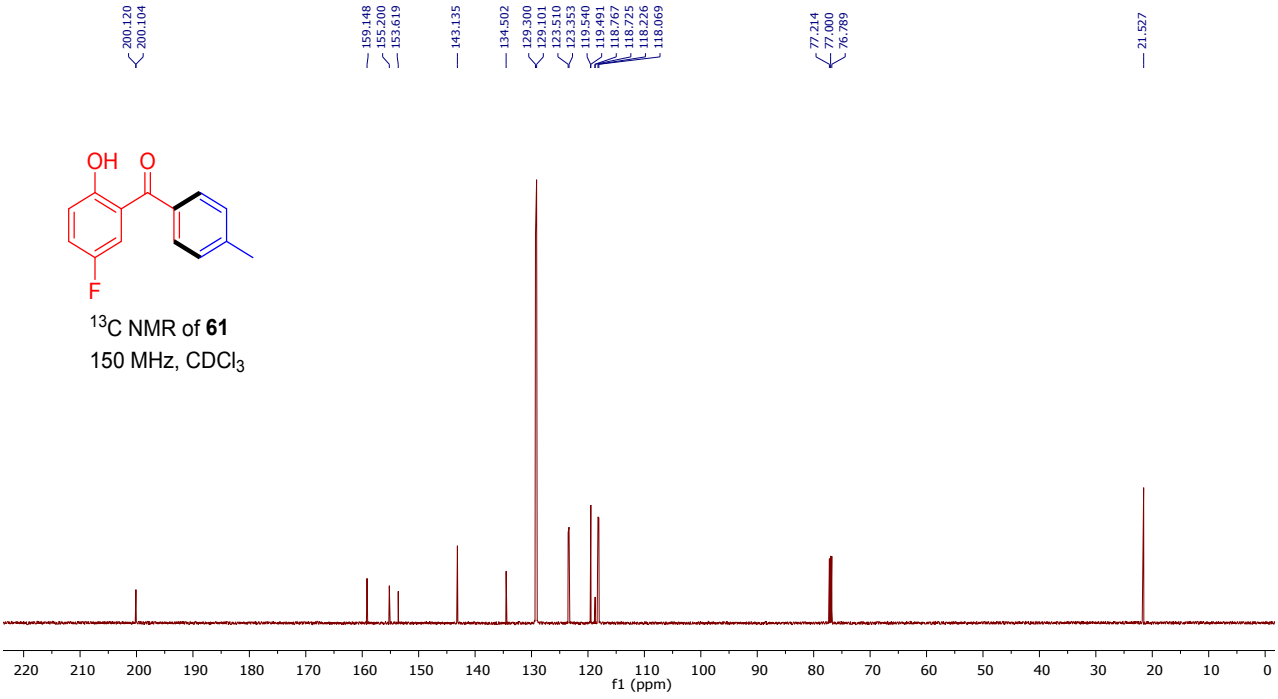
^{1}H NMR of **60**
600 MHz, $CDCl_3$



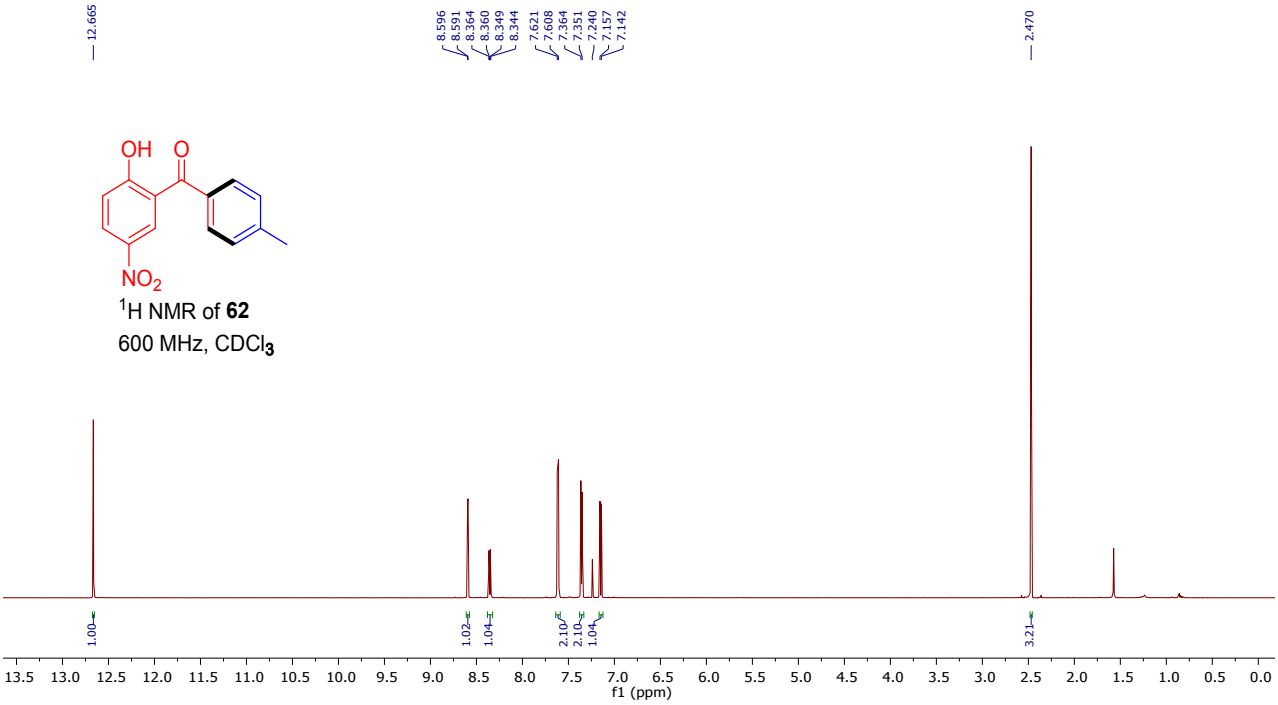
^{13}C NMR of **60**
150 MHz, CDC_{l3}



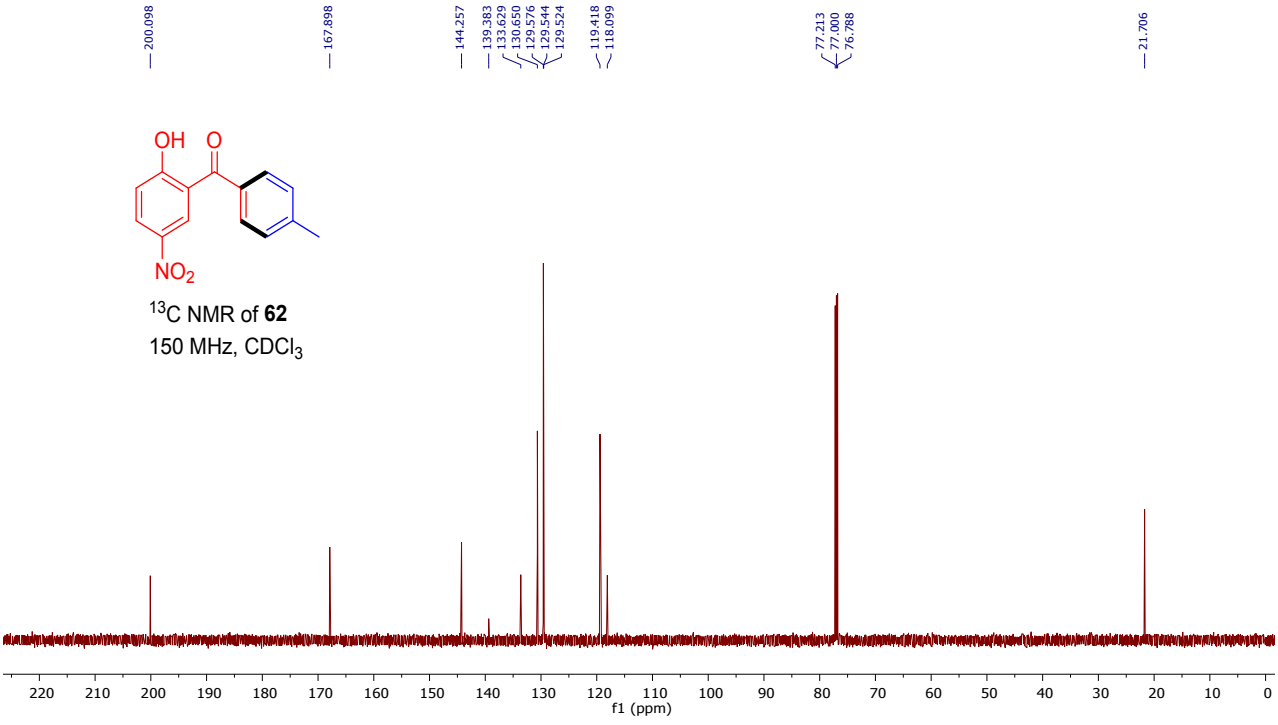
^{1}H NMR of **61**
600 MHz, $CDCl_3$



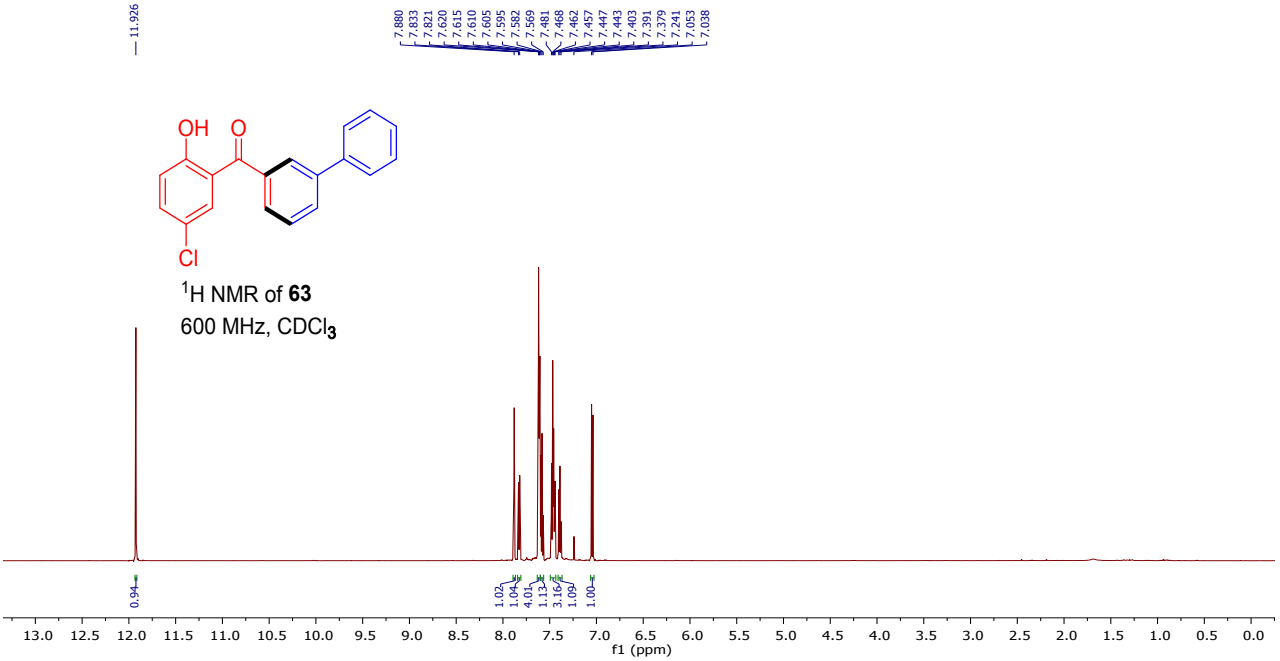
^{13}C NMR of **61**
150 MHz, $CDCl_3$



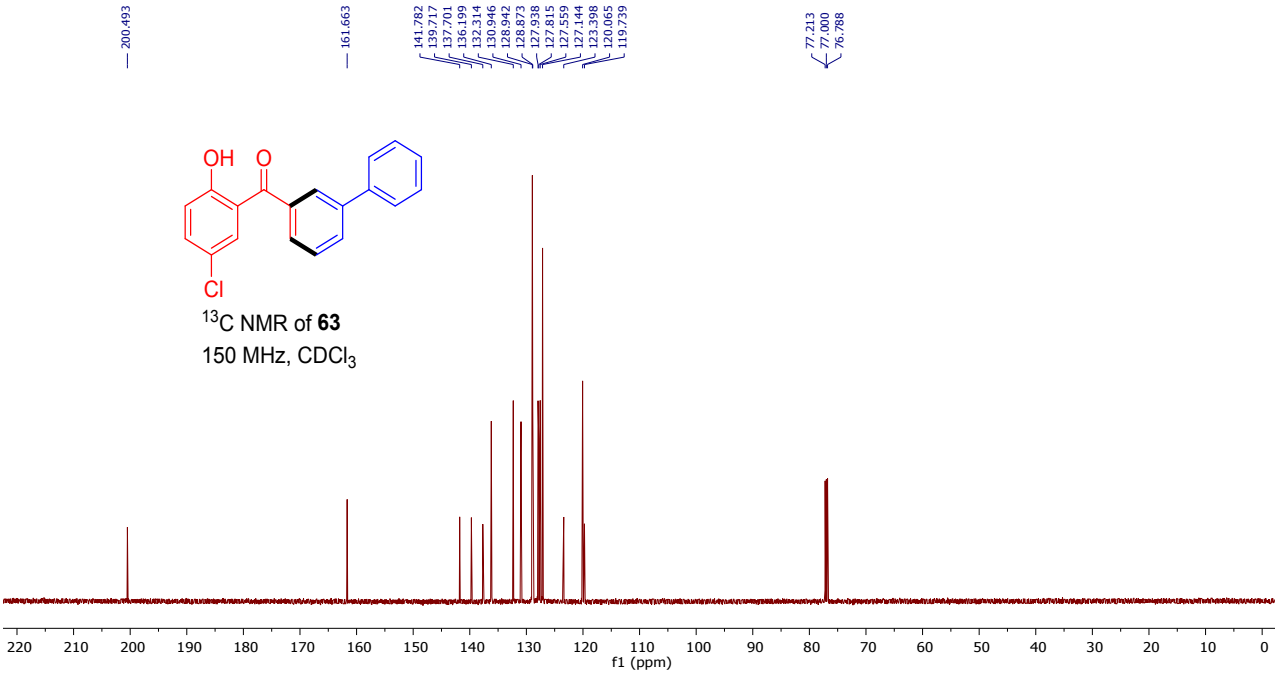
^{1}H NMR of **62**
600 MHz, $CDCl_3$



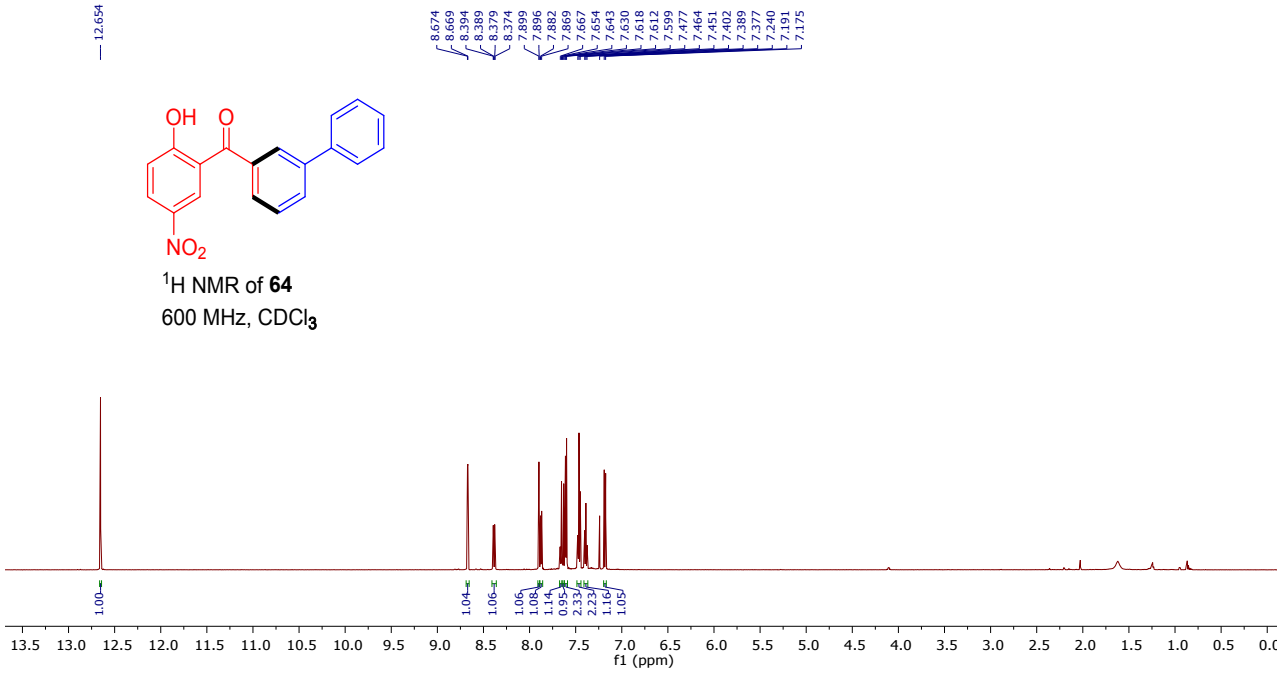
^{13}C NMR of **62**
150 MHz, $CDCl_3$



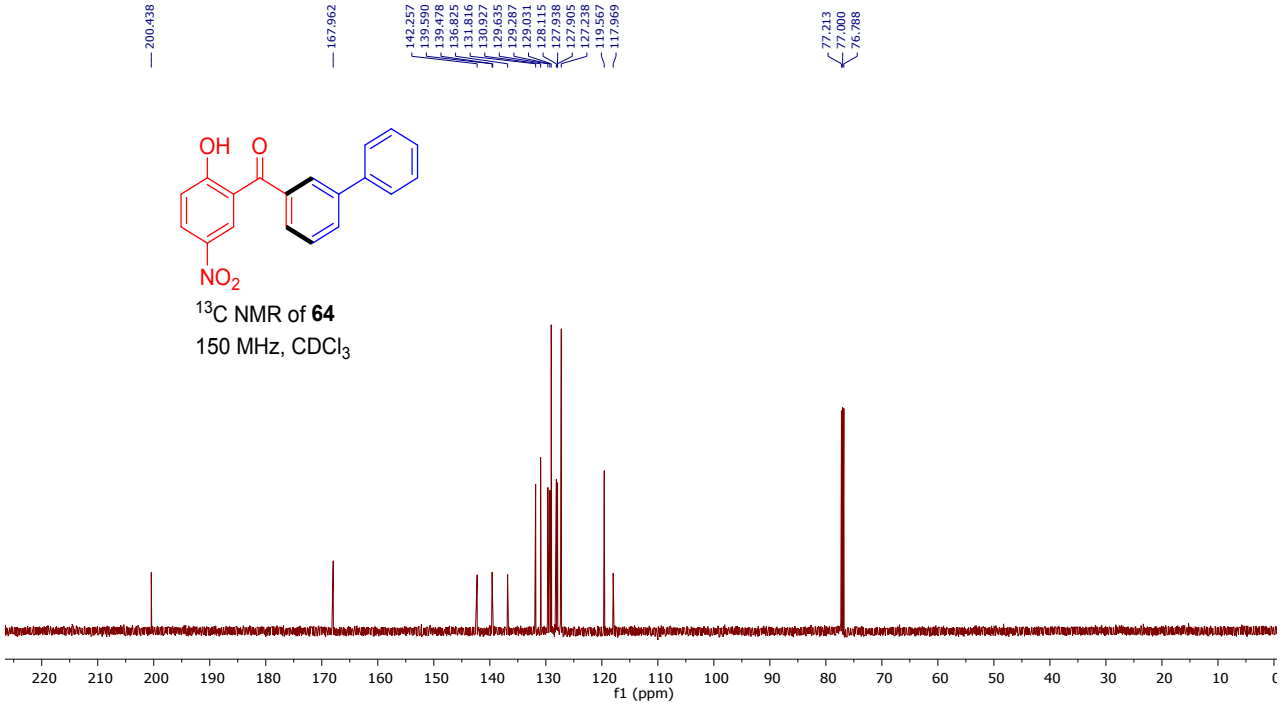
^{1}H NMR of **63**
600 MHz, $CDCl_3$



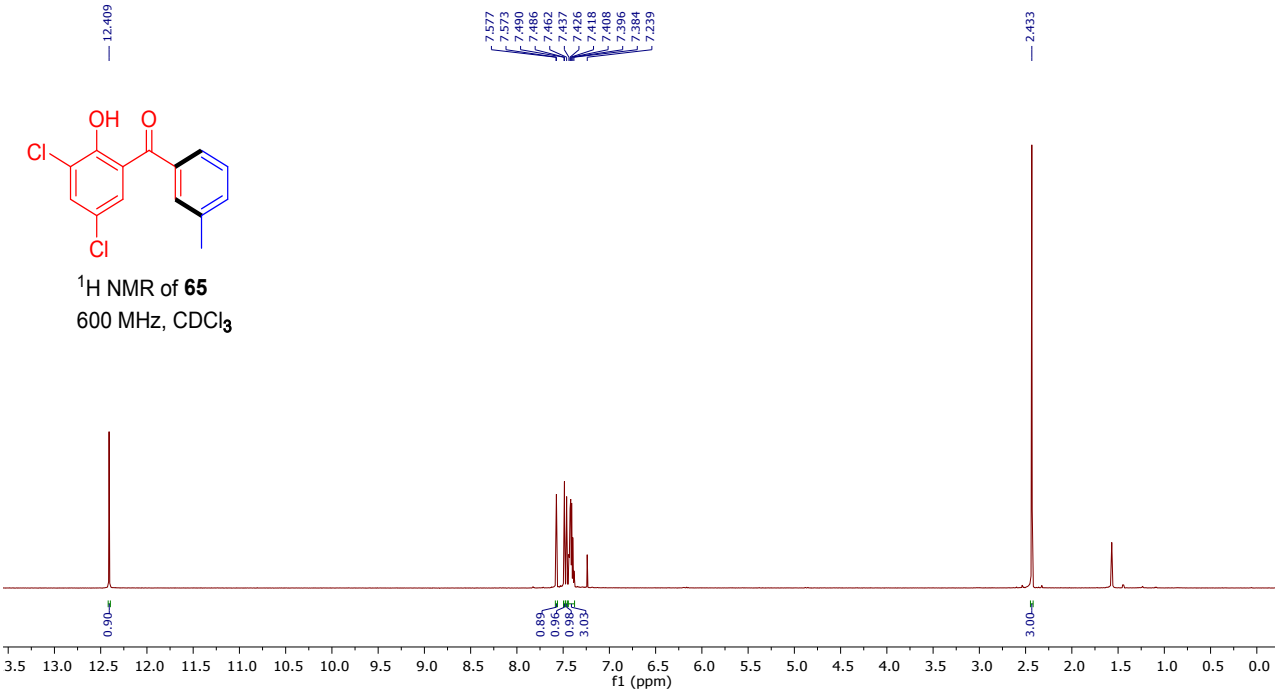
^{13}C NMR of **63**
150 MHz, $CDCl_3$



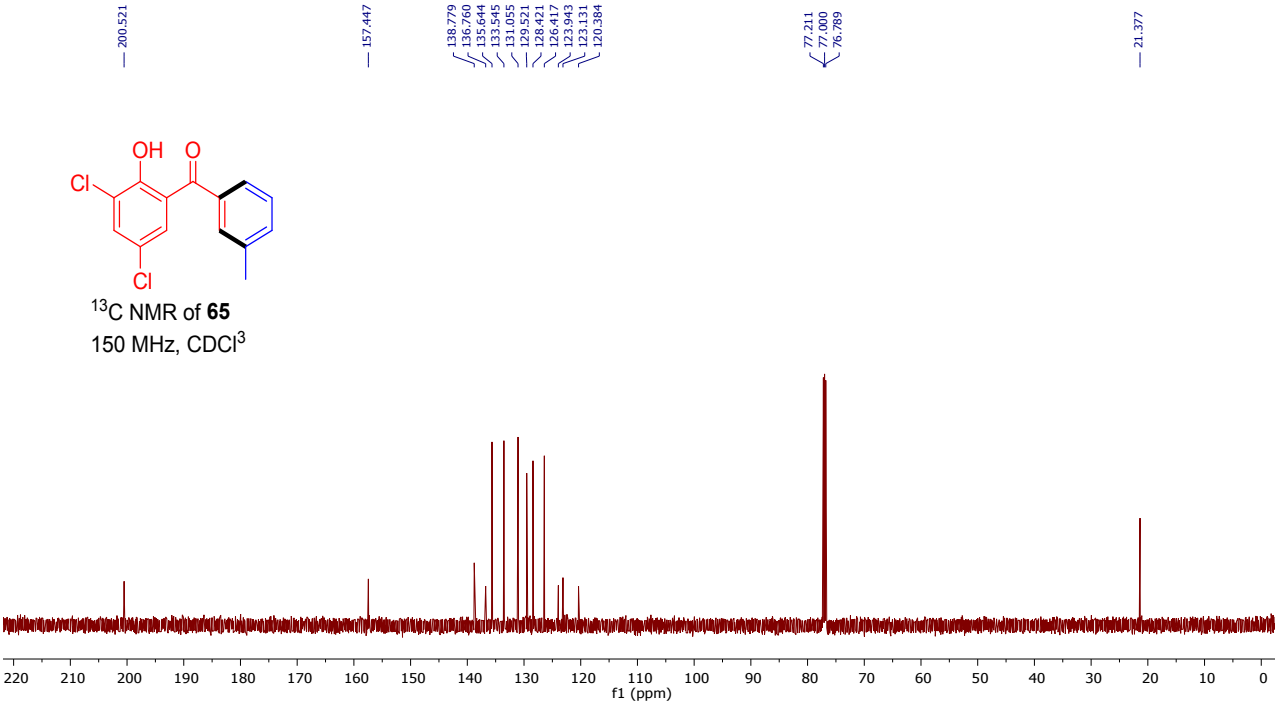
^{1}H NMR of **64**
600 MHz, $CDCl_3$



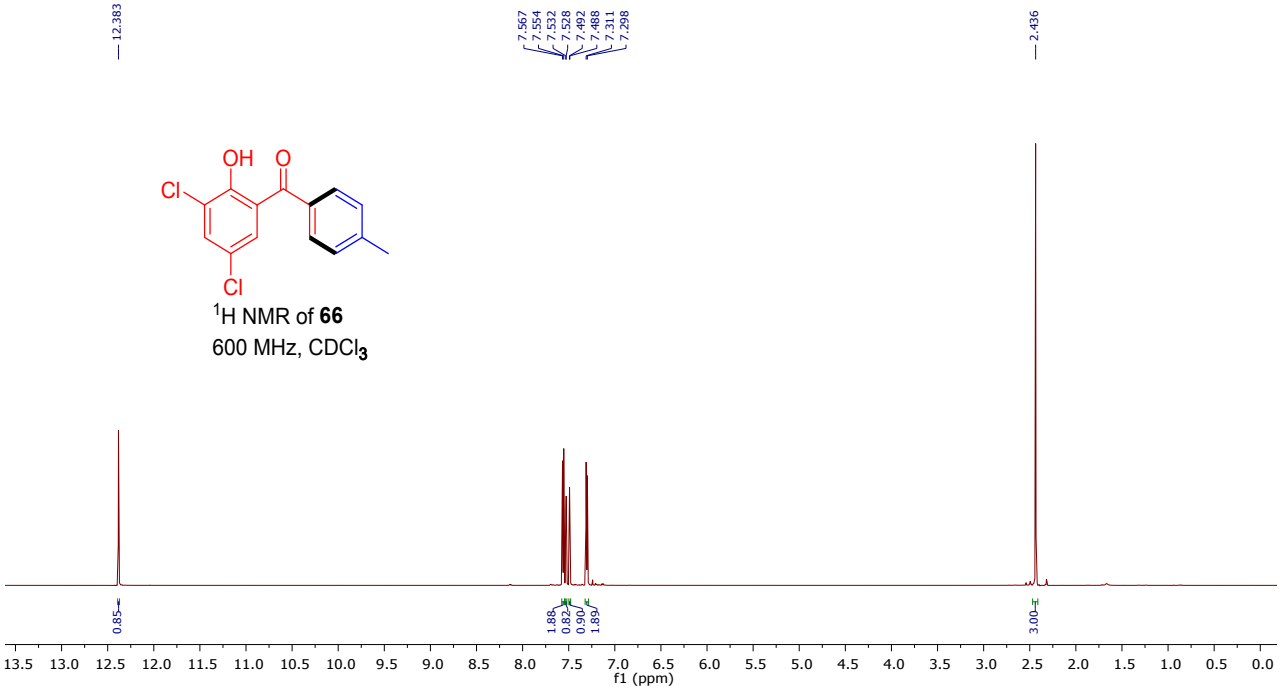
^{13}C NMR of **64**
150 MHz, $CDCl_3$



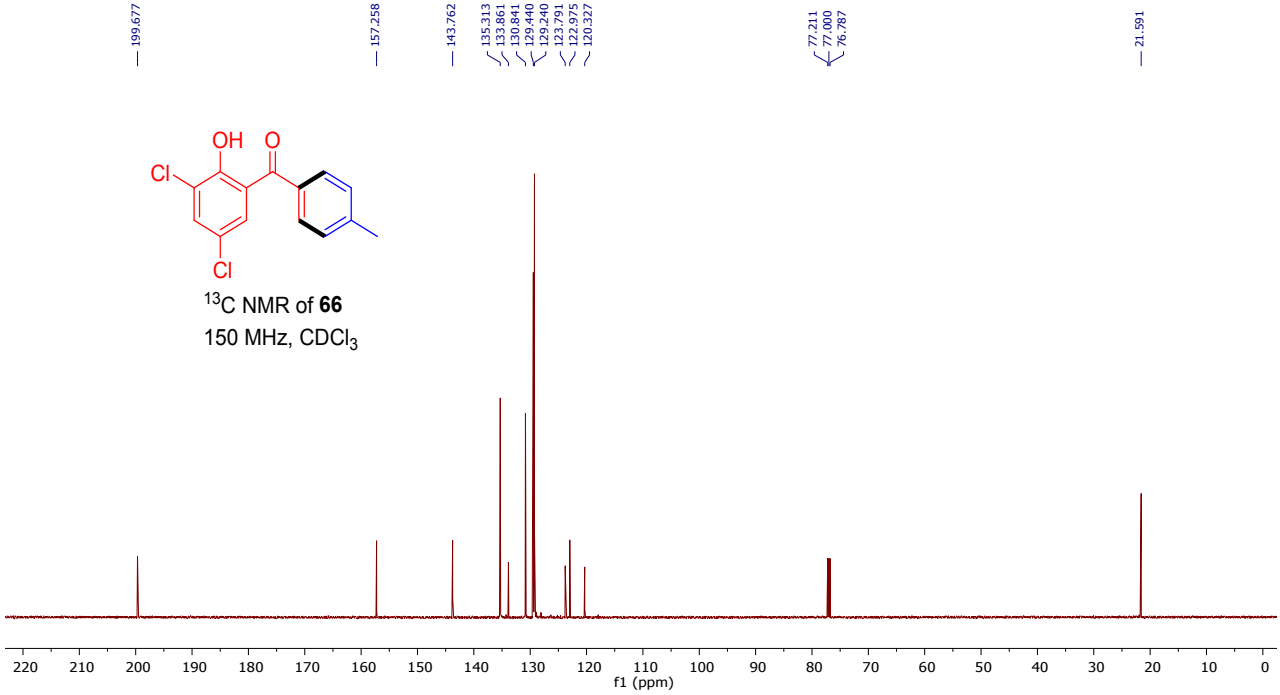
^{1}H NMR of **65**
600 MHz, $CDCl_3$



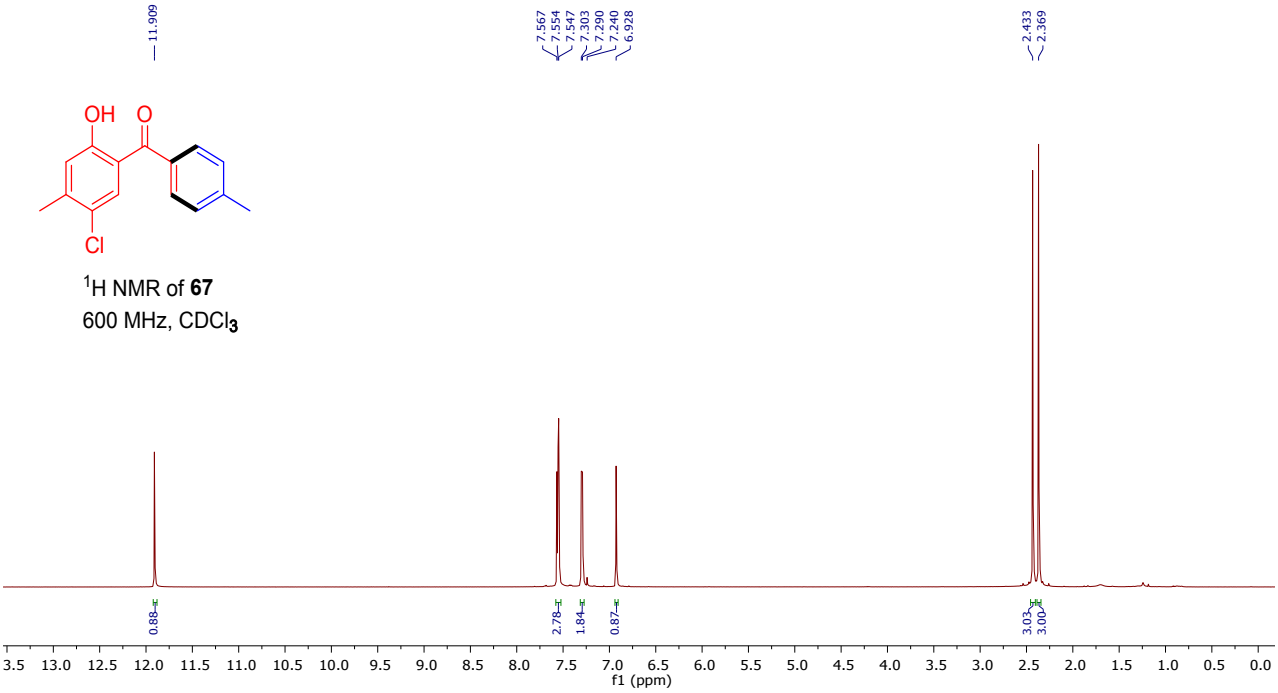
^{13}C NMR of **65**
150 MHz, $CDCl^3$



