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Supporting Information

Reaction of imidazo[1,2-a]pyridines with coumarin-3-carboxylic acids: A domino Michael addition/decarboxylation/oxidation/ annulation

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Contents

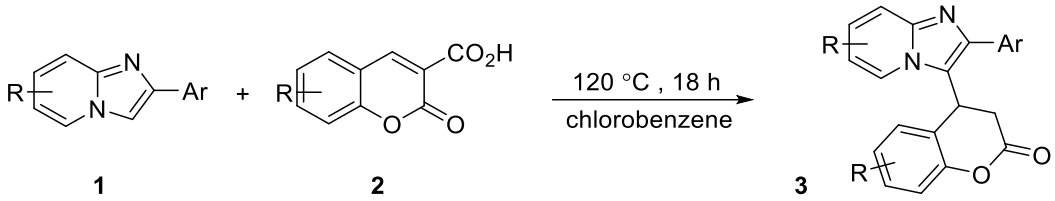
1. General Information

All purchased reagents were obtained from commercial sources and used without prior purification. 2-aryl-imidazo[1,2- a]pyridines derivatives was synthesized according to the literature. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. The products were purified by preparative column chromatography on silica gel (0.063-0.200 mm; Merck). ^{1}H and ^{13}C-NMR Spectra: were recorded on Bruker, 500 Advance instrument in $CDCl_3$ and DMSO; δ in ppm, *J* in Hz. Mass spectrometry was obtained on Agilent 5975C VL MSD (Ion source: EI+, 70eV, 230°C). The high-resolutionmass spectra (HRMS) were obtained on an Agilent technologies 6530 Q-TOF-LC-MS. The mass accuracy performance verification was achieved using the G1969-85001 ESTOF reference mass solution kit.

2. Experimental section

2.1 General procedure for the synthesis of 4-(2-arylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3):

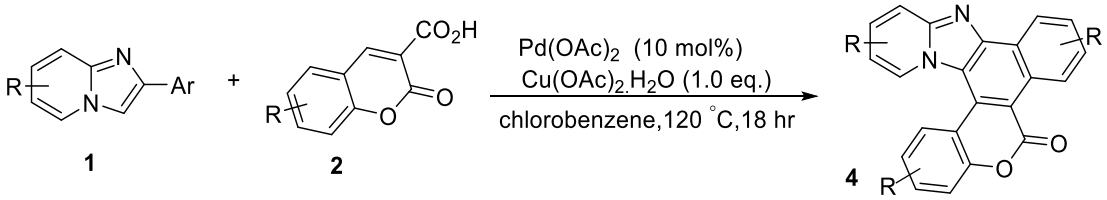
2-aryl-imidazo[1,2-α]pyridine **1** (0.1 mmol) and coumarin-3-carboxylic acid **2** (0.15 mmol) were dissolved in 1.5 mL of chlorobenzene in a sealed tube, and the resulting mixture was heated in an oil bath at 120 ˚C for 18 hours. The contents were poured into saturated $NaHCO_3$ solution (10 mL) and were extracted with EtOAc (3 × 10 mL). Combined organic phases dried over $MgSO_4$, and the solvent was removed in reduced pressure. The residue was purified with column chromatography using hexane and EtOAc as eluent in (9:1) ratio. In some cases, pouring the crude mixture into $NaHCO_3$ solution led to precipitation. The precipitate was filtered and washed with brine. The resulting solid was then subjected to column chromatography.



1 2 3

2.2 General procedure for the synthesis of 6H-dibenzo[3',4':7',8']isochromeno[6',5':4,5]imidazo [1,2-a]pyridin-6-one (4) :

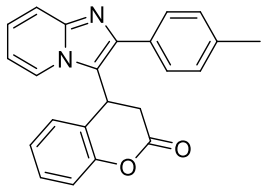
$Cu(OAC)_2.H_2O$ (1.0 eq) and $Pd(OAc)_2$ (10 mol%) were added to a solution of **1** (0.1 mmol) and **2** (0.15 mmol) in chlorobenzene (1.5 mL), then the mixture was heated in an oil bath at 120 ˚C for 18 hours. After this time, the reaction mixture was cooled to room temperature and transferred to a saturated solution of $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL), and the organic phase was dried using $MgSO_4$. The solvent was removed at reduced pressure and the residue was purified with column chromatography using hexane and EtOAc as eluent.



1 2 4

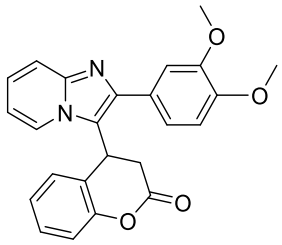
1. Characterization of the products

4-(2-(p-tolyl)imidazo[1,2-a]pyridine-3-yl)chroman-2-one (3a)



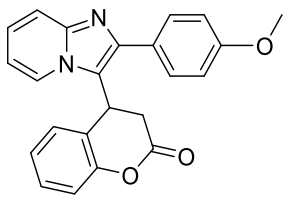
White solid, Yield : 69%, m.p. 249-250 ˚C; ^{1}H NMR (500 MHz, DMSO-d6) δ 7.99 (d, J = 7.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.8 Hz, 1H), 7.28 (t, J = 7.9 Hz, 1H), 7.24 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 6.78 (t, J = 6.8 Hz, 1H), 6.52 (d, J = 7.6 Hz, 1H), 5.45 (dd, J = 14.4, 5.5 Hz, 1H), 3.59 (m, 1H), 2.91 (dd, J = 16.4, 5.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.4, 152.0, 145.4, 145.3, 137.6, 131.8, 129.5, 129.4, 129.0, 126.6, 126.4, 125.05, 122.5, 117.7, 117.6, 116.2, 112.4, 31.5, 31.0, 21.3. MS (EI) m/z (relative intensity) 354 (M^+, 100) 353 (17), 311 (54), 221 (22), 208 (12), 195 (13),78 (23). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{23}H_{19}N_2O_2$, 355.1447; found, 355.1482.

4-(2-(3,4-dimethoxyphenyl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3b)



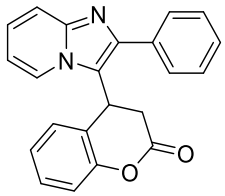
White solid, Yield : 83%, m.p. 222-223 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 9.1 Hz, 1H), 7.58 (d, J = 6.9 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.26 – 7.15 (m, 3H), 7.09 – 6.98 (m, 2H), 6.89 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 6.8 Hz, 1H), 5.26 (dd, J = 14.6, 5.2 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.32 (t, J = 15.4 Hz, 1H), 2.92 (dd, J = 16.3, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 151.5, 149.3, 149.3, 146.2, 145.6, 129.6, 126.773, 126.7, 125.2, 124.6, 124.3, 121.9, 120.9, 118.27, 117.8, 115.1, 112.5, 112.1, 111.1, 56.0, 55.9, 31.9, 31.5. MS (EI) m/z (relative intensity) 400 (M^+, 100), 399 (37), 371 (31), 327 (12.5), 221 (8), 78 (10). $C_{24}H_{20}N_2O_4$ (400): calcd. C, 71.99; H, 5.03; N, 7.00; found C, 71.67; H, 5.12; N, 7.06.

4-(2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3c)



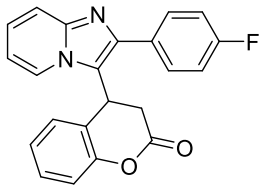
White solid, Yield : 75%, m.p. 211-213 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 9.1 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.33 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.18 (d, J = 8.3 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 7.8 Hz, 2H), 6.76 (d, J = 7.7 Hz, 1H), 6.69 (t, J = 6.9 Hz, 1H), 5.22 (dd, J = 14.6, 5.2 Hz, 1H), 3.81 (s, 3H), 3.30 (t, J = 15.4 Hz, 1H), 2.90 (dd, J = 16.5, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 159.8, 151.5, 146.1, 145.7, 130.0, 129.6, 126.7, 126.2, 125.2, 124.6, 124.4, 121.6, 118.2, 117.8, 114.8, 114.3, 112.5, 55.3, 31.8, 31.5. MS (EI) m/z (relative intensity) 370 (M^+, 100), 327 (47), 297 (12), 221 (14), 195 (13), 78 (19). $C_{23}H_{18}N_2O_3$ (370): calcd. C, 74.58; H, 4.90; N, 7.56; found C, 74.81; H, 4.83; N, 7.67.

4-(2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3d)



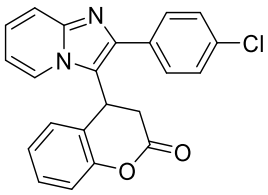
White solid, Yield : 65%, m.p. 252-253 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 9.1 Hz, 1H), 7.43 (d, J = 6.9 Hz, 1H), 7.38 (d, J = 7.3 Hz, 2H), 7.22 (t, J = 7.4 Hz, 2H), 7.20 – 7.11 (m,2H), 7.06 – 7.02 (m,1 H), 6.97 (d, J = 8.2 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.59 – 6.50 (m, 2H), 5.08 (dd, J = 14.5, 5.3 Hz, 1H), 3.22 – 3.11 (m, 1H), 2.71 (dd, J = 16.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 151.4, 145.93, 145.5, 133.9, 129.4, 128.6, 128.6, 128.1, 126.5, 125.1, 124.7, 124.6, 121.4, 118.0, 117.5, 115.3, 112.4, 31.7, 31.3. MS (EI) m/z (relative intensity) 340 (M^+, 100), 297 (54), 221 (42), 194 (15), 78 (23). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{22}H_{17}N_2O_2$, 341.1290; found, 341.1318.

4-(2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3e)



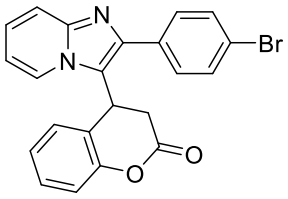
White solid, Yield : 57%, m.p. 243-245 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.31 (dd, J = 8.4, 5.4 Hz, 2H), 7.10 (t, J = 7.8 Hz, 1H), 7.01 (t, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.86 (t, J = 8.6 Hz, 2H), 6.80 (t, J = 7.6 Hz, 1H), 6.51 (d, J = 7.1 Hz, 2H), 5.00 (dd, J = 14.3, 5.3 Hz, 1H), 3.12 (dd, J = 16.3, 14.3 Hz, 1H), 2.67 (dd, J = 16.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.76, 163.59, 161.62, 151.41, 145.56, 145.08, 130.49, 130.42, 130.10, 130.07, 129.52, 126.50, 125.13, 124.79, 124.61, 121.33, 118.11, 117.64, 115.67, 115.50, 115.31, 112.57, 31.75, 31.32. MS (EI) m/z (relative intensity) 358 (M^+, 100), 357 (7.7), 339 (0.3), 315 (62), 221 (29), 173 (10). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{22}H_{16}FN_2O_2$, 359.1196; found, 359.1204.

4-(2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3f)



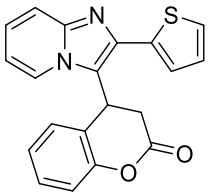
White solid, Yield : 61%, m.p. 236-238 ˚C; ^{1}H NMR (500 MHz, DMSO-d6) δ 8.00 (d, J = 6.9 Hz, 1H), 7.65 (dd, J = 17.7, 8.2 Hz, 3H), 7.46 (d, J = 9.0 Hz, 2H), 7.32 (dt, J = 19.6, 8.0 Hz, 2H), 7.18 (d, J = 8.2 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.80 (t, J = 6.8 Hz, 1H), 6.52 (d, J = 7.6 Hz, 1H), 5.47 (dd, J = 14.1, 5.6 Hz, 1H), 3.58 (t, J = 15.2 Hz, 1H), 2.94 (dd, J = 16.5, 5.6 Hz, 1H).^{13}C NMR (126 MHz, DMSO-d6) δ 167.36, 152.01, 145.40, 144.11, 133.53, 133.09, 130.78, 129.42, 128.92, 126.58, 125.38, 125.05, 122.24, 117.82, 117.61, 116.84, 112.61, 31.53, 30.94. MS (EI) m/z (relative intensity) 376 (M^{+} ^{37}Cl, 35), 374 (M^{+} ^{35}Cl, 100), 373 (7), 331 (46), 297 (34), 221 (31), 195 (12), 78 (31). $C_{22}H_{15}ClN_2O_2$ (374): calcd. C, 70.50; H, 4.03; N, 7.47; found C, 70.76; H, 4.18; N, 7.43.

4-(2-(4-bromophenyl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3g)



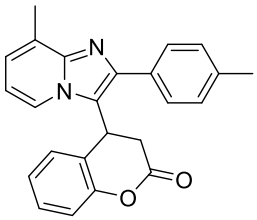
White solid, Yield : 80%, m.p. 257-259 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 9.1 Hz, 1H), 7.59 (dd, J = 14.4, 7.4 Hz, 3H), 7.51 (d, J = 8.1 Hz, 2H), 7.40 (t, J = 7.9 Hz, 1H), 7.28 (d, J = 10.1 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 6.77 (t, J = 6.9 Hz, 1H), 5.25 (dd, J = 14.5, 5.2 Hz, 1H), 3.33 (t, J = 15.4 Hz, 1H), 2.97 (dd, J = 16.3, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 151.2, 145.3, 144.3, 133.0, 131.4, 130.2, 129.2, 126.3, 124.9, 124.8, 124.7, 121.8, 121.3, 117.7, 117.3, 115.7, 112.3, 31.5, 30.9. MS (EI) m/z (relative intensity) 420 (M^{+} ^{81}Br, 100), 418 (M^{+} ^{79}Br, 97), 375 (41), 297 (56), 221 (43), 195 (16), 78 (22). $C_{22}H_{15}BrN_2O_2$ (419): calcd. C, 63.02; H, 3.61; N, 6.68; found C, 63.43; H, 3.72; N, 6.54.

4-(2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3i)



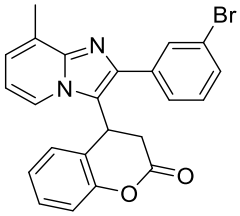
Green solid, Yield : 71%, m.p. 244-245 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 9.1 Hz, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.35 (dd, J = 5.1, 1.2 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.23 – 7.13 (m, 3H), 7.04 (dd, J = 5.1, 3.6 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 6.67 (t, J = 6.9 Hz, 1H), 5.42 (dd, J = 14.4, 5.5 Hz, 1H), 3.30 (dd, J = 16.4, 14.4 Hz, 1H), 2.95 (dd, J = 16.4, 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 151.4, 145.6, 139.7, 136.1, 129.6, 127.7, 126.7, 126.6, 126.0, 125.2, 125.1, 124.51, 121.0, 118.1, 117.7, 115.3, 112.7, 31.6, 31.4. MS (EI) m/z (relative intensity) 346 (M^{+},100), 303 (86), 221 (6), 200 (13), 78 (19). HRMS (ESI): m/z: $[M + H]^{+}$ calc. for $C_{20}H_{15}N_2O_2S$, 347.0854; found, 347.0868.

4-(8-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)chroman-2-one (3k)



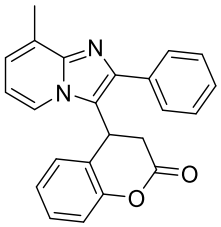
White solid, Yield : 67%, m.p. 162-164 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.35 (t, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.65 (t, *J* = 6.9 Hz, 1H), 5.22 (dd, *J* = 14.6, 5.3 Hz, 1H), 3.36 – 3.26 (m, 1H), 2.93 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.71 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 151.6, 146.0, 145.8, 138.3, 130.8, 129.5, 129.5, 128.9, 128.4, 126.9, 125.2, 123.7, 122.3, 121.7, 117.8, 115.6, 112.7, 31.9, 31.6, 21.3, 17.3. MS (EI) m/z (relative intensity) 368 (M^{+}, 100), 367 (15), 325 (50), 235 (27), 297 (6), 208 (6), 92 (12). $C_{24}H_{20}N_2O_2$ (368): calcd. C, 78.24; H, 5.47; N, 7.60; found C, 78.54; H, 5.54; N, 7.66.

4-(2-(3-bromophenyl)-8-methylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3l)



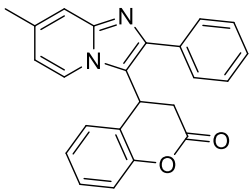
White solid, Yield : 30%, m.p. 173-176 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.43 (dd, J = 11.2, 7.4 Hz, 2H), 7.35 (t, J = 7.9 Hz, 1H), 7.27 (d, J = 9.3 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.05 (t, J = 7.7 Hz, 2H), 6.78 (d, J = 7.7 Hz, 1H), 6.65 (t, J = 6.9 Hz, 1H), 5.17 (dd, J = 14.2, 5.4 Hz, 1H), 3.29 (t, J = 14.5 Hz, 1H), 2.92 (dd, J = 16.4, 5.3 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 151.5 , 144.1, 136.2, 132.0, 131.2, 130.1, 129.6, 128.5, 127.4, 126.7, 125.2, 123.8, 122.8, 122.4, 121.3, 117.7, 116.2, 112.9, 31.9, 31.5, 17.2. MS (EI) m/z (relative intensity) 434 (M^+ ^{81}Br, 100), 432 (M^+ ^{79}Br, 98), 389 (29), 311 (34), 286 (10), 235 (55), 92 (24). $C_{23}H_{17}BrN_2O_2$ (433): calcd. C, 63.75; H, 3.95; N, 6.47; found C, 63.27; H, 3.91; N, 6.38.

4-(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3m)



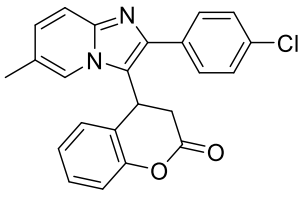
White solid, Yield : 53%, m.p. 225-227 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.43 (dt, *J* = 18.6, 7.3 Hz, 4H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 5.3 Hz, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.66 (t, *J* = 6.9 Hz, 1H), 5.23 (dd, *J* = 14.6, 5.3 Hz, 1H), 3.31 (t, *J* = 15.5 Hz, 1H), 2.94 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 151.6, 146.1, 145.8, 133.8, 129.6, 129.1, 128.8, 128.5, 128.4, 126.8, 125.2, 123.8, 122.4, 121.6, 117.8, 115.8, 112.7, 31.9, 31.6, 17.3. MS (EI) m/z (relative intensity) 354 (M^+, 100), 311 (48), 295 (26), 235 (49), 208 (20), 92(13). $C_{23}H_{18}N_2O_2$ (354): calcd. C, 77.95; H, 5.12; N, 7.90; found C, 77.68; H, 5.16; N, 7.73.

4-(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3n)



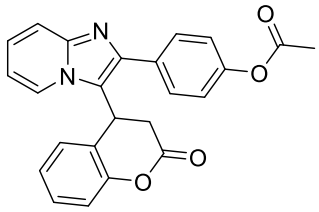
White solid, Yield : 73%, m.p. 254-256 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 3H), 7.44 (t, *J* = 7.7 Hz, 3H), 7.42 – 7.33 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 7.1 Hz, 1H), 5.23 (dd, *J* = 14.6, 5.3 Hz, 1H), 3.29 (t, *J* = 15.5 Hz, 1H), 2.94 (dd, *J* = 16.4, 5.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 151.6, 146.1, 145.7, 136.2, 133.6, 129.6, 128.8, 128.8, 128.4, 126.8, 125.2, 123.8, 121.6, 117.8, 116.7, 115.4, 114.7, 32.0, 31.5, 21.3. MS (EI) m/z (relative intensity) 354 (M^+, 100), 311 (70), 235 (59), 209 (27), 92 (43), 65 (37). $C_{23}H_{18}N_2O_2$ (354): calcd. C, 77.95; H, 5.12; N, 7.90; found C, 77.82; H, 5.21; N, 7.94.

4-(2-(4-chlorophenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3o)



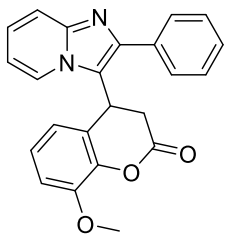
White solid, Yield : 51%, m.p. 277-279 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 9.2 Hz, 1H), 7.51 (d, J = 7.3 Hz, 2H), 7.39 (dd, J = 14.9, 7.5 Hz, 3H), 7.31 (s, 1H), 7.22 (d, J = 8.1 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.80 (d, J = 7.7 Hz, 1H), 5.18 (dd, J = 14.4, 5.2 Hz, 1H), 3.32 (t, J = 15.4 Hz, 1H), 2.92 (dd, J = 16.4, 5.1 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 151.4, 144.76, 144.6, 134.2, 132.5, 130.0, 129.6, 128.9, 128.3, 126.6, 125.2, 122.7, 122.0, 121.5, 117.8, 117.6, 115.3, 31.9, 31.4, 18.4. MS (EI) m/z (relative intensity) 390 (M^+ ^{37}Cl, 36), 388 (M^+ ^{35}Cl, 100), 345 (56), 311 (32), 235 (33), 209 (12), 92 (17). $C_{23}H_{17}ClN_2O_2$ (388): calcd. C, 71.04; H, 4.41; N, 7.20; found C, 71.33; H, 4.56; N, 7.29.

4-(3-(2-oxochroman-4-yl)imidazo[1,2-a]pyridin-2-yl)phenyl acetate (3p)



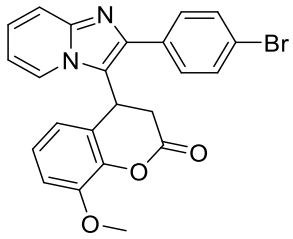
White solid, Yield : 59%, m.p. 231-233 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.1 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 (t, *J* = 8.7 Hz, 3H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.80 – 6.73 (m, 2H), 5.27 (dd, *J* = 14.5, 5.3 Hz, 1H), 3.32 (t, *J* = 15.4 Hz, 1H), 2.97 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 166.6, 151.6, 150.9, 145.7, 145.1, 131.0, 129.9, 129.7, 126.6, 125.3, 125.2, 124.6, 122.1, 121.1, 118.4, 117.9, 115.5, 112.9, 31.8, 31.5, 21.2. MS (EI) m/z (relative intensity) 398 (M^+, 57), 356 (100), 313 (56), 221(23), 195 (13), 43 (14). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{24}H_{19}N_2O_4$, 399.1345; found, 399.1299.

8-methoxy-4-(2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3q)



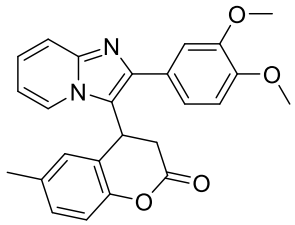
White solid, Yield : 77%, m.p. 234-236 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.86 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.75 (t, *J* = 6.8 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.27 (dd, *J* = 14.6, 5.3 Hz, 1H), 3.94 (s, 3H), 3.32 (t, *J* = 15.4 Hz, 1H), 2.94 (dd, *J* = 16.3, 5.1 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 148.3, 145.8, 145.7, 140.8, 133.4, 128.9, 128.84, 128.6, 125.2, 125.1, 124.6, 122.6, 118.3, 117.9, 115.7, 112.8, 112.2, 56.2, 31.7, 31.7. MS (EI) m/z (relativeintensity) 370 (M^+, 100), 327 (28), 221 (37), 194 (54), 78 (31). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{23}H_{19}N_2O_3$, 371.1396; found, 371.1417.

4-(2-(4-bromophenyl)imidazo[1,2-a]pyridin-3-yl)-8-methoxychroman-2-one (3r)



White solid, Yield : 81%, m.p. 239-241 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.0 Hz, 1H), 7.20 (d, J = 9.1 Hz, 1H), 7.08 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.86 – 6.78 (m, 1H), 6.58 – 6.48 (m, 2H), 6.33 (t, J = 6.4 Hz, 1H), 5.86 (d, J = 7.3 Hz, 1H), 4.84 (dd, J = 14.0, 5.3 Hz, 1H), 3.45 (s, 3H), 2.96 (t, J = 15.1 Hz, 1H), 2.44 (dd, J = 16.3, 4.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.05, 147.67, 145.17, 144.03, 140.38, 132.96, 131.26, 130.15, 124.92, 124.69, 122.37, 121.76, 117.53, 117.41, 115.91, 112.26, 111.83, 55.71, 31.30, 31.09. MS (EI) m/z (relative intensity) 450 (M^+ ^{81}Br, 100), 448 (M^+ ^{79}Br, 98), 405 (25), 377 (6), 327 (25), 299 (26), 274 (52), 251 (17), 176 (51), 154 (16),78 (49). $C_{23}H_{17}BrN_2O_3$ (449): calcd. C, 61.48; H, 3.81; N, 6.23; found C, 61.19; H, 3.88; N, 6.13.

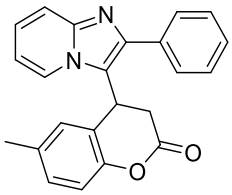
4-(2-(3,4-dimethoxyphenyl)imidazo[1,2-a]pyridin-3-yl)-6-methylchroman-2-one (3t)



White solid, Yield : 75%, m.p. 196-199 ^{0}C; ^{1}H NMR (500 MHz $CDCl_3$) δ 7.76 (d, J = 9.1 Hz, 1H), 7.61 (d, J = 6.9 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.15 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.76 (t, J = 6.8 Hz, 1H), 6.61 (s, 1H), 5.24 (dd, J = 14.5, 5.2 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.39 – 3.24 (m, 1H), 2.91 (dd, J = 16.3, 5.2 Hz, 1H), 2.19 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 167.23, 149.44, 149.33, 149.31, 146.18, 145.65, 135.08, 130.04, 126.86, 126.75, 124.58, 124.29, 121.5, 120.96, 118.3, 117.6, 115.3, 112.5, 112.1, 111.1, 56.0, 55.9, 32.0, 31.5, 20.8. MS (EI) m/z (relative intensity) 414

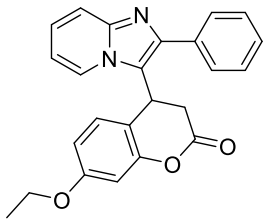
(M^+,100), 385 (25), 357 (16), 327 (3). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{25}H_{23}N_2O_4$, 415.1658; found, 415.1685.

6-methyl-4-(2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3v)



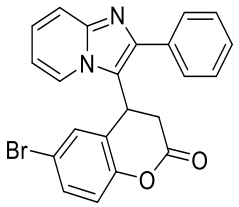
White solid, Yield : 70%, m.p. 229-231 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 9.1 Hz, 1H), 7.61 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 6.9 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.73 (t, J = 6.8 Hz, 1H), 6.58 (s, 1H), 5.24 (dd, J = 14.6, 5.3 Hz, 1H), 3.29 (t, J = 15.5 Hz, 1H), 2.90 (dd, J = 14.7, 5.3 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 149.4, 145.7, 135.1, 133.8, 130.1, 128.7, 128.3, 126.7, 124.7, 124.6, 121.0, 118.3, 117.5, 115.5, 112.6, 31.8, 31.4, 20.7. MS (EI) m/z (relative intensity) 354 (M^+, 100), 312 (46), 236 (5.4), 194 (32), 78 (19). $C_{23}H_{18}N_2O_2$ (354): calcd. C, 77.95; H, 5.12; N, 7.90; found C, 77.86; H, 5.12; N, 7.90.

7-ethoxy-4-(2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3w)



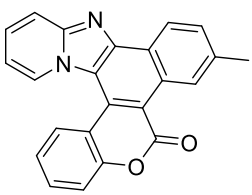
White solid, Yield : 76%, m.p. 197-199 ^{0}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.64 (dd, *J* = 15.9, 8.3 Hz, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.79 (t, *J* = 6.9 Hz, 1H), 6.75 (s, 1H), 6.56 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 5.36 (dd, *J* = 14.1, 5.5 Hz, 1H), 3.99 (q, *J* = 7.1, 6.4 Hz, 2H), 3.56 (t, *J* = 15.2 Hz, 1H), 2.91 (dd, *J* = 16.3, 5.5 Hz, 1H), 1.31 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.4, 159.5, 152.71, 145.3, 134.8, 129.1, 128.9, 128.1, 127.2, 126.5, 125.0, 117.8, 116.8, 113.8, 112.40, 111.3, 103.7, 63.9, 31.7, 30.5, 14.96. MS (EI) m/z(relative intensity) 384 (M^+, 100), 342 (36), 313 (30), 265 (23), 194 (19), 78 (11). $C_{24}H_{20}N_2O_3$ (384): calcd. C, 74.98; H, 5.24; N, 7.29; found C, 74.65; H, 5.17; N, 7.18.

6-bromo-4-(2-phenylimidazo[1,2-a]pyridin-3-yl)chroman-2-one (3x)



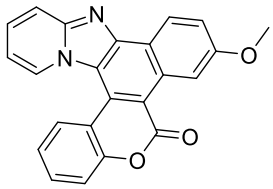
White solid, Yield : 50%, m.p. 250-252 ˚C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.41 – 7.34 (m, 1H), 7.35 – 7.28 (m, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.85 (t, *J* = 6.8 Hz, 1H), 6.62 (s, 1H), 5.53 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.62 – 3.51 (m, 1H), 2.95 (dd, *J* = 16.2, 5.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.9, 151.4, 145.5, 145.4, 134.6, 132.2, 129.1, 128.9, 128.3, 126.4, 125.4, 125.0, 119.9, 117.9, 116.7, 115.8, 112.7, 31.3, 30.9. MS (EI) m/z (relative intensity) 420 (M^+ ^{81}Br, 100), 418 (M^+ ^{79}Br, 98), 376 (37), 299 (18), 221 (19), 194 (37), 78 (22). $C_{22}H_{15}BrN_2O_2$ (419): calcd. C, 63.02; H, 3.61; N, 6.68; found C, 63.36; H, 3.67; N, 6.74.

8-methyl-6H-dibenzo[3',4':7',8'] ochromeno[6',5':4,5] isimidazo[1,2-a] pyridin-6-one (4a)



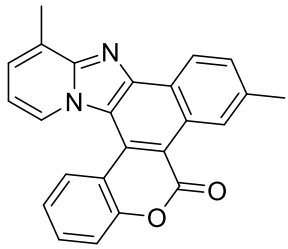
Yellow solid, Yield : 58%, m.p. 249-250 ˚C; ^{1}H NMR (500 MHz, DMSO-d6) δ 9.42 (s, 1H), 8.92 (d, J = 6.9 Hz, 1H), 8.69 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.17 (t, J = 6.8 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 151.1, 150.786, 147.6, 139.1, 131.0, 130.5, 129.6, 129.5, 128.4, 128.2, 127.1, 126.6, 124.9, 123.3, 123.1, 118.6, 118.4, 117.5, 116.0, 111.5, 111.3, 22.6. MS (EI) m/z (relative intensity) 350 (M^+, 100), 349 (13), 322 (30), 293 (13), 161 (15), 133 (6), 78 (4). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{23}H_{15}N_2O_2$, 351.1134; found, 351.1151.

8-methoxy-6H-dibenzo[3',4':7',8']isochromeno[6',5':4,5]imidazo[1,2-a]pyridin-6-one (4b)



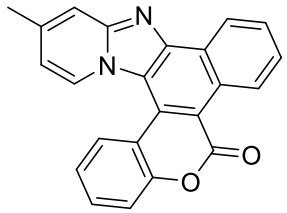
Yellow solid, Yield : 49%, m.p. 228-230 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.92 (d, *J* = 7.0 Hz, 1H), 8.85 (d, *J* = 8.9 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 9.9 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 6.7 Hz, 1H), 4.08 (s, 3H). MS (EI) m/z (relative intensity) 366 (M^+, 100), 323 (16), 295 (21), 238 (3), 133 (10), 97 (3). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{23}H_{15}N_2O_3$, 367.1083; found, 367.1081.

8,12-dimethyl-6H-dibenzo[3',4':7',8']isochromeno[6',5':4,5]imidazo[1,2-a]pyridin-6-one (4c)



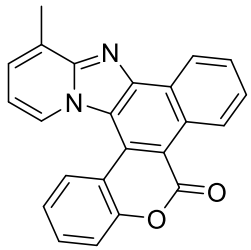
Yellow solid, Yield : 53%, m.p. 278-280 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.87 (d, J = 6.5Hz, 1H), 8.71 (d, J = 7.1 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 6.86 (t, J = 6.0 Hz, 1H), 2.85 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 151.2, 139.0, 130.86, 130.6, 129.4, 128.6, 128.0, 127.1, 126.8, 126.2, 125.2, 123.4, 123.3, 117.5, 116.1, 111.4, 111.2, 22.6, 17.6. MS (EI) m/z (relative intensity) 364 (M^+, 100), 363 (15), 336 (15), 168 (8). HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{24}H_{17}N_2O_2$, 365.1290; found, 365.1318.

13-methyl-6H-dibenzo[3',4':7',8']isochromeno[6',5':4,5]imidazo[1,2-a]pyridin-6-one (4d)



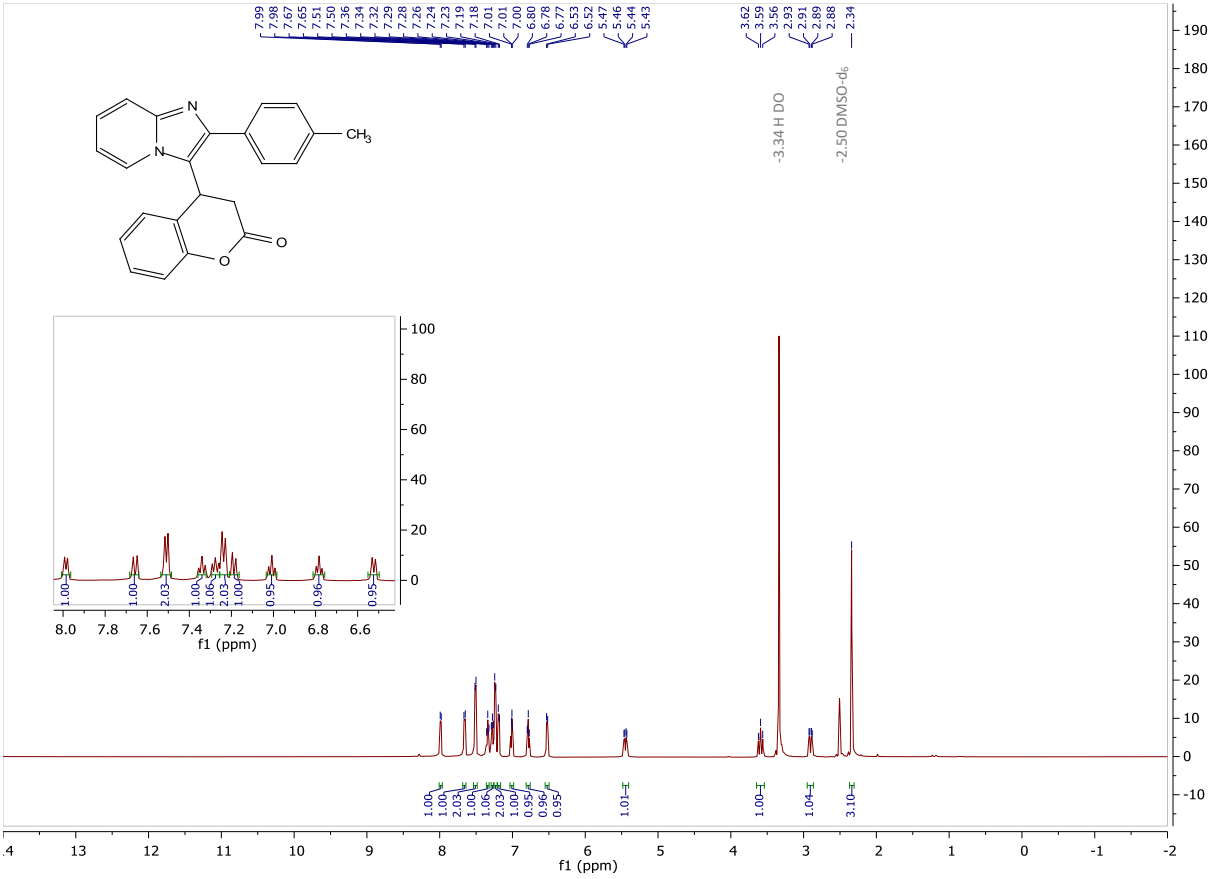
Yellow solid, Yield : 39%, m.p. 239-241 ˚C; ^{1}H NMR (500 MHz, DMSO-d6) δ 9.63 (d, *J* = 9.1 Hz, 1H), 8.87 – 8.77 (m, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.79 (s, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 10.7 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 151.3, 137.6, 131.5, 130.6, 129.8, 128.3, 128.27, 127.9, 127.79, 127., 126.5, 125.87, 123.9, 123.7, 117.8, 115.8, 115.7, 115.6, 113.1, 109.9, 21.9. MS (EI) m/z (relative intensity) 350 (M^+, 100), 322 (27), 293 (14), 161 (20), 133 (3). $C_{23}H_{14}N_2O_2$ (350): calcd. C, 78.84; H, 4.03; N, 8.00; found C, 78.56; H, 4.13; N, 8.26.

12-methyl-6H-dibenzo[3',4':7',8']isochromeno[6',5':4,5]imidazo[1,2-a]pyridin-6-one (4e)

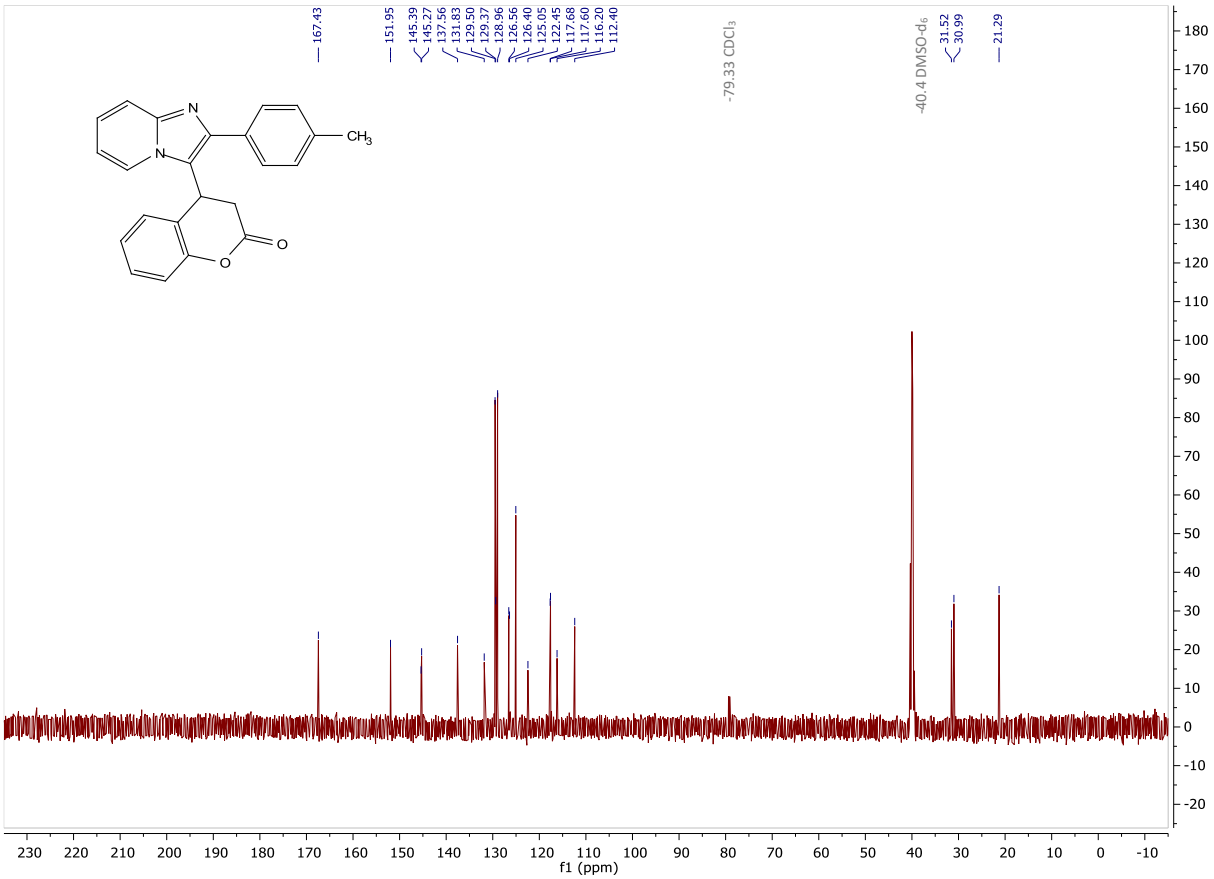


Yellow solid, Yield : 43%, m.p. 263-265 ˚C; ^{1}H NMR (500 MHz, DMSO-d6) δ 9.55 (d, *J* = 7.5 Hz, 1H), 8.75 (dd, *J* = 22.2, 6.5 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (dd, *J* = 13.0, 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 6.7 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$-DMSO-d6) δ 160.0, 151.0, 131.2, 130.2, 129.4, 128.9, 128.3, 128.1, 127.6, 127.4, 126.6, 126.3, 126.2, 123.8, 123.5, 119.1, 117.4, 115.6, 112.2, 111.8, 17.6. MS (EI) m/z (relative intensity) 350 (M^+, 100), 321 (17), 293 (10), 161 (12), 132 (3). $C_{23}H_{14}N_2O_2$ (350): calcd. C, 78.84; H, 4.03; N, 8.00; found C, 78.38; H, 4.21; N, 8.17.

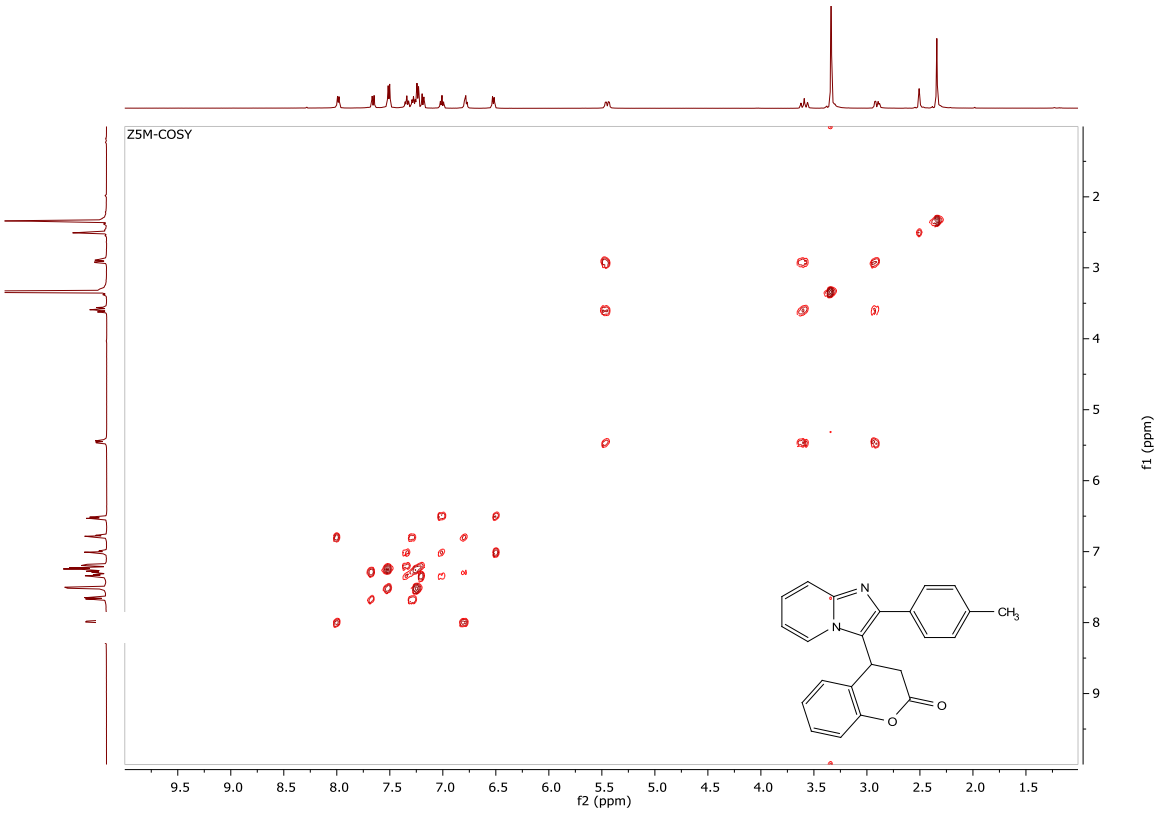
^{1}H NMR spectrum of (3a)

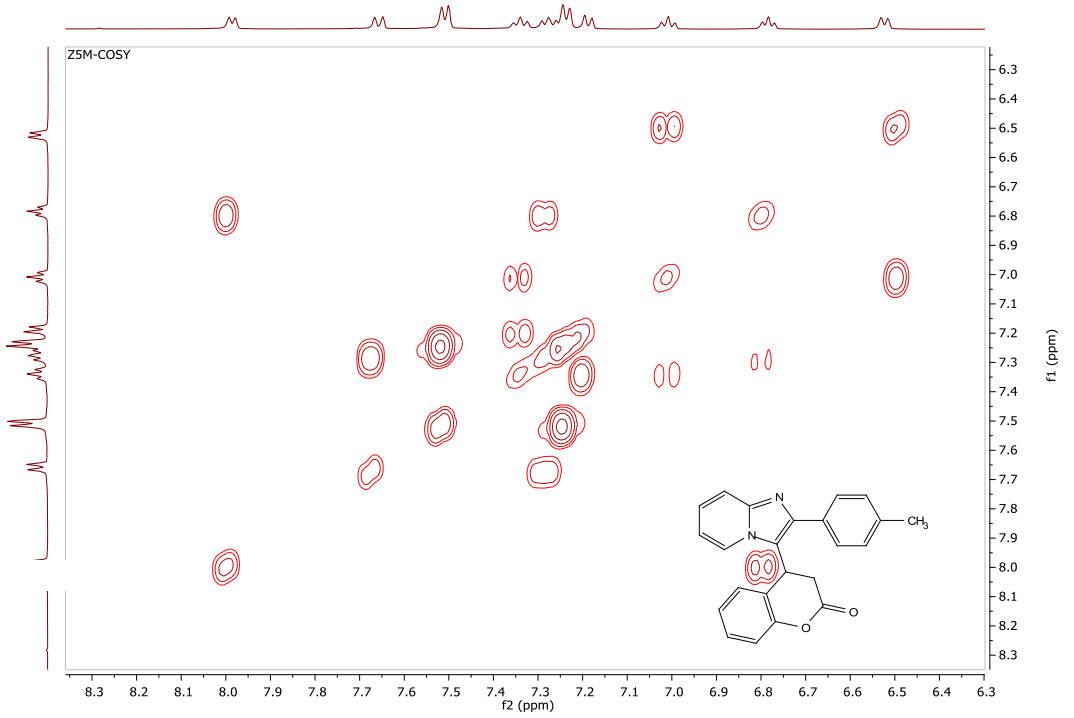


^{13}C NMR spectrum of (3a)

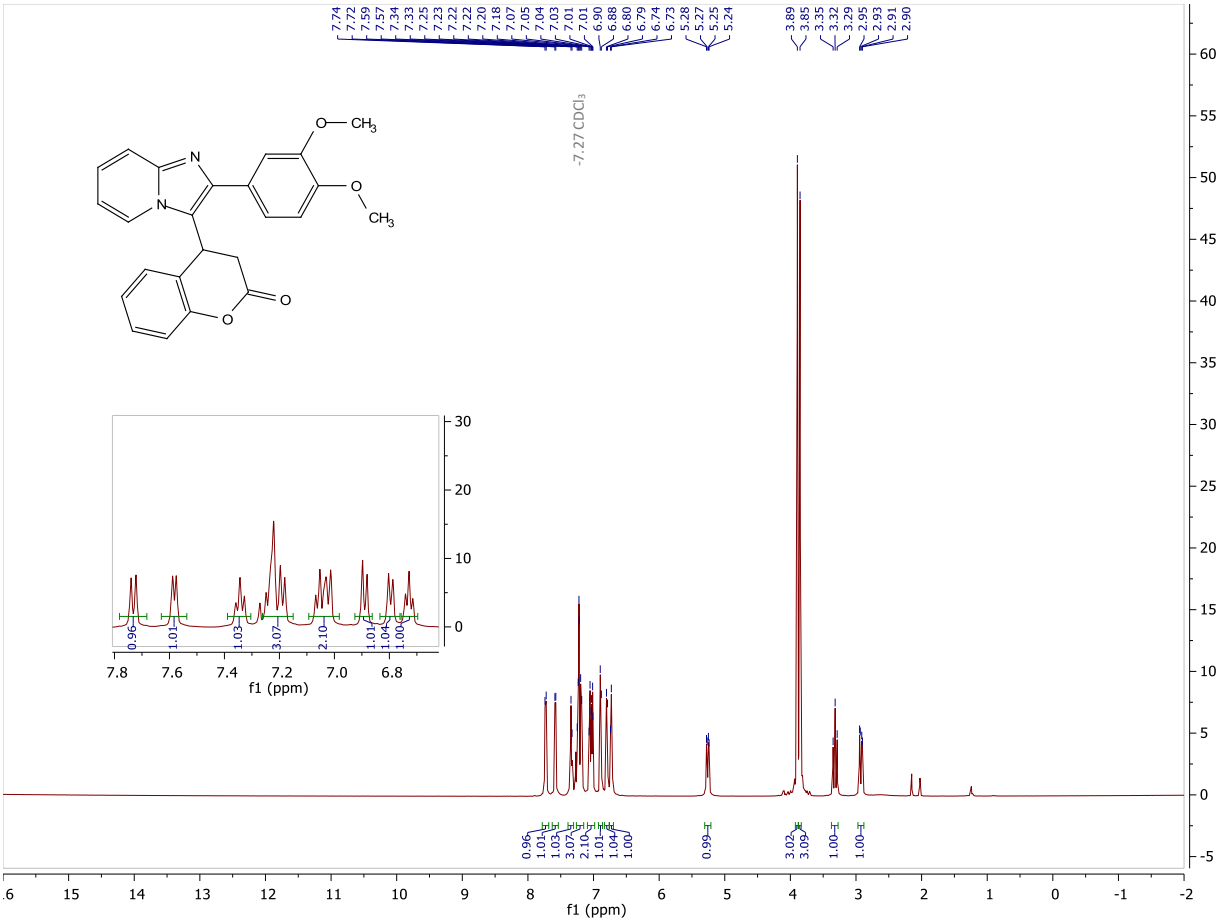


H,H-COSY NMR spectrum of (3a)

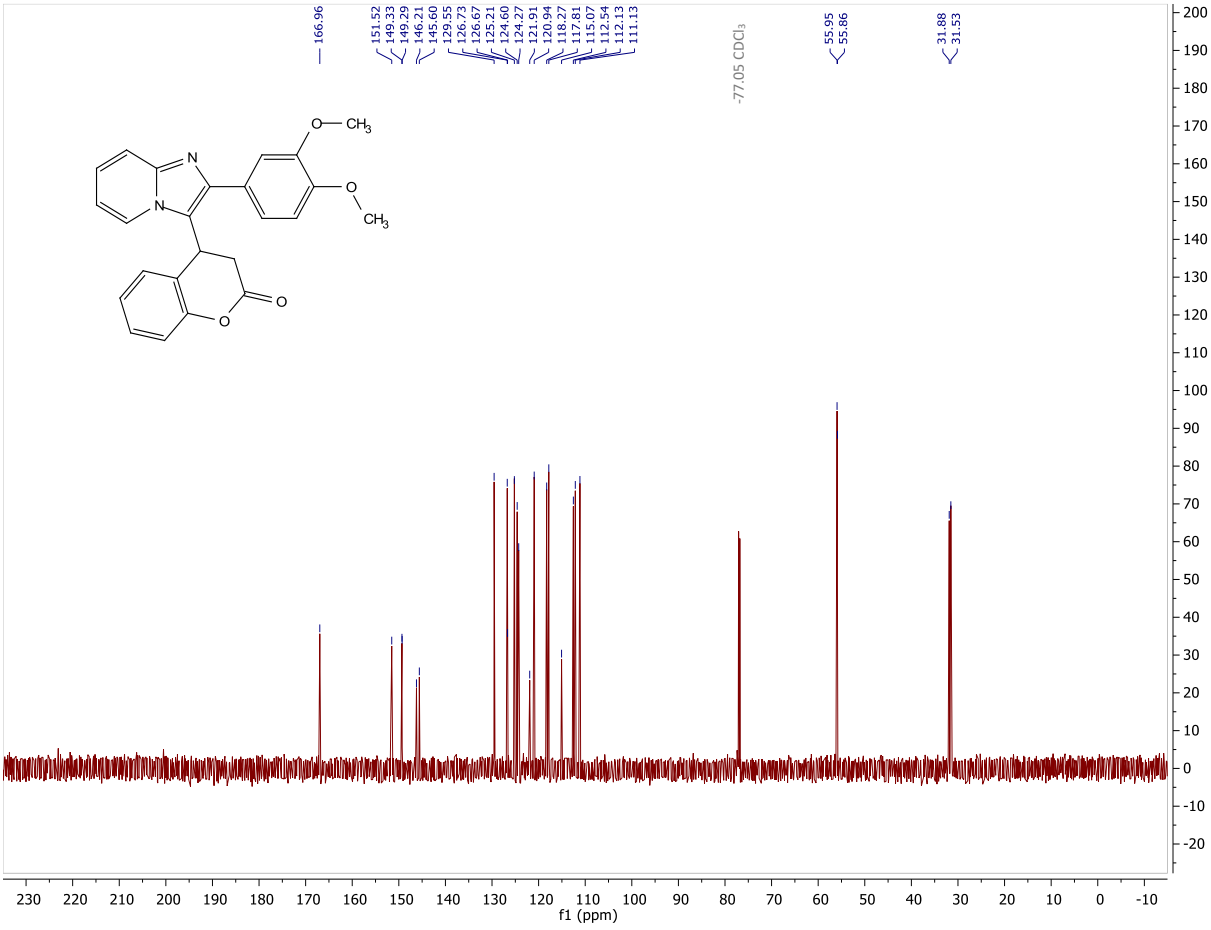




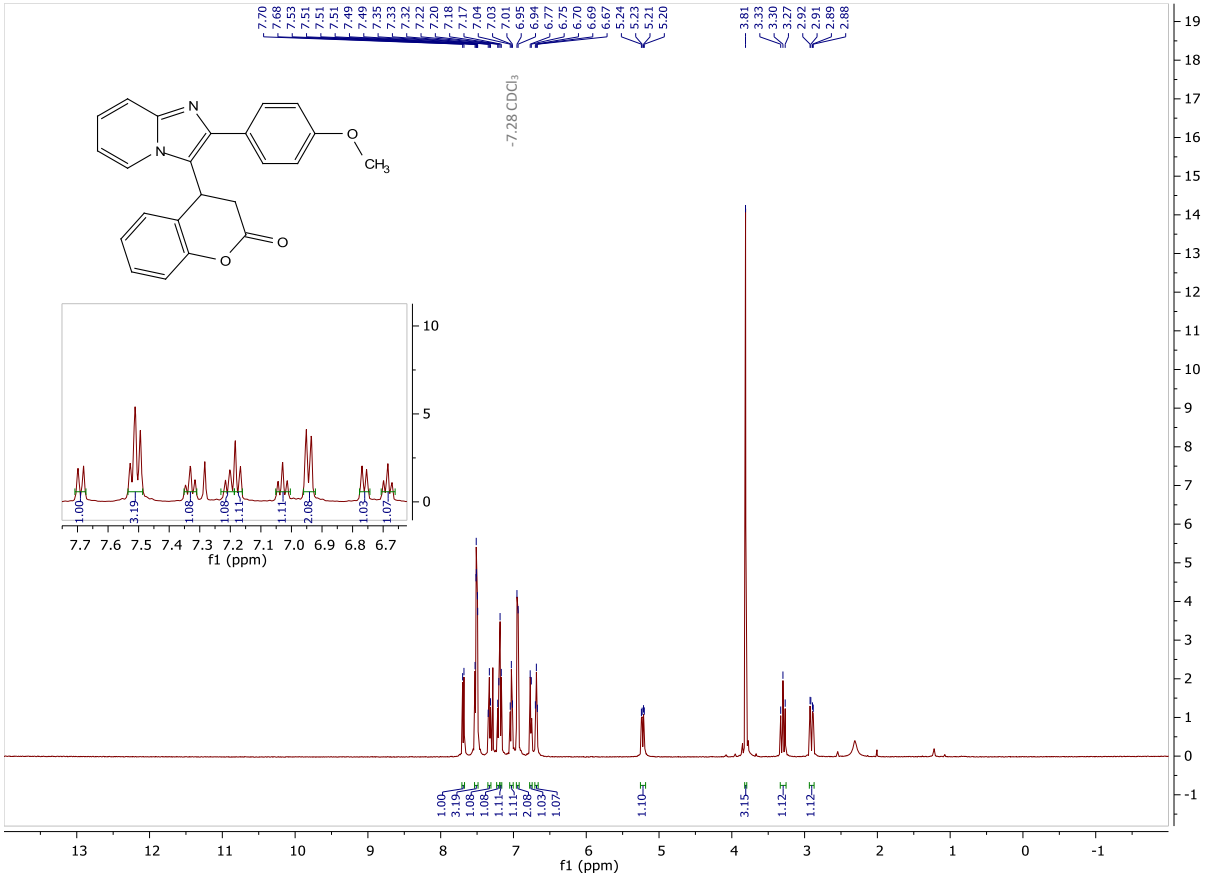
^{1}H NMR spectrum of (3b)



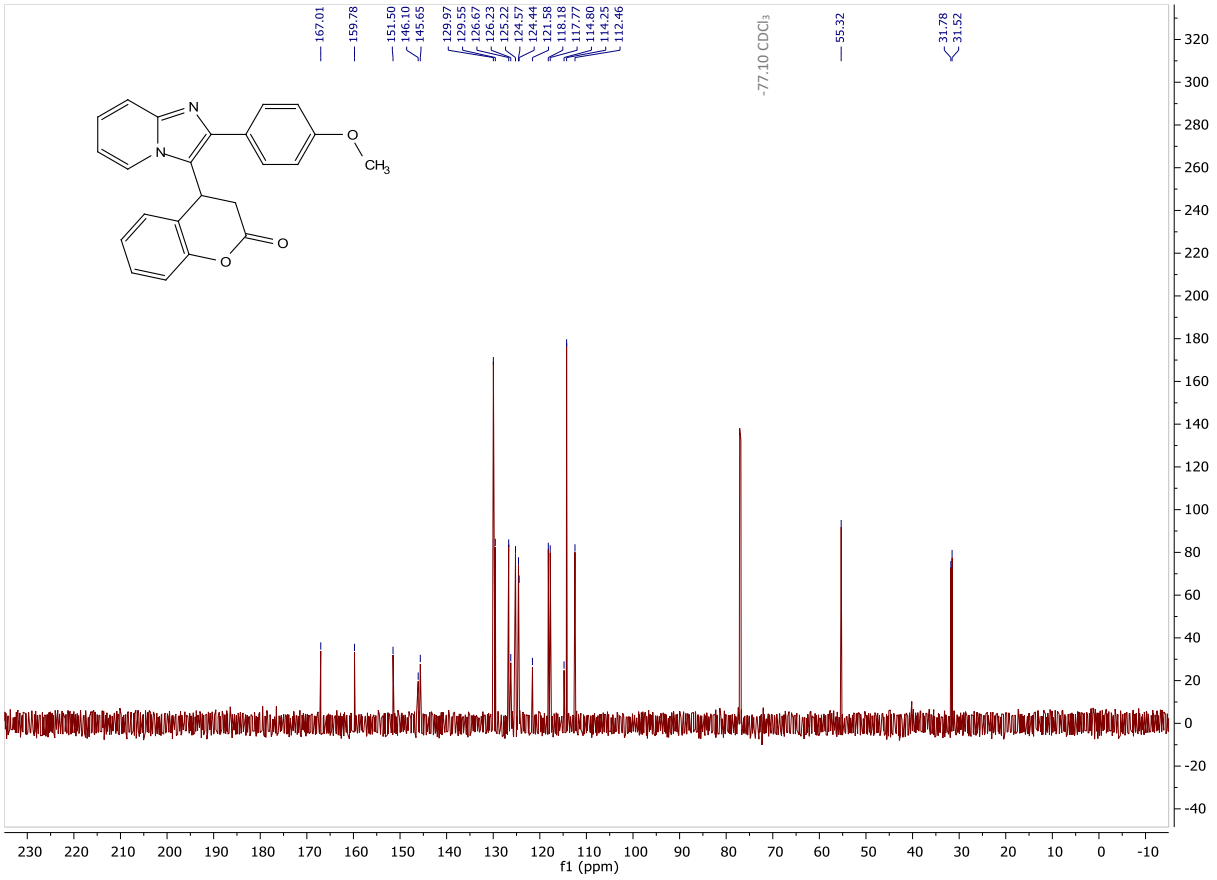
^{13}C NMR spectrum of (3b)



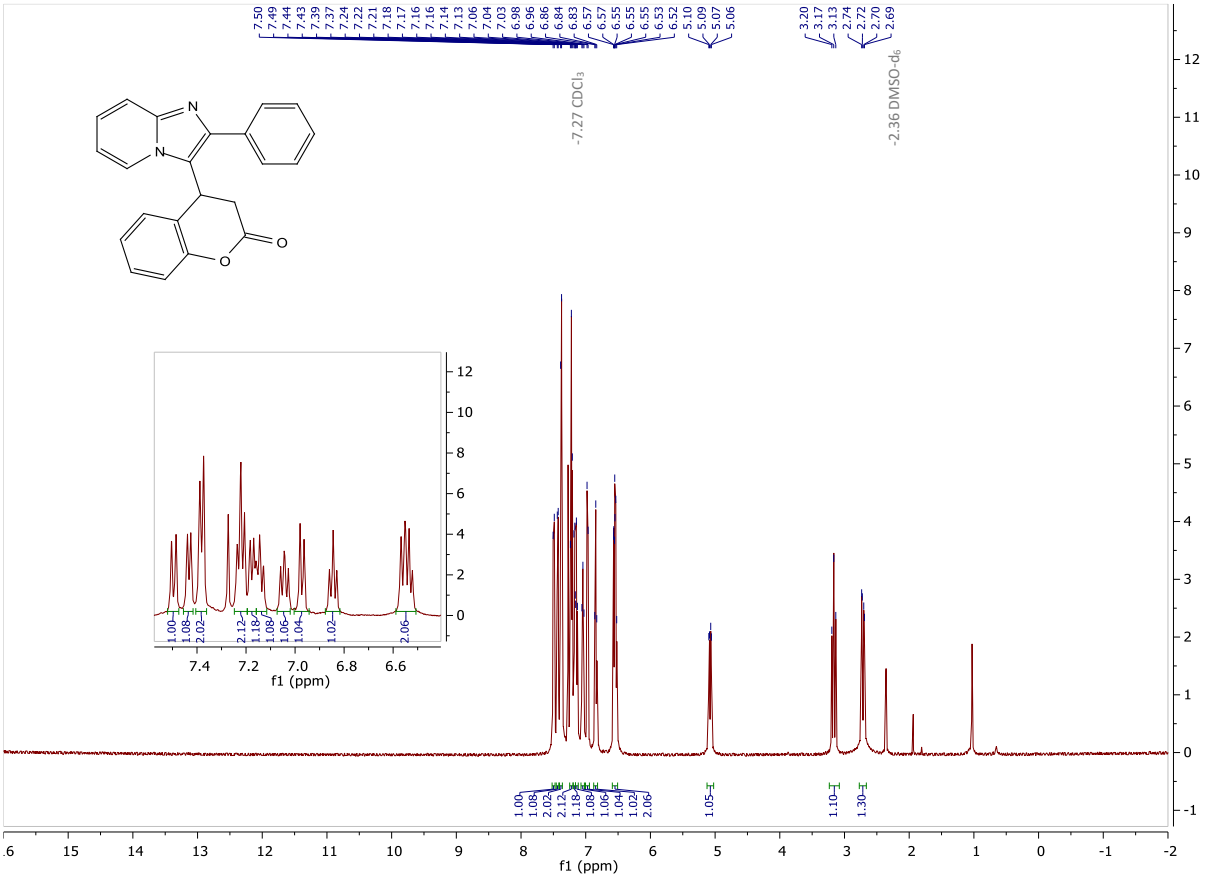
^{1}H NMR spectrum of (3c)



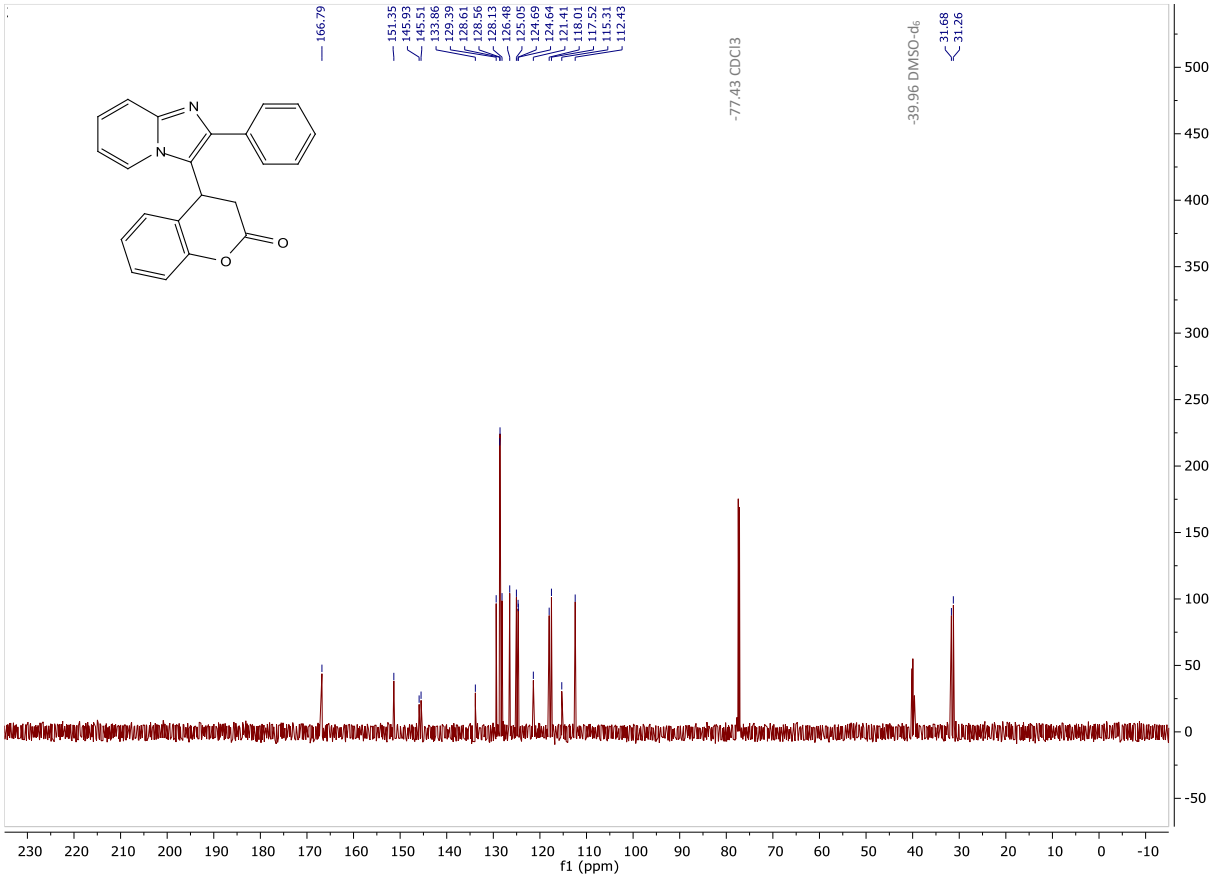
^{13}C NMR spectrum of (3c)



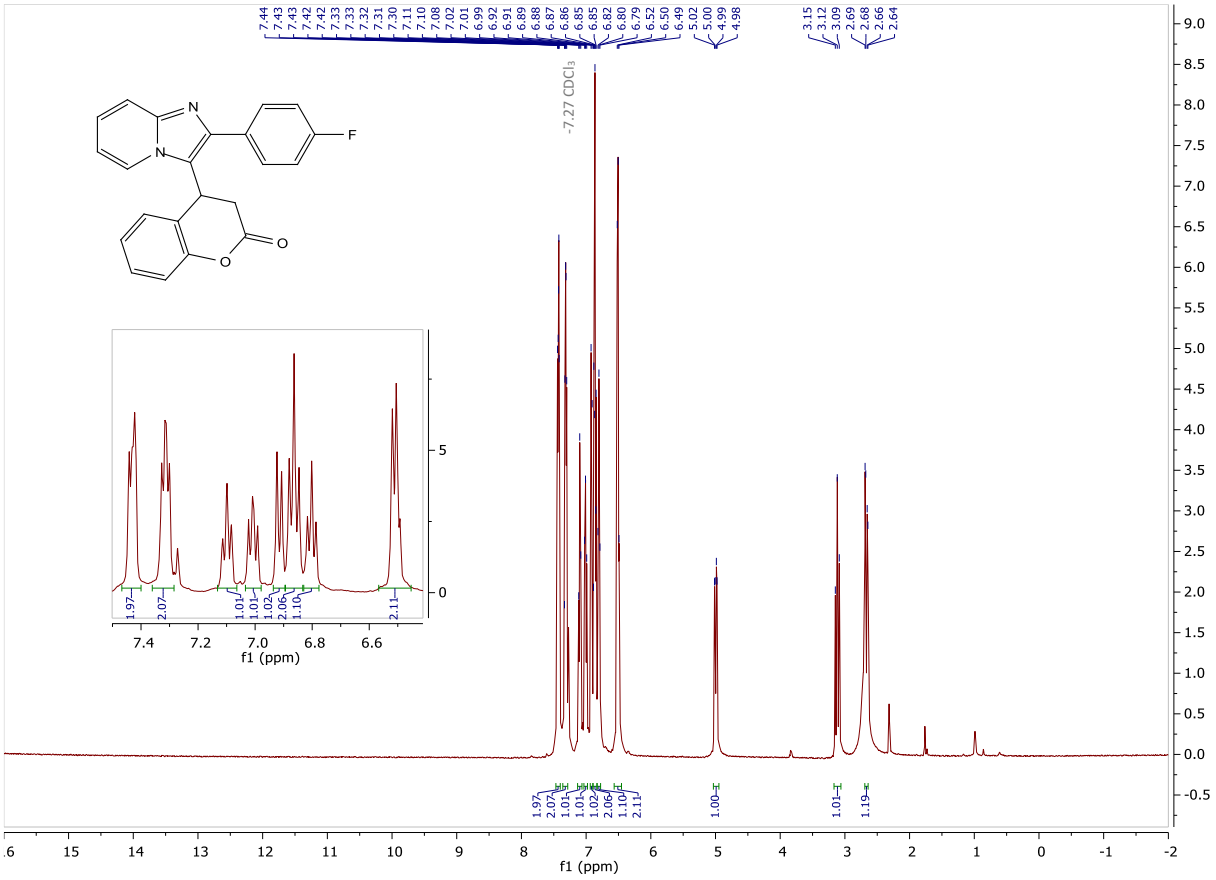
^{1}H NMR spectrum of (3d)



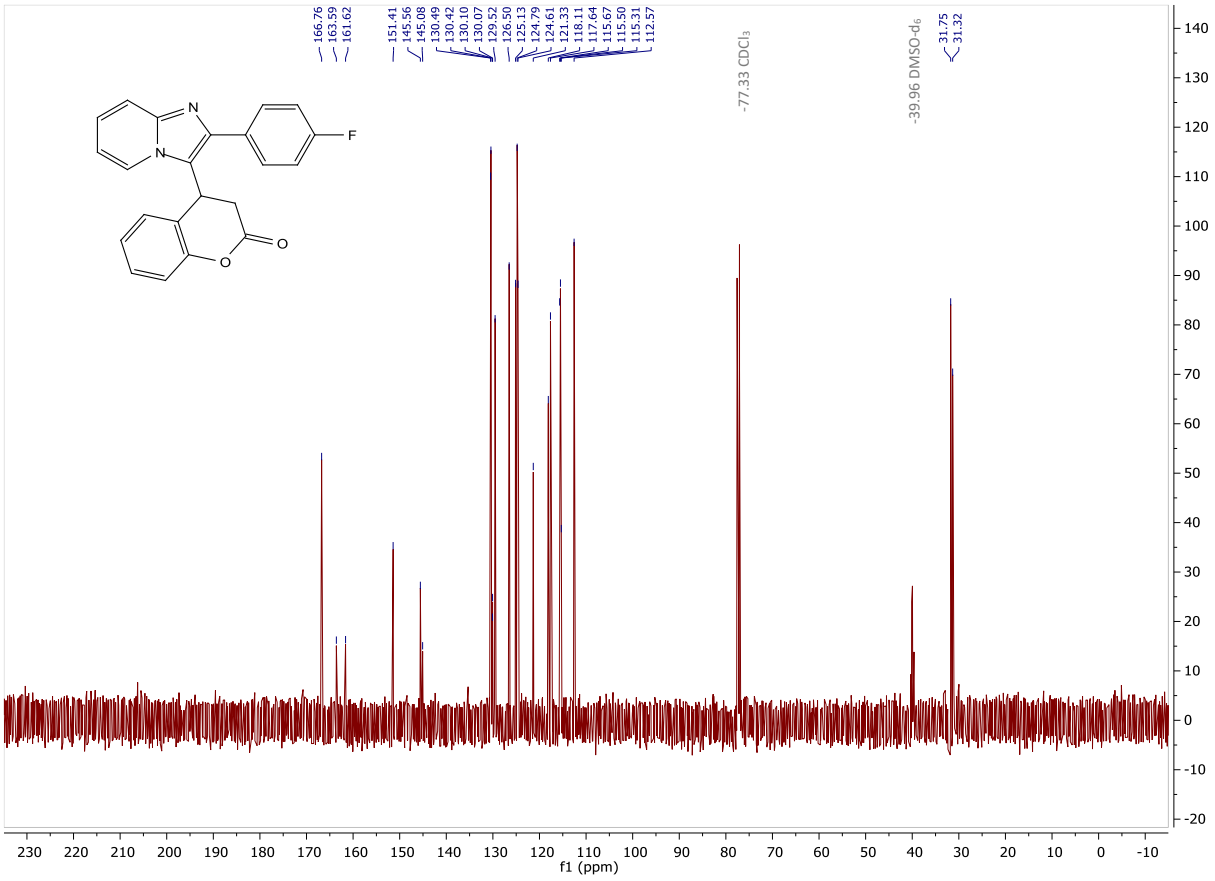
^{13}C NMR spectrum of (3d)



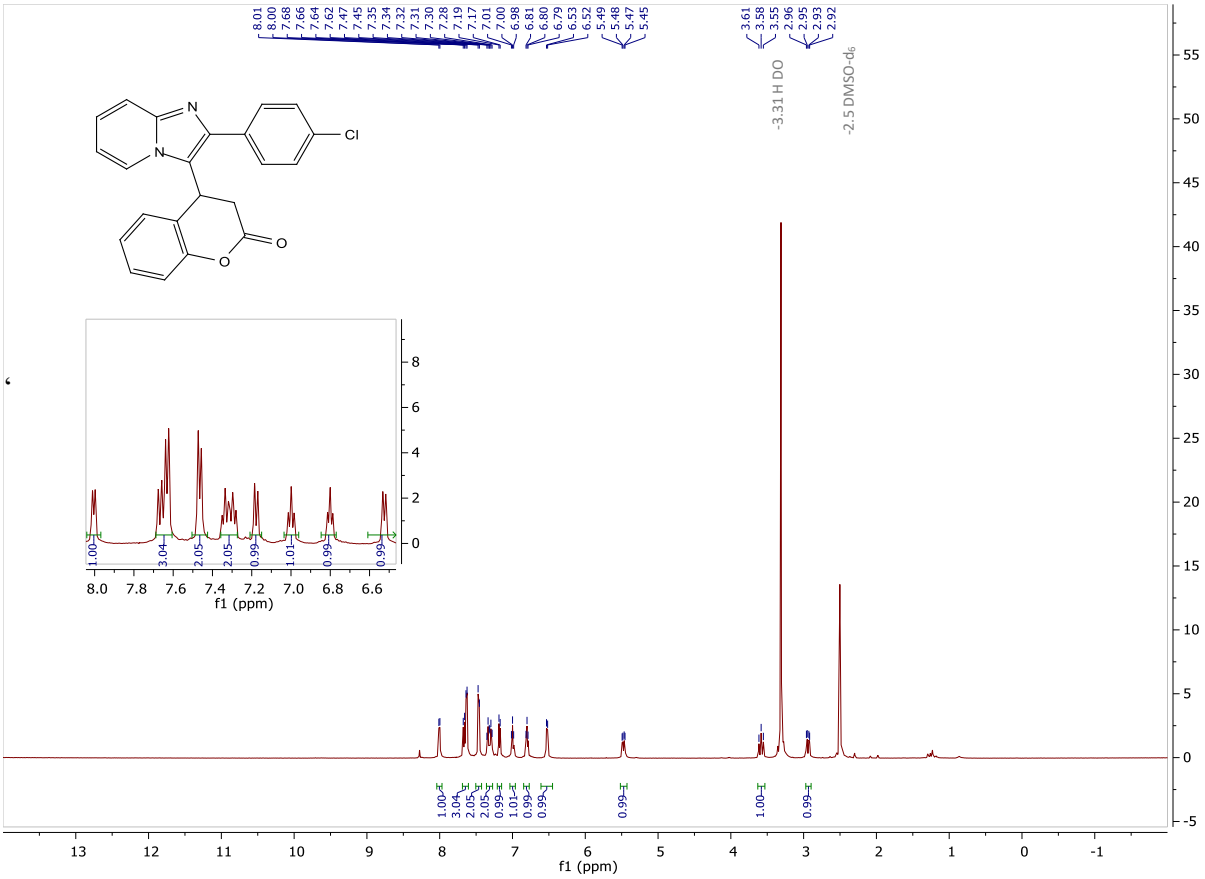
^{1}H NMR spectrum of (3e)



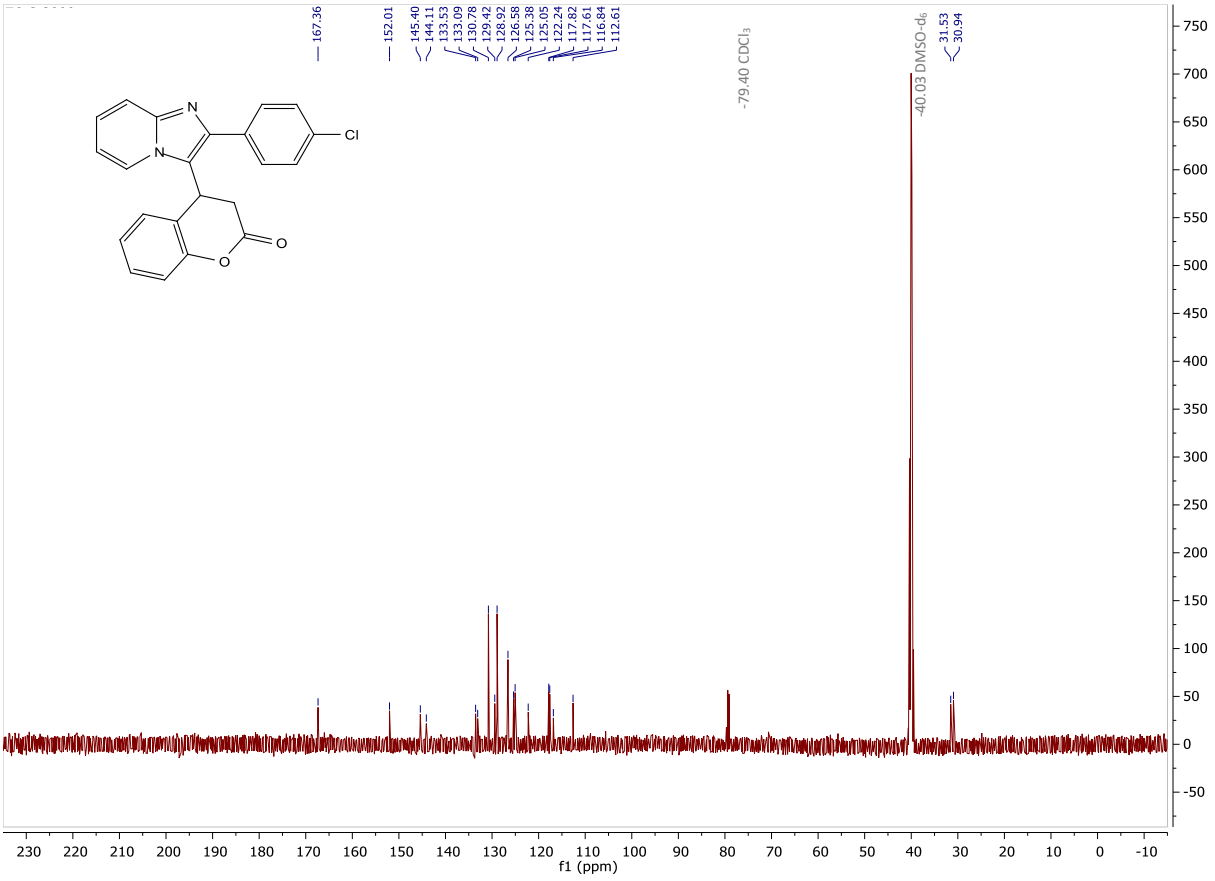
^{13}C NMR spectrum of (3e)



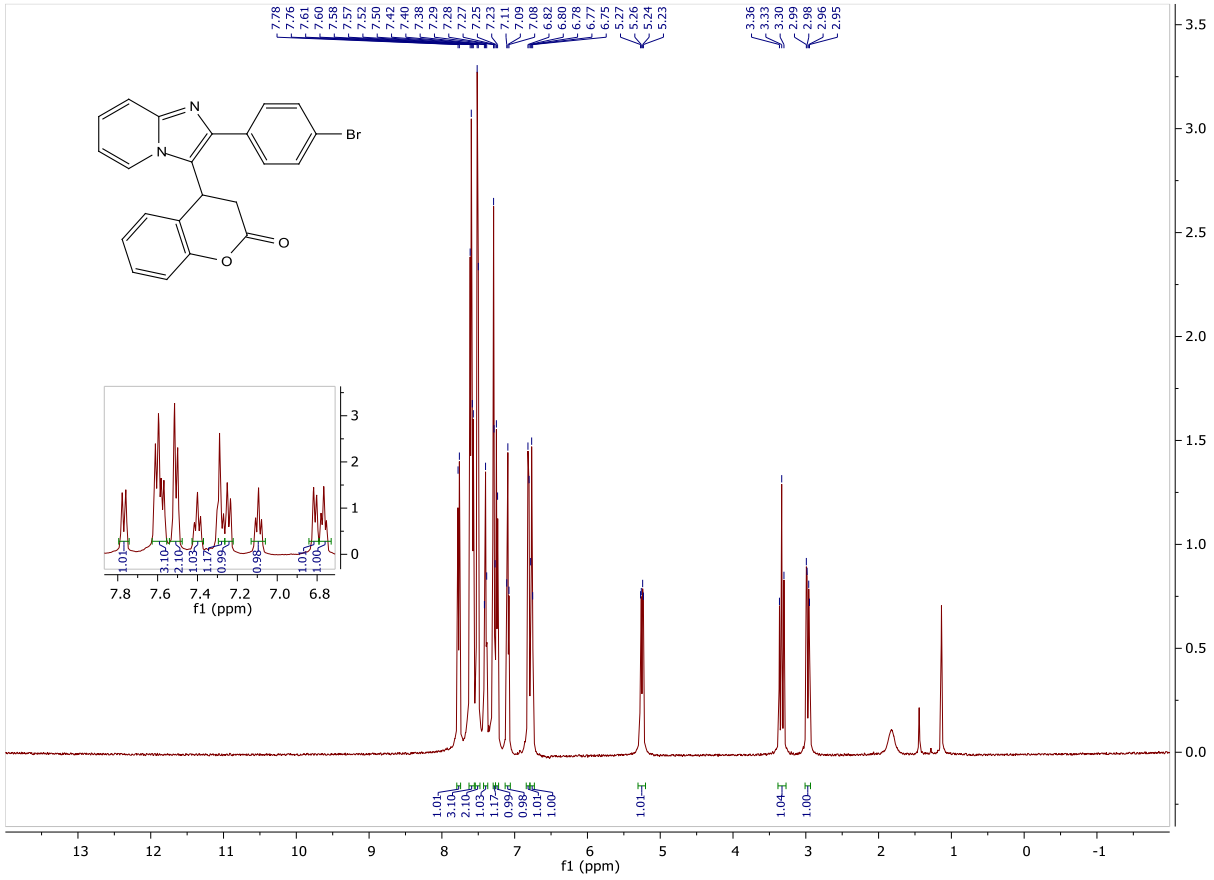
^{1}H NMR spectrum of (3f)



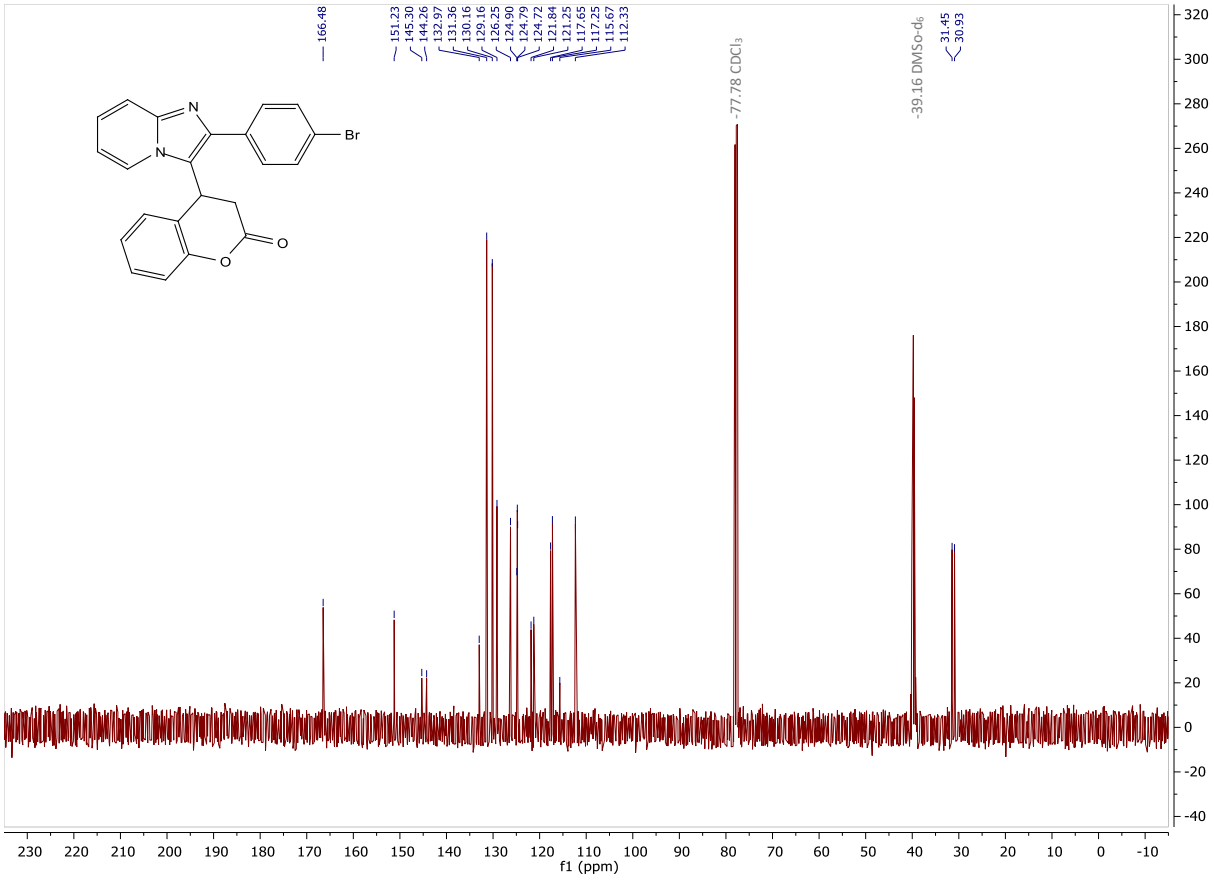
^{13}C NMR spectrum of (3f)



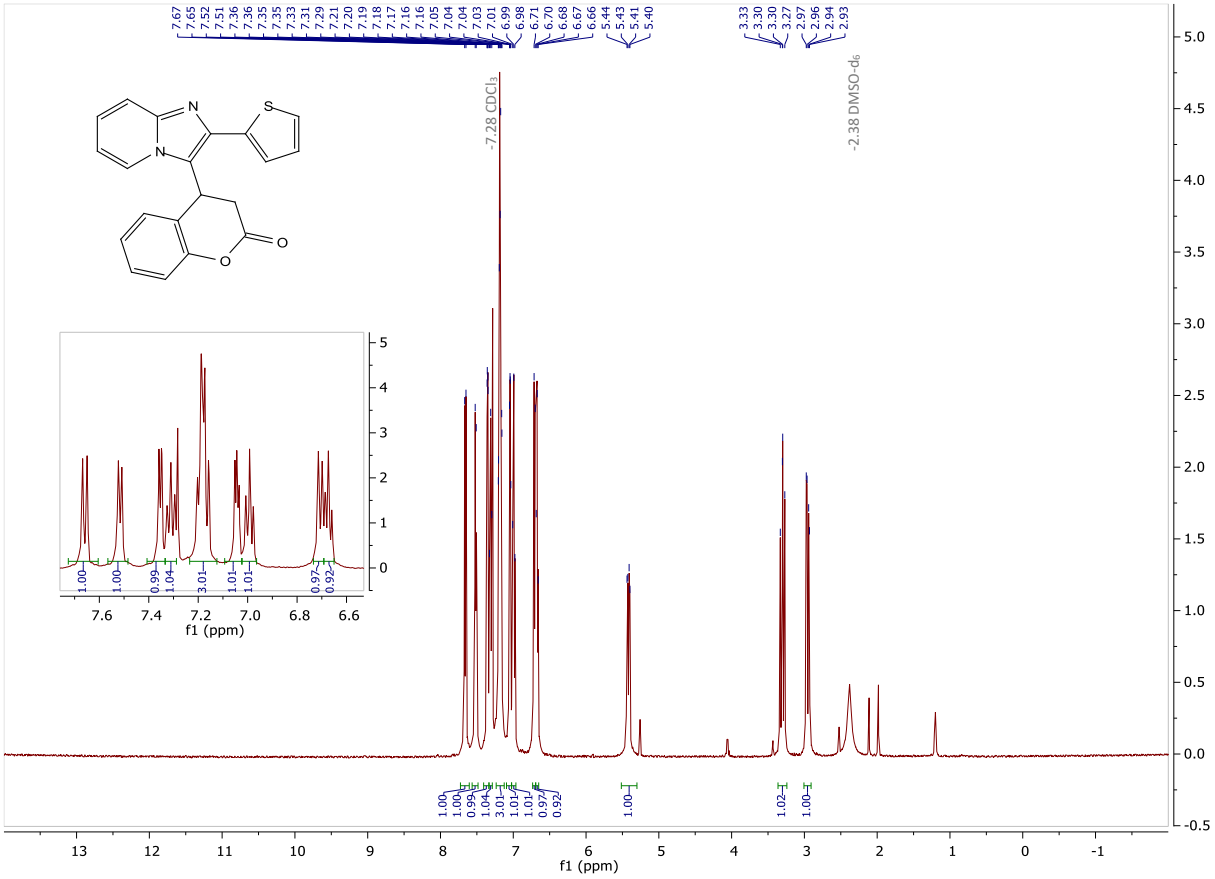
^{1}H NMR spectrum of (3g)



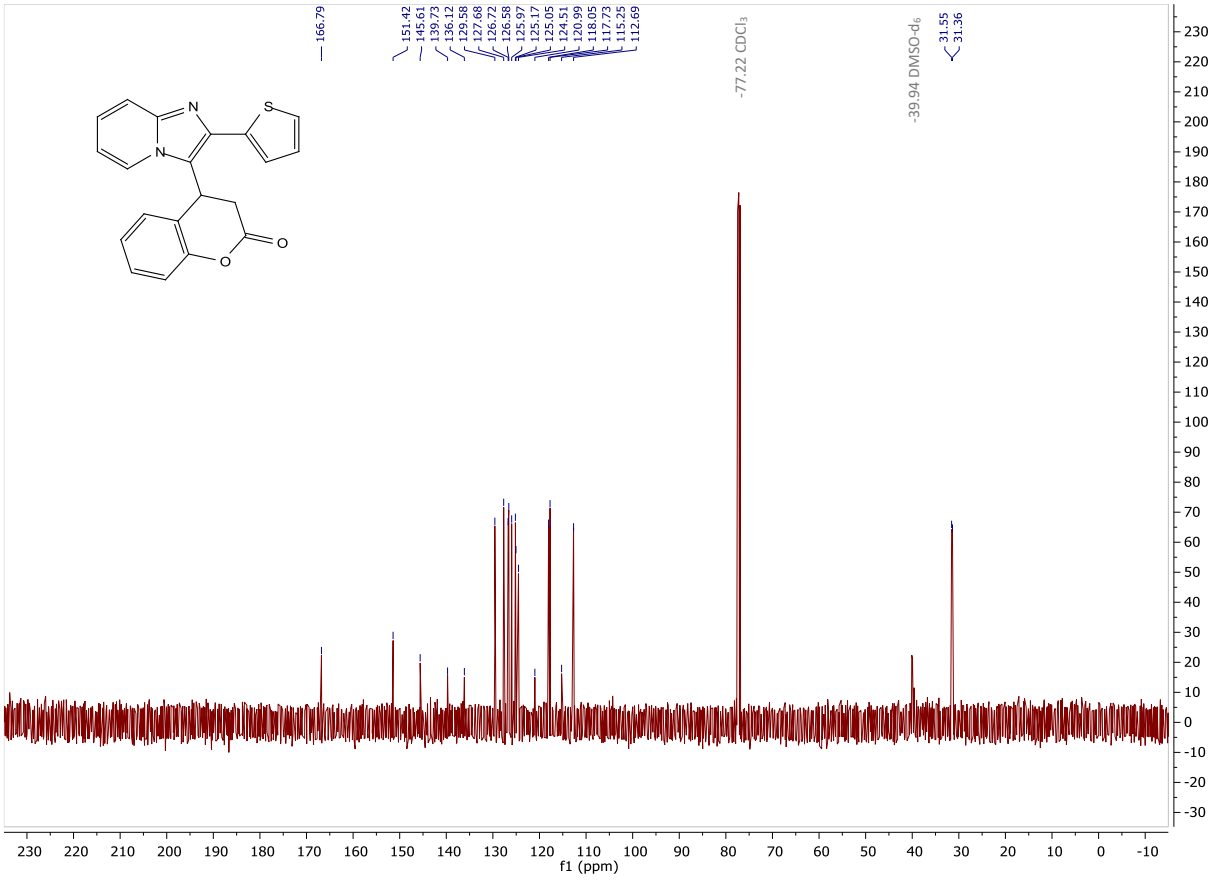
^{13}C NMR spectrum of (3g)



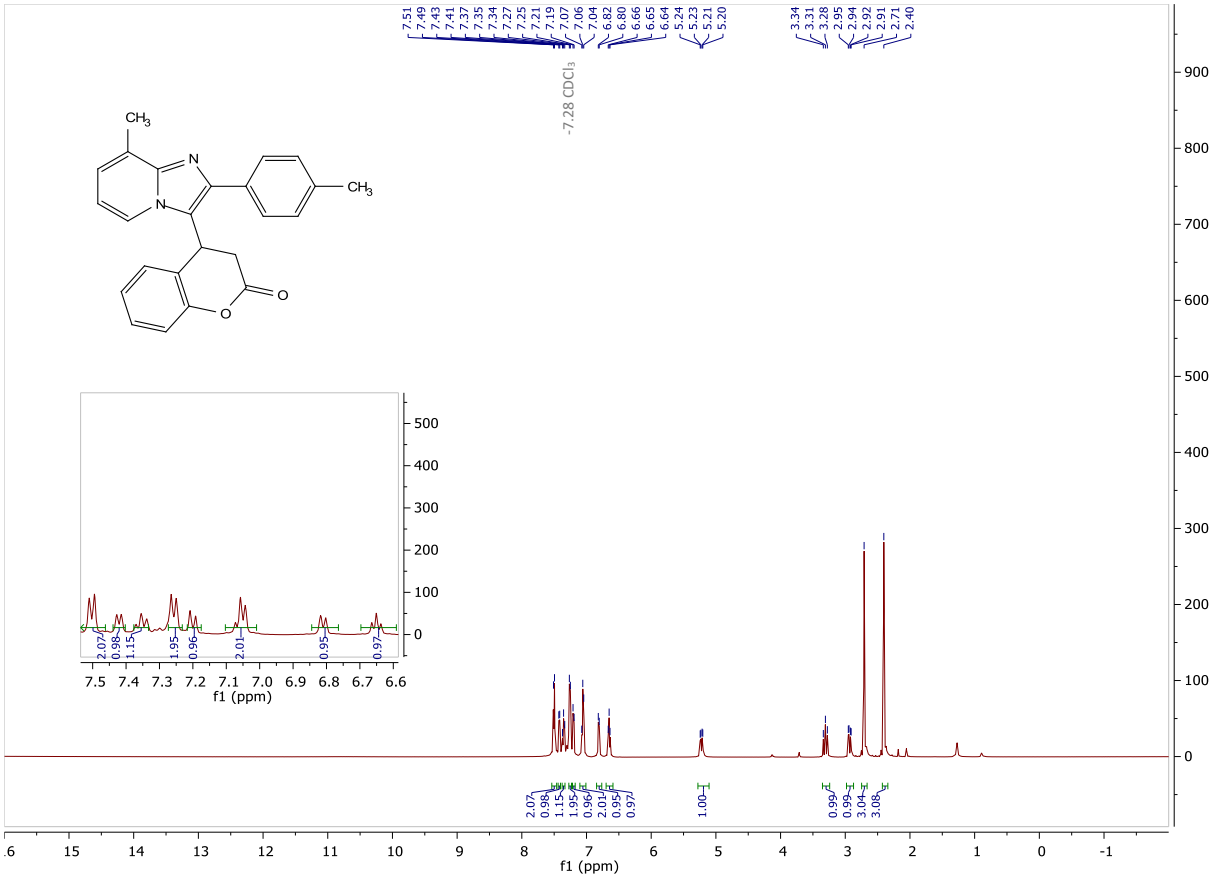
^{1}H NMR spectrum of (3i)



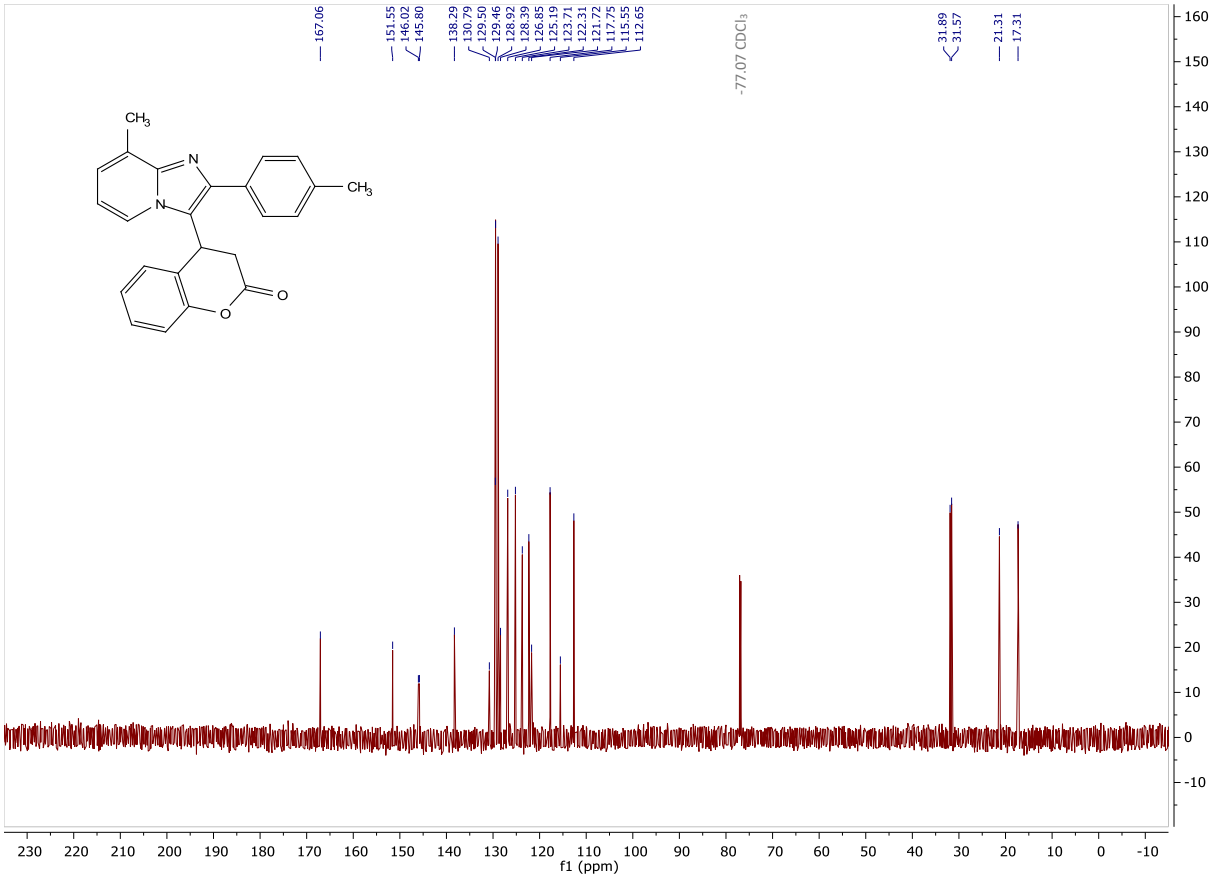
^{13}C NMR spectrum of (3i)



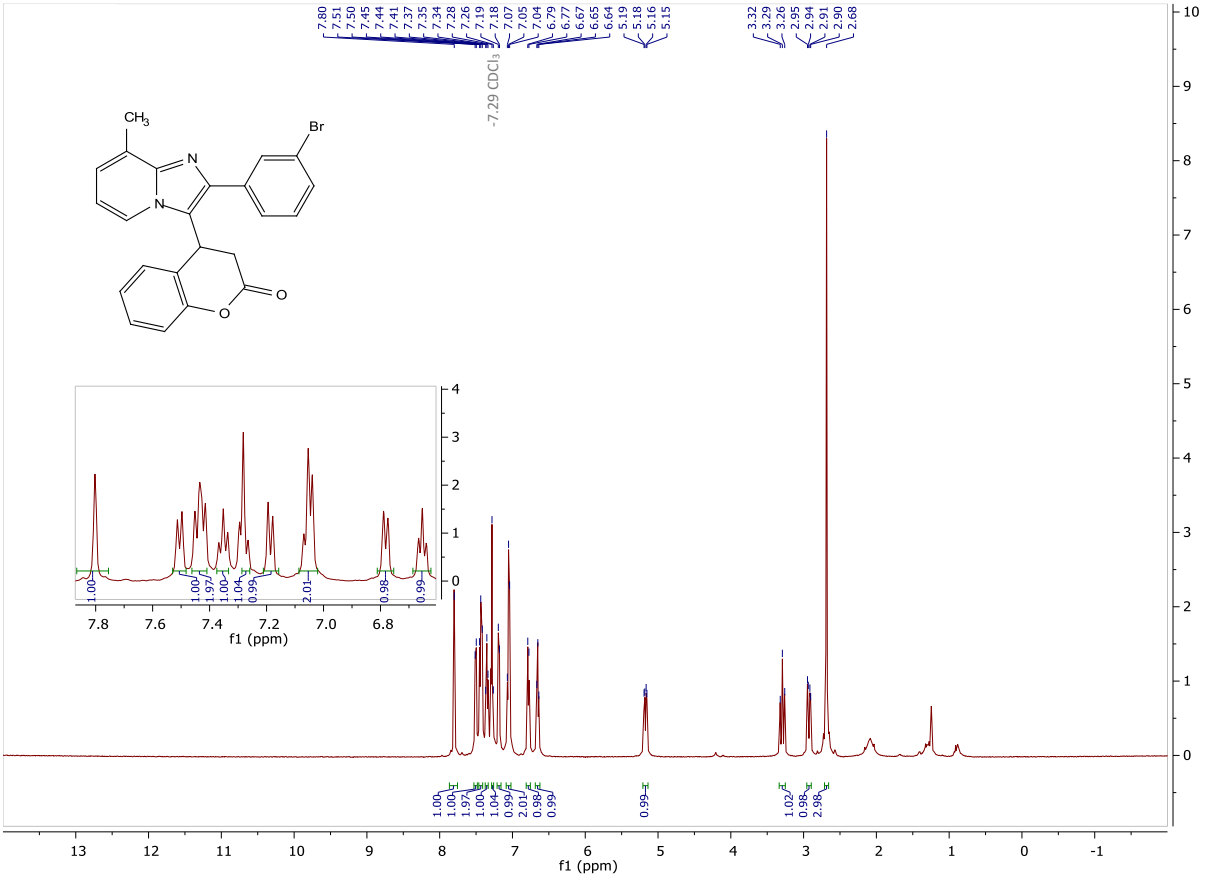
^{1}H NMR spectrum of (3k)



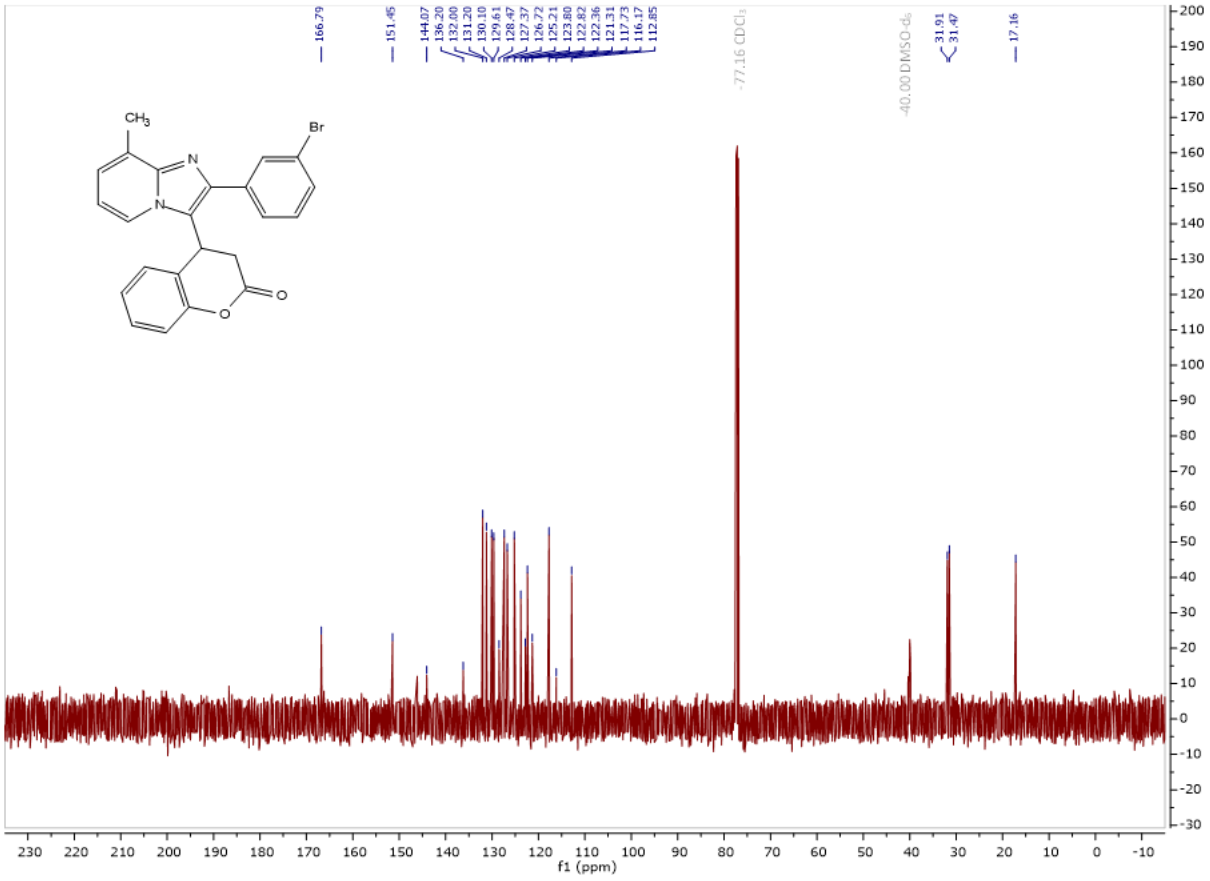
^{13}C NMR spectrum of (3k)



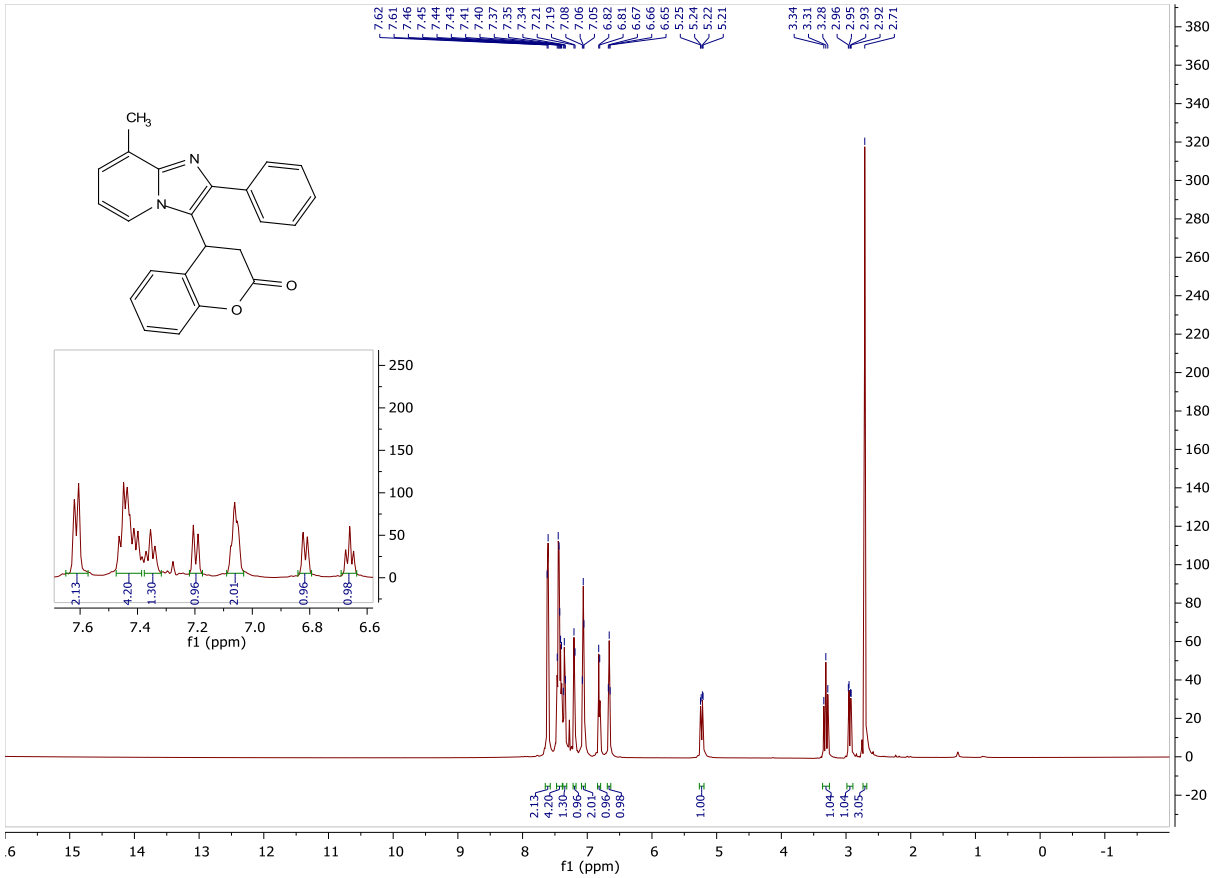
^{1}H NMR spectrum of (3l)



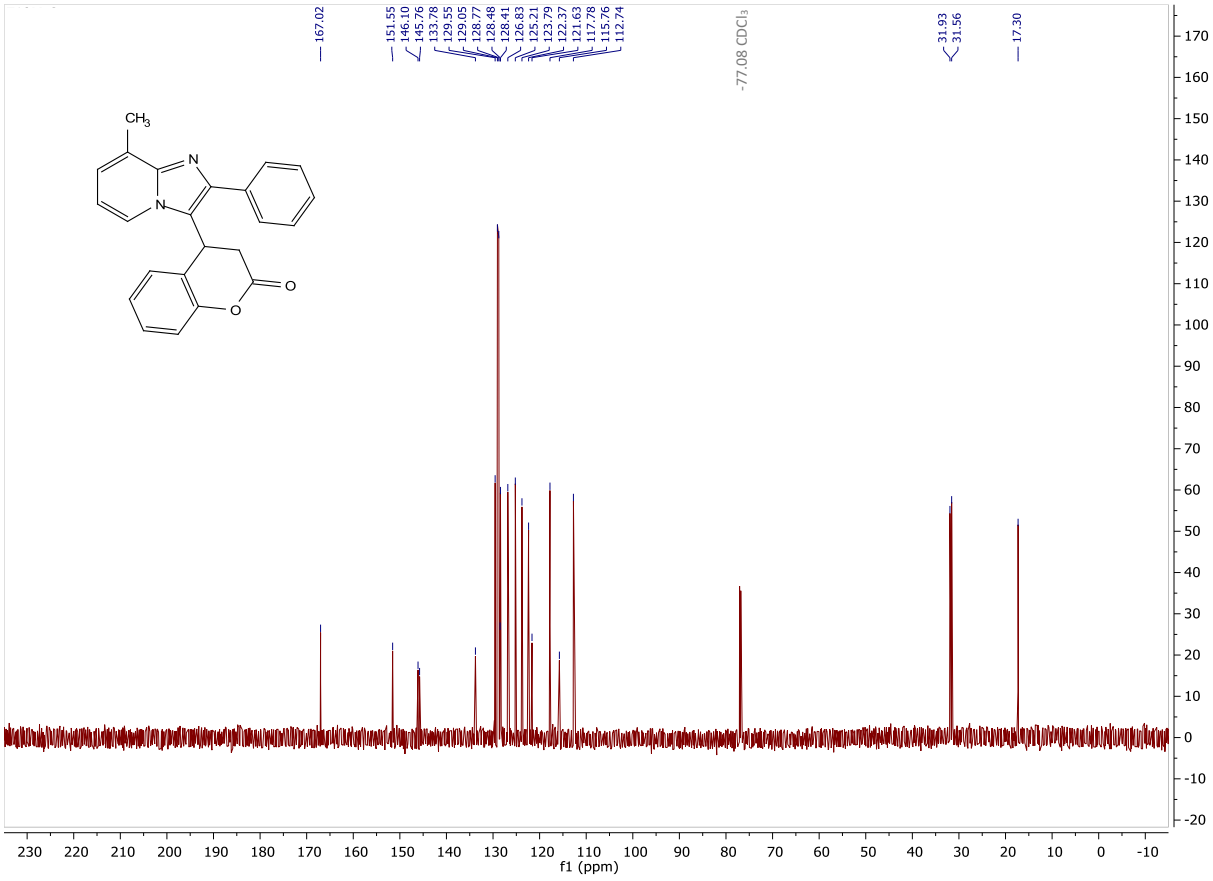
^{13}C NMR spectrum of (3l)



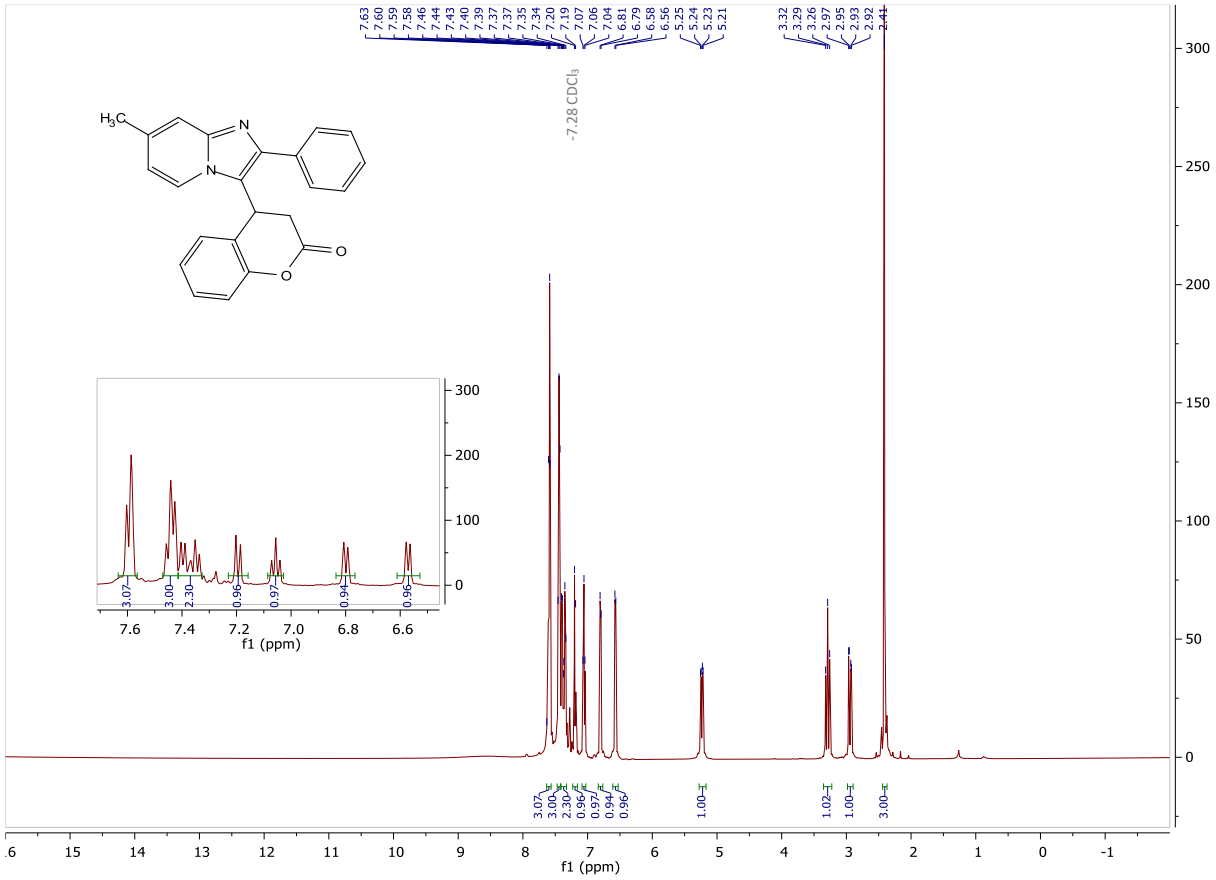
^{1}H NMR spectrum of (3m)



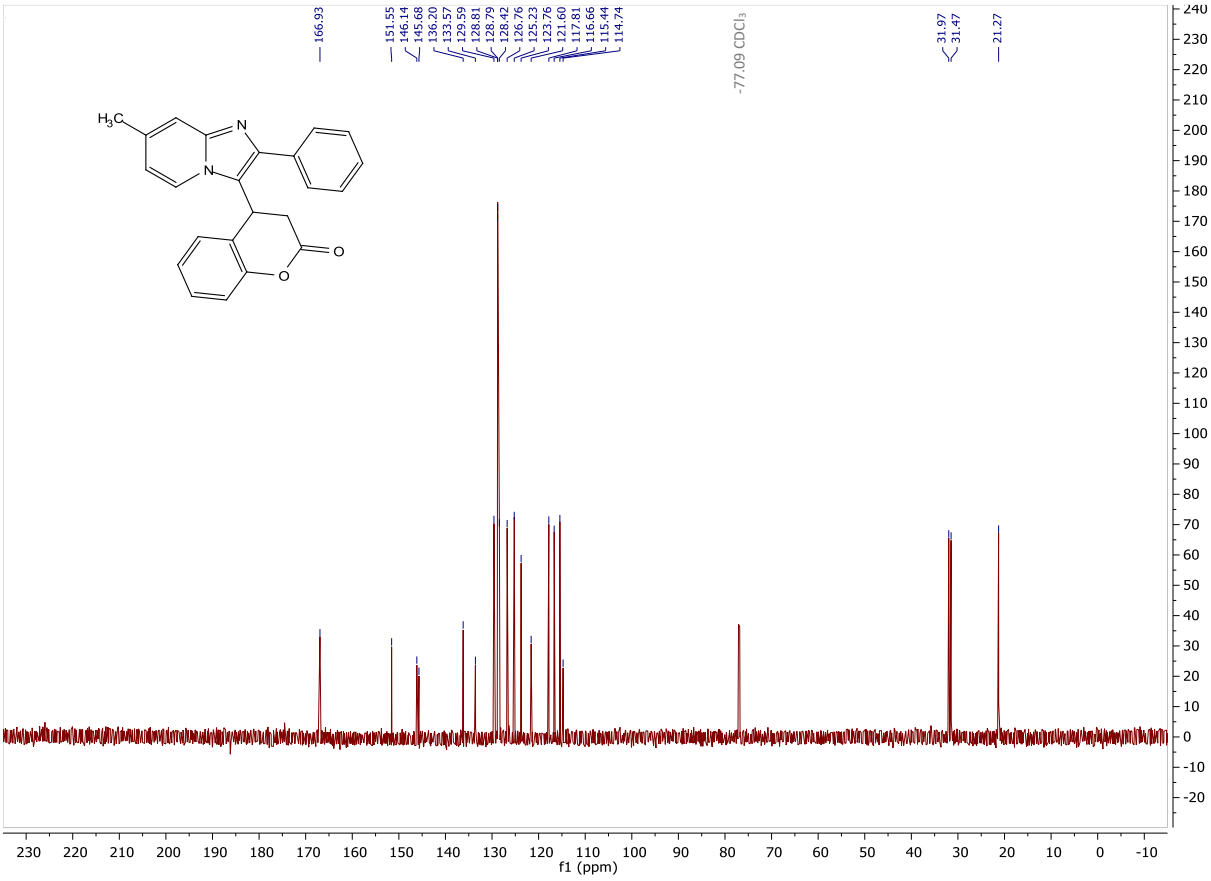
^{13}C NMR spectrum of (3m)



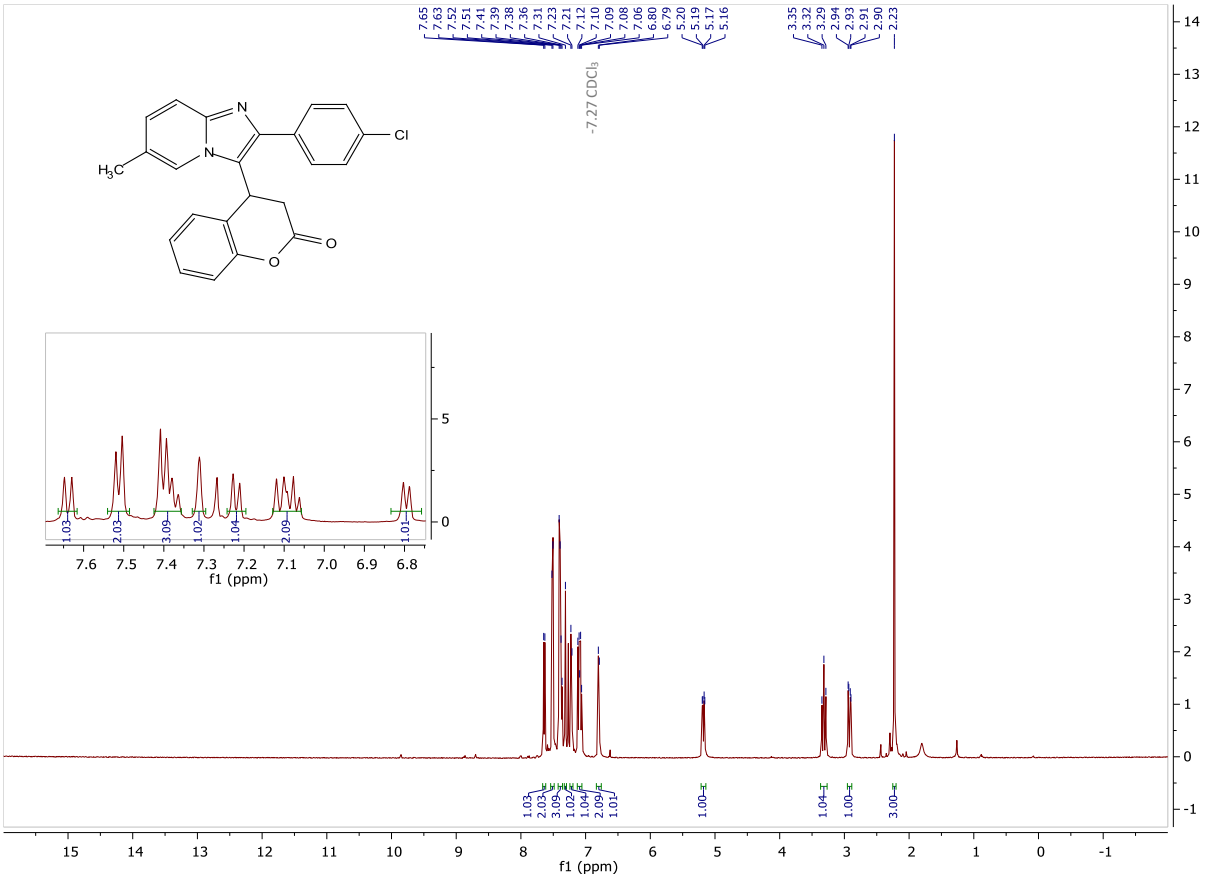
^{1}H NMR spectrum of (3n)



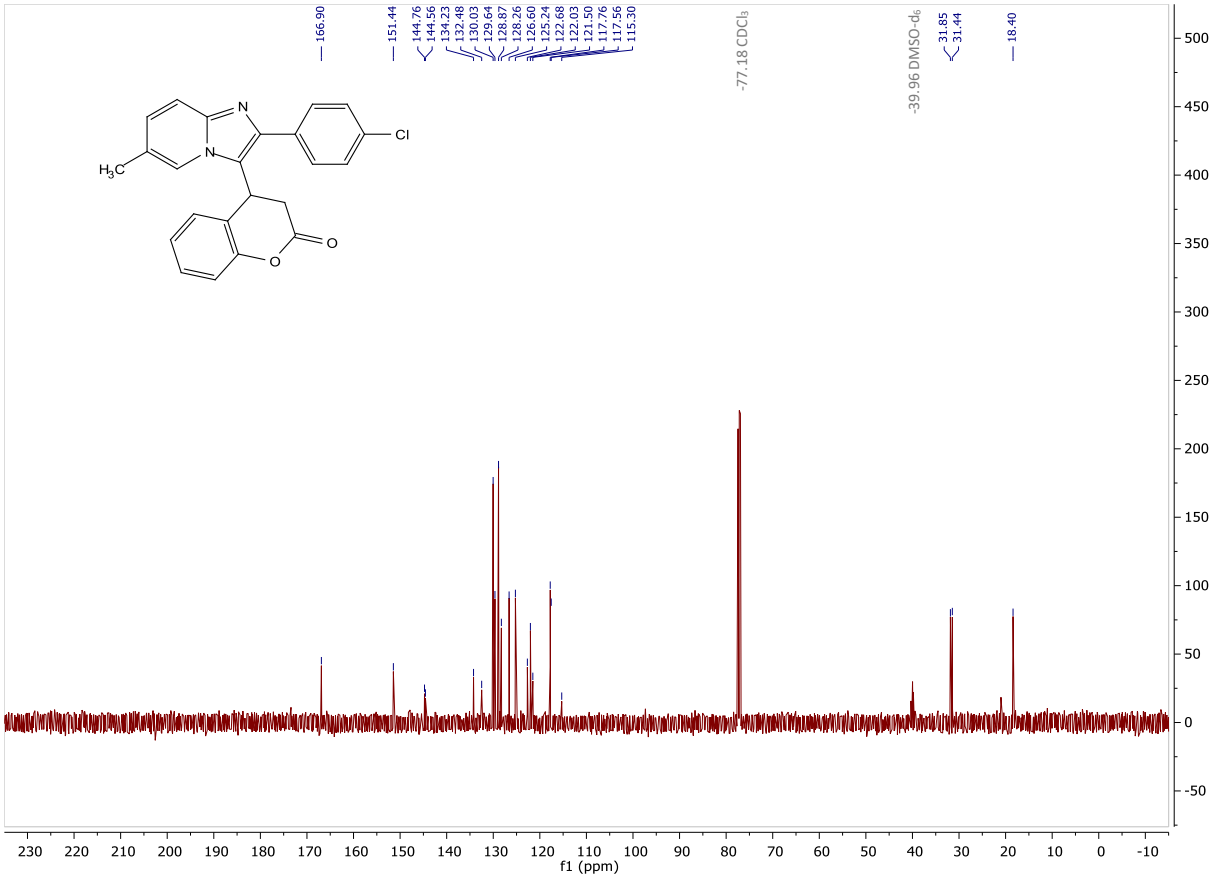
^{13}C NMR spectrum of (3n)



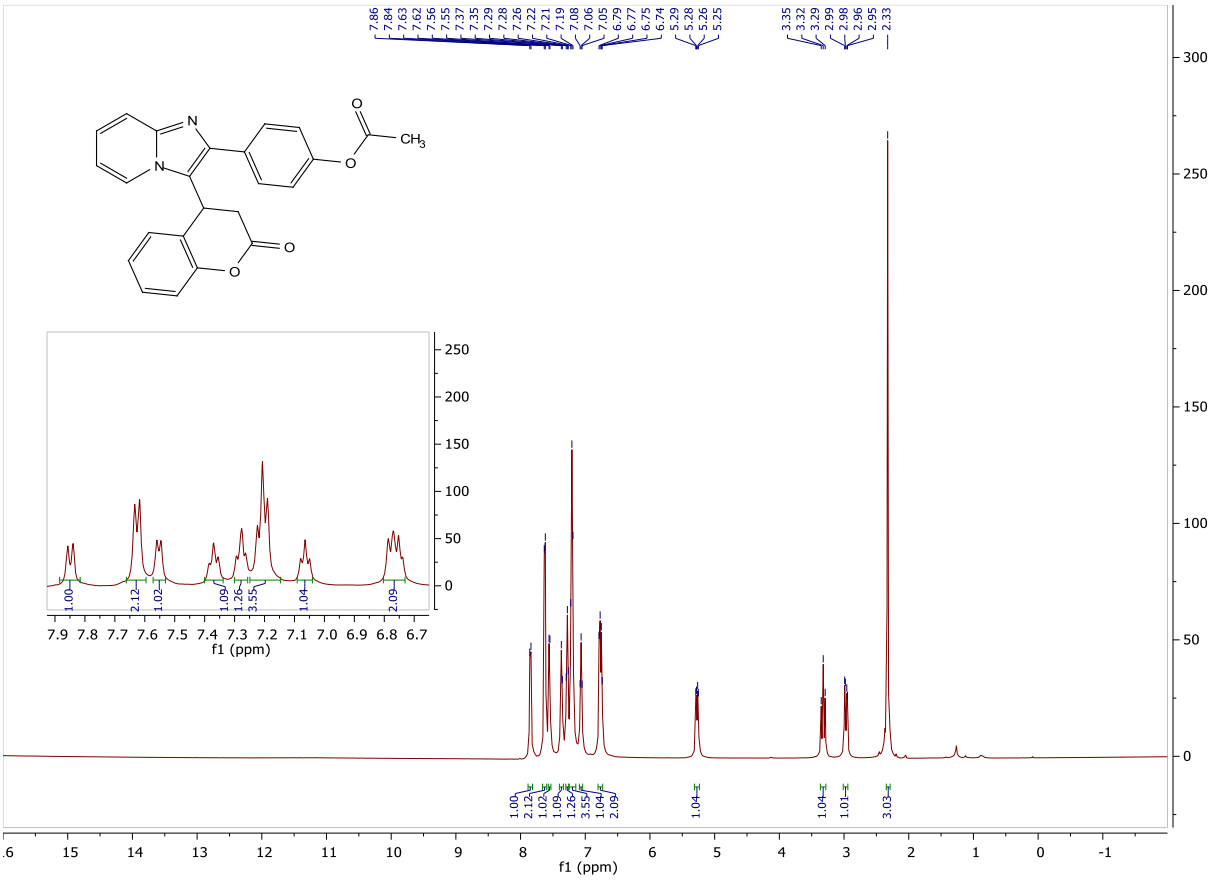
^{1}H NMR spectrum of (3o)



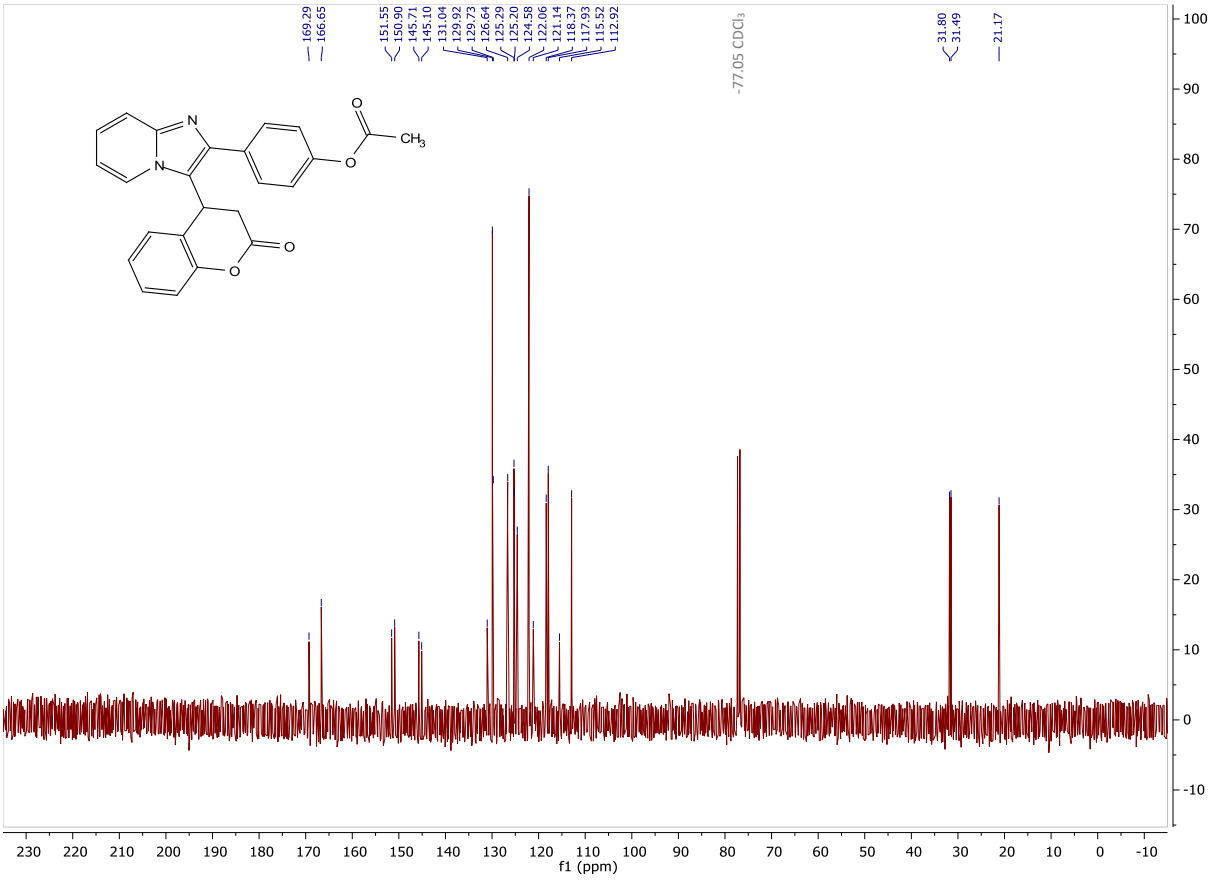
^{13}C NMR spectrum of (3o)



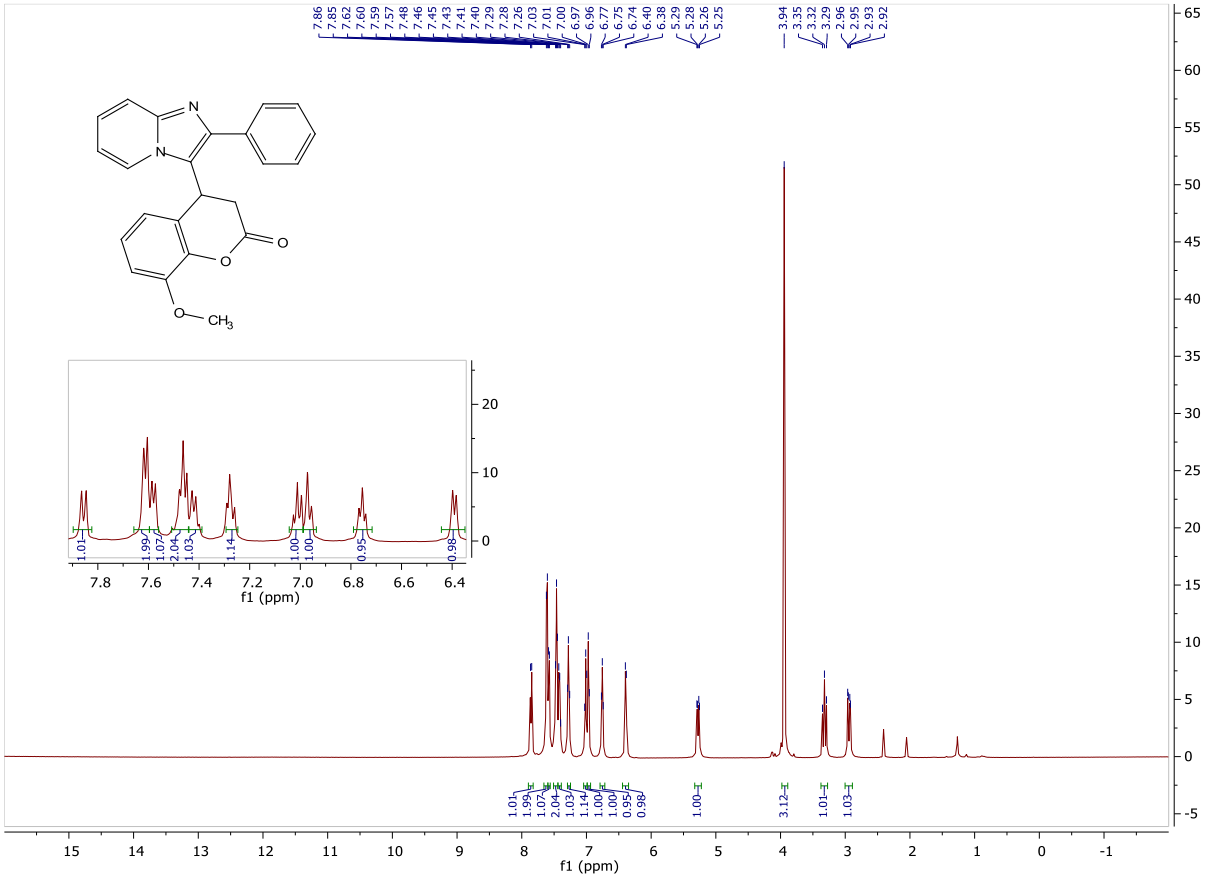
^{1}H NMR spectrum of (3p)



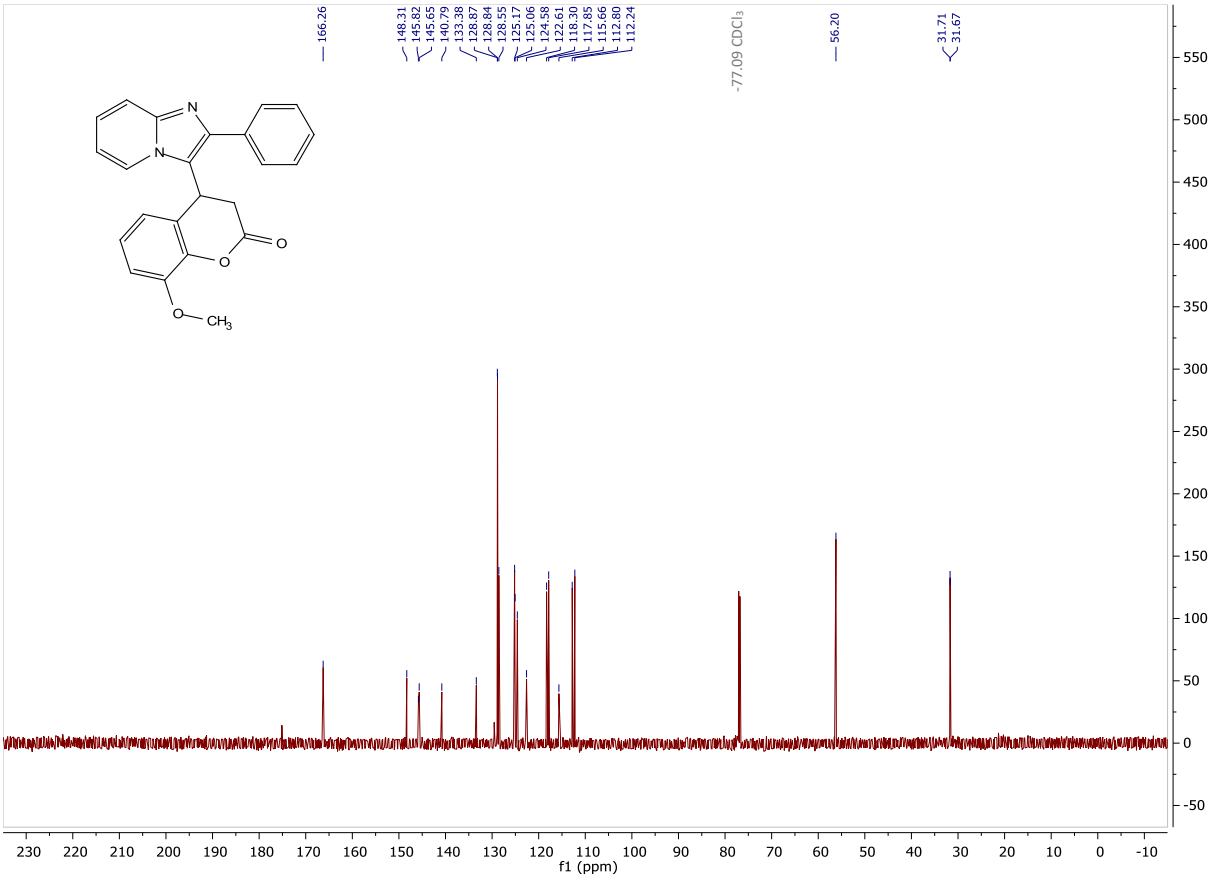
^{13}C NMR spectrum of (3p)



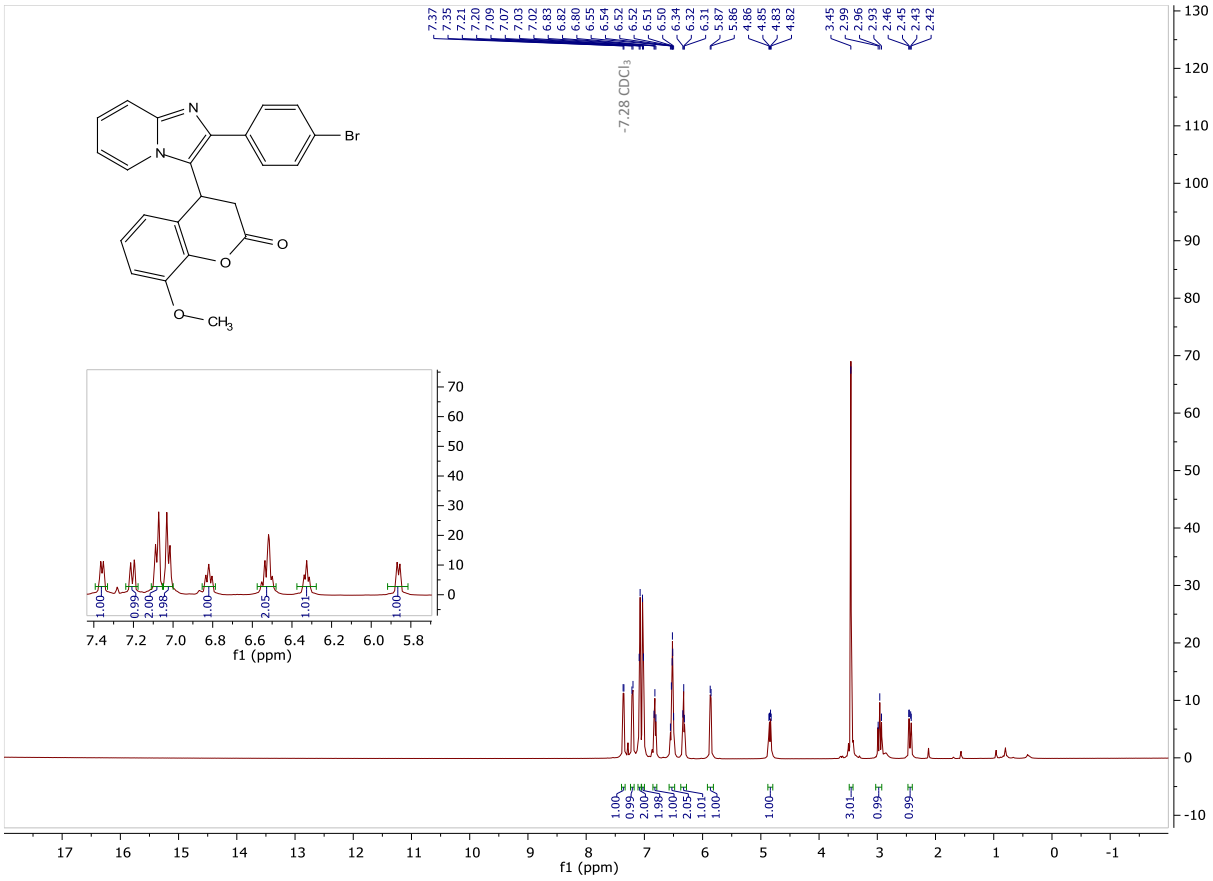
^{1}H NMR spectrum of (3q)



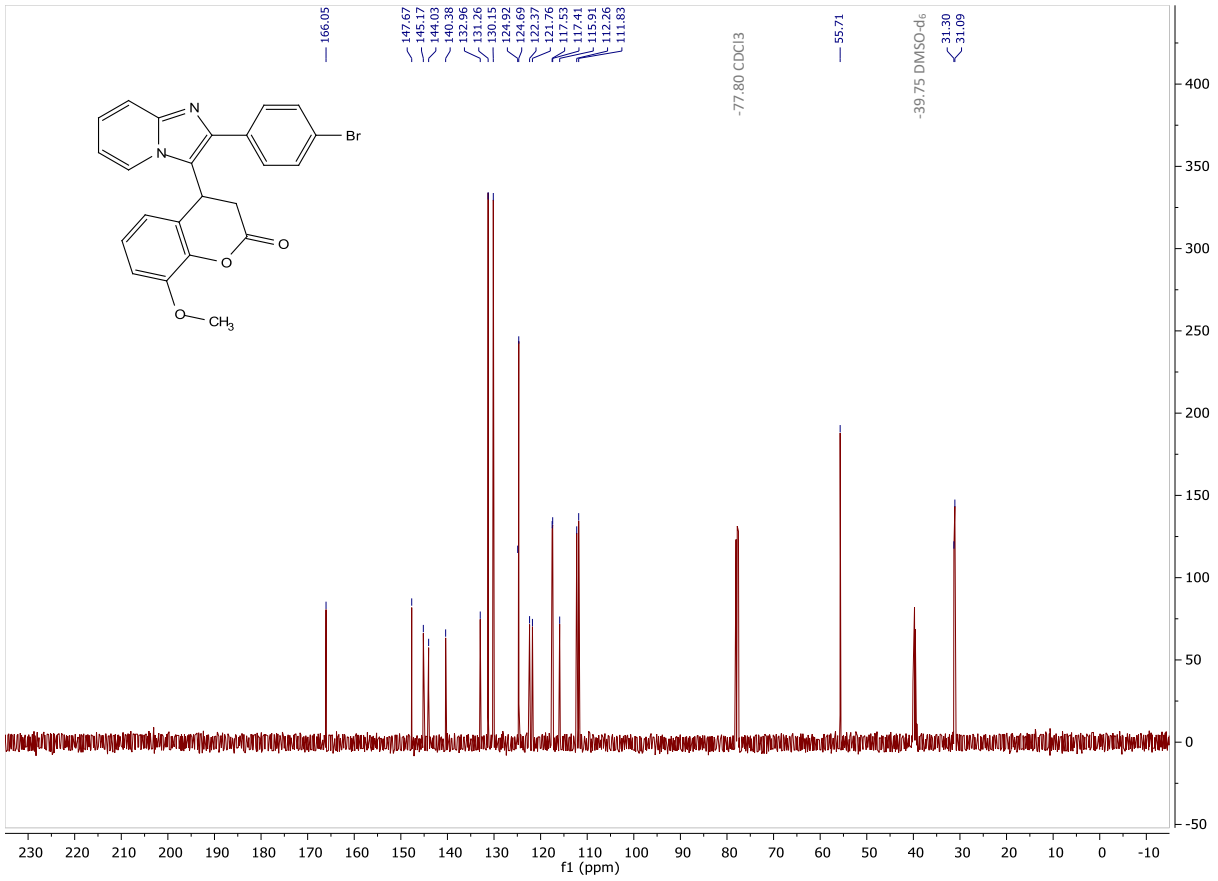
^{13}C NMR spectrum of (3q)



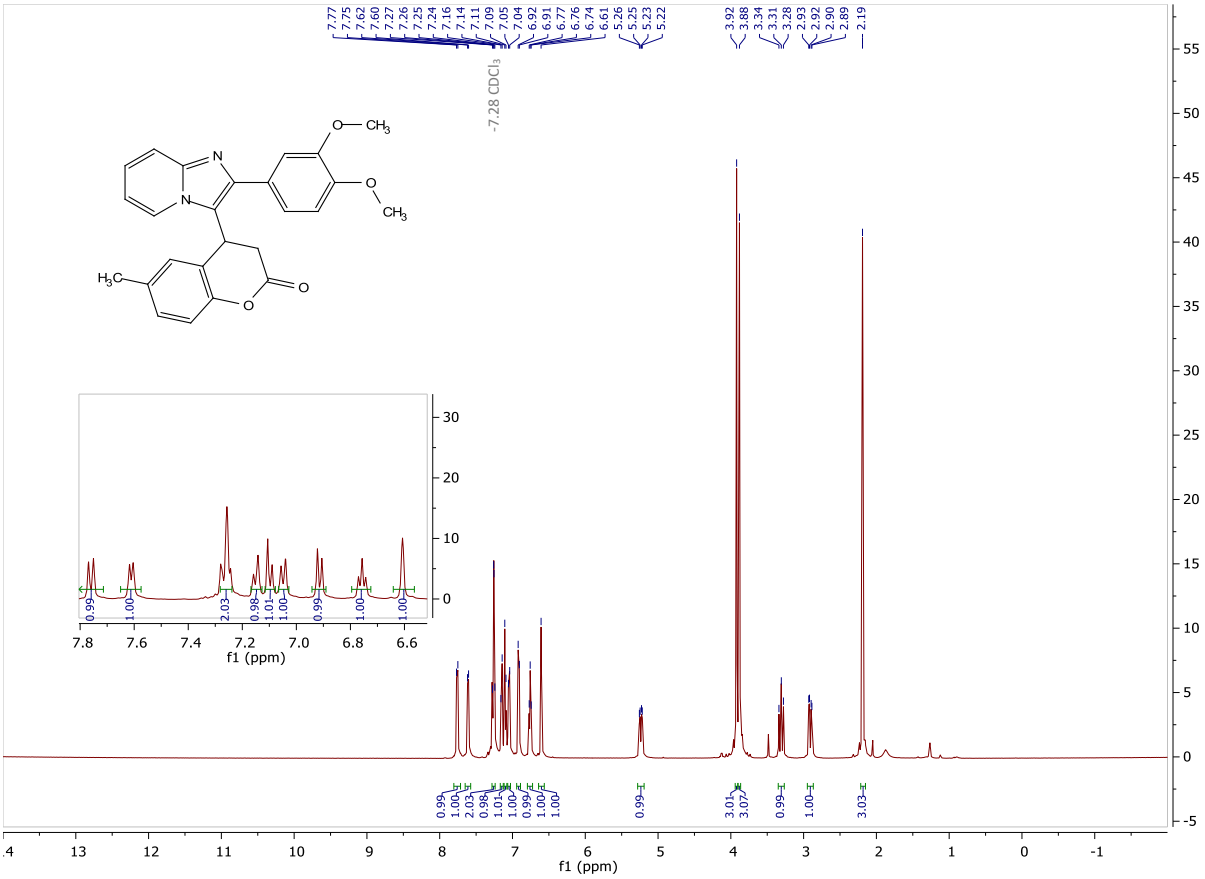
^{1}H NMR spectrum of (3r)



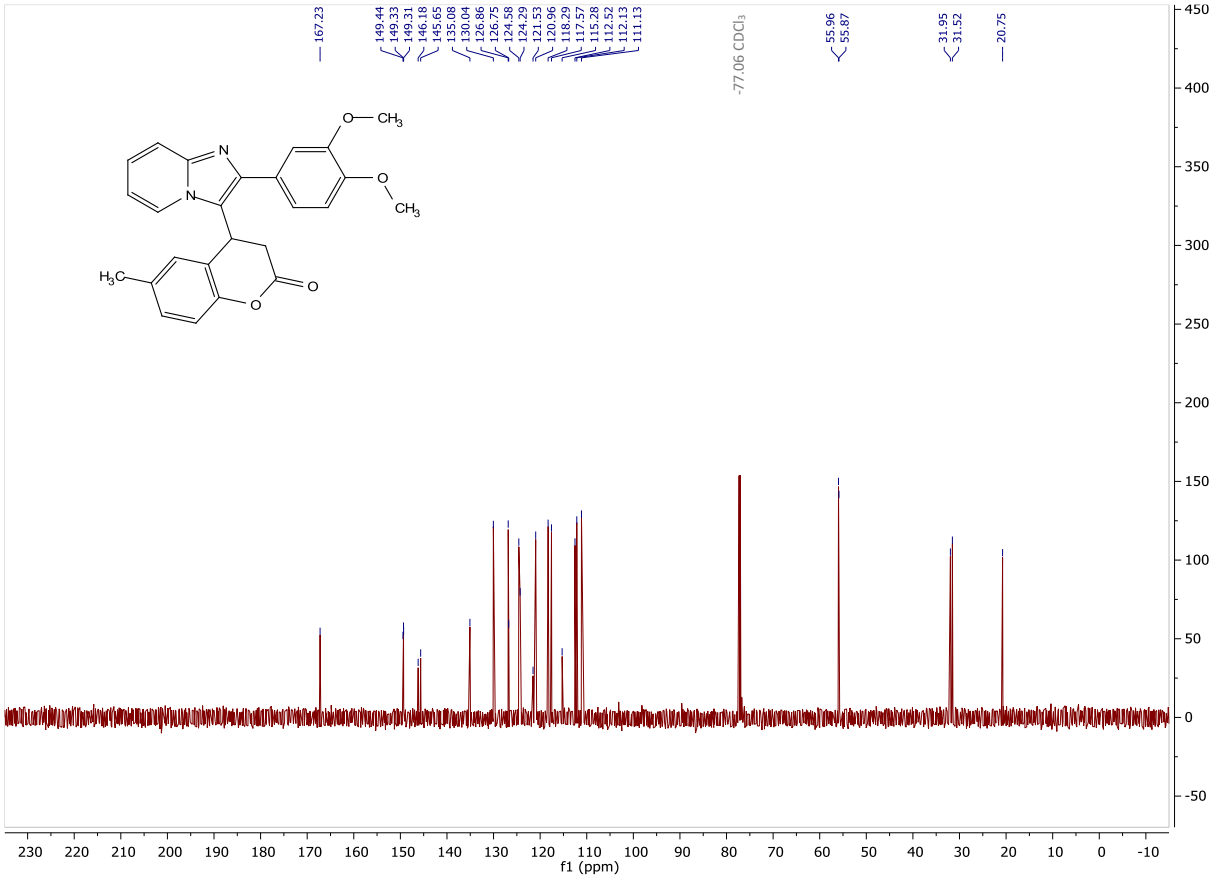
^{13}C NMR spectrum of (3r)



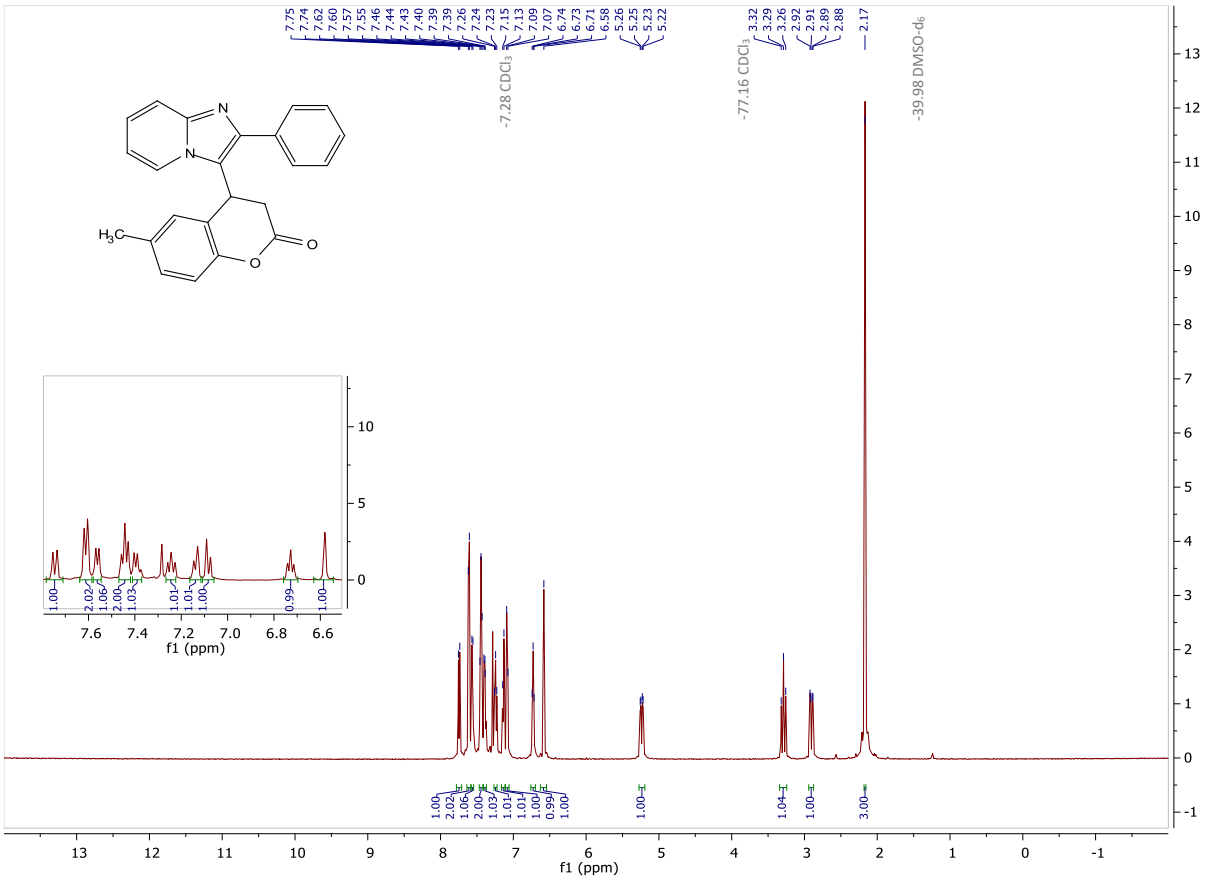
^{1}H NMR spectrum of (3t)



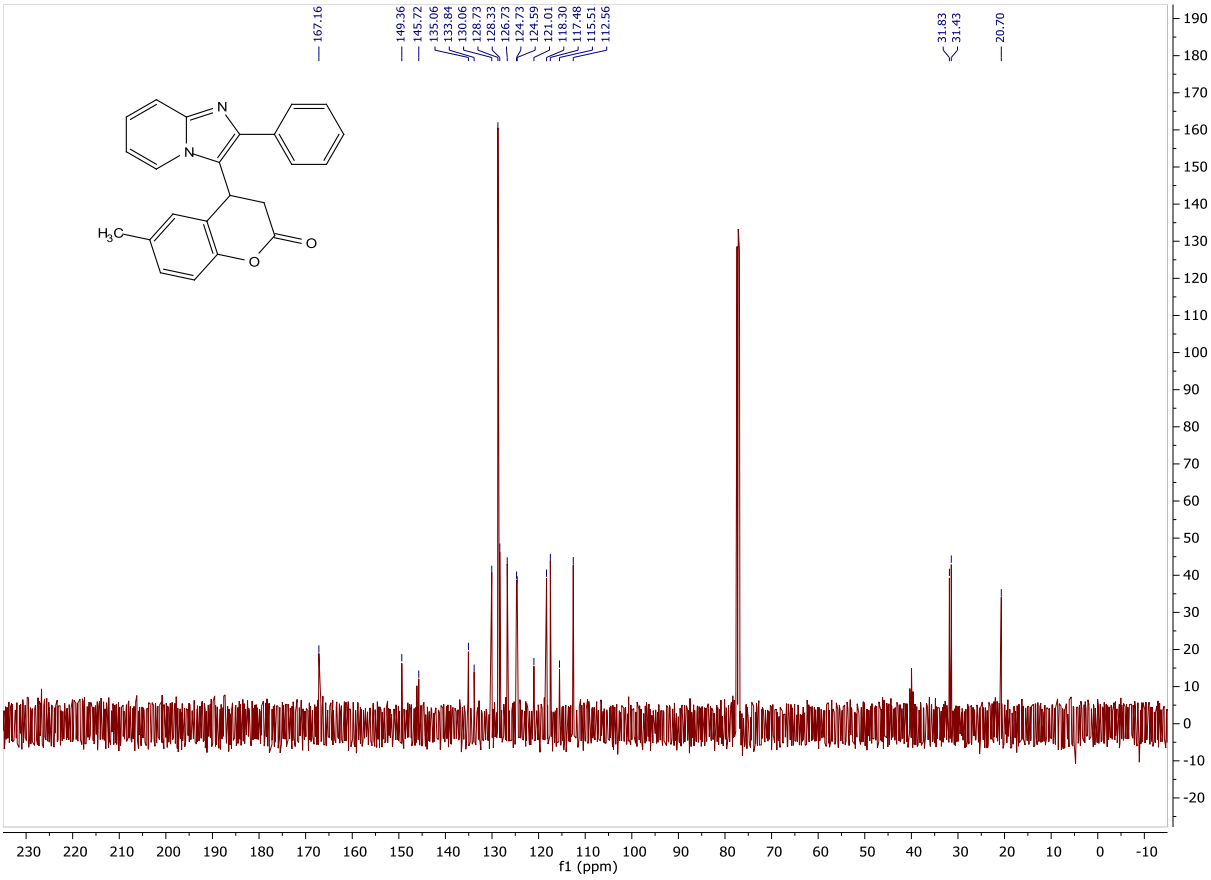
^{13}C NMR spectrum of (3t)



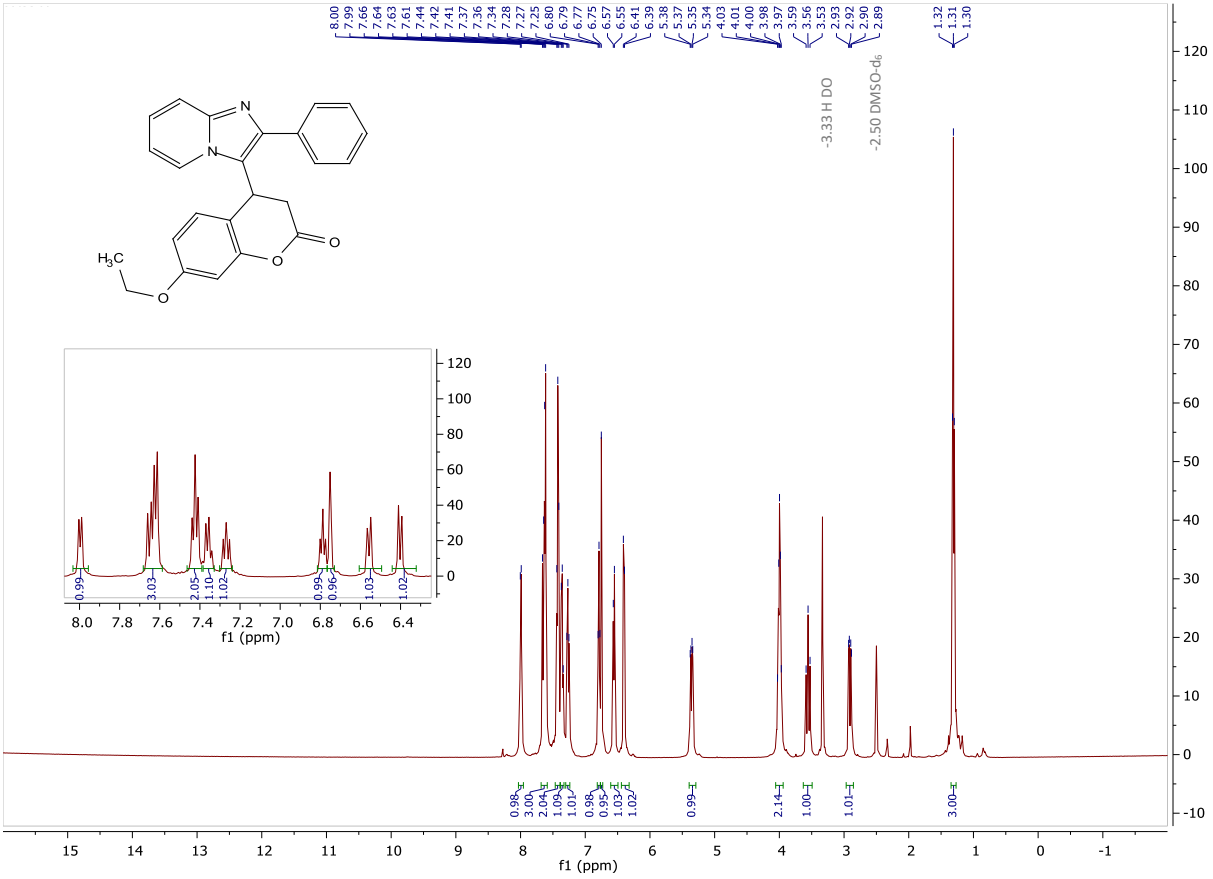
^{1}H NMR spectrum of (3v)



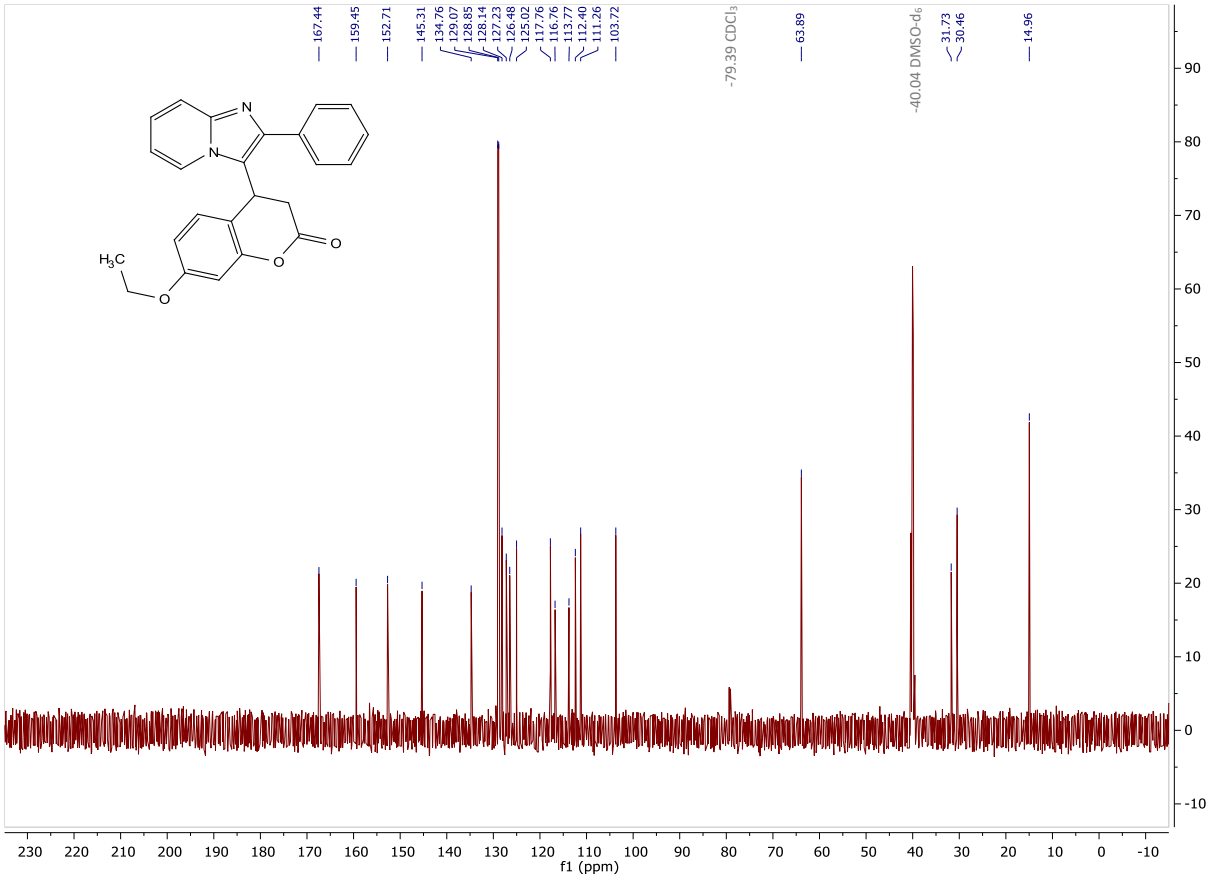
^{13}C NMR spectrum of (3v)



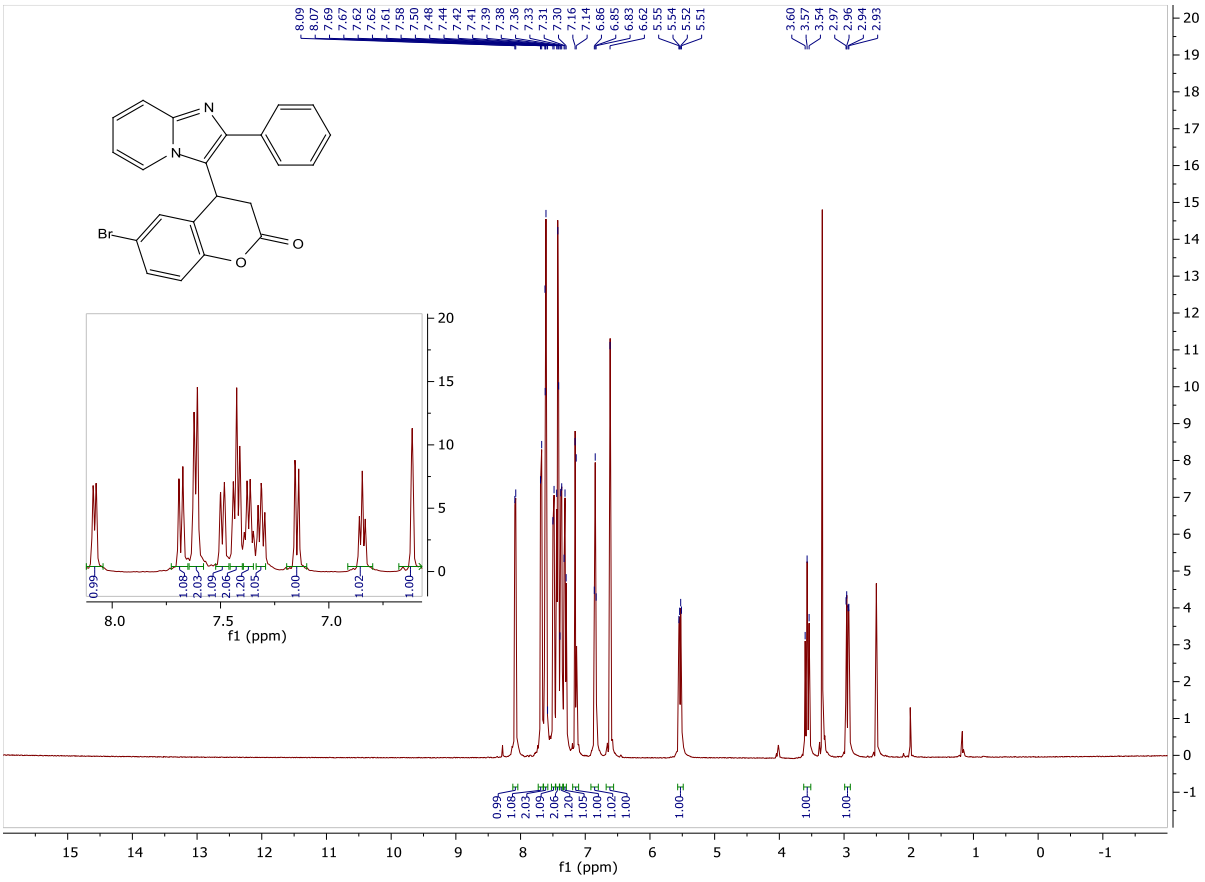
^{1}H NMR spectrum of (3w)



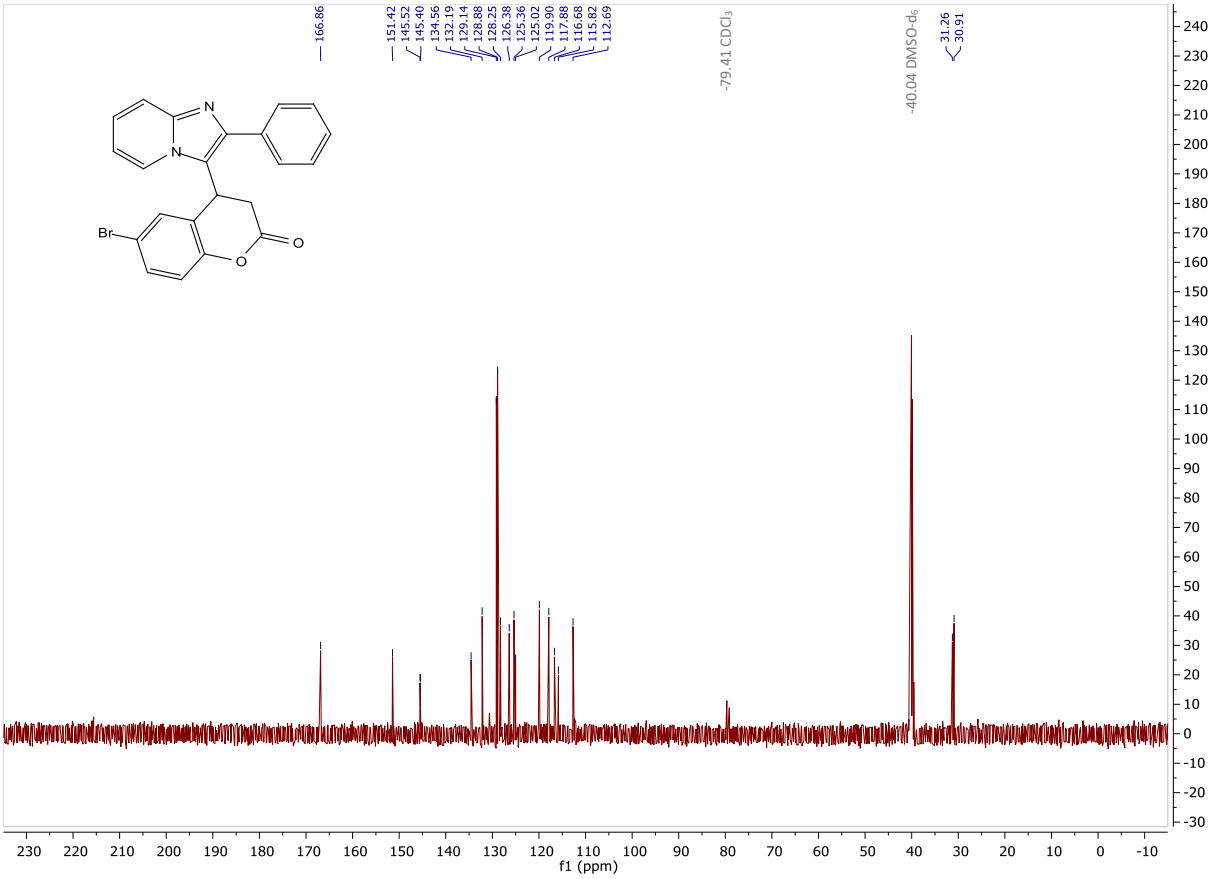
^{13}C NMR spectrum of (3w)



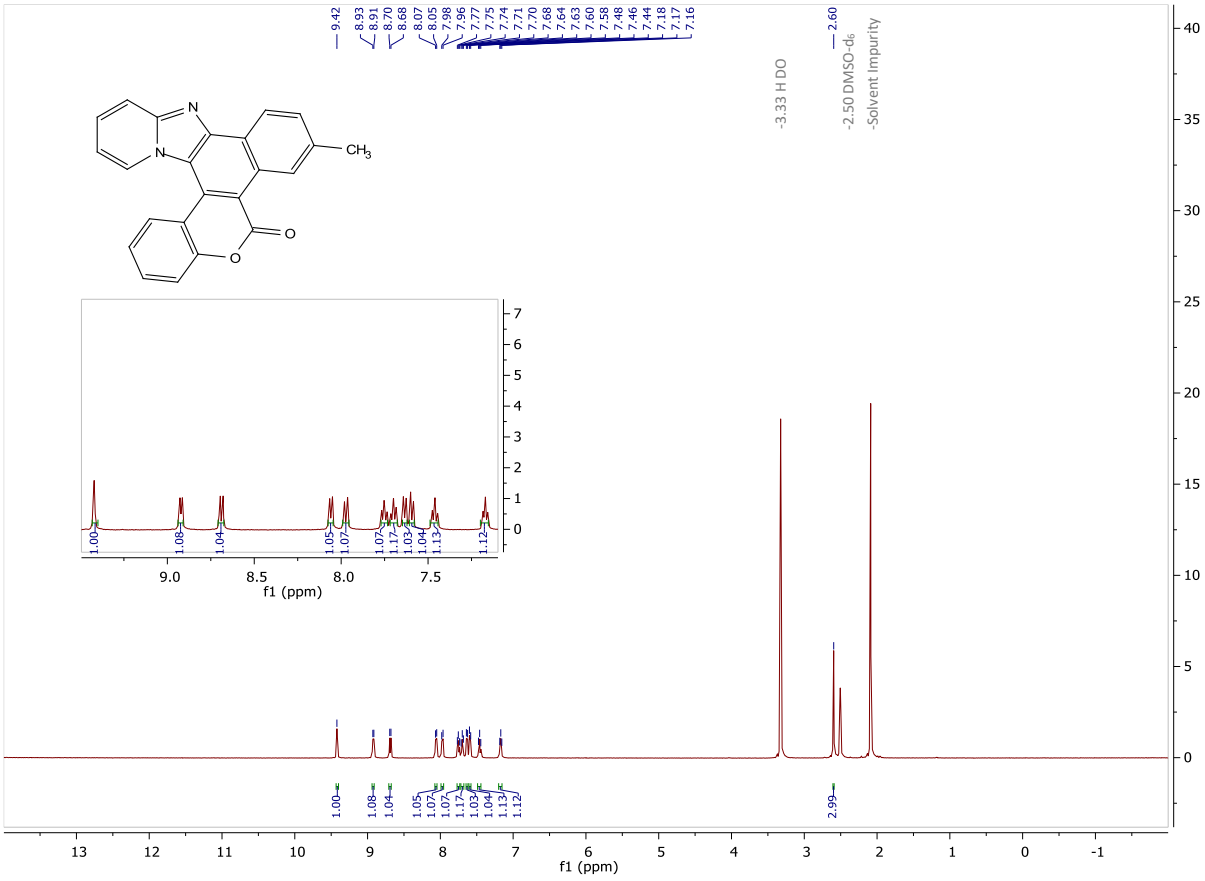
^{1}H NMR spectrum of (3x)



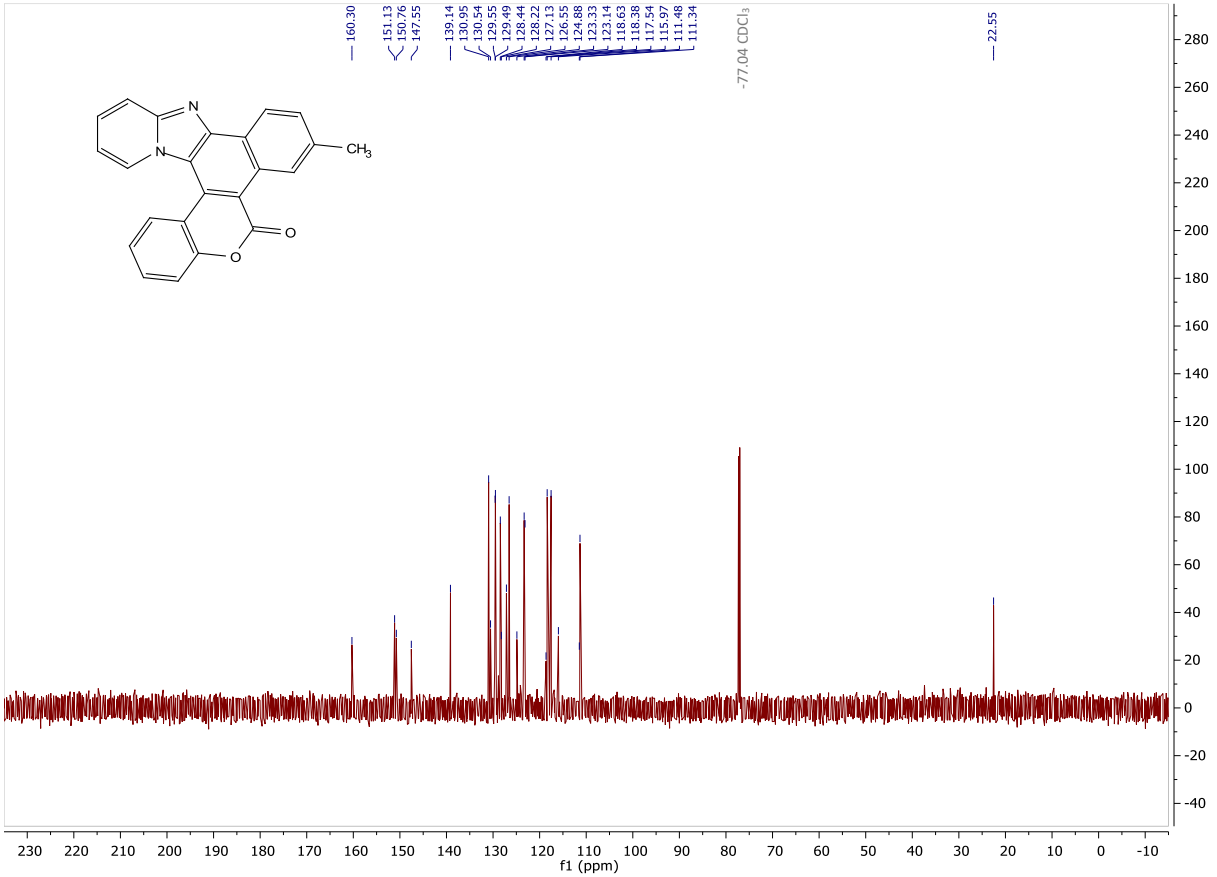
^{13}C NMR spectrum of (3x)



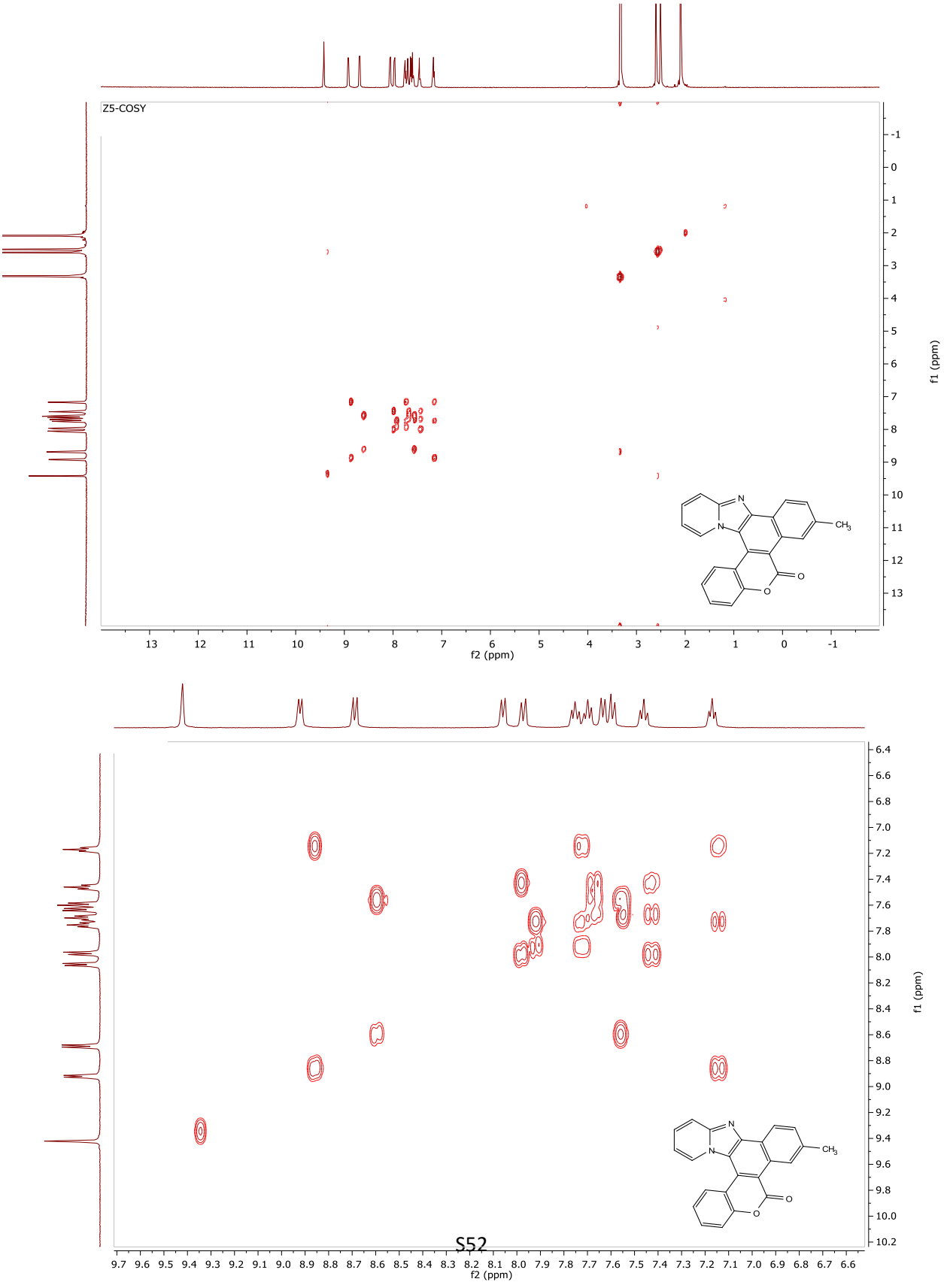
^{1}H NMR spectrum of (4a)



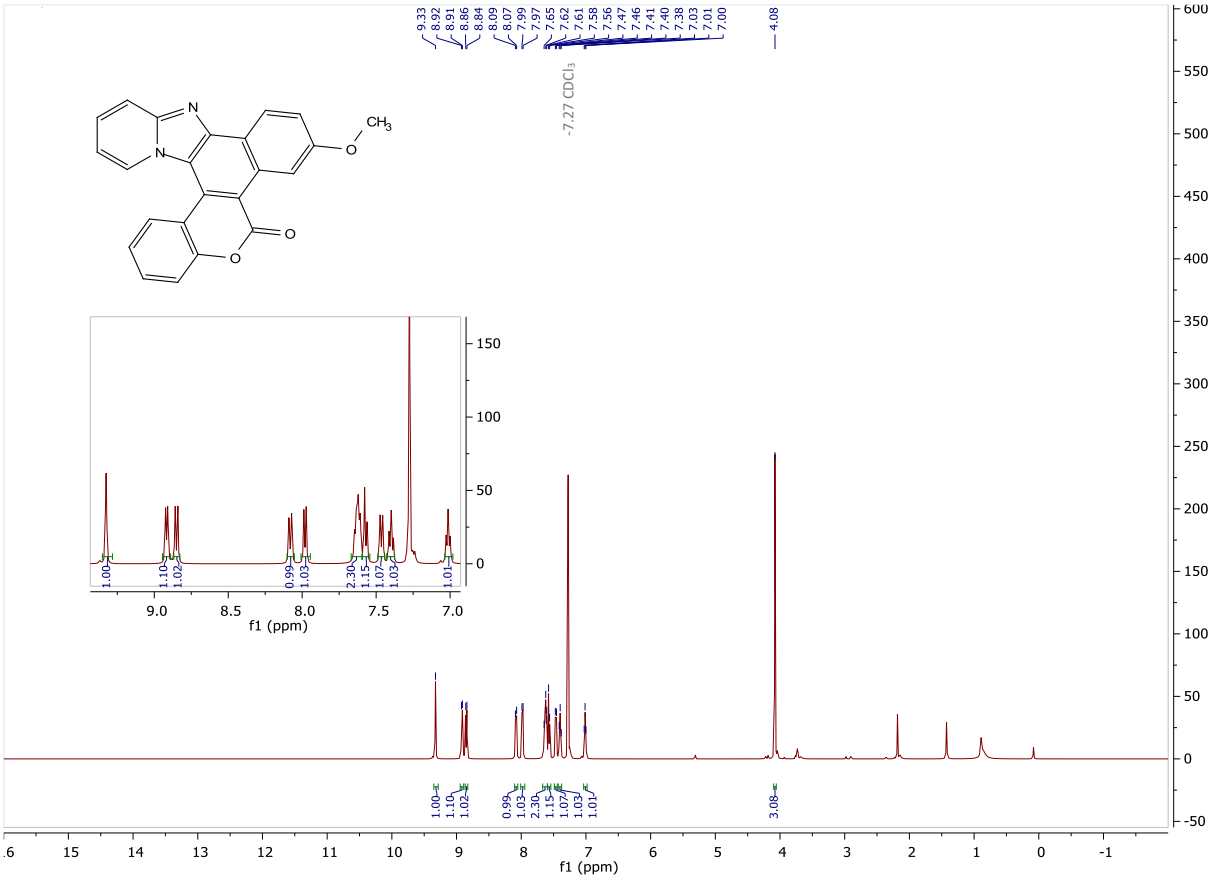
^{13}C NMR spectrum of (4a)



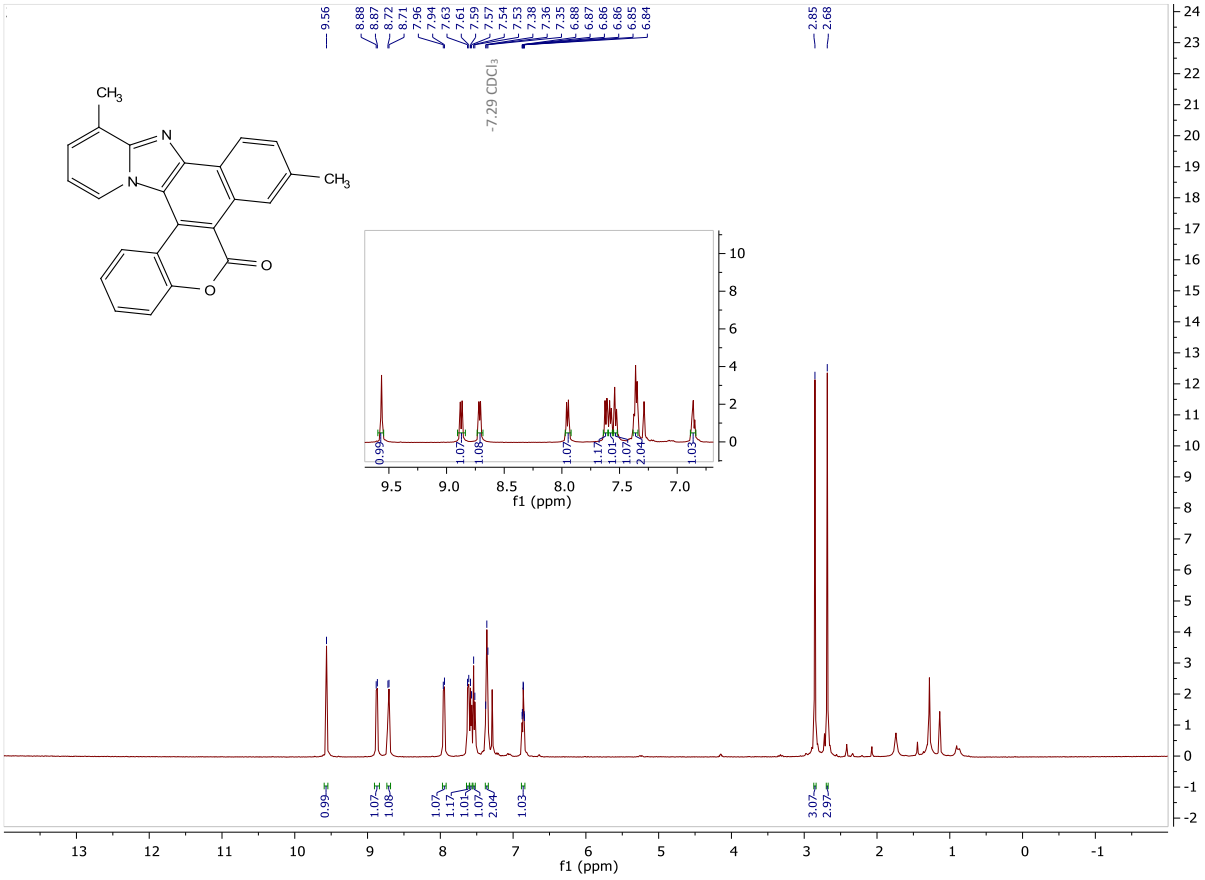
HH-COSY NMR Spectrum of (4a)



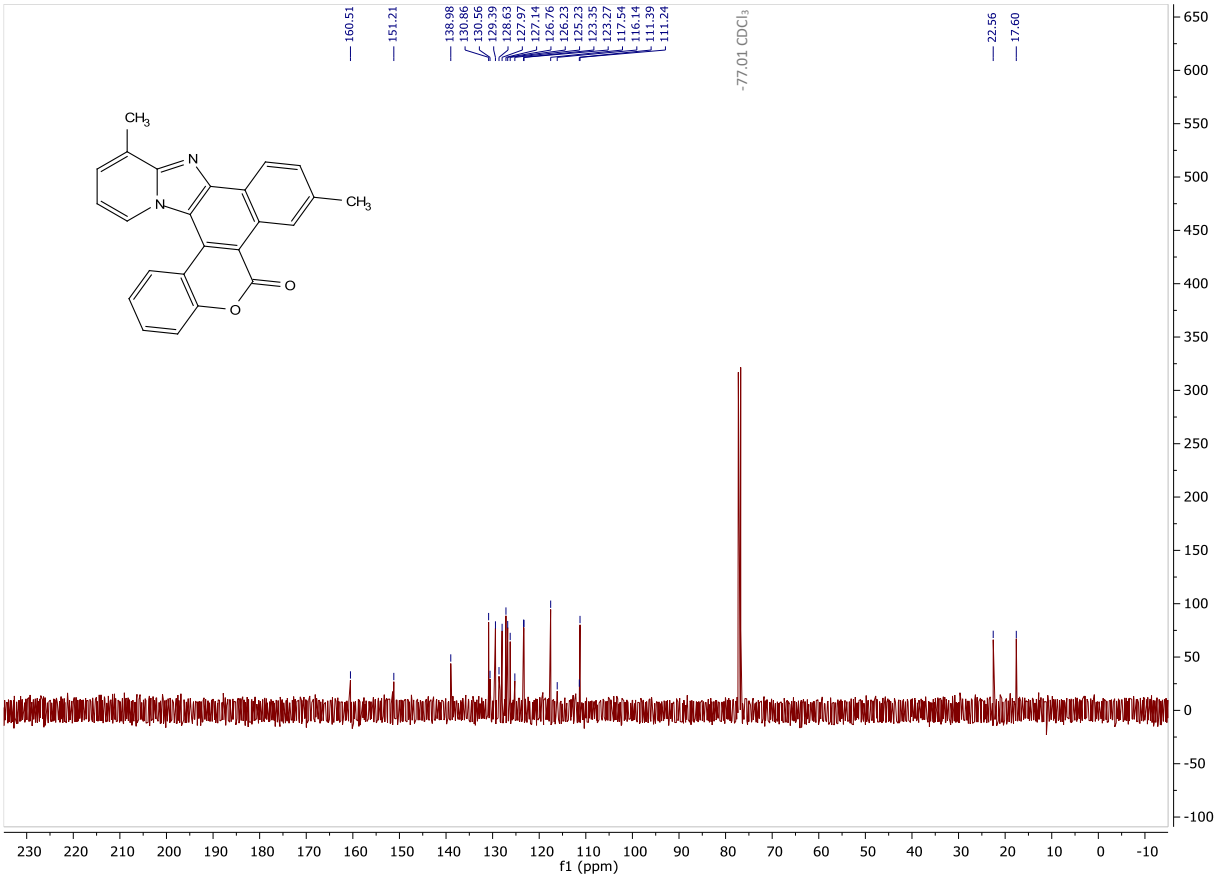
^{1}H NMR spectrum of (4b)



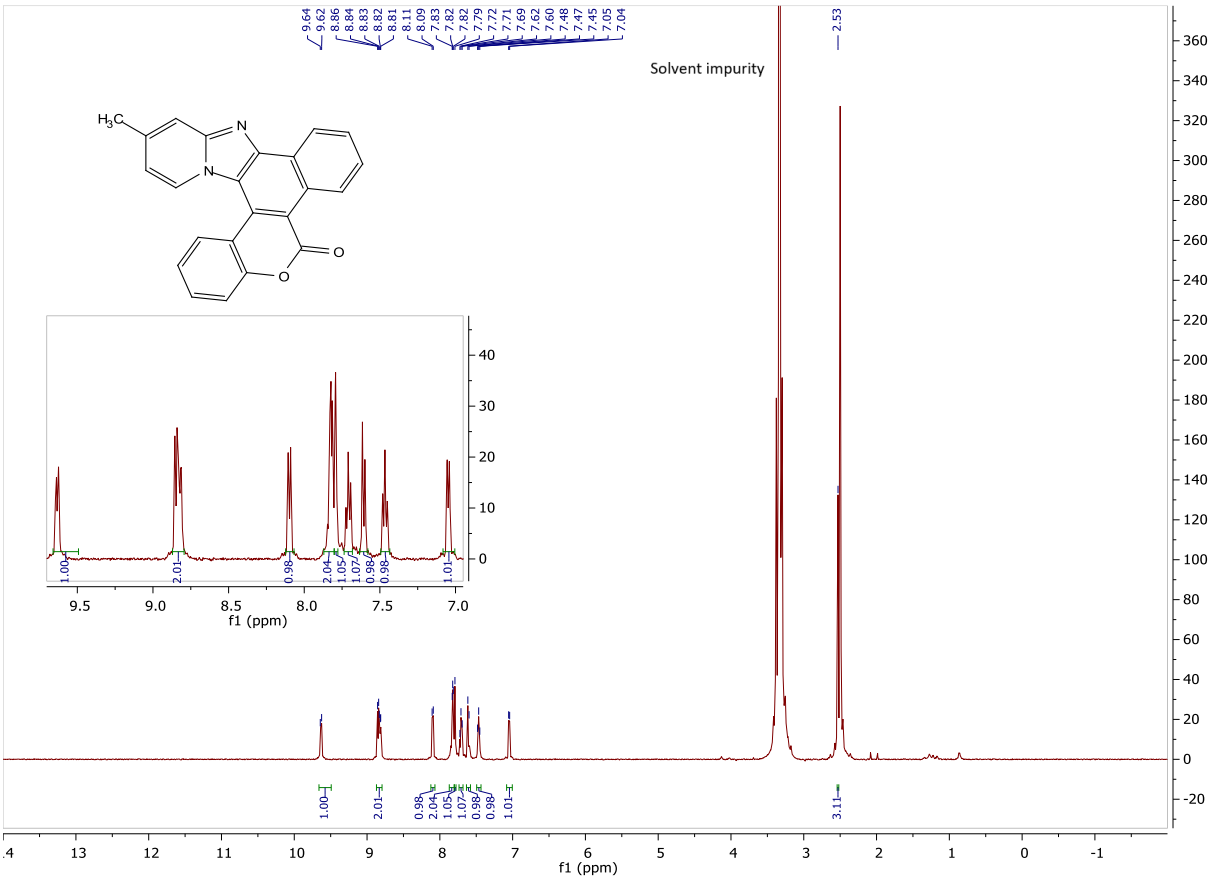
^{1}H NMR spectrum of (4c)



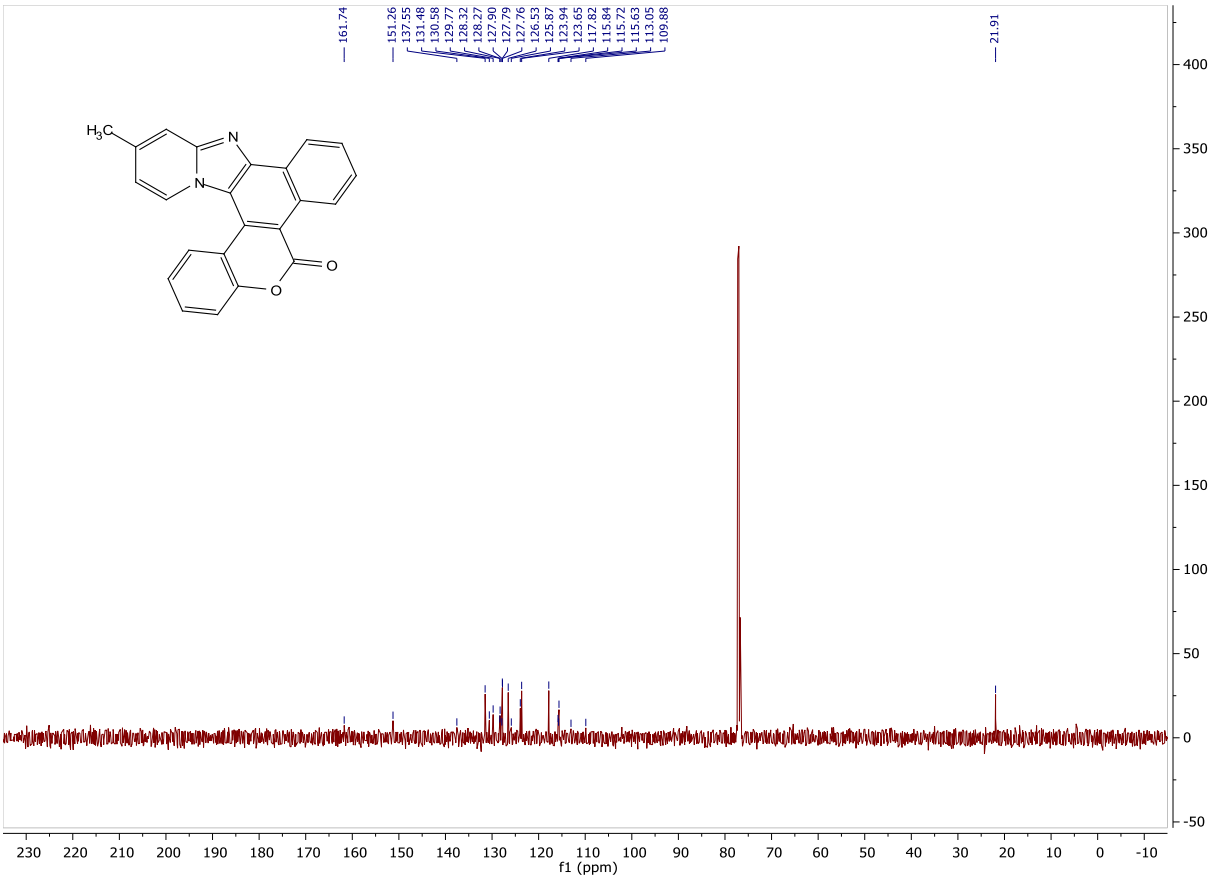
^{13}C NMR spectrum of (4c)



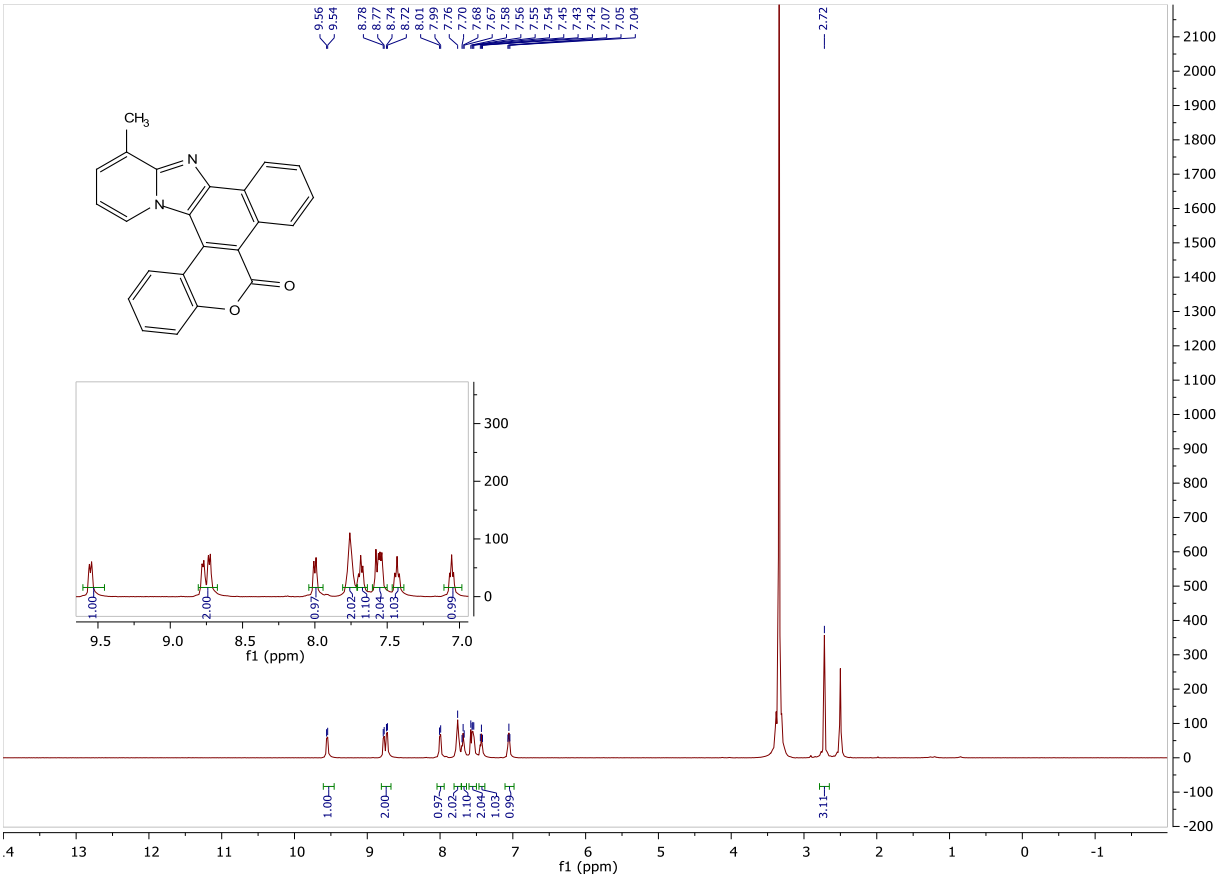
^{1}H NMR spectrum of (4d)



^{13}C NMR spectrum of (4d)



^{1}H NMR spectrum of (4e)



^{13}C NMR spectrum of (4e)