Electronic Supplementary Material (ESI) for ChemComm.

**Supporting Information**

# Highly Fluorescent 1,2-Dihydropyrimido[1,6-*α*]indole: An efficient metal free Synthesis and Photophysical Study

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## Experimental Section:

### General Methods

All reactions were carried out in oven dried glassware with magnetic stirring. All solvents were purified and dried according to standard methods prior to use. All the starting materials were prepared by reported methods.[1,2] $^1H$ spectra were recorded on 400 MHz, 500 MHz or 700 MHz in $CDCl_3$ and $CD_3CN$, $^{13}C$ NMR spectra were recorded on 100 MHz, 125 MHz and 175 MHz in $CDCl_3$ and $CD_3CN$ using TMS or residual solvent signals as internal standard. Data for $^1H$ NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for $^{13}C$ NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained by the ESI (Q-TOF) ionization sources. IR spectra were measured with Bruker FT/IR Vector 22 spectrometer. Routine monitoring of reactions were performed using precoated silica gel TLC plates from E-Merck. All the chromatographic separations were carried out by using silica gel (Acme's, 230-400 mesh). Melting points were recorded by using a melting point apparatus and are uncorrected.

**General procedure for the synthesis of 1,2-dihydropyrimido[1,6-α]indoles 3aa-am:** 1*H*-indole-2-carbaldehydes **1a-d** (Figure 1) (0.3 mmol) was dissolved in dry toluene and 4Å (70 mg) molecular sieves were added to it. After stirring at room temperature for 30 minutes, ethyl *N*-arylideneglycinate **2a-o** (Figure 1) (0.45 mmol) and DBU (0.39 mmol equiv) were added to it. The reaction mixture was allowed to stire at the same temperature for 10 h, filtered it through short celite pad and then toluene was removed under reduced pressure to get a residue. The residue was purified by silica gel column chromatography (5-8% ethyl acetate in petroleum ether) to get pure compounds **3aa-an** and **3ba-da** (Scheme 1).

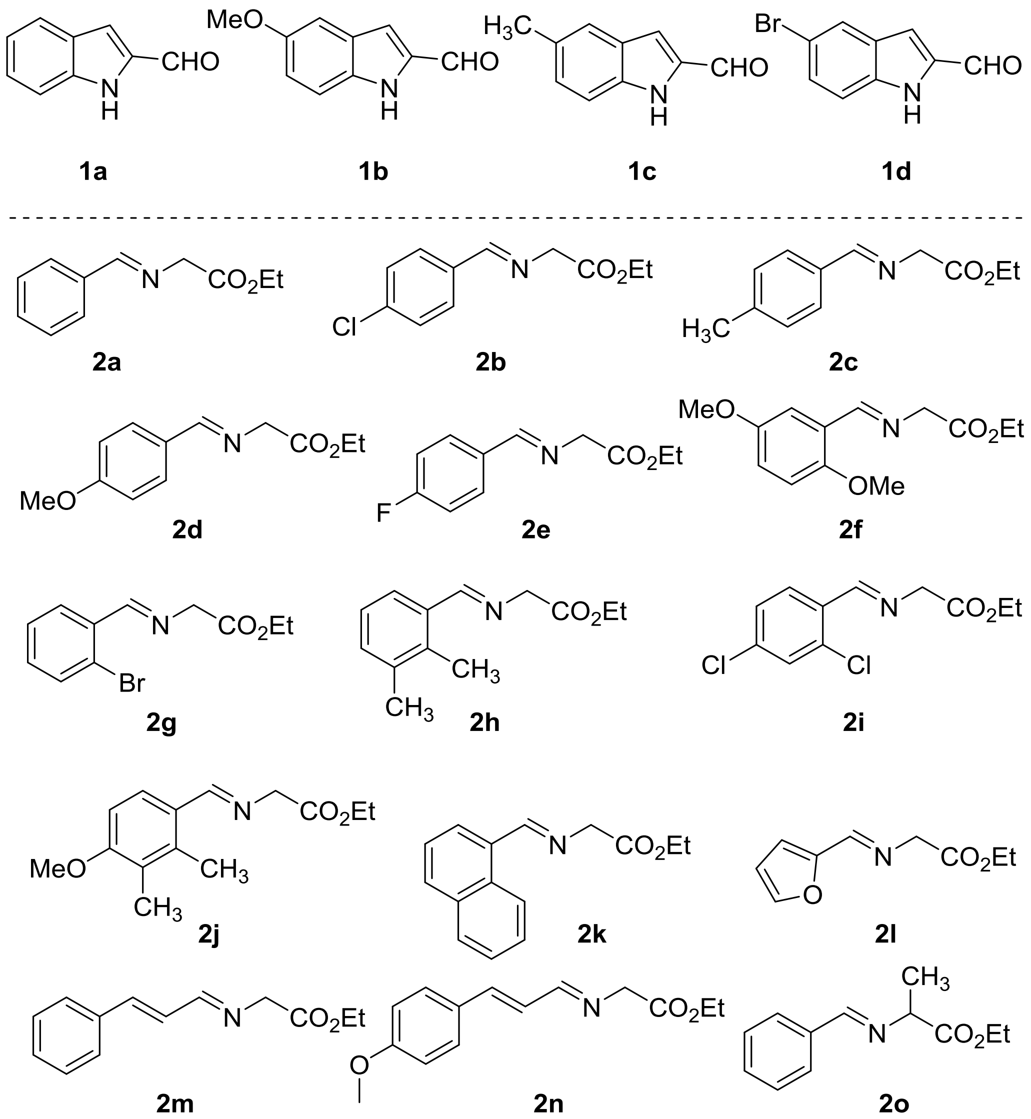
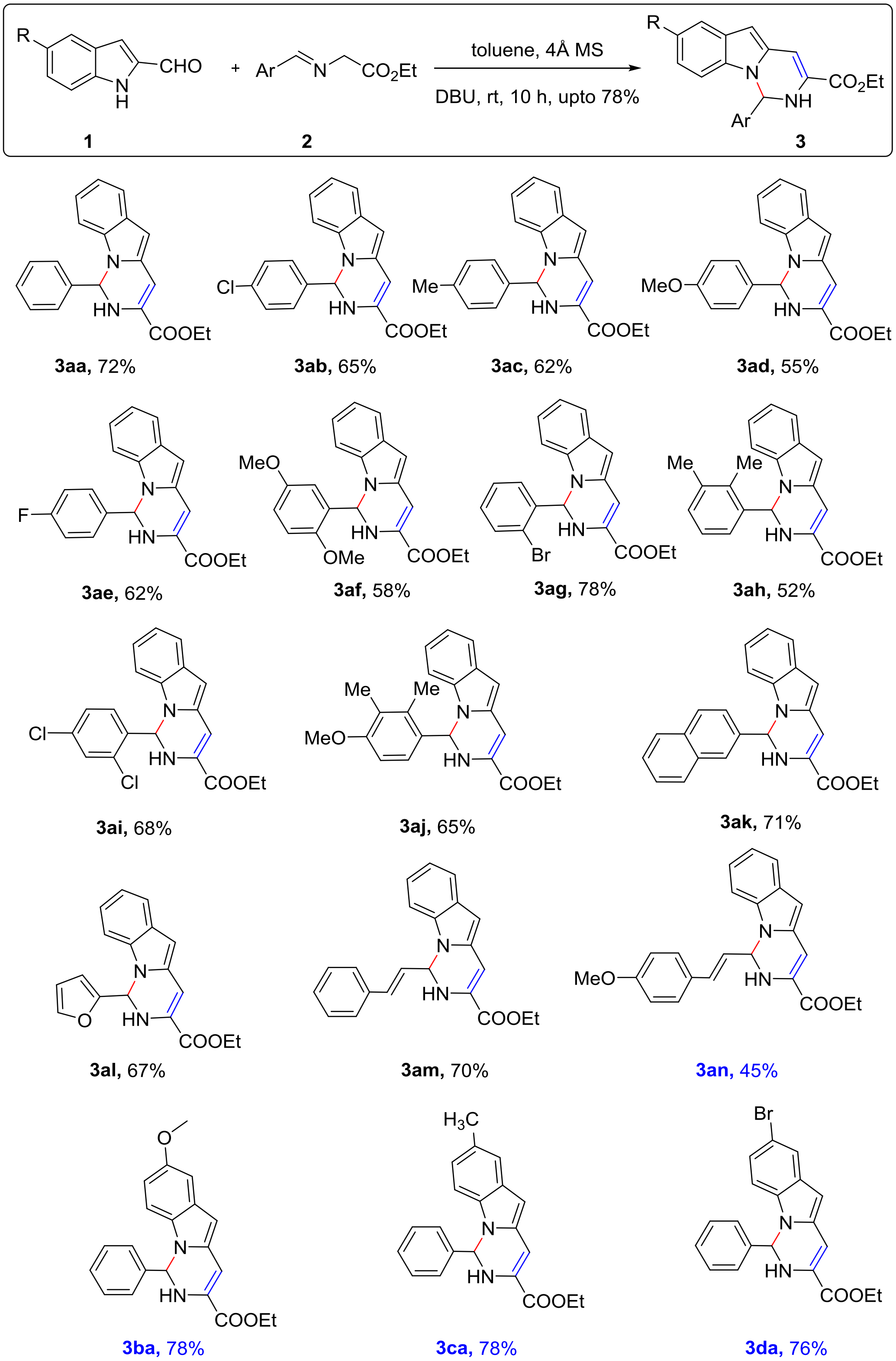
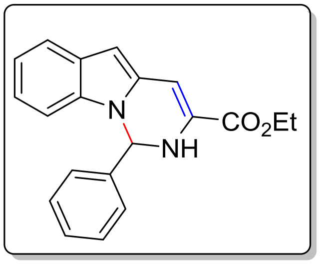


**Figure 1:** Different Indole-2- carbaldehydes (**1a-d**) and ethyl *N*-arylideneglycinate (**2a-o**) used in the reactions.

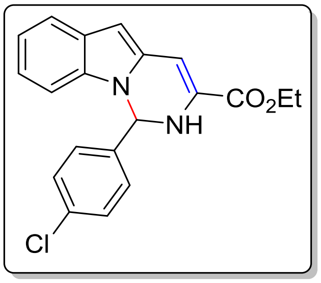


**Scheme 1:** General reaction scheme for the synthesis of pyrimidoindole derivatives.

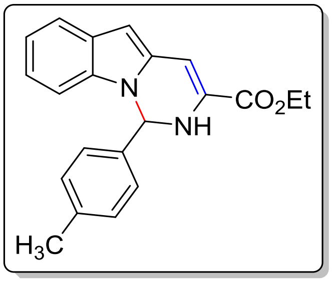
The compound **3aa** was obtained as a yellow solid in 72% yield (74.5 mg). M.P. (84-85) °C; **$^{1}$H NMR (700 MHz, $CD_3CN$):** δ 1.32 (t, 3H, *J* = 7.14 Hz), 4.26 (q, 2H, *J* = 7.12 Hz), 5.84 (s, 1H), 6.62-6.63 (m, 2H), 6.90 (d, 1H, *J* = 2.56 Hz), 7.03-7.08 (m, 4H), 7.11-7.13 (m, 1H), 7.27-7.29 (m, 2H), 7.56-7.57 (m, 1H); **$^{13}$C NMR (175 MHz, $CD_3CN$)**: δ 14.5, 62.5, 68.4, 99.0, 101.0, 110.6, 121.3, 121.4, 123.2, 126.5, 129.6, 129.7, 130.4, 130.7, 134.6, 136.4, 142.3, 164.4. HRMS (ES+) calc. for $C_{20}H_{19}N_2O_2$ [M+H]+: 319.1441 found: 319.1453. IR (film): 3388, 2920, 2356, 1700, 1620, 1477, 1318, 1246, 1137, 1012, 776 cm$^{-1}$.



The compound **3ab** was obtained as a yellow solid in 65% yield (79.4 mg). M.P. (62-63) °C; **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 1.34 (t, 3H, *J* = 7.15 Hz), 4.28 (q, 2H, *J* = 7.12 Hz), 5.07 (s, 1H), 6.57 (s, 1H), 6.64 (d, 2H, *J* = 8.68 Hz), 6.75-6.77 (m, 1H), 7.01-7.06 (m, 3H), 7.24-7.26 (m, 2H), 7.53-7.55 (m, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 14.2, 61.7, 68.3, 99.6, 101.2, 109.7, 120.5, 120.6, 122.6, 127.4, 128.6, 129.2, 129.8, 133.2, 134.9, 135.6, 138.8, 163.7. HRMS (ES+) calc. for $C_{20}H_{18}ClN_2O_2$ [M+H]+: 352.0979 found: 352.0976. IR (film): 3382, 2914, 2361, 1702, 1485, 1320, 1249, 1084, 1012, 821 cm$^{-1}$

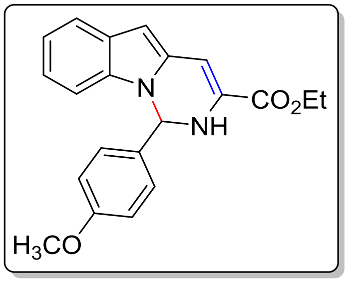


The compound **3ac** was obtained as a yellow liquid in 62% yield (75.8 mg). **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 1.34 (t, 3H, *J* = 7.14 Hz), 2.31 (s, 3H), 4.27 (q, 2H, *J* = 7.11 Hz), 5.04 (s, 1H), 6.56 (s, 1H), 6.59 (bs, 1H), 6.65 (bs, 1H), 6.69-6.71 (m, 1H), 6.95-7.04 (m, 2H), 7.06-7.11 (m, 4H), 7.52-7.54 (m, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 14.2, 21.2, 61.6, 69.1, 99.4, 100.9, 110.0, 120.3, 120.4, 122.3, 126.2, 129.1, 129.6, 129.8, 133.6, 135.8, 137.3, 139.0, 163.8.

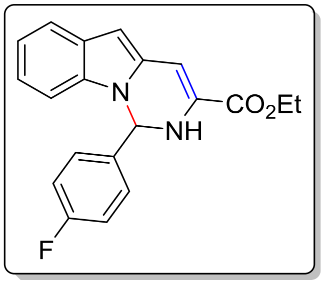


HRMS (ES+) calc. for $C_{21}H_{21}N_2O_2$ $[M+H]^+$: 333.1598 found: 333.1608. IR (film): 3372, 2914, 2851, 1702, 1594, 1320, 1243, 1127, 1015, 774 cm$^{-1}$’\m\j\

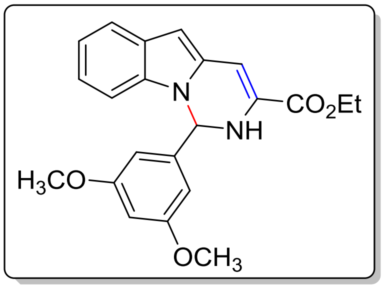
The compound **3ad** was obtained as a yellow liquid in 55% yield (75.2 mg). **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.39 (t, 3H, *J* = 7.13 Hz), 3.81 (s, 3H), 4.32 (q, 2H, *J* = 7.12 Hz), 5.05 (s, 1H), 6.59-6.60 (m, 2H), 6.68-6.70 (m, 2H), 6.86-6.89 (m, 2H), 6.99-7.07 (m, 2H), 7.18-7.21 (m, 2H), 7.56-7.58 (m, 1H); **$^{13}$C NMR (125 MHz, CDCl$_3$**): δ 14.2, 55.3, 61.6, 69.1, 99.5, 101.0, 110.2, 114.3, 120.2, 120.4, 122.3, 127.8, 129.3, 129.9, 132.3, 133.8, 135.8, 160.2, 163.8. HRMS (ES+) calc. for $C_{21}H_{19}N_2O_3$ $[M-H]^+$: 347.1390 found: 347.1408. IR (film): 3372, 2914, 2361, 1708, 1604, 1511, 1318, 1249, 1169, 829, 750 cm$^{-1}$.



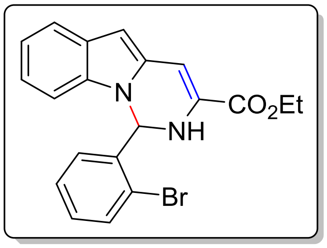
The compound **3ae** was obtained as a yellow liquid in 62% yield (75.7 mg). **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.39 (t, 3H, *J* = 7.14 Hz), 4.31-4,35 (m, 2H), 5.09 (s, 1H), 6.62 (s, 1H), 6.66 (d, 1H, *J* = 1.44 Hz), 6.71 (d, 1H, *J* = 1.51 Hz), 6.74-6.76 (m, 1H), 7.00-7.09 (m, 4H), 7.17-7.20 (m, 2H), 7.58-7.59 (m, 1H); **$^{13}$C NMR (125 MHz, CDCl$_3$**): δ 14.2, 61.7, 68.5, 99.5, 101.2, 109.8, 115.9, 116.1, 120.5, 120.5, 122.5, 128.0, 128.0, 128.8, 129.8, 133.4, 135.6, 136.2, 136.2, 162.0, 163.7, 164.0. HRMS (ES+) calc. for $C_{20}H_{16}FN_2O_2$ $[M-H]^+$: 335.1190 found: 335.1201. IR (film): 3395, 2927, 2844, 2360, 1719, 1600, 1467, 1248, 1073, 738 cm$^{-1}$.



