

Supporting information

Visible-Light Mediated, Oxygen-Promoted Regioselective Cross Dehydrogenative Coupling of Coumarins and Dimethylanilines

Tavinder Singh^a, Ganesh Chandra Upreti^a, Shivani Arora^a, Himanshu Chauhan^a, and Anand Singh^{a,b} *

^aDepartment of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India

^b Department of Sustainable Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, India

Contents

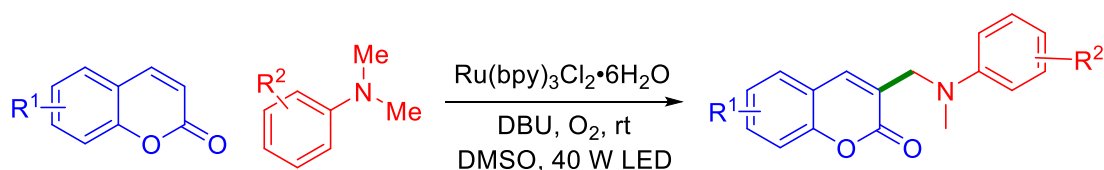
1. General Information	SI-1
2. General Procedures	SI-2
3. Detailed Procedures for mmol scale synthesis.....	SI-2
4. TEMPO & BHT Experiments.....	SI-3
5. Analytical Data for products	SI-3
6. References.....	SI-12
7. ¹ H and ¹³ C Spectra.....	SI-13

1. General Information

Unless otherwise noted, all chemicals were purchased from commercial sources and used without further purification. Yields refer to chromatographically pure material. All solvents were used as purchased, without purification. MeCN were used as after drying and distillation. Reactions were monitored by thin-layer chromatography (TLC) performed on 0.25 mm Merck silica gel plates (60F-254) using UV light. Merck silica gel (mesh size 100-200) was used for flash column chromatography. NMR

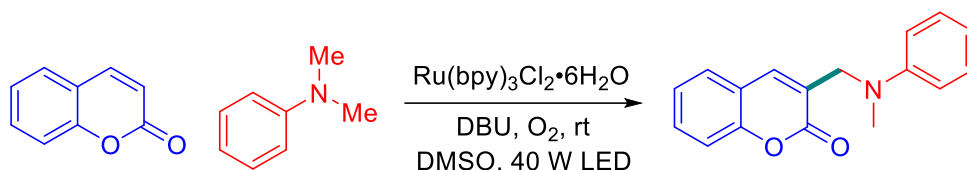
spectra were recorded on JEOL 500 (^1H : 500 MHz, ^{13}C : 125 MHz) or 400 (^1H : 400 MHz, ^{13}C : 100 MHz) spectrometer in CDCl_3 having TMS 0.03% as internal standard. Mass spectrometric data were obtained using WATERS-Q-TOF Premier-ESI-MS and GC-MS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of doublet, m = multiplet. Coumarin derivatives and dimethyl aniline derivatives were prepared according to the literature reports.

2. General Procedure



An oven dried vial equipped with a magnetic stir bar was charged with coumarin derivative (0.34 mmol), dimethyl aniline (4.0 equiv.), DBU (2 equiv.) and $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (2 mol%), followed by distilled dry DMSO (2 mL). After addition of solvent, reaction mixture was stirred under O_2 atmosphere (O_2 balloon) at rt under 40W LED illumination. After the completion of reaction (confirmed by TLC), reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/ petroleum ether).

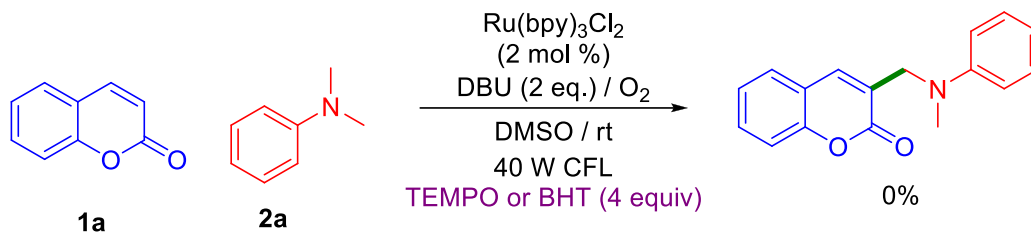
3. 1 mmol scale synthesis:



A dried 50 mL round bottom equipped with a magnetic stir bar was charged coumarin **1a** (1.03 mmol), N,N -dimethylaniline **2a** (4 equiv.), DBU (2 equiv.),

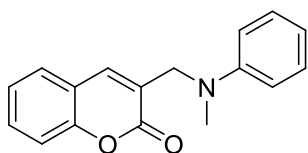
Ru(bpy)₃Cl₂·6H₂O (2 mol%) and 6 mL dry DMSO. After addition of solvent, reaction mixture was stirred under O₂ atmosphere (O₂ balloon) at rt under 40W LED illumination. After the completion of reaction (confirmed by TLC), reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/ petroleum ether).

4. TEMPO & BHT Experiments:



An oven dried vial equipped with a magnetic stir bar was charged with coumarin **1a** (0.34 mmol), *N,N*-dimethylaniline **2a** (4.0 equiv.), DBU (2 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), followed by distilled dry DMSO (2 mL) and TEMPO or BHT (4 equiv) was added. After the addition of solvent, reaction mixture was stirred under O₂ atmosphere (O₂ balloon) at rt under 40W CFL illumination. After 24 h, no product formation was observed.

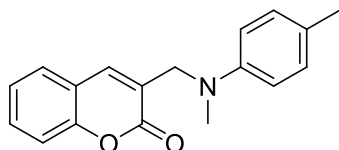
5. Analytical Data of Synthesized Products:



3-((Methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (**3a**):

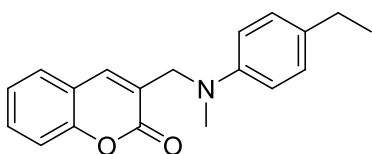
According to the general procedure, 2*H*-chromen-2-one (50 mg, 0.342 mmol) and *N,N*-dimethyl aniline (4.0 equiv, 1.37 mmol) provided **3a** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (76 mg, 84 %). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 1606, 1704, 1754, 3070, 3405. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.41 –

7.32 (m, 2H), 7.26 – 7.21 (m, 3H), 6.79 – 6.69 (m, 3H), 4.43 (s, 2H), 3.11 (s, 3H). ¹³C NMR (125MHz, Chloroform-*d*) δ 161.3, 153.2, 149.0, 137.8, 131.1, 129.5, 127.8, 125.5, 124.5, 119.3, 117.1, 116.6, 112.1, 52.8, 39.0. HRMS: exact mass calculated for C₁₇H₁₅NO₂ [M+Na]⁺ 288.1000, found 288.1012.



3-((methyl(*p*-tolyl)amino)methyl)-2*H*-chromen-2-one

(3b): According to the general procedure, 2*H*-chromen-2-one (50 mg, 0.342 mmol) and *N,N*,4-trimethylaniline (3.0 equiv, 1.37 mmol) provided **3b** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (76 mg, 80%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1522, 1610, 1713, 2918. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.36 (dd, *J* = 19.2, 7.4 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.39 (s, 2H), 3.08 (s, 3H), 2.25 (s, 3H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 161.3, 153.1, 147.0, 137.9, 131.0, 130.0, 127.8, 126.4, 125.8, 119.4, 116.6, 112.3, 53.0, 39.2, 20.3. exact mass calculated for C₁₈H₁₇NO₂ [M+H]⁺ 280.1332, found 280.1332.

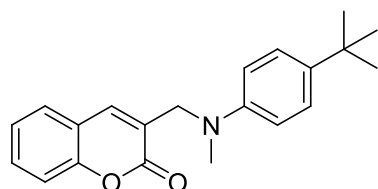


3-(((4-ethylphenyl)(methyl)amino)methyl)-2*H*-

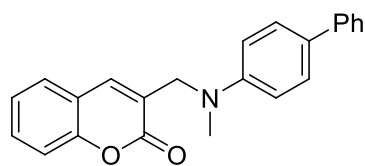
chromen-2-one (3c): According to the general

procedure, 2*H*-chromen-2-one (50 mg, 0.342 mmol) and 4-ethyl-*N,N*-dimethylaniline (4.0 equiv, 1.37 mmol) provided **3c** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (67 mg, 67%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1523, 1609, 1709, 2868, 2923, 2959. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.37 (dd, *J* = 20.8, 8.0 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 4.41 (s, 2H), 3.10 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (125MHz,

Chloroform-*d*) δ 161.3, 153.2, 147.2, 137.9, 133.0, 131.1, 128.8, 127.8, 125.8, 124.5, 119.4, 116.6, 112.3, 53.1, 39.2, 27.9, 16.0. HRMS: Exact mass calculated for $C_{19}H_{19}NO_2[M+H]^+$ 294.1489, found 294.1489.

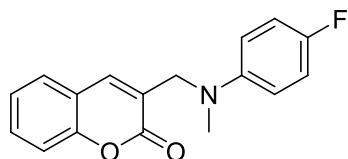


3-(((4-*tert*-Butylphenyl)(methyl)amino)methyl)-2H-chromen-2-one (3d): According to the general procedure **2**, 2*H*-chromen-2-one (50 mg, 0.342 mmol) and 4-*tert*-butyl-*N,N*-dimethylaniline (4.0 equiv, 1.37 mmol) provided **3d** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (104 mg, 95%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1522, 1609, 1706, 2866, 2958, 3045, 3408. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.46 (m, 2H), 7.39 (dd, $J = 23.3, 7.9$ Hz, 2H), 7.32 – 7.22 (m, 3H), 6.70 (d, $J = 8.8$ Hz, 2H), 4.42 (s, 2H), 3.11 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.3, 153.2, 147.0, 139.9, 137.9, 131.1, 127.9, 126.3, 125.9, 124.5, 119.4, 116.6, 111.9, 53.1, 39.1, 33.9, 31.6. HRMS: exact mass calculated for $C_{21}H_{23}NO_2[M+H]^+$ 322.1802, found 322.1802



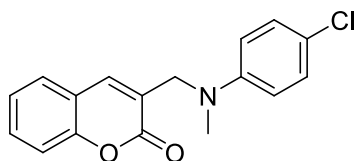
3-((Biphenyl-4-yl(methyl)amino)methyl)-2H-chromen-2-one (3e): According to the general procedure **2**, 2*H*-chromen-2-one (25 mg, 0.17 mmol) and *N,N*-dimethylbiphenyl-4-amine (4.0 equiv, 0.68 mmol) provided **3e** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (36 mg, 62%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1526, 1610, 1718, 2918, 3029. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.46 (m, 6H), 7.43 – 7.34 (m, 4H), 7.28 – 7.21 (m, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 4.49 (s, 2H), 3.17 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.3, 153.2, 148.4, 141.0, 137.9, 131.2, 130.0, 128.8, 128.1, 127.9, 126.4, 126.3,

125.3, 124.6, 119.3, 116.6, 112.4, 52.8, 39.1. HRMS: Exact mass calculated for $C_{23}H_{19}NO_2$ $[M+Na]^+$ 364.1313, found 364.1330.



3-(((4-Fluorophenyl)(methyl)amino)methyl)-2H-chromen-2-one (3f): According to the general procedure,

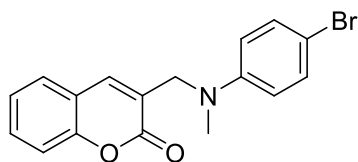
2H-chromen-2-one (50 mg, 0.342 mmol) and 4-fluoro-*N,N*-dimethylaniline (4.0 equiv, 1.37 mmol) provided **3f** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (36 mg, 36%). IR (neat): ν_{max}/cm^{-1} : 1610, 1713, 2923. 1H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 2H), 7.43 – 7.32 (m, 2H), 7.28 – 7.21 (m, 1H), 6.97 – 6.90 (m, 2H), 6.64 (dd, $J = 9.2, 4.2$ Hz, 2H), 4.38 (s, 2H), 3.07 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.2, 156.7, 153.1, 145.7, 137.9, 131.2, 127.8, 125.4, 124.5, 119.26, 116.6, 115.8 (d, $J = 22.2$ Hz), 113.2 (d, $J = 7.3$ Hz), 53.4, 39.5. HRMS: Exact mass calculated for $C_{17}H_{14}FNO_2$ $[M+H]^+$ 284.1081, found 284.1081.



3-(((4-Chlorophenyl)(methyl)amino)methyl)-2H-chromen-2-one (3g): According to the general

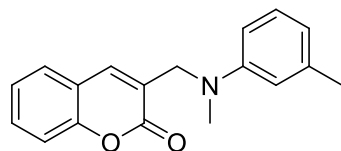
procedure, 2H-chromen-2-one (40 mg, 0.27 mmol) and 4-chloro-*N,N*-dimethylaniline (4.0 equiv, 1.09 mmol) provided **3g** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (58 mg, 71%). IR (neat): ν_{max}/cm^{-1} : 1597, 1608, 1718, 2920. 1H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 1H), 7.41 – 7.30 (m, 3H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.18 – 7.12 (m, 2H), 6.61 (d, $J = 9.1$ Hz, 2H), 4.39 (s, 2H), 3.09 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.1, 153.2, 147.5, 137.9, 131.3, 129.2, 127.8, 125.0,

124.6, 122.0, 119.1, 116.6, 113.3, 52.9, 39.2. HRMS: Exact mass calculated for $C_{17}H_{14}ClNO_2[M+H]^+$ 300.0786, found 300.0786.

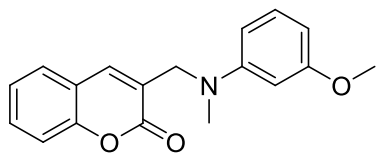


3-(((4-Bromophenyl)(methyl)amino)methyl)-2H-chromen-2-one (3h): According to the general procedure, 2H-chromen-2-one (50 mg, 0.342 mmol) and 4-bromo-

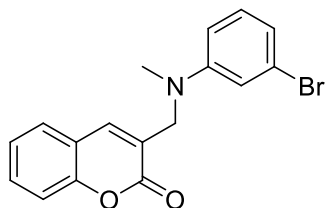
N,N-dimethylaniline (4.0 equiv, 1.01 mmol) provided **3h** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (88 mg, 75%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1608, 1707, 2087, 2955, 3452. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 1H), 7.41 – 7.31 (m, 3H), 7.30 – 7.20 (m, 3H), 6.57 (d, $J = 9.0$ Hz, 2H), 4.40 (s, 2H), 3.09 (s, 3H). ^{13}C NMR (125MHz, Chloroform-*d*) δ 161.1, 153.1, 148.0, 137.9, 132.1, 131.3, 127.8, 124.9, 124.6, 119.2, 116.6, 113.7, 109.1, 52.7, 39.2. HRMS: Exact mass calculated for $C_{17}H_{14}BrNO_2 [M+H]^+$ 344.0281, found 344.0281.



