One-Pot Synthesis of 1,3-Oxazin-4-ones through an Ir-Catalyzed Mild Formal Condensation Reaction of Secondary Amides with Acyl Chlorides

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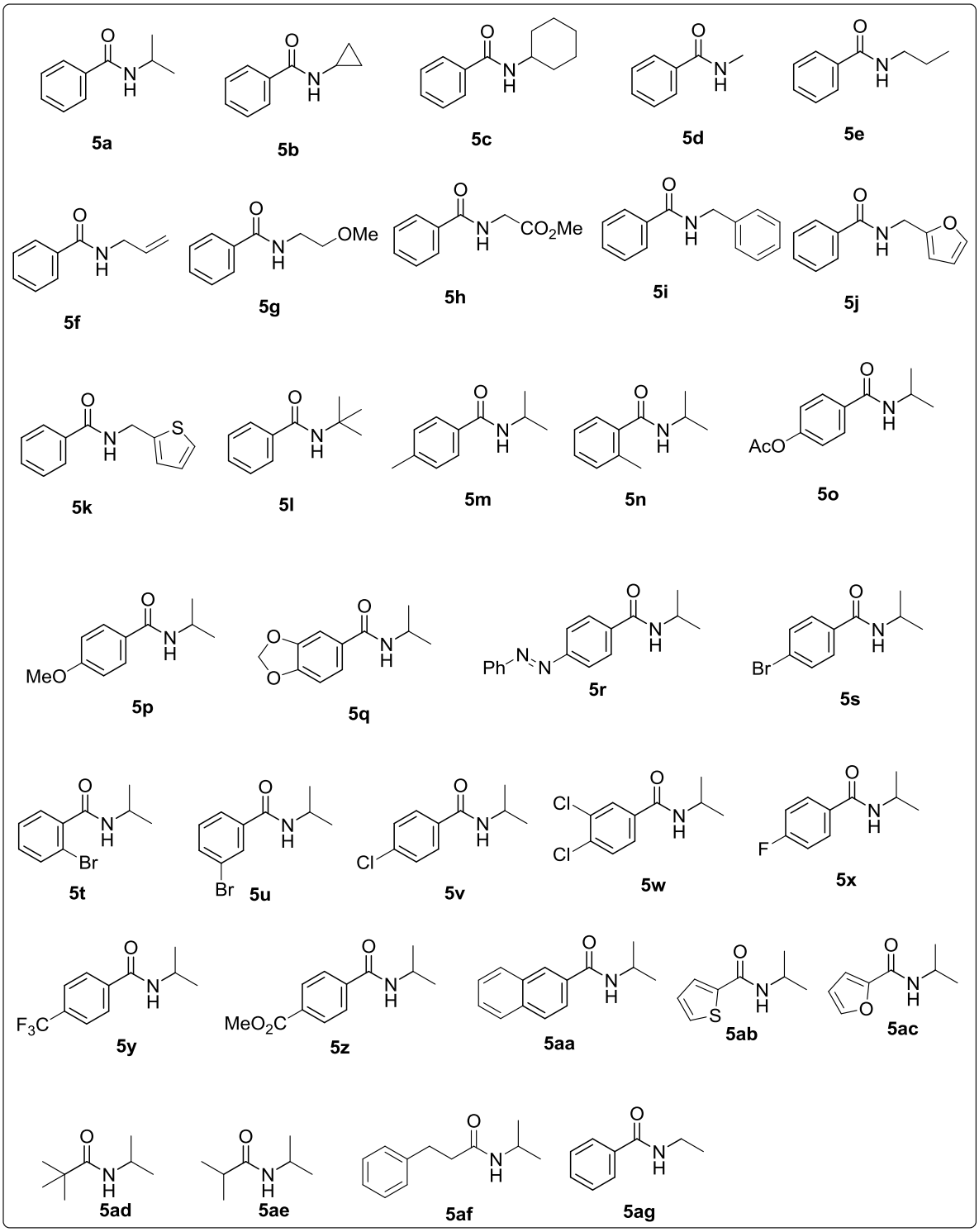
1. General Information

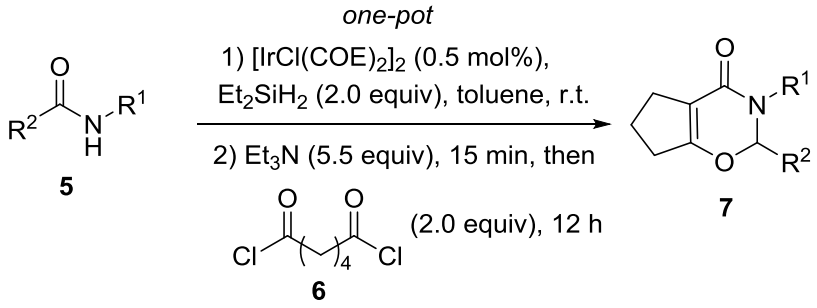
Melting points were determined by a Switzerland Büchi M-560 automatic melting point apparatus. Infrared spectra were measured with a Nicolet Avatar 330 FT-IR spectrometer using film KBr pellet techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometer with $CDCl_3$ as solvent. Chemical shifts (δ) are reported in ppm and respectively referenced to either the internal standard Me_4Si or solvent signals (Me_4Si at 0 ppm for ^{1}H NMR and $CDCl_3$ at 77.0 ppm for ^{13}C NMR). HRMS spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. Unless otherwise stated, reactions were performed in oven-dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Flash column chromatography was performed with silica gel (200-300 mesh), eluting with AcOEt / Petroleum ether (EA / PE). Toluene was distilled over sodium under N_2. All other commercially available compounds were used as received.

Table S1. The structures of amides used



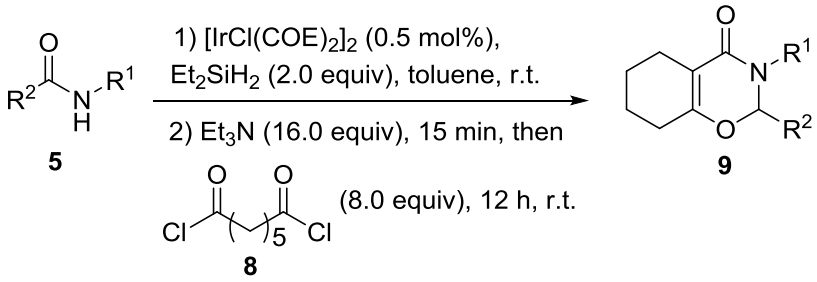
3. Experiment Details

3.1 General Procedure A for Synthesis of 2,3,6,7-tetrahydrocyclopenta[*e*]-1,3-oxazin-4-one 7.



To a solution of secondary amide **5** (0.50 mmol, 1.0 equiv) and $[IrCl(COE)_2]_2$ (2.2 mg, 0.5 mol%, weighted in the glove box) in toluene (2.5 mL, 0.2 M) was added Et_2SiH_2 (130 μL, 1.0 mmol, 2.0 equiv) at room temperature. The mixture was stirred at the same temperature until complete consumption of amide (monitored by TLC). Then Et_3N (382 μL, 2.75 mmol, 5.5 equiv) was added. After being stirred for 15 min, to the reaction mixture a solution of adipoyl chloride **6** (146 μL, 1.0 mmol, 2.0 equiv) in toluene (1.0 mL) was added dropwise and stirred for 12 h at room temperature. The resulted mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (elution AcOEt / Petroleum ether) to provide the corresponding 1,3-oxazin-4-ones **7**.

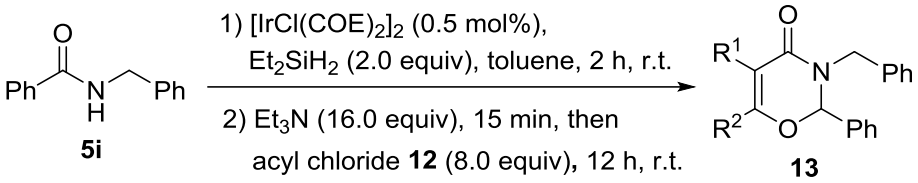
3.2 General Procedure B for Synthesis of 2,3,5,6,7,8-hexahydro-4*H*-benzo[*e*]-1,3-oxazin-4-one 9.



To a solution of secondary amide **5** (0.50 mmol, 1.0 equiv.) and $[IrCl(COE)_2]_2$ (2.2 mg, 0.5 mol%, weighted in the glove box) in toluene (2.5 mL, 0.2 M) was added Et_2SiH_2 (130 μL, 1.0 mmol, 2.0 equiv) at room temperature. The mixture was stirred at the

same temperature until complete consumption of amide (monitored by TLC). Then Et_3N (1.1 mL, 8.0 mmol, 16.0 equiv) was added. After being stirred for 15 min, to the reaction mixture a solution of pimeloyl chloride **8** (654 μL, 4.0 mmol, 8.0 equiv) in toluene (4.0 mL) was added dropwise and stirred for 12 h at room temperature. The resulted mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (elution: AcOEt / Petroleum ether) to provide the corresponding 1,3-oxazin-4-ones **9**.

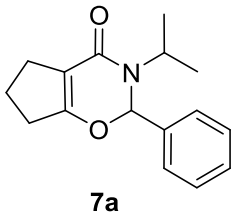
3.3 General Procedure B for Synthesis of 2,3-dihydro-4*H*-1,3-oxazin-4-one 13.



To a solution of secondary amide **5i** (0.50 mmol, 1.0 equiv.) and $[IrCl(COE)_2]_2$ (2.2 mg, 0.5 mol%, weighted in the glove box) in toluene (2.5 mL, 0.2 M) was added Et_2SiH_2 (130 μL, 1.0 mmol, 2.0 equiv) at room temperature. The mixture was stirred at the same temperature until complete consumption of amide (monitored by TLC). Then Et_3N (1.1 mL, 8.0 mmol, 16.0 equiv) was added. After being stirred for 15 min, to the reaction mixture a solution of acyl chloride **12** (4.0 mmol, 8.0 equiv) in toluene (4.0 mL) was added dropwise and stirred for 12 h at room temperature. The resulted mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (elution: AcOEt / Petroleum ether) to provide the corresponding 1,3-oxazin-4-ones **13**.

4. Preparation and Characterization of 1,3-oxazin-4-ones

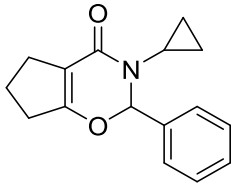
3-Isopropyl-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7a)



7a

Following the general procedure A, the reaction of secondary amide **5a** (82 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7a** (110 mg, yield: 86%) as a white solid; Mp 95-98 °C; IR (film) ν_{max}: 2967, 2870, 1660, 1439, 1311, 1204, 1041, 912, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.40 (m, 2H), 7.39-7.31 (m, 3H), 6.37 (s, 1H), 4.86 (septet, J = 6.9 Hz, 1H), 2.67-2.53 (m, 1H), 2.51-2.30 (m, 2H), 2.25-2.12 (m, 1H), 1.95-1.81 (m, 1H), 1.78-1.67 (m, 1H), 1.29 (d, J = 6.9 Hz, 3H), 1.05 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 162.2, 138.5, 128.7, 128.0 (2C), 126.9 (2C), 111.0, 85.0, 43.8, 31.2, 25.7, 21.3, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{16}H_{20}NO_2$ 258.1489, found 258.1484.

3-Cyclopropyl-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7b)

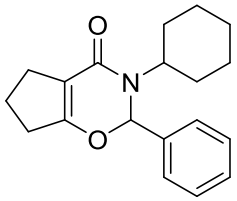


7b

Following the general procedure A, the reaction of secondary amide **5b** (81 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7b** (116 mg, yield: 91%) as a white solid; Mp 106-109 °C; IR (film) ν_{max}: 2960, 2869, 1669, 1455, 1429, 1364, 1299, 1235, 1109, 1028, 941, 759, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 5H), 6.29 (s, 1H), 2.64-2.51 (m, 2H), 2.50-2.34 (m, 2H), 2.32-2.18 (m, 1H), 1.96-1.83 (m, 1H), 1.82-1.70 (m, 1H), 1.05-0.93 (m, 1H), 0.87-0.78 (m, 1H), 0.77-0.64 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 163.9, 137.4, 128.9, 128.3 (2C), 126.5 (2C), 109.9, 90.4, 31.3, 26.9, 25.6, 19.5, 9.0, 6.3 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$

cacld for $C_{16}H_{17}NO_2Na$ 278.1151, found 278.1150.

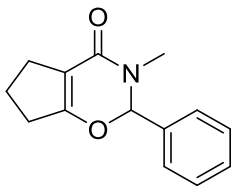
3-Cyclohexyl-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7c)



7c

Following the general procedure A, the reaction of secondary amide **5c** (102 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7c** (144 mg, yield: 97%) as a white solid; Mp 131-134 °C; IR (film) ν_{max}: 2930, 2855, 1660, 1533, 1439, 1310, 1216, 1129, 917, 894, 739, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.40 (m, 2H), 7.38-7.30 (m, 3H), 6.39 (s, 1H), 4.56-4.43 (m, 1H), 2.68-2.54 (m, 1H), 2.52-2.29 (m, 2H), 2.26-2.11 (m, 1H), 1.91-1.30 (m, 10H), 1.13-0.94 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 162.1, 138.7, 128.7, 127.0 (2C), 126.9 (2C), 111.1, 85.3, 51.6, 31.5, 31.3, 31.2, 25.8, 25.7, 25.6, 25.3, 19.4 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{19}H_{23}NO_2Na$ 320.1621, found 320.1616.

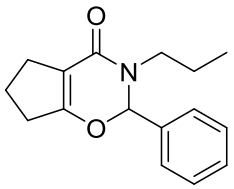
3-Methyl-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7d)



7d

Following the general procedure, the reaction of secondary amide **5d** (68 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7d** (86 mg, yield: 75%) as a white solid; Mp 117-120 °C; IR (film) ν_{max}: 2923, 2867, 1667, 1440, 1405, 1317, 1303, 1212, 1075, 758, 740, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 5H), 6.15 (s, 1H), 2.82 (s, 3H), 2.64-2.48 (m, 3H), 2.46-2.35 (m, 1H), 1.99-1.87 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 163.6, 136.0, 129.6, 128.7 (2C), 127.2 (2C), 109.7, 91.5, 31.3, 30.4, 26.0, 19.7 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{14}H_{15}NO_2Na$ 252.0995, found 252.0991.

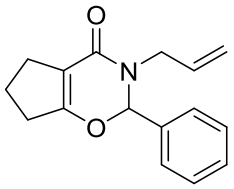
2-Phenyl-3-propyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7e)



7e

Following the general procedure A, the reaction of secondary amide **5e** (82 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7e** (96 mg, yield: 74%) as a white solid; Mp 95-97 °C; IR (film) ν_{max}: 2964, 2871, 1664, 1464, 1447, 1425, 1299, 1218, 1093, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 5H), 6.21 (s, 1H), 3.95-3.72 (m, 1H), 2.86-2.71 (m, 1H), 2.67-2.55 (m, 1H), 2.53-2.39 (m, 2H), 2.37-2.24 (m, 1H), 1.96-1.76 (m, 2H), 1.62-1.46 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 162.9, 136.6, 129.3, 128.4 (2C), 127.0 (2C), 110.1, 89.8, 45.2, 31.3, 25.8, 21.7, 19.6, 11.2 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{19}NO_2Na$ 280.1308, found 280.1303.

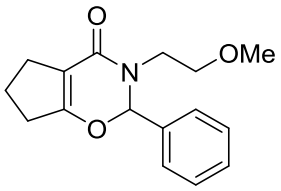
3-Allyl-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7f)



7f

Following the general procedure A, the reaction of secondary amide **5f** (81 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7f** (87 mg, yield: 68%) as a white solid; Mp 86-89 °C; IR (film) ν_{max}: 2956, 2839, 1664, 1444, 1216, 1080, 922, 741, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 5H), 6.21 (s, 1H), 5.84-5.67 (m, 1H), 5.10 (m, 2H), 4.63 (d, J = 15.7 Hz, 1H), 3.34 (dd, J = 15.7, 6.5 Hz, 1H), 2.64-2.43 (m, 3H), 2.40-2.26 (m, 1H), 2.00-1.78 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 162.6, 136.1, 133.0, 129.4, 128.4 (2C), 127.2 (2C), 117.4, 109.8, 89.2, 45.2, 31.3, 25.9, 19.6 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{16}H_{18}NO_2$ 256.1332, found 256.1327.

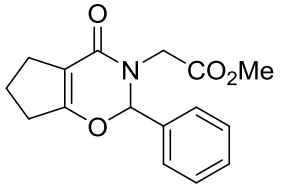
3-(2-Methoxyethyl)-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7g)



7g

Following the general procedure A, the reaction of secondary amide **5g** (90 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7g** (101 mg, yield: 74%) as a white solid; Mp 89-92 °C; IR (film) ν_{max}: 2927, 1666, 1464, 1446, 1421, 1362, 1302, 1209, 1118, 1080, 756, 738, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 5H, 6.39 (s, 1H),), 3.96 (dt, J = 14.5, 4.3 Hz, 1H), 3.58-3.48 (m, 1H), 3.44-3.36 (m, 1H), 3.22 (s, 3H), 3.18-3.07 (m, 1H), 2.63-2.53 (m, 1H), 2.52-2.37 (m, 2H), 2.34-2.22 (m, 1H), 1.97-1.73 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 162.8, 136.7, 129.1, 128.3 (2C), 127.1 (2C), 109.7, 90.6, 71.3, 58.6, 43.1, 31.3, 25.8, 19.5, ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{19}NO_3Na$ 296.1257, found 296.1252.

Methyl 2-(4-oxo-2-phenyl-4,5,6,7-tetrahydrocyclopenta[e][1,3]oxazin-3(2H)-yl) acetate (7h)

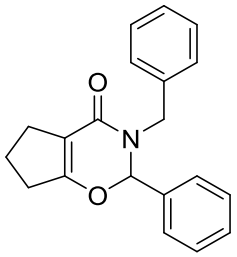


7h

Following the general procedure A, the reaction of secondary amide **5h** (97 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7h** (105 mg, yield: 73%) as a white solid; Mp 97-100 °C; IR (film) ν_{max}: 2951, 2921, 1749, 1668, 1427, 1396, 1210, 1074, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52-7.36 (m, 5H), 6.37 (s, 1H), 4.47 (d, J = 17.7 Hz, 1H), 3.61 (s, 3H), 3.24 (d, J = 17.7 Hz, 1H), 2.65-2.57 (m, 2H), 2.54 (t, J = 7.7 Hz, 2H), 2.06-1.93 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 169.9, 164.1, 134.2, 130.3, 128.8 (2C), 127.8 (2C), 109.6, 91.4, 51.9, 43.8, 31.1, 25.9, 19.8 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{17}NO_4Na$ 310.1050,

found 310.1046.

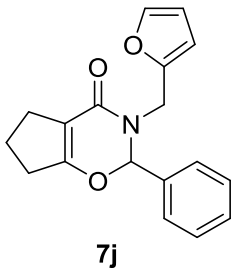
3-Benzyl-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7i)



7i

Following the general procedure A, the reaction of secondary amide **5i** (106 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7i** (127 mg, yield: 83%) as a white solid; Mp 78-81 °C; IR (film) ν_{max}: 2922, 2867, 1664, 1462, 1440, 1361, 1301, 1213, 1078, 756, 736, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.19 (m, 8H) ppm; 7.13 (d, J = 6.6 Hz, 2H), 6.15 (s, 1H), 5.37 (d, J = 15.4 Hz, 1H), 3.82 (d, J = 15.5 Hz, 1H), 2.72-2.61 (m, 1H), 2.60-2.45 (m, 2H), 2.41-2.29 (m, 1H), 2.00-1.79 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 162.9, 137.0, 135.6, 129.4, 128.4 (3C), 127.6 (2C), 127.23 (2C), 127.21 (2C), 109.5, 89.1, 45.9, 31.3, 25.9, 19.6 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{20}H_{19}NO_2Na$ 328.1308, found 328.1302.

3-(Furan-2-ylmethyl)-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7j)

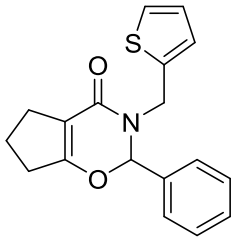


7j

Following the general procedure A, the reaction of secondary amide **5j** (101 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7j** (130 mg, yield: 88%) as a white solid; Mp 92-95 °C; IR (film) ν_{max}: 2923, 2868, 1665, 1460, 1443, 1300, 1205, 1075, 1012, 738, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 5H), 7.30-7.26 (m, 1H), 6.34-6.21 (m, 2H), 6.14 (d, J = 2.8 Hz, 1H), 5.11 (d, J = 15.8 Hz,

1H), 3.98 (d, J = 15.8 Hz, 1H), 2.68-2.56 (m, 1H), 2.55-2.43 (m, 2H), 2.42-2.29 (m, 1H), 1.99-1.78 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 162.6, 150.4, 142.0, 135.8, 129.4, 128.4 (2C), 127.2 (2C), 110.2, 109.6, 108.3, 89.7, 39.1, 31.3, 25.8, 19.6 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{18}H_{17}NO_3Na$ 318.1101, found 318.1095.

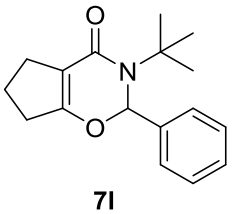
2-Phenyl-3-(thiophen-2-ylmethyl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7k)



7k

Following the general procedure A, the reaction of secondary amide **5k** (109 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7k** (141 mg, yield: 90%) as a white solid; Mp 80-83 °C; IR (film) ν_{max}: 2921, 2866, 1663, 1459, 1443, 1367, 1299, 1210, 853, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.32 (m, 5H), 7.18 (d, J = 4.9 Hz, 1H), 6.89-6.84 (m, 1H), 6.73 (d, J = 2.7 Hz, 1H), 6.22 (s, 1H), 5.32 (d, J = 15.6 Hz, 1H), 4.05 (d, J = 15.6 Hz, 1H), 2.79-2.60 (m, 1H), 2.59-2.45 (m, 2H), 2.43-2.33 (m, 1H), 1.99-1.84 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 162.8, 139.7, 135.6, 129.6, 128.5 (2C), 127.4 (2C), 126.5, 126.4, 125.3, 109.5, 89.7, 40.9, 31.3, 25.9, 19.6 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{18}H_{17}NO_2SNa$ 334.0872, found 334.0865.

3-(tert-Butyl)-2-phenyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7l)

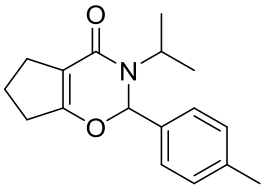


7l

Following the general procedure A, the reaction of secondary amide **5l** (89 mg, 0.50

mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7l** (69 mg, yield: 51%) as a white solid; Mp 103-106 °C; IR (film) ν_{max}: 2965, 2925, 1635, 1540, 1491, 1451, 1364, 1312, 1218, 718, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45-7.40 (m, 2H), 7.36-7.29 (m, 3H), 6.62 (s, 1H), 2.60-2.52 (m, 1H), 2.47-2.39 (m, 1H), 2.33-2.25 (m, 1H), 2.22-2.12 (m, 1H), 1.93-1.80 (m, 1H), 1.75-1.65 (m, 1H), 1.52 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 163.8, 139.0, 128.7, 128.1 (2C), 127.0 (2C), 112.5, 87.0, 56.9, 31.1, 29.1 (3C), 25.7, 19.6 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{17}H_{22}NO_2$ 272.1645, found 272.1644.

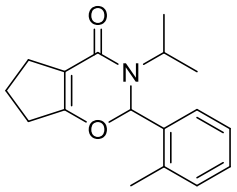
3-Isopropyl-2-(p-tolyl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7m)



7m

Following the general procedure A, the reaction of secondary amide **5m** (89 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7m** (136 mg, yield: 88%) as a white solid; Mp 116-119 °C; IR (film) ν_{max}: 2971, 1659, 1541, 1507, 1445, 1369, 1298, 1203, 1041, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.7 Hz, 2H), 7.15 (d, J = 7.4 Hz, 2H), 6.33 (s, 1H), 4.84 (septet, J = 6.5 Hz, 1H), 2.68-2.55 (m, 1H), 2.68-2.55 (m, 1H), 2.51-2.36 (m, 2H), 2.34 (s, 3H), 2.25-2.13 (m, 1H), 1.95-1.81 (m, 1H), 1.80-1.66 (m, 1H), 1.28 (d, J = 6.5 Hz, 3H), 1.04 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 162.2, 138.6, 135.5, 128.7 (2C), 126.9 (2C), 110.8, 85.0, 43.7, 31.2, 25.7, 21.2, 21.0, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{17}H_{21}NO_2Na$ 294.1465, found 294.1460.

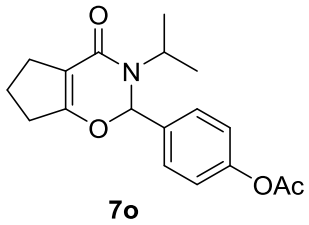
3-Isopropyl-2-(o-tolyl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7n)



7n

Following the general procedure A, the reaction of secondary amide **5n** (89 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7n** (117 mg, yield: 86%) as a white solid; Mp 101-103 °C; IR (film) ν_{max}: 2966, 2878, 1745, 1661, 1440, 1370, 1202, 1040, 921, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 6.5 Hz, 2H), 7.21 (d, J = 7.0 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 6.49 (s, 1H), 4.80 (septet, J = 6.5 Hz, 1H), 2.70-2.58 (m, 1H), 2.51 (s, 3H), 2.49-2.38 (m, 2H), 2.23-2.09 (m, 1H), 1.96-1.82, 1.29 (d, J = 6.5 Hz, 3H), 1.81-1.69 (m, 1H), (m, 1H), 0.94 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 162.6, 136.6, 135.3, 131.0, 129.0, 127.7, 125.2, 110.2, 83.7, 43.7, 31.2, 25.9, 21.2, 20.5, 19.5, 19.3 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{17}H_{22}NO_2$ 272.1645, found 272.1640.

4-(3-Isopropyl-4-oxo-2,3,4,5,6,7-hexahydrocyclopenta[e][1,3]oxazin-2-yl)phenyl acetate (7o)

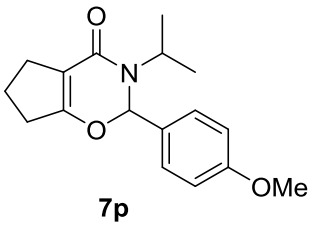


7o

Following the general procedure A, the reaction of secondary amide **5o** (111 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7o** (134 mg, yield: 85%) as a white solid; Mp 120-123 °C; IR (film) ν_{max}: 2970, 2926, 2872, 1762, 1664, 1504, 1445, 1370, 1200, 1164, 1016, 913, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.7 Hz, 2H)， 7.09 (d, J = 7.6 Hz, 2H), 6.37 (s, 1H), 4.87 (septet, J = 7.1 Hz, 1H), 2.67-2.57 (m, 1H), 2.52-2.42 (m, 1H), 2.41-2.34 (m, 1H), 2.30 (s, 3H), 2.26-2.16 (m, 1H), 1.96-1.84 (m, 1H), 1.83-1.70 (m, 1H), 1.29 (d, J = 7.1 Hz, 3H), 1.06 (d, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 165.9, 162.1, 150.9, 136.0, 128.1 (2C), 121.2 (2C), 111.0, 84.4, 43.9, 31.2, 25.7, 21.2, 20.9, 20.5, 19.3 ppm;

HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{18}H_{22}NO_4$ 316.1543, found 316.1541.

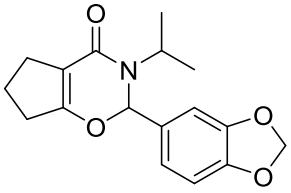
3-Isopropyl-2-(4-methoxyphenyl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7p)



7p

Following the general procedure A, the reaction of secondary amide **5p** (97 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7p** (113 mg, yield: 78%) as a white solid; Mp 103-106 °C; IR (film) ν_{max}: 2970, 2869, 1659, 1512, 1444, 1307, 1253, 1173, 1033, 823, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.1 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.29 (s, 1H), 4.79 (septet, J = 6.7 Hz, 1H), 3.77 (s, 1H), 2.64-2.51 (m, 1H), 2.46-2.29 (m, 2H), 2.23-2.09 (m, 1H), 1.92-1.79 (m, 1H), 1.77-1.63 (m, 1H), 1.24 (d, J = 6.7 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 162.3, 160.0, 130.5, 128.3 (2C), 113.4 (2C), 110.7, 85.0, 55.1, 43.8, 31.3, 25.8, 21.2, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{17}H_{22}NO_3$ 288.1594, found 288.1587.

2-(Benzo[d][1,3]dioxol-5-yl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7q)

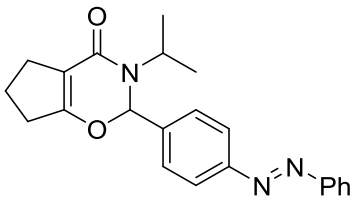


7q

Following the general procedure A, the reaction of secondary amide **5q** (104 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7q** (142 mg, yield: 94%) as a white solid; Mp 123-126 °C; IR (film) ν_{max}: 2971, 1660, 1490, 1431, 1298, 1241, 1203, 1098, 1038, 929, 872, 791 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.90 (app. d, J = 11.7 Hz, 2H), 6.75 (d, J = 7.9 Hz, 1H), 6.28 (s, 1H), 5.97 (s, 2H), 4.82 (septet, J =

6.6 Hz, 1H), 2.68-2.56 (m, 1H), 2.51-2.34 (m, 2H), 2.29-2.18 (m, 1H), 1.96-1.85 (m, 1H), 1.84-1.71 (m, 1H), 1.27 (d, J = 6.6 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 162.1, 148.0, 147.7, 132.5, 120.9, 110.8, 107.6, 107.4, 101.2, 85.0, 43.8, 31.3, 25.8, 21.3, 20.4, 19.4 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{17}H_{20}NO_4$ 302.1387, found 302.1382.

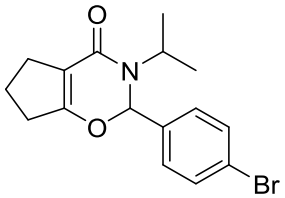
(E)-3-Isopropyl-2-(4-(phenyldiazenyl)phenyl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7r)



7r

Following the general procedure A, the reaction of secondary amide **5r** (134 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7r** (155 mg, yield: 86%) as a white solid; Mp 140-143 °C; IR (film) ν_{max}: 2972, 2867, 1659, 1533, 1442, 1221, 1040, 880, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.85 (m, 4H), 7.58 (d, J = 7.5 Hz, 2H), 7.55-7.45 (m, 3H), 6.41 (s, 1H), 4.92 (septet, J = 6.4 Hz, 1H), 2.70-2.57 (m, 1H), 2.54-2.42 (m, 1H), 2.41-2.31 (m, 1H), 2.28-2.15 (m, 1H), 1.97-1.84 (m, 1H), 1.78-1.67 (m, 1H), 1.31 (d, J = 6.4 Hz, 3H), 1.09 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 162.2, 152.9, 152.5, 141.3, 131.3, 129.1 (2C), 127.9 (2C), 122.9 (2C), 122.5 (2C), 111.4, 84.7, 43.9, 31.4, 25.8, 21.4, 20.6, 19.5 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for$C_{22}H_{23}N_3O_2Na$ 384.1682, found 384.1675.

2-(4-Bromophenyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7s)

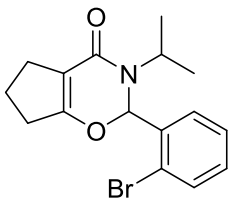


7s

Following the general procedure A, the reaction of secondary amide **5s** (121 mg, 0.50

mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7s** (147 mg, yield: 87%) as a white solid; Mp 107-109 °C; IR (film) ν_{max}: 2972, 2868, 1656, 1485, 1442, 1225, 1201, 1010, 808, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 7.5 Hz, 2H) , 7.31 (d, J = 7.5 Hz, 2H), 6.32 (s, 1H), 4.88 (septet, J = 6.5 Hz, 1H), 2.67-2.56 (m, 1H), 2.52-2.40 (m, 1H), 2.40-2.30 (m, 1H), 2.25-2.13 (m, 1H), 1.96-1.84 (m, 1H), 1.81-1.69 (m, 1H), 1.28 (d, J = 6.5 Hz, 3H), 1.05 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 162.0, 137.7, 131.3 (2C), 128.7 (2C), 123.0, 111.2, 84.3, 43.8, 31.3, 25.7, 21.3, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{18}BrNO_2Na$ 358.0413, found 358.0406.

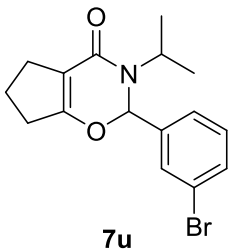
2-(2-Bromophenyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7t)



7t

Following the general procedure A, the reaction of secondary amide **5t** (121 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7t** (144 mg, yield: 86%) as a white solid; Mp 100-103 °C; IR (film) ν_{max}: 2971, 2869, 1667, 1429, 1369, 1204, 1026, 930, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 7.7, 1.3 Hz, 1H) , 7.36 (dd, J = 7.6, 1.8 Hz, 1H), 7.30-7.21 (m, 2H), 6.65 (s, 1H), 4.83 (septet, J = 6.9 Hz, 1H), 2.73-2.58 (m, 1H), 2.53-2.39 (m, 2H), 2.25-2.12 (m, 1H), 1.99-1.85 (m, 1H), 1.83-1.71 (m, 1H), 1.83-1.71 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 162.1, 136.4, 133.5, 130.6, 129.3, 126.8, 123.0, 109.9, 84.6, 43.5, 31.2, 25.8, 20.8, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{18}BrNO_2Na$ 358.0413, found 358.0405.

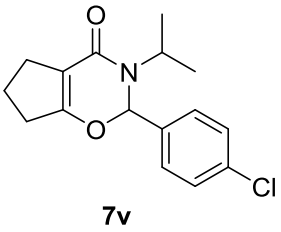
2-(3-Bromophenyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7u)



7u

Following the general procedure A, the reaction of secondary amide **5u** (121 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7u** (154 mg, yield: 91%) as a white solid; Mp 121-124 °C; IR (film) ν_{max}: 2971, 2924, 2868, 1658, 1446, 1421, 1299, 1222, 1203, 1129, 1041, 786 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H) , 7.47 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H) , 6.33 (s, 1H), 4.88 (septet, *J* = 6.9 Hz, 1H), 2.66-2.56 (m, 1H), 2.53-2.42 (m, 1H), 2.41-2.31 (m, 1H), 2.29-2.17 (m, 1H), 1.85-1.84 (m, 1H), 1.82-1.70 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 161.8, 141.0, 131.9, 129.9, 129.6, 125.5, 122.4, 111.2, 84.1, 43.9, 31.2, 25.7, 21.3, 20.5, 19.3 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{18}BrNO_2Na$ 358.0413, found 358.0407.

2-(4-Chlorophenyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7v)

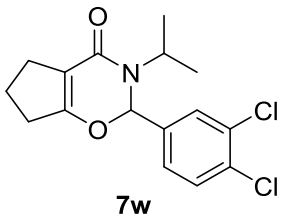


7v

Following the general procedure A, the reaction of secondary amide **5v** (99 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7v** (135 mg, yield: 93%) as a white solid; Mp 98-101 °C; IR (film) ν_{max}: 2972, 2869, 1659, 1488, 1443, 1224, 1091, 929, 809, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.34 (s, 1H), 4.88 (septet, *J* = 6.7 Hz, 1H), 2.68- 2.56 (m, 1H), 2.53-2.40 (m, 1H), 2.40-2.30 (m, 1H), 2.25-2.12 (m, 1H), 1.97-1.82 (m, 1H), 1.81-1.67 (m, 1H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H),ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): δ 165.9, 162.0, 137.2, 134.7, 128.4 (2C), 128.3 (2C), 111.1, 84.3, 43.8, 31.2, 25.7, 21.3, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + Na]^+$ cacld for $C_{16}H_{18}ClNO_2Na$ 314.0918, found 314.0913.