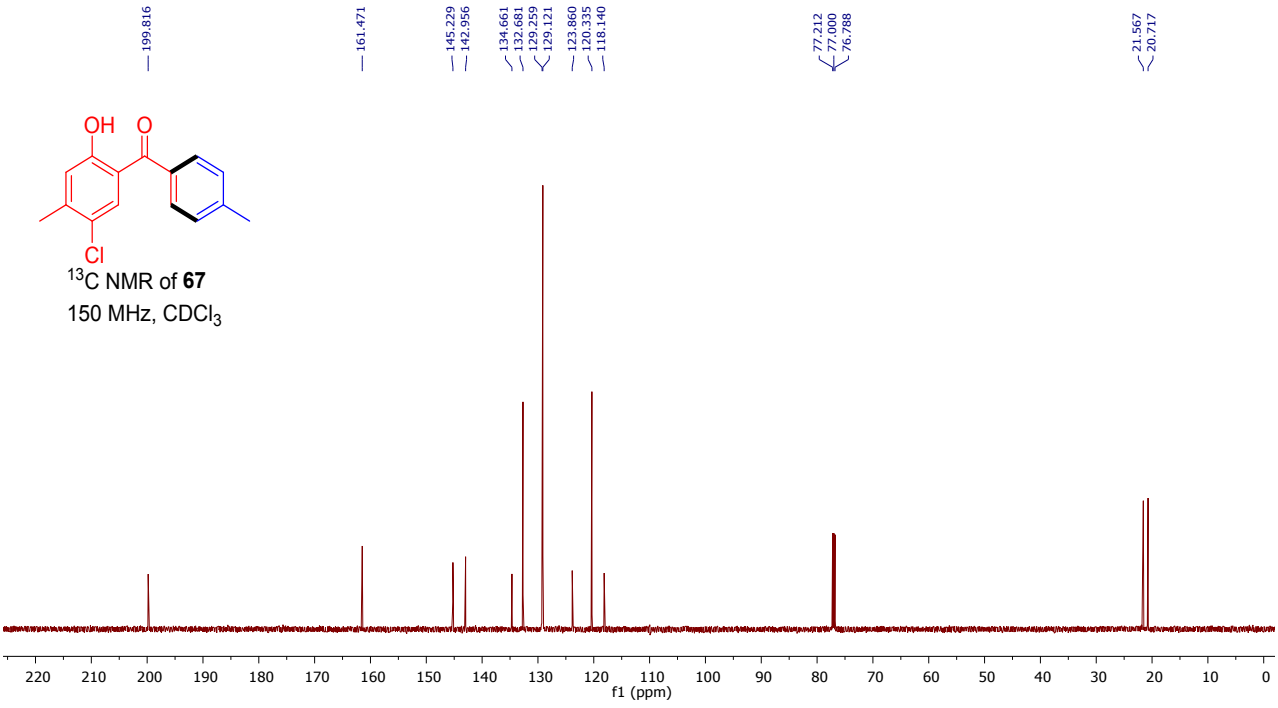
^{1}H NMR of **66**
600 MHz, $CDCl_3$



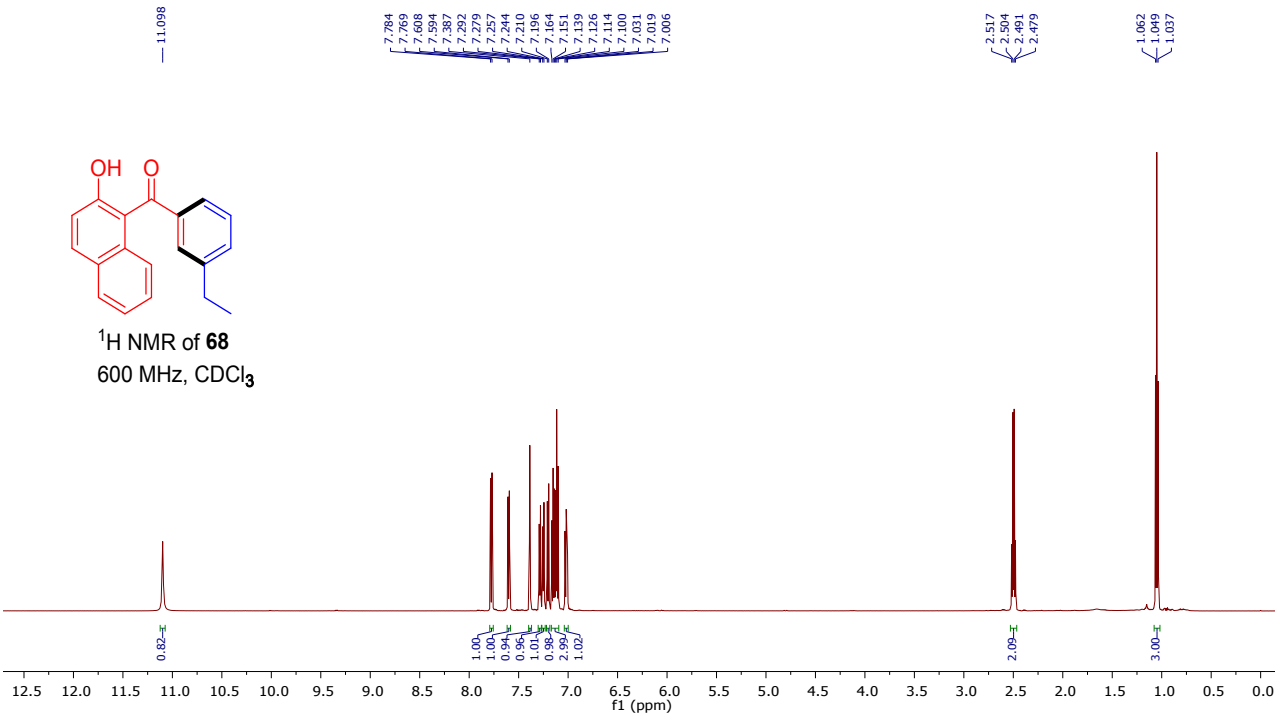
^{13}C NMR of **66**
150 MHz, $CDCl_3$



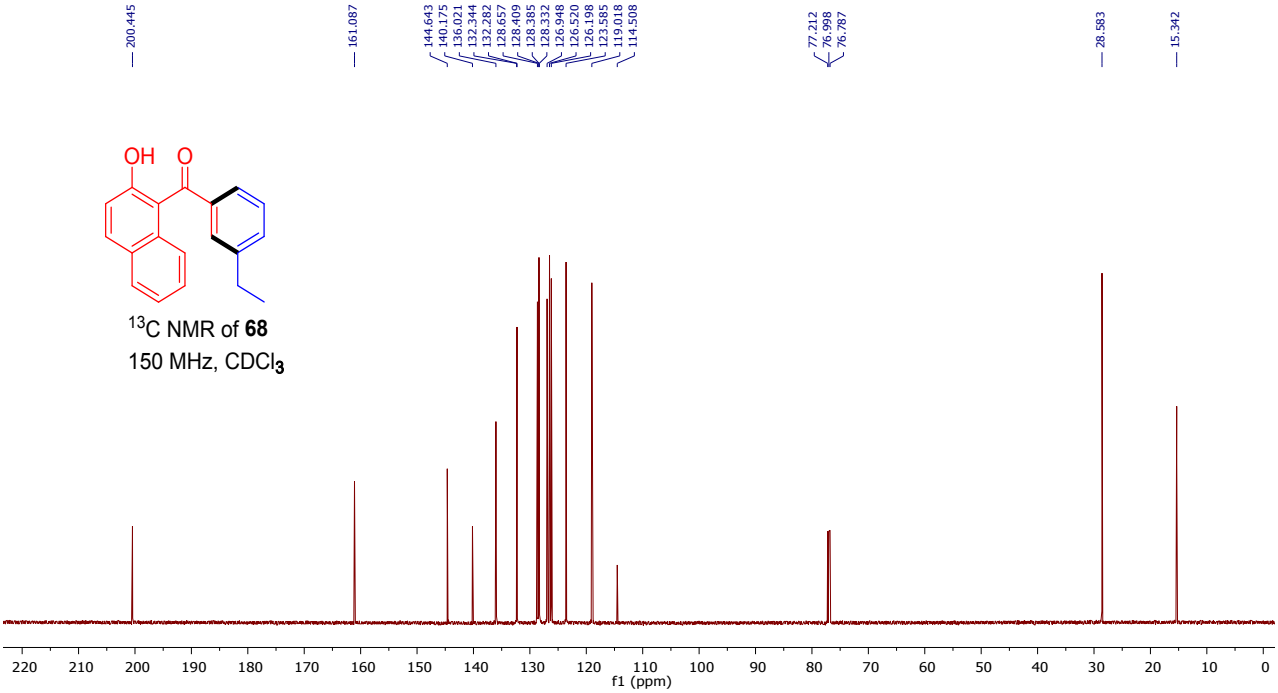
^{1}H NMR of **67**
600 MHz, $CDCl_3$



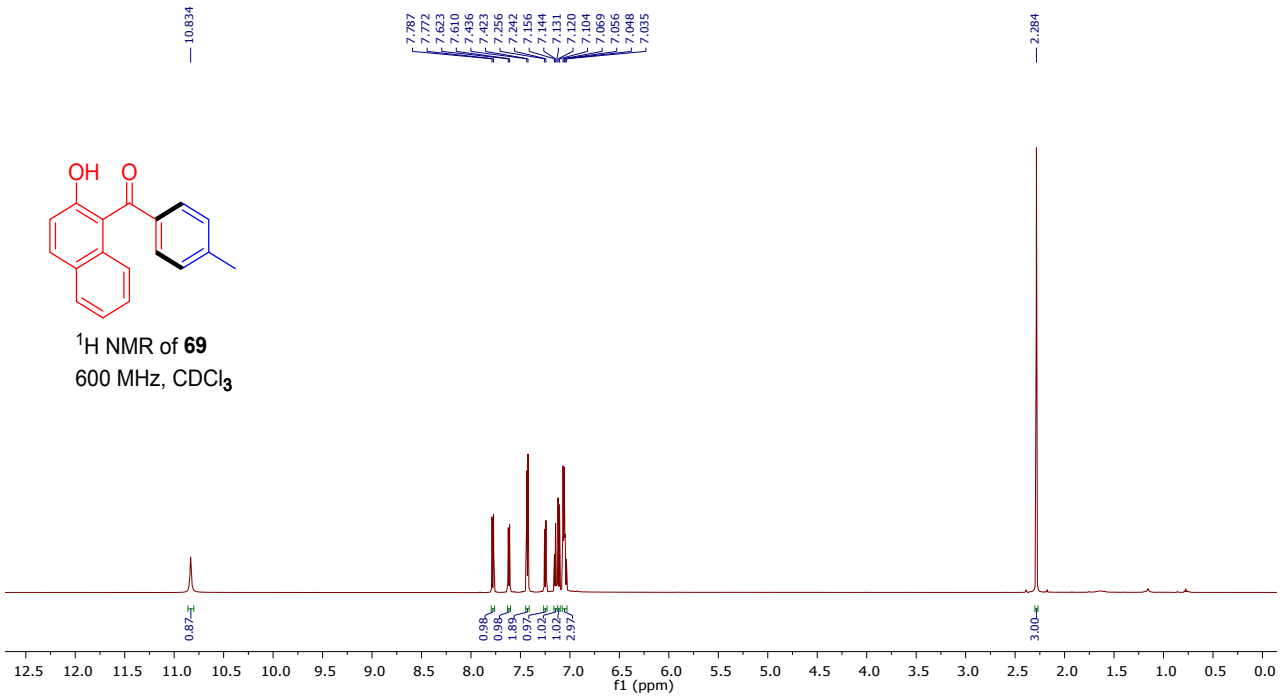
^{13}C NMR of **67**
150 MHz, $CDCl_3$



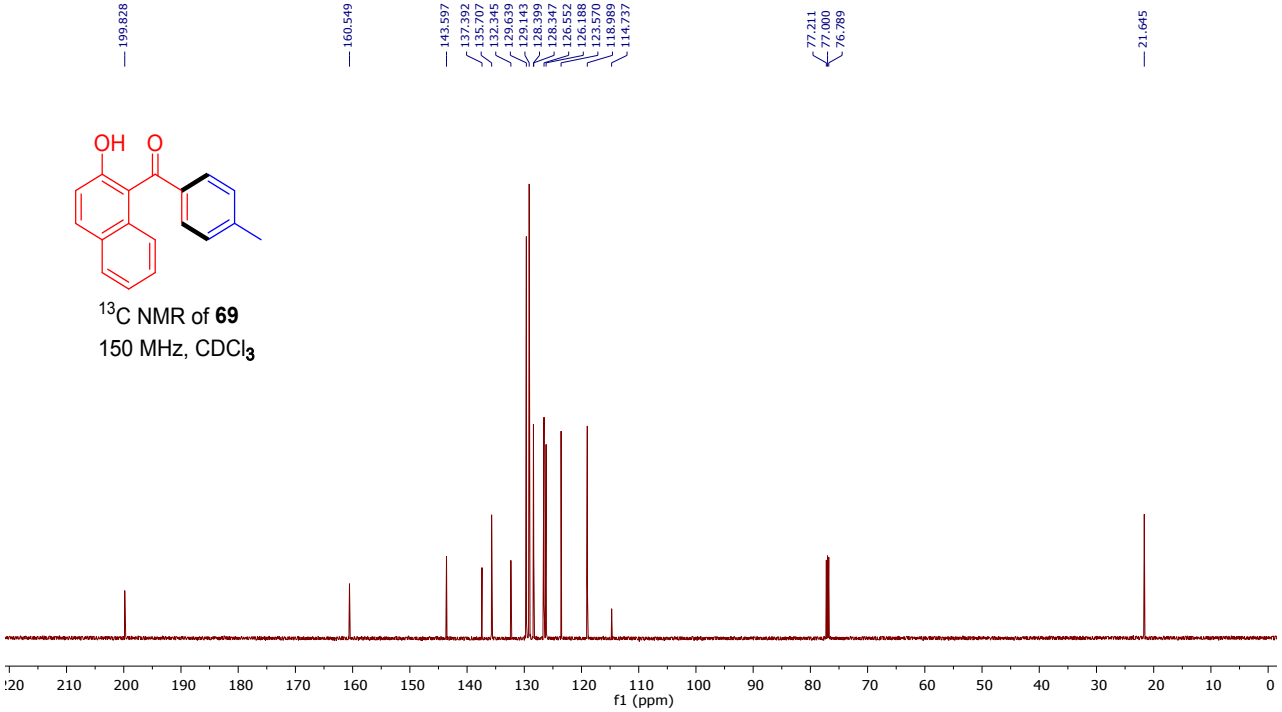
^{1}H NMR of **68**
600 MHz, $CDCl_3$



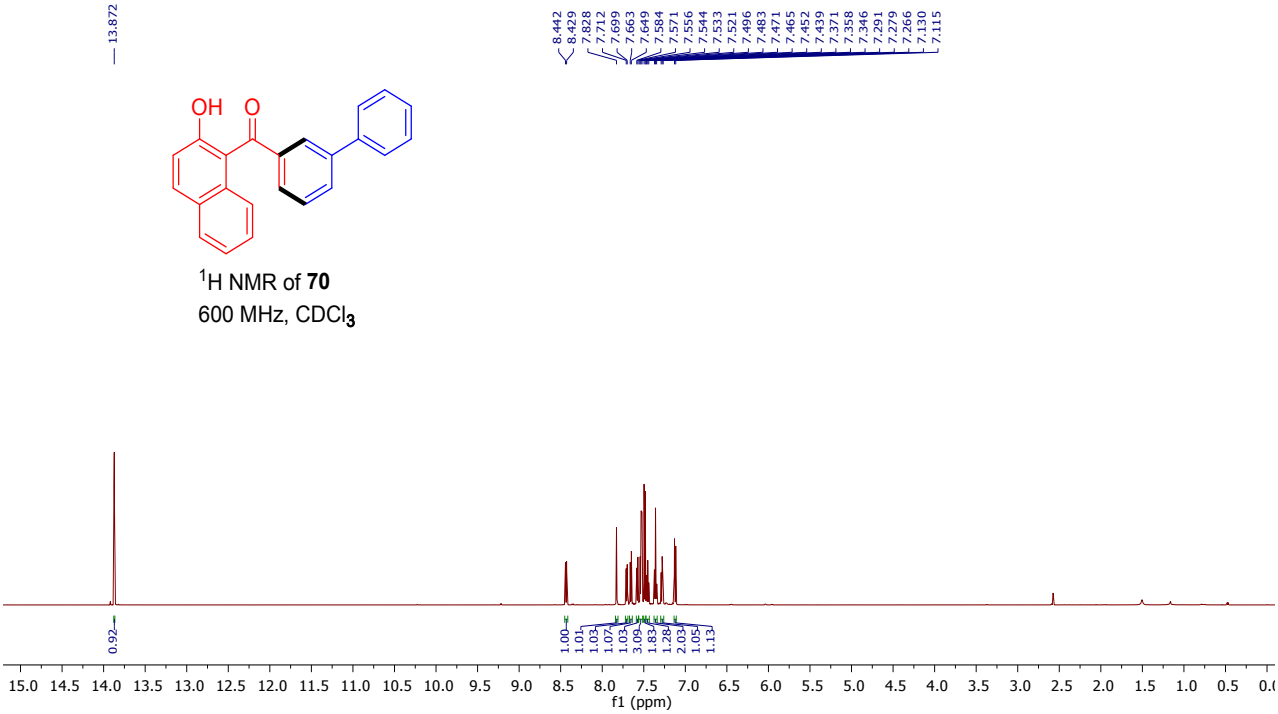
^{13}C NMR of **68**
150 MHz, $CDCl_3$



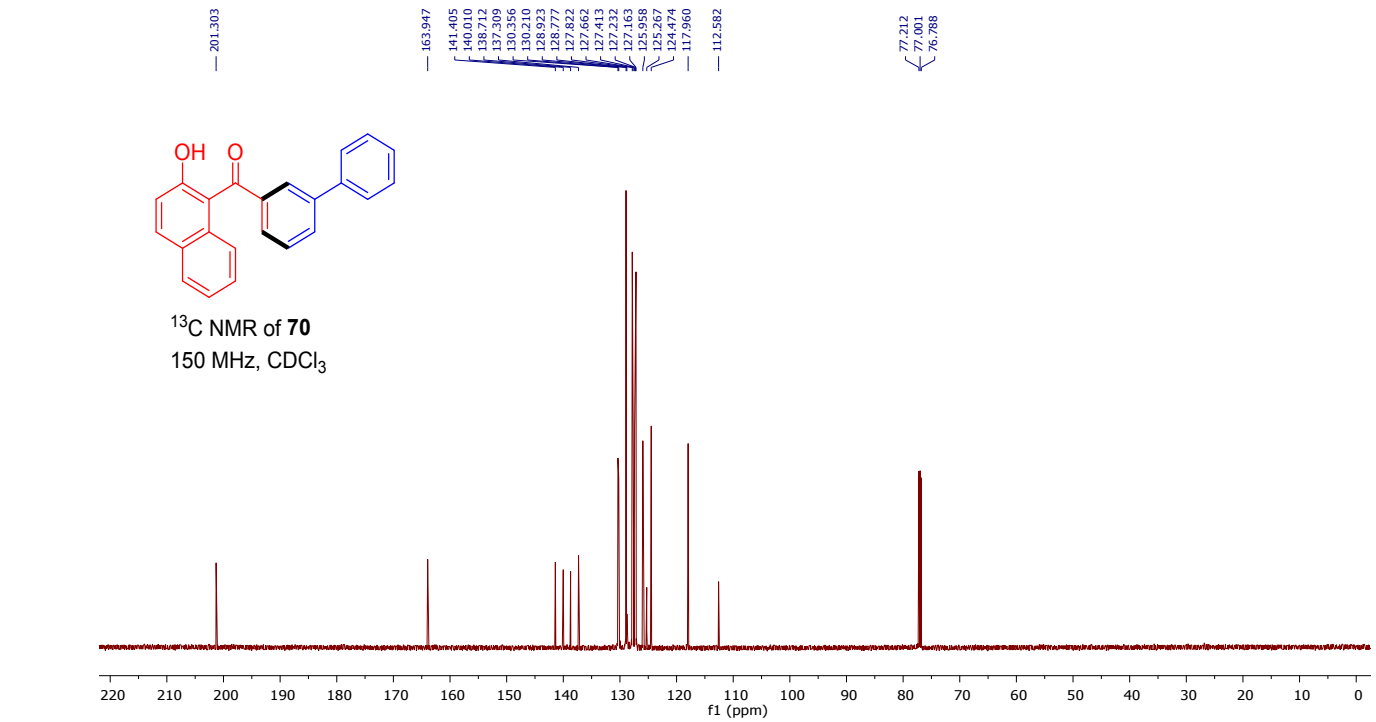
^{1}H NMR of **69**
600 MHz, $CDCl_3$



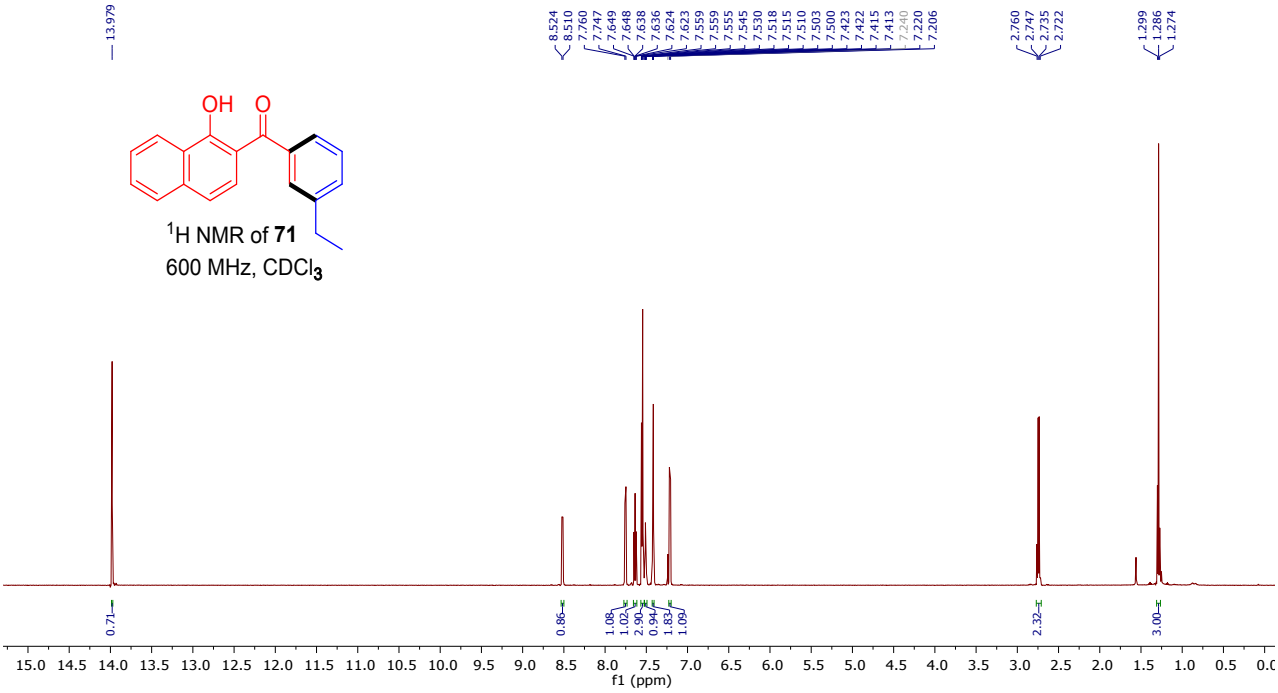
^{13}C NMR of **69**
150 MHz, $CDCl_3$

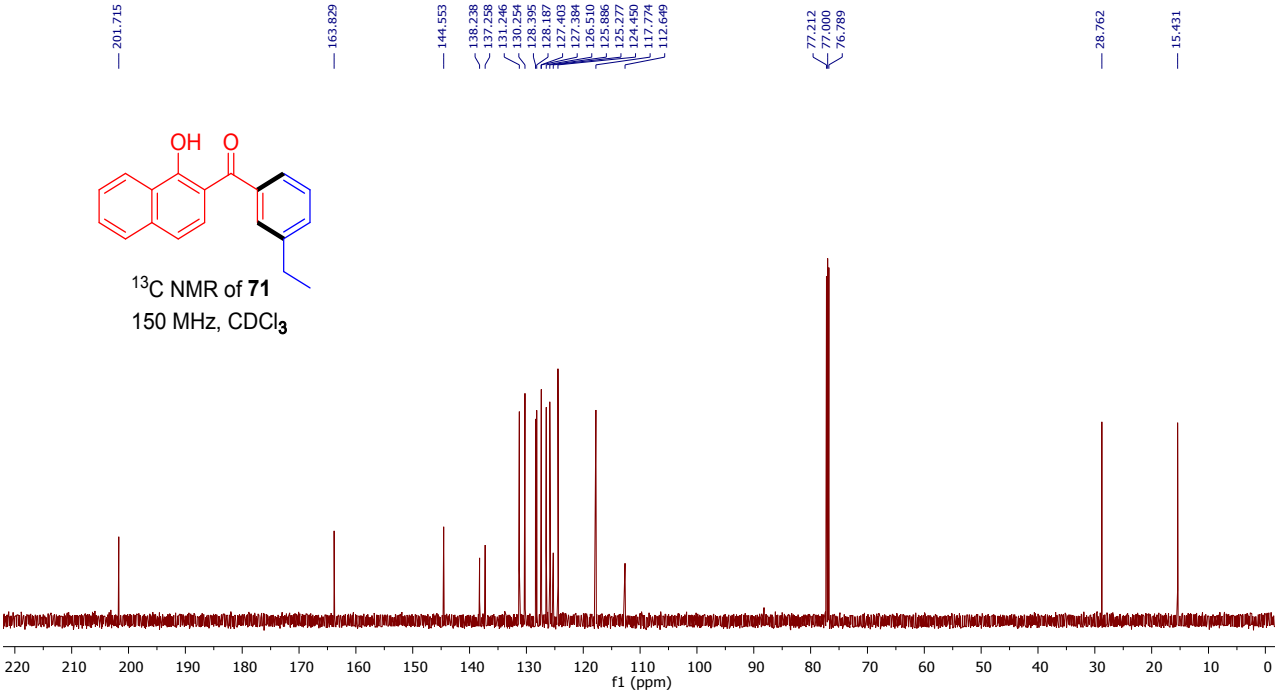


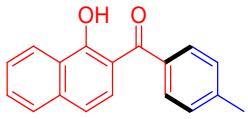
^{1}H NMR of **70**
600 MHz, $CDCl_3$



^{13}C NMR of **70**
150 MHz, $CDCl_3$

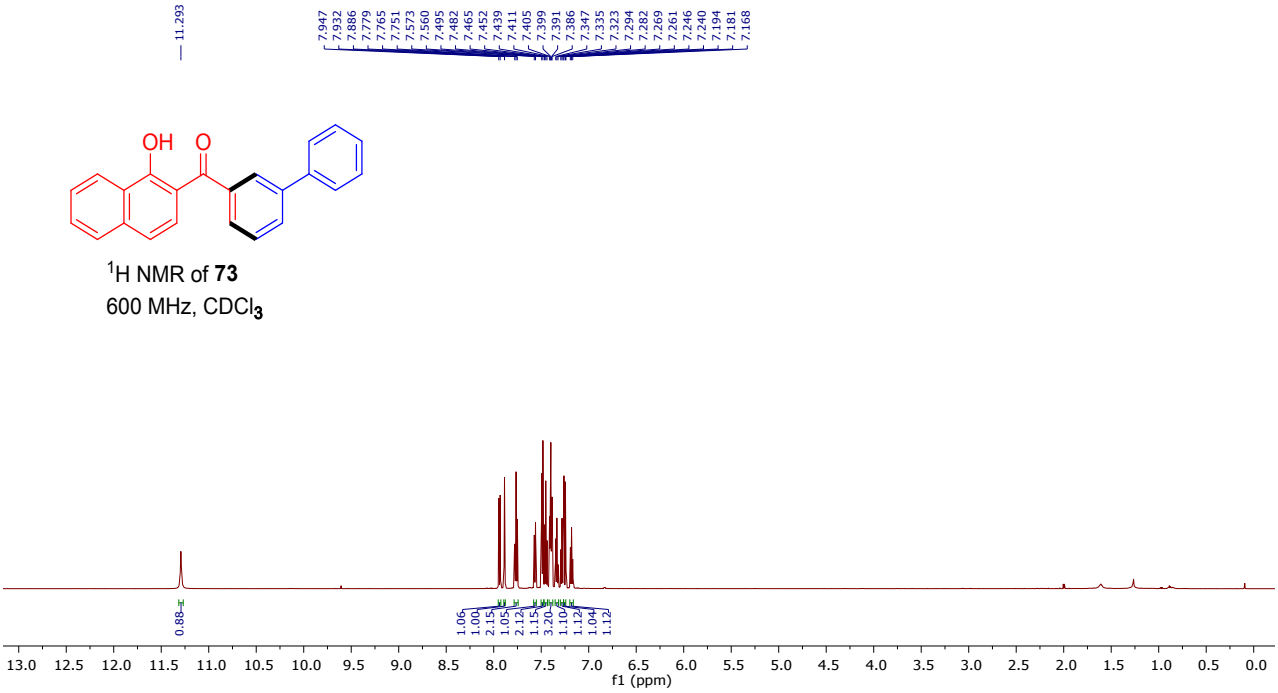

OH
O
^{1}H NMR of **71**
600 MHz, $CDCl_3$
f1 (ppm)


OH
O
^{13}C NMR of **71**
150 MHz, $CDCl_3$
f1 (ppm)