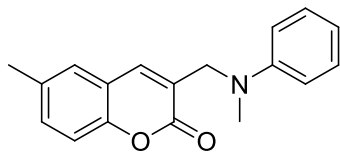
3-(((Methyl(*m*-tolyl)amino)methyl)-2H-chromen-2-one (3i): According to the general procedure, 2H-chromen-2-one (50 mg, 0.342 mmol) and *N,N*,3-trimethylaniline (4.0 equiv, 1.37 mmol) provided **3i** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (64 mg, 67%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1601, 1707, 2917, 3043. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 2H), 7.43 – 7.33 (m, 2H), 7.28 – 7.21 (m, 1H), 7.14 (dd, $J = 8.9, 7.5$ Hz, 1H), 6.62 – 6.51 (m, 3H), 4.43 (s, 2H), 3.10 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.3, 153.2, 149.2, 139.2, 137.7, 131.0, 129.3, 127.8, 125.6, 124.5, 119.4, 118.1, 116.6, 112.8, 109.3, 52.8, 39.0, 22.0. HRMS: Exact mass calculated for $C_{18}H_{17}NO_2 [M+H]^+$ 280.1332, found 280.1345.



3-(((3-Methoxyphenyl)(methyl)amino)methyl)-2H-chromen-2-one (3j): According to the general procedure, 2H-chromen-2-one (50 mg, 0.342 mmol) and 3-methoxy-*N,N*-dimethylaniline (4.0 equiv, 1.37 mmol) provided **3j** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (62 mg, 61%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1576, 1608, 1718, 2835, 2934. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 2H), 7.36 (dd, $J = 24.8, 8.6$ Hz, 2H), 7.28 – 7.20 (m, 1H), 7.14 (t, $J = 8.2$ Hz, 1H), 6.32 (dt, $J = 8.1, 2.6$ Hz, 2H), 6.26 (t, $J = 2.3$ Hz, 1H), 4.41 (s, 2H), 3.77 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.0, 153.1, 150.4, 143.5, 137.8, 131.9, 131.1, 130.2, 127.8, 125.3, 124.5, 116.6, 105.2, 101.8, 98.8, 55.2, 52.7, 39.0. HRMS: Exact mass calculated for $\text{C}_{18}\text{H}_{17}\text{NO}_3[\text{M}+\text{H}]^+$ 296.1281, found 296.1288.

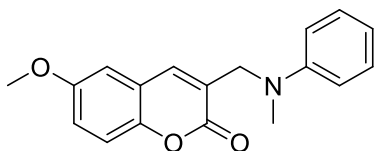


3-(((3-Bromophenyl)(methyl)amino)methyl)-2H-chromen-2-one (3k): According to the general procedure, 2H-chromen-2-one (50 mg, 0.342 mmol) and 3-bromo-*N,N*-dimethylaniline (4.0 equiv, 1.37 mmol) provided **3k** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (78 mg, 66 %). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1556, 1607, 1703, 2917. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 1H), 7.43 – 7.32 (m, 3H), 7.28 – 7.21 (m, 1H), 7.06 (t, $J = 8.0$ Hz, 1H), 6.88 – 6.82 (m, 2H), 6.62 – 6.56 (m, 1H), 4.41 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.1, 153.2, 150.2, 137.8, 131.3, 130.7, 127.9, 124.8, 124.6, 123.8, 120.0, 119.2, 116.6, 114.8, 110.7, 52.6, 39.0. HRMS: Exact mass calculated for $\text{C}_{17}\text{H}_{14}\text{BrNO}_2[\text{M}+\text{H}]^+$ 344.0281, found 344.0287.



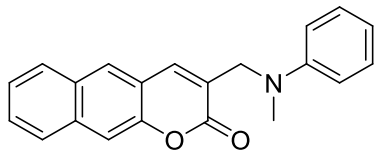
6-Methyl-3-((methyl(phenyl)amino)methyl)-2H-chromen-2-one (4a):

According to the general procedure, 6-methyl-2H-chromen-2-one (50 mg, 0.312 mmol) and *N,N*-dimethyl aniline (3.0 equiv, 1.25 mmol) provided **4a** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (72 mg, 82%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1615, 1718, 2923, 3029, 3060, 3417. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 7.31 – 7.20 (m, 4H), 7.17 (s, 1H), 6.73 (dd, $J = 22.1, 7.8$ Hz, 3H), 4.43 (s, 2H), 3.11 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.5, 151.3, 149.0, 137.8, 134.2, 132.1, 129.5, 127.7, 125.2, 119.1, 117.1, 116.3, 112.1, 52.8, 39.0, 20.8. HRMS: Exact mass calculated for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 280.1332, found 280.1338.



6-Methoxy-3-((methyl(phenyl)amino)methyl)-2H-chromen-2-one (4b):

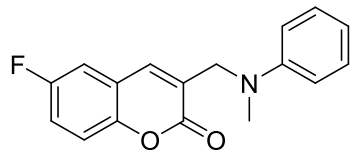
According to the general procedure, 6-methoxy-2H-chromen-2-one (50 mg, 0.283 mmol) and *N,N*-dimethyl aniline (4.0 equiv, 1.14 mmol) provided **4b** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (63 mg, 75%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1640, 1712, 2925, 3242, 3373. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 (s, 1H), 7.30 – 7.21 (m, 3H), 7.06 (dd, $J = 9.1, 2.9$ Hz, 1H), 6.82 (d, $J = 2.9$ Hz, 1H), 6.74 (dd, $J = 24.3, 7.8$ Hz, 3H), 4.43 (s, 2H), 3.79 (s, 3H), 3.12 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.4, 156.2, 149.0, 147.6, 137.6, 129.5, 125.7, 119.7, 119.1, 117.6, 117.1, 112.0, 109.8, 55.9, 52.8, 39.0. HRMS: Exact mass calculated for $\text{C}_{18}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 296.1281, found 296.1285.



3-((Methyl(phenyl)amino)methyl)-2H-

benzo[g]chromen-2-one(4c): According to the general procedure, 2H-benzo[g]chromen-2-one (50 mg, 0.254

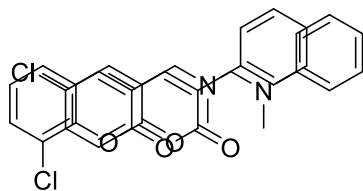
mmol) and *N,N*-dimethyl aniline (4.0 equiv, 1.02 mmol) provided **4c** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (37 mg, 46%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1368, 1506, 1598, 1714. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 7.88 – 7.82 (m, 1H), 7.67 – 7.56 (m, 4H), 7.36 (d, $J = 8.5$ Hz, 1H), 7.30 – 7.23 (m, 2H), 6.80 – 6.73 (m, 3H), 4.51 (s, 2H), 3.15 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.4, 150.1, 149.1, 138.6, 134.5, 129.5, 128.5, 127.9, 127.2, 125.0, 124.5, 123.9, 123.0, 122.2, 117.2, 114.8, 112.1, 52.8, 39.1. exact mass calculated for $\text{C}_{21}\text{H}_{17}\text{NO}_2$ [$\text{M}+\text{NH}_4$] $^+$ 333.1603, found 333.1664.



6-Fluoro-3-((methyl(phenyl)amino)methyl)-2H-

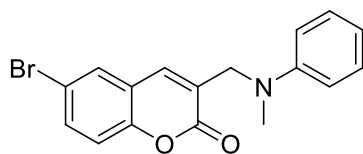
chromen-2-one (4d): According to the general procedure, 6-fluoro-2H-chromen-2-one (50 mg, 0.30 mmol) and *N,N*-

dimethylaniline (4.0 equiv, 1.22 mmol) provided **4d** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (19 mg, 22%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1714, 2923, 3064. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 7.32 (dd, $J = 9.1, 4.4$ Hz, 1H), 7.28 – 7.15 (m, 3H), 7.07 (dd, $J = 8.0, 2.9$ Hz, 1H), 6.76 (t, $J = 7.2$ Hz, 1H), 6.70 (d, $J = 7.9$ Hz, 2H), 4.43 (s, 2H), 3.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.9, 157.9, 149.3, 148.9, 136.8, 129.5, 126.9, 120.1 (d, $J = 8.8$ Hz), 118.5 (d, $J = 24.4$ Hz), 118.1 (d, $J = 8.4$ Hz), 117.3, 113.1 (d, $J = 23.9$ Hz), 112.1, 52.9, 39.1. HRMS: Exact mass calculated for $\text{C}_{17}\text{H}_{14}\text{FNO}_2$ [$\text{M}+\text{H}$] $^+$ 284.1081, found 284.1076.



6-Chloro-3-((methyl(phenyl)amino)methyl)-2H-chromen-2-one (4e):

According to the general procedure, 6-chloro-2*H*-chromen-2-one (50 mg, 0.276 mmol) and *N,N*-dimethyl aniline (4.0 equiv, 1.11 mmol) provided **4e** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (25 mg, 30%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1601, 1722, 2921. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, $J = 8.8$ Hz, 1H), 7.36 (s, 2H), 7.31 – 7.19 (m, 3H), 6.72 (dd, $J = 30.1, 7.7$ Hz, 3H), 4.42 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.6, 151.5, 148.8, 136.6, 131.0, 129.8, 129.5, 127.1, 126.9, 120.4, 118.0, 117.4, 112.1, 52.8, 39.1. HRMS: Exact mass calculated for $\text{C}_{17}\text{H}_{14}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$ 300.0786, found 300.0782.

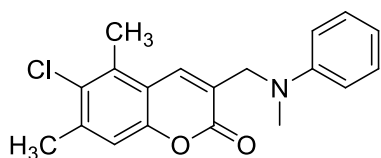


6-Bromo-3-((methyl(phenyl)amino)methyl)-2H-chromen-2-one (4f):

According to the general procedure, 6-bromo-2*H*-chromen-2-one (50 mg, 0.2 mmol) and *N,N*-dimethylaniline (4.0 equiv, 0.8 mmol) provided **4f** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (37 mg, 48%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1600, 1722, 2850, 2918. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.50 (m, 2H), 7.36 (s, 1H), 7.27 – 7.19 (m, 3H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 8.2$ Hz, 2H), 4.43 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.6, 152.0, 148.8, 136.5, 133.8, 130.1, 129.5, 126.9, 120.9, 118.3, 117.4, 117.1, 112.1, 52.8, 39.0. HRMS: Exact mass calculated for $\text{C}_{17}\text{H}_{14}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$ 344.0281, found 344.0281.

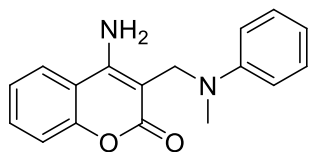
8-Chloro-3-((methyl(phenyl)amino)methyl)-2H-chromen-2-one (4g): According to the general procedure, 8-chloro-2*H*-chromen-2-one (50 mg, 0.276 mmol) and *N,N*-dimethylaniline (4.0 equiv, 1.11 mmol) provided **4g** after flash column

chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (15 mg, 18%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1507, 1601, 1725, 2918. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.53 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.44 (s, 1H), 7.29 (d, $J = 7.8$ Hz, 1H), 7.25 – 7.20 (m, 2H), 7.17 (t, $J = 7.8$ Hz, 1H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.70 (d, $J = 8.2$ Hz, 2H), 4.44 (s, 2H), 3.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.1, 148.9, 137.4, 131.5, 129.5, 126.5, 126.3, 124.7, 121.5, 120.6, 117.3, 112.1, 52.8, 39.1. HRMS: Exact mass calculated for $\text{C}_{17}\text{H}_{14}\text{ClNO}_2[\text{M}+\text{H}]^+$ 300.0786, found 300.0789.



**6-Chloro-5,7-dimethyl-3-
((methyl(phenyl)amino)methyl)-2H-chromen-2-one**

(4h) According to the general procedure, 6-chloro-5,7-dimethyl-2H-chromen-2-one (50 mg, 0.239 mmol) and *N,N*-dimethylaniline (4.0 equiv, 0.958 mmol) provided **4h** after flash column chromatography (5% Ethyl acetate in petroleum ether) as yellow liquid (34 mg, 43%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$: 1601, 1718, 2922. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.24 (dd, $J = 8.1, 6.8$ Hz, 2H), 7.09 (s, 1H), 6.75 (dd, $J = 14.2, 7.6$ Hz, 3H), 4.43 (s, 2H), 3.10 (s, 3H), 2.44 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.9, 151.6, 149.2, 140.1, 134.9, 133.3, 130.8, 129.4, 124.5, 117.4, 117.1, 116.2, 112.5, 53.1, 39.1, 21.7, 16.0. HRMS: Exact mass calculated for $\text{C}_{19}\text{H}_{18}\text{ClNO}_2[\text{M}+\text{Na}]^+$ 350.0924, found 350.0911.



