Supporting Information

Green and Effective Synthesis of Multisubstituted α-Pyrones *via* K_2CO_3 Catalyzed Formal Insertion of Ketenimines into C(CO)-C Bonds of 1,3-Diketones

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1) General Information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 or Jeol 400 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s=singlet, d=doublet, t = triplet, q=quartet, h=heptet, m=multiplet, br=broad.

Anhydrous solvents, palladium catalysts, Brønsted base catalysts, and 1,3-diphenylpropane-1,3-dione were purchased from Energy Chemical. Unless otherwise stated, all purchased reagents were used without further purification. All reactions involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere in dried Schlenk tube. The isonitriles,[1] diazo compounds,[2] ketenimines,[3] and 1,3-diones[4] were prepared using the literature procedures.

Detailed photophysical studies were performed on compounds **49-51** in solution state (10^{-5} M). As for absorption measurements, those solution samples were tested by Cary 60 (Agilent) equipment. PL studies were conducted by using Edinburgh FLS1000 fluorescent spectrometer, in which steady state PL spectra were excited at 365 nm by using Xe_2 xenon lamp, and PL transient decay curves were obtained by using a picosecond pulsed LED (EPLED-365) as light-exciting source. Absolute PL quantum efficiency (φ_{PL}) of those samples were further measured by using a built-in integration sphere accessory that was coupled to FLS1000 equipment. All those sample were measured in air. To minimize the influence of air on the resultant PL transient and φ_{PL}, all those solution sample were freshly prepared in nitrogen-filled glovebox and then transferred to outside for measuring as soon as possible. Moreover, transient PL photophysical fitting and studies shown in Table S2 were performed according to the standard PL photophysical theory in OLEDs.[5]

[1] a) X.-H. Zhao, X.-H. Liu, H.-J. Mei, J. Guo, L.-L. Lin, X.-M. Feng, *Angew. Chem. Int. Ed.* **2015**, *54*, 4032-4035; b) J. M. Saya, B. Oppelaar, R. C. Cioc, G. van der Heijden, C. M. L. Vande Velde, R. V. A. Orru, E. Ruijter, *Chem. Commun.* **2016**, *52*, 12482-12485; c) Z. He, M. Bae, J. Wu, T. F. Jamison, *Angew. Chem. Int. Ed.* **2014**, *53*, 14451-14455.

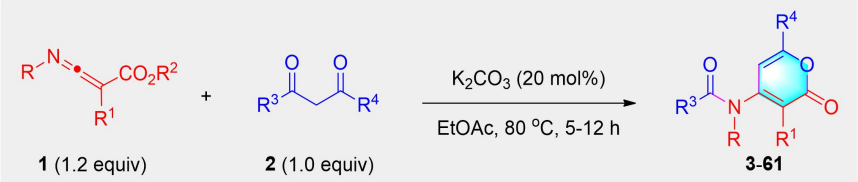
[2] Y. Xia, D. Qiu, J. Wang, *Chem. Rev.* **2017**, *117*, 13810-13889.

[3] a) J. Luo, G.-S. Chen, S.-J. Chen, Z.-D. Li, Y.-L. Zhao, Y.-L. Liu, *Adv. Synth. Catal.* **2020**, *362*, 3635-3643; b) Z. Liu, S. Cao, J. Wu, G. Zanoni, P. Sivaguru, X. Bi, *ACS Catal.* **2020**, *10*, 12881-12887.

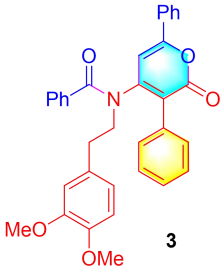
[4] a) Y. Ning, Q. Song, P. Sivaguru, L. Wu, E. A. Anderson, Xihe Bi, *Org. Lett.* **2022**, *24*, 631-636; b) K. Wu, T. Zhang, Z. Wang, L. Wang, L. Zhan, S. Gong, C. Zhong, Z.-H. Lu, S. Zhang, C. Yang, *J. Am. Chem. Soc.* **2018**, *140*, 8877-8886; c) Q. Zhang, H. Kuwabara, W. J. Potscavage Jr., S. Huang, Y. Hatae, T. Shibata, C. Adachi, *J. Am. Chem. Soc.* **2014**, *136*, 18070-18081.

[5] Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, *Adv. Mater.* **2014**, *26*, 7931-7958.

2) General Procedure and Spectral Data of Products 3-61

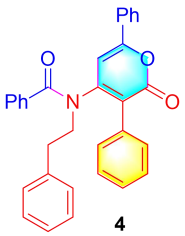


To a 10.0 mL Schlenk tube were successively added ketenimines **1** (0.12 mmol), 1,3-diketones **2** (0.10 mmol), anhydrous EtOAc (1.0 mL), and K_2CO_3 (20 mol%). The reaction mixture was stirred vigorously at 80 °C under N_2 atmosphere till full consumption of 1,3-diketones **2** by TLC analysis. The reaction mixture was then concentrated by rotary vaporation, and the residue was subjected to column chromatography using petroleum ether/ethyl acetate (from 10:1-1:1) as eluent to afford the desired products **3-61**.



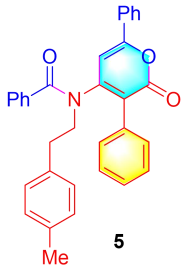
3

The reaction was run at 80 °C for 5 h, affording product **3** as a pale yellow solid (49.4 mg, 93% yield, m.p. = 151-152 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.00 (brm, 2H), 3.47 (brm, 1H), 3.77 (s, 3H), 3.85 (s, 3H), 4.35 (brm, 1H), 5.77 (s, 1H), 6.72 (s, 1H), 6.79 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 4.5 Hz, 2H), 7.04 (d, J = 7.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 2H), 7.29-7.37 (m, 4H), 7.42-7.47 (m, 3H), 7.54-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.69, 162.22, 158.57, 153.54, 149.22, 147.98, 134.51, 131.69, 131.23, 131.16, 130.03, 130.41, 128.81, 128.79, 128.40, 128.27, 127.99, 127.80, 125.40, 121.25, 120.72, 112.35, 102.39, 55.78, 55.73, 53.17, 33.04; IR (ATR): 1709, 1668, 1632, 1548, 1514, 1438, 1315, 1260, 1237, 1153, 1141, 1026, 904, 769, 691, 644, 572. HRMS (ESI): Exact mass calcd for $C_{34}H_{29}NO_5Na$ $[M+Na]^+$: 554.1938, Found: 554.1932.



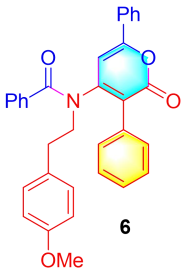
4

The reaction was run at 80 °C for 5 h, affording product **4** as a pale yellow solid (46.2 mg, 98% yield, m.p. = 182-183 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 (brm, 2H), 3.81 (brm, 2H), 5.79 (s, 1H), 6.99-7.00 (m, 2H), 7.06-7.08 (m, 2H), 7.18-7.26 (m, 4H), 7.32-7.35 (m, 4H), 7.37-7.47 (m, 6H), 7.55 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.83, 162.30, 158.61, 153.50, 139.31, 134.60, 131.31, 131.16, 131.05, 130.46, 129.87, 129.48, 128.90, 128.73, 128.49, 128.36, 128.03, 127.89, 126.94, 125.60, 120.83, 102.49, 52.97, 33.70; IR (ATR): 1708, 1651, 1629, 1548, 1494, 1450, 1395, 1321, 796, 755, 695, 642, 574. HRMS (ESI): Exact mass calcd for $C_{32}H_{25}NO_3Na$ $[M+Na]^+$: 494.1727, Found: 494.1717.



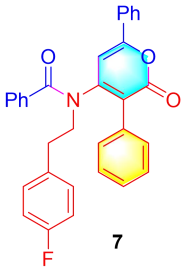
5

The reaction was run at 80 °C for 5 h, affording product **5** as a pale yellow solid (45.1 mg, 93% yield, m.p. = 181-182 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.04 (brm, 2H), 3.49-4.29 (brm, 2H), 5.68 (s, 1H), 6.97-6.98 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.18-7.23 (m, 4H), 7.31-7.39 (m, 4H), 7.41-7.47 (m, 3H), 7.54 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.77, 162.31, 158.44, 153.70, 136.62, 136.34, 134.65, 131.32, 131.13, 130.97, 130.52, 129.90, 129.58, 129.45, 128.76, 128.46, 128.33, 128.06, 127.85, 125.51, 120.89, 102.49, 53.34, 33.16, 21.07; IR (ATR): 1706, 1653, 1627, 1544, 1497, 1442, 1391, 1317, 814, 786, 768, 717, 692, 643, 573. HRMS (ESI): Exact mass calcd for $C_{33}H_{27}NO_3Na$ $[M+Na]^+$: 508.1883, Found: 508.1877.



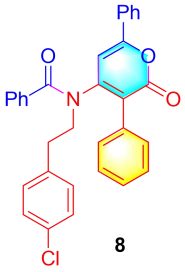
6

The reaction was run at 80 °C for 5 h, affording product **6** as a pale green solid (44.6 mg, 89% yield, m.p. = 163-164 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02 (brm, 2H), 3.51-4.25 (brm, 2H), 3.79 (s, 3H), 5.74 (s, 1H), 6.91-6.94 (m, 2H), 6.99 (d, *J* = 4.8 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.30-7.38 (m, 4H), 7.41-7.49 (m, 3H), 7.54-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.77, 162.33, 158.68, 158.49, 153.68, 134.67, 131.34, 131.28, 131.13, 131.03, 130.49, 129.88, 128.79, 128.48, 128.35, 128.03, 127.88, 125.55, 120.86, 114.24, 102.59, 55.20, 53.36, 32.80; IR (ATR): 1707, 1661, 1631, 1547, 1512, 1396, 1241, 1174, 1032, 826, 787, 769, 721, 697, 641, 572. HRMS (ESI): Exact mass calcd for $C_{33}H_{27}NO_4Na$ $[M+Na]^+$: 524.1832, Found: 524.1824.

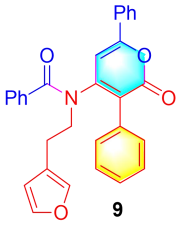


7

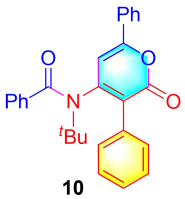
The reaction was run at 80 °C for 5 h, affording product **7** as a pale yellow solid (47.4 mg, 97% yield, m.p. = 175-176 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (brm, 2H), 3.81 (brm, 2H), 5.81 (s, 1H), 7.00-7.01 (m, 2H), 7.05-7.10 (m, 4H), 7.18-7.23 (m, 4H), 7.30-7.40 (m, 4H), 7.43-7.48 (m, 3H), 7.55-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.80, 162.27, 161.91 (d, *J* = 245 Hz), 158.73, 153.36, 134.94, 134.51, 131.28, 131.26, 131.19, 130.88 (d, *J* = 8.0 Hz), 130.43, 129.82, 128.90, 128.57, 128.42, 128.00, 127.97, 125.49, 120.81, 115.72 (d, *J* = 21 Hz), 102.47, 52.83, 32.98; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.60; IR (ATR): 1711, 1658, 1622, 1534, 1503, 1402, 1211, 1152, 1045, 851, 781, 751, 682, 636, 557. HRMS (ESI): Exact mass calcd for $C_{32}H_{24}FNO_3Na$ $[M+Na]^+$: 512.1632, Found: 512.1627.



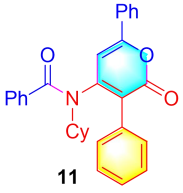
The reaction was run at 80 °C for 5 h, affording product **8** as a pale yellow solid (48.0 mg, 95% yield, m.p. = 184-185 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.04 (brm, 2H), 3.75 (brm, 2H), 5.73 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.16-7.23 (m, 4H), 7.30-7.35 (m, 3H), 7.35-7.39 (m, 3H), 7.47-7.49 (m, 3H), 7.53-7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.75, 162.22, 158.79, 153.38, 137.90, 134.43, 133.02, 131.29, 131.22, 131.17, 130.86, 130.35, 129.83, 129.03, 129.01, 128.56, 128.38, 128.01, 127.95, 125.46, 120.96, 102.25, 52.90, 33.06; IR (ATR): 1706, 1662, 1630, 1545, 1489, 1445, 1395, 1277, 1172, 1085, 1016, 932, 814, 769, 721, 697, 643, 574, 544. HRMS (ESI): Exact mass calcd for $C_{32}H_{24}NO_3ClNa$ $[M+Na]^+$: 528.1337, Found: 528.1326.



The reaction was run at 80 °C for 6 h, affording product **9** as a pale yellow solid (42.0 mg, 91% yield, m.p. = 108-109 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (brm, 2H), 3.65-4.15 (brm, 2H), 6.01 (s, 1H), 6.14 (s, 1H), 6.37-6.39 (m, 1H), 7.03 (brs, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.33-7.38 (m, 4H), 7.42 (s, 1H), 7.44-7.51 (m, 3H), 7.71-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.83, 162.38, 158.64, 153.39, 152.76, 141.72, 134.53, 131.31, 131.16, 131.08, 130.61, 129.85, 128.83, 128.50, 128.39, 128.00, 127.90, 125.62, 120.59, 110.87, 107.83, 102.59, 49.86, 26.17; IR (ATR): 1703, 1653, 1628, 1538, 1494, 1443, 1392, 1324, 1181, 1076, 919, 163, 746, 682, 641, 604, 570. HRMS (ESI): Exact mass calcd for $C_{30}H_{23}NO_4Na$ $[M+Na]^+$: 484.1519, Found: 484.1510.

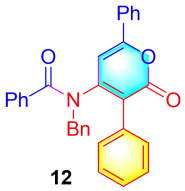


The reaction was run at 80 °C for 12 h, affording product **10** as a pale-green solid (22.4 mg, 53% yield, m.p. = 109-110 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (s, 9H), 6.66 (s, 1H), 7.09-7.12 (m, 2H), 7.19-7.23 (m, 4H), 7.28-7.33 (m, 1H), 7.36-7.38 (m, 3H), 7.49-7.53 (m, 3H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.30, 162.62, 157.08, 151.61, 137.71, 131.42, 131.26, 130.57, 130.13, 129.77, 129.11, 128.78, 127.98, 127.68, 127.48, 125.70, 125.58, 106.49, 60.55, 29.23; IR (ATR): 1696, 1652, 1622, 1548, 1451, 1370, 1331, 1179, 769, 689, 661, 630, 571. HRMS (ESI): Exact mass calcd for $C_{28}H_{25}NO_3Na$ $[M+Na]^+$: 446.1727, Found: 446.1718.



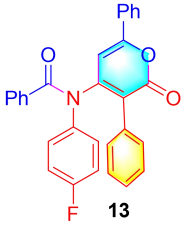
The reaction was run at 80 °C for 8 h, affording product **11** as a pale green solid (37.7 mg, 84% yield, m.p. = 92-93 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09-1.23 (m, 3H), 1.62-1.67 (m, 3H), 1.76-1.84 (m, 4H), 4.05 (s, 1H), 6.71 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.16 (brs, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.33-7.37 (m, 4H), 7.50-7.51 (m, 3H), 7.85-7.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.18,

162.50, 157.78, 151.03, 135.72, 131.70, 131.12, 130.75, 130.52, 129.87, 129.01, 128.46, 128.15, 127.95, 127.45, 125.60, 104.68, 60.47, 31.81, 26.09, 25.35; IR (ATR): 1701, 1651, 1629, 1540, 1495, 1450, 1301, 903, 765, 687, 646, 567. HRMS (ESI): Exact mass calcd for $C_{30}H_{27}NO_3Na$ $[M+Na]^+$: 472.1883, Found: 472.1875.



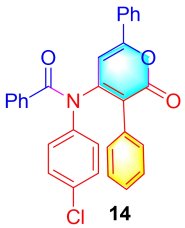
12

The reaction was run at 80 °C for 8 h, affording product **12** as a pale green solid (39.8 mg, 87% yield, m.p. = 141-142 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.79 (brs, 2H), 6.54 (s, 1H), 6.94 (d, J = 6.0 Hz, 2H), 7.20-7.26 (m, 4H), 7.30-7.39 (m, 9H), 7.43-7.49 (m, 3H), 7.64-7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.78, 162.40, 158.54, 152.58, 136.44, 134.36, 131.22, 131.14, 130.59, 129.68, 128.93, 128.89, 128.50, 128.40, 128.36, 128.11, 128.02, 125.54, 120.71, 102.74, 52.19; IR (ATR): 1723, 1661, 1629, 1551, 1492, 1448, 1400, 1327, 1270, 1027, 906, 796, 761, 699, 645, 628, 604, 571. HRMS (ESI): Exact mass calcd for $C_{31}H_{23}NO_3Na$ $[M+Na]^+$: 480.1570, Found: 480.1560.



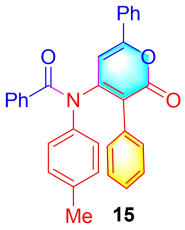
13

The reaction was run at 80 °C for 5 h, affording product **13** as a pale green solid (42.4 mg, 92% yield, m.p. = 186-187 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (s, 1H), 6.84 (d, J = 6.0 Hz, 4H), 7.17-7.21 (m, 4H), 7.23-7.26 (m, 5H), 7.35 (tt, J = 7.2, 1.2 Hz, 1H), 7.42-7.49 (m, 3H), 7.80-7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.92, 162.64, 160.78 (d, J = 247 Hz), 159.11, 153.07, 137.43 (d, J = 2.8 Hz), 133.91, 131.74, 131.43, 131.10, 130.73, 129.42, 128.92, 128.87, 128.47, 128.31, 128.26, 128.18, 128.02, 125.64, 122.07, 116.03 (d, J = 23 Hz), 103.04; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.91; IR (ATR): 1721, 1658, 1613, 1551, 1456, 1431, 1322, 1245, 1072, 1002, 889, 789, 667, 653, 627, 569. HRMS (ESI): Exact mass calcd for $C_{30}H_{20}NFO_3Na$ $[M+Na]^+$: 484.1319, Found: 484.1319.



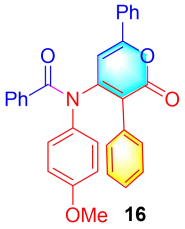
14

The reaction was run at 80 °C for 5 h, affording product **14** as a pale yellow solid (44.8 mg, 94% yield, m.p. = 193-194 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68 (t, J = 4.0 Hz, 1H), 6.86 (s, 2H), 7.14-7.27 (m, 11H), 7.38 (t, J = 5.2 Hz, 1H), 7.46-7.49 (m, 3H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.78, 162.54, 159.15, 152.79, 139.88, 133.70, 132.33, 131.56, 131.13, 130.58, 129.35, 129.19, 128.89, 128.85, 128.50, 128.29, 128.02, 127.56, 125.60, 122.23, 102.92; IR (ATR): 1718, 1649, 1607, 1548, 1486, 1447, 1316, 1288, 1091, 1011, 936, 829, 785, 685, 653, 626, 599, 572. HRMS (ESI): Exact mass calcd for $C_{30}H_{20}ClNO_3Na$ $[M+Na]^+$: 500.1024, Found: 500.1025.



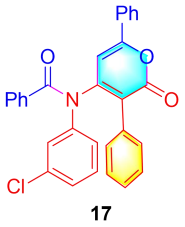
15

The reaction was run at 80 °C for 5 h, affording product **15** as a pale green solid (41.6 mg, 91% yield, m.p. = 165-166 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 6.62 (s, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.14-7.18 (m, 2H), 7.21-7.26 (m, 7H), 7.32 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.41-7.45 (m, 3H), 7.79-7.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.86, 162.74, 158.95, 153.00, 138.78, 136.86, 134.30, 131.88, 131.17, 130.94, 130.87, 129.82, 129.47, 128.89, 128.85, 128.31, 128.22, 127.83, 126.40, 125.62, 122.06, 103.07, 20.95; IR (ATR): 1711, 1657, 1619, 1551, 1511, 1448, 1289, 1177, 1070, 1026, 791, 766, 689, 636, 609, 566, 513. HRMS (ESI): Exact mass calcd for $C_{31}H_{23}NO_3Na$ $[M+Na]^+$: 480.1570, Found: 480.1568.



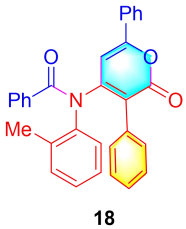
16

The reaction was run at 80 °C for 5 h, affording product **16** as a pale green solid (44.0 mg, 93% yield, m.p. = 168-169 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 3H), 6.66 (s, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.23-7.27 (m, 6H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.42-7.46 (m, 3H), 7.80-7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.85, 162.79, 158.89, 158.08, 153.06, 134.17, 134.07, 131.89, 131.10, 130.94, 130.77, 129.38, 128.83, 128.31, 128.24, 127.84, 125.57, 121.73, 114.37, 103.00, 55.37; IR (ATR): 1712, 1653, 1607, 1549, 1507, 1447, 1245, 1172, 1026, 831, 792, 766, 689, 639, 609, 562, 519. HRMS (ESI): Exact mass calcd for $C_{31}H_{23}NO_4Na$ $[M+Na]^+$: 496.1519, Found: 496.1520.



17

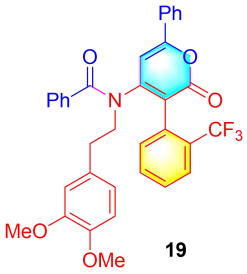
The reaction was run at 80 °C for 10 h, affording product **17** as a pale yellow solid (44.8 mg, 94% yield, m.p. = 193-194 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.77 (s, 1H), 6.92 (s, 1H), 7.06-7.12 (m, 2H), 7.15-7.16 (m, 2H), 7.20-7.23 (m, 2H), 7.23-7.27 (m, 5H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.44-7.49 (m, 3H), 7.82 (dd, *J* = 7.5, 2.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.83, 162.55, 159.25, 152.75, 142.52, 134.70, 133.72, 131.71, 131.46, 131.18, 130.68, 129.90, 129.44, 128.94, 128.91, 128.59, 128.33, 128.08, 126.89, 126.59, 125.70, 124.69, 122.40, 102.97; IR (ATR): 1719, 1662, 1631, 1552, 1474, 1324, 1076, 917, 763, 686, 596. HRMS (ESI): Exact mass calcd for $C_{30}H_{20}ClNO_3Na$ $[M+Na]^+$: 500.1024, Found: 500.1020.



18

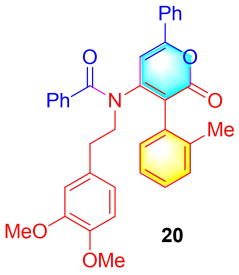
The reaction was run at 80 °C for 10 h, affording product **18** as a pale green solid (42.5 mg, 93% yield, m.p. = 189-190 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.11 (s, 3H), 6.47 (s, 1H), 7.03-7.11 (m, 4H), 7.16-7.24 (m, 7H), 7.28 (brm, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.41-7.47 (m, 3H), 7.73-7.74 (m, 2H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 169.73, 162.90, 158.52, 152.98, 140.21, 135.16, 134.17, 131.94, 131.63, 131.50, 130.99, 130.83, 129.50, 128.89, 128.69, 128.28, 128.12, 127.98, 127.94, 127.16, 125.62, 119.95, 102.57, 18.71; IR (ATR): 1721, 1675, 1623, 1547, 1462, 1401, 1375, 1062, 932, 757, 682, 574. HRMS (ESI): Exact mass calcd for $C_{31}H_{23}NO_3Na$ $[M+Na]^+$: 480.1570, Found: 480.1566.



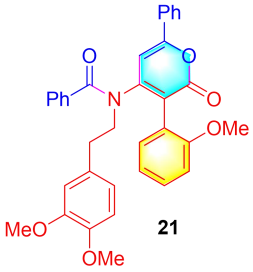
19

The reaction was run at 80 °C for 12 h, affording product **19** as a pale yellow solid (37.1 mg, 62% yield, m.p. = 167-168 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 2.79-2.86 (m, 1H), 2.91-2.98 (m, 1H), 3.54 (brm, 1H), 3.74 (s, 3H), 3.86 (s, 3H), 3.89 (brm, 1H), 5.94 (s, 1H), 6.62 (s, 1H), 6.70 (dd, J = 8.0, 1.2 Hz, 1H), 6.78-6.91 (m, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.43-7.49 (m, 5H), 7.52 (t, J = 7.6 Hz, 1H), 7.60-7.62 (m, 2H), 7.70 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.73, 161.91, 159.24, 153.82, 149.28, 148.06, 134.75, 132.29, 131.83, 131.56, 131.28, 131.17, 130.41, 129.70, 129.42, 129.40, 129.20, 128.91, 128.42, 128.24, 127.49 (q, J = 3.3 Hz), 123.87 (q, J = 273 Hz), 121.19, 112.30, 111.32, 102.66, 55.87, 55.72, 52.98, 33.42; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.09; IR (ATR): 1717, 1672, 1610, 1544, 1450, 1398, 1366, 1055, 913, 742, 657, 565. HRMS (ESI): Exact mass calcd for $C_{35}H_{28}NO_5F_3Na$ $[M+Na]^+$: 622.1812, Found: 622.1812.



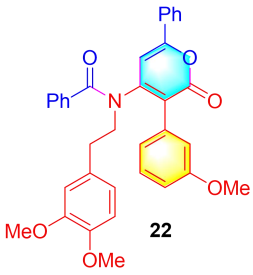
20

The reaction was run at 80 °C for 12 h, affording product **20** as a pale yellow solid (39.2 mg, 72% yield, m.p. = 155-156 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 (brm, 3H), 2.85-2.91 (m, 1H), 3.09 (brs, 1H), 3.54 (brs, 1H), 3.75 (s, 3H), 3.91 (s, 3H), 4.24 (brm, 1H), 5.79 (s, 1H), 6.70 (s, 1H), 6.78-6.80 (m, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 7.11 (brm, 3H), 7.20-7.30 (m, 4H), 7.39 (t, J = 7.6 Hz, 1H), 7.43-7.48 (m, 3H), 7.58-7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.72, 161.21, 159.10, 154.91, 149.31, 148.07, 134.87, 131.43, 131.14, 130.78, 130.59, 130.52, 129.89, 128.98, 128.89, 128.45, 128.10, 125.70, 125.52, 121.29, 112.52, 111.34, 55.90, 55.79, 33.15, 18.99; IR (ATR): 1714, 1654, 1630, 1550, 1517, 1447, 1390, 1319, 1261, 1243, 1160, 1136, 1080, 1028, 911, 864, 805, 762, 716, 689, 640, 580, 544. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_5Na$ $[M+Na]^+$: 568.2094, Found: 568.2101.



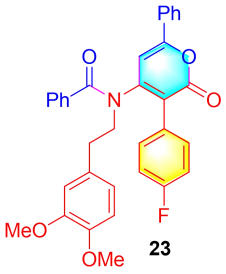
21

The reaction was run at 80 °C for 12 h, affording product **21** as a pale yellow solid (32.0 mg, 57% yield, m.p. = 143-144 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.92 (brm, 2H), 3.64 (brm, 4H), 3.77 (s, 3H), 3.85 (s, 3H), 4.12 (brm, 1H), 5.75 (s, 1H), 6.69 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.85-6.89 (m, 3H), 7.18-7.25 (m, 4H), 7.31-7.45 (m, 6H), 7.52-7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.60, 158.31, 149.20, 147.94, 134.79, 131.88, 131.17, 130.87, 130.73, 130.25, 129.45, 128.78, 128.38, 127.91, 125.45, 121.27, 120.62, 120.16, 115.29, 112.45, 111.24, 110.70, 102.53, 55.82, 55.78, 55.18, 52.28, 33.20; IR (ATR): 1702, 1668, 1637, 1549, 1514, 1452, 1398, 1320, 1286, 1239, 1154, 1139, 1024, 911, 858, 804, 774, 757, 722, 696, 665, 647, 626, 569, 523. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_6Na$ $[M+Na]^+$: 584.2044, Found: 584.2047.



22

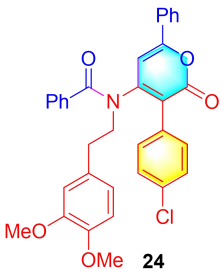
The reaction was run at 80 °C for 10 h, affording product **22** as a pale yellow solid (48.8 mg, 87% yield, m.p. = 92-93 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03 (brm, 2H), 3.51 (brm, 1H), 3.70 (s, 3H), 3.77 (s, 3H), 3.86 (s, 3H), 4.26 (brm, 1H), 5.77 (s, 1H), 6.40 (s, 1H), 6.60 (d, *J* = 7.2 Hz, 1H), 6.72 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.87-6.89 (m, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.42-7.46 (m, 3H), 7.54-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.67, 162.17, 159.29, 158.68, 153.73, 149.32, 148.07, 134.62, 132.43, 131.81, 131.17, 131.10, 130.47, 129.33, 128.86, 128.07, 127.83, 125.47, 121.93, 121.31, 120.52, 115.11, 114.69, 112.44, 111.33, 102.38, 55.84, 55.79, 55.07, 53.27, 33.12; IR (ATR): 1704, 1654, 1630, 1514, 1492, 1452, 1390, 1317, 1266, 1240, 1157, 1025, 837, 805, 775, 715, 691, 642, 628. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_6Na$ $[M+Na]^+$: 584.2044, Found: 584.2054.



23

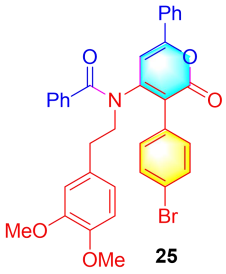
The reaction was run at 80 °C for 5 h, affording product **23** as a pale yellow solid (52.7 mg, 96% yield, m.p. = 197-198 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (brm, 2H), 3.72 (brm, 2H), 3.77 (s, 3H), 3.87 (s, 3H), 5.79 (s, 1H), 6.73 (s, 1H), 6.80 (d, *J* = 9.2 Hz, 1H), 6.89-6.93 (m, 3H), 6.98-7.02 (m, 2H), 7.05-7.07 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.42-7.49 (m, 3H), 7.55-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.63, 162.51 (d, *J* = 248 Hz), 162.19, 158.90, 153.78, 149.37, 148.13, 134.41, 131.84 (d, *J* = 8.0 Hz), 131.72, 131.39, 131.21, 130.39, 128.89, 128.03, 127.92, 127.23 (d, *J* = 3.2 Hz), 125.49, 121.31, 119.84, 115.54, 115.33, 112.46, 111.37, 102.13, 55.86, 55.80, 53.35, 33.10. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.16; IR (ATR): 1710, 1668, 1627, 1544, 1515, 1436, 1387, 1259,

1238, 1140, 1085, 1024, 910, 844, 807, 772, 715, 694, 644, 592, 518. HRMS (ESI): Exact mass calcd for $C_{34}H_{28}FNO_5Na$ $[M+Na]^+$: 572.1844, Found: 572.1840.



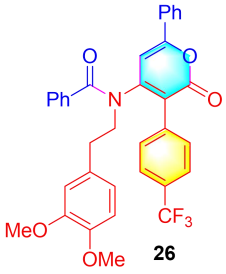
24

The reaction was run at 80 °C for 5 h, affording product **24** as a pale yellow solid (53.7 mg, 95% yield, m.p. = 173-174 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (brm, 2H), 3.63 (brm, 1H), 3.77 (s, 3H), 3.88 (s, 3H), 4.12 (brm, 1H), 5.78 (s, 1H), 6.73 (s, 1H), 6.80-6.91 (m, 4H), 7.04-7.06 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.26-7.29 (m, 2H), 7.37 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.43-7.48 (m, 3H), 7.55-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.60, 161.99, 159.08, 153.92, 149.38, 148.14, 134.46, 134.37, 131.68, 131.42, 131.27, 130.34, 129.76, 128.91, 128.57, 128.06, 127.97, 125.52, 121.31, 119.60, 112.44, 111.38, 102.11, 55.86, 55.81, 53.38, 33.09; IR (ATR): 1703, 1654, 1612, 1533, 1501, 1424, 1390, 1267, 1244, 1136, 1095, 1033, 931, 861, 767, 721, 652, 574. HRMS (ESI): Exact mass calcd for $C_{34}H_{28}NO_5ClNa$ $[M+Na]^+$: 588.1548, Found: 588.1543.



25

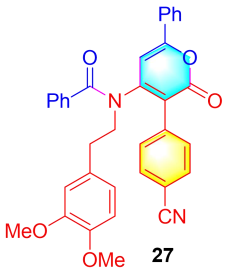
The reaction was run at 80 °C for 5 h, affording product **25** as a pale yellow solid (57.2 mg, 94% yield, m.p. = 168-169 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (brm, 2H), 3.62 (brm, 1H), 3.77 (s, 3H), 3.87 (s, 3H), 4.14 (brm, 1H), 5.78 (s, 1H), 6.73 (s, 1H), 6.78-6.82 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.35-7.39 (m, 1H), 7.41-7.48 (m, 5H), 7.54-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.60, 161.92, 159.10, 153.89, 149.39, 148.15, 134.37, 131.68, 131.53, 131.43, 131.29, 130.35, 130.25, 128.91, 128.07, 127.98, 125.53, 122.73, 121.32, 119.61, 112.45, 111.39, 102.12, 55.87, 55.81, 53.39, 33.10. IR (ATR): 1720, 1657, 1631, 1550, 1511, 1412, 1355, 1243, 1255, 1124, 1045, 1032, 925, 832, 673, 567. HRMS (ESI): Exact mass calcd for $C_{34}H_{28}BrNO_5Na$ $[M+Na]^+$: 632.1043, Found: 632.1041.



26

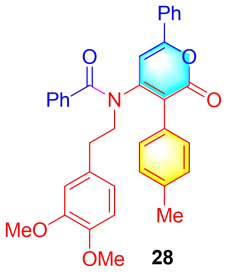
The reaction was run at 80 °C for 5 h, affording product **26** as a pale yellow solid (55.1 mg, 92% yield, m.p. = 190-191 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 (brm, 2H), 3.65 (brm, 1H), 3.77 (s, 3H), 3.88 (s, 3H), 4.08 (brm, 1H), 5.81 (s, 1H), 6.74 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.44-7.49 (m, 3H), 7.53-7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.40, 161.80, 159.67, 154.51, 149.46, 148.22, 135.15 (q, *J* = 1.2 Hz), 134.14, 131.68, 131.55, 131.47, 130.35, 130.26, 130.04, 128.96, 128.02, 128.00, 125.61, 125.20 (q, *J* = 3.7 Hz), 123.89 (q, *J* = 272 Hz), 121.35, 119.16, 112.47,

111.44, 101.85, 55.88, 55.82, 53.65, 33.06; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82; IR (ATR): 1713, 1671, 1628, 1543, 1521, 1402, 1378, 1225, 1154, 1033, 934, 815, 663, 587. HRMS (ESI): Exact mass calcd for $C_{35}H_{28}F_3NO_5Na$ $[M+Na]^+$: 622.1812, Found: 622.1804.



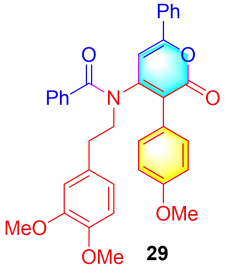
27

The reaction was run at 80 °C for 5 h, affording product **27** as a pale yellow solid (51.7 mg, 93% yield, m.p. = 172-173 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08 (brm, 2H), 3.72 (brm, 1H), 3.76 (s, 3H), 3.88 (s, 3H), 4.10 (brm, 1H), 5.80 (s, 1H), 6.74 (d, *J* = 1.2 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.95-6.98 (m, 4H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.38 (tt, *J* = 7.6, 1.6 Hz, 1H), 7.44-7.50 (m, 3H), 7.54-7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.28, 161.42, 160.10, 154.84, 149.48, 148.24, 136.33, 133.96, 131.86, 131.72, 131.62, 130.79, 130.11, 128.98, 128.06, 128.05, 125.65, 121.33, 118.60, 118.45, 112.47, 111.75, 111.46, 101.59, 55.89, 55.81, 53.72, 33.00. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82; IR (ATR): 2247, 1715, 1662, 1633, 1534, 1501, 1397, 1345, 1218, 1133, 1044, 985, 857, 678, 596. HRMS (ESI): Exact mass calcd for $C_{35}H_{28}N_2O_5Na$ $[M+Na]^+$: 579.1890, Found: 579.1882.



28

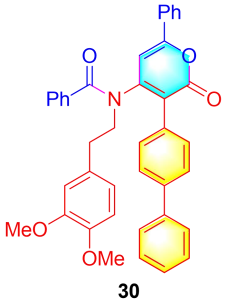
The reaction was run at 80 °C for 5 h, affording product **28** as a pale yellow solid (46.9 mg, 86% yield, m.p. = 121-122 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.00 (brm, 2H), 3.42 (brm, 1H), 3.78 (s, 3H), 3.86 (s, 3H), 4.33 (brm, 1H), 5.76 (s, 1H), 6.71 (s, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.86-6.90 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.42-7.47 (m, 3H), 7.54-7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.89, 162.47, 158.30, 153.26, 149.29, 148.05, 138.51, 134.73, 131.75, 131.17, 131.01, 130.57, 129.70, 129.10, 128.85, 128.32, 128.09, 127.89, 125.45, 121.31, 120.93, 112.43, 111.31, 102.70, 55.85, 55.82, 53.02, 33.21, 21.36. IR (ATR): 1717, 1663, 1631, 1538, 1498, 1432, 1378, 1294, 1165, 1136, 1047, 834, 734, 675, 568. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_5Na$ $[M+Na]^+$: 568.2094, Found: 568.2096.



29

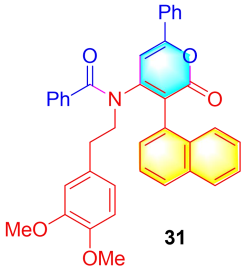
The reaction was run at 80 °C for 5 h, affording product **29** as a pale yellow solid (47.1 mg, 84% yield, m.p. = 151-152 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.00 (brm, 2H), 3.46 (brm, 1H), 3.78 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 4.35 (brm, 1H), 5.76 (s, 1H), 6.72 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.84-6.89 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.36 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.42-7.46 (m, 3H), 7.53-7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.90, 162.56, 159.64, 158.11, 152.97, 149.29,

148.05, 134.69, 131.73, 131.17, 130.96, 130.56, 129.44, 128.84, 128.00, 127.87, 125.41, 123.47, 121.30, 120.60, 113.87, 112.43, 111.31, 102.61, 55.84, 55.80, 55.27, 52.97, 33.17; IR (ATR): 1709, 1670, 1626, 1542, 1507, 1449, 1394, 1253, 1174, 1141, 1084, 1028, 905, 829, 772, 721, 693, 640, 562. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_6Na$ $[M+Na]^+$: 584.2044, Found: 584.2036.



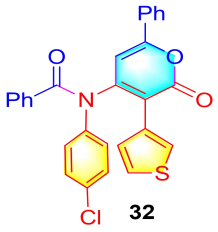
30

The reaction was run at 80 °C for 5 h, affording product **30** as a pale yellow solid (55.2 mg, 91% yield, m.p. = 166-167 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (brm, 2H), 3.56 (brm, 1H), 3.78 (s, 3H), 3.87 (s, 3H), 4.40 (brm, 1H), 5.80 (s, 1H), 6.74 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 7.04-7.08 (m, 4H), 7.19 (t, J = 8.0 Hz, 2H), 7.34-7.41 (m, 2H), 7.43-7.50 (m, 5H), 7.54-7.58 (m, 4H), 7.63-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.79, 162.36, 158.67, 153.63, 149.33, 148.08, 141.12, 140.35, 134.55, 131.75, 131.27, 131.14, 130.48, 130.28, 128.89, 128.82, 128.05, 127.92, 127.59, 127.06, 126.99, 125.50, 121.33, 120.38, 112.43, 111.33, 102.44, 102.44, 55.85, 55.81, 53.30, 33.15; IR (ATR): 1716, 1657, 1627, 1546, 1515, 1447, 1390, 1319, 1246, 1158, 1026, 910, 837, 810, 764, 721, 689, 645, 625, 574. HRMS (ESI): Exact mass calcd for $C_{40}H_{33}NO_5Na$ $[M+Na]^+$: 630.2251, Found: 630.2256.



31

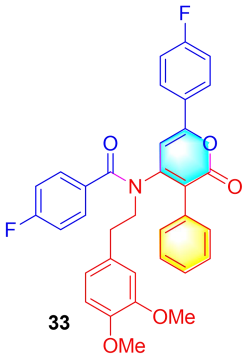
The reaction was run at 80 °C for 10 h, affording product **31** as a pale yellow solid (47.1 mg, 81% yield, m.p. = 180-181 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.83-2.85 (brm, 2H), 3.57 (brm, 1H), 3.72 (s, 3H), 3.87 (s, 4H), 5.96 (s, 1H), 6.56 (s, 1H), 6.64 (s, 1H), 6.84-7.04 (m, 6H), 7.16-7.25 (m, 3H), 7.39-7.43 (m, 1H), 7.46-7.50 (m, 4H), 7.64-7.65 (m, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.76, 162.02, 159.27, 155.82, 149.22, 148.00, 134.77, 133.58, 131.48, 131.30, 131.20, 130.60, 129.64, 129.22, 128.92, 128.43, 128.12, 127.89, 126.45, 125.79, 125.61, 125.20, 124.61, 121.20, 112.40, 111.29, 102.77, 55.88, 55.80, 33.22. IR (ATR): 1719, 1664, 1629, 1547, 1535, 1441, 1378, 1310, 1268, 1048, 975, 878, 805, 747, 587. HRMS (ESI): Exact mass calcd for $C_{38}H_{31}NO_5Na$ $[M+Na]^+$: 604.2094, Found: 604.2092.



32

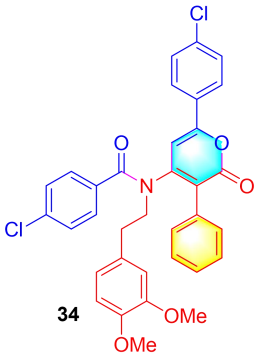
The reaction was run at 80 °C for 8 h, affording product **32** as a pale yellow solid (41.1 mg, 85% yield, m.p. = 117-118 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.57 (s, 1H), 7.02 (d, J = 5.0 Hz, 1H), 7.11 (brm, 2H), 7.20-7.24 (m, 5H), 7.30 (d, J = 7.5 Hz, 2H), 7.35-7.38 (m, 2H), 7.44-7.49 (m, 3H), 7.78-7.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.81, 161.90, 158.79,

139.50, 133.92, 132.69, 131.58, 131.23, 130.79, 130.52, 129.59, 128.99, 128.30, 128.15, 128.01, 127.37, 126.81, 125.60, 125.26, 117.94, 102.69; IR (ATR): 1726, 1673, 1628, 1556, 1488, 1447, 1287, 1089, 1012, 851, 791, 764, 689, 675, 652, 635, 605, 575, 515. HRMS (ESI): Exact mass calcd for $C_{28}H_{18}ClNO_3SNa$ $[M+Na]^+$: 506.0588, Found: 506.0581.



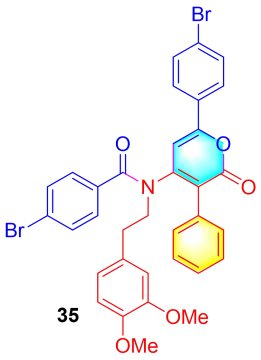
33

The reaction was run at 80 °C for 5 h, affording product **33** as a pale yellow solid (53.9 mg, 95% yield, m.p. = 221-222 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (brm, 2H), 3.55 (brm, 1H), 3.78 (s, 3H), 3.89 (s, 3H), 4.34 (brm, 1H), 5.62 (s, 1H), 6.74 (s, 1H), 6.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.84-6.92 (m, 5H), 6.96-7.01 (m, 2H), 7.12-7.17 (m, 2H), 7.28-7.35 (m, 3H), 7.52-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.55, 164.41 (d, *J* = 252 Hz), 164.28 (d, *J* = 252 Hz), 161.95, 158.02 (d, *J* = 1.3 Hz), 153.52, 149.46, 148.20, 131.97, 131.11, 130.70 (d, *J* = 3.4 Hz), 130.38 (d, *J* = 9.2 Hz), 129.84, 128.56, 128.39, 127.74, 127.66, 126.69 (d, *J* = 3.2 Hz), 121.43, 120.70, 116.15 (d, *J* = 22.2 Hz), 114.99 (d, *J* = 21.9 Hz), 112.50, 111.40, 101.59, 55.93, 55.86, 53.65, 33.05; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.22, -107.65. IR (ATR): 1714, 1662, 1617, 1543, 1476, 1434, 1276, 1077, 1021, 869, 758, 676, 664, 648, 582. HRMS (ESI): Exact mass calcd for $C_{34}H_{27}F_2NO_5Na$ $[M+Na]^+$: 590.1750, Found: 590.1751.



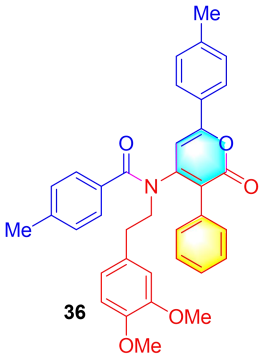
34

The reaction was run at 80 °C for 5 h, affording product **34** as a pale yellow solid (55.1 mg, 92% yield, m.p. = 215-216 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (brm, 2H), 3.43 (brm, 1H), 3.79 (s, 3H), 3.89 (s, 3H), 4.41 (brm, 1H), 5.65 (s, 1H), 6.74 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.89-6.93 (m, 5H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.29-7.36 (m, 3H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.58, 161.80, 157.83, 153.21, 149.47, 148.22, 137.48, 137.42, 132.89, 131.86, 130.96, 129.87, 129.37, 129.22, 128.82, 128.65, 128.42, 128.12, 126.70, 121.44, 121.22, 112.43, 111.40, 102.02, 55.95, 55.88, 53.64, 33.02; IR (ATR): 1717, 1665, 1627, 1545, 1511, 1490, 1440, 1391, 1264, 1153, 1086, 1011, 904, 819, 787, 753, 698, 637, 575. HRMS (ESI): Exact mass calcd for $C_{34}H_{27}Cl_2NO_5Na$ $[M+Na]^+$: 622.1158, Found: 622.1169.



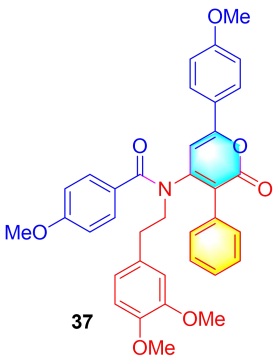
35

The reaction was run at 80 °C for 5 h, affording product **35** as a pale yellow solid (63.9 mg, 93% yield, m.p. = 205-206 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94 (brm, 2H), 3.41 (brm, 1H), 3.79 (s, 3H), 3.89 (s, 3H), 4.42 (brm, 1H), 5.65 (s, 1H), 6.74-6.78 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.88-6.92 (m, 3H), 7.29-7.34 (m, 5H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.68, 161.77, 157.89, 153.16, 149.47, 148.22, 133.33, 132.19, 131.83, 131.09, 130.94, 129.86, 129.51, 129.25, 128.67, 128.42, 126.84, 125.91, 125.85, 121.44, 121.33, 112.40, 111.39, 102.03, 55.94, 55.88, 53.62, 33.01; IR (ATR): 1713, 1663, 1627, 1586, 1544, 1510, 1486, 1441, 1389, 1270, 1151, 1068, 1008, 903, 817, 786, 750, 699, 636, 573. HRMS (ESI): Exact mass calcd for $C_{34}H_{27}Br_2NO_5Na$ $[M+Na]^+$: 710.0148, Found: 710.0152.



36

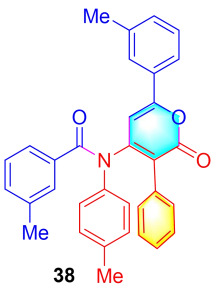
The reaction was run at 80 °C for 5 h, affording product **36** as a pale yellow solid (50.8 mg, 91% yield, m.p. = 190-191 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3H), 2.35 (s, 3H), 2.94 (brm, 2H), 3.45 (brm, 1H), 3.73 (s, 3H), 3.81 (s, 3H), 4.12 (brm, 1H), 5.67 (s, 1H), 6.67 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.89-6.94 (m, 6H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.23-7.27 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.80, 162.50, 158.83, 154.02, 149.26, 148.00, 141.66, 131.85, 131.46, 129.91, 129.56, 128.48, 128.33, 128.26, 128.20, 127.79, 125.41, 121.33, 120.24, 112.40, 111.29, 101.90, 55.85, 55.79, 53.13, 33.15, 21.44, 21.42. IR (ATR): 1716, 1658, 1612, 1538, 1524, 1487, 1455, 1378, 1257, 1158, 1052, 948, 779, 567. HRMS (ESI): Exact mass calcd for $C_{36}H_{33}NO_5Na$ $[M+Na]^+$: 582.2251, Found: 582.2240.



37

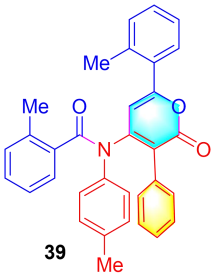
The reaction was run at 80 °C for 8 h, affording product **37** as a pale yellow solid (54.4 mg, 92% yield, m.p. = 136-137 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01 (brm, 2H), 3.60 (brm, 2H), 3.77 (s, 3H), 3.78 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 5.64 (s, 1H), 6.65-6.69 (m, 2H), 6.72-6.73 (m, 1H), 6.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.87-6.90 (m, 1H), 6.92-6.95 (m, 4H), 7.00-7.04 (m, 2H), 7.28-7.30 (m, 3H), 7.49-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.27, 162.57, 161.96, 161.89, 158.86, 154.45, 149.25, 147.98, 132.06, 131.59, 130.17, 129.88, 128.97, 128.23, 128.19, 127.24, 126.96, 123.08, 121.31, 119.33, 114.24, 113.06, 112.52, 111.30, 100.84, 55.86, 55.81,

55.47, 55.29, 53.27, 33.13; IR (ATR): 1700, 1656, 1605, 1539, 1509, 1442, 1390, 1321, 1241, 1184, 1023, 853, 824, 782, 744, 698, 639, 612, 563. HRMS (ESI): Exact mass calcd for $C_{36}H_{33}NO_7Na$ $[M+Na]^+$: 614.2149, Found: 614.2155.



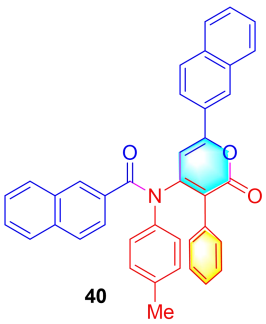
38

The reaction was run at 80 °C for 5 h, affording product **38** as a pale green solid (44.6 mg, 92% yield, m.p. = 196-197 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.29 (s, 3H), 2.40 (s, 3H), 6.60 (s, 1H), 6.86 (s, 2H), 6.96-7.03 (m, 5H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.21-7.25 (m, 5H), 7.27 (brs, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.14, 162.89, 159.13, 153.17, 138.84, 138.74, 137.85, 136.75, 134.28, 131.94, 131.88, 131.77, 130.82, 129.79, 129.52, 128.73, 128.24, 128.16, 127.42, 126.35, 126.23, 125.66, 122.78, 121.87, 103.09, 21.36, 21.17, 20.97; IR (ATR): 1708, 1662, 1627, 1548, 1509, 1432, 1345, 1297, 909, 782, 726, 693, 566. HRMS (ESI): Exact mass calcd for $C_{33}H_{27}NO_3Na$ $[M+Na]^+$: 508.1883, Found: 508.1889.



39

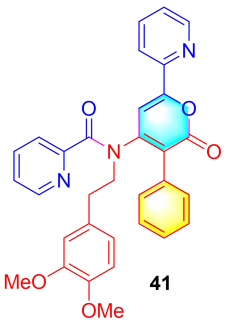
The reaction was run at 80 °C for 5 h, affording product **39** as a pale green solid (41.2 mg, 85% yield, m.p. = 181-182 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.25 (s, 3H), 2.51 (s, 3H), 6.45 (s, 1H), 6.59 (s, 2H), 6.82-6.83 (m, 2H), 6.91-6.94 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.27-7.32 (m, 7H), 7.36 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.32, 163.22, 160.56, 152.64, 138.17, 136.78, 136.73, 134.35, 132.11, 131.65, 131.32, 130.72, 130.42, 129.83, 129.56, 129.37, 129.11, 128.48, 128.25, 127.85, 126.33, 126.08, 124.97, 122.37, 107.77, 20.90, 19.65. IR (ATR): 1714, 1657, 1632, 1541, 1498, 1447, 1355, 1278, 935, 774, 712, 678, 558. HRMS (ESI): Exact mass calcd for $C_{33}H_{27}NO_3Na$ $[M+Na]^+$: 508.1883, Found: 508.1879.



40

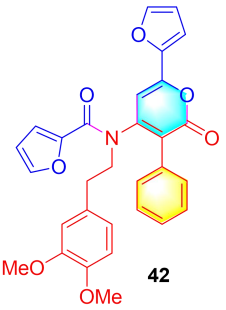
The reaction was run at 80 °C for 8 h, affording product **40** as a pale yellow solid (47.9 mg, 86% yield, m.p. = 171-172 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 6.84 (s, 1H), 6.93-7.02 (m, 4H), 7.24-7.28 (m, 6H), 7.45-7.61 (m, 5H), 7.71-7.78 (m, 3H), 7.85-7.89 (m, 3H), 7.93-7.95 (m, 1H), 8.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.93, 162.89, 158.94, 153.22, 138.75, 136.88, 134.23, 132.92, 132.13, 131.93, 131.65, 130.37, 129.91, 129.47, 128.98, 128.88, 128.66, 128.36, 128.24, 127.84, 127.73, 127.68, 127.58, 127.36, 126.97, 126.53, 126.40, 126.20, 124.83, 122.17, 121.90, 103.46, 20.95; IR (ATR): 1697, 1655, 1624, 1509, 1432, 1350, 1270, 1193, 1125, 947,

905, 867, 817, 735, 700, 563. HRMS (ESI): Exact mass calcd for $C_{39}H_{27}NO_3Na$ $[M+Na]^+$: 580.1883, Found: 580.1895.



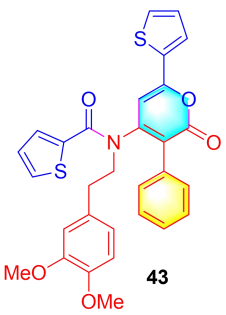
41

The reaction was run at 80 °C for 8 h, affording product **41** as a pale yellow solid (33.0 mg, 62% yield, m.p. = 151-152 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 (brm, 2H), 3.39 (brm, 1H), 3.76 (s, 3H), 3.83 (s, 3H), 4.11 (brm, 1H), 6.66-6.75 (m, 3H), 6.93 (s, 1H), 7.28-7.34 (m, 5H), 7.37-7.42 (m, 2H), 7.59-7.61 (m, 1H), 7.70 (td, *J* = 7.6, 1.6 Hz, 1H), 7.77-7.81 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 4.0 Hz, 1H), 8.57-8.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.66, 162.65, 156.01, 149.69, 148.93, 148.39, 147.69, 147.55, 136.99, 136.83, 132.06, 130.79, 129.61, 129.00, 128.54, 128.50, 128.26, 128.21, 125.71, 124.81, 124.70, 120.94, 120.32, 111.99, 111.16, 105.87, 55.74, 51.53, 33.79; IR (ATR): 1737, 1655, 1622, 1560, 1515, 1441, 1236, 1156, 1025, 810, 746, 696, 618. HRMS (ESI): Exact mass calcd for $C_{32}H_{27}N_3O_5Na$ $[M+Na]^+$: 556.1843, Found: 556.1846.



42

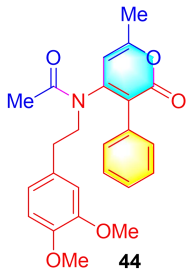
The reaction was run at 80 °C for 8 h, affording product **42** as a pale yellow solid (44.4 mg, 87% yield, m.p. = 142-143 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (brm, 2H), 3.64 (brm, 1H), 3.78 (s, 3H), 3.80 (s, 3H), 3.88 (brm, 1H), 5.88 (s, 1H), 6.43 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.64-6.67 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 3.6 Hz, 1H), 6.99 (d, *J* = 3.6 Hz, 1H), 7.24-7.25 (m, 1H), 7.26-7.27 (m, 1H), 7.32-7.37 (m, 3H), 7.41-7.42 (m, 1H), 7.49-7.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.94, 158.86, 153.35, 150.17, 149.01, 147.85, 147.17, 145.82, 144.99, 144.96, 131.56, 130.75, 129.32, 128.70, 128.54, 120.97, 119.74, 117.66, 112.52, 112.20, 112.03, 111.91, 111.14, 101.72, 55.74, 55.72, 51.33, 33.56; IR (ATR): 1711, 1672, 1636, 1515, 1466, 1388, 1261, 1155, 1016, 884, 749, 698, 592. HRMS (ESI): Exact mass calcd for $C_{30}H_{25}NO_7Na$ $[M+Na]^+$: 534.1523, Found: 534.1522.



43

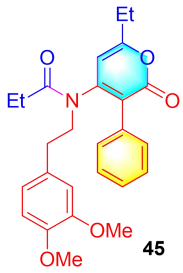
The reaction was run at 80 °C for 8 h, affording product **43** as a pale yellow solid (48.9 mg, 90% yield, m.p. = 165-166 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.92 (brm, 2H), 3.70 (brm, 2H), 3.78 (s, 3H), 3.81 (s, 3H), 5.64 (s, 1H), 6.67 (d, *J* = 1.6 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.09 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.13-7.17 (m, 2H), 7.25-7.26 (m, 1H), 7.32-7.35 (m, 3H), 7.42 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.43 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.46 (dd, *J* = 4.8, 1.2 Hz, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 162.46, 161.76, 154.39, 153.51, 149.03, 147.78, 137.43, 134.30, 131.34, 131.33, 131.30, 131.22, 129.51, 129.39, 128.62, 128.54, 128.34, 127.76, 127.13, 121.13, 120.60, 112.25, 111.25, 102.15, 55.75, 55.72, 52.66, 33.16; IR (ATR): 1707, 1647, 1614, 1535, 1440, 1419, 1392, 1301, 1262, 1234, 1158, 1026, 856, 809, 786, 731, 695, 636, 569. HRMS (ESI): Exact mass calcd for $C_{30}H_{25}NO_5S_2Na$ $[M+Na]^+$: 566.1066, Found: 566.1068.



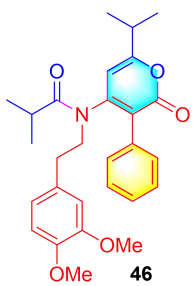
44

The reaction was run at 80 °C for 8 h, affording product **44** as a pale yellow solid (20.4 mg, 50% yield, m.p. = 132-133 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H), 2.21 (s, 3H), 2.65 (brm, 1H), 2.79 (brm, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 3.91 (brm, 1H), 5.41 (s, 1H), 6.61 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H), 7.26-7.29 (m, 2H), 7.33-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.94, 163.26, 160.76, 152.74, 148.95, 147.79, 131.38, 130.87, 129.06, 128.82, 128.72, 120.82, 111.97, 111.12, 106.26, 55.85, 50.07, 33.59, 22.95, 19.74; IR (ATR): 1713, 1665, 1634, 1561, 1515, 1440, 1345, 1237, 1140, 1027, 944, 853, 792, 750, 699, 657, 569. HRMS (ESI): Exact mass calcd for $C_{24}H_{25}NO_5Na$ $[M+Na]^+$: 430.1625, Found: 430.1633.



45

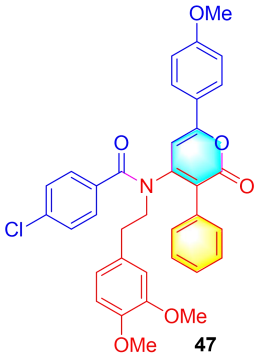
The reaction was run at 80 °C for 8 h, affording product **45** as a pale yellow solid (34.8 mg, 80% yield, m.p. = 108-109 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 1.11 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 2.26 (q, J = 8.4 Hz, 2H), 2.48 (q, J = 7.6 Hz, 2H), 2.63-2.80 (brm, 3H), 3.74-3.90 (brm, 1H), 3.82 (s, 3H), 3.83 (s, 3H), 5.39 (s, 1H), 6.59-6.62 (m, 2H), 6.75 (d, J = 8.0 Hz, 1H), 7.26-7.27 (m, 2H), 7.31-7.36 (m, 1H), 7.37-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.63, 165.47, 163.32, 152.85, 148.89, 147.71, 131.51, 130.87, 129.07, 128.72, 128.65, 120.95, 120.79, 111.92, 111.08, 104.74, 55.80, 50.20, 33.68, 28.04, 26.67, 10.65, 9.35. IR (ATR): 1718, 1657, 1623, 1547, 1502, 1477, 1332, 1245, 1135, 1011, 924, 878, 765, 744, 686, 645. HRMS (ESI): Exact mass calcd for $C_{26}H_{29}NO_5Na$ $[M+Na]^+$: 458.1938, Found: 458.1939.



46

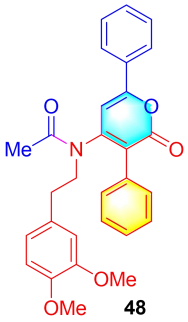
The reaction was run at 80 °C for 10 h, affording product **46** as a pale-green solid (38.4 mg, 83% yield, m.p. = 92-93 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 0.95 (brs, 3H), 1.09 (brs, 3H), 1.19 (d, J = 6.8 Hz, 6H), 2.58-2.72 (m, 3H), 2.89 (brm, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 3.91 (brm, 1H), 5.33 (s, 1H), 6.62 (d, J = 7.2 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H), 7.26-7.28 (m, 2H), 7.31-7.35 (m, 1H), 7.37-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.69, 169.12, 163.34, 153.18, 148.94, 147.75, 131.54, 129.32, 128.64, 120.91, 111.98, 111.10, 102.92,

55.80, 50.94, 33.50, 32.67, 32.42, 20.54, 20.00, 19.90, 19.75, 19.01. IR (ATR): 1714, 1664, 1617, 1532, 1499, 1466, 1387, 1236, 1175, 1023, 952, 886, 748, 741, 687. HRMS (ESI): Exact mass calcd for $C_{28}H_{33}NO_5Na$ $[M+Na]^+$: 486.2251, Found: 486.2258.



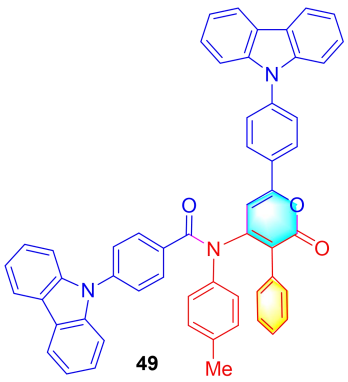
47

The reaction was run at 80 °C for 6 h, affording the product as a separable mixture of two regioisomers (1.6:1.0 ratio) (pale yellow solid, 29.8 mg, 50% yield of the major regioisomer **47**, m.p. = 152-153 °C); NMR data of the major regioisomer **47** was listed below: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02 (brm, 2H), 3.78 (s, 3H), 3.79 (s, 3H), 3.87 (brm, 5H), 5.67 (s, 1H), 6.67-6.70 (m, 2H), 6.72-6.73 (m, 1H), 6.79 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.95-6.97 (m, 2H), 7.00-7.04 (m, 2H), 7.28-7.35 (m, 3H), 7.41-7.43 (m, 2H), 7.46-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.27, 162.16, 162.01, 157.44, 153.98, 149.37, 148.09, 137.25, 132.09, 131.30, 130.17, 129.84, 129.18, 129.02, 128.49, 128.34, 126.83, 126.70, 121.42, 120.73, 113.16, 112.55, 111.35, 102.60, 55.94, 55.87, 55.35, 53.32, 33.15; IR (ATR): 1718, 1662, 1603, 1546, 1510, 1440, 1389, 1256, 1168, 1087, 1031, 904, 824, 774, 750, 698, 628,609, 572. HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NO_6ClNa$ $[M+Na]^+$: 618.1654, Found: 618.1648.

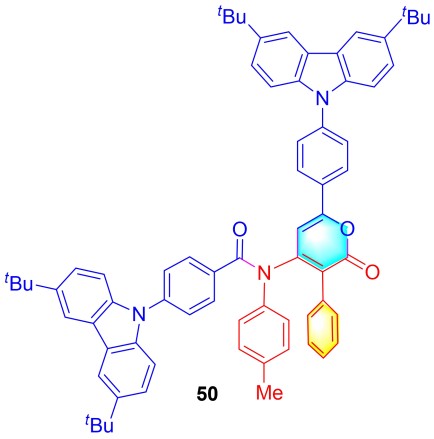


48

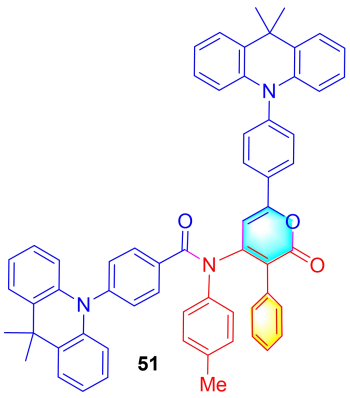
The reaction was run at 80 °C for 8 h, affording the product as a separable mixture of two regioisomers (1.3:1 ratio) (pale yellow solid, 16.9 mg, 36% yield of the major regioisomer **48**, m.p. = 45-46 °C); NMR data of the major regioisomer **48** was listed below: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 3H), 2.93 (brm, 2H), 3.79 (brm, 5H), 3.89 (s, 3H), 5.27 (s, 1H), 6.63 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.96-6.97 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.28-7.31 (m, 3H), 7.37 (t, *J* = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.78, 163.12, 160.53, 153.17, 149.12, 147.96, 134.60, 131.35, 131.27, 131.13, 129.74, 128.38, 127.94, 127.90, 121.04, 119.80, 112.40, 111.28, 104.96, 55.99, 55.83, 52.55, 33.50, 19.88; IR (ATR): 1717, 1639, 1612, 1559, 1514, 1440, 1261, 1142, 1026, 935, 789, 696, 568. HRMS (ESI): Exact mass calcd for $C_{29}H_{27}NO_5Na$ $[M+Na]^+$: 492.1781, Found: 492.1784.



The reaction was run at 80 °C for 12 h, affording product **49** as a yellow solid (63.7 mg, 81% yield, m.p. = 215-216 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 6.77 (s, 1H), 7.02 (brm, 2H), 7.13-7.15 (m, 2H), 7.29-7.37 (m, 11H), 7.40-7.49 (m, 10H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 8.14 (t, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.02, 162.55, 158.25, 152.75, 140.40, 140.23, 140.19, 140.10, 138.63, 137.38, 132.68, 131.78, 130.55, 130.14, 129.47, 129.30, 128.61, 128.45, 127.25, 126.97, 126.51, 126.16, 126.11, 125.95, 123.70, 123.66, 120.49, 120.44, 120.42, 109.65, 109.53, 103.13, 21.07; IR (ATR): 1718, 1670, 1599, 1509, 1448, 1336, 1225, 1170, 746, 722, 564. HRMS (ESI): Exact mass calcd for $C_{55}H_{37}N_3O_3Na$ $[M+Na]^+$: 810.2727, Found: 810.2741.

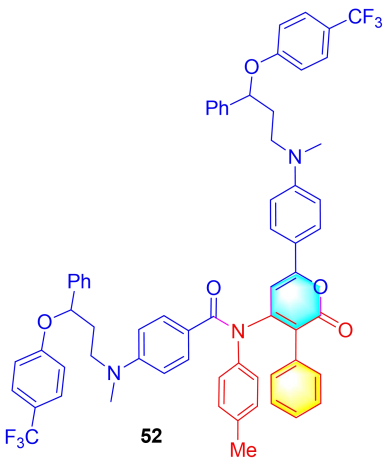


The reaction was run at 80 °C for 12 h, affording product **50** as a yellow solid (61.7 mg, 61% yield, m.p. = 234-235 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50-1.51 (m, 36H), 2.40 (s, 3H), 6.81 (s, 1H), 7.06 (brm, 2H), 7.16-7.18 (m, 2H), 7.34-7.38 (m, 7H), 7.44-7.53 (m, 10H), 7.73 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.11, 162.58, 158.35, 152.85, 143.49, 143.47, 140.93, 140.74, 138.68, 138.48, 138.42, 137.25, 132.09, 131.80, 130.47, 130.10, 129.47, 128.69, 128.52, 128.41, 127.18, 126.47, 126.38, 125.40, 123.79, 123.74, 123.68, 116.36, 116.31, 109.14, 109.05, 102.98, 34.72, 34.70, 31.92, 31.91, 21.05; IR (ATR): 1723, 1681, 1602, 1511, 1471, 1363, 1293, 1177, 809, 696, 610, 566. HRMS (ESI): Exact mass calcd for $C_{71}H_{69}N_3O_3Na$ $[M+Na]^+$: 1034.5231, Found: 1034.5233.



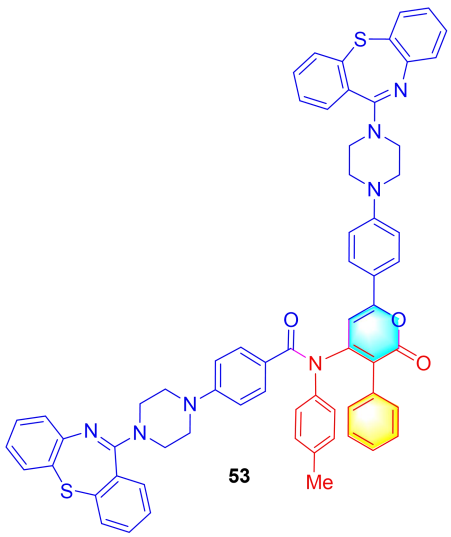
The reaction was run at 80 °C for 12 h, affording product **51** as a yellow solid (49.6 mg, 57% yield, m.p. = 131-132 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (s, 6H), 1.70 (s, 6H), 2.35 (s, 3H), 6.15 (d, *J* = 7.6 Hz, 2H), 6.27 (d, *J* = 7.2 Hz, 2H), 6.78 (s, 1H), 6.96-7.01 (m, 10H), 7.10-7.12 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.33-7.36 (m, 5H), 7.45-7.49 (m, 8H), 8.09 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.29, 158.26, 143.96, 140.41, 140.27, 138.55, 137.46, 134.02, 131.80, 131.29, 130.76, 130.45, 130.33, 130.31, 130.02, 129.52, 128.67, 128.49, 128.22, 126.57, 126.40, 126.27, 125.37,

125.31, 120.97, 114.01, 113.96, 103.42, 35.98, 35.95, 31.18, 31.04, 21.07; IR (ATR): 1717, 1674, 1591, 1509, 1447, 1268, 1046, 743, 695, 623. HRMS (ESI): Exact mass calcd for $C_{61}H_{49}N_3O_3Na$ $[M+Na]^+$: 894.3666, Found: 894.3664.



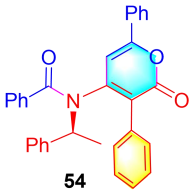
52

The reaction was run at 80 °C for 12 h, affording product **52** as a yellow solid (56.8 mg, 53% yield, m.p. = 115-116 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10-2.26 (m, 4H), 2.31 (s, 3H), 2.91 (s, 3H), 2.99 (s, 3H), 3.49-3.57 (m, 2H), 3.62 (t, *J* = 7.2 Hz, 2H), 5.17 (ddd, *J* = 16.4, 8.0, 4.4 Hz, 2H), 6.35 (d, *J* = 9.2 Hz, 2H), 6.39 (s, 1H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.88-6.92 (m, 6H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.16-7.20 (m, 5H), 7.26-7.37 (m, 10H), 7.42-7.46 (m, 4H), 7.63 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.88, 163.52, 160.18, 159.73, 154.72, 150.89, 150.59, 140.35, 140.31, 139.92, 135.92, 132.49, 131.25, 129.69, 129.62, 128.89, 128.88, 128.04, 128.01, 127.93, 127.63, 127.19, 126.84, 126.82, 126.80, 126.78, 126.75, 126.26, 125.56, 125.54, 124.28 (q, *J* = 270 Hz), 123.02 (q, *J* = 33 Hz), 123.00 (q, *J* = 33 Hz), 118.72, 118.33, 115.65, 111.44, 110.18, 100.30, 77.87, 77.80, 48.67, 38.54, 35.84, 35.81, 20.96; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.60, -61.61; IR (ATR): 1706, 1656, 1599, 1516, 1321, 1178, 1107, 1066, 820, 754, 698, 636, 564. HRMS (ESI): Exact mass calcd for $C_{65}H_{55}F_6N_3O_5Na$ $[M+Na]^+$: 1094.3938, Found: 1094.3932.



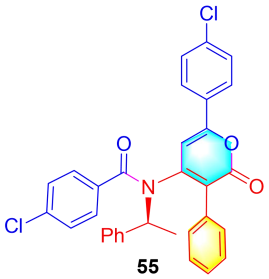
53

The reaction was run at 80 °C for 12 h, affording product **53** as a yellow solid (75.1 mg, 72% yield, m.p. = 219-220 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 3.23-3.43 (m, 9H), 3.66 (brm, 7H), 6.45 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.86-6.94 (m, 6H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.09-7.12 (m, 2H), 7.17-7.23 (m, 9H), 7.29-7.42 (m, 8H), 7.52-7.55 (m, 2H), 7.70 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.56, 166.87, 163.26, 160.68, 160.66, 159.26, 154.20, 152.83, 152.60, 148.59, 148.56, 140.03, 140.00, 139.57, 136.23, 133.91, 132.32, 132.21, 130.99, 129.73, 129.60, 129.14, 128.93, 128.36, 128.04, 127.93, 127.91, 127.87, 127.02, 126.29, 125.26, 124.20, 123.13, 121.31, 119.79, 114.75, 113.46, 101.13, 47.57, 47.40, 46.34, 20.97; IR (ATR): 1707, 1657, 1596, 1510, 1478, 1365, 1225, 1008, 932, 760, 695, 561. HRMS (ESI): Exact mass calcd for $C_{65}H_{53}N_7O_3S_2Na$ $[M+Na]^+$: 1066.3651, Found: 1066.3658.



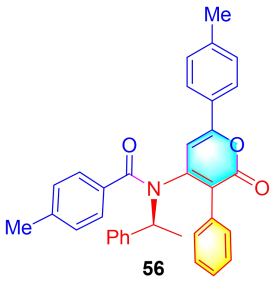
54

The reaction was run at 80 °C for 12 h, affording product **54** as a pale yellow solid (40.0 mg, 85% yield, m.p. = 145-146 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 13.91 min, t_r (minor) = 17.38 min) gave the isomeric composition of the product: 99% ee, $[\alpha]^{25}_{D}$ = -120.1 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69 (brs, 3H), 6.39 (brm, 3H), 6.90-7.23 (brm, 5H), 7.31-7.47 (brm, 12H), 7.58 (brm, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.98, 162.57, 157.72, 136.89, 135.18, 130.95, 130.60, 129.90, 128.87, 128.36, 128.17, 128.06, 127.79, 127.03, 125.44, 17.38; IR (ATR): 1712, 1654, 1626, 1542, 1495, 1450, 1401, 1291, 905, 690, 562. HRMS (ESI): Exact mass calcd for $C_{32}H_{25}NO_3Na$ $[M+Na]^+$: 494.1727, Found: 494.1723.



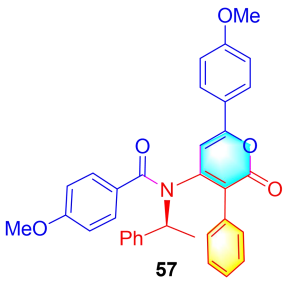
55

The reaction was run at 80 °C for 12 h, affording product **55** as a pale yellow solid (45.2 mg, 84% yield, m.p. = 166-167 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 24.78 min, t_r (minor) = 10.72 min) gave the isomeric composition of the product: 98% ee, $[\alpha]^{25}_{D}$ = -234.2 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69 (brs, 3H), 6.29 (brm, 3H), 7.02 (brm, 3H), 7.20 (brm, 2H), 7.31-7.41 (brm, 10H), 7.48-7.52 (brm, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.55, 162.13, 156.76, 150.36, 137.24, 133.47, 131.10, 129.84, 129.24, 129.13, 128.97, 128.56, 125.50, 128.29, 128.23, 126.97, 126.67, 17.30; IR (ATR): 1718, 1662, 1627, 1544, 1489, 1394, 1296, 1090, 1012, 822, 755, 696, 572. HRMS (ESI): Exact mass calcd for $C_{32}H_{23}NO_3Cl_2Na$ $[M+Na]^+$: 562.0947, Found: 562.0943.



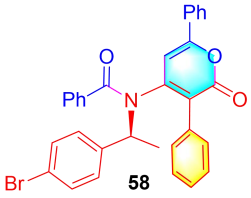
56

The reaction was run at 80 °C for 12 h, affording product **56** as a pale yellow solid (40.4 mg, 81% yield, m.p. = 151-152 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 9.06 min, t_r (minor) = 7.62 min) gave the isomeric composition of the product: 95% ee, $[\alpha]^{25}_{D}$ = -135.1 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (brs, 3H), 2.34 (s, 3H), 2.40 (s, 3H), 6.31 (brm, 3H), 7.03 (brm, 6H), 7.22 (d, J = 8.0 Hz, 2H), 7.29-7.38 (brm, 7H), 7.47-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.78, 157.95, 151.20, 141.56, 141.39, 132.40, 131.48, 129.96, 129.57, 128.78, 128.20, 128.09, 127.90, 127.02, 125.39, 21.43, 17.36; IR (ATR): 1711, 1652, 1598, 1556, 1502, 1298, 1232, 1165, 1009, 843, 759, 684, 635, 605, 574. HRMS (ESI): Exact mass calcd for $C_{34}H_{29}NO_3Na$ $[M+Na]^+$: 522.2040, Found: 522.2047.



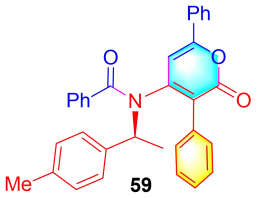
57

The reaction was run at 80 °C for 12 h, affording product **57** as a pale yellow solid (39.8 mg, 75% yield, m.p. = 160-161 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 16.30 min, t_r (minor) = 12.73 min) gave the isomeric composition of the product: 98% ee, $[\alpha]^{25}_{D}$ = -261.3 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (brs, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 5.97-6.27 (brm, 2H), 6.70 (d, *J* = 6.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.99-7.08 (brm, 4H), 7.27-7.30 (brm, 3H), 7.32-7.41 (brm, 5H), 7.55 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.09, 162.82, 161.90, 161.76, 157.92, 151.71, 131.68, 129.98, 129.93, 128.79, 128.09, 127.84, 127.54, 127.18, 126.96, 123.17, 114.30, 113.23, 55.44, 55.32, 17.35; IR (ATR): 1714, 1646, 1601, 1539, 1506, 1302, 1248, 1176, 1018, 838, 764, 697, 650, 614, 568. HRMS (ESI): Exact mass calcd for $C_{34}H_{30}NO_5$ $[M+H]^+$: 532.2118, Found: 532.2121.



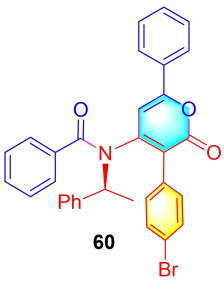
58

The reaction was run at 80 °C for 12 h, affording product **58** as a pale yellow solid (39.5 mg, 72% yield, m.p. = 149-150 °C); HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 25/75, 1.0 mL/min, 230 nm; t_r (major) = 16.89 min, t_r (minor) = 18.22 min) gave the isomeric composition of the product: 97% ee, $[\alpha]^{25}_{D}$ = -75.1 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.69 (brs, 3H), 5.23-6.40 (brm, 2H), 6.97-7.39 (m, 12H), 7.44-7.49 (m, 5H), 7.62 (brm, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.44, 162.44, 157.98, 135.02, 131.89, 131.18, 131.12, 130.50, 129.83, 129.02, 128.81, 128.48, 128.23, 127.79, 125.49, 122.02, 17.51; IR (ATR): 1712, 1659, 1626, 1542, 1489, 1398, 1290, 1074, 1007, 905, 765, 688, 646, 565. HRMS (ESI): Exact mass calcd for $C_{32}H_{24}BrNO_3Na$ $[M+Na]^+$: 572.0832, Found: 572.0833.



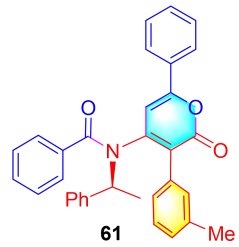
59

The reaction was run at 80 °C for 12 h, affording product **59** as a pale yellow solid (30.6 mg, 63% yield, m.p. = 139-140 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 9.06 min, t_r (minor) = 7.62 min) gave the isomeric composition of the product: 95% ee, $[\alpha]^{25}_{D}$ = -153.2 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.77 (brs, 3H), 2.38 (s, 3H), 5.43-6.51 (m, 2H), 7.19-7.44 (m, 15H), 7.58-7.76 (brm, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.63, 157.58, 137.93, 137.33, 130.89, 130.71, 129.94, 129.47, 128.85, 128.36, 128.13, 127.86, 127.77, 127.10, 127.06, 125.48, 21.03, 17.36. IR (ATR): 1720, 1647, 1613, 1565, 1511, 1392, 1247, 1135, 1012, 863, 747, 689, 631, 621, 586. HRMS (ESI): Exact mass calcd for $C_{33}H_{28}NO_3$ $[M+H]^+$: 486.2064, Found: 486.2070.