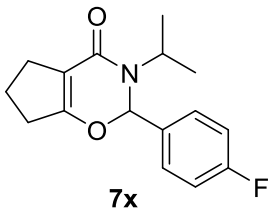
2-(3,4-Dichlorophenyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7w)



7w

Following the general procedure A, the reaction of secondary amide **5w** (116 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7w** (148 mg, yield: 90%) as a white solid; Mp 129-132 °C; IR (film) ν_{max}: 2973, 2869, 1656, 1442, 1407, 1390, 1372, 1299, 1221, 1202, 1131, 1031, 932, 899, 872, 852, 821, 755, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 6.30 (s, 1H), 4.89 (septet, *J* = 6.7 Hz, 1H), 2.69-2.56 (m, 1H), 2.55-2.43 (m, 1H), 2.42-2.30 (m, 1H), 2.29-2.17 (m, 1H), 2.00-1.85 (m, 1H), 1.85-1.71 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1 , 161.8, 139.2, 133.2, 132.7, 130.2, 129.0, 126.3, 111.5, 83.7, 44.0, 31.3, 25.8, 21.4, 20.6, 19.4 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{16}H_{18}Cl_2NO_2$ 326.0709, found 326.0703.

2-(4-Fluorophenyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7x)

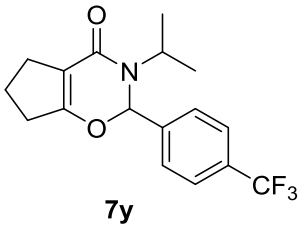


7x

Following the general procedure A, the reaction of secondary amide **5x** (91 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7x** (107 mg, yield: 78%) as

a white solid; Mp 106-109 °C; IR (film) ν_{max}: 2973, 2871, 1655, 1508, 1443, 1370, 1226, 1157, 827, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.32 (m, 2H), 7.07-6.94 (m, 2H), 6.31 (s, 1H), 4.84 (septet, J = 6.9 Hz, 1H), 2.66-2.53 (m, 1H), 2.50-2.38 (m, 1H), 2.38-2.28 (m, 1H), 2.23-2.10 (m, 1H), 1.93-1.81 (m, 1H), 1.79-1.67 (m, 1H), 1.25 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 162.9 (d, J_{C-F} = 248.5 Hz), 162.1, 134.5 (d, J_{C-F} = 3.0 Hz), 128.9 (d, J_{C-F} = 8.3 Hz, 2C), 115.1 (d, J_{C-F} = 21.7 Hz, 2C), 111.1, 84.5, 43.9, 31.3, 25.8, 21.3, 20.5, 19.4 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for$C_{16}H_{19}FNO_2$ 276.1394, found 276.1392.

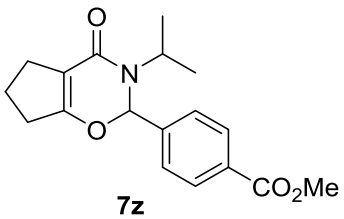
3-Isopropyl-2-(4-(trifluoromethyl)phenyl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7y)



7y

Following the general procedure A, the reaction of secondary amide **5y** (116 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7y** (135 mg, yield: 83%) as a white solid; Mp 110-113 °C; IR (film) ν_{max}: 2974, 2874, 1659, 1444, 1337, 1164, 1127, 1068, 1017, 825, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H) 6.36 (s, 1H), 4.88 (septet, J = 6.9 Hz, 1H), 2.64-2.53 (m, 1H), 2.51-2.39 (m, 1H), 2.37-2.26 (m, 1H), 2.23- 2.10 (m, 1H), 1.95-1.80 (m, 1H), 1.78-1.65 (m, 1H), 1.27 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 166.1, 142.7, 131.0 (q, J_{C-F} = 32.4 Hz), 127.4 (2C), 125.2 (q, J_{C-F} = 3.8 Hz, 2C), 123.8 (q, J_{C-F} = 272.1 Hz, 2C), 111.5, 84.2, 43.9, 31.3, 25.8, 21.4, 20.6, 19.4 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{17}H_{19}F_3NO_2$ 326.1362, found 326.1361.

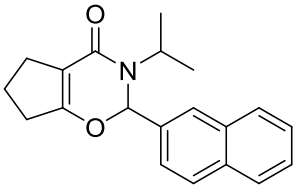
Methyl 4-(3-isopropyl-4-oxo-2,3,4,5,6,7-hexahydrocyclopenta[e][1,3]oxazin-2-yl) benzoate (7z)



7z

Following the general procedure A, the reaction of secondary amide **5z** (111 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7z** (142 mg, yield: 90%) as a white solid; Mp 121-124 °C; IR (film) ν_{max}: 2972, 2873, 1725, 1659, 1540, 1442, 1279, 1203, 1108, 1019, 816, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 7.7 Hz, 2H) , 7.53 (d, J = 7.7 Hz, 2H), 6.40 (s, 1H), 4.91 (septet, J = 6.5 Hz, 1H), 2.69-2.56 (m, 1H), 3.92 (s, 3H), 2.53-2.42 (m, 1H), 2.39-2.28 (m, 1H), 2.26-2.13 (m, 1H), 1.97-1.82 (m, 1H), 1.80-1.66 (m, 1H) , 1.30 (d, J = 6.5 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 166.0, 161.9, 143.5, 130.6, 129.3 (2C), 127.0 (2C), 111.3, 84.4, 52.0, 43.8, 31.2, 25.7, 21.3, 20.5, 19.3 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{18}H_{22}NO_4$ 316.1543, found 316.1538.

3-Isopropyl-2-(naphthalen-2-yl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7aa)

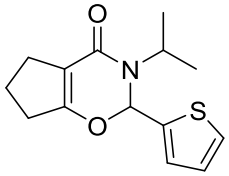


7aa

Following the general procedure A, the reaction of secondary amide **5aa** (107 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7aa** (130 mg, yield: 84%) as a white solid; Mp 138-141 °C; IR (film) ν_{max}: 2970, 2869, 1656, 1447, 1430, 1370, 1295, 1200, 1041, 861, 821, 785, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90-7.70 (m, 4H) 7.57 (d, J = 8.5 Hz, 1H), 7.54-7.45 (m, 2H), 6.52 (s, 1H), 4.95 (septet, J = 6.6 Hz, 1H), 2.70-2.57 (m, 1H), 2.52-2.40 (m, 1H), 2.39-2.29 (m, 1H), 2.21-2.10 (m, 1H), 1.92-1.79 (m, 1H), 1.73-1.59 (m, 1H), 1.32 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 162.3, 135.7, 133.3, 132.5, 128.3, 128.2, 127.4, 126.6, 126.5, 126.4, 124.5, 111.1, 85.1, 43.9, 31.2,

25.8, 21.4, 20.5, 19.3 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{20}H_{22}NO_2$ 308.1645, found 308.1638.

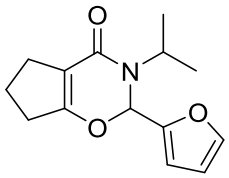
3-Isopropyl-2-(thiophen-2-yl)-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7ab)



7ab

Following the general procedure A, the reaction of secondary amide **5ab** (85 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7ab** (100 mg, yield: 76%) as a white solid; Mp 82-85 °C; IR (film) ν_{max}: 2969, 2917, 1656, 1636, 1436, 1369, 1291, 1200, 1127, 1034, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 1H) , 7.09 (br. s, 1H), 6.93 (br. s, 1H), 6.55 (s, 1H), 4.81 (septet, J = 6.6 Hz, 1H), 2.74- 2.58 (m, 1H), 2.55-2.38 (m, 2H) , 2.39-2.26 (m, 1H), 2.04-1.75 (m, 2H), 1.28 (d, J = 6.6 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 161.5, 142.9, 127.2, 126.3, 126.2, 111.3, 82.3, 44.0, 31.4, 25.8, 21.1, 20.8, 19.5 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{14}H_{18}NO_2S$ 264.1053, found 264.1049.

2-(Furan-2-yl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7ac)

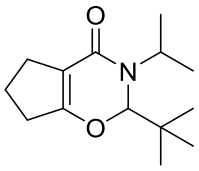


7ac

Following the general procedure A, the reaction of secondary amide **5ac** (104 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7ac** (87 mg, yield: 70%) as a white solid; Mp 90-93 °C; IR (film) ν_{max}: 2964, 2867, 1743, 1663, 1439, 1373, 1208, 1013, 859, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 6.38-6.30 (m, 3H), 4.79 (septet, J = 6.6 Hz, 1H), 2.72-2.58 (m, 1H), 2.55-2.40 (m, 2H), 2.39-2.28

(m, 1H), 2.02-1.78 (m, 2H), 1.26 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 161.7, 151.2, 143.1, 110.9, 110.4, 110.3, 79.8, 43.7, 31.2, 26.0, 21.0, 20.8, 19.7 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{14}H_{18}NO_3$ 248.1281, found 248.1276.

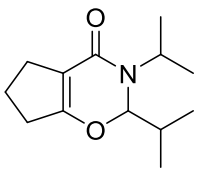
2-(tert-Butyl)-3-isopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7ad)



7ad

Following the general procedure A, the reaction of secondary amide **5ad** (72 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7ad** (97 mg, yield: 82%) as a white solid; Mp 80-83 °C; IR (film) ν_{max}: 2951, 2864, 1663, 1634, 1482, 1417, 1303, 1185, 1096, 960, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92 (s, 1H), 3.62 (septet, J = 6.8 Hz, 1H), 2.65- 2.54 (m, 1H), 2.54-2.42 (m, 2H), 2.41-2.32 (m, 1H), 2.00-1.82 (m, 2H), 1.52 (d, J = 6.8 Hz, 3H), 1.33 (d, J = 6.8 Hz, 3H), 0.99 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 163.9, 110.0, 97.8, 53.9, 39.4, 30.9, 26.3 (3C), 25.4, 21.5, 20.6, 19.5 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{14}H_{24}NO_2$ 238.1802, found 238.1798.

2,3-Diisopropyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7ae)

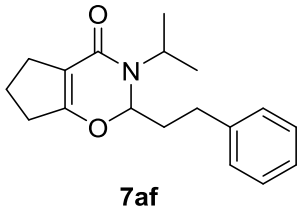


7ae

Following the general procedure A, the reaction of secondary amide **5ae** (65 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7ae** (73 mg, yield: 65%) as a yellow oil; IR (film) ν_{max}: 2967, 2875, 1757, 1654, 1444, 1367, 1215, 1127, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.96 (d, J = 7.3 Hz, 1H), 4.37 (septet, J = 6.6 Hz,

1H), 2.69-2.57 (m, 1H), 2.55-2.40 (m, 3H), 2.39-2.29 (m, 1H), 2.00-1.89 (m, 2H), 1.26 (d, J = 6.5 Hz, 3H), 1.23 (d, J = 6.7 Hz, 3H), 0.98 (t, J = 7.7 Hz, 6H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 163.0, 110.1, 92.5, 47.3, 31.5, 31.1, 25.9, 21.7, 21.2, 19.6, 19.0, 18.6 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{13}H_{22}NO_2$ 224.1645, found 224.1641.

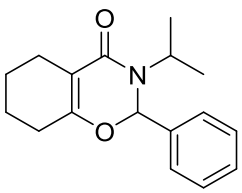
3-Isopropyl-2-phenethyl-2,3,6,7-tetrahydrocyclopenta[e][1,3]oxazin-4(5H)-one (7af)



7af

Following the general procedure A, the reaction of secondary amide **5af** (96 mg, 0.50 mmol) gave, after FC (eluent: EA / PE = 1: 3), oxazinone **7af** (60 mg, yield: 42%) as a yellow oil; IR (film) ν_{max}: 2964, 2871, 1744, 1661, 1452, 1369, 1304, 1216, 1042, 848, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.16 (m, 3H), 7.35-7.28 (m, 2H), 5.28 (d, J = 8.0 Hz, 1H), 4.62 (septet, J = 6.6 Hz, 1H), 2.82-2.68 (m, 3H), 2.67-2.58 (m, 1H), 2.55-2.43 (m, 2H), 2.39-2.28 (m, 1H), 2.00-1.87 (m, 2H), 1.76-1.61 (m, 1H), 1.11 (d, J = 6.6 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 161.3, 140.4, 128.5, 128.4 (2C), 126.2 (2C), 109.8, 85.2, 43.5, 34.6, 31.5, 31.1, 26.0, 21.3, 20.7, 19.7 ppm; HRMS (ESI) *m/z*: $[M + H]^+$ cacld for $C_{18}H_{24}NO_2$ 286.1802, found 286.1795.

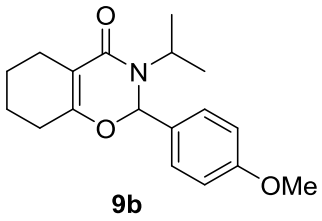
3-Isopropyl-2-phenyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9a)



9a

Following the general procedure B, the reaction of secondary amide **5a** (82 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9a** (117 mg, yield: 86%) as a white solid; Mp 103-105 ℃; IR (film) ν_{max} 2926, 2854, 1663, 1639, 1457, 1435, 1228, 1215, 762, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.30 (m, 5H), 6.17 (s, 1H), 4.83 (septet, J = 6.9 Hz, 1H), 2.41-2.28 (m, 1H), 2.18-2.02 (m, 2H), 1.82-1.72 (m, 1H), 1.70-1.55 (m, 2H), 1.56-1.43 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H), 1.22-1.16 (m, 1H), 1.04 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 158.9, 138.7, 128.7, 128.1 (2C), 127.0 (2C), 109.3, 82.7, 44.3, 27.4, 21.8, 21.7, 21.3, 21.2, 20.2 ppm; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{17}H_{21}NO_2Na$ 294.1465, found 294.1471.

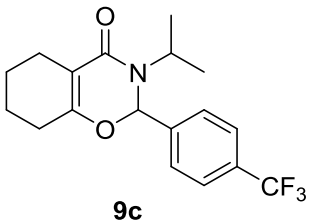
3-Isopropyl-2-(4-methoxyphenyl)-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9b)



9b

Following the general procedure B, the reaction of secondary amide **5p** (97 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9b** (128 mg, yield: 85%) as a white solid; Mp 102-104 ℃; IR (film) ν_{max} 2956, 2925, 2854, 1721, 1667, 1614, 1586, 1463, 1378, 1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 6.95-6.78 (m, 2H), 6.17 (s, 1H), 4.77 (hept, J = 6.9 Hz, 1H), 3.81 (s, 3H), 2.41-2.28 (m, 1H), 2.21-2.01 (m, 2H), 1.88-1.69 (m, 2H), 1.70-1.55 (m, 2H), 1.55-1.39 (m, 1H), 1.29 (d, J = 6.9 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 159.9, 158.7, 130.8, 128.3 (2C), 113.4 (2C), 109.0, 82.6, 55.2, 44.2, 27.4, 21.9, 21.7, 21.2, 21.2, 20.2 ppm; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{18}H_{23}NO_3Na$ 324.1570 found 324.1571.

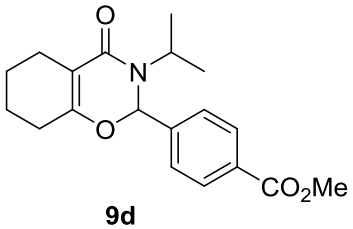
3-Isopropyl-2-(4-(trifluoromethyl)phenyl)-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9c)



9c

Following the general procedure B, the reaction of secondary amide **5y** (116 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9c** (115 mg, yield: 68%) as a white solid; Mp 110-112 ℃; IR (film) ν_{max} 2937, 2860, 1662, 1640, 1442, 1411, 1326, 1166, 1128, 1112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.48 (m, 4H), 6.24 (s, 1H), 4.87 (septet, J = 6.9 Hz, 1H), 2.42-2.23 (m, 1H), 2.20-2.00 (m, 2H), 1.85-1.73 (m, 1H), 1.72-1.57 (m, 2H), 1.57-1.43 (m, 1H), 1.31 (d, J = 6.9 Hz, 3H), 1.27-1.17 (m, 1H), 1.05 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7, 159.2, 142.9, 131.0 (q, J_{C-F} = 32.5 Hz), 127.3 (2C), 125.2 (q, J_{C-F} = 3.7 Hz, 2C), 123.9 (q, J_{C-F} = 272.2 Hz), 109.6, 81.8, 44.3, 27.4, 21.7, 21.6, 21.4, 21.2, 20.3 ppm; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{18}H_{20}F_3NO_2Na$ 362.1338, found 362.1338.

Methyl 4-(3-isopropyl-4-oxo-3,4,5,6,7,8-hexahydro-2H-benzo[e] [1,3]oxazin-2-yl) benzoate (9d)

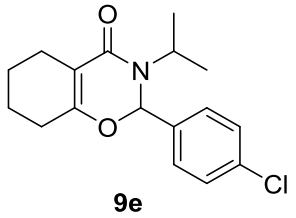


9d

Following the general procedure B, the reaction of secondary amide **5z** (111 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9d** (140 mg, yield: 85%) as a white solid; Mp 106-108 ℃; IR (film) ν_{max} 2956, 2926, 2854, 1726, 1663, 1644, 1494, 1438, 1311, 1278 cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 6.23 (s, 1H), 4.87 (septet, J = 7.0 Hz, 1H), 3.92 (s, 3H), 2.39-2.27 (m, 1H), 2.16-2.03 (m, 2H), 1.83-1.70 (m, 1H), 1.66-1.56 (m, 2H), 1.55-1.44 (m, 1H), 1.30 (d, J = 7.0 Hz, 3H), 1.23-1.11 (m, 1H), 1.05 (d, J = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 162.8, 159.1, 143.8, 130.6, 129.4 (2C), 127.0 (2C), 109.6, 82.0, 52.2, 44.2, 27.5, 21.8, 21.6, 21.4, 21.2, 20.2 ppm; HRMS (ESI) m/z [M + Na]+ calcd for $C_{19}H_{23}NO_4Na$ 352.1519, found 352.1519.

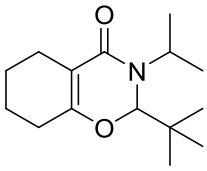
2-(4-Chlorophenyl)-3-isopropyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9e)



9e

Following the general procedure B, the reaction of secondary amide **5v** (99 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9e** (127 mg, yield: 83%) as a white solid; Mp 116-118 ℃; IR (film) ν_{max} 2924, 2852, 1661, 1634, 1441, 1404, 1310, 1291, 1227, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 4H), 6.17 (s, 1H), 4.83 (septet, J = 6.9 Hz, 1H), 2.41-2.28 (m, 1H), 2.18-2.03 (m, 2H), 1.82-1.72 (m, 1H), 1.71-1.56 (m, 2H), 1.56-1.43 (m, 1H), 1.29 (d, J = 6.9 Hz, 3H), 1.27-1.16 (m, 1H), 1.03 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8, 158.9, 137.4, 134.7, 128.4 (2C), 128.4 (2C), 109.4, 81.9, 44.2, 27.4, 21.8, 21.7, 21.3, 21.2, 20.2 ppm; HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{20}ClNO_2Na$ 328.1075, found 328.1081.

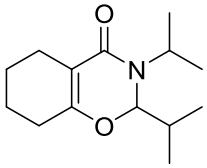
2-(tert-Butyl)-3-isopropyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9f)



9f

Following the general procedure B, the reaction of secondary amide **5ad** (72 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9f** (60 mg, yield: 48%) as a white solid; Mp 66-68 ℃; IR (film) ν_{max} 2959, 2931, 2869, 1674, 1640, 1479, 1457, 1398, 1380, 1309 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 1H), 3.44 (septet, J = 6.8 Hz, 1H), 2.38-2.26 (m, 1H), 2.21-2.01 (m, 3H), 1.79-1.69 (m, 2H), 1.68-1.58 (m, 1H), 1.56 (d, J = 6.8 Hz, 3H), 1.50-1.39 (m, 1H), 1.36 (d, J = 6.8 Hz, 3H), 0.99 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.3, 159.8, 107.9, 95.3, 54.7, 39.5, 26.9, 26.5 (3C), 22.1, 21.9, 21.5, 20.8, 20.3 ppm; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{25}NO_2Na$ 274.1778, found 274.1778.

2,3-Diisopropyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9g)

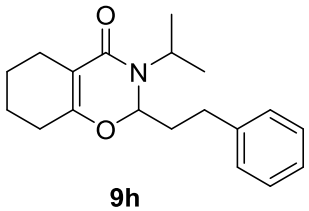


9g

Following the general procedure B, the reaction of secondary amide **5ae** (65 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9g** (56 mg, yield: 47%) as colorless oil; IR (film) ν_{max} 2960, 2929, 2873, 2857, 1659, 1641, 1450, 1398, 1393, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.81 (d, J = 7.3 Hz, 1H), 4.26 (septet, J = 6.9 Hz, 1H), 2.41-2.26 (m, 2H), 2.22-2.06 (m, 3H), 1.81-1.69 (m, 2H), 1.65-1.53 (m, 1H), 1.53-1.43 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H), 1.24 (d, J = 6.9 Hz, 3H), 0.97 (t, J = 6.6 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.4, 159.6, 108.0, 89.8, 47.9, 31.6, 27.1, 22.1, 21.9, 21.3, 21.2, 21.1, 18.9,

18.5 ppm; HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{14}H_{23}NO_2Na$ 260.1621, found 260.1621.

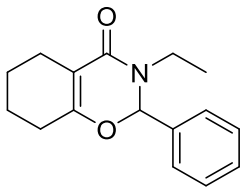
3-Isopropyl-2-phenethyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9h)



9h

Following the general procedure B, the reaction of secondary amide **5af** (96 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9h** (37 mg, yield: 25%) as colorless oil; IR (film) ν_{max} 2932, 2858, 1772, 1716, 1662, 1637, 1586, 1495, 1460, 1442 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 2H), 7.25-7.10 (m, 3H), 5.15 (dd, *J* = 9.6, 2.7 Hz, 1H), 4.58 (septet, *J* = 6.9 Hz, 1H), 2.81-2.61 (m, 3H), 2.41-2.30 (m, 1H), 2.26-2.11 (m, 2H), 2.08-1.97 (m, 1H), 1.83-1.71 (m, 2H), 1.67-1.46 (m, 3H), 1.13 (d, *J* = 6.9Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 158.2, 140.6, 128.6 (2C), 128.4 (2C), 126.2, 107.8, 82.5, 43.8, 34.4, 31.6, 27.2, 22.1, 22.0, 21.3, 21.0, 20.6 ppm; HRMS (ESI) m/z [M + Na]+ calcd for $C_{19}H_{25}NO_2Na$ 322.1778, found 322.1778.

3-Ethyl-2-phenyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9i)

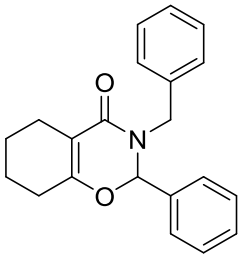


9i

Following the general procedure B, the reaction of secondary amide **5ag** (75 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9i** (106 mg, yield: 82%) as colorless oil; IR (film) ν_{max} 2923, 2851, 1664, 1646, 1470, 1446, 1417, 762, 733, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.50-7.35 (m, 5H), 6.08 (s, 1H), 3.76 (dq, J = 14.1, 7.2 Hz, 1H), 2.95 (dq, J = 14.1, 7.1 Hz, 1H), 2.38-2.28 (m, 1H), 2.28-2.12 (m, 2H), 2.05-1.95 (m, 1H), 1.67-1.55 (m, 3H), 1.55-1.44 (m, 1H), 1.08 (t, J = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 160.6, 136.6, 129.4, 128.5 (2C), 127.3 (2C), 108.1, 87.6, 38.5, 27.3, 21.9, 21.8, 21.3, 13.6 ppm; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{19}NO_2Na$ 280.1308 found 280.1314.

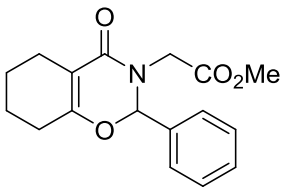
3-Benzyl-2-phenyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9j)



9j

Following the general procedure B, the reaction of secondary amide **5i** (106 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9j** (142 mg, yield: 89%) as colorless oil; IR (film) ν_{max} 2956, 2926, 2855, 1664, 1495, 1435, 1414, 1184, 965, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 3H), 7.30-7.26 (m, 3H), 7.25-7.19 (m, 2H), 7.15-7.10 (m, 2H), 6.02 (s, 1H), 5.29 (d, J = 15.5 Hz, 1H), 3.84 (d, J = 15.5 Hz, 1H), 2.43-2.25 (m, 2H), 2.23-2.09 (m, 1H), 2.05-1.94 (m, 1H), 1.69-1.58 (m, 3H), 1.57-1.42 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1, 161.0, 137.1, 135.9, 129.4, 128.4 (4C), 127.8 (2C), 127.4 (2C), 127.2, 107.7, 87.0, 46.4, 27.3, 21.9, 21.8, 21.4 ppm; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{21}NO_2Na$ 342.1465, found 342.1465.

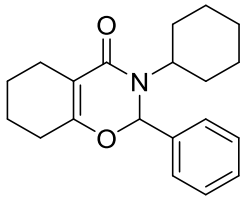
Methyl 2-(4-oxo-2-phenyl-5,6,7,8-tetrahydro-2H-benzo[e][1,3] oxazin-3(4H)-yl) acetate (9k)



9k

Following the general procedure B, the reaction of secondary amide **5h** (97 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9k** (104 mg, yield: 69%) as a white solid; Mp 94-96 ℃; IR (film) ν_{max} 2922, 2851, 1748, 1664, 1458, 1420, 1397, 1210, 1182, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.46-7.40 (m, 3H), 6.27 (s, 1H), 4.48 (d, J = 17.7 Hz, 1H), 3.64 (s, 3H), 3.23 (d, J = 17.7 Hz, 1H), 2.40-2.32 (m, 2H), 2.28-2.15 (m, 2H), 1.84-1.73 (m, 2H), 1.65-1.49 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 165.7, 163.7, 134.6, 130.3, 128.9 (2C), 128.0 (2C), 107.3, 89.3, 52.0, 44.1, 27.2, 21.9 (2C), 21.5 ppm; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{19}NO_4Na$ 324.1206, found 324.1207.

3-Cyclohexyl-2-phenyl-2,3,5,6,7,8-hexahydro-4H-benzo[e][1,3]oxazin-4-one (9l)

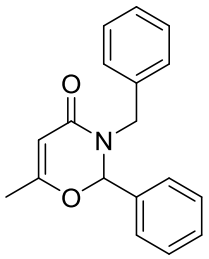


9l

Following the general procedure B, the reaction of secondary amide **5c** (102 mg, 0.5 mmol) with pimeloyl chloride (654 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **9l** (117 mg, yield: 75%) as a white solid; Mp 154-156 ℃; IR (film) ν_{max} 2922, 2851, 1663, 1636, 1493, 1433, 1392, 761, 735, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.40 (m, 2H), 7.39-7.30 (m, 3H), 6.38 (s, 1H), 4.49 (tt, J = 12.2, 3.7 Hz, 1H), 2.69-2.54 (m, 1H), 2.52-2.39 (m, 1H), 2.39-2.29 (m, 1H), 2.24-2.11 (m, 1H), 2.10-1.14 (m, 12H), 1.13-0.93 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9, 158.7, 138.9, 128.6, 128.0 (2C), 127.0 (2C), 109.3, 82.9, 52.0, 31.5, 30.9, 27.4,

25.8, 25.8, 25.4, 21.8, 21.7, 21.2 ppm; HRMS (ESI) *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{25}NO_2Na$ 334.1778, found 334.1780.

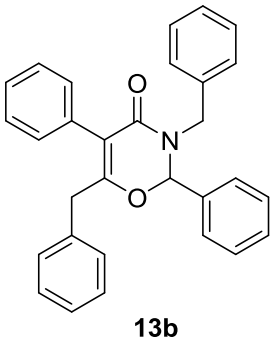
3-Benzyl-6-methyl-2-phenyl-2,3-dihydro-4H-1,3-oxazin-4-one (13a)



13a

Following the general procedure C, the reaction of secondary amide **5i** (106 mg, 0.5 mmol) with acetyl chloride (284 μL, 4.0 mmol) gave, after FC (eluent: EA / PE = 1: 20), oxazinone **13a** (117 mg, yield: 84%) as colorless oil; IR (film) ν_{max} 2920, 2850, 1669, 1633, 1470, 1429, 1389, 1357, 729, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.32-7.24 (m, 5H), 7.16-7.10 (m, 2H), 6.08 (s, 1H), 5.36 (d, *J* = 15.4 Hz, 1H), 5.33 (s, 1H), 3.80 (d, *J* = 15.4 Hz, 1H), 1.87 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 163.5, 136.8, 135.5, 129.6, 128.6 (2C), 128.5 (2C), 127.8 (2C), 127.5, 127.4 (2C), 100.1, 87.7, 46.2, 19.7 ppm; HRMS (ESI) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}NO_2Na$ 302.1151, found 302.1155.

3,6-Dibenzyl-2,5-diphenyl-2,3-dihydro-4H-1,3-oxazin-4-one (13b)

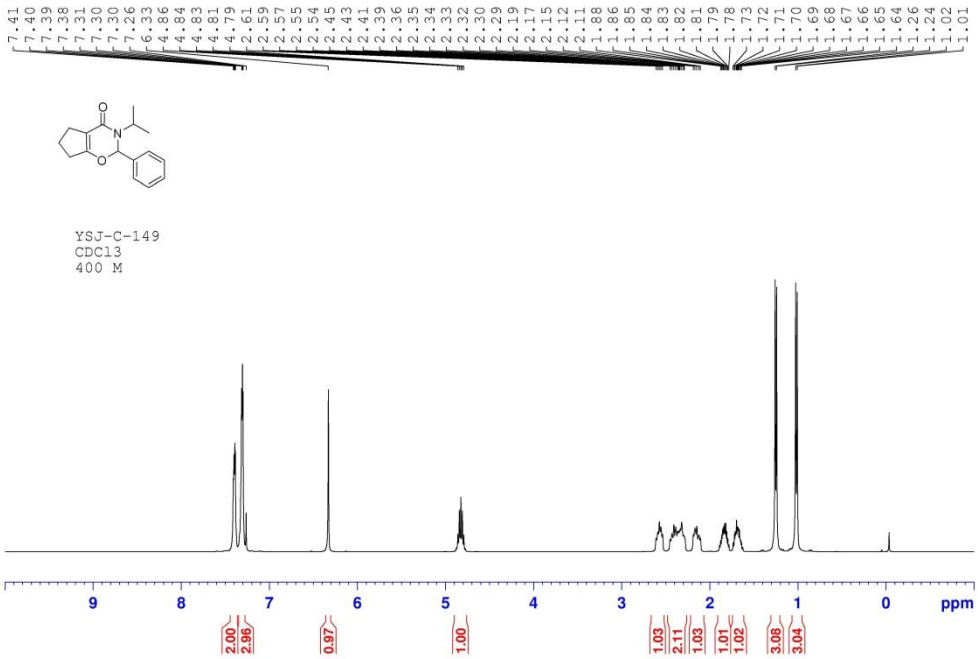


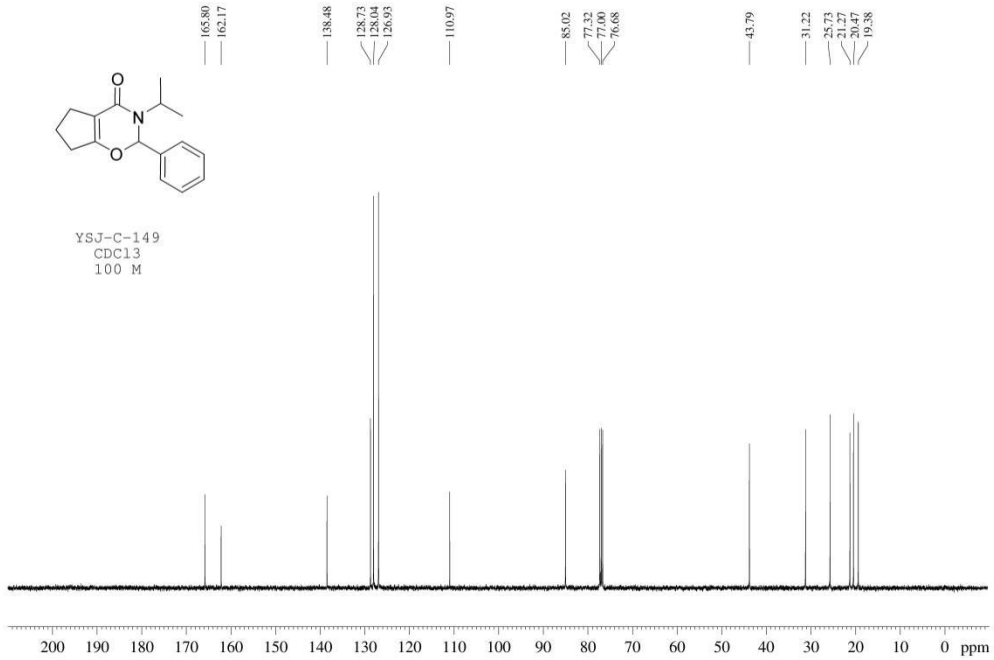
13b

Following the general procedure C, the reaction of secondary amide **5i** (106 mg, 0.5 mmol) with phenylacetyl chloride (529 μL, 4.0 mmol) gave, after FC (eluent: EA / PE

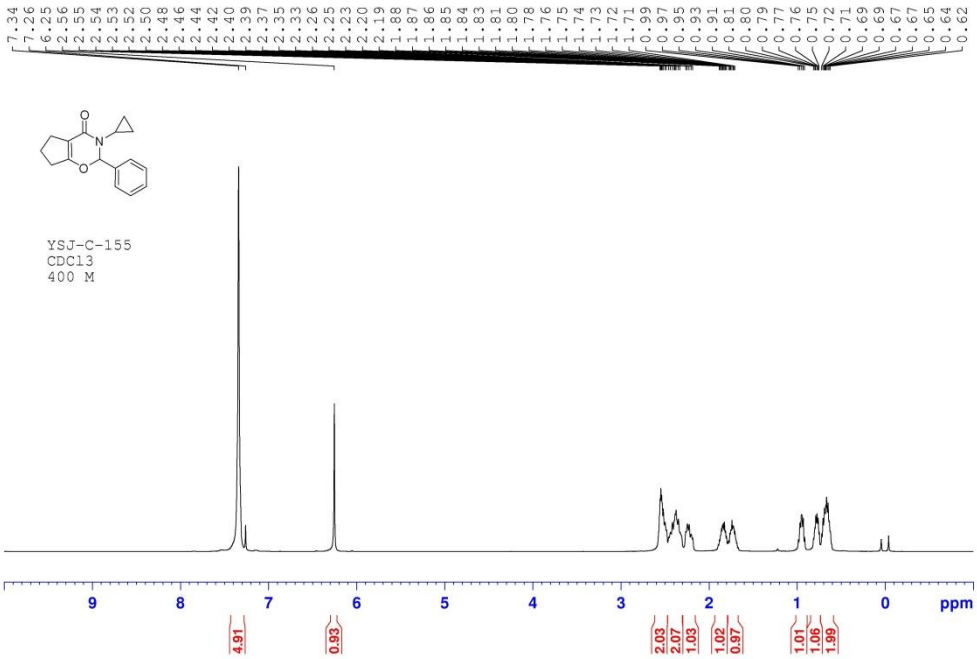
= 1: 20), oxazinone **13b** (196 mg, yield: 91%) as light yellow oil; IR (film) ν_{max} 2920, 2850, 1656, 1495, 1454, 1443, 1427, 781, 744, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 3H), 7.31-7.20 (m, 10H), 7.18-7.07 (m, 5H), 6.88-6.77 (m, 2H), 6.12 (s, 1H), 5.39 (d, J = 15.2 Hz, 1H), 3.88 (d, J = 15.2 Hz, 1H), 3.44-3.31 (dd, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.2, 160.9, 136.7, 135.8, 135.3, 133.2, 131.0 (2C), 129.3, 128.7 (2C), 128.6 (2C), 128.29 (2C), 128.26 (2C), 128.1 (4C), 127.5 (2C), 127.3 (2C), 126.4, 114.6, 86.9, 47.0, 37.5 ppm; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{30}H_{25}NO_2Na$ 454.1778, found 454.1778.