4-Amino-3-((methyl(phenyl)amino)methyl)-2H-chromen-2-one (4i): According to the general procedure, 4-amino-2H-chromen-2-one (50 mg, 0.31 mmol) and *N,N*-dimethyl

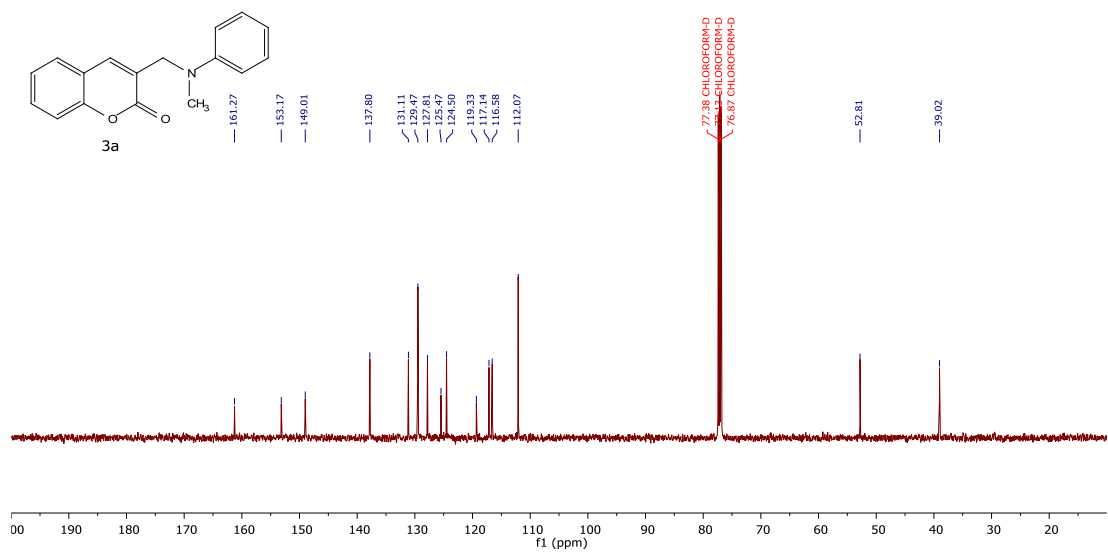
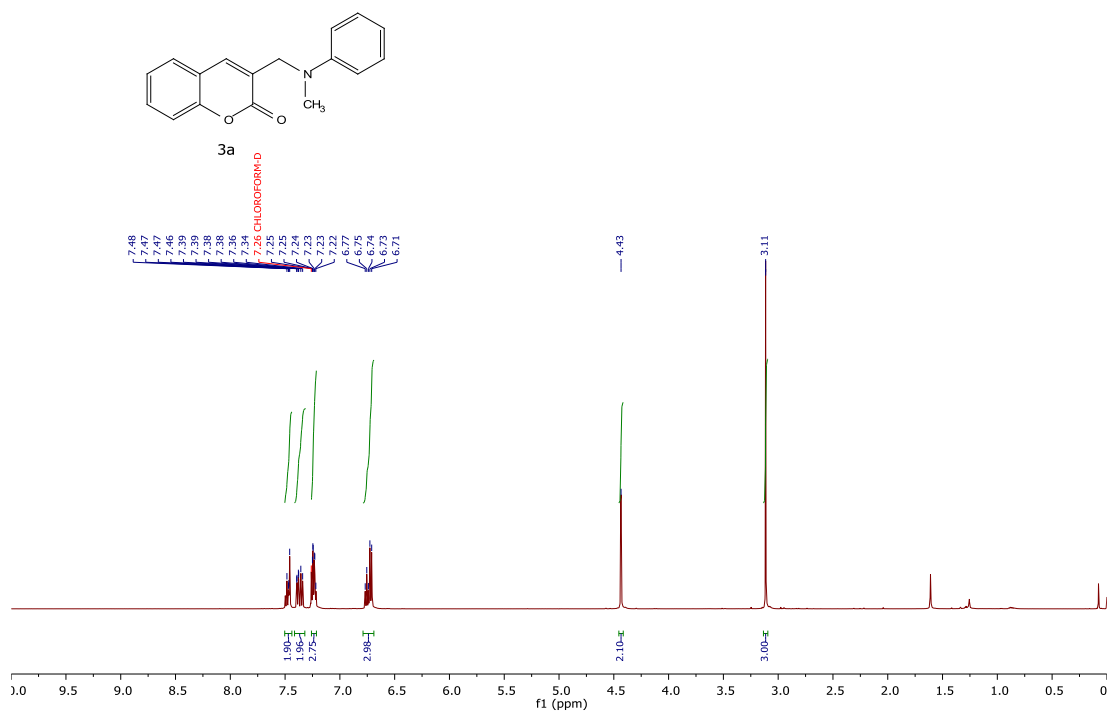
aniline (4.0 equiv, 1.24 mmol) provided **4i** after flash column chromatography (15% Ethyl acetate in petroleum ether) as yellow liquid (37 mg, 55%). IR (neat): $\nu_{\max}/\text{cm}^{-1}$

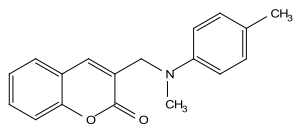
¹: 1637, 1605, 2799, 3239, 3351. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.49 (t, *J* = 7.8 Hz, 1H), 7.35 (dd, *J* = 24.8, 8.5 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 2H), 3.87 (s, 2H), 2.88 (s, 3H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 163.6, 152.9, 149.7, 149.6, 131.4, 128.8, 126.1, 123.5, 120.6, 117.6, 114.6, 113.3, 99.5, 40.8, 29.9. HRMS: Exact mass calculated for C₁₇H₁₆N₂O² [M+H]⁺ 281.1285, found 281.1280.

6. References:

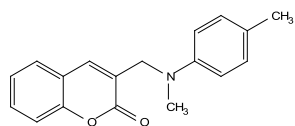
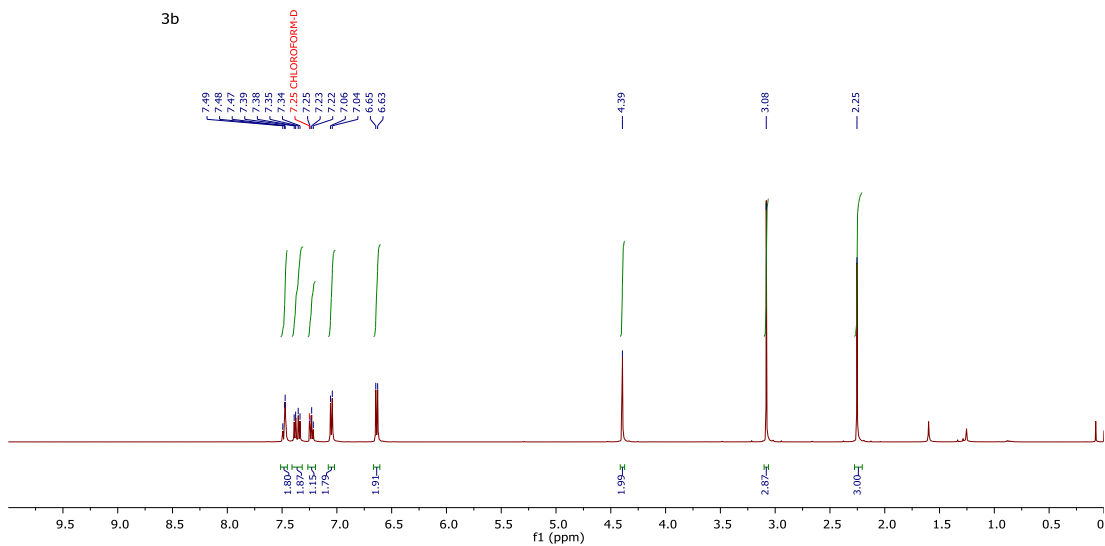
1. Wu, Q.L., Guo, J., Huang, G.B., Chan, A.S., Weng, J. and Lu, G., 2020. Visible-light-promoted radical cross-coupling of para-quinone methides with N-substituted anilines: an efficient approach to 2, 2-diarylethylamines. *Organic & Biomolecular Chemistry*, 18(5), pp.860-864.
2. Zhao, Y.R., Li, L. and Xuan, J., 2023. Direct Synthesis of Indolines via Cyclization of Tertiary Aryl Amines with Iodonium Ylides under Sole Visible Light Irradiation. *Advanced Synthesis & Catalysis*, 365(1), pp.110-115.
3. Gadakh, S.K., Dey, S. and Sudalai, A., 2015. Rh-Catalyzed synthesis of coumarin derivatives from phenolic acetates and acrylates via C–H bond activation. *The Journal of organic chemistry*, 80(22), pp.11544-11550.
4. Dubuffet, T., Loutz, A. and Lavielle, G., 1999. An efficient large scale synthesis of coumarins by a dealkylative boron-mediated ring closure of 3-(ortho-methoxyaryl) propenoic esters. *Synthetic communications*, 29(6), pp.929-936.

7. ^1H & ^{13}C spectra:

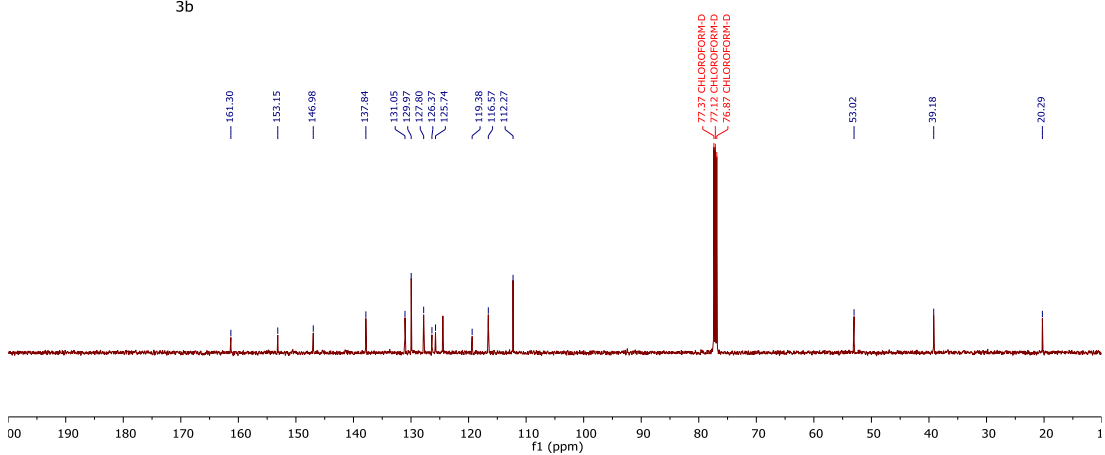


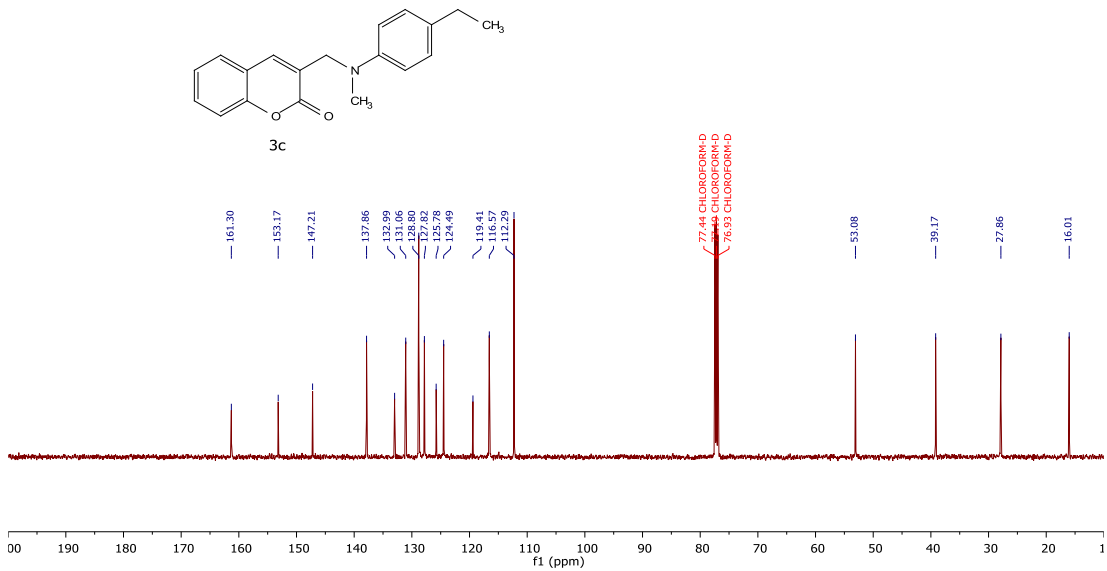
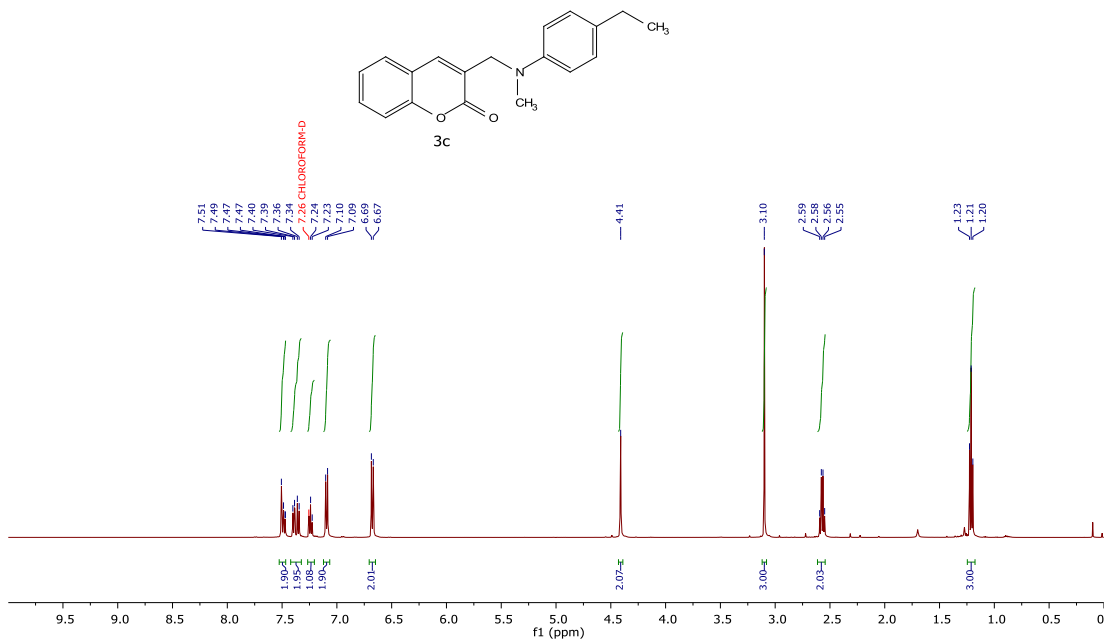