60

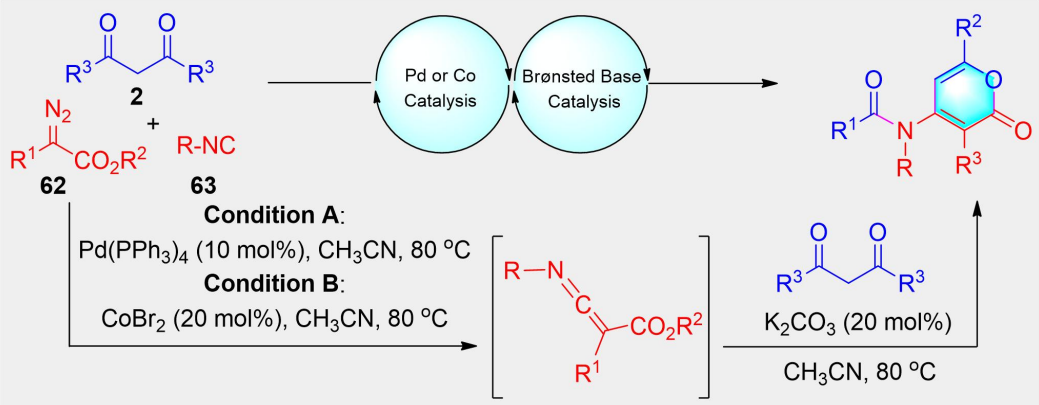
The reaction was run at 80 °C for 12 h, affording product **60** as a pale yellow solid (40.6 mg, 74% yield, m.p. = 163-164 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 10.51 min, t_r (minor) = 20.61 min) gave the isomeric composition of the product: 94% ee, $[\alpha]^{25}_{D}$ = -165.2 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71 (brs, 3H), 5.93-6.41 (brm, 3H), 6.83 (brm, 2H), 7.15 (brm, 2H), 7.36-7.49 (brm, 12H), 7.59-7.60 (brm, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.59, 162.21, 158.15, 150.94, 140.94, 134.98, 131.56, 131.32, 131.15, 130.46, 128.93, 128.21, 127.75, 127.10, 125.48, 122.63, 102.01, 56.21, 17.54; IR (ATR): 1715, 1647, 1625, 1540, 1494, 1449, 1388, 1290, 1071, 909, 826, 766, 696, 647, 515. HRMS (ESI): Exact mass calcd for $C_{32}H_{24}BrNO_3Na$ $[M+Na]^+$: 572.0832, Found: 572.0824.



61

The reaction was run at 80 °C for 10 h, affording product **61** as a pale yellow solid (42.7 mg, 88% yield, m.p. = 150-151 °C); HPLC analysis (Chiralcel OD, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 10.34 min, t_r (minor) = 12.51 min) gave the isomeric composition of the product: 99% ee, $[\alpha]^{25}_{D}$ = -114.1 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (brs, 3H), 2.27 (s, 3H), 6.49-6.85 (brm, 3H), 7.13-7.24 (brm, 6H), 7.37-7.48 (brm, 10H), 7.60 (brm, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.54, 162.62, 157.63, 150.59, 137.63, 135.18, 130.97, 130.87, 130.73, 130.65, 129.15, 128.87, 128.84, 128.03, 127.83, 127.09, 126.62, 125.44, 21.49, 17.42. IR (ATR): 1718, 1654, 1612, 1561, 1488, 1438, 1377, 1286, 1082, 942, 875, 735, 664. HRMS (ESI): Exact mass calcd for $C_{33}H_{27}NO_3Na$ $[M+Na]^+$: 508.1883, Found: 508.1884.

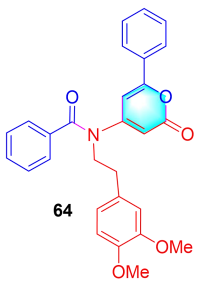
3) General Procedure for the One-Pot Synthesis of Di- and Trisubstituted α-Pyrones



The preparation of 3,4,6-trisubstituted α-pyrones: To an oven-dried Schlenk tube (10 mL) were successively added [$Pd(PPh_3)_4$] (10 mol%), anhydrous CH_3CN (1.0 mL), *α*-diazoacetates **62** (0.12 mmol), and isonitriles **63** (0.10 mmol). The reaction mixture was stirred vigorously at 80 °C under N_2 atmosphere. After the full consumption of isonitriles **63** by TLC analysis, 1,3-diketones **2** (0.10 mmol) and K_2CO_3 (0.02 mmol) were added successively, and then the reaction mixture was stirred at 80 °C till completion. The reaction mixture was concentrated by rotary vaporation, and the residue was subjected to column chromatography using petroleum ether/ethyl acetate (from 5:1-1:1) as eluent to afford the desired 3,4,6-trisubstituted α-pyrones. The NMR data of these products were the same as described above.

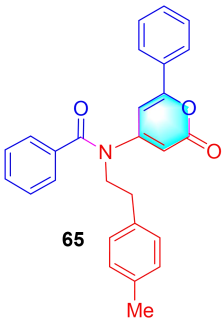
The preparation of 4,6-disubstituted α-pyrones: To an oven-dried Schlenk tube (10 mL) were successively added $CoBr_2$ (20 mol%), anhydrous MeCN (1 mL), *α*-diazoacetates **62** (0.12 mmol), isocyanides **63** (0.10 mmol), 1,3-diketones **2** (0.10 mmol) and K_2CO_3 (0.02 mmol). The tube was backfilled with N_2. After stirring at 80 °C for 12 h, the reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 5:1-1:1) to give the desired 4,6-disubstituted α-pyrones.

4) Spectral Data of 4,6-Disubstituted α-Pyrones

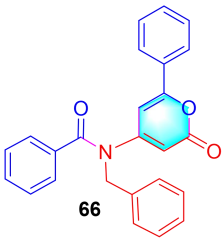


The reaction was run at 80 °C for 12 h, affording product **64** as a pale yellow solid (16.8 mg, 37% yield, m.p. = 128-129 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 3.02 (t, J = 7.2 Hz, 2H), 3.83 (s, 6H), 4.13 (t, J = 7.2 Hz, 2H), 5.75 (d, J = 2.0 Hz, 1H), 5.92 (d, J = 2.0 Hz, 1H), 6.74 (d, J = 2.0 Hz, 1H), 6.78-6.84 (m, 2H), 7.34-7.49 (m, 8H), 7.50-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.50, 162.47, 159.63, 157.77, 149.16, 148.02, 134.94, 131.84, 131.15,

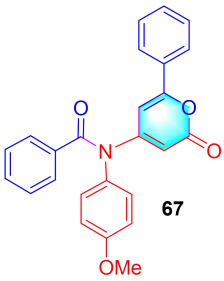
130.77, 130.61, 128.84, 128.75, 128.51, 125.59, 121.13, 112.21, 111.38, 103.79, 101.47, 55.86, 51.62, 33.71; IR (ATR): 1701, 1654, 1625, 1515, 1449, 1409, 1260, 1139, 1026, 822, 794, 765, 726, 687, 632. HRMS (ESI): Exact mass calcd for $C_{28}H_{25}NO_5Na$ $[M+Na]^+$: 478.1625, Found: 478.1622.



The reaction was run at 80 °C for 12 h, affording product **65** as a pale yellow solid (16.4 mg, 40% yield, m.p. = 103-104 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.04 (t, J = 7.2 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H), 5.69 (d, J = 2.0 Hz, 1H), 5.87 (d, J = 2.0 Hz, 1H), 7.15 (s, 4H), 7.35-7.49 (m, 8H), 7.50-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.51, 162.46, 159.57, 157.88, 136.63, 135.19, 134.98, 131.79, 131.10, 130.80, 129.50, 129.09, 128.81, 128.76, 128.51, 125.61, 104.06, 101.42, 51.81, 33.72, 21.01; IR (ATR): 1708, 1660, 1624, 1540, 1496, 1406, 1302, 1160, 1080, 918, 817, 795, 762, 729, 697, 631, 558. HRMS (ESI): Exact mass calcd for $C_{27}H_{23}NO_3Na$ $[M+Na]^+$: 432.1570, Found: 432.1566.



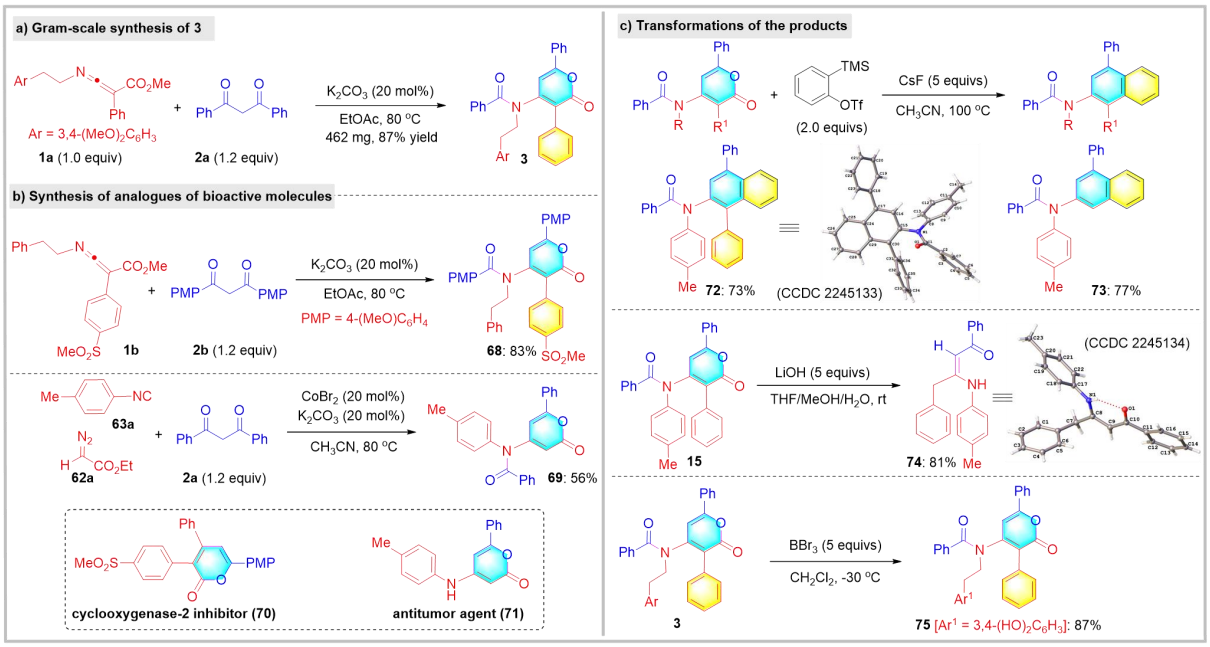
The reaction was run at 80 °C for 12 h, affording product **66** as a pale yellow solid (19.8 mg, 52% yield, m.p. = 89-90 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (s, 2H), 5.88 (d, J = 1.6 Hz, 1H), 6.22 (d, J = 1.6 Hz, 1H), 7.29-7.37 (m, 7H), 7.39-7.45 (m, 5H), 7.48-7.53 (m, 1H), 7.64-7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.87, 162.58, 159.30, 157.28, 136.18, 134.84, 132.05, 131.11, 130.82, 129.03, 128.87, 128.84, 128.59, 127.90, 127.03, 125.62, 102.67, 101.47, 52.36; IR (ATR): 1717, 1663, 1623, 1539, 1494, 1451, 1278, 1074, 966, 832, 765, 691, 594. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}NO_3Na$ $[M+Na]^+$: 404.1257, Found: 404.1262.



The reaction was run at 80 °C for 12 h, affording product **67** as a pale yellow solid (22.6 mg, 57% yield, m.p. = 107-108 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 3H), 5.56 (d, J = 1.6 Hz, 1H), 6.80-6.84 (m, 2H), 6.96 (d, J = 2.0 Hz, 1H), 7.03-7.07 (m, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.33-7.43 (m, 4H), 7.50-7.52 (m, 2H), 7.74-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.90, 163.19, 159.32, 159.20, 157.76, 134.71, 133.27, 131.45, 131.27, 130.85, 129.62, 129.18, 128.80, 128.23, 125.76, 115.15, 102.98, 100.36, 55.45; IR

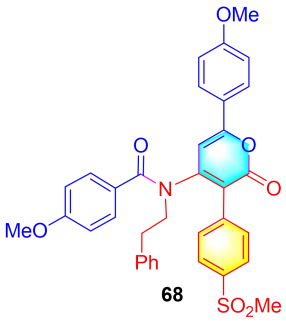
(ATR): 1725, 1660, 1627, 1539, 1511, 1447, 1410, 1284, 1175, 1091, 1026, 901, 828, 792, 705, 602, 527. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}NO_4Na$ $[M+Na]^+$: 420.1206, Found: 420.1211.

5) Scale-Up Reaction and Transformations of The Products



The scale-up synthesis of 3: To an oven-dried 10.0 mL Schlenk tube were successively added ketenimine **1a** (1.2 mmol), 1,3-diketone **2a** (1.0 mmol), anhydrous EtOAc (6 mL), and K_2CO_3 (20 mol%). The reaction mixture was stirred vigorously at 80 °C under N_2 atmosphere till full consumption of 1,3-diketone **2a** by TLC analysis. The reaction mixture was then concentrated by rotary vaporation, and the residue was subjected to column chromatography using petroleum ether/ethyl acetate (from 5:1-1:1) as eluent to afford the desired product **3** in 87% yield (462 mg, pale yellow solid). The full characterization data of this compound have been described in page S4.

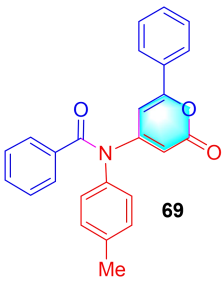
The synthesis of 68: To an oven-dried 10.0 mL Schlenk tube were successively added ketenimine **1b** (0.12 mmol), 1,3-diketone **2b** (0.10 mmol), anhydrous EtOAc (1 mL), and K_2CO_3 (20 mol%). The reaction mixture was stirred vigorously at 80 °C under N_2 atmosphere till full consumption of 1,3-diketone **2b** by TLC analysis. The reaction mixture was then concentrated by rotary vaporation, and the residue was subjected to column chromatography using petroleum ether/ethyl acetate (from 5:1-1:1) as eluent to afford the desired product **68** in 83% yield (50.5 mg, pale yellow solid, m.p. = 182-183 °C).



68

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (s, 3H), 3.13 (brm, 2H), 3.80 (s, 3H), 3.90 (s, 3H), 3.98 (brm, 2H), 5.69 (s, 1H), 6.66-6.69 (m, 2H), 6.93-6.97 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.25-7.28 (m, 2H), 7.36 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.41-7.45 (m, 2H), 7.50-7.54 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.79, 162.32, 162.17, 161.90, 160.20, 155.64, 139.46, 139.39, 137.62, 130.91, 130.02, 129.54, 128.98, 127.59, 127.09, 127.00, 126.20, 122.54, 116.83, 114.21, 113.29, 99.96, 55.50, 55.36, 53.41, 44.46, 33.58; IR (ATR): 1691, 1646, 1604, 1508, 1313, 1250, 1147, 1020, 833, 761, 707, 648, 555. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_7SNa$ $[M+Na]^+$: 632.1713, Found: 632.1713.

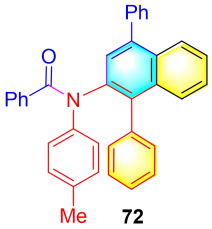
The synthesis of 69: To an oven-dried Schlenk tube (10 mL) were successively added $CoBr_2$ (20 mol%), anhydrous MeCN (1 mL), ethyl diazoacetate **62a** (0.12 mmol), 1-isocyano-4-methylbenzene **63a** (0.10 mmol), 1,3-dione **2a** (0.10 mmol) and K_2CO_3 (0.02 mmol). The tube was backfilled with N_2. After stirring at 80 °C for 12 h, the reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 5:1-1:1) to give compound **69** in 56% yield (21.3 mg, pale yellow solid, m.p. = 93-94 °C).



69

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 5.55 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.33-7.43 (m, 4H), 7.51-7.53 (m, 2H), 7.74-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.88, 163.16, 159.34, 157.71, 138.49, 138.11, 134.66, 131.52, 131.27, 130.85, 130.59, 129.24, 128.80, 128.22, 125.76, 103.28, 100.49, 21.03. IR (ATR): 1711, 1654, 1612, 1501, 1412, 1233, 1124, 1050, 853, 747, 663, 576. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}NO_3Na$ $[M+Na]^+$: 404.1257, Found: 404.1251.

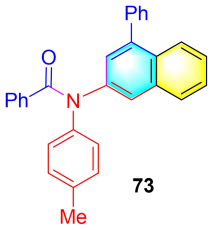
The synthesis of 72: To an oven-dried sealed tube (10 mL) were successively added compound **15** (0.10 mmol), anhydrous MeCN (1.0 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.30 mmol), and caesium fluoride (0.50 mmol). The tube was backfilled with N_2. After stirring at 100 °C for 10 h, the reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 6:1-3:1) to give compound **72** in 73% yield (35.7 mg, pale yellow solid, m.p. = 197-198 °C).



72

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 6.58 (brs, 2H), 6.78 (d, J = 6.4 Hz, 2H), 7.10-7.14 (m, 3H), 7.21-7.25 (m, 3H), 7.31-7.46 (m, 7H), 7.47-7.63 (m, 6H), 7.96 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.66, 141.38, 141.35, 141.27, 139.90, 138.37, 138.26, 138.11, 136.87, 136.83, 136.81, 136.76, 136.09, 135.06, 134.04, 131.06, 130.62, 130.16, 130.04, 129.93, 129.01, 128.89, 128.43, 128.27, 127.67, 127.51, 127.49, 127.07, 126.43, 126.19, 126.15, 126.11, 20.82; IR (ATR): 1656, 1611, 1509, 1487, 1397, 1272, 882, 756, 693, 583. HRMS (ESI): Exact mass calcd for $C_{36}H_{27}NONa$ $[M+Na]^+$: 512.1985, Found: 512.1987.

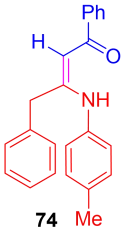
The synthesis of 73: To an oven-dried sealed tube (10 mL) were successively added compound **69** (0.10 mmol), anhydrous MeCN (1.0 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.30 mmol), and caesium fluoride (0.50 mmol). The tube was backfilled with N_2. After stirring at 100 °C for 10 h, the reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 6:1-3:1) to give compound **73** in 77% yield (31.8 mg, pale yellow solid, m.p. = 103-104 °C).



73

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 7.10 (s, 4H), 7.20-7.24 (m, 2H), 7.28-7.32 (m, 2H), 7.36-7.46 (m, 7H), 7.51-7.53 (m, 2H), 7.56 (d, J = 2.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.85, 141.29, 141.22, 140.99, 139.75, 136.32, 136.21, 134.06, 130.15, 129.97, 129.83, 129.18, 128.23, 128.18, 127.91, 127.47, 127.45, 126.71, 126.33, 126.14, 125.90, 124.70, 21.01; IR (ATR): 1662, 1613, 1542, 1493, 1386, 1281, 1187, 1065, 809, 729, 687. HRMS (ESI): Exact mass calcd for $C_{30}H_{23}NONa$ $[M+Na]^+$: 436.1672, Found: 436.1668.

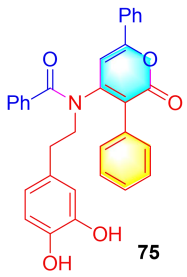
The synthesis of 74: To a 3.0 mL vial were successively added compound **15** (0.10 mmol), THF (0.40 mL), MeOH (0.40 mL), H_2O (0.20 mL), and LiOH (1.0 mmol). After stirring at rt for 1.5 h, the reaction mixture was extracted with EtOAc (3 mL× 3). The combined organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 3:1-1:1) to give compound **74** in 81% yield (26.5 mg, pale yellow solid, m.p. = 73-74 °C).



74

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.74 (s, 2H), 5.82 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.11-7.14 (m, 4H), 7.20-7.30 (m, 3H), 7.38-7.46 (m, 3H), 7.84-7.87 (m, 2H), 13.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.81, 164.65, 140.04, 136.77, 136.10, 135.59, 130.85, 129.67, 128.82, 128.53, 128.22, 127.06, 126.74, 125.56, 94.33, 38.58, 20.96. IR (ATR): 3453, 1722, 1653, 1604, 1553, 1477, 1392, 1245, 1132, 1047, 846, 733, 659. HRMS (ESI): Exact mass calcd for $C_{23}H_{21}NONa$ $[M+Na]^+$: 350.1515, Found: 350.1512.

The synthesis of 75: To an oven-dried Schlenk tube (10 mL) were successively added compound **3** (0.10 mmol), anhydrous CH_2Cl_2 (2.0 mL), and BBr_3 (0.50 mmol). The tube was backfilled with N_2. After stirring at -30 °C for 8 h, the reaction mixture was quenched with H_2O (6.0 mL) and then extracted with CH_2Cl_2 (5 mL× 3). The combined organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 1:1-1:2) to give compound **75** in 87% yield (43.8 mg, yellow oil).

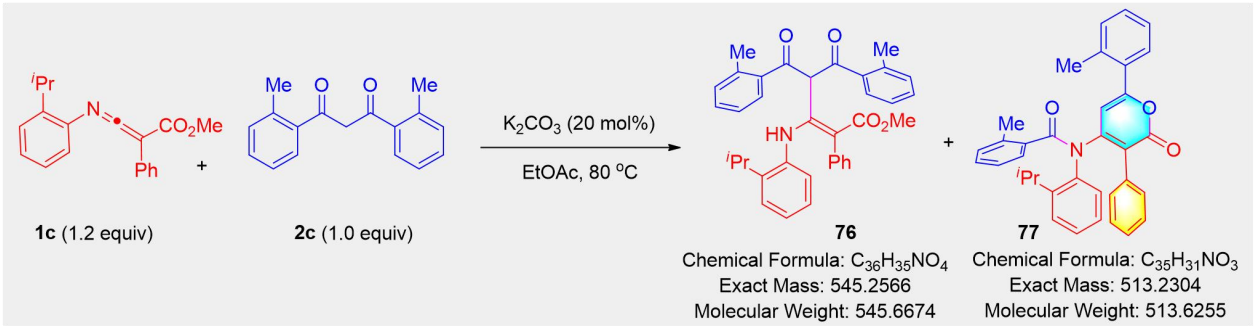


75

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84 (brm, 2H), 3.50 (brm, 2H), 5.76 (s, 1H), 6.03 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 6.81-6.83 (m, 2H), 6.89 (d, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 2H), 7.28-7.34 (m, 4H), 7.41-7.43 (m, 3H), 7.54-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.41, 162.61, 158.83, 153.70, 144.21, 143.23, 134.33, 131.51, 131.30, 131.18, 131.11, 130.32, 130.31, 129.89, 128.97, 128.59, 128.39, 128.03, 127.93, 125.58, 121.50, 116.24, 115.52, 102.49, 53.49, 49.54, 32.86; IR (ATR): 3325, 1657, 1619, 1529, 1444, 1286, 927, 772, 697, 626, 577. HRMS (ESI): Exact mass calcd for $C_{32}H_{25}NO_5Na$ $[M+Na]^+$: 526.1625, Found: 526.1622.

6) Mechanistic Studies

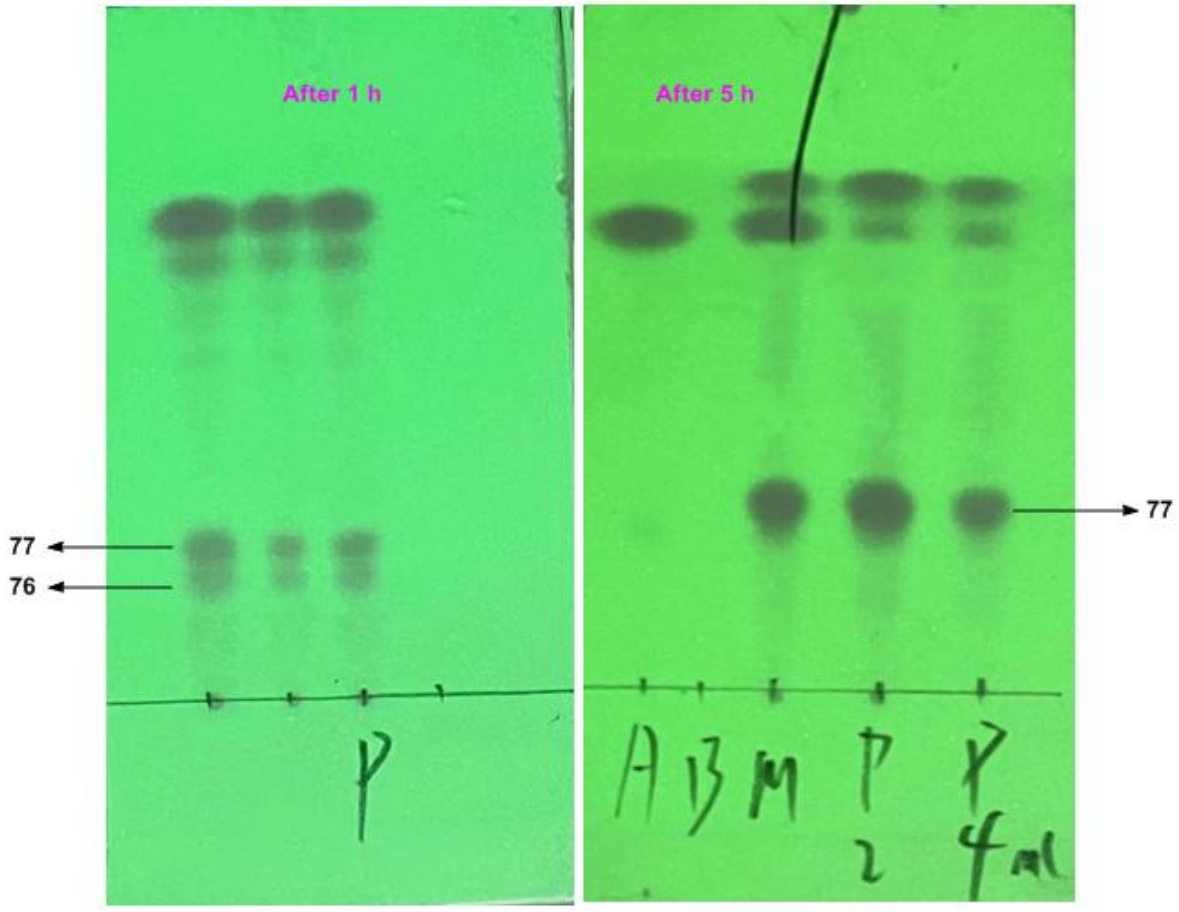
We studied the reaction mechanism of K_2CO_3 catalyzed formal insertion of ketenimines into C(CO)-C bonds of 1,3-diketones by a series of control experiments. Finally, we found that when the reaction of 2-isopropylphenyl substituted ketenimine **1c** and 1,3-di-*o*-tolylpropane-1,3-dione **2c** was stirred at 80 °C for 1 h, both the Mannich adduct **76** and α-pyrone **77** could be detected through TLC and LC-MS analysis. However, despite the large steric hindrance, the Mannich adduct **76** was almost fully converted into *α*-pyrone **77** after the reaction mixture was stirred at 80 °C for 5 h. The structure of compound **77** was characterized by NMR, IR and HRMS.



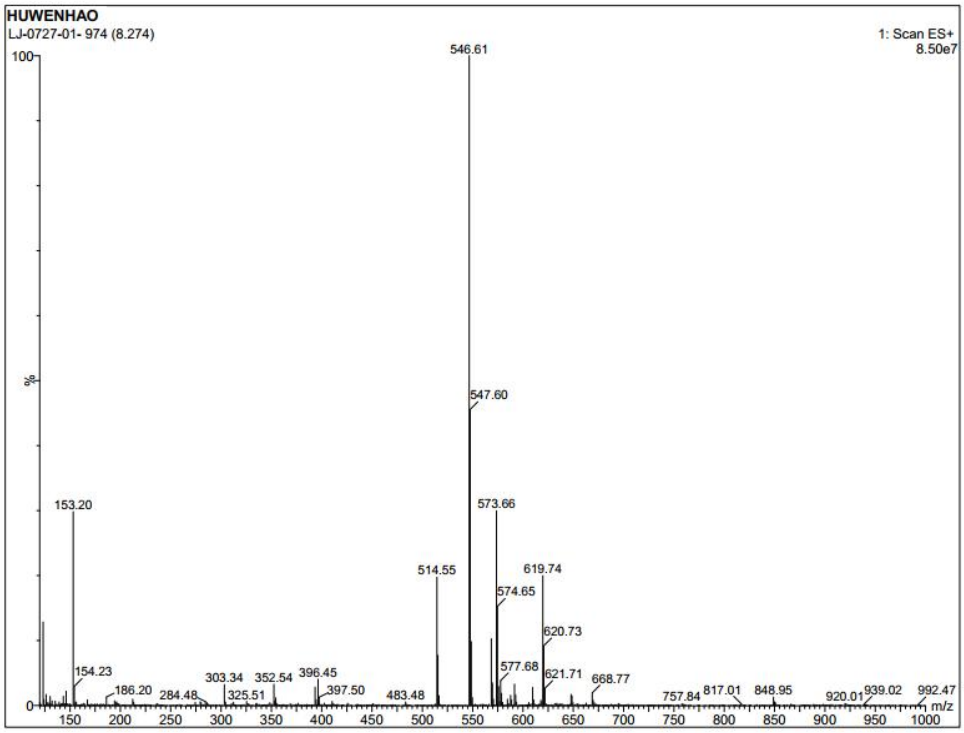
1c (1.2 equiv) **2c** (1.0 equiv)

76
Chemical Formula: $C_{36}H_{35}NO_4$
Exact Mass: 545.2566
Molecular Weight: 545.6674

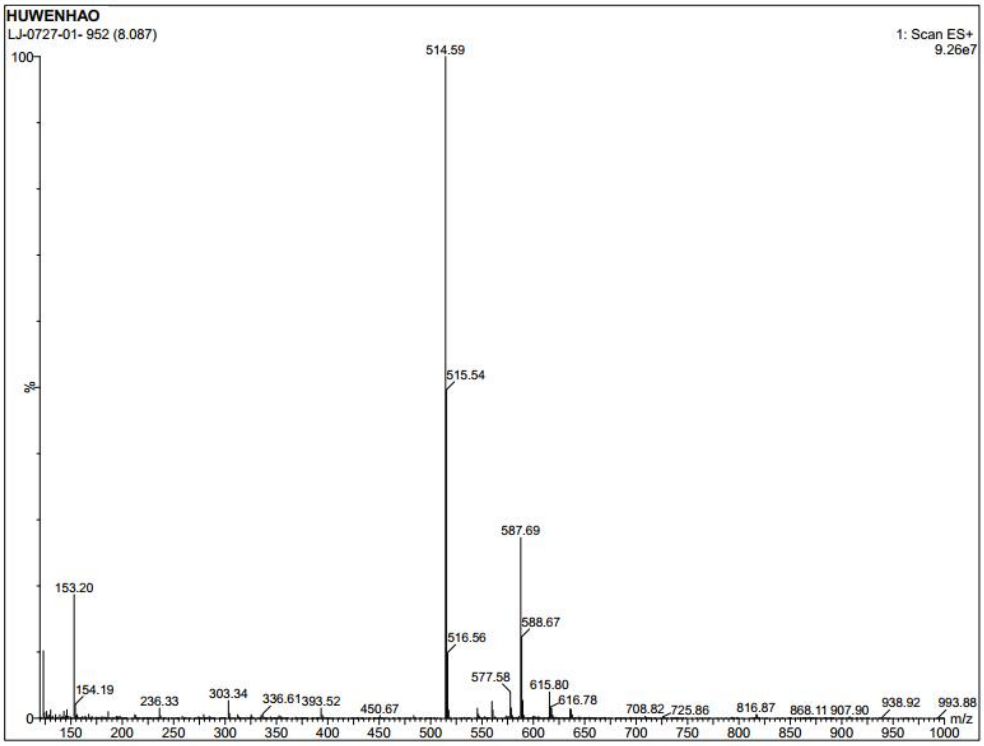
77
Chemical Formula: $C_{35}H_{31}NO_3$
Exact Mass: 513.2304
Molecular Weight: 513.6255



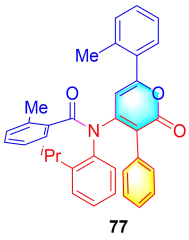
Monitoring the reaction by TLC



After 1 h



After 5 h



77

The reaction was run at 80 °C for 5 h, affording product **77** as a pale green solid (35.9 mg, 70% yield, m.p. = 195-196 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 (d, J = 5.0 Hz, 3H), 1.19 (d, J = 7.0 Hz, 3H), 2.31 (brs, 3H), 2.46 (brs, 3H), 3.18 (brm, 1H), 6.15-6.66 (m, 3H), 6.91-7.18 (m, 7H), 7.24-7.28 (m, 6H), 7.37 (t, J = 7.5 Hz, 1H), 7.47-7.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.71, 163.40, 159.79, 138.29, 136.68, 132.41, 131.77, 131.28, 130.40, 130.34, 129.56, 129.06, 128.38, 128.33, 128.08, 127.64, 127.06, 126.14, 124.76, 107.82, 28.39, 23.85, 23.34, 20.71, 19.93. IR (ATR): 1702, 1676, 1603, 1534, 1423, 1396, 1283, 956, 782, 773, 652, 565. HRMS (ESI): Exact mass calcd for $C_{35}H_{31}NO_3Na$ $[M+Na]^+$: 536.2196, Found: 536.2191.

7) Device Fabrication and Characterizations

At first, we prepared single component **51** or SimCP2 solution (10 mg ml^{-1}, chlorobenzene as solvent) in N_2-filled glovebox and then thoroughly dissolved by successive heat stirring at 50 °C for 2 h. After that, the blended solutions at different blending ratios (SimCP2:**51**, (100-x):x, x= 1~7 wt.%) were prepared by blending these solutions as required. For device fabrications, ITO-covered glass substrate (ITO thickness = 110 nm, sheet resistance = 15 Ω sq^{-1}) was cleaned and dried using routine method and then processed by UV-ozone treatment in air for 25 min (ref. J. Ye, Y. He, K. Li, L. Liu, C. Xi, Z. Liu, Y. Ma, B. Zhang, Y. Bao, W. Wang, Y. Cheng, L. Niu, *ACS Appl. Mater. Interfaces* **2022**, *14*, 17698-17708). After that, water dispersion of PEDOT:PSS (Clevious PVP AI4083, Heraeus) was spin-coated onto the ITO substrate and then dried in air drying oven at 120 °C (30 min.). The thickness of such PEDOT:PSS layer was about 50 nm. Subsequently, the device samples were transferred into N_2-filled glovebox. Those SimCP2:**51** blended solutions were spin-coated onto the surface of ITO/PEDOT:PSS at 1800 rpm (1 min.), followed by thermal annealing at 100 °C (30 min.) to obtain the emissive layer with a thickness of ca. 30 nm. Finally, those device samples were loaded into thermal evaporating chamber (Angstrom Engineering Corp., Canada, EVOVAC) for the subsequent thermal evaporation of DPEPO (10 nm)/TmPyPB (50 nm)/LiF (1nm)/Al (100 nm) in sequence. The base pressure for thermal evaporation is generally less than 5×10^{-6} mbar and the deposition rate is 0.1 nm s^{-1}. The emissive area of each device is 3.5×4 mm^2, as defined by the overlap zone byetewen the Al top electrode and ITO bottom electrode. All those preparing procedures, except for the ITO and PEDOT:PSS layer, were performed under the protection of N_2-filled glove box (mBraun- UNIlab, Shanghai, $[O_2] < 0.1$ ppm, $[H_2O] < 0.1$ ppm).

Those as-fabricated OLEDs were then measured by commercial OLED testing equipment (FS-2000TR, Fstar, Soochow, China), in which current-voltage source Keithley 2400 and high-resolution spectroradiometer CS2000A were inter-connected and computer-controlled by a home-made software. During the measurement, luminance and EL spectra were directly measured by CS2000A. All those OLEDs were not encapsulated and tested in air. For the calculations of EQE performance parameters, these OLEDs were routinely assumed as Lambert emitters.

8) Physical and Material Properties

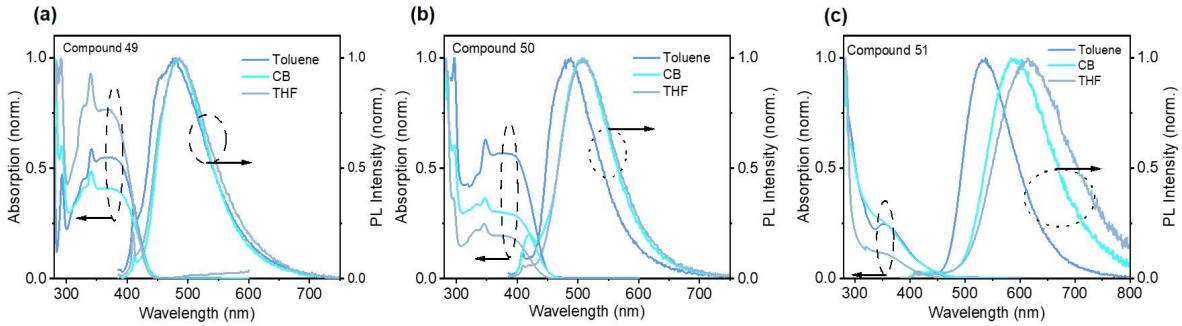


Figure S1. Absorption and PL spectra of compounds **49** (a), **50** (b) and **51** (c), respectively, in different solvent (10^{-5}M).

Table S1. Photophysical parameters of **49-51** in different solvents.

Compound	Solvent	$\lambda_{abs.}$ [a] [nm]	λ_{PL} [a] [nm]	E_g [a] [nm]	FWHM [nm]
49	Toluene	340	475	2.81	108
	CB	340	482	2.82	97
	THF	341	484	2.85	106
50	Toluene	347	485	2.77	93
	CB	345	507	2.74	99
	THF	345	510	2.80	103
51	Toluene	353	533	2.69	104
	CB	352	590	2.86	134
	THF	320	615	2.92	156

[a] Measured in solution with a concentration of 10^{-5} M.

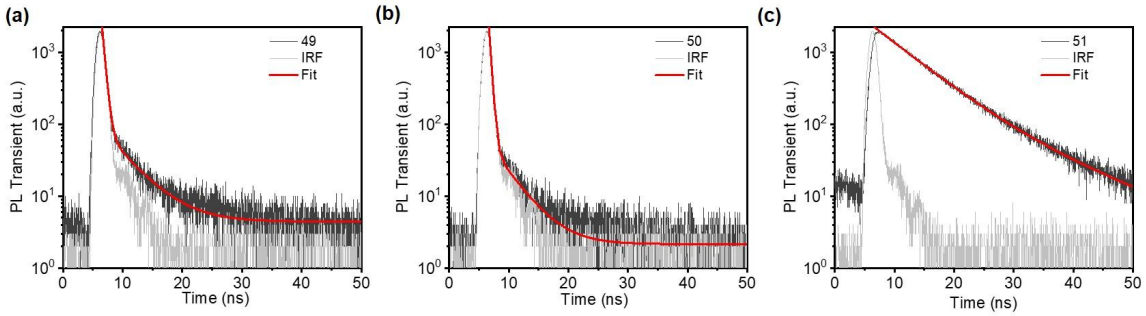


Figure S2. PL transient decay of compounds **49** (a), **50** (b) and **51** (c), respectively, in solution (10^{-5}M, CB as solvent).

Table S2. Fitting results of PL transient decays of **49-51** in solution.

Compound	τ_1 [ns]	A_1	τ_2 [ns]	A_2	χ^2	τ_{ave} [ns]
49	0.4455	1624.506	4.4219	76.6985	1.3865	1.7143
50	0.3385	1155.333	3.6333	48.0219	1.2854	1.3550
51	6.5389	1934.428	23.1639	102.3752	1.0211	9.1635

[a] The average lifetime calculated by $\tau_{ave} = \sum A_i\tau_i^2/\sum A_i\tau_i$, where A_i is the pre-exponential for lifetime τ_i (i = 1, 2) shown in the Table.

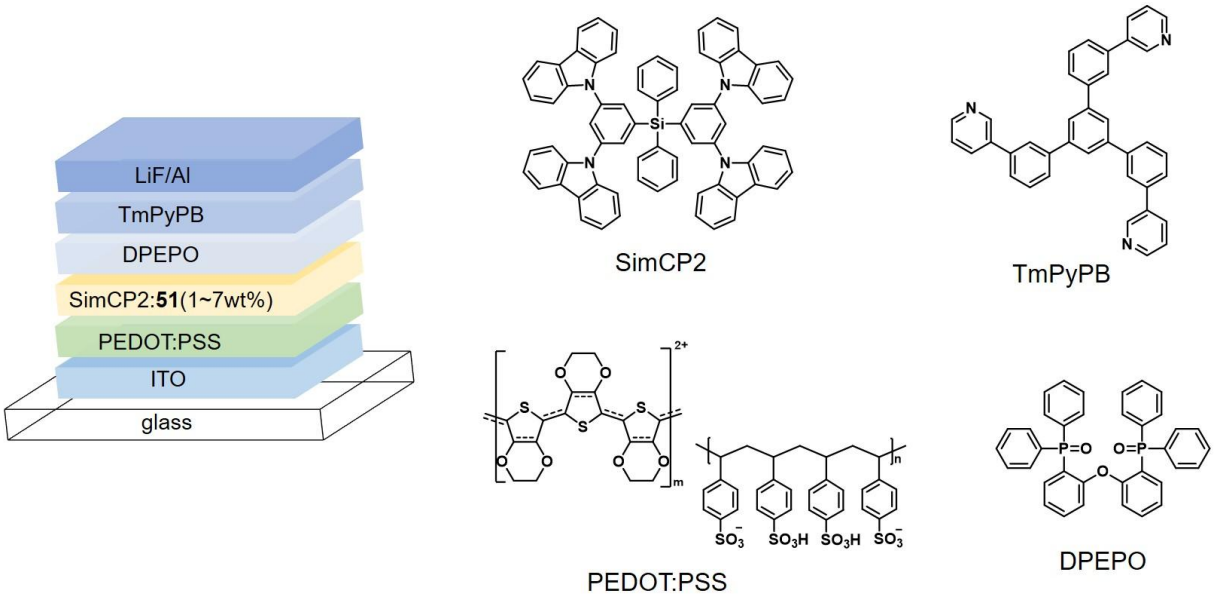


Figure S3. Chemical structures of materials (except **51**) using in solution-processed OLEDs.

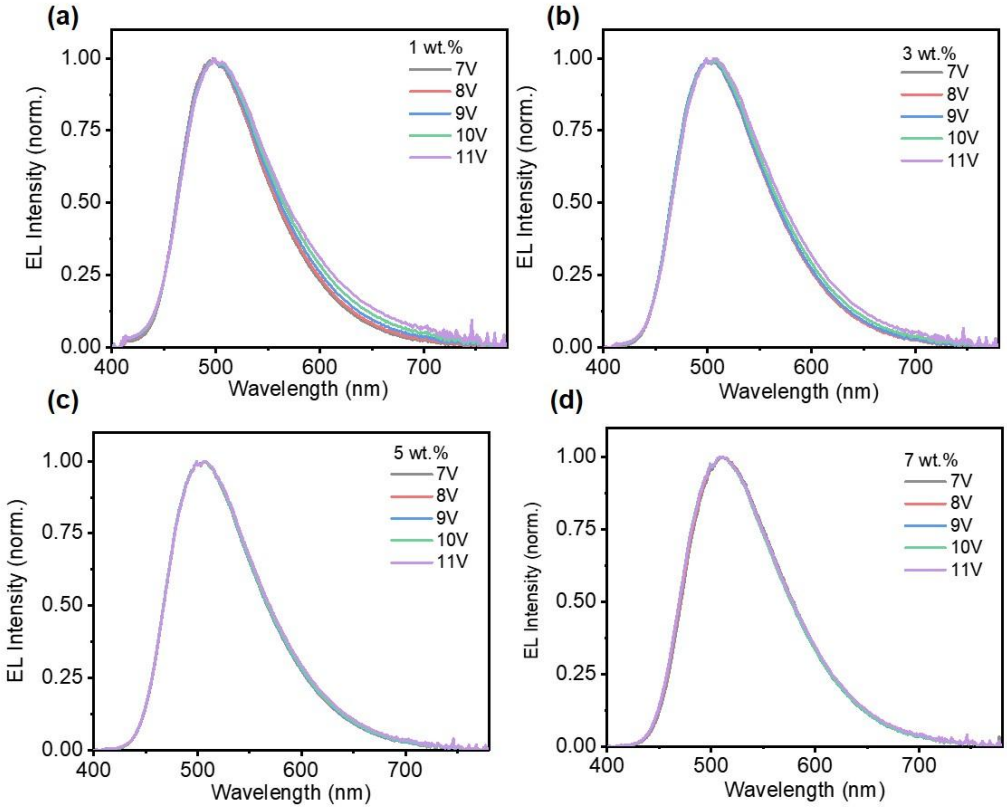
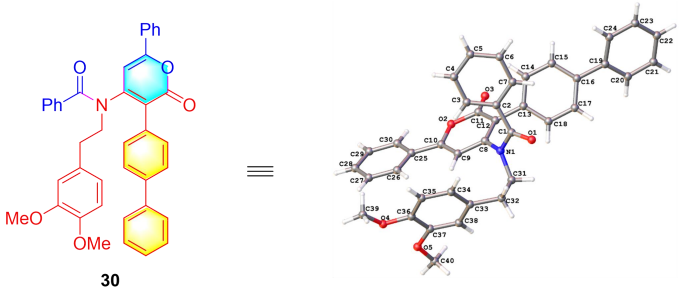


Figure S4. Bias-dependent EL spectra of solution-processed OLEDs using **47** dopant at different doping concentrations, i.e. 1 wt.% (a), 3 wt.% (b), 5 wt.% (c) and 7 wt.% (d), respectively.

9) X-Ray Crystallographic Data for Compounds 30, 47, 48, 72 and 74

Data intensity of **30** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 292.99(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2245130 (**30**).



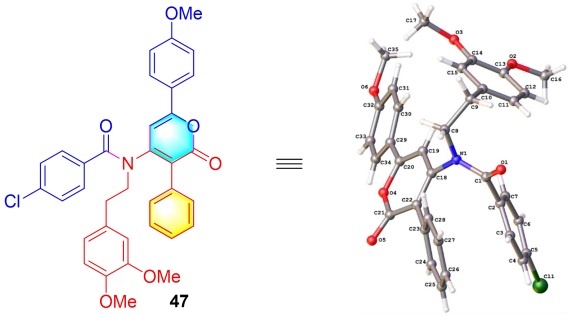
30

X-ray structure of product **30**

Crystal data.

Empirical formula	$C_{40}H_{33}NO_5$
Formula weight	607.67
Temperature/K	292.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.5520(14)
b/Å	10.2862(10)
c/Å	23.234(3)
α/°	90
β/°	95.963(10)
γ/°	90
Volume/Å^3	3221.2(6)
Z	4
ρ_{calc}g/cm^3	1.253
μ/mm^{-1}	0.082
F(000)	1280.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θrange for data collection/°	4.334 to 59.21
Index ranges	-18 ≤ h ≤ 14, -13 ≤ k ≤ 10, -32 ≤ l ≤ 22
Reflections collected	16913
Independent reflections	7598 [R_{int} = 0.0563, R_{sigma} = 0.1036]
Data/restraints/parameters	7598/0/418
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0724, wR_2 = 0.1445
Final R indexes [all data]	R_1 = 0.1788, wR_2 = 0.1931
Largest diff. peak/hole / e Å^{-3}	0.36/-0.21

Data intensity of **47** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 150.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2245131 (**47**).

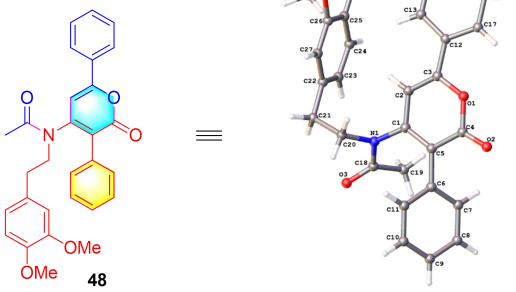


X-ray structure of product **47**

Crystal data.

Empirical formula	$C_{35}H_{30}ClNO_6$
Formula weight	596.05
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4332(5)
b/Å	10.0121(4)
c/Å	27.9684(13)
α/°	90
β/°	98.050(4)
γ/°	90
Volume/Å^3	2892.7(2)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	1.577
F(000)	1248.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θrange for data collection/°	6.384 to 147.464
Index ranges	$-12 \le h \le 12$, $-8 \le k \le 12$, $-34 \le l \le 29$
Reflections collected	10780
Independent reflections	5666 [R_{int} = 0.0409, R_{sigma} = 0.0602]
Data/restraints/parameters	5666/0/392
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1325
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1478
Largest diff. peak/hole / e Å^{-3}	0.30/-0.39

Data intensity of **48** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 150.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2245132 (**48**).

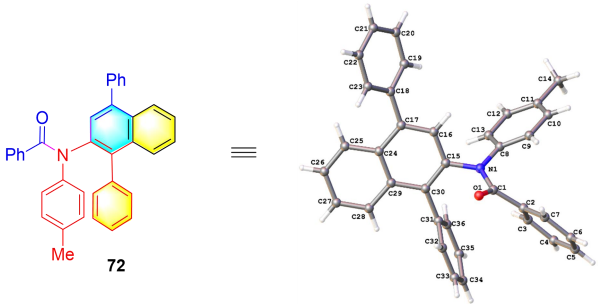


48

X-ray structure of product **48**

Crystal data.	
Empirical formula	$C_{29}H_{27}NO_5$
Formula weight	469.51
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.0361(5)
b/Å	14.2348(5)
c/Å	16.7656(6)
α/°	79.529(3)
β/°	88.302(3)
γ/°	75.050(4)
Volume/Å^3	2501.88(18)
Z	4
ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	0.085
F(000)	992.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θrange for data collection/°	4.214 to 59.222
Index ranges	-13 ≤ h ≤ 15, -18 ≤ k ≤ 19, -22 ≤ l ≤ 22
Reflections collected	21663
Independent reflections	11671 [R_{int} = 0.0320, R_{sigma} = 0.0651]
Data/restraints/parameters	11671/0/637
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1368
Final R indexes [all data]	R_1 = 0.0963, wR_2 = 0.1608
Largest diff. peak/hole / e Å^{-3}	1.12/-0.22

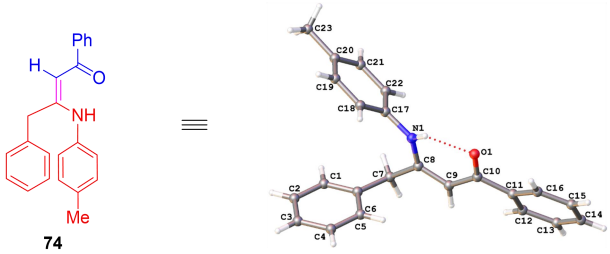
Data intensity of **72** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 170.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2245133 (**72**).



X-ray structure of product **72**

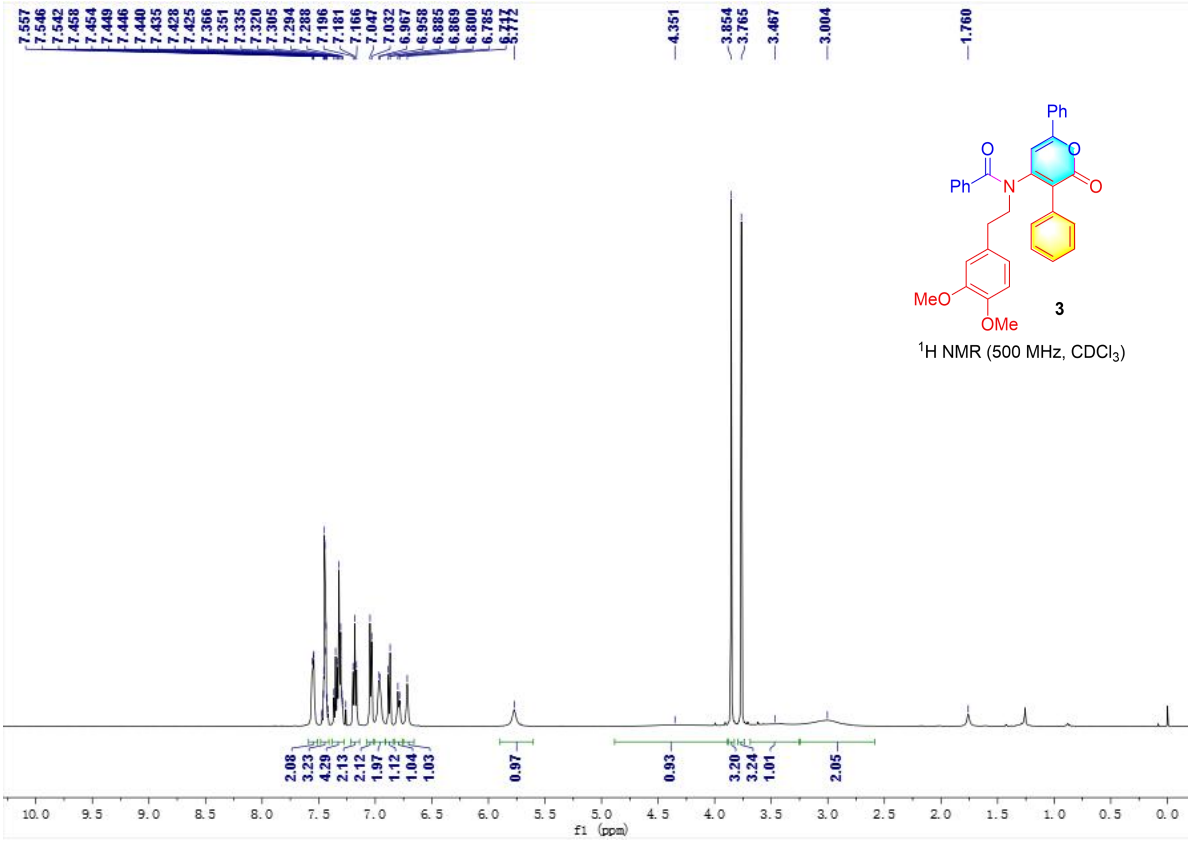
Crystal data.	
Empirical formula	$C_{36}H_{27}NO$
Formula weight	489.58
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.3653(9)
b/Å	11.5399(8)
c/Å	12.1483(9)
α/°	86.936(6)
β/°	75.711(7)
γ/°	69.063(7)
Volume/Å^3	1314.21(19)
Z	2
ρ_{calc}g/cm^3	1.237
μ/mm^{-1}	0.568
F(000)	516.0
Crystal size/mm^3	0.14 × 0.12 × 0.10
Radiation	Cu Kα (λ = 1.54184)
2Θrange for data collection/°	7.514 to 146.72
Index ranges	-12 ≤ h ≤ 12, -10 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	8974
Independent reflections	5121 [R_{int} = 0.0343, R_{sigma} = 0.0471]
Data/restraints/parameters	5121/0/344
Goodness-of-fit on F^2	1.164
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1269
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.1374
Largest diff. peak/hole / e Å^{-3}	0.18/-0.26

Data intensity of **74** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 170.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2245134 (**74**).

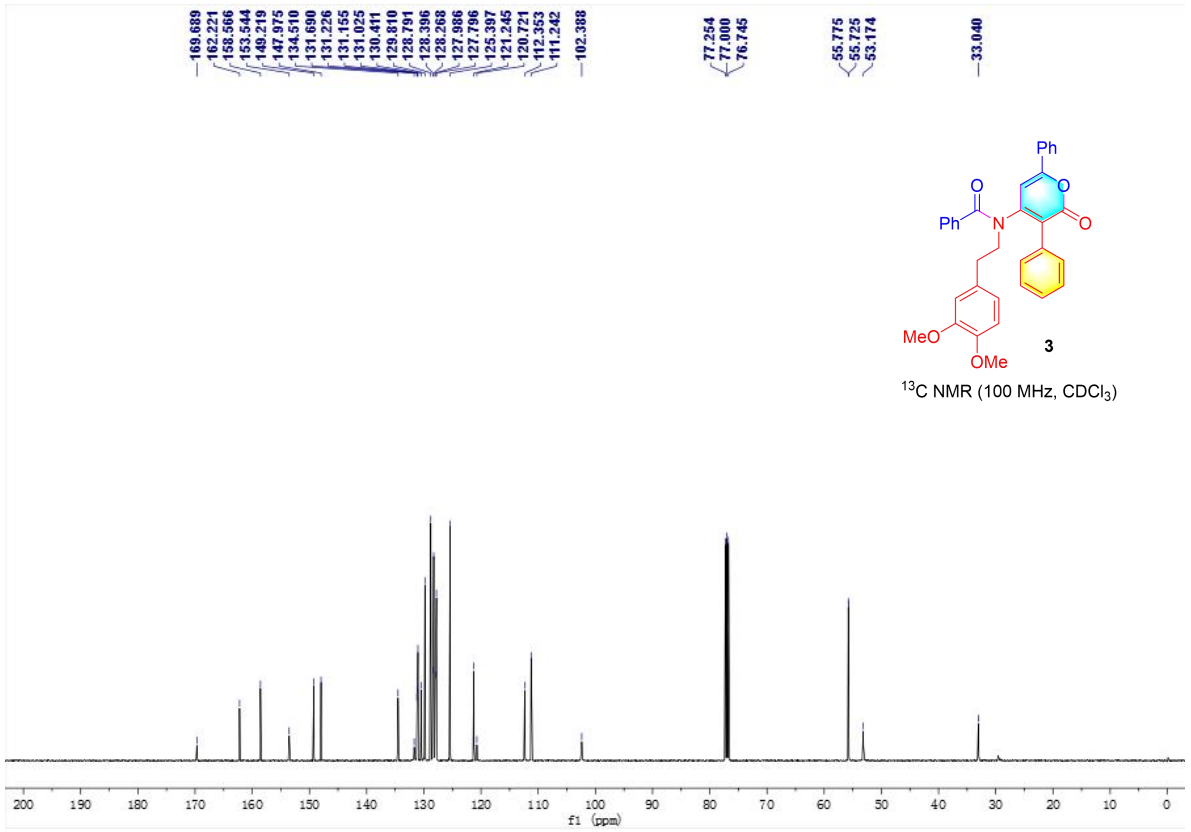


Crystal data.	
Empirical formula	$C_{23}H_{21}NO$
Formula weight	327.41
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.8318(4)
b/Å	11.6046(8)
c/Å	26.5835(15)
α/°	86.525(5)
β/°	87.942(5)
γ/°	87.181(5)
Volume/Å^3	1792.6(2)
Z	4
ρ_{calc}g/cm^3	1.213
μ/mm^{-1}	0.571
F(000)	696.0
Crystal size/mm^3	0.14 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θrange for data collection/°	6.666 to 148.43
Index ranges	-7 ≤ h ≤ 5, -14 ≤ k ≤ 14, -32 ≤ l ≤ 32
Reflections collected	12192
Independent reflections	7010 [R_{int} = 0.0461, R_{sigma} = 0.0583]
Data/restraints/parameters	7010/0/453
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0614, wR_2 = 0.1720
Final R indexes [all data]	R_1 = 0.0868, wR_2 = 0.1892
Largest diff. peak/hole / e Å^{-3}	0.40/-0.28

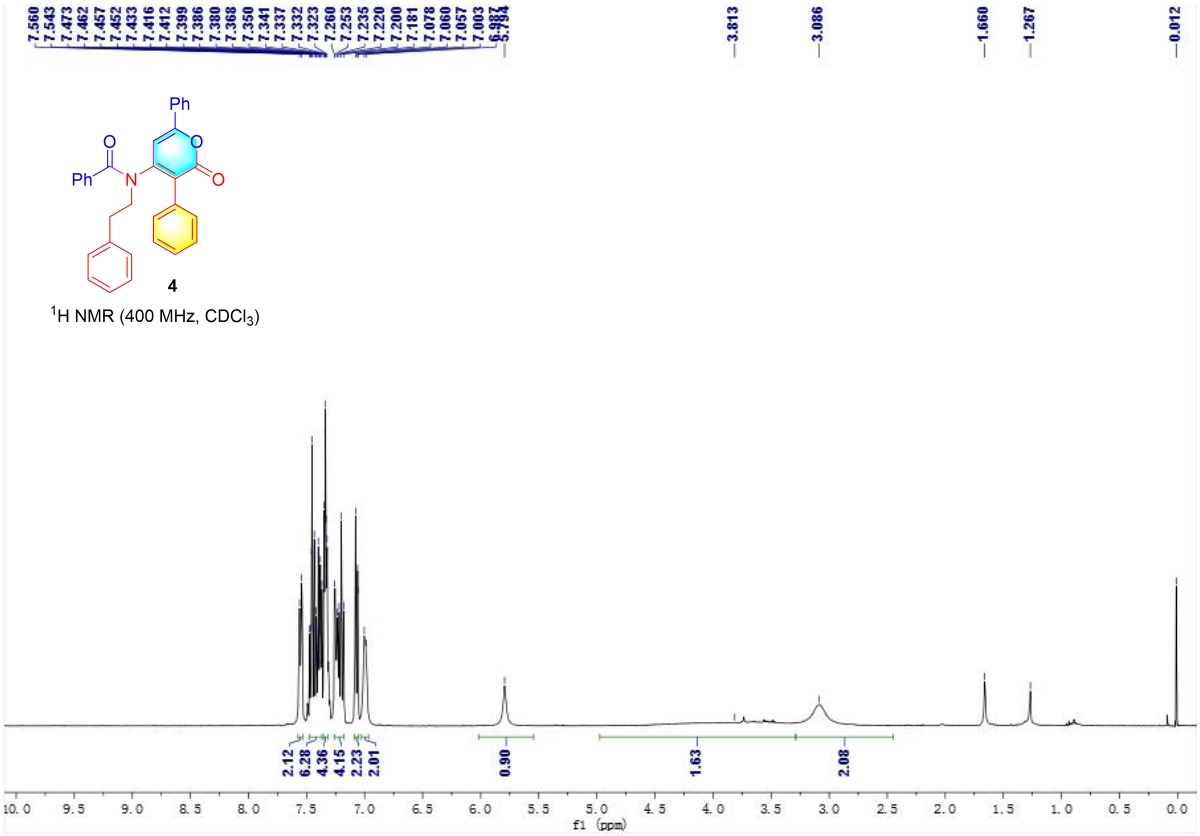
10) Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products 3-76



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

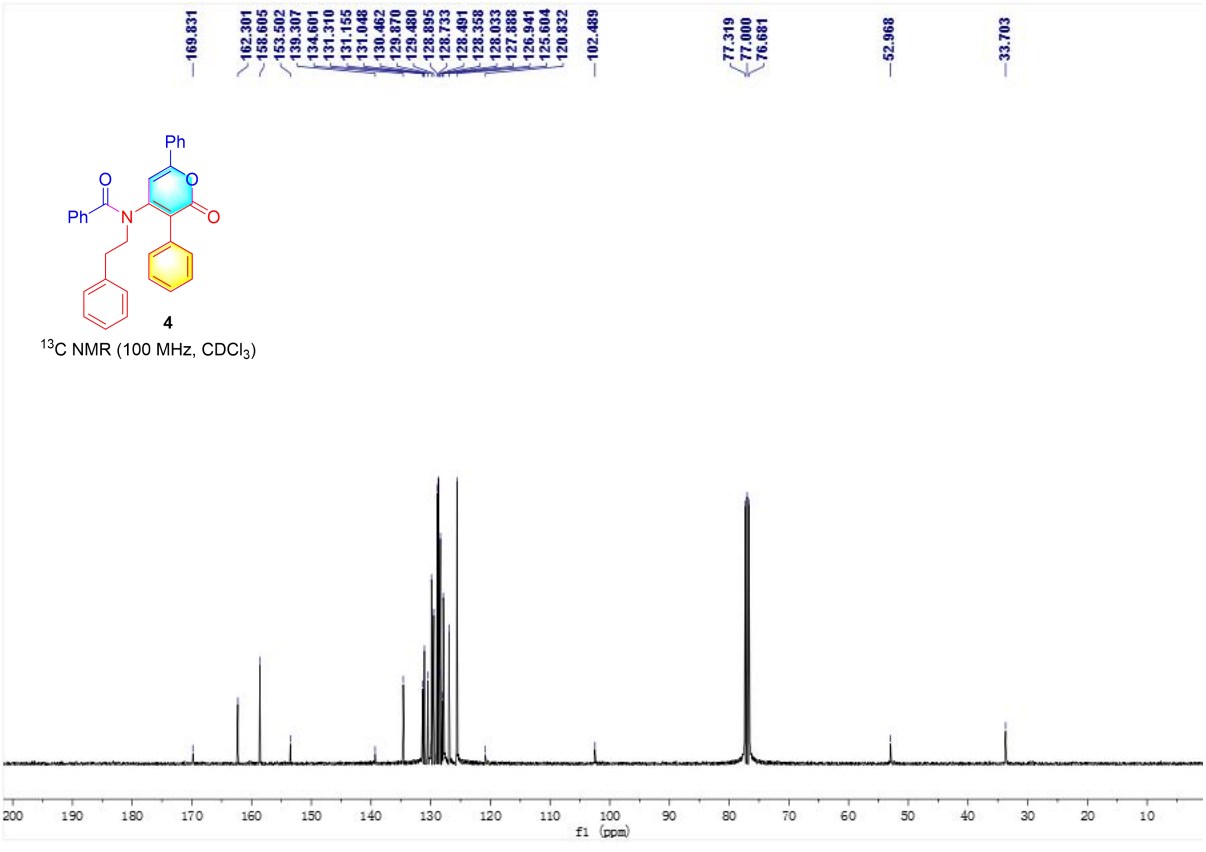


^{13}C NMR (100 MHz, $CDCl_3$)



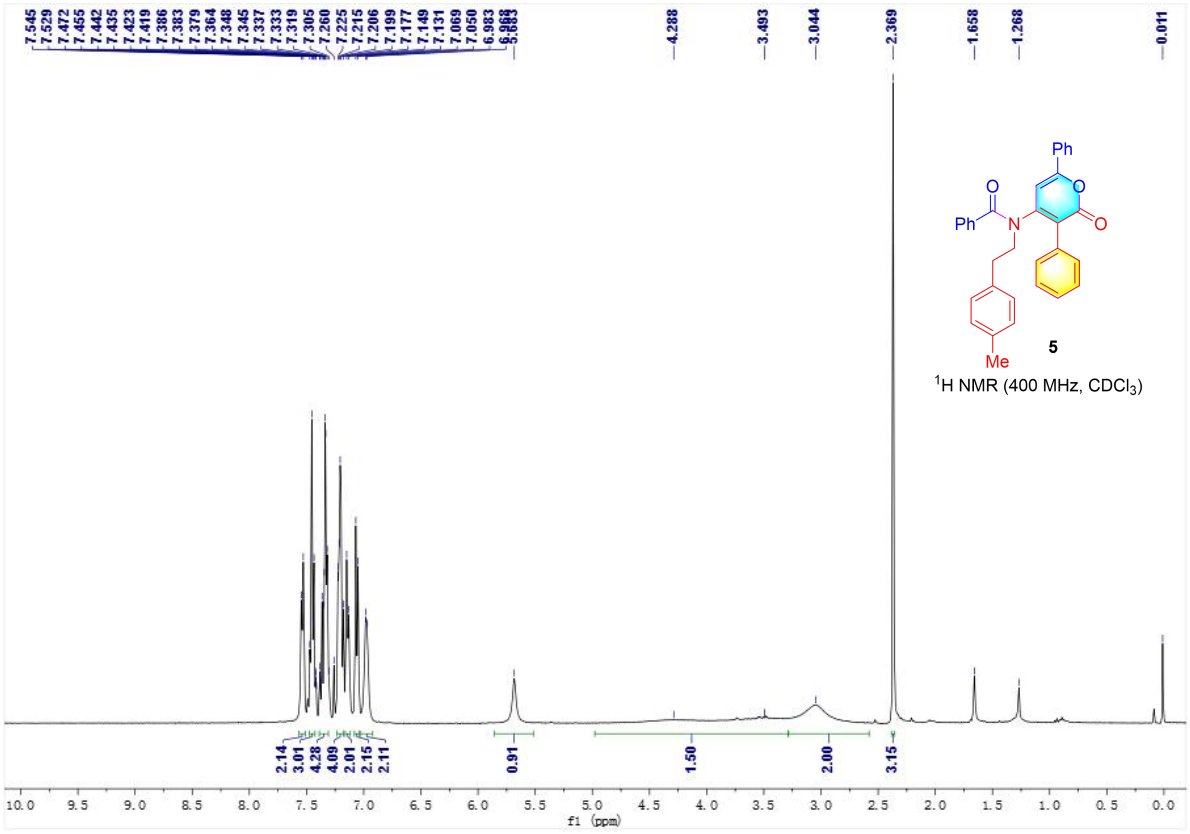
4

^{1}H NMR (400 MHz, $CDCl_3$)

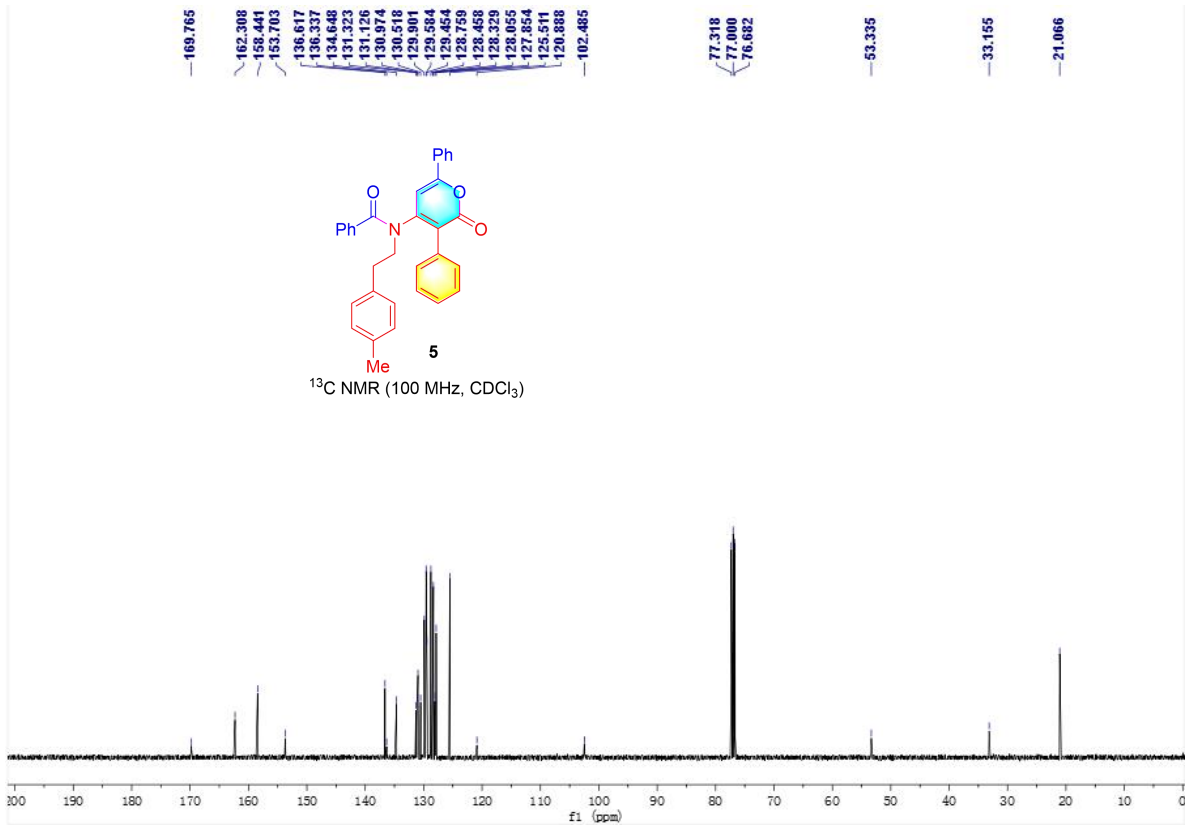


4

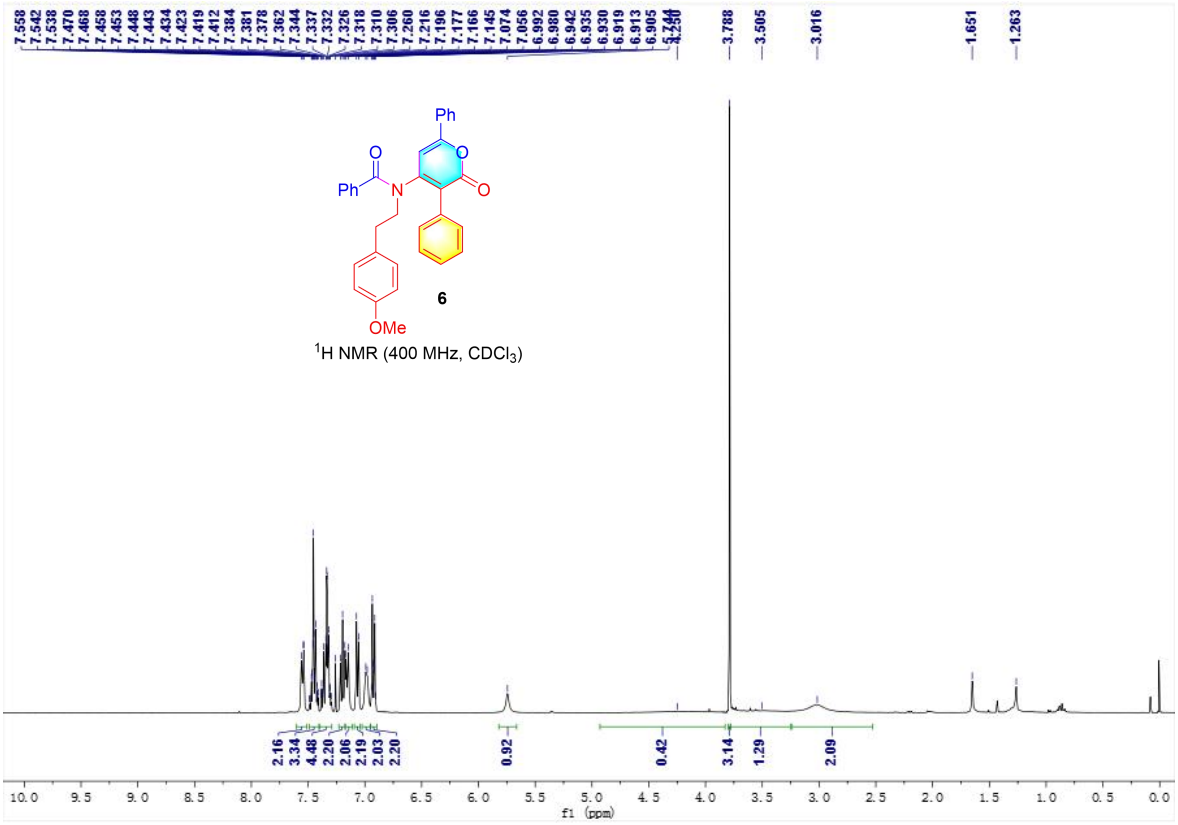
^{13}C NMR (100 MHz, $CDCl_3$)

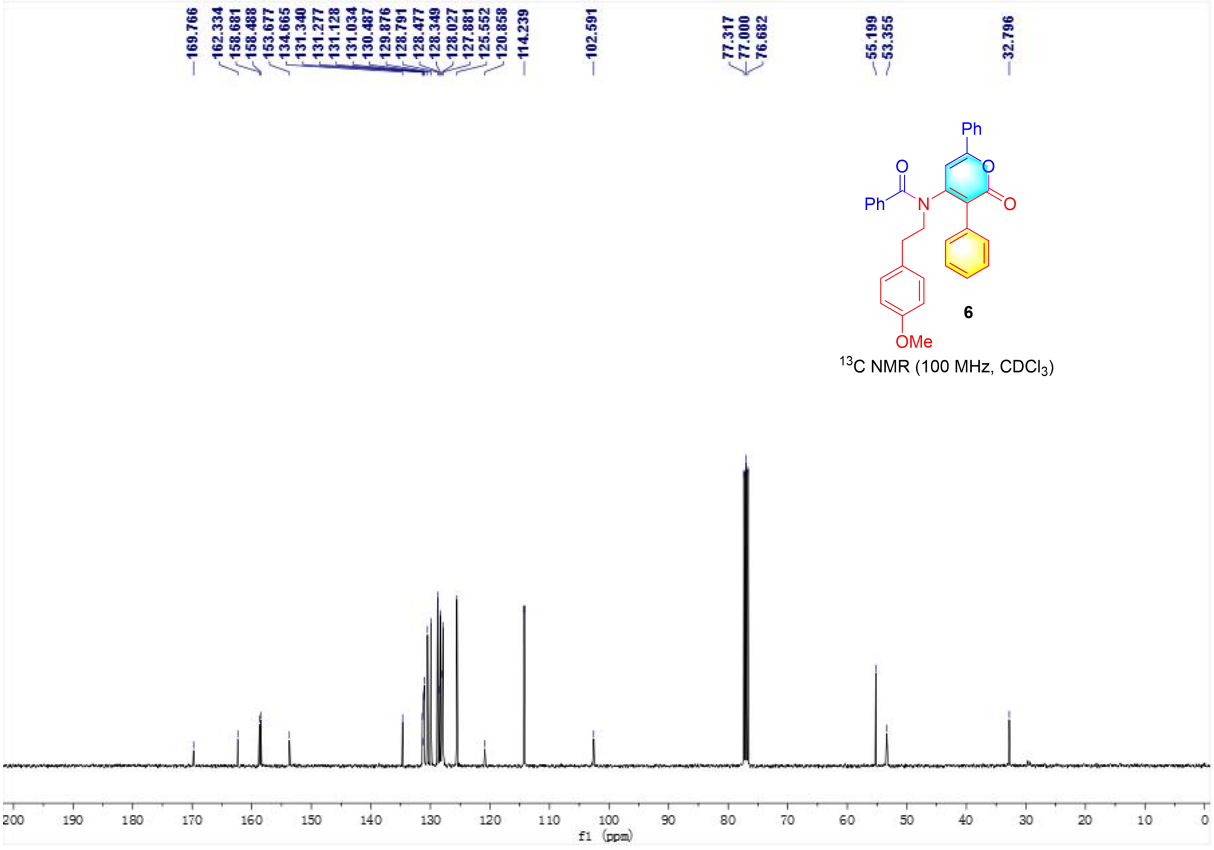


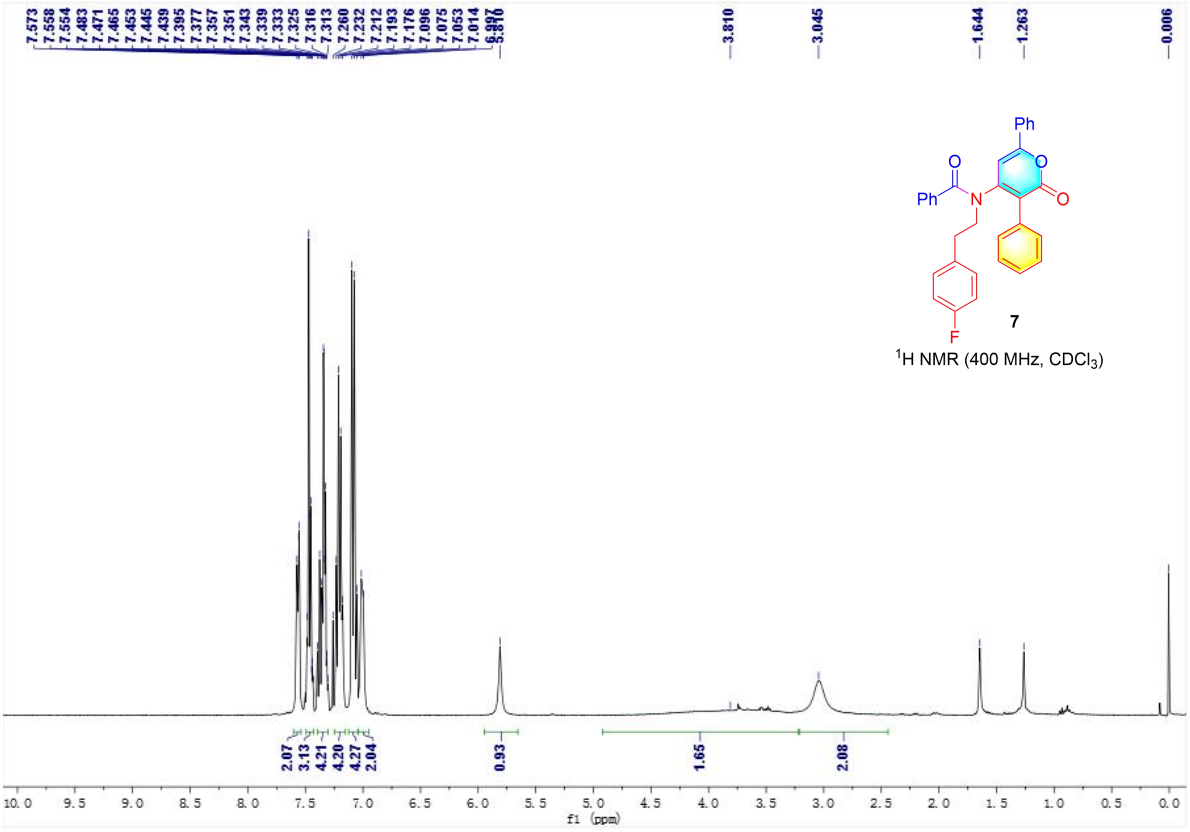
^{1}H NMR (400 MHz, $CDCl_3$)