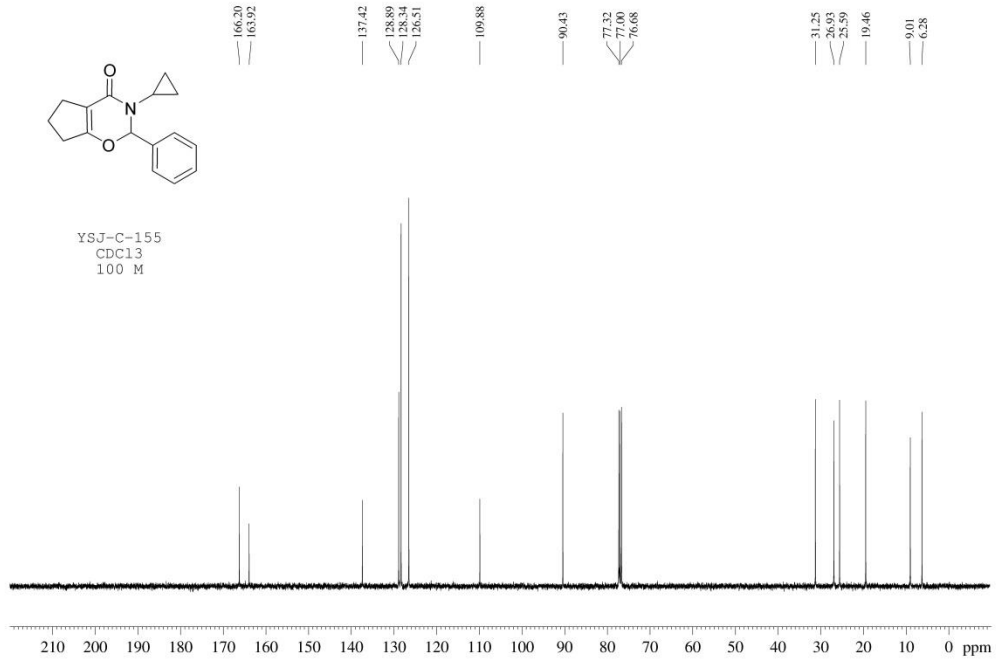
^{1}H and ^{13}C NMR spectra of compound 7a



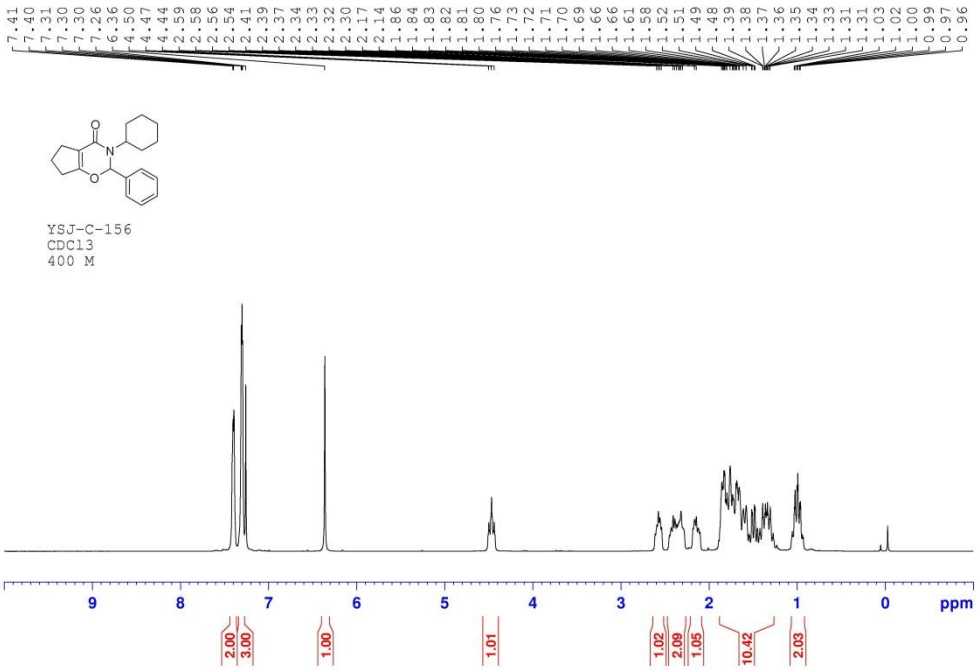


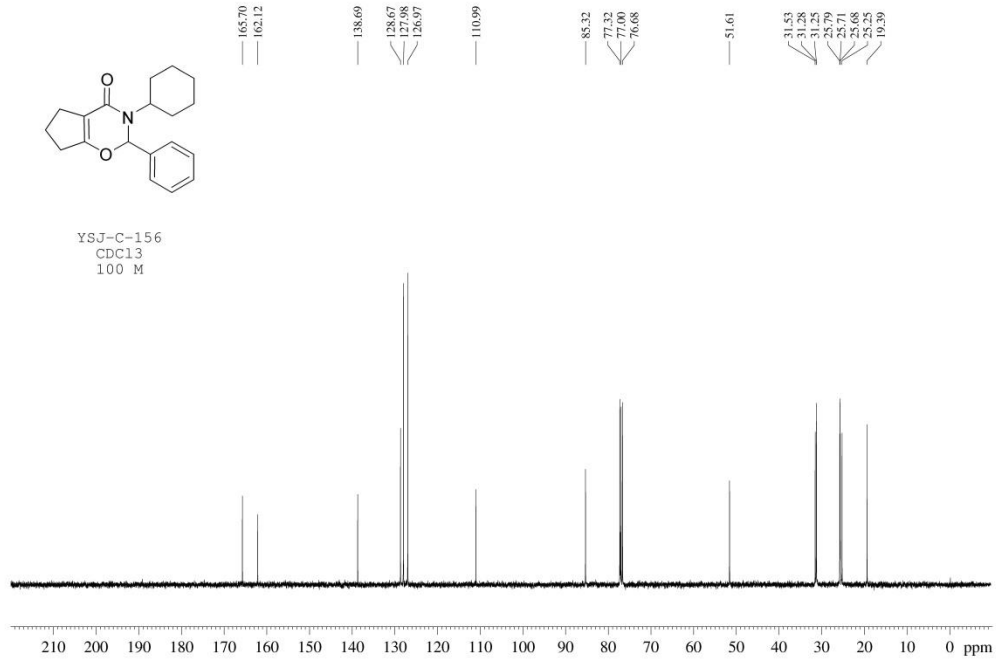
^{1}H and ^{13}C NMR spectra of compound 7b



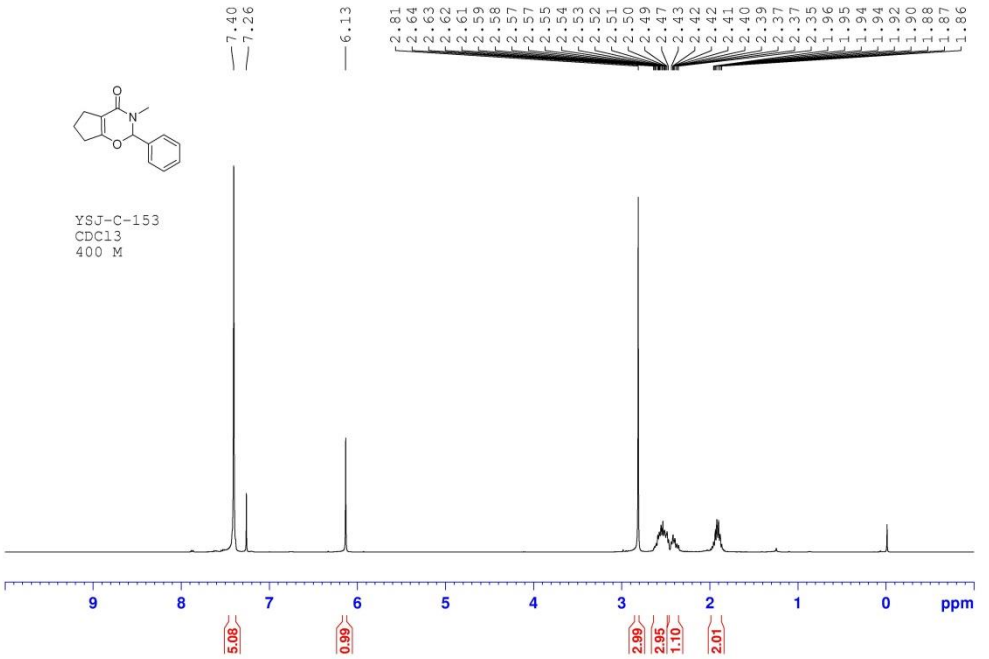


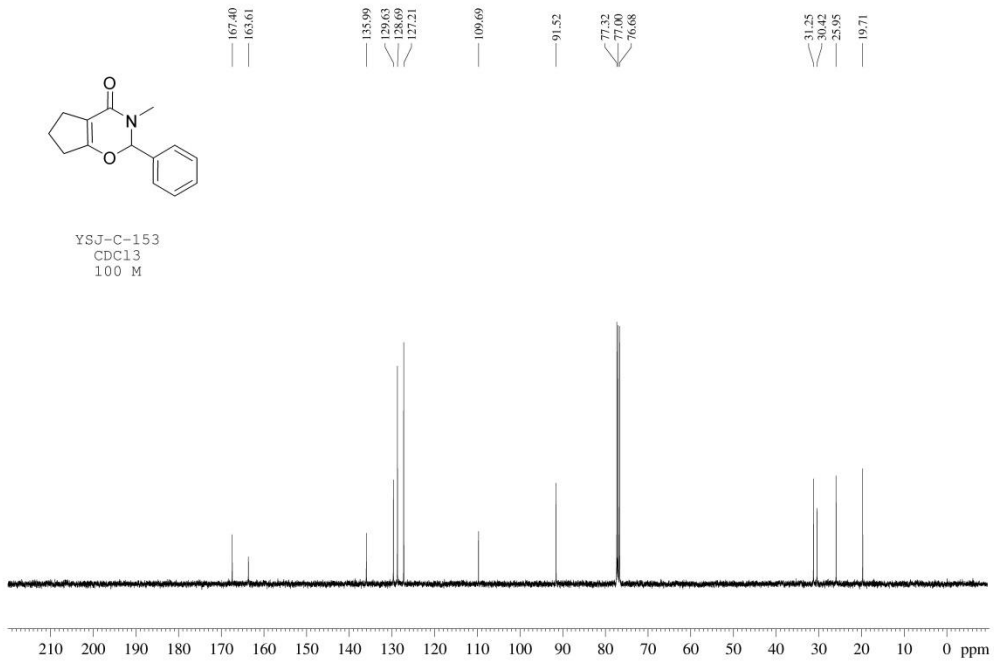
^{1}H and ^{13}C NMR spectra of compound 7c



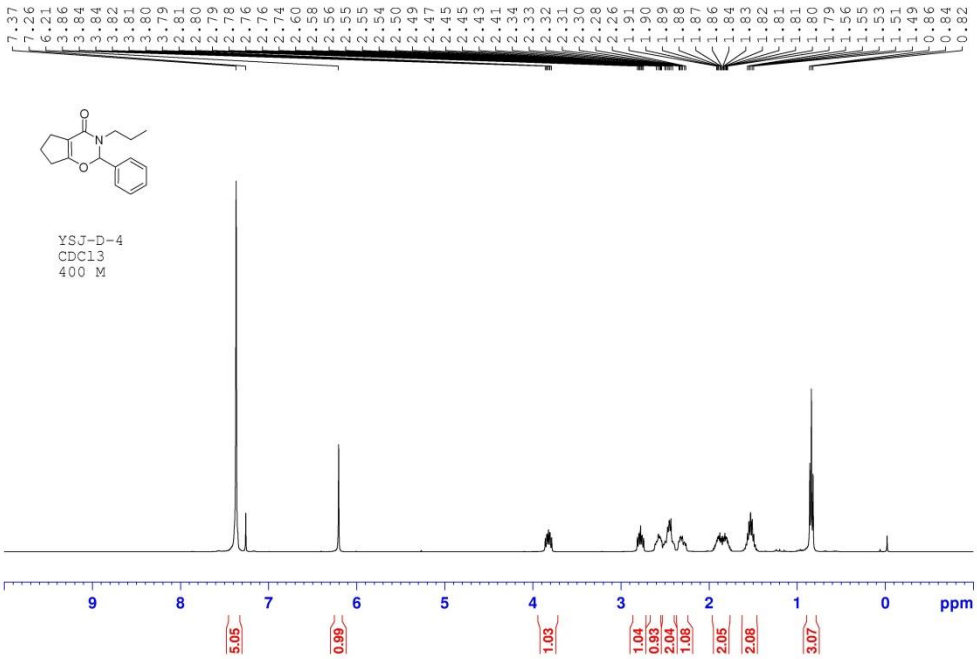


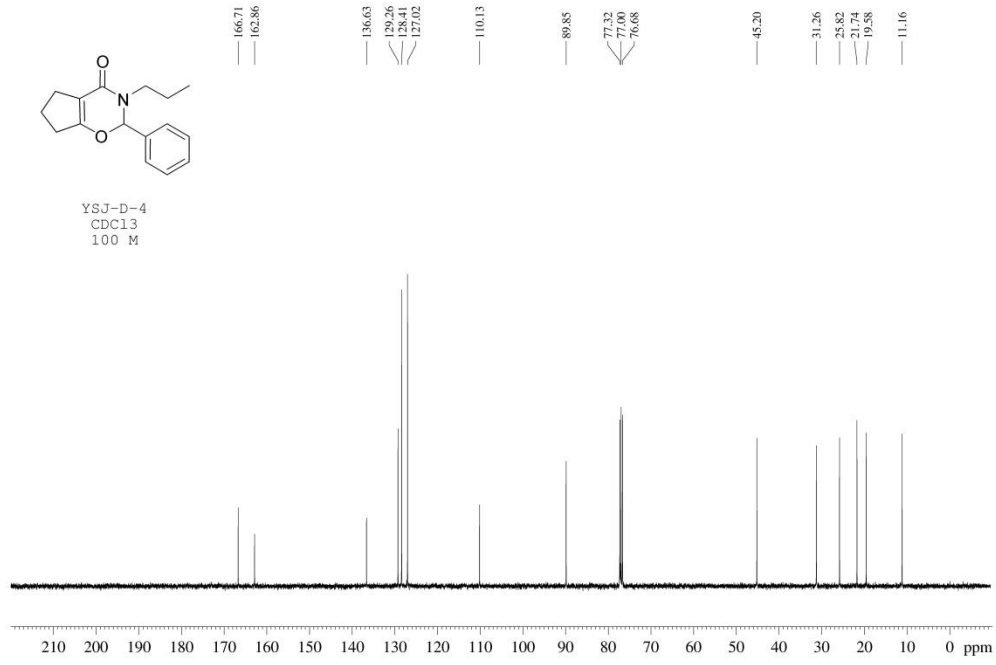
^{1}H and ^{13}C NMR spectra of compound 7d



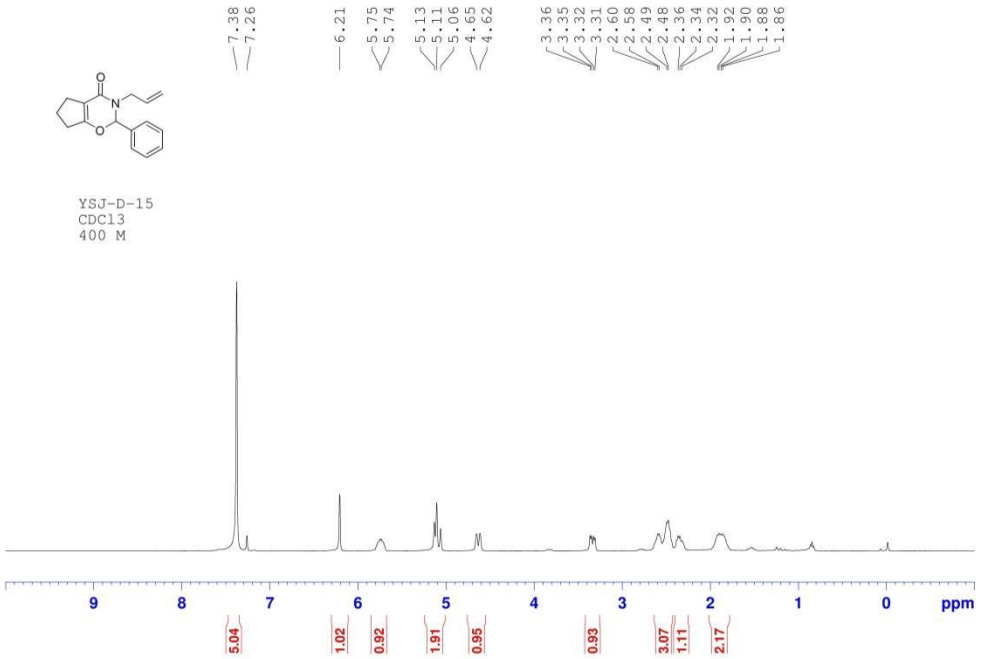


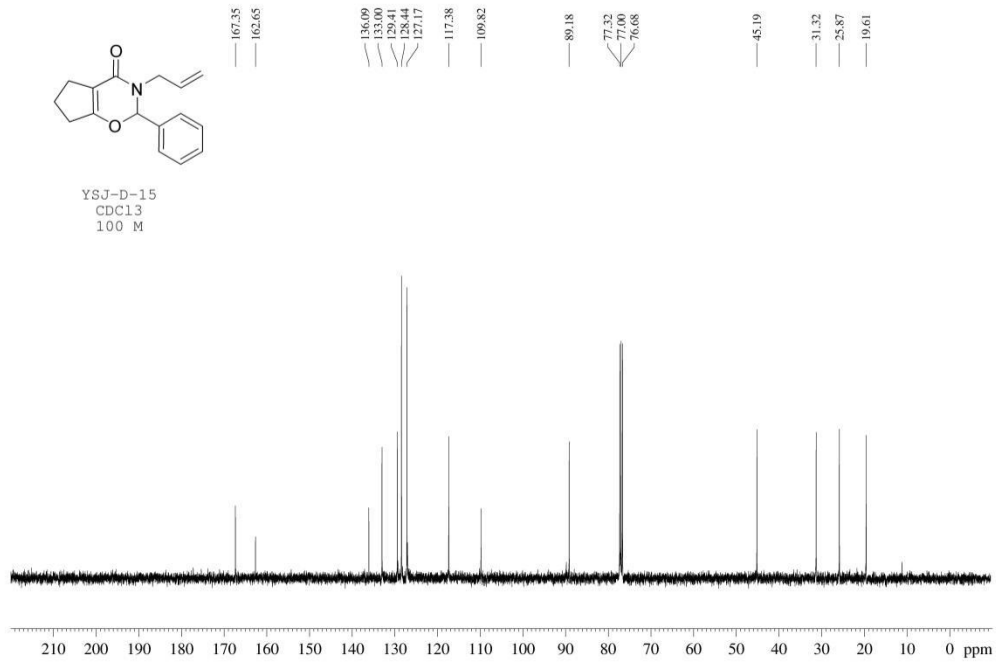
^{1}H and ^{13}C NMR spectra of compound 7e



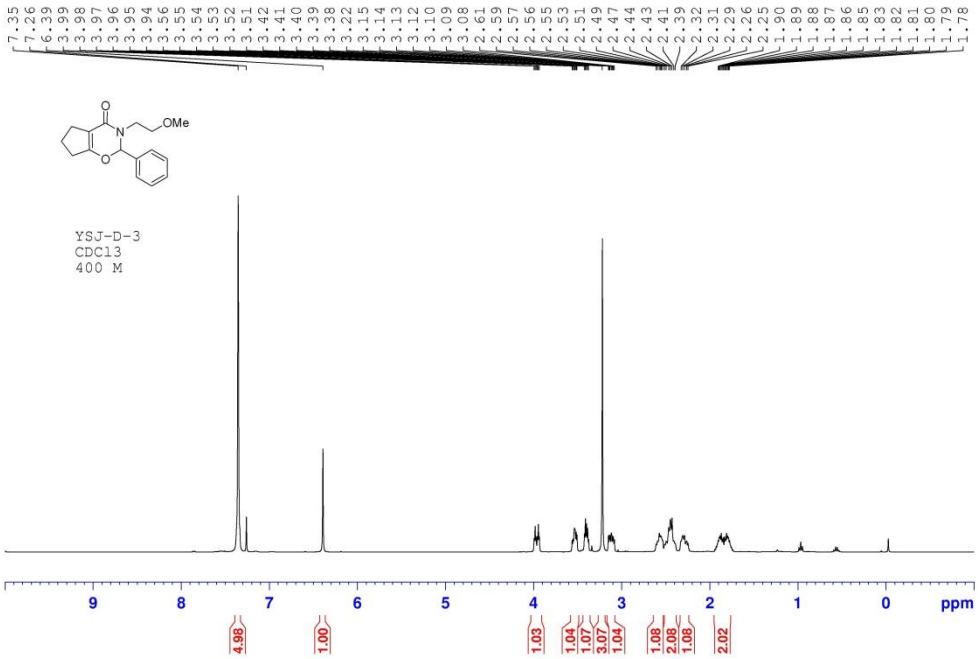


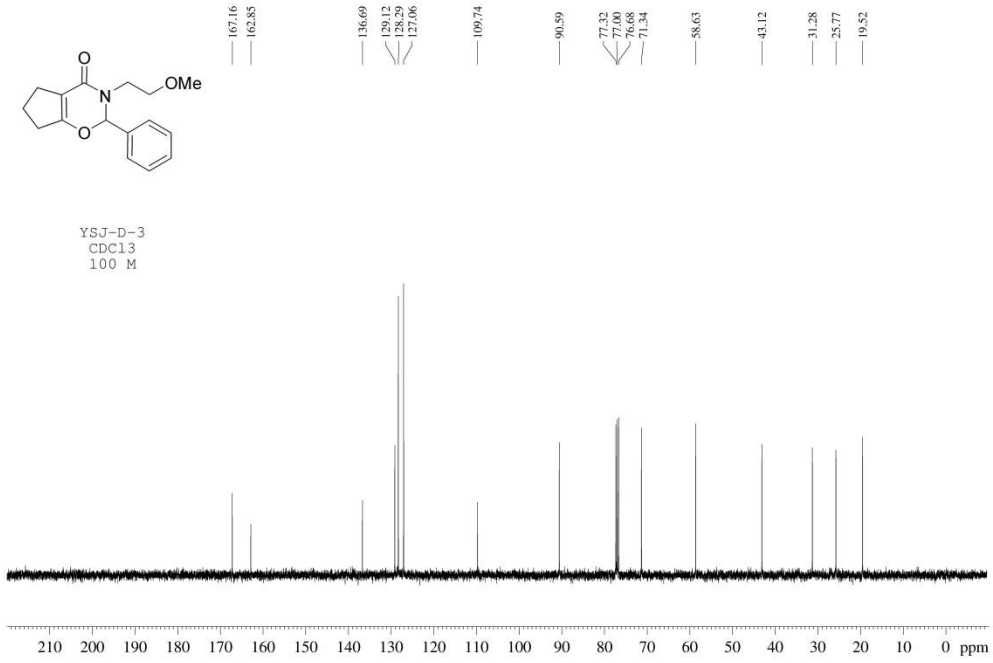
^{1}H and ^{13}C NMR spectra of compound 7f



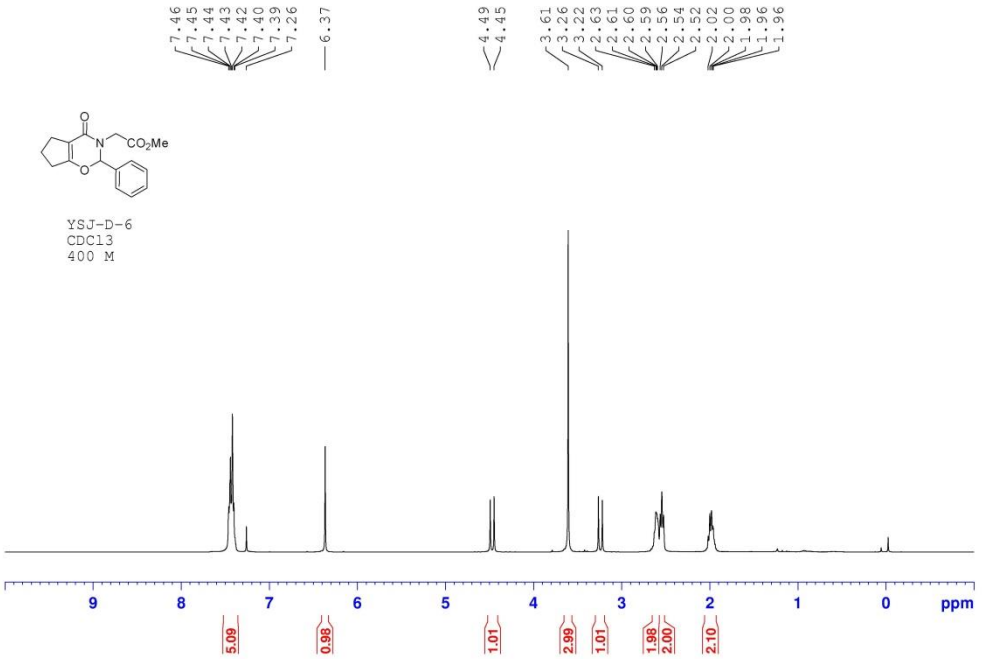


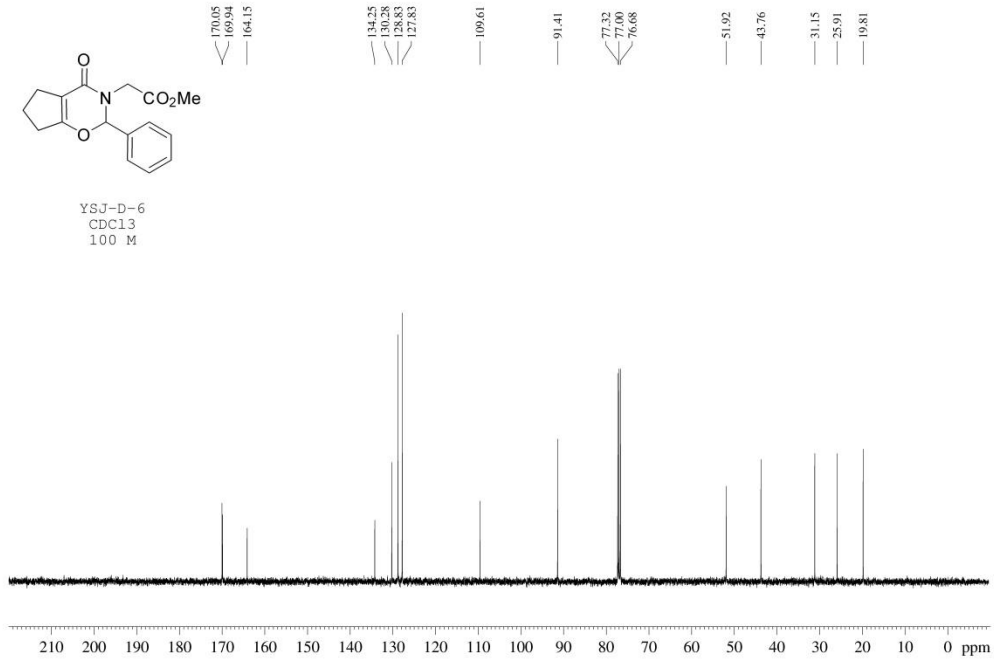
^{1}H and ^{13}C NMR spectra of compound 7g



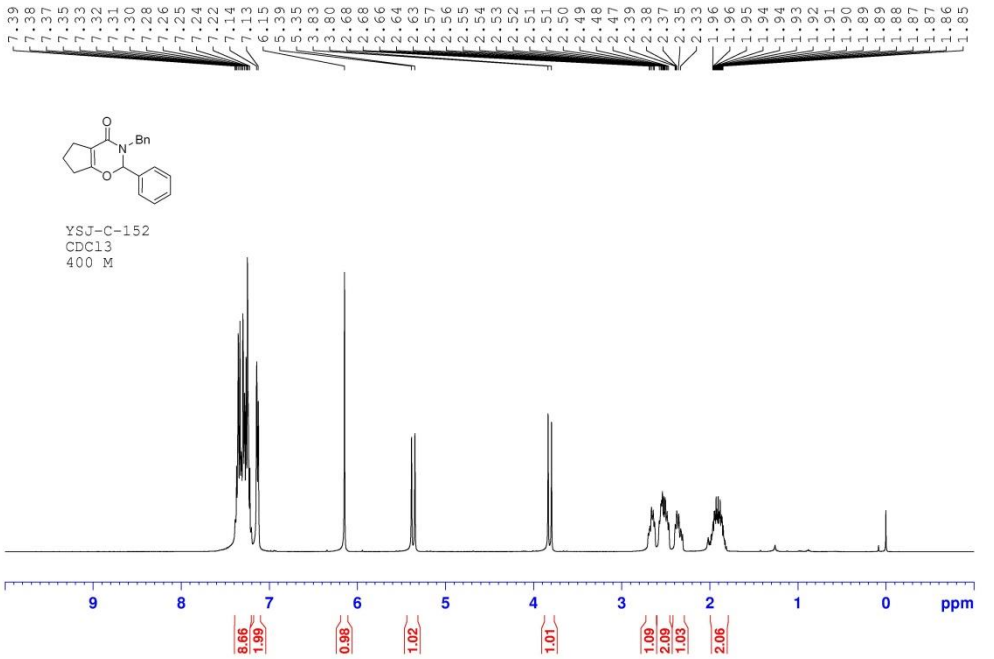


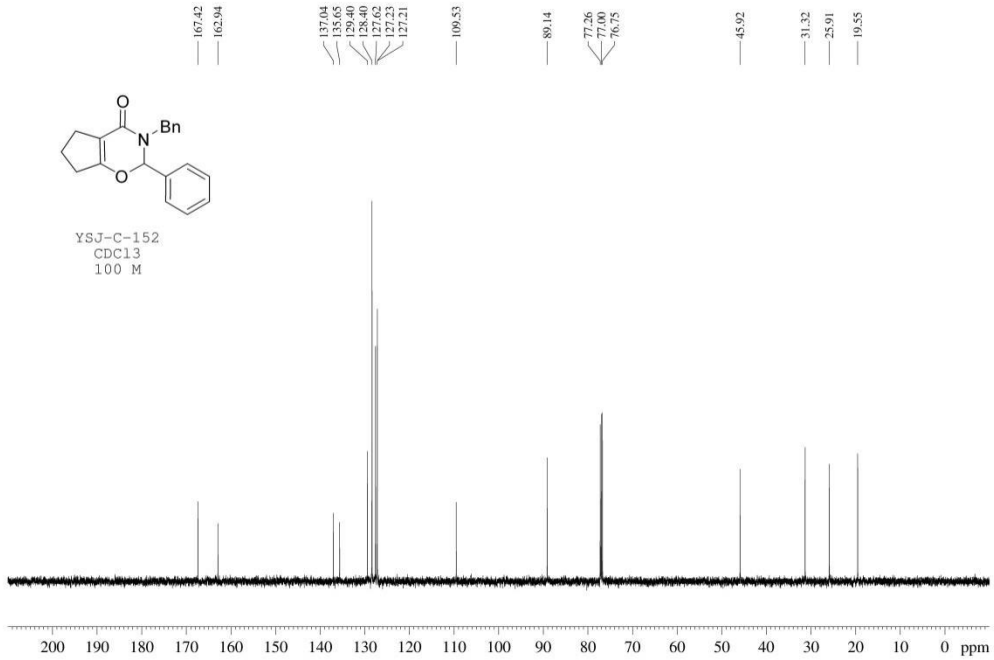
^{1}H and ^{13}C NMR spectra of compound 7h



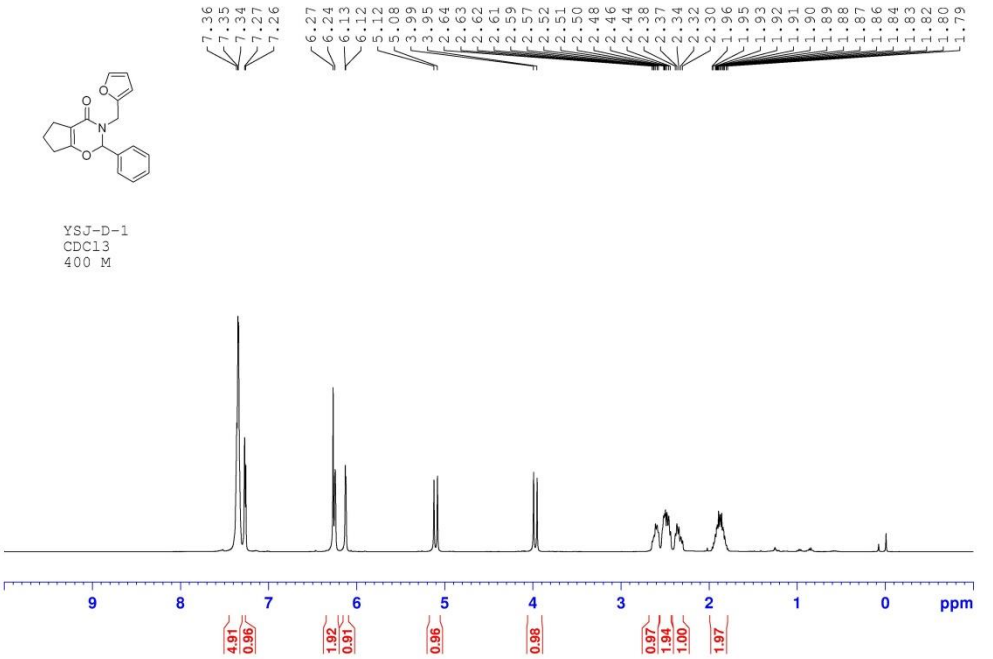


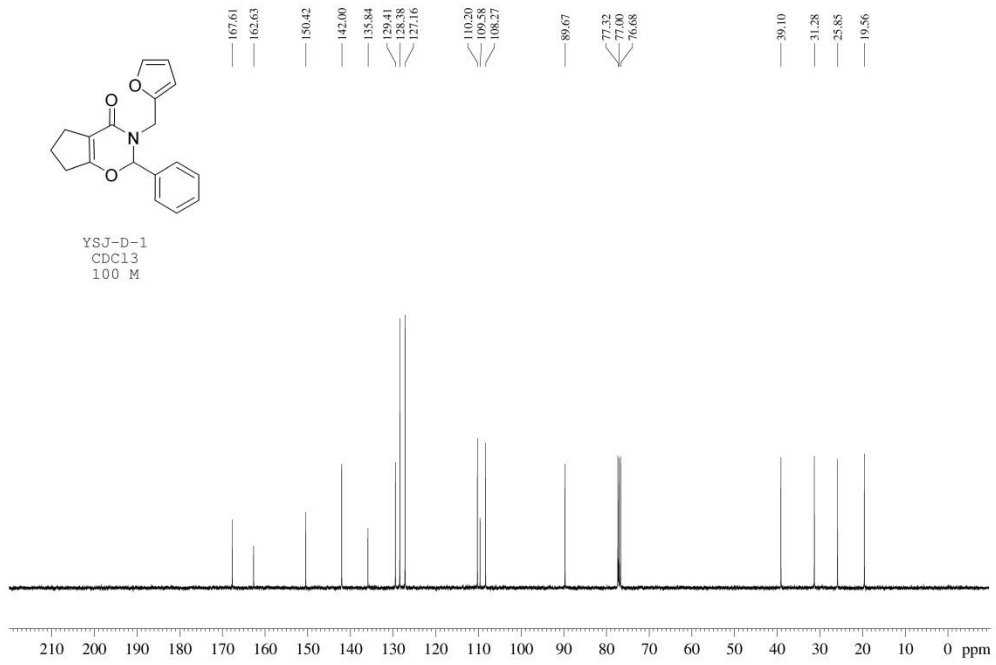
^{1}H and ^{13}C NMR spectra of compound 7i