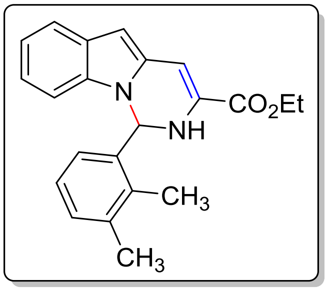
The compound **3af** was obtained as a yellow solid in 58% yield (88.5 mg). M.P. (70-71) $^{\circ}$C; **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.35 (t, 3H, *J* = 7.12 Hz), 3.46 (s, 3H), 3.98 (s, 3H), 4.23-4.33 (m, 2H), 5.43 (d, 1H, *J* = 3.05 Hz),



5.67 (s, 1H), 6.61 (s, 1H), 6.66 (d, 1H, *J* = 1.52 Hz), 6.70-6.73 (m, 1H), 6.86 (d, 1H, *J* = 8.86 Hz), 7.06-7.13 (m, 4H), 7.60-7.62 (m, 1H); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 55.3, 55.9, 61.4, 63.2, 99.4, 100.4, 109.2, 111.2, 112.4, 113.1, 120.3, 120.5, 122.5, 128.3, 129.3, 129.4, 133.6, 135.5, 149.9, 153.2, 163.9. HRMS (ES+) calc. for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1652 found: 379.1652. IR (film): 3393, 2925, 2835, 1705, 1601, 1493, 1318, 1246, 1042, 729 cm$^{-1}$.

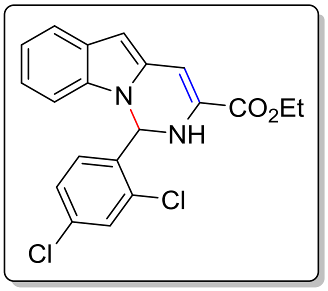


The compound **3ag** was obtained as a yellow solid in 78% yield (101.3 mg). M.P. (85-86) °C; **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.38 (t, 3H, *J* = 7.16 Hz), 4.27-4.34 (m, 2H), 5.74 (s, 1H), 6.10-6.14 (m, 1H), 6.68 (s, 1H), 6.74 (d, 1H, *J* = 1.53 Hz), 7.00-7.04 (m, 2H), 7.10-7.15 (m, 3H), 7.20 (d, 1H, *J* = 2.09 Hz), 7.62-7.66 (m, 2H); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 61.7, 66.9, 99.2, 100.7, 109.3, 120.6, 120.7, 121.0, 122.7, 126.9, 127.9, 128.4, 129.6, 130.1, 133.2, 133.4, 135.3, 138.1, 163.6. HRMS (ES+) calc. for $C_{20}H_{16}BrN_2O_2$ $[M-H]^+$: 395.0390 found: 395.0376. IR (film): 3382, 2973, 2351, 1702, 1596, 1320, 1246, 1132, 1010, 774 cm$^{-1}$.

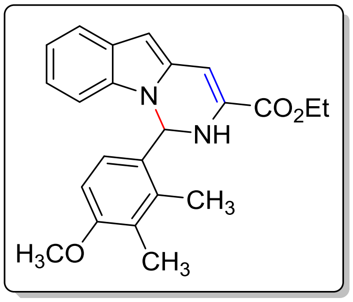


The compound **3ah** was obtained as a yellow liquid in 52% yield (72.7 mg). **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.39 (t, 3H, *J* = 7.12 Hz), 2.37 (s, 3H), 2.43 (s, 3H), 4.30-4.34 (m, 2H), 5.00 (s, 1H), 6.56 (d, 1H, *J* = 8.26 Hz), 6.62-6.63 (m, 2H), 6.69 (d, 1H, *J* = 1.40 Hz), 6.93-7.07 (m, 4H), 7.19 (d, 1H, *J* = 7.42 Hz), 7.58 (d, 1H, *J* = 7.85 Hz); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 14.7, 21.0, 61.6, 99.1, 100.9, 110.0, 120.2, 120.3, 122.4, 125.1, 126.0, 129.3, 129.9, 130.7, 134.1, 135.9, 136.8, 138.0, 163.8. HRMS (ES+) calc. for $C_{22}H_{23}N_2O_2$ $[M+H]^+$: 347.1754 found: 347.1758. IR (film): 3393, 2925, 2356, 1702, 1479, 1320, 1249, 1137, 1025, 774 cm$^{-1}$.

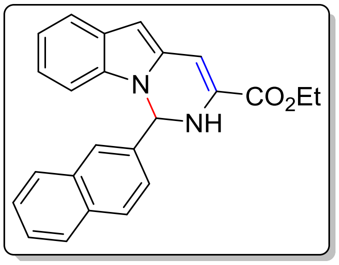
The compound **3ai** was obtained as a yellow liquid in 68% yield (92.9 mg). **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.37 (t, 3H, *J* = 7.15 Hz), 4.26-4.33 (m, 2H), 5.60 (s, 1H), 5.97 (d, 1H, *J* = 8.38 Hz), 6.65 (s, 1H), 6.70 (d, 1H, *J* = 1.51 Hz), 6.93-6.95 (m, 1H), 6.99-7.01 (m, 1H), 7.11-7.15 (m, 2H), 7.17 (d, 1H, *J* = 2.11 Hz), 7.46 (d, 1H, *J* = 2.10 Hz), 7.61-7.63 (m, 1H); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 61.7, 64.3, 99.4, 101.0,109.1, 120.7, 120.8, 122.9, 127.6, 127.6, 128.2, 129.5, 129.8, 131.8, 133.1, 135.0, 135.1, 135.3, 163.5. HRMS (ES+) calc. for $C_{20}H_{15}Cl_2N_2O_2$ $[M-H]^+$: 385.0505 found: 385.0514. IR (film): 3392, 2925, 2855, 2360, 1707, 1599, 1369, 1247, 1139, 1017 cm$^{-1}$.



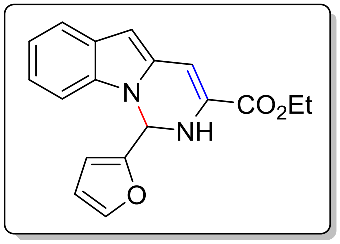
The compound **3aj** was obtained as a yellow liquid in 65% yield (73.4 mg). **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.38 (t, 3H, *J* = 7.14 Hz), 2.23 (s, 3H), 2.41 (s, 3H), 3.82 (s, 3H), 4.29-4.34 (m, 2H), 4.94 (s, 1H), 6.52 (d, 1H, *J* = 8.29 Hz), 6.59 (s, 1H), 6.62-6.68 (m, 3H), 6.83 (s, 1H), 6.93-6.97 (m, 1H), 7.02-7.05 (m, 1H), 7.55-7.57 (m, 1H); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 11.9, 14.1, 14.2, 15.2, 22.7, 29.7, 31.9, 55.4, 61.6, 99.1, 100.8, 107.7, 110.2, 120.1, 120.3, 122.3, 125.8, 126.3, 128.9, 129.6, 129.9, 134.4, 136.0, 157.9, 163.8. HRMS (ES+) calc. for $C_{23}H_{23}N_2O_3$ $[M-H]^+$: 375.1703 found: 375.1702. IR (film): 3381, 2923, 2847, 2360, 2334, 1721, 1598, 1263, 1101, 1019, 749 cm$^{-1}$.



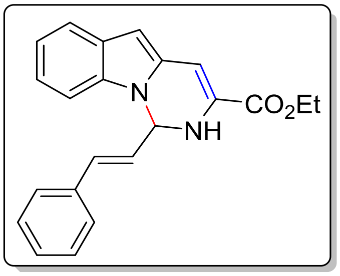
The compound **3ak** was obtained as a yellow liquid in 71% yield (90.6 mg). **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.39 (t, 3H, *J* = 7.12 Hz), 4.30-4.35 (m, 2H), 5.21 (s, 1H), 6.70 (s, 1H), 6.78 (d, 1H, *J* = 1.49 Hz), 6.80-6.82 (m, 1H), 6.85 (d, 1H, *J* = 1.52 Hz), 6.99-7.02 (m, 1H), 7.07-7.11 (m, 1H),



7.39 (dd, 1H, *J* = 1.82 Hz, 8.52 Hz), 7.52-7.55 (m, 2H), 7.62-7.64 (m, 2H), 7.82-7.86 (m, 3H); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.3, 61.7, 69.5, 99.3, 101.3, 110.1, 120.4, 120.5, 122.5, 123.8, 125.3, 126.5, 126.6, 127.8, 128.3, 129.0, 129.4, 129.9, 133.0, 133.6, 135.9, 137.6, 163.7. HRMS (ES+) calc. for $C_{24}H_{21}N_2O_2$ [M+H]$^+$: 369.1598 found: 369.1590. IR (film): 3377, 2920, 1702, 1623, 1599, 1477, 1368, 1246, 1137, 1010, 747 cm$^{-1}$.



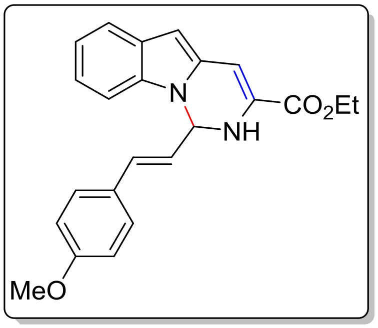
The compound **3al** was obtained as a yellow solid in 77% yield (69.4 mg). M.P. (65-66) °C; **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.40 (t, 3H, *J* = 7.14 Hz), 4.33-4.38 (m, 2H), 5.34 (s, 1H), 5.80-5.81 (m, 1H), 6.21 (dd, 1H, *J* = 1.81 Hz, 3.24 Hz), 6.59 (s, 1H), 6.73 (d, 1H, *J* = 1.43 Hz), 6.81 (d, 1H, *J* = 1.86 Hz), 7.11-7.15 (m, 2H), 7.17-7.20 (m, 1H), 7.35-7.36 (m, 1H), 7.60-7.62 (m, 1H); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 61.7, 62.3, 100.5, 101.3, 107.2, 109.2, 110.3, 120.3, 120.6, 122.7, 128.9, 129.6, 132.8, 135.6, 142.9, 151.4, 163.7. HRMS (ES+) calc. for $C_{18}H_{17}N_2O_3$ [M+H]$^+$: 309.1234 found: 309.1236. IR (film): 3383, 2360, 1704, 1601, 1479, 1371, 1250, 1139, 1012, 734 cm$^{-1}$.



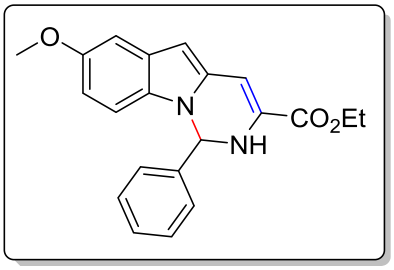
The compound **3am** was obtained as a yellow solid in 70% yield (78.5 mg). M.P. (79-80) °C; **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.37 (t, 3H, *J* = 7.12 Hz), 4.32 (q, 2H, *J* = 7.12 Hz), 4.97 (s, 1H), 6.27-6.36 (m, 2H), 6.50-6.53 (m, 2H), 6.62 (d, 1H, *J* = 1.49 Hz), 7.04-7.08 (m, 1H), 7.11-7.16 (m, 1H), 7.20-7.24 (m, 3H), 7.25-7.28 (m, 2H), 7.29-7.32 (m, 2H), 7.53 (d, 1H, *J* = 7.93 Hz); **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.3, 61.7, 68.0, 99.6, 100.1, 109.5, 120.3, 120.6, 122.5, 125.4, 126.9, 128.4, 128.6, 128.7, 129.8, 131.6, 132.4, 135.3, 135.5, 163.8. HRMS (ES+)

calc. for $C_{22}H_{20}NaN_2O_2$ [M+Na]$^+$: 367.1417 found: 367.1426. IR (film): 3326, 2926, 1726, 1607, 1450, 1207, 1086, 1025, 863, 754 cm$^{-1}$.

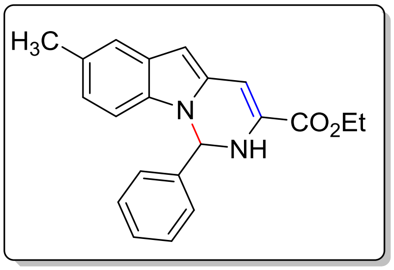
The compound **3an** was obtained as a yellow gum in 45% yield (36 mg). **$^1$H NMR (400 MHz, CDCl$_3$):** δ 1.37 (t, 3H, *J* = 7.12 Hz), 3.81 (s, 3H), 4.32 (q, 2H, *J* = 7.10 Hz), 4.95 (s, 1H), 6.21-6.35 (m, 2H), 6.43 (bs, 1H), 6.49-6.56 (m, 1H), 6.60-6.64 (m, 1H), 7.00 (d, 1H, *J* = 2.49 Hz), 7.11-7.18 (m, 3H), 7.22-7.23 (m, 1H), 7.28-7.32 (m, 3H); **$^{13}$C NMR (100 MHz, CDCl$_3$)**: δ 14.1, 22.7, 31.9, 55.8, 61.6, 68.3, 99.7, 100.8, 102.3, 110.2, 112.7, 125.6, 126.9, 128.6, 130.3, 130.9, 131.7, 133.1, 135.3, 154.5, 163.8. HRMS (ES+) calc. for $C_{23}H_{23}N_2O_3$ [M+H]$^+$: 375.1703 found: 375.1696. IR (film): 3421, 3378, 2958, 2521, 1804, 1639, 1471, 1209, 1081, 865, 749 cm$^{-1}$.



The compound **3ba** was obtained as a yellow solid in 78% yield (80.7 mg). M.P. (125-126) °C; **$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.38 (t, 3H, *J* = 7.18 Hz), 3.83 (s, 3H), 4.32 (q, 2H, *J* = 7.18 Hz), 5.10 (s, 1H), 6.55-6.69 (m, 5H), 7.04 (s, 1H), 7.22-7.36 (m, 5H). **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 55.7, 61.6, 69.5, 99.5, 100.8, 102.1, 110.8, 112.5, 126.3, 128.9, 129.0, 129.2, 130.4, 131.2, 134.3, 140.1, 154.5, 163.8. HRMS (ES+) calc. for $C_{21}H_{21}N_2O_3$ [M+H]$^+$: 349.1547 found: 349.1565. IR (film): 3384, 2919, 2528, 2368, 1809, 1772, 1609, 1519, 1379, 1246, 1176, 849, 786 cm$^{-1}$

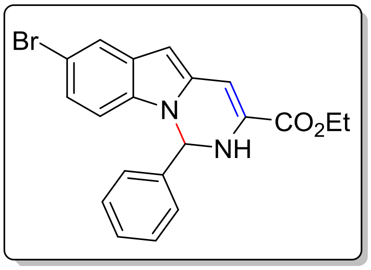


The compound **3ca** was obtained as a brown solid in 78% yield (78.2 mg). M.P. (109-110) °C;



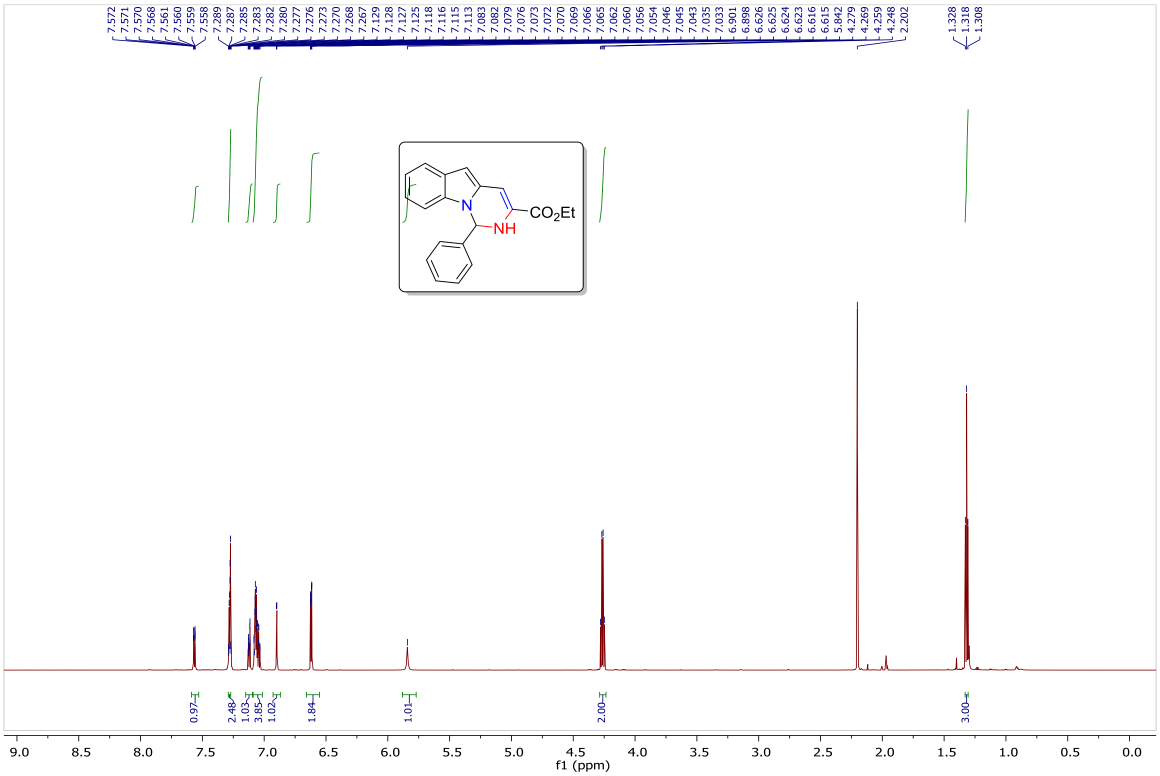
**$^1$H NMR (500 MHz, CDCl$_3$):** δ 1.37 (t, 3H, *J* = 7.14 Hz), 2.39 (s, 3H), 4.32 (q, 2H, *J* = 7.11 Hz), 5.08 (s, 1H), 6.53 (s, 1H), 6.61-6.63 (m, 2H), 6.69 (s, 1H), 6.84 (d, 1H, *J* = 8.42 Hz), 7.20-7.22 (m, 2H), 7.32-7.36 (m, 4H). **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 21.3, 61.6, 69.3, 99.7, 100.6, 109.7, 120.1, 124.0, 126.2, 128.8, 128.9, 129.1, 129.6, 130.1, 133.6, 134.2, 140.3, 163.8. HRMS (ES+) calc. for $C_{21}H_{21}N_2O_2$ $[M+H]^+$: 333.1598 found: 333.1601. IR (film): 3372, 2916, 2878, 1746, 1681, 1556, 1329, 1286, 1208, 1130, 1011, 786 cm$^{-1}$

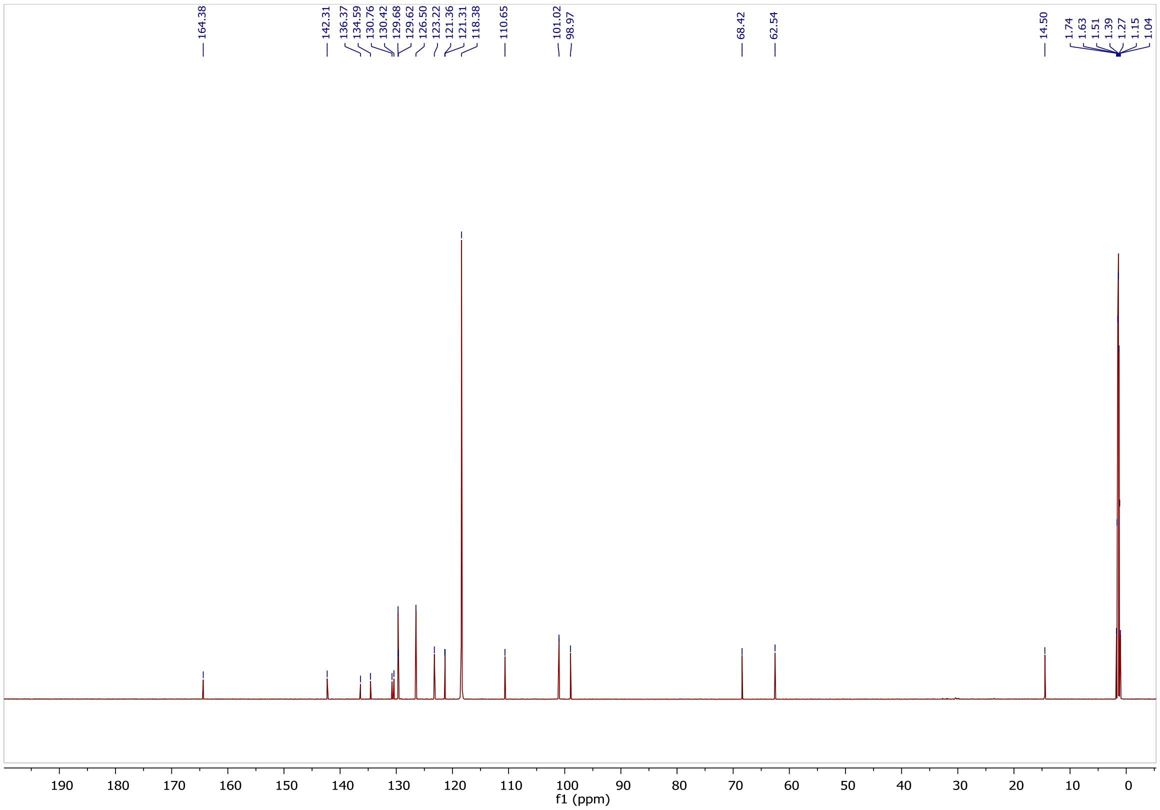
The compound **3da** was obtained as a yellow solid in 76% yield (160 mg). M.P. (92-93) °C;



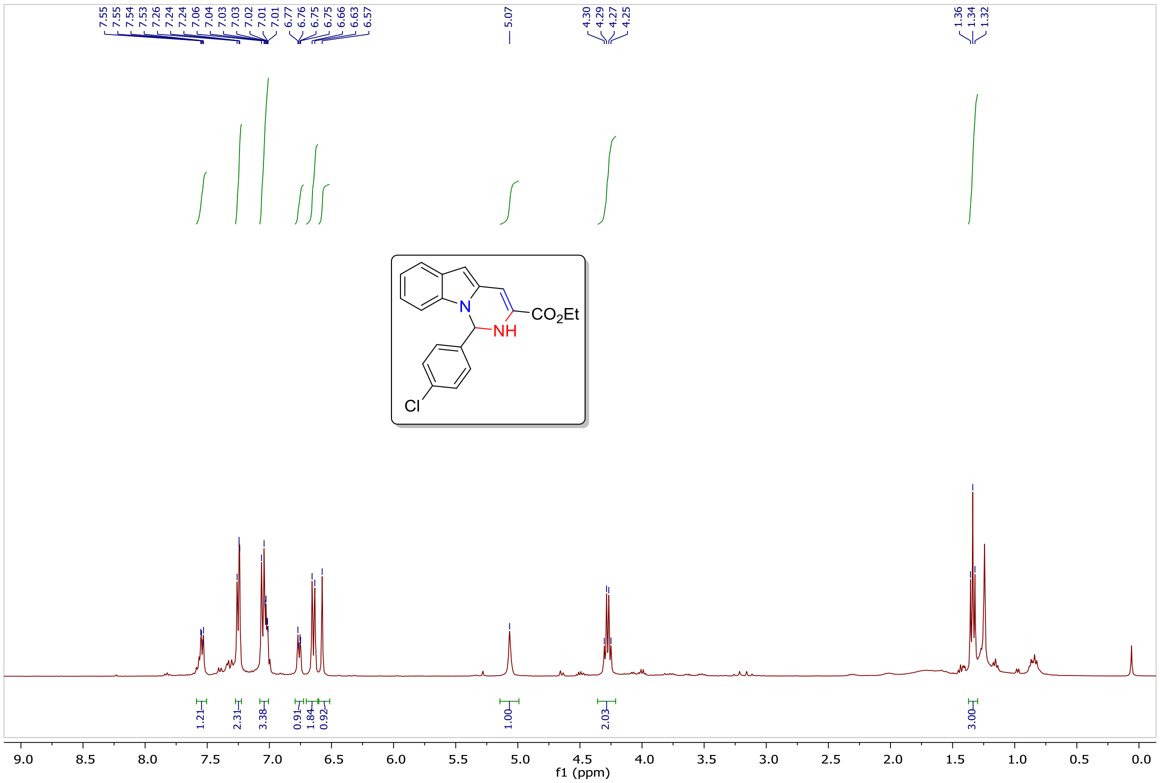
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 1.34 (t, 3H, *J* = 7.14 Hz), 4.27 (q, 2H, *J* = 7.14 Hz), 5.06 (s, 1H), 6.57-6.66 (m, 3H), 6.75-6.77 (m, 1H), 7.01-7.07 (m, 3H), 7.23-7.26 (m, 3H), 7.53-7.57 (m, 1H). **$^{13}$C NMR (125 MHz, CDCl$_3$)**: δ 14.2, 61.7, 68.3, 99.6, 101.3, 109.7, 120.5, 120.6, 122.6, 127.4, 128.6, 129.2, 129.8, 133.2, 134.9, 135.6, 138.8, 163.7. HRMS (ES+) calc. for $C_{20}H_{18}BrN_2O_2$ $[M+H]^+$: 397.0546 found: 397.0523. IR (film): 3381, 2973, 2354, 1708, 1597, 1568, 1304, 1258, 1129, 1010, 846 cm$^{-1}$

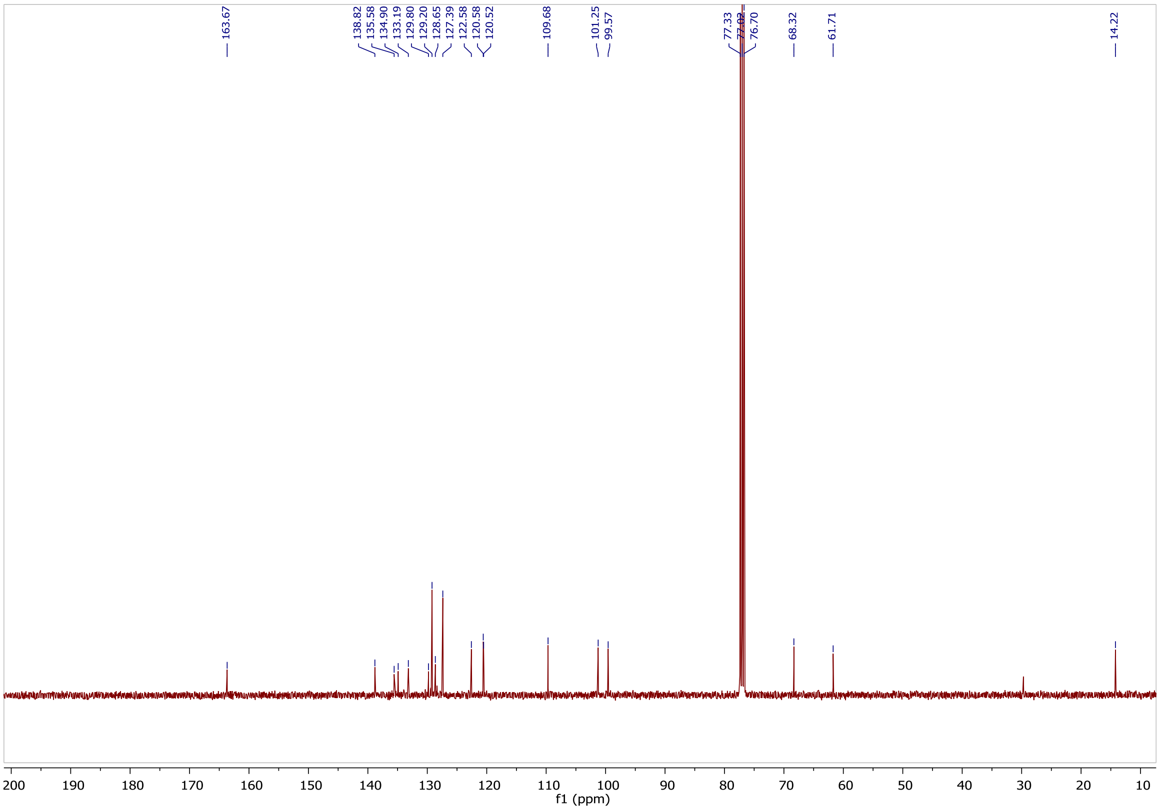
# NMR spectra of compound 3aa



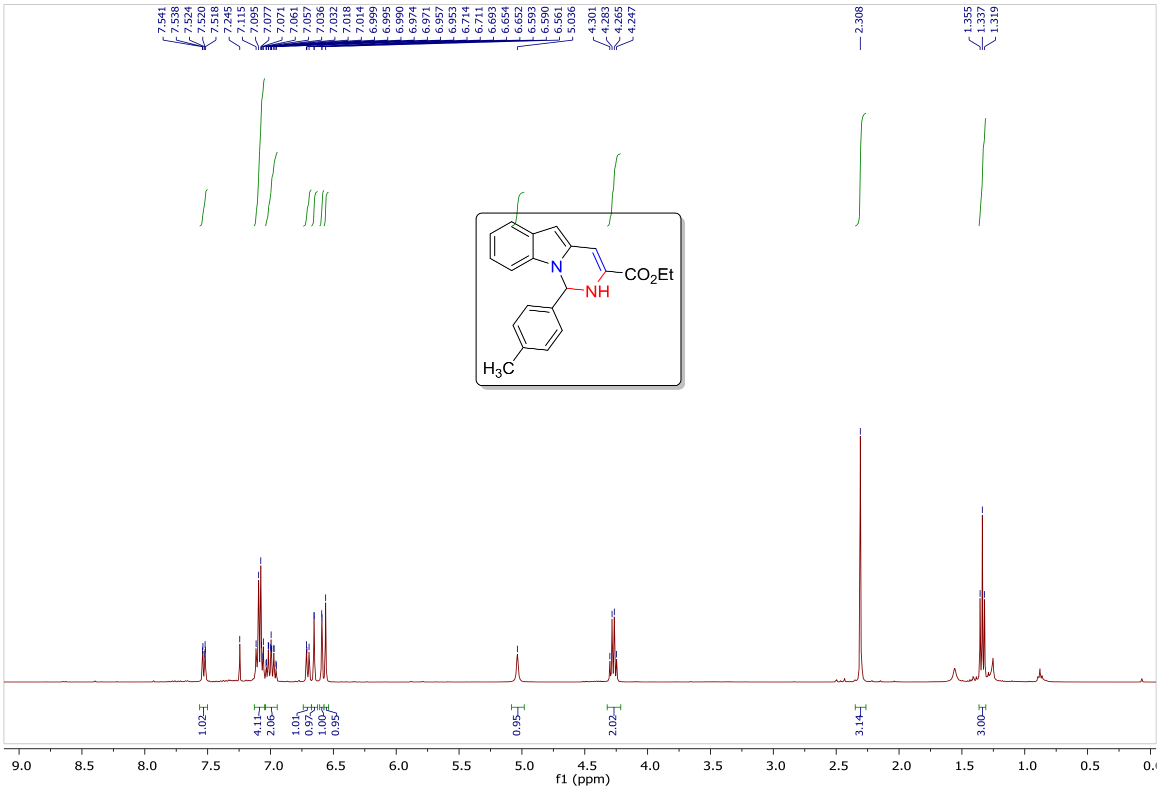


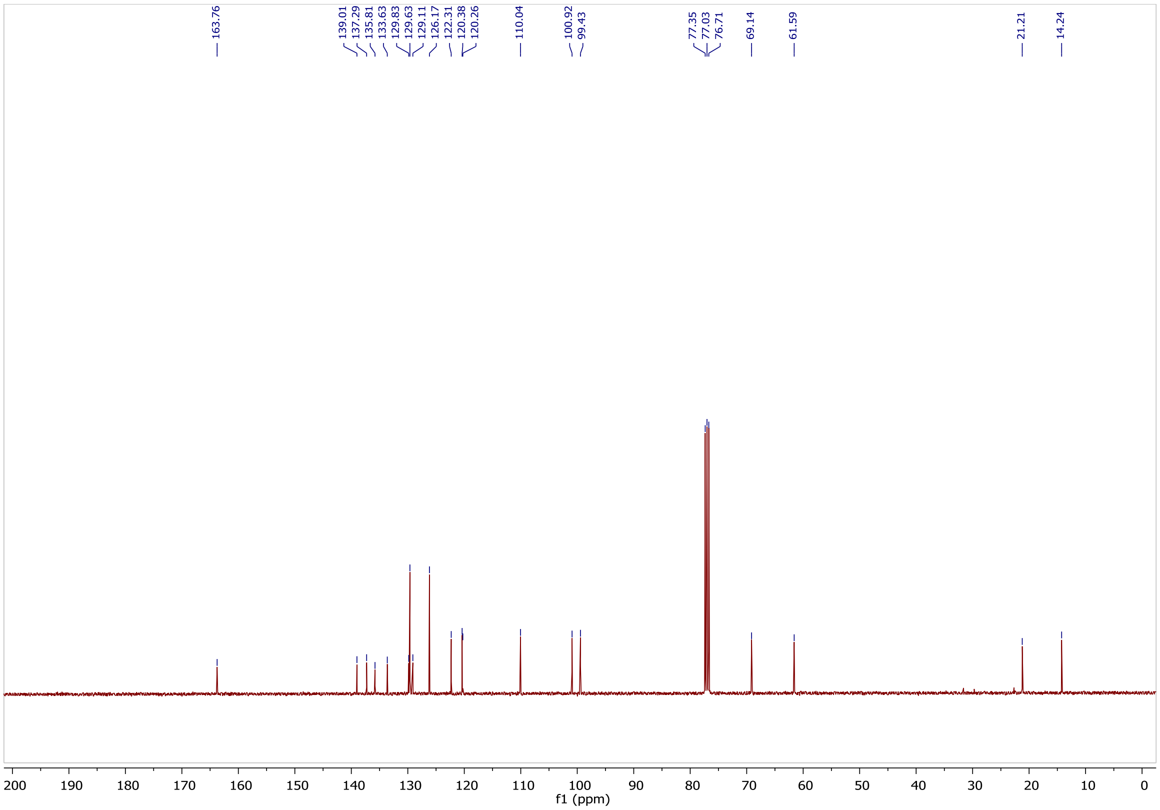
# NMR spectra of compound 3ab



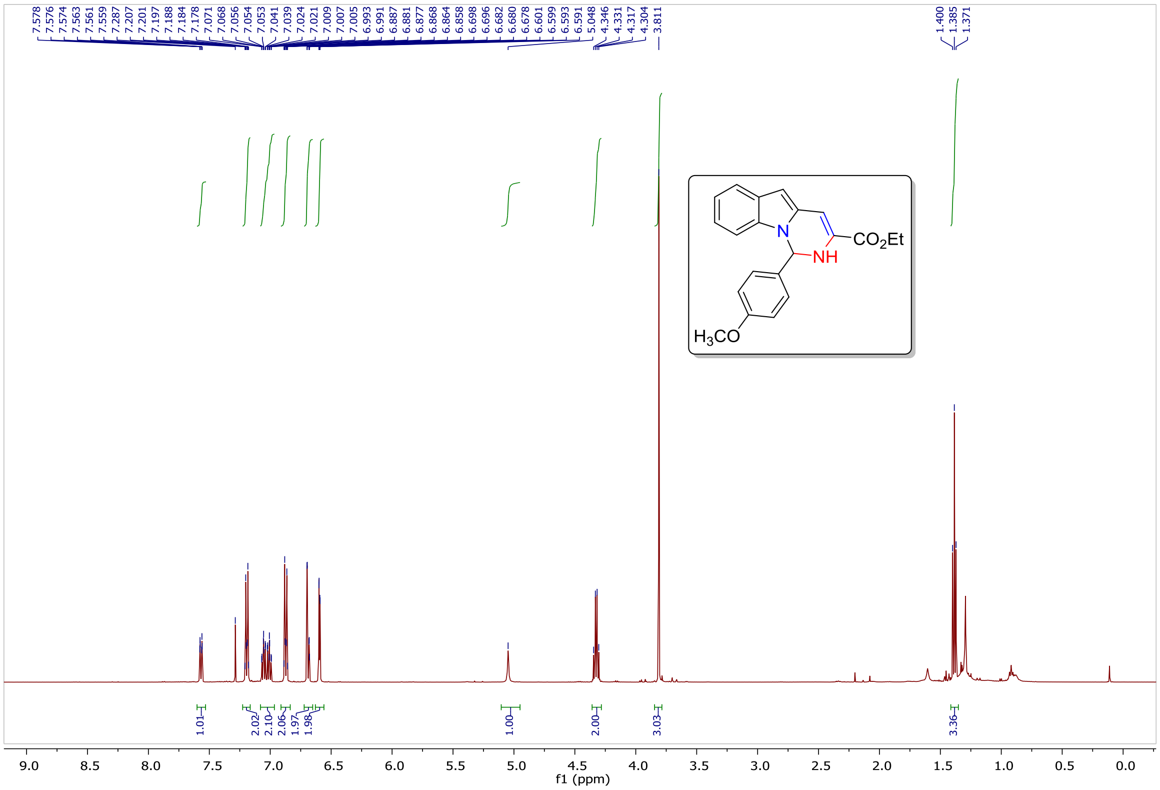


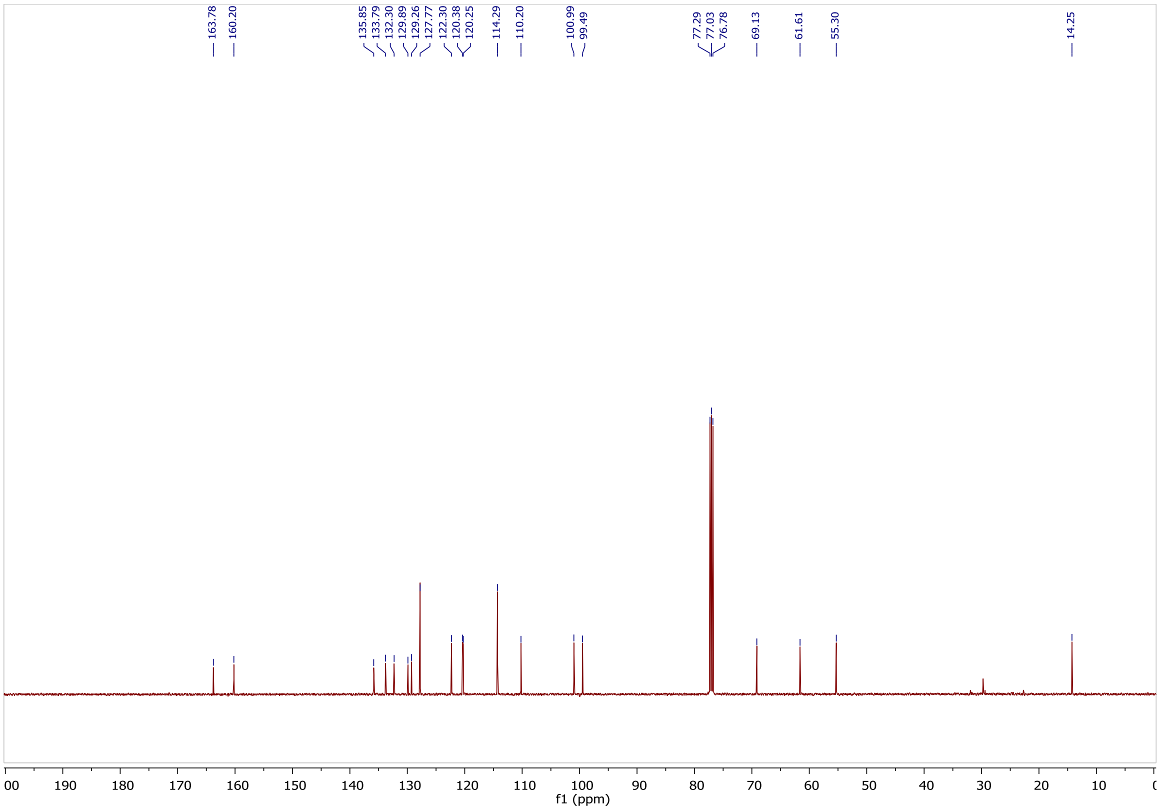
# NMR spectra of compound 3ac



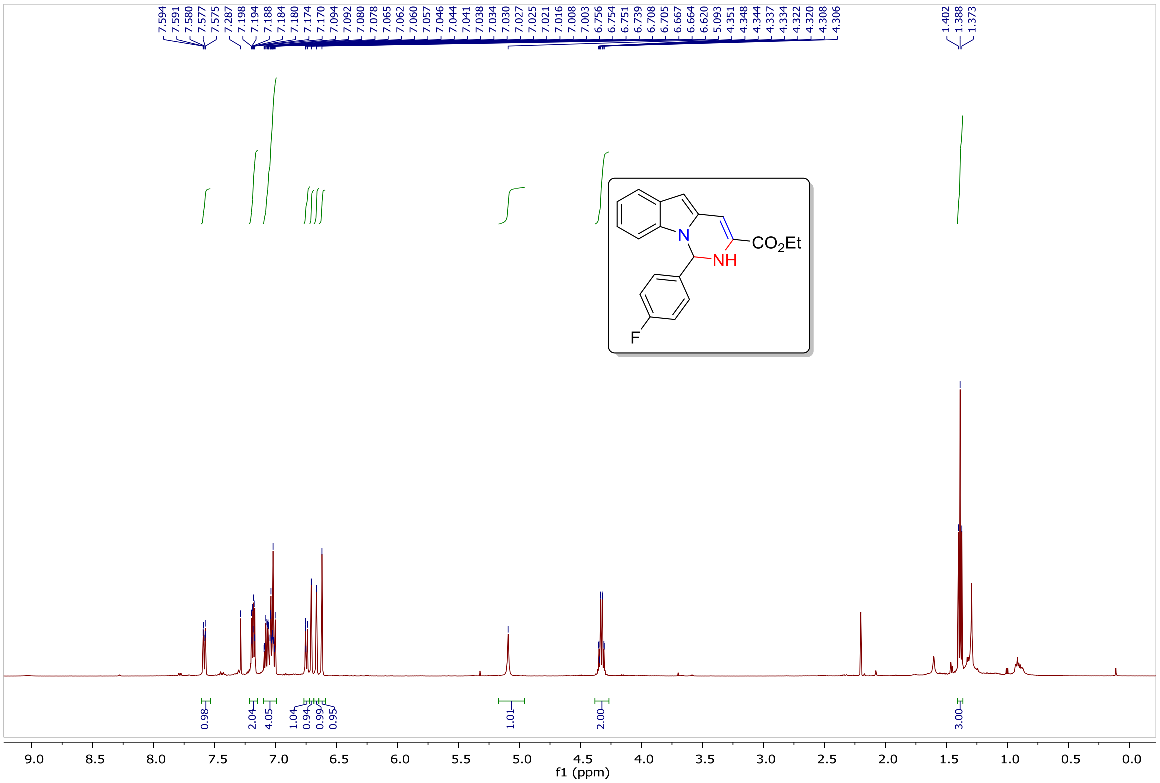


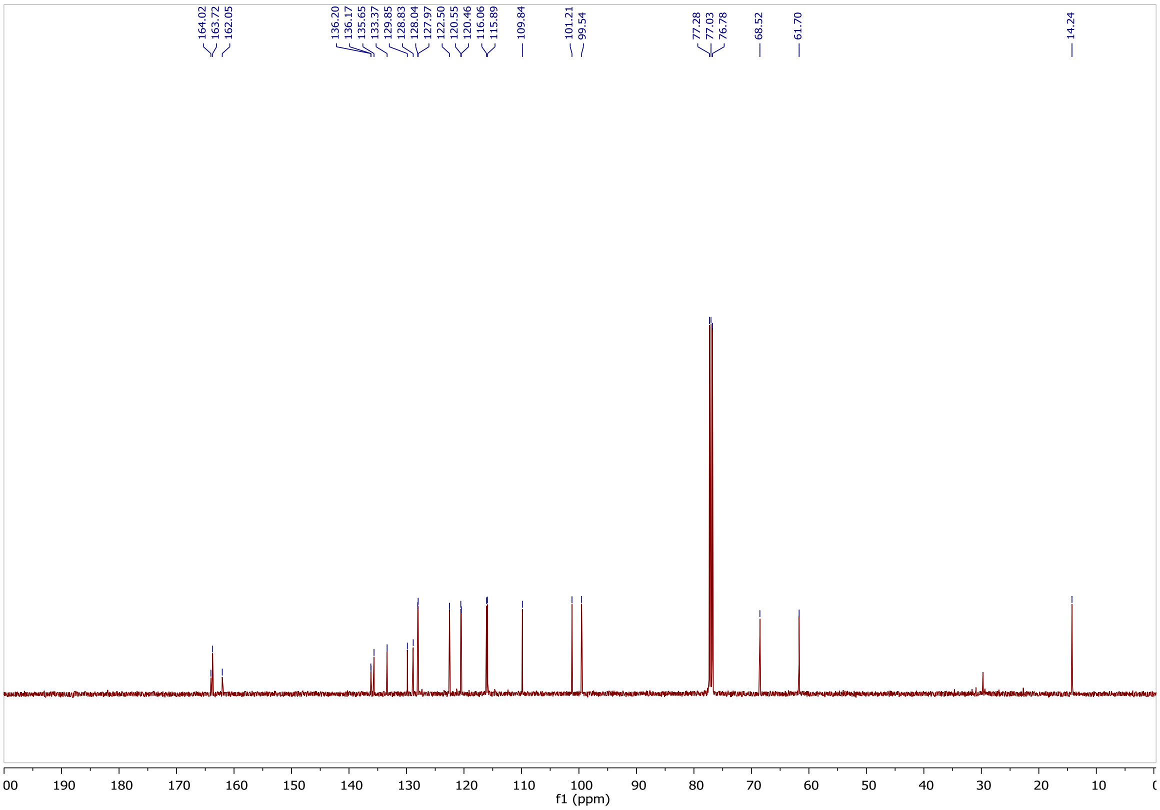
# NMR spectra of compound 3ad



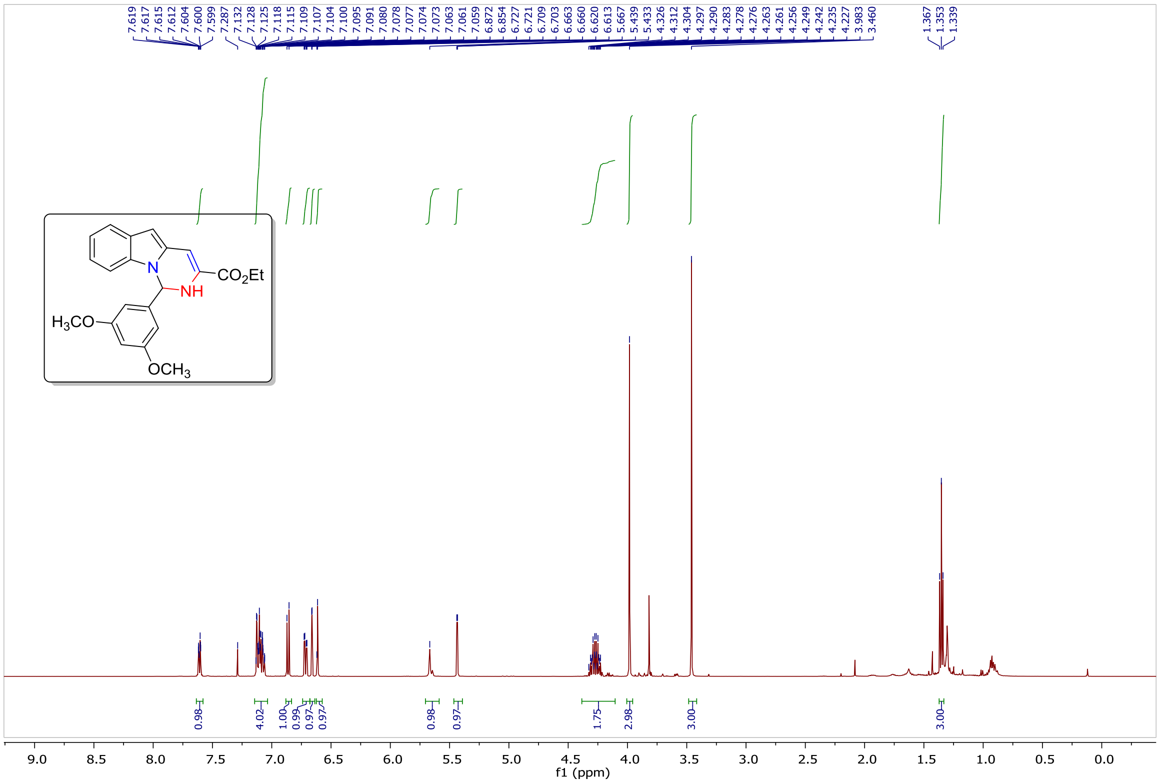


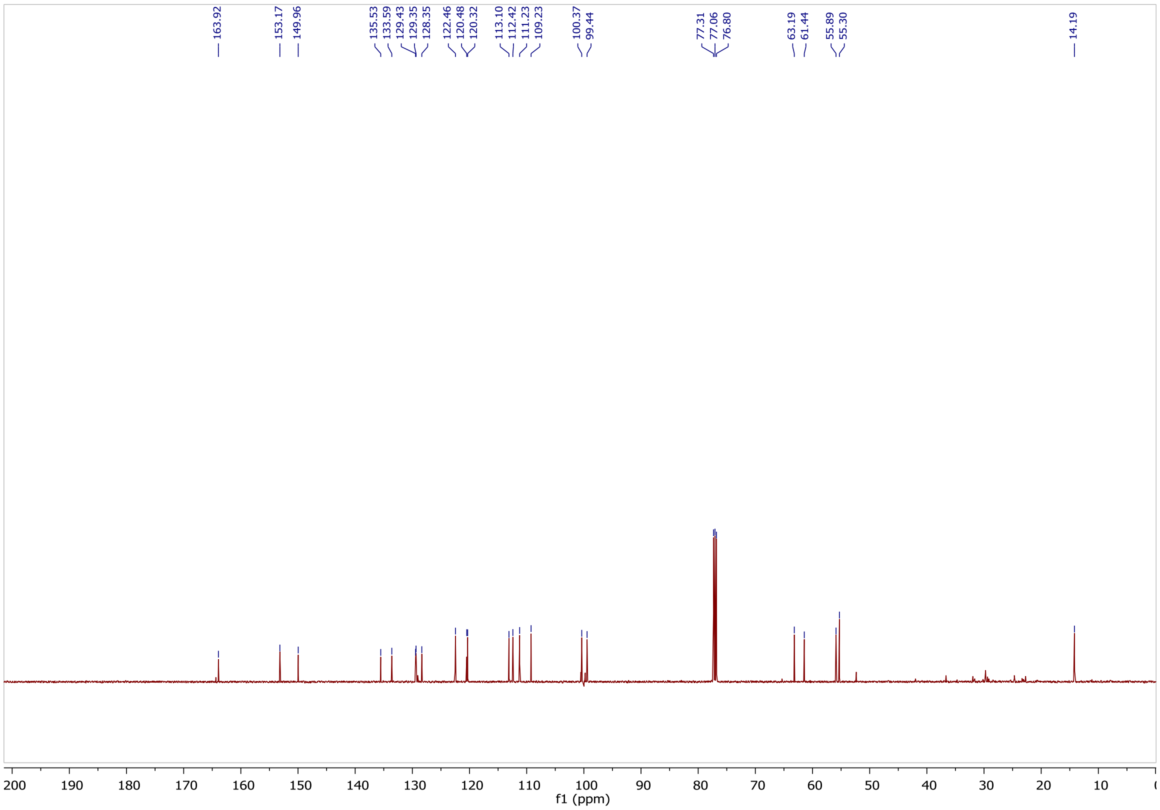
# NMR spectra of compound 3ae



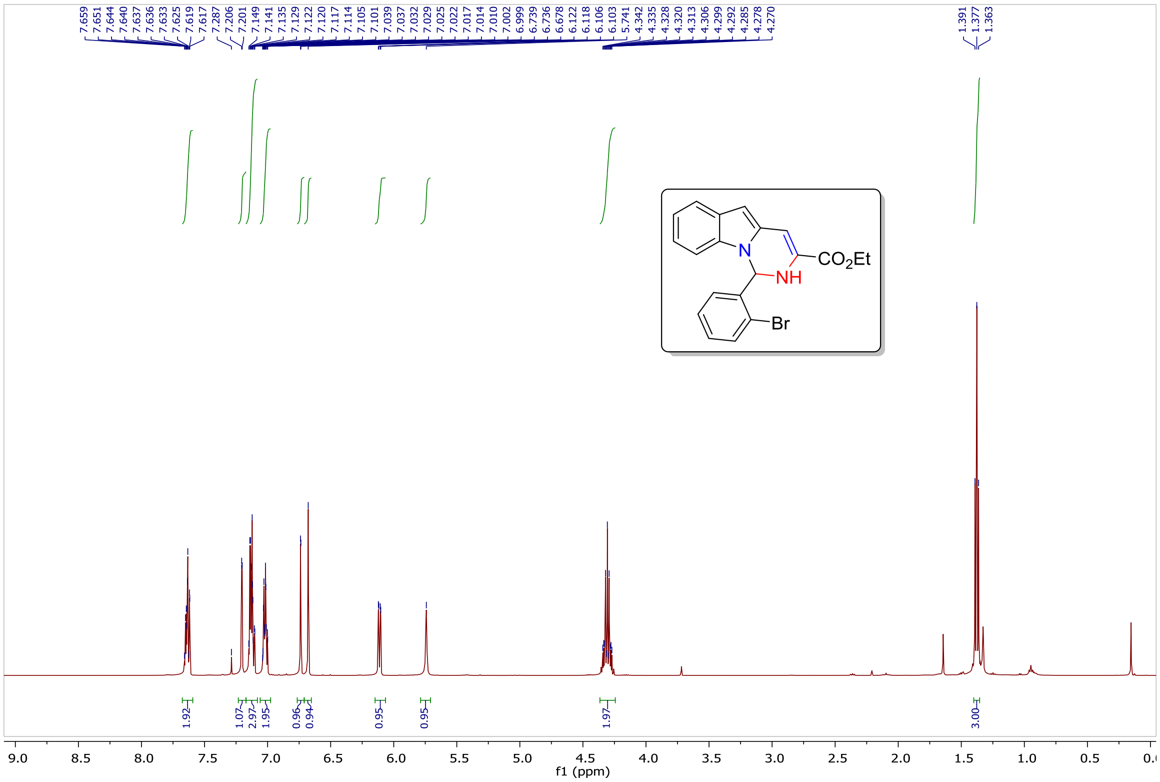


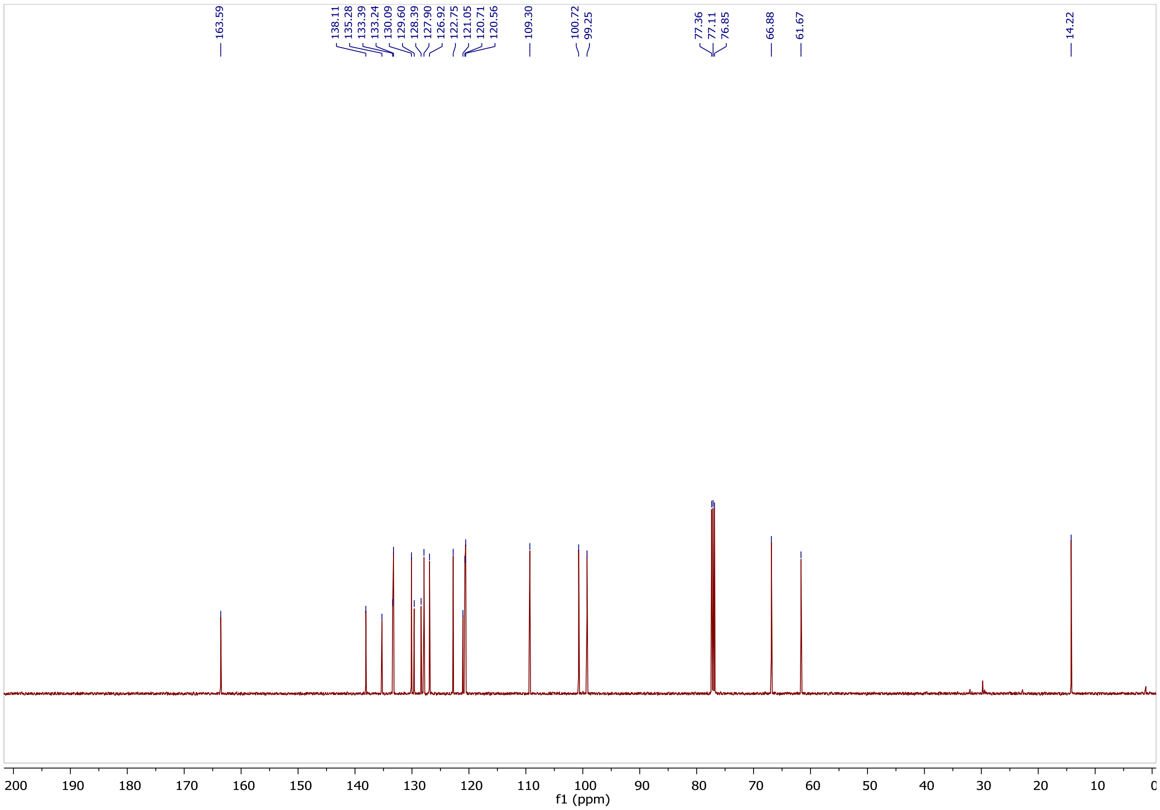
# NMR spectra of compound 3af



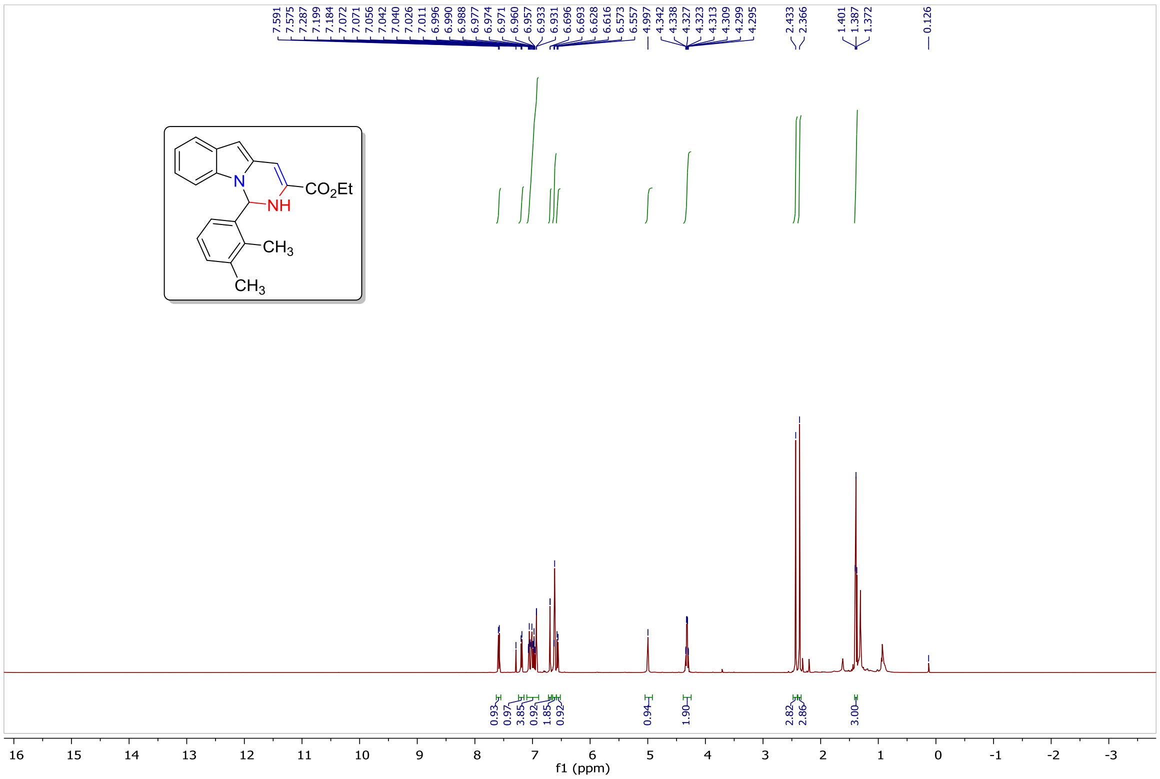


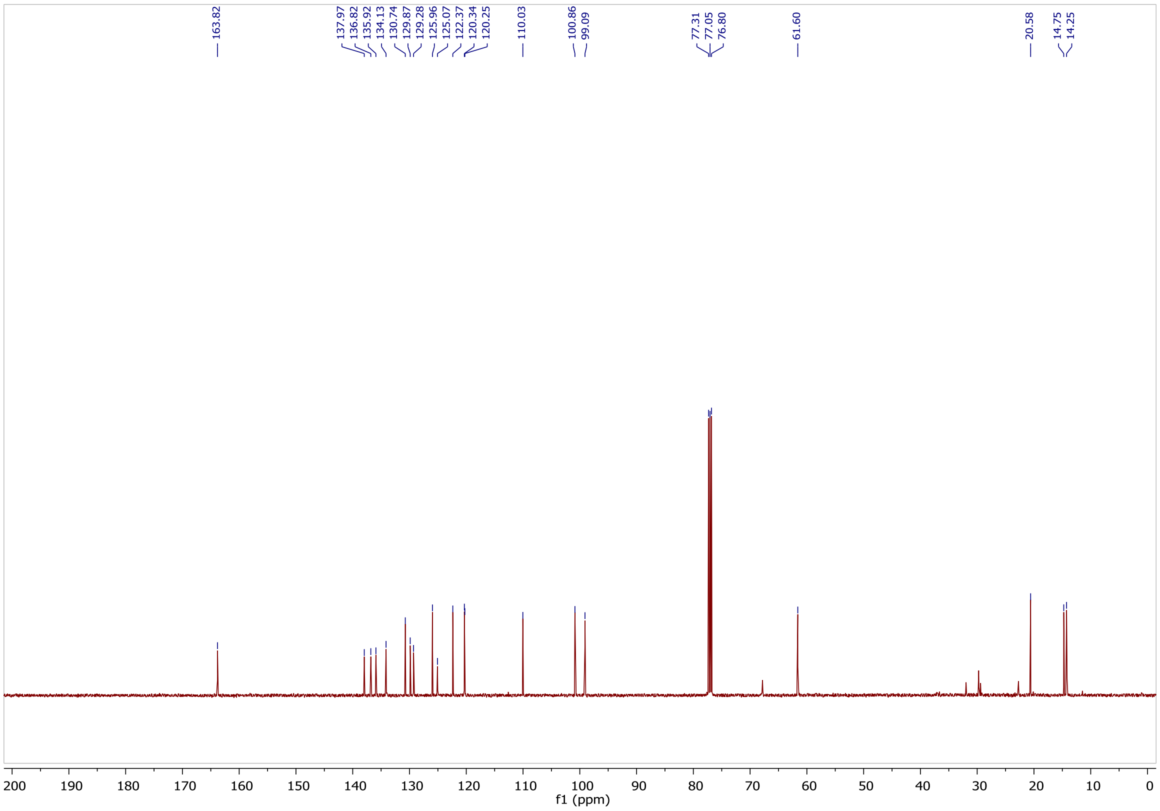
# NMR spectra of compound 3ag



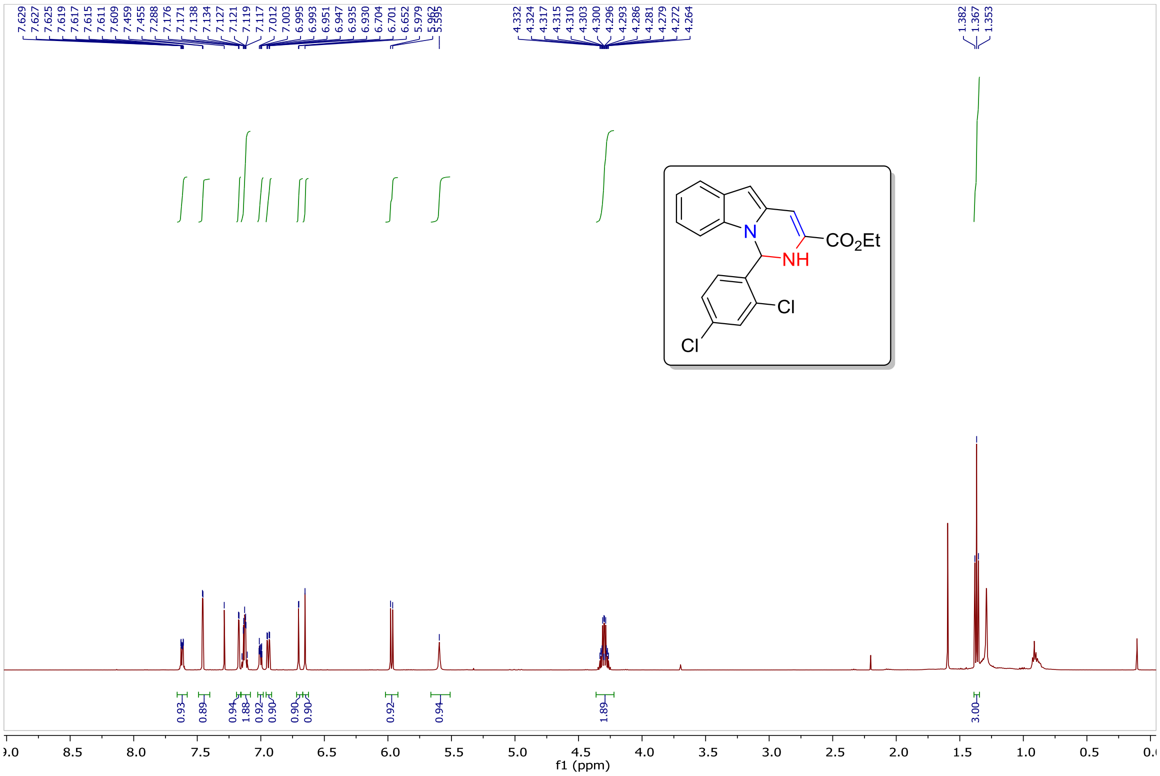


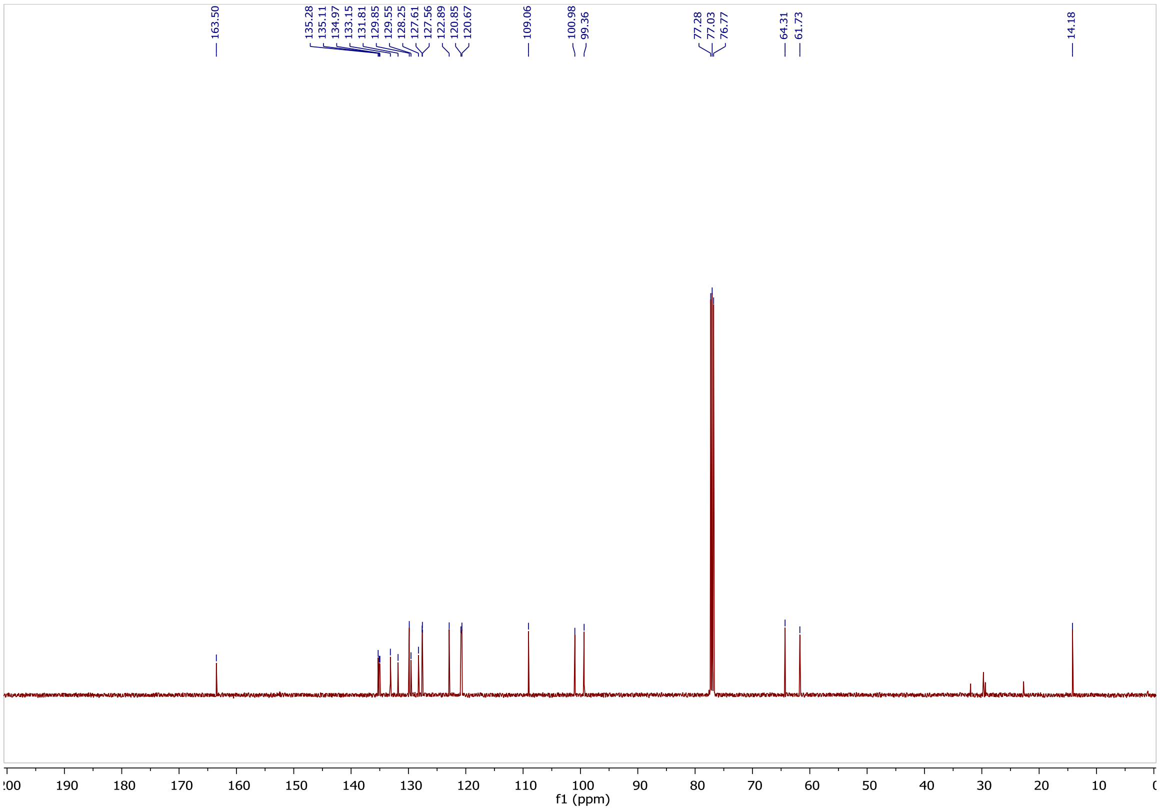
## NMR spectra of compound 3ah



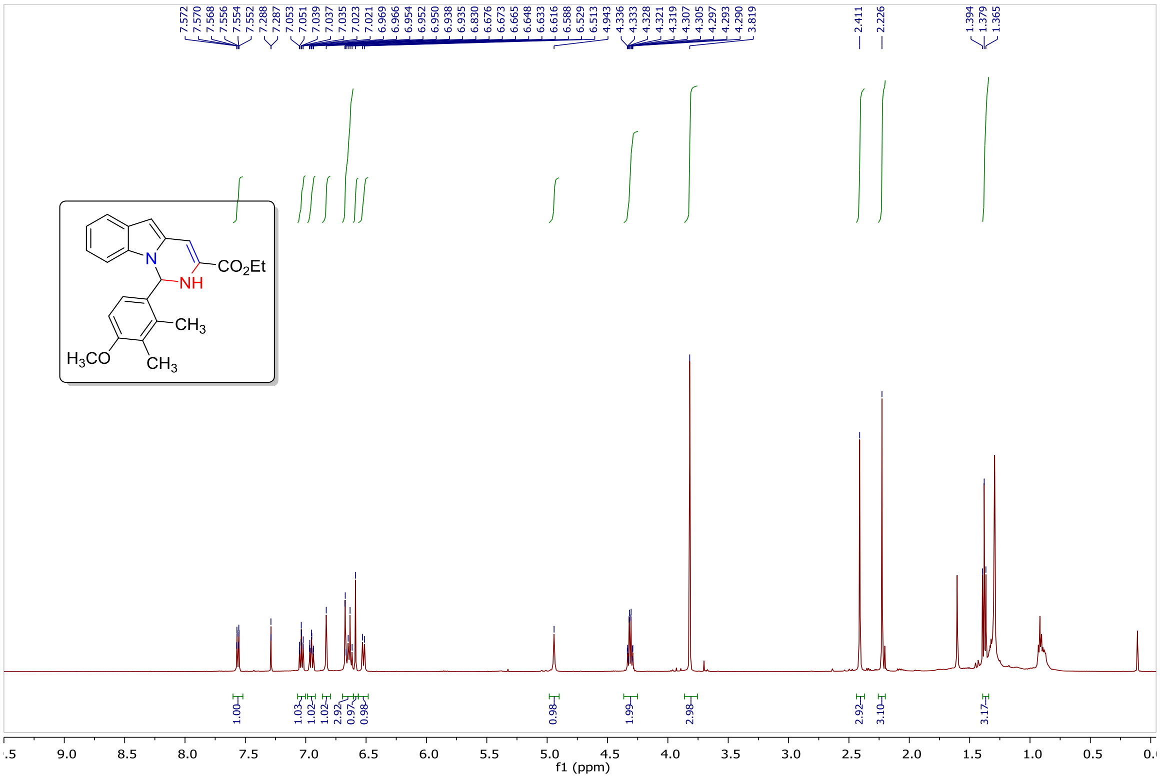


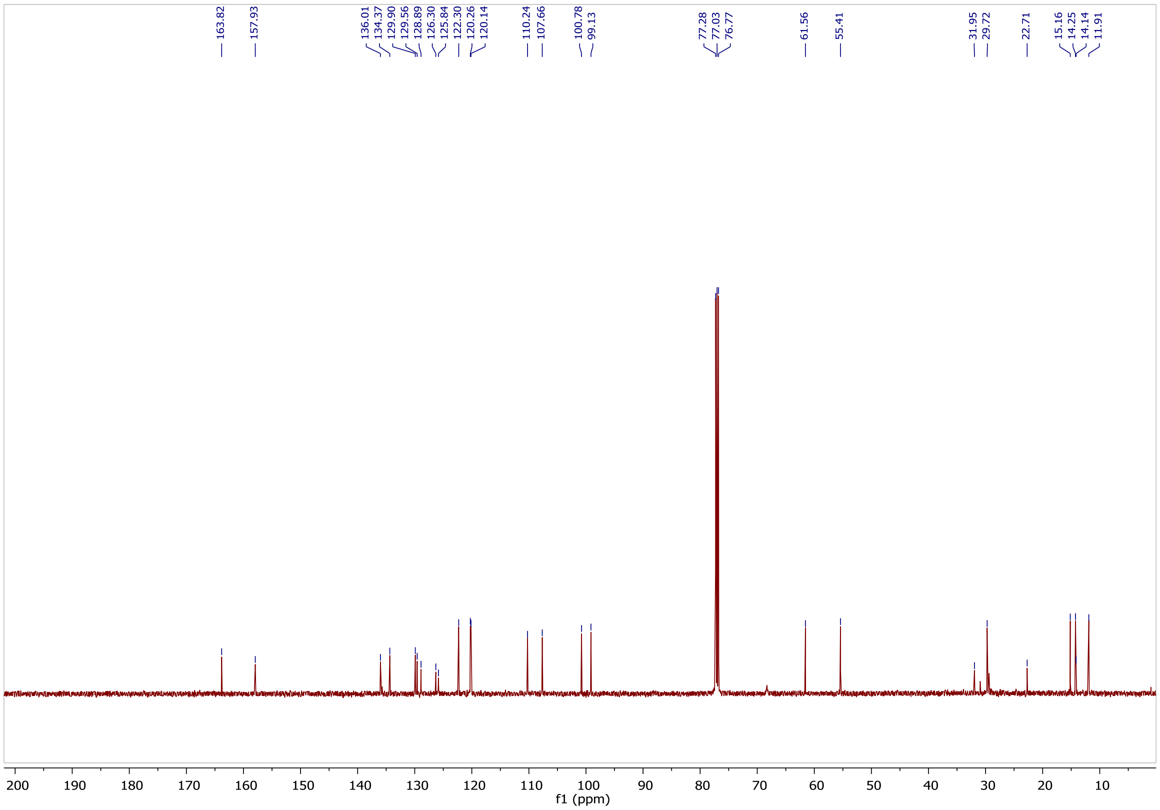
# NMR spectra of compound 3ai



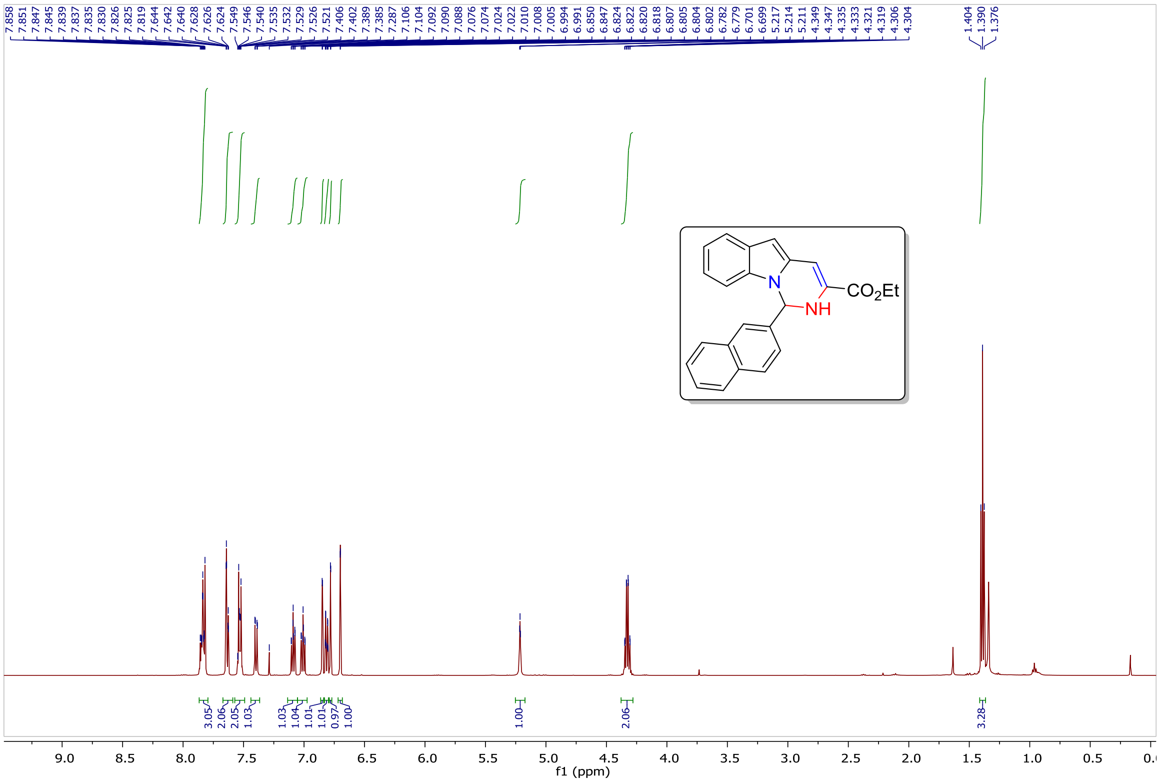


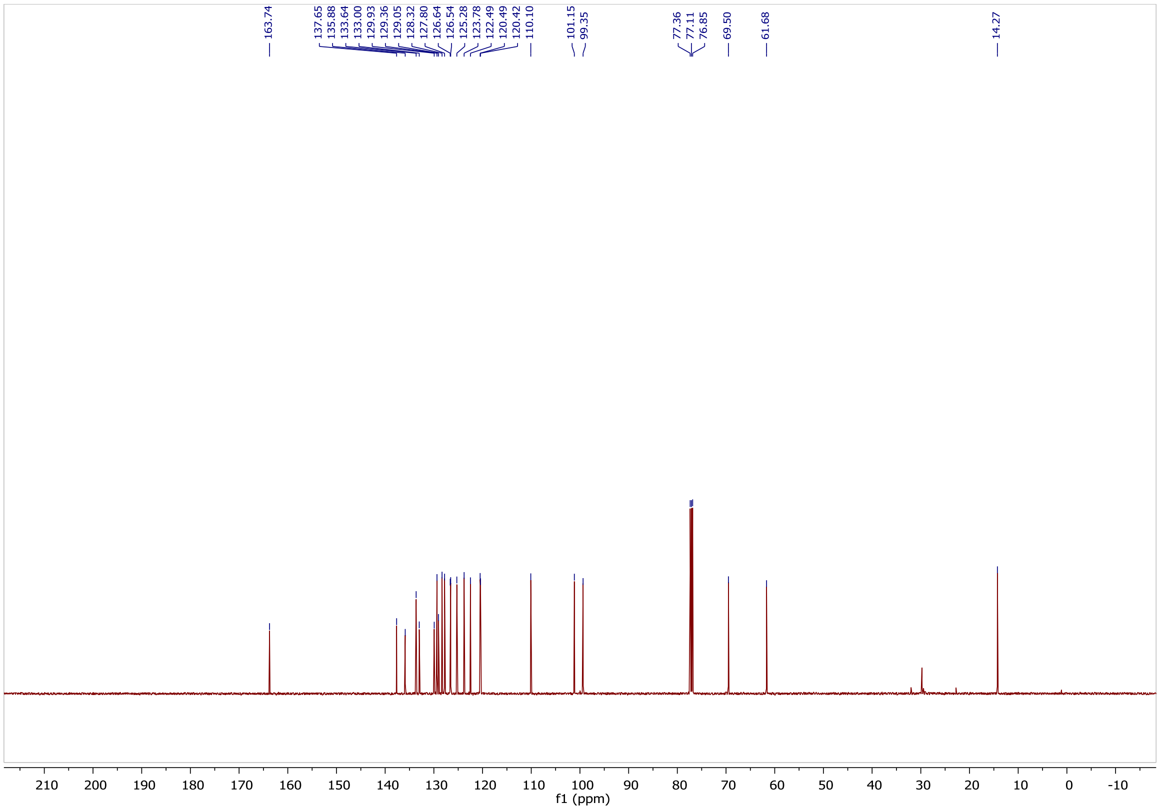
# NMR spectra of compound 3aj



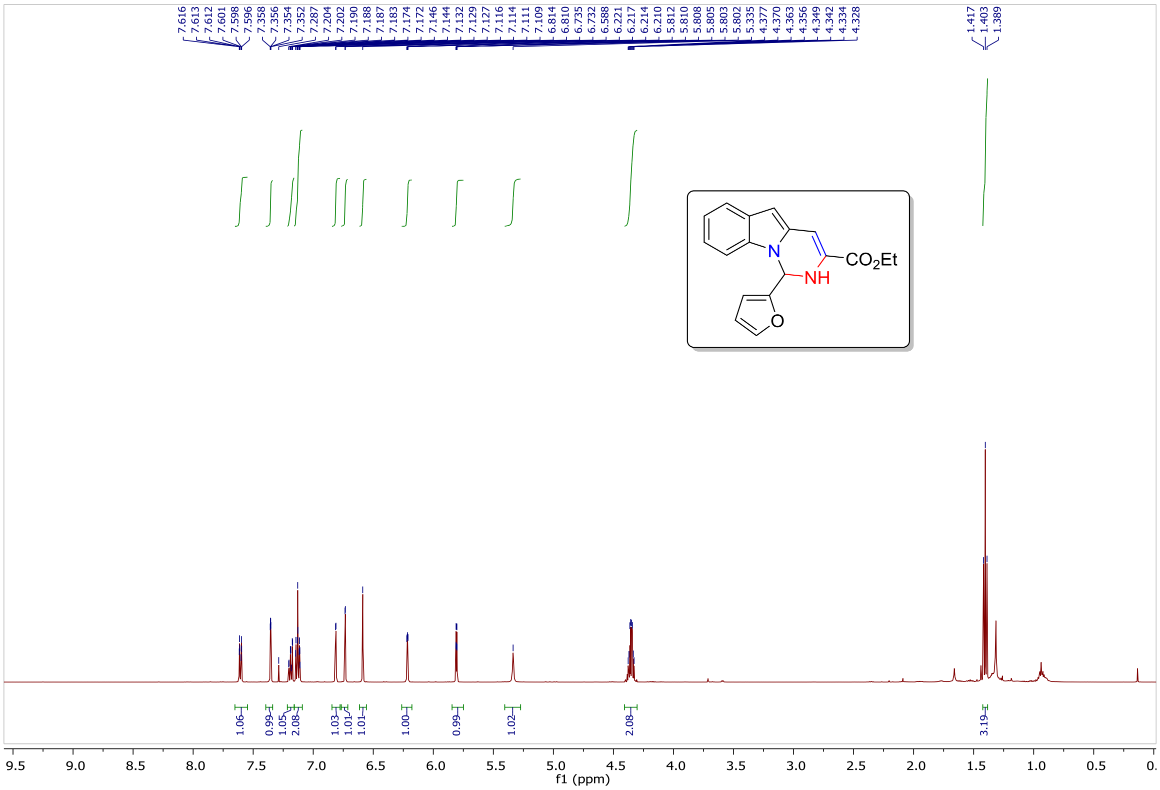


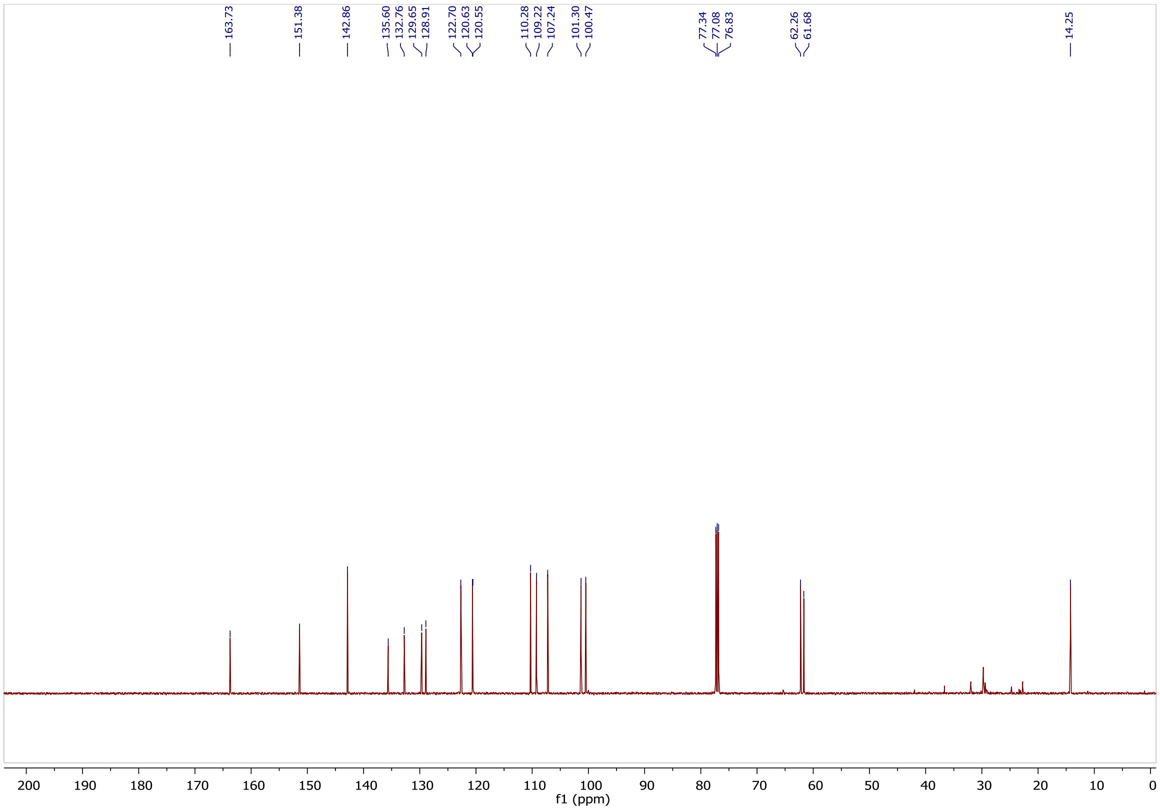
# NMR spectra of compound 3ak



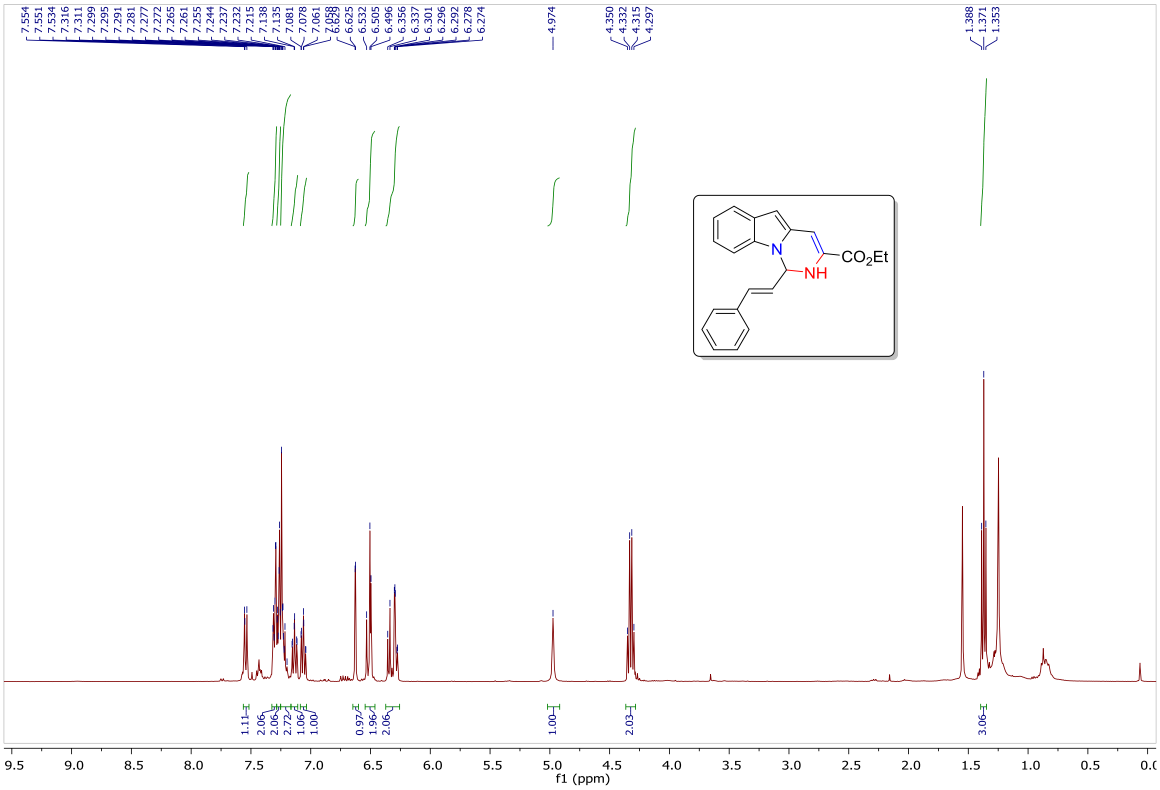


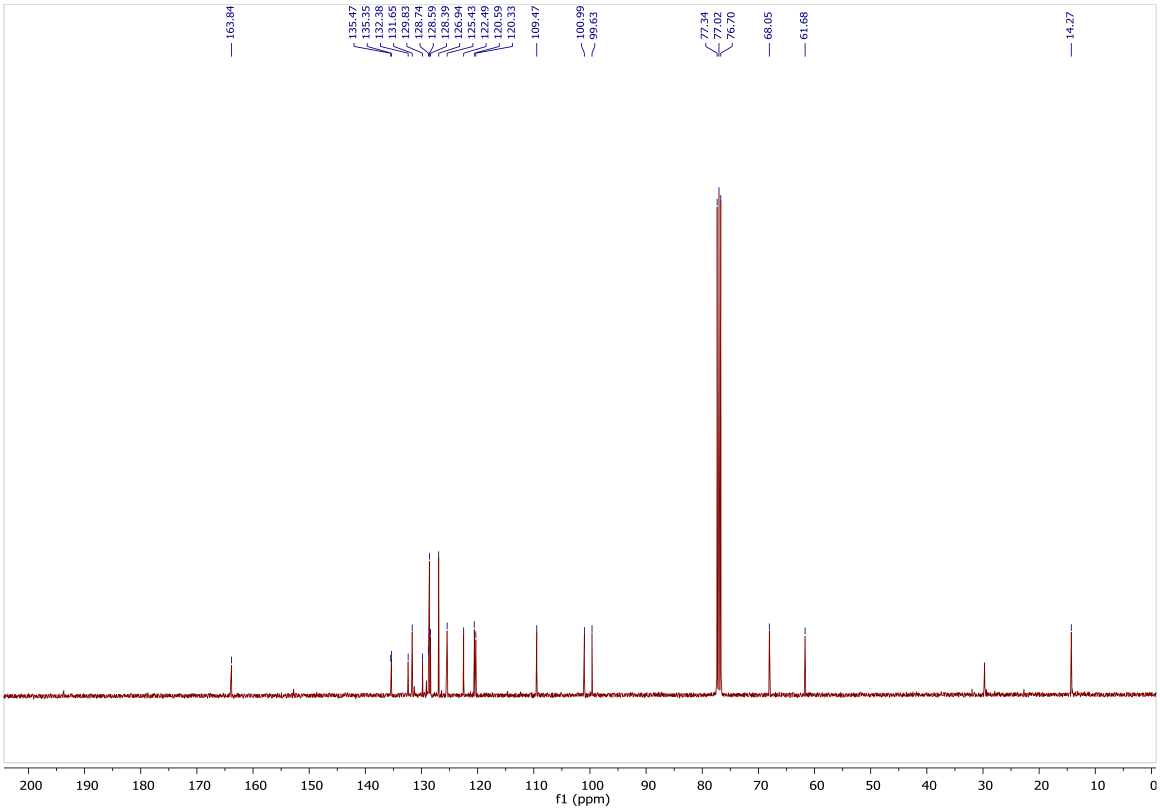
# NMR spectra of compound 3al



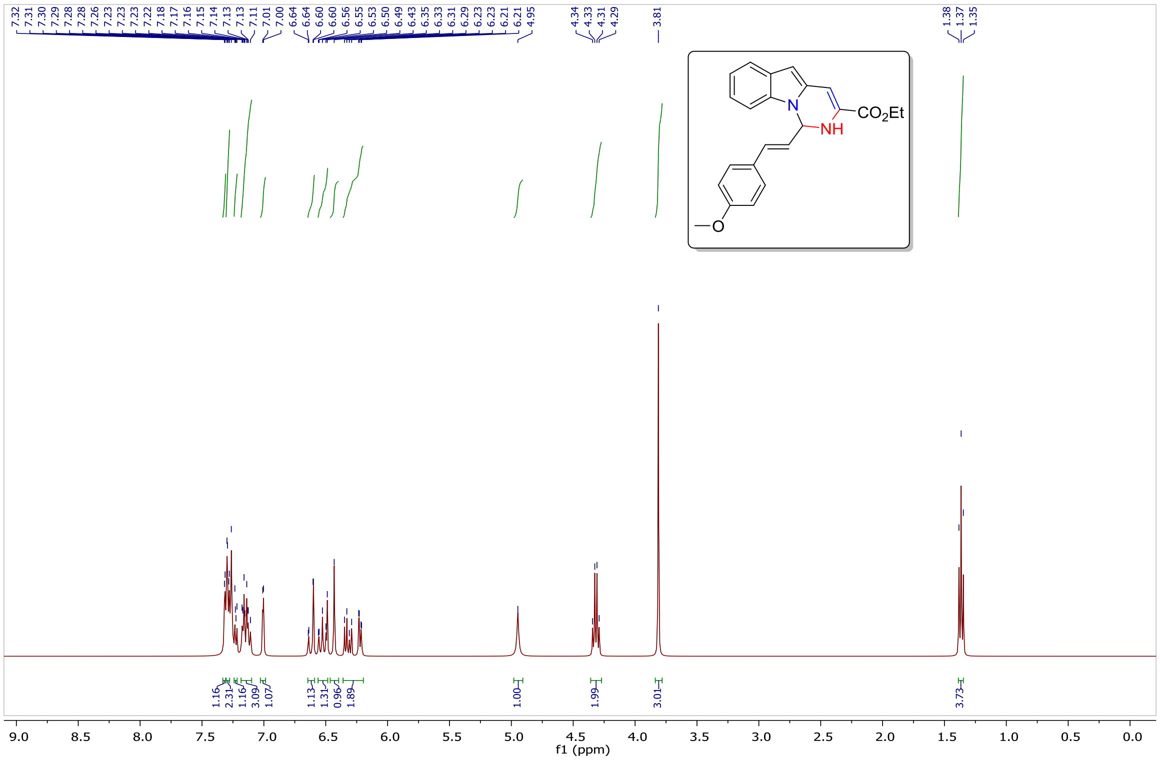


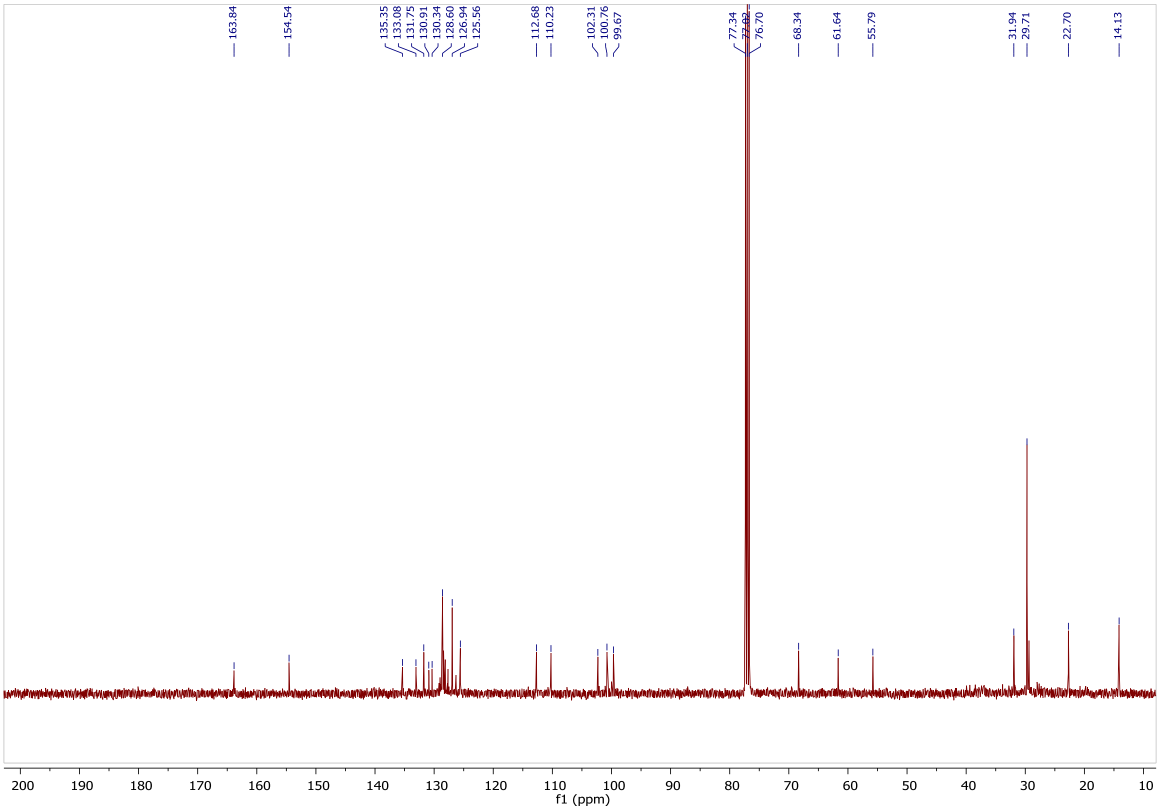
# NMR spectra of compound 3am



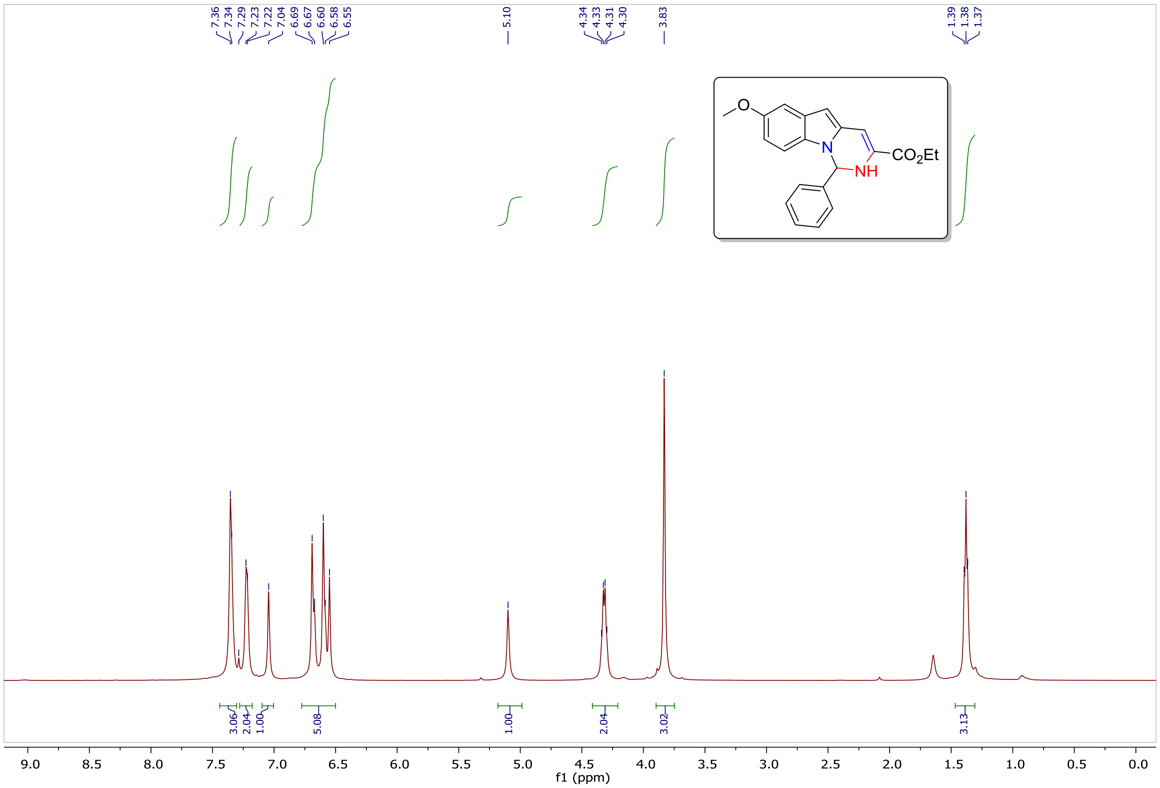


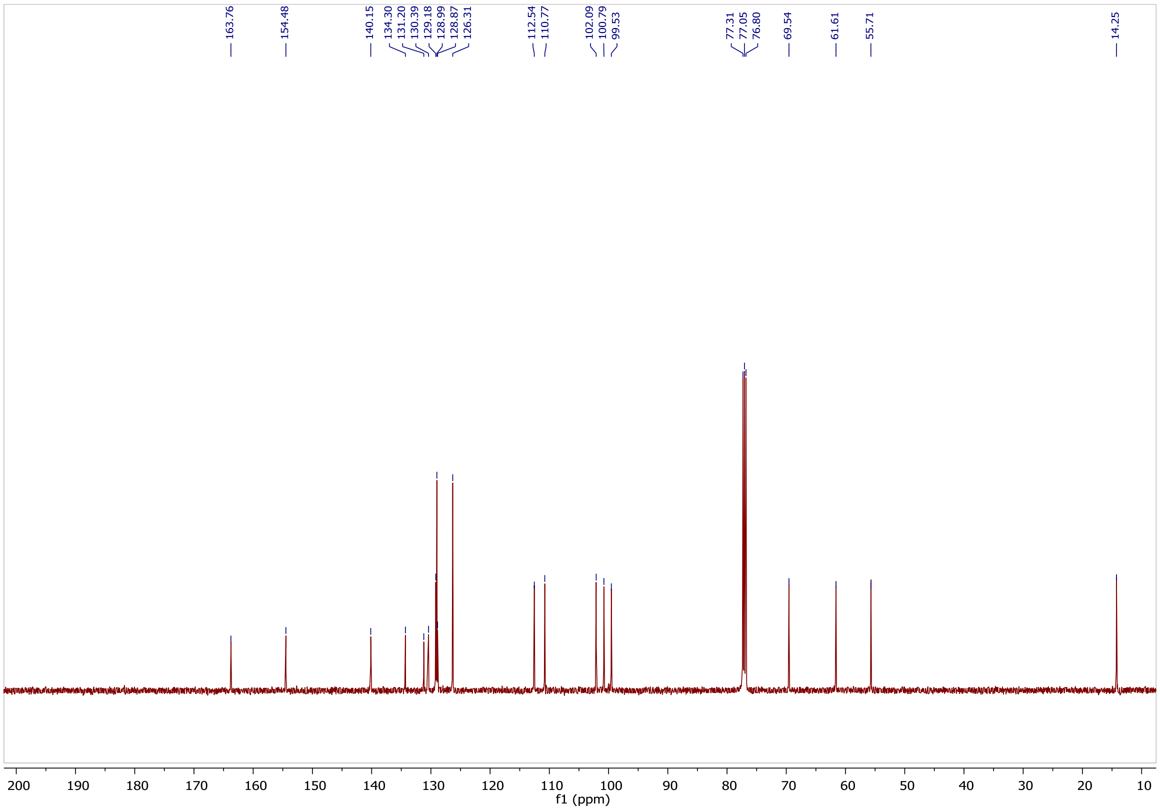
# NMR spectra of compound 3an



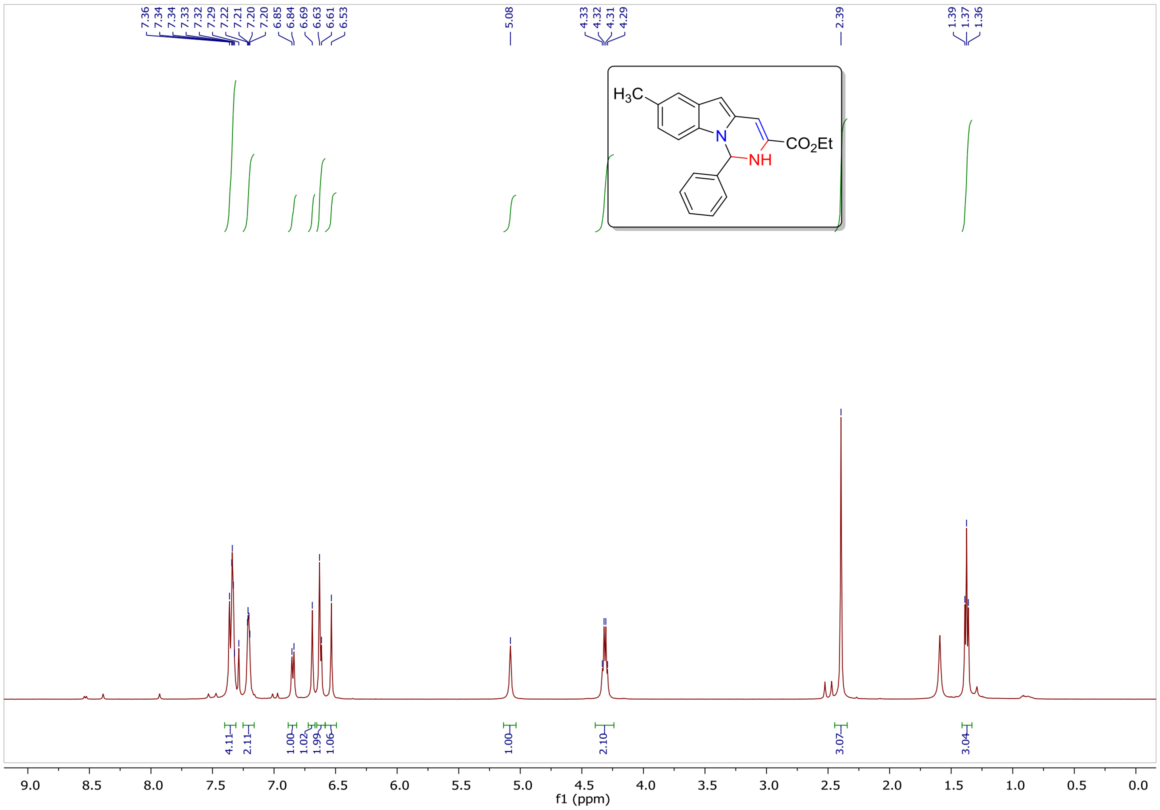


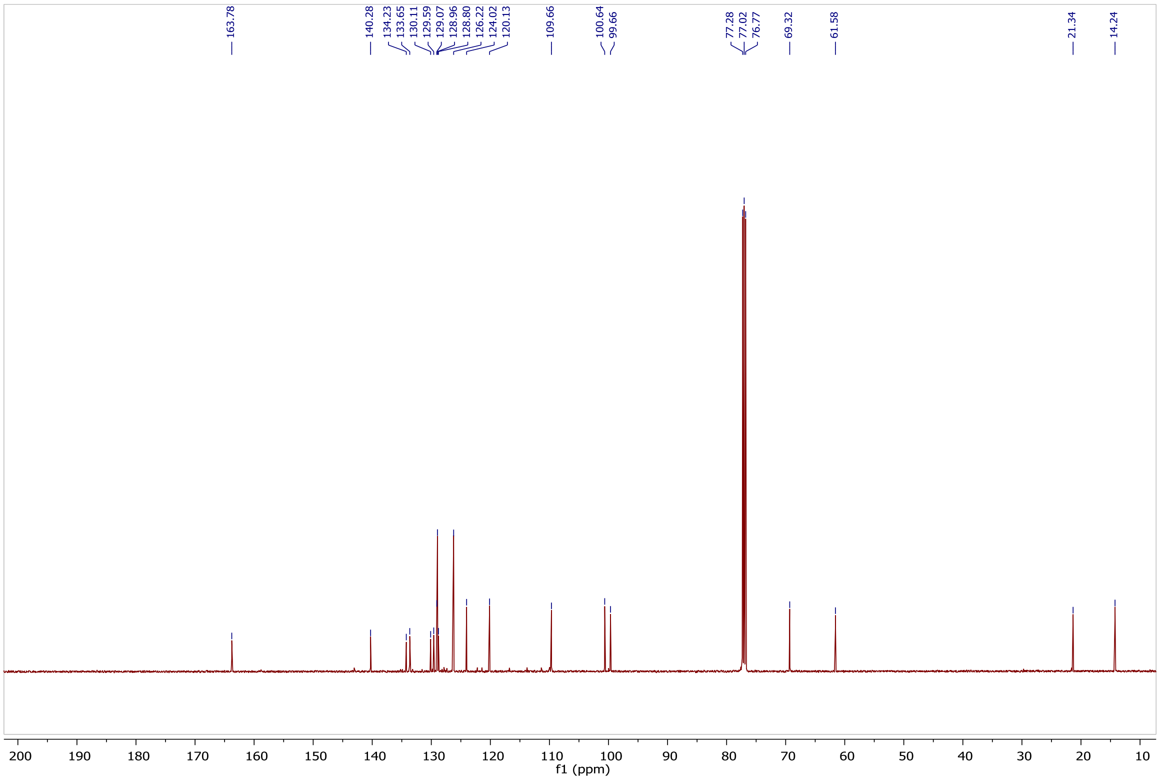
# NMR spectra of compound 3ba



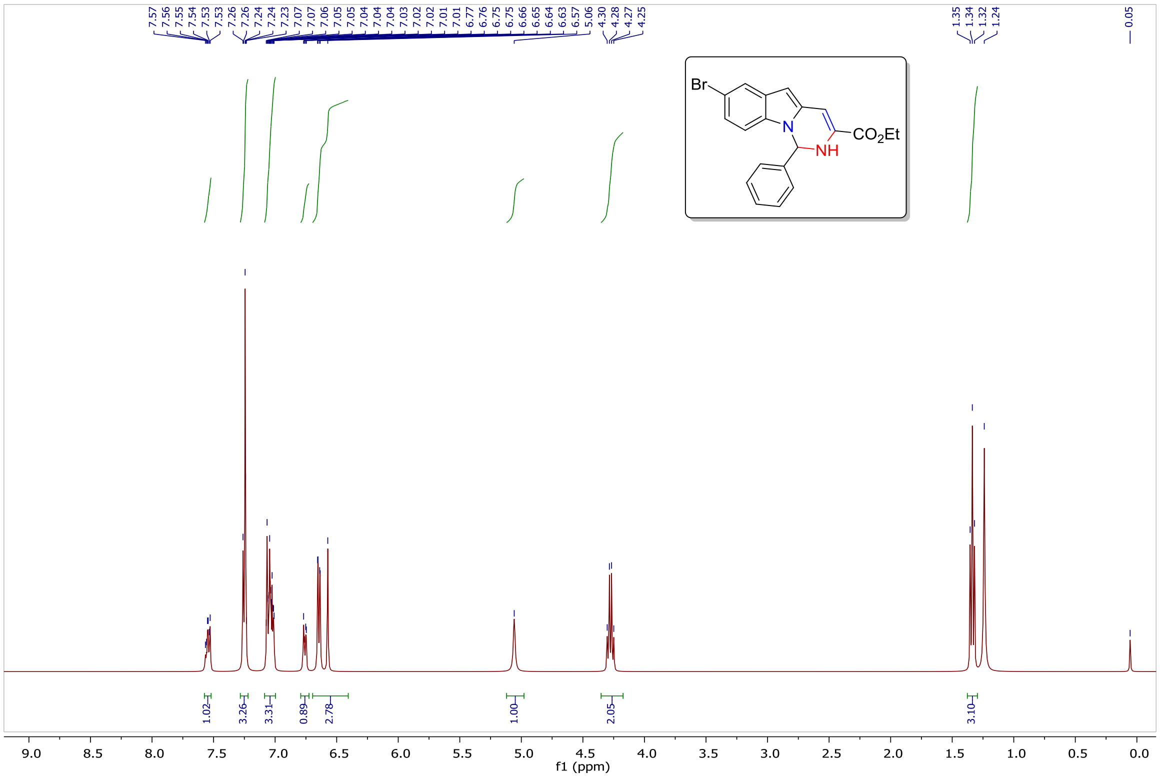


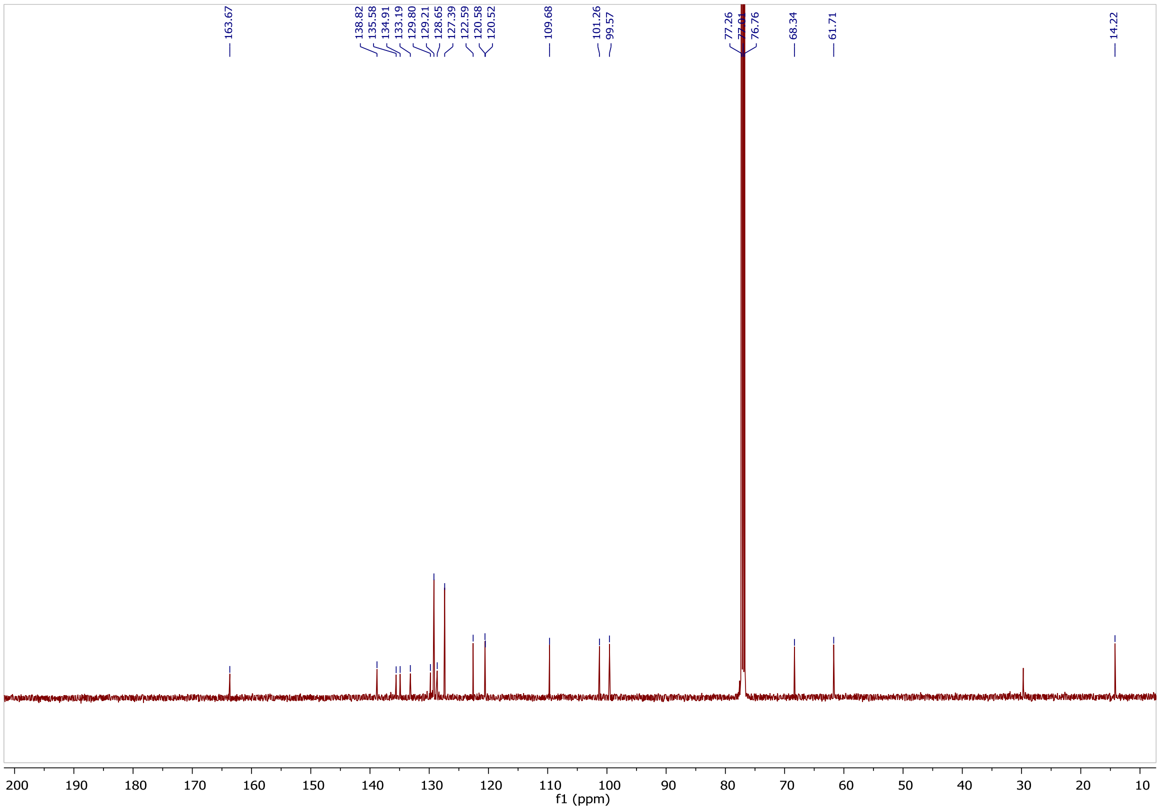
# NMR spectra of compound 3ca





# NMR spectra of compound 3da





## Photophysical studies

**Steady State Absorption:** Steady state absorption measurements were done on carry 100 UV/VIS spectrophotometer. Quartz cell with optical path length of 10 mm was used for all steady-state measurements. Solvents dichloromethane, hexane, methanol and DMSO, were obtained from Sigma-Aldrich (spectroscopic grade).

**Steady-state fluorescence emission studies and Fluorescence decay measurements:** Steady-state fluorescence emission measurements were done on a Horiba JobinYvonfluorolog 3-111. Spectroscopic-grade solvents were used for measuring electrochemical and optical properties. Quartz cell with optical path length of 10 mm was used for all steady-state measurements. The measurements of spontaneous fluorescence decay were done on time- correlated singlephoton counting system (Deltaflex) from HORIBA. All molecules were excited by using DD-375L picosecond diodes (Deltadiode) and all the molecules were probed at their emission maxima. Fwhm at 375 nm excitation was around 167 ps. Quantum yield was calculated according to the following formula and Coumarin 153 as a reference.

$QY = [QY_{ref} \text{ x } I \text{ x } A_{ref} \text{ x } \eta 2] / [A \text{ x } I_{ref} \text{ x } \eta^2_{ref}]$;

where QY = quantum yield; ref = reference (Coumarin 153); A = Absorbance; I = integrated

fluorescence intensity; η = refractive index of the solvent.

**Table 1**. Optical data for **3aa**

| **Solvent** | **$\lambda_{abs}$ (nm)** | **ε ($10^4 M^{-1} cm^{-1}$)** | **$\lambda_{em}$(nm)** | **τ (ns)** | **ϕ*** |
|---|---|---|---|---|---|
| **HEX** | 368 | 3.04 | 429, 405 | 1.1 | 0.26 |
| **DCM** | 375 | 2.97 | 457 | 0.8 | 0.18 |
| **MeOH** | 376 | 2.87 | 456 | 0.8 | 0.11 |
| **DMSO** | 383 | 2.74 | 457 | 2.8 | 0.37 |

**Table 2**. Optical data for **3al**

| **Solvent** | **$\lambda_{abs}$ (nm)** | $\varepsilon$ ($10^4 M^{-1} cm^{-1}$) | **$\lambda_{em}$(nm)** | **$\tau$ (ns)** | **$\phi$*** |
|---|---|---|---|---|---|
| HEX | 365 | 1.38 | 424, 401 | 1.1 | 0.75 |
| DCM | 369 | 1.40 | 436 | 1.4 | 0.85 |
| MeOH | 379 | 1.31 | 451 | 0.82 | 0.71 |
| DMSO | 376 | 1.37 | 453 | 2.8 | 1.0 |

*Fluorescence quantum yields were calculated using coumarin 153 ($\phi$= 0.53 in ethanol)[3]

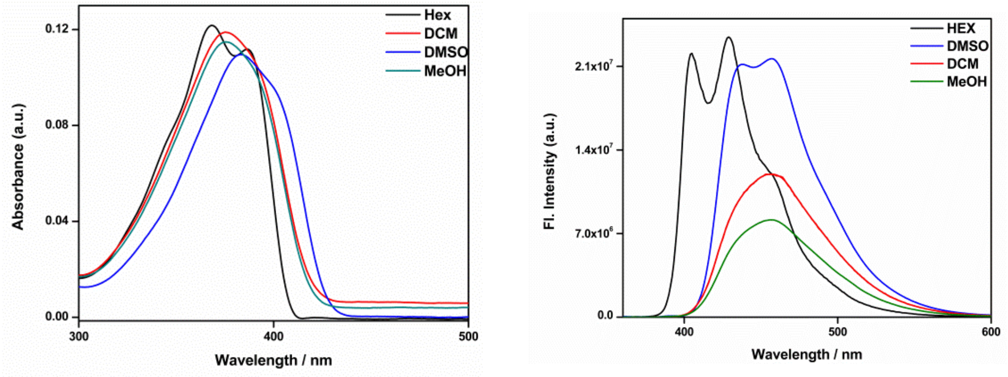


**Figure2**. Absorption and emission features of **3aa**

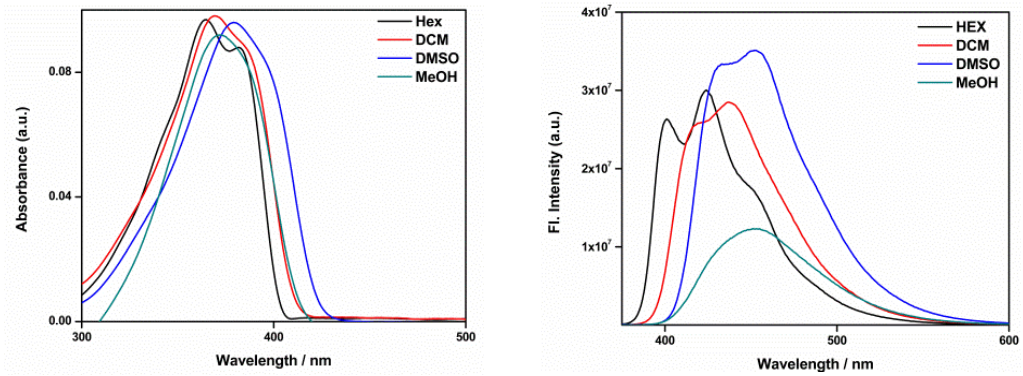


**Figure3**. Absorption and emission features of **3al**

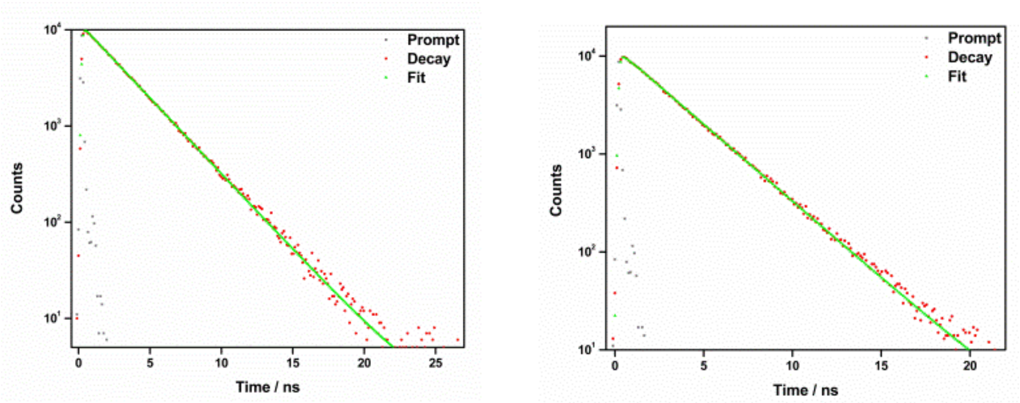


**Figure4**. Absorption and emission features of two molecules (starting from left) **3aa** and **3al** in DMSO ($\lambda_{exc}$ 375 nm)

**References:**

1. C. Zheng, Y. Lu, J. Zhang, X. Chen, Z. Chai, W. Ma and G. Zhao, *Chem. Eur. J.* 2010, **16**, 5853-5857.

2. (a) L. Dai, D. Xu, L. W. Tang and Z. M. Zhou, *Chem. Cat. Chem.* 2015, **7**, 1078; (b) A. López-Pérez, J. Adrio and J. C. Carretero, *Angew. Chem. Int. Ed*. 2009, **48**, 340; (c) I. Oura, K. Shimizu, K. Ogata and S.-I. Fukuzawa, *Org. Lett*. 2010, **12**, 1752.

3. C. Wurth, M. Grabolle, J. Pauli, M. Spieles and U. R. Genger, *Nat. Protoc*. 2013, **8**, 1535.