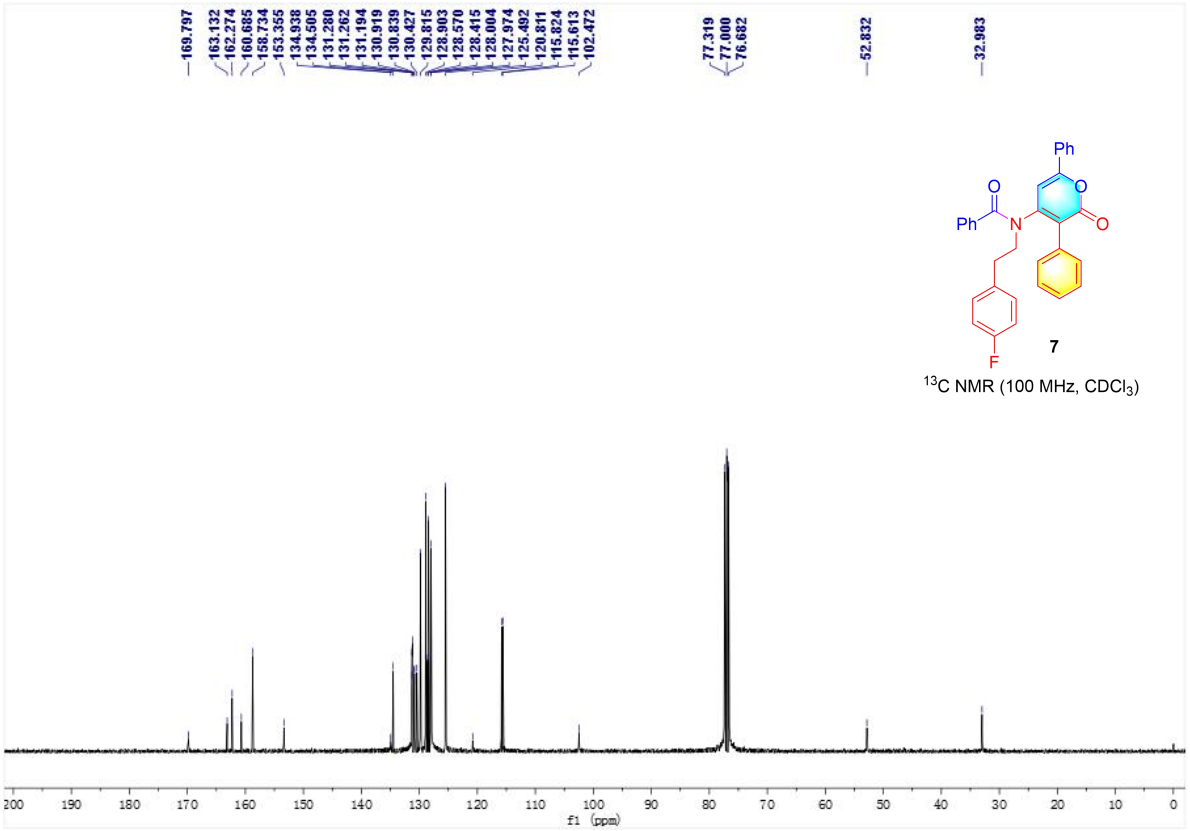
^{13}C NMR (100 MHz, $CDCl_3$)


Ph
O
O
Ph
N
O
OMe
6
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

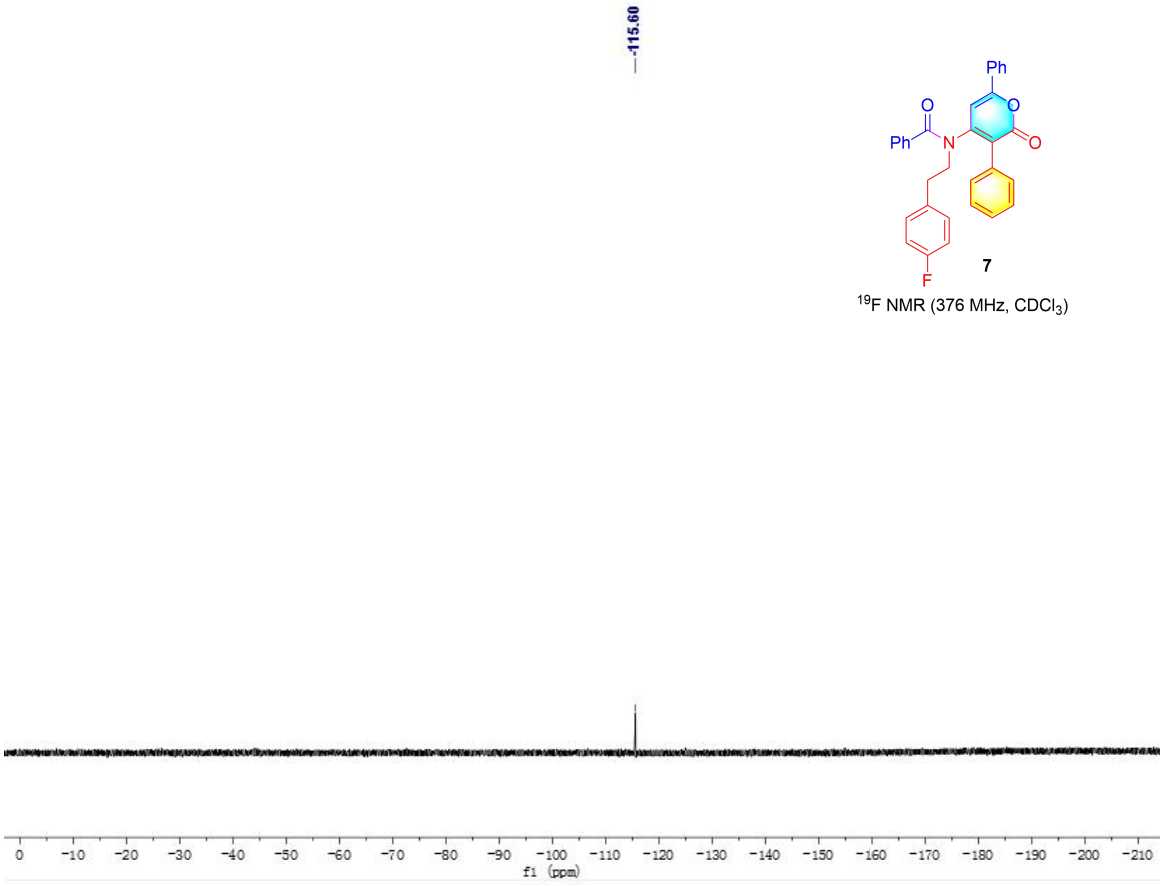

Ph
O
O
Ph
N
O
OMe
6
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

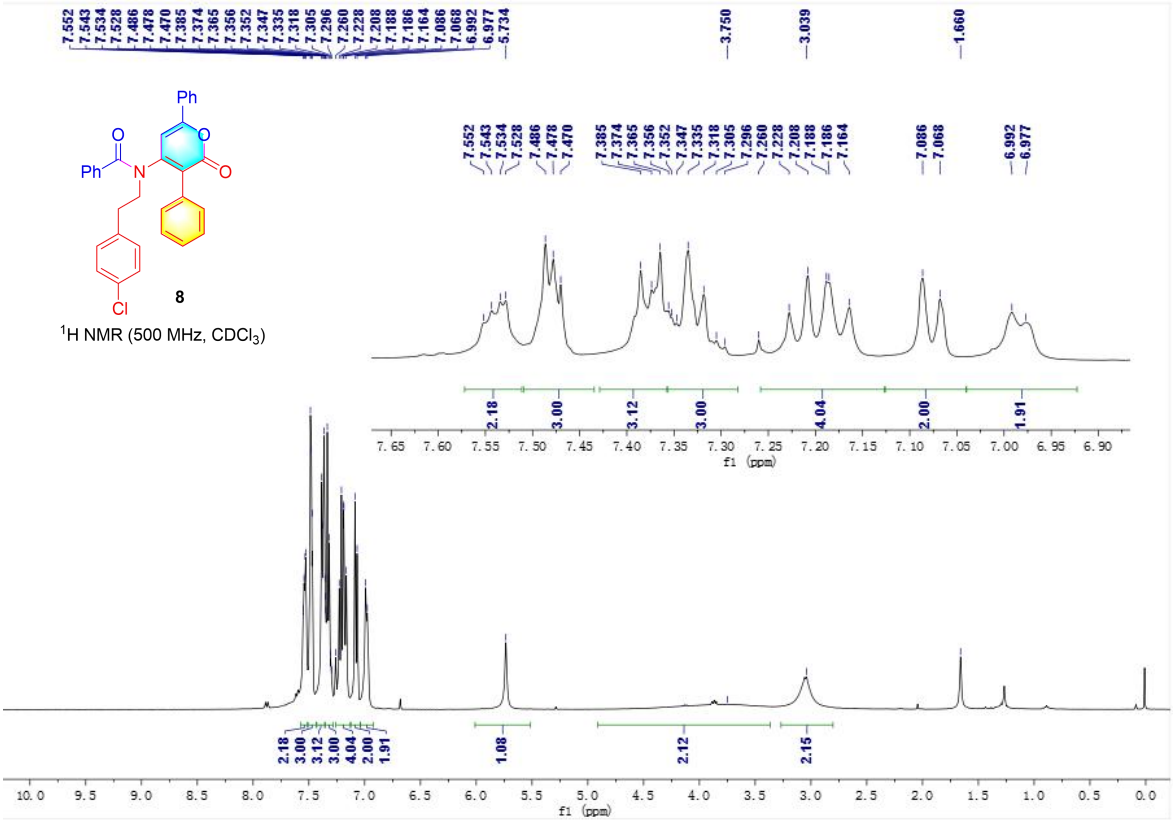


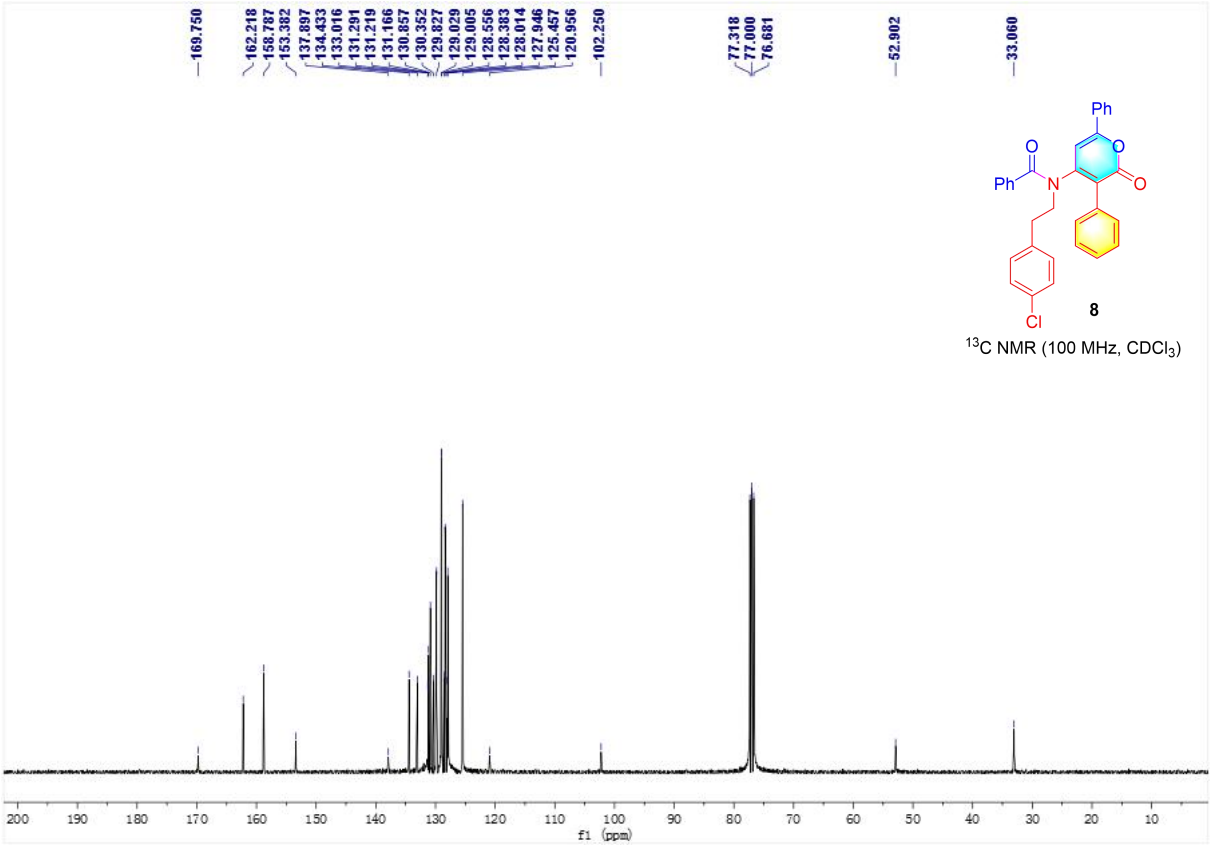
^{13}C NMR (100 MHz, $CDCl_3$)

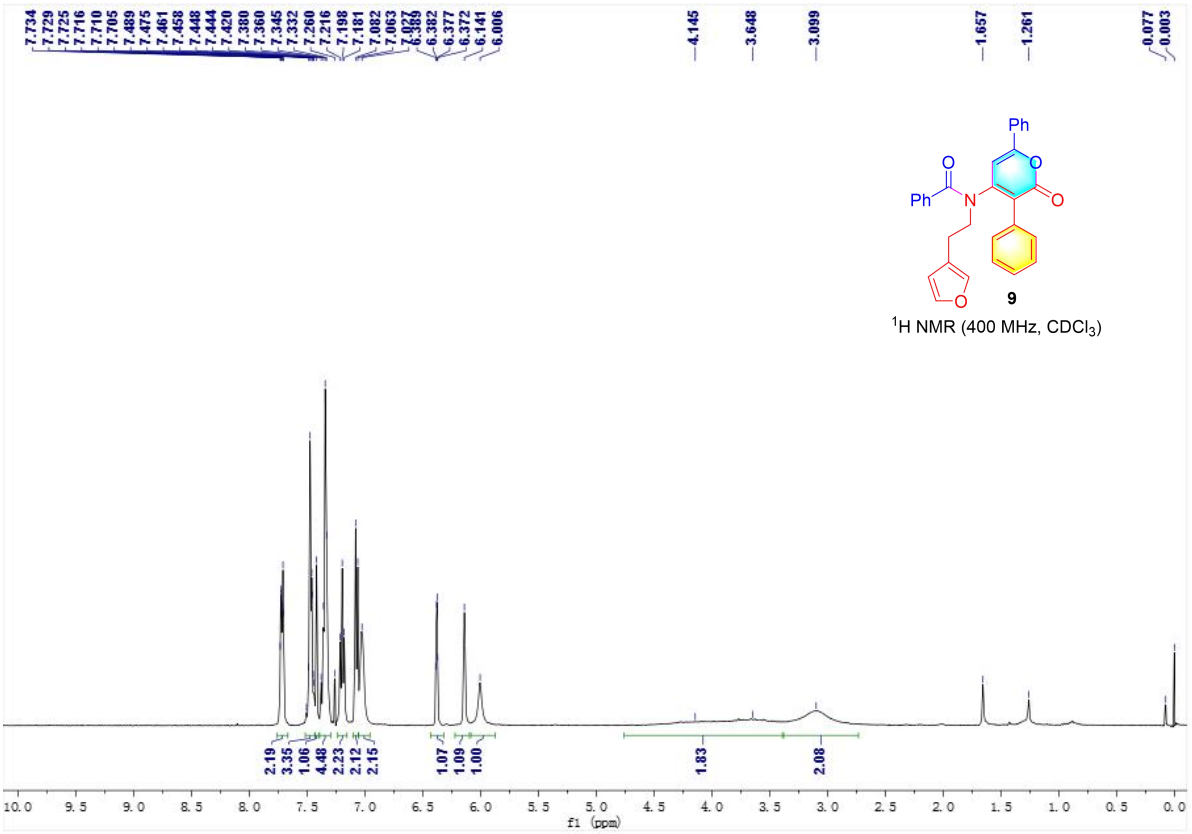


7

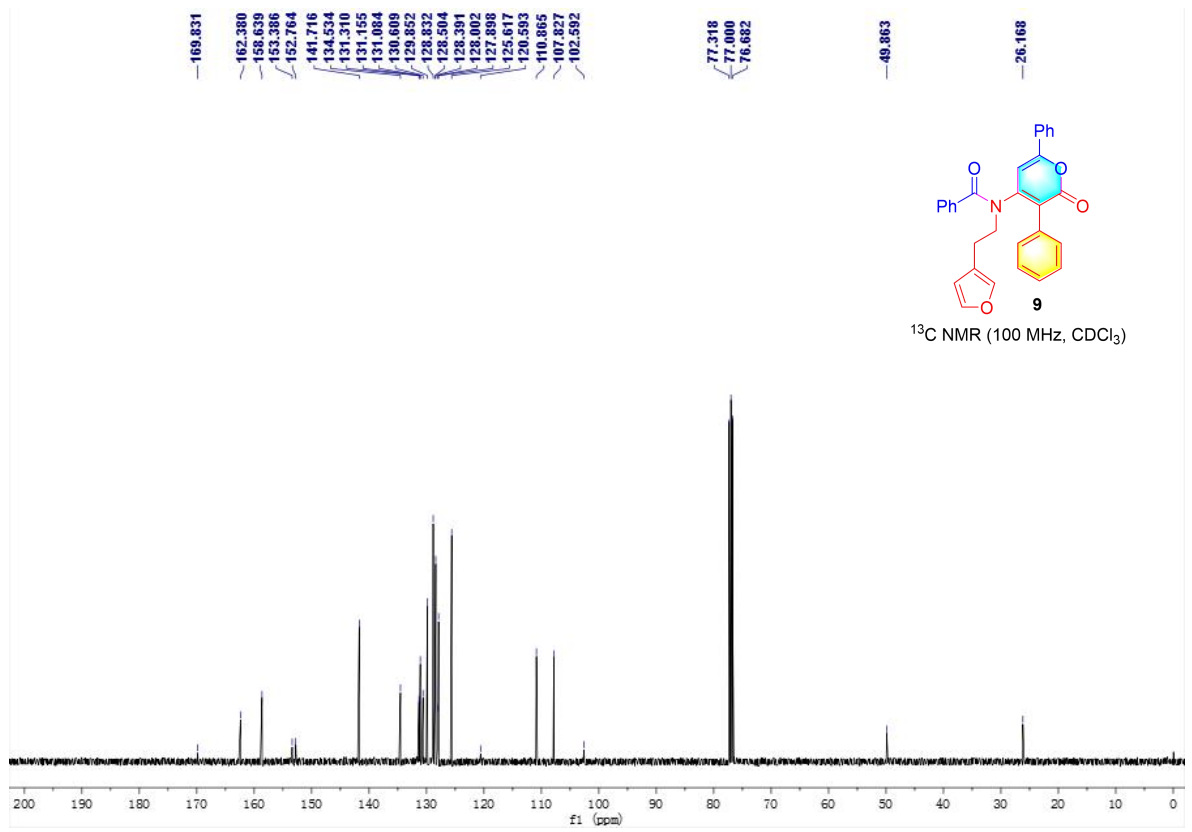
^{19}F NMR (376 MHz, $CDCl_3$)


8
1H NMR (500 MHz, CDCl3)

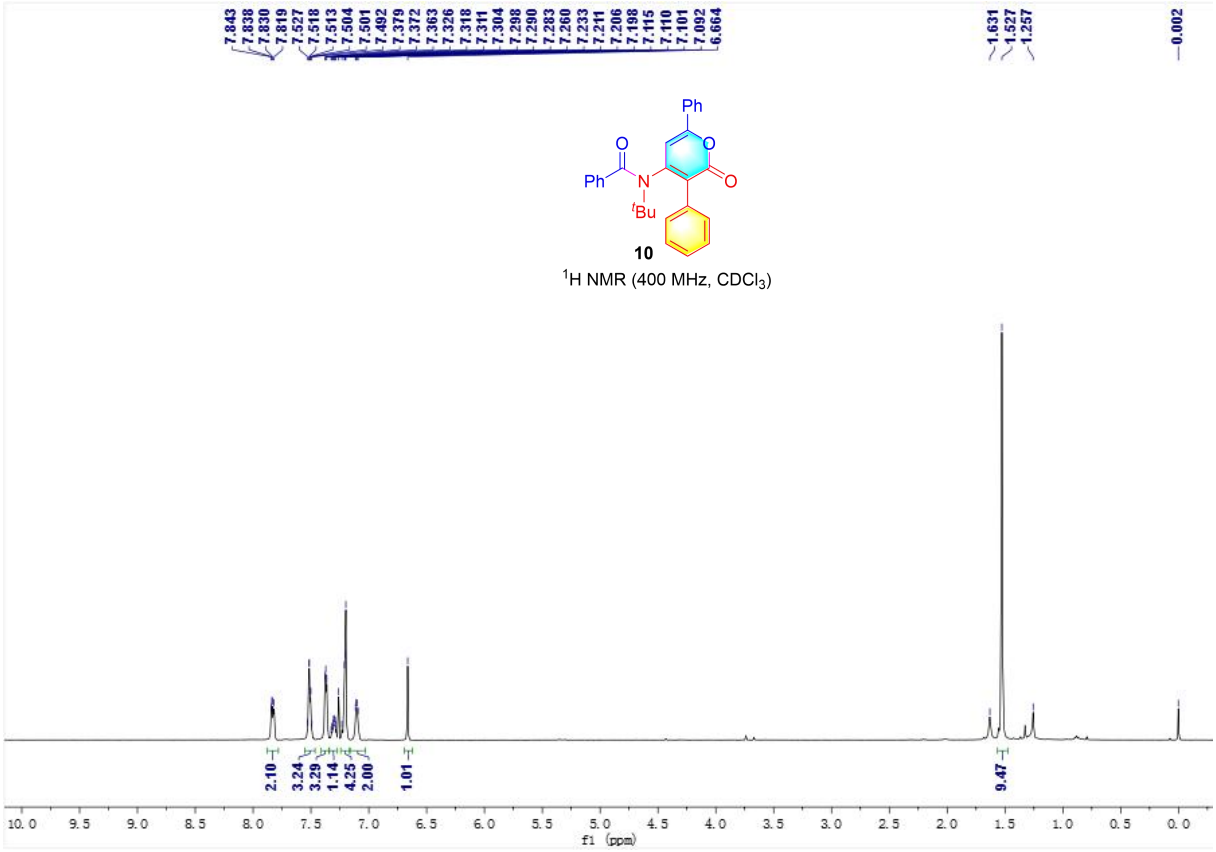

8
13C NMR (100 MHz, CDCl3)



^{1}H NMR (400 MHz, $CDCl_3$)

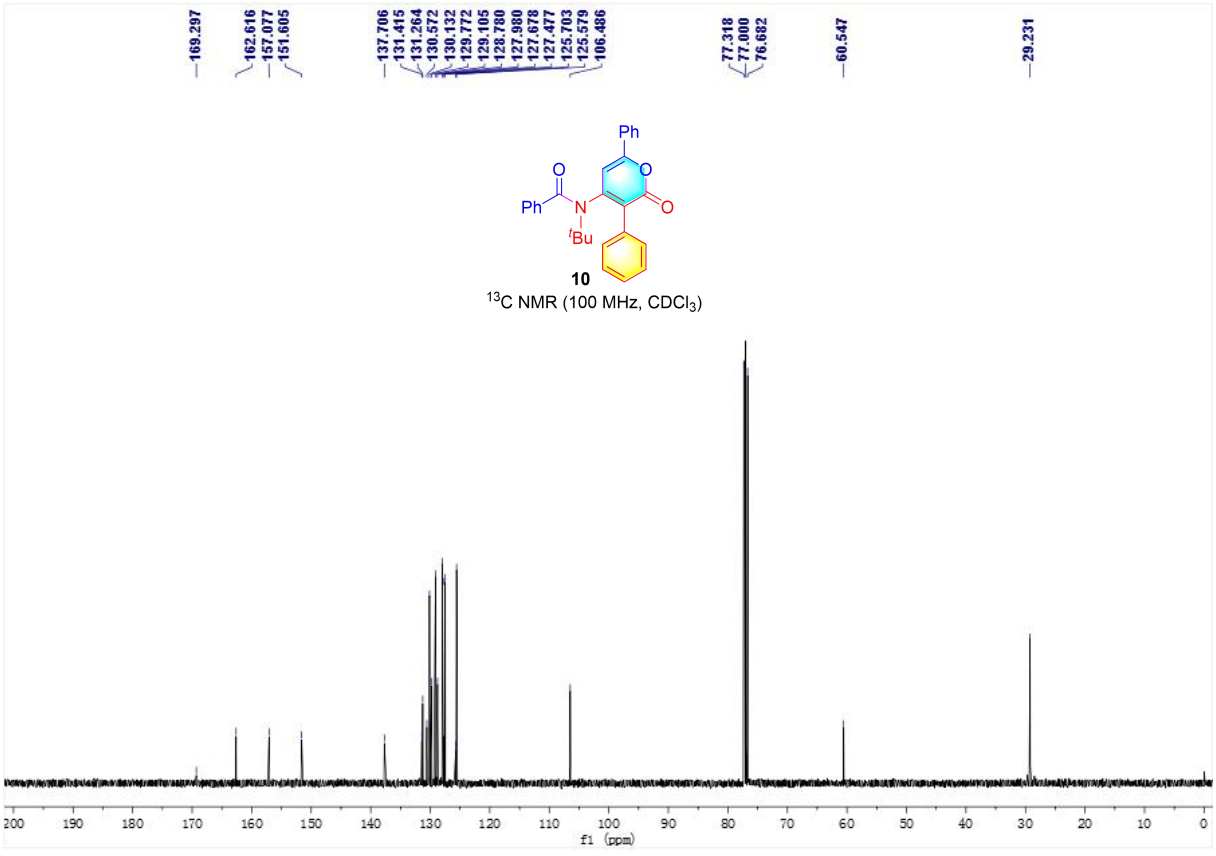


^{13}C NMR (100 MHz, $CDCl_3$)



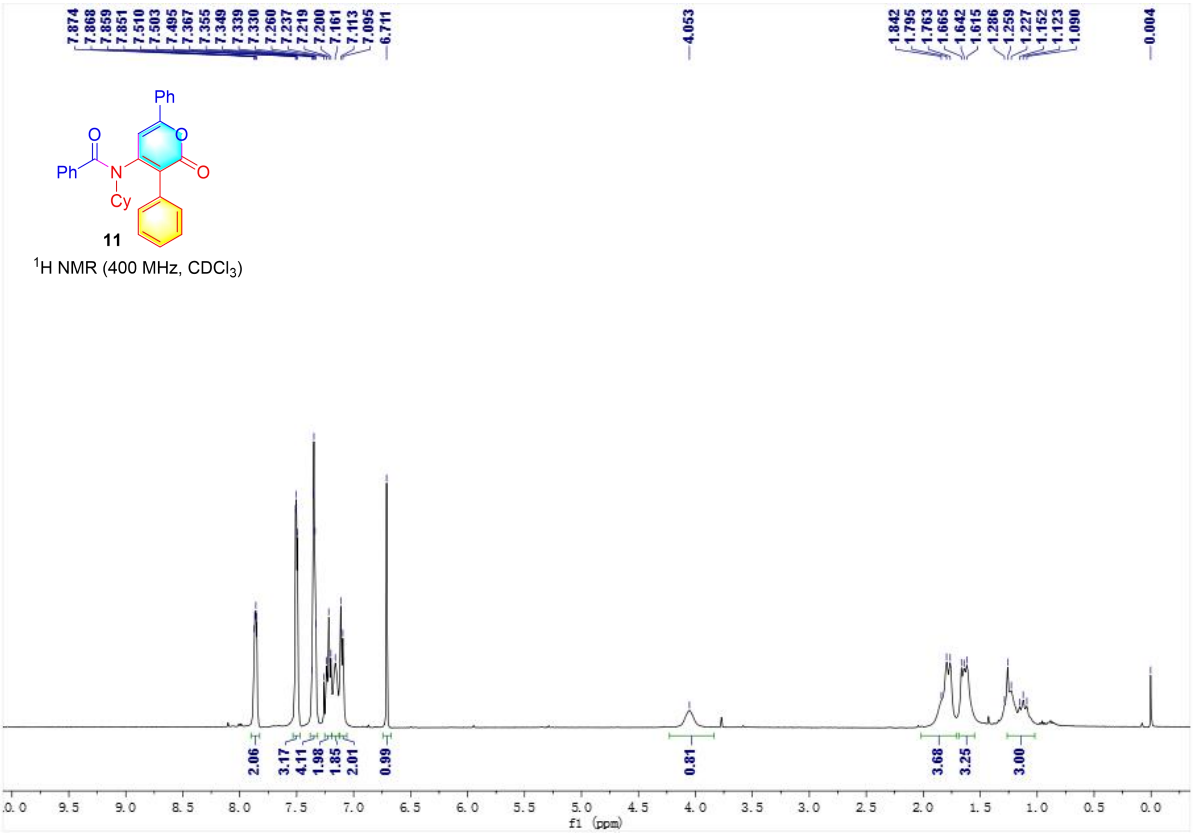
10

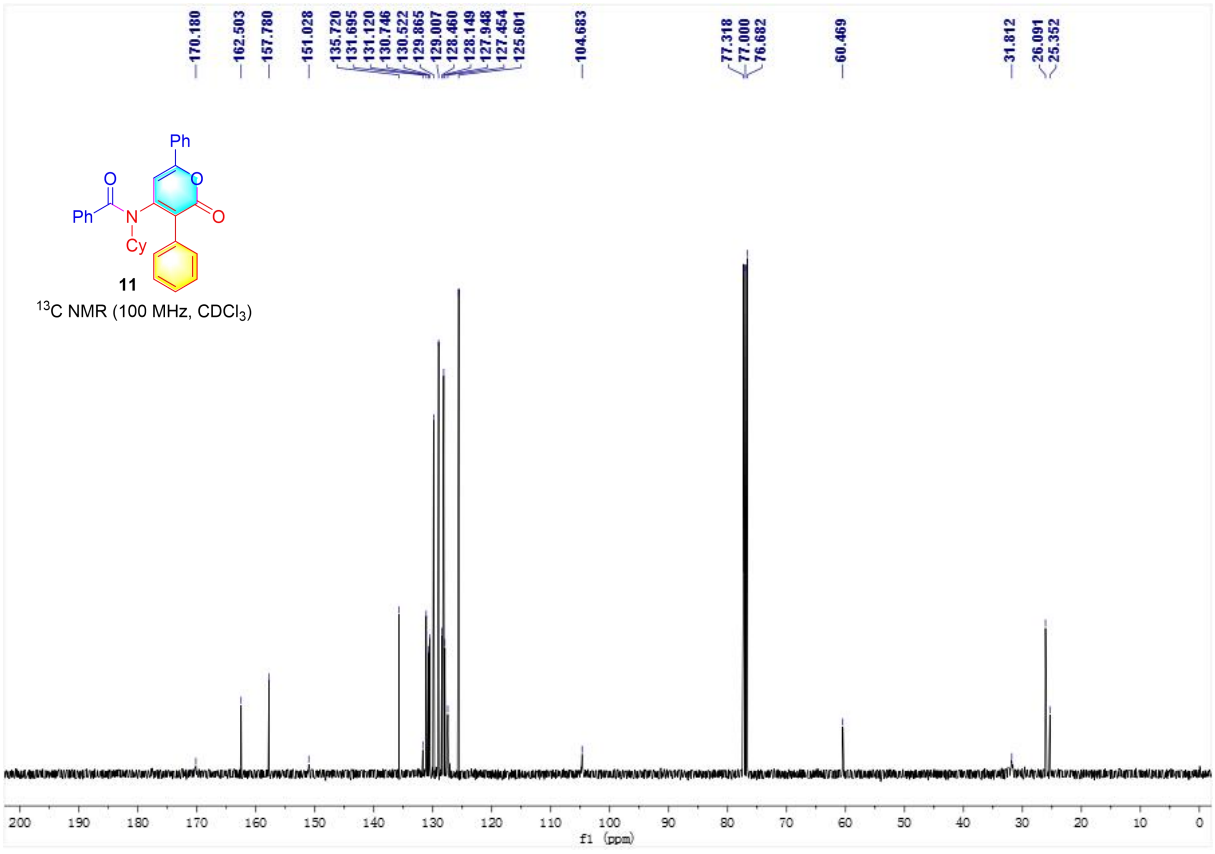
^{1}H NMR (400 MHz, $CDCl_3$)

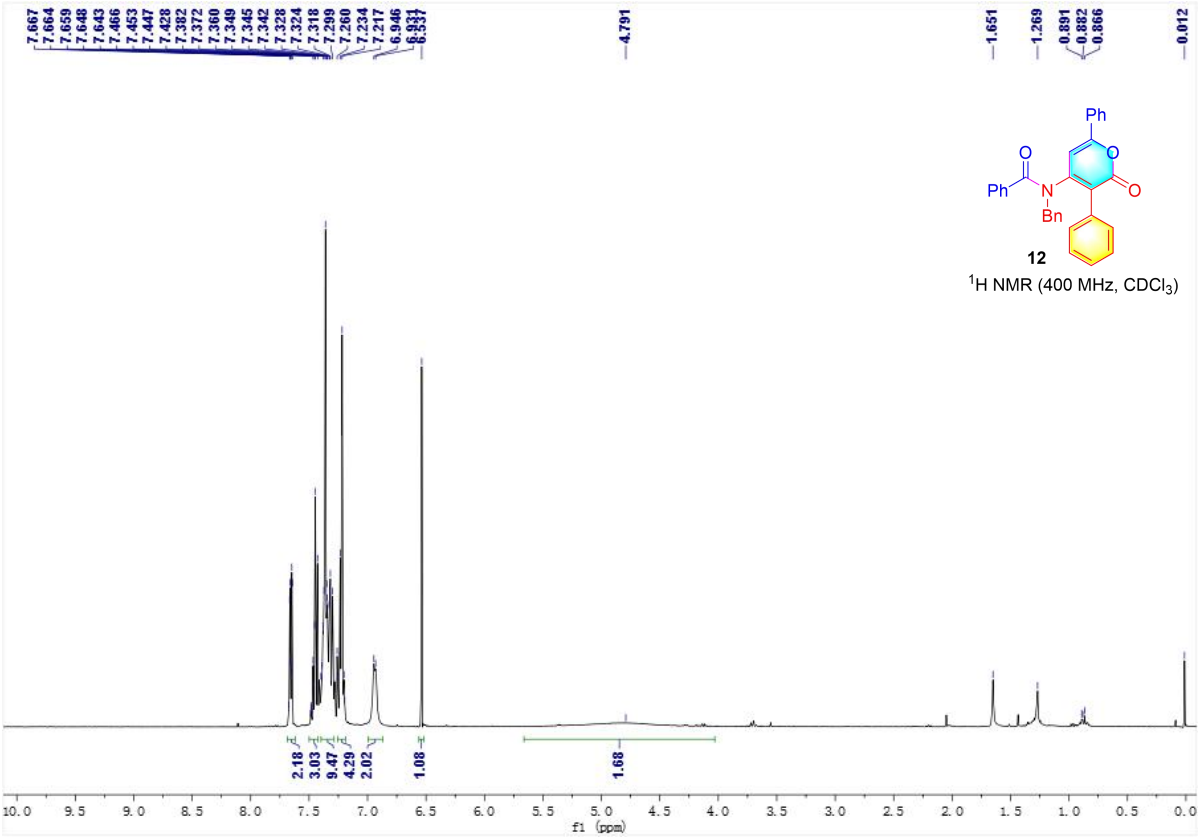


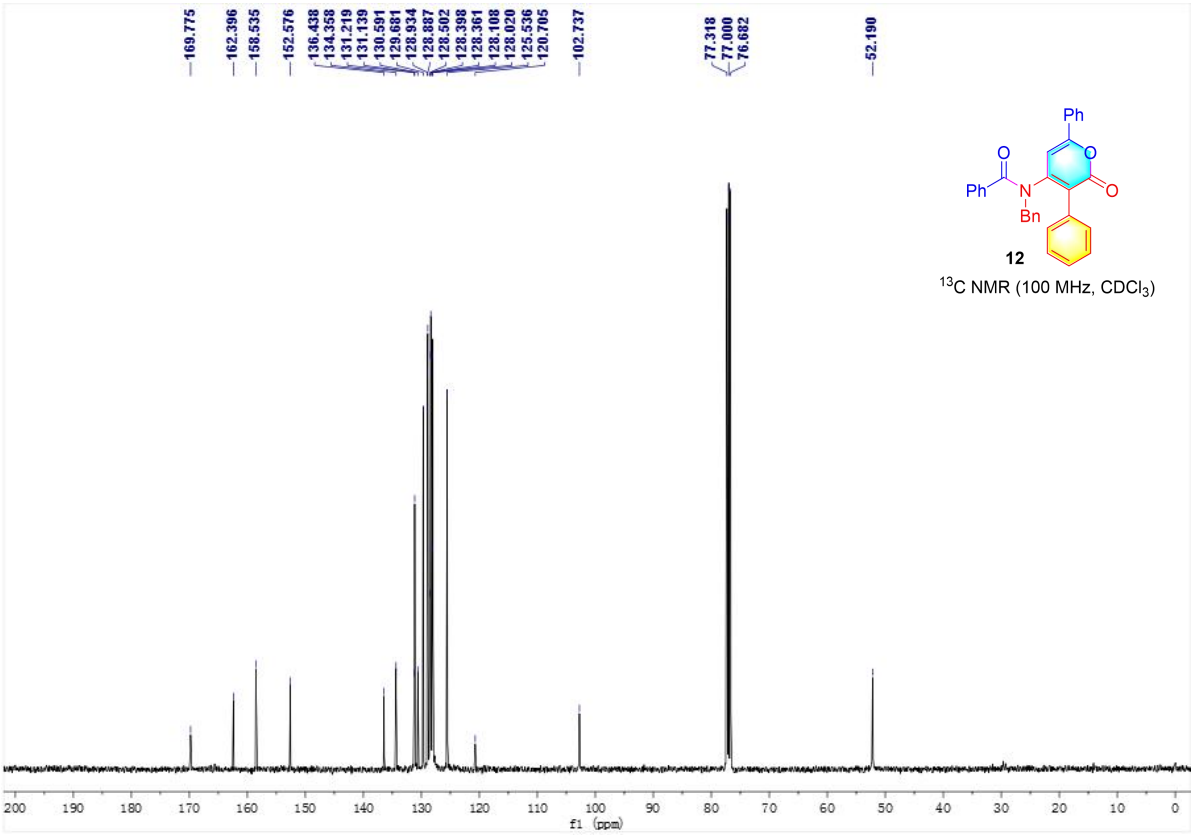
10

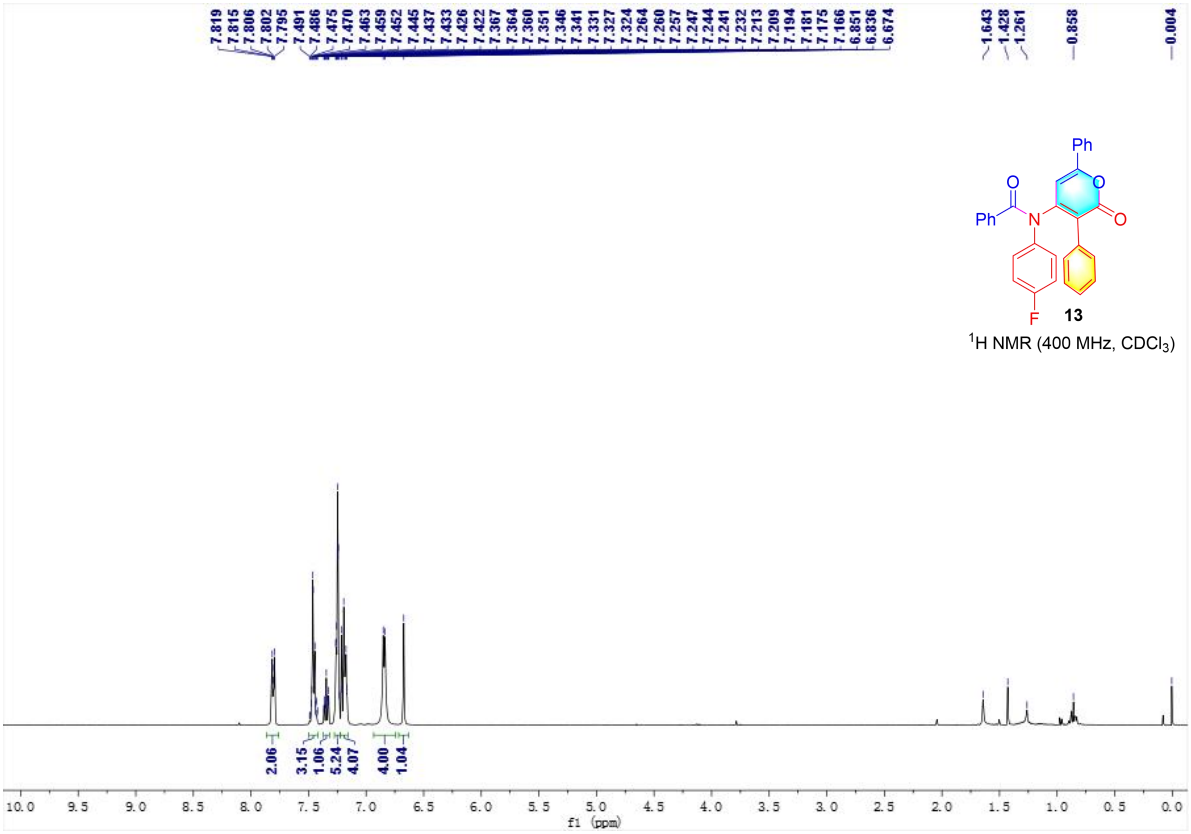
^{13}C NMR (100 MHz, $CDCl_3$)


7.874
7.868
7.859
7.851
7.510
7.503
7.495
7.367
7.355
7.349
7.339
7.330
7.260
7.237
7.219
7.200
7.161
7.113
7.095
6.711
4.053
1.842
1.795
1.763
1.665
1.642
1.615
1.286
1.259
1.227
1.152
1.123
1.090
0.004
Ph
O
O
Ph
N
Cy
O
11
1H NMR (400 MHz, CDCl3)
2.06
3.17
4.11
1.98
1.83
2.01
0.99
0.81
3.68
3.25
3.00
f1 (ppm)

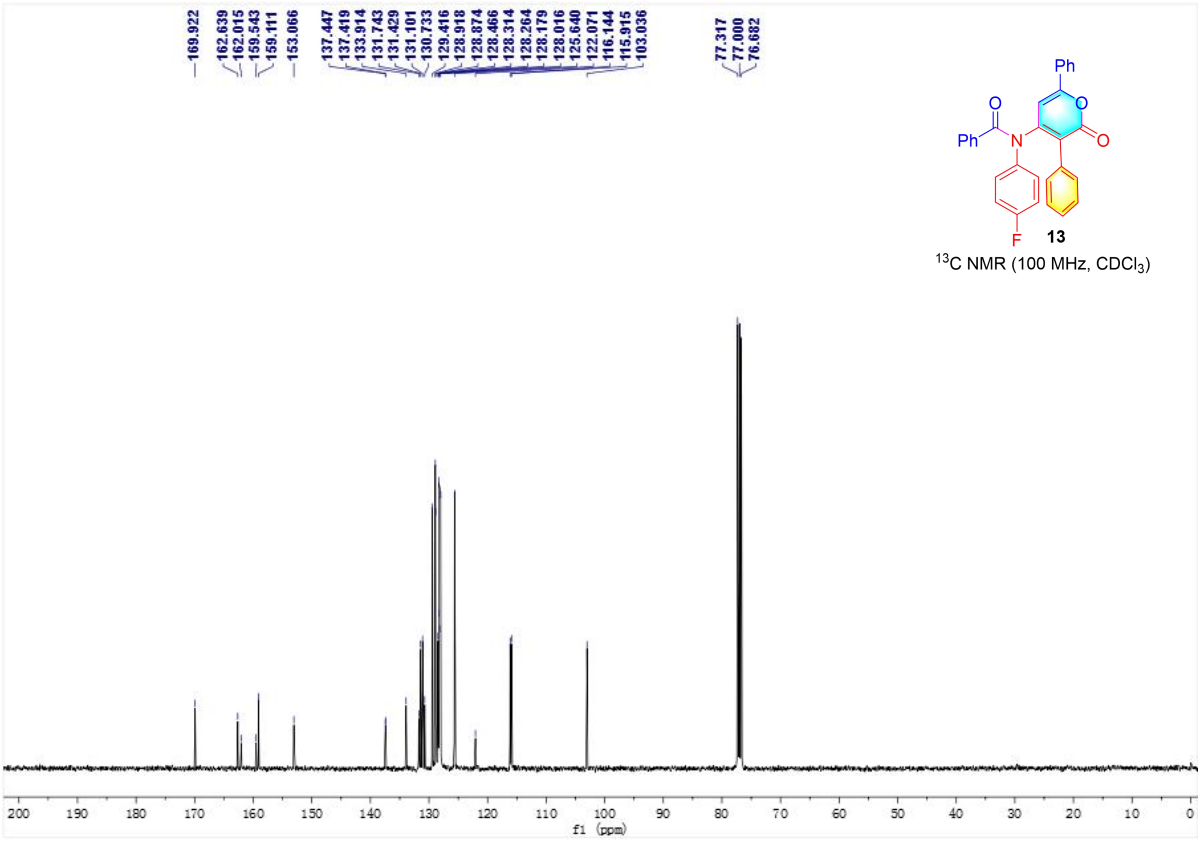

170.180
162.503
157.780
151.028
135.720
131.695
131.120
130.746
130.522
129.865
129.007
128.460
128.149
127.948
127.454
125.601
104.683
77.318
77.000
76.682
60.469
31.812
26.091
25.352
Ph
O
O
Ph
N
Cy
O
11
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.667
7.664
7.659
7.648
7.643
7.466
7.453
7.447
7.428
7.382
7.372
7.360
7.349
7.345
7.342
7.328
7.324
7.318
7.299
7.260
7.234
7.217
6.946
6.931
6.331
4.791
1.651
1.269
0.891
0.882
0.866
0.012
Ph
O
O
Ph
N
O
Bn
12
^{1}H NMR (400 MHz, $CDCl_3$)
2.18
3.03
9.47
4.29
2.02
1.08
1.68
f1 (ppm)

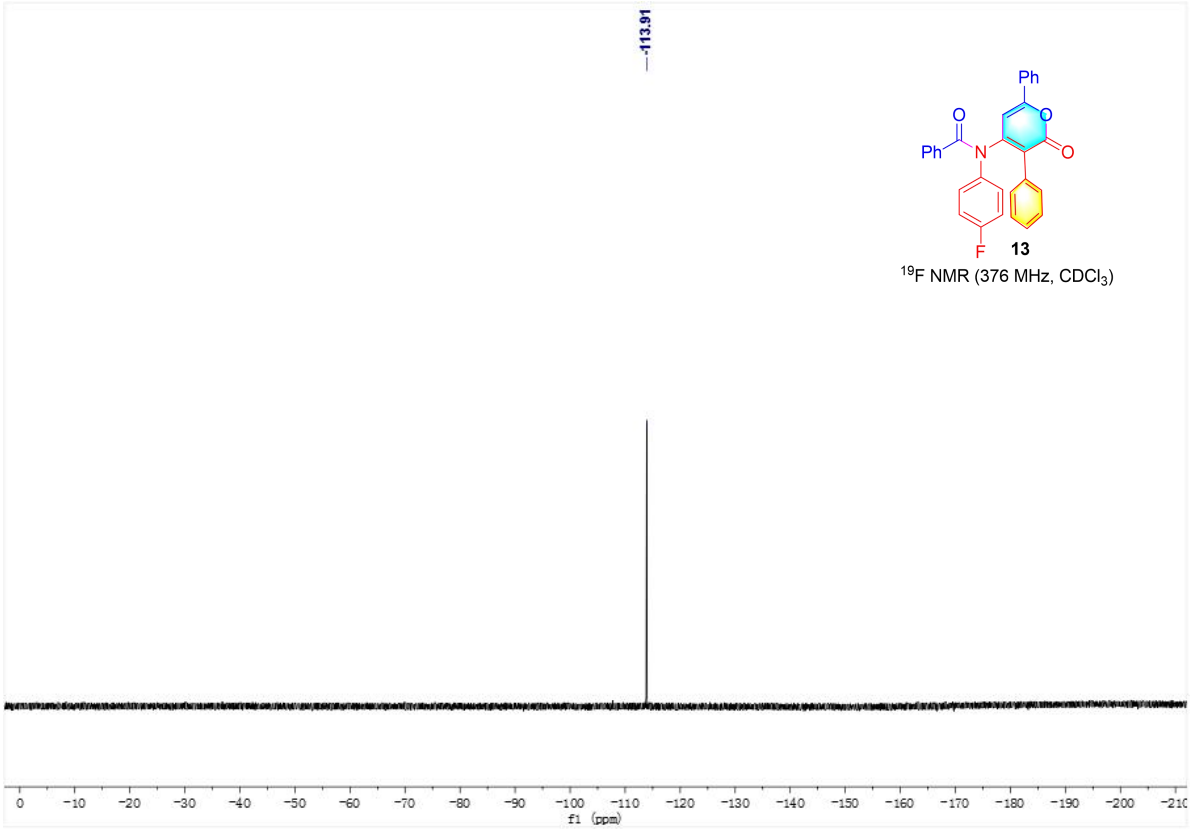

169.775
162.396
158.535
152.576
136.438
134.358
131.219
131.139
130.591
129.681
128.934
128.887
128.502
128.398
128.361
128.108
128.020
125.536
120.705
102.737
77.318
77.000
76.682
52.190
Ph
O
O
Ph
N
O
Bn
12
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



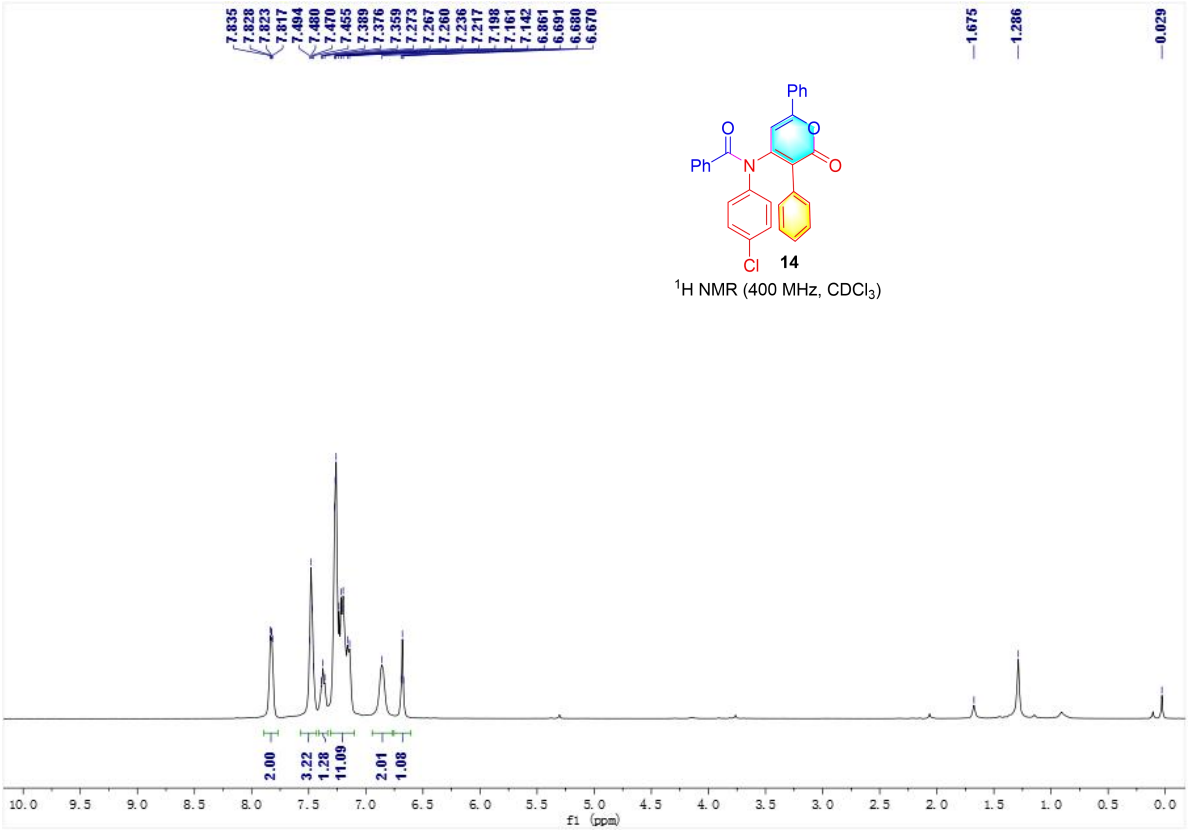
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

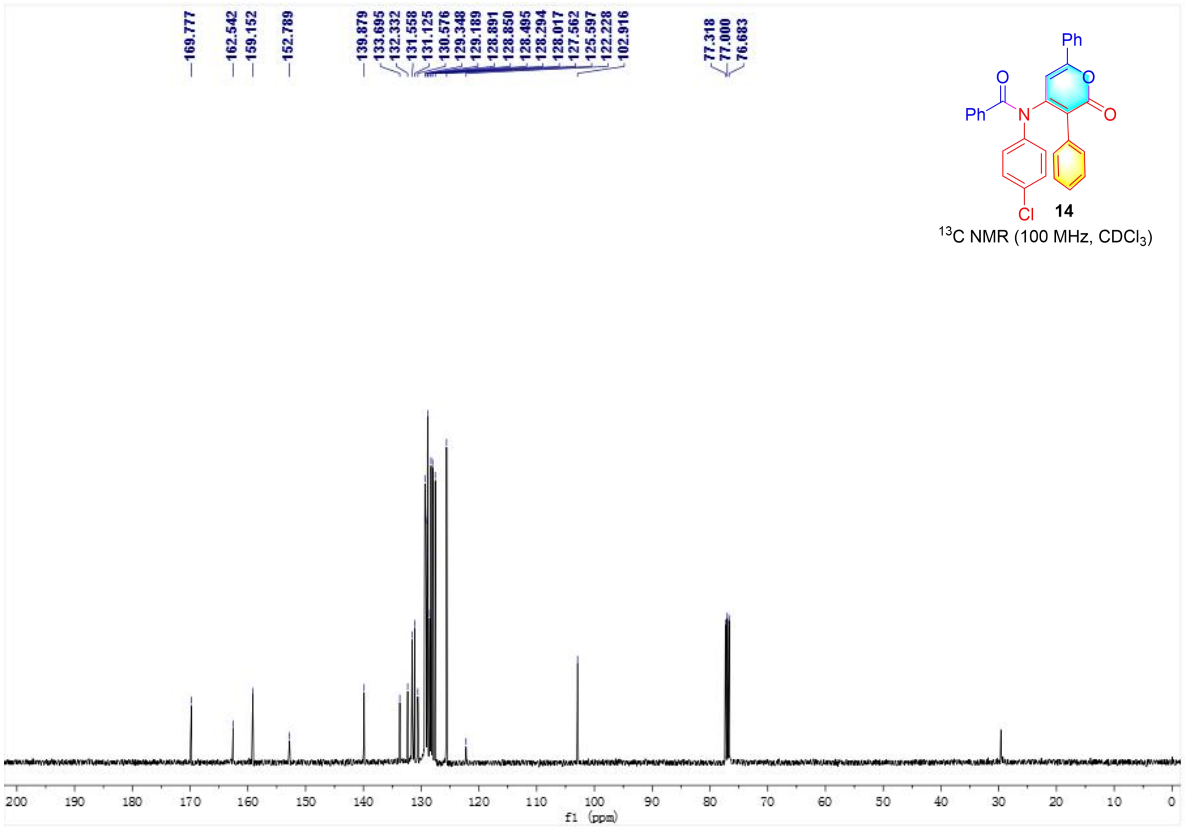


^{19}F NMR (376 MHz, $CDCl_3$)



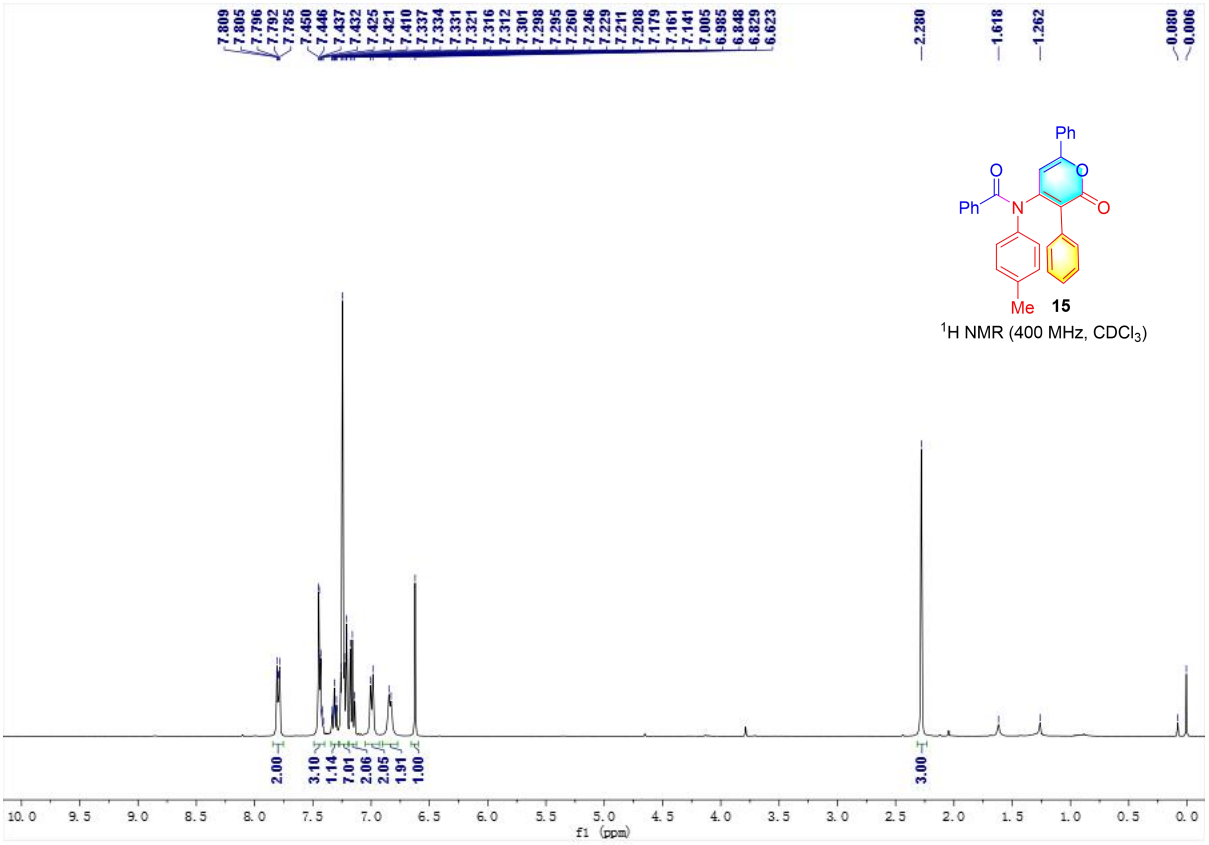
14

^{1}H NMR (400 MHz, $CDCl_3$)

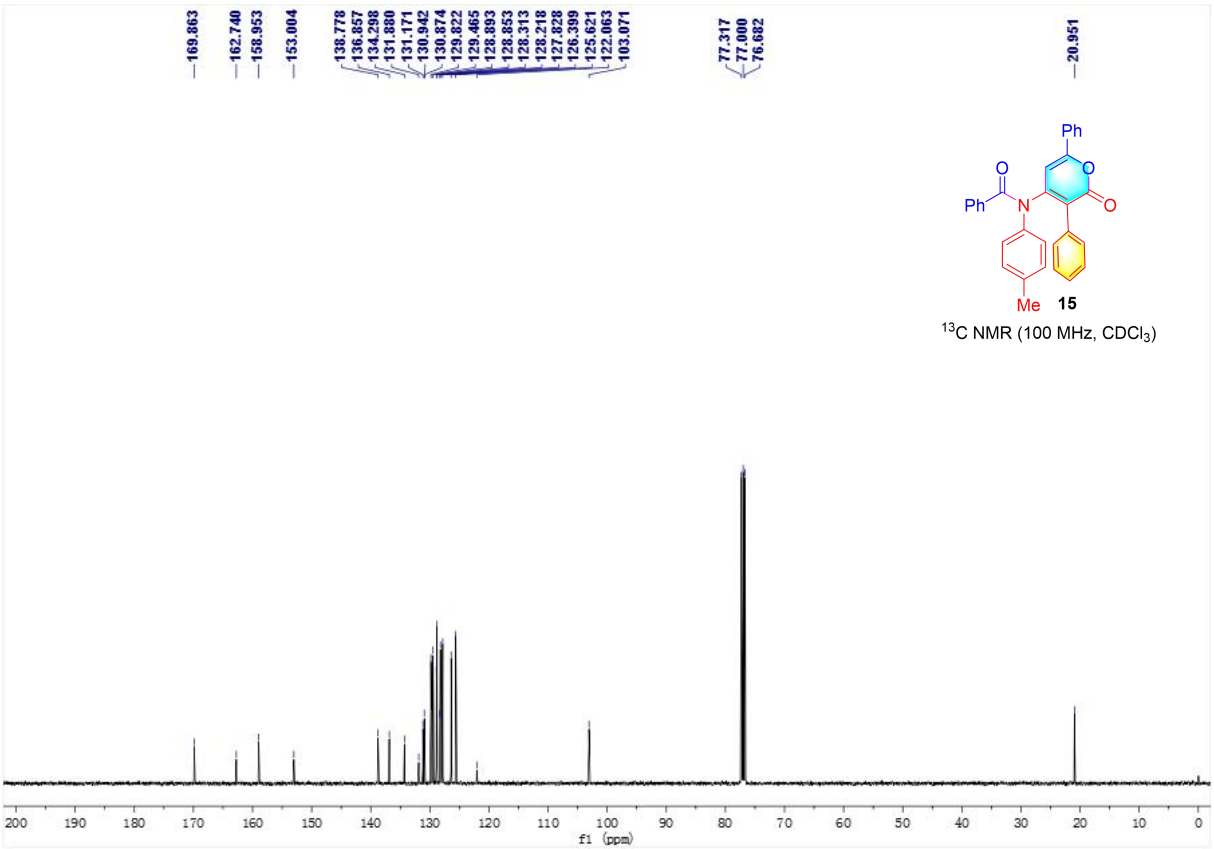


14

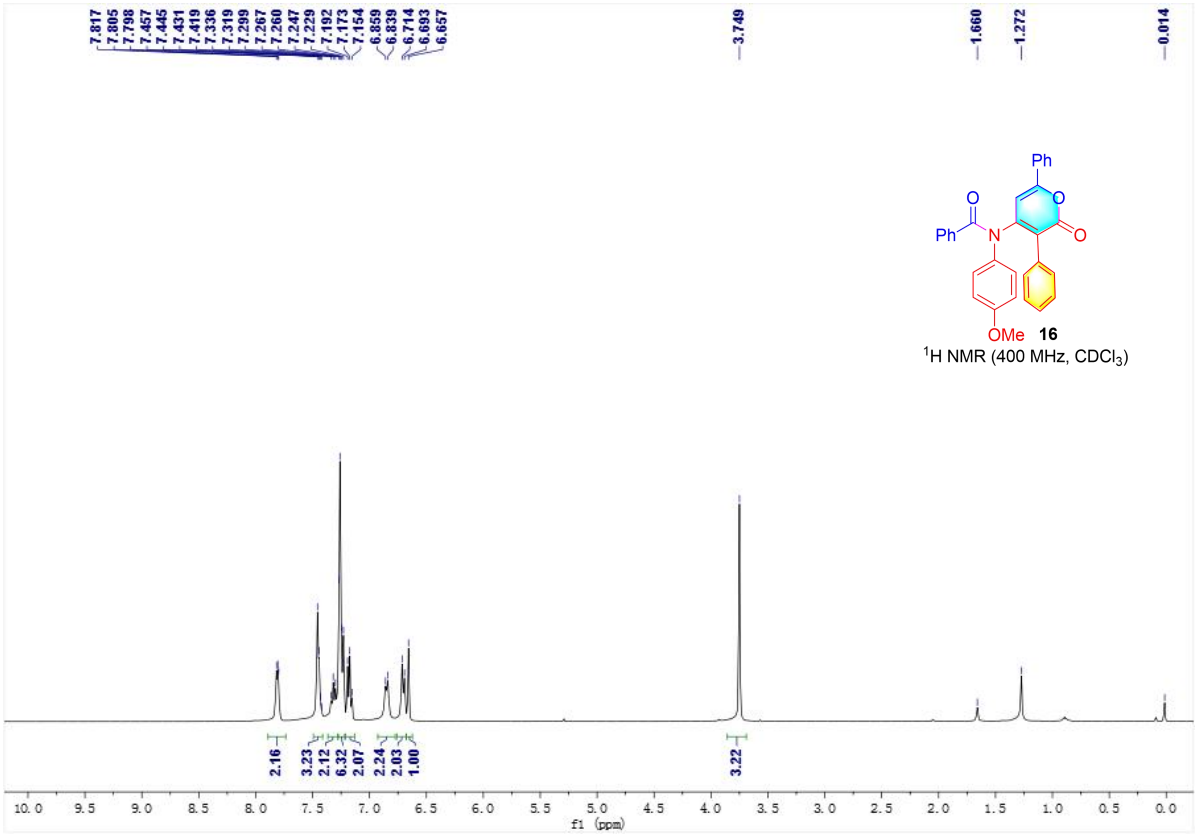
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

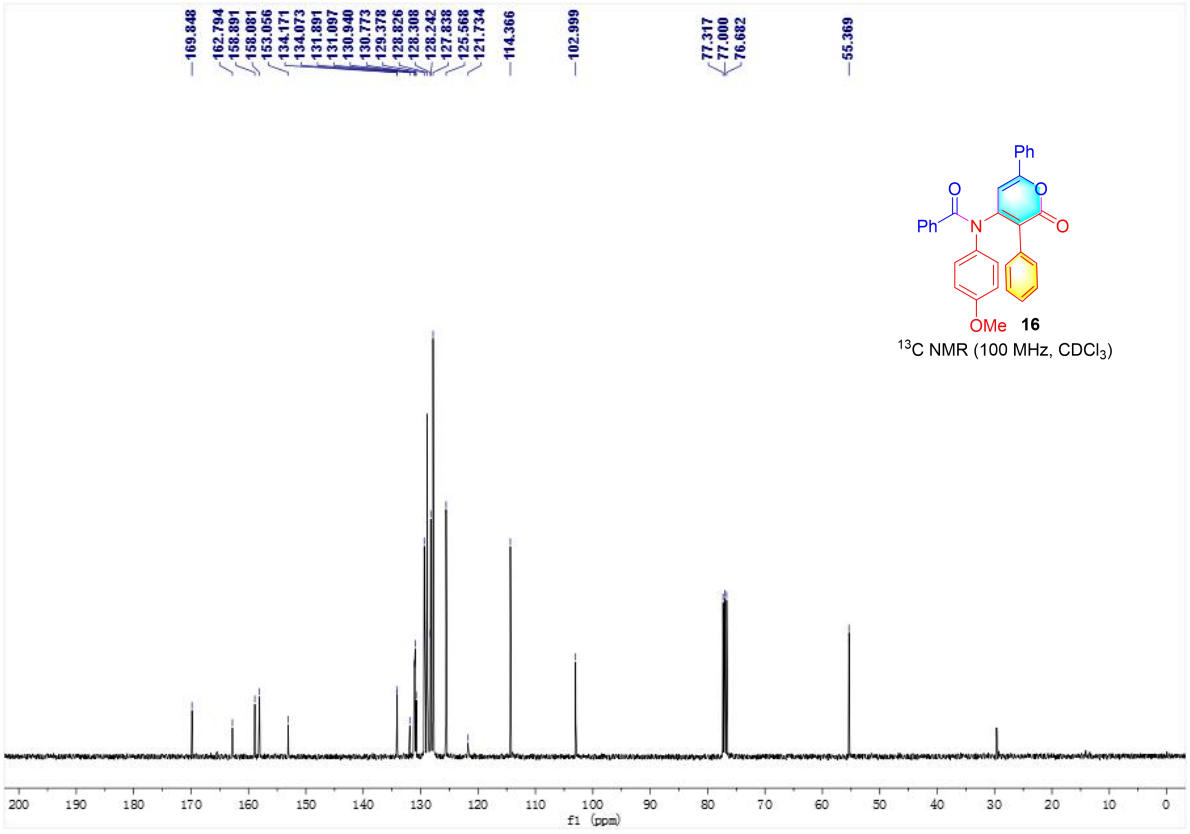


^{13}C NMR (100 MHz, $CDCl_3$)



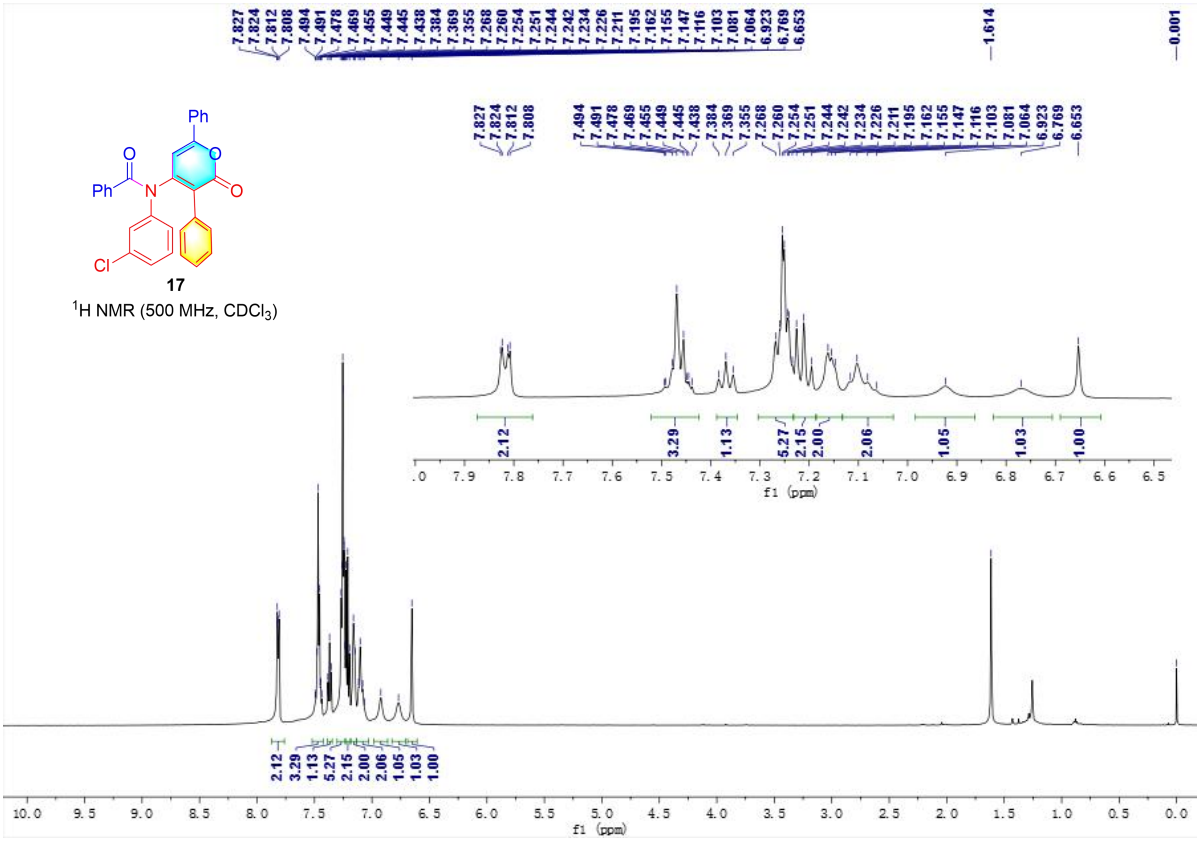
16

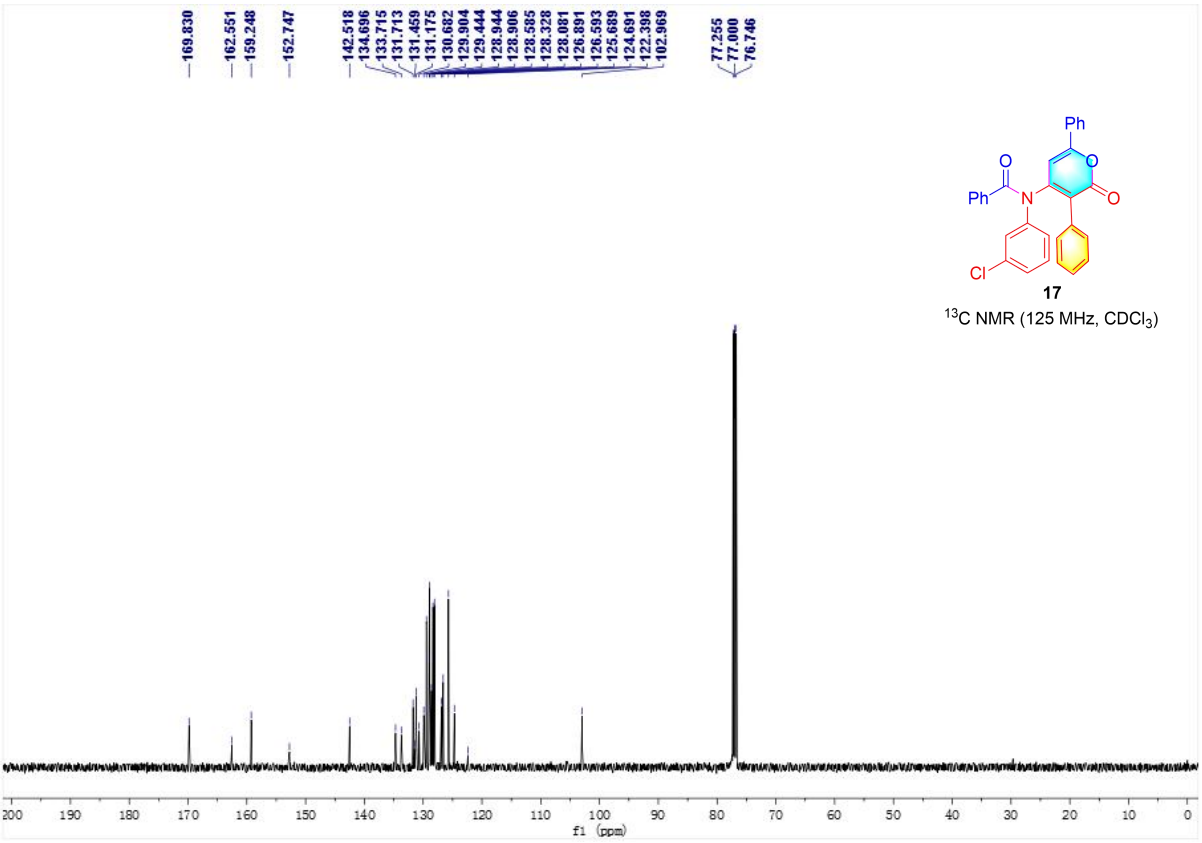
^{1}H NMR (400 MHz, $CDCl_3$)

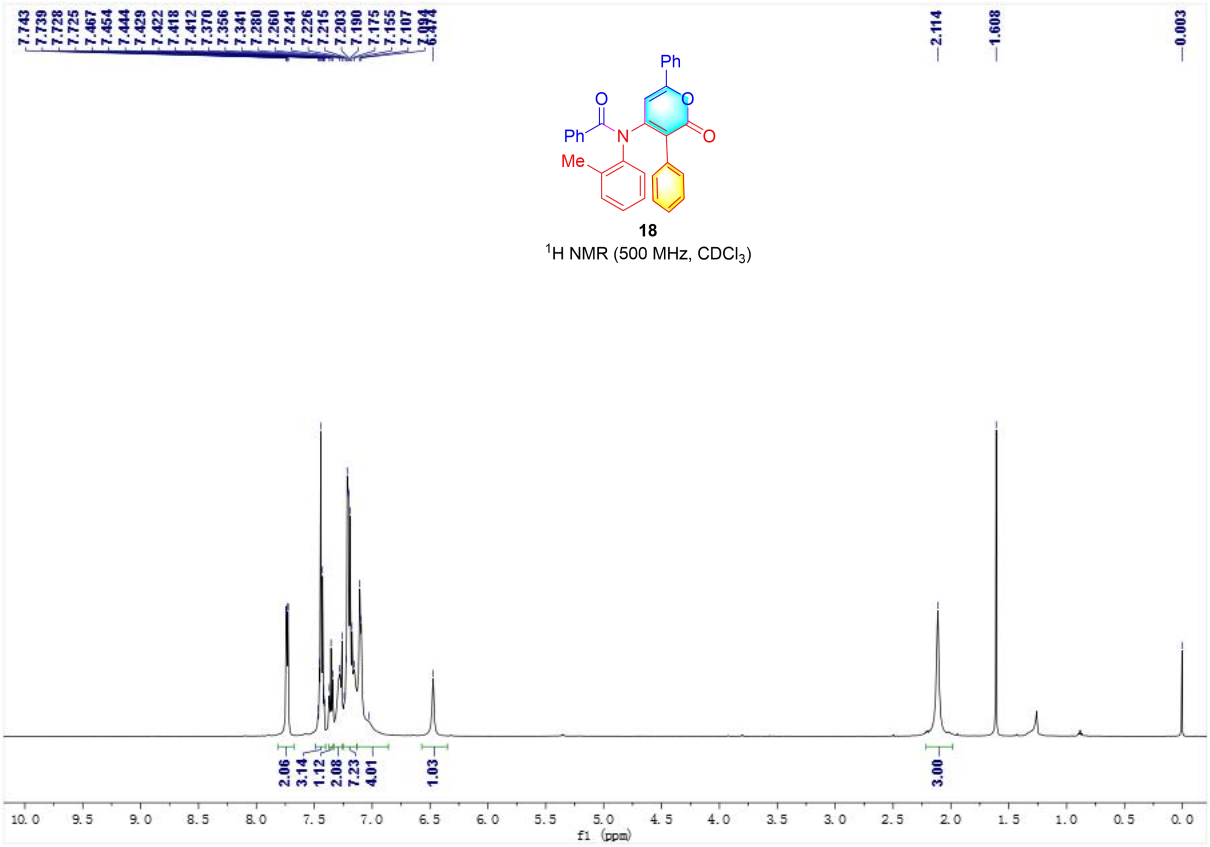


16

^{13}C NMR (100 MHz, $CDCl_3$)

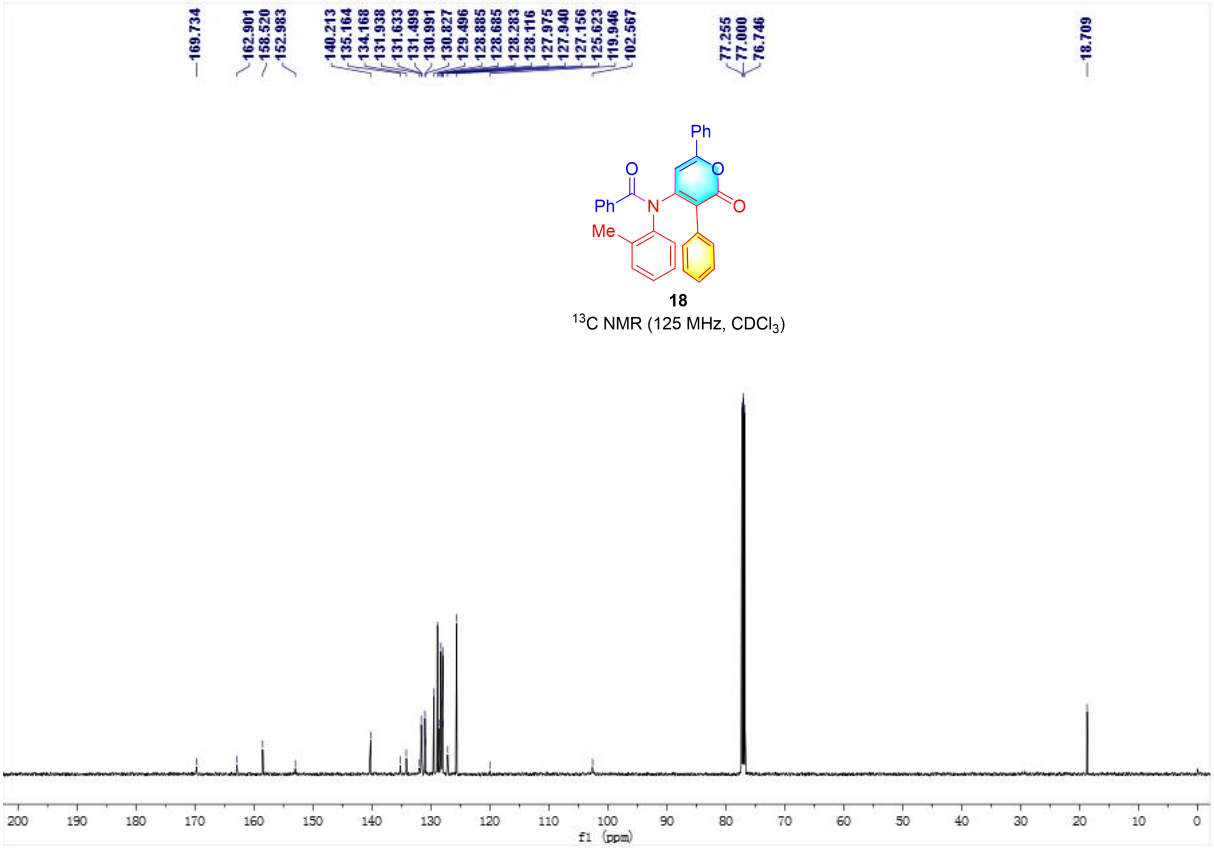

17
1H NMR (500 MHz, CDCl3)
f1 (ppm)