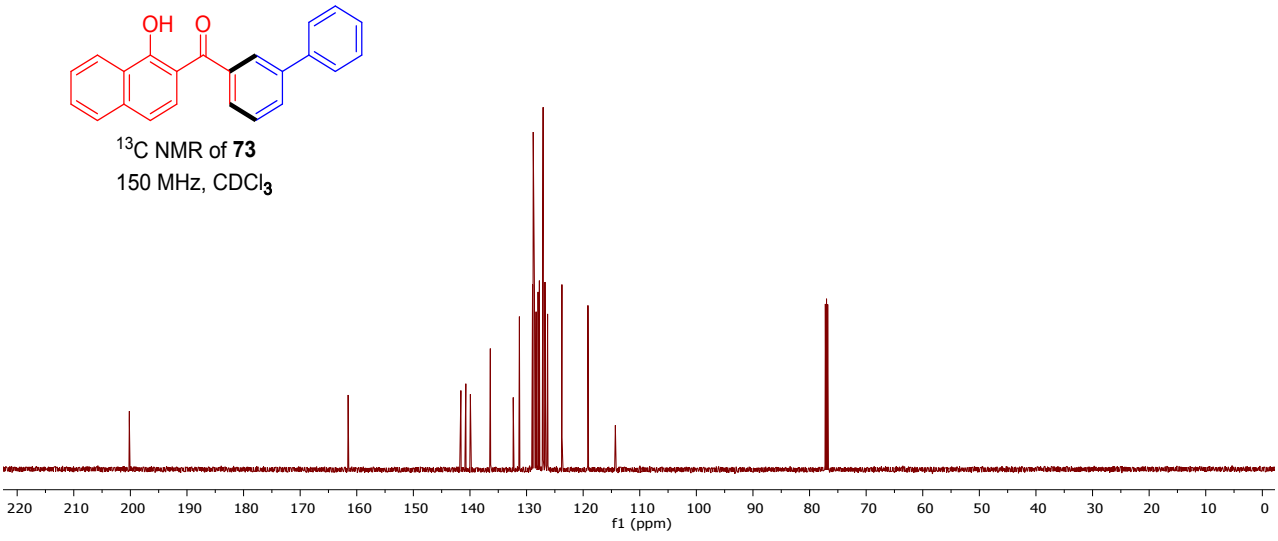


^{1}H NMR of **72**
600 MHz, $CDCl_3$

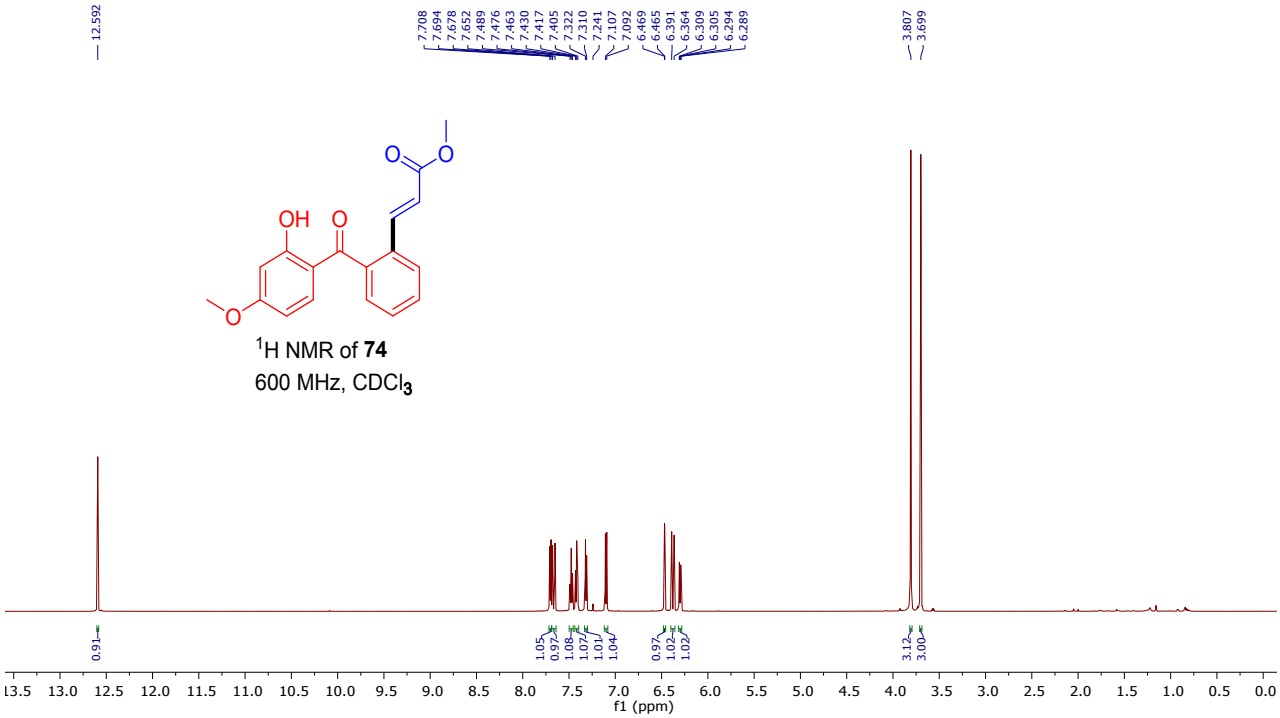
^{13}C NMR of **72**
150 MHz, $CDCl_3$



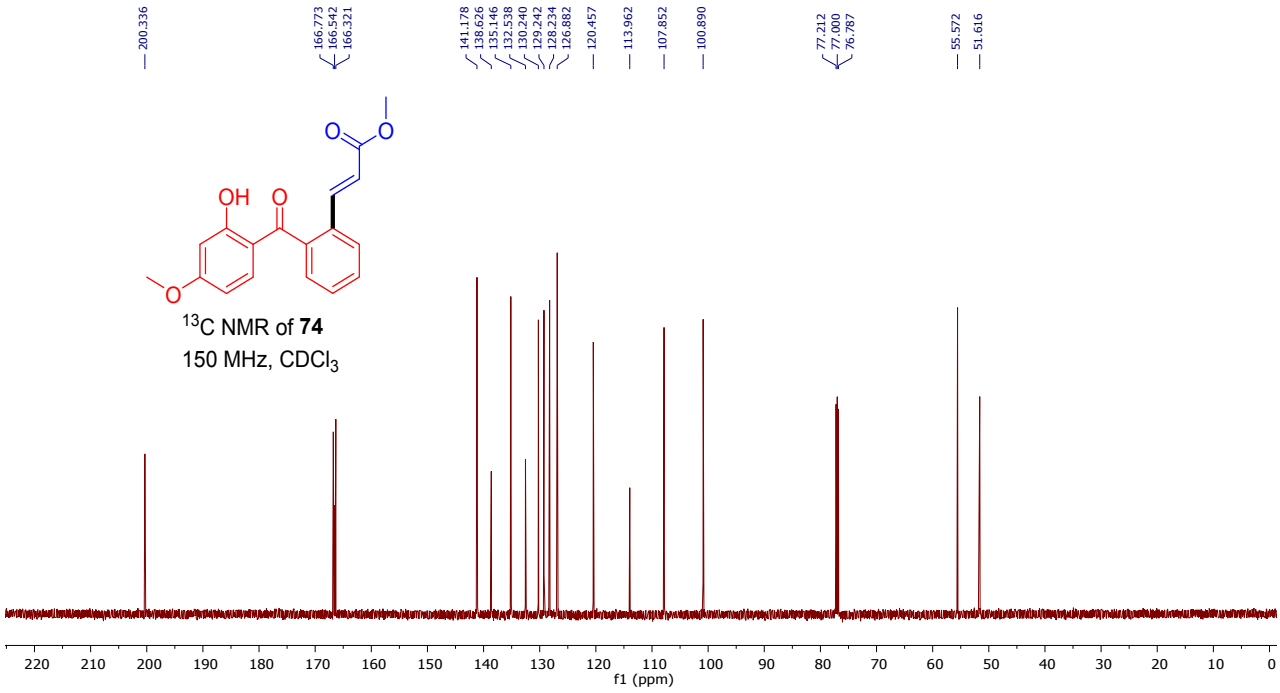
^{1}H NMR of **73**
600 MHz, $CDCl_3$



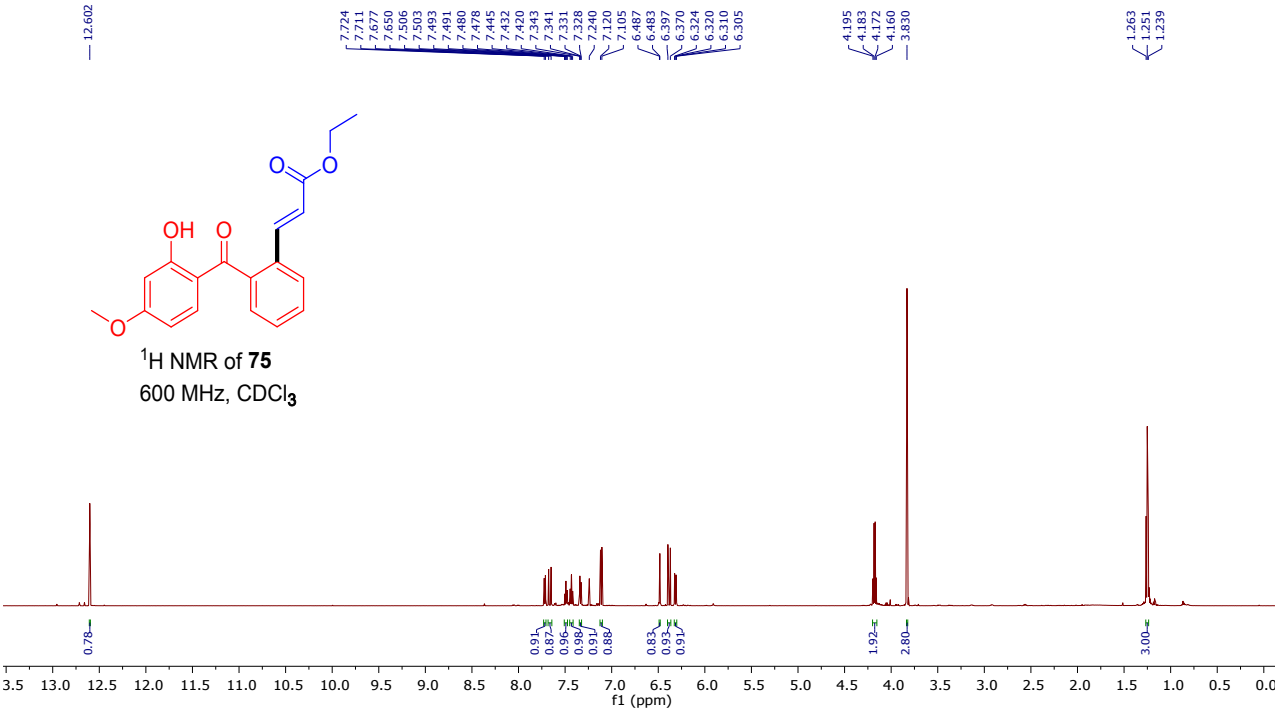
^{13}C NMR of **73**
150 MHz, $CDCl_3$



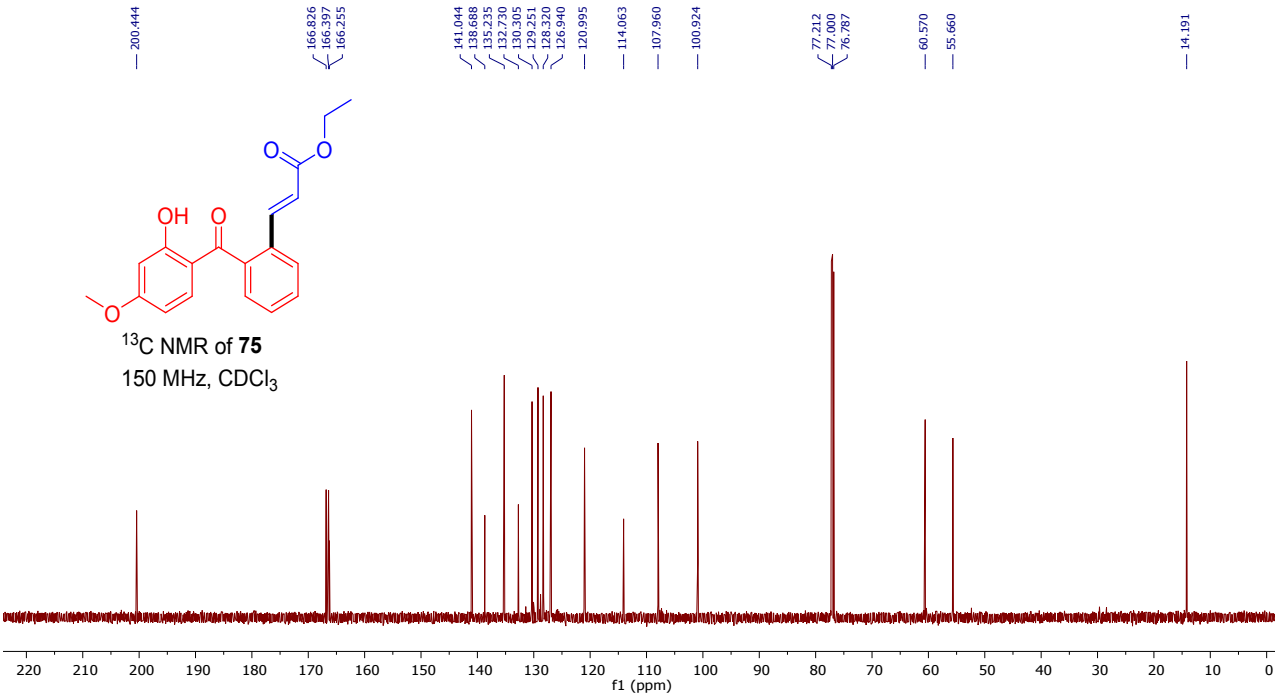
^{1}H NMR of **74**
600 MHz, $CDCl_3$



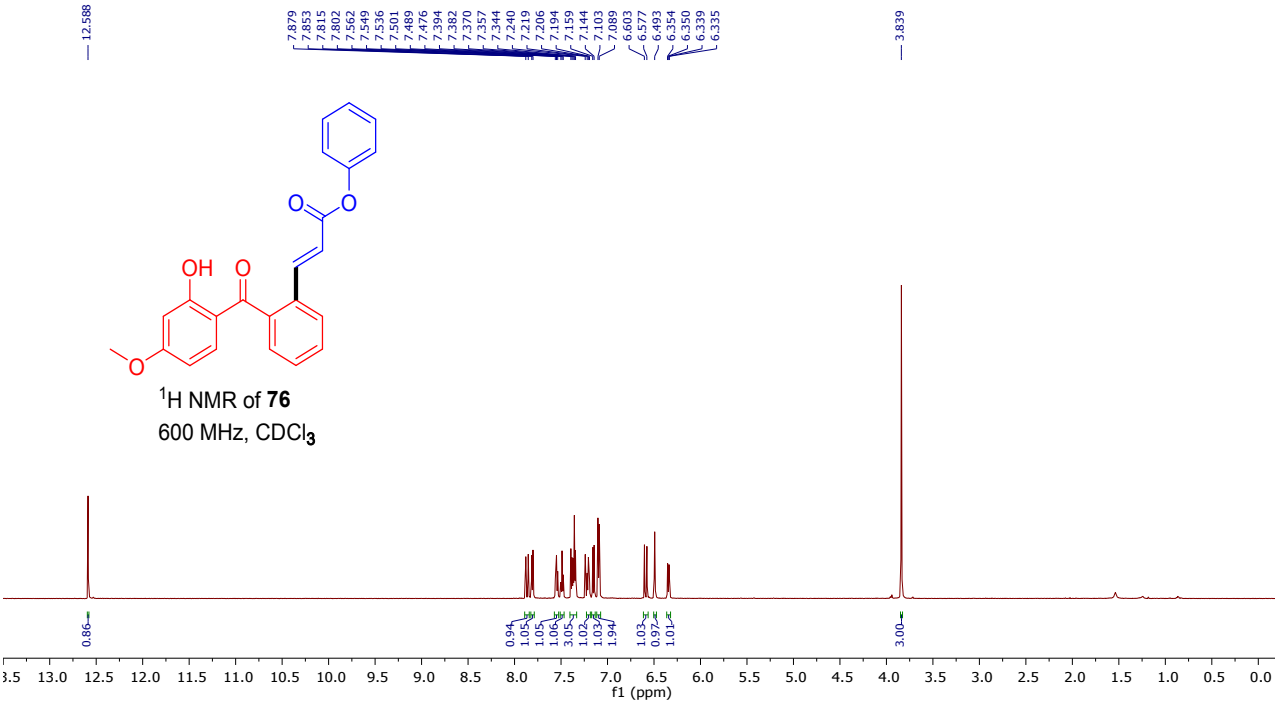
^{13}C NMR of **74**
150 MHz, $CDCl_3$



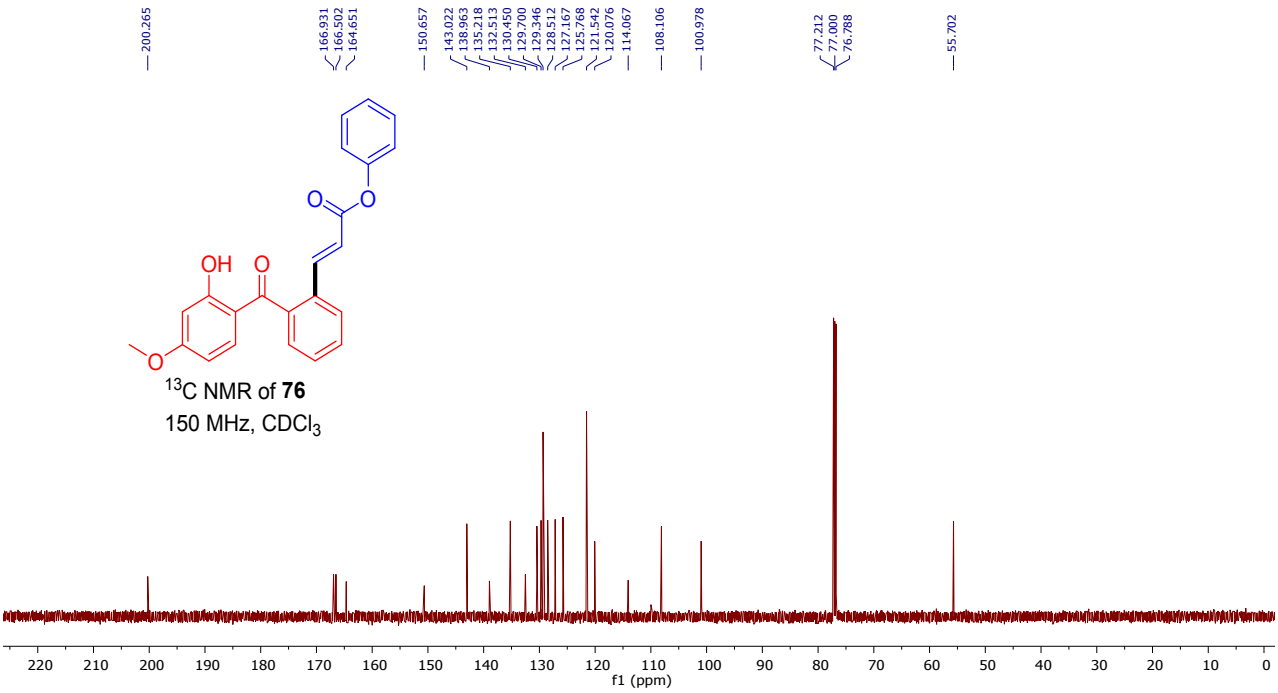
^{1}H NMR of **75**
600 MHz, $CDCl_3$



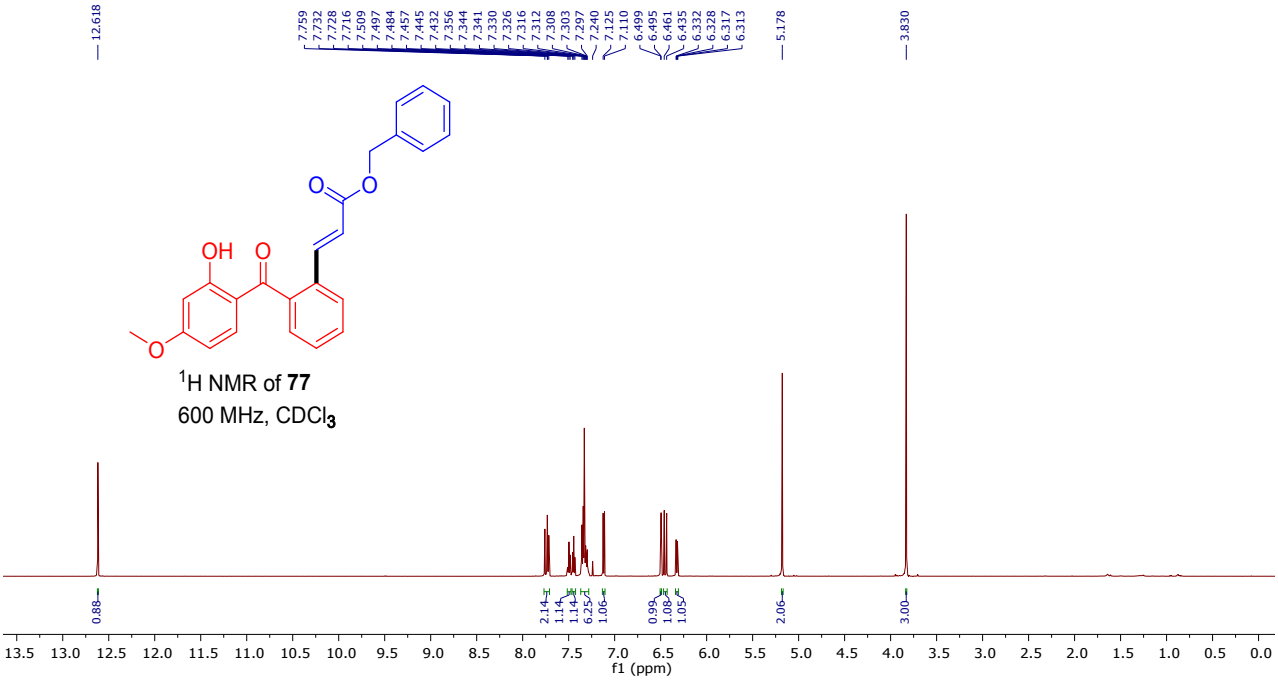
^{13}C NMR of **75**
150 MHz, $CDCl_3$



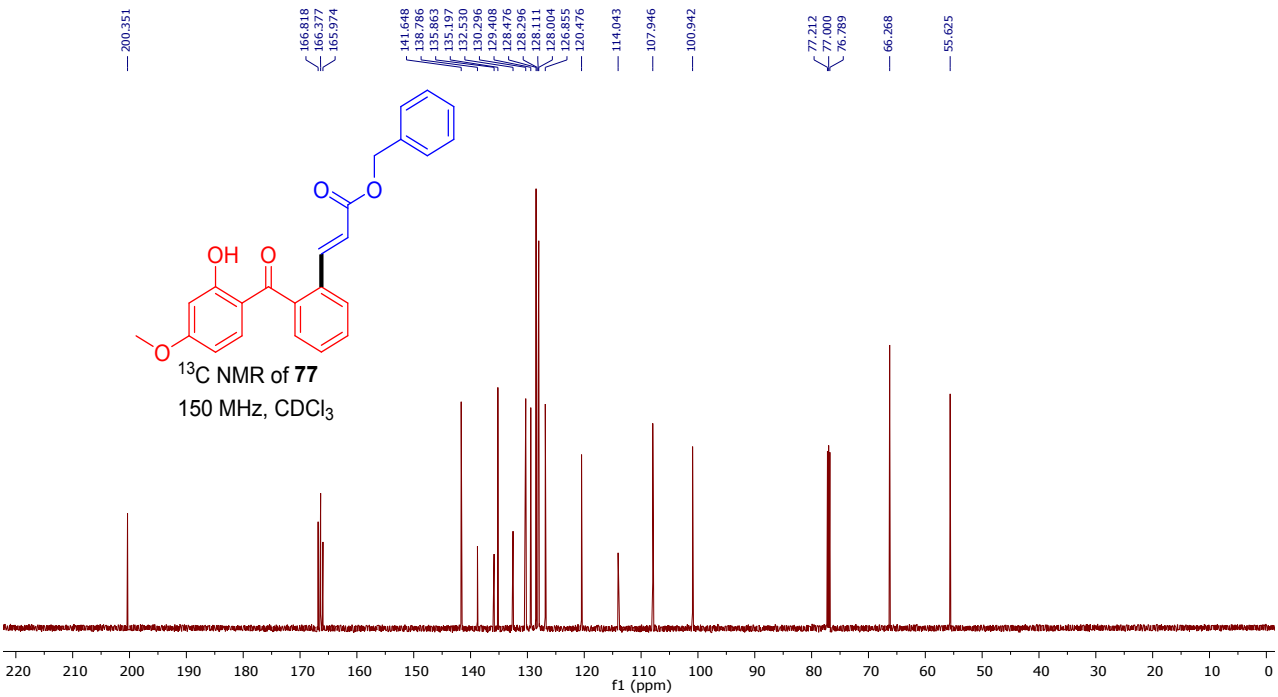
^{1}H NMR of **76**
600 MHz, $CDCl_3$



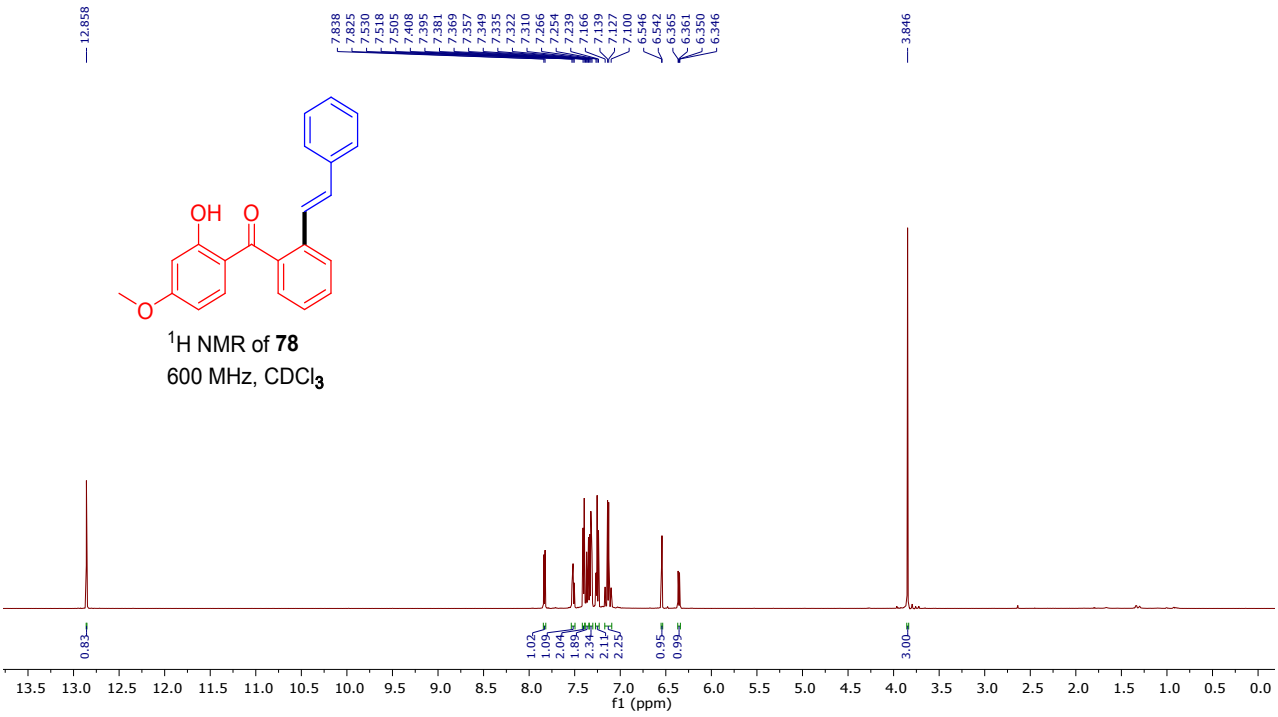
^{13}C NMR of **76**
150 MHz, $CDCl_3$



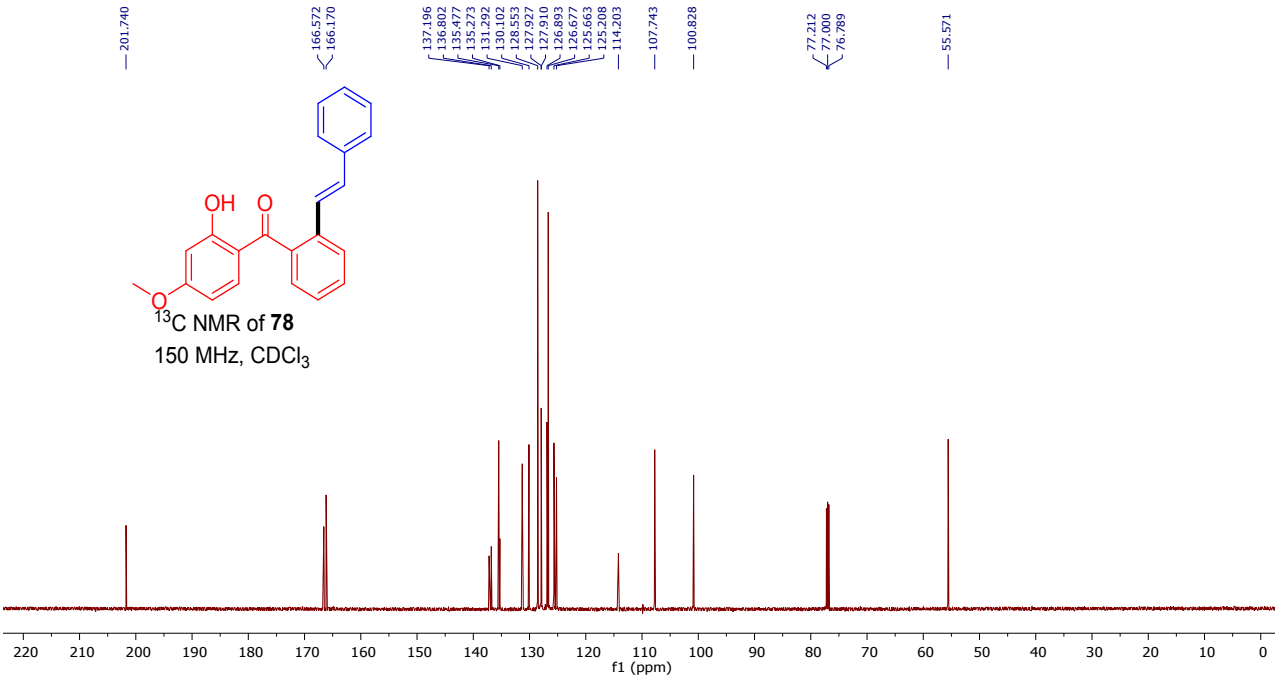
^{1}H NMR of **77**
600 MHz, $CDCl_3$



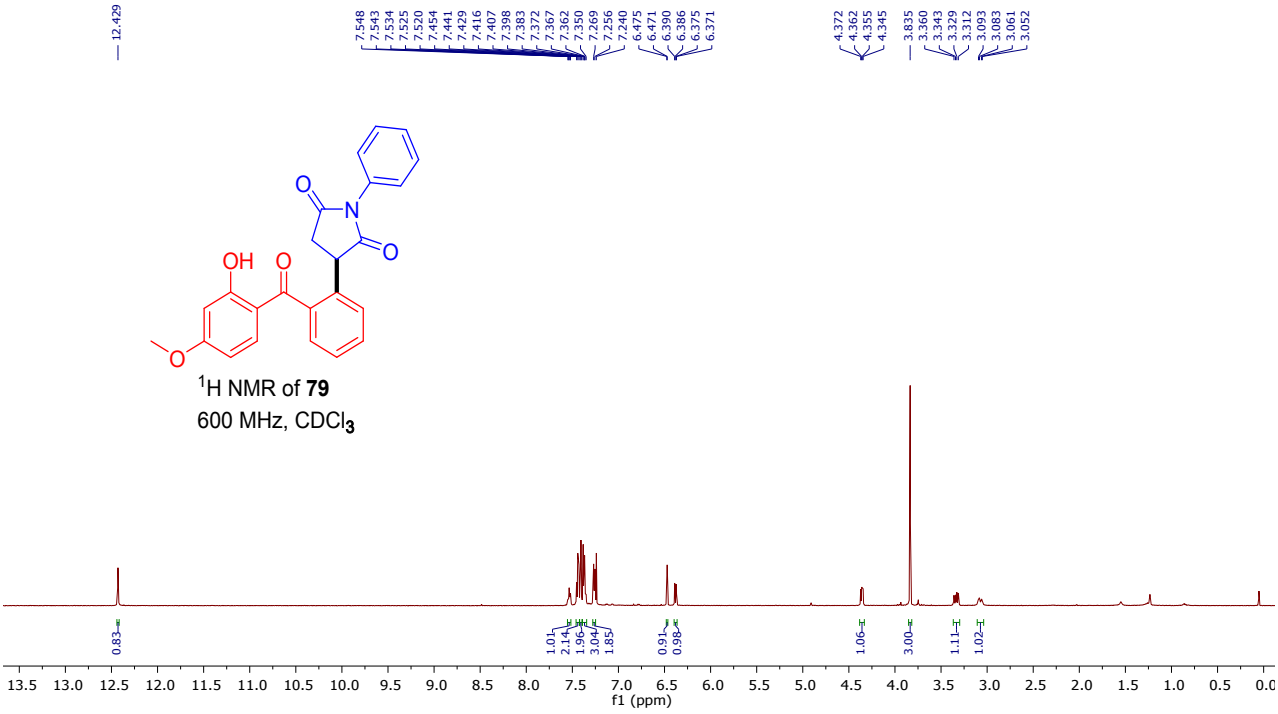
^{13}C NMR of **77**
150 MHz, $CDCl_3$



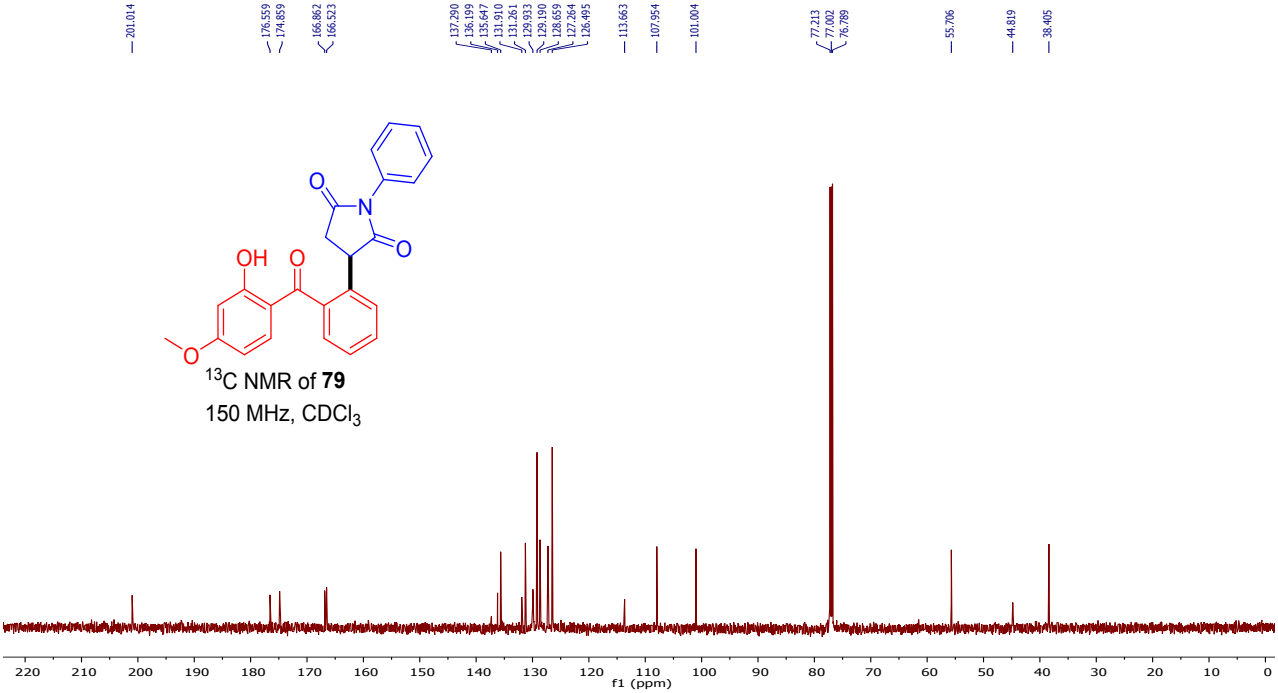
^{1}H NMR of **78**
600 MHz, $CDCl_3$



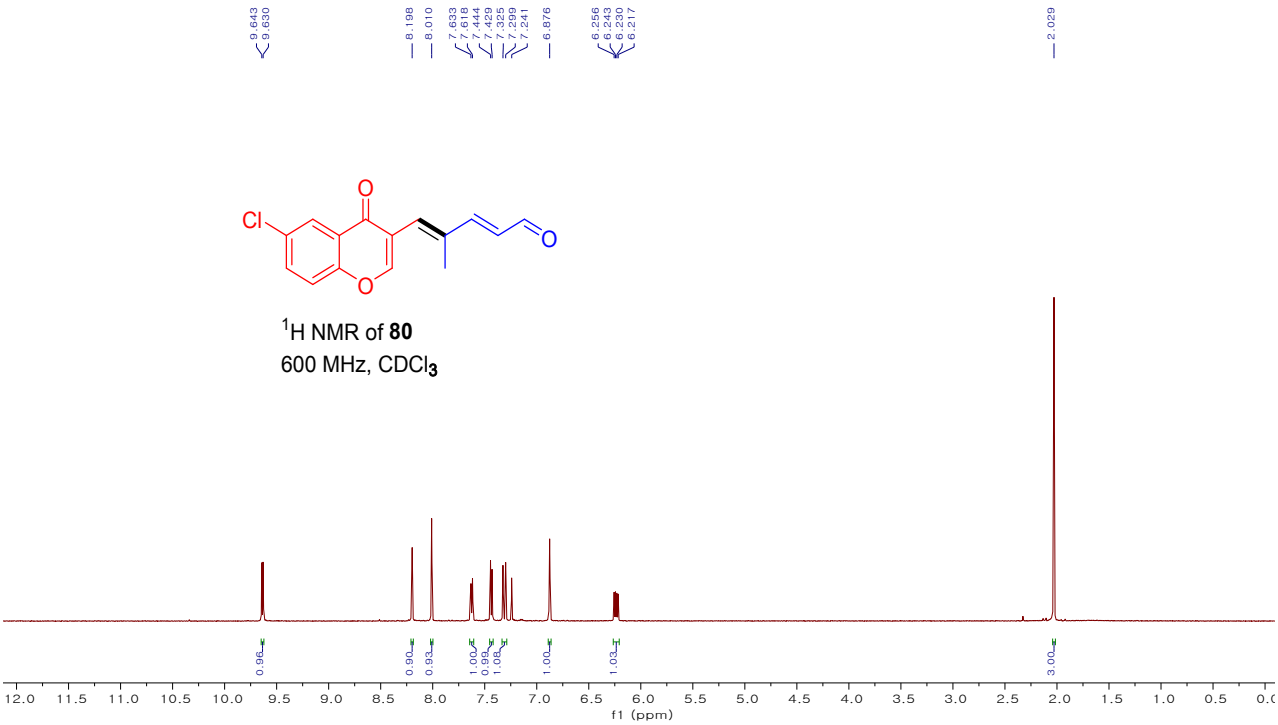
^{13}C NMR of **78**
150 MHz, $CDCl_3$



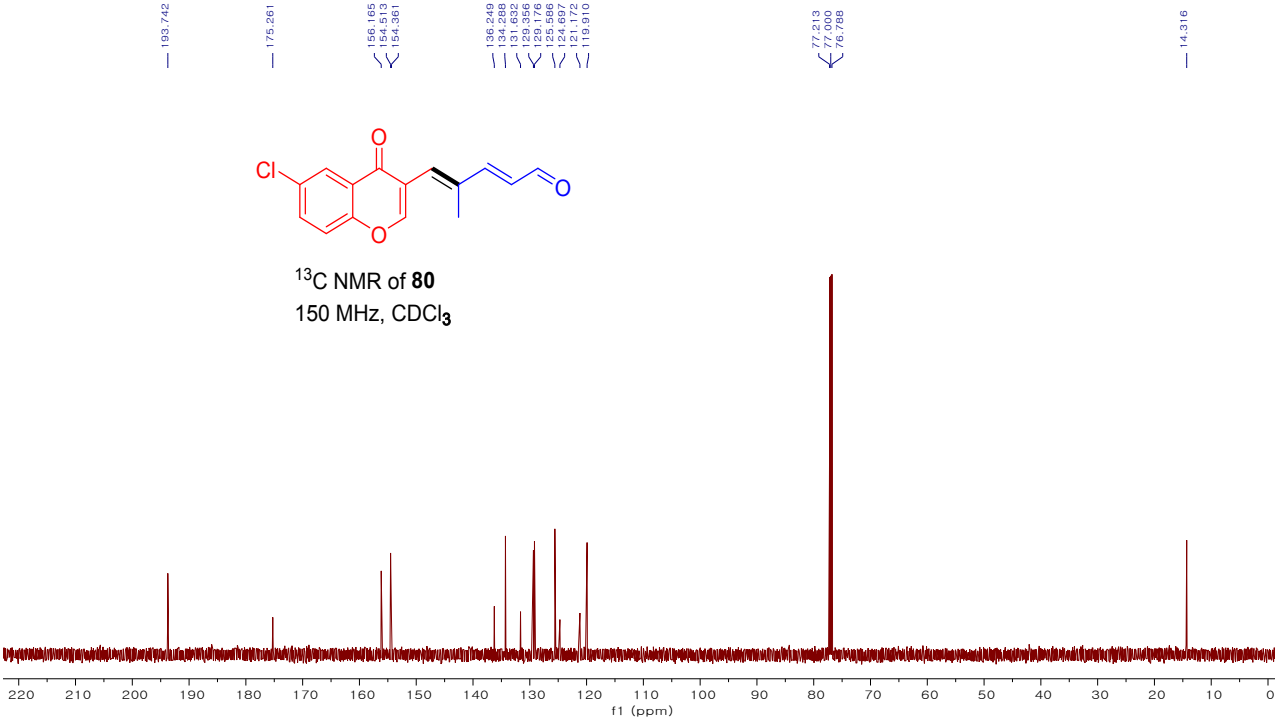
^{1}H NMR of **79**
600 MHz, $CDCl_3$



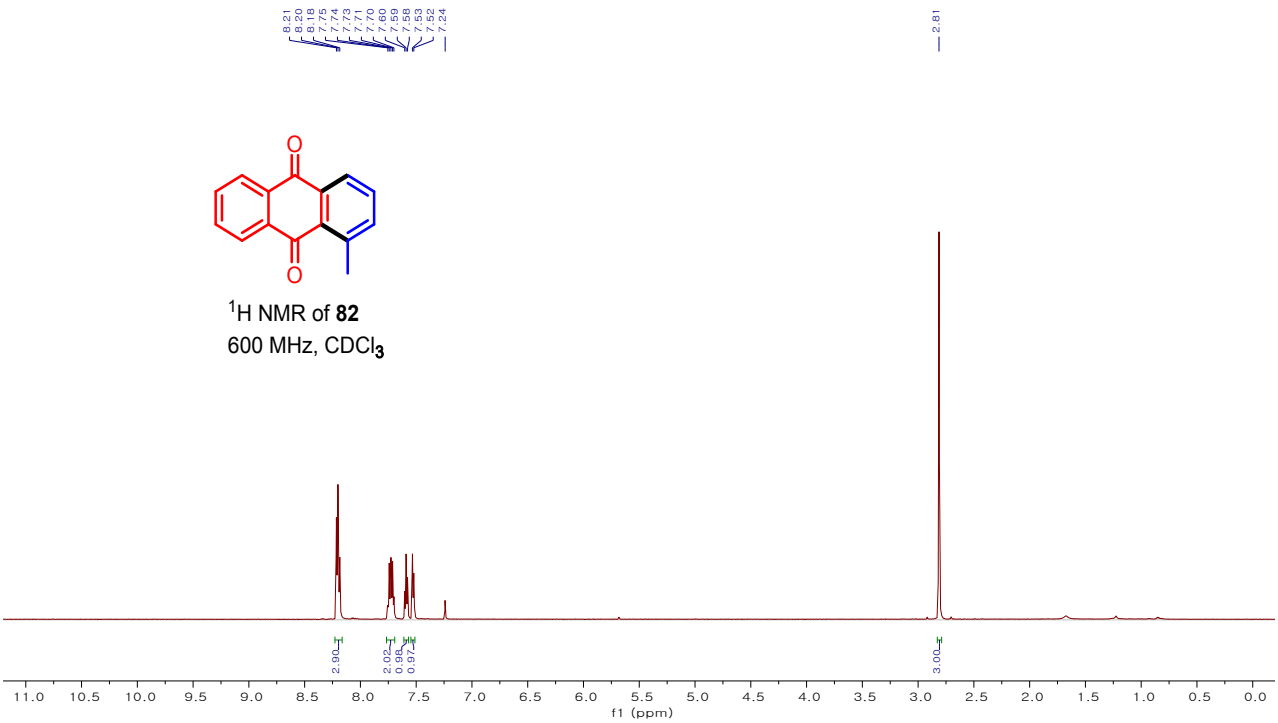
^{13}C NMR of **79**
150 MHz, $CDCl_3$



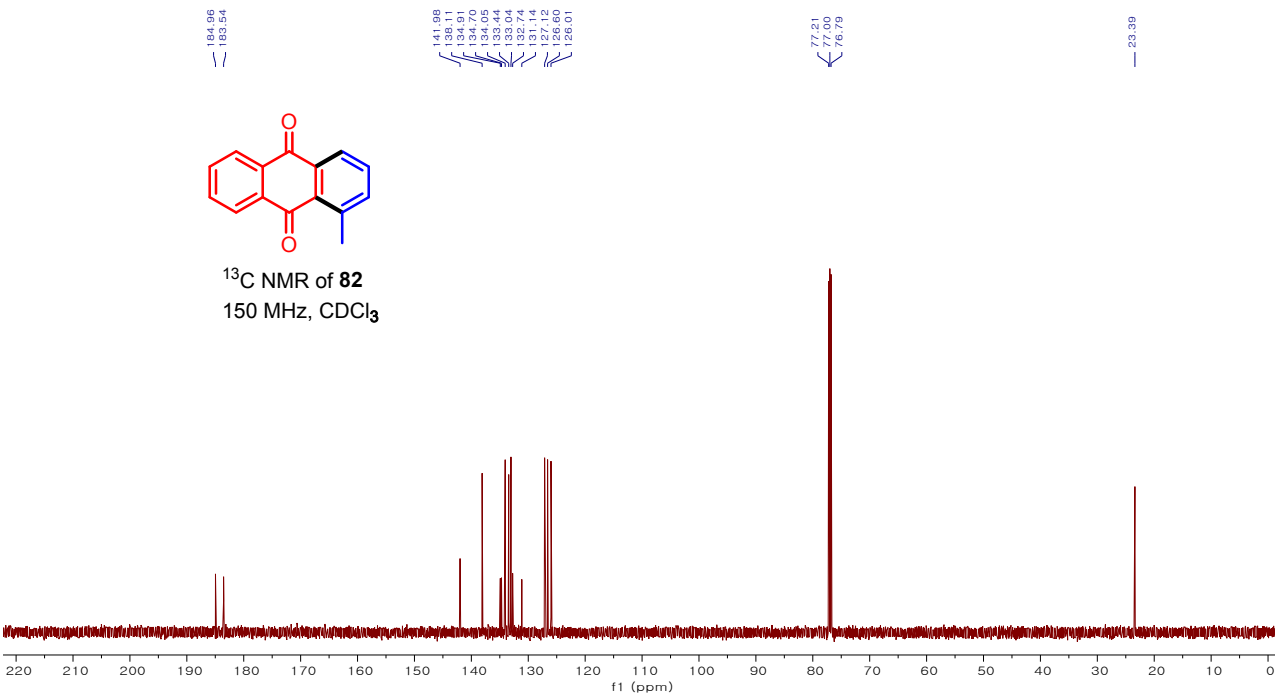
^{1}H NMR of **80**
600 MHz, $CDCl_3$



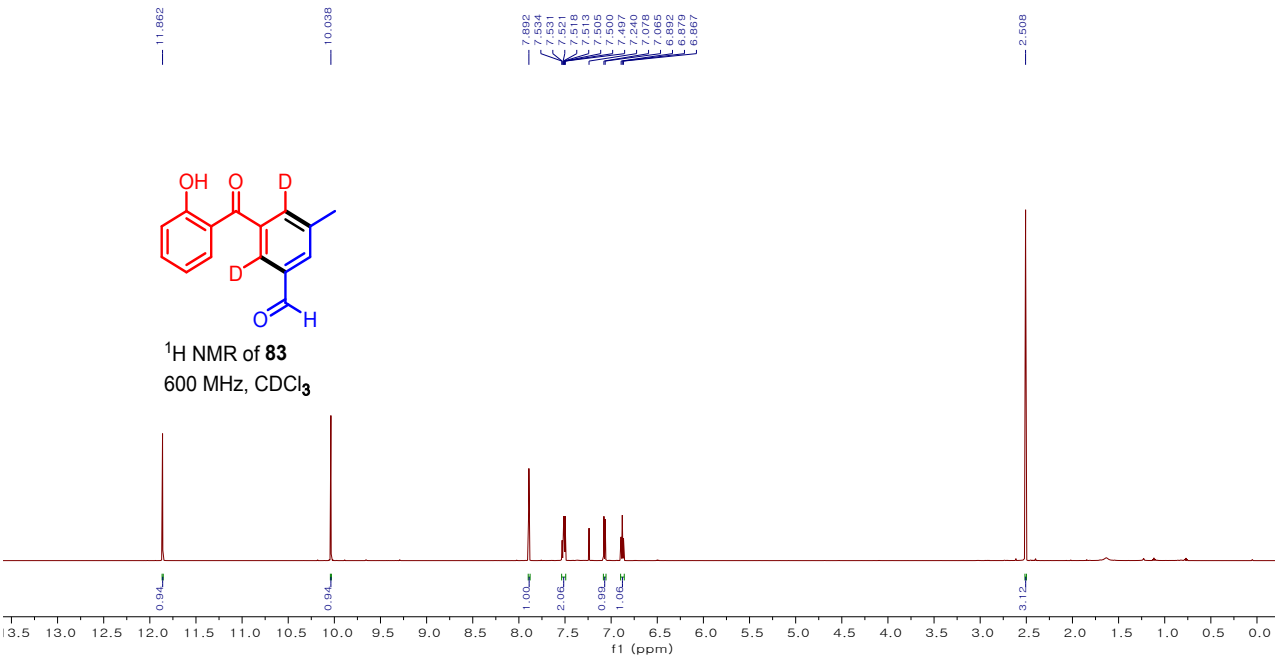
^{13}C NMR of **80**
150 MHz, $CDCl_3$



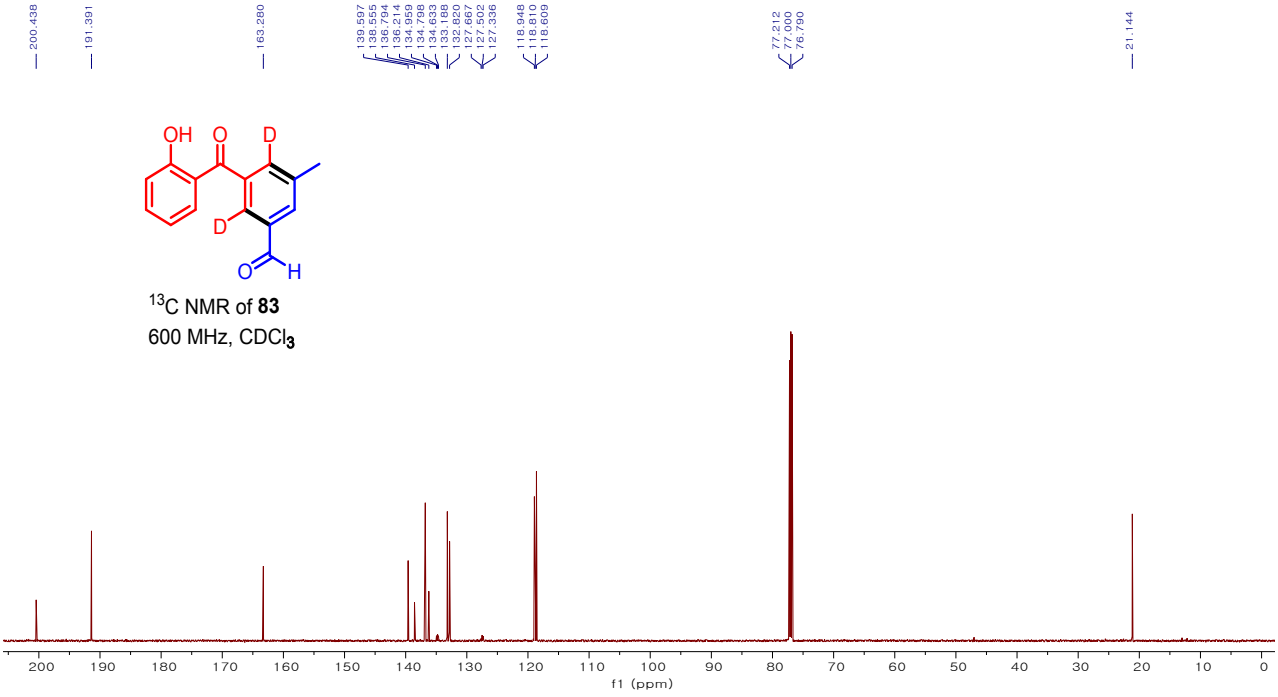
^{1}H NMR of **82**
600 MHz, $CDCl_3$



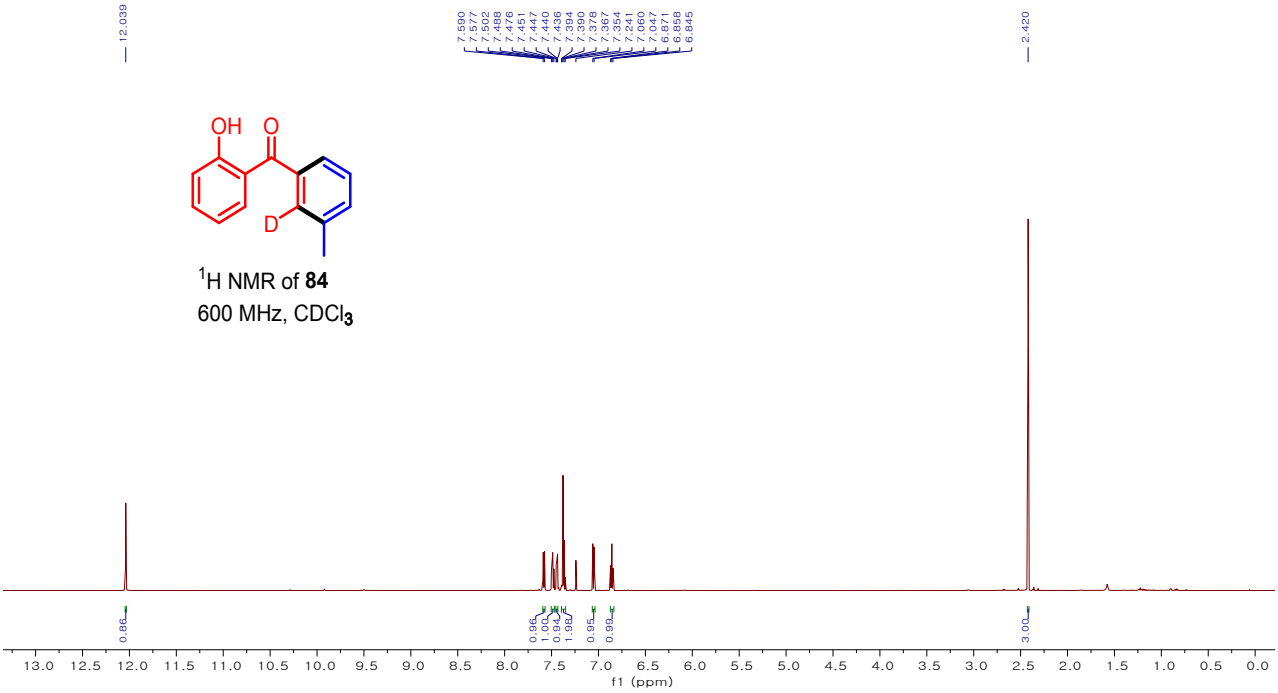
^{13}C NMR of **82**
150 MHz, $CDCl_3$



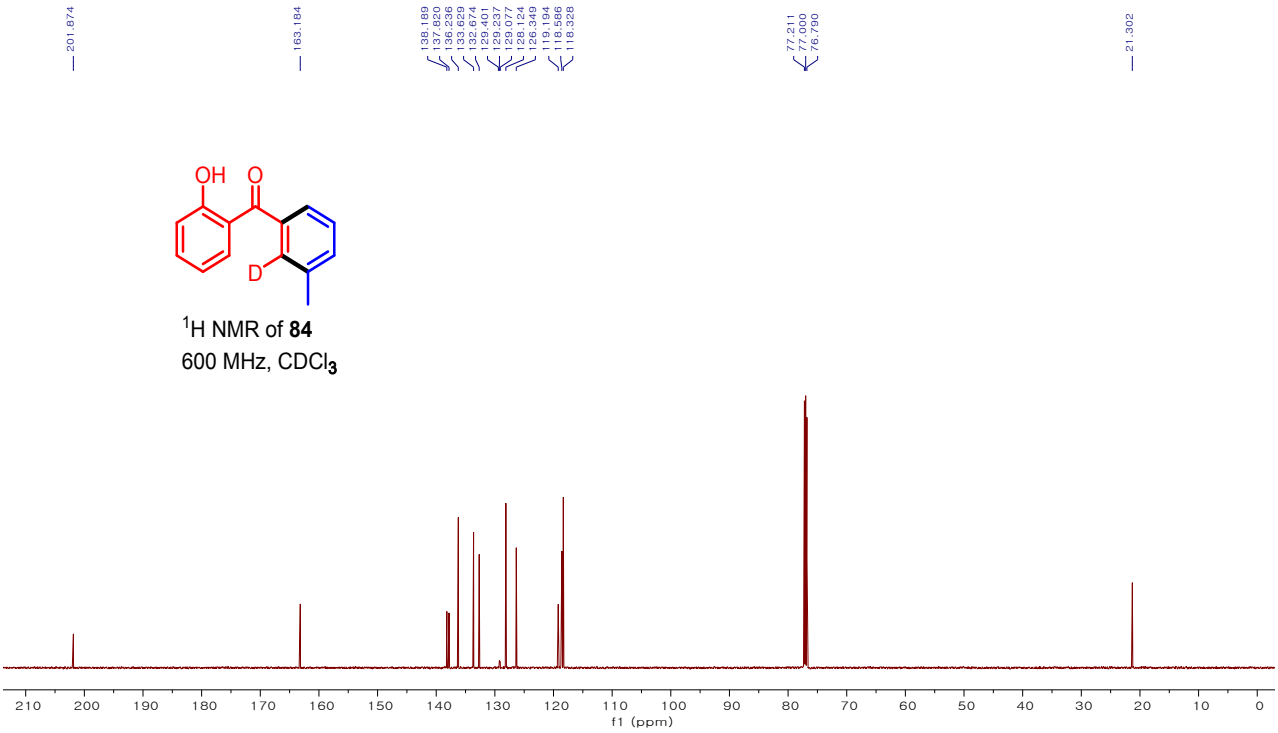