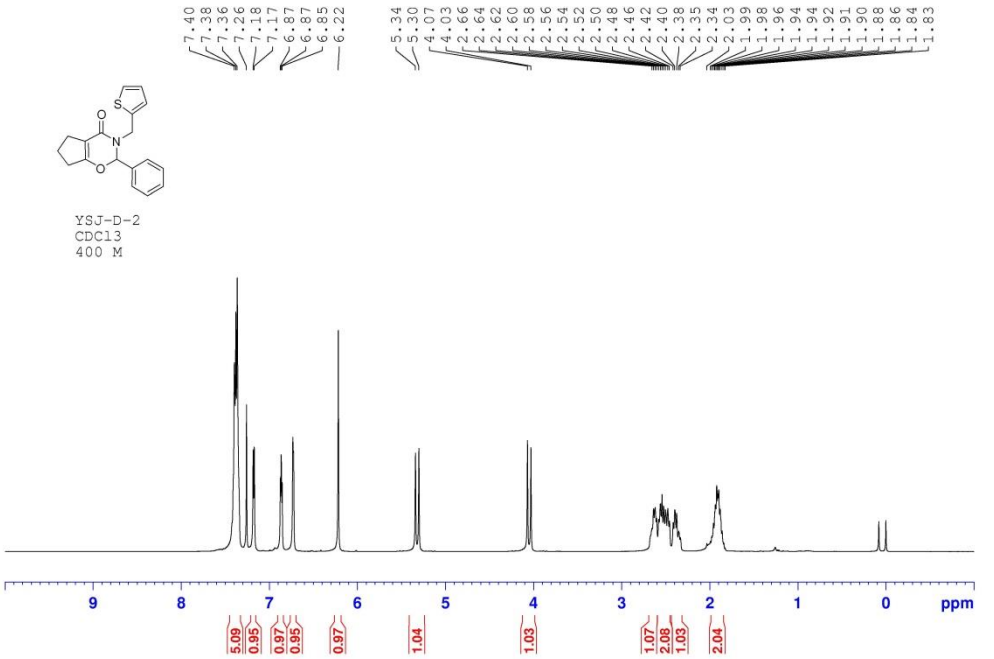


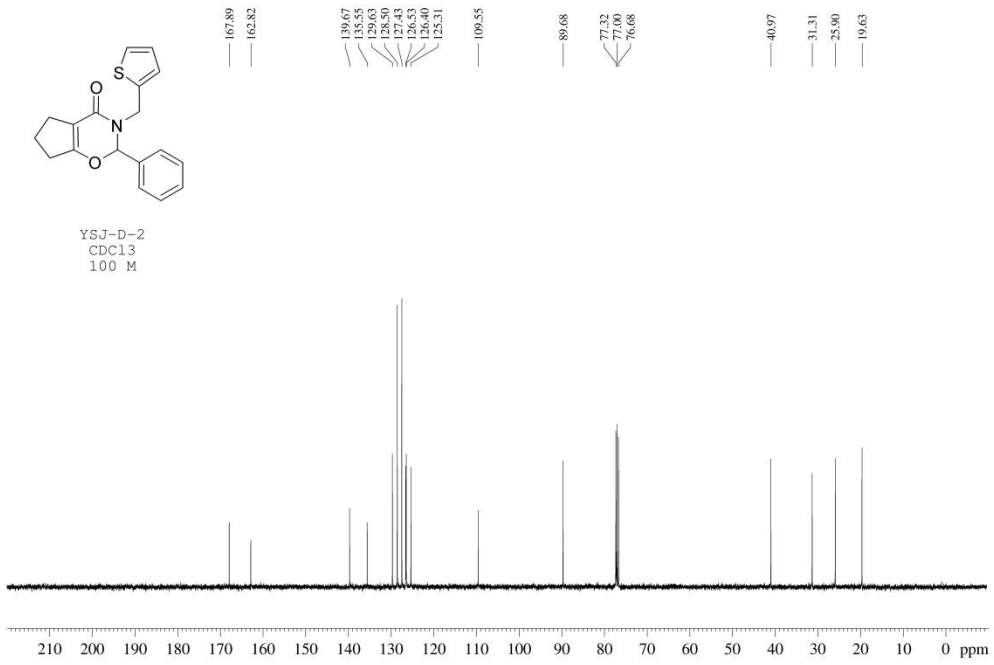
^{1}H and ^{13}C NMR spectra of compound 7j



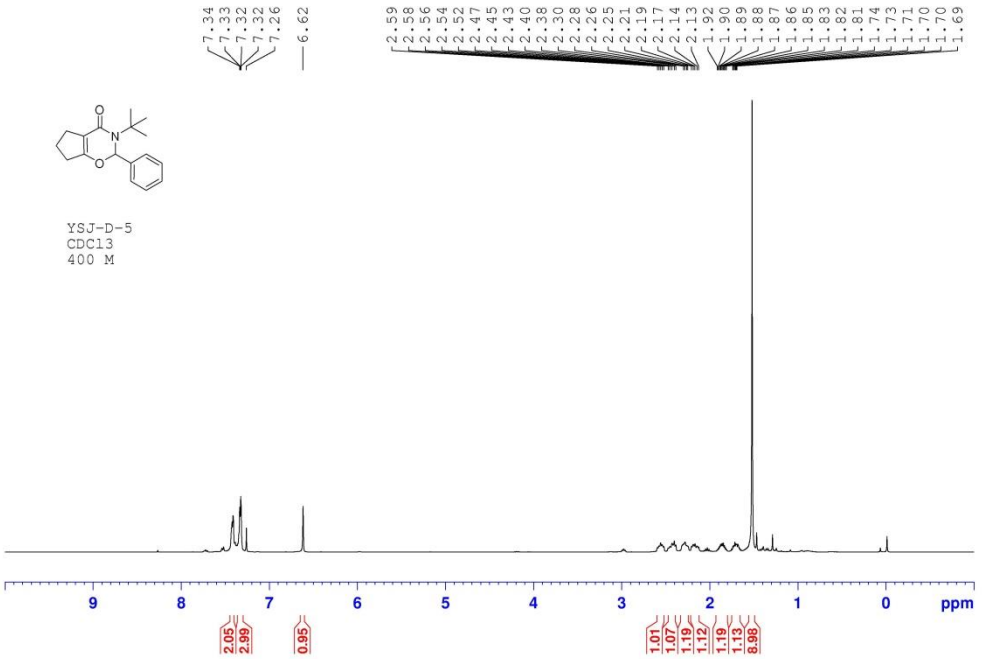


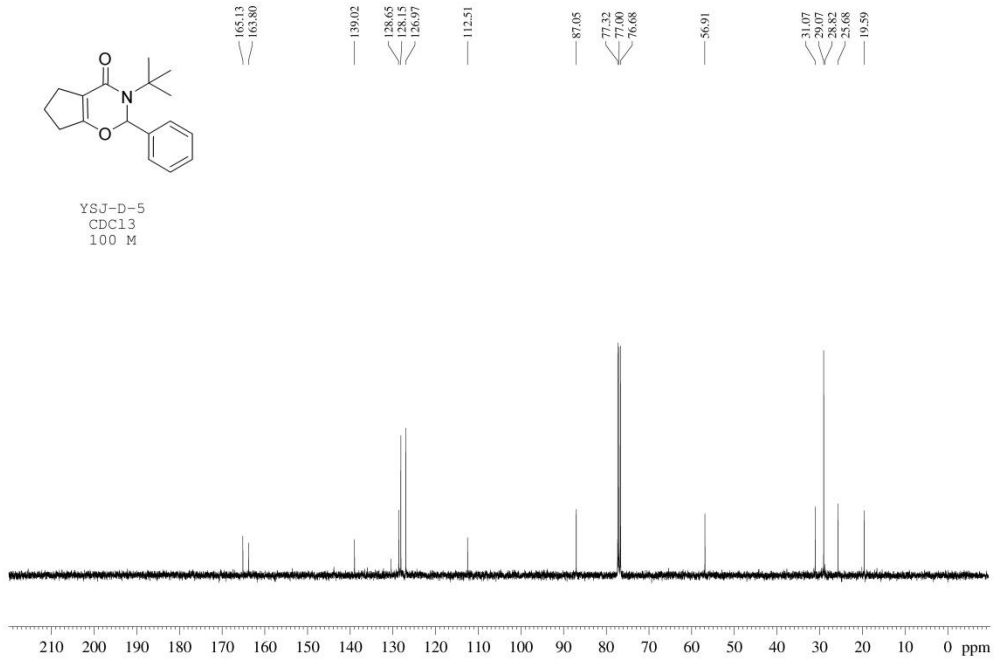
^{1}H and ^{13}C NMR spectra of compound 7k



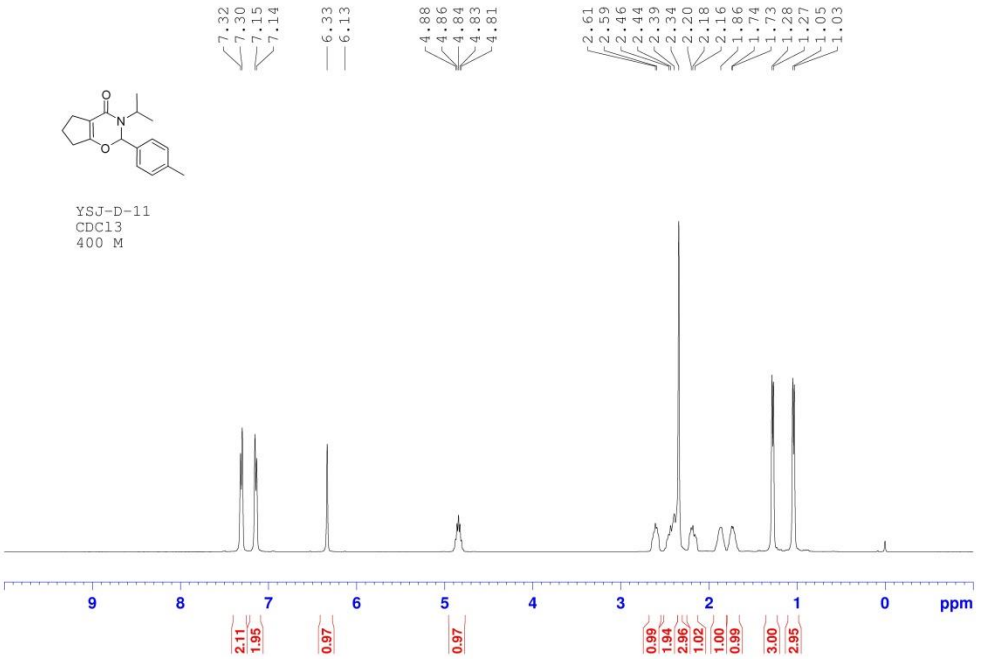


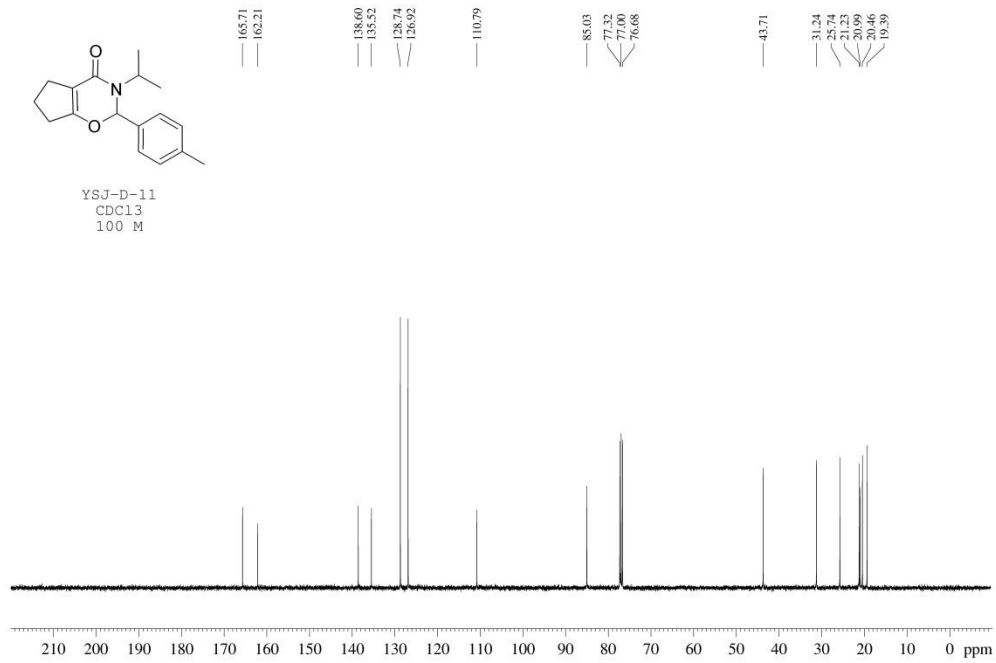
^{1}H and ^{13}C NMR spectra of compound 7l



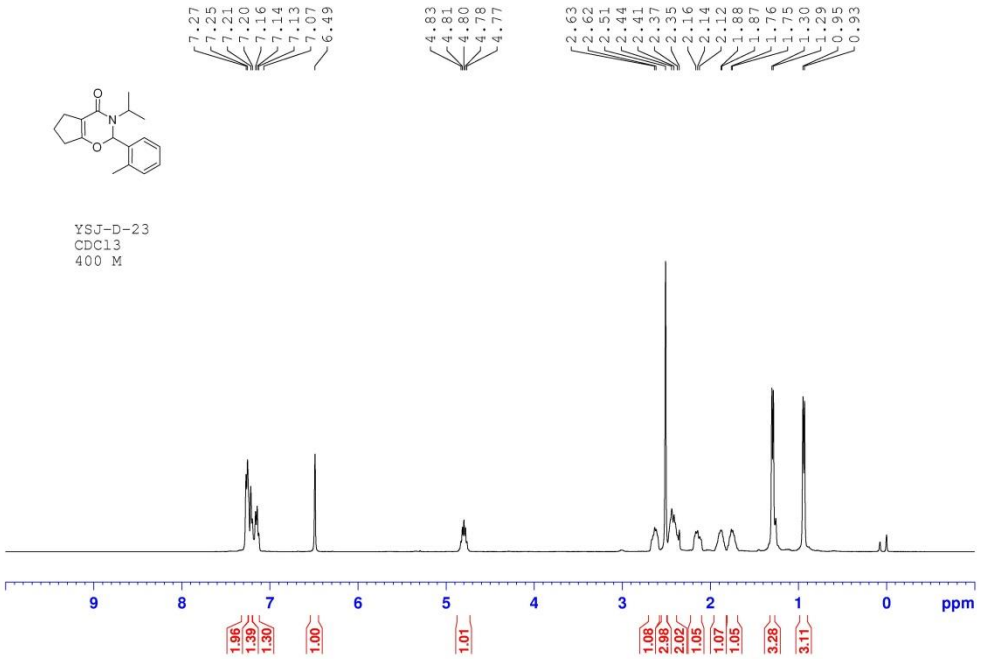


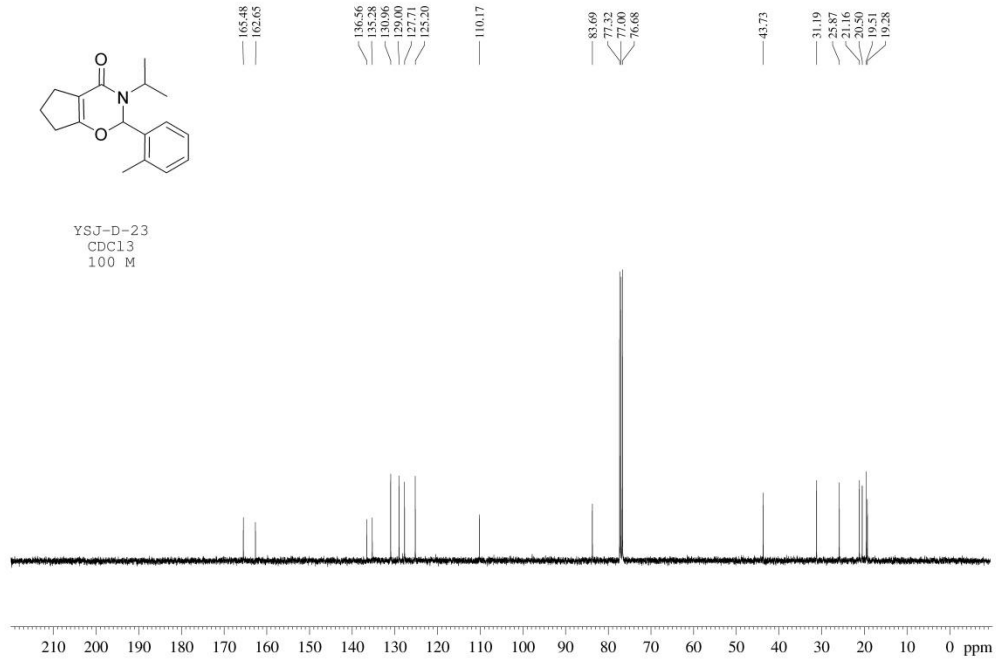
^{1}H and ^{13}C NMR spectra of compound 7m



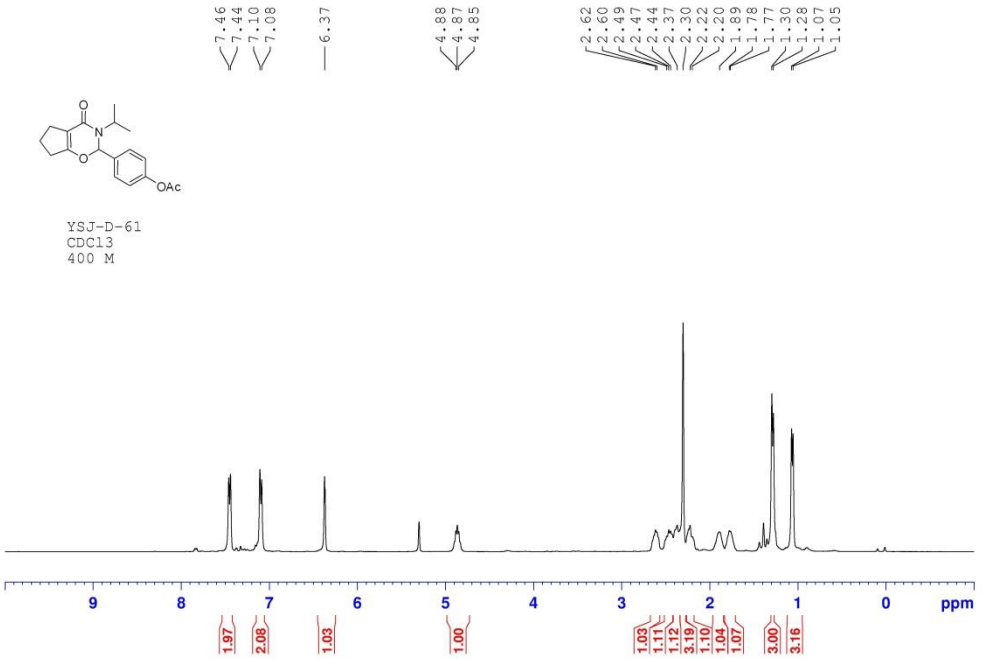


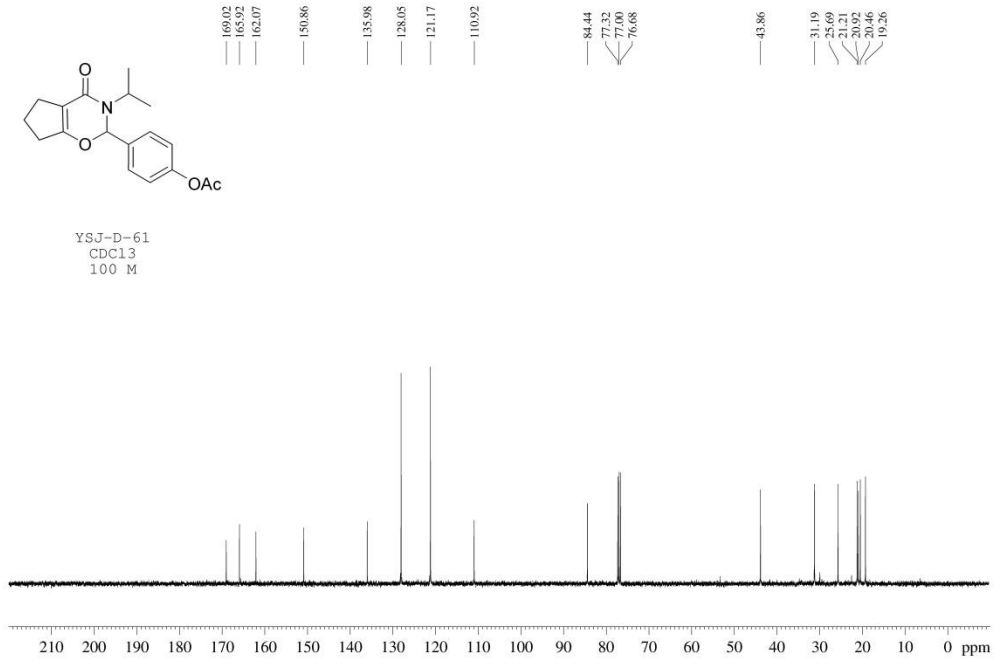
^{1}H and ^{13}C NMR spectra of compound 7n



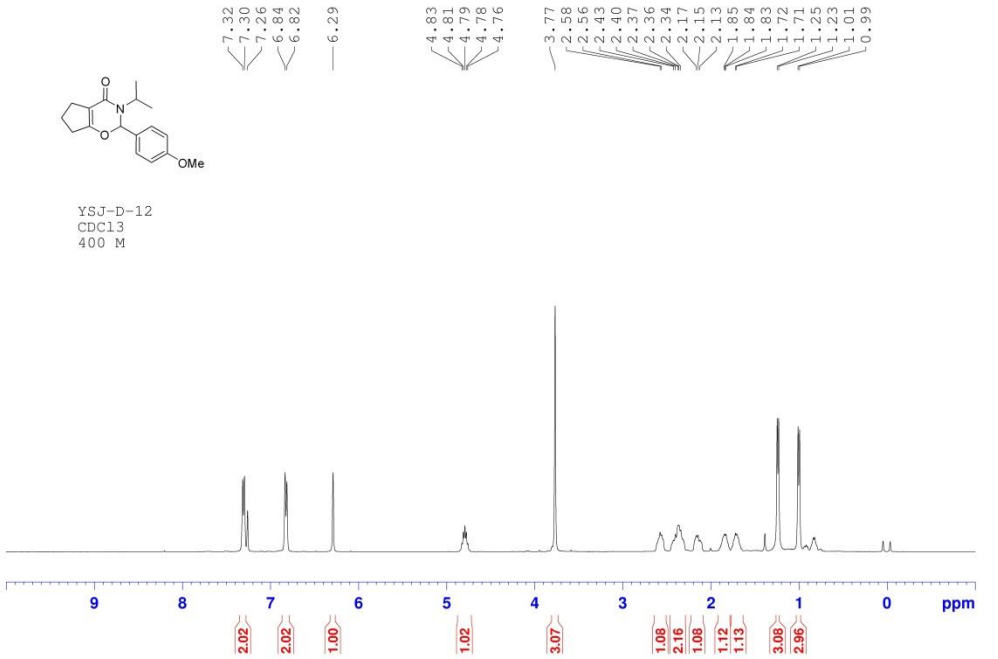


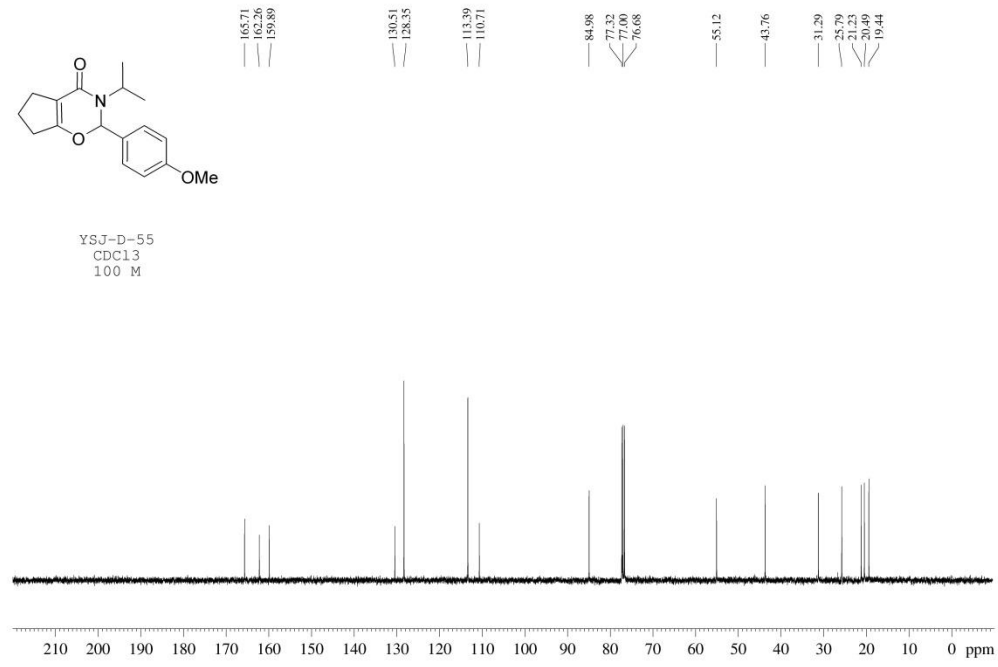
^{1}H and ^{13}C NMR spectra of compound 7o



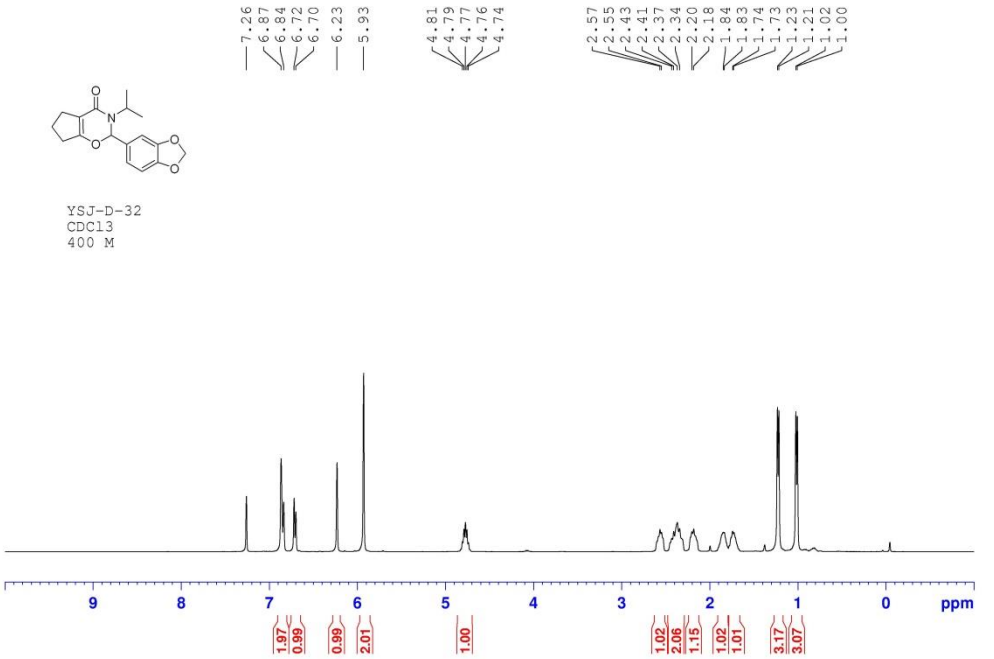


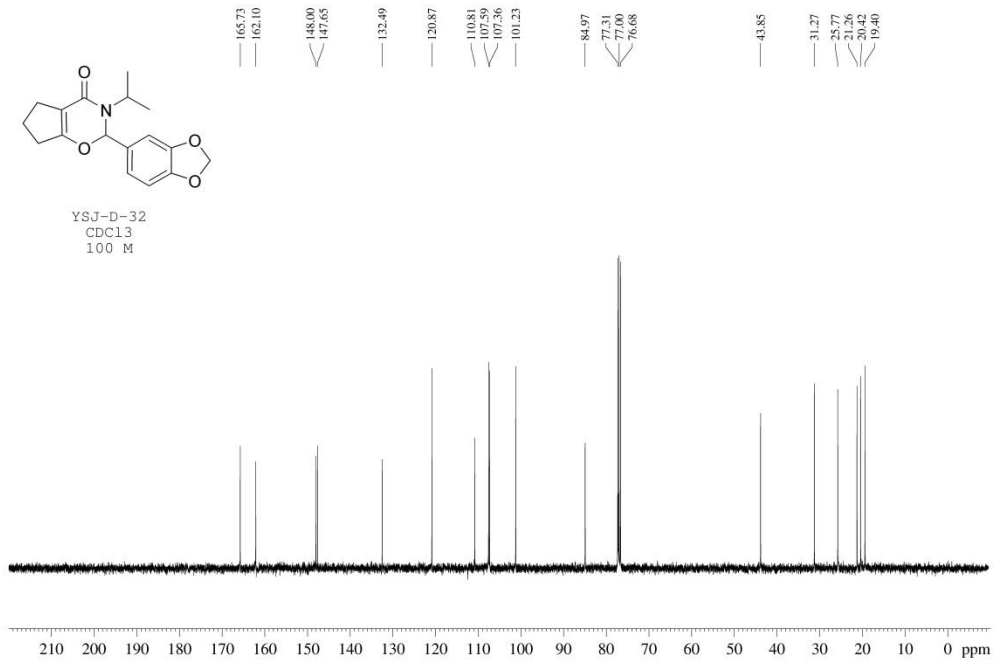
^{1}H and ^{13}C NMR spectra of compound 7p