17
13C NMR (125 MHz, CDCl3)
f1 (ppm)



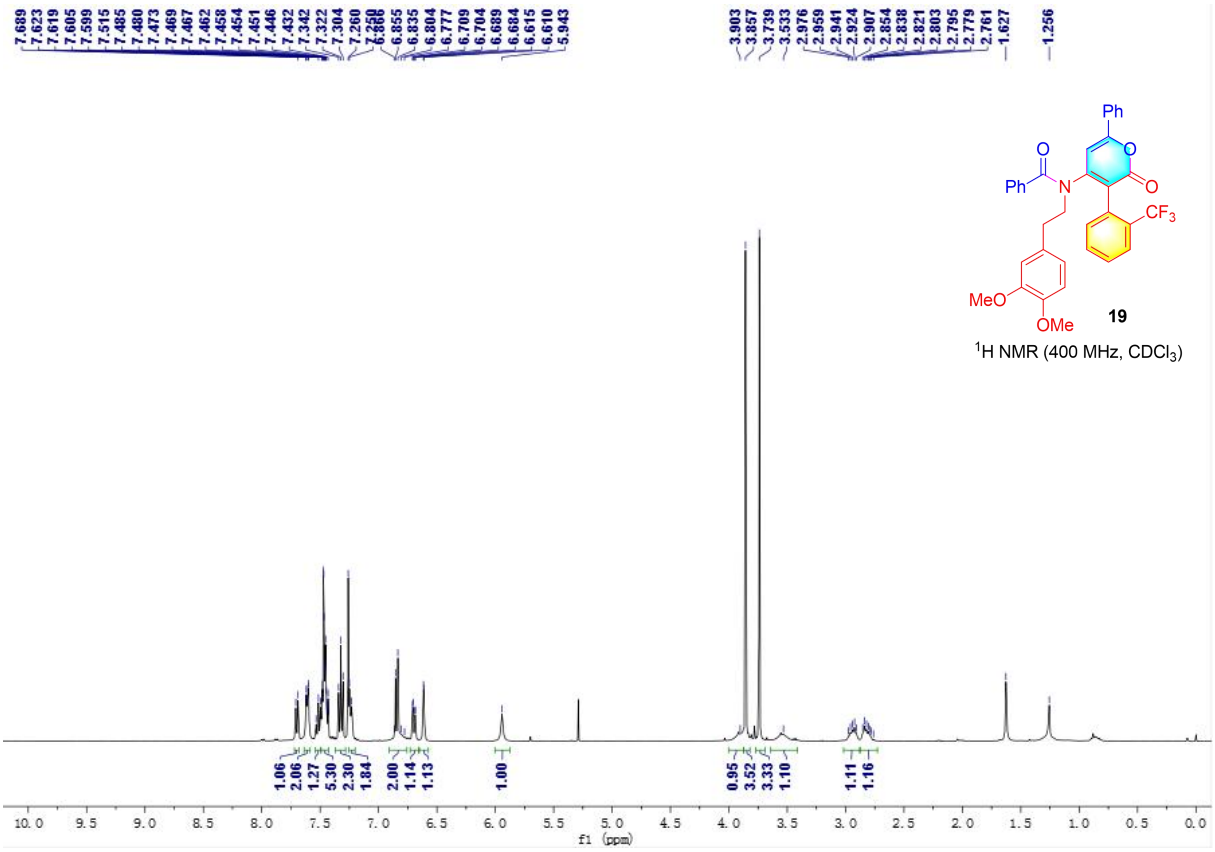
18

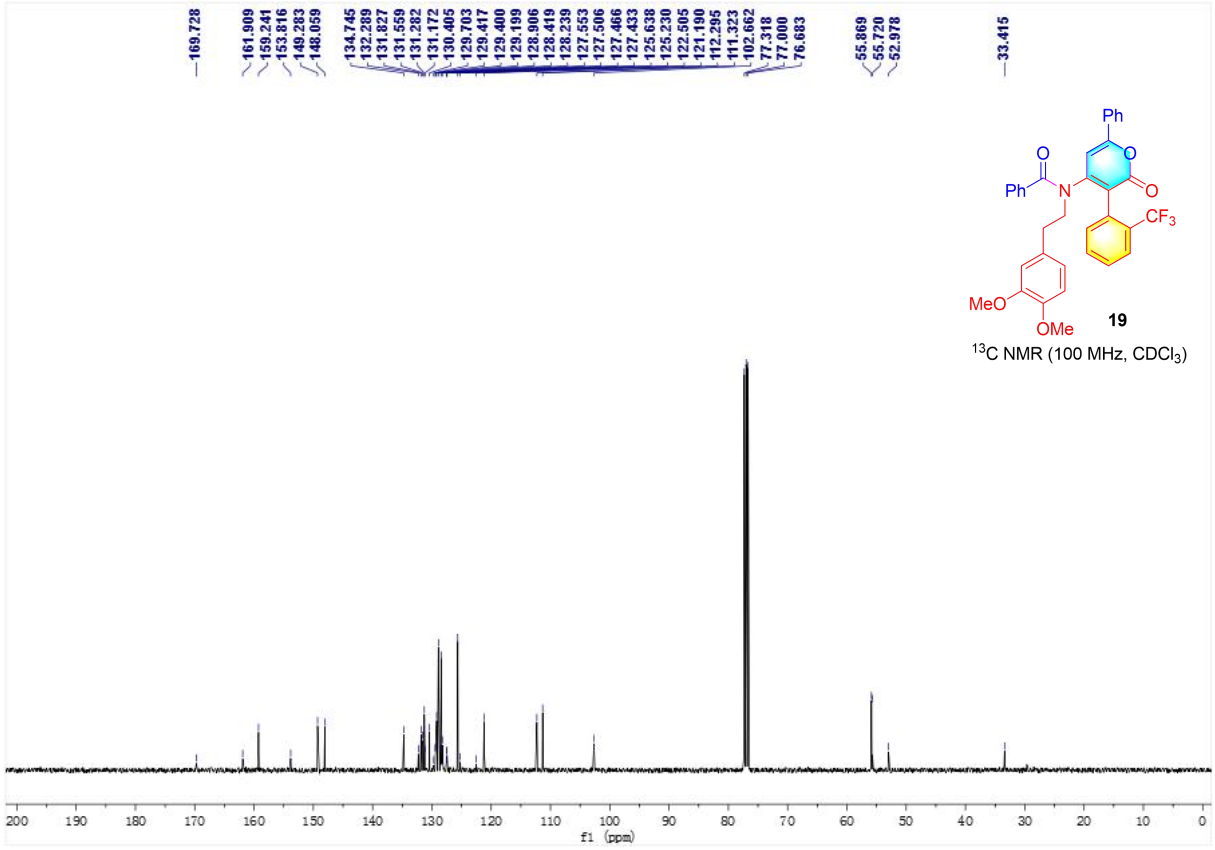
^{1}H NMR (500 MHz, $CDCl_3$)

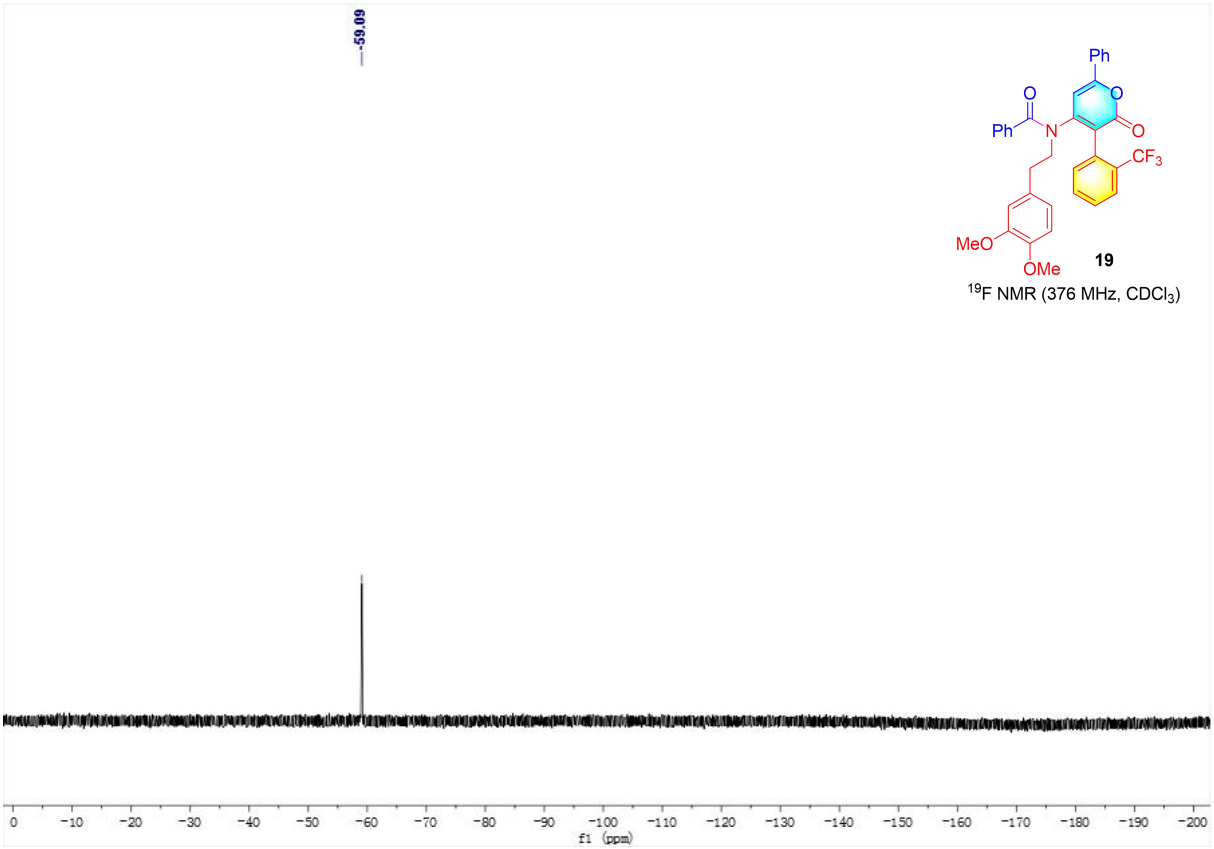


18

^{13}C NMR (125 MHz, $CDCl_3$)

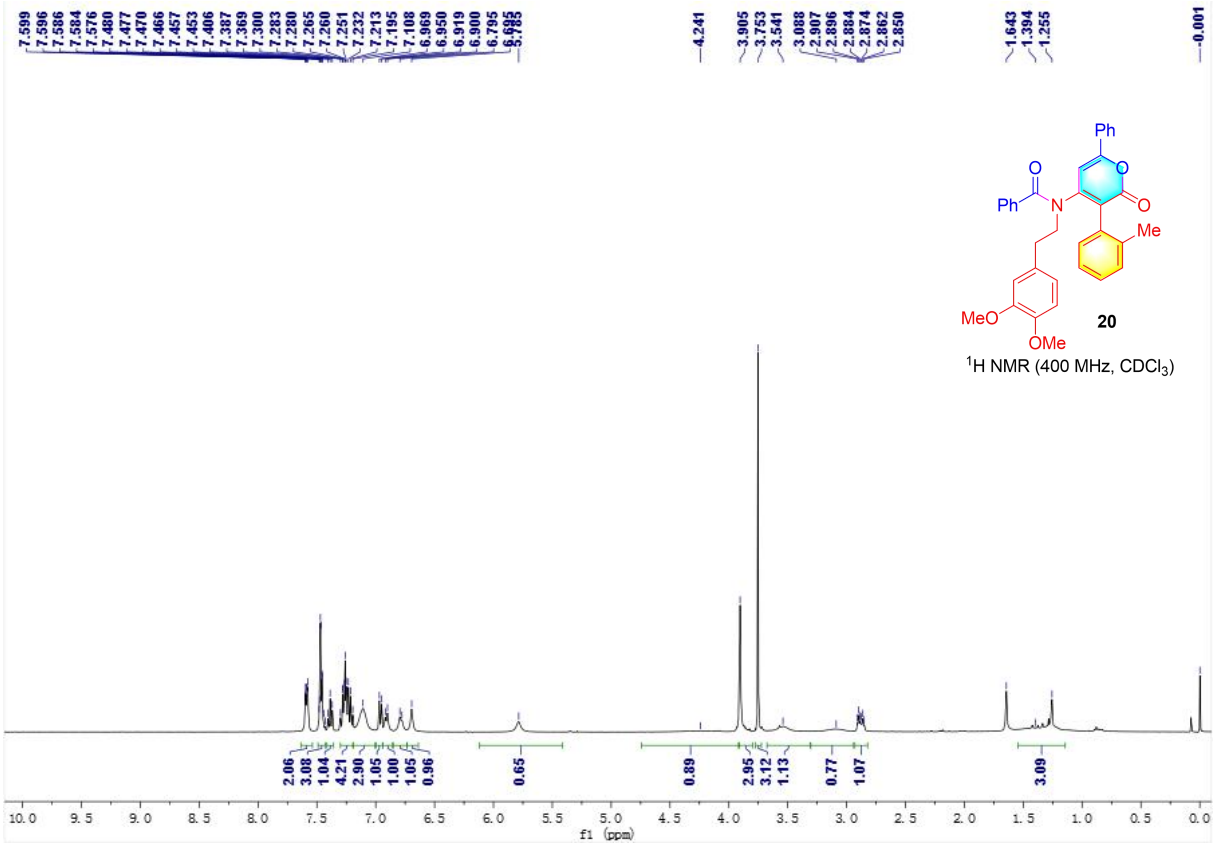

Ph
O
Ph
N
O
O
CF3
MeO
OMe
19
1H NMR (400 MHz, CDCl3)
f1 (ppm)

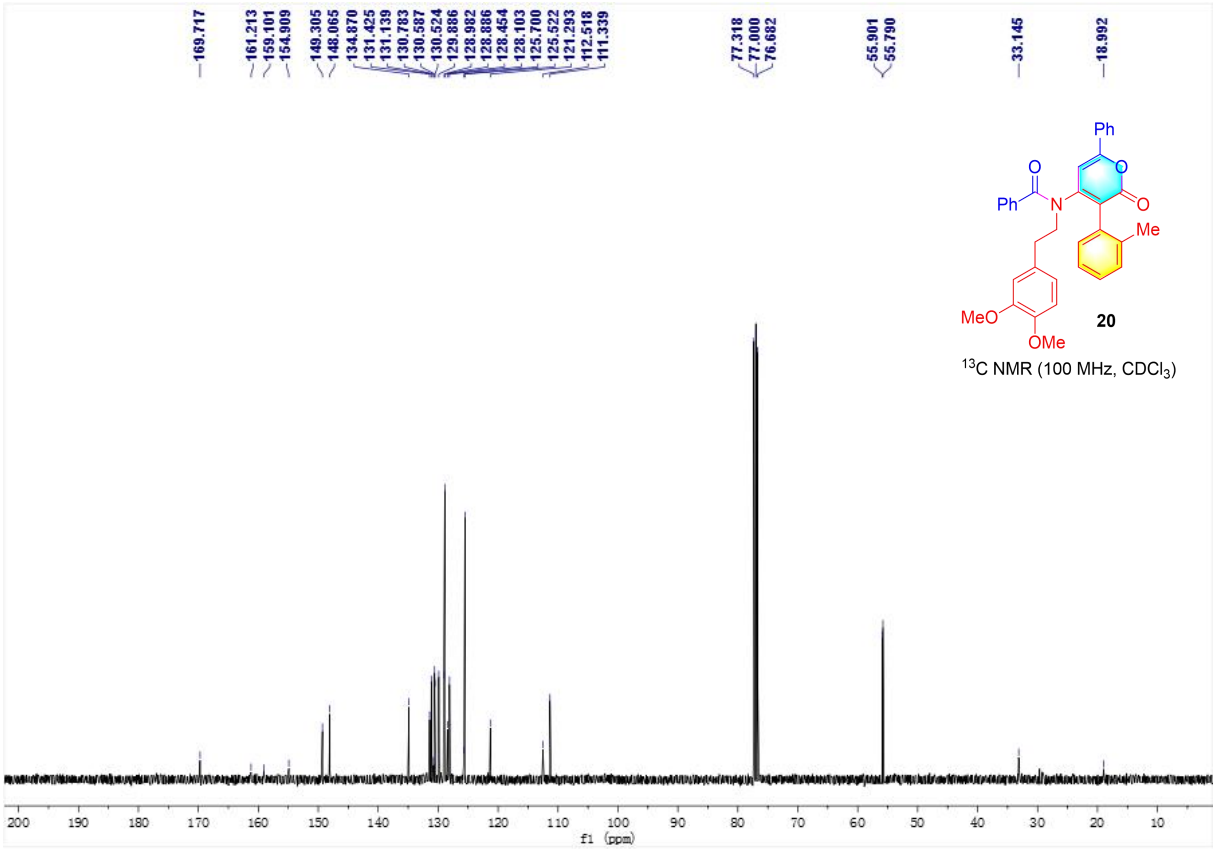

Ph
O
Ph
N
O
O
CF3
MeO
OMe
19
13C NMR (100 MHz, CDCl3)
f1 (ppm)

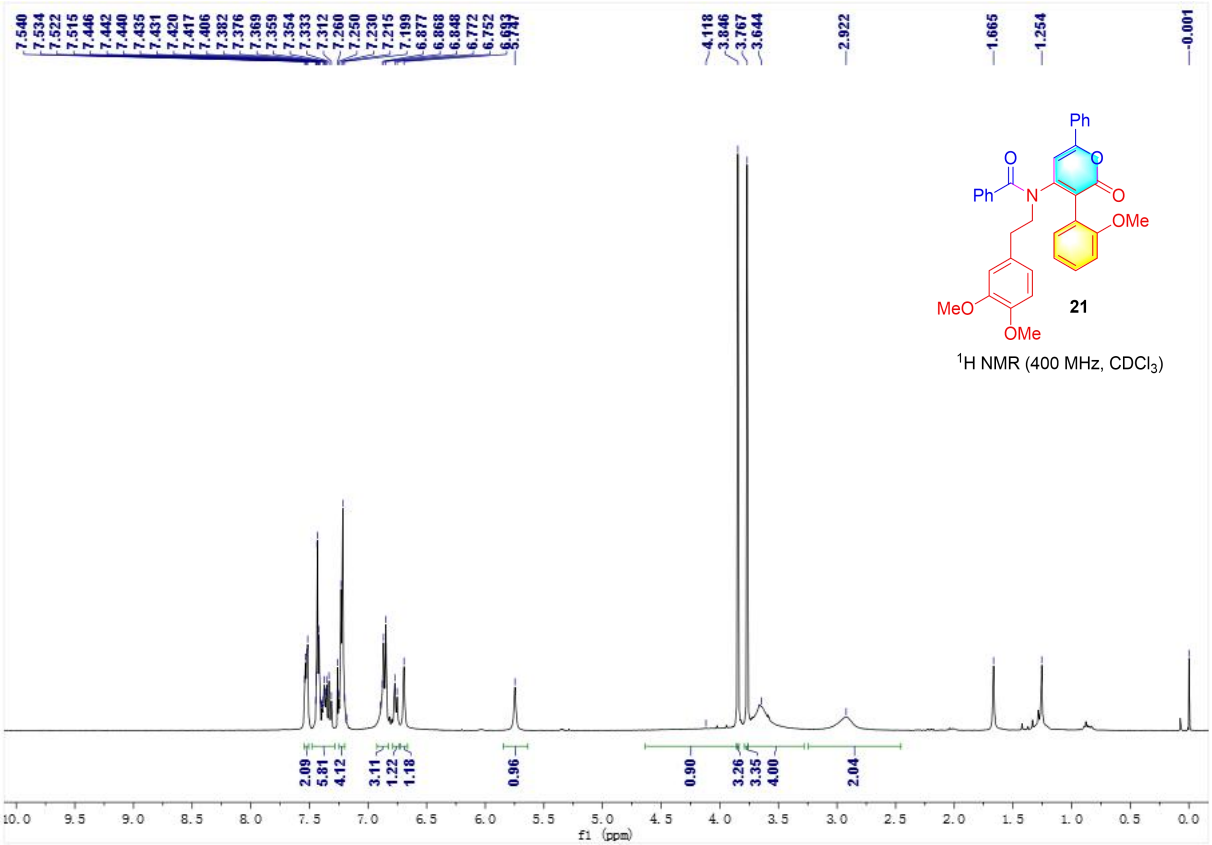


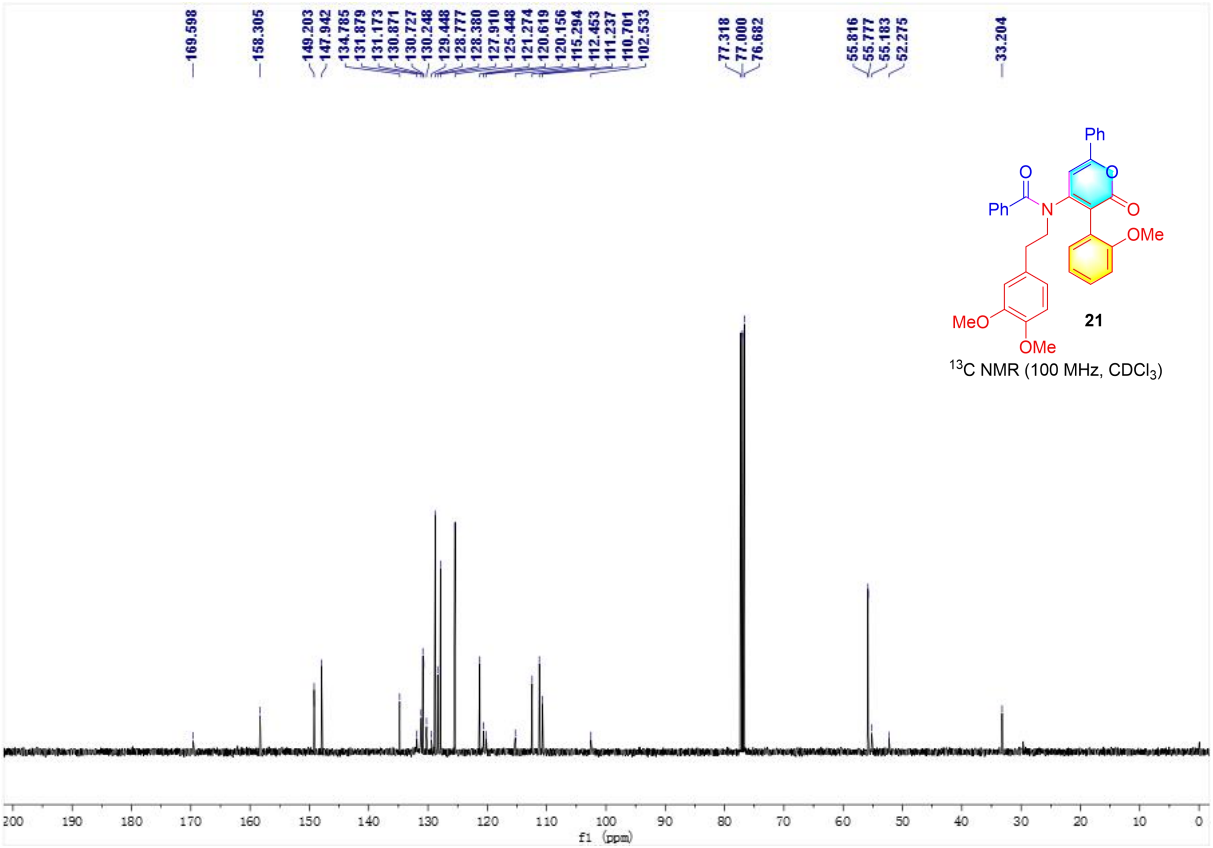
19

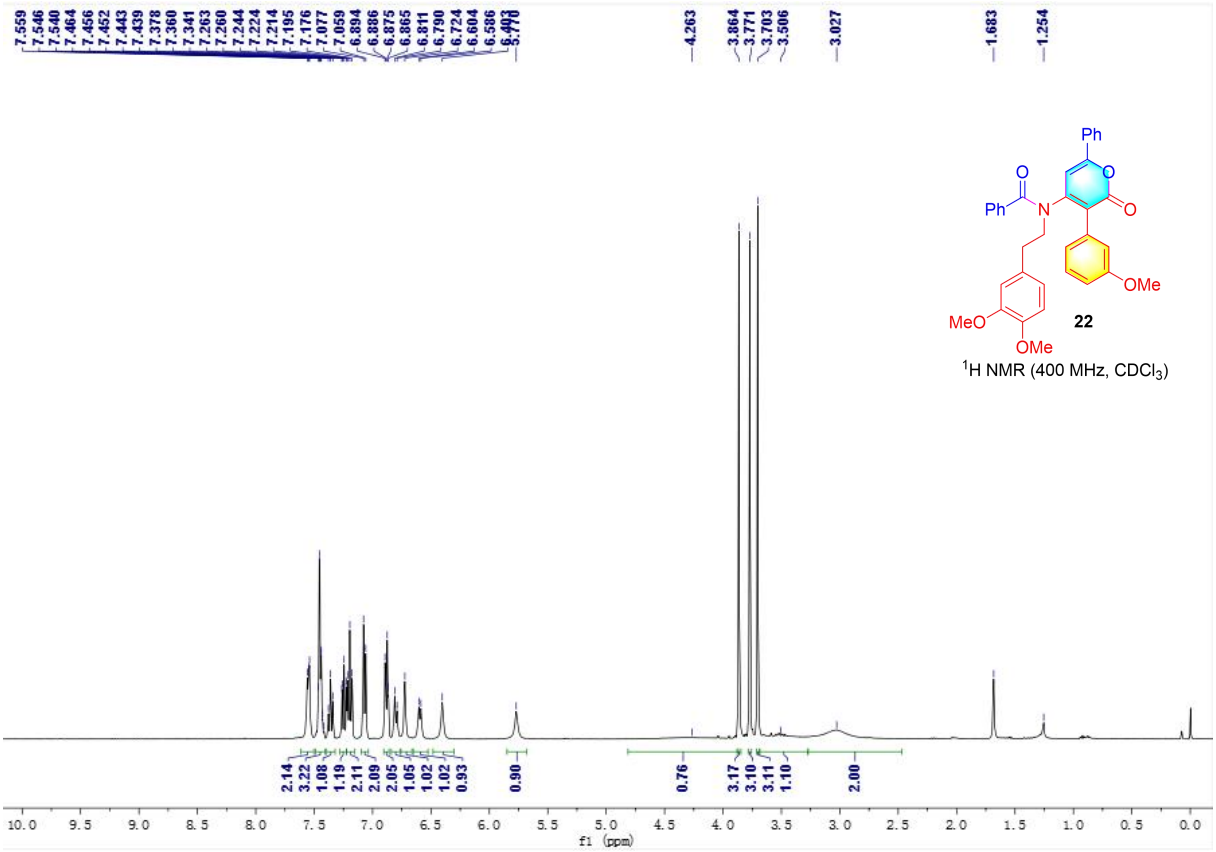
^{19}F NMR (376 MHz, $CDCl_3$)

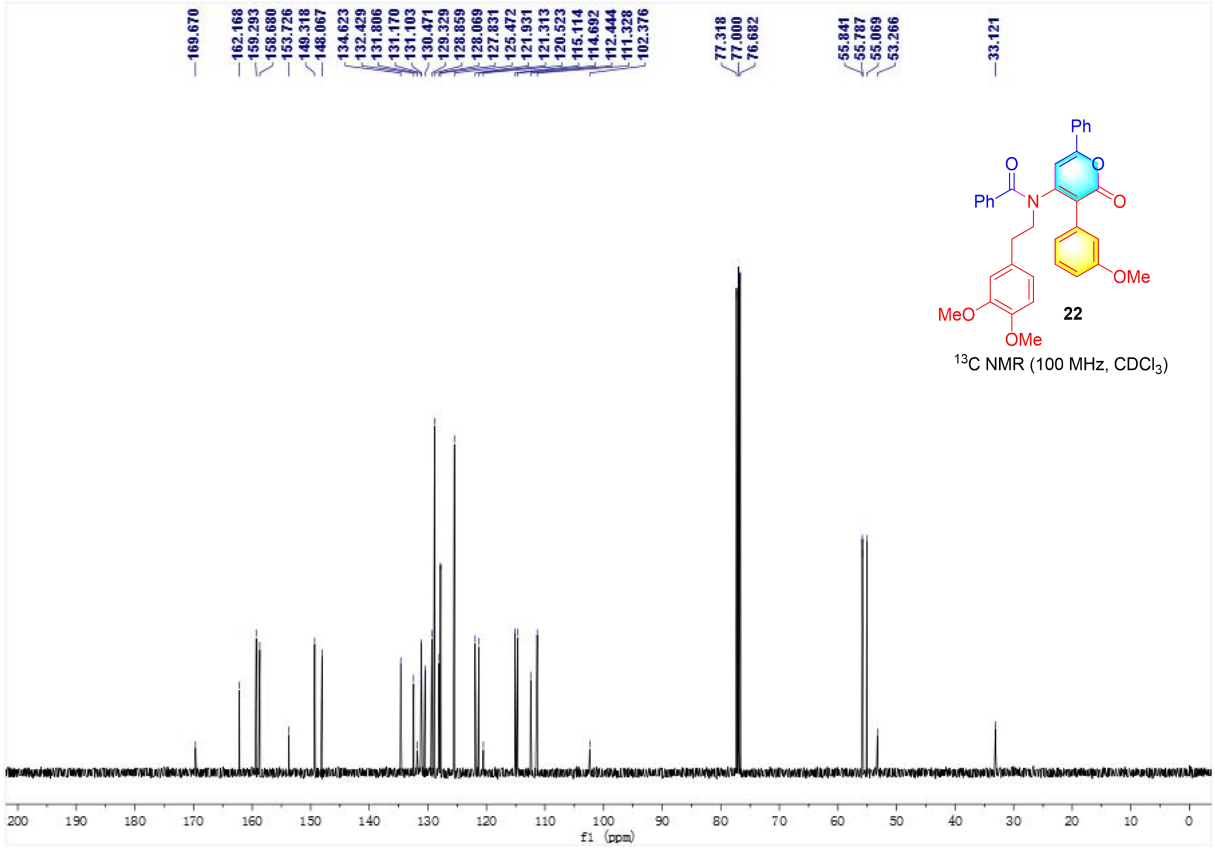

7.599 7.596 7.586 7.584 7.576 7.480 7.477 7.470 7.466 7.457 7.453 7.406 7.387 7.369 7.300 7.283 7.280 7.265 7.260 7.251 7.232 7.213 7.195 7.108 6.969 6.950 6.919 6.900 6.795 6.695 6.685 5.785
4.241
3.905 3.753 3.541
3.088 2.907 2.896 2.884 2.874 2.862 2.850
1.643 1.394 1.255
-0.001
Ph
O
Ph
N
O
O
Me
MeO
OMe
20
^{1}H NMR (400 MHz, $CDCl_3$)
2.06 3.08 1.04 4.21 2.90 1.05 1.00 1.05 0.96 0.65 0.89 2.95 3.12 1.13 0.77 1.07 3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

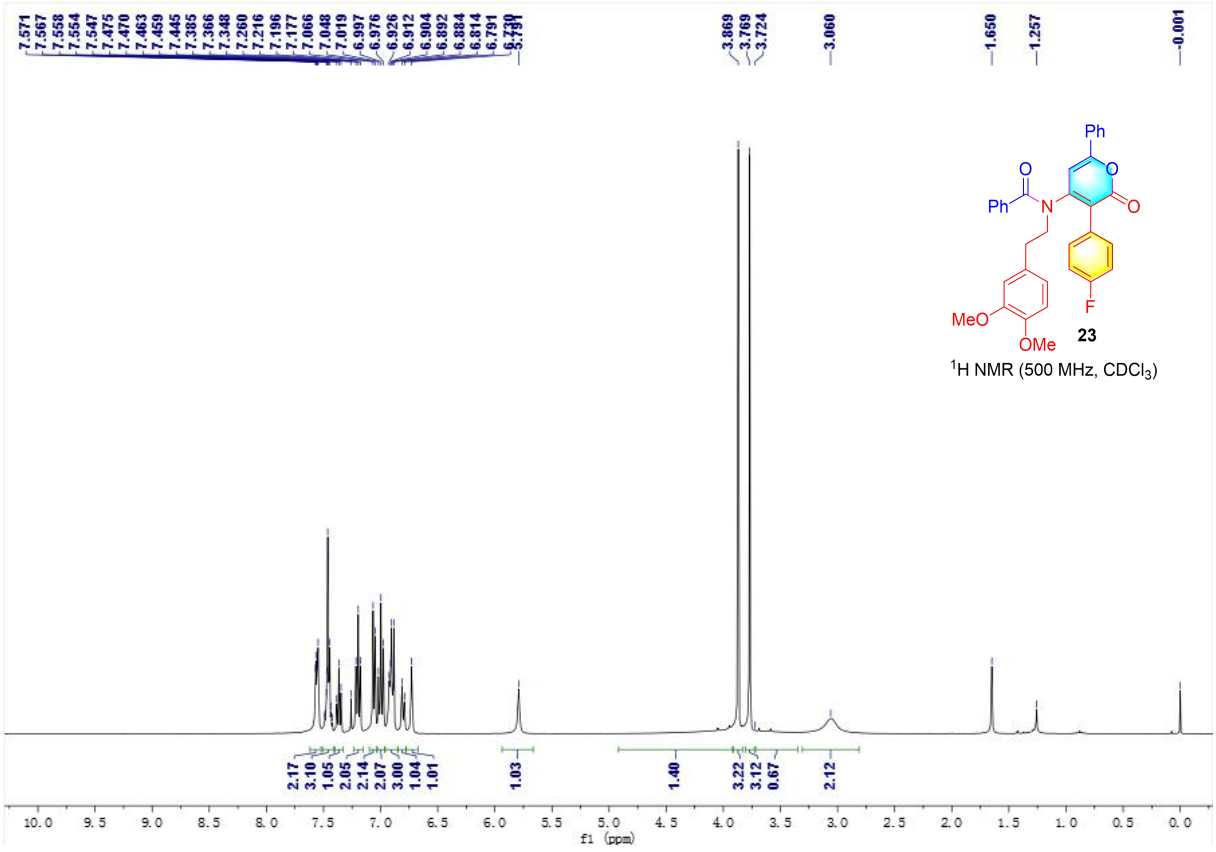

169.717
161.213 159.101 154.909 149.305 148.065 134.870 131.425 131.139 130.783 130.587 130.524 129.886 128.982 128.886 128.454 128.103 125.700 125.522 121.293 112.518 111.339
77.318 77.000 76.682
55.901 55.790
33.145
18.992
Ph
O
Ph
N
O
O
Me
MeO
OMe
20
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.540
7.534
7.522
7.515
7.446
7.442
7.440
7.435
7.431
7.420
7.417
7.406
7.382
7.376
7.369
7.359
7.354
7.333
7.312
7.260
7.250
7.230
7.215
7.199
6.877
6.868
6.848
6.772
6.752
6.693
4.118
3.846
3.767
3.644
2.922
1.665
1.254
0.001
2.09
5.81
4.12
3.11
1.22
1.18
0.96
0.90
3.26
3.35
4.00
2.04
f1 (ppm)
Ph
O
Ph
N
O
O
OMe
MeO
OMe
21
1H NMR (400 MHz, CDCl3)

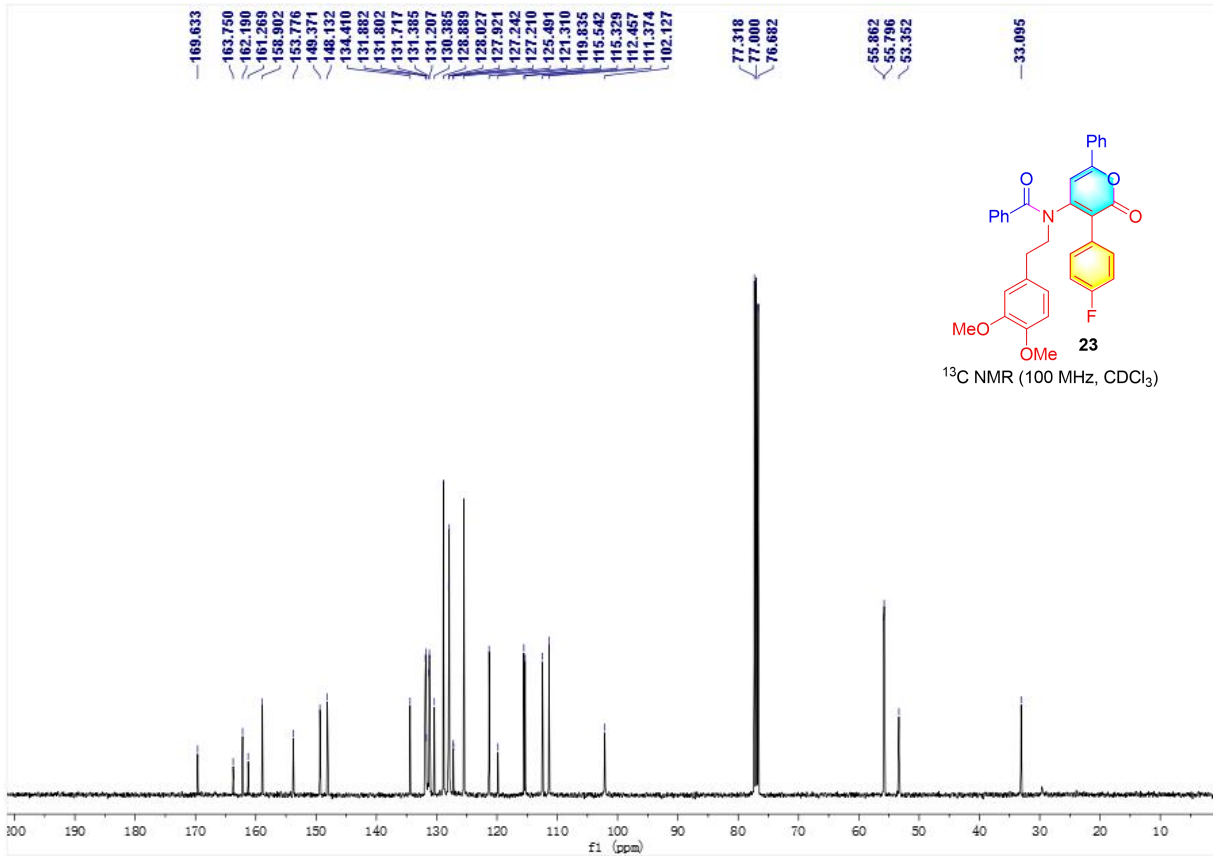

169.598
158.305
149.203
147.942
134.785
131.879
131.173
130.871
130.727
130.248
129.448
128.777
128.380
127.910
125.448
121.274
120.619
120.156
115.294
112.453
111.237
110.701
102.533
77.318
77.000
76.682
55.816
55.777
55.183
52.275
33.204
f1 (ppm)
Ph
O
Ph
N
O
O
OMe
MeO
OMe
21
13C NMR (100 MHz, CDCl3)


7.559
7.546
7.540
7.464
7.456
7.452
7.443
7.439
7.378
7.360
7.341
7.263
7.260
7.244
7.224
7.214
7.195
7.176
7.077
7.059
6.894
6.886
6.875
6.865
6.811
6.790
6.724
6.604
6.586
4.263
3.864
3.771
3.703
3.506
3.027
1.683
1.254
2.14
3.22
1.08
1.19
2.11
2.09
2.05
1.05
1.02
1.02
0.93
0.90
0.76
3.17
3.10
3.11
1.10
2.00
f1 (ppm)
Ph
O
O
Ph
N
O
OMe
MeO
OMe
22
1H NMR (400 MHz, CDCl3)

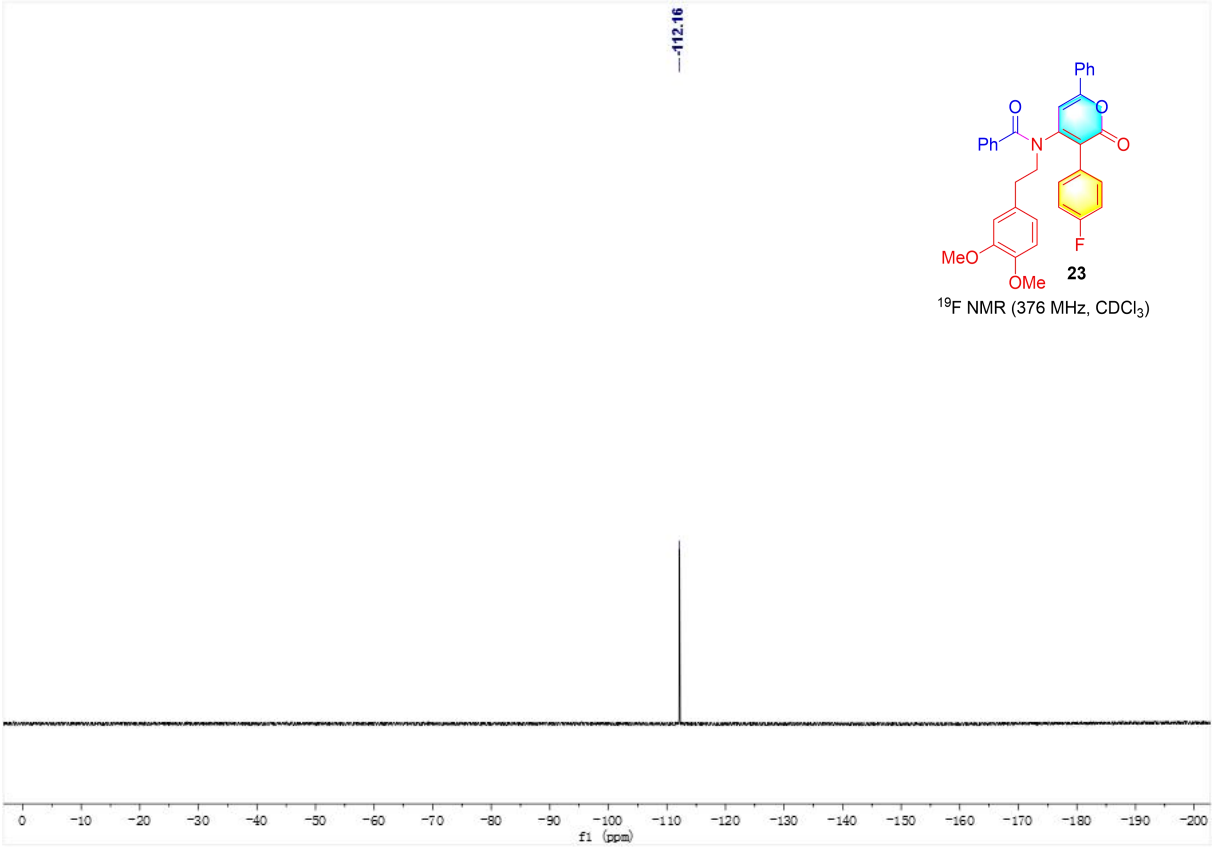

169.670
162.168
159.293
158.680
153.726
149.318
148.067
134.623
132.429
131.806
131.170
131.103
130.471
129.329
128.859
128.069
127.831
125.472
121.931
121.313
120.523
115.114
114.692
112.444
111.328
102.376
77.318
77.000
76.682
55.841
55.787
55.069
53.266
33.121
f1 (ppm)
Ph
O
O
Ph
N
O
OMe
MeO
OMe
22
13C NMR (100 MHz, CDCl3)



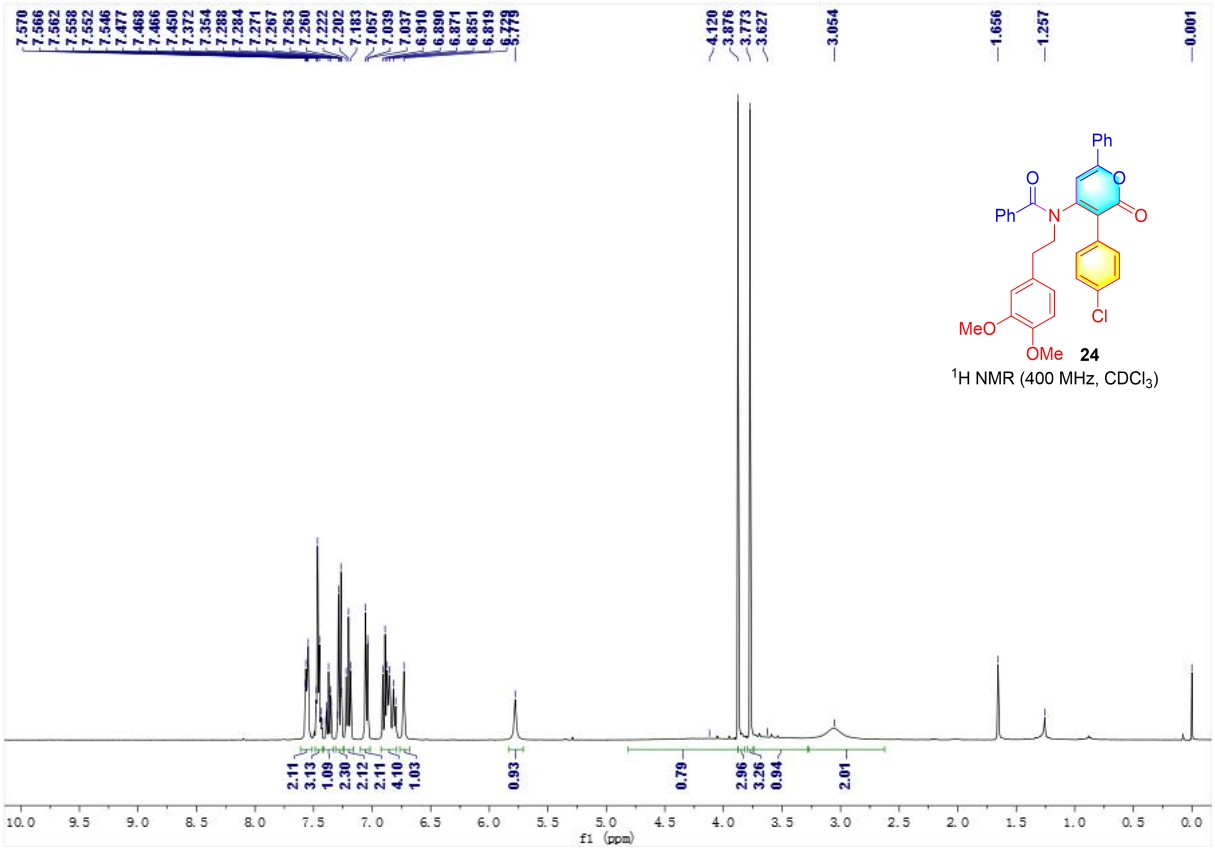
^{1}H NMR (500 MHz, $CDCl_3$)

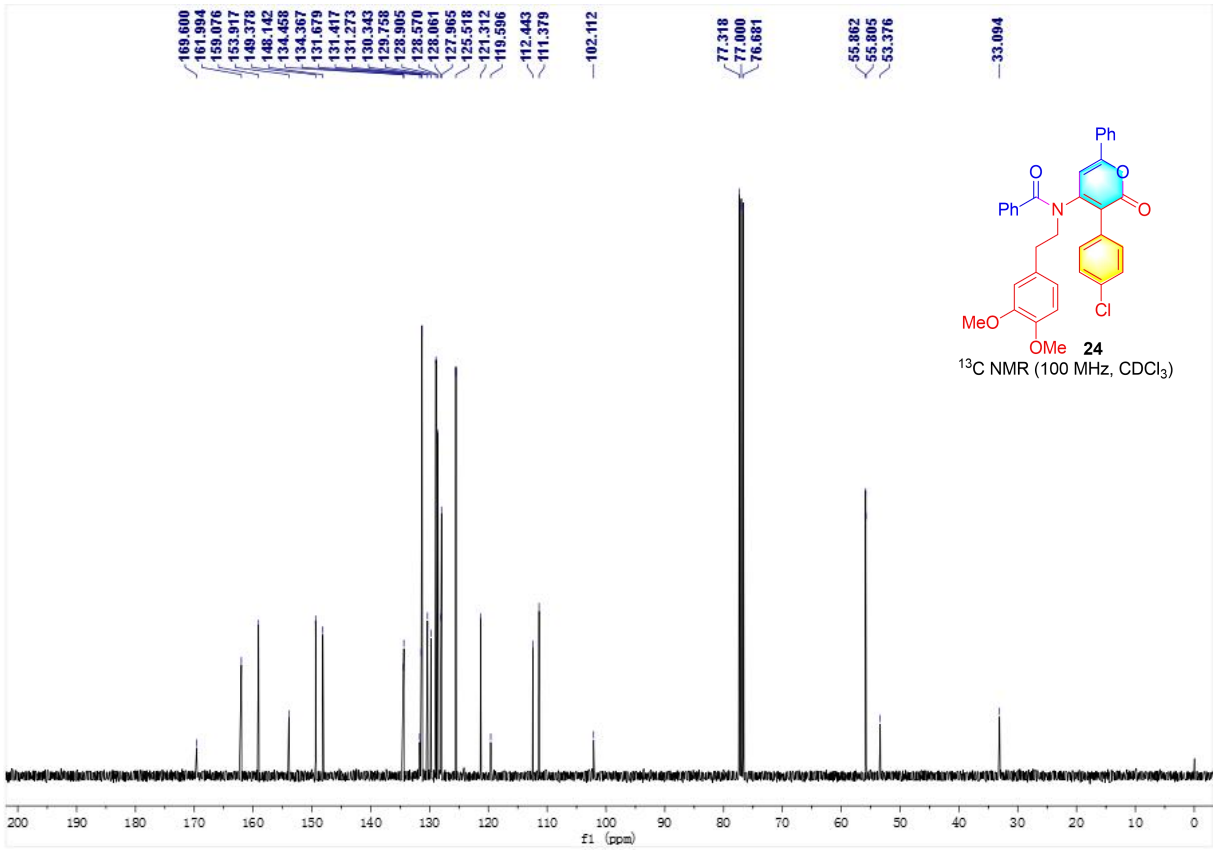


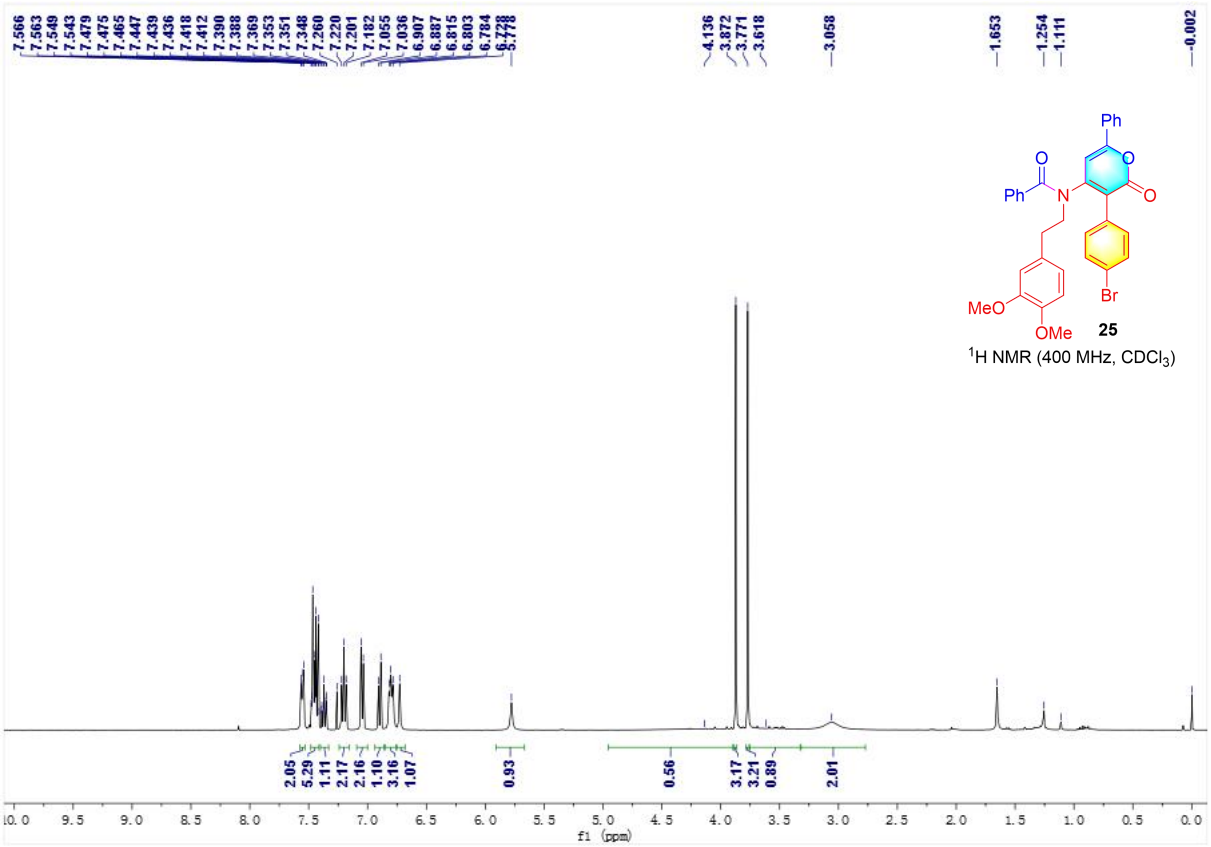
^{13}C NMR (100 MHz, $CDCl_3$)



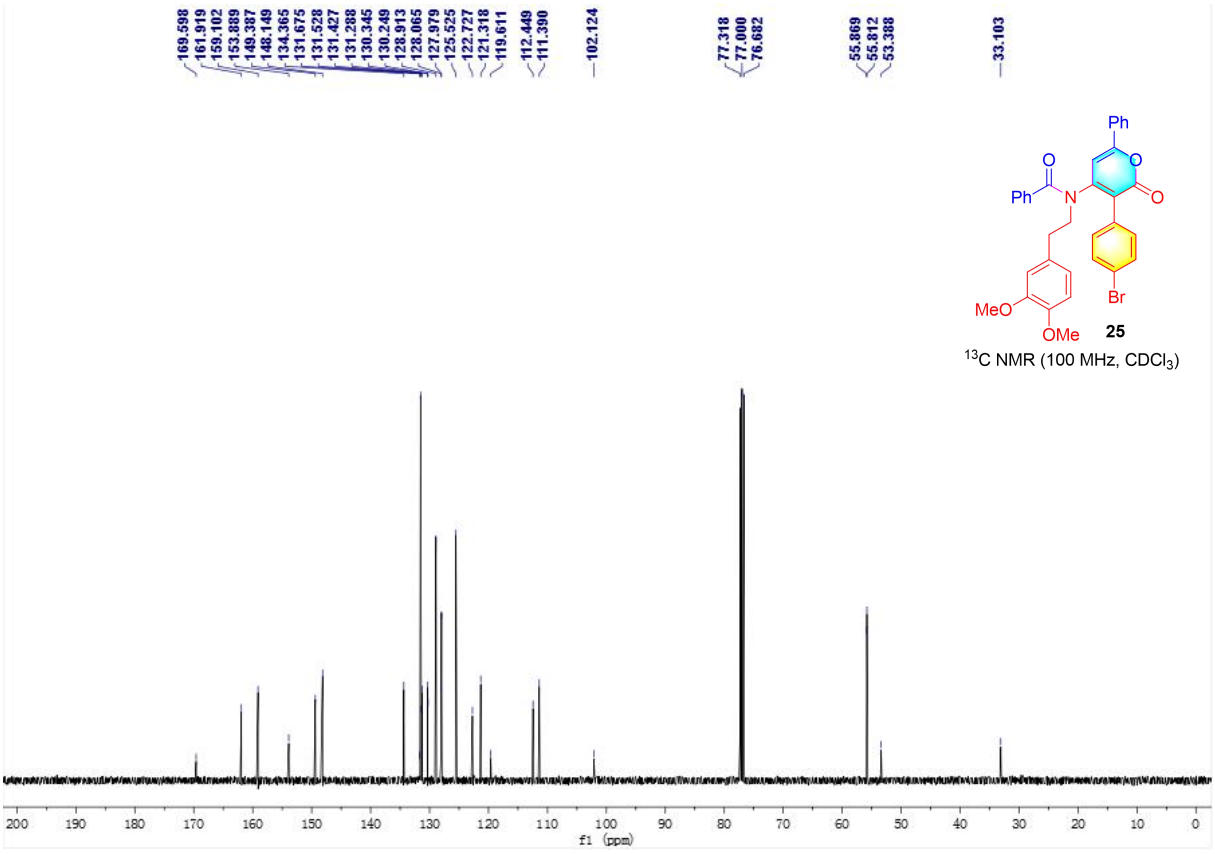
^{19}F NMR (376 MHz, $CDCl_3$)


7.570
7.566
7.562
7.558
7.552
7.546
7.477
7.468
7.466
7.450
7.372
7.354
7.288
7.284
7.271
7.267
7.263
7.260
7.222
7.202
7.183
7.057
7.039
7.037
6.910
6.890
6.871
6.851
6.819
4.120
3.876
3.773
3.627
3.054
1.656
1.257
0.001
2.11
3.13
1.09
2.30
2.12
2.11
4.10
1.03
0.93
0.79
2.96
3.26
0.94
2.01
f1 (ppm)
Ph
O
Ph
N
O
O
Cl
MeO
OMe
24
^{1}H NMR (400 MHz, $CDCl_3$)

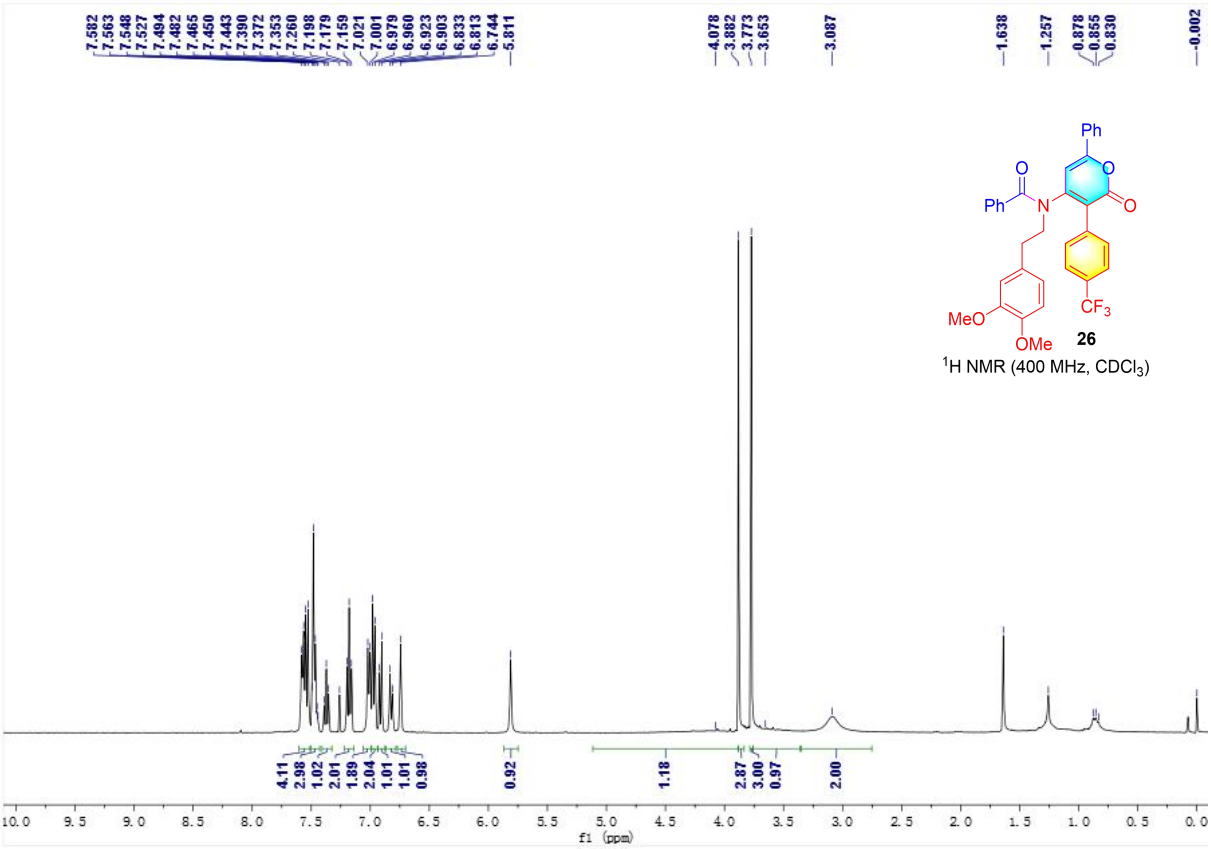

169.600
161.994
159.076
153.917
149.378
148.142
134.458
134.367
131.679
131.417
131.273
130.343
129.758
128.905
128.570
128.061
127.965
125.518
121.312
119.596
112.443
111.379
102.112
77.318
77.000
76.681
55.862
55.805
53.376
33.094
f1 (ppm)
Ph
O
Ph
N
O
O
Cl
MeO
OMe
24
^{13}C NMR (100 MHz, $CDCl_3$)

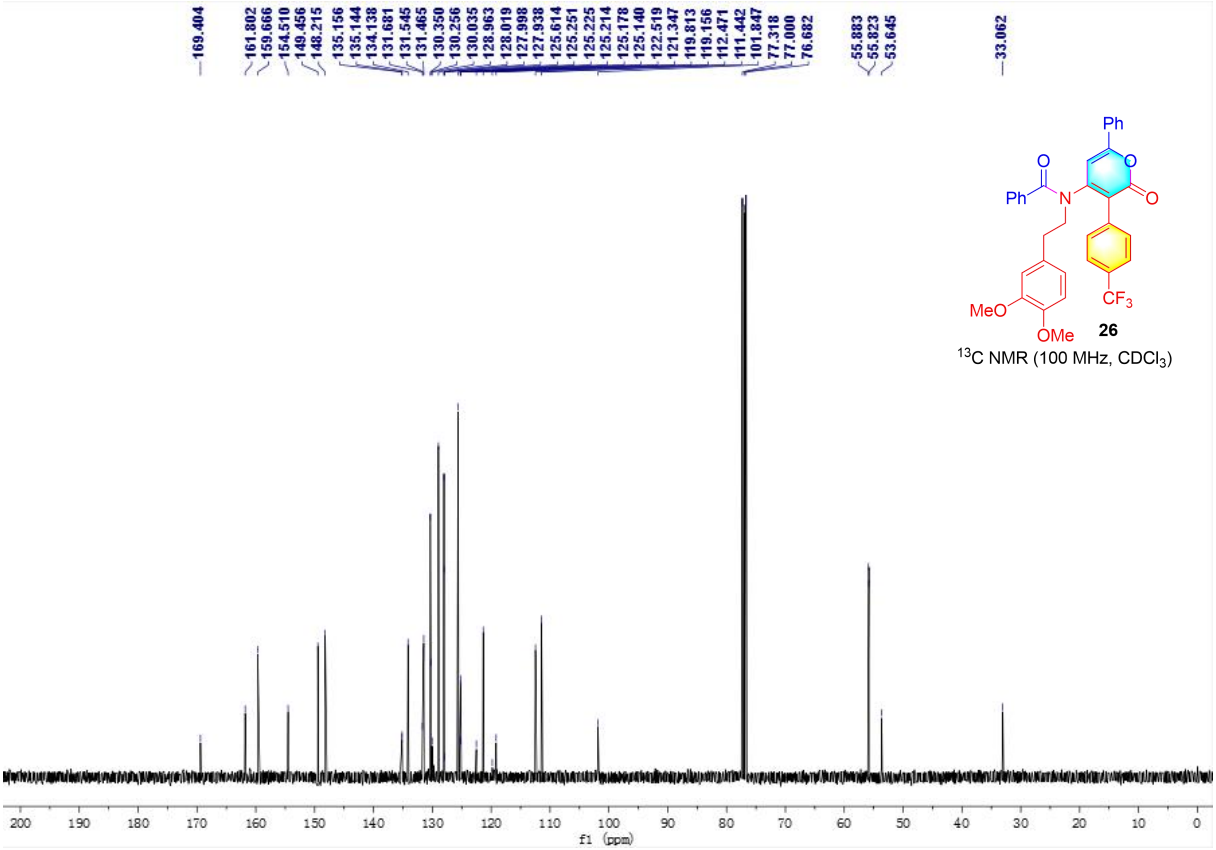


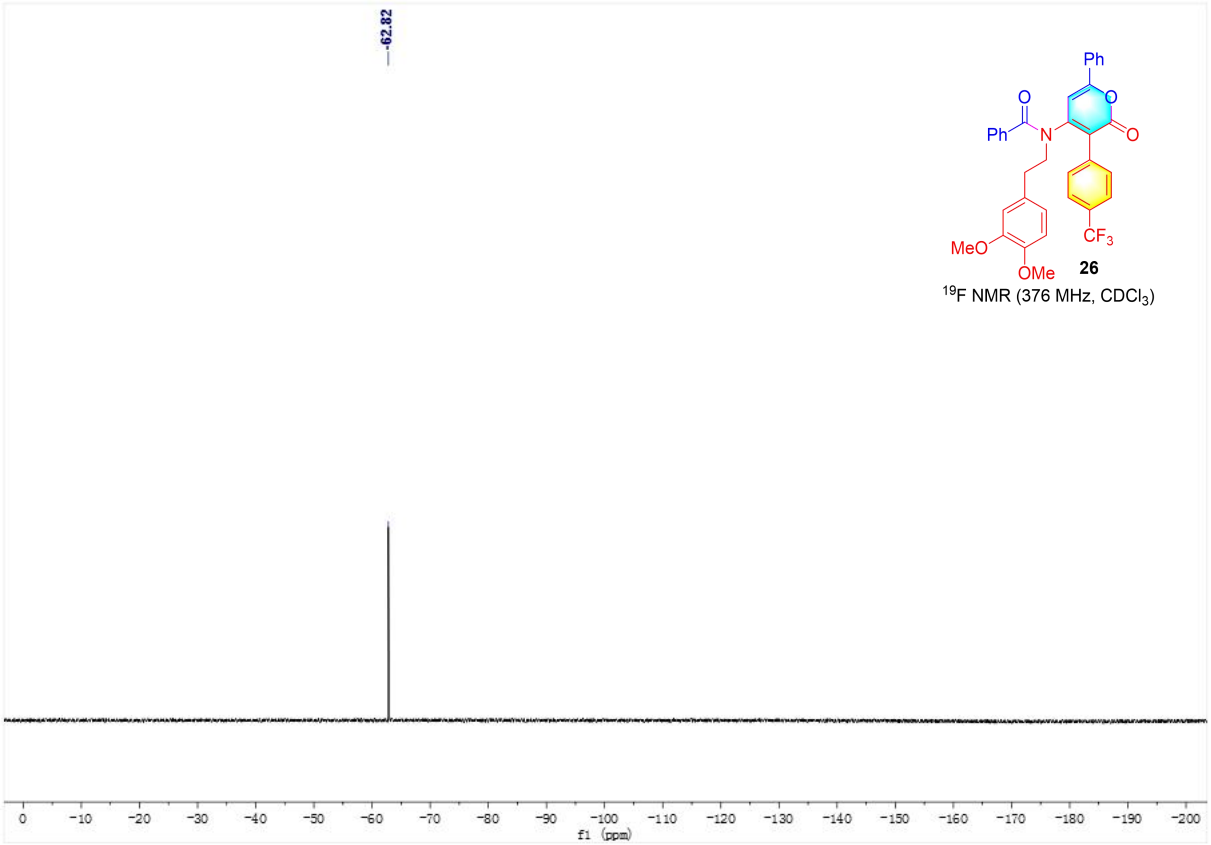
^{1}H NMR (400 MHz, $CDCl_3$)

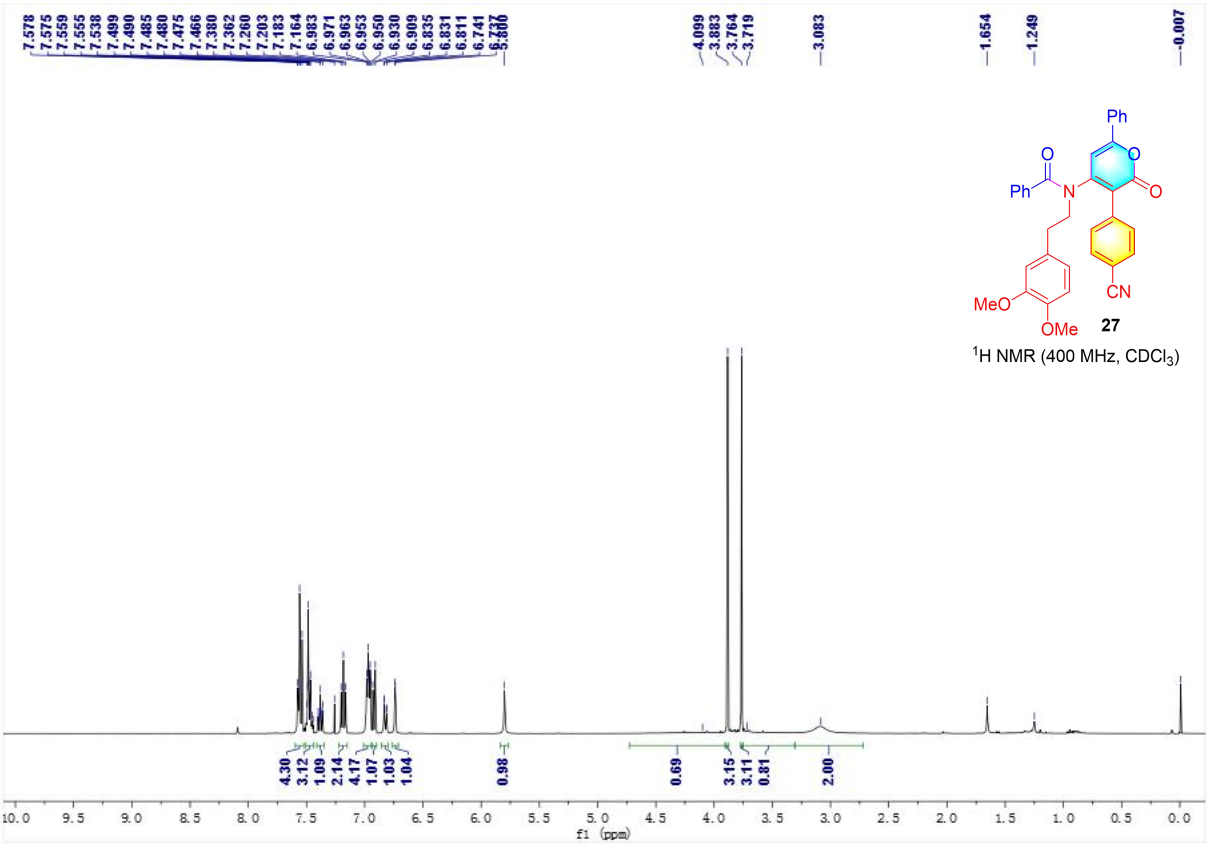


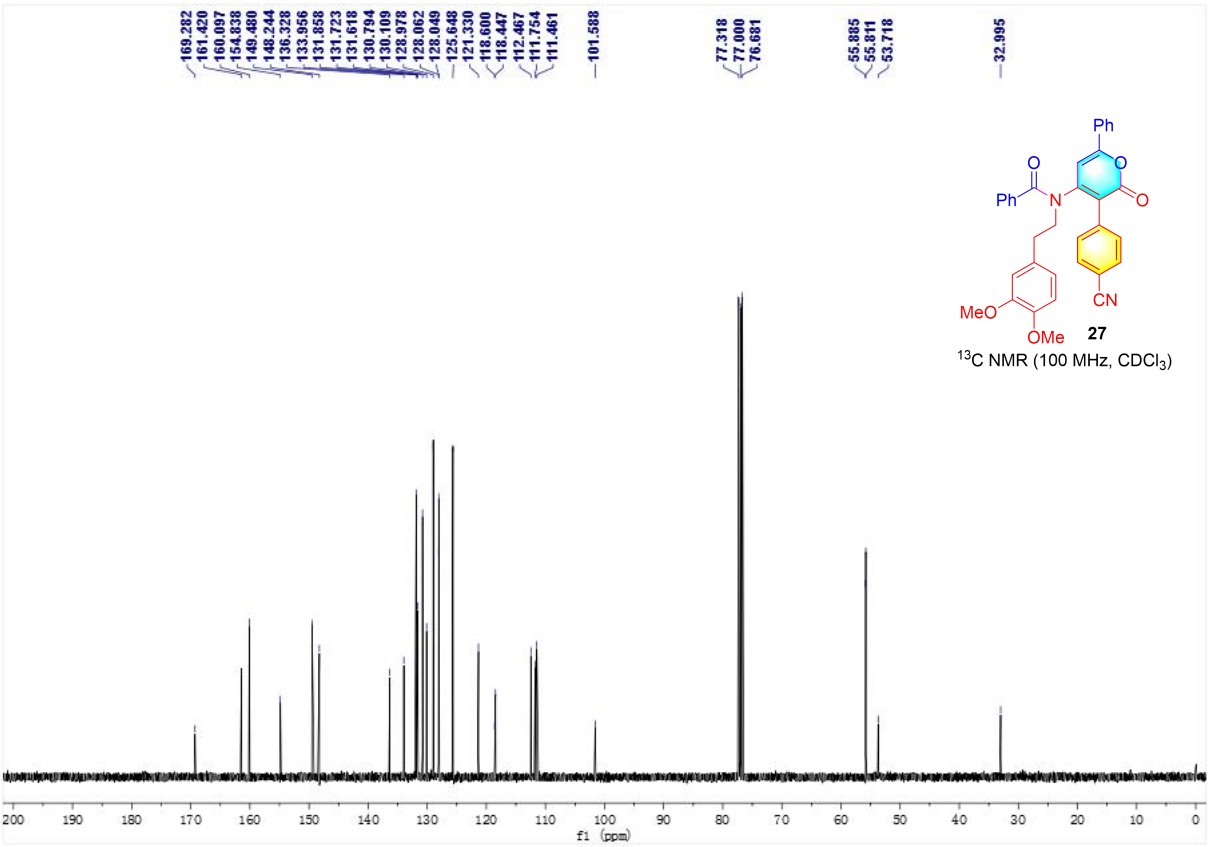
^{13}C NMR (100 MHz, $CDCl_3$)

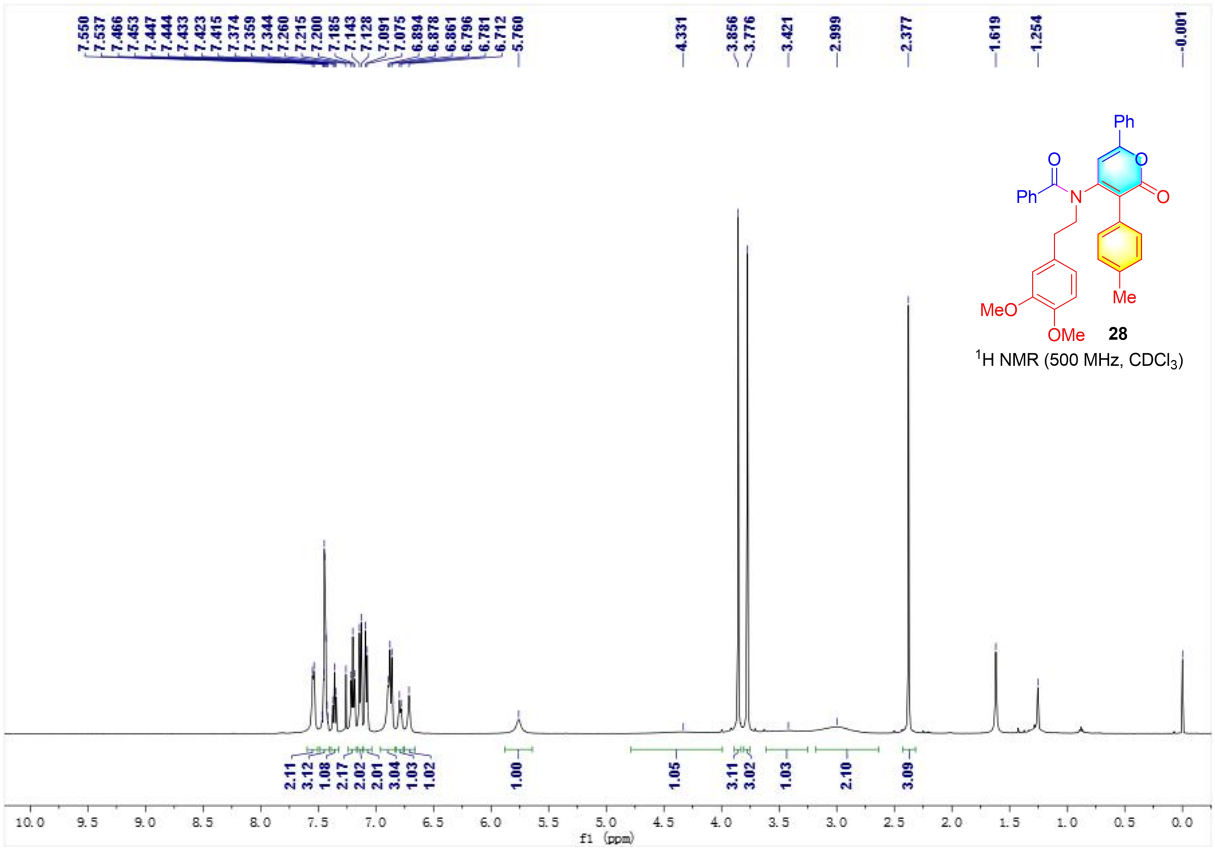

7.582
7.563
7.548
7.527
7.494
7.482
7.465
7.450
7.443
7.390
7.372
7.353
7.260
7.198
7.179
7.159
7.021
7.001
6.979
6.960
6.923
6.903
6.833
6.813
6.744
5.811
4.078
3.882
3.773
3.653
3.087
1.638
1.257
0.878
0.855
0.830
-0.002
4.11
2.98
1.02
2.01
1.89
2.04
1.01
1.01
0.98
0.92
1.18
2.87
3.00
0.97
2.00
f1 (ppm)
Ph
O
Ph
N
O
O
MeO
OMe
CF3
26
1H NMR (400 MHz, CDCl3)


169.404
161.802
159.666
154.510
149.456
148.215
135.156
135.144
134.138
131.681
131.545
131.465
130.350
130.256
130.035
128.963
128.019
127.998
127.938
125.614
125.251
125.225
125.214
125.178
125.140
122.519
121.347
119.813
119.156
112.471
111.442
101.847
77.318
77.000
76.682
55.883
55.823
53.645
33.062
f1 (ppm)
Ph
O
Ph
N
O
O
MeO
OMe
CF3
26
13C NMR (100 MHz, CDCl3)

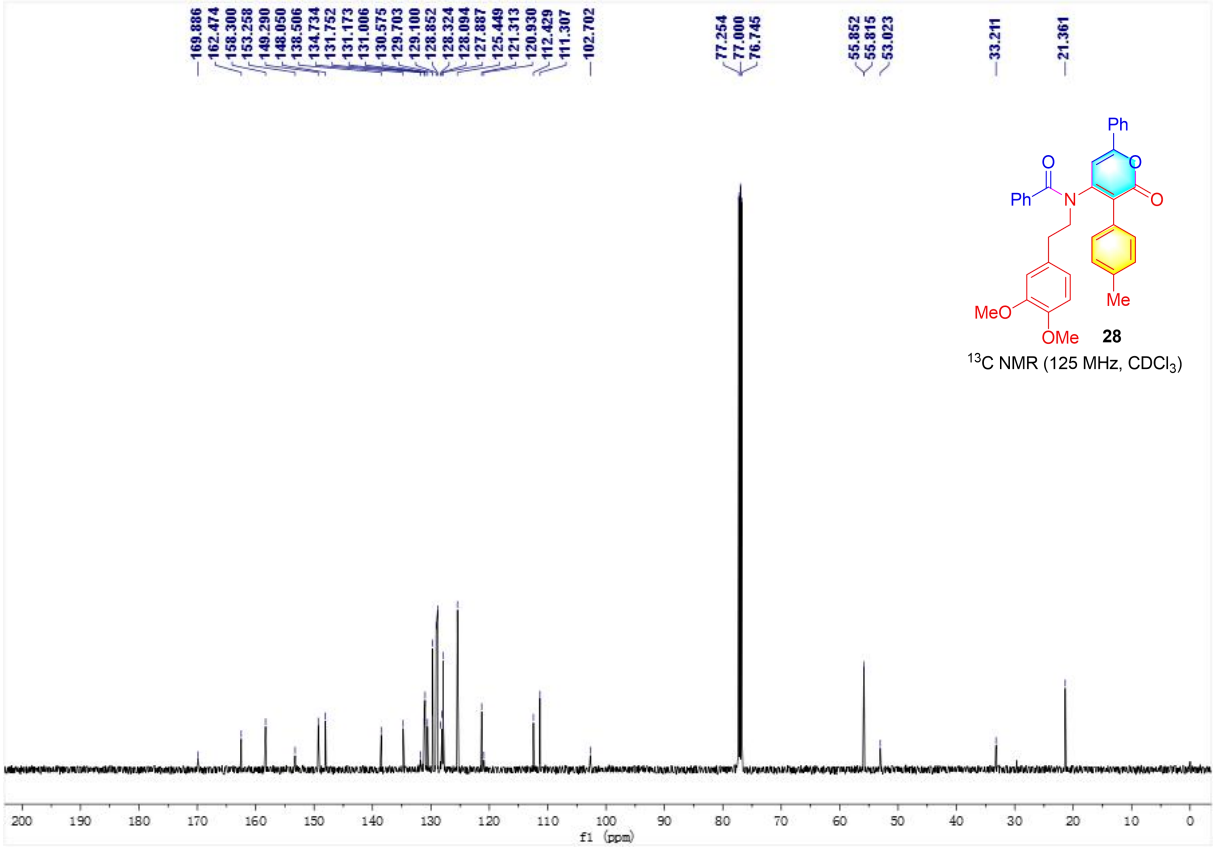

-62.82
Ph
O
O
Ph
N
O
MeO
OMe
CF3
26
19F NMR (376 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