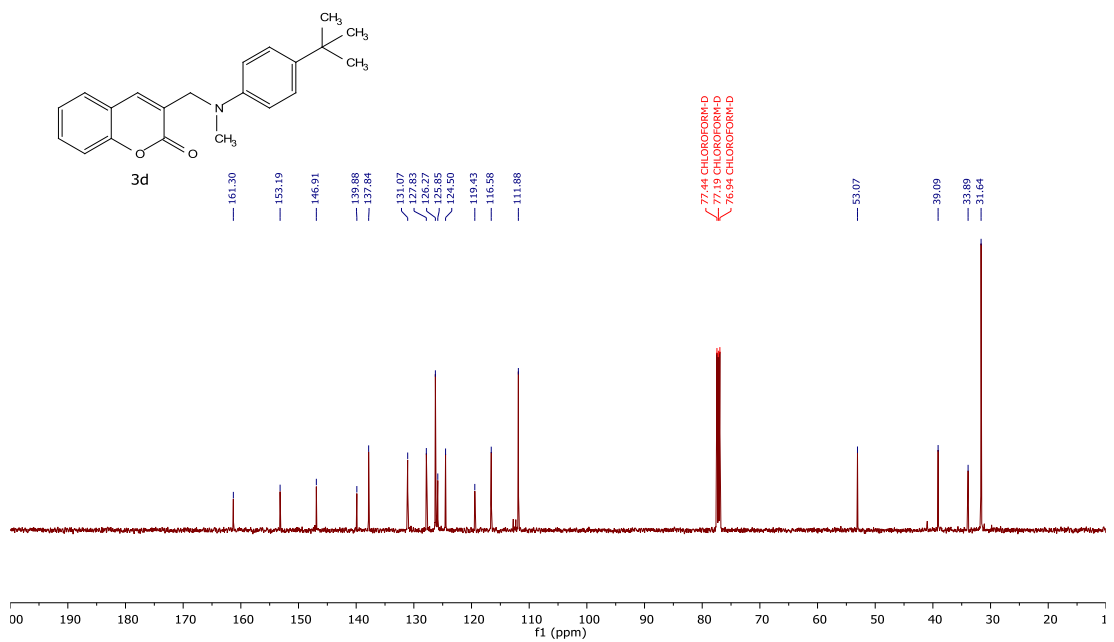
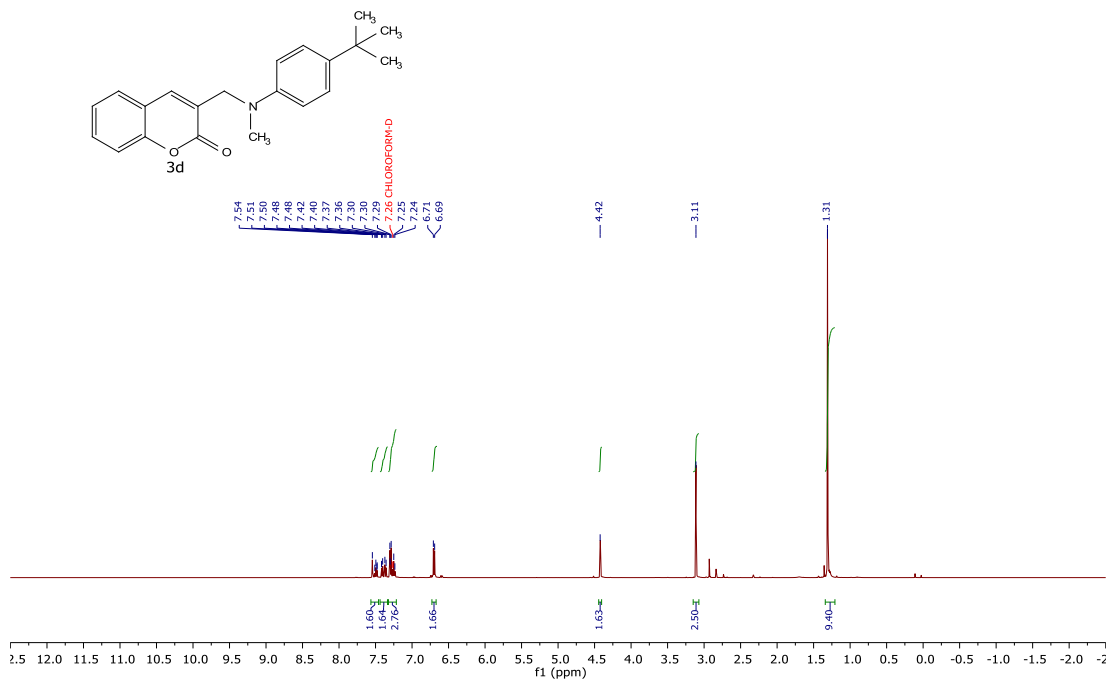
3b

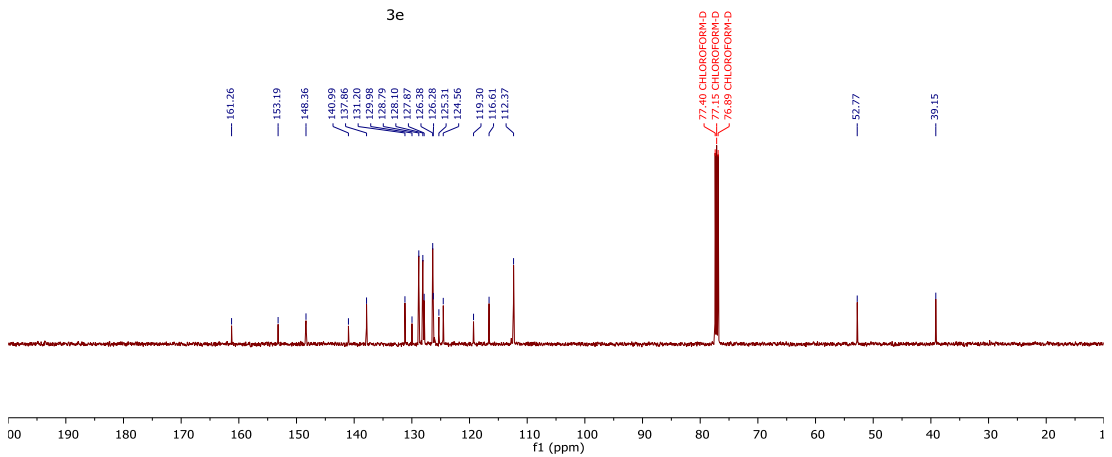
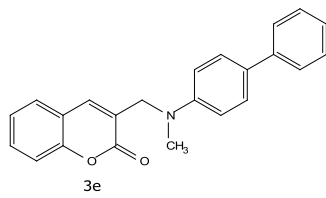
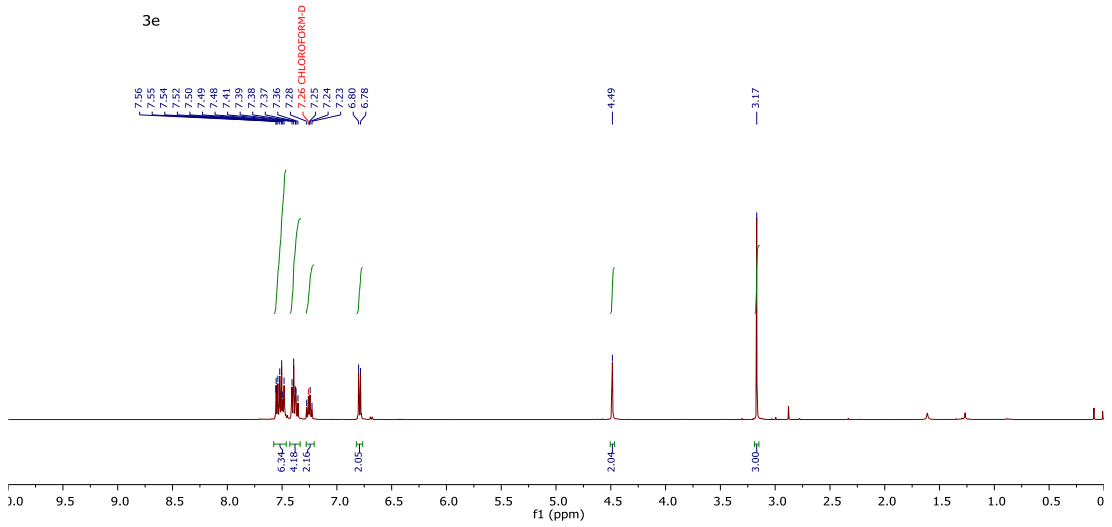
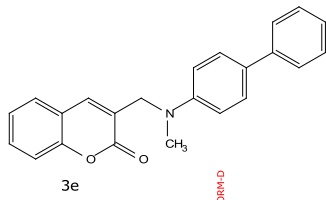


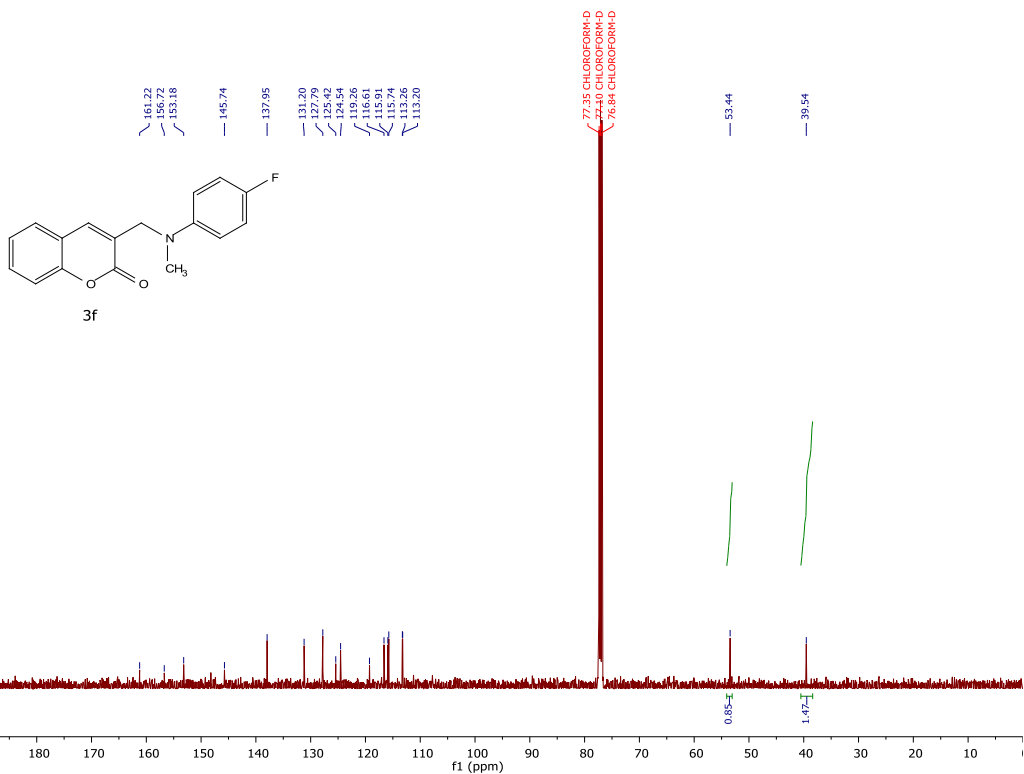
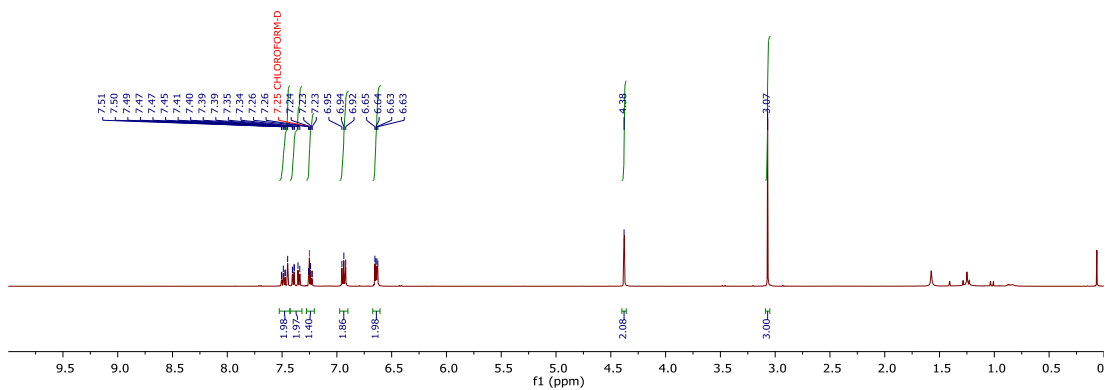
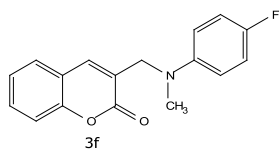
3b