^{1}H NMR of **83**
600 MHz, $CDCl_3$



^{13}C NMR of **83**
600 MHz, $CDCl_3$



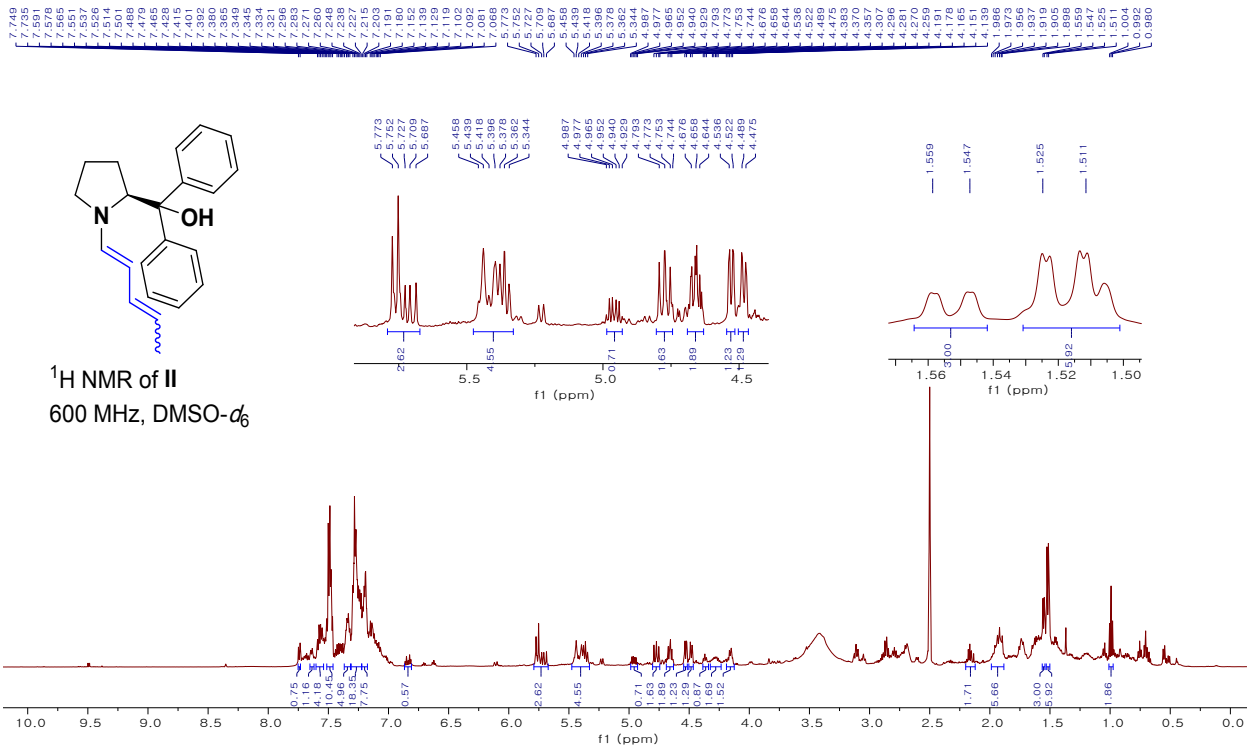
^{1}H NMR of **84**
600 MHz, $CDCl_3$



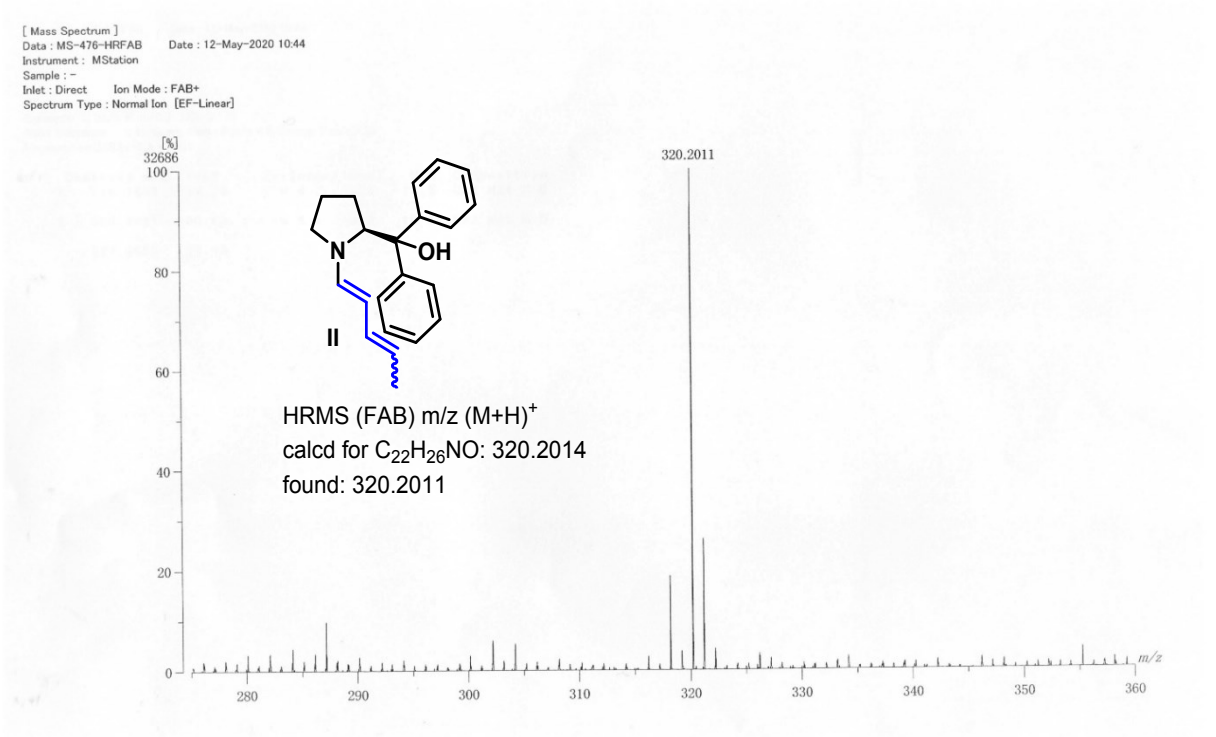
^{1}H NMR of **84**
600 MHz, $CDCl_3$

The intermediate **II** could not be isolated by column chromatography, but was confirmed by NMR study through mixing of **2a** and Cat. **II** in DMSO-d_6. In the ^{1}H NMR of the mixture, an aldehyde peak of **2a** was disappeared and newly-made double bond peaks adjacent to the methyl peak in related to intermediate **II** were shown. The formation of **II** was also confirmed by HRMS analysis.

The ^{1}H NMR spectra of crude reaction mixture for intermediate **II**:

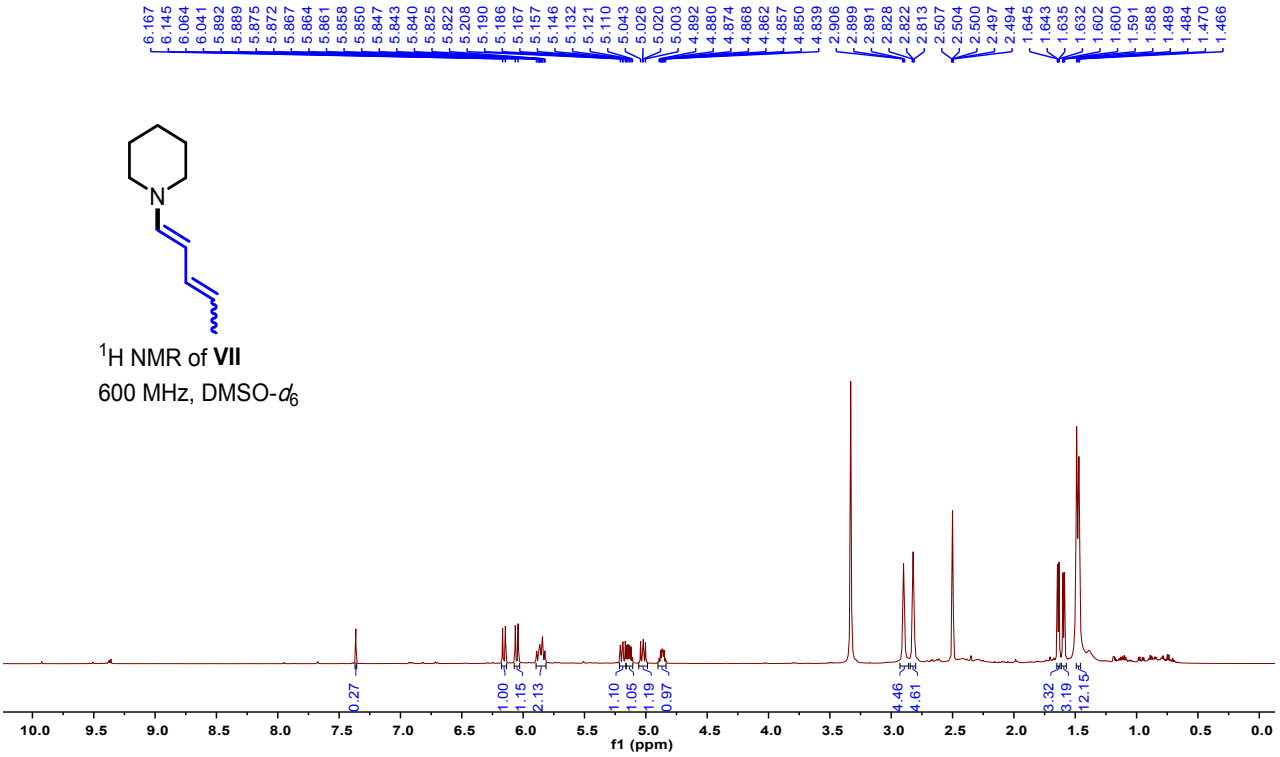


HRMS spectra of intermediate **II:**

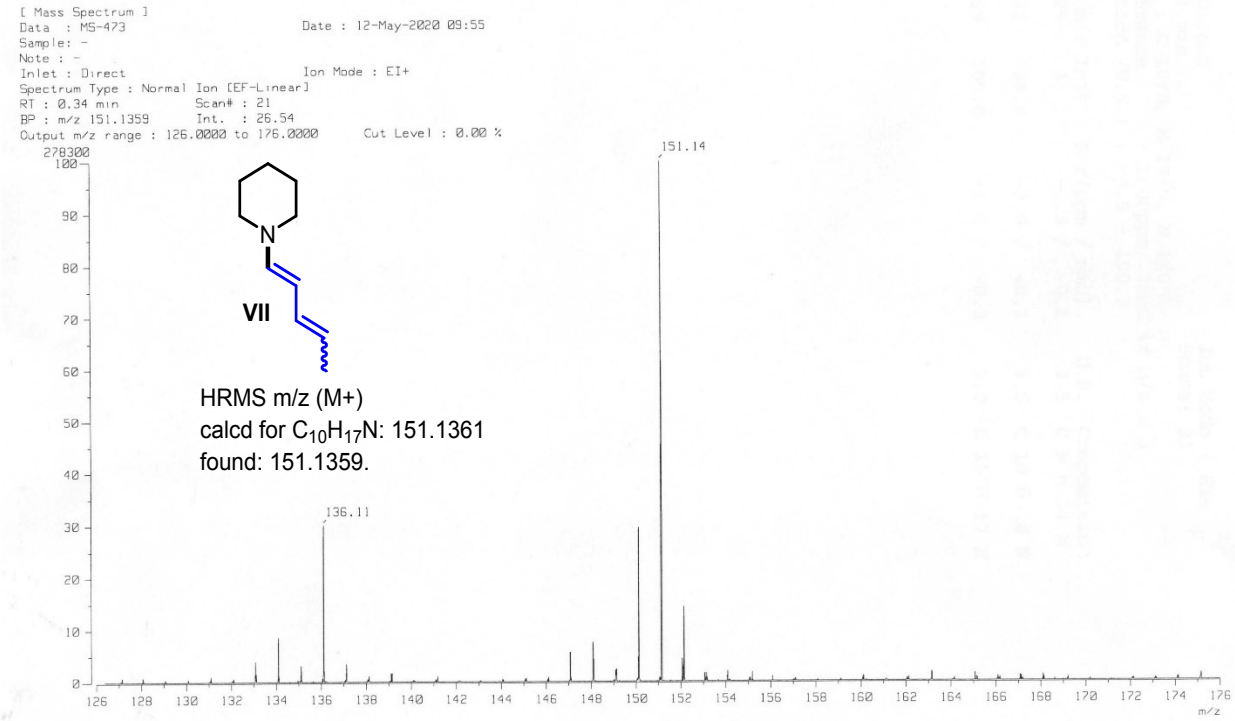


The intermediate **VII** was confirmed by the crude ^{1}H NMR through the reaction of **2a** with Cat. **VI** in benzene. The formation of **II** was also confirmed by HRMS analysis.

^{1}H NMR and ^{13}C NMR spectra of intermediate **II**



HRMS spectra of intermediate **VII**


[Mass Spectrum]
Data : MS-473
Date : 12-May-2020 09:55
Sample: -
Note : -
Inlet : Direct
Ion Mode : EI+
Spectrum Type : Normal Ion [EF-Linear]
RT : 0.34 min
Scan# : 21
BP : m/z 151.1359
Int. : 26.54
Output m/z range : 126.0000 to 176.0000
Cut Level : 0.00 %
278300
151.14
136.11
m/z
VII
HRMS m/z (M+)
calcd for C10H17N: 151.1361
found: 151.1359.

8. GCMS analysis:

The samples of pure formic acid and crude reaction mixture were analyzed over Shimadzu GCMS-QP2010 Ultra to determine the presence of HCOOH by a gas chromatography equipped with a SH-Rxi-1ms column (I.D: 0.25 mm, length 30 m, film thickness 0.25 µm) and a flame ionization detector (280 ^{o}C max.). The temperature was initially set at 40 ^{o}C (5 min) and was then increased with a rate of 5 ^{o}C/min (42 min) upto 250 ^{o}C. The retention time for reference formic acid in EtOH was observed at 5.53 min. In order to confirm the presence of formic acid in the reaction mixture, we analyzed the crude sample using the same parameters. The peak observed at 5.48 min confirmed the presence of formic acid in the reaction mixture.

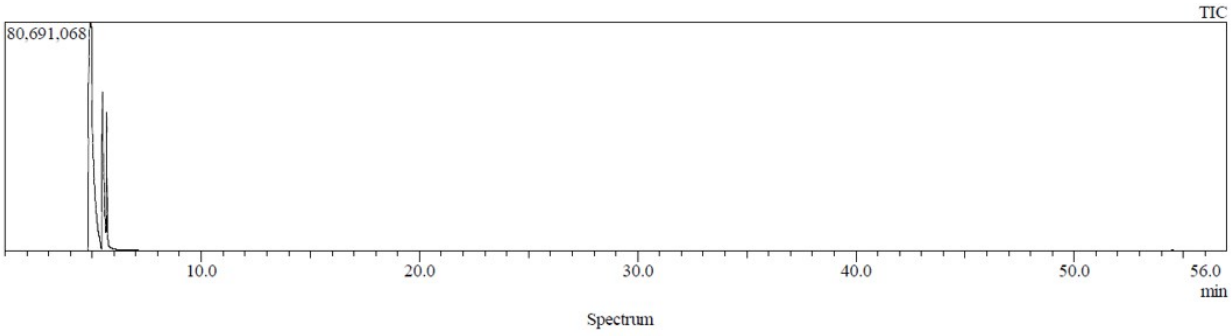


Figure S1. GC spectra of the pure formic acid in ethanol.

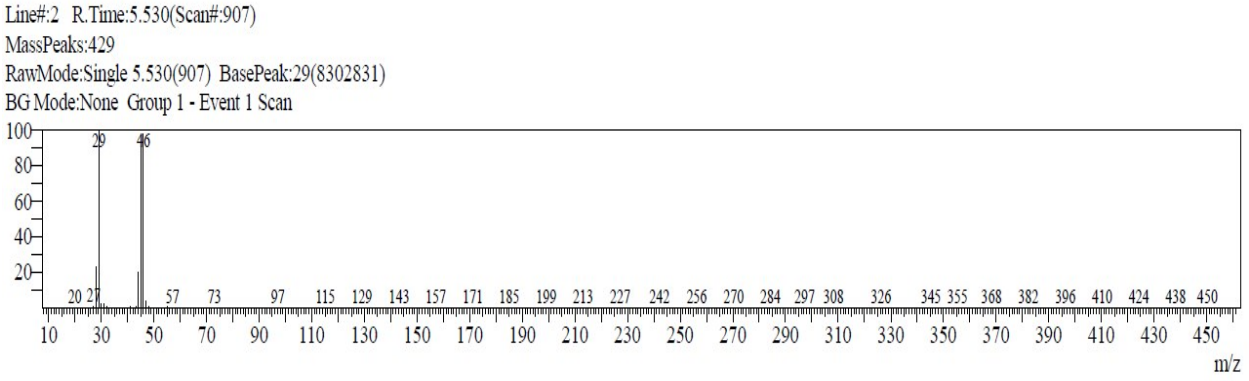


Figure S2. Mass spectrum of the GC peak at 5.53 min of retention time for pure Formic acid.

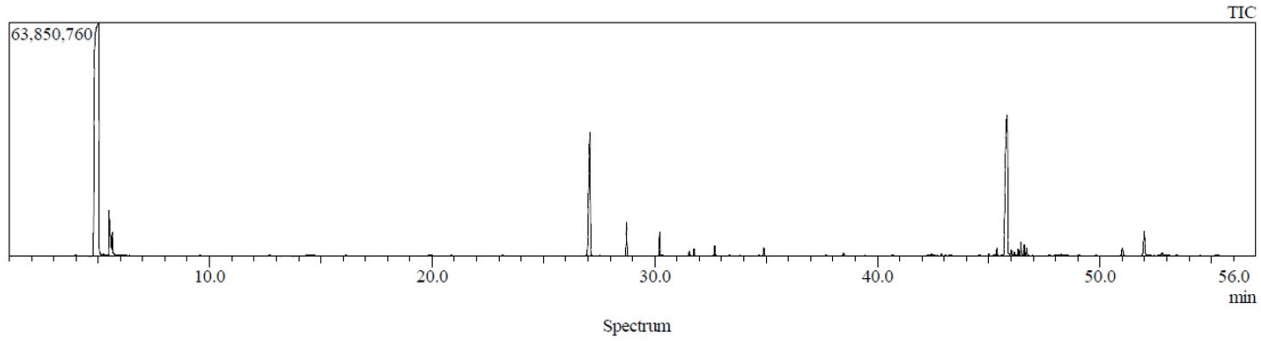


Figure S3. GC specta of the crude reaction mixture obtained from reaction between **1a** and **2a** in the presence of Cat **VI** with ethanol as solvent.

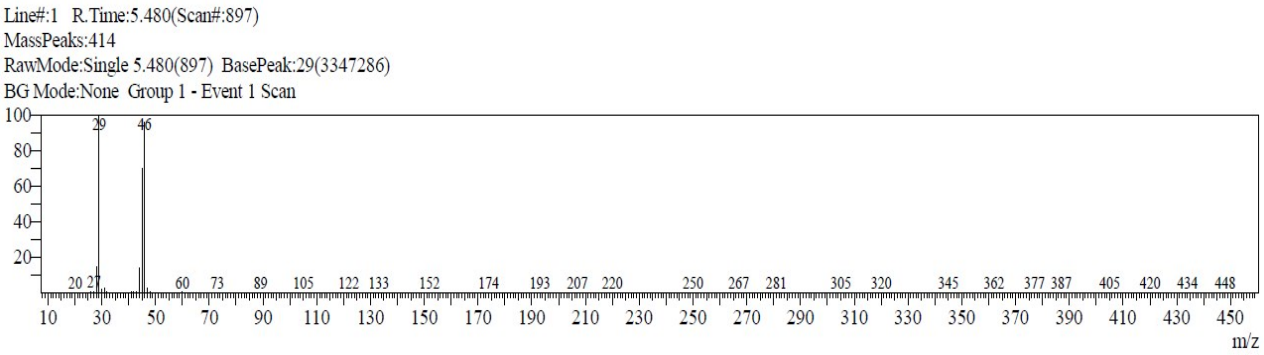


Figure S4. Mass spectrum of the GC peak at 5.48 min of retention time for crude reaction mixture.

9. Energy-minimization calculation:

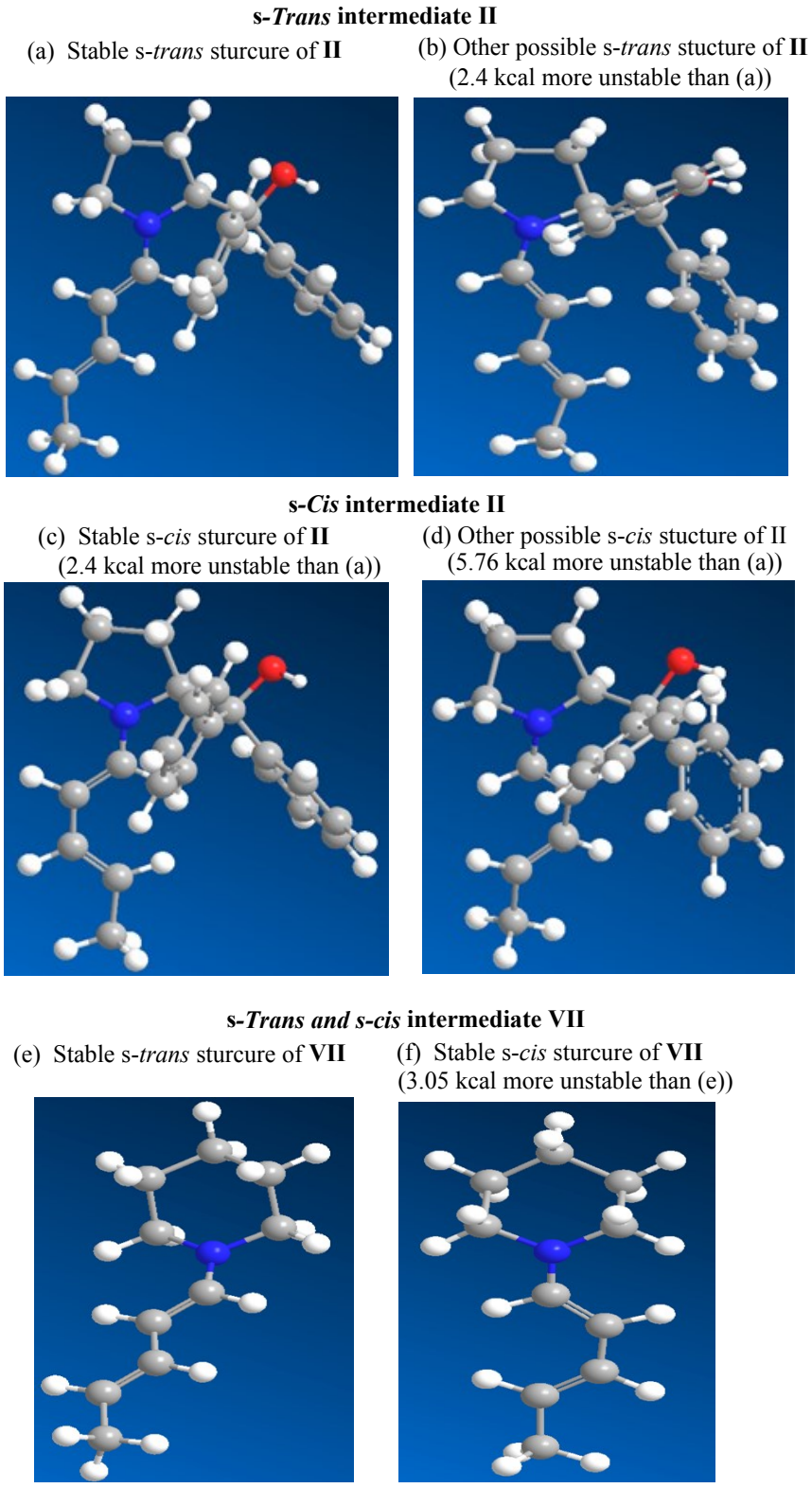
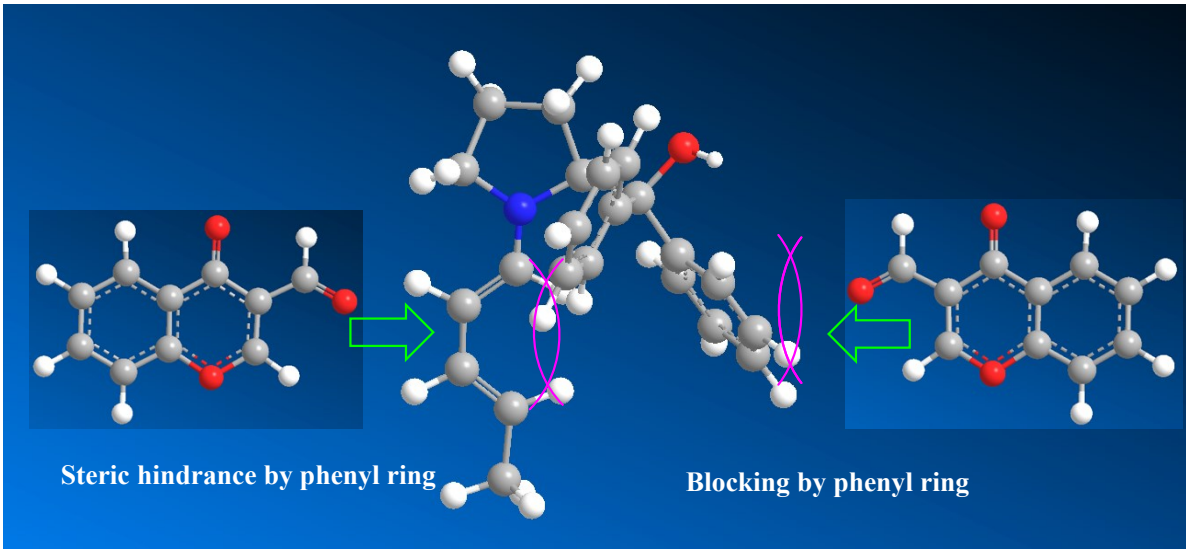


Figure S5. Energy minimized structures of **II** and **VII** by MM2 of ChemBio3D

Chemoselectivity Control

(a) Less possibility of Diels-Alder reaction from intermediate **II**



(b) High possibility of Diels-Alder reaction from intermediate **VII**

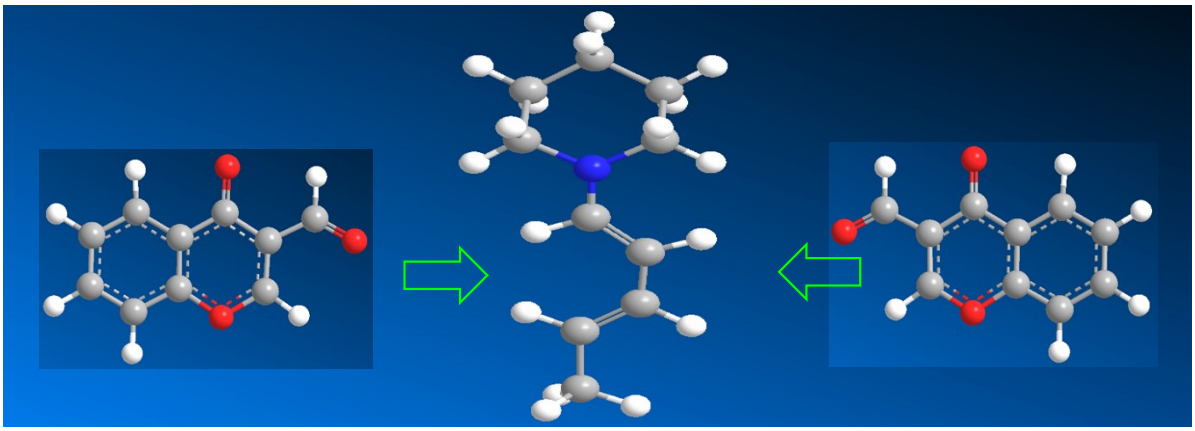


Figure S6. Chemoselectivity control through intermediate **II** and **VII**

9. UV-Absorption studies