7.578
7.575
7.559
7.555
7.538
7.499
7.490
7.485
7.480
7.475
7.466
7.380
7.362
7.260
7.203
7.183
7.164
6.983
6.971
6.963
6.953
6.950
6.930
6.909
6.835
6.831
6.811
6.741
4.099
3.883
3.764
3.719
3.083
1.654
1.249
0.007
Ph
O
Ph
N
O
O
MeO
OMe
CN
27
1H NMR (400 MHz, CDCl3)
4.30
3.12
1.09
2.14
4.17
1.07
1.03
1.04
0.98
0.69
3.15
3.11
0.81
2.00
f1 (ppm)

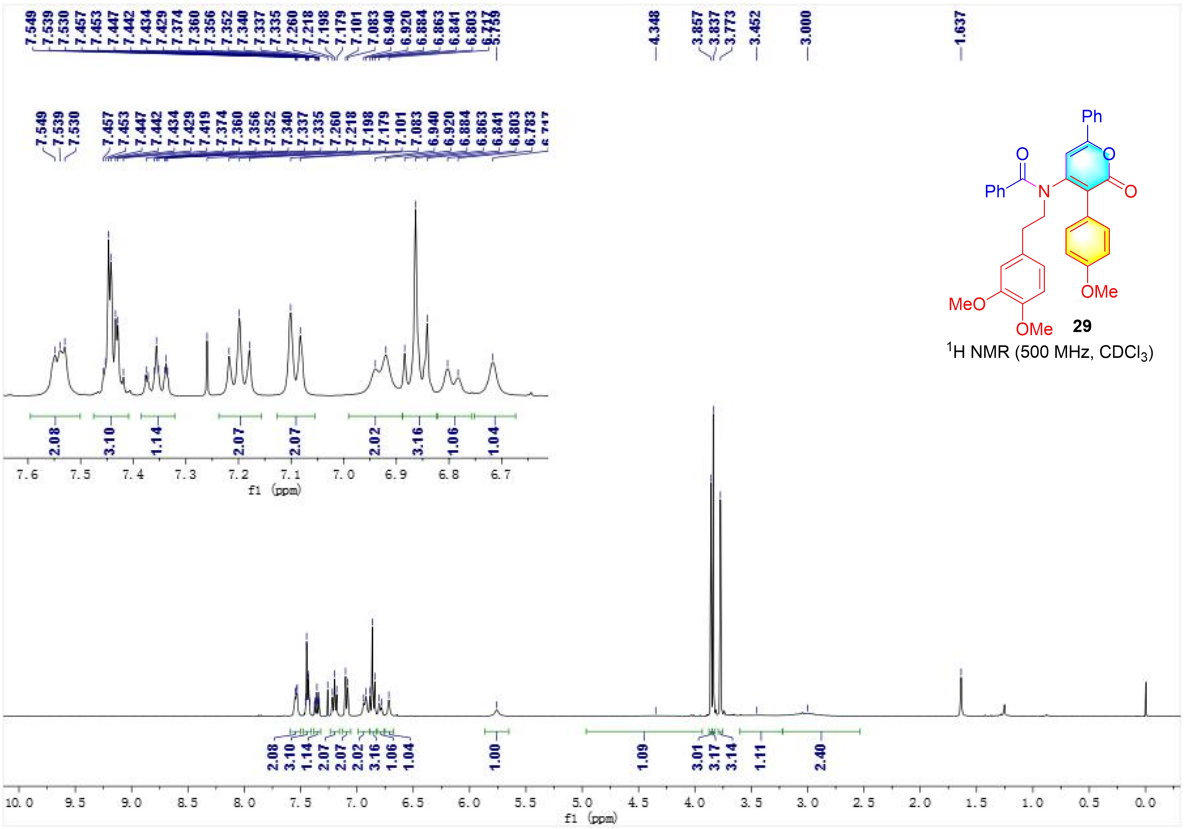

169.282
161.420
160.097
154.838
149.480
148.244
136.328
133.956
131.858
131.723
131.618
130.794
130.109
128.978
128.062
128.049
125.648
121.330
118.600
118.447
112.467
111.754
111.461
101.588
77.318
77.000
76.681
55.885
55.811
53.718
32.995
Ph
O
Ph
N
O
O
MeO
OMe
CN
27
13C NMR (100 MHz, CDCl3)
f1 (ppm)



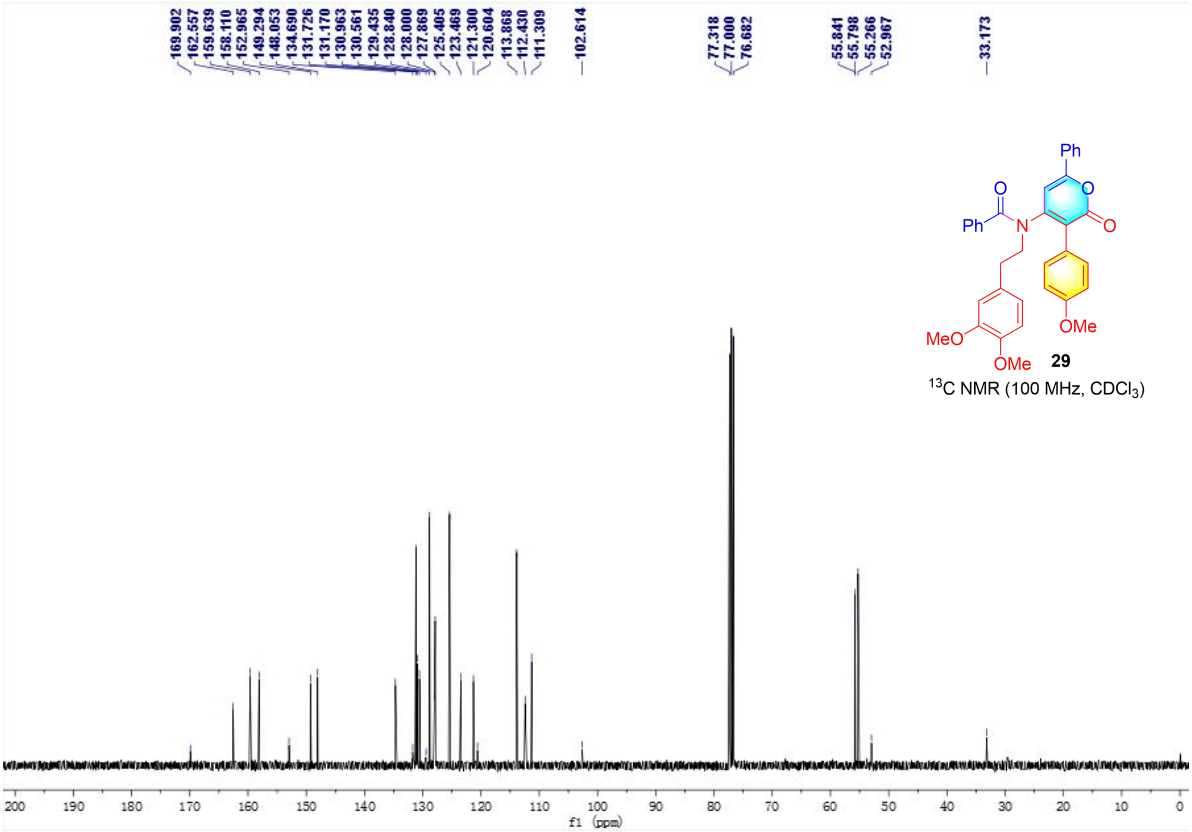
^{1}H NMR (500 MHz, $CDCl_3$)



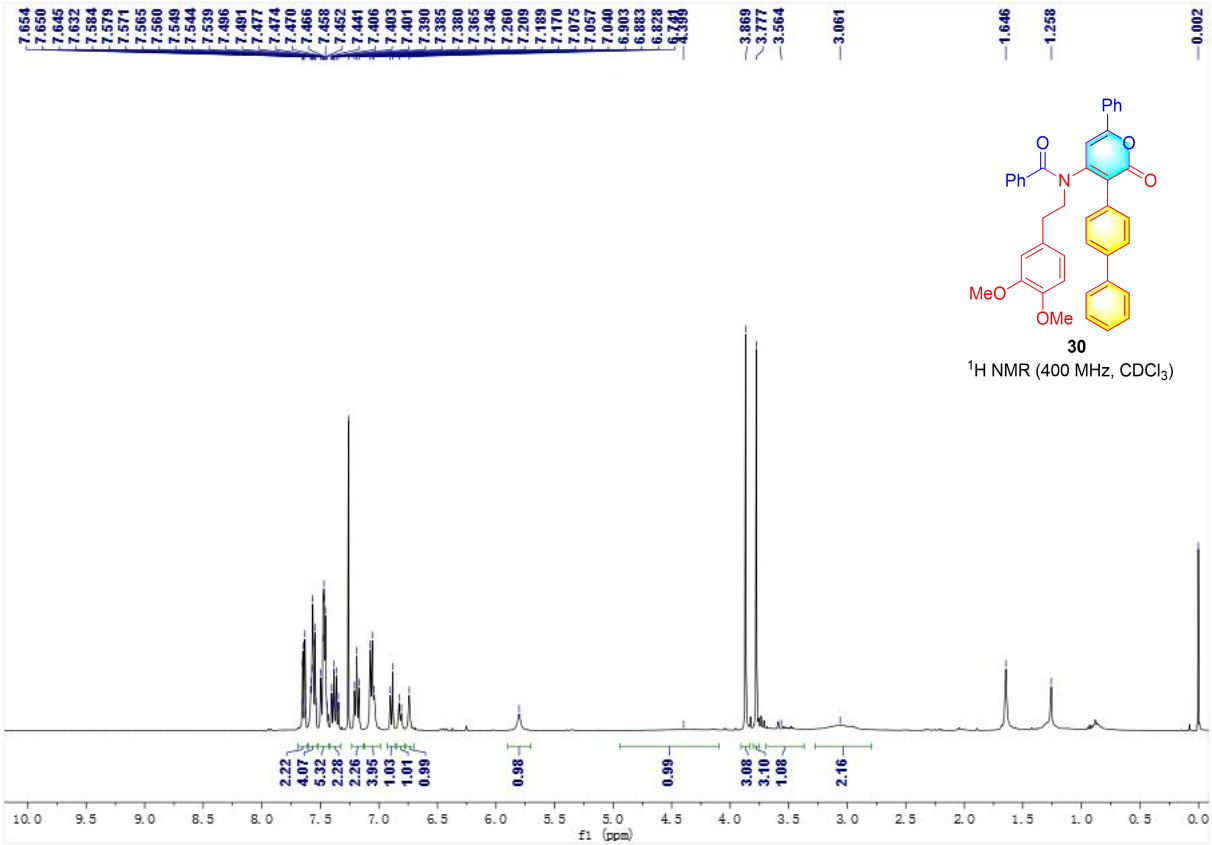
^{13}C NMR (125 MHz, $CDCl_3$)



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

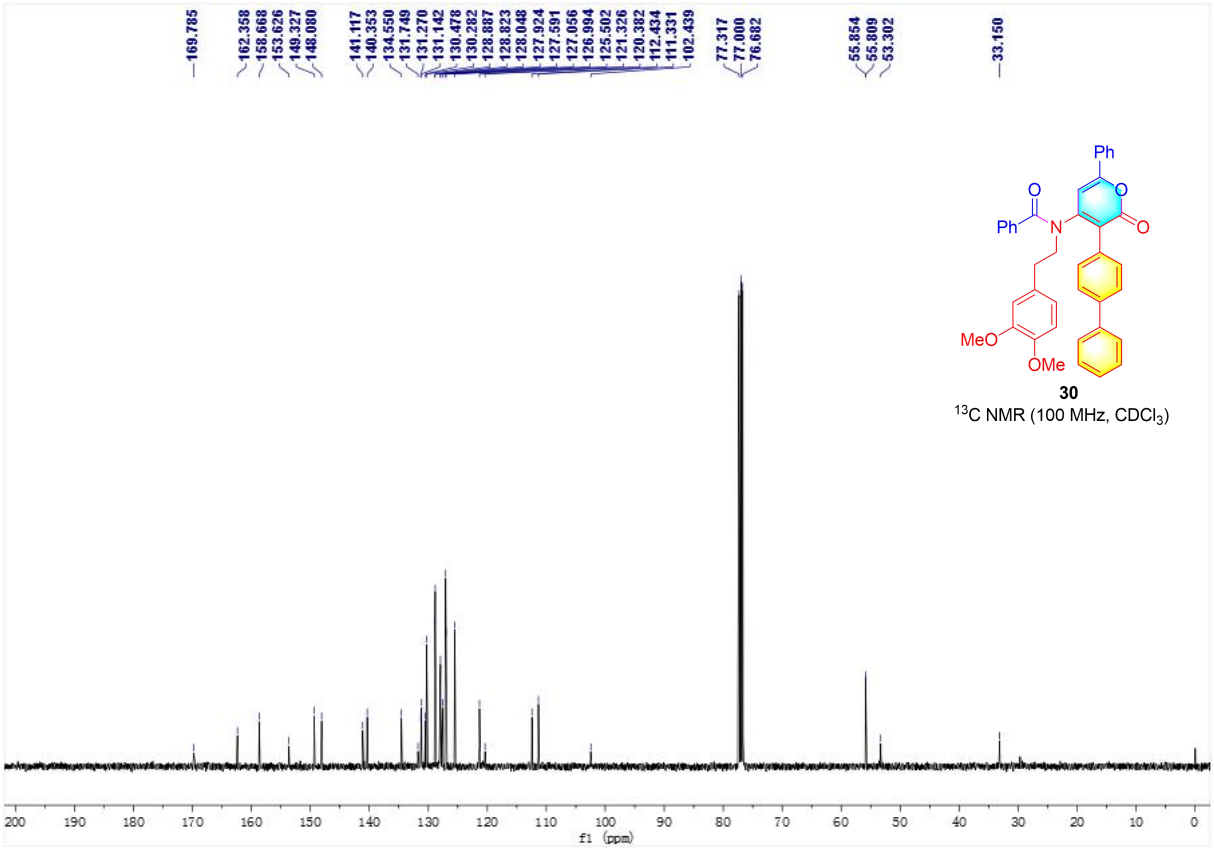


^{13}C NMR (100 MHz, $CDCl_3$)



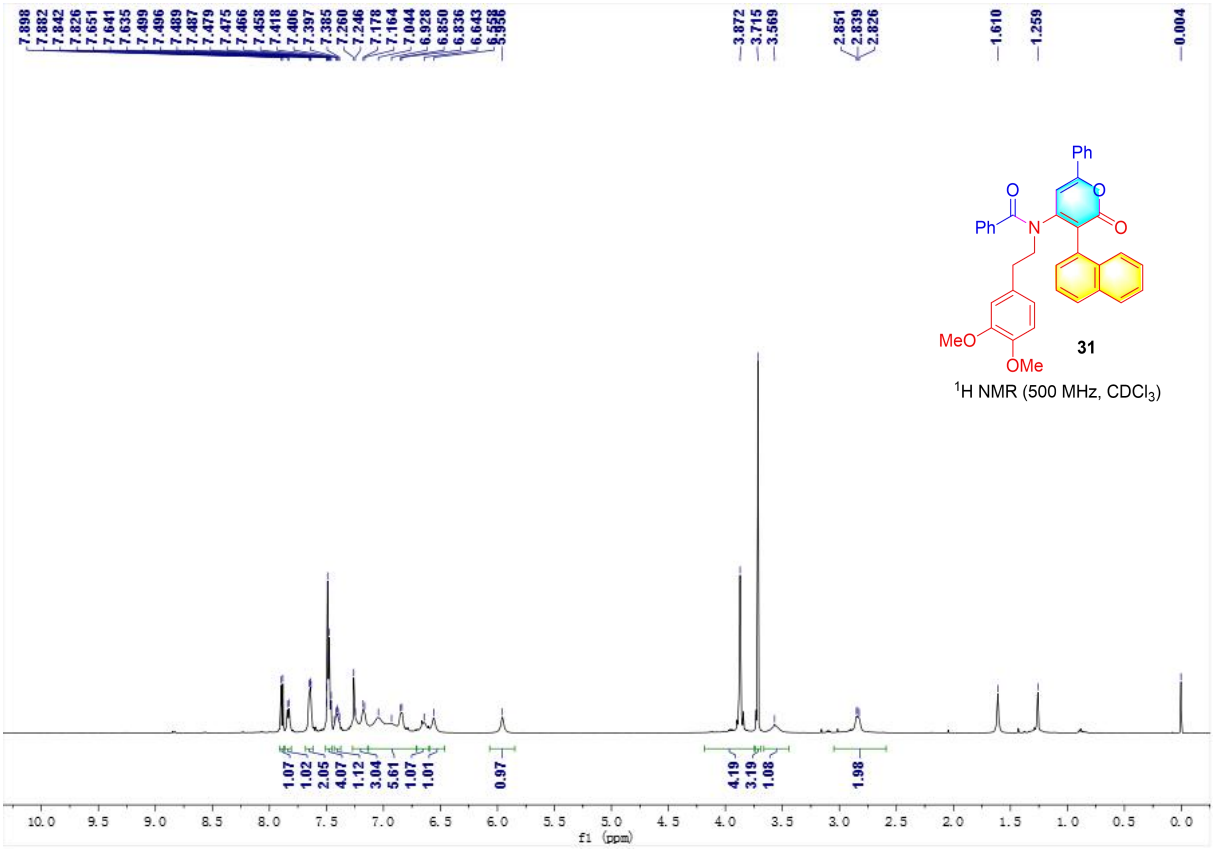
30

^{1}H NMR (400 MHz, $CDCl_3$)

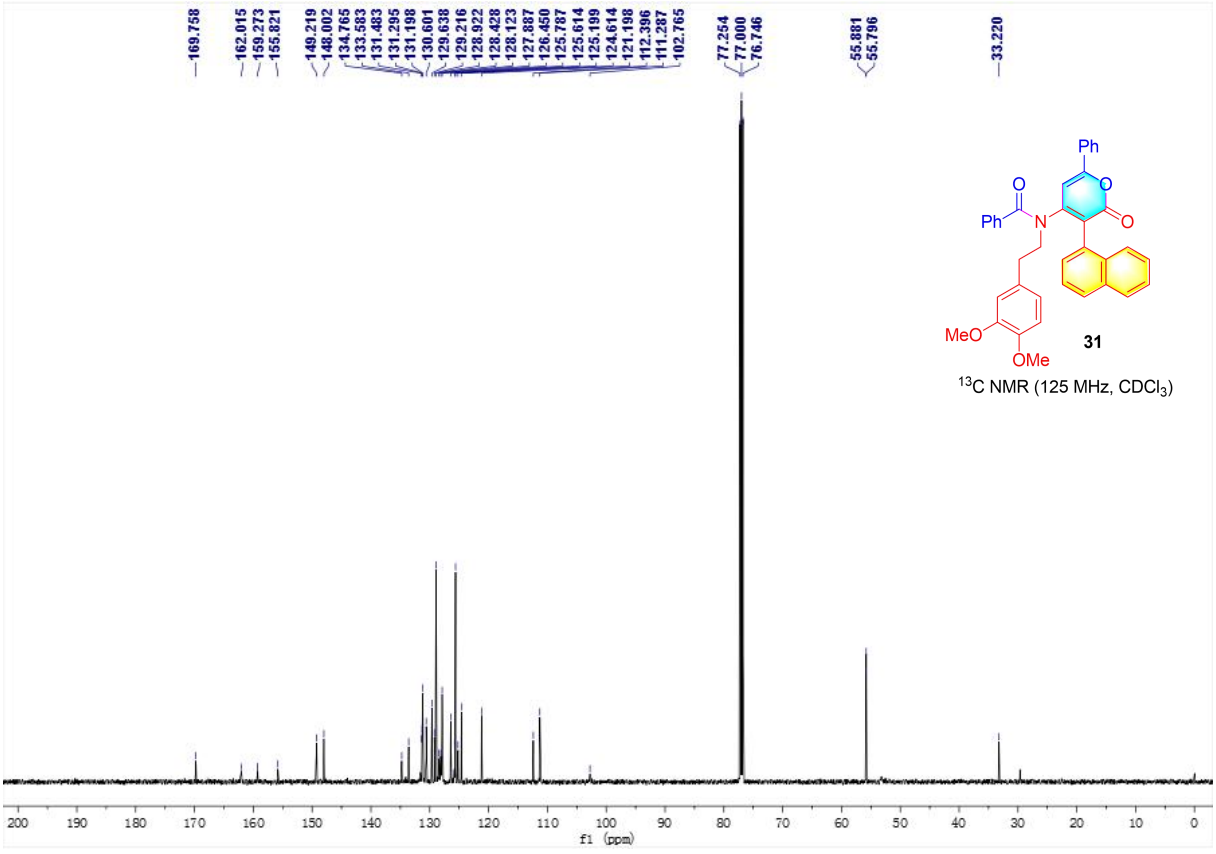


30

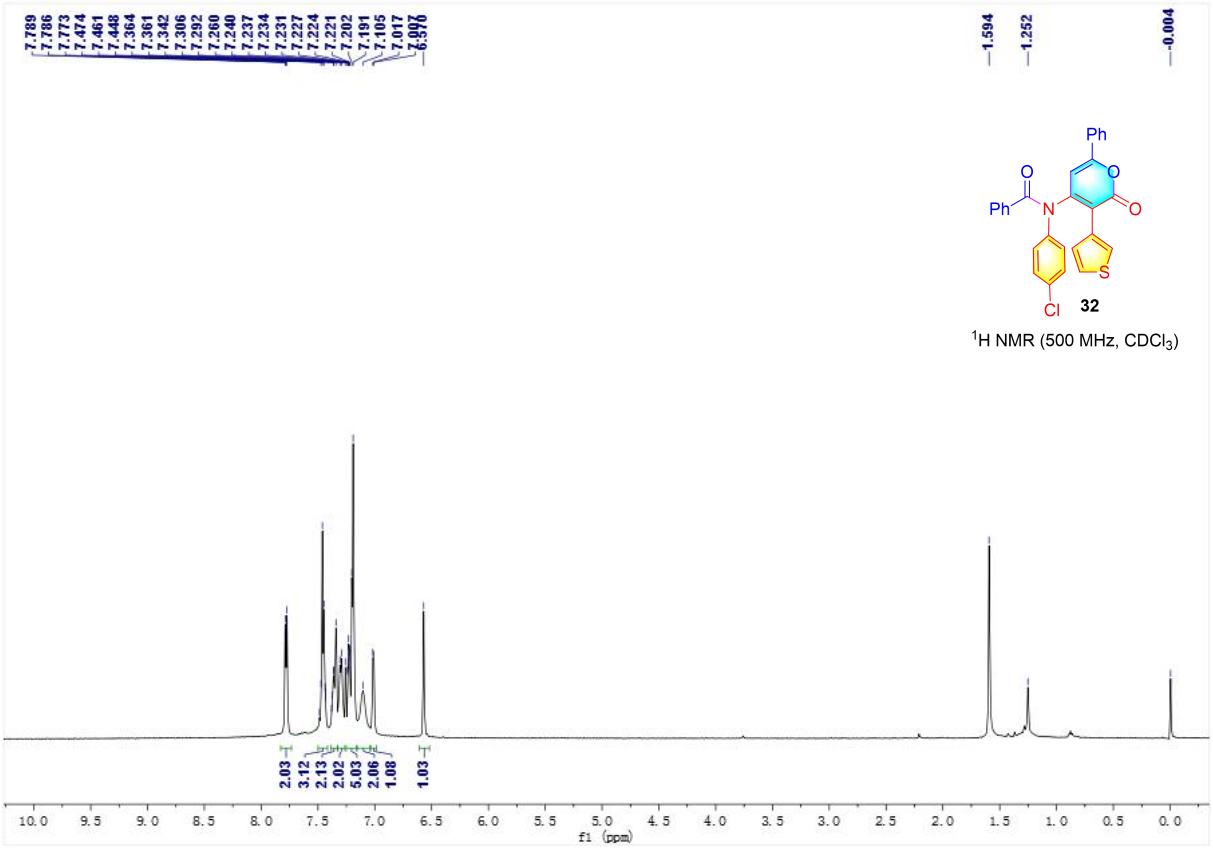
^{13}C NMR (100 MHz, $CDCl_3$)



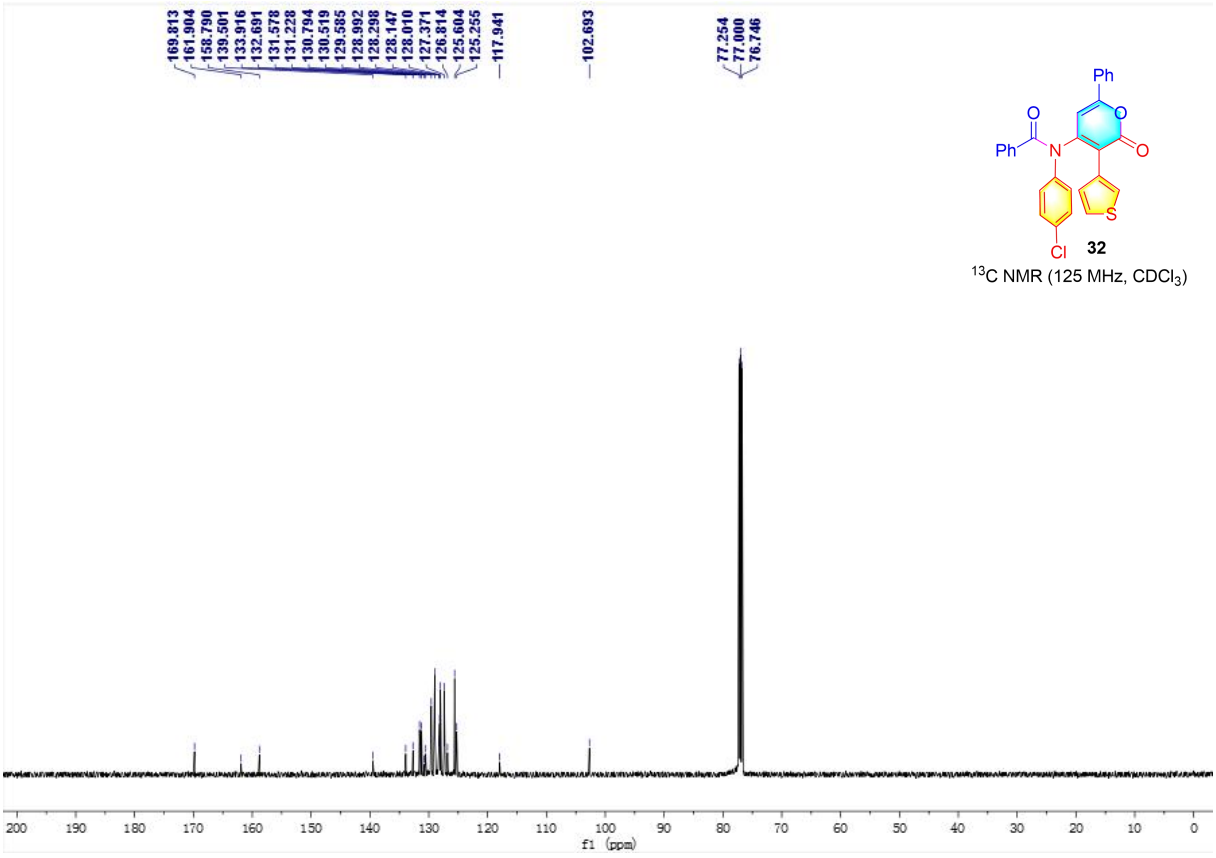
^{1}H NMR (500 MHz, $CDCl_3$)



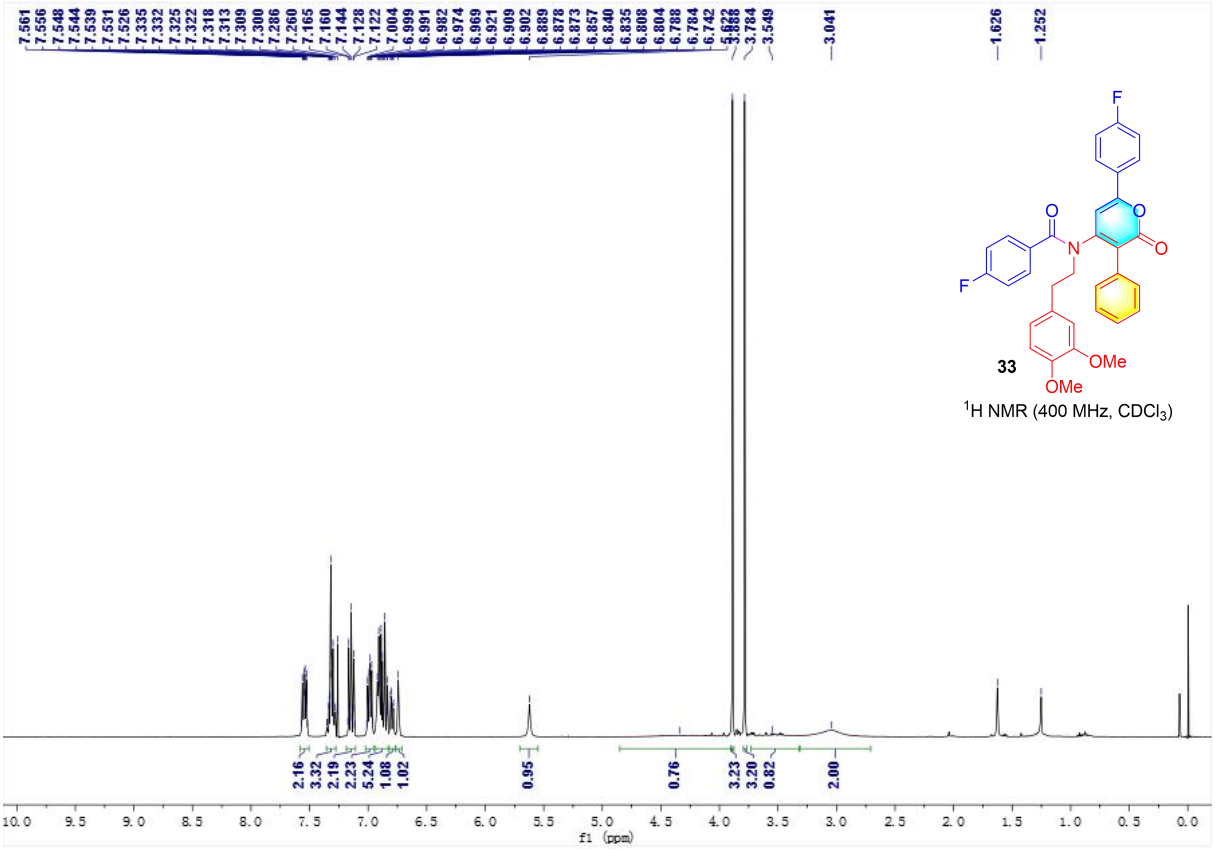
^{13}C NMR (125 MHz, $CDCl_3$)



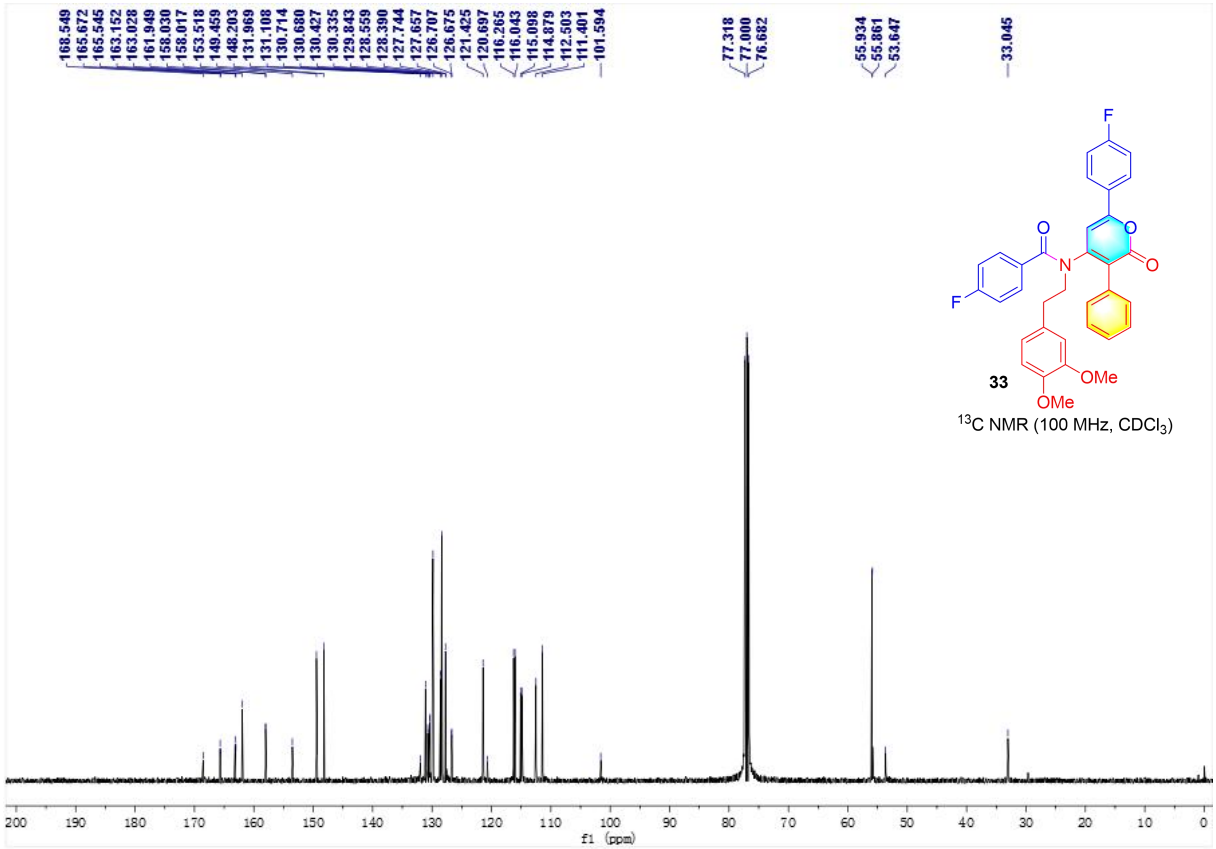
^{1}H NMR (500 MHz, $CDCl_3$)



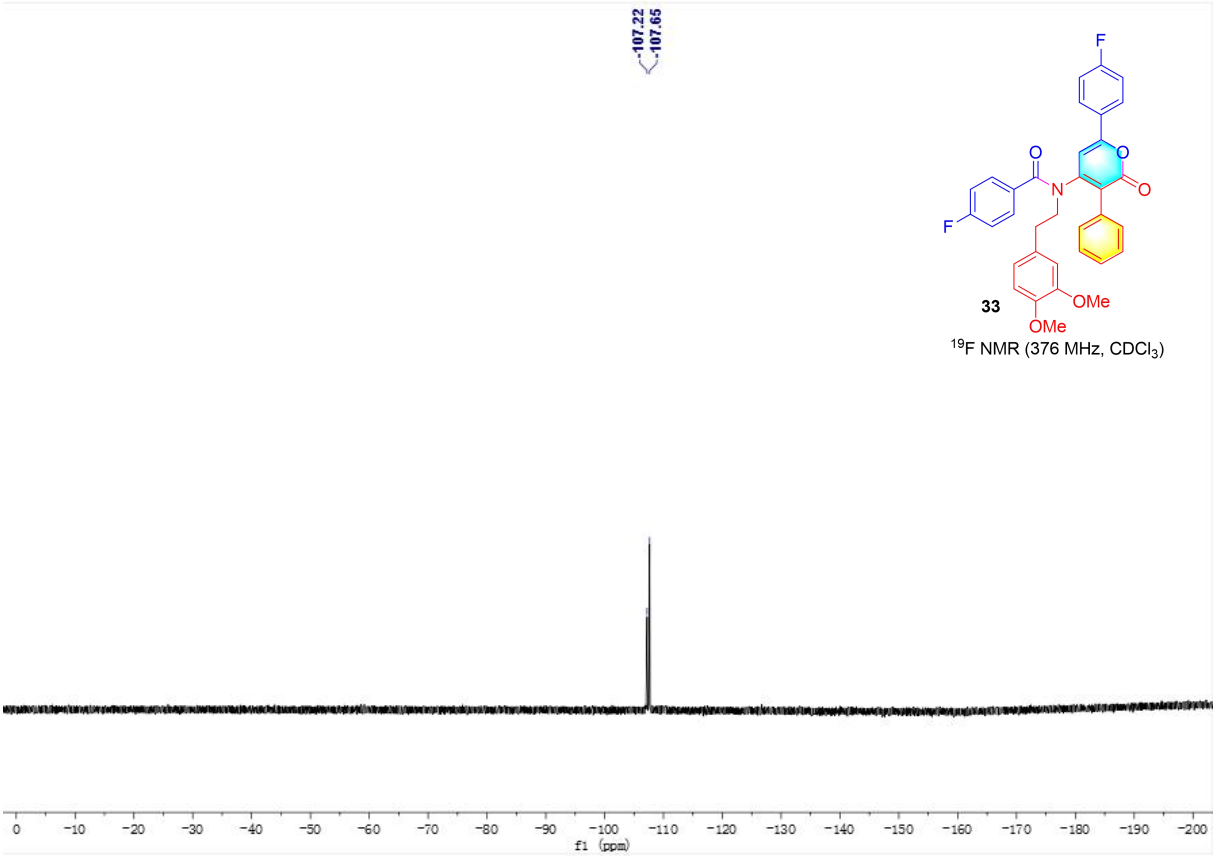
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

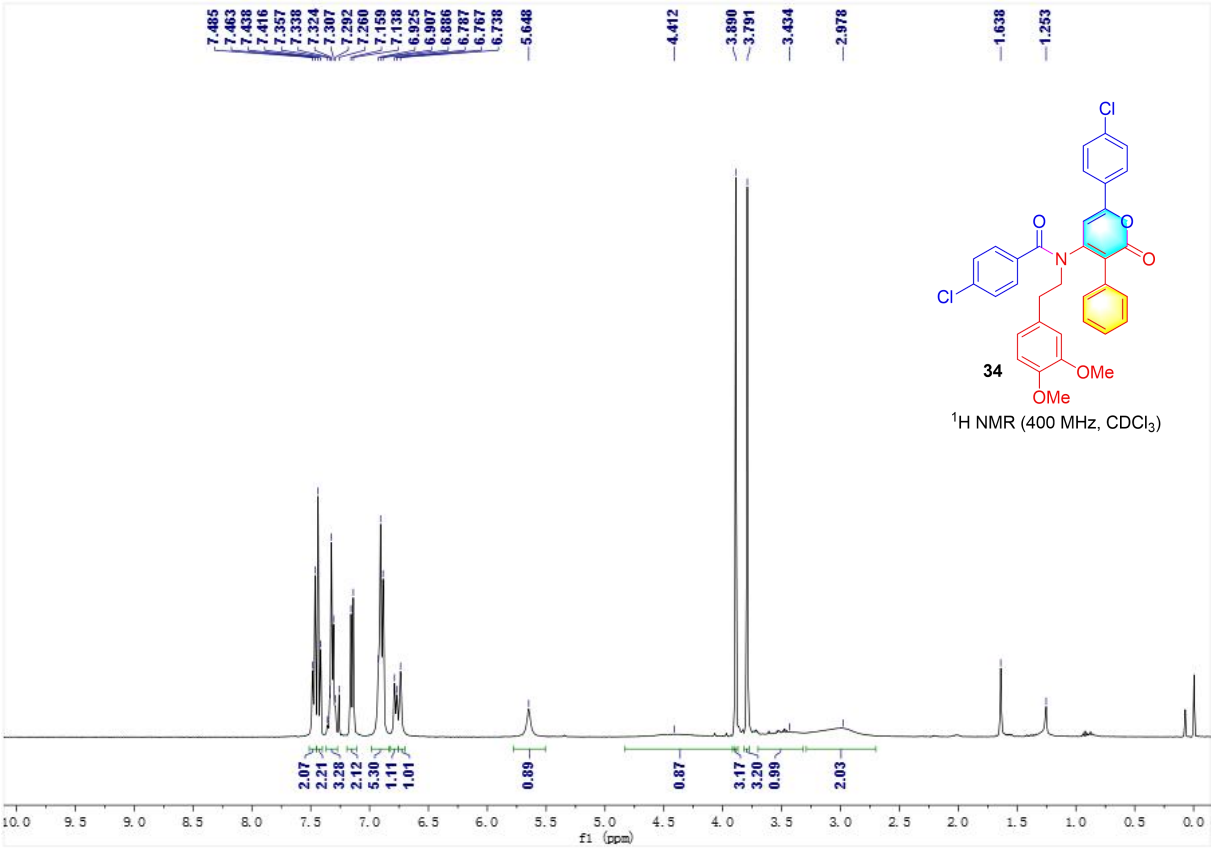


^{13}C NMR (100 MHz, $CDCl_3$)

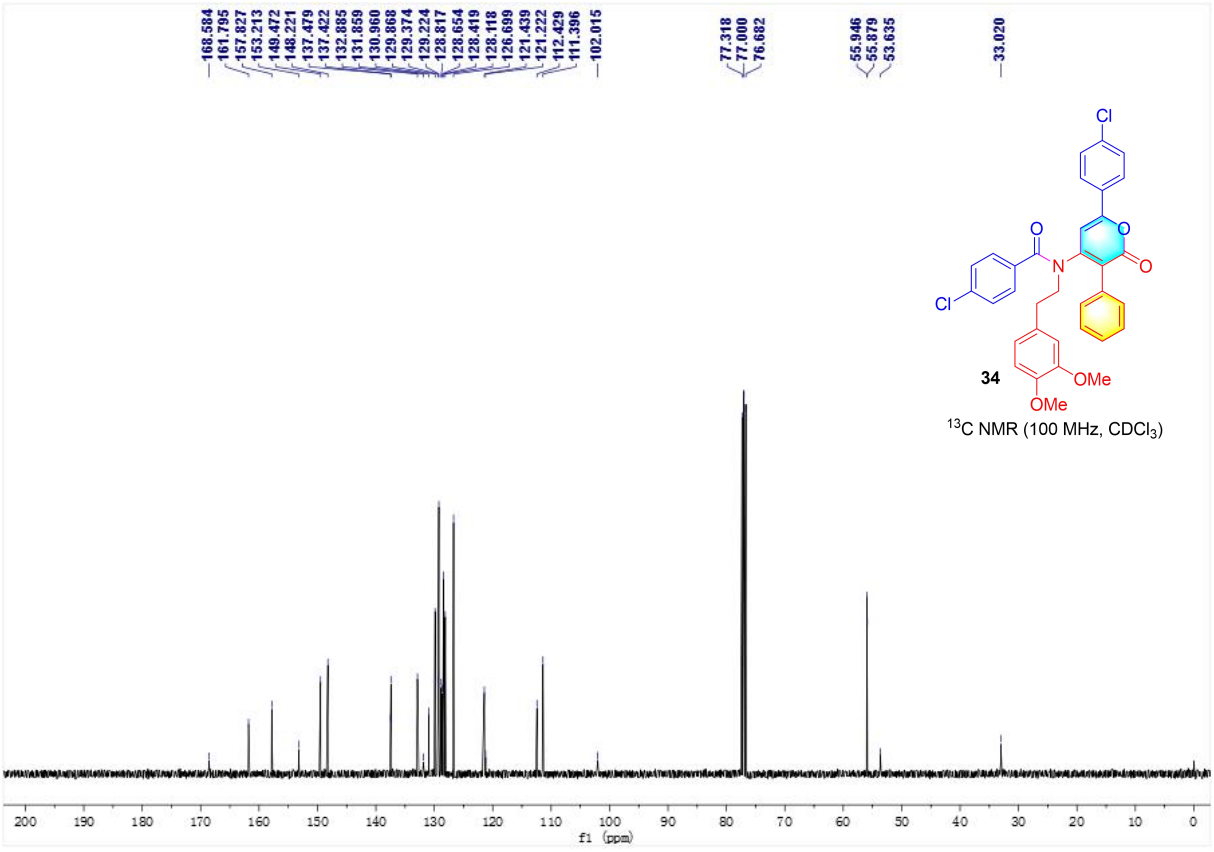


33

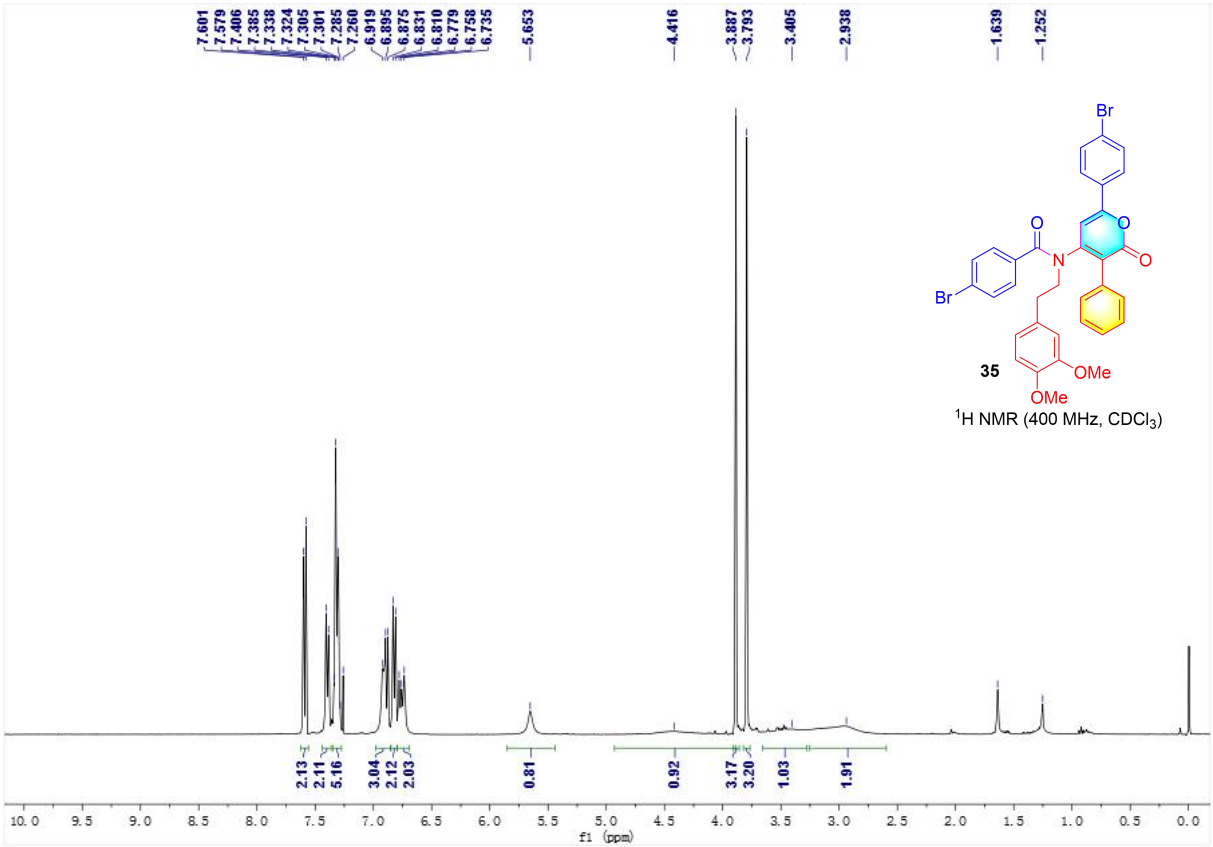
^{19}F NMR (376 MHz, $CDCl_3$)



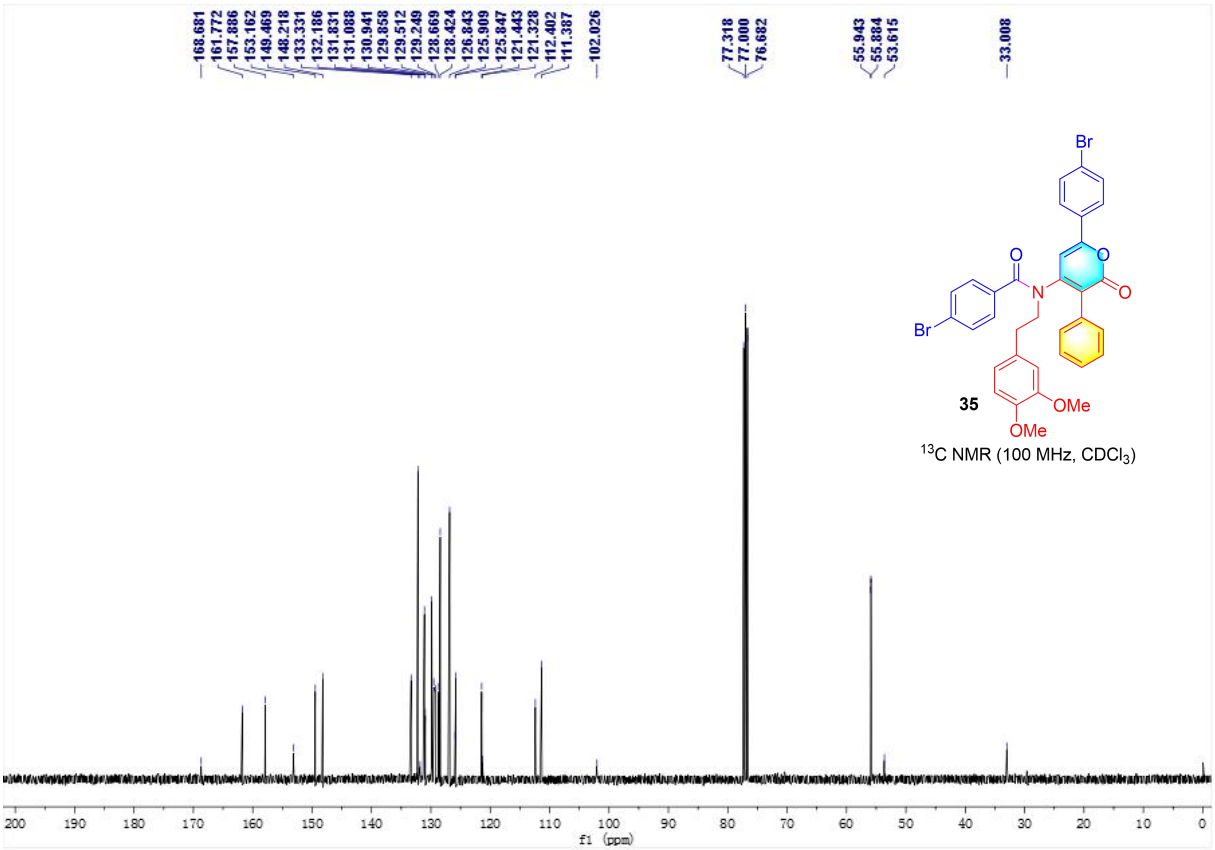
^{1}H NMR (400 MHz, $CDCl_3$)



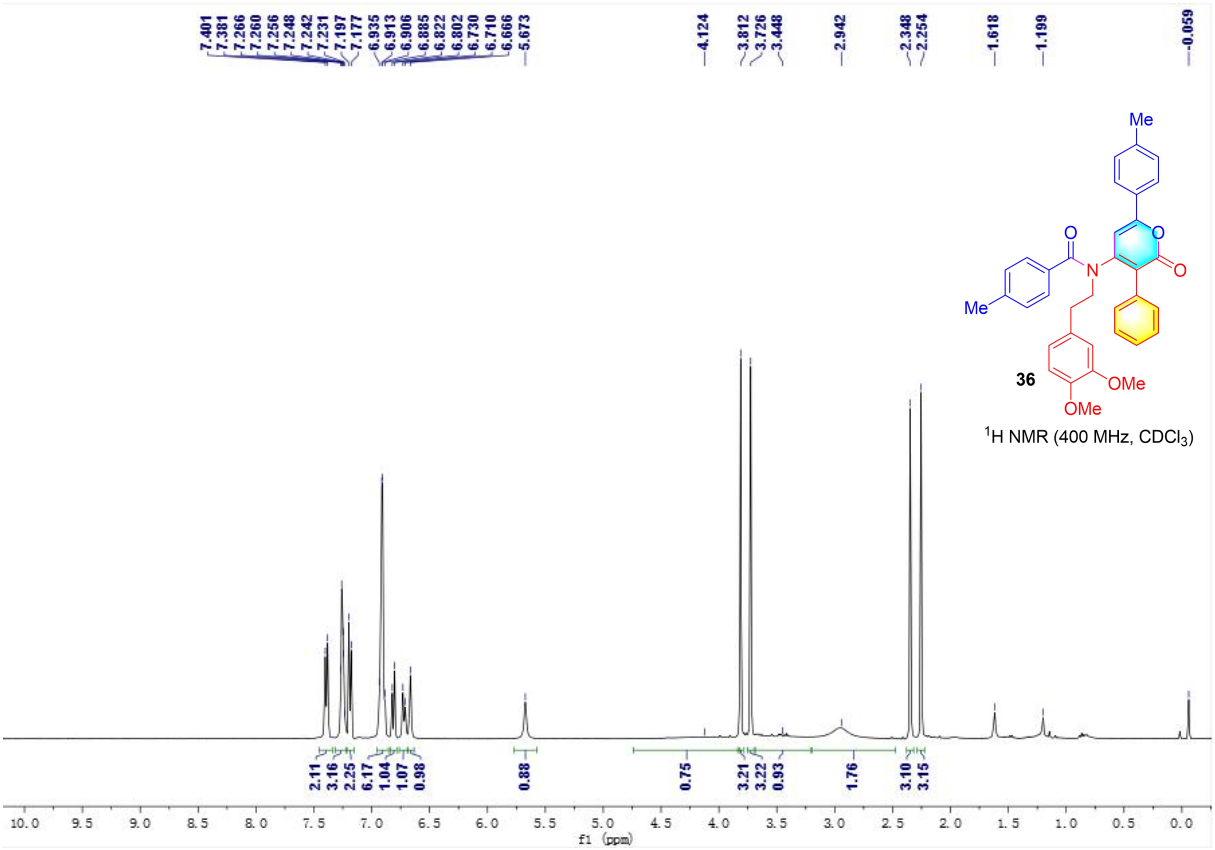
^{13}C NMR (100 MHz, $CDCl_3$)



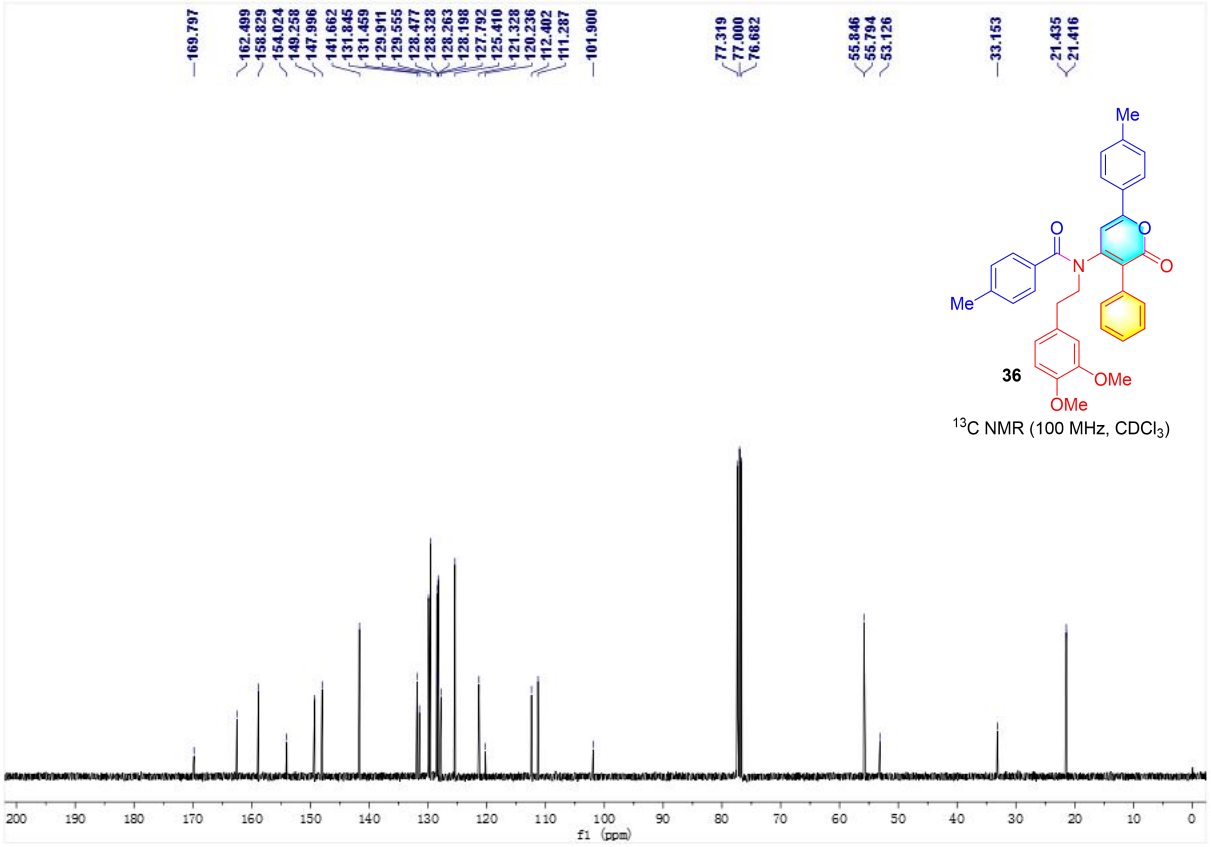
^{1}H NMR (400 MHz, $CDCl_3$)



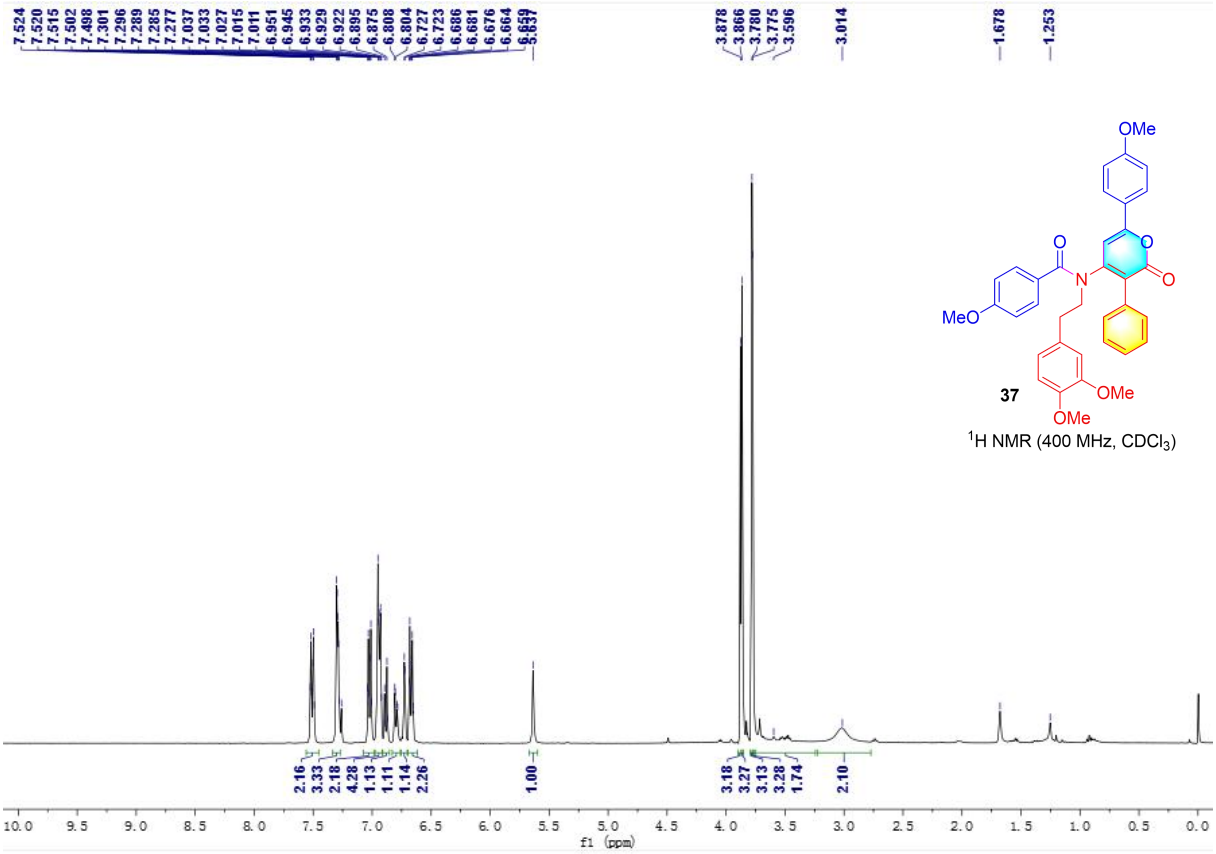
^{13}C NMR (100 MHz, $CDCl_3$)



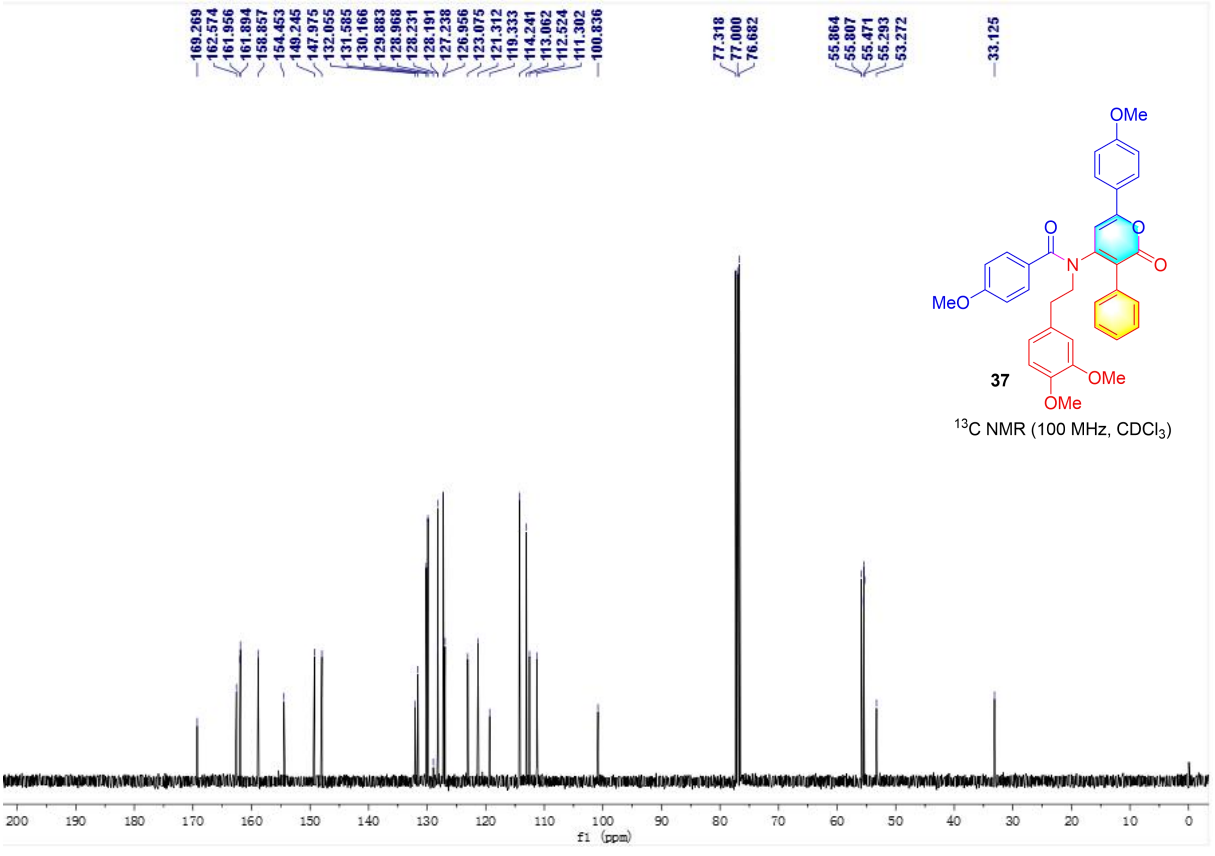
^{1}H NMR (400 MHz, $CDCl_3$)



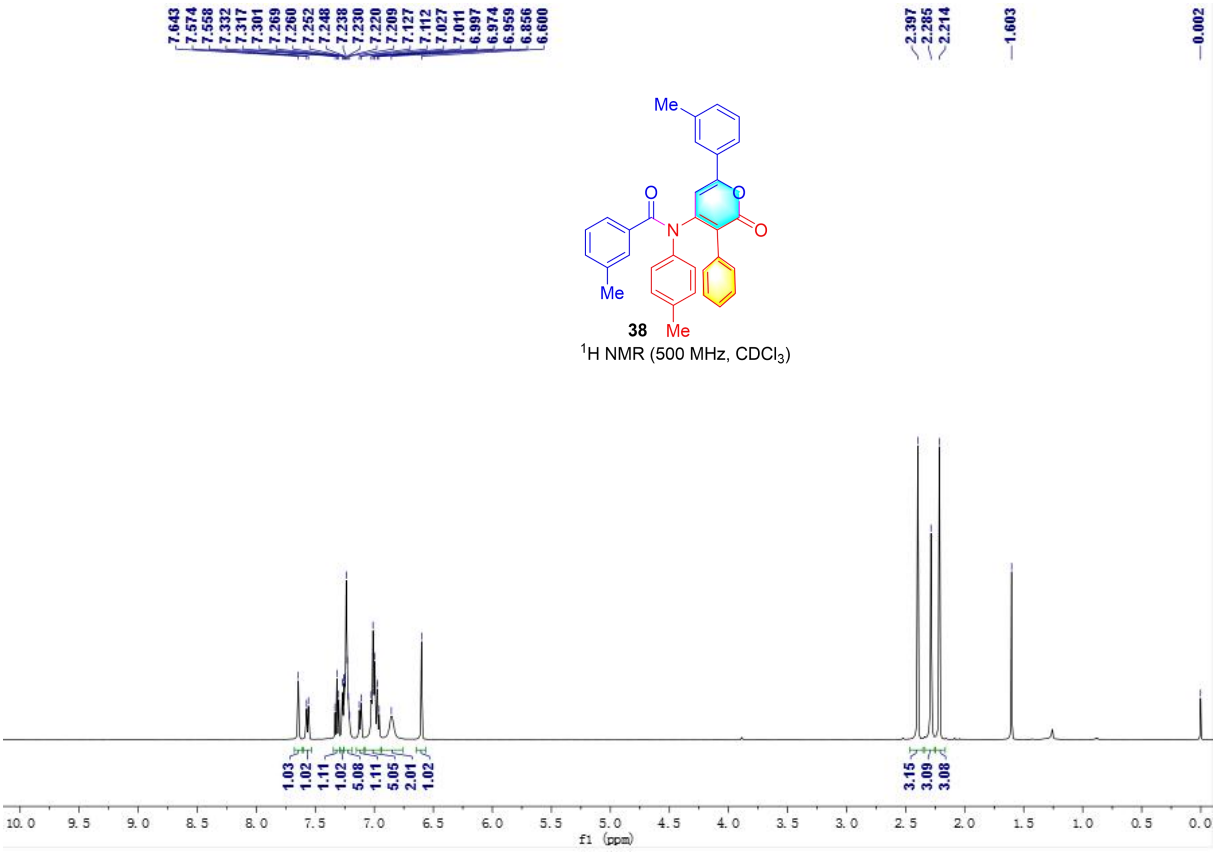
^{13}C NMR (100 MHz, $CDCl_3$)



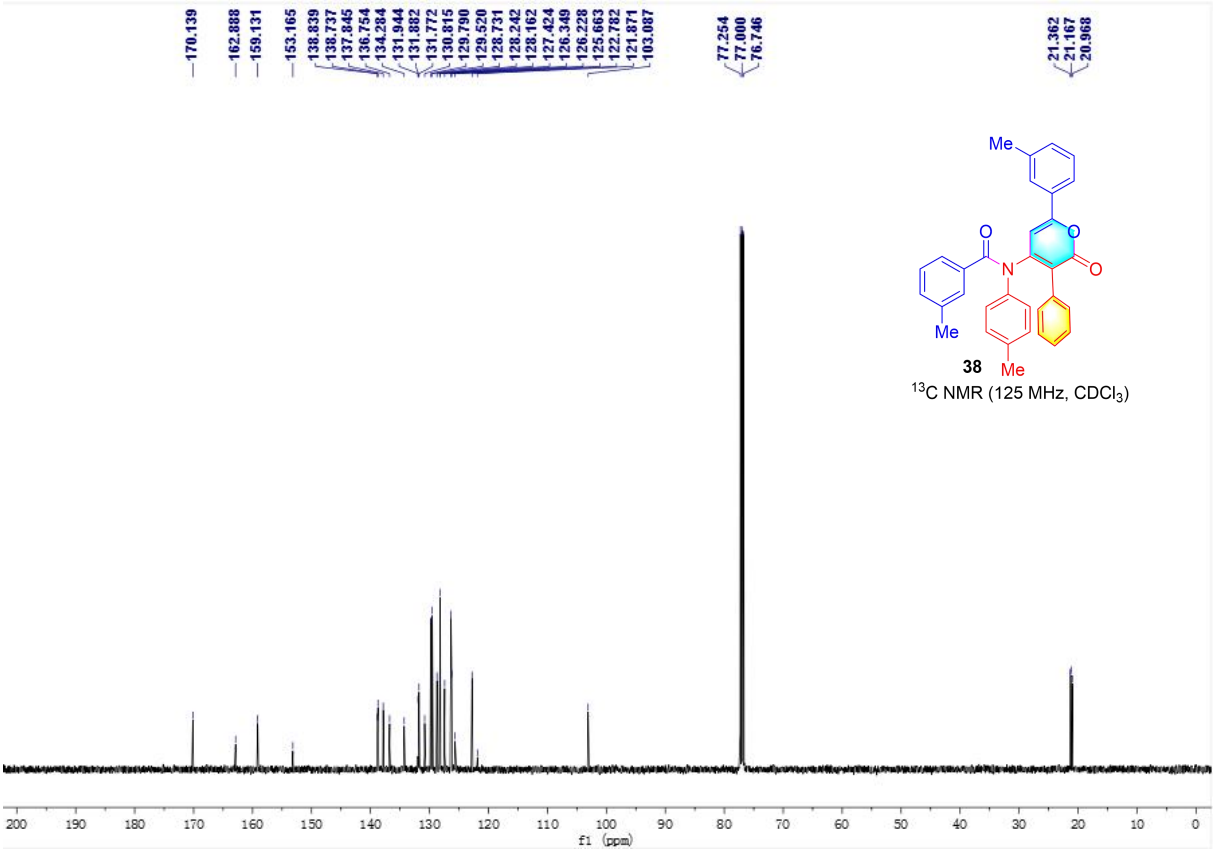
^{1}H NMR (400 MHz, $CDCl_3$)



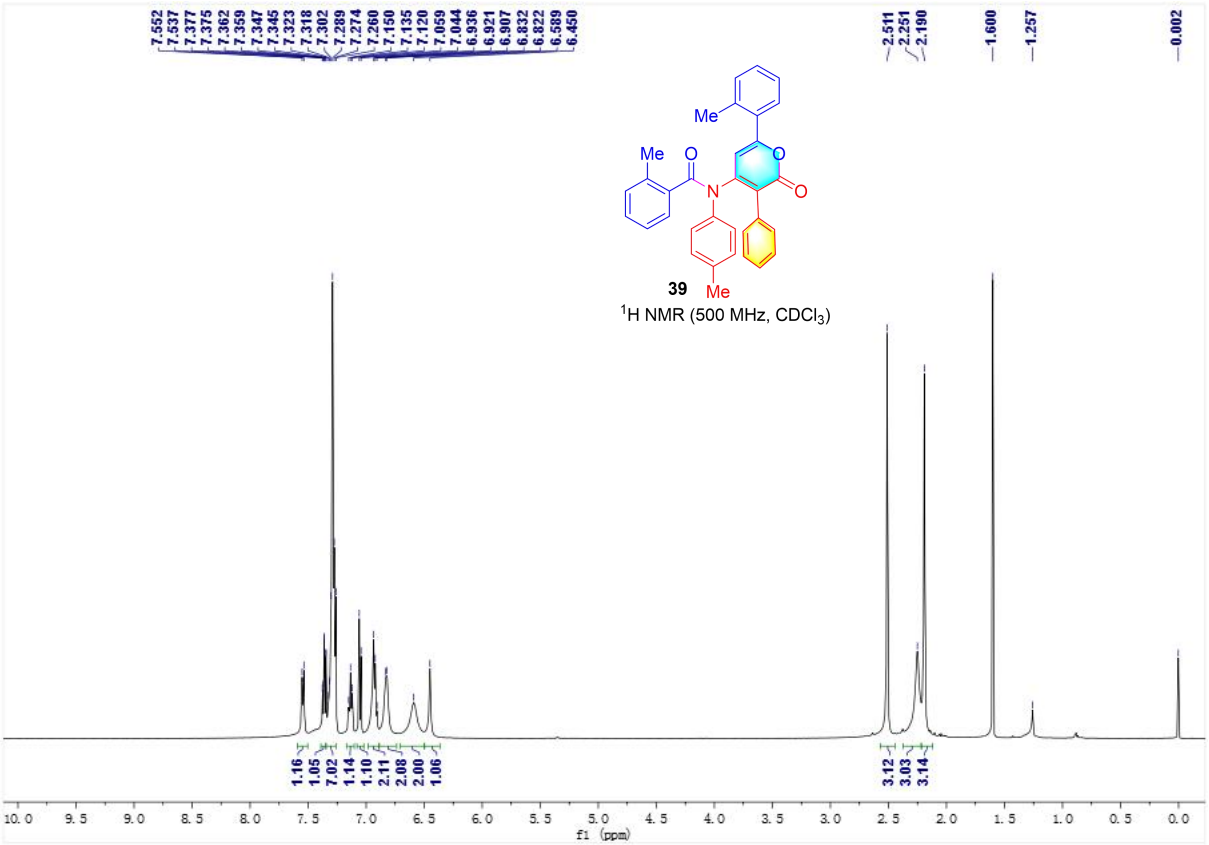
^{13}C NMR (100 MHz, $CDCl_3$)



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

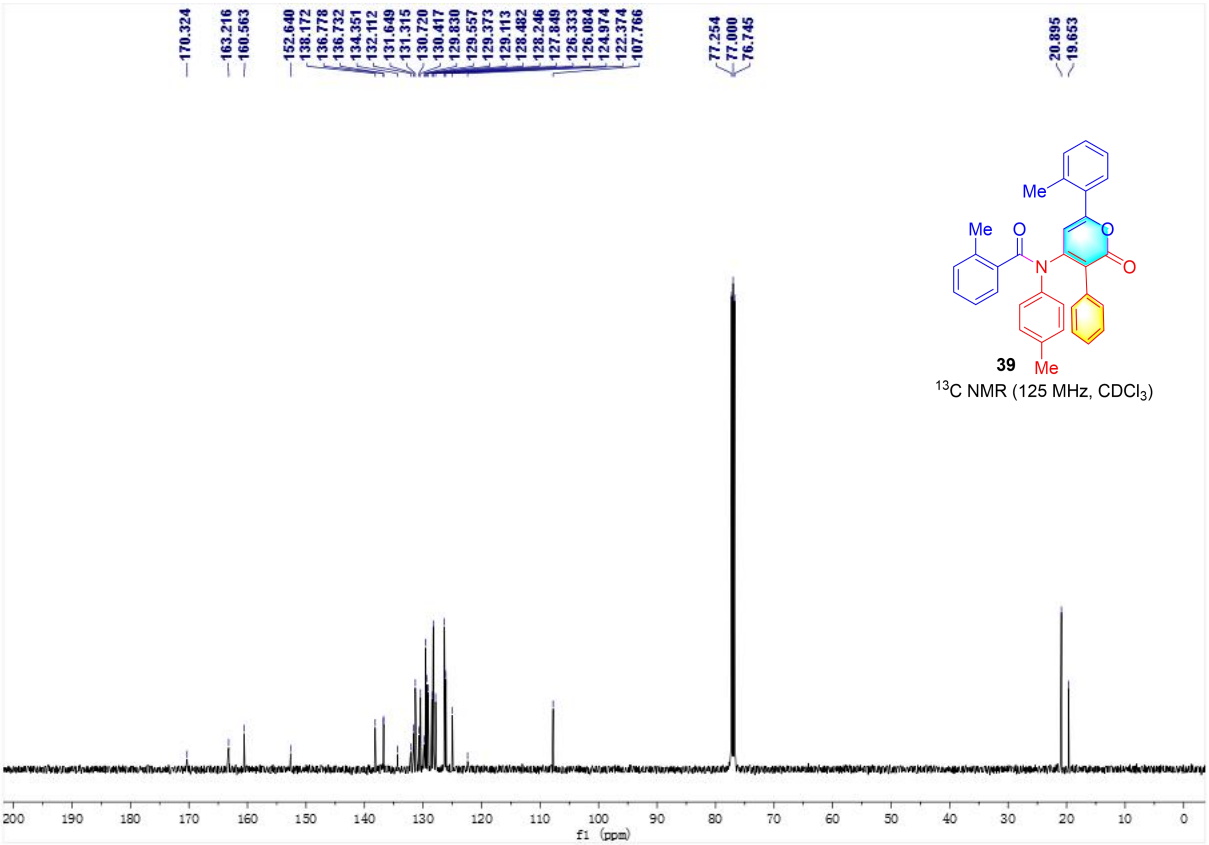


^{13}C NMR (125 MHz, $CDCl_3$)



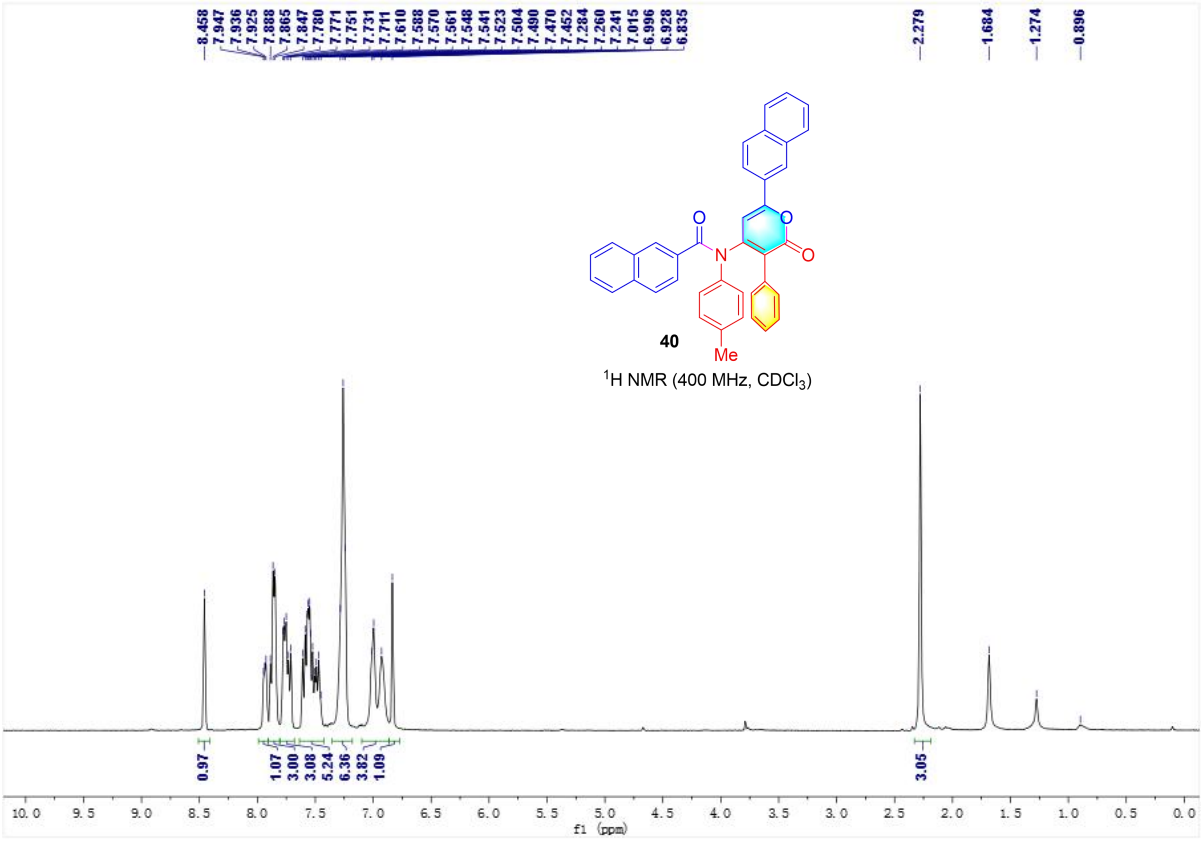
39

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



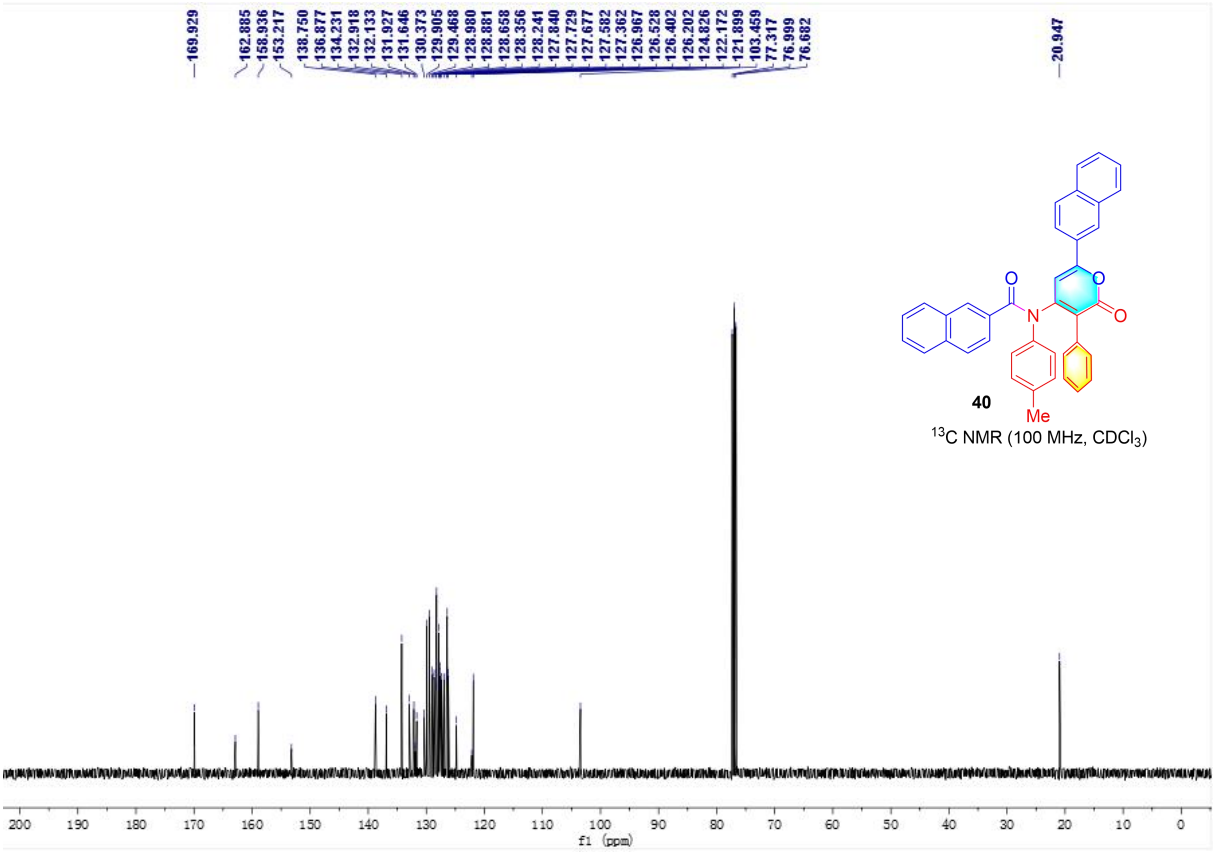
39

^{13}C NMR (125 MHz, $CDCl_3$)



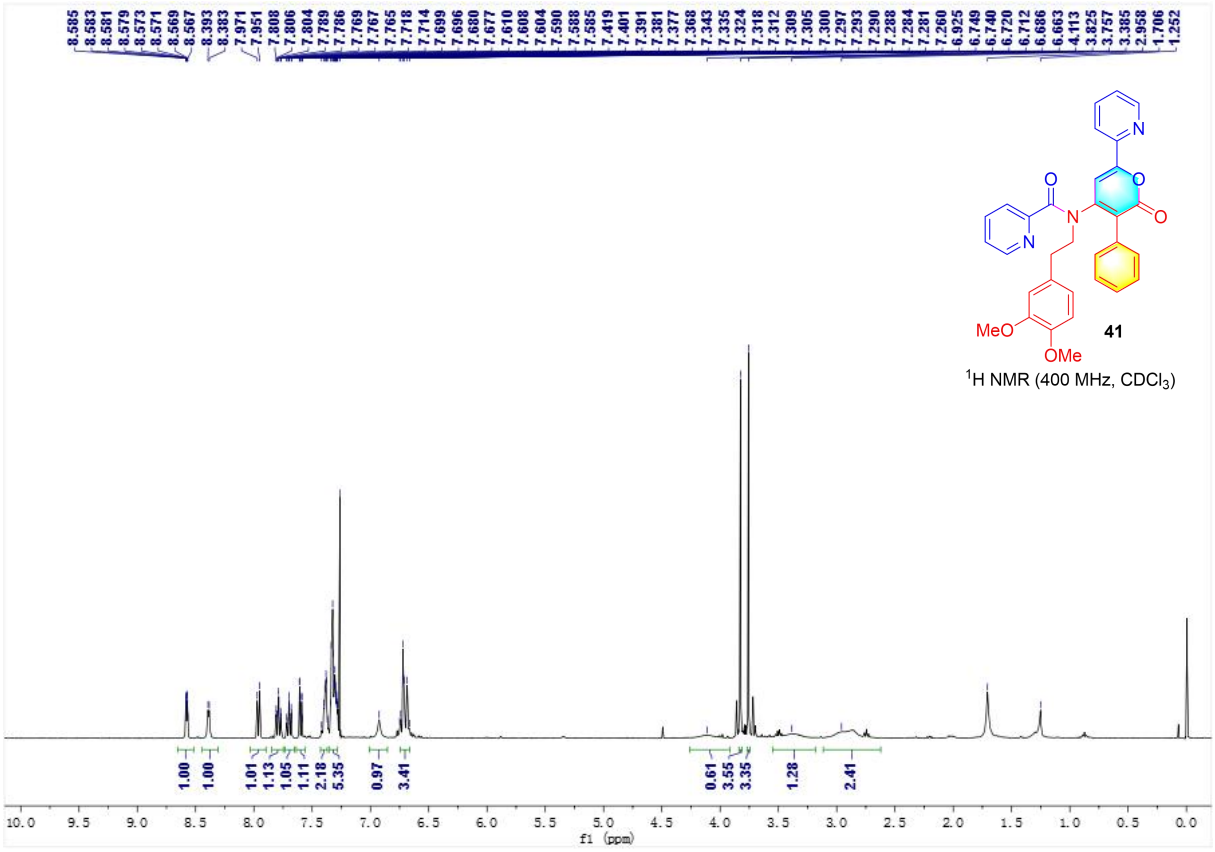
40

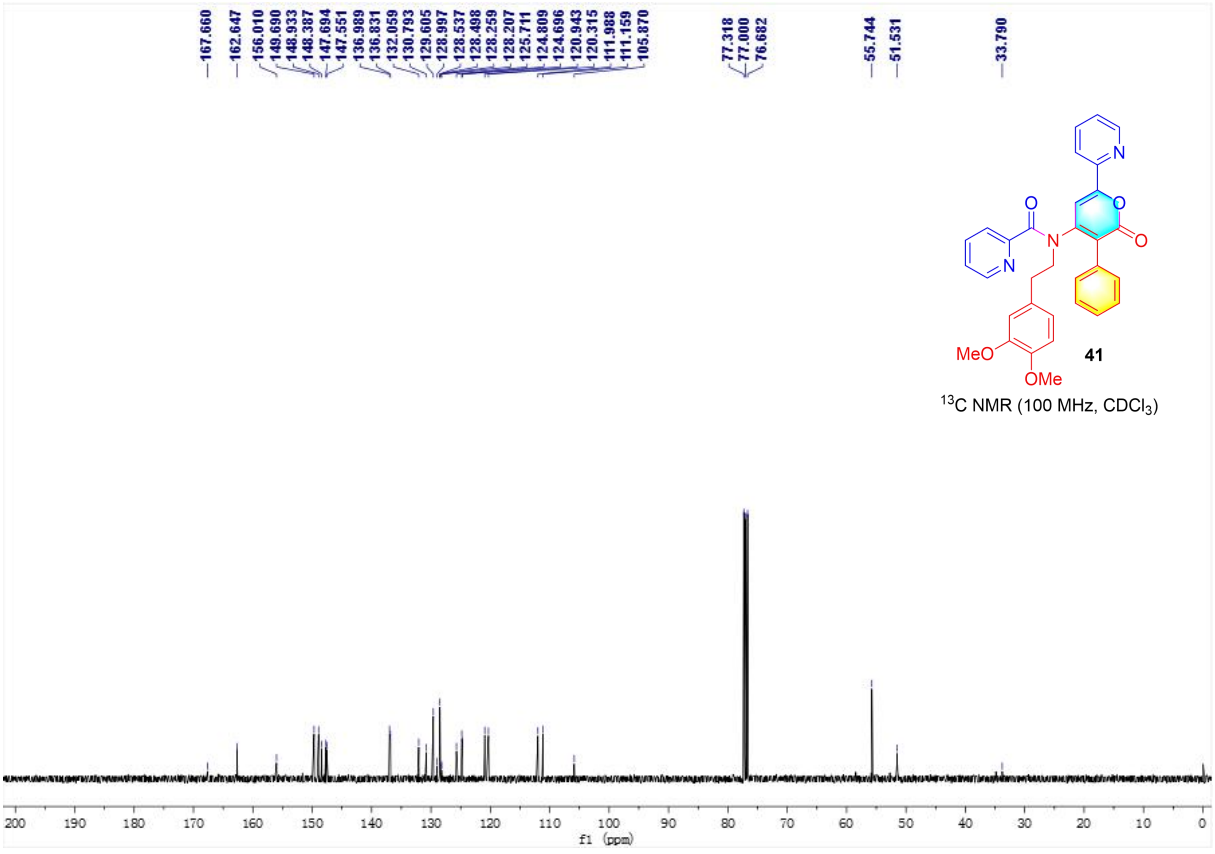
^{1}H NMR (400 MHz, $CDCl_3$)

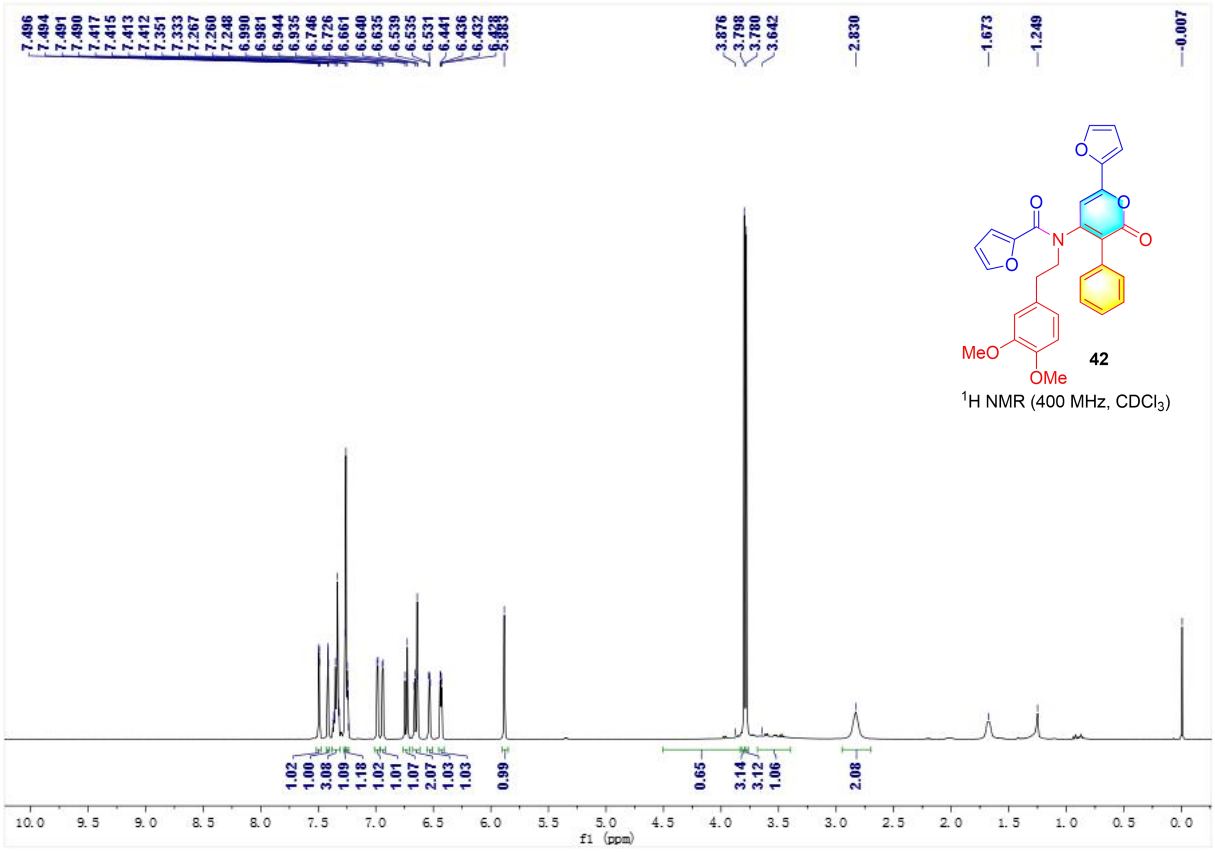


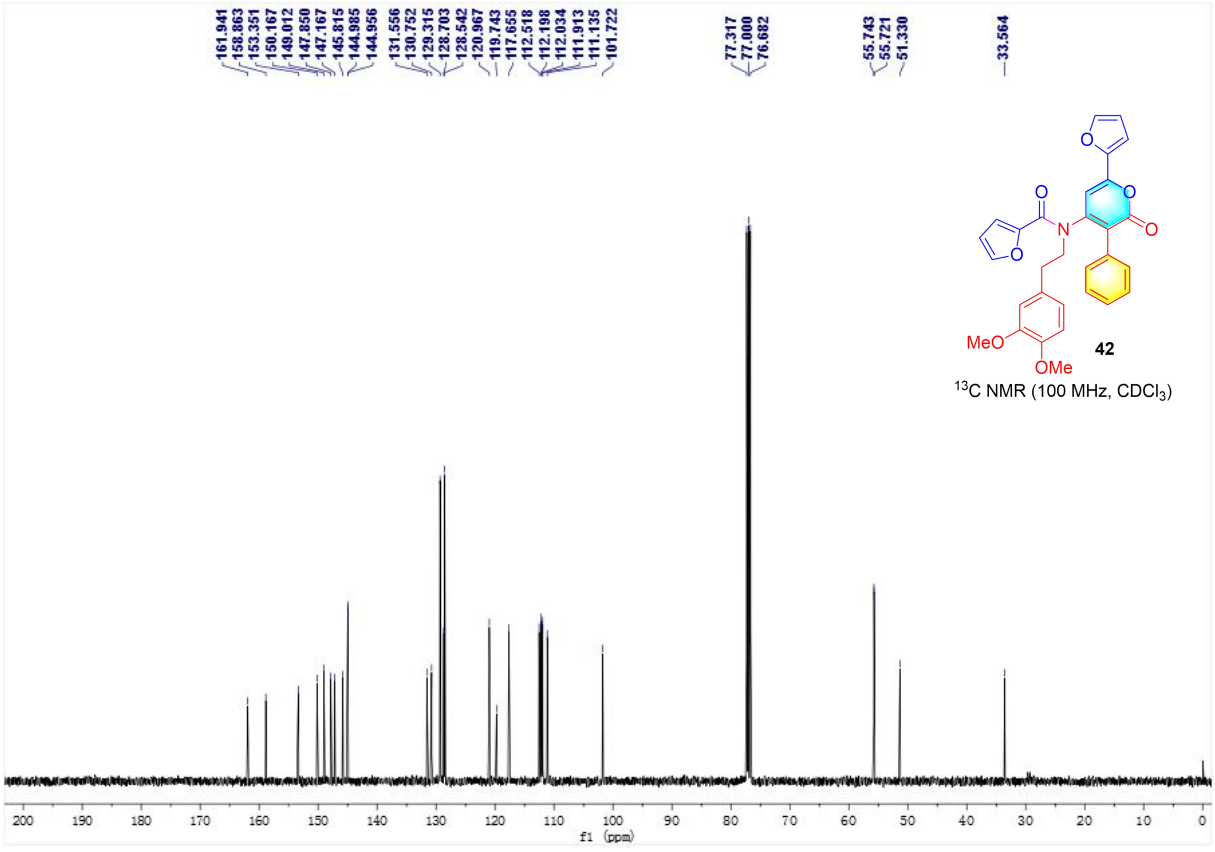
40

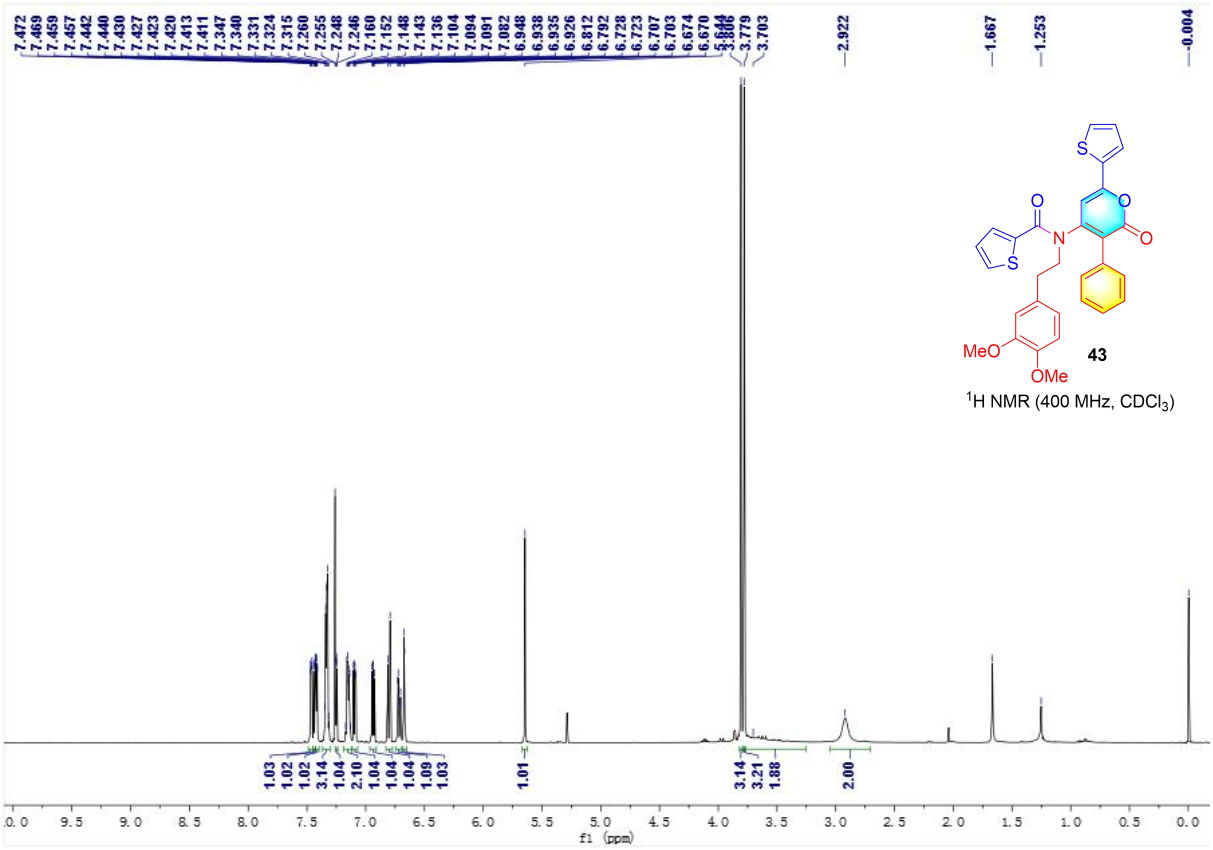
^{13}C NMR (100 MHz, $CDCl_3$)

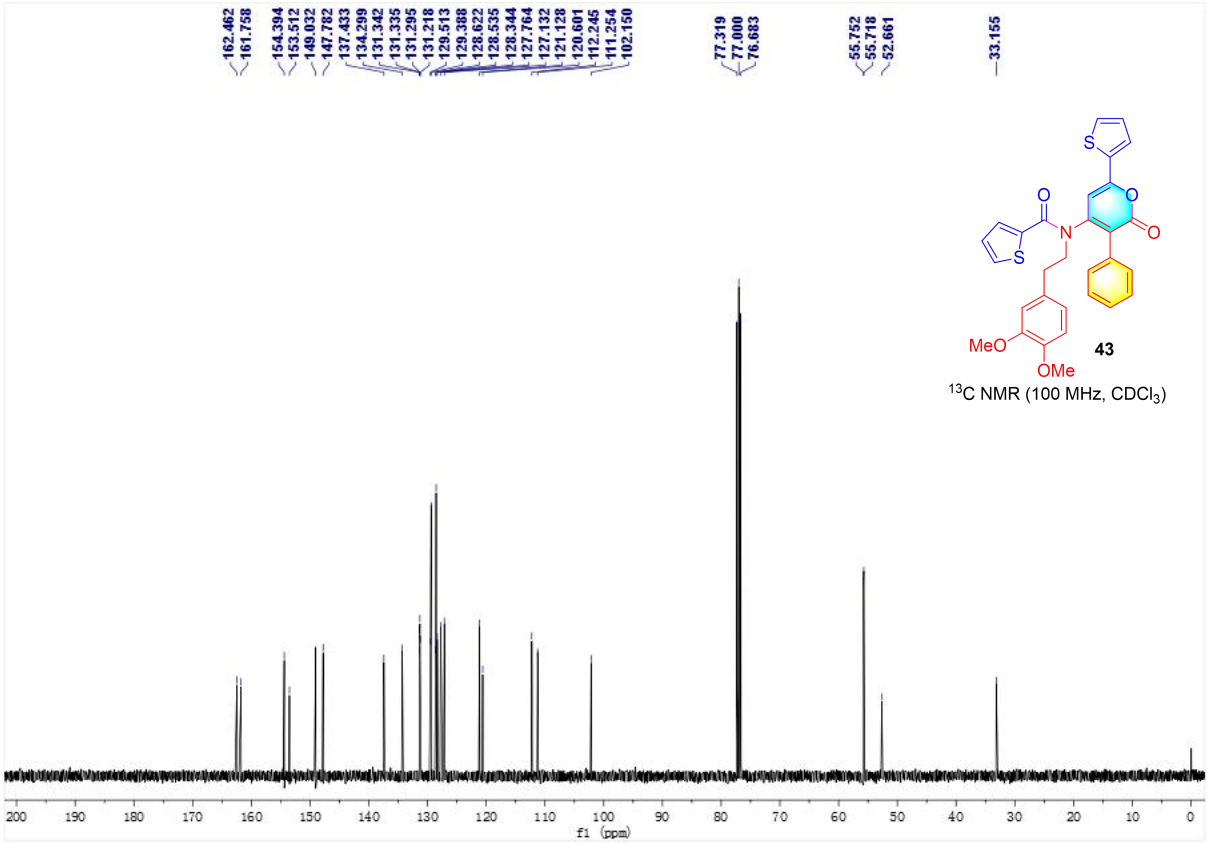

8.585 8.583 8.581 8.579 8.573 8.571 8.569 8.567 8.393 8.383 7.971 7.951 7.808 7.806 7.804 7.789 7.786 7.769 7.767 7.765 7.718 7.714 7.699 7.696 7.680 7.677 7.610 7.608 7.604 7.590 7.588 7.585 7.419 7.401 7.391 7.381 7.377 7.368 7.343 7.335 7.324 7.318 7.312 7.309 7.305 7.300 7.297 7.293 7.290 7.288 7.284 7.281 7.260 6.925 6.749 6.740 6.720 6.712 6.686 6.663 4.413 3.825 3.757 3.385 2.958 1.706 1.252
1.00 1.00 1.01 1.13 1.05 1.11 2.18 5.35 0.97 3.41 0.61 3.55 3.35 1.28 2.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
MeO
OMe
41
^{1}H NMR (400 MHz, $CDCl_3$)

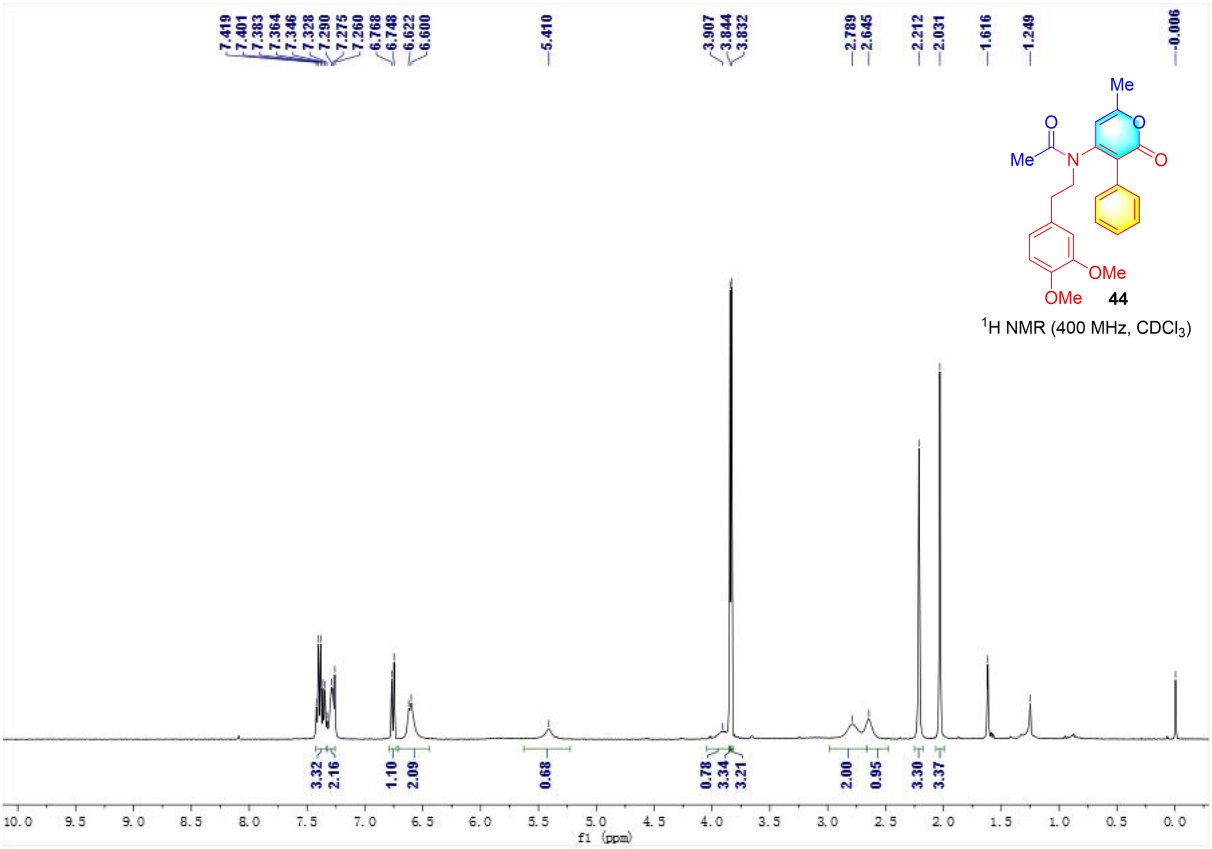

167.660 162.647 156.010 149.690 148.933 148.387 147.694 147.551 136.989 136.831 132.059 130.793 129.605 128.997 128.537 128.498 128.259 128.207 125.711 124.809 124.696 120.943 120.315 111.988 111.159 105.870
77.318 77.000 76.682
55.744 51.531
33.790
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
MeO
OMe
41
^{13}C NMR (100 MHz, $CDCl_3$)


7.496
7.494
7.491
7.490
7.417
7.415
7.413
7.412
7.351
7.333
7.267
7.260
7.248
6.990
6.981
6.944
6.935
6.746
6.726
6.661
6.640
6.635
6.539
6.535
6.531
6.441
6.436
6.432
3.876
3.798
3.780
3.642
2.830
1.673
1.249
0.007
1.02
1.00
3.08
1.09
1.18
1.02
1.01
1.07
2.07
1.03
1.03
0.99
0.65
3.14
3.12
1.06
2.08
f1 (ppm)
MeO
OMe
42
1H NMR (400 MHz, CDCl3)

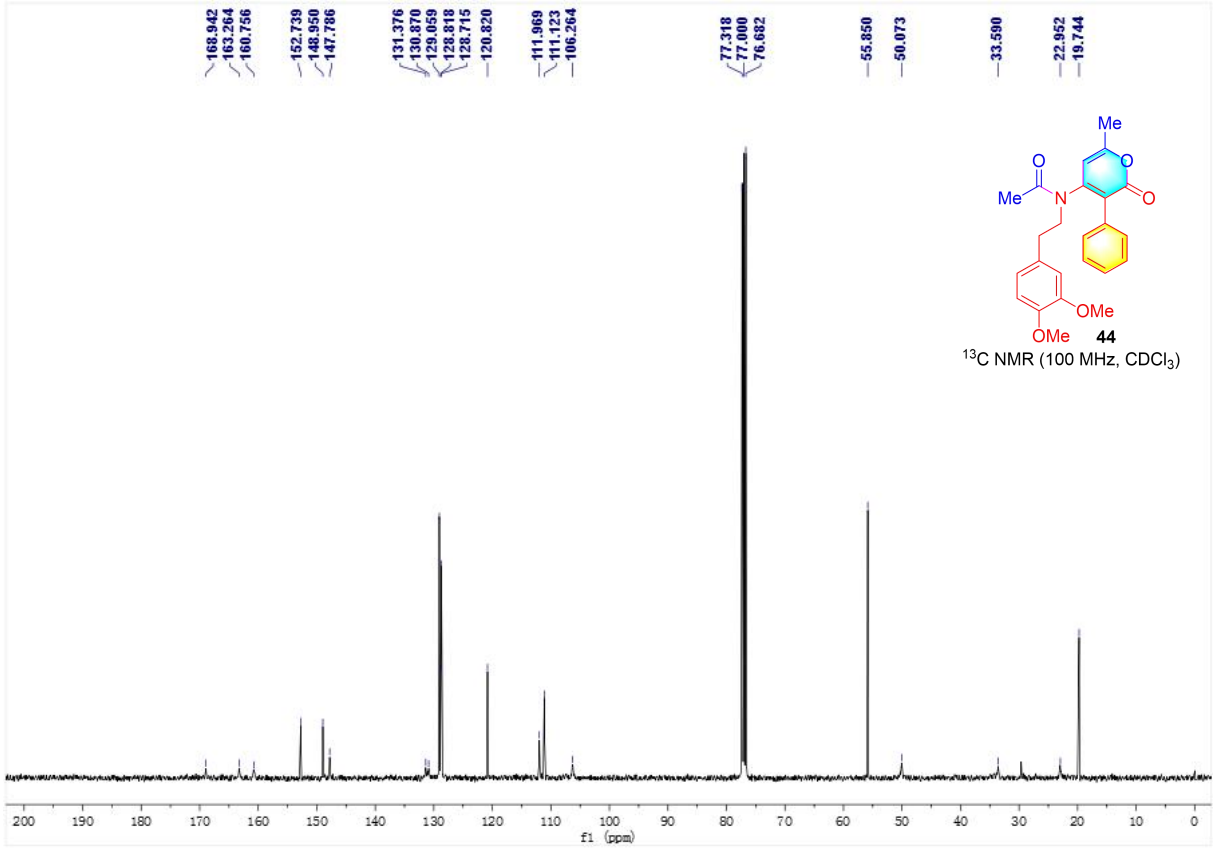

161.941
158.863
153.351
150.167
149.012
147.850
147.167
145.815
144.985
144.956
131.556
130.752
129.315
128.703
128.542
120.967
119.743
117.655
112.518
112.198
112.034
111.913
111.135
101.722
77.317
77.000
76.682
55.743
55.721
51.330
33.564
f1 (ppm)
MeO
OMe
42
13C NMR (100 MHz, CDCl3)


43
1H NMR (400 MHz, CDCl3)
f1 (ppm)

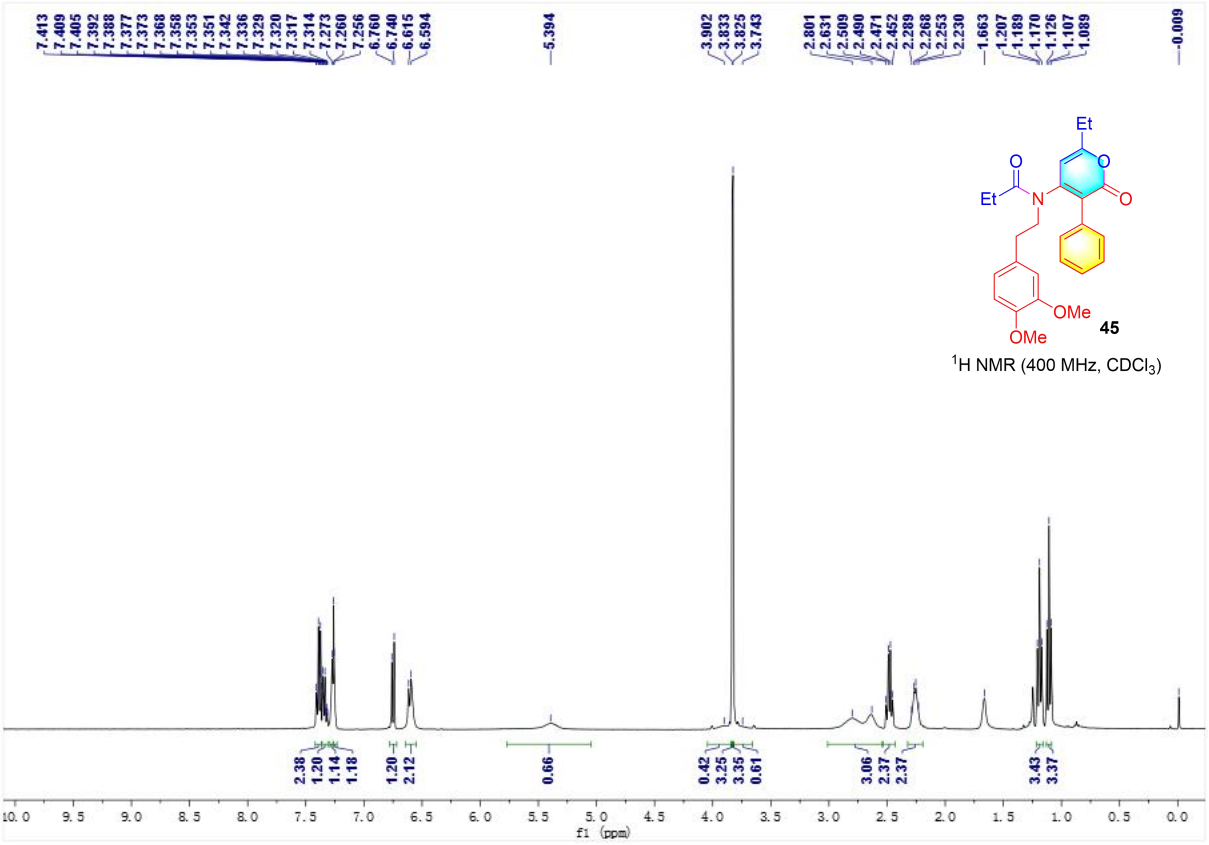

43
13C NMR (100 MHz, CDCl3)
f1 (ppm)



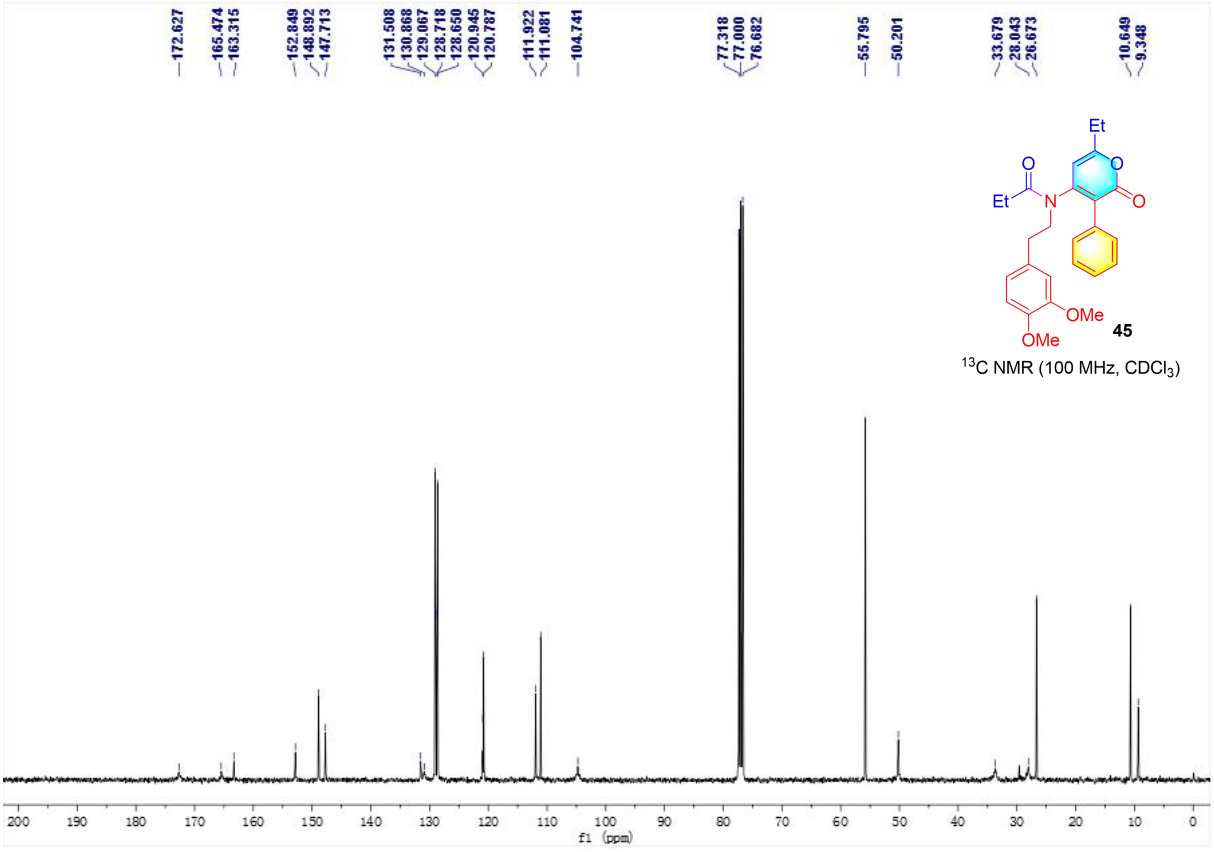
^{1}H NMR (400 MHz, $CDCl_3$)



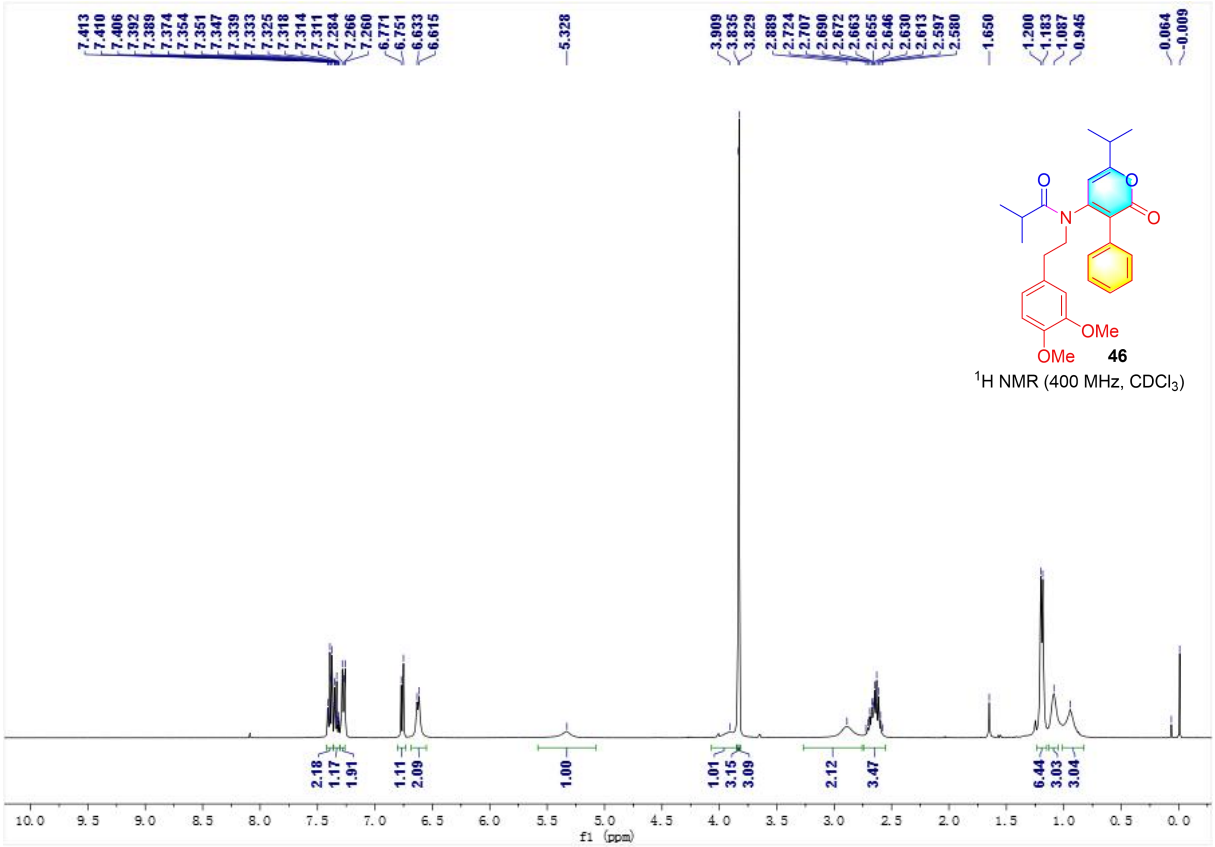
^{13}C NMR (100 MHz, $CDCl_3$)

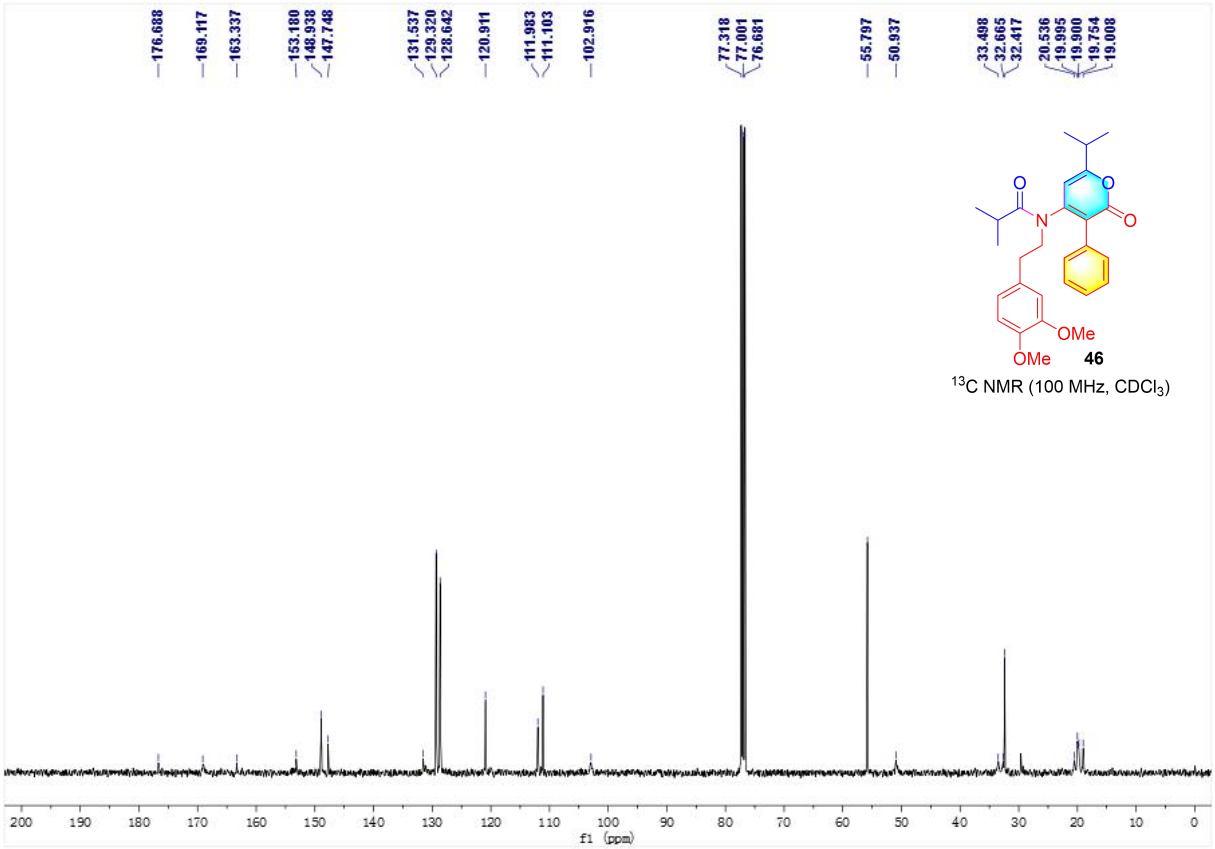


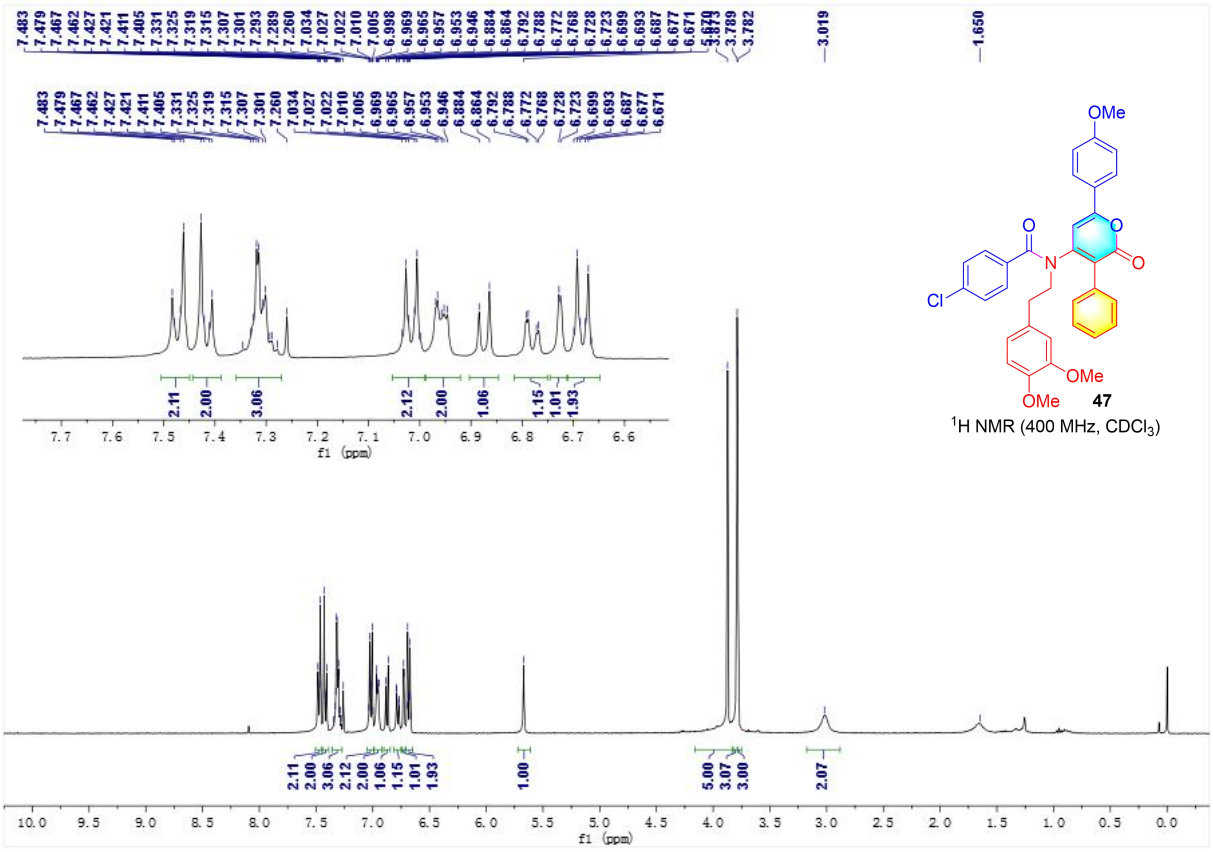
^{1}H NMR (400 MHz, $CDCl_3$)

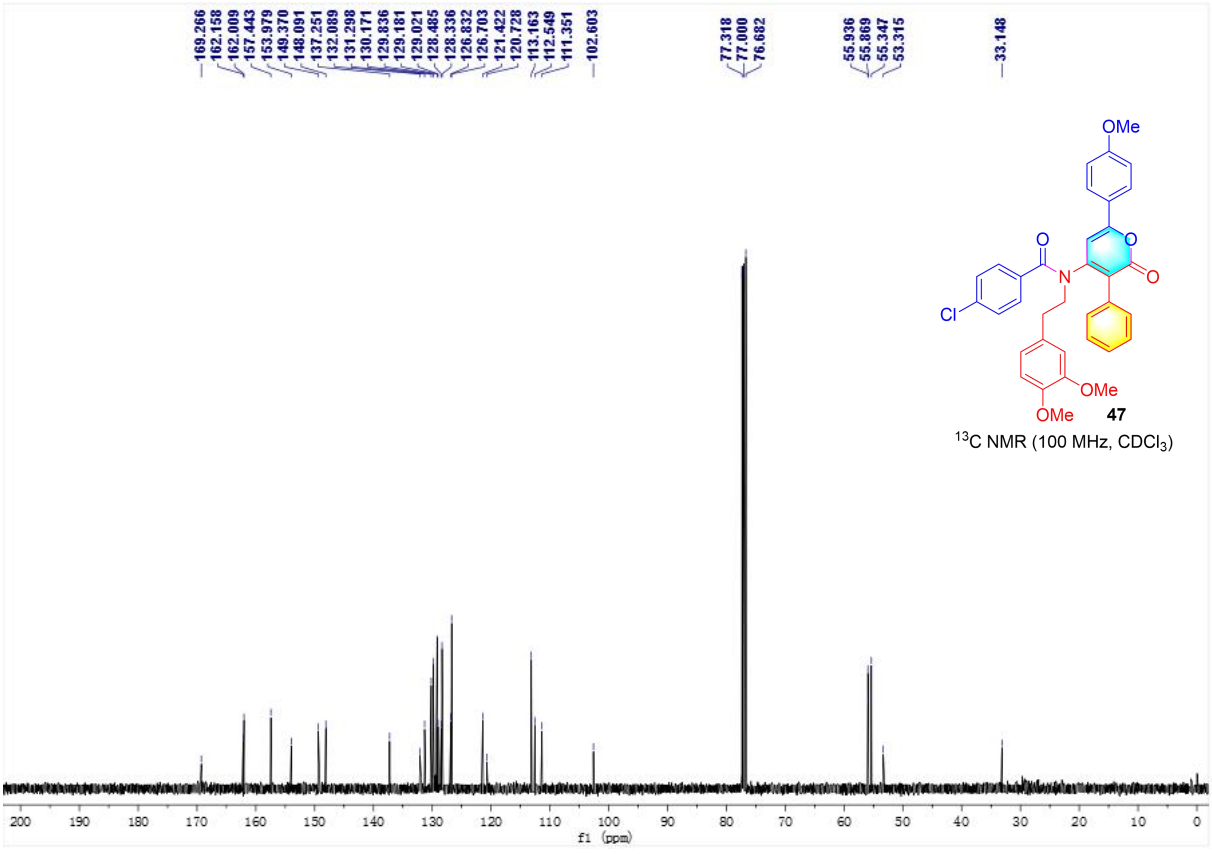


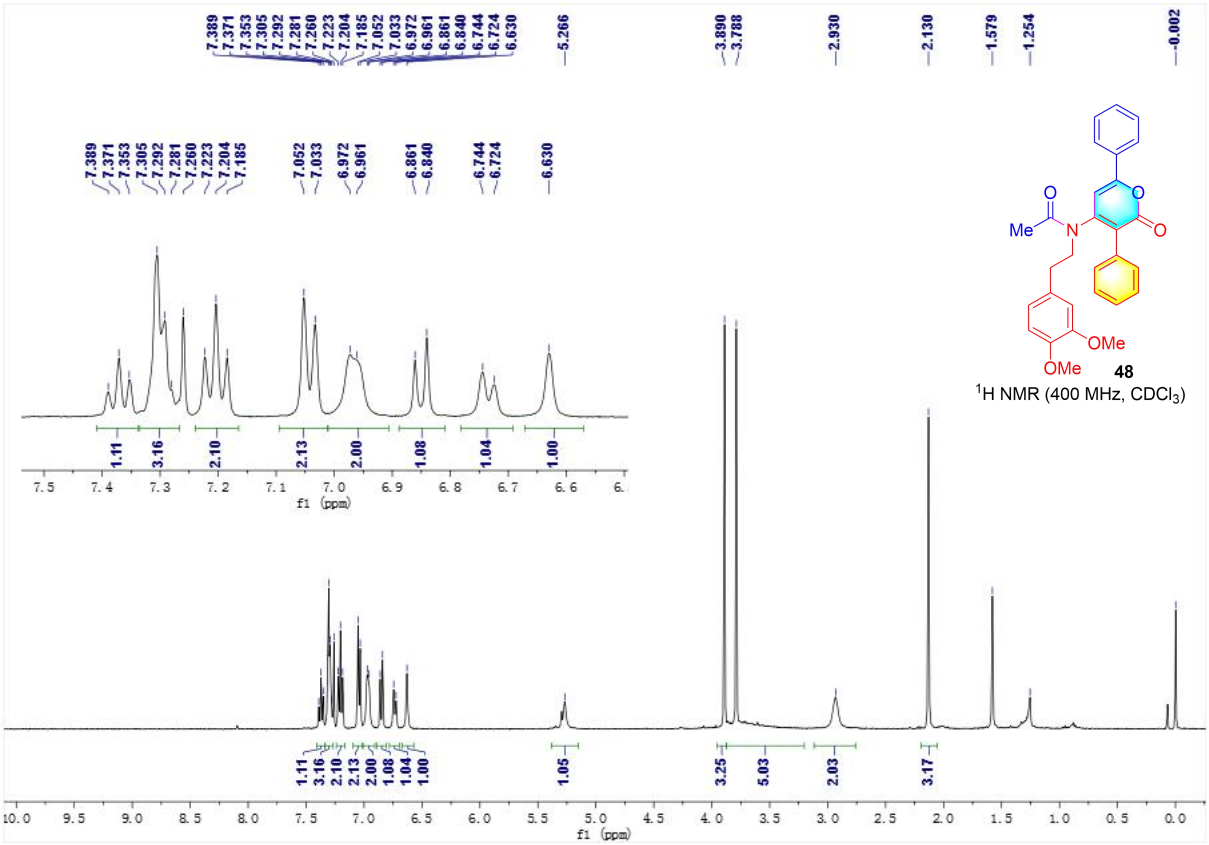
^{13}C NMR (100 MHz, $CDCl_3$)


7.413
7.410
7.406
7.392
7.389
7.374
7.354
7.351
7.347
7.339
7.333
7.325
7.318
7.314
7.311
7.284
7.266
7.260
6.771
6.751
6.633
6.615
5.328
3.909
3.835
3.829
2.889
2.724
2.707
2.690
2.672
2.663
2.655
2.646
2.630
2.613
2.597
2.580
1.650
1.200
1.183
1.087
0.945
0.064
-0.009
OMe
OMe
46
^{1}H NMR (400 MHz, $CDCl_3$)
2.18
1.17
1.91
1.11
2.09
1.00
1.01
3.15
3.09
2.12
3.47
6.44
3.03
3.04
f1 (ppm)

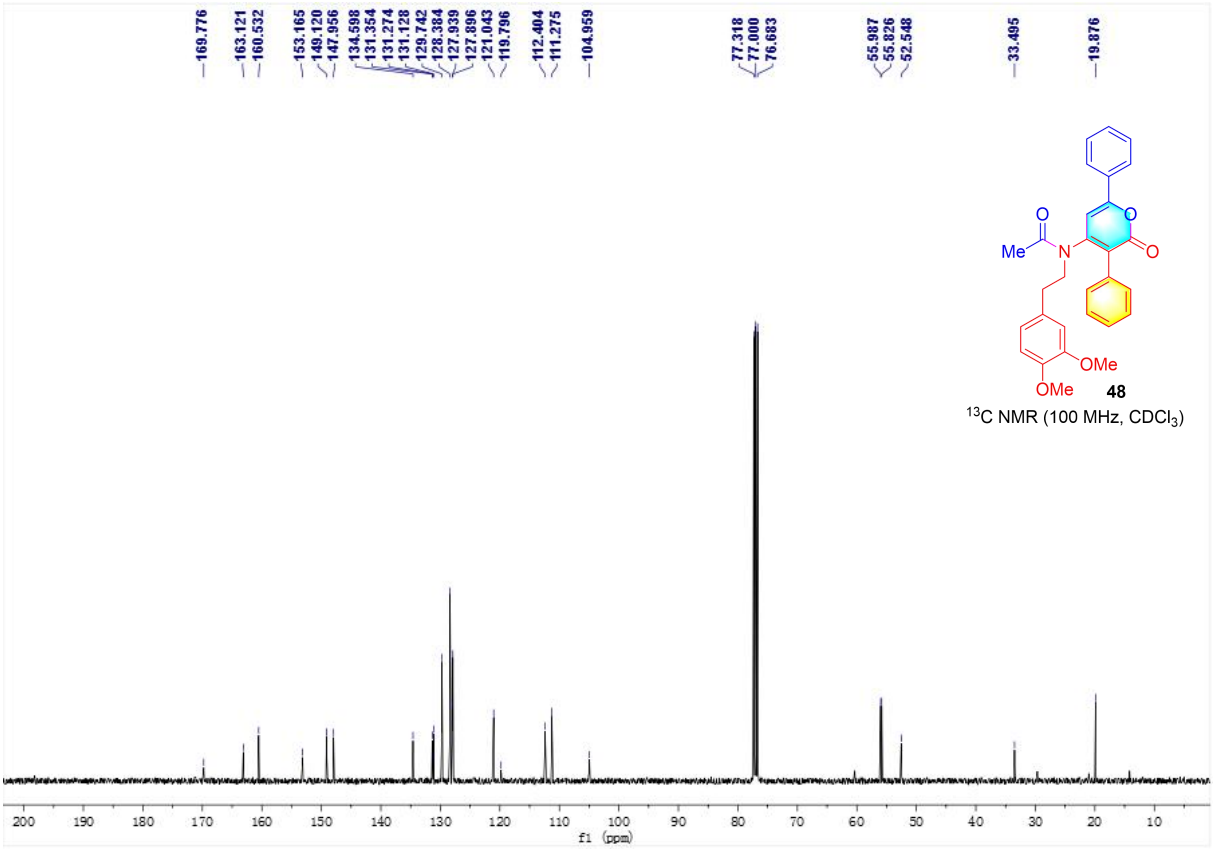

176.688
169.117
163.337
153.180
148.938
147.748
131.537
129.320
128.642
120.911
111.983
111.103
102.916
77.318
77.001
76.681
55.797
50.937
33.498
32.665
32.417
20.536
19.995
19.900
19.754
19.008
OMe
OMe
46
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


OMe
O
O
N
O
Cl
OMe
OMe
47
^{1}H NMR (400 MHz, $CDCl_3$)

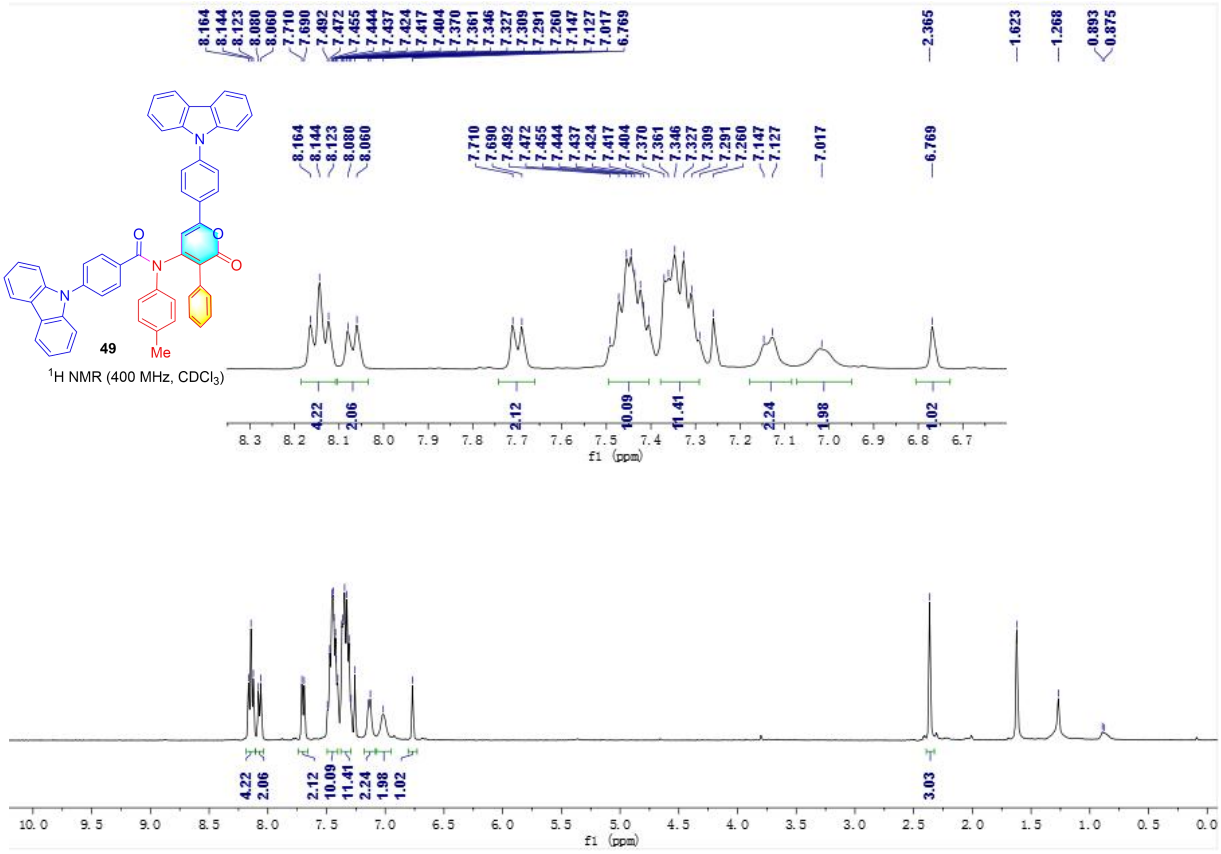

OMe
O
O
N
O
Cl
OMe
OMe
47
^{13}C NMR (100 MHz, $CDCl_3$)

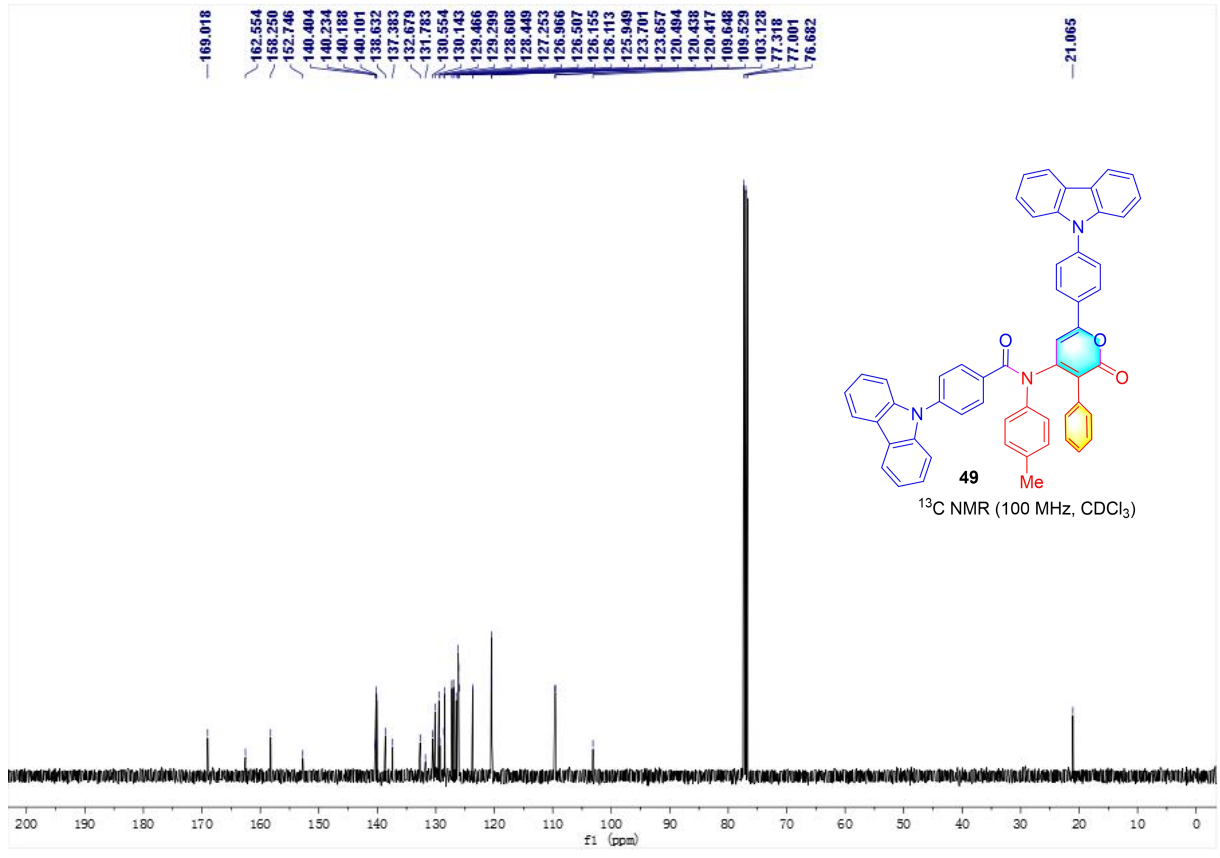


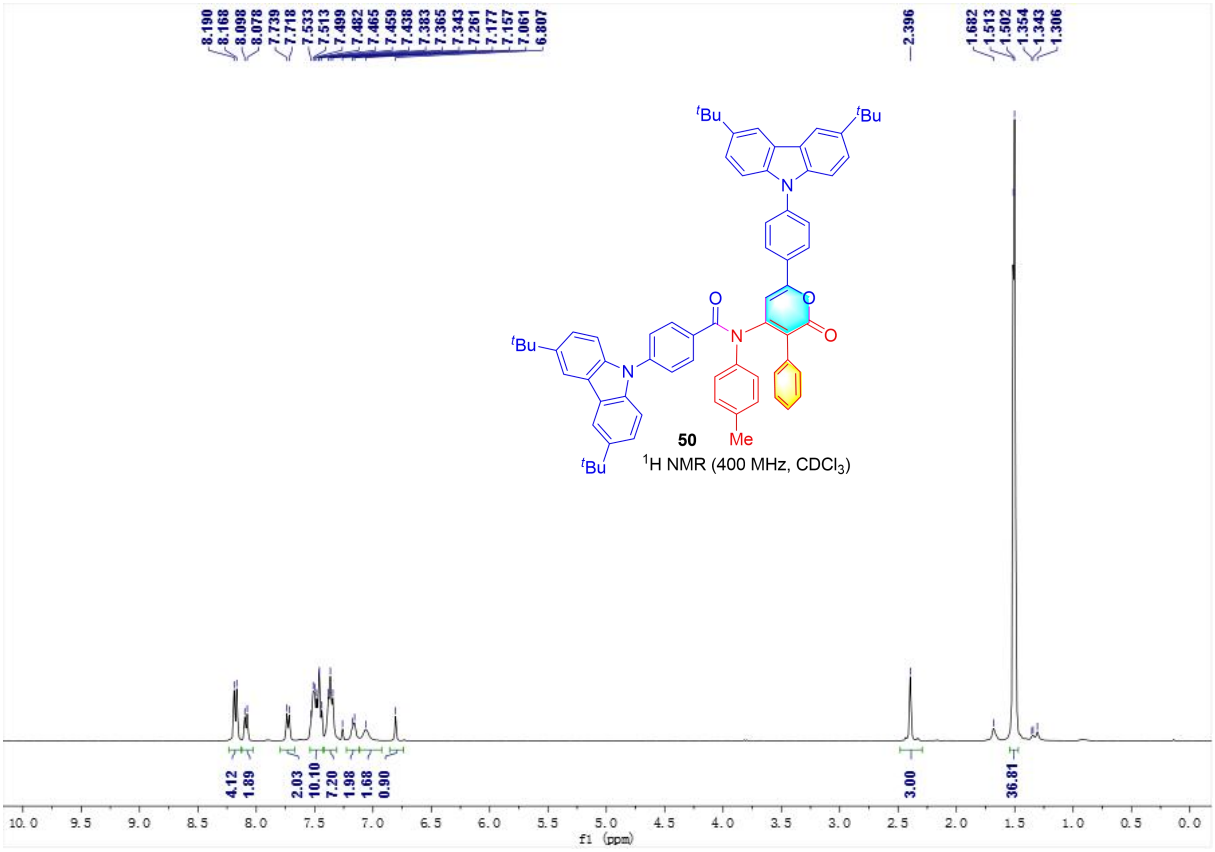
^{1}H NMR (400 MHz, $CDCl_3$)

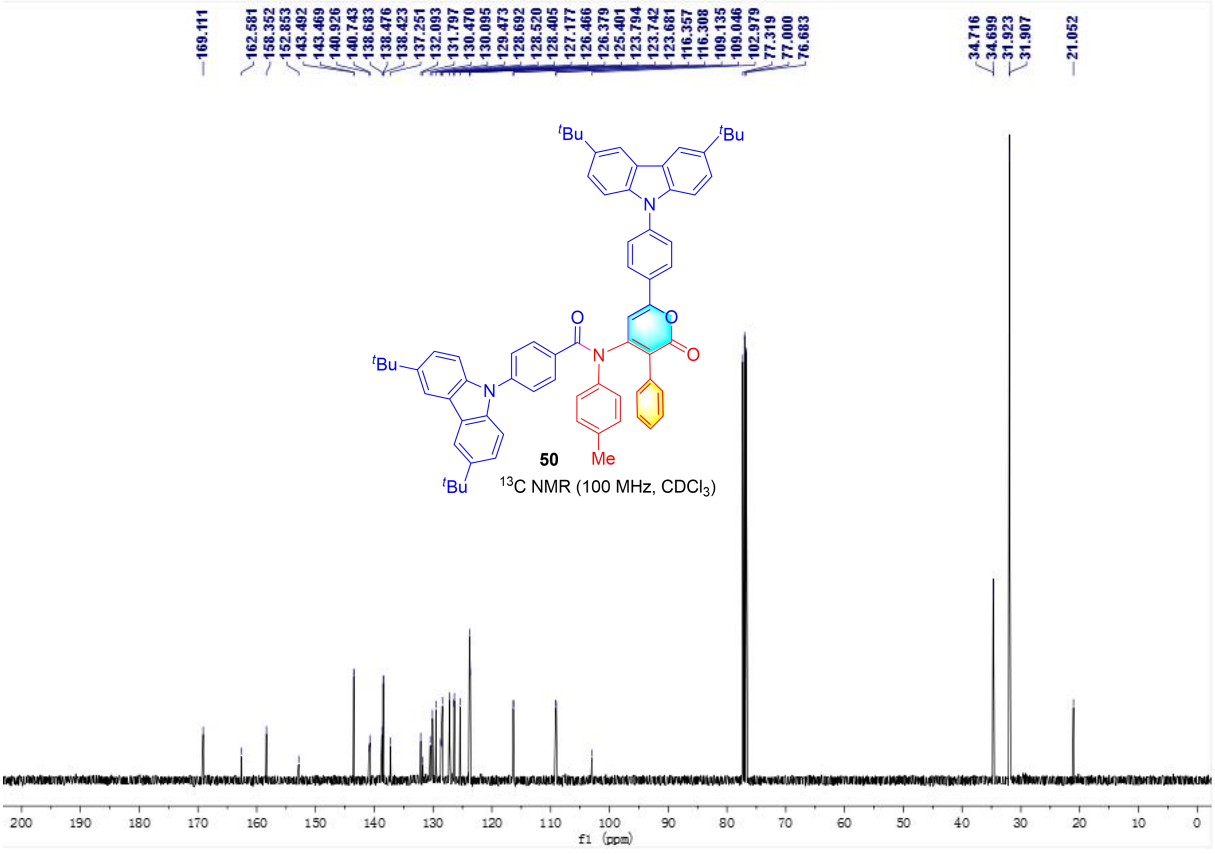


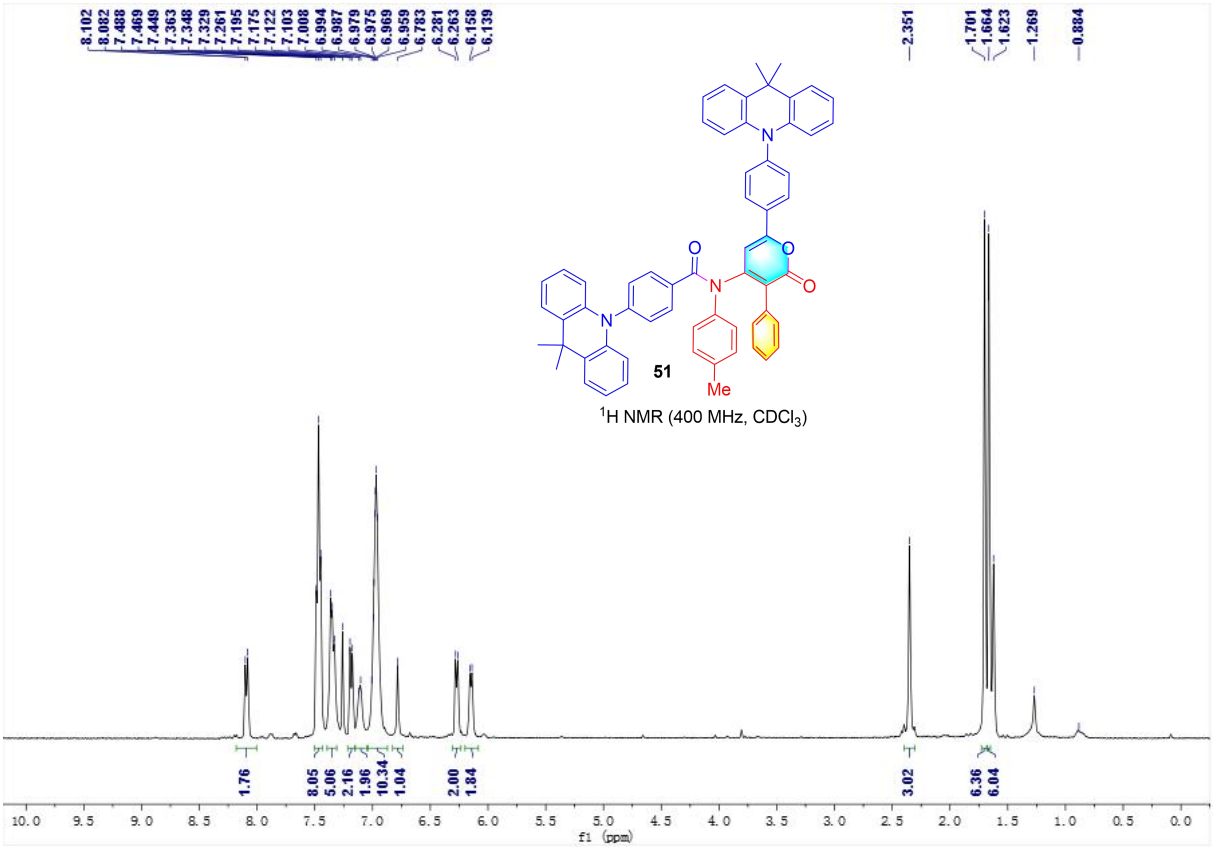
^{13}C NMR (100 MHz, $CDCl_3$)


49
Me
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

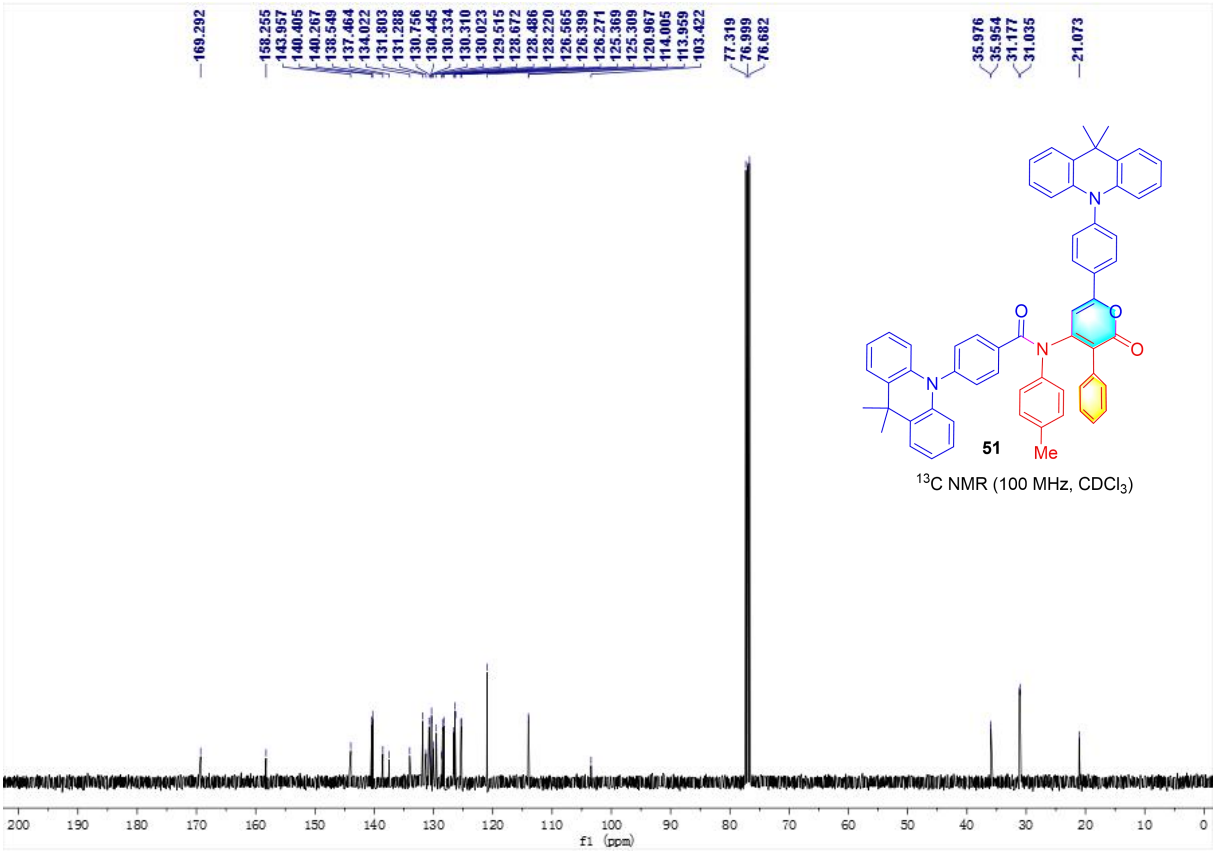

49
Me
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


8.190
8.168
8.098
8.078
7.739
7.718
7.533
7.513
7.499
7.482
7.465
7.459
7.438
7.383
7.365
7.343
7.261
7.177
7.157
7.061
6.807
2.396
1.682
1.513
1.502
1.354
1.343
1.306
tBu
tBu
N
O
O
O
N
O
tBu
N
tBu
50
Me
1H NMR (400 MHz, CDCl3)
4.12
1.89
2.03
10.10
7.20
1.98
1.68
0.90
3.00
36.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

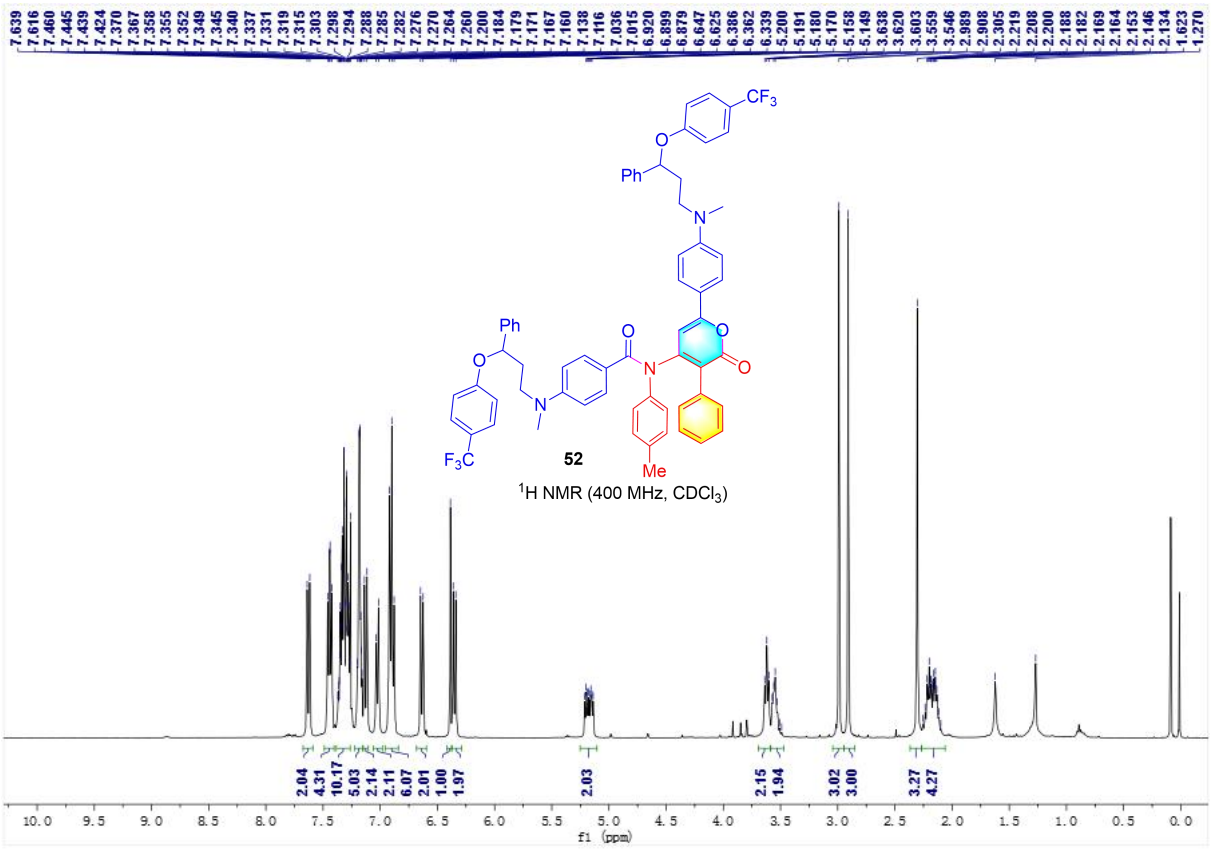

169.111
162.581
158.352
152.853
143.492
143.469
140.926
140.743
138.683
138.476
138.423
137.251
132.093
131.797
130.470
130.095
129.473
128.692
128.520
128.405
127.177
126.466
126.379
125.401
123.794
123.742
123.681
116.357
116.308
109.135
109.046
102.979
77.319
77.000
76.683
34.716
34.699
31.923
31.907
21.052
tBu
tBu
N
O
O
O
N
O
tBu
N
tBu
50
Me
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

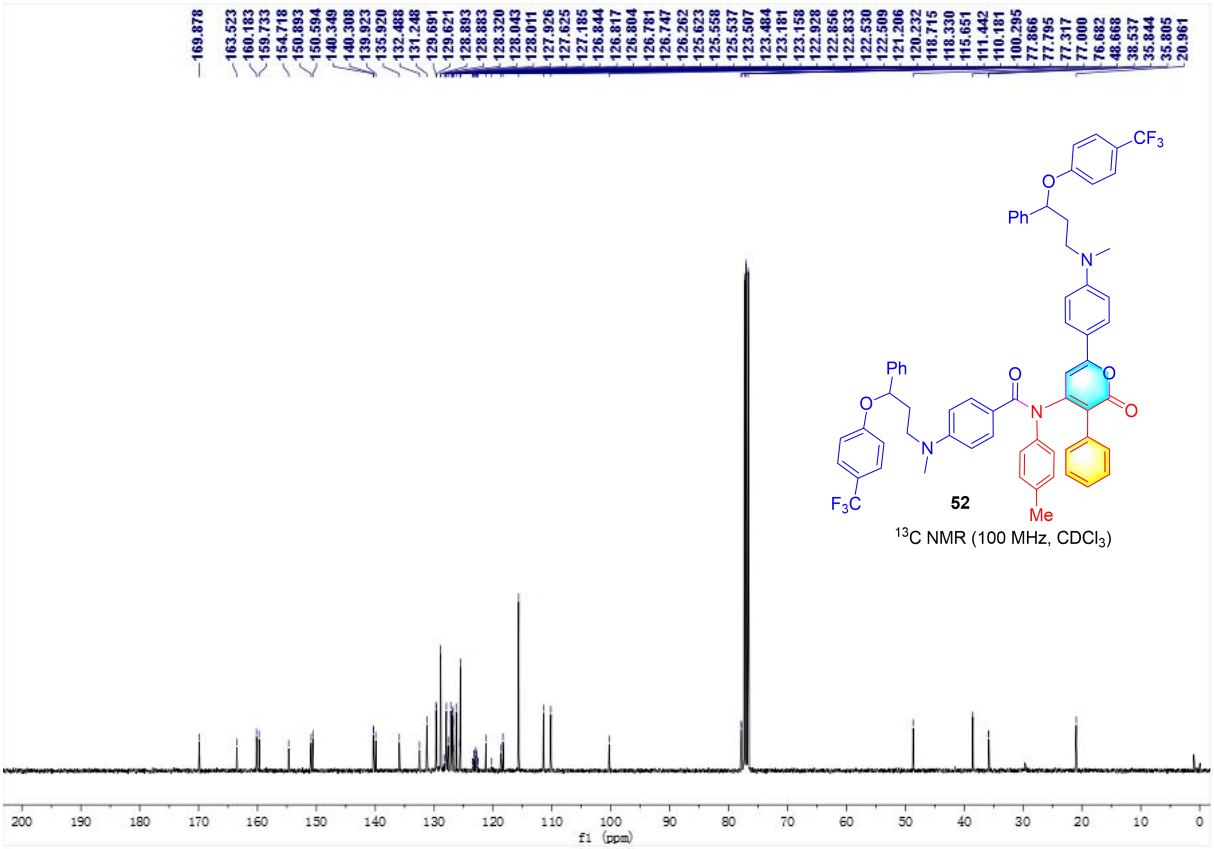


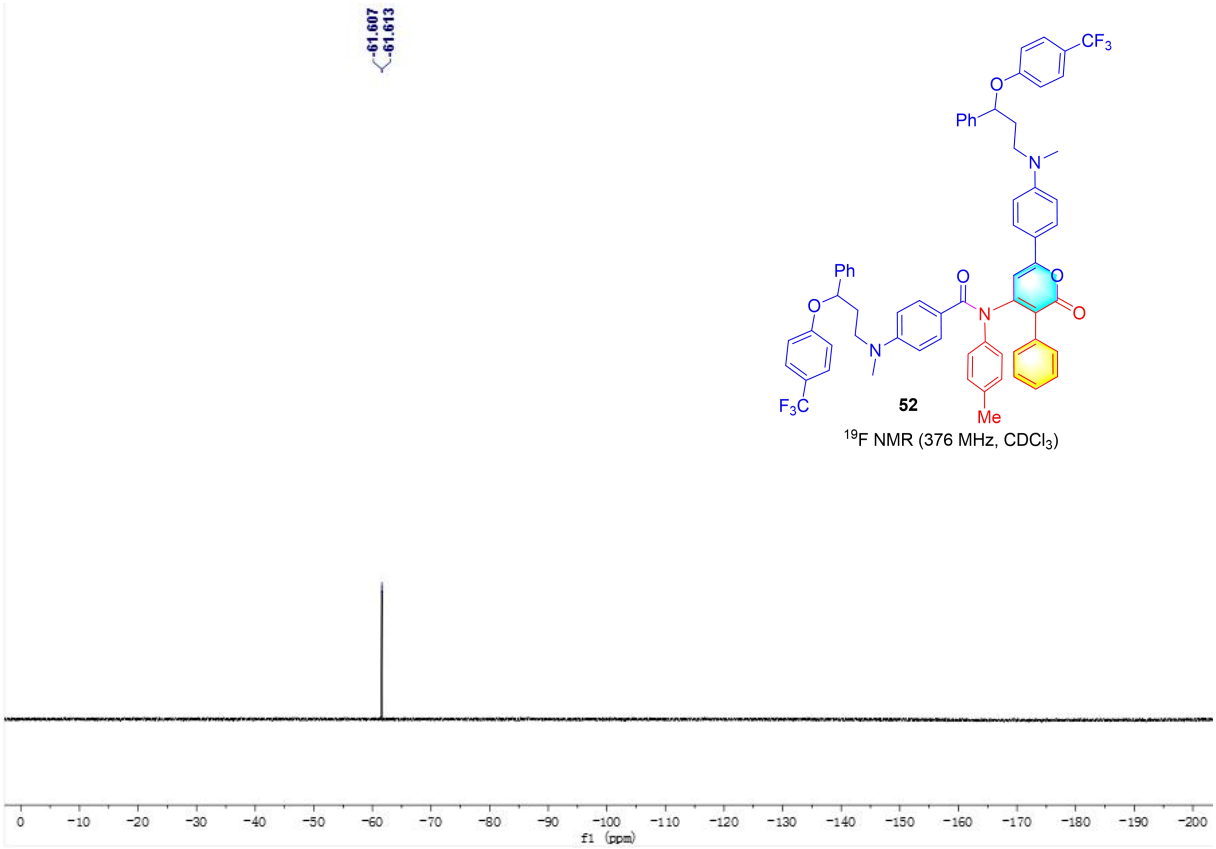
^{1}H NMR (400 MHz, $CDCl_3$)



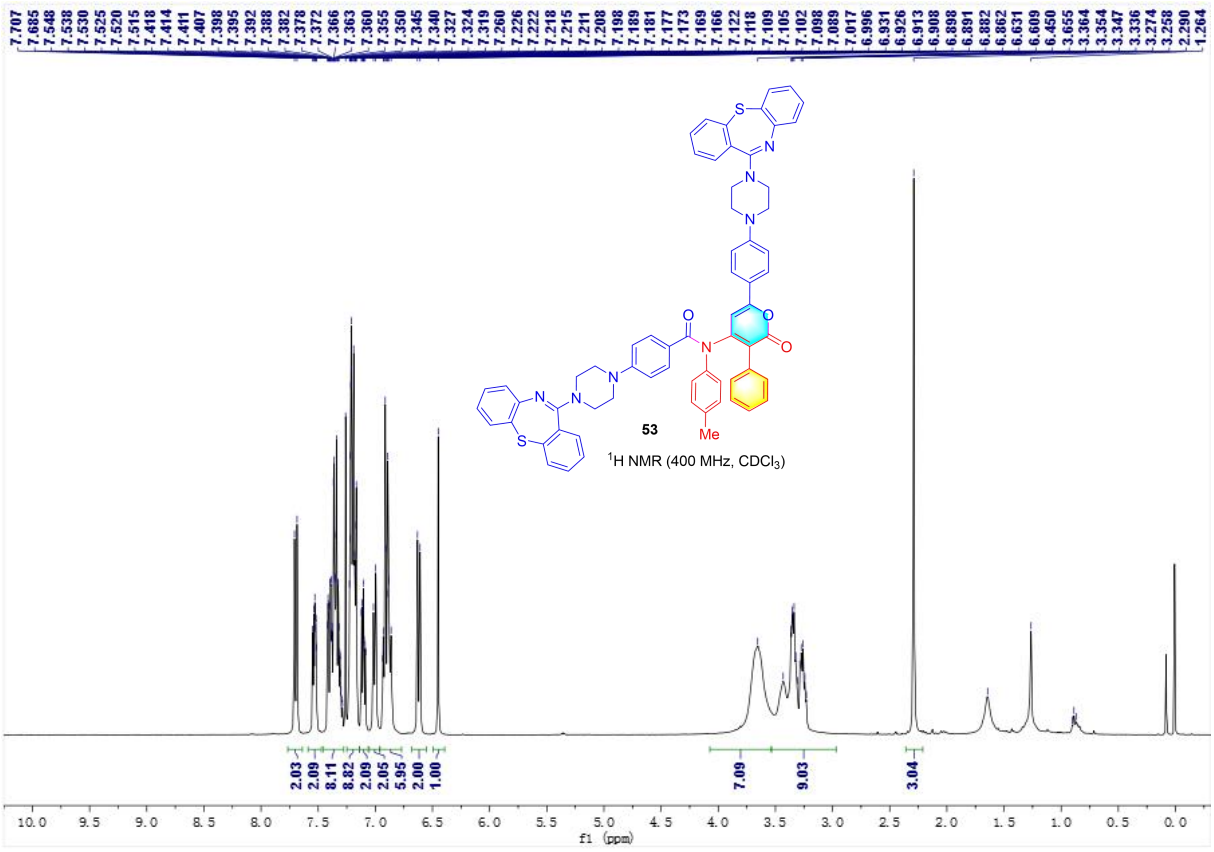
^{13}C NMR (100 MHz, $CDCl_3$)

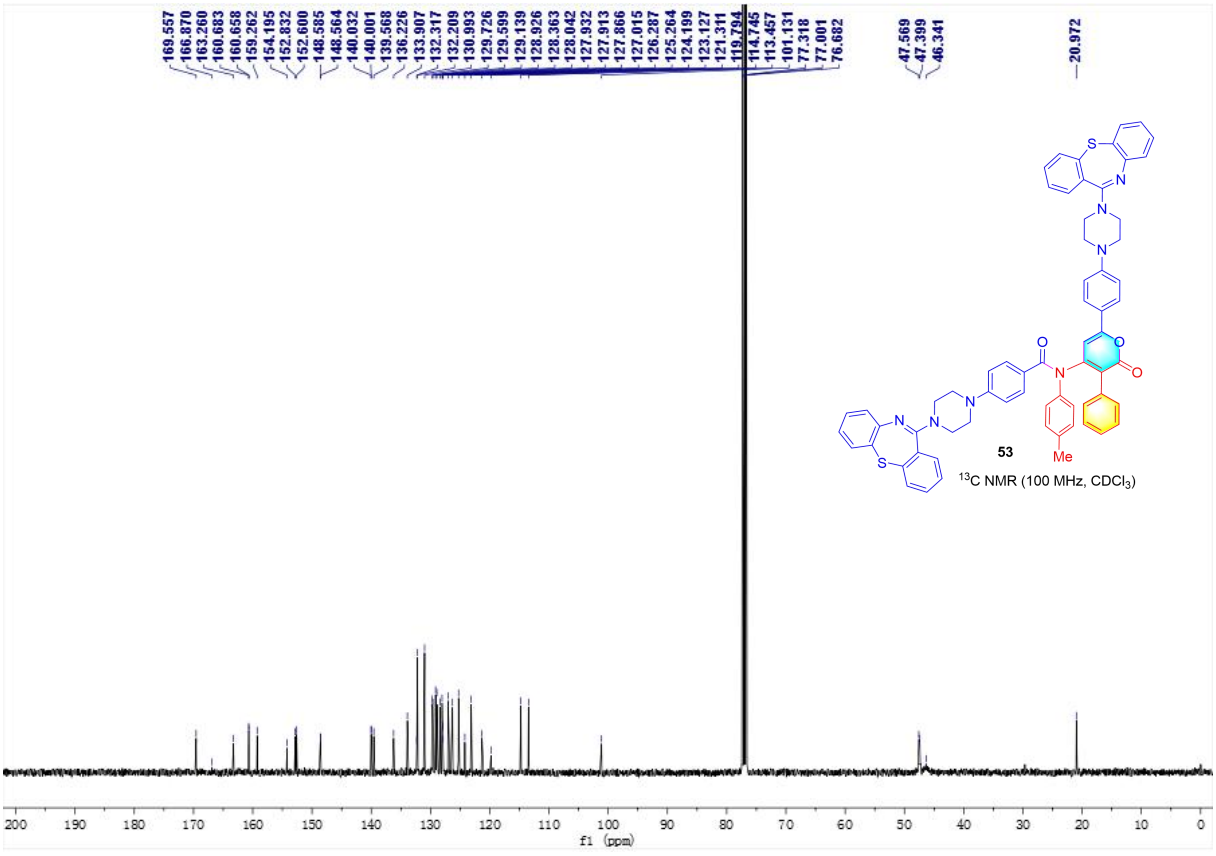

52
^{1}H NMR (400 MHz, CDCl$_3$)

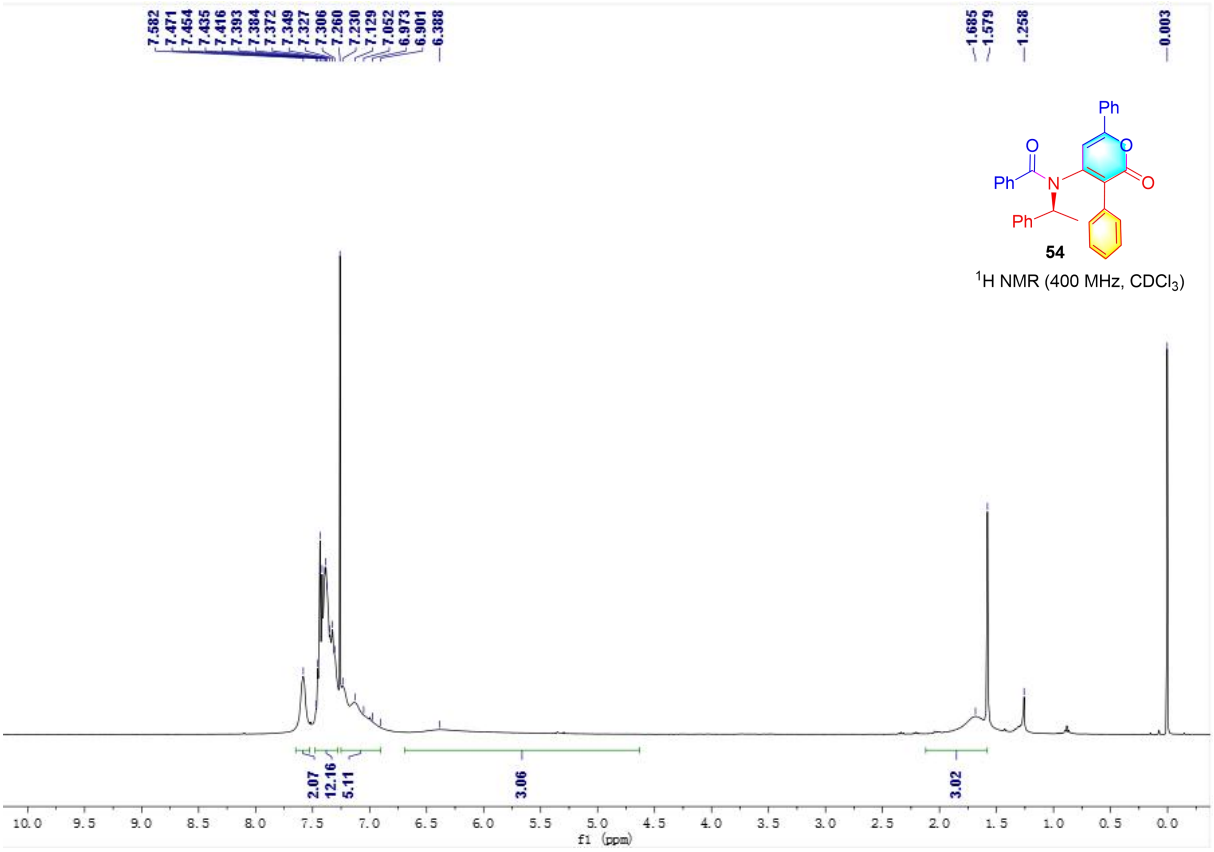

52
^{13}C NMR (100 MHz, CDCl$_3$)



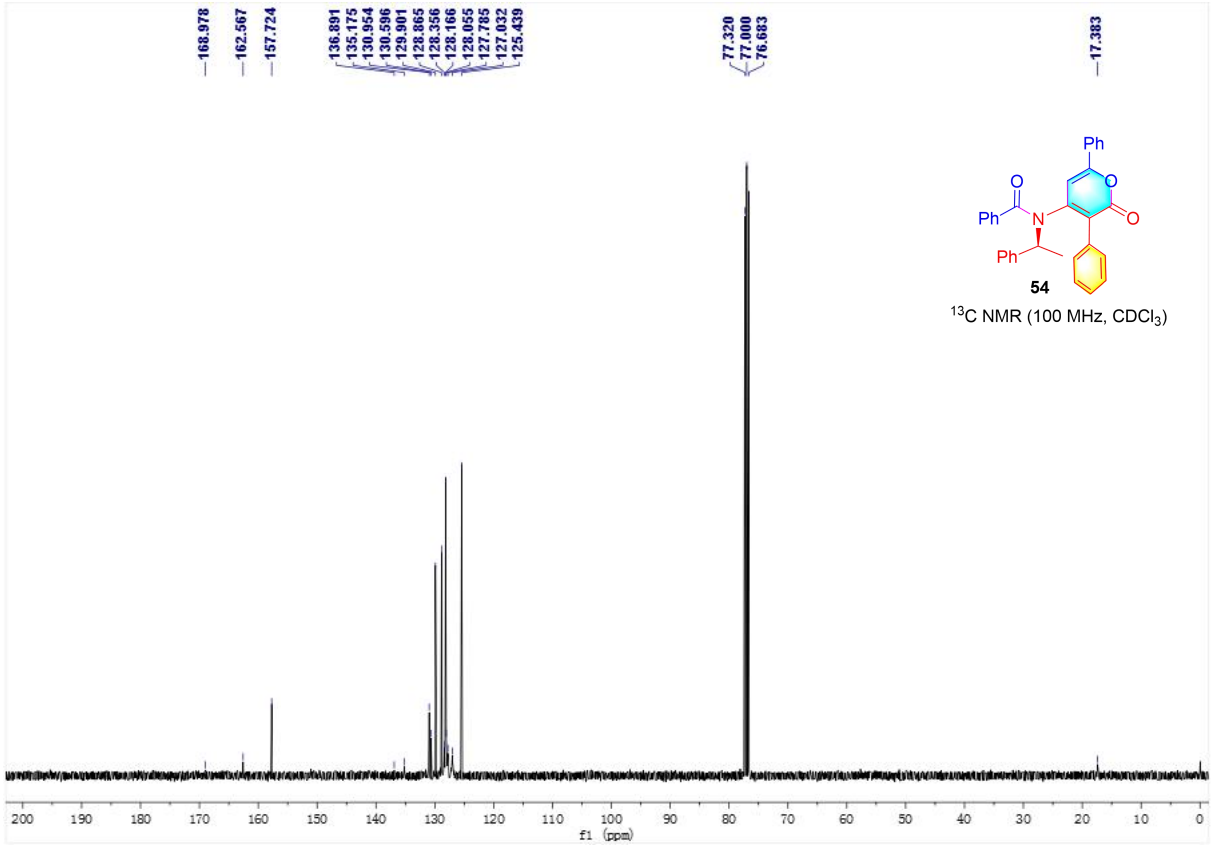
^{19}F NMR (376 MHz, $CDCl_3$)


53
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

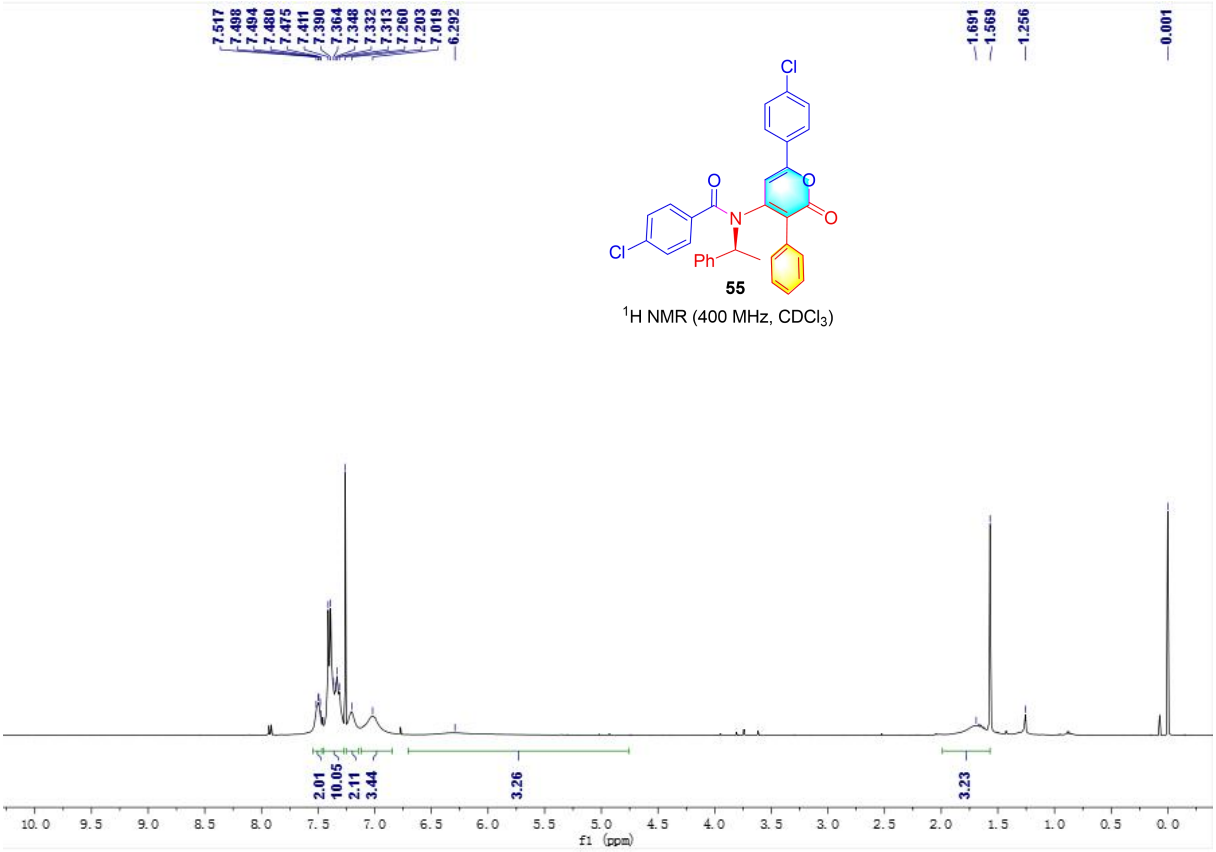

53
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



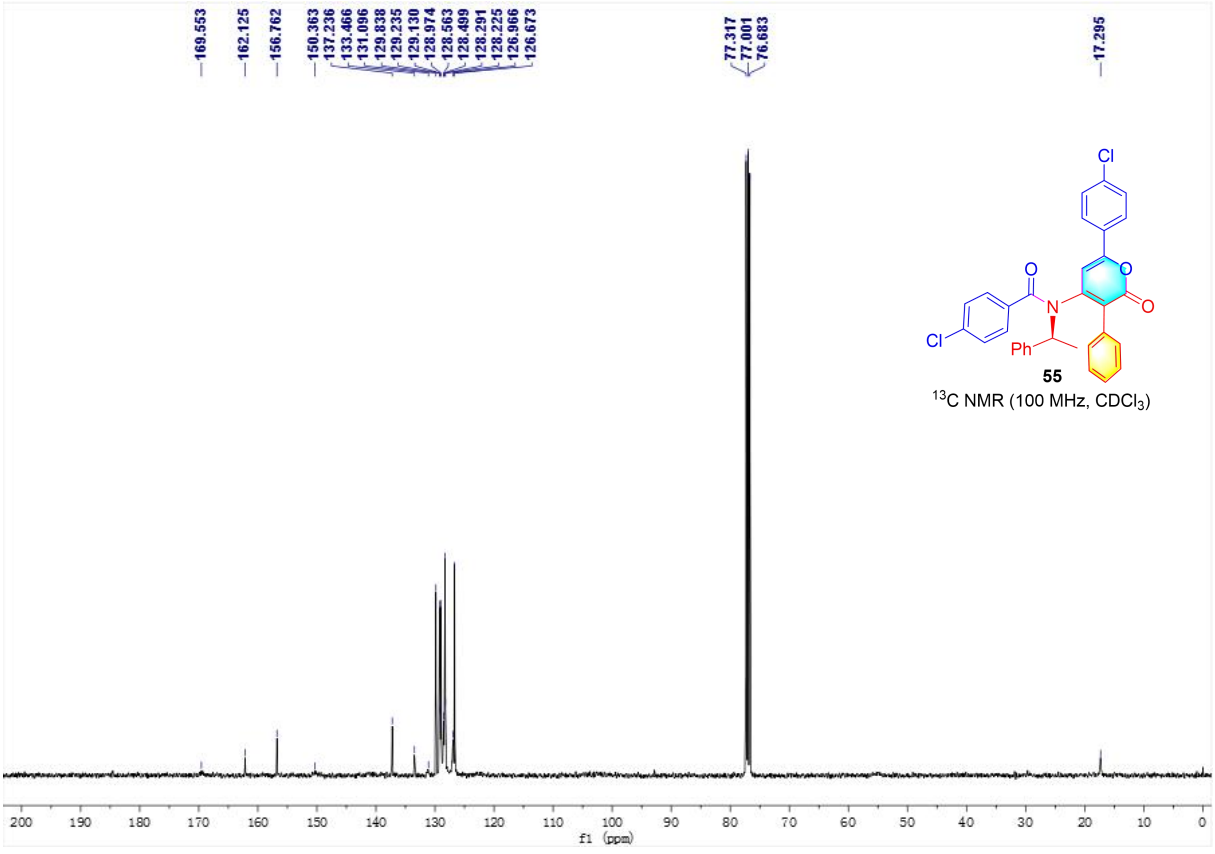
^{1}H NMR (400 MHz, $CDCl_3$)



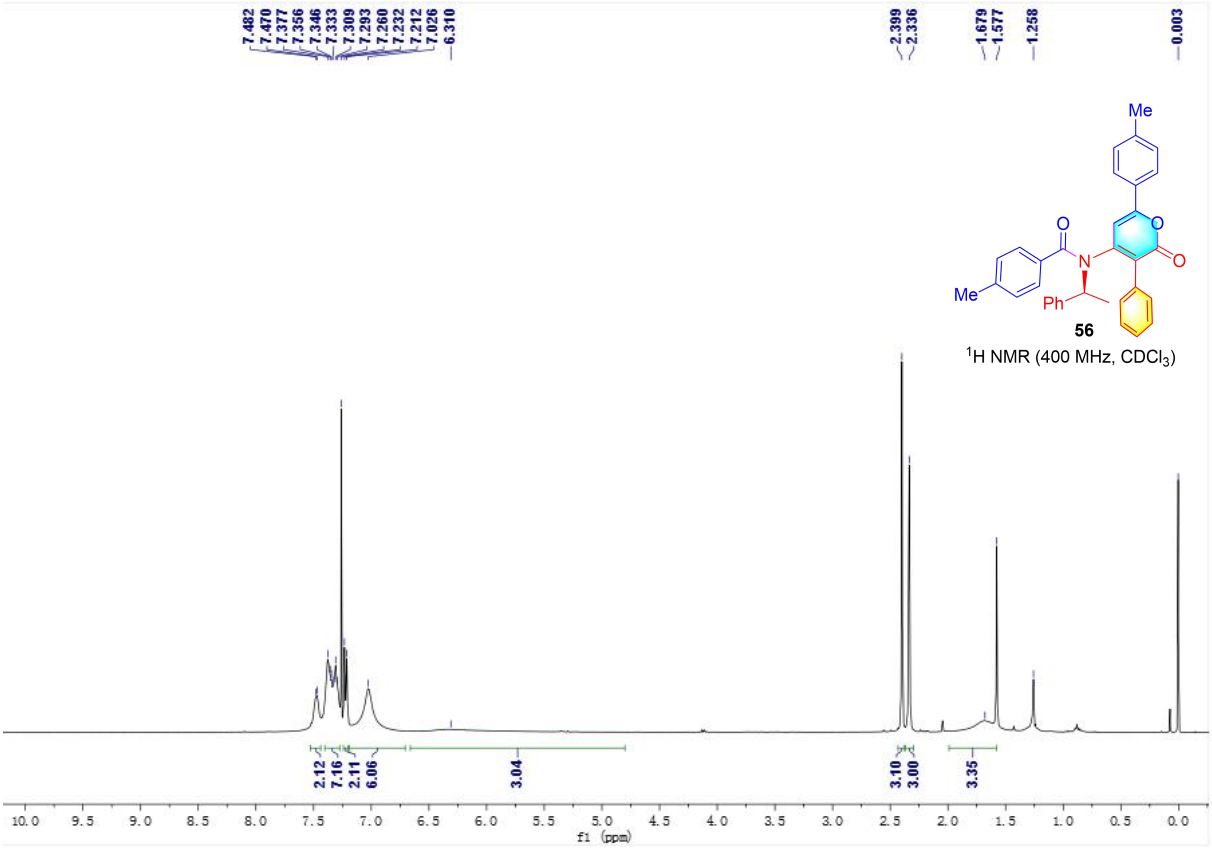
^{13}C NMR (100 MHz, $CDCl_3$)



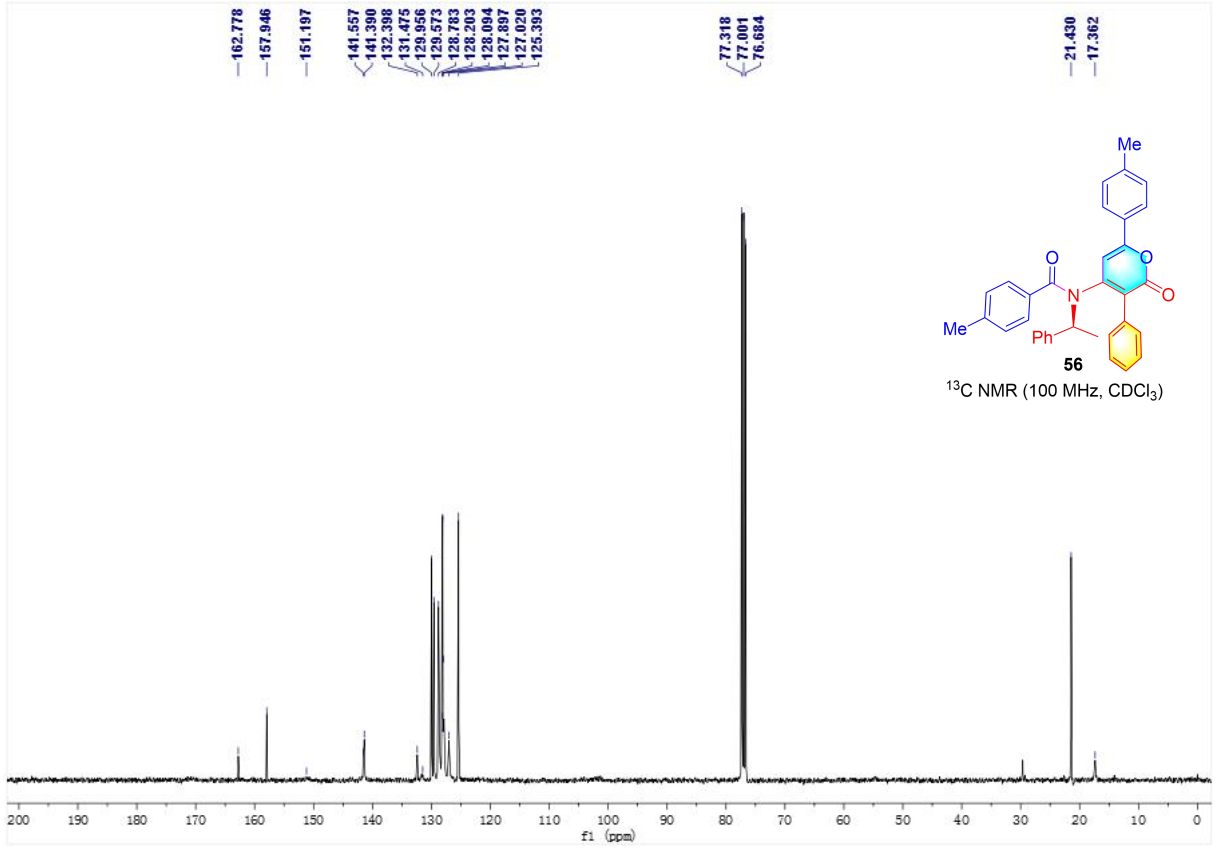
^{1}H NMR (400 MHz, $CDCl_3$)



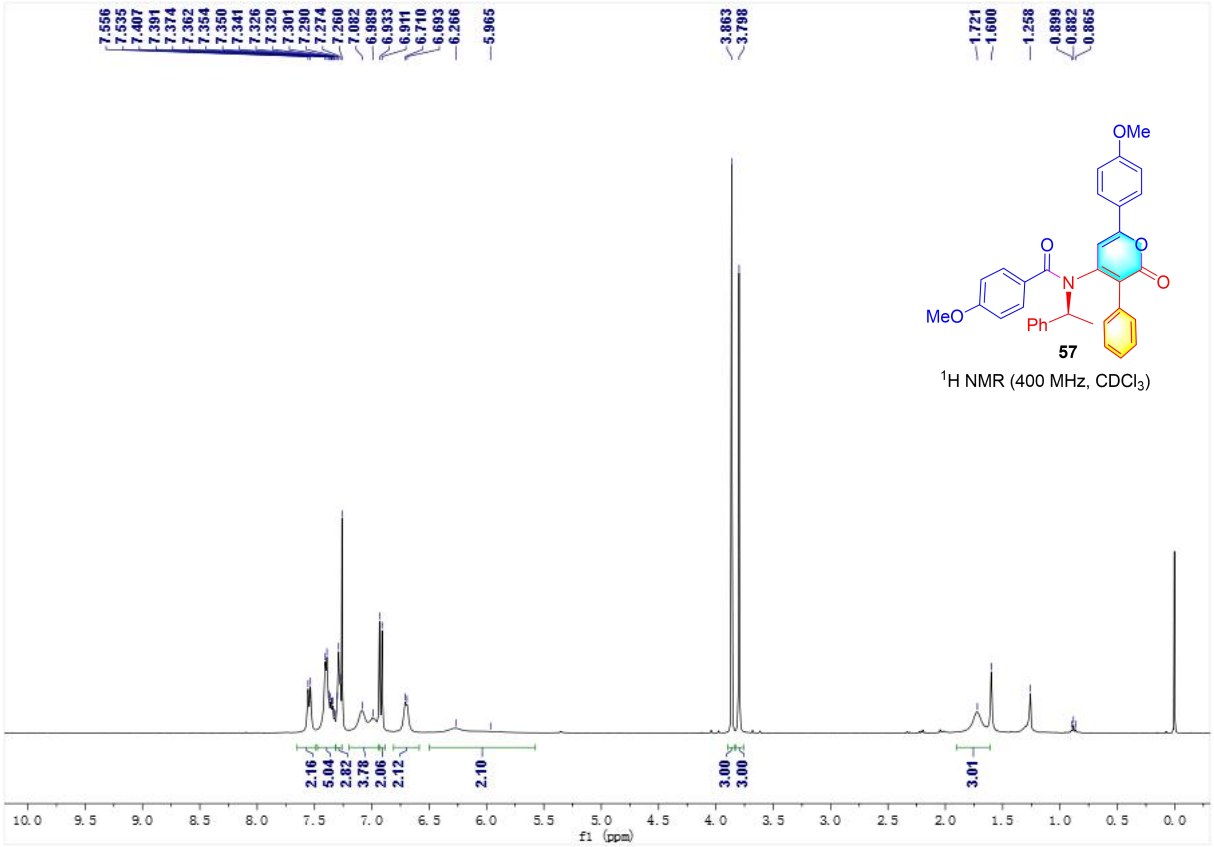
^{13}C NMR (100 MHz, $CDCl_3$)



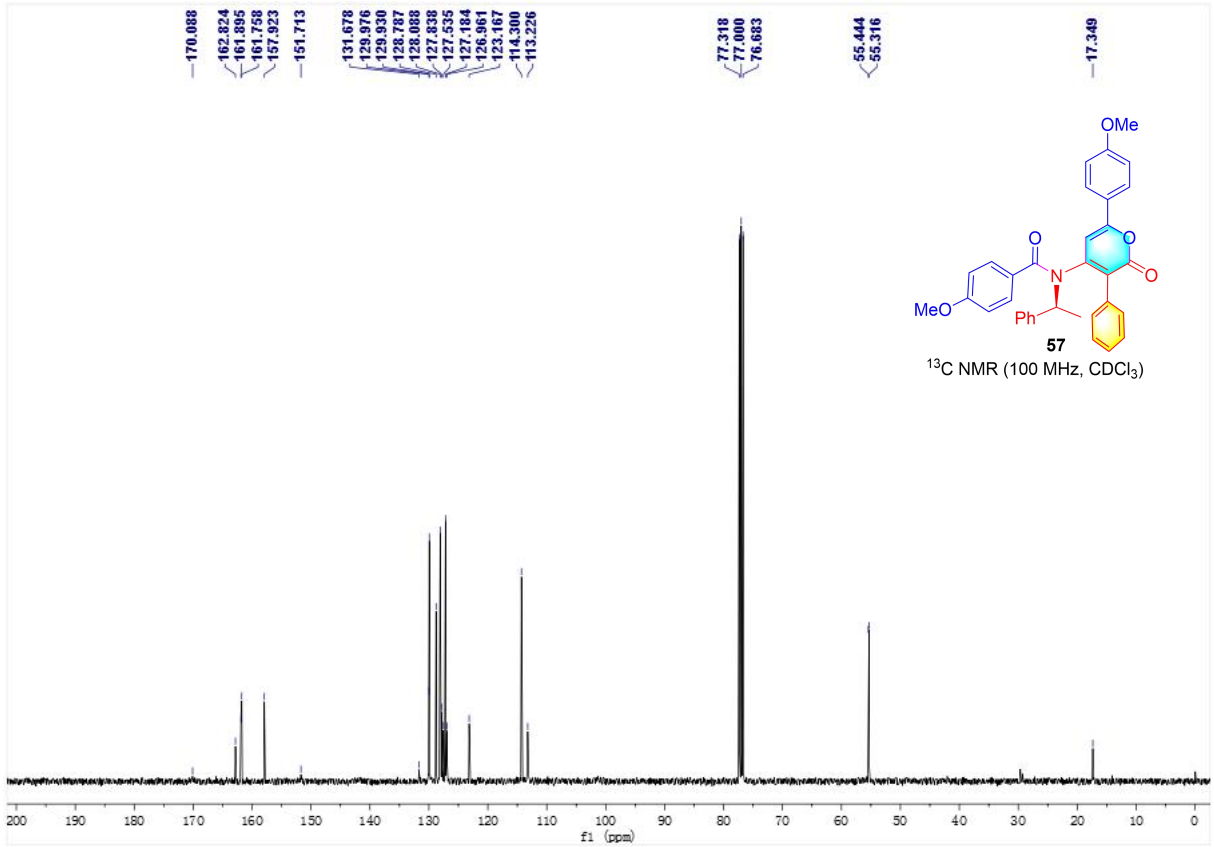
^{1}H NMR (400 MHz, $CDCl_3$)



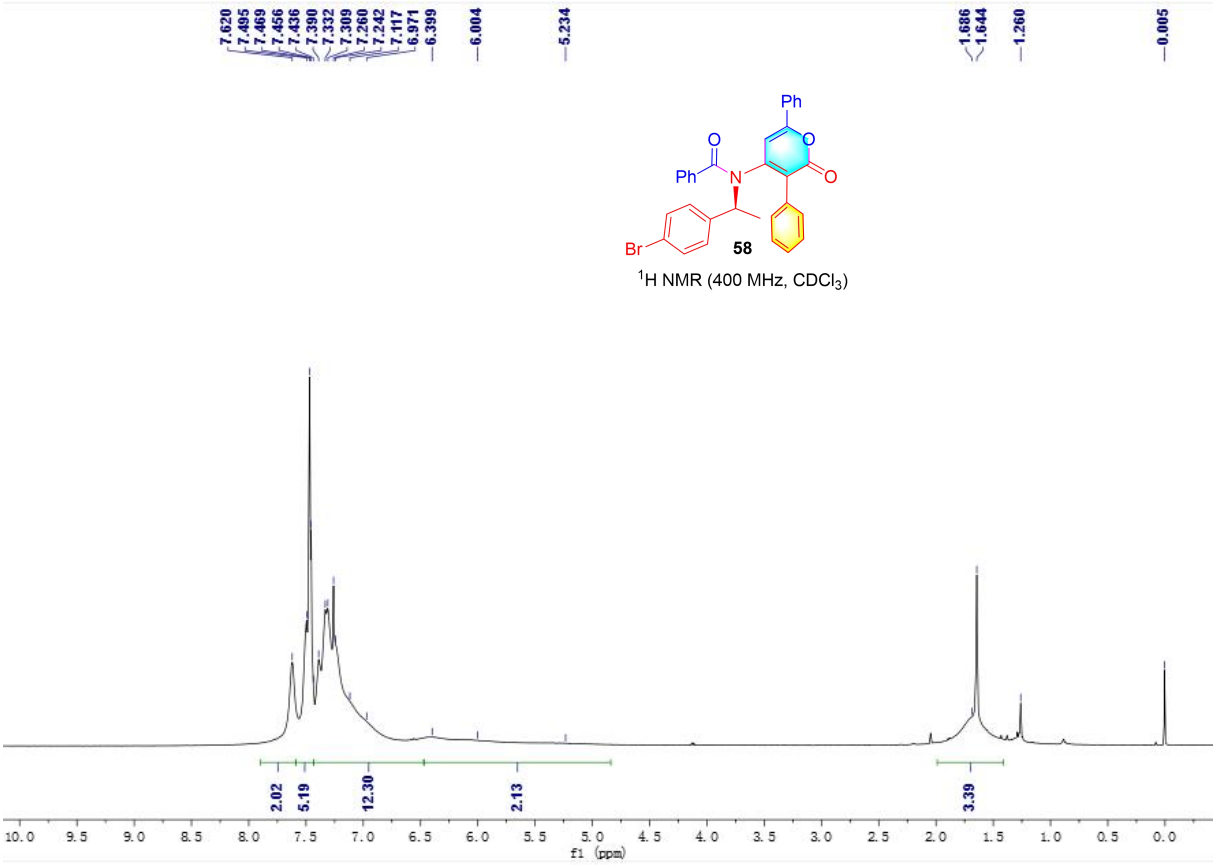
^{13}C NMR (100 MHz, $CDCl_3$)



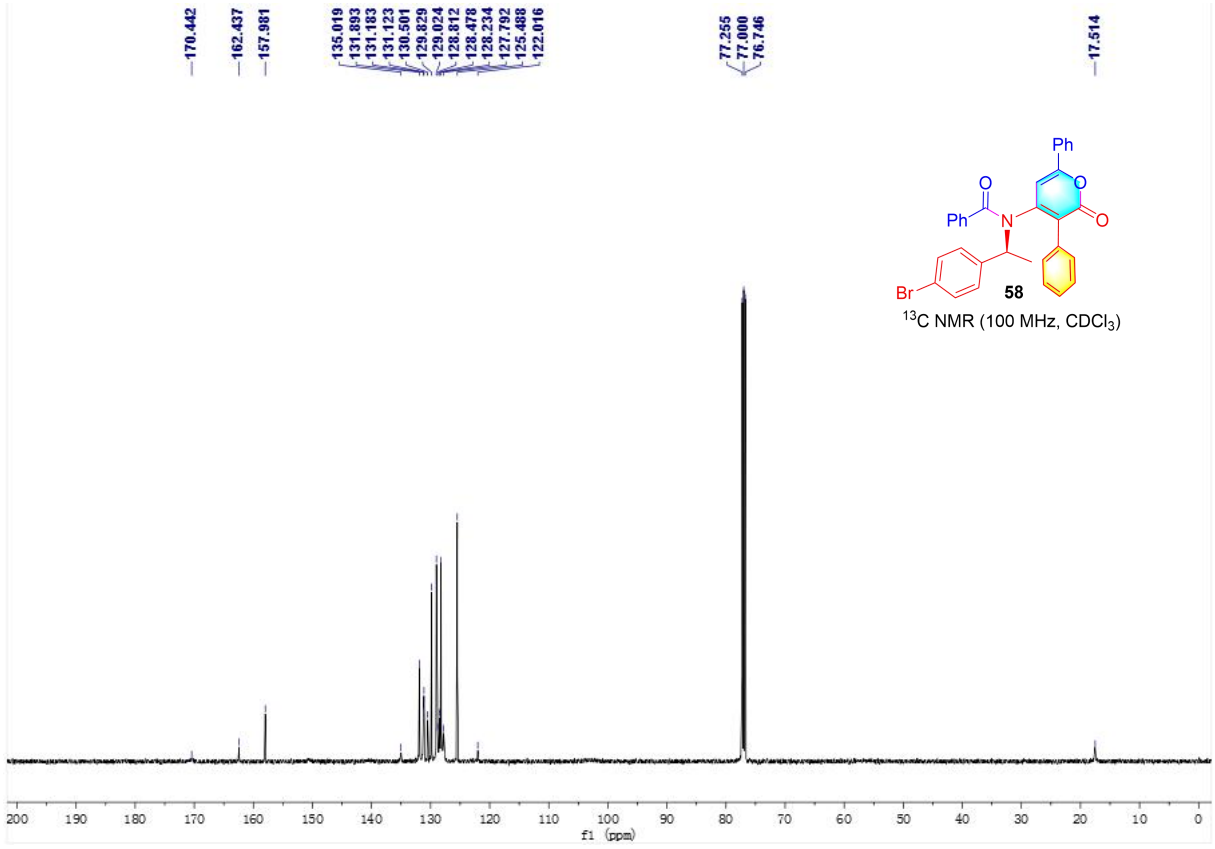
^{1}H NMR (400 MHz, $CDCl_3$)



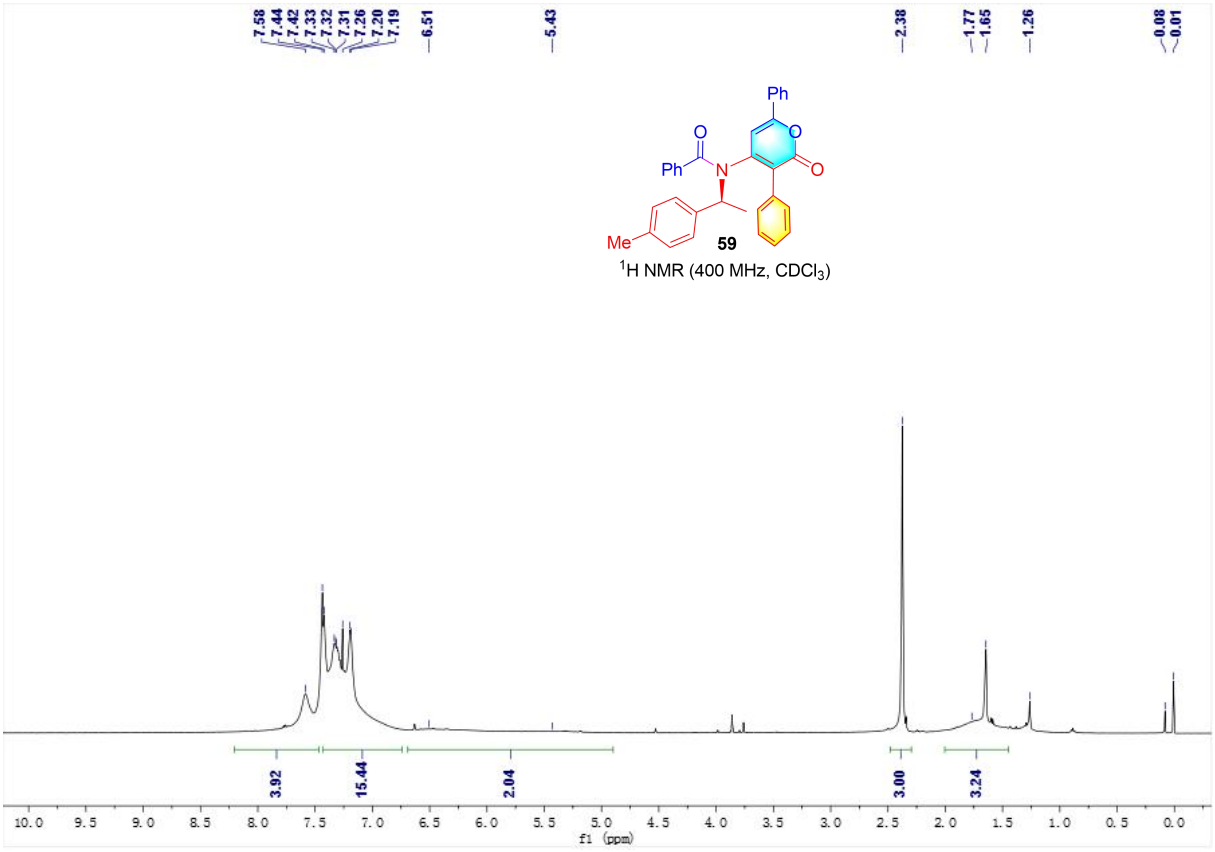
^{13}C NMR (100 MHz, $CDCl_3$)



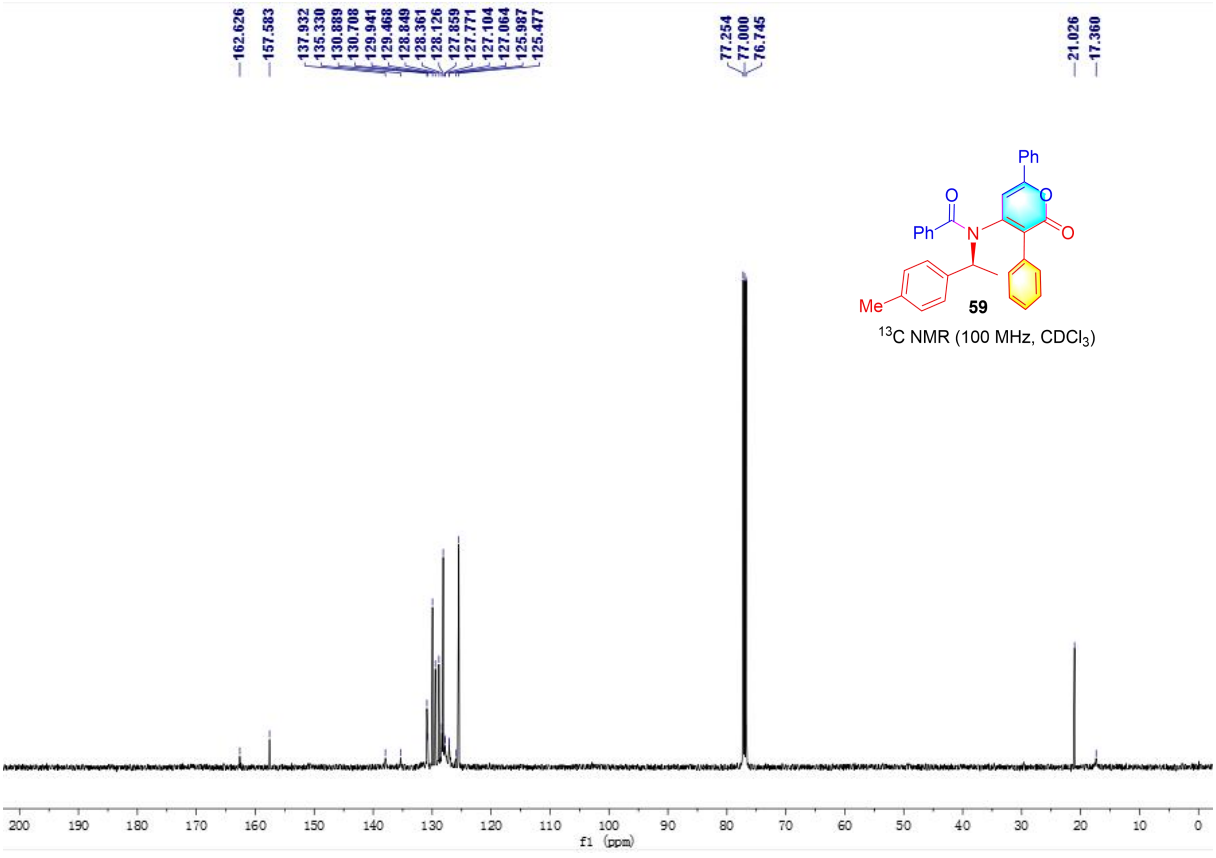
^{1}H NMR (400 MHz, $CDCl_3$)



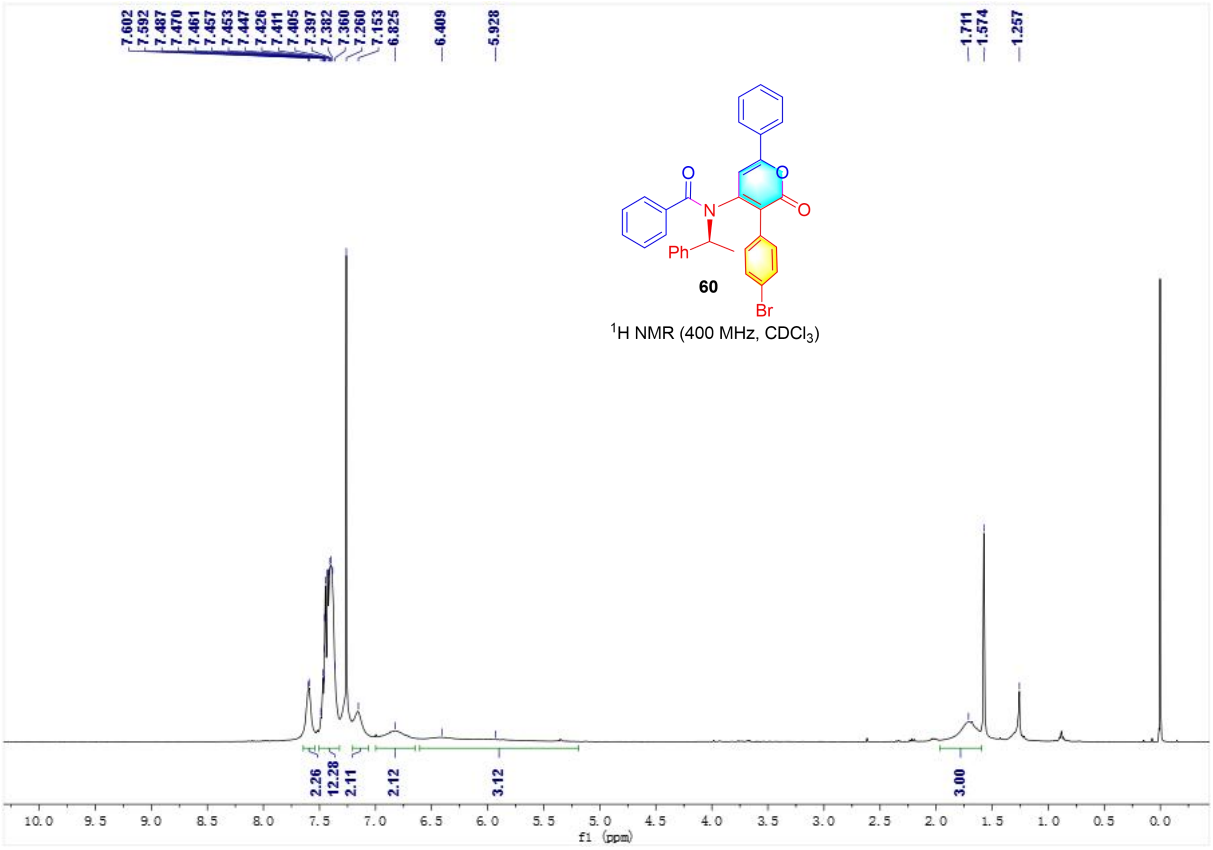
^{13}C NMR (100 MHz, $CDCl_3$)



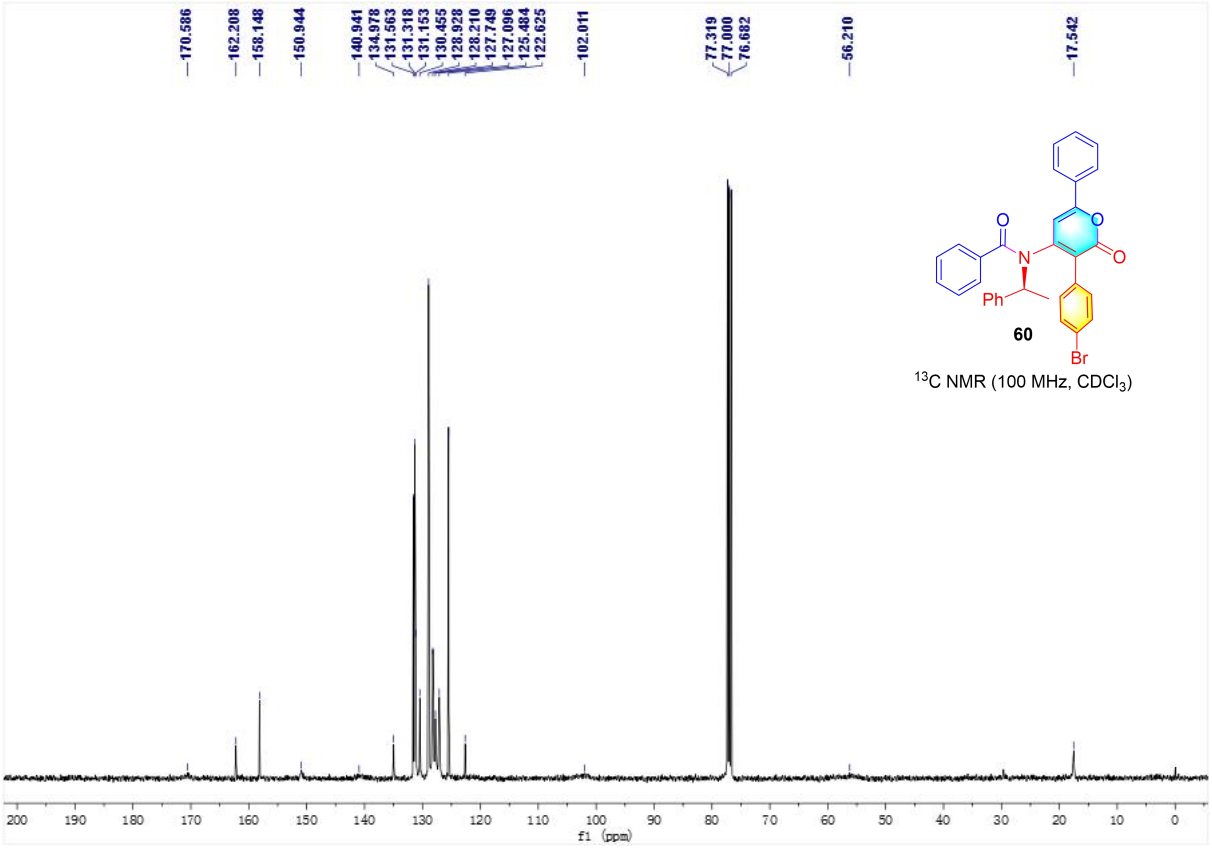
^{1}H NMR (400 MHz, $CDCl_3$)



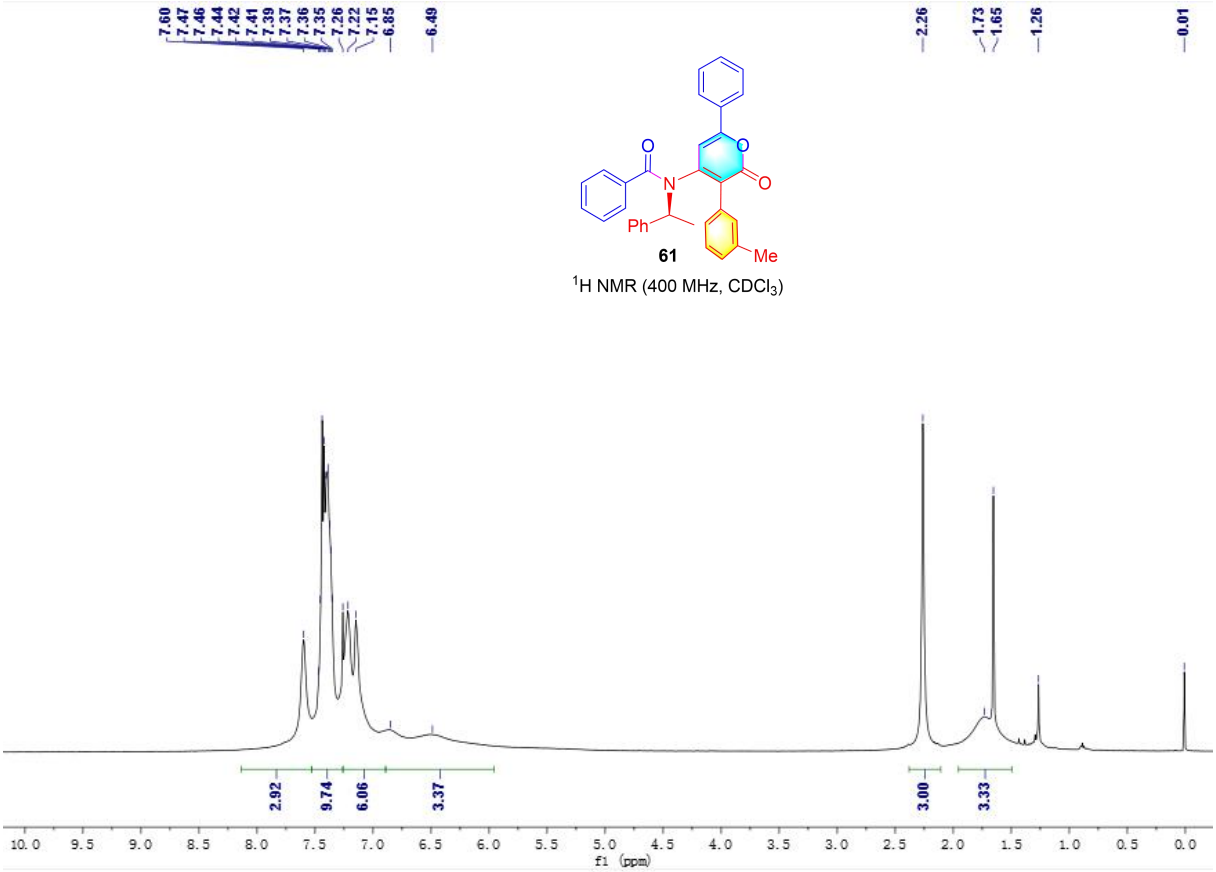
^{13}C NMR (100 MHz, $CDCl_3$)



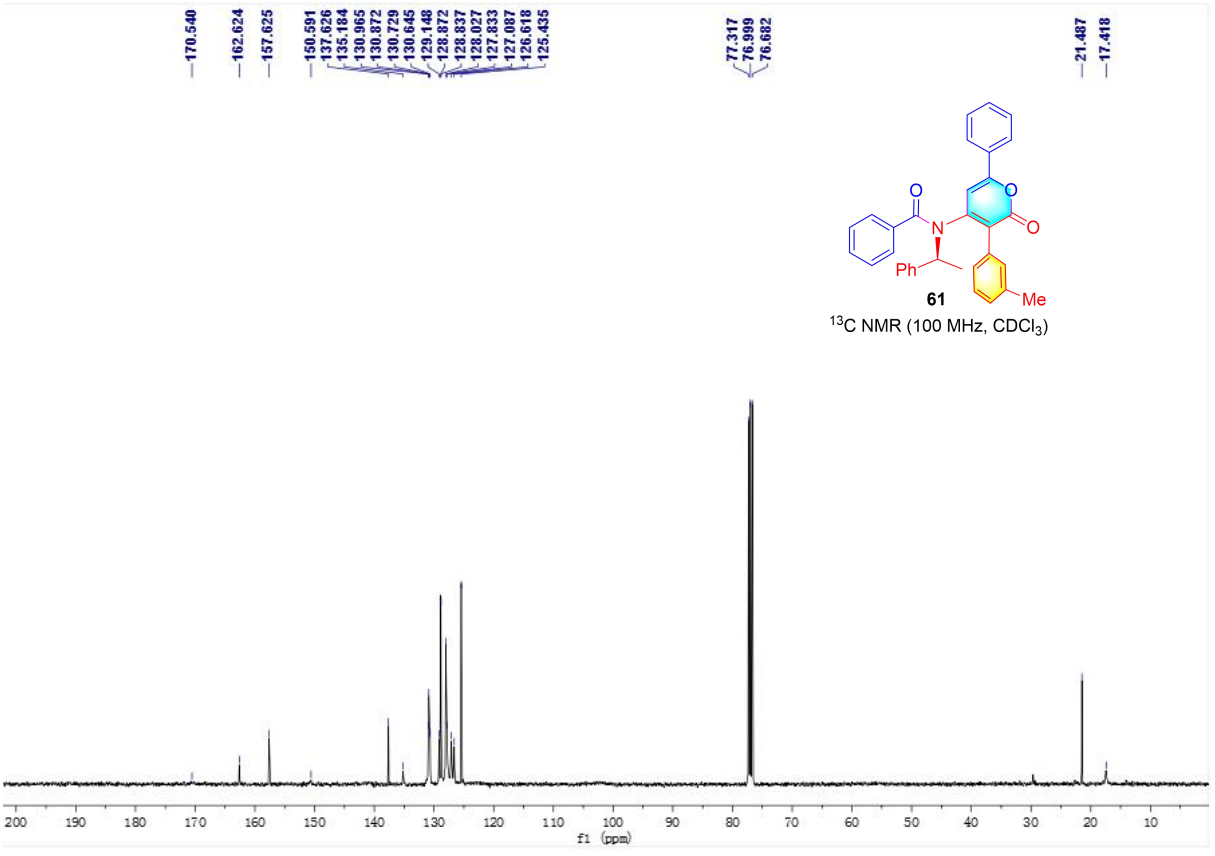
^{1}H NMR (400 MHz, $CDCl_3$)



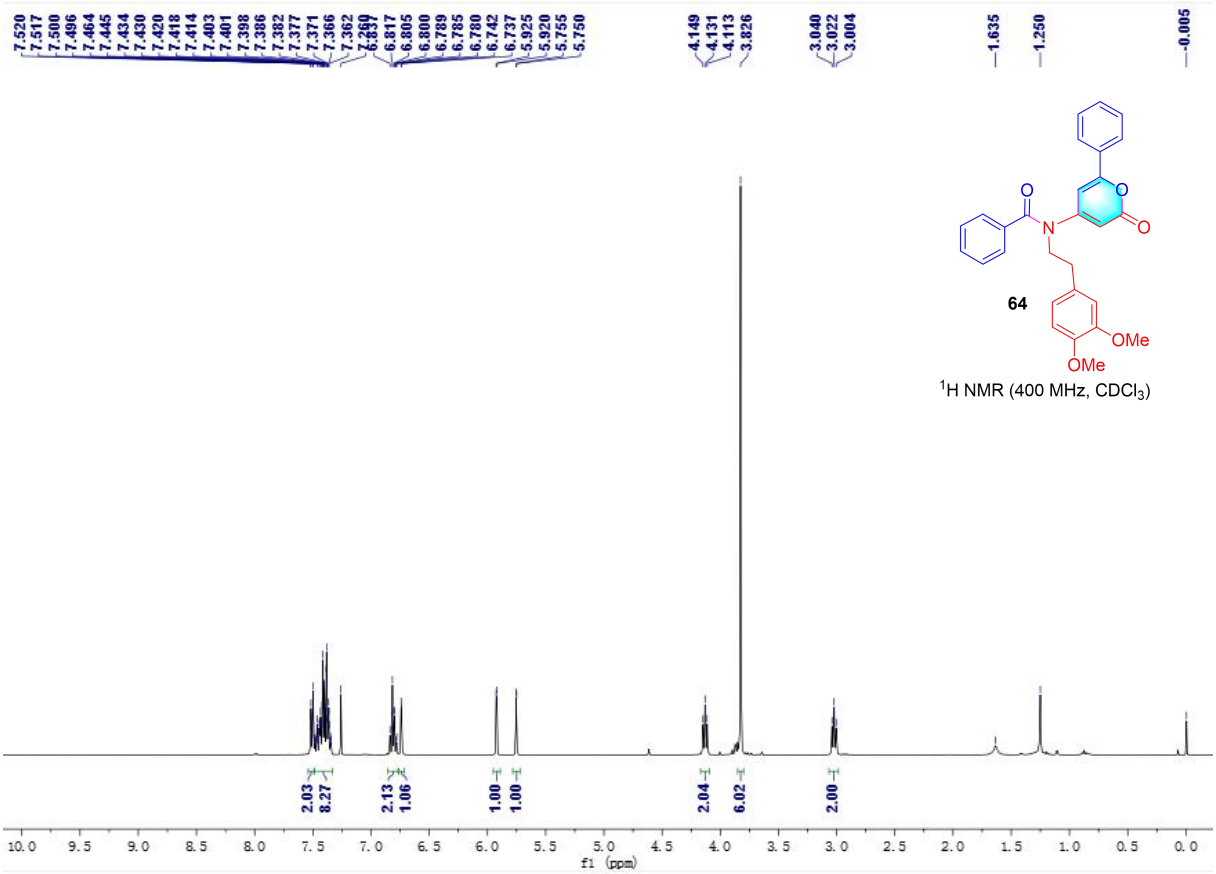
^{13}C NMR (100 MHz, $CDCl_3$)

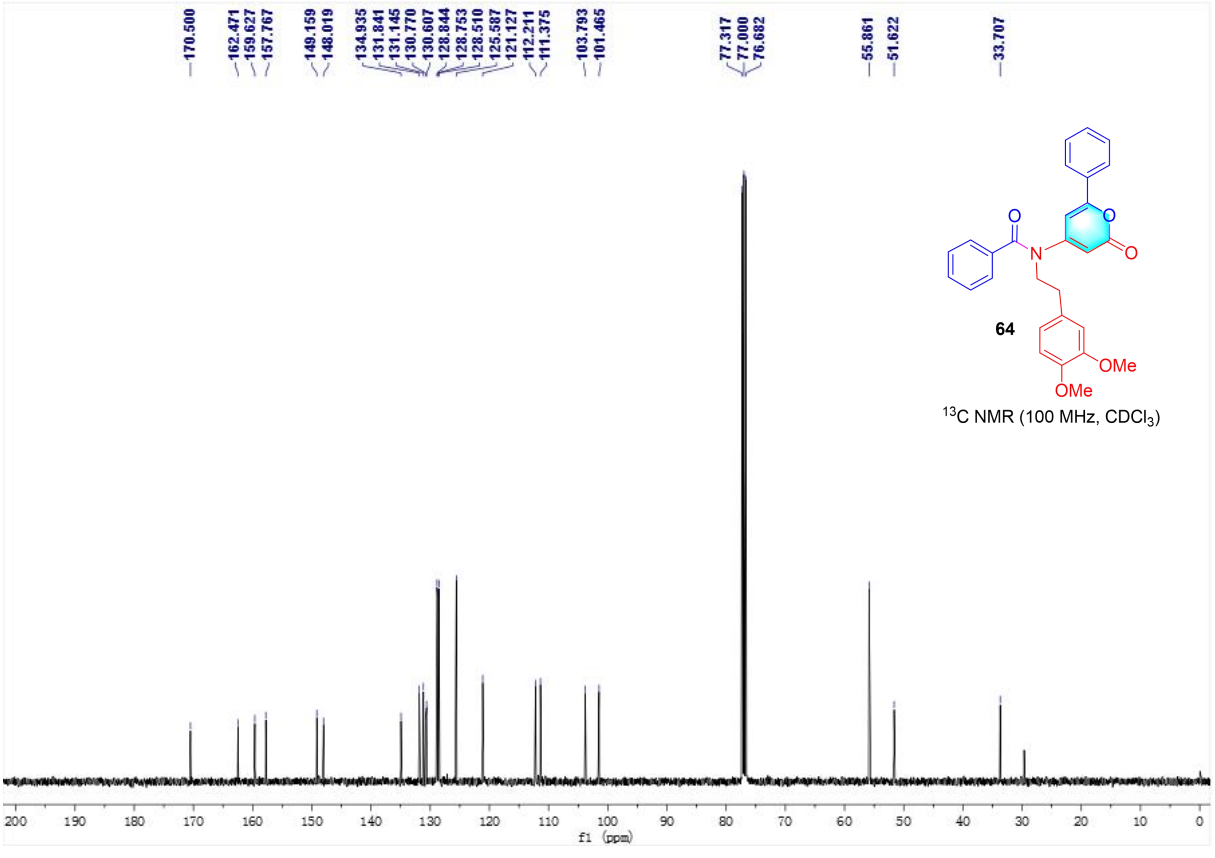


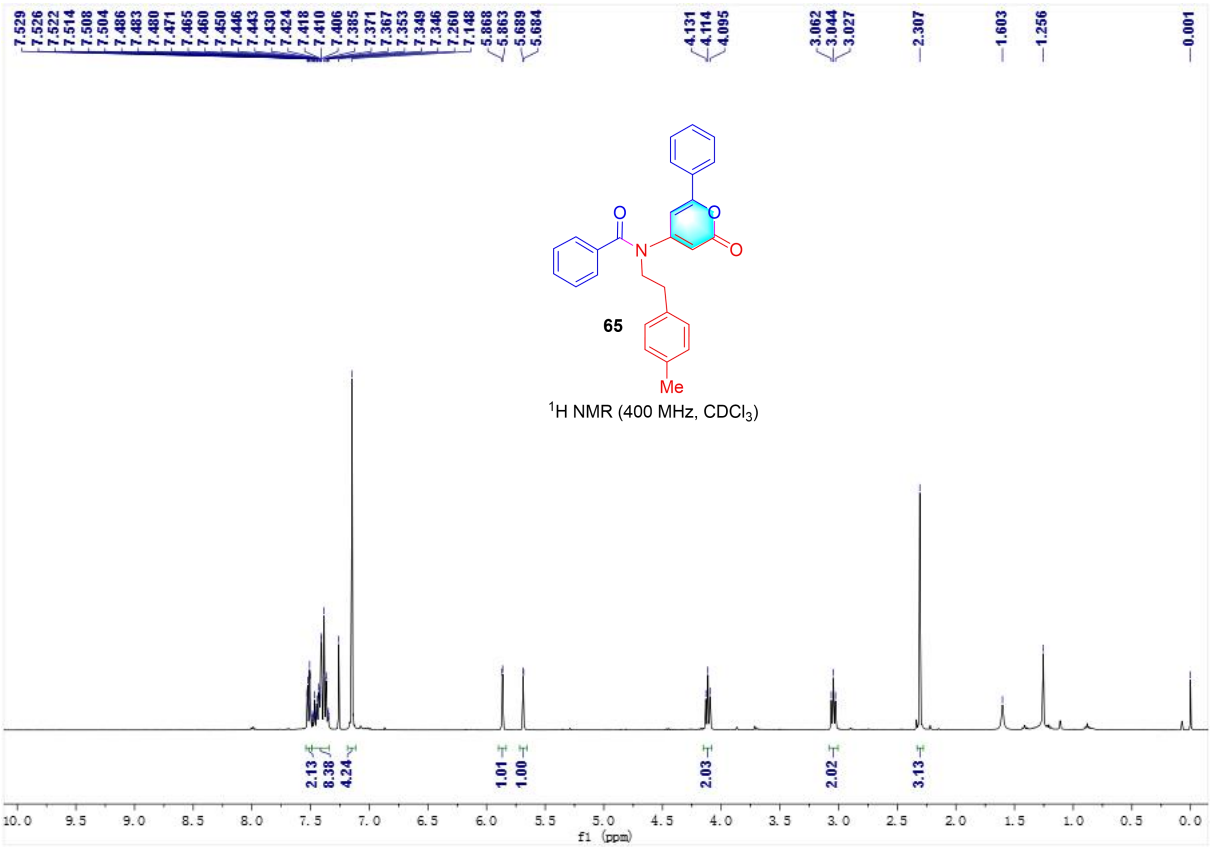
^{1}H NMR (400 MHz, $CDCl_3$)



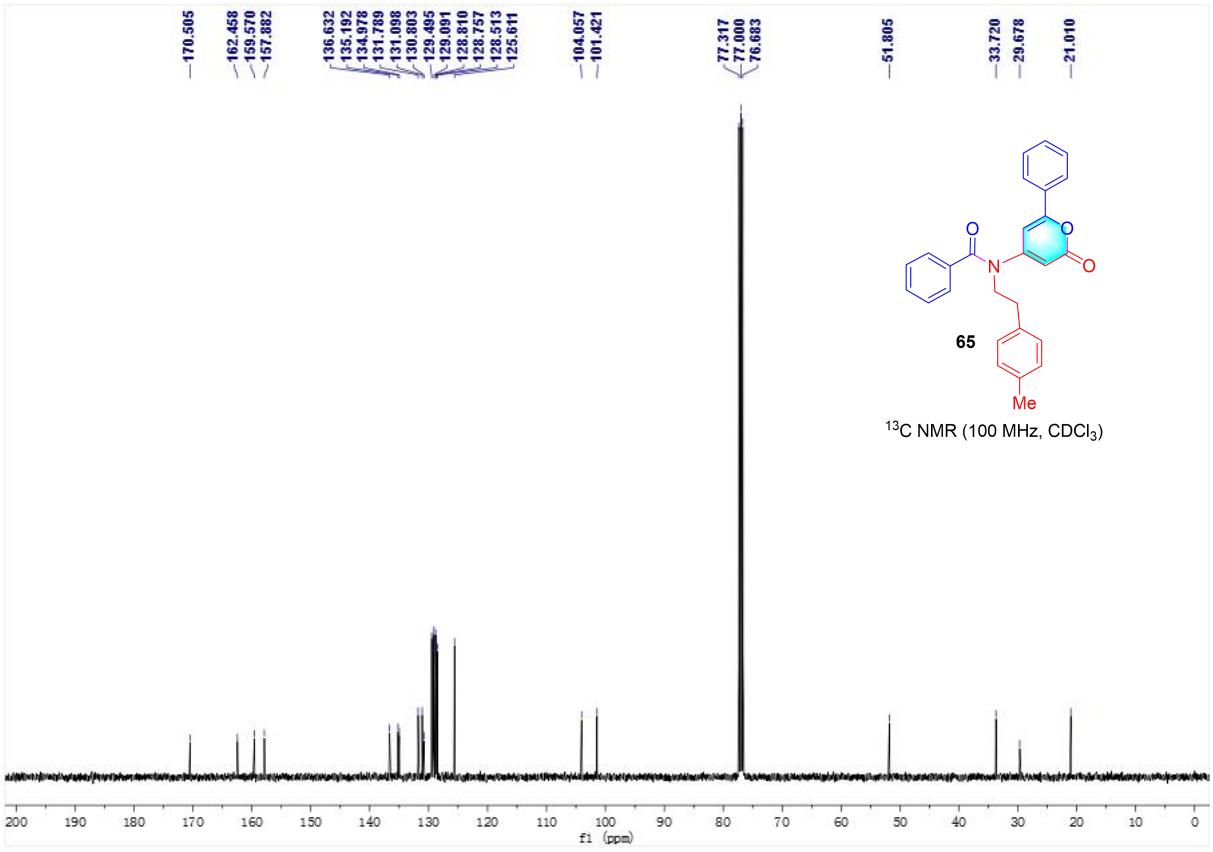
^{13}C NMR (100 MHz, $CDCl_3$)


7.520
7.517
7.500
7.496
7.464
7.445
7.434
7.430
7.420
7.418
7.414
7.403
7.401
7.398
7.386
7.382
7.377
7.371
7.366
7.362
6.817
6.805
6.800
6.789
6.785
6.780
6.742
6.737
5.925
5.920
5.755
5.750
4.149
4.131
4.113
3.826
3.040
3.022
3.004
1.635
1.250
0.005
2.03
8.27
2.13
1.06
1.00
1.00
2.04
6.02
2.00
f1 (ppm)
64
OMe
OMe
^{1}H NMR (400 MHz, $CDCl_3$)

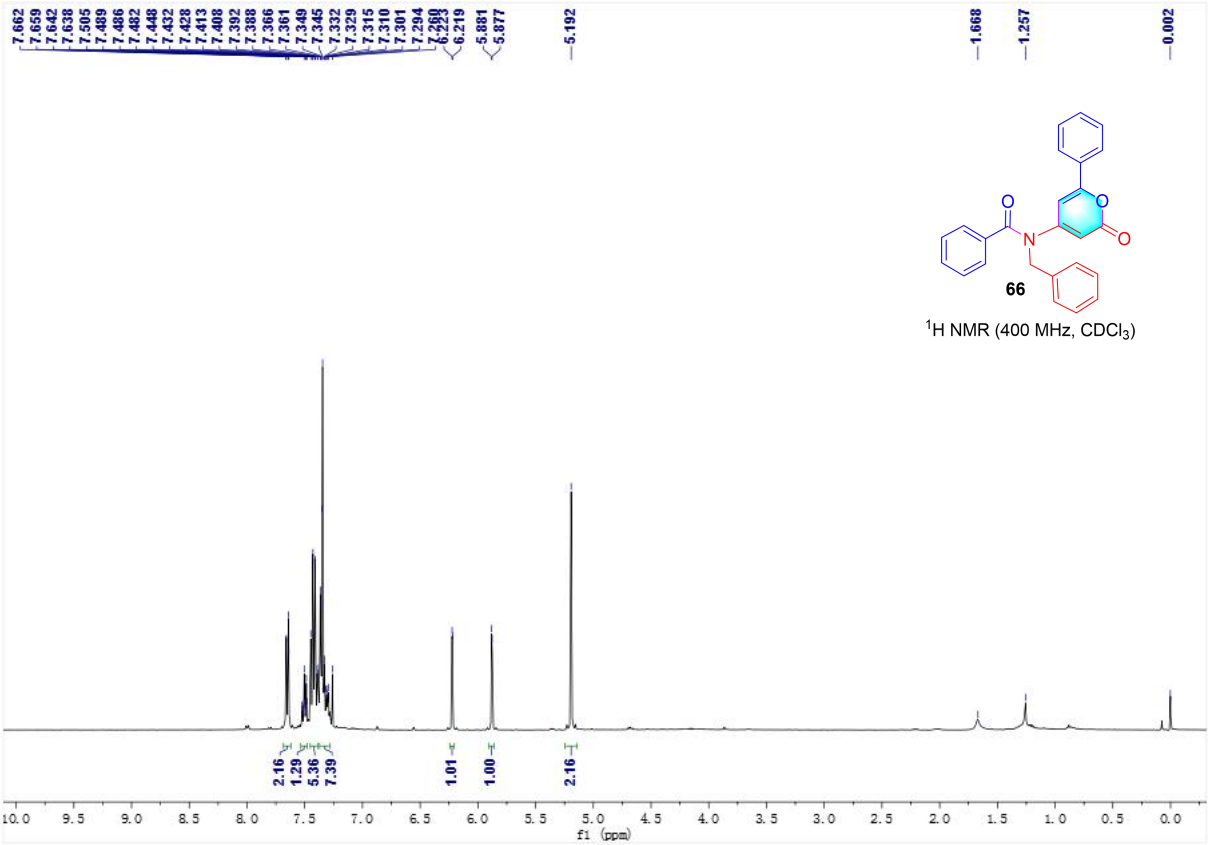

170.500
162.471
159.627
157.767
149.159
148.019
134.935
131.841
131.145
130.770
130.607
128.844
128.753
128.510
125.587
121.127
112.211
111.375
103.793
101.465
77.317
77.000
76.682
55.861
51.622
33.707
f1 (ppm)
64
OMe
OMe
^{13}C NMR (100 MHz, $CDCl_3$)



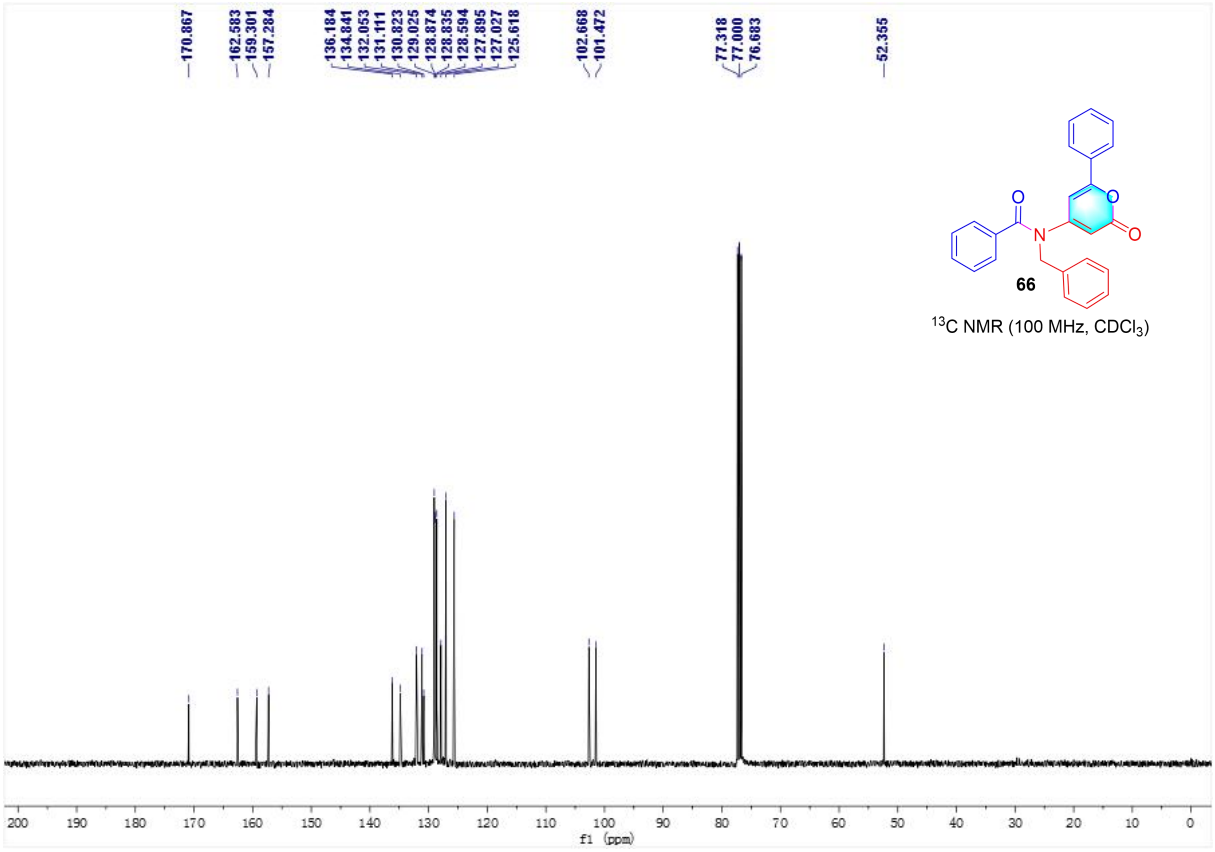
^{1}H NMR (400 MHz, $CDCl_3$)



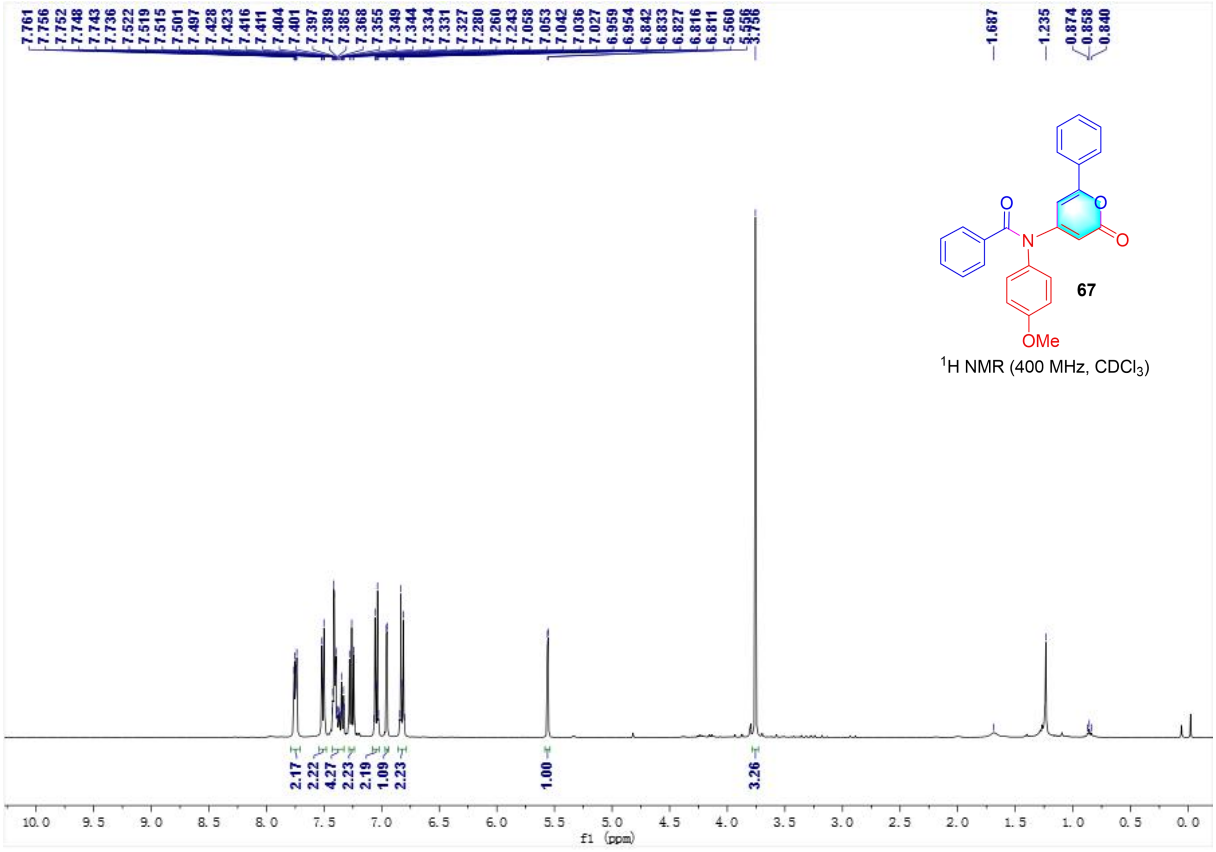
^{13}C NMR (100 MHz, $CDCl_3$)



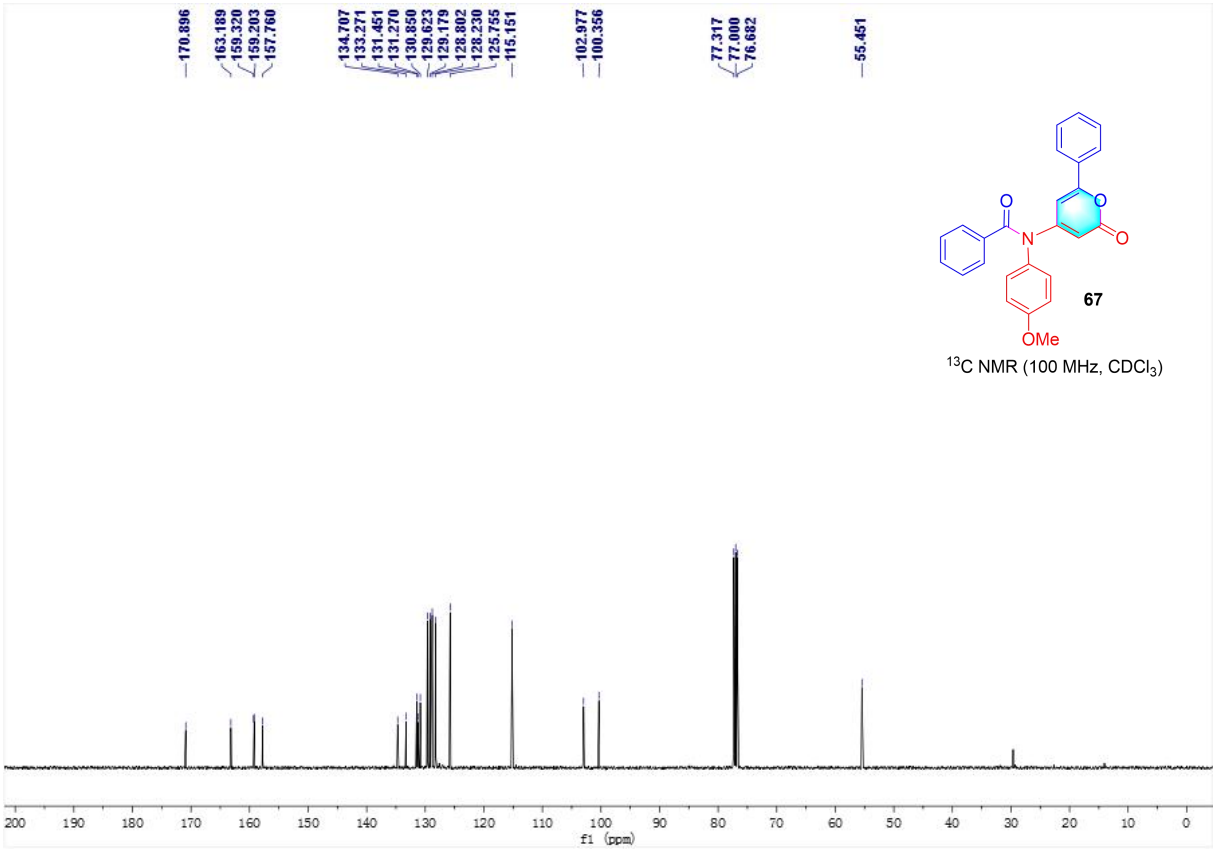
^{1}H NMR (400 MHz, $CDCl_3$)



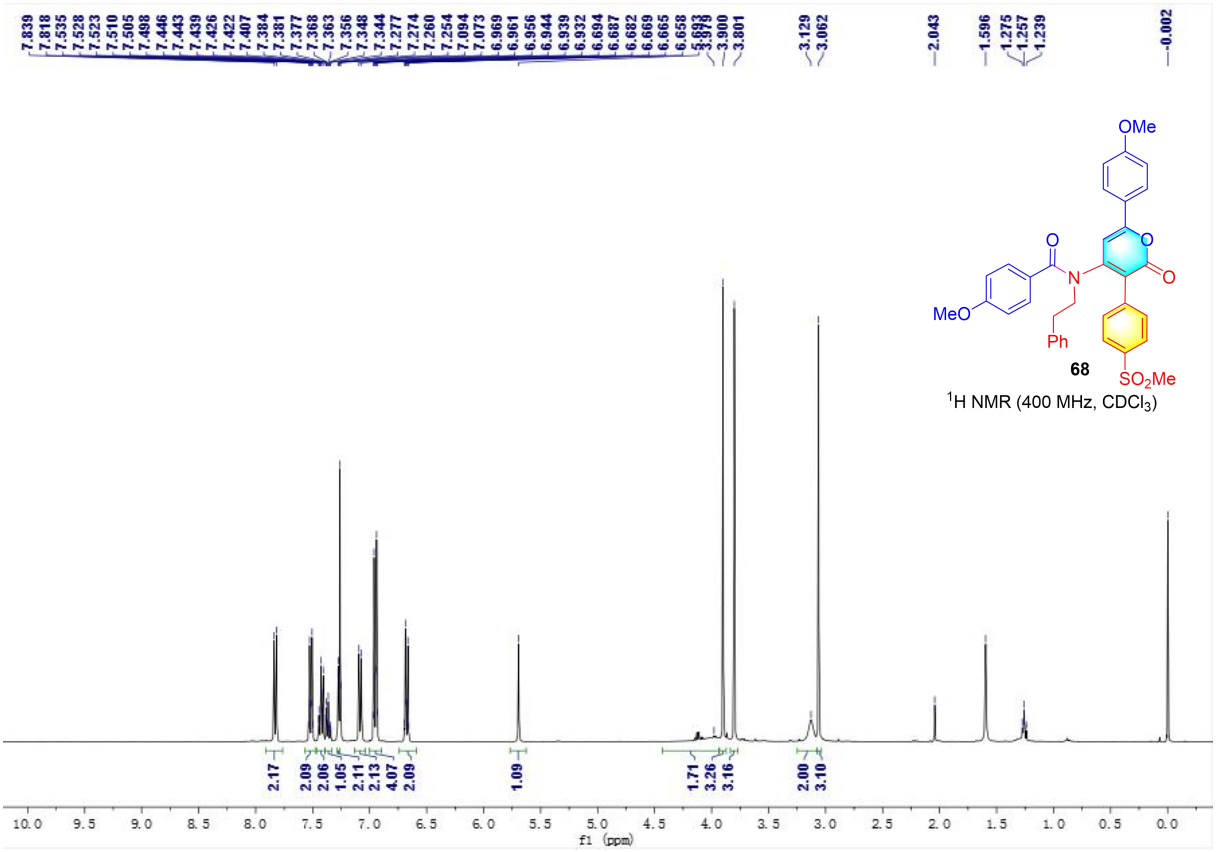
^{13}C NMR (100 MHz, $CDCl_3$)

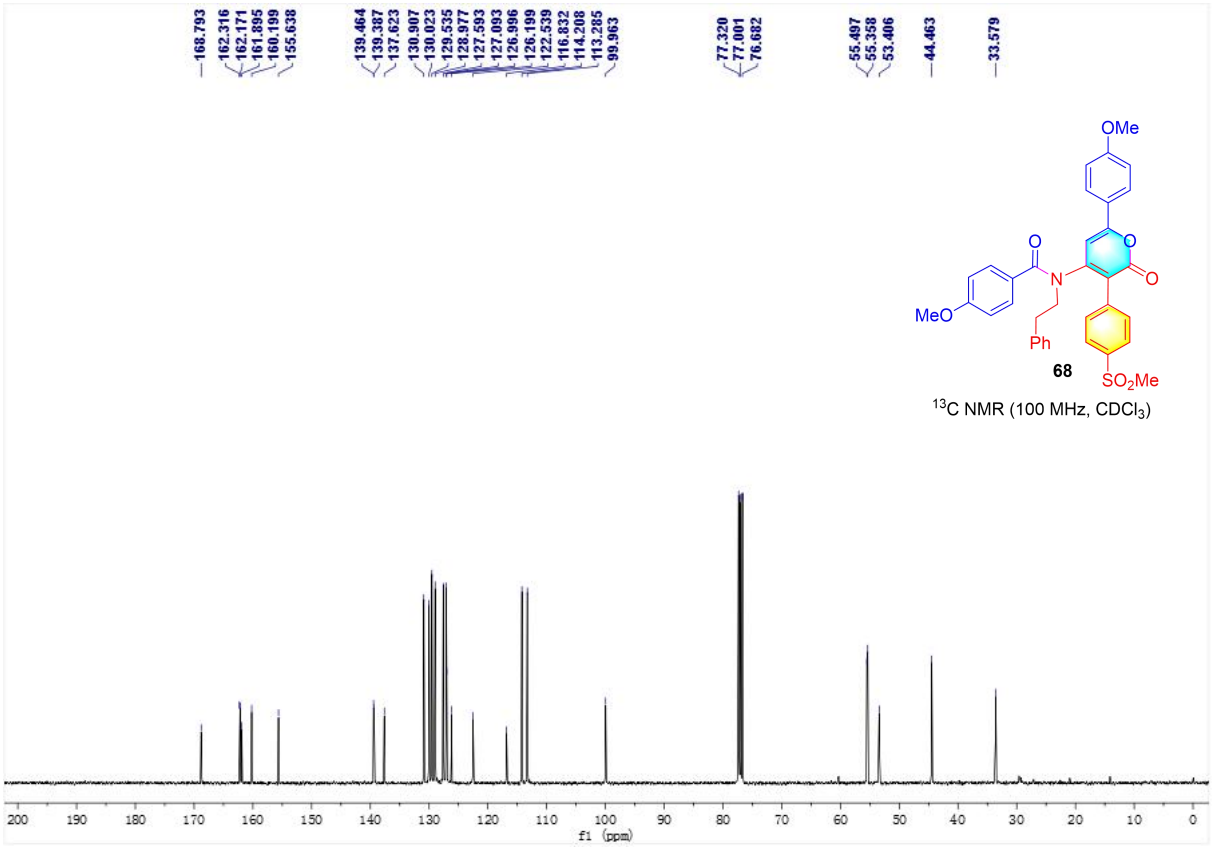


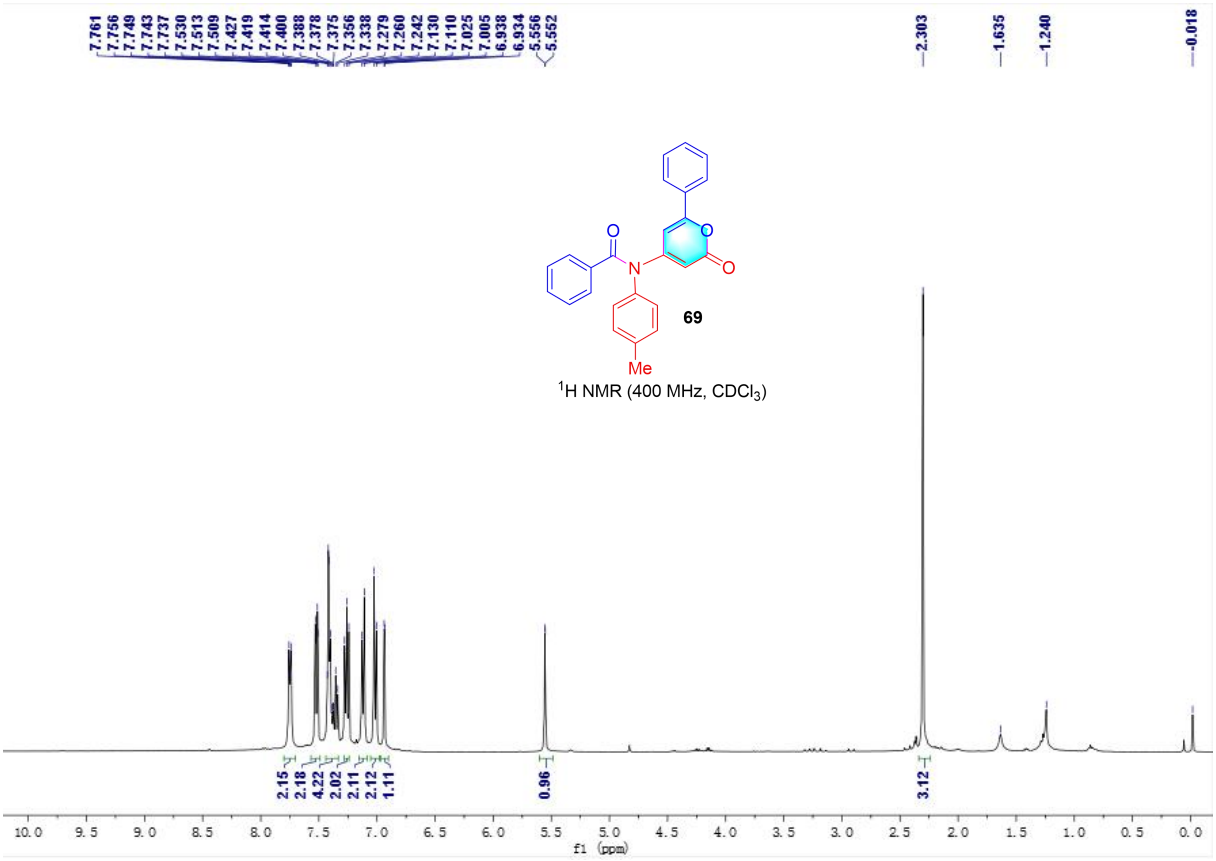
^{1}H NMR (400 MHz, $CDCl_3$)



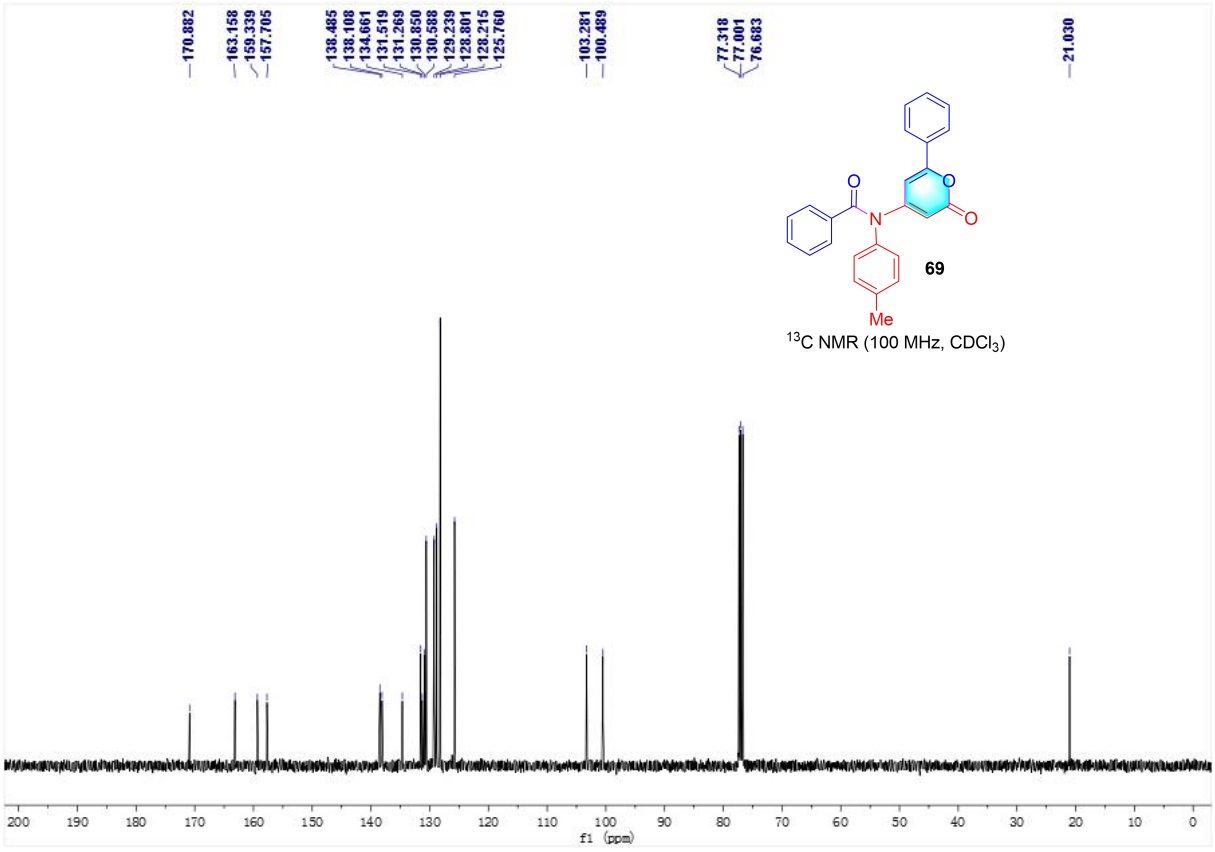
^{13}C NMR (100 MHz, $CDCl_3$)


OMe
MeO
Ph
68
SO2Me
1H NMR (400 MHz, CDCl3)

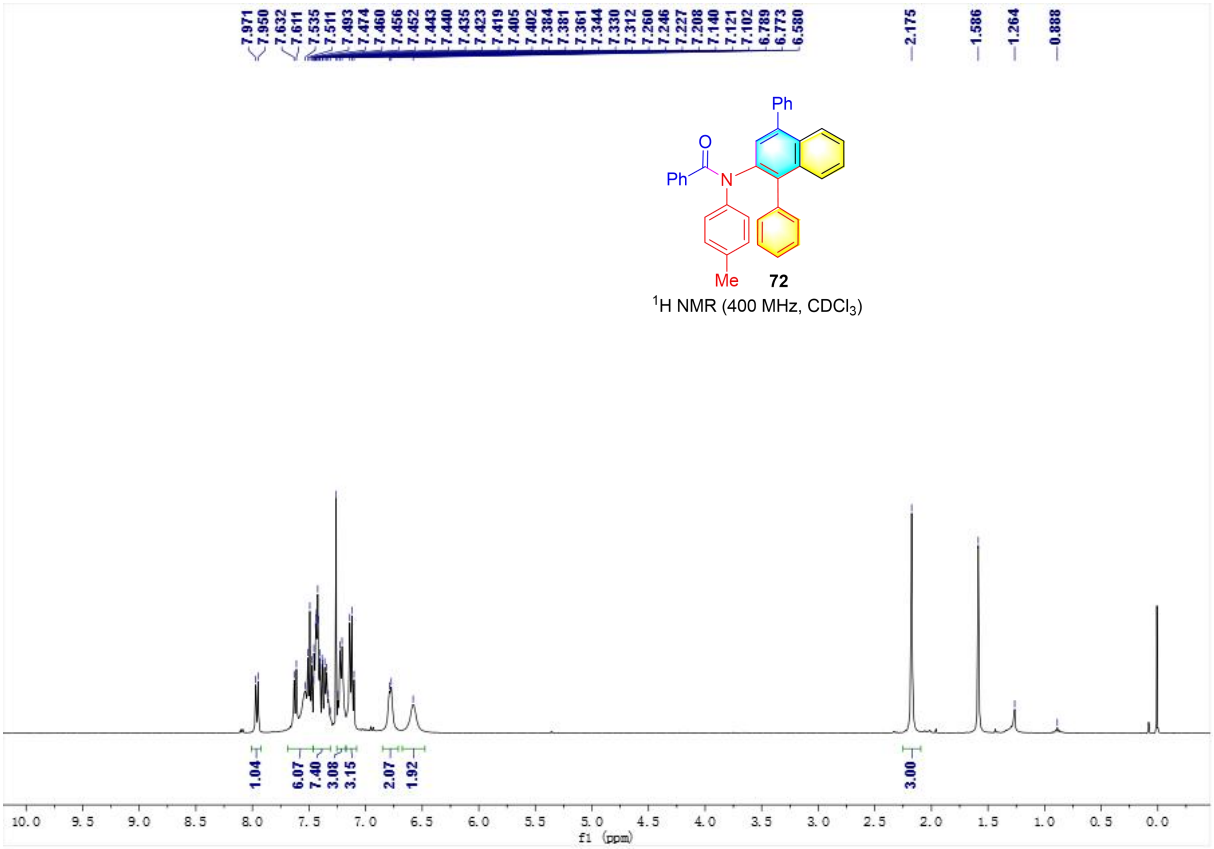

OMe
MeO
Ph
68
SO2Me
13C NMR (100 MHz, CDCl3)



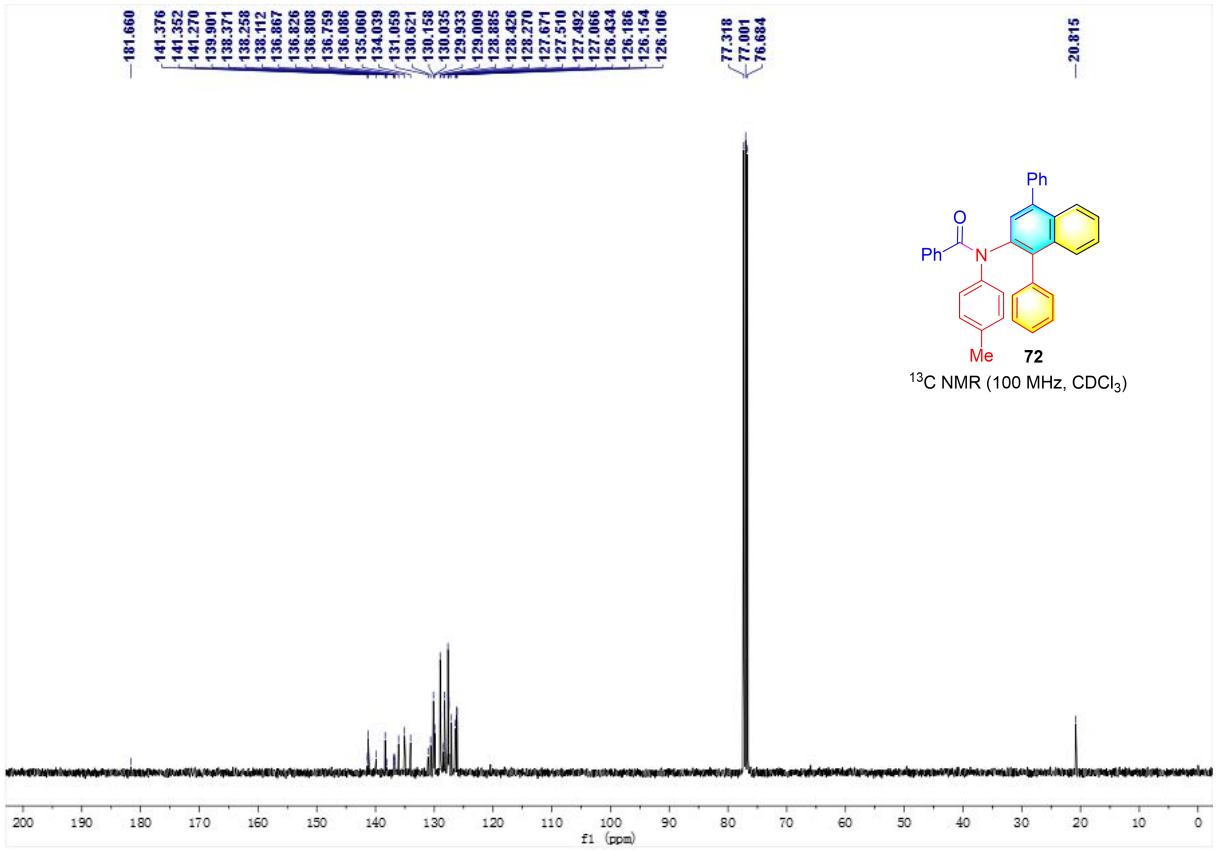
^{1}H NMR (400 MHz, $CDCl_3$)



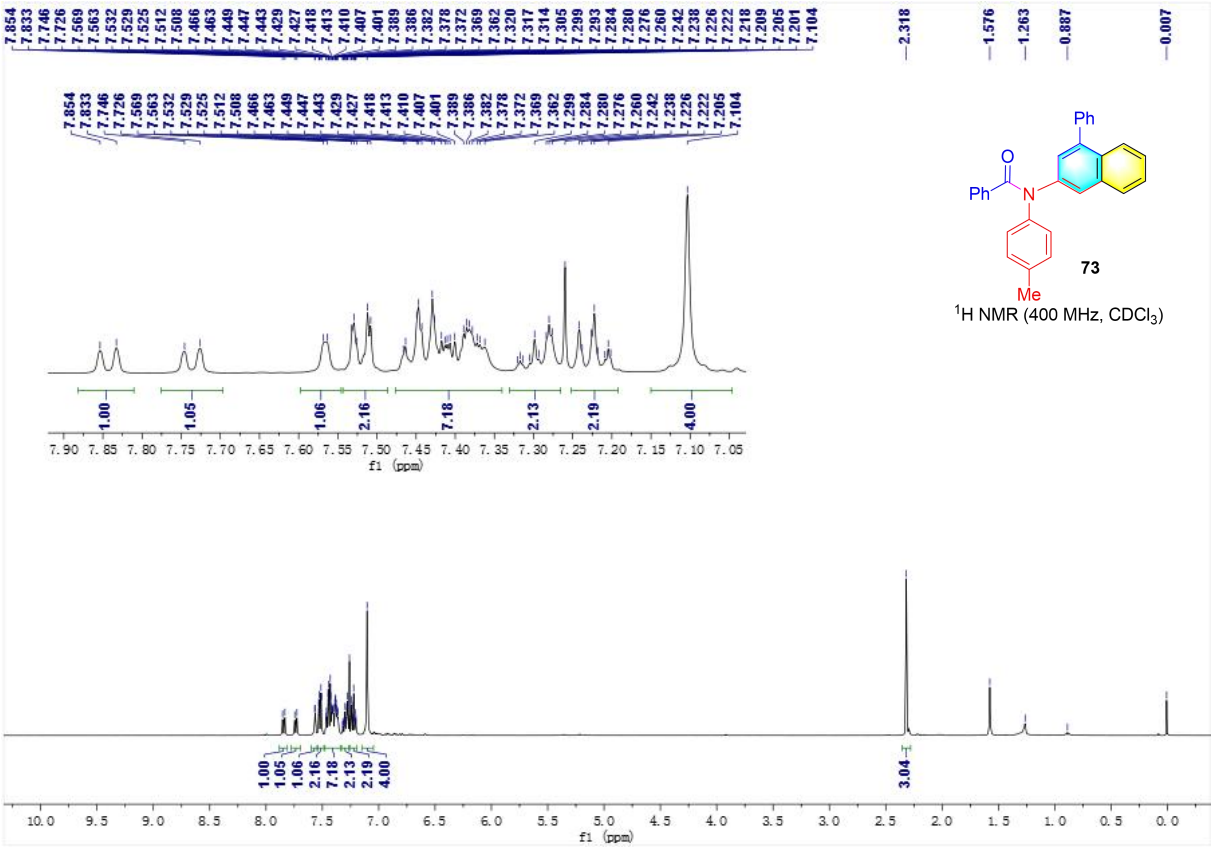
^{13}C NMR (100 MHz, $CDCl_3$)

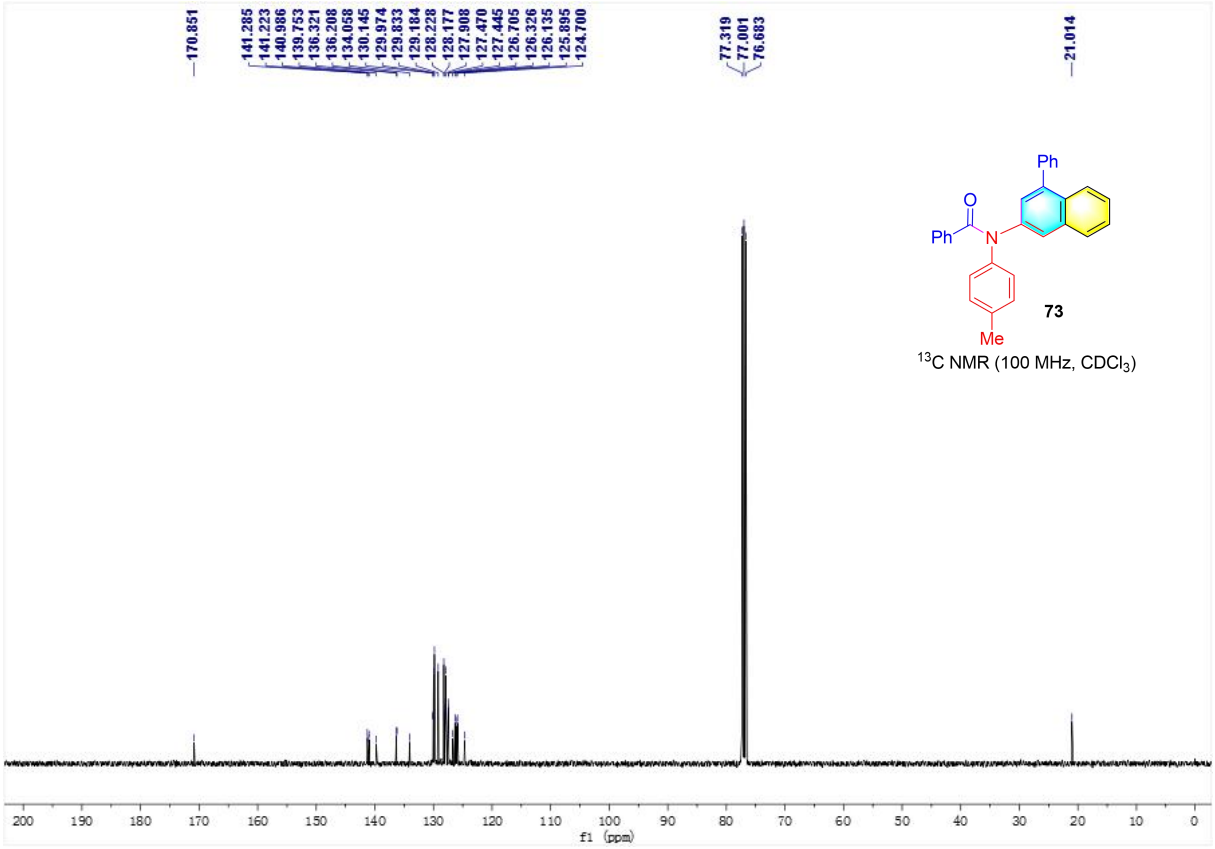


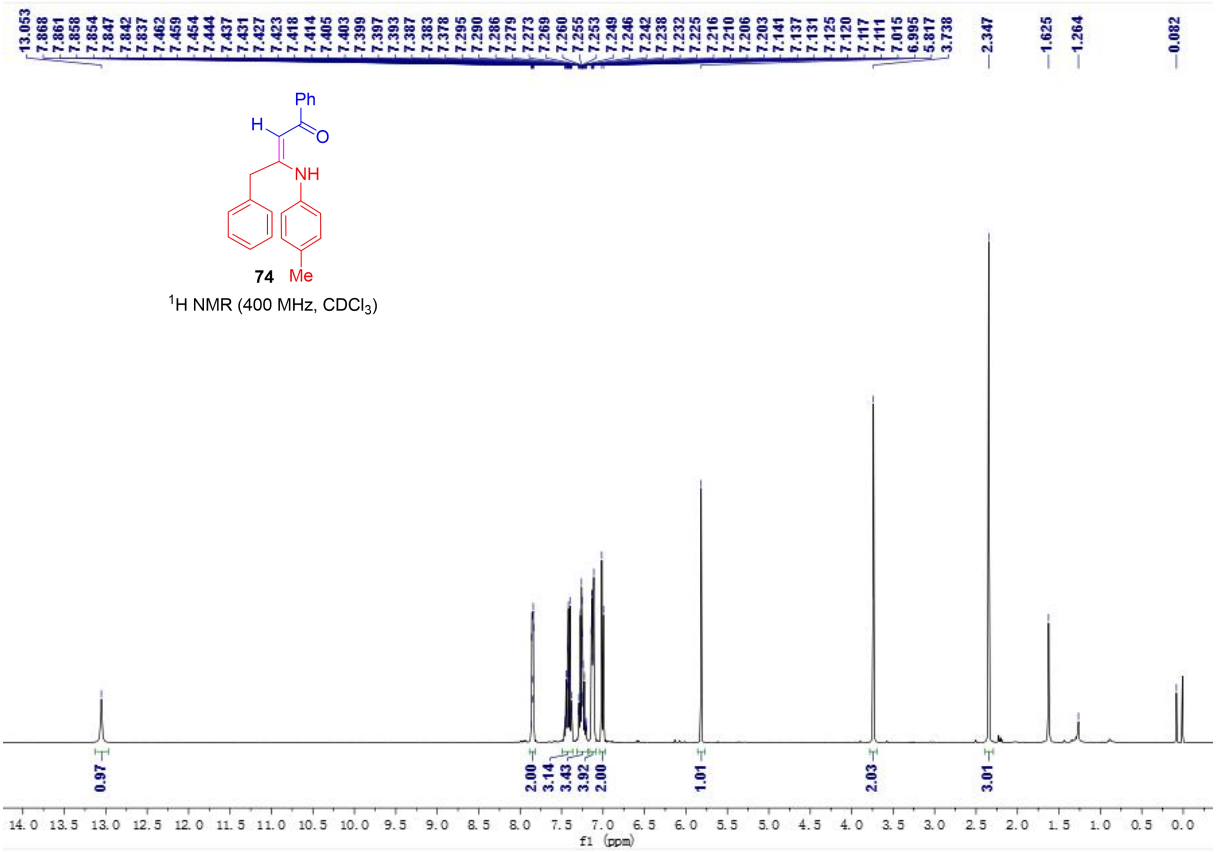
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

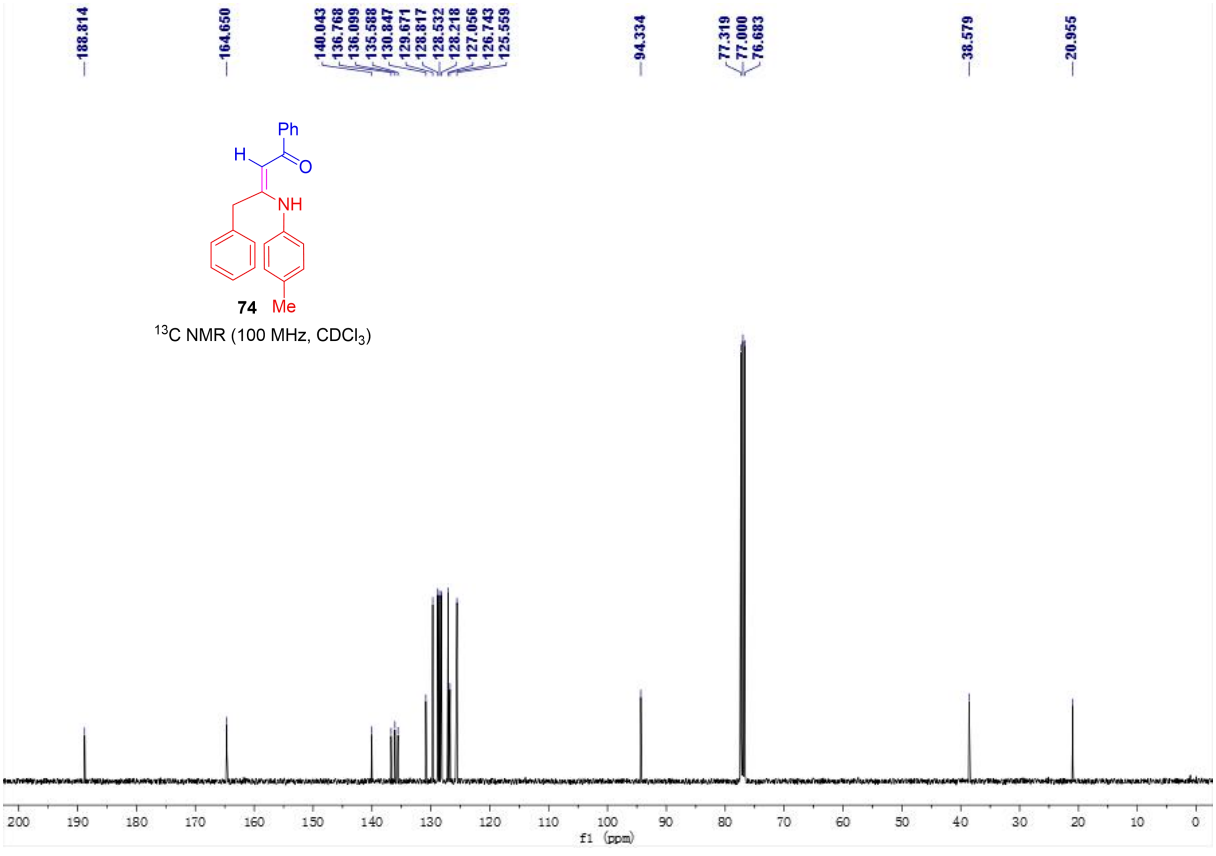

Ph
O
Ph
N
Me
73
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Ph
O
Ph
N
Me
73
13C NMR (100 MHz, CDCl3)
f1 (ppm)



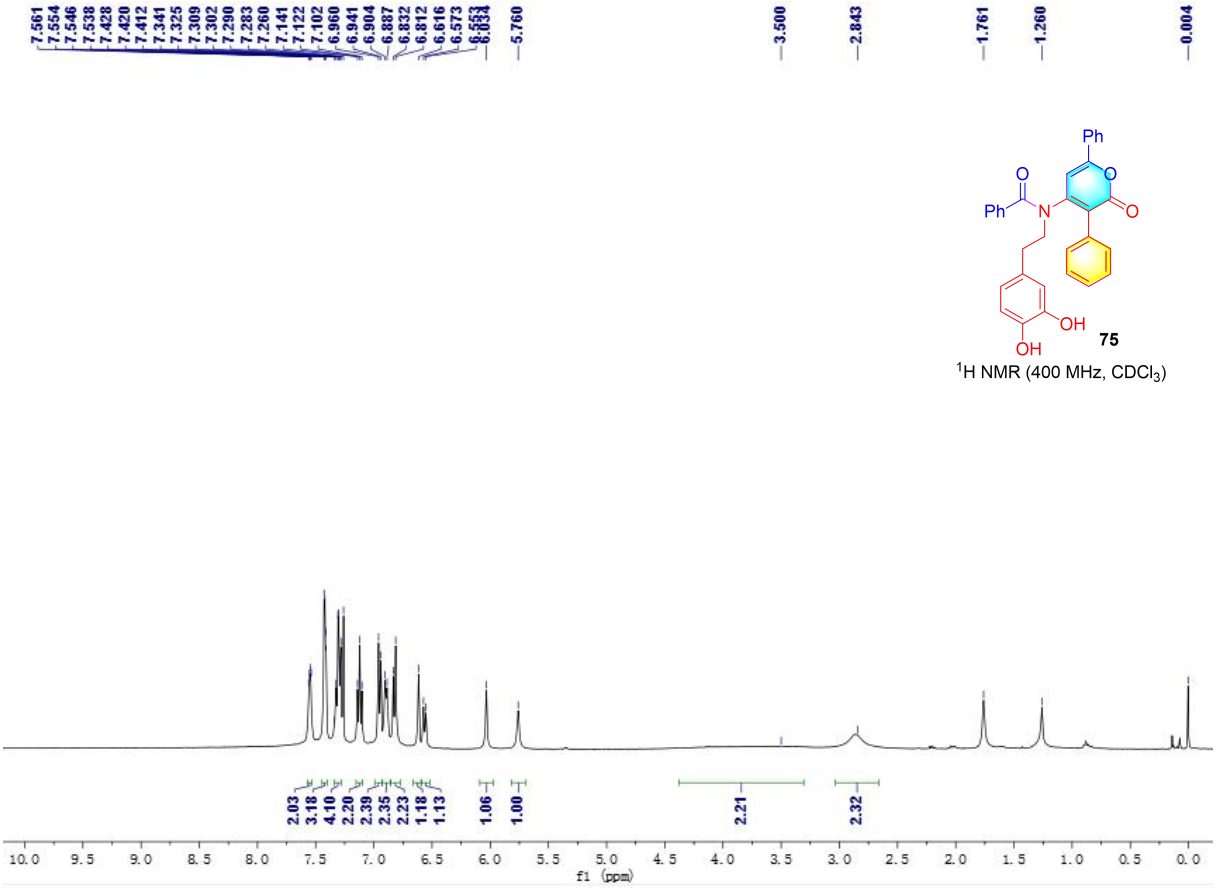
74

^{1}H NMR (400 MHz, $CDCl_3$)

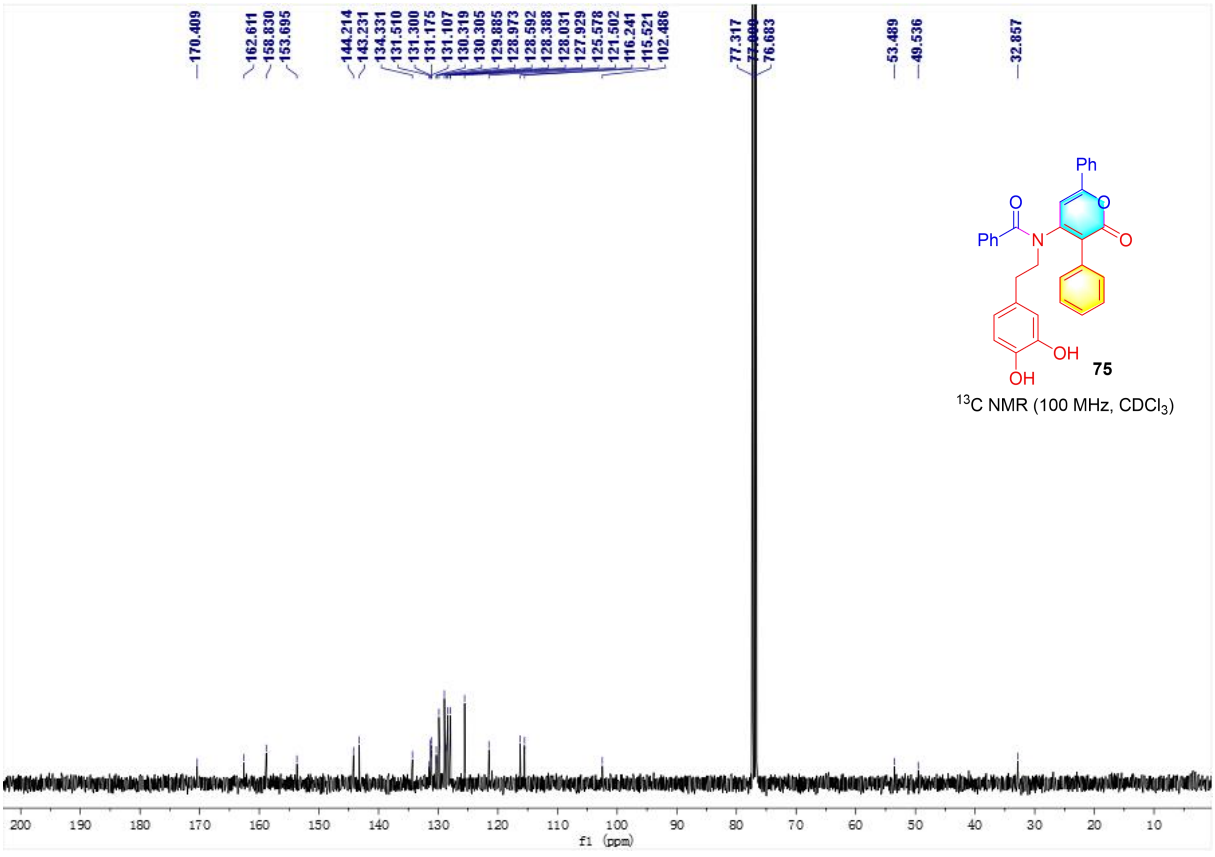


74

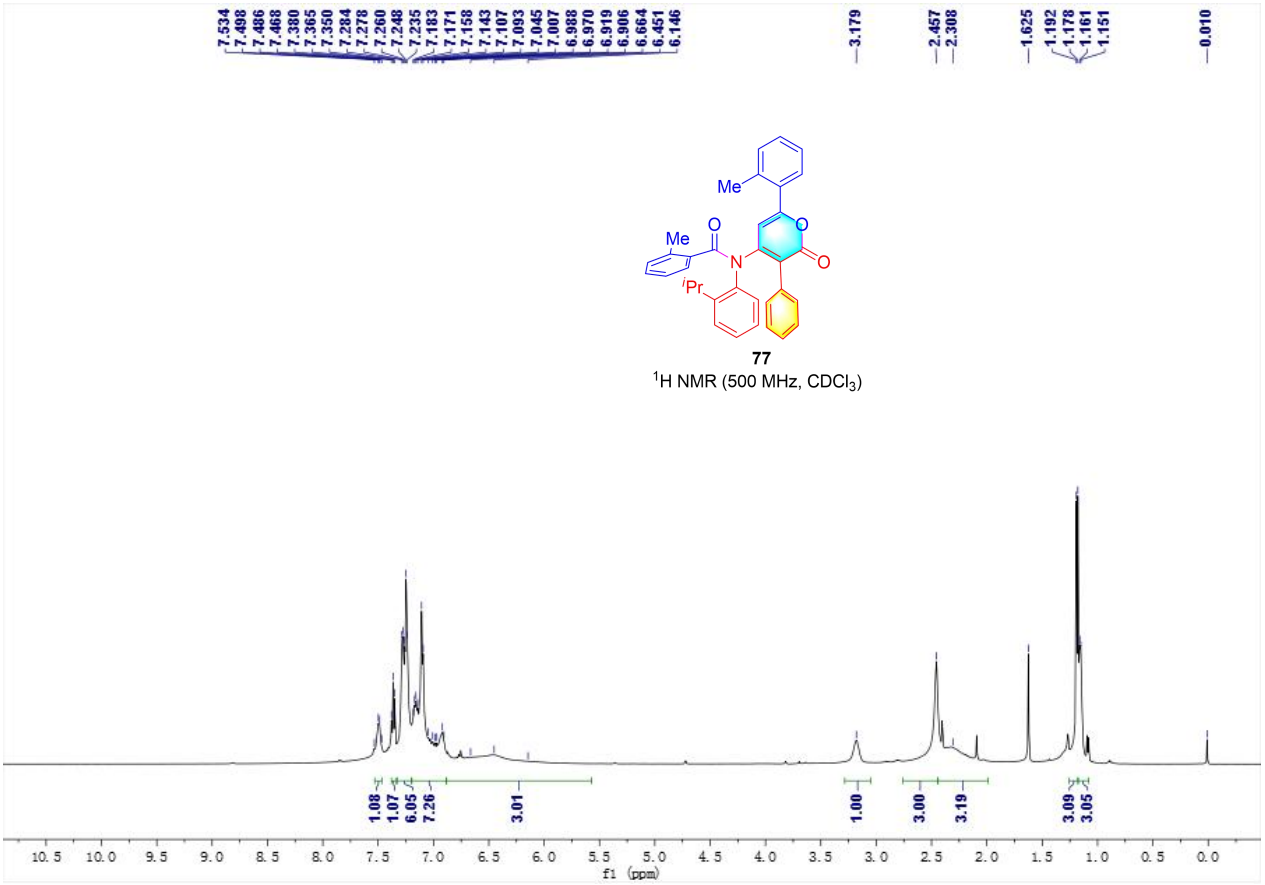
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

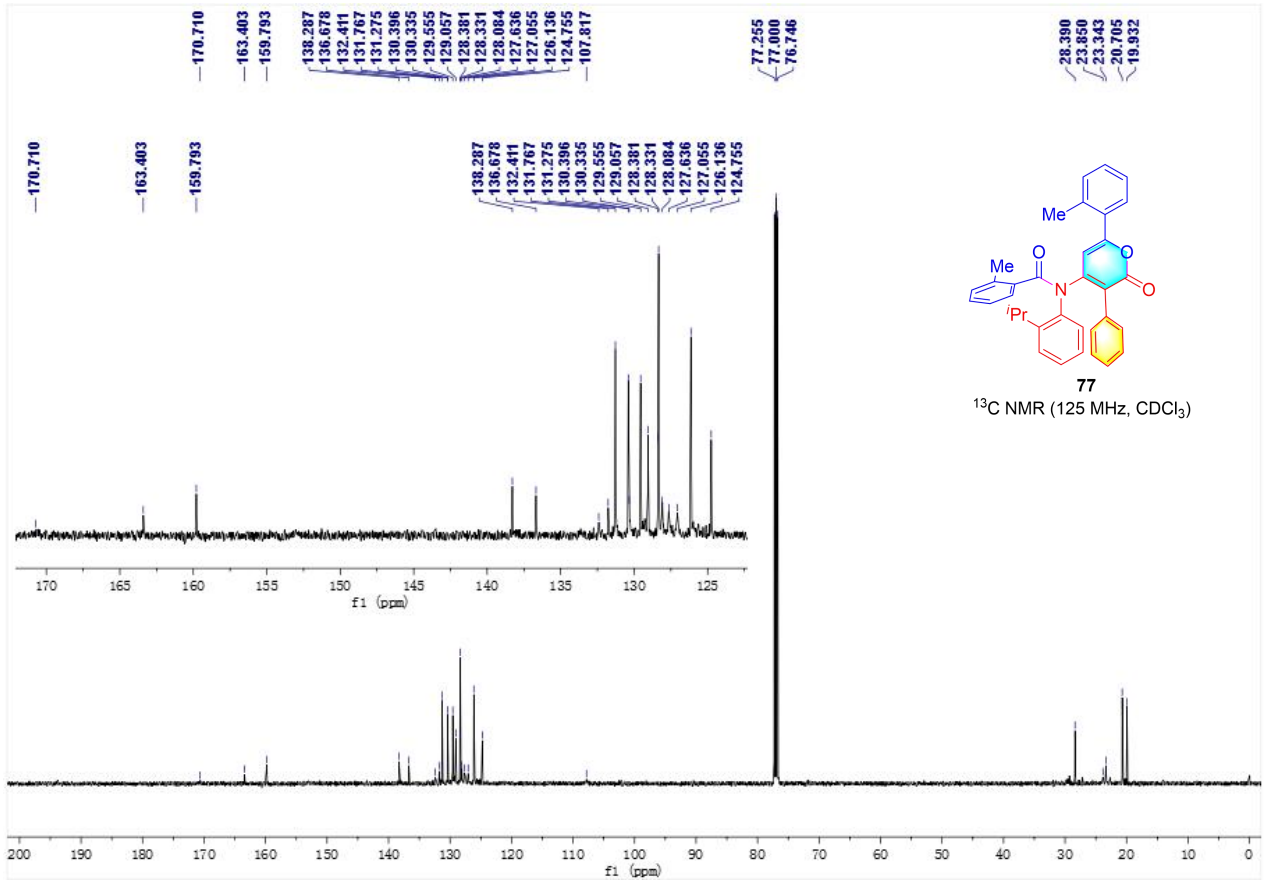


^{13}C NMR (100 MHz, $CDCl_3$)



77

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



77

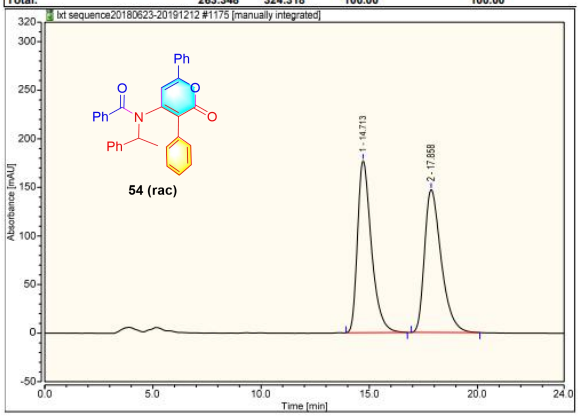
^{13}C NMR (125 MHz, $CDCl_3$)

11) Copies of HPLC Spectra of Products 54-61

Peak Integration Report

Sample Name:	LJ-20210129-80-20-OD-RAC	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	27.33

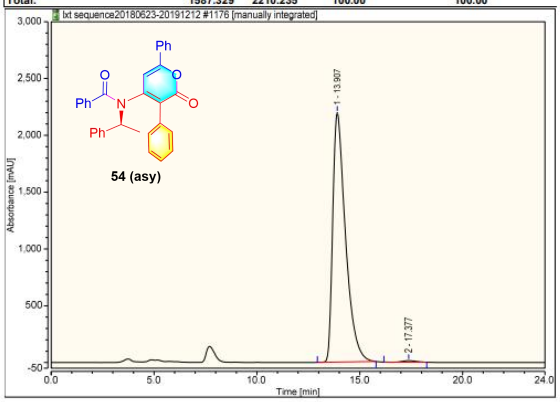
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14.713	131.793	177.215	50.05	54.64
2		17.858	131.555	147.103	49.95	45.36
Total:			263.348	324.318	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210129-80-20-OD-ASY	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	24.66

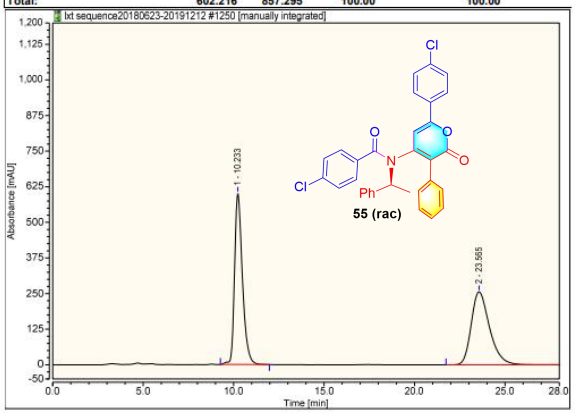
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		13.907	1577.994	2197.025	99.41	99.40
2		17.377	9.336	13.210	0.59	0.60
Total:			1587.329	2210.235	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210423-80-20-OD-4-Cl-ketong-Rac	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	30.18

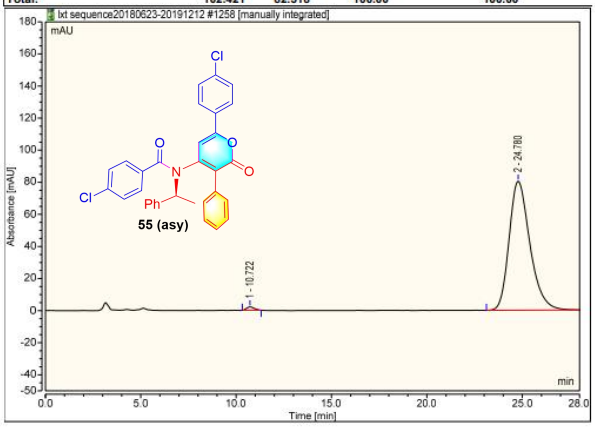
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		10.233	302.229	601.116	50.19	70.12
2		23.565	299.987	256.179	49.81	29.88
Total:			602.216	857.295	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210426-80-20-OD-4-Cl-ketone-Asy	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	38.88

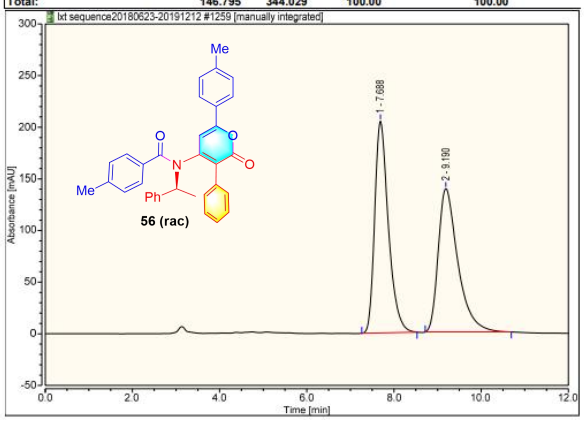
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		10.722	0.972	2.087	0.95	2.53
2		24.780	101.449	80.431	99.05	97.47
Total:			102.421	82.518	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210426-80-20-OD-4-Me-ketone-Rac	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	13.55

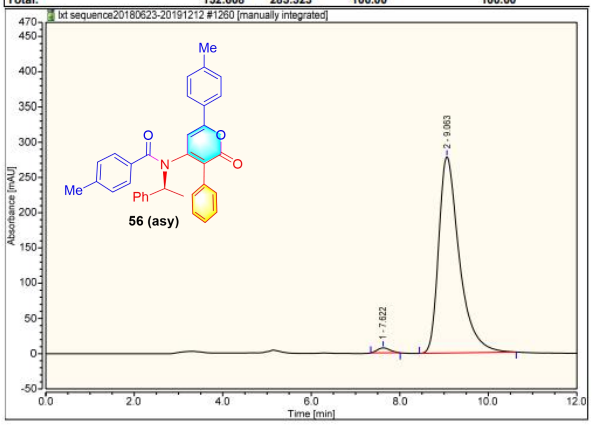
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7.688	74.576	205.248	50.80	59.66
2		9.190	72.219	138.780	49.20	40.34
Total:			146.795	344.029	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210426-80-20-OD-4-Me-ketone-Asy	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	15.39

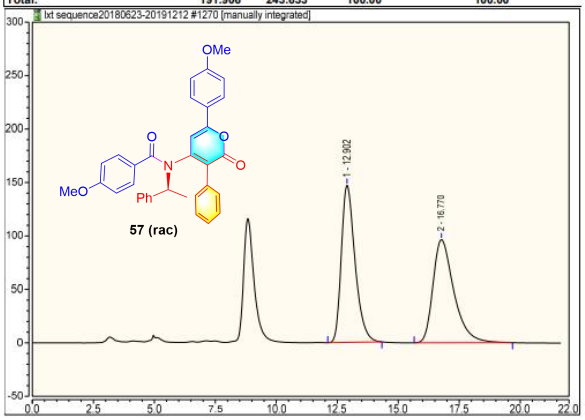
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7.622	2.358	7.066	1.55	2.47
2		9.063	150.250	278.458	98.45	97.53
Total:			152.608	285.523	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210512-80-20-OD-4-OMe-ketone-Rac-2	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	21.67

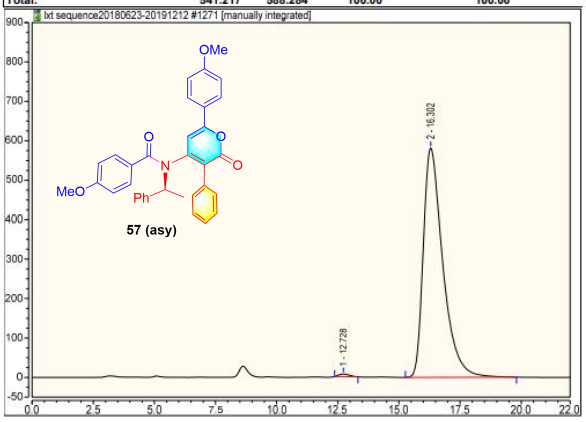
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.902	95.957	147.145	50.00	60.40
2		16.770	95.949	96.488	50.00	39.60
Total:			191.906	243.633	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210512-80-20-OD-4-OMe-ketone-Asy	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	23.41

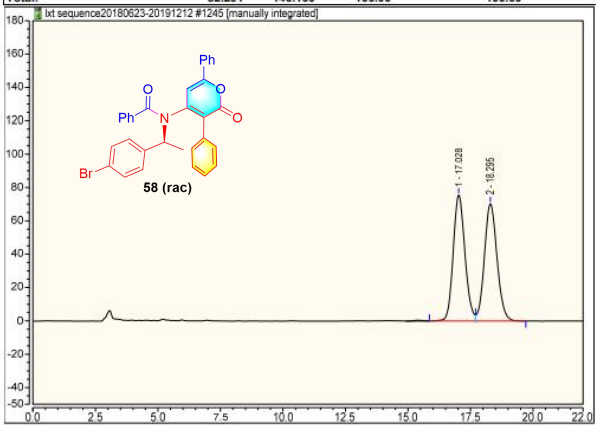
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.728	3.277	6.584	0.61	1.12
2		16.302	537.940	581.700	99.39	98.88
Total:			541.217	588.284	100.00	100.00



Peak Integration Report

Sample Name:	LJ-20210423-75-25-AD-H-4-Br-NC-Rac	*Inj. Vol.:*	1.00
Injection Type:	Check Standard	*Dilution Factor:*	1.0000
Instrument Method:	lxt	*Operator:*	Administrator
Inj. Date / Time:	############## Check Standard	*Run Time:*	25.84

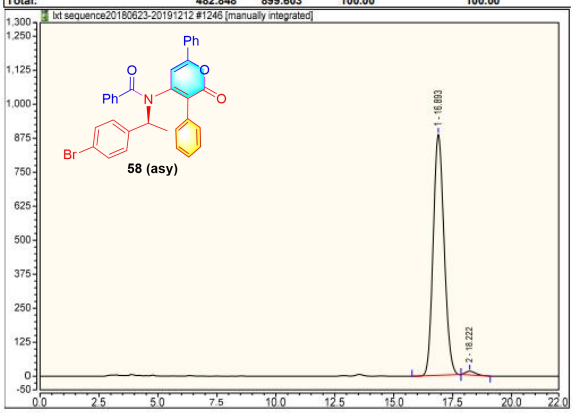
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		17.028	41.089	75.638	49.93	51.77
2		18.295	41.202	70.462	50.07	48.23
Total:			**82.291**	**146.100**	**100.00**	**100.00**



Peak Integration Report

Sample Name:	LJ-20210423-75-25-AD-H-4-Br-NC-Asy	*Inj. Vol.:*	1.00
Injection Type:	Check Standard	*Dilution Factor:*	1.0000
Instrument Method:	lxt	*Operator:*	Administrator
Inj. Date / Time:	############## Check Standard	*Run Time:*	29.50

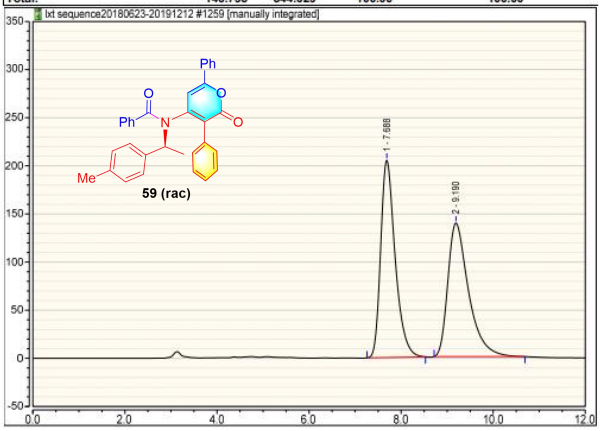
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		16.893	475.905	885.731	98.56	98.46
2		18.222	6.943	13.871	1.44	1.54
Total:			**482.848**	**899.603**	**100.00**	**100.00**



Peak Integration Report

Sample Name:	LJ-20210426-80-20-OD-4-Me-ketone-Rac	*Inj. Vol.:*	1.00
Injection Type:	Check Standard	*Dilution Factor:*	1.0000
Instrument Method:	lxt	*Operator:*	Administrator
Inj. Date / Time:	############## Check Standard	*Run Time:*	13.55

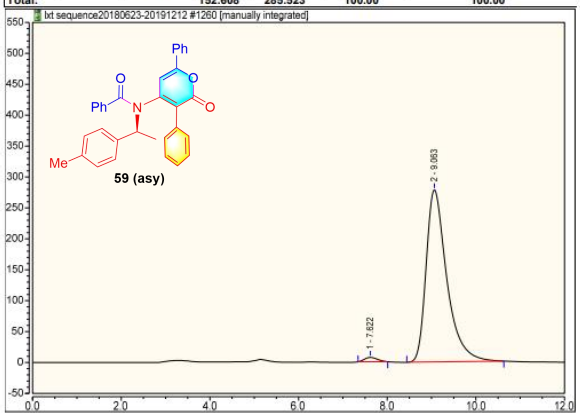
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7.688	74.576	205.248	50.80	59.66
2		9.190	72.219	138.780	49.20	40.34
Total:			**146.795**	**344.029**	**100.00**	**100.00**



Peak Integration Report

Sample Name:	LJ-20210426-80-20-OD-4-Me-ketone-Asy	*Inj. Vol.:*	1.00
Injection Type:	Check Standard	*Dilution Factor:*	1.0000
Instrument Method:	lxt	*Operator:*	Administrator
Inj. Date / Time:	############## Check Standard	*Run Time:*	15.39

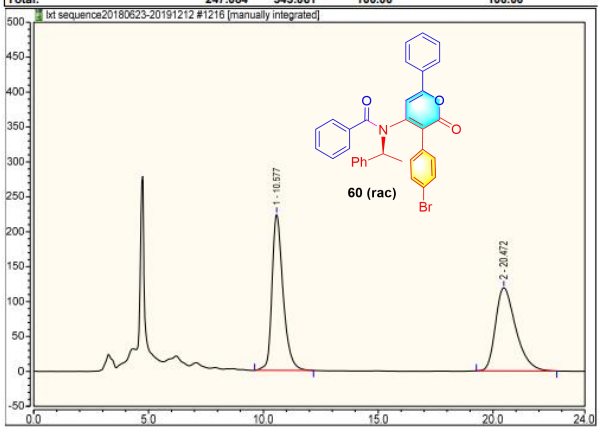
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7.622	2.358	7.066	1.55	2.47
2		9.063	150.250	278.458	98.45	97.53
Total:			**152.608**	**285.523**	**100.00**	**100.00**



Peak Integration Report

Sample Name:	lj-20210406-4Br-N2-Rac-80-20-OD	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	30.09

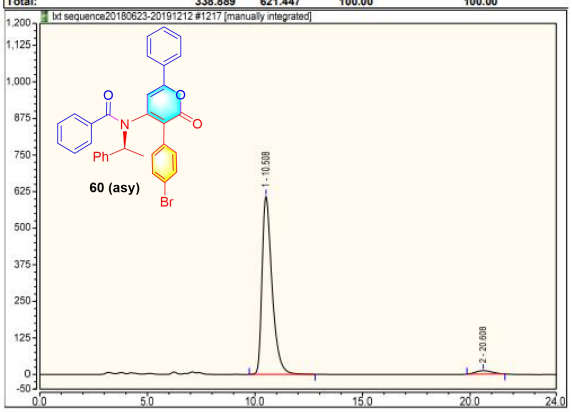
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		10.577	125.154	223.864	50.65	65.25
2		20.472	121.930	119.197	49.35	34.75
Total:			247.084	343.061	100.00	100.00



Peak Integration Report

Sample Name:	lj-20210406-4Br-N2-Asy-80-20-OD	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	30.18

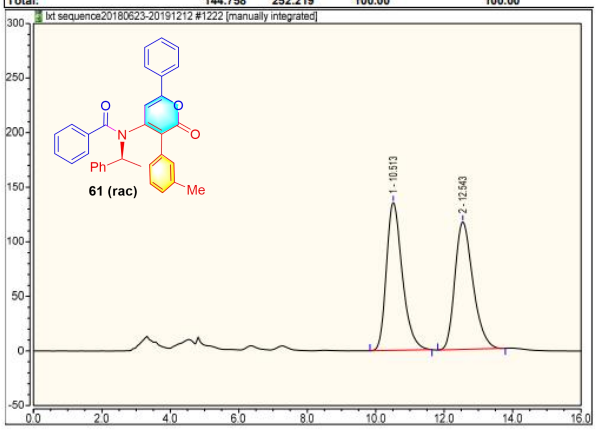
No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		10.508	328.659	609.872	96.98	98.14
2		20.608	10.230	11.575	3.02	1.86
Total:			338.889	621.447	100.00	100.00



Peak Integration Report

Sample Name:	lj-20210409-3-Me-N2-Rac-80-20-OD	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	20.87

No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		10.513	73.086	135.491	50.49	53.72
2		12.543	71.672	116.728	49.51	46.28
Total:			144.758	252.219	100.00	100.00



Peak Integration Report

Sample Name:	lj-20210409-3-Me-N2-Asy-80-20-OD	Inj. Vol.:	1.00
Injection Type:	Check Standard	Dilution Factor:	1.0000
Instrument Method:	lxt	Operator:	Administrator
Inj. Date / Time:	########## Check Standard	Run Time:	19.67

No.	Time min	Peak Name	Peak Type	Area mAU*min	Height mAU	Amount n.a.
No.	Peak Nam	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		10.340	1253.528	2470.842	99.30	99.33
2		12.513	8.861	16.773	0.70	0.67
Total:			1262.389	2487.615	100.00	100.00