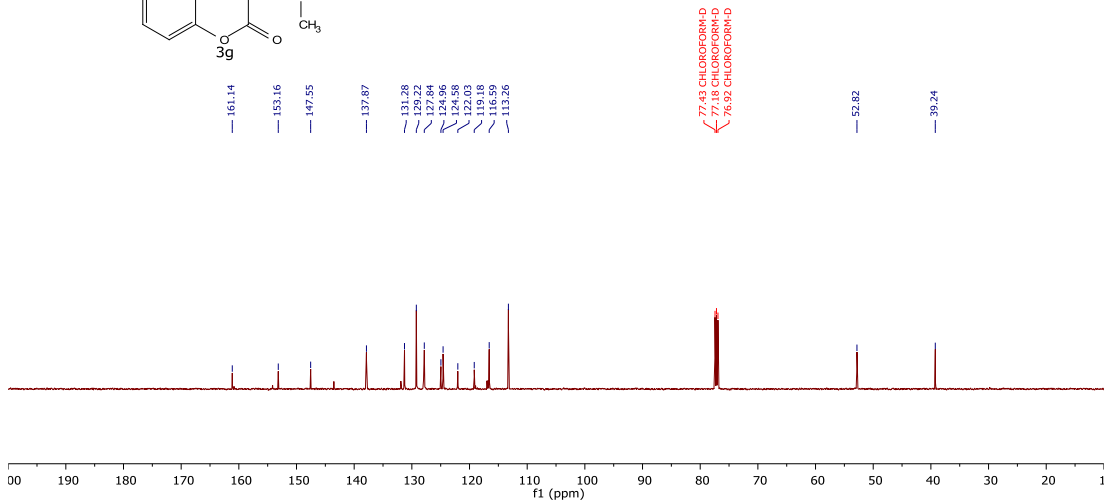
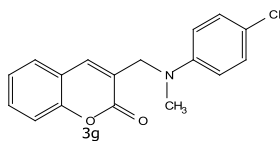
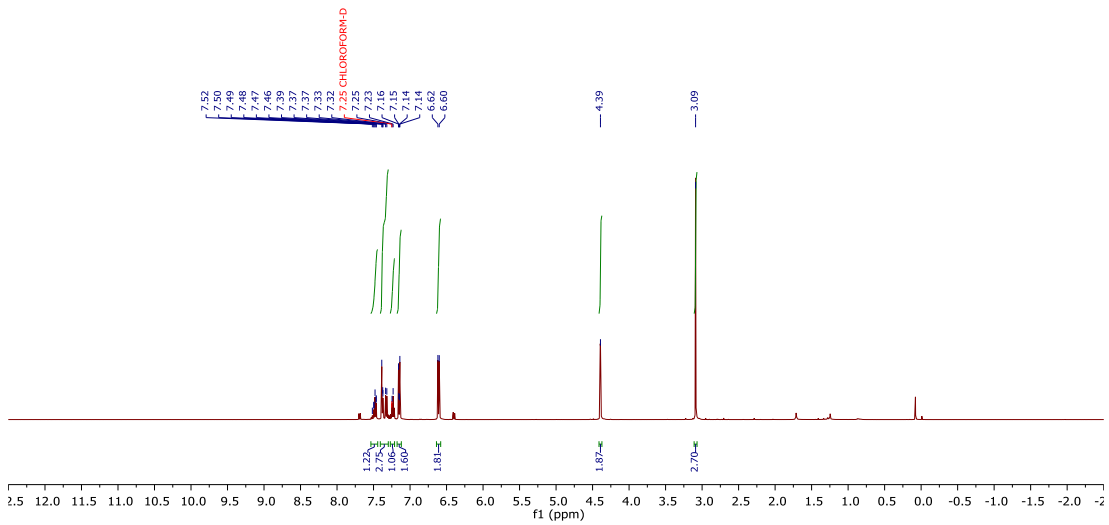
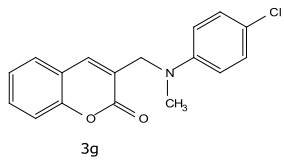


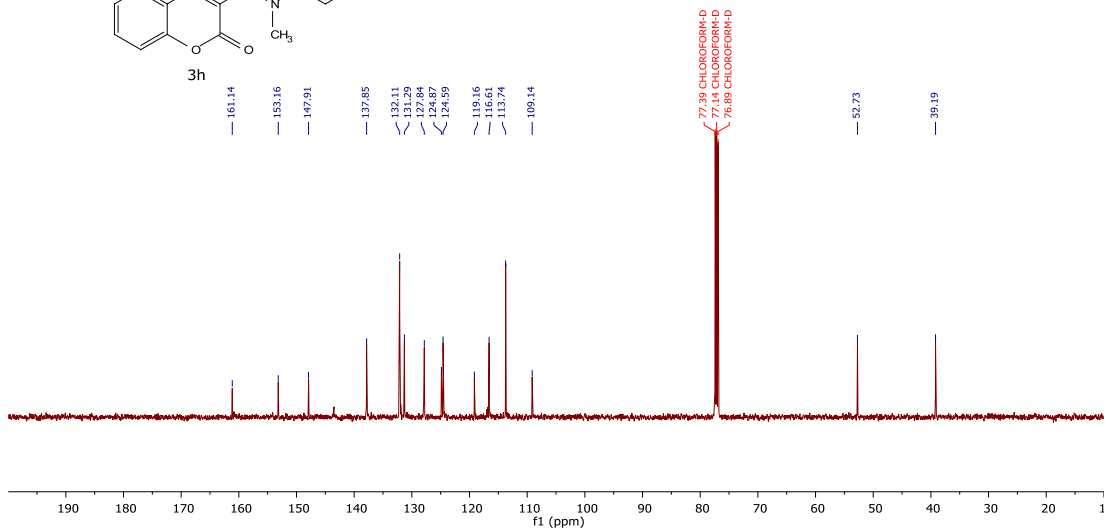
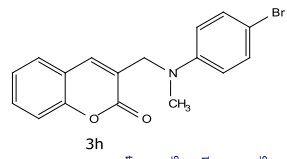
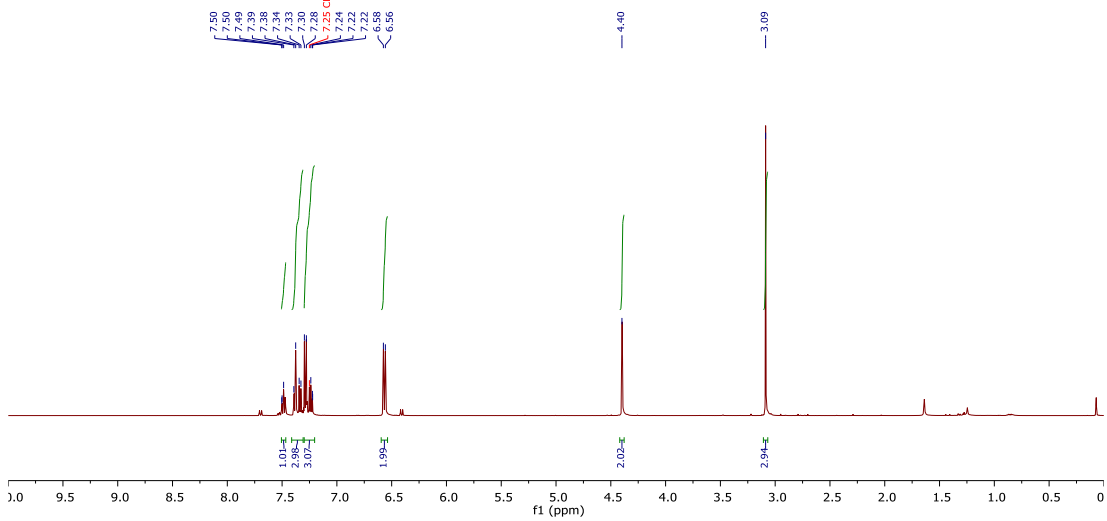
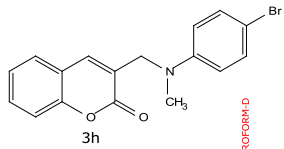


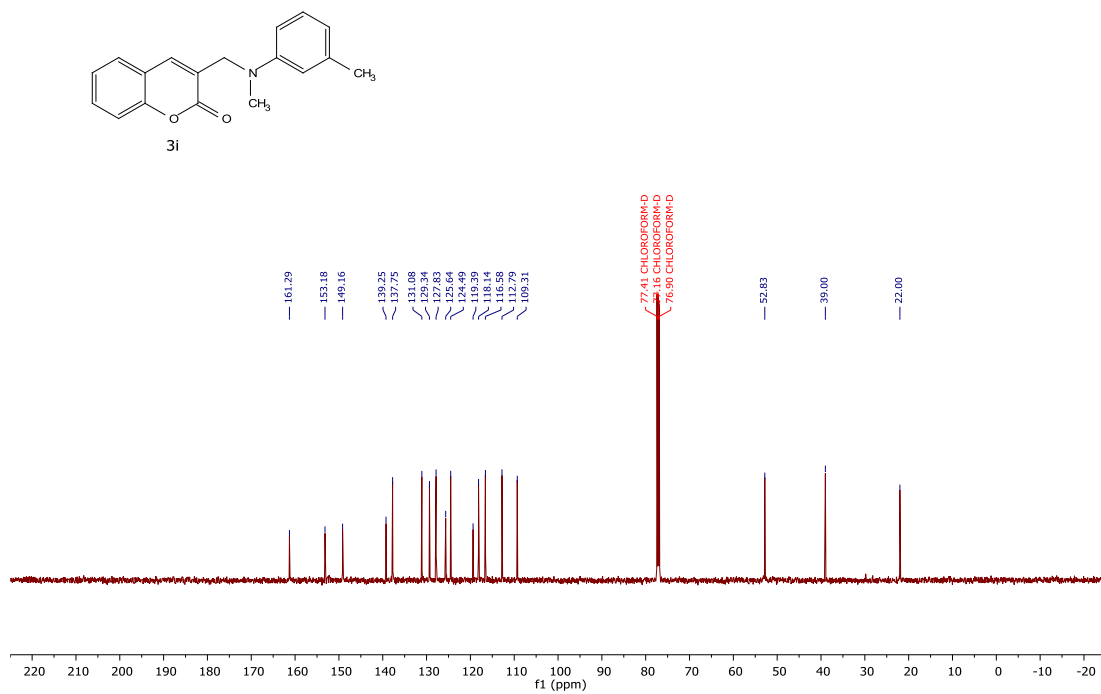
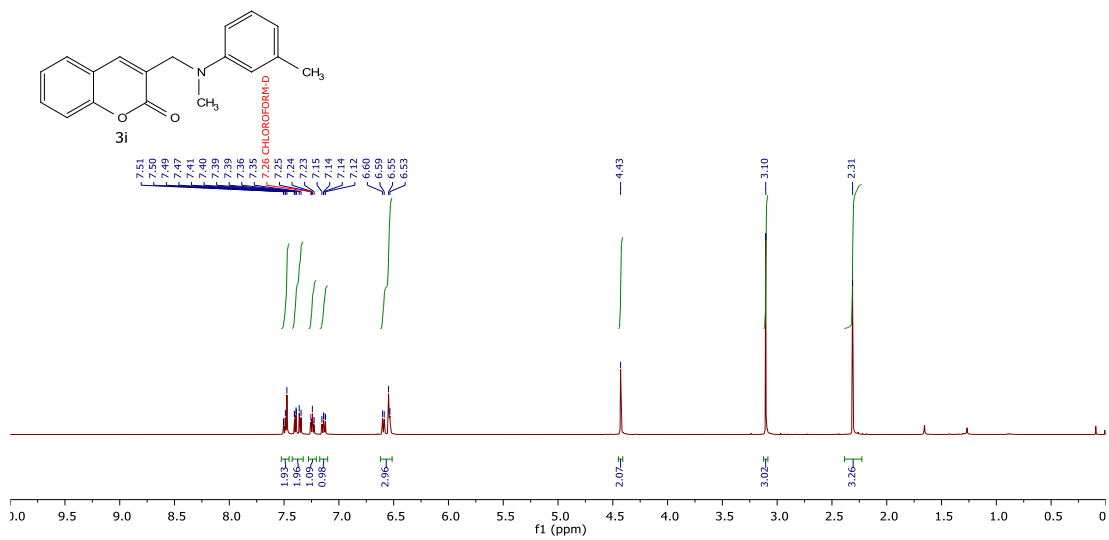


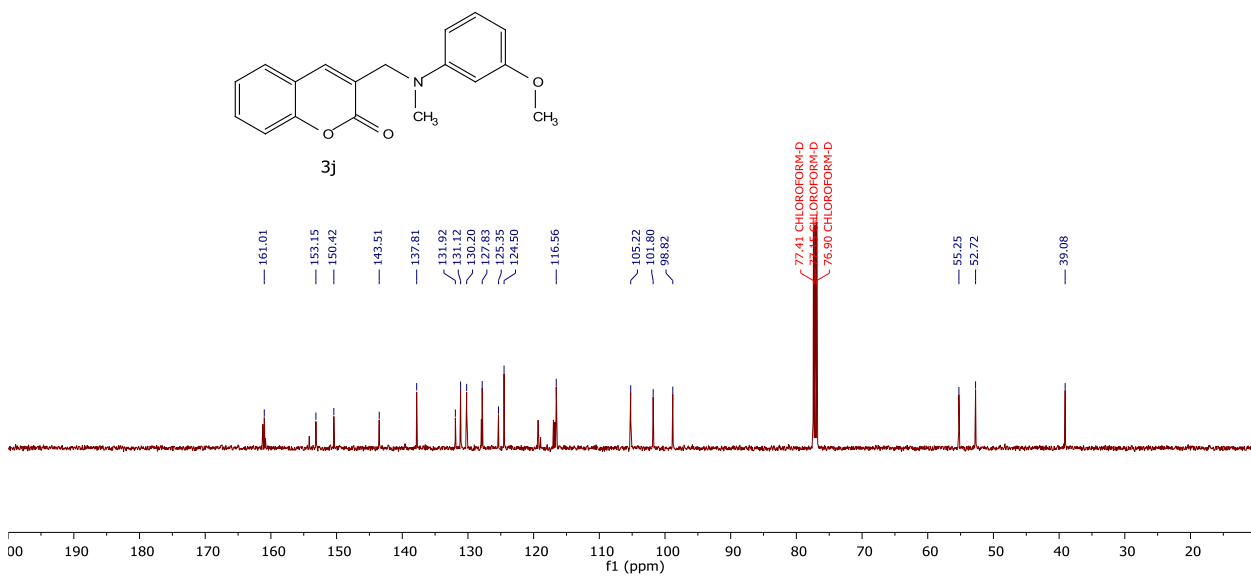
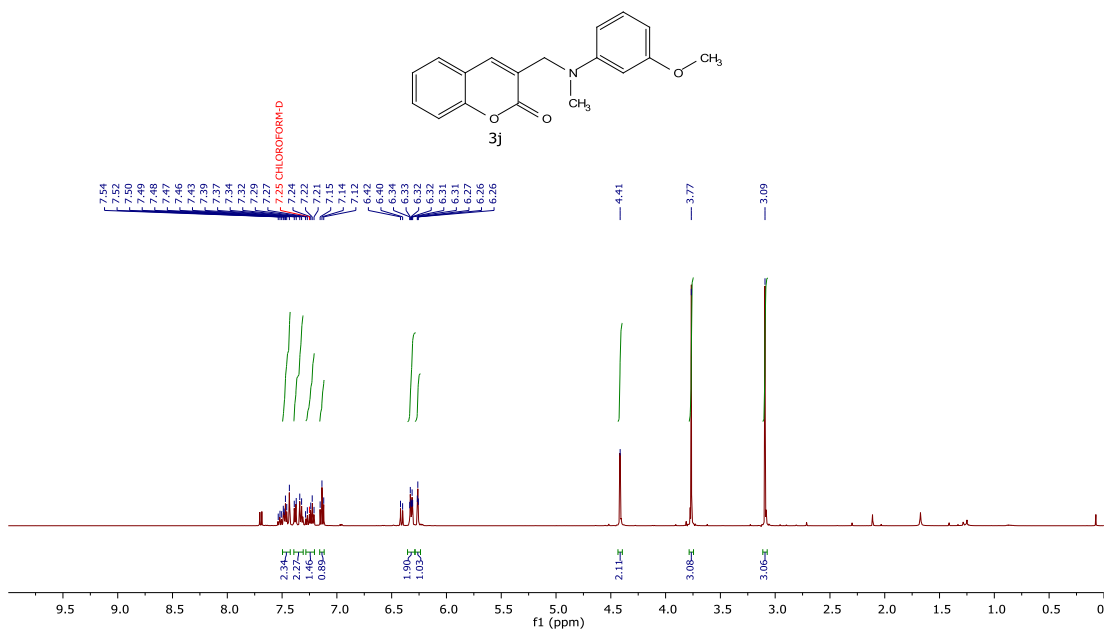


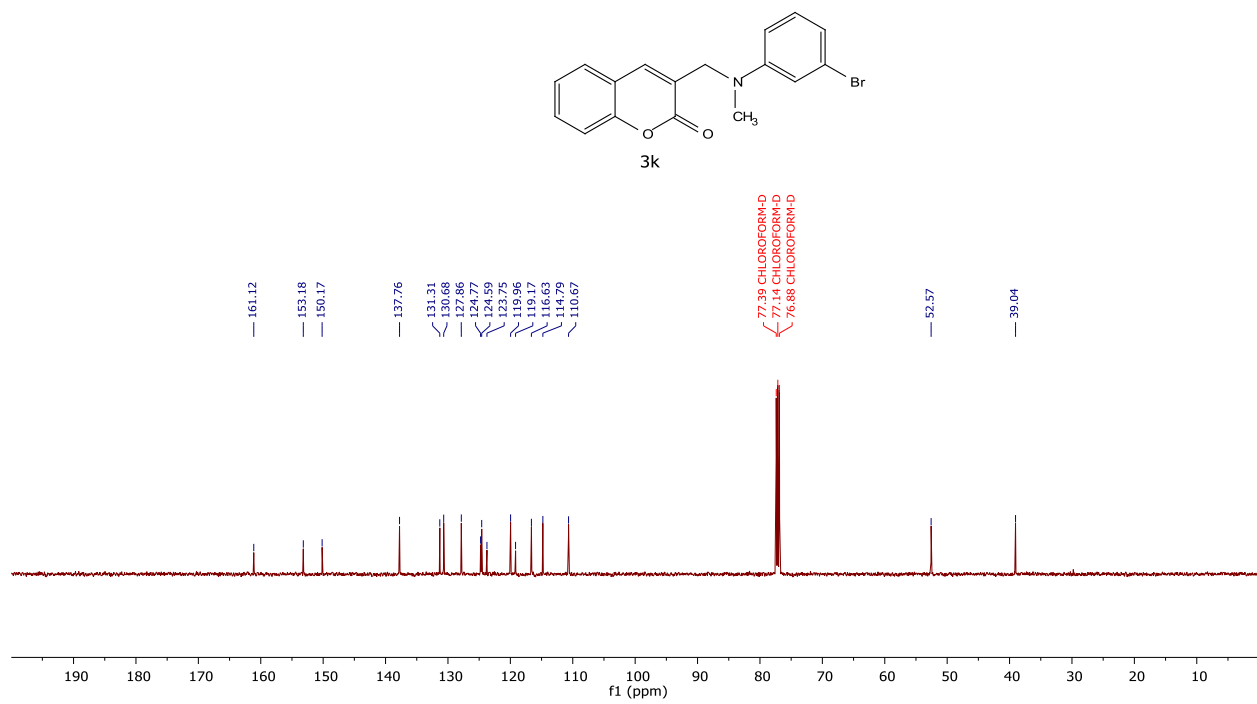
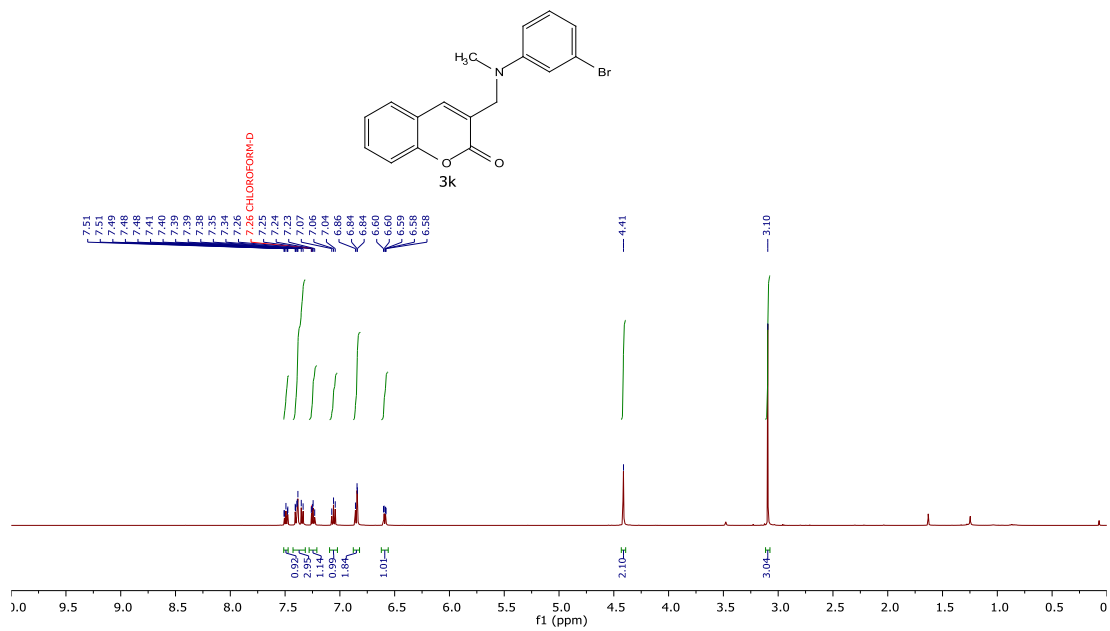


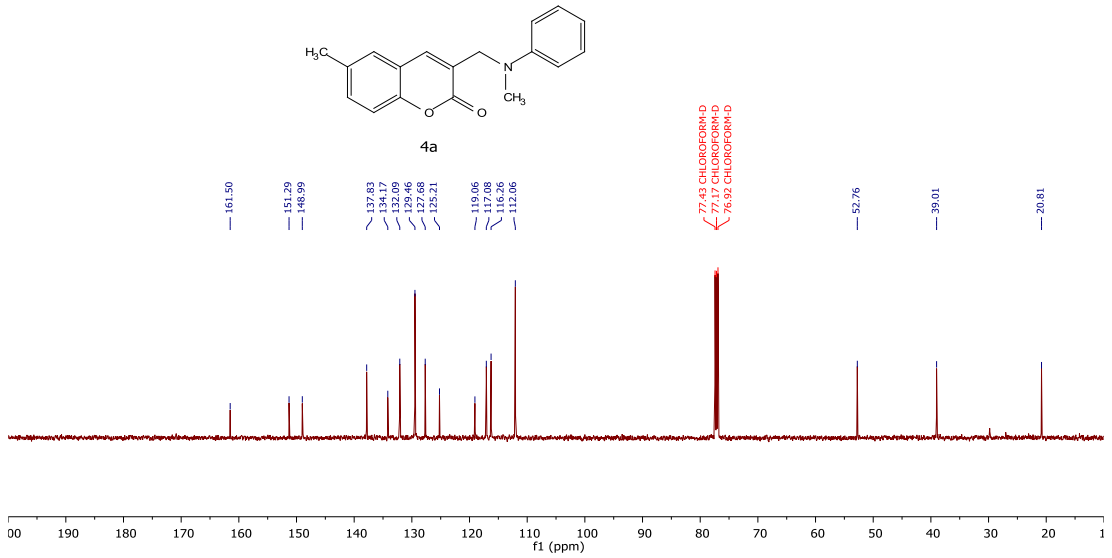
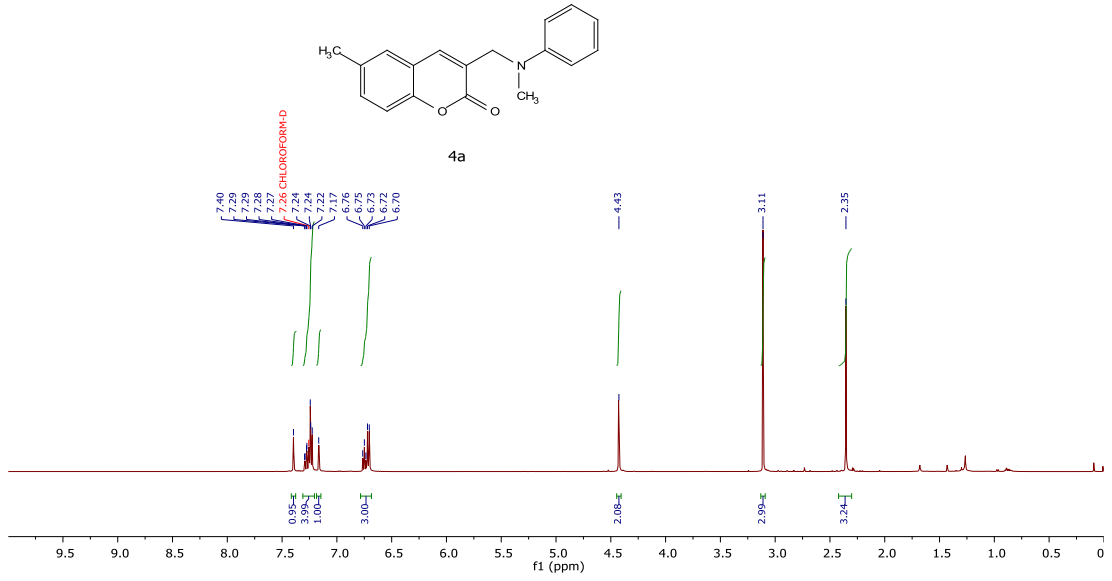


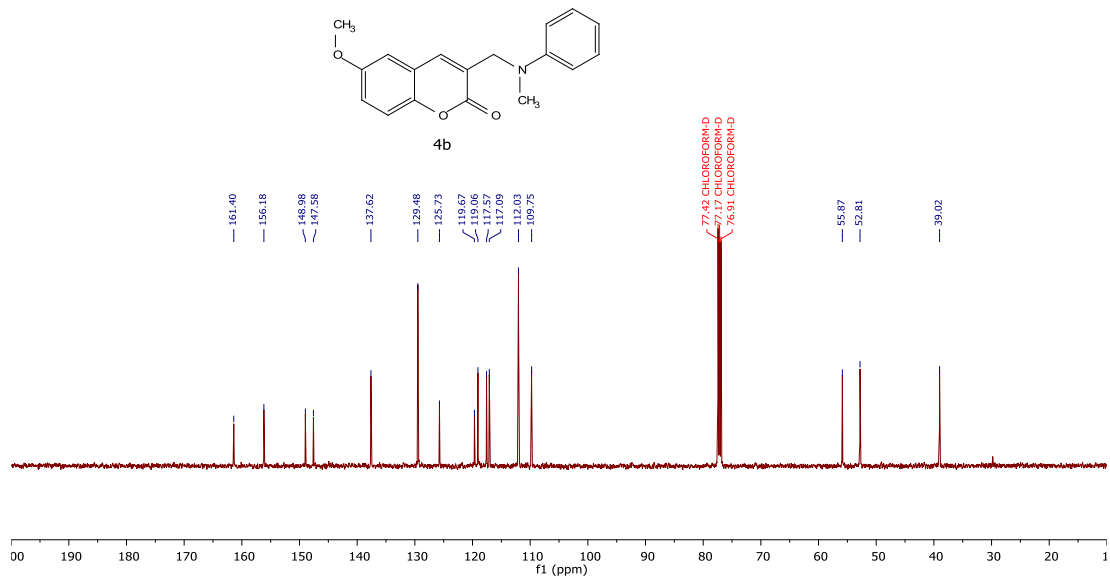
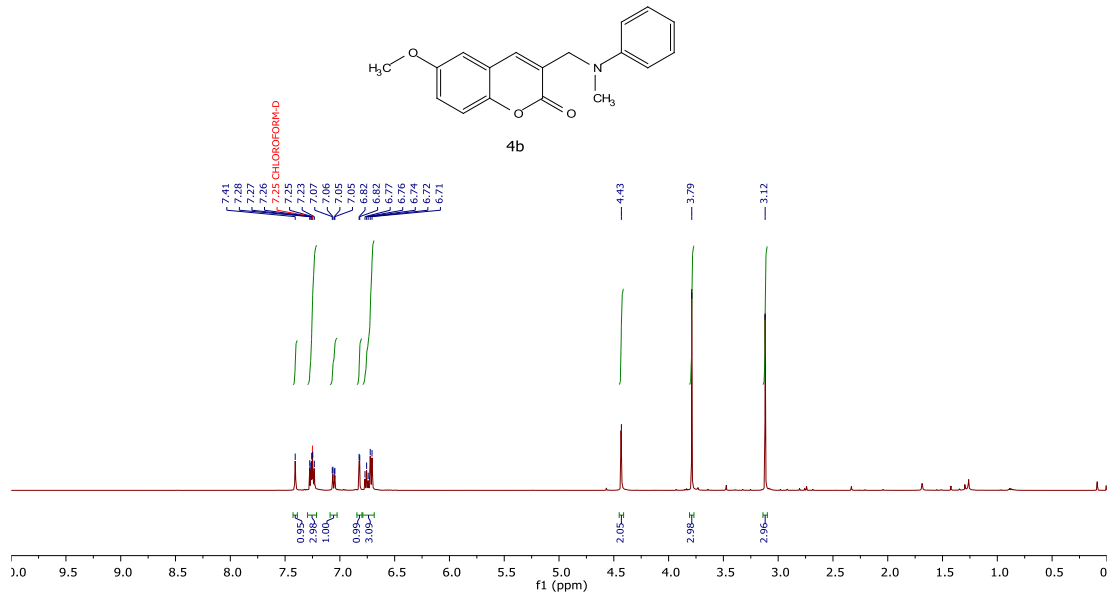


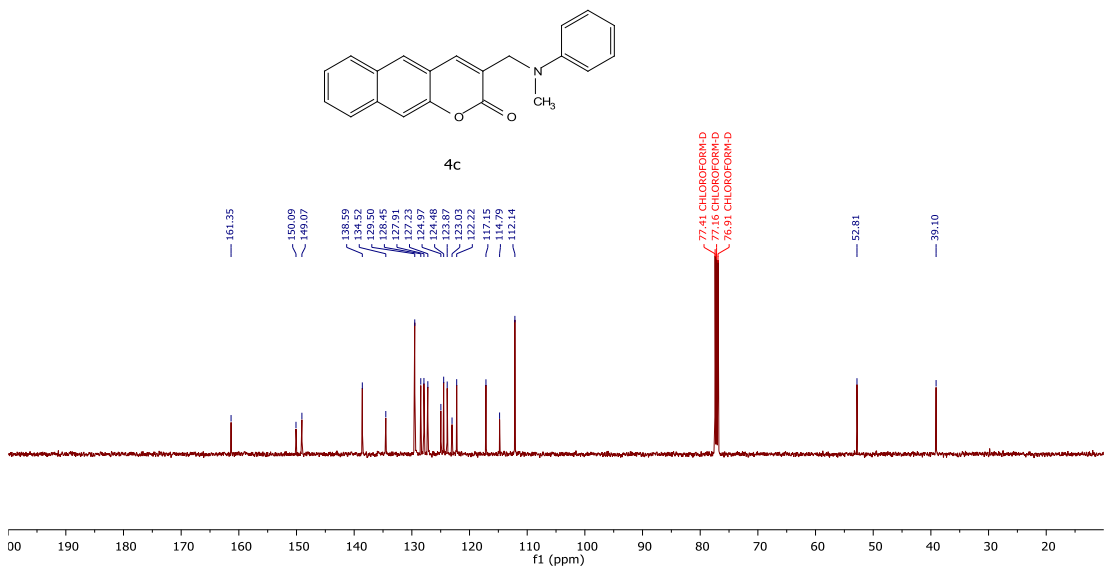
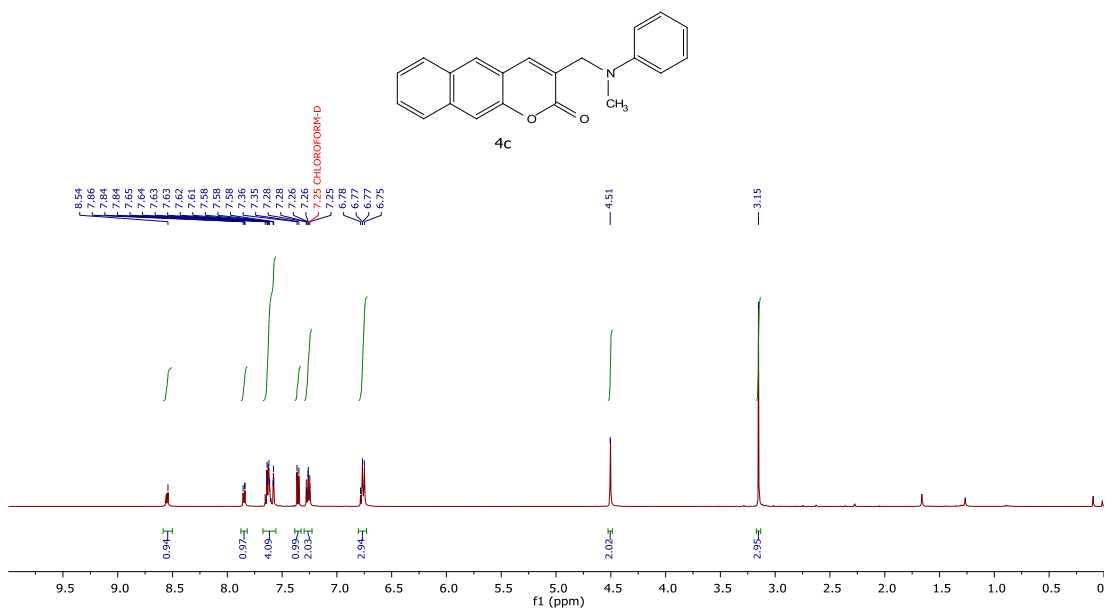


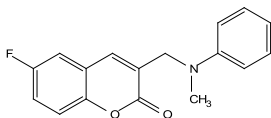




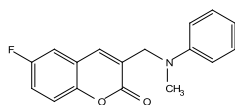
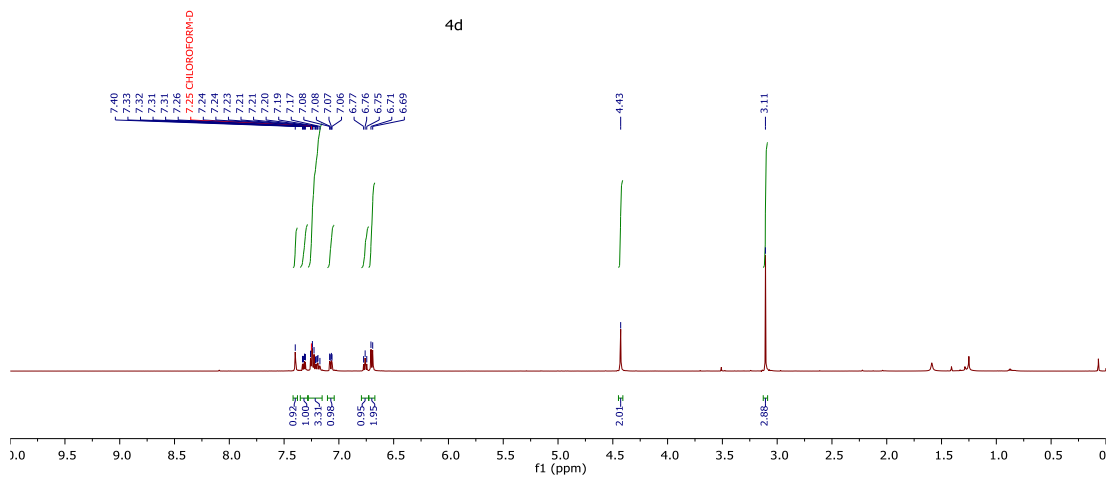




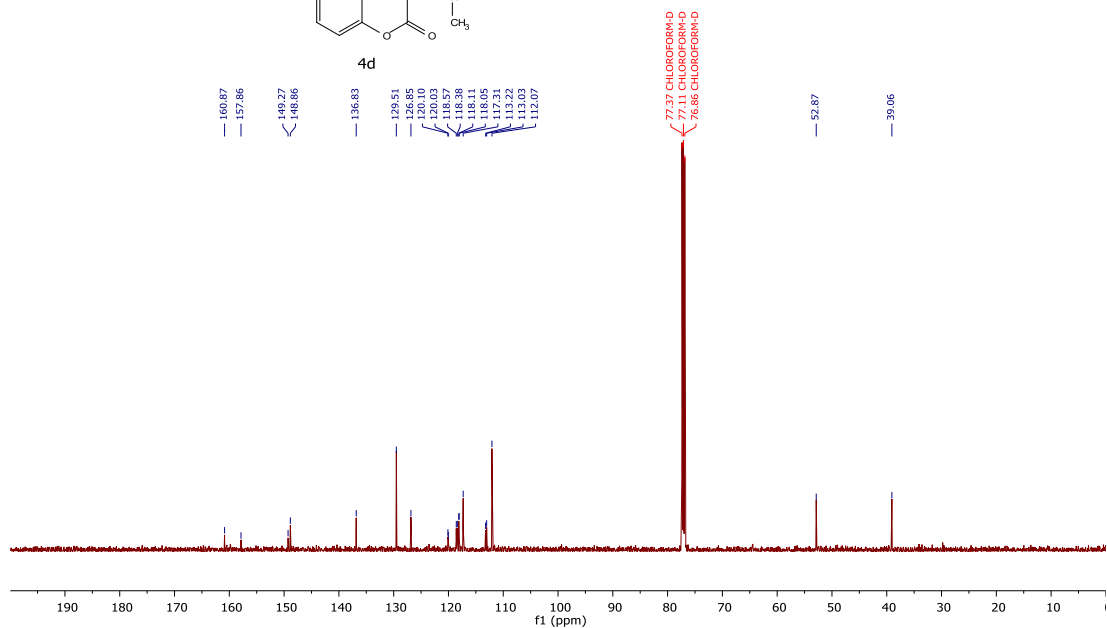


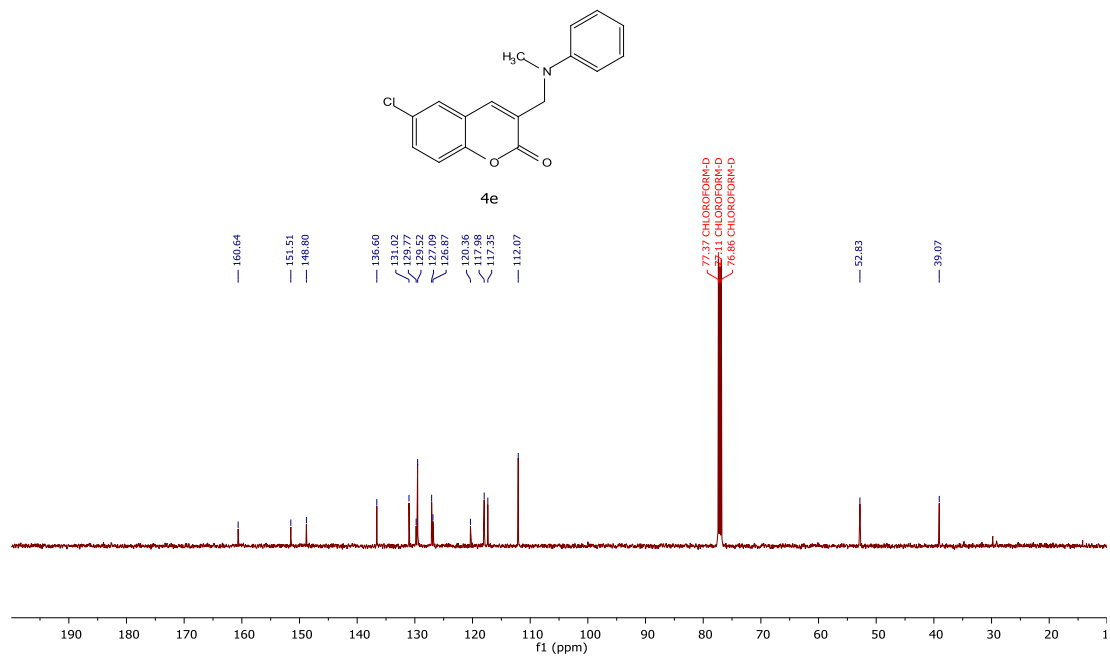
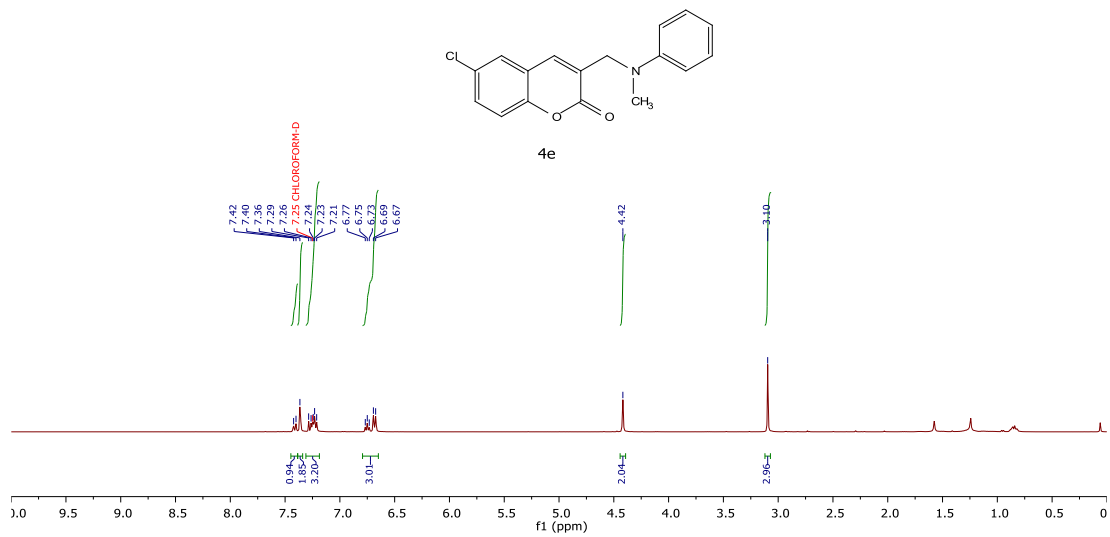


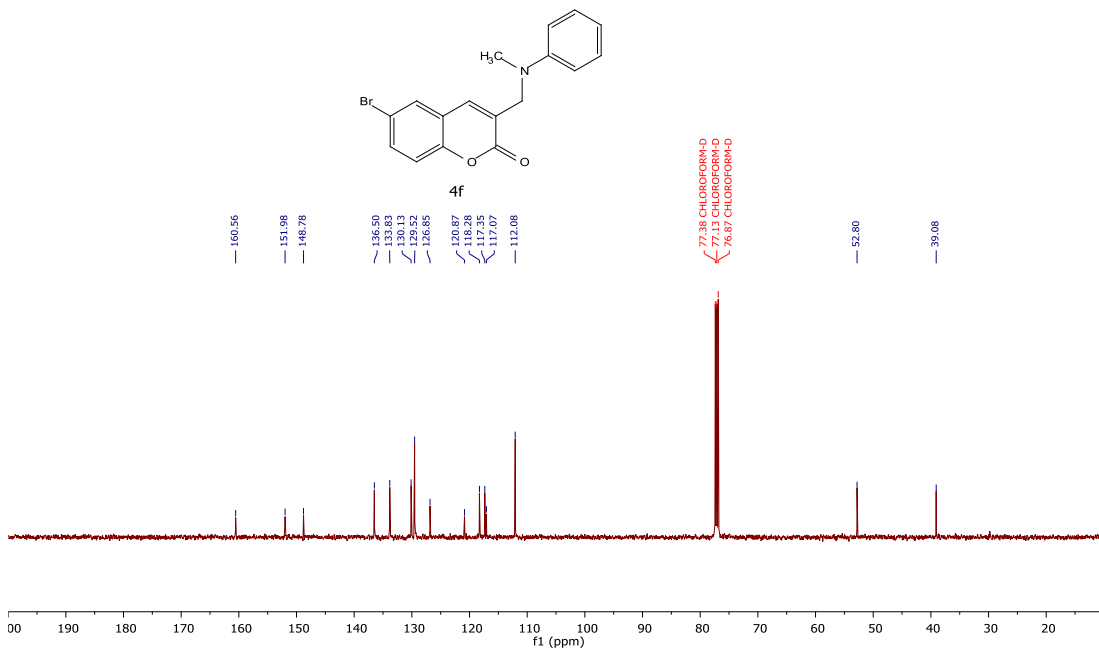
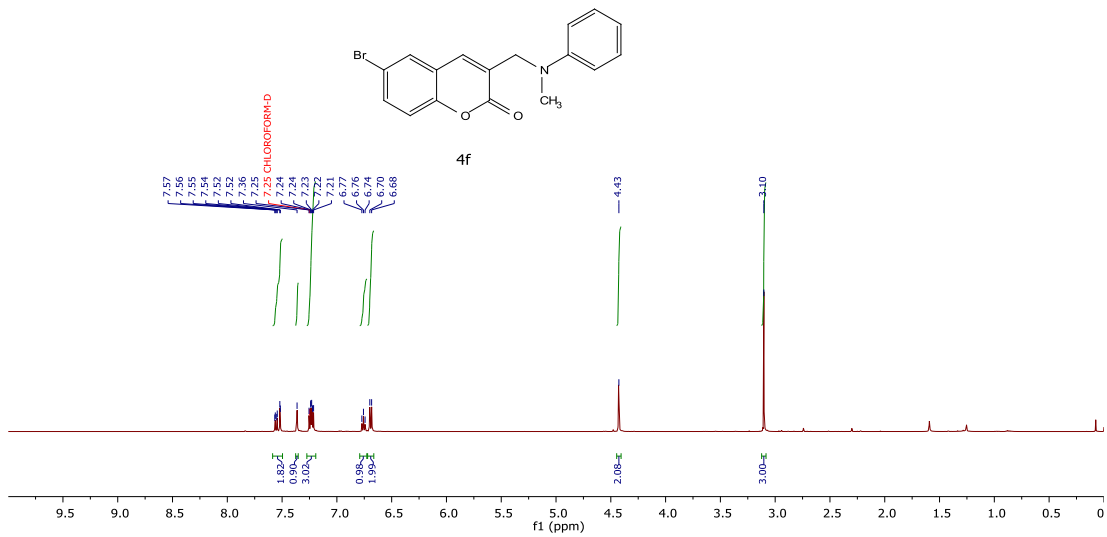
4d

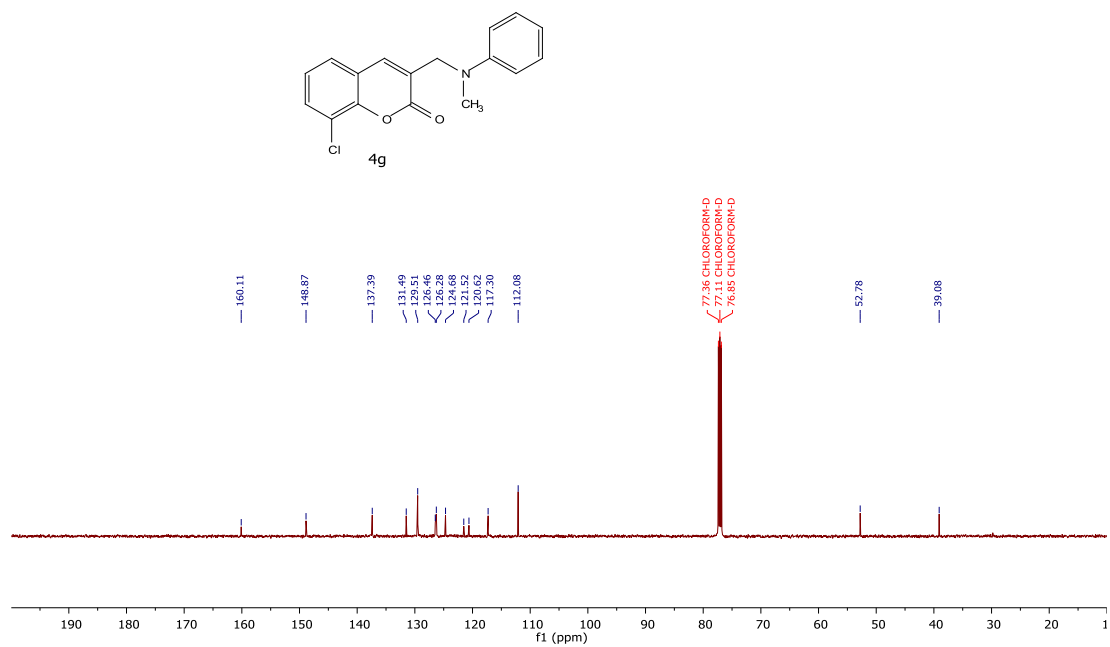
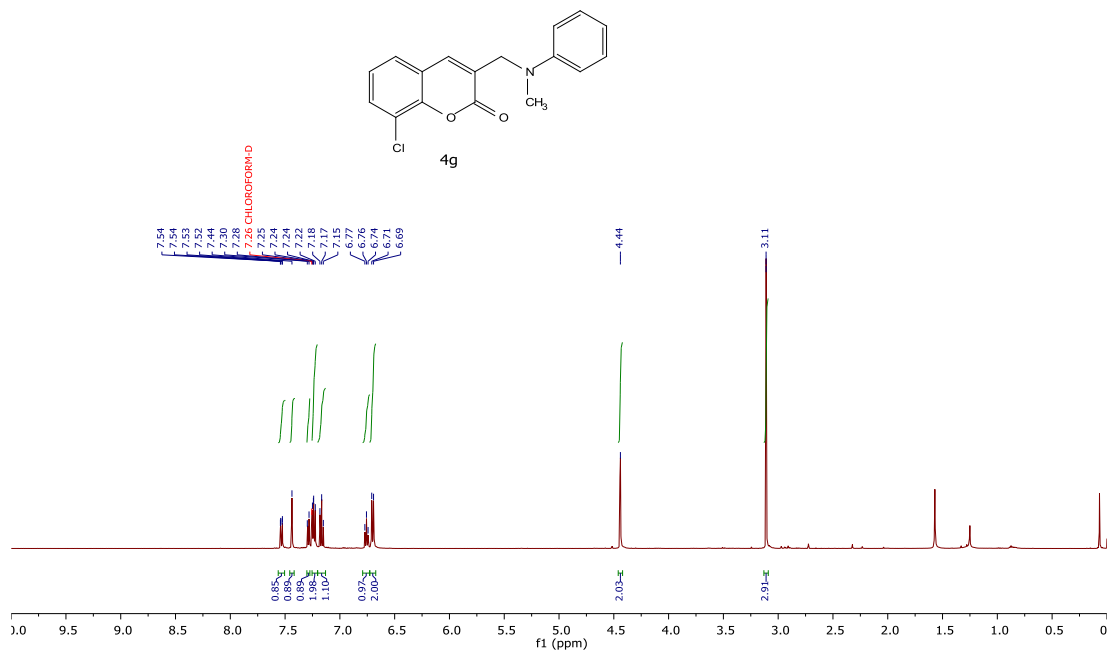


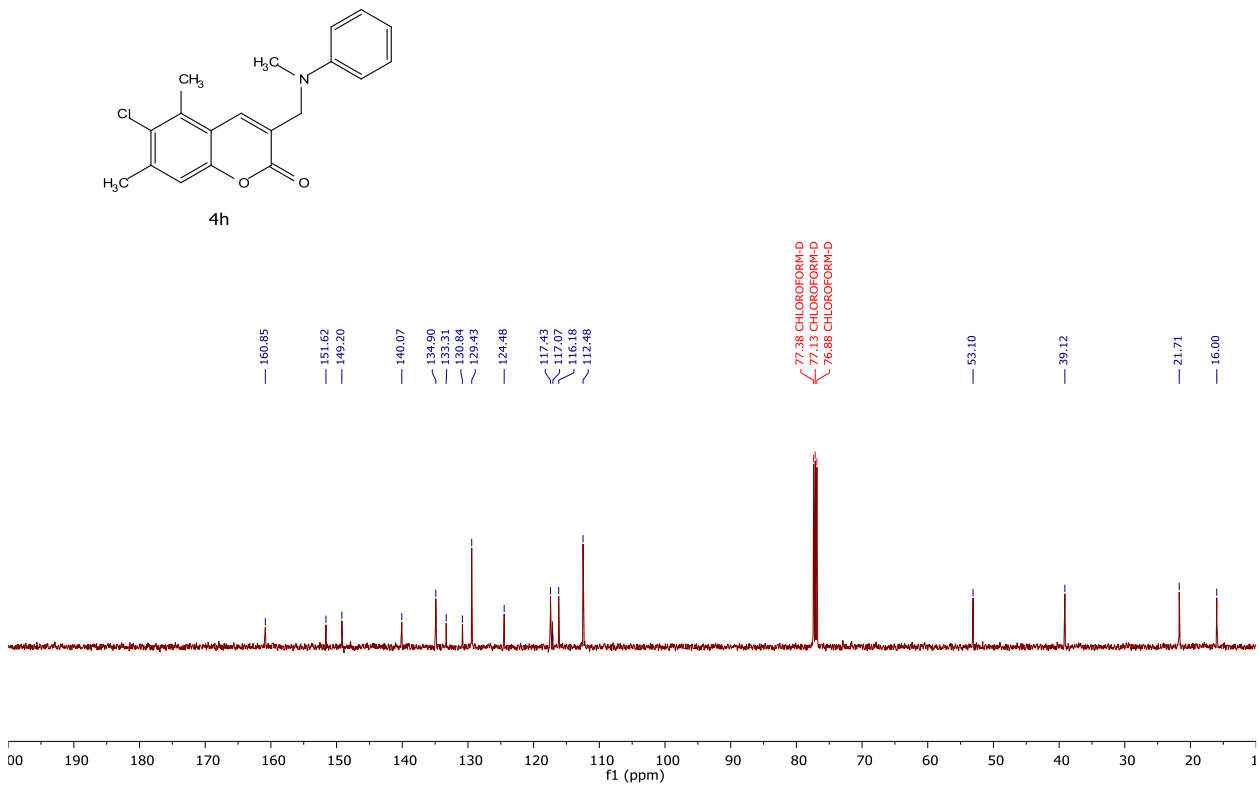
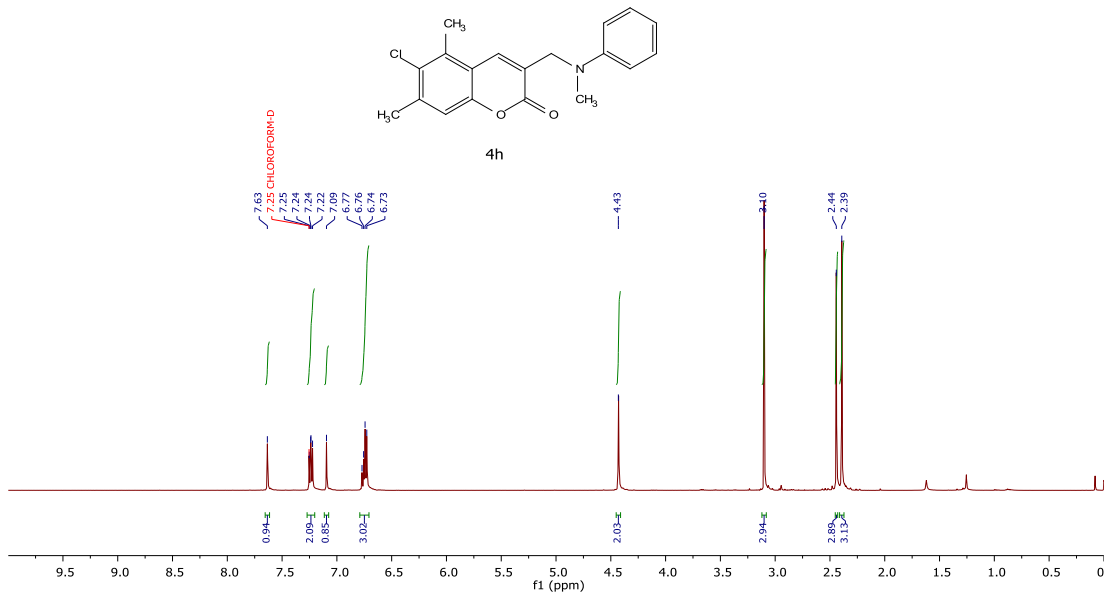
4d

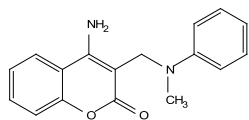




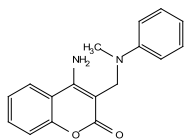
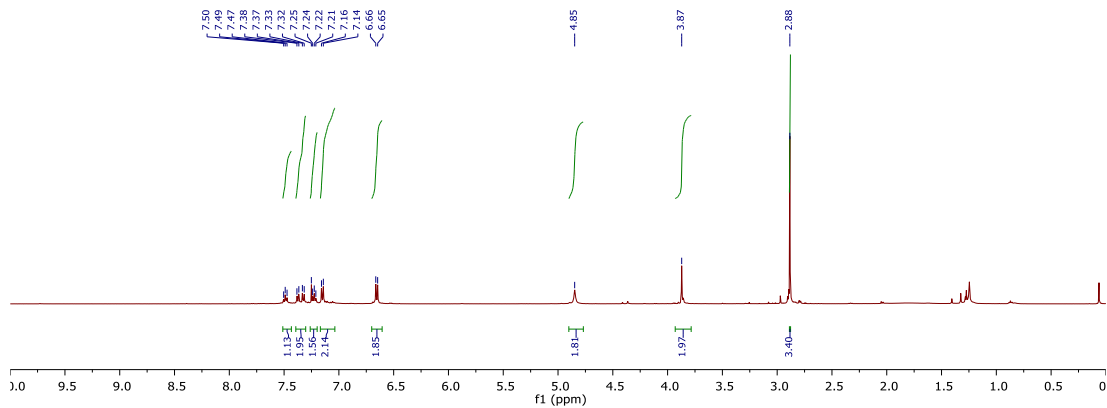








4i



4i