Absorbance spectra of the tested compounds were recorded at room temperature (298 K) using UV/Vis spectrophotometer (Optizen UV-3200). The samples were prepared using ethanol as solvent (Sigma-Aldrich, HPLC Grade) at a concentration of 25 μM. The data were corrected for solvent background by the instrument's calibration using ethanol as a blank. The absorption spectra of samples in solution were obtained in the range of 220-500 nm at 1 nm interval in triplicates. The critical wavelength (λ_c) and UVA/UVB ratio were calculated using equation (1) and (2), respectively, as shown below.

$$\int_{290}^{\lambda_c} A(\lambda)d\lambda = 0.9\int_{290}^{400} A(\lambda)d\lambda \quad (1)$$

$$\frac{UVA}{UVB} = \frac{\int_{320}^{400} A(\lambda)d\lambda \Big/ \int_{320}^{400} d\lambda}{\int_{290}^{320} A(\lambda)d\lambda \Big/ \int_{290}^{320} d\lambda} \quad (2)$$

Determination of Sun Protection Factor (SPF)

Five milligrams of each sample were weighed and dissolved in 25 mL of ethanol followed by ultrasonication for 5 min to prepare solution of 200 μg/ml. The absorption spectra of samples in solution were obtained in the range of 290 to 450 nm using 1 cm quartz cell, and ethanol as a blank. The absorption data were obtained in the range of 290 to 320, every 5 nm, and 3 determinations were made at each point, followed by the application of Mansur equation.

$$SPF_{spectrophootometric} = CF \times \sum_{290}^{320} EE\,(\lambda) \times I\,(\lambda) \times Abs\,(\lambda) \quad (3)$$

Where: CF – correction factor (= 10); EE (λ) – erythemal effect spectrum; I (λ) –solar intensity spectrum; Abs (λ)- spectrophotometric absorbance values at corresponding wavelength. The values of [EE (λ) x I (λ)] are constants as shown in Table S1.