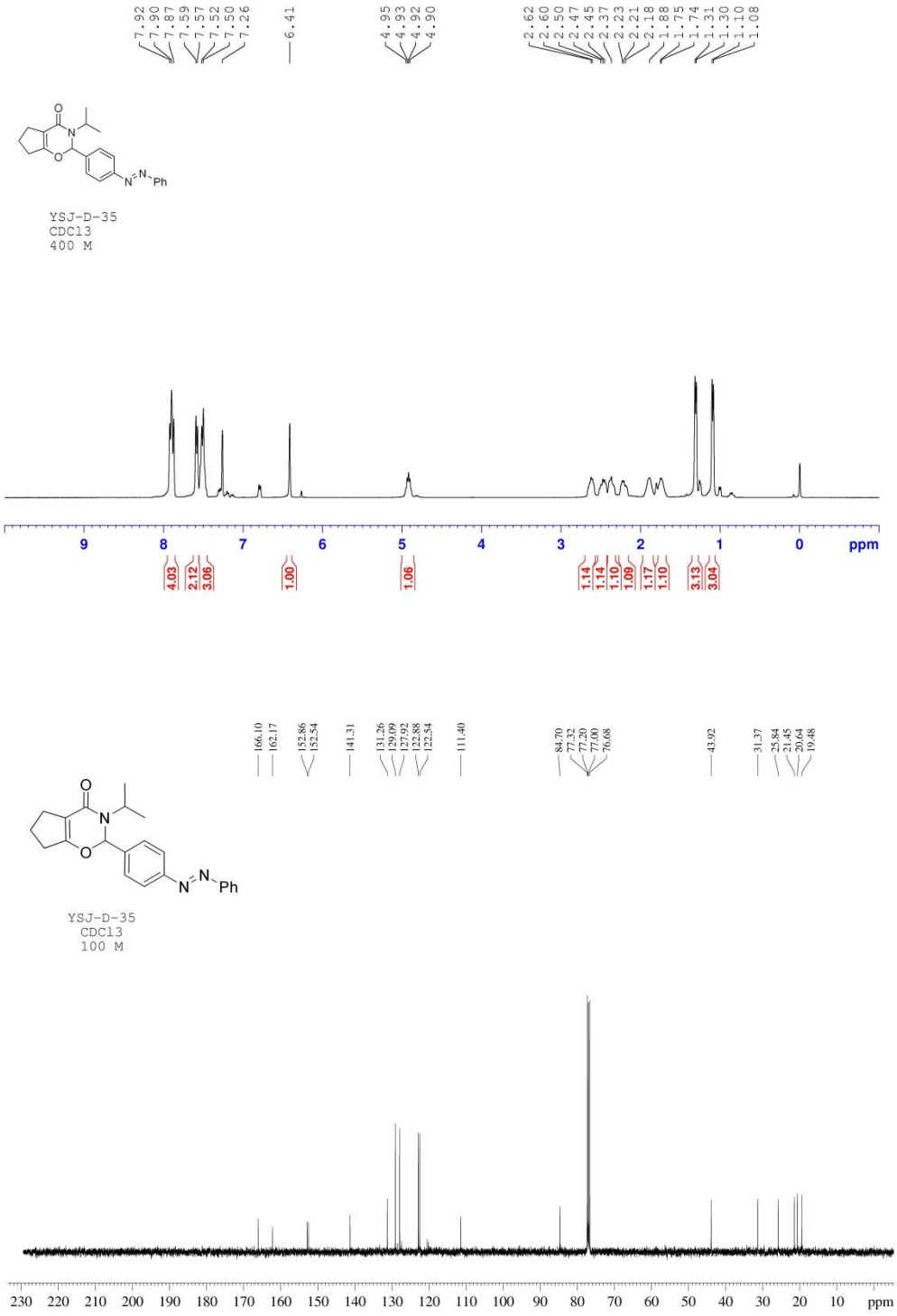


^{1}H and ^{13}C NMR spectra of compound 7q

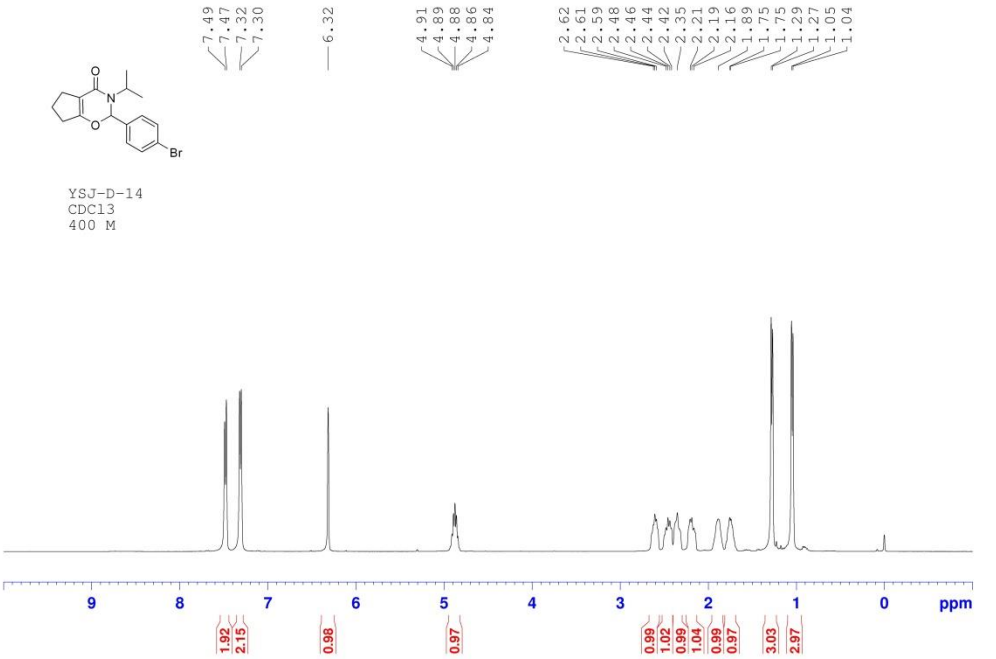


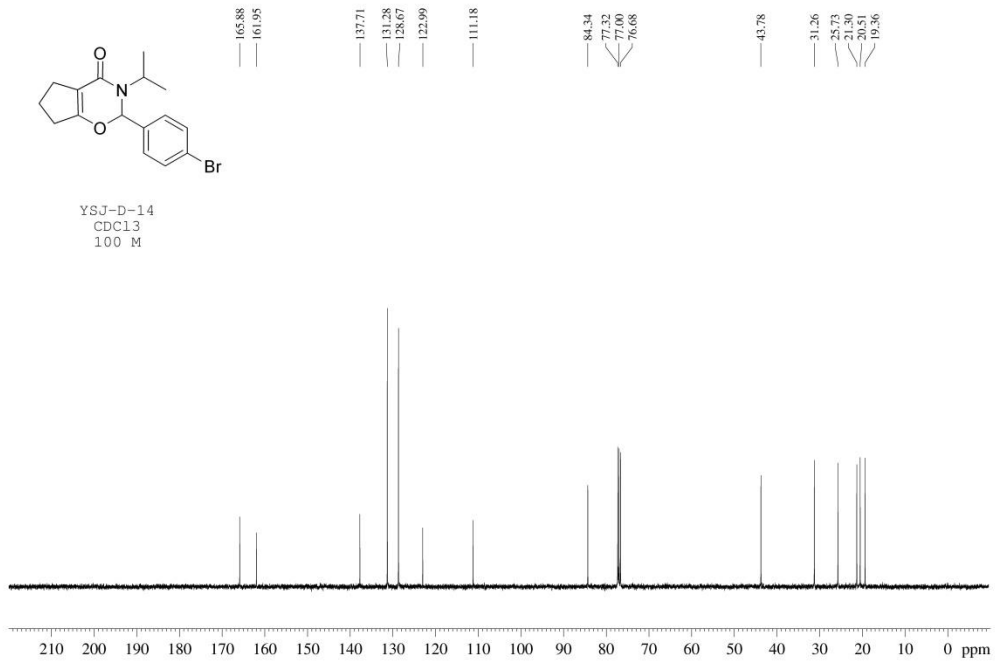


^{1}H and ^{13}C NMR spectra of compound 7r

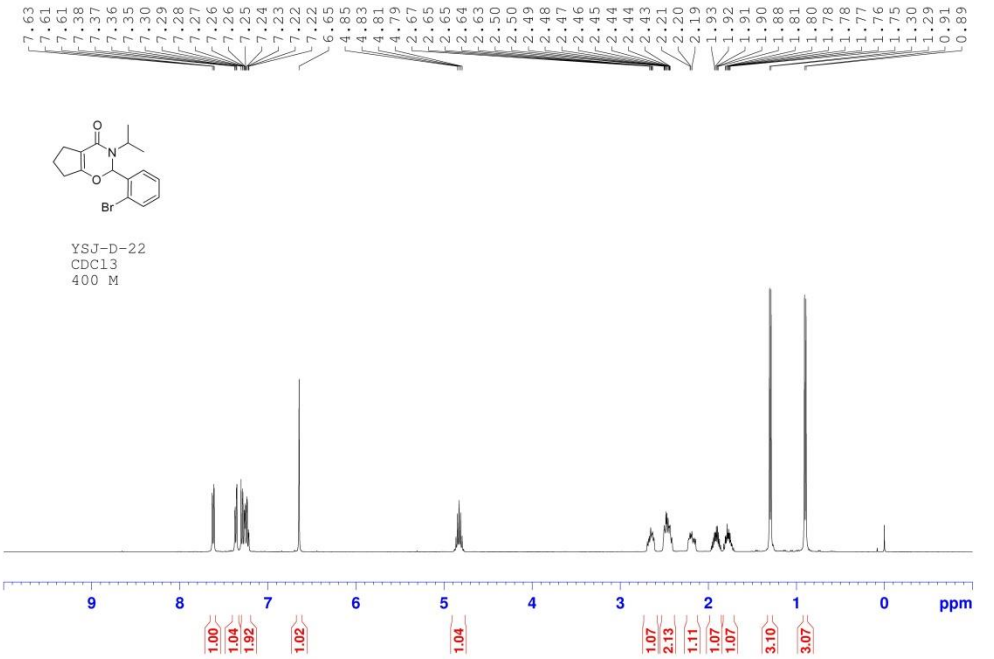


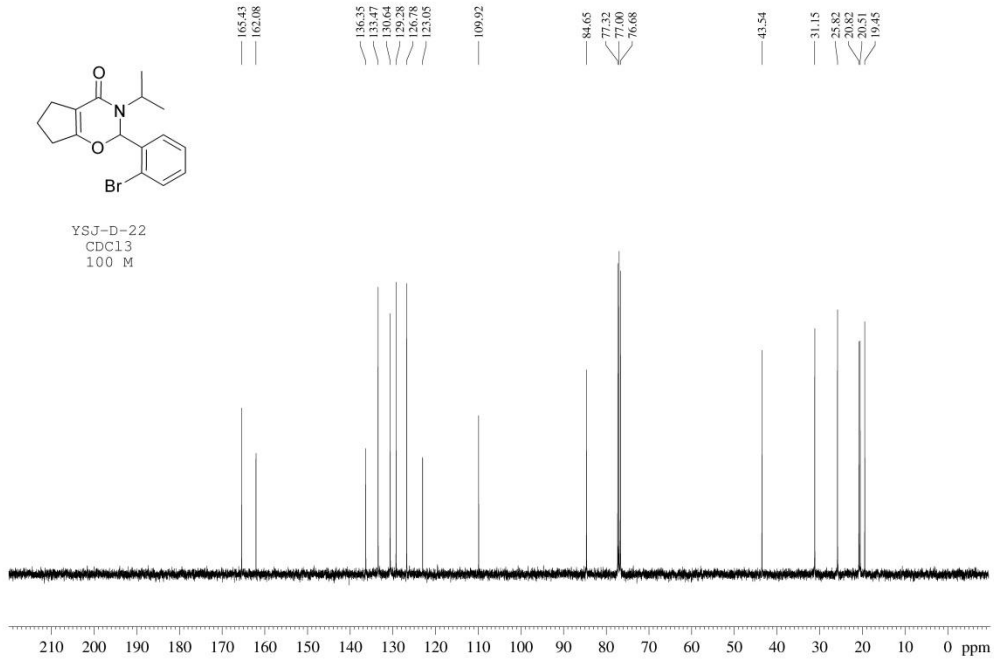
^{1}H and ^{13}C NMR spectra of compound 7s



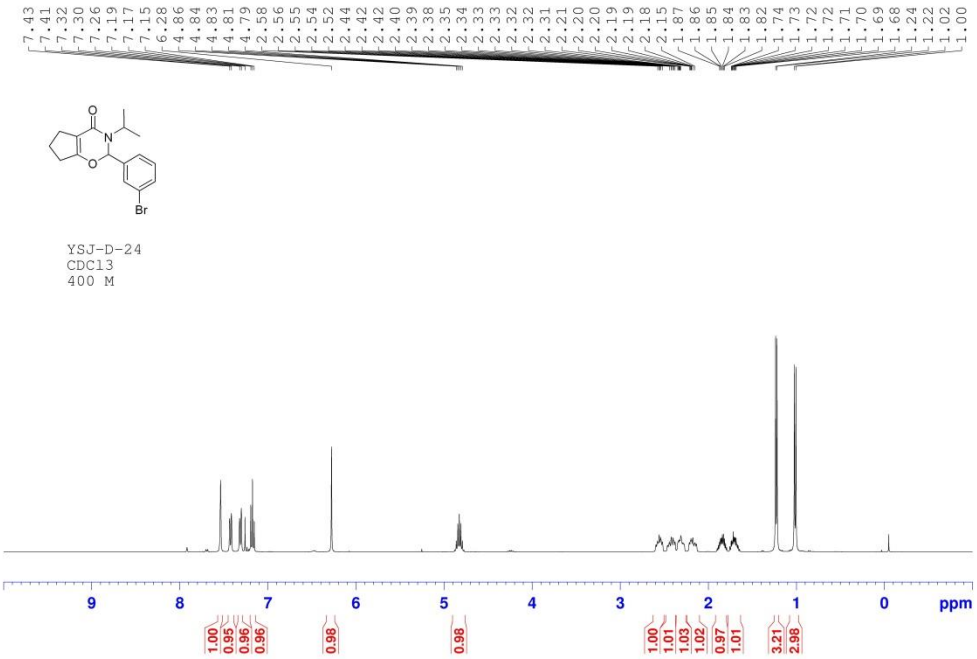


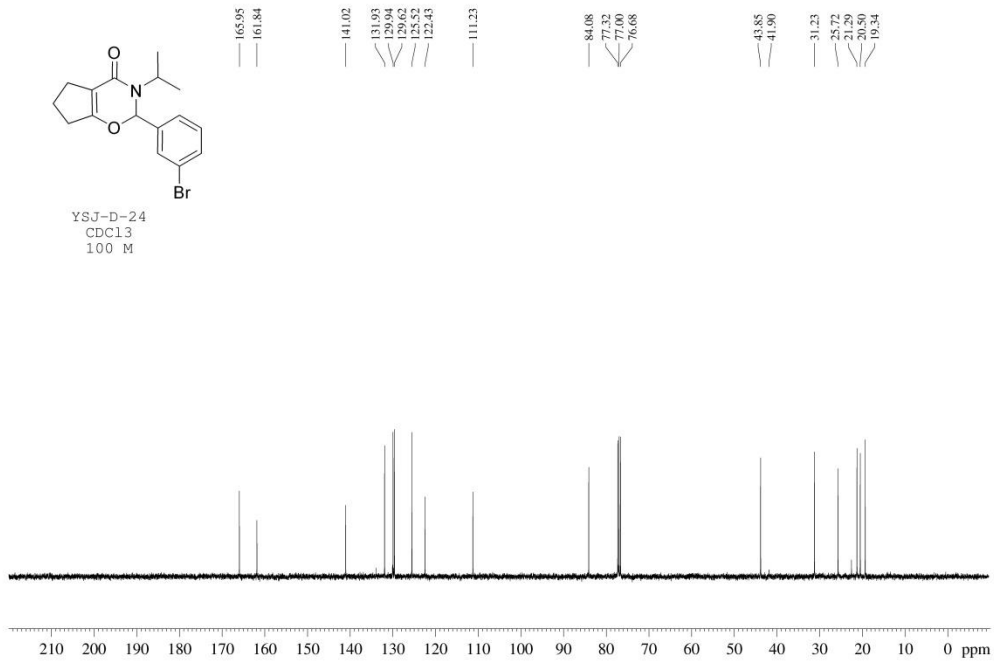
^{1}H and ^{13}C NMR spectra of compound 7t



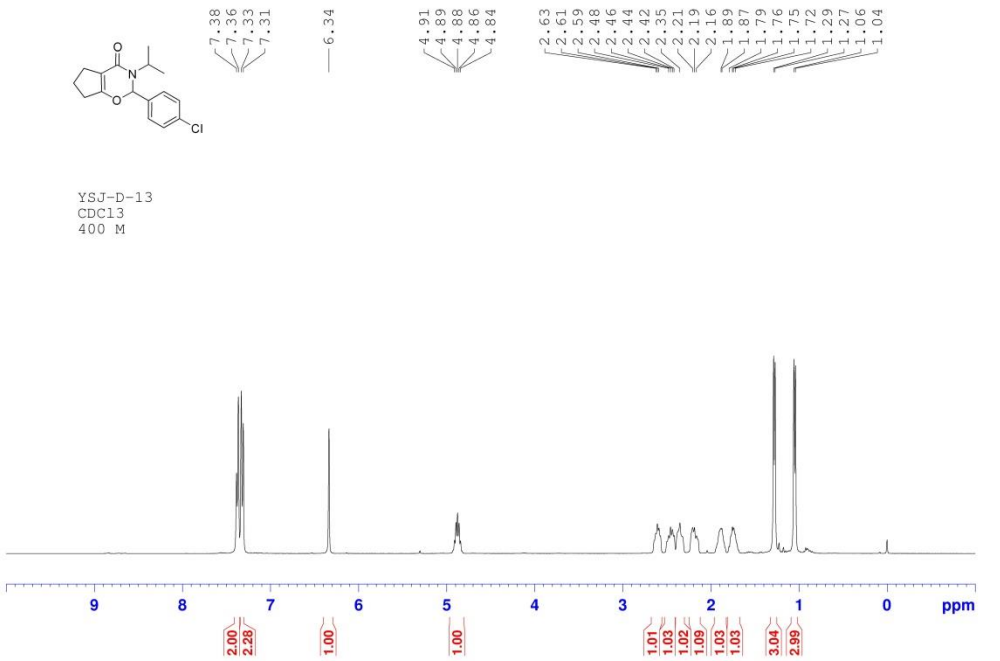


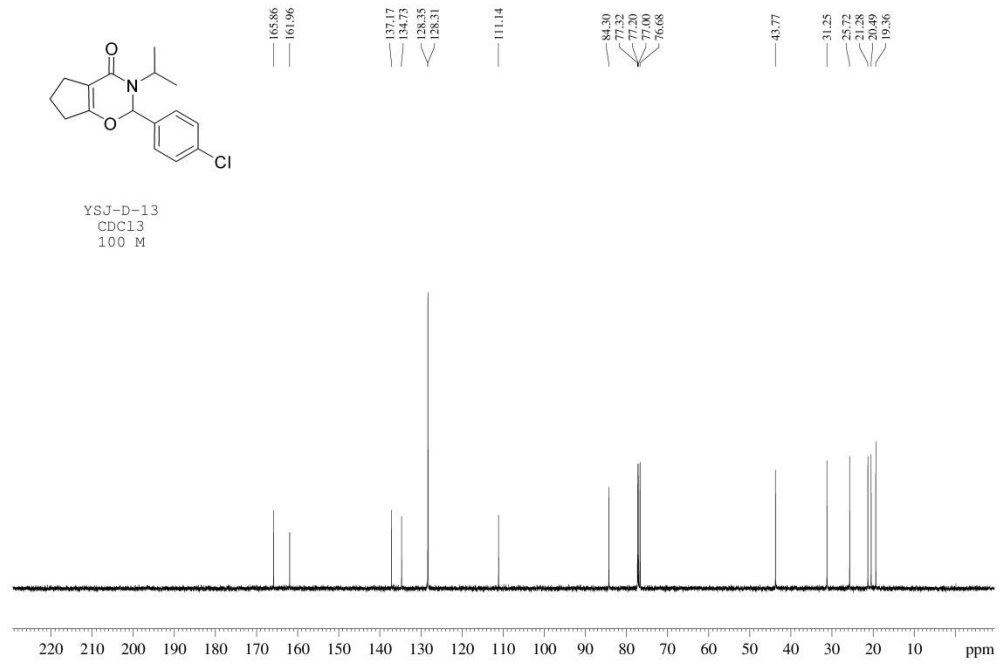
^{1}H and ^{13}C NMR spectra of compound 7u



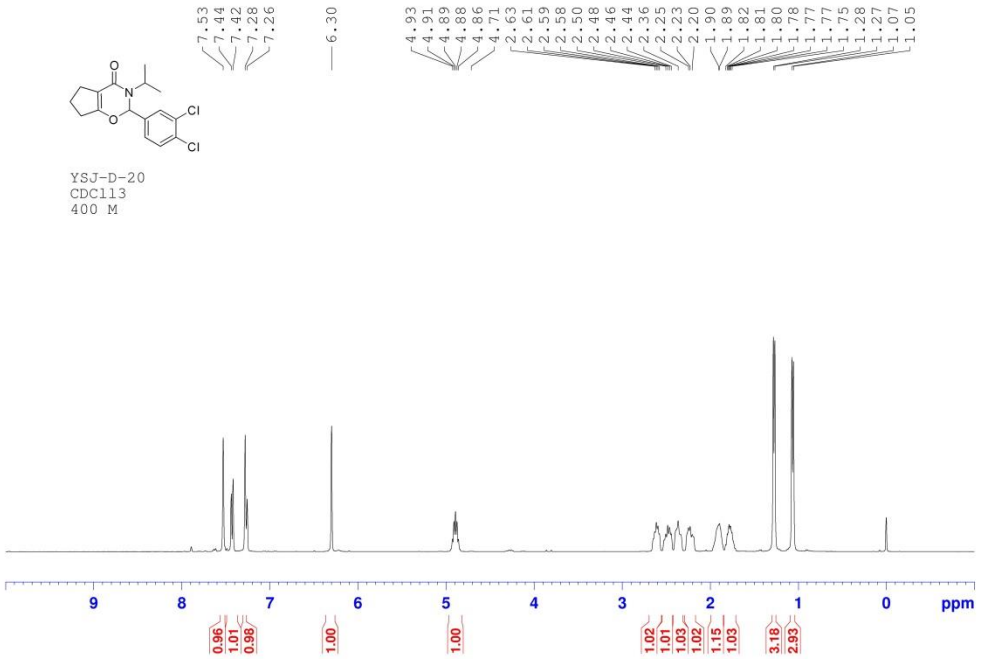


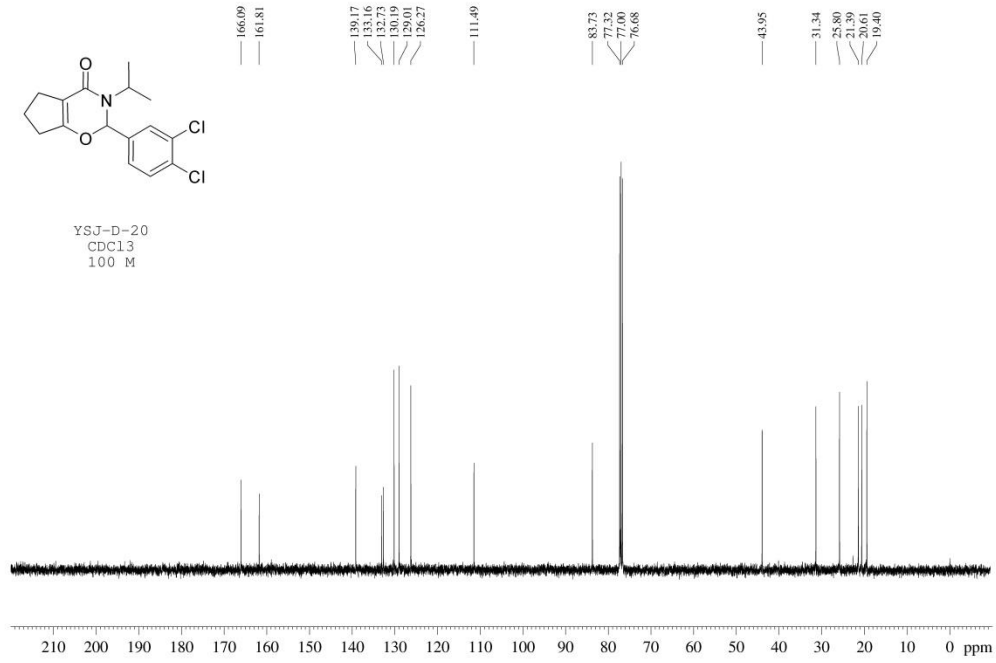
^{1}H and ^{13}C NMR spectra of compound 7v



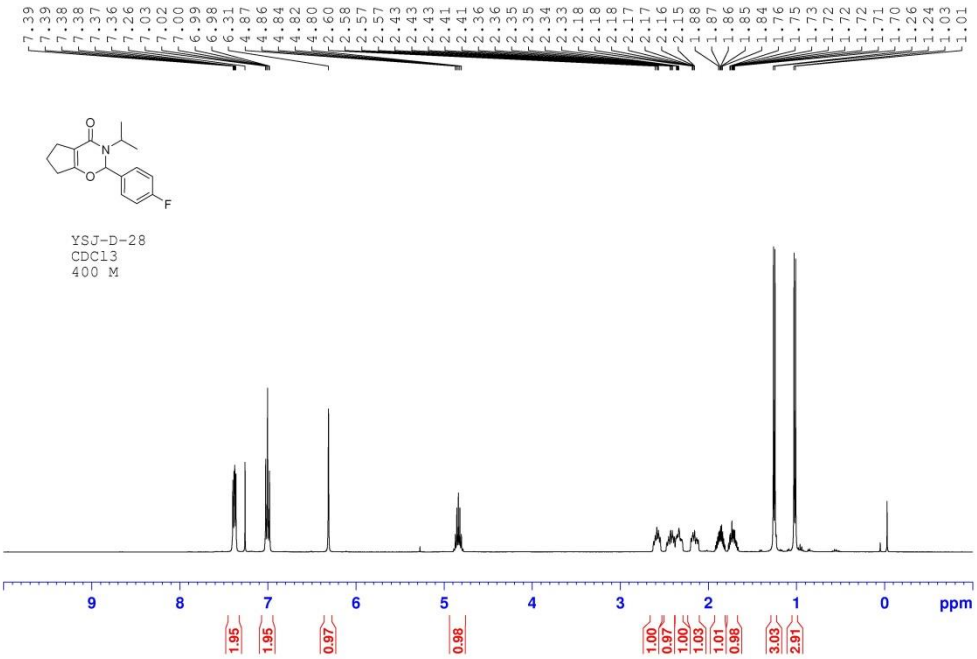


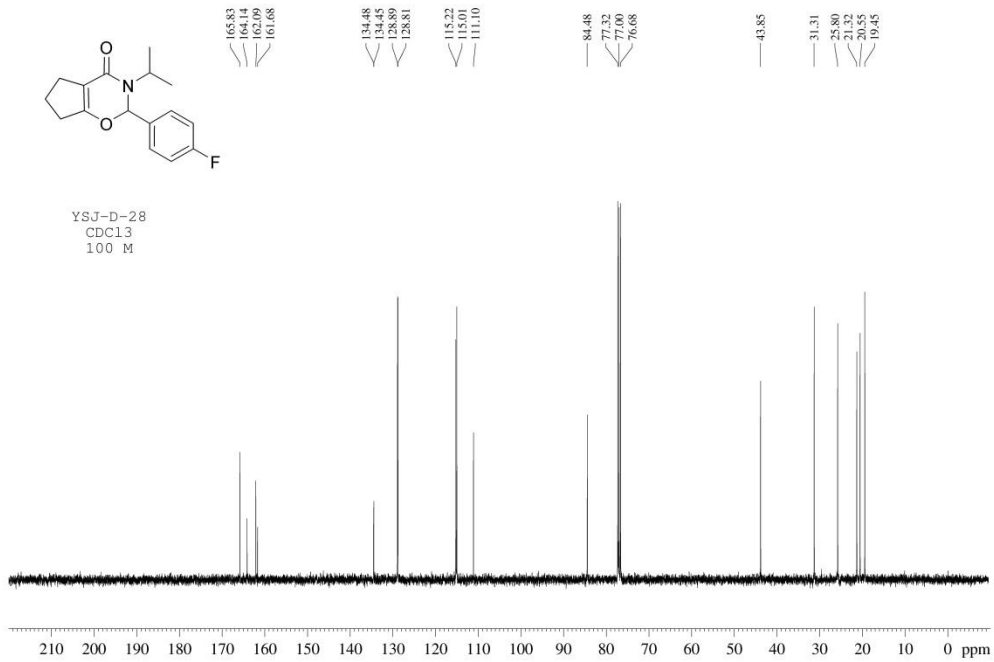
^{1}H and ^{13}C NMR spectra of compound 7w



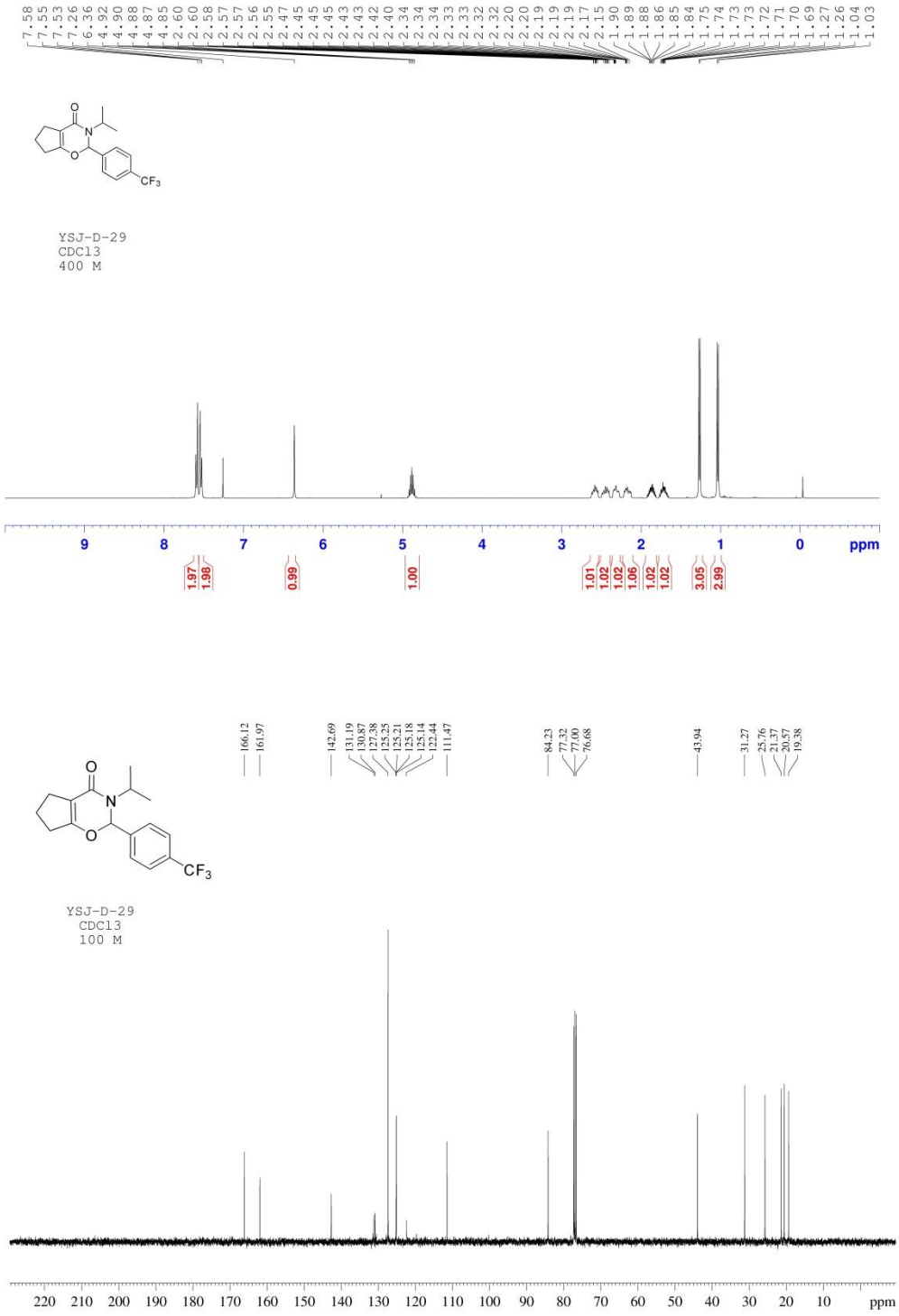


^{1}H and ^{13}C NMR spectra of compound 7x

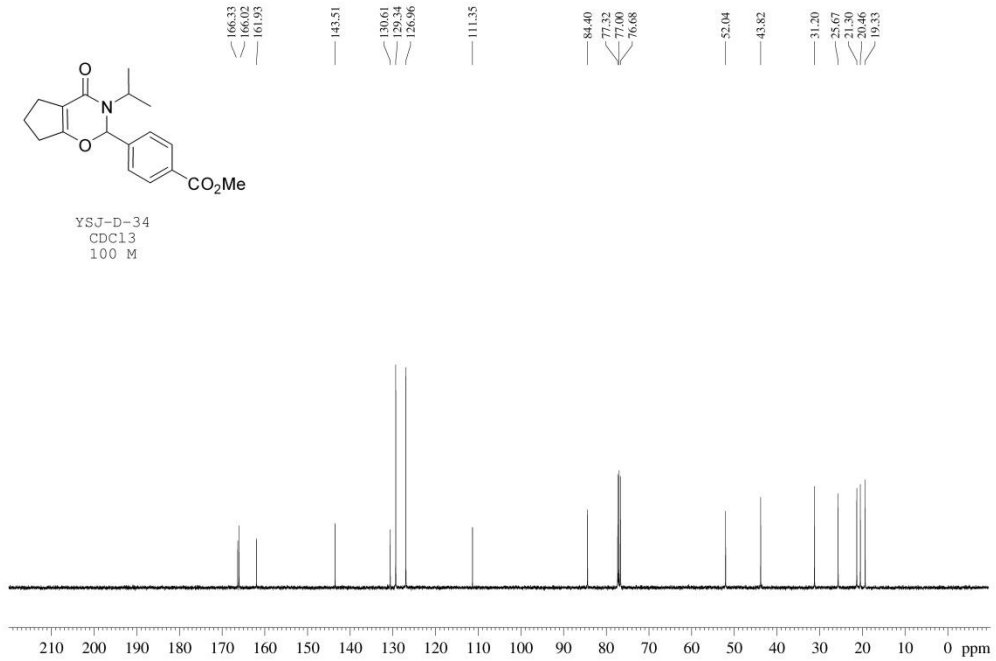


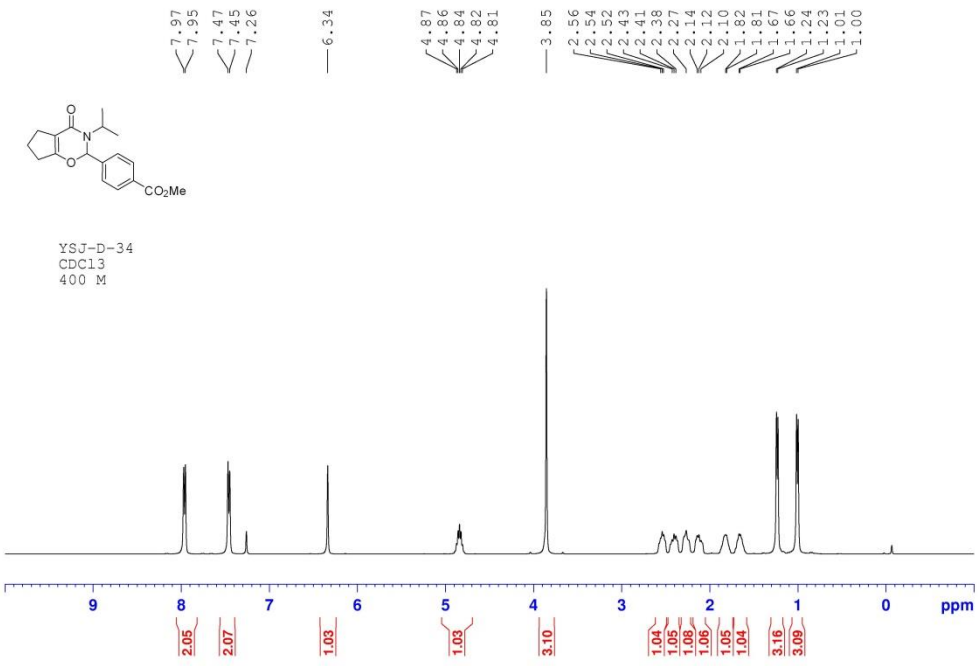


^{1}H and ^{13}C NMR spectra of compound 7y

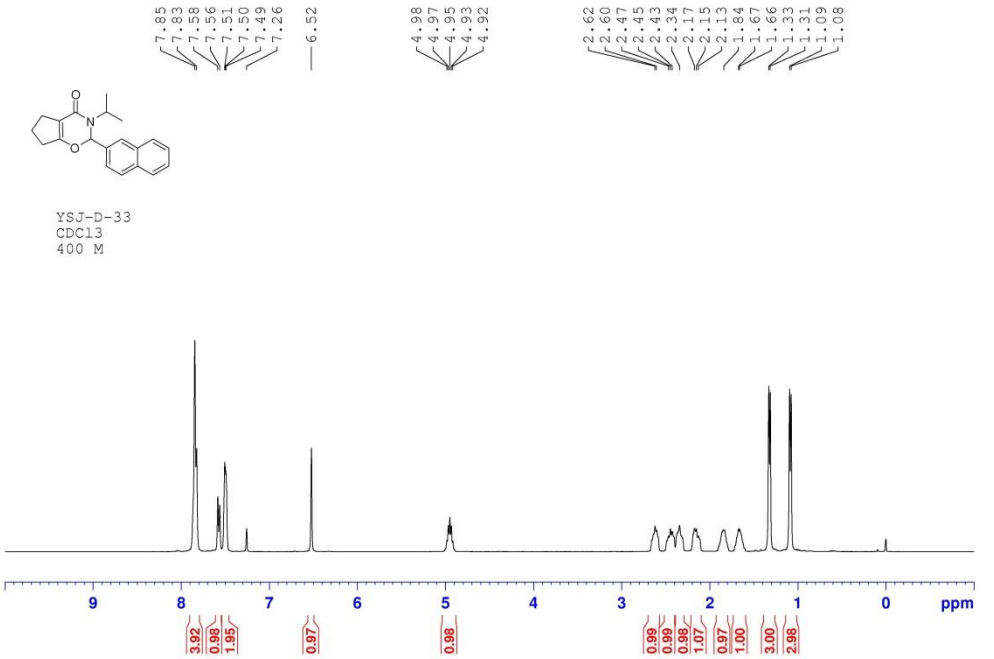


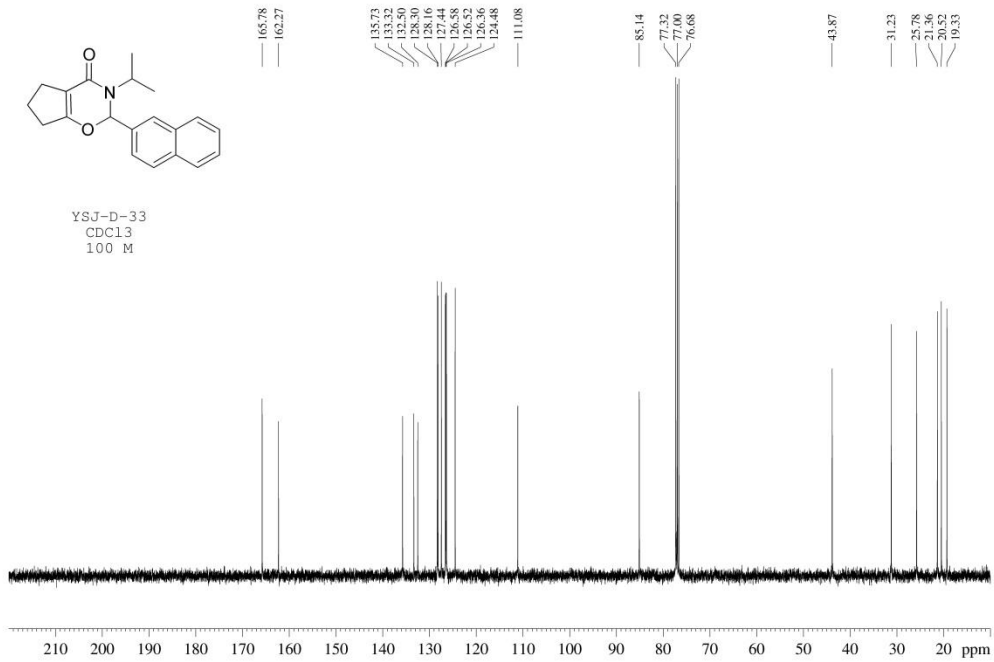
^{1}H and ^{13}C NMR spectra of compound 7z