Table S1. Normalized product function used in the calculation of SPF

Wavelength (λ nm)	EE x I (normalized)
290	0.0150
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0839
320	0.0180
Total	1

EE – erythemal effect spectrum; I – solar intensity spectrum

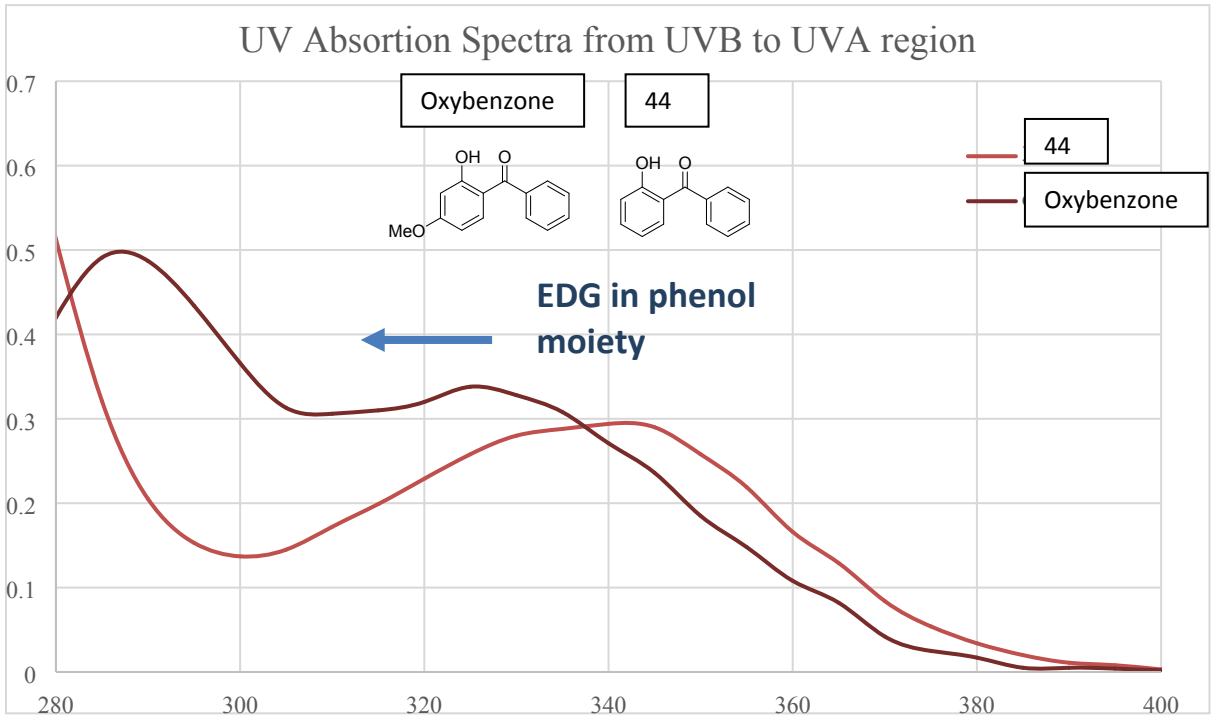


Figure S7. Structure-activity relationship of **44** and OBZ

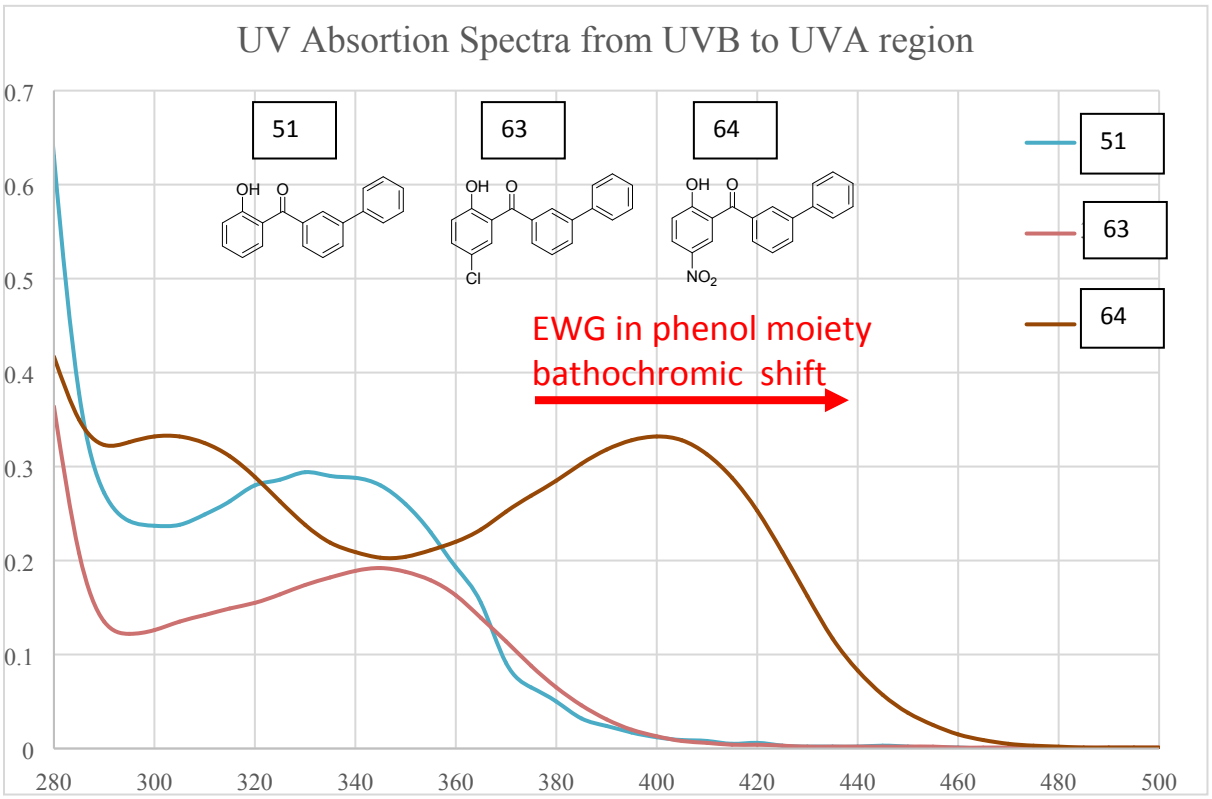


Figure S8. Structure-activity relationship of **51**, **63**, **64**

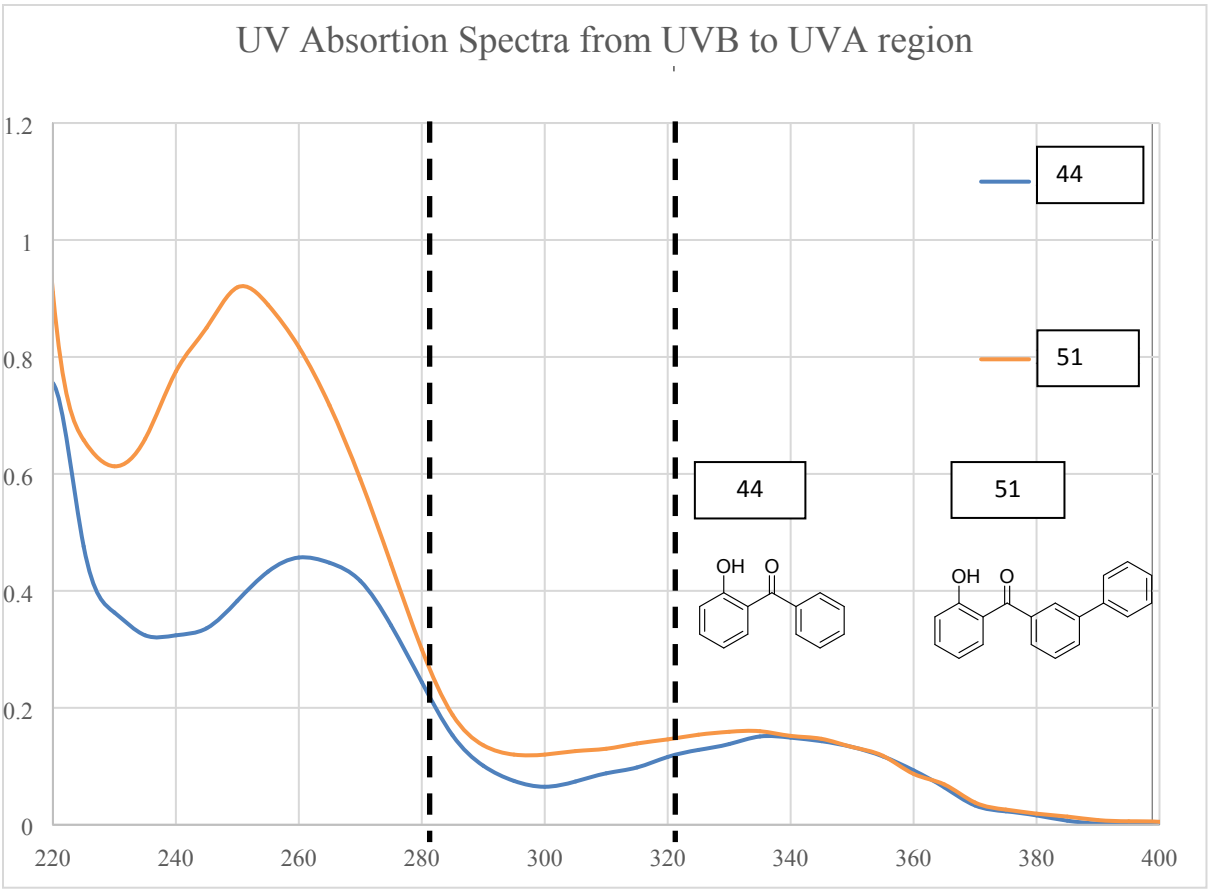


Figure S9. Structure-activity relationship of **44** and **51**

10. X-ray structure and data for compound 5

Empirical Formula C_{16} H_{14} O_3, M = 254.27, Monoclinic, Space group $P_{21/c}$, a = 13.6722(4) Å, b = 21.2561(6) Å, c = 8.9159(2) Å, V = 2577.50(12) Å^3, Z = 8, T = 223(2) K, ρ_{calcd} = 1.311 Mg/m^3, $2\Theta_{max.}$ = 25.242°, Refinement of 349 parameters on 6382 independent reflections out of 81761 collected reflections (R_{int} = 0.0330) led to R1 = 0.0499 [I >2σ(I)], wR_2 = 0.1507 (all data) and S = 1.067 with the largest difference peak and hole of 0.297 and -0.198 e.Å^{-3} respectively. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1991823). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

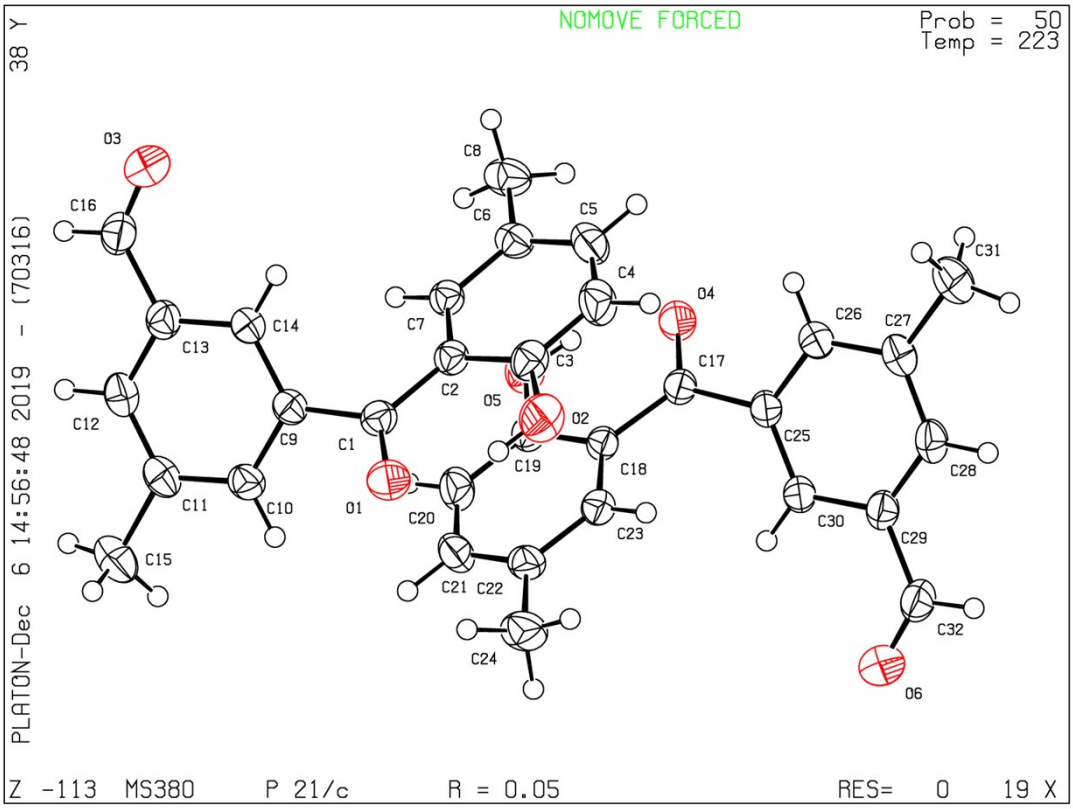


Figure S10. X-ray crystal structure of compound **5**.

Table S2. Crystal data and structure refinement for **5**.

Identification code	**5**	
Empirical formula	$C_{16}H_{14}O_3$	
Formula weight	254.27	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.6722(4) Å	α= 90°.
	b = 21.2561(6) Å	β= 95.8770(10)°.
	c = 8.9159(2) Å	γ = 90°.
Volume	2577.50(12) Å^3	
Z	8	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	1072	
Crystal size	0.444 x 0.262 x 0.114 mm^3	
Theta range for data collection	1.778 to 28.317°.	
Index ranges	-18<=h<=18, -28<=k<=28, -11<=l<=11	
Reflections collected	81761	
Independent reflections	6382 [R(int) = 0.0330]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7191	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6382 / 0 / 349	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1428	
R indices (all data)	R1 = 0.0580, wR2 = 0.1507	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.297 and -0.198 e.Å^{-3}	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3748(1)	5836(1)	8937(2)	31(1)
O(1)	3660(1)	5760(1)	10292(1)	44(1)
C(2)	3780(1)	5299(1)	7905(2)	29(1)
C(3)	3865(1)	4685(1)	8489(2)	35(1)
C(4)	3898(1)	4180(1)	7500(2)	44(1)
C(5)	3835(1)	4275(1)	5972(2)	41(1)
C(6)	3720(1)	4877(1)	5345(2)	33(1)
C(7)	3693(1)	5376(1)	6329(2)	29(1)
O(2)	3910(1)	4561(1)	9981(1)	50(1)
C(8)	3629(1)	4972(1)	3665(2)	43(1)
C(9)	3823(1)	6496(1)	8375(1)	31(1)
C(10)	3186(1)	6950(1)	8861(2)	34(1)
C(11)	3247(1)	7579(1)	8439(2)	36(1)
C(12)	3969(1)	7746(1)	7521(2)	37(1)
C(13)	4619(1)	7301(1)	7050(2)	34(1)
C(14)	4551(1)	6672(1)	7479(2)	32(1)
C(15)	2563(1)	8060(1)	9011(2)	50(1)
C(16)	5371(1)	7494(1)	6067(2)	42(1)
O(3)	5996(1)	7155(1)	5673(2)	63(1)
C(17)	1342(1)	4127(1)	5581(1)	29(1)
O(4)	1469(1)	4142(1)	4226(1)	39(1)
C(18)	1295(1)	4708(1)	6464(1)	27(1)
C(19)	1203(1)	5291(1)	5710(2)	32(1)
C(20)	1115(1)	5838(1)	6541(2)	41(1)
C(21)	1140(1)	5815(1)	8088(2)	42(1)
C(22)	1274(1)	5246(1)	8881(2)	35(1)
C(23)	1349(1)	4704(1)	8046(2)	31(1)
O(5)	1186(1)	5347(1)	4201(1)	42(1)
C(24)	1328(1)	5228(1)	10576(2)	49(1)
C(25)	1209(1)	3498(1)	6290(1)	29(1)
C(26)	1808(1)	3001(1)	5917(2)	33(1)

C(27)	1679(1)	2394(1)	6453(2)	35(1)
C(28)	930(1)	2295(1)	7375(2)	36(1)
C(29)	330(1)	2785(1)	7755(2)	33(1)
C(30)	460(1)	3391(1)	7205(2)	30(1)
C(31)	2320(1)	1860(1)	6022(2)	51(1)
C(32)	-429(1)	2662(1)	8782(2)	42(1)
O(6)	-987(1)	3046(1)	9198(2)	56(1)

Table S4. Bond lengths [Å] and angles [°] for **5**.

C(1)-O(1)	1.2375(16)
C(1)-C(2)	1.4695(18)
C(1)-C(9)	1.4961(18)
C(2)-C(3)	1.4055(18)
C(2)-C(7)	1.4076(18)
C(3)-O(2)	1.3515(18)
C(3)-C(4)	1.393(2)
C(4)-C(5)	1.372(2)
C(4)-H(4)	0.9400
C(5)-C(6)	1.398(2)
C(5)-H(5)	0.9400
C(6)-C(7)	1.3800(18)
C(6)-C(8)	1.504(2)
C(7)-H(7)	0.9400
O(2)-H(2)	0.8300
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(8)-H(8C)	0.9700
C(9)-C(14)	1.3904(18)
C(9)-C(10)	1.3982(18)
C(10)-C(11)	1.394(2)
C(10)-H(10)	0.9400
C(11)-C(12)	1.391(2)
C(11)-C(15)	1.509(2)
C(12)-C(13)	1.393(2)
C(12)-H(12)	0.9400
C(13)-C(14)	1.3956(19)
C(13)-C(16)	1.476(2)
C(14)-H(14)	0.9400
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(15)-H(15C)	0.9700
C(16)-O(3)	1.199(2)
C(16)-H(16)	0.9400

C(17)-O(4)	1.2380(16)
C(17)-C(18)	1.4700(17)
C(17)-C(25)	1.4980(17)
C(18)-C(23)	1.4045(18)
C(18)-C(19)	1.4078(17)
C(19)-O(5)	1.3490(17)
C(19)-C(20)	1.392(2)
C(20)-C(21)	1.377(2)
C(20)-H(20)	0.9400
C(21)-C(22)	1.404(2)
C(21)-H(21)	0.9400
C(22)-C(23)	1.3805(18)
C(22)-C(24)	1.506(2)
C(23)-H(23)	0.9400
O(5)-H(5A)	0.8300
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(24)-H(24C)	0.9700
C(25)-C(30)	1.3923(18)
C(25)-C(26)	1.3971(18)
C(26)-C(27)	1.3925(19)
C(26)-H(26)	0.9400
C(27)-C(28)	1.393(2)
C(27)-C(31)	1.509(2)
C(28)-C(29)	1.390(2)
C(28)-H(28)	0.9400
C(29)-C(30)	1.3951(18)
C(29)-C(32)	1.476(2)
C(30)-H(30)	0.9400
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(31)-H(31C)	0.9700
C(32)-O(6)	1.201(2)
C(32)-H(32)	0.9400

O(1)-C(1)-C(2)	121.50(12)

O(1)-C(1)-C(9)	117.72(12)
C(2)-C(1)-C(9)	120.78(11)
C(3)-C(2)-C(7)	118.23(12)
C(3)-C(2)-C(1)	119.76(12)
C(7)-C(2)-C(1)	121.98(12)
O(2)-C(3)-C(4)	118.12(13)
O(2)-C(3)-C(2)	122.67(13)
C(4)-C(3)-C(2)	119.21(13)
C(5)-C(4)-C(3)	120.84(14)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	121.66(13)
C(4)-C(5)-H(5)	119.2
C(6)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	117.28(13)
C(7)-C(6)-C(8)	121.69(13)
C(5)-C(6)-C(8)	121.03(13)
C(6)-C(7)-C(2)	122.73(12)
C(6)-C(7)-H(7)	118.6
C(2)-C(7)-H(7)	118.6
C(3)-O(2)-H(2)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(14)-C(9)-C(10)	119.81(13)
C(14)-C(9)-C(1)	121.51(12)
C(10)-C(9)-C(1)	118.51(12)
C(11)-C(10)-C(9)	121.45(13)
C(11)-C(10)-H(10)	119.3
C(9)-C(10)-H(10)	119.3
C(12)-C(11)-C(10)	118.07(13)
C(12)-C(11)-C(15)	121.80(14)
C(10)-C(11)-C(15)	120.10(14)

C(11)-C(12)-C(13)	121.08(13)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	120.40(13)
C(12)-C(13)-C(16)	119.67(13)
C(14)-C(13)-C(16)	119.92(13)
C(9)-C(14)-C(13)	119.17(13)
C(9)-C(14)-H(14)	120.4
C(13)-C(14)-H(14)	120.4
C(11)-C(15)-H(15A)	109.5
C(11)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(11)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(3)-C(16)-C(13)	124.61(15)
O(3)-C(16)-H(16)	117.7
C(13)-C(16)-H(16)	117.7
O(4)-C(17)-C(18)	121.33(11)
O(4)-C(17)-C(25)	117.96(11)
C(18)-C(17)-C(25)	120.69(11)
C(23)-C(18)-C(19)	118.57(12)
C(23)-C(18)-C(17)	122.14(11)
C(19)-C(18)-C(17)	119.29(12)
O(5)-C(19)-C(20)	117.58(12)
O(5)-C(19)-C(18)	123.12(12)
C(20)-C(19)-C(18)	119.30(13)
C(21)-C(20)-C(19)	120.56(14)
C(21)-C(20)-H(20)	119.7
C(19)-C(20)-H(20)	119.7
C(20)-C(21)-C(22)	121.60(13)
C(20)-C(21)-H(21)	119.2
C(22)-C(21)-H(21)	119.2
C(23)-C(22)-C(21)	117.39(13)
C(23)-C(22)-C(24)	121.41(14)
C(21)-C(22)-C(24)	121.19(13)

C(22)-C(23)-C(18)	122.47(13)
C(22)-C(23)-H(23)	118.8
C(18)-C(23)-H(23)	118.8
C(19)-O(5)-H(5A)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(30)-C(25)-C(26)	119.91(12)
C(30)-C(25)-C(17)	121.45(12)
C(26)-C(25)-C(17)	118.44(12)
C(27)-C(26)-C(25)	121.44(13)
C(27)-C(26)-H(26)	119.3
C(25)-C(26)-H(26)	119.3
C(26)-C(27)-C(28)	117.97(13)
C(26)-C(27)-C(31)	120.87(14)
C(28)-C(27)-C(31)	121.15(13)
C(29)-C(28)-C(27)	121.22(12)
C(29)-C(28)-H(28)	119.4
C(27)-C(28)-H(28)	119.4
C(28)-C(29)-C(30)	120.39(13)
C(28)-C(29)-C(32)	119.26(12)
C(30)-C(29)-C(32)	120.32(13)
C(25)-C(30)-C(29)	119.06(12)
C(25)-C(30)-H(30)	120.5
C(29)-C(30)-H(30)	120.5
C(27)-C(31)-H(31A)	109.5
C(27)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(27)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
O(6)-C(32)-C(29)	125.47(14)
O(6)-C(32)-H(32)	117.3