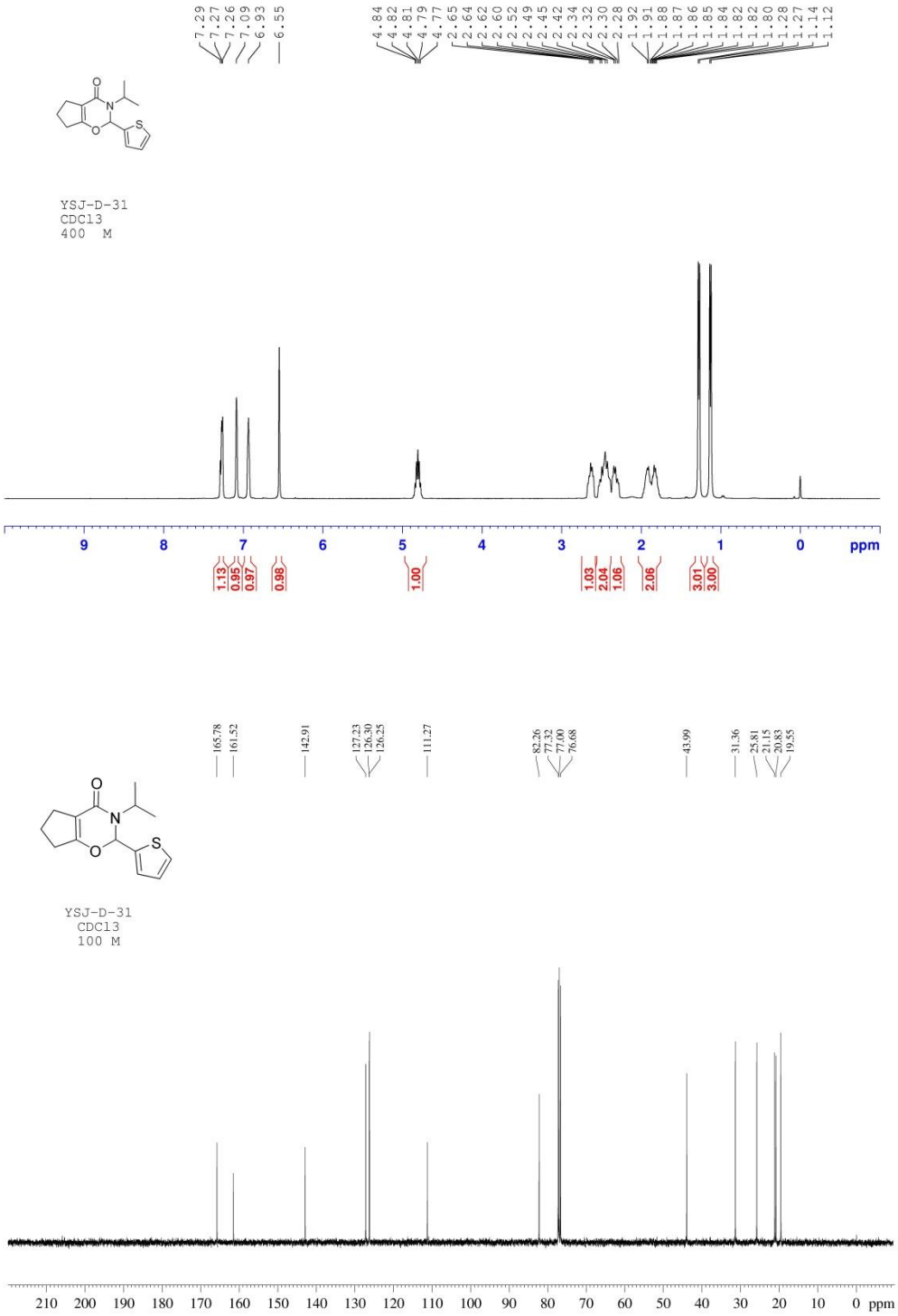


^{1}H and ^{13}C NMR spectra of compound 7aa

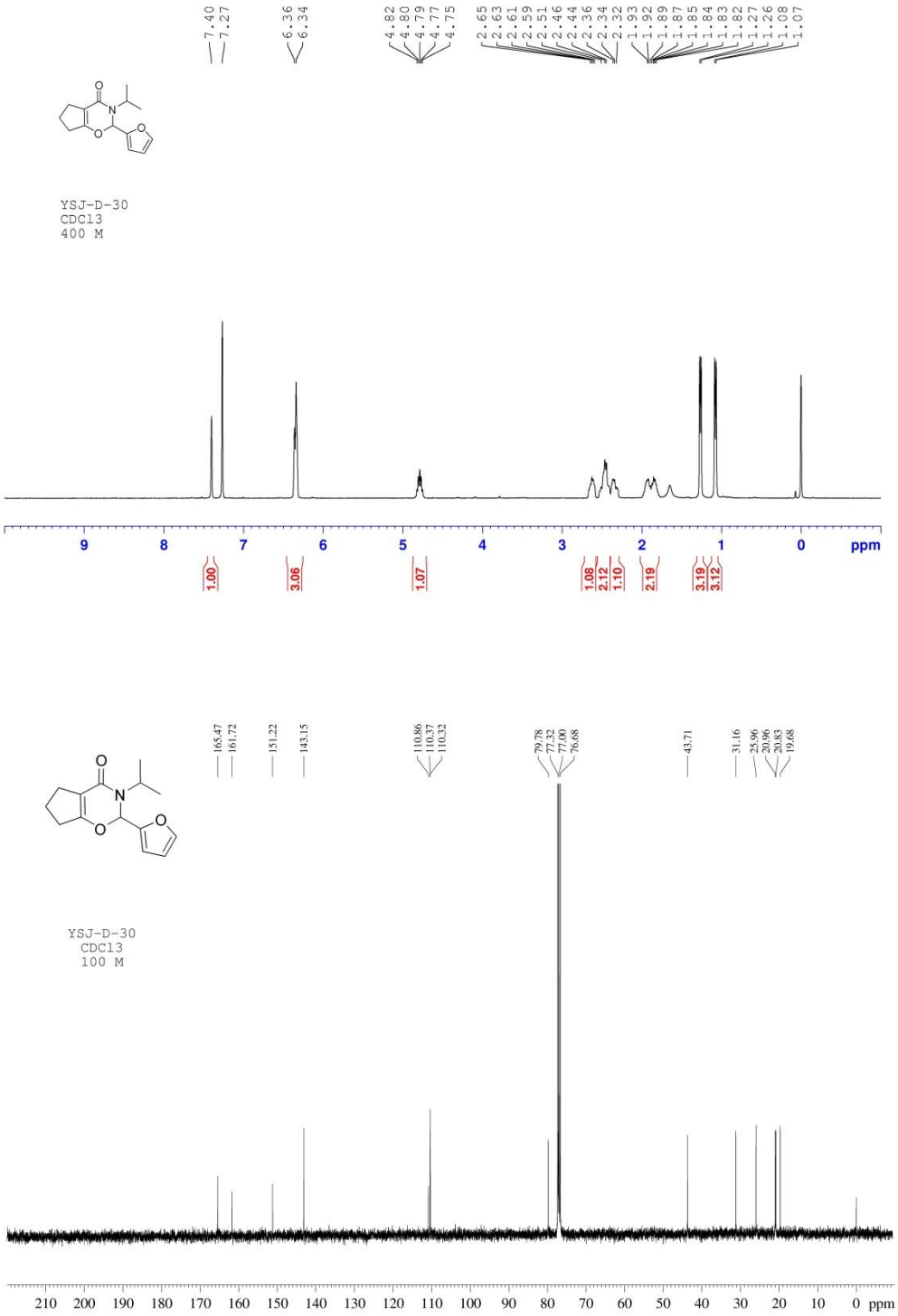




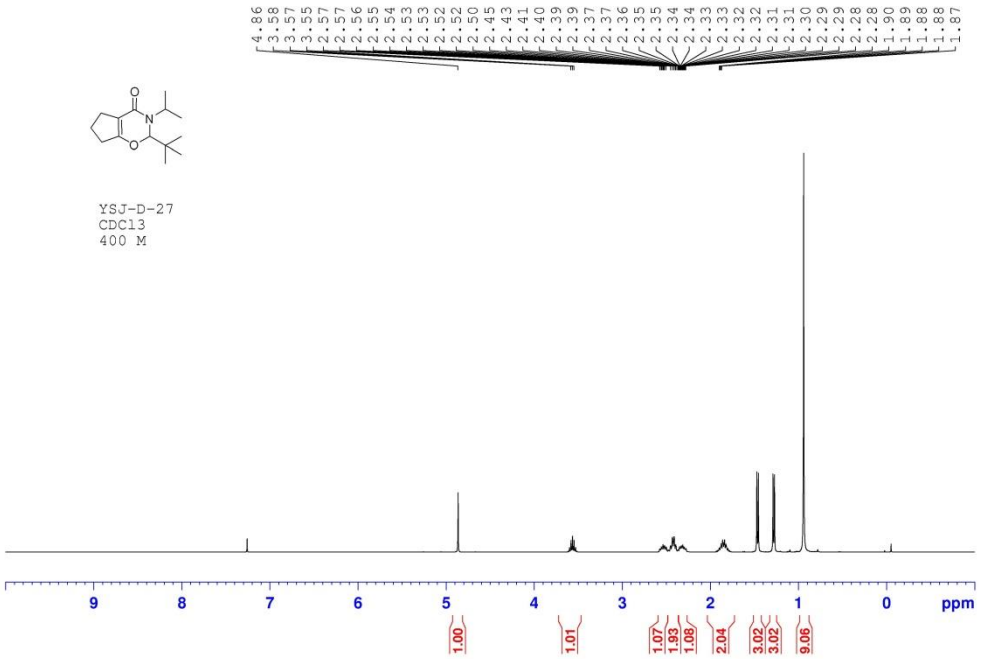
^{1}H and ^{13}C NMR spectra of compound 7ab

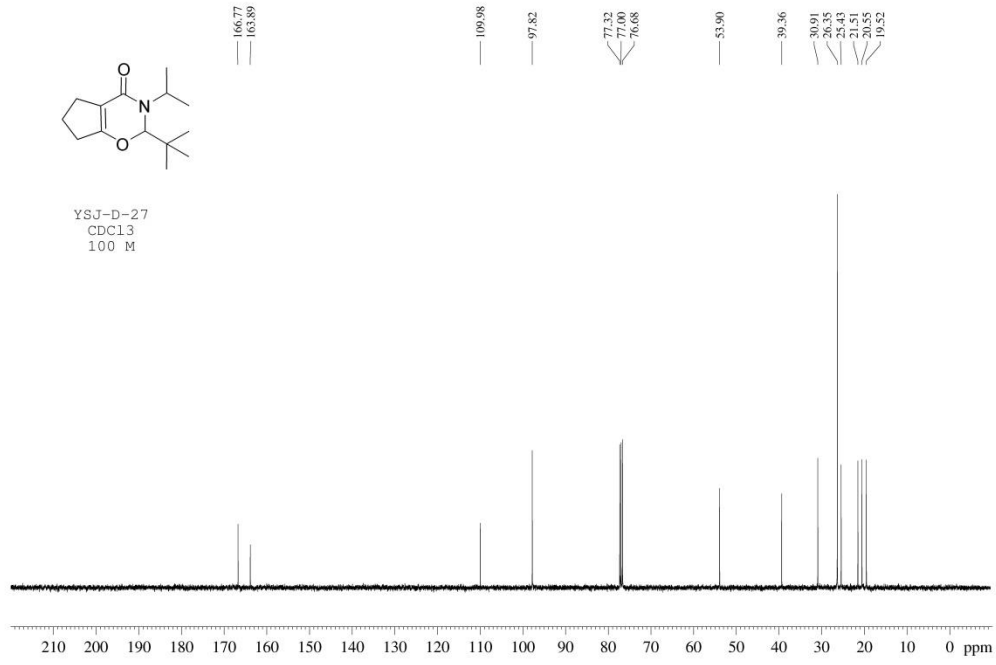


^{1}H and ^{13}C NMR spectra of compound 7ac

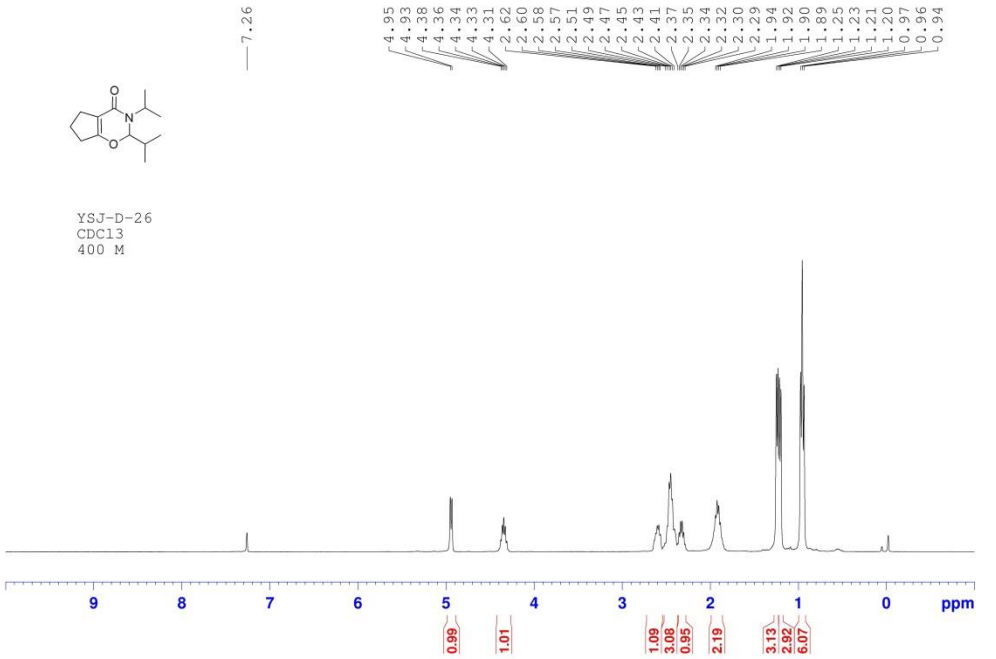


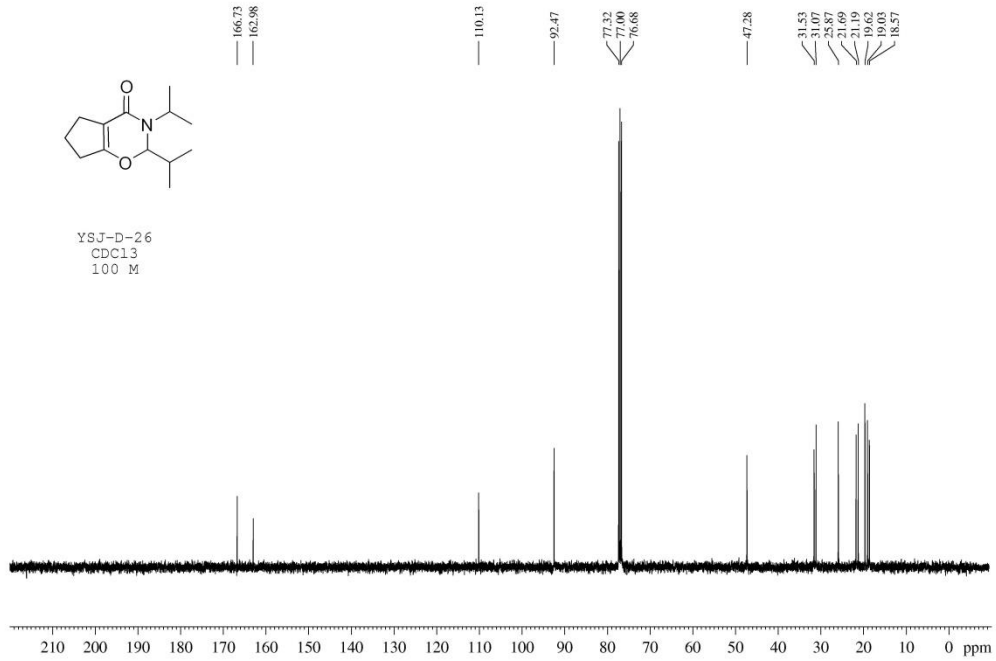
^{1}H and ^{13}C NMR spectra of compound 7ad



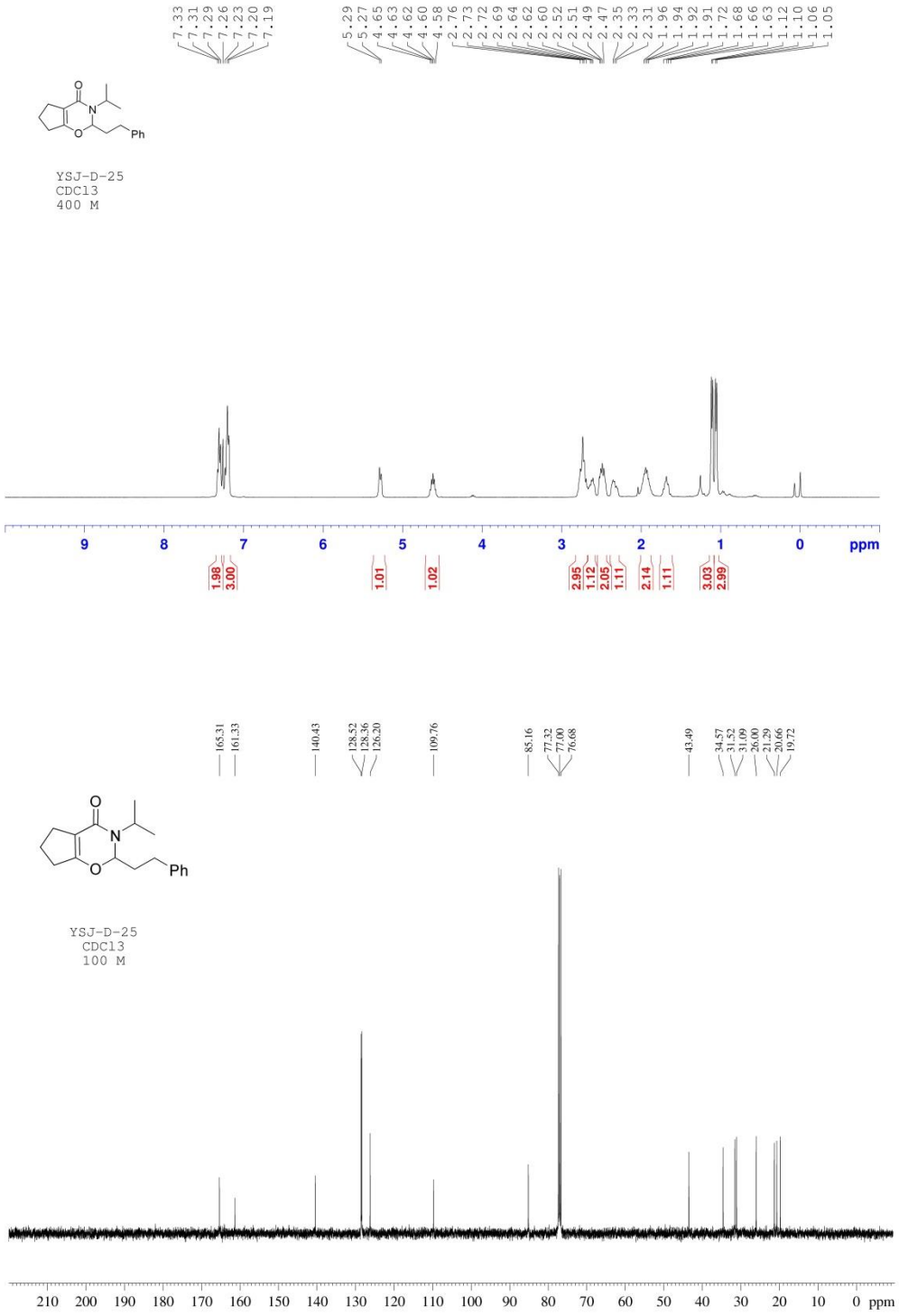


^{1}H and ^{13}C NMR spectra of compound 7ae

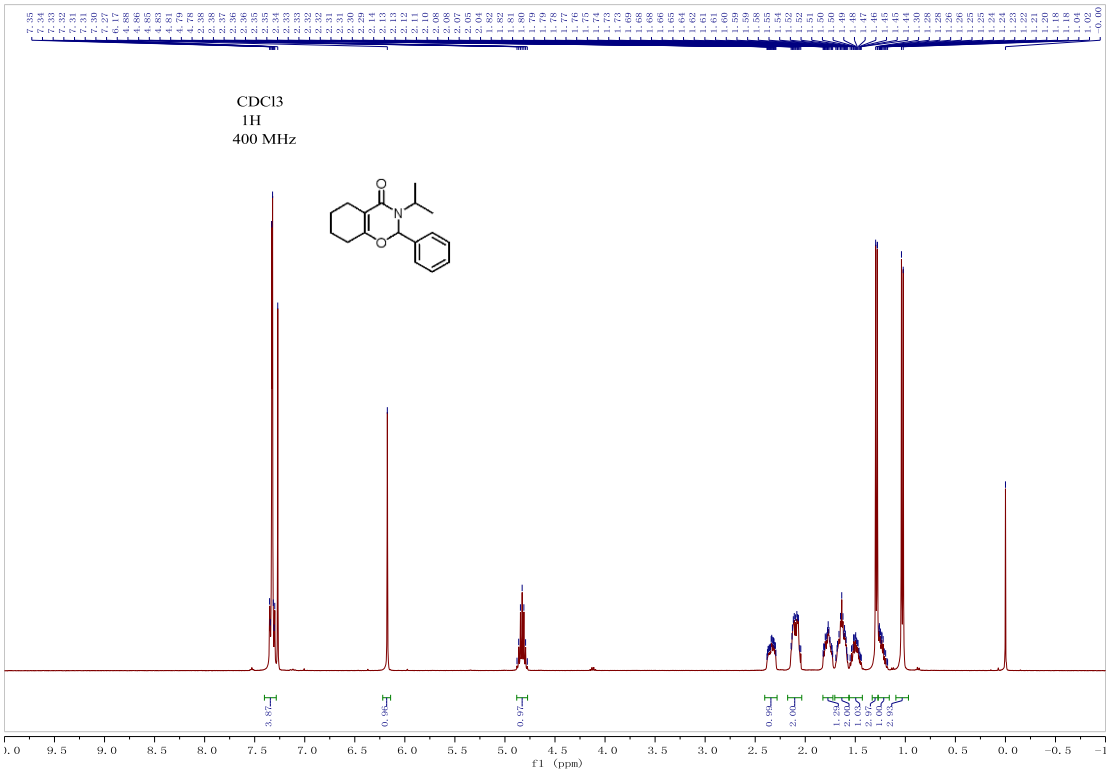


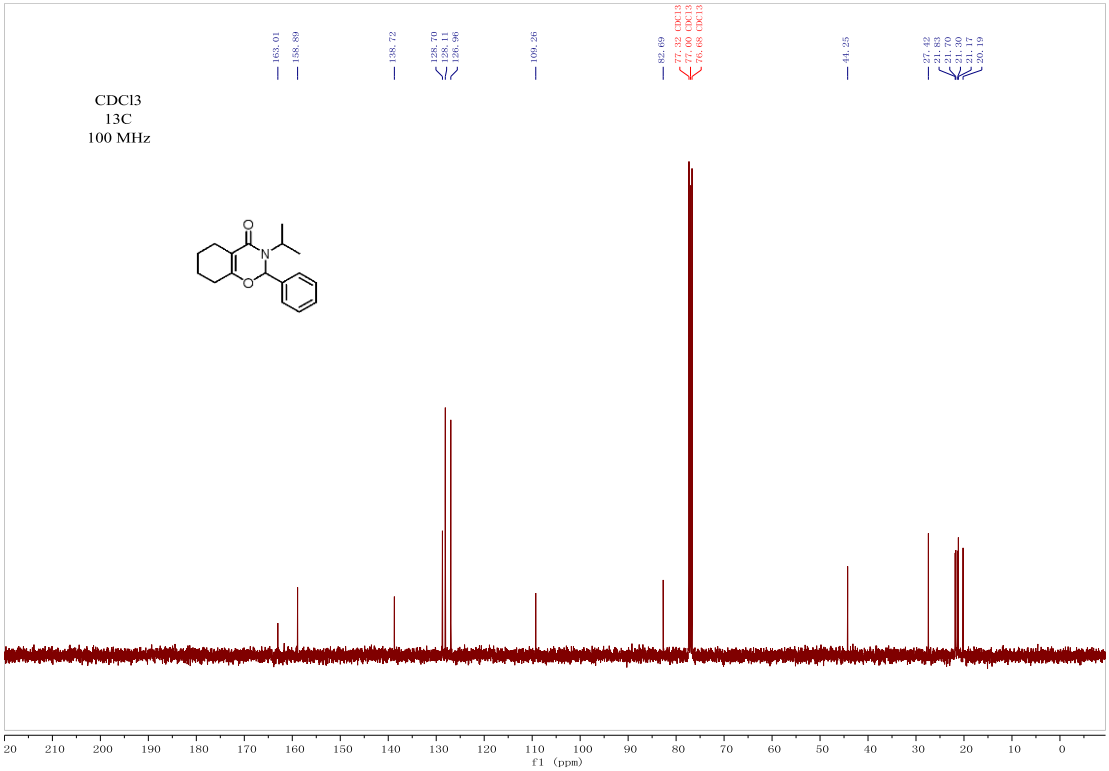


^{1}H and ^{13}C NMR spectra of compound 7af

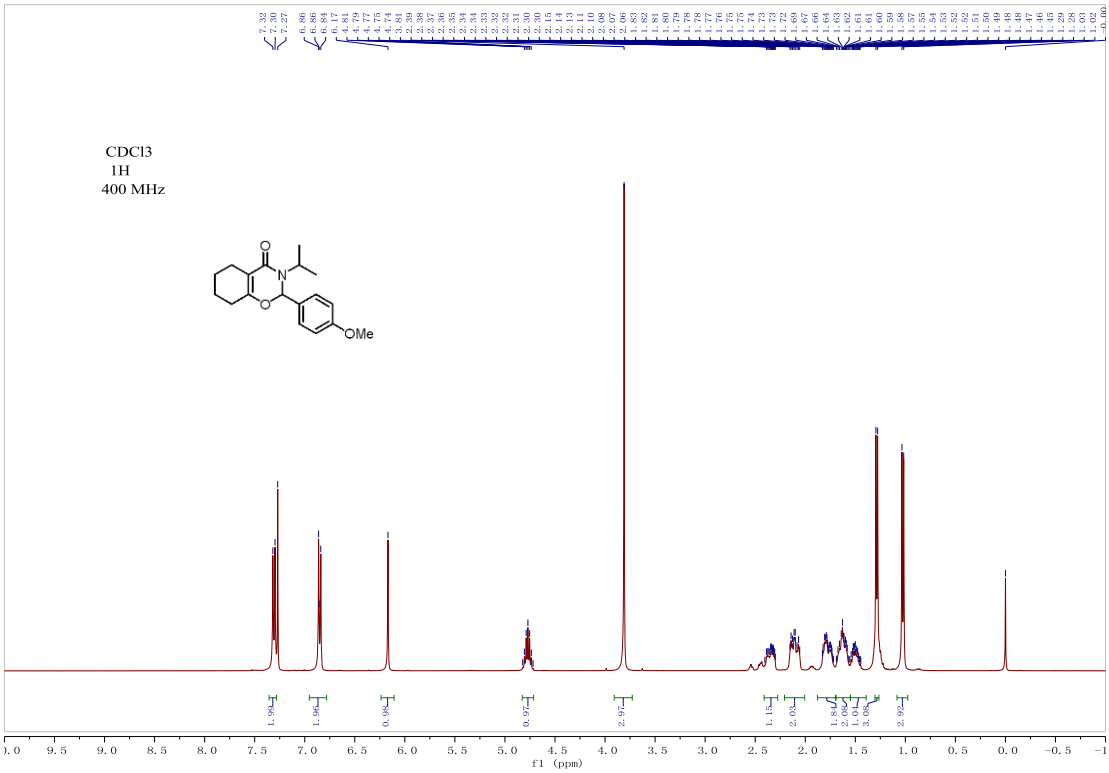


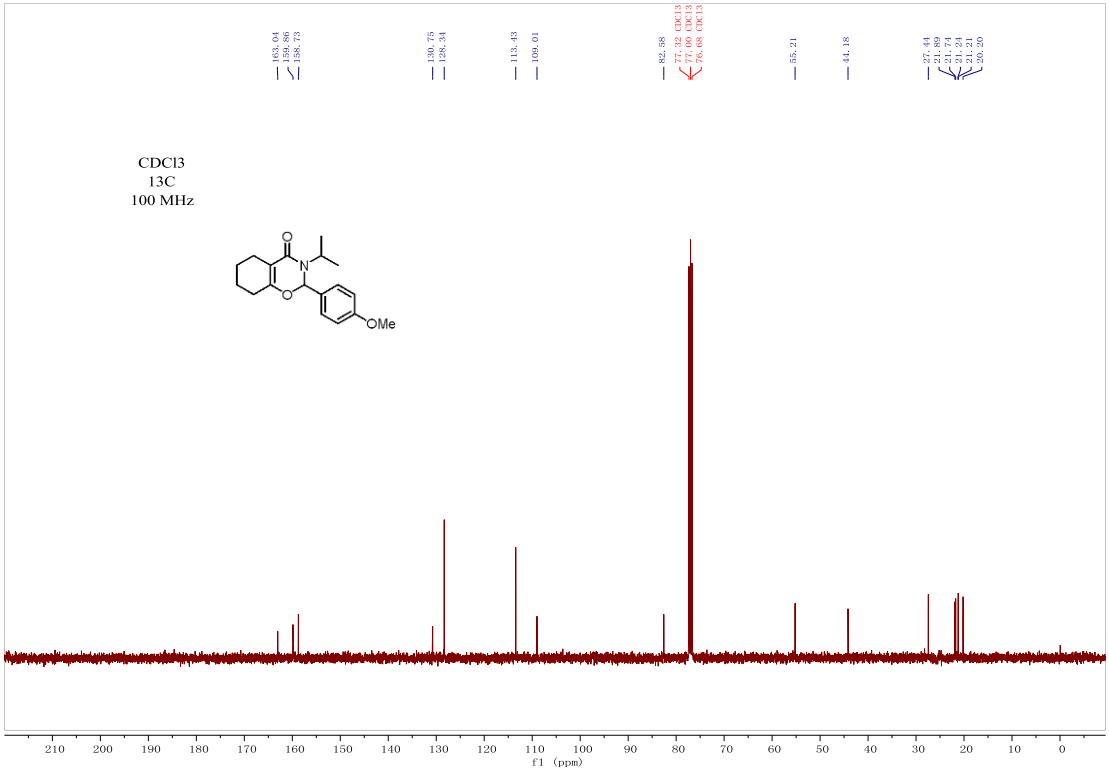
^{1}H and ^{13}C NMR spectra of compound 9a



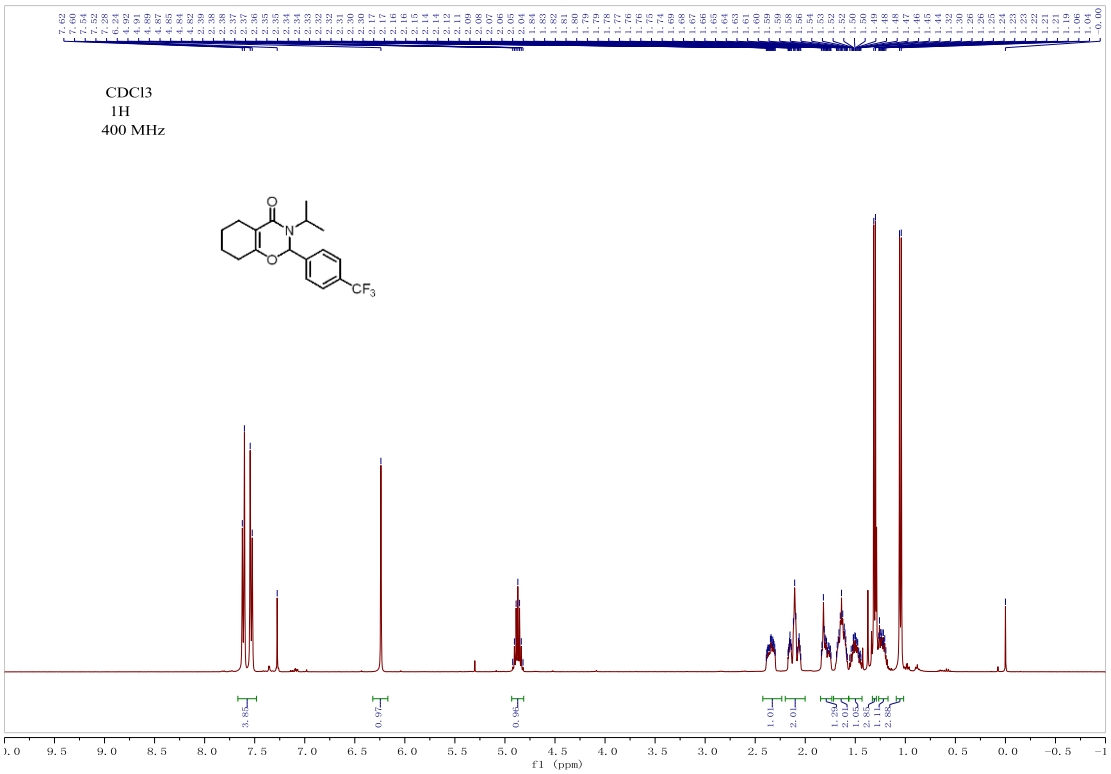


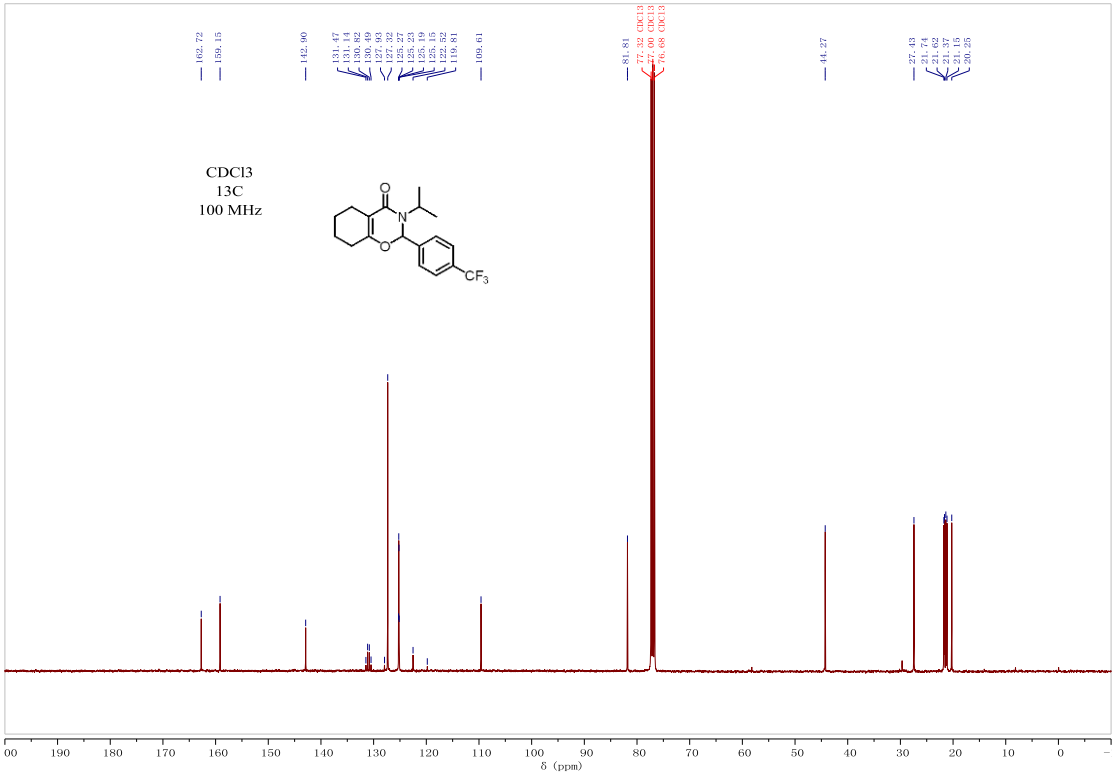
^{1}H and ^{13}C NMR spectra of compound 9b



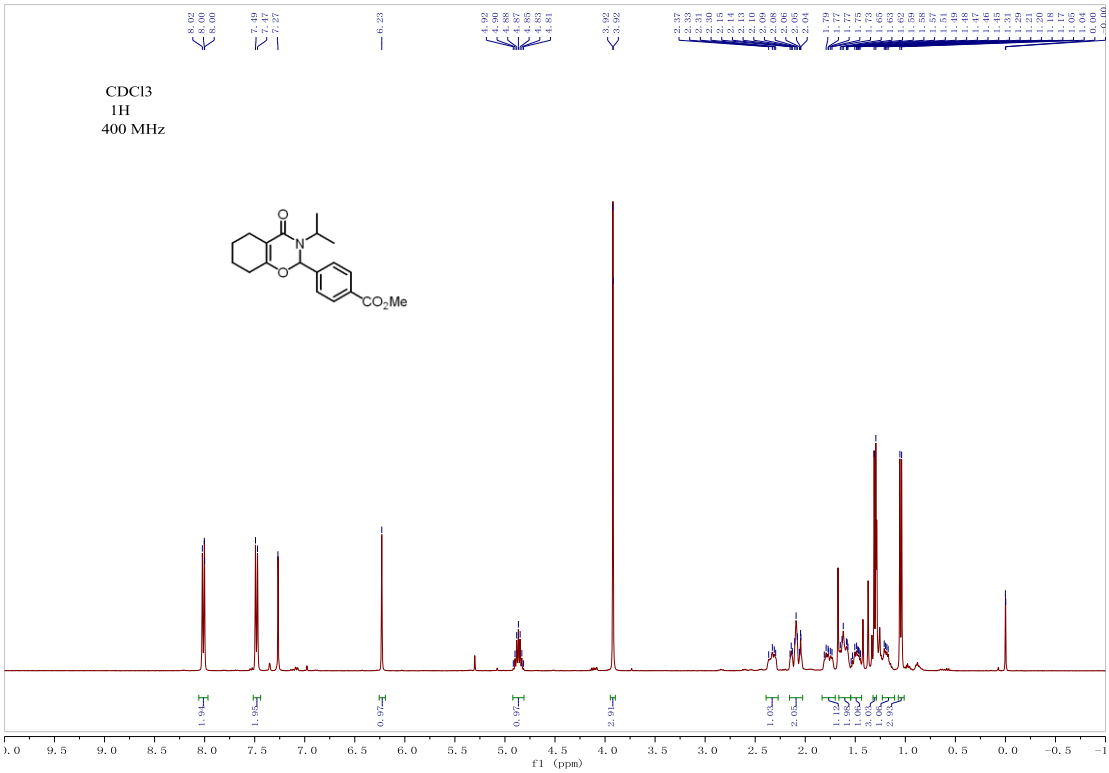


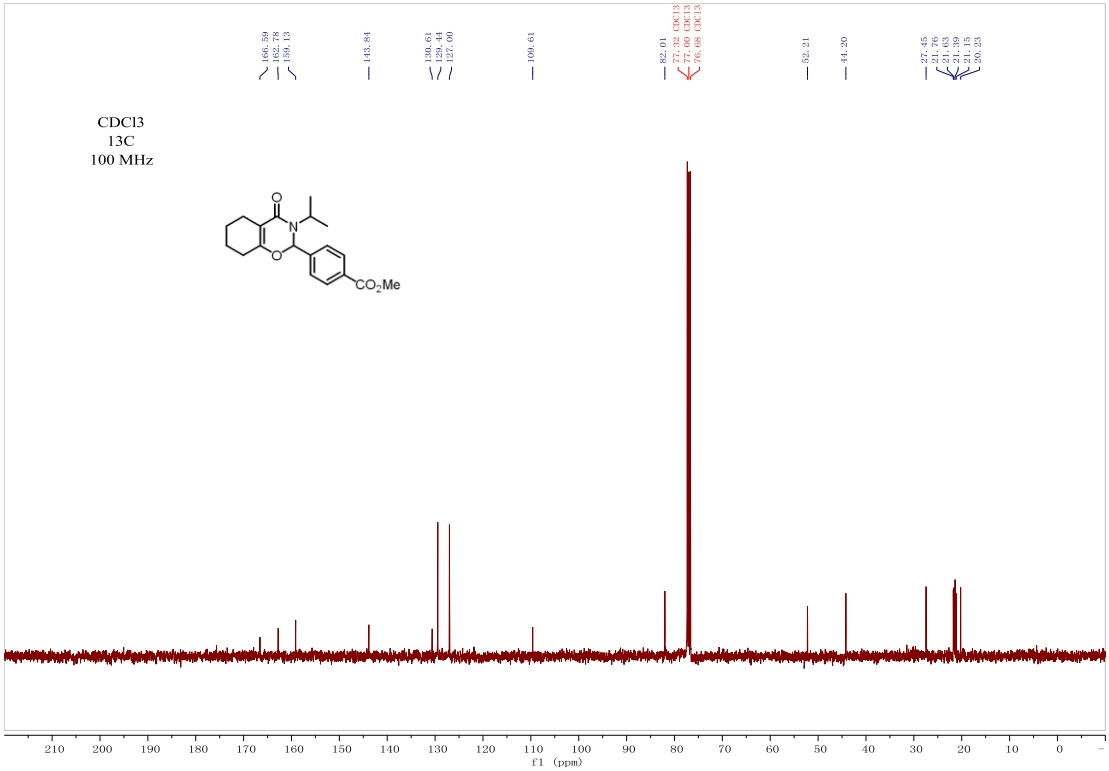
^{1}H and ^{13}C NMR spectra of compound 9c



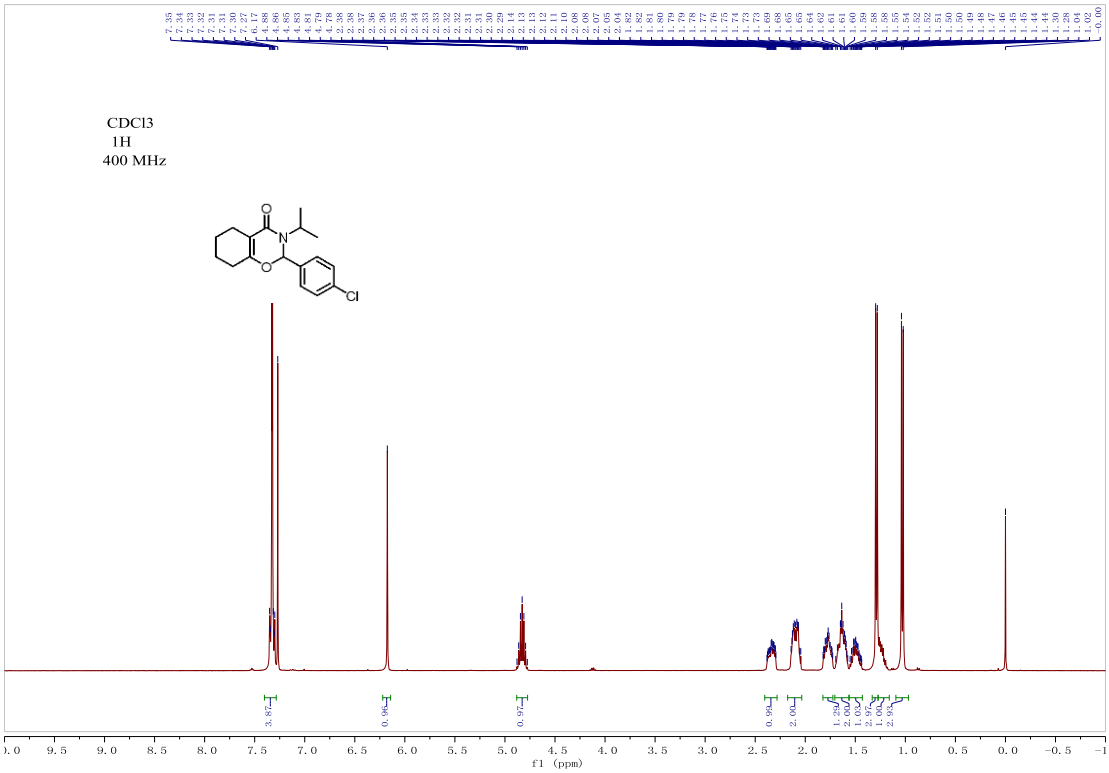


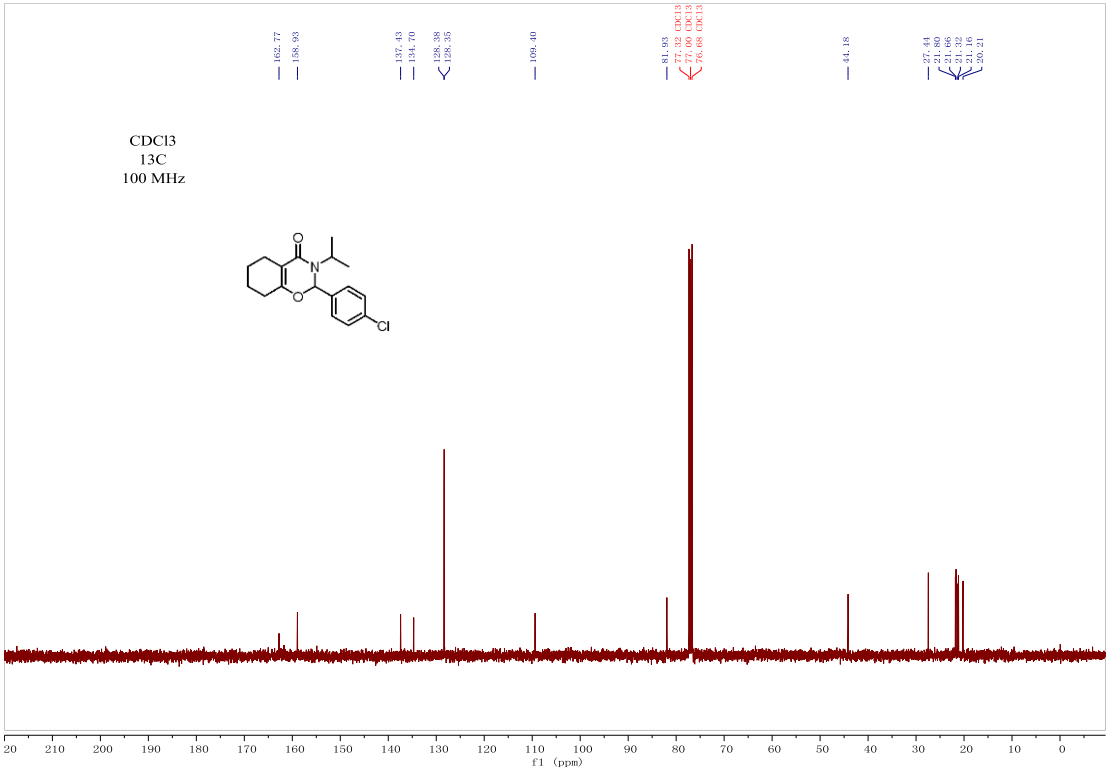
^{1}H and ^{13}C NMR spectra of compound 9d



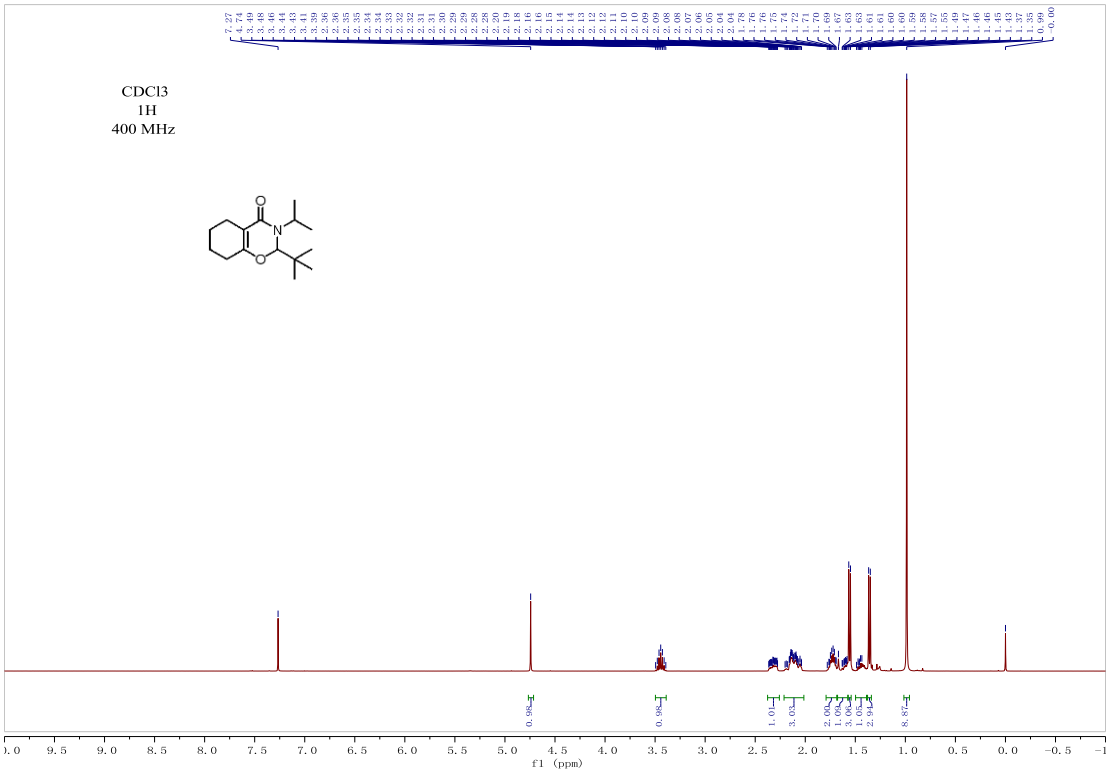


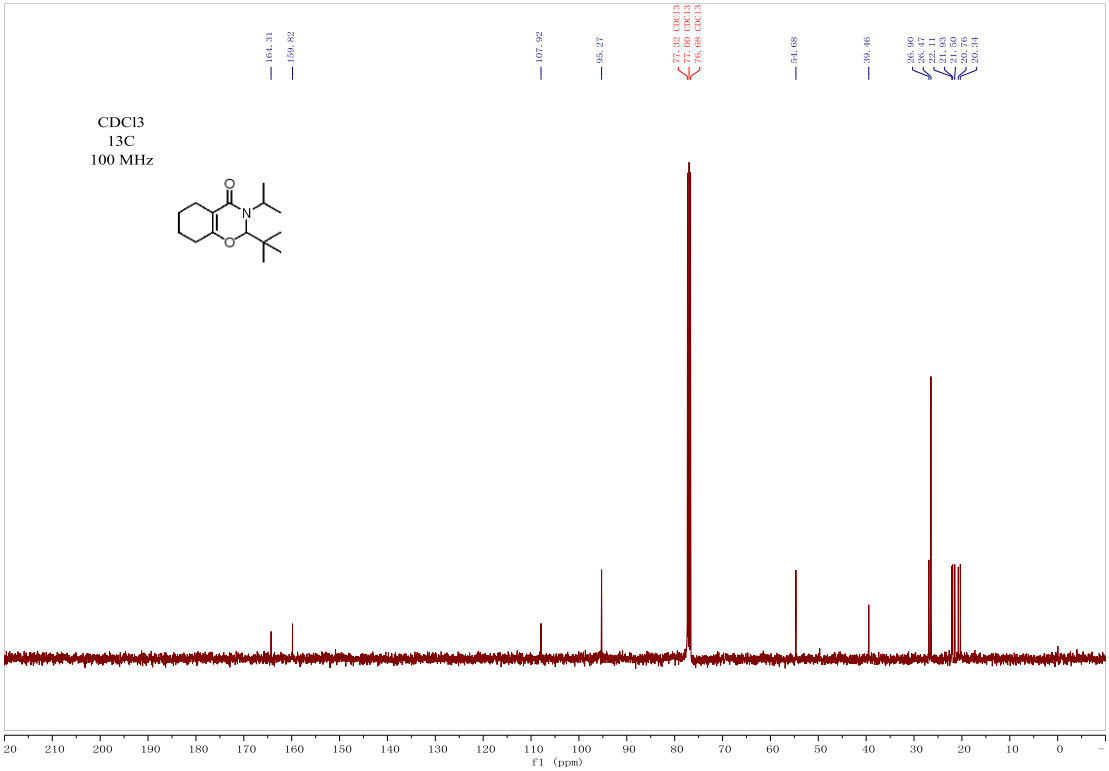
^{1}H and ^{13}C NMR spectra of compound 9e



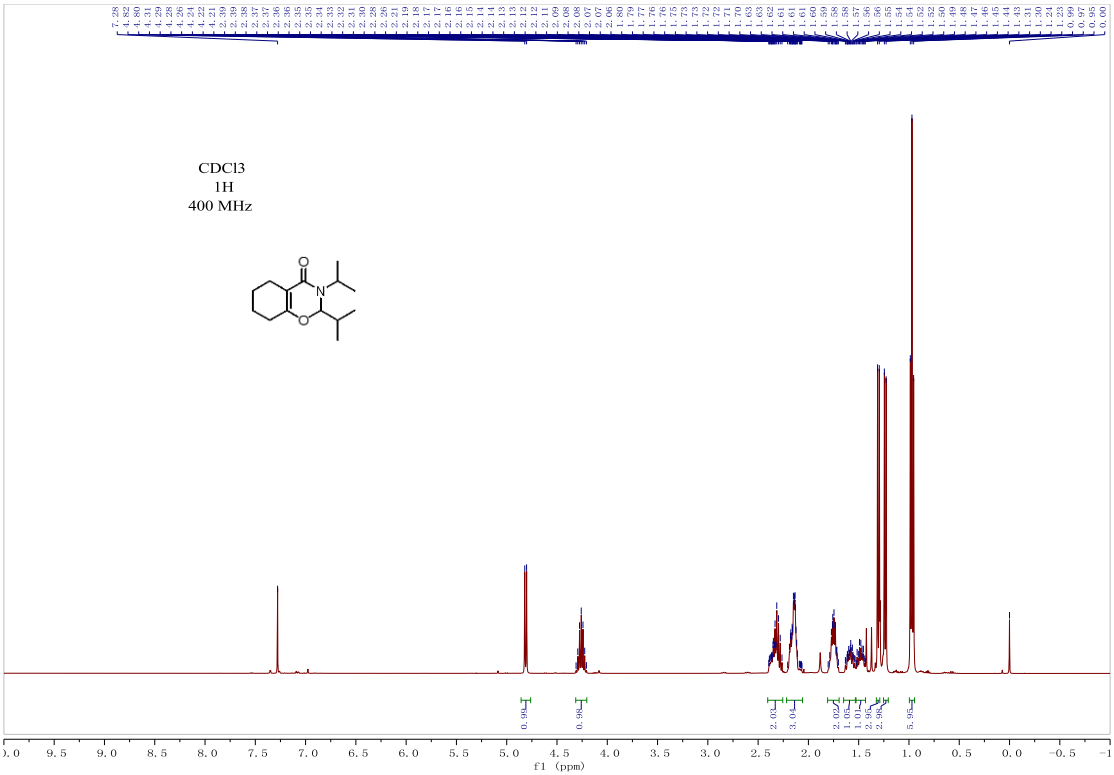


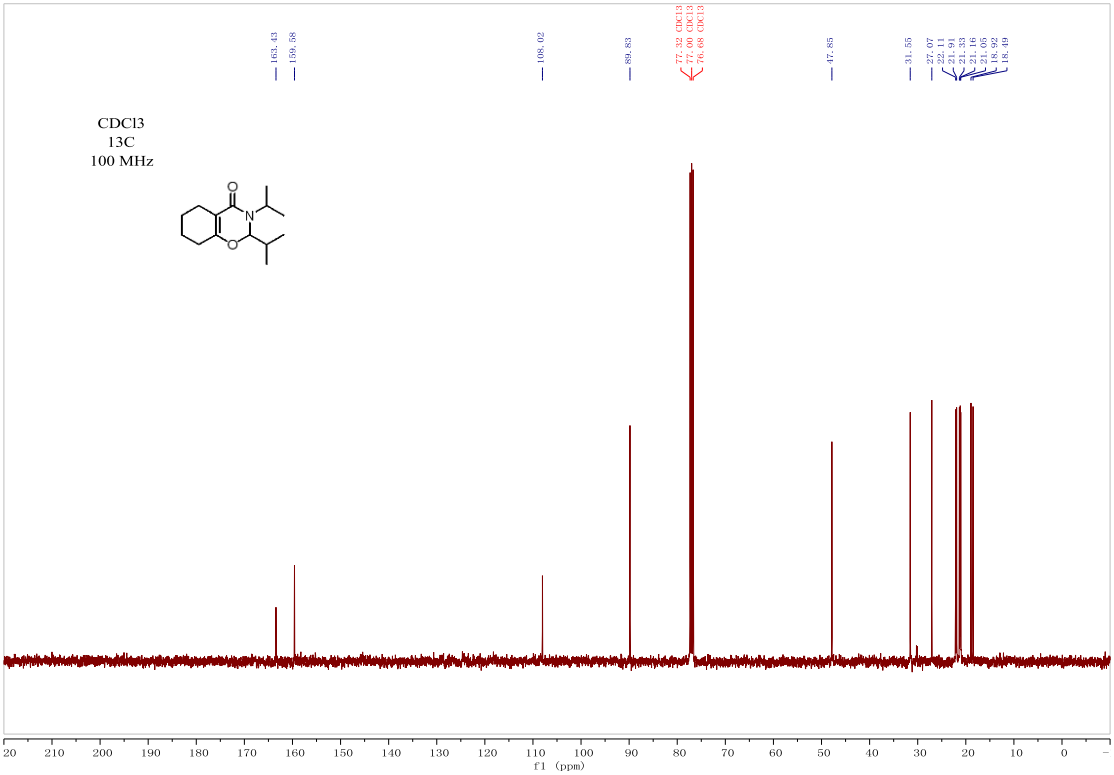
^{1}H and ^{13}C NMR spectra of compound 9f



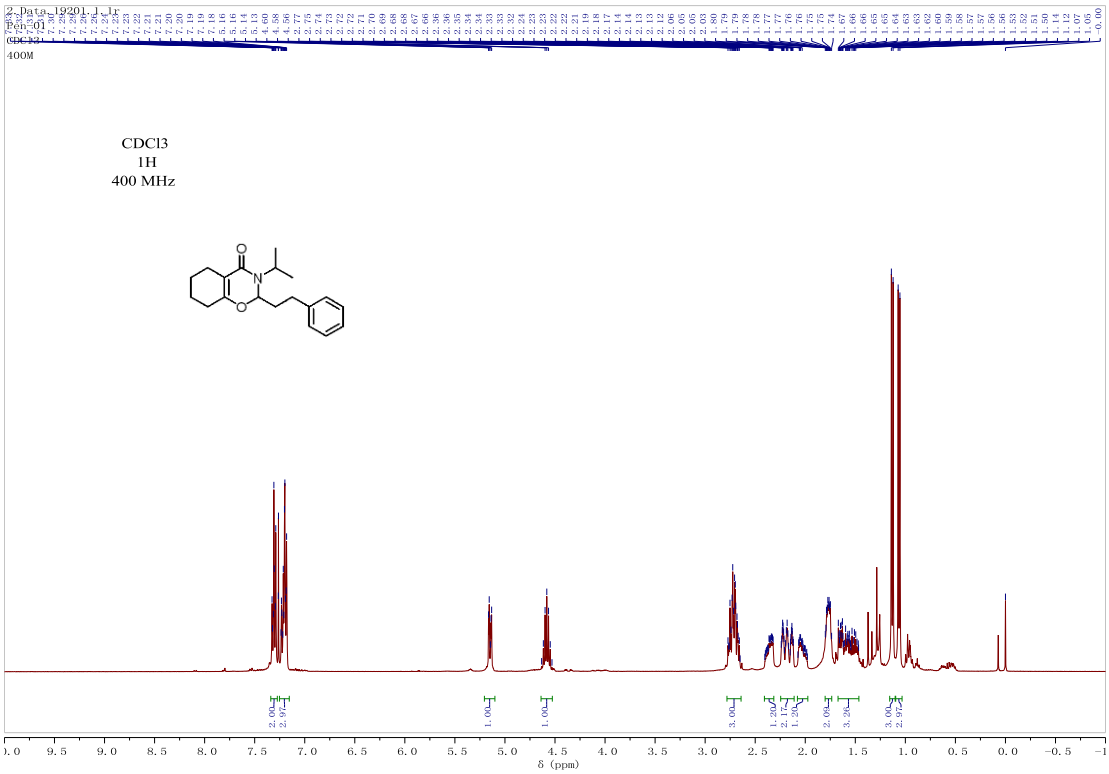


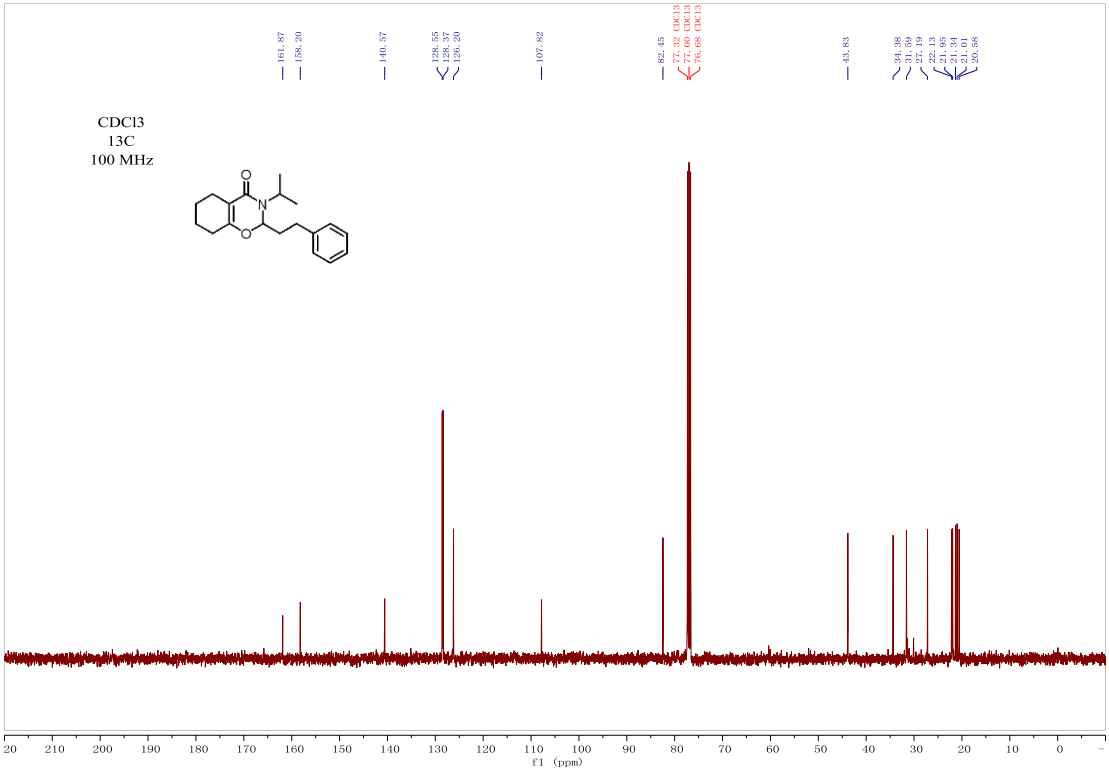
^{1}H and ^{13}C NMR spectra of compound 9g



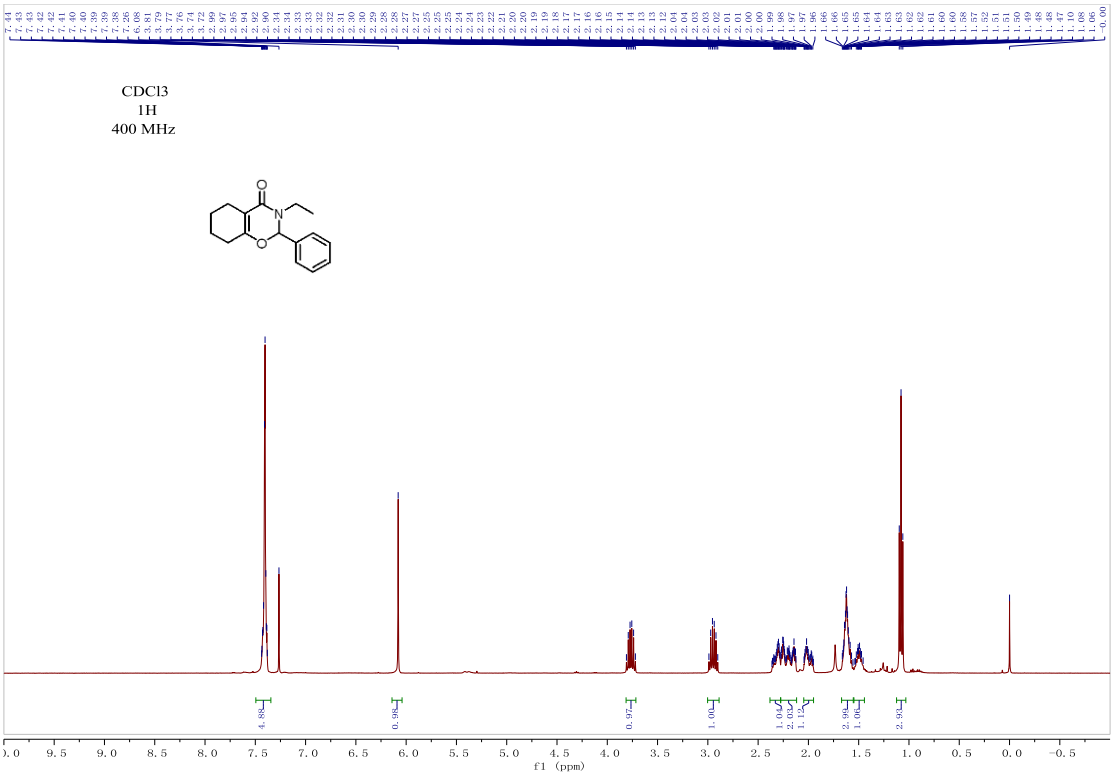


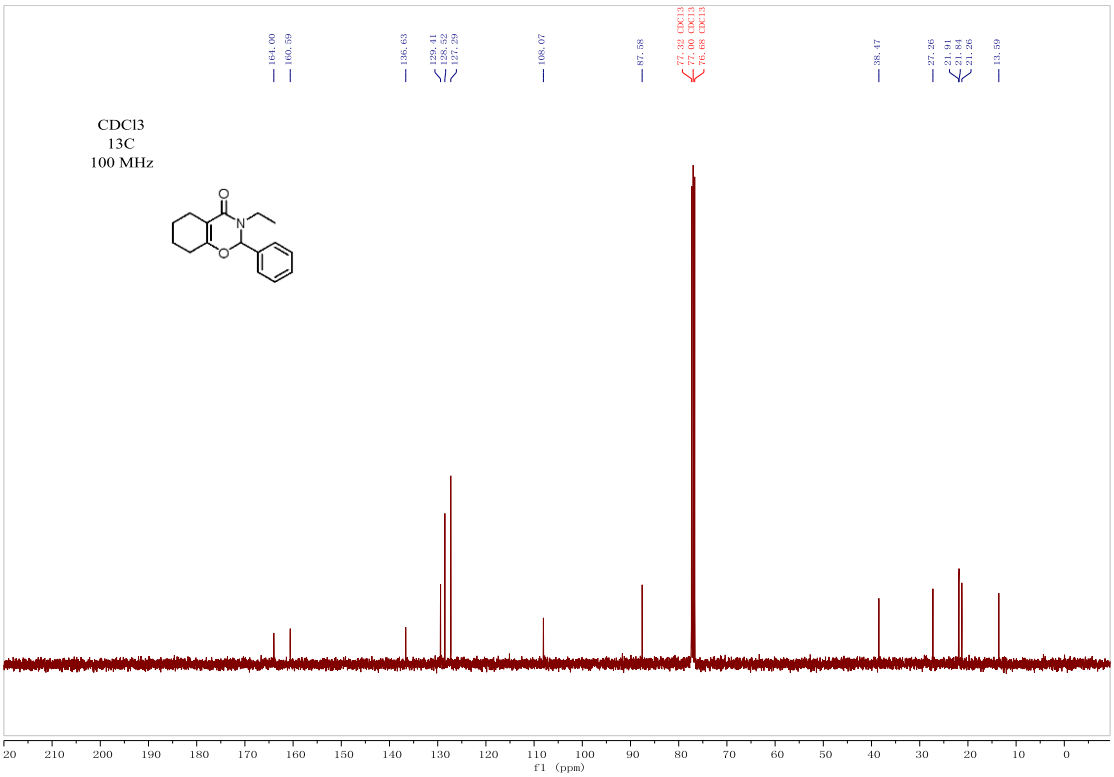
^{1}H and ^{13}C NMR spectra of compound 9h



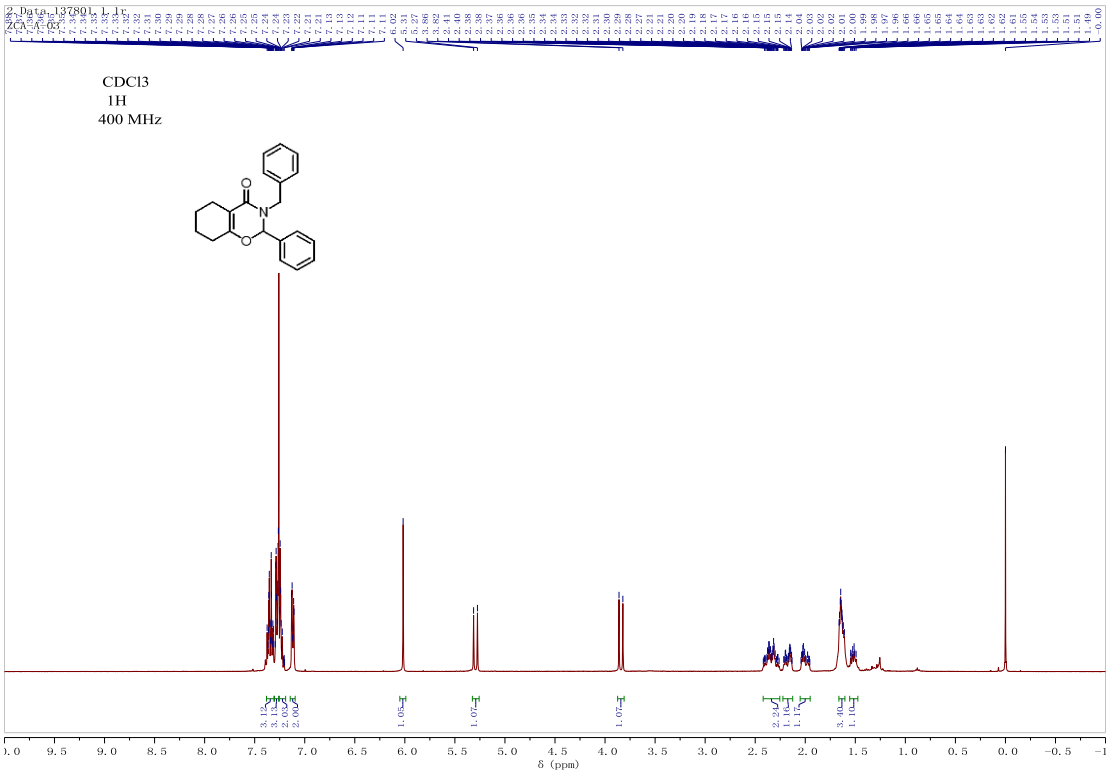


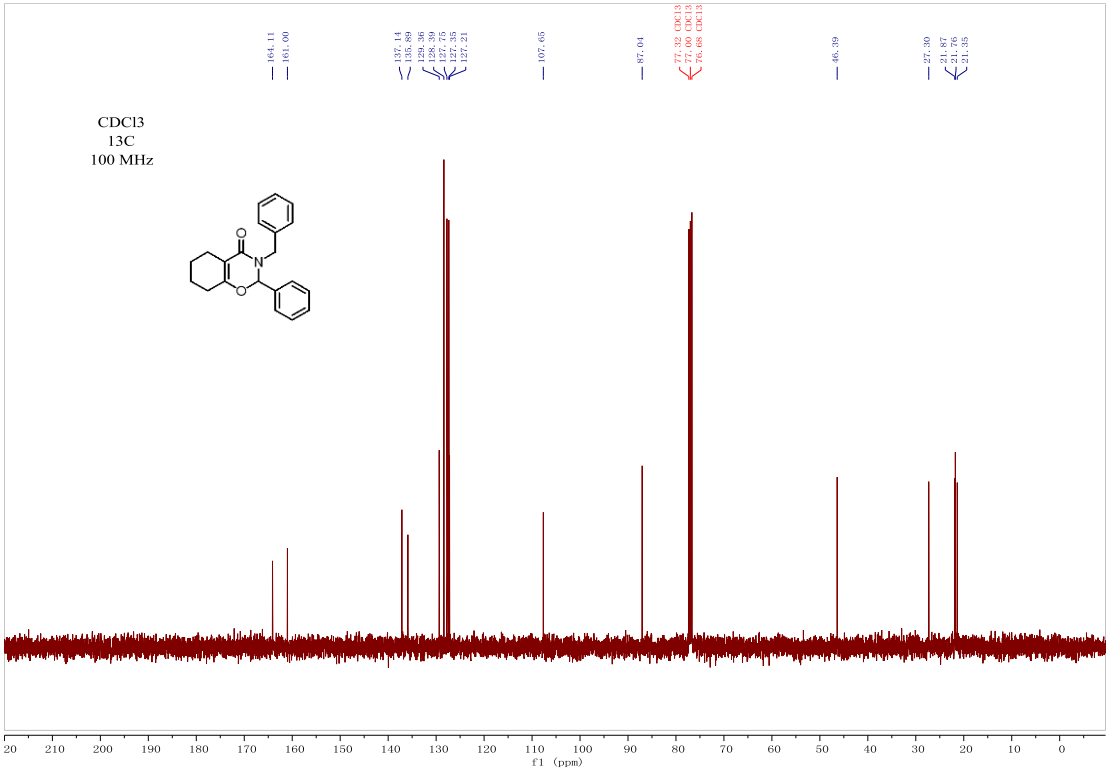
^{1}H and ^{13}C NMR spectra of compound 9i



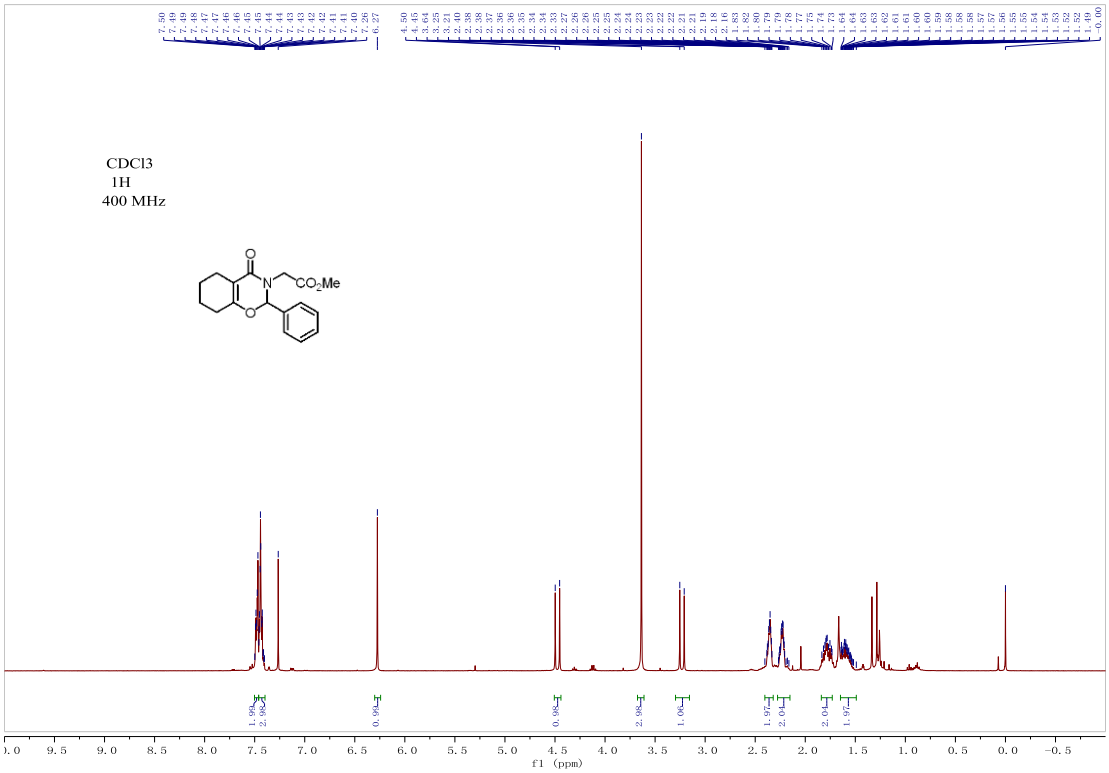


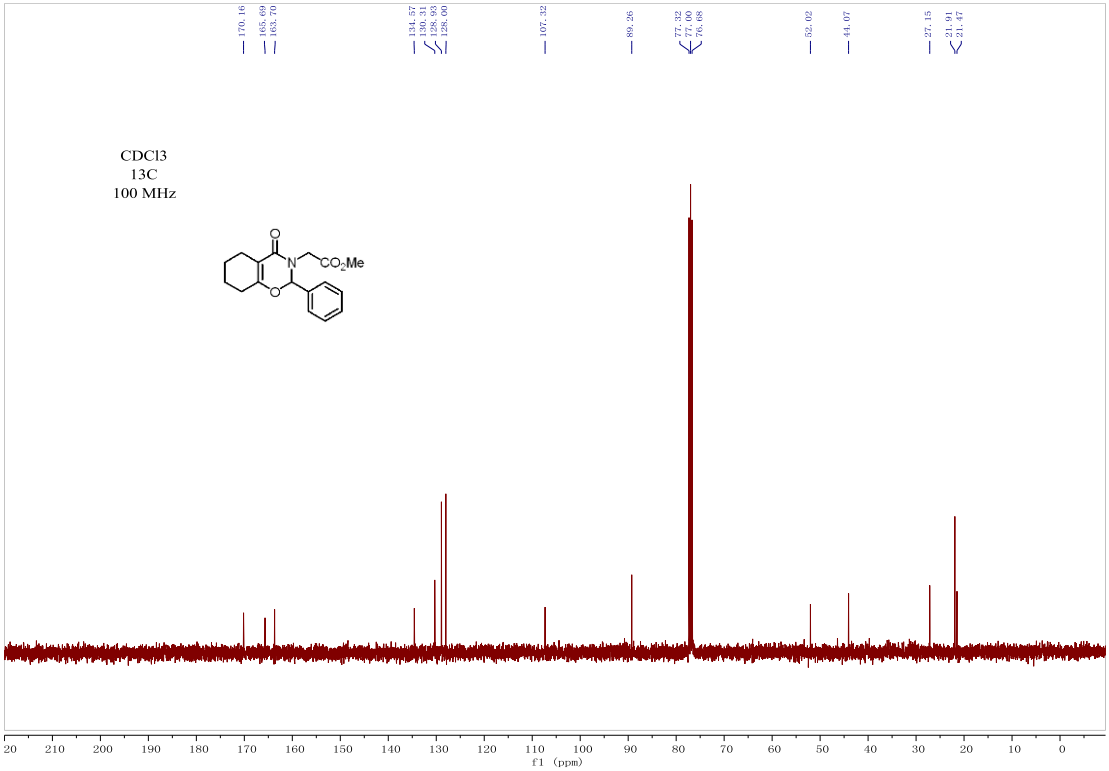
^{1}H and ^{13}C NMR spectra of compound 9j



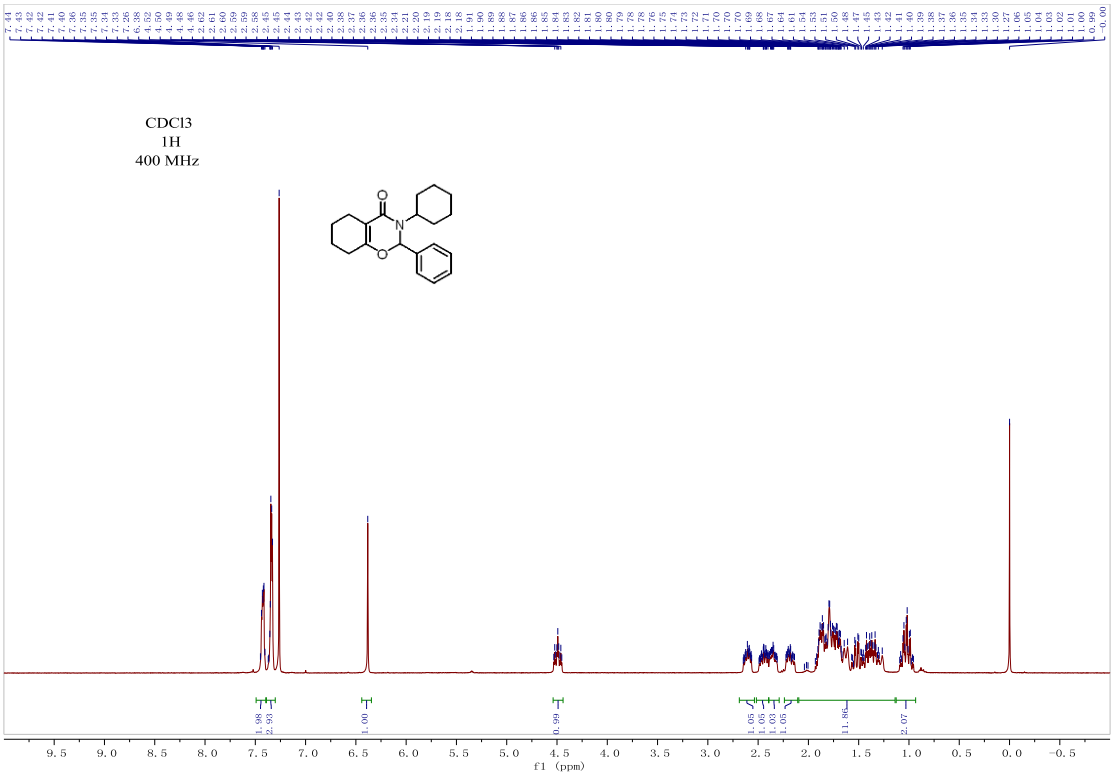


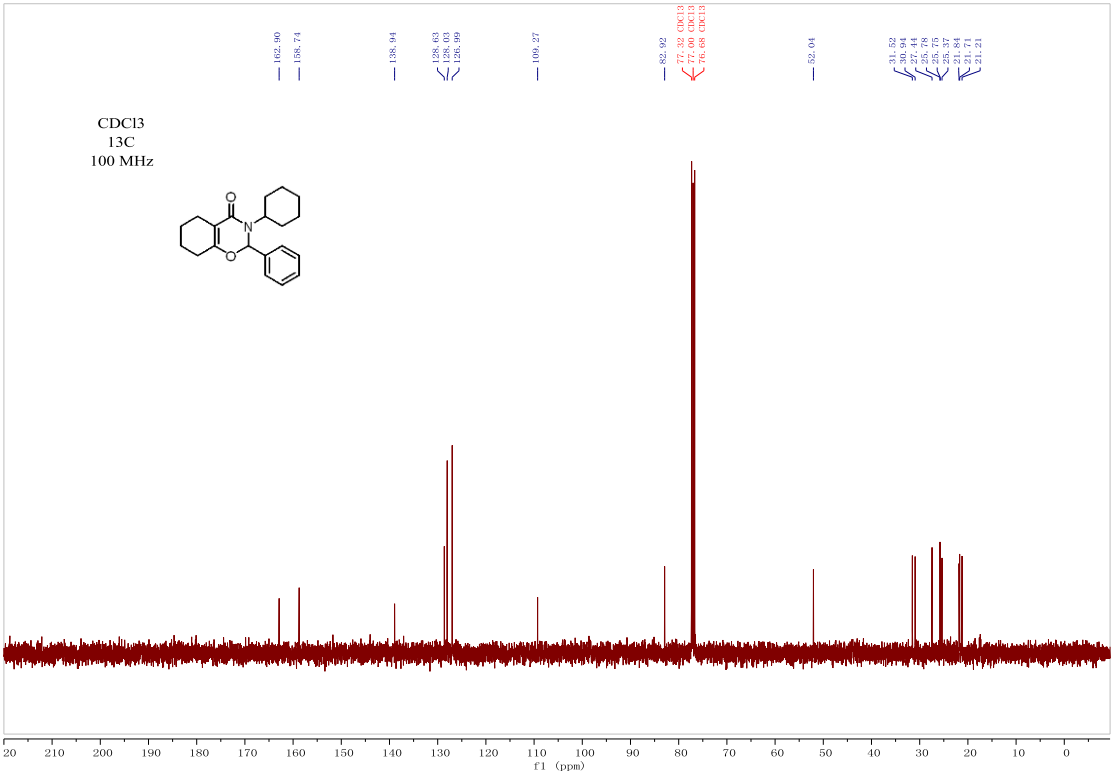
^{1}H and ^{13}C NMR spectra of compound 9k



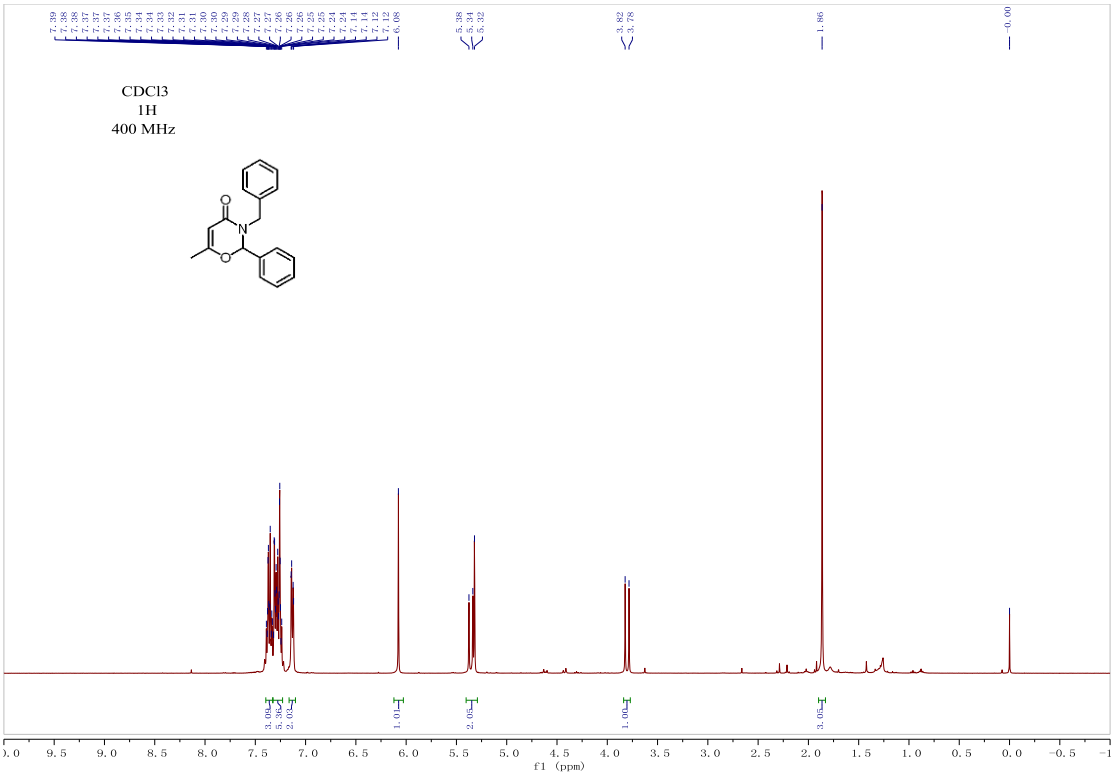


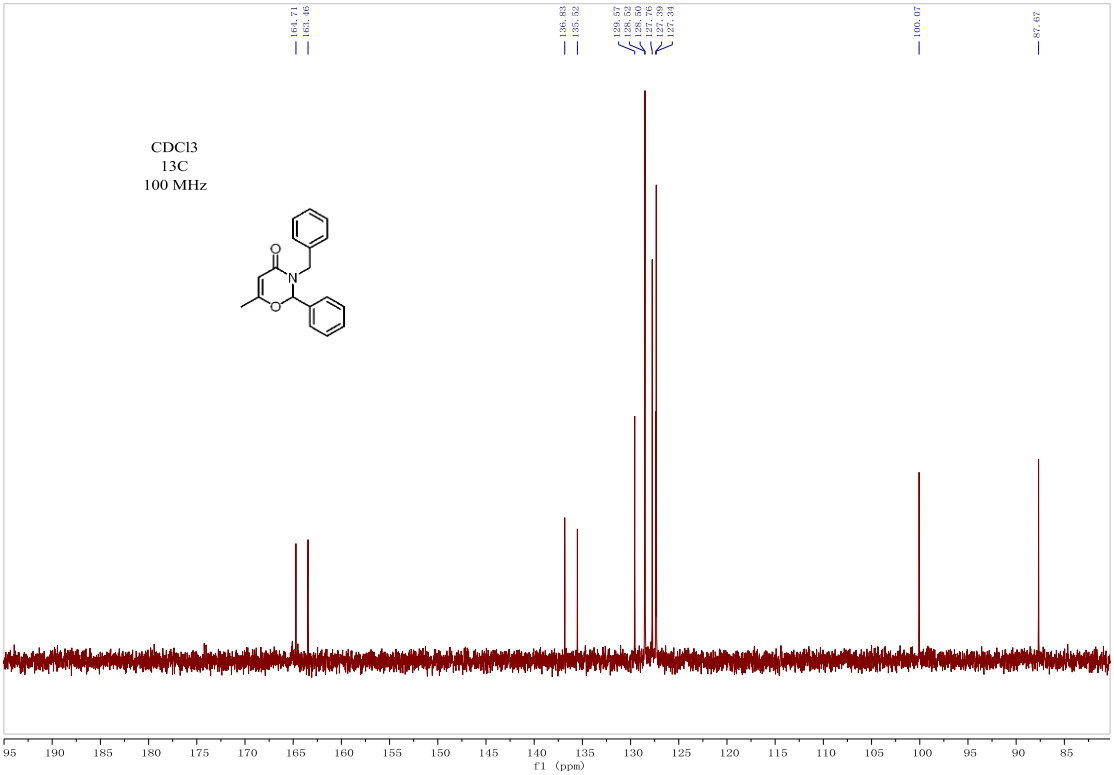
^{1}H and ^{13}C NMR spectra of compound 9l



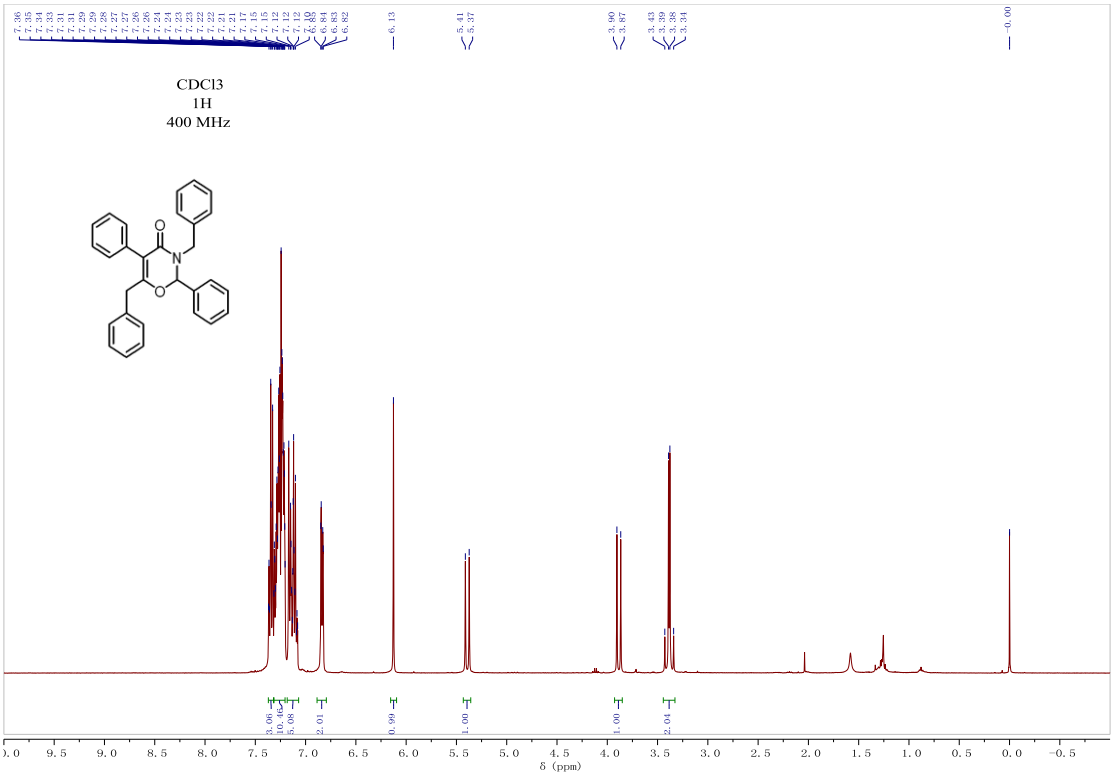


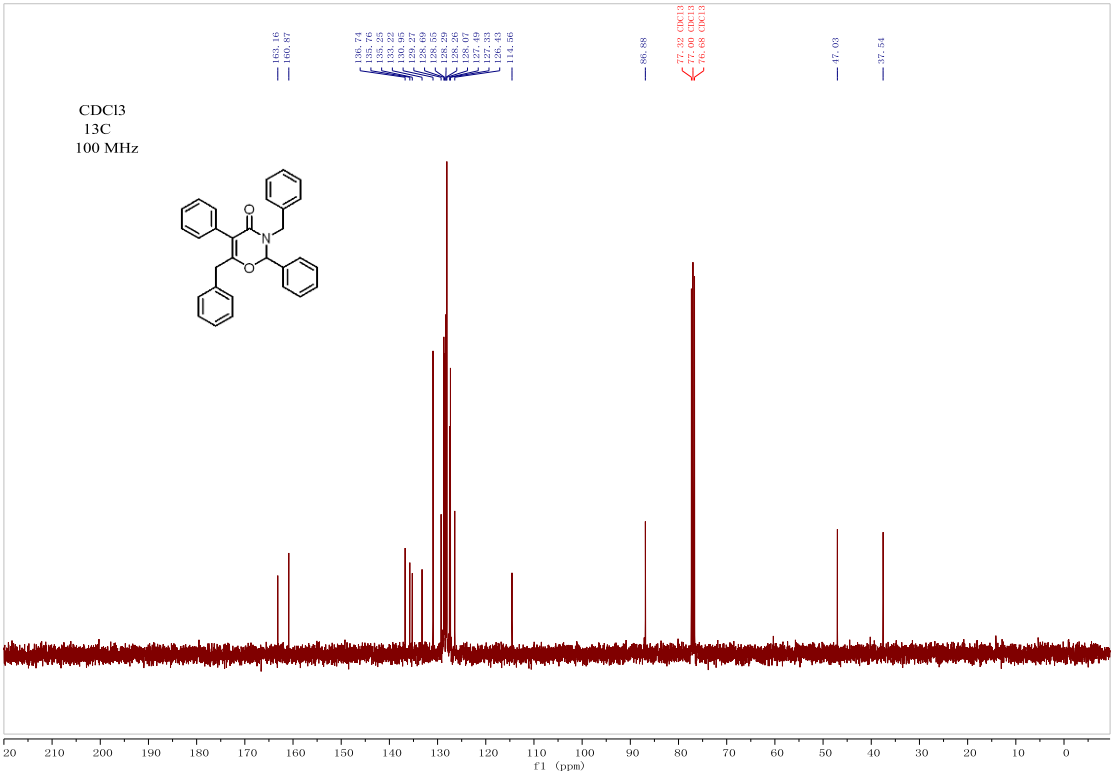
^{1}H and ^{13}C NMR spectra of compound 13a





^{1}H and ^{13}C NMR spectra of compound 13b





CCDC 2213238-2213241 contain the crystallographic data for compounds **7a**, **7c**, **9a**, **9b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Single crystals of $C_{16}H_{19}NO_2$ [**exp_3599, CCDC 2213238**] were obtained by slow evaporation of an AcOEt/*n*-hexane solution of **7a**. A suitable crystal was selected and mounted on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimisation.

Crystal Data for $C_{16}H_{19}NO_2$ [**exp_3599, CCDC 2213238**] (*M* =257.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.96412(10) Å, b = 13.49912(14) Å, c = 12.50563(16) Å, β = 103.1964(13)°, V = 1308.96(3) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.682 mm^{-1}, *Dcalc* = 1.306 g/cm^3, 12781 reflections measured (9.782° ≤ 2Θ ≤ 143.514°), 2487 unique (R_{int} = 0.0290, R_{sigma} = 0.0207) which were used in all calculations. The final R_1 was 0.0339 (I > 2σ(I)) and wR_2 was 0.0866 (all data).

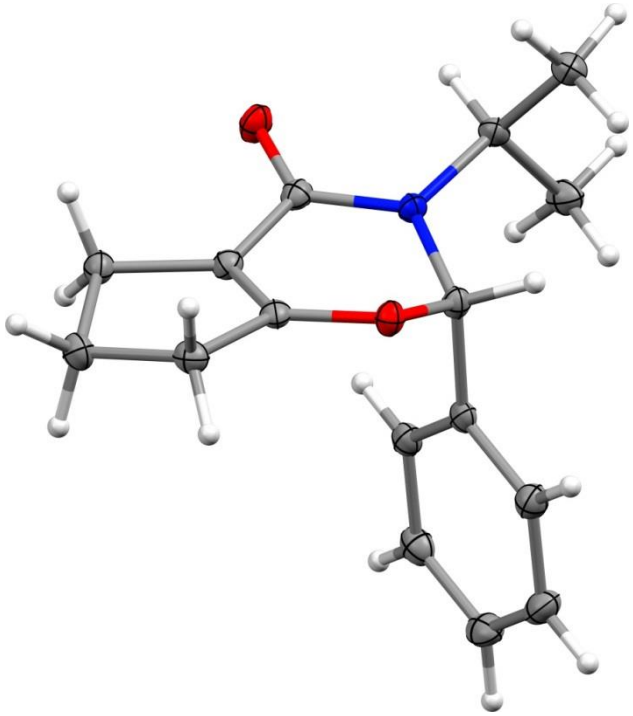


Figure S1. The single crystal X-ray structure of compound **7a** [**CCDC 2213238**]. Thermal ellipsoids are drawn at the 50% probability level.

Single crystals of $C_{19}H_{23}NO_2$ [**exp_3588, CCDC 2213239**] were obtained by slow evaporation of an AcOEt/*n*-hexane solution of **7c**. A suitable crystal was selected and mounted on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimisation.

Crystal Data for $C_{19}H_{23}NO_2$ [**exp_3588, CCDC 2213239**] (M =297.38 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 15.8861(2) Å, b = 9.81570(10) Å, c = 10.53650(10) Å, β = 105.7530(10) °, V = 1581.28(3) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.633 mm^{-1}, *Dcalc* = 1.249 g/cm^3, 15471 reflections measured (5.78° ≤ 2Θ ≤ 143.644°), 3038 unique (R_{int} = 0.0460, R_{sigma} = 0.0300) which were used in all calculations. The final R_1 was 0.0429 (I > 2σ(I)) and wR_2 was 0.1118 (all data).

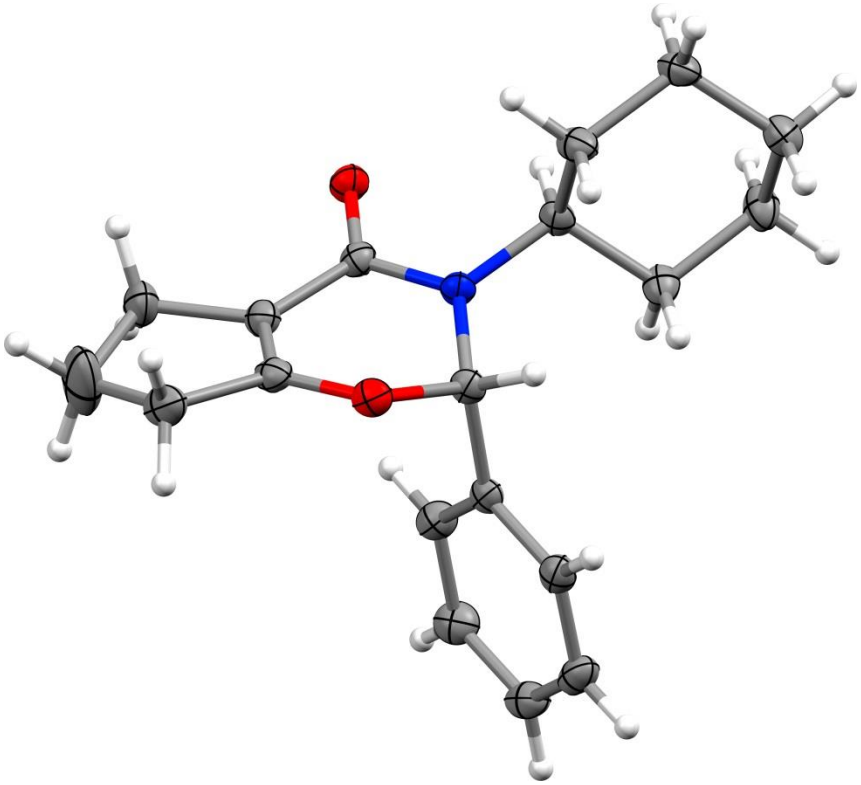


Figure S2. The single crystal X-ray structure of compound **7c** [**CCDC 2213239**]. Thermal ellipsoids are drawn at the 50% probability level.

Single crystals of $C_{17}H_{21}NO_2$ [**exp_1468_1, CCDC 2213240**] were obtained by slow evaporation of a dichloromethane/petroleum ether solution of **9a**. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimisation.

Crystal Data for $C_{17}H_{21}NO_2$ [**exp_1468_1, CCDC 2213240**] (*M* =271.362 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 9.91528(16) Å, *b* = 10.40381(18) Å, *c* = 28.3425(4) Å, *V* = 2923.71(8) Å^3, *Z* = 8, *T* = 100.00(10) K, μ(Cu Kα) = 0.636 mm^{-1}, *Dcalc* = 1.233 g/cm^3, 7062 reflections measured (10.9° ≤ 2Θ ≤ 146.7 °), 2852 unique (R_{int} = 0.0240, R_{sigma} = 0.0252) which were used in all calculations. The final R_1 was 0.0381 (I>=2u(I)) and wR_2 was 0.1023 (all data).

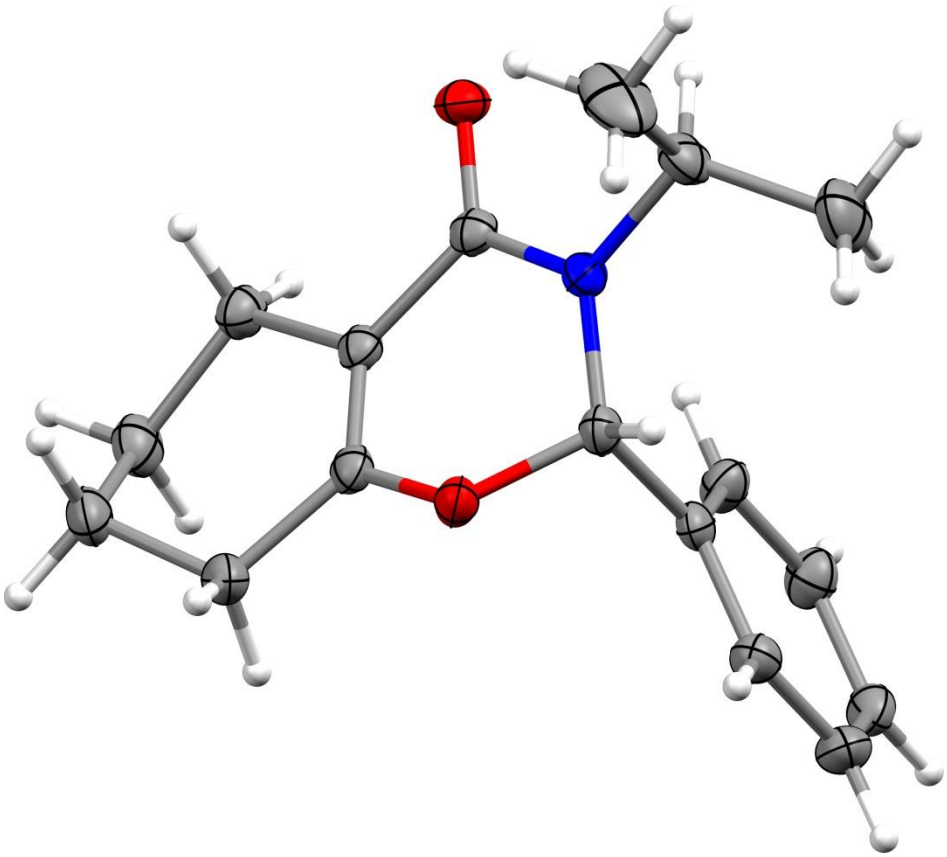


Figure S3. The single crystal X-ray structure of compound **9a** [**CCDC 2213240**]. Thermal ellipsoids are drawn at the 50% probability level.

Single crystals of $C_{18}H_{23}NO_3$ [**exp_1495_1, CCDC 2213241**] were obtained by slow evaporation of a dichloromethane/petroleum ether solution of **9b**. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimisation.

Crystal Data for $C_{18}H_{23}NO_3$ [**exp_1495_1, CCDC 2213241**] (*M* =301.37 g/mol): monoclinic, space group C2/c (no. 15), *a* = 15.7240(3) Å, *b* = 12.93561(17) Å, *c* = 17.1001(3) Å, *β* = 110.2436(19) °, *V* = 3263.31(9) Å^3, *Z* = 8, *T* = 293 K, μ(Cu Kα) = 0.666 mm^{-1}, *Dcalc* = 1.227 g/cm^3, 6163 reflections measured (9.092° ≤ 2Θ ≤ 147.596 °), 3209 unique (R_{int} = 0.0117, R_{sigma} = 0.0141) which were used in all calculations. The final R_1 was 0.0450 (I > 2σ(I)) and wR_2 was 0.1374 (all data).

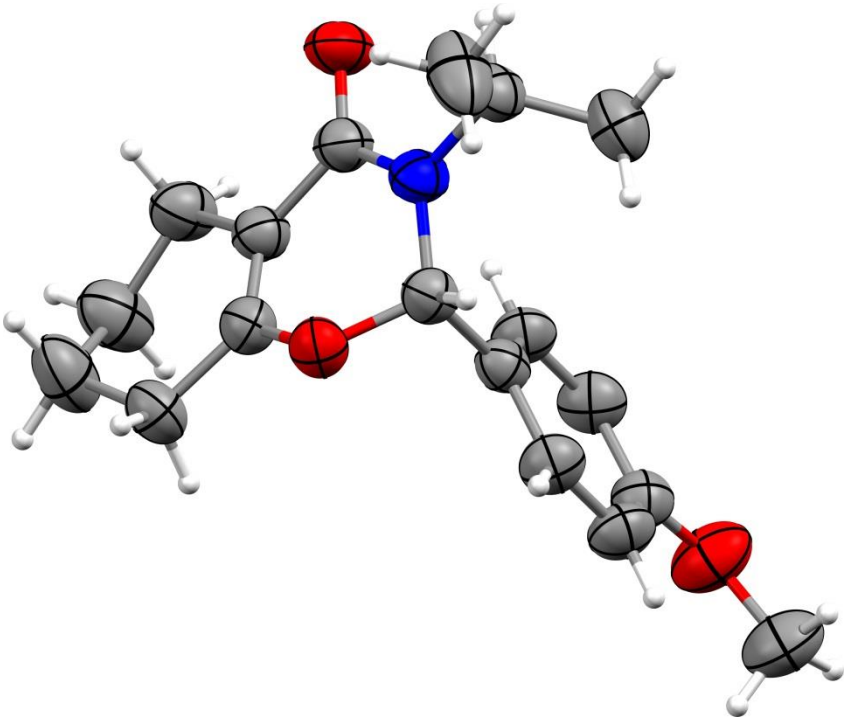


Figure S4. The single crystal X-ray structure of compound **9b** [**CCDC 2213241**]. Thermal ellipsoids are drawn at the 50% probability level.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.