C(29)-C(32)-H(32) 117.3

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	32(1)	33(1)	30(1)	0(1)	4(1)	-2(1)
O(1)	58(1)	45(1)	30(1)	1(1)	10(1)	-3(1)
C(2)	27(1)	29(1)	31(1)	1(1)	3(1)	-1(1)
C(3)	34(1)	33(1)	38(1)	7(1)	2(1)	1(1)
C(4)	48(1)	28(1)	56(1)	4(1)	4(1)	6(1)
C(5)	39(1)	33(1)	51(1)	-11(1)	4(1)	3(1)
C(6)	26(1)	38(1)	35(1)	-7(1)	2(1)	0(1)
C(7)	28(1)	29(1)	31(1)	0(1)	3(1)	0(1)
O(2)	67(1)	43(1)	40(1)	14(1)	6(1)	2(1)
C(8)	40(1)	57(1)	34(1)	-11(1)	4(1)	-1(1)
C(9)	34(1)	30(1)	28(1)	-4(1)	3(1)	-2(1)
C(10)	34(1)	35(1)	32(1)	-7(1)	4(1)	-2(1)
C(11)	38(1)	33(1)	36(1)	-8(1)	-3(1)	2(1)
C(12)	45(1)	29(1)	35(1)	-3(1)	-2(1)	-2(1)
C(13)	40(1)	32(1)	31(1)	-3(1)	3(1)	-6(1)
C(14)	36(1)	30(1)	32(1)	-5(1)	6(1)	-3(1)
C(15)	51(1)	40(1)	58(1)	-13(1)	1(1)	9(1)
C(16)	52(1)	35(1)	40(1)	-3(1)	9(1)	-13(1)
O(3)	64(1)	54(1)	76(1)	-4(1)	35(1)	-9(1)
C(17)	30(1)	27(1)	30(1)	1(1)	4(1)	-2(1)
O(4)	54(1)	34(1)	30(1)	-1(1)	9(1)	-5(1)
C(18)	25(1)	25(1)	32(1)	0(1)	4(1)	-2(1)
C(19)	29(1)	29(1)	38(1)	4(1)	4(1)	0(1)
C(20)	42(1)	25(1)	57(1)	2(1)	7(1)	3(1)
C(21)	38(1)	31(1)	57(1)	-13(1)	10(1)	1(1)
C(22)	30(1)	39(1)	38(1)	-10(1)	7(1)	-4(1)
C(23)	30(1)	30(1)	32(1)	-1(1)	4(1)	-3(1)
O(5)	54(1)	35(1)	36(1)	10(1)	4(1)	1(1)
C(24)	51(1)	60(1)	37(1)	-15(1)	9(1)	-7(1)
C(25)	35(1)	24(1)	29(1)	-1(1)	3(1)	-3(1)
C(26)	36(1)	29(1)	34(1)	-2(1)	5(1)	0(1)

C(27)	42(1)	27(1)	36(1)	-2(1)	-1(1)	3(1)
C(28)	49(1)	25(1)	33(1)	2(1)	-1(1)	-3(1)
C(29)	41(1)	28(1)	29(1)	1(1)	3(1)	-6(1)
C(30)	35(1)	25(1)	31(1)	-1(1)	4(1)	-2(1)
C(31)	58(1)	33(1)	63(1)	-3(1)	8(1)	11(1)
C(32)	54(1)	34(1)	40(1)	1(1)	11(1)	-12(1)
O(6)	62(1)	52(1)	57(1)	-2(1)	26(1)	-5(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5**.

	x	y	z	U(eq)
H(4)	3964	3769	7885	53
H(5)	3871	3927	5329	49
H(7)	3613	5784	5931	35
H(2)	3846	4893	10451	75
H(8A)	3315	5373	3418	65
H(8B)	3234	4636	3177	65
H(8C)	4278	4967	3315	65
H(10)	2706	6828	9486	40
H(12)	4018	8167	7213	44
H(14)	4993	6372	7166	39
H(15A)	2795	8172	10041	75
H(15B)	1907	7884	8980	75
H(15C)	2548	8432	8380	75
H(16)	5358	7913	5726	51
H(20)	1038	6227	6042	49
H(21)	1064	6189	8626	50
H(23)	1440	4318	8555	37
H(5A)	1261	4995	3824	63
H(24A)	676	5290	10889	74
H(24B)	1762	5559	10995	74
H(24C)	1581	4823	10936	74
H(26)	2308	3077	5291	40
H(28)	830	1889	7748	43
H(30)	48	3721	7449	37
H(31A)	2123	1474	6490	77
H(31B)	3001	1951	6364	77
H(31C)	2247	1810	4935	77
H(32)	-480	2249	9141	51

Table S7. Torsion angles [°] for **5**.

O(1)-C(1)-C(2)-C(3)	-9.9(2)
C(9)-C(1)-C(2)-C(3)	170.00(12)
O(1)-C(1)-C(2)-C(7)	167.78(13)
C(9)-C(1)-C(2)-C(7)	-12.27(19)
C(7)-C(2)-C(3)-O(2)	-177.17(12)
C(1)-C(2)-C(3)-O(2)	0.6(2)
C(7)-C(2)-C(3)-C(4)	2.5(2)
C(1)-C(2)-C(3)-C(4)	-179.73(13)
O(2)-C(3)-C(4)-C(5)	178.73(14)
C(2)-C(3)-C(4)-C(5)	-0.9(2)
C(3)-C(4)-C(5)-C(6)	-1.0(2)
C(4)-C(5)-C(6)-C(7)	1.3(2)
C(4)-C(5)-C(6)-C(8)	-178.54(14)
C(5)-C(6)-C(7)-C(2)	0.32(19)
C(8)-C(6)-C(7)-C(2)	-179.81(12)
C(3)-C(2)-C(7)-C(6)	-2.2(2)
C(1)-C(2)-C(7)-C(6)	-179.96(12)
O(1)-C(1)-C(9)-C(14)	131.50(14)
C(2)-C(1)-C(9)-C(14)	-48.45(18)
O(1)-C(1)-C(9)-C(10)	-43.84(18)
C(2)-C(1)-C(9)-C(10)	136.22(13)
C(14)-C(9)-C(10)-C(11)	1.5(2)
C(1)-C(9)-C(10)-C(11)	176.93(12)
C(9)-C(10)-C(11)-C(12)	-0.4(2)
C(9)-C(10)-C(11)-C(15)	-178.63(13)
C(10)-C(11)-C(12)-C(13)	-0.8(2)
C(15)-C(11)-C(12)-C(13)	177.45(14)
C(11)-C(12)-C(13)-C(14)	0.8(2)
C(11)-C(12)-C(13)-C(16)	179.54(13)
C(10)-C(9)-C(14)-C(13)	-1.4(2)
C(1)-C(9)-C(14)-C(13)	-176.72(12)
C(12)-C(13)-C(14)-C(9)	0.3(2)
C(16)-C(13)-C(14)-C(9)	-178.41(13)
C(12)-C(13)-C(16)-O(3)	175.63(16)

C(14)-C(13)-C(16)-O(3)	-5.6(2)
O(4)-C(17)-C(18)-C(23)	-166.96(13)
C(25)-C(17)-C(18)-C(23)	14.69(19)
O(4)-C(17)-C(18)-C(19)	12.35(19)
C(25)-C(17)-C(18)-C(19)	-166.00(12)
C(23)-C(18)-C(19)-O(5)	177.19(12)
C(17)-C(18)-C(19)-O(5)	-2.1(2)
C(23)-C(18)-C(19)-C(20)	-3.49(19)
C(17)-C(18)-C(19)-C(20)	177.17(12)
O(5)-C(19)-C(20)-C(21)	-179.15(13)
C(18)-C(19)-C(20)-C(21)	1.5(2)
C(19)-C(20)-C(21)-C(22)	1.4(2)
C(20)-C(21)-C(22)-C(23)	-2.1(2)
C(20)-C(21)-C(22)-C(24)	178.30(14)
C(21)-C(22)-C(23)-C(18)	0.0(2)
C(24)-C(22)-C(23)-C(18)	179.57(13)
C(19)-C(18)-C(23)-C(22)	2.8(2)
C(17)-C(18)-C(23)-C(22)	-177.88(12)
O(4)-C(17)-C(25)-C(30)	-133.28(14)
C(18)-C(17)-C(25)-C(30)	45.13(18)
O(4)-C(17)-C(25)-C(26)	41.65(18)
C(18)-C(17)-C(25)-C(26)	-139.95(13)
C(30)-C(25)-C(26)-C(27)	-0.5(2)
C(17)-C(25)-C(26)-C(27)	-175.56(12)
C(25)-C(26)-C(27)-C(28)	0.1(2)
C(25)-C(26)-C(27)-C(31)	179.02(14)
C(26)-C(27)-C(28)-C(29)	-0.1(2)
C(31)-C(27)-C(28)-C(29)	-179.01(14)
C(27)-C(28)-C(29)-C(30)	0.5(2)
C(27)-C(28)-C(29)-C(32)	-177.67(13)
C(26)-C(25)-C(30)-C(29)	0.93(19)
C(17)-C(25)-C(30)-C(29)	175.78(12)
C(28)-C(29)-C(30)-C(25)	-0.9(2)
C(32)-C(29)-C(30)-C(25)	177.26(12)
C(28)-C(29)-C(32)-O(6)	179.60(16)
C(30)-C(29)-C(32)-O(6)	1.4(2)

Symmetry transformations used to generate equivalent atoms:

Table S8. Hydrogen bonds for **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(4)	0.83	1.87	2.5905(15)	145.1
O(2)-H(2)...O(1)	0.83	1.87	2.5919(17)	145.5

Symmetry transformations used to generate equivalent atoms:

X-ray structure and data for compound 34

Empirical Formula C_{19} H_{14} O_3, M = 290.30, Monoclinic, Space group $P_{21/c}$, a = 7.3618(3) Å, b = 7.4104(2) Å, c = 25.4612(9) Å, V = 1383.11(8) Å^3, Z = 4, T = 223(2) K, ρ_{calcd} = 1.394 Mg/m^3, $2\Theta_{max.}$ = 25.242°, Refinement of 201 parameters on 3455 independent reflections out of 42946 collected reflections (R_{int} = 0.0371) led to R1 = 0.0429 [I >2σ(I)], wR_2 = 0.1157 (all data) and S = 1.069 with the largest difference peak and hole of 0.313 and -0.188 e.Å^{-3} respectively. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1991825). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

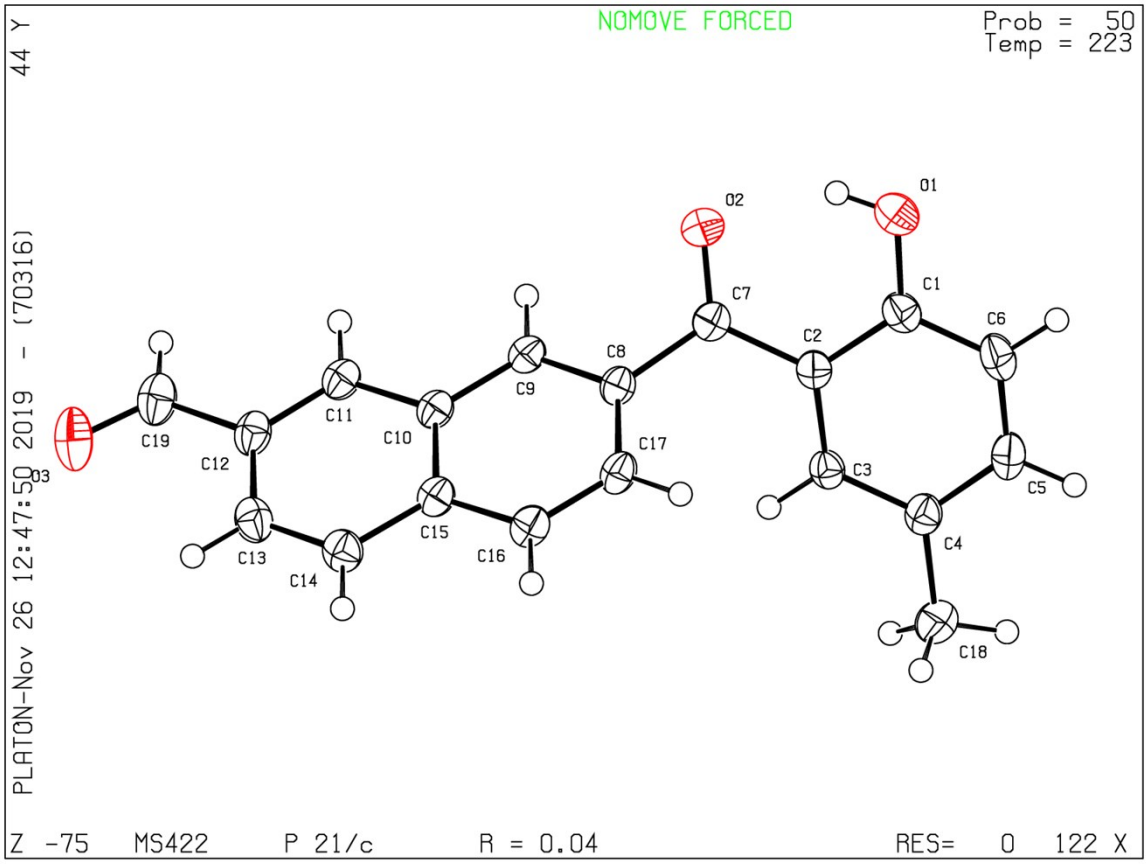


Figure S11. X-ray crystal structure of compound **34**.

Table S9. Crystal data and structure refinement for **34**.

Identification code	**34**	
Empirical formula	$C_{19}H_{14}O_3$	
Formula weight	290.30	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.3618(3) Å	α= 90°.
	b = 7.4104(2) Å	β= 95.2808(14)°.
	c = 25.4612(9) Å	γ = 90°.
Volume	1383.11(8) Å^3	
Z	4	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	608	
Crystal size	0.259 x 0.248 x 0.166 mm^3	
Theta range for data collection	2.864 to 28.591°.	
Index ranges	-9<=h<=9, -9<=k<=9, -33<=l<=34	
Reflections collected	42946	
Independent reflections	3455 [R(int) = 0.0371]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7171	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3455 / 0 / 201	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1088	
R indices (all data)	R1 = 0.0504, wR2 = 0.1157	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.313 and -0.188 e.Å^{-3}	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **34**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5489(2)	6522(2)	8219(1)	28(1)
C(2)	4238(2)	5351(2)	8432(1)	23(1)
C(3)	2499(2)	5138(2)	8165(1)	24(1)
C(4)	1989(2)	6012(2)	7692(1)	27(1)
C(5)	3282(2)	7125(2)	7485(1)	31(1)
C(6)	4998(2)	7378(2)	7742(1)	32(1)
O(1)	7184(1)	6851(2)	8457(1)	42(1)
C(7)	4725(2)	4482(2)	8948(1)	24(1)
O(2)	5876(1)	5172(1)	9268(1)	34(1)
C(8)	3856(2)	2743(2)	9082(1)	24(1)
C(9)	3561(2)	2413(2)	9601(1)	24(1)
C(10)	2853(2)	738(2)	9751(1)	24(1)
C(11)	2518(2)	374(2)	10280(1)	27(1)
C(12)	1845(2)	-1267(2)	10418(1)	28(1)
C(13)	1479(2)	-2629(2)	10032(1)	31(1)
C(14)	1781(2)	-2321(2)	9520(1)	30(1)
C(15)	2477(2)	-629(2)	9364(1)	25(1)
C(16)	2813(2)	-259(2)	8836(1)	27(1)
C(17)	3474(2)	1383(2)	8697(1)	26(1)
C(18)	133(2)	5749(2)	7404(1)	39(1)
C(19)	1516(2)	-1583(2)	10973(1)	36(1)
O(3)	969(2)	-2987(2)	11145(1)	48(1)

Table S11. Bond lengths [Å] and angles [°] for **34**.

C(1)-O(1)	1.3588(17)
C(1)-C(6)	1.3879(19)
C(1)-C(2)	1.4093(17)
C(2)-C(3)	1.4022(17)
C(2)-C(7)	1.4786(16)
C(3)-C(4)	1.3884(17)
C(3)-H(3)	0.9400
C(4)-C(5)	1.3977(19)
C(4)-C(18)	1.503(2)
C(5)-C(6)	1.381(2)
C(5)-H(5)	0.9400
C(6)-H(6)	0.9400
O(1)-H(1)	0.8300
C(7)-O(2)	1.2314(16)
C(7)-C(8)	1.4920(18)
C(8)-C(9)	1.3805(17)
C(8)-C(17)	1.4159(17)
C(9)-C(10)	1.4117(17)
C(9)-H(9)	0.9400
C(10)-C(11)	1.4186(17)
C(10)-C(15)	1.4231(17)
C(11)-C(12)	1.3706(19)
C(11)-H(11)	0.9400
C(12)-C(13)	1.416(2)
C(12)-C(19)	1.4756(18)
C(13)-C(14)	1.3634(19)
C(13)-H(13)	0.9400
C(14)-C(15)	1.4252(18)
C(14)-H(14)	0.9400
C(15)-C(16)	1.4155(17)
C(16)-C(17)	1.3683(18)
C(16)-H(16)	0.9400
C(17)-H(17)	0.9400
C(18)-H(18A)	0.9700

C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-O(3)	1.2113(19)
C(19)-H(19)	0.9400

O(1)-C(1)-C(6)	117.56(12)
O(1)-C(1)-C(2)	122.99(12)
C(6)-C(1)-C(2)	119.44(12)
C(3)-C(2)-C(1)	118.83(11)
C(3)-C(2)-C(7)	121.22(11)
C(1)-C(2)-C(7)	119.79(11)
C(4)-C(3)-C(2)	122.04(12)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(3)-C(4)-C(5)	117.49(12)
C(3)-C(4)-C(18)	121.60(12)
C(5)-C(4)-C(18)	120.90(12)
C(6)-C(5)-C(4)	121.86(12)
C(6)-C(5)-H(5)	119.1
C(4)-C(5)-H(5)	119.1
C(5)-C(6)-C(1)	120.30(12)
C(5)-C(6)-H(6)	119.8
C(1)-C(6)-H(6)	119.8
C(1)-O(1)-H(1)	109.5
O(2)-C(7)-C(2)	120.22(12)
O(2)-C(7)-C(8)	119.41(11)
C(2)-C(7)-C(8)	120.36(11)
C(9)-C(8)-C(17)	119.83(12)
C(9)-C(8)-C(7)	118.70(11)
C(17)-C(8)-C(7)	121.25(11)
C(8)-C(9)-C(10)	120.56(11)
C(8)-C(9)-H(9)	119.7
C(10)-C(9)-H(9)	119.7
C(9)-C(10)-C(11)	121.63(12)
C(9)-C(10)-C(15)	119.48(11)
C(11)-C(10)-C(15)	118.89(12)

C(12)-C(11)-C(10)	120.65(12)
C(12)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7
C(11)-C(12)-C(13)	120.41(12)
C(11)-C(12)-C(19)	118.72(13)
C(13)-C(12)-C(19)	120.87(13)
C(14)-C(13)-C(12)	120.43(13)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	120.59(12)
C(13)-C(14)-H(14)	119.7
C(15)-C(14)-H(14)	119.7
C(16)-C(15)-C(10)	118.68(12)
C(16)-C(15)-C(14)	122.28(12)
C(10)-C(15)-C(14)	119.04(11)
C(17)-C(16)-C(15)	120.94(12)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(16)-C(17)-C(8)	120.50(11)
C(16)-C(17)-H(17)	119.8
C(8)-C(17)-H(17)	119.8
C(4)-C(18)-H(18A)	109.5
C(4)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(4)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(3)-C(19)-C(12)	124.88(15)
O(3)-C(19)-H(19)	117.6
C(12)-C(19)-H(19)	117.6

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **34**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	30(1)	26(1)	29(1)	-1(1)	7(1)	-3(1)
C(2)	28(1)	20(1)	22(1)	-1(1)	5(1)	1(1)
C(3)	28(1)	19(1)	24(1)	-1(1)	5(1)	0(1)
C(4)	33(1)	22(1)	25(1)	0(1)	3(1)	3(1)
C(5)	42(1)	26(1)	25(1)	5(1)	6(1)	2(1)
C(6)	39(1)	28(1)	32(1)	4(1)	13(1)	-5(1)
O(1)	34(1)	50(1)	41(1)	7(1)	1(1)	-14(1)
C(7)	26(1)	25(1)	22(1)	-2(1)	4(1)	3(1)
O(2)	37(1)	37(1)	28(1)	-1(1)	-3(1)	-7(1)
C(8)	25(1)	23(1)	23(1)	2(1)	2(1)	4(1)
C(9)	26(1)	26(1)	21(1)	-1(1)	1(1)	2(1)
C(10)	23(1)	26(1)	23(1)	1(1)	2(1)	4(1)
C(11)	27(1)	31(1)	23(1)	1(1)	3(1)	3(1)
C(12)	25(1)	33(1)	27(1)	7(1)	5(1)	6(1)
C(13)	30(1)	27(1)	36(1)	6(1)	5(1)	2(1)
C(14)	33(1)	24(1)	32(1)	0(1)	3(1)	3(1)
C(15)	26(1)	23(1)	25(1)	1(1)	2(1)	6(1)
C(16)	35(1)	23(1)	24(1)	-3(1)	2(1)	5(1)
C(17)	33(1)	26(1)	20(1)	1(1)	3(1)	5(1)
C(18)	40(1)	37(1)	37(1)	7(1)	-7(1)	-1(1)
C(19)	38(1)	40(1)	31(1)	8(1)	10(1)	6(1)
O(3)	60(1)	45(1)	41(1)	15(1)	21(1)	3(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **34**.

	x	y	z	U(eq)
H(3)	1653	4380	8310	28
H(5)	2974	7718	7163	37
H(6)	5839	8134	7593	39
H(1)	7290	6369	8753	63
H(9)	3835	3310	9857	29
H(11)	2760	1267	10540	32
H(13)	1025	-3753	10131	37
H(14)	1527	-3233	9267	36
H(16)	2579	-1153	8577	33
H(17)	3677	1609	8344	32
H(18A)	102	4612	7214	58
H(18B)	-123	6731	7156	58
H(18C)	-780	5735	7655	58
H(19)	1747	-624	11211	43

Table S14. Torsion angles [°] for **34**.

O(1)-C(1)-C(2)-C(3)	178.13(12)
C(6)-C(1)-C(2)-C(3)	-2.47(18)
O(1)-C(1)-C(2)-C(7)	2.72(19)
C(6)-C(1)-C(2)-C(7)	-177.89(12)
C(1)-C(2)-C(3)-C(4)	1.51(18)
C(7)-C(2)-C(3)-C(4)	176.86(11)
C(2)-C(3)-C(4)-C(5)	0.15(18)
C(2)-C(3)-C(4)-C(18)	178.94(12)
C(3)-C(4)-C(5)-C(6)	-0.9(2)
C(18)-C(4)-C(5)-C(6)	-179.68(13)
C(4)-C(5)-C(6)-C(1)	-0.1(2)
O(1)-C(1)-C(6)-C(5)	-178.77(13)
C(2)-C(1)-C(6)-C(5)	1.8(2)
C(3)-C(2)-C(7)-O(2)	-151.40(12)
C(1)-C(2)-C(7)-O(2)	23.90(18)
C(3)-C(2)-C(7)-C(8)	29.91(17)
C(1)-C(2)-C(7)-C(8)	-154.79(11)
O(2)-C(7)-C(8)-C(9)	33.64(17)
C(2)-C(7)-C(8)-C(9)	-147.66(12)
O(2)-C(7)-C(8)-C(17)	-141.09(13)
C(2)-C(7)-C(8)-C(17)	37.60(17)
C(17)-C(8)-C(9)-C(10)	-1.05(18)
C(7)-C(8)-C(9)-C(10)	-175.86(11)
C(8)-C(9)-C(10)-C(11)	-179.25(11)
C(8)-C(9)-C(10)-C(15)	1.30(18)
C(9)-C(10)-C(11)-C(12)	-179.41(11)
C(15)-C(10)-C(11)-C(12)	0.04(18)
C(10)-C(11)-C(12)-C(13)	0.22(19)
C(10)-C(11)-C(12)-C(19)	-179.90(12)
C(11)-C(12)-C(13)-C(14)	-0.4(2)
C(19)-C(12)-C(13)-C(14)	179.71(13)
C(12)-C(13)-C(14)-C(15)	0.3(2)
C(9)-C(10)-C(15)-C(16)	-0.55(18)
C(11)-C(10)-C(15)-C(16)	179.98(11)

C(9)-C(10)-C(15)-C(14)	179.35(11)
C(11)-C(10)-C(15)-C(14)	-0.12(18)
C(13)-C(14)-C(15)-C(16)	179.83(12)
C(13)-C(14)-C(15)-C(10)	-0.07(19)
C(10)-C(15)-C(16)-C(17)	-0.43(19)
C(14)-C(15)-C(16)-C(17)	179.67(12)
C(15)-C(16)-C(17)-C(8)	0.69(19)
C(9)-C(8)-C(17)-C(16)	0.06(19)
C(7)-C(8)-C(17)-C(16)	174.73(12)
C(11)-C(12)-C(19)-O(3)	-178.06(14)
C(13)-C(12)-C(19)-O(3)	1.8(2)

Symmetry transformations used to generate equivalent atoms:

Table S15. Hydrogen bonds for **34** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.83	1.96	2.6657(15)	142.2

Symmetry transformations used to generate equivalent atoms: