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Supporting Information

Redox-Neutral Dual Functionalization of Electron-Deficient Alkenes

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Supporting Information

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A. General Information

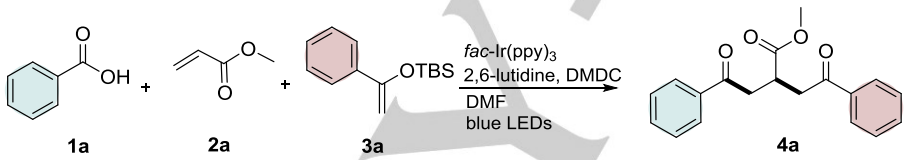
Commercial chemicals and solvents were used as received without prior purification, except for 2,6-lutidine and the electron-poor olefins (**2 a-h**) which were distilled before use. All reactions were monitored by TLC (Merck silica gel 60 F254), GC or ^{1}H-NMR. Conversions and yields provided by ^{1}H-NMR was obtained using 2,5-dimethylfuran or 1,3,5-dimethoxybenzene as the internal standard. ^{1}H-spectra were obtained at either 400 or 500 MHz and ^{13}C-NMR spectra at 101 or 126 MHz using a Varian 400 or a 500 spectrometer, respectively. Residual solvent peaks were used as reference. Column chromatography was performed by manual flash chromatography (wet-packed silica, 0.04 - 0.063 mm). HRMS analysis was performed on a Xevo G2-XS QTof Quadrupole Time-of-Flight mass spectrometer with a Waters Acquity CSH C18, 1.7 um, 2.1 x100 mm column eluting with a gradient of 1-95% acetonitrile in MQ-water containing 0.1% formic acid. Compounds **3 a-h** were prepared from the corresponding ketones following literature procedure[1] Dry tetrahydrofuran (THF) was obtained by distillation over sodium/benzophenone.

Materials

Commercially available reagents were purchased from Sigma Aldrich, Alfa Aesar or VWR and used as received unless otherwise noted.

B. Optimization Studies

Table S1. Selected optimization studies (0.1 mmol scale)



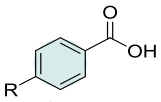
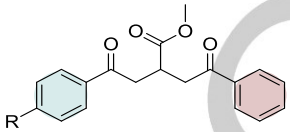
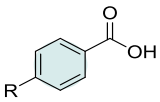
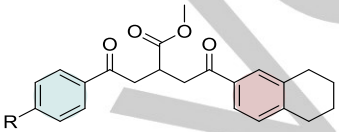
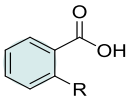
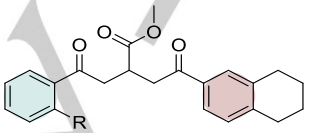
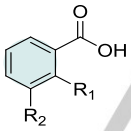
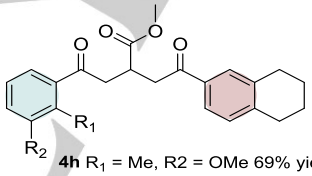
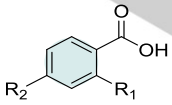
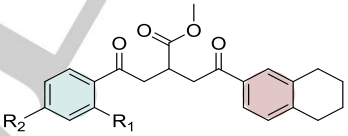
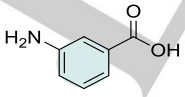
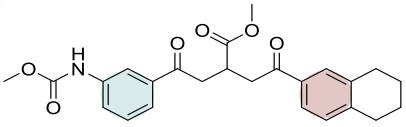
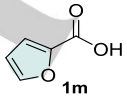
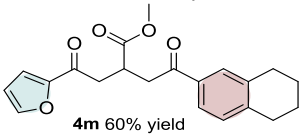
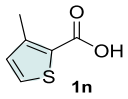
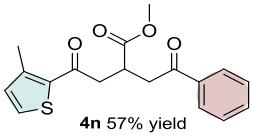
1a 2a 3a 4a

Entry	1a (equiv)	2a (equiv)	3a (equiv)	4a[a] Yield [%]	Notes[b]
1	1.5	1	3	46	3 equiv 2,6-lutidine, DMA as solvent
2	1.5	1	3	36	3 equiv 2,6-lutidine,CH_3CN as solvent
3	1.5	1	3	-	trifluoroethanol:DMF 1:1 as solvent
4	1.5	1	3	70	3 eq of trifluoroethanol as additive
5	1.5	1	3	74	3 equiv 2,6-lutidine
6	2	1	3	89	3 equiv 2,6-lutidine, 4 equiv DMDC
7	1.5	1	3	55	no lutidine
8	2	1	2	99	70 h
9	2	1	2	33	23 h
10	1.5	1	3	74	
11	2	1	1.5	81	
12	2	1	2	99	
13	2	2	1	90	5 mol% of *fac*-Ir(ppy)3
14	2	1	2	-	Control experiment without *fac*-Ir(ppy)$_3$
15	2	1	2	-	Control experiment without blue LEDs
16	2	1	2	-	Control experiment without DMDC

[a] NMR yield using 2,5-dimethylfuran as internal standard. [b] Standard conditions if nothing else is noted: 48 h under blue LEDs, DMF as solvent, 2 mol% of *fac*-Ir(ppy)$_3$, 3 equiv of DMDC, 0.5 equiv of 2,6-lutidine. DMF = dimethylformamide, DMA = dimethylacetamide, DMDC = dimethyl dicarbonate.

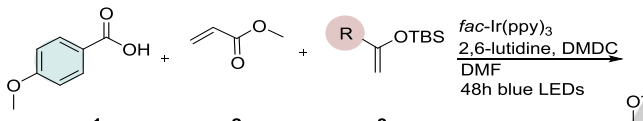
C. Scope of the different substrates

Table S2. Scope of the carboxylic acids **1**[a]

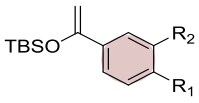
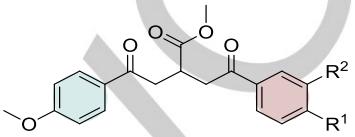
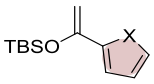
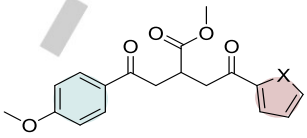
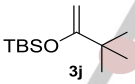
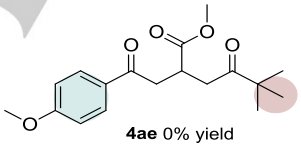
Entry	1	4
1	 **1a** R = H **1p** R = NO_2	 **4a** R = H 94% yield **4ac** R = NO_2 0% NMR yield
2	 **1b** R = Cl **1d** R = OiPr **1c** R = OMe **1e** R = OH **1o** R = CF_3	 **4b** R = Cl 54% yield **4d** R = OiPr 53% yield **4c** R = OMe 97% yield **4e** R = OCOMe 54% yi **4ab** R = CF_3 10% NMR yield
3	 **1f** R = Cl **1g** R = Me	 **4f** R = Cl 54% yield **4g** R = Me 75% yield
4	 **1h** R_1 = Me, R2 = OMe **1i** R_1 = Me, R2 = CF_3	 **4h** R_1 = Me, R2 = OMe 69% yield **4i** R_1 = Me, R2 = CF_3 33% yield
5	 **1j** R_1 = Me, R2 = Me **1k** R_1 = Me, R2 = Cl	 **4j** R_1 = Me, R2 = OM 61% yield **4k** R_1 = Me, R2 = Cl 62% yield
6	 **1l**	 **4l** 53% yield
7	 **1m**	 **4m** 60% yield
8	 **1n**	 **4n** 57% yield

[a] Reaction time 48 h under blue LEDs, DMF as solvent, 5 mol% of *fac*-Ir(ppy)$_3$, 3 equiv of DMDC, 0.5 equiv of 2,6-lutidine. Isolated yields. DMF = dimethylformamide, DMA = dimethylacetamide, DMDC = dimethyl dicarbonate.

Table S3. Scope of the electron-rich olefins **3** [a]

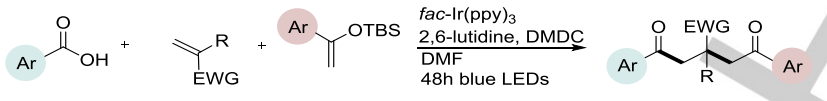


1c **2a** **3** **4**

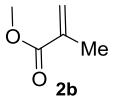
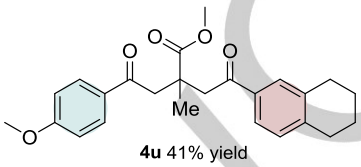
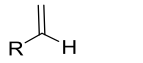
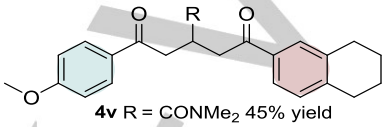
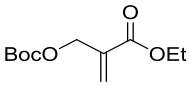
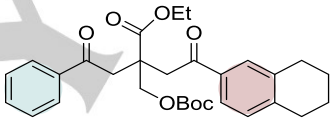
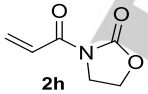
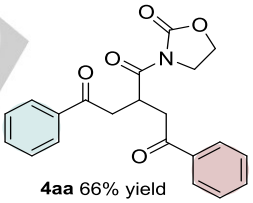
Entry	3	4
1	 **3c** R_1 = Cl, R_2 = H **3e** R_1 = OMe, R_2 = OMe **3d** R_1 = t-Bu, R_2 = H **3f** R_1 = OMe, R_2 = H **3i** R_1 = CF_3, R_2 = H	 **4o** R^1 = Cl, R^2 = H 46% yield **4p** R^1 = t-Bu, R^2 = H 61% yield **4q** R^1 = OMe, R^2 = OMe 34% yield **4r** R^1 = OMe, R^2 = H 63% yield **4ad** R_1 = CF_3, R_2 = H 0% NMR yield
2	 **3g** X = O **3h** X = S	 **4s** X = O 40% yield **4t** X = S 50% yield
3	 **3j**	 **4ae** 0% yield

[a] Reaction time 48 h under blue LEDs, DMF as solvent, 2 mol% of *fac*-Ir(ppy)$_3$, 3 equiv of DMDC, 0.5 equiv of 2,6-lutidine. Isolated yields. DMF = dimethylformamide, DMA = dimethylacetamide, DMDC = dimethyl dicarbonate.

Table S4. Scope of the electron-poor olefins **2** [a]



1 **2** **3** **4**

Entry	**2**	**4**
1	 **2b**	 **4u** 41% yield
2	 **2c** R = $CONMe_2$ **2d** R = CN **2e** R = COMe **2f** R = SO_2Ph	 **4v** R = $CONMe_2$ 45% yield **4w** R = CN 52% yield **4x** R = COMe 47% yield **4y** R = SO_2Ph 66% yield
3	 **2g**	 **4z** 63% yield
4	 **2h**	 **4aa** 66% yield

[a] Reaction time 48 h under blue LEDs, DMF as solvent, 2 mol% of *fac*-Ir(ppy)$_3$, 3 equiv of DMDC, 0.5 equiv of 2,6-lutidine. Isolated yields. DMF = dimethylformamide, DMA = dimethylacetamide, DMDC = dimethyl dicarbonate.

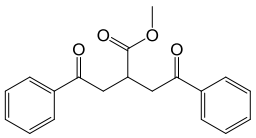
C. General Procedures for the Photocatalytic Reaction

General Method

Carboxylic acid **1** (0.4 mmol) and *fac*-Ir(ppy)$_3$ (5 mol%) were added into a 10 mL vial equipped with a teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with nitrogen. Then 2 mL of dried (over 3 Å MS) DMF (sparged with nitrogen for 20 minutes) was added followed by 2,6-lutidine (11.6 µL, 0.1 mmol), electron-rich olefin **3** (0.2 mmol), dimethyl dicarbonate (DMDC) (64.4 µL, 0.6 mmol) and electron-poor olefin **2** (0.4 mmol) in that order (unless otherwise stated). The above mixture was then sparged with nitrogen for 5 minutes. The vial was capped sealed with teflon tape and irradiated (at approximately 4 cm away from the light source) with 8 W blue LEDs (λmax = 460 nm) under vigorous stirring at room temperature. After 48 hours the reaction crude was transferred into a 50 mL separation funnel using 15 mL of ethyl acetate. The mixture was washed with water (25 mL) and brine (25 mL x2). The organic phase was then separated and dried over anhydrous $MgSO_4$. The $MgSO_4$ was then filtered off and the solvent was removed under vacuum. Purification by flash chromatography on silica gel provided the desired product.

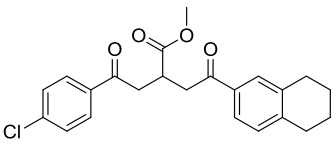
D. Products Characterization

methyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (**4a – Table 1**)



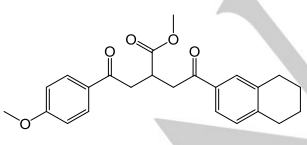
The reaction was carried out following a modified procedure of the general method starting from benzoic acid **1a** (48.8 mg, 0.4 mmol), methyl acrylate **2a** (18 µL, 0.2 mmol) and tert-butyldimethyl((1-phenylvinyl)oxy)silane **3a** (98.6 µL, 0.4 mmol) using 2 mol% of *fac*-Ir(ppy)$_3$. Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a yellowish solid (58 mg, 99% yield). HRMS calcd for ($C_{19}H_{19}O_4$): 311.1283, found 311.1290. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.01 – 7.93 (m, 4H), 7.61 – 7.52 (m, 2H), 7.50 – 7.41 (m, 4H), 3.70 (s, 3H), 3.69 – 3.62 (m, 1H), 3.57 (dd, J = 17.9, 5.7 Hz, 2H), 3.37 (dd, J = 17.7, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 197.8, 174.8, 136.4, 133.3, 128.6, 128.0, 52.1, 39.5, 35.8.

methyl 4-(4-chlorophenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4b - Table 1**)



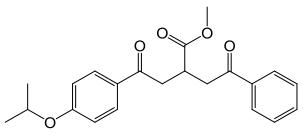
The reaction was carried out following the general method starting from 4-chlorobenzoic acid **1b** (62.6 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (57 mg, 75% yield). HRMS calcd for ($C_{23}H_{24}O_4Cl$): 399.1363, found 399.1363. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.95 – 7.84 (m, 2H), 7.71 – 7.62 (m, 2H), 7.48 – 7.38 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 3.69 (s, 3H), 3.61 (dtd, *J* = 6.9, 6.1, 5.1 Hz, 1H), 3.51 (ddd, *J* = 17.9, 6.4, 5.7 Hz, 2H), 3.39 – 3.25 (m, 2H), 2.82 – 2.75 (m, 4H), 1.83 – 1.76 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 197.5, 196.7, 174.7, 143.6, 139.7, 137.5, 134.8, 133.9, 129.5, 129.3, 128.9, 128.9, 125.0, 52.1, 39.4, 39.3, 35.8, 29.6, 29.3, 22.9, 22.7.

methyl 4-(4-methoxyphenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4c - Table 1**)



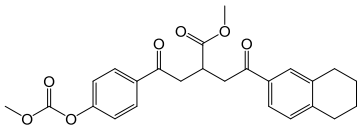
The reaction was carried out following the general method starting from *p*-anisic acid **1c** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (64 mg, 80% yield). HRMS calcd for ($C_{24}H_{27}O_5$): 395.1858, found 395.1860. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.69 – 7.63 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.95 – 6.88 (m, 2H), 3.85 (s, 3H), 3.69 (s, 3H), 3.60 (q, *J* = 6.1 Hz, 1H), 3.50 (ddd, *J* = 17.7, 11.0, 5.8 Hz, 2H), 3.32 (ddd, *J* = 17.7, 9.1, 6.5 Hz, 2H), 2.79 (p, *J* = 3.3 Hz, 4H), 1.80 (ddd, *J* = 6.6, 3.8, 2.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 196.3, 175.0, 163.6, 143.4, 137.4, 134.0, 130.3, 129.6, 129.3, 129.0, 125.1, 113.7, 55.4, 52.0, 39.4, 39.1, 36.0, 29.6, 29.3, 22.9, 22.8.

methyl 4-(4-isopropoxyphenyl)-4-oxo-2-(2-oxo-2-phenylethyl)butanoate (**4d - Table 1**)



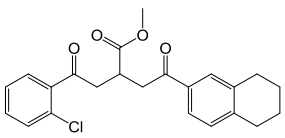
The reaction was carried out following the general method starting from 4-isopropoxybenzoic acid **1d** (65.7 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-phenylvinyl)oxy)silane **3a** (98.6 µL, 0.4 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a yellowish oil (39 mg, 53% yield). HRMS calcd for ($C_{22}H_{25}O_5$): 369.1702, found 369.1703. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.94 – 7.89 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 6.92 – 6.85 (m, 2H), 4.63 (hept, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.66 – 3.60 (m, 1H), 3.53 (ddd, *J* = 29.1, 17.8, 5.8 Hz, 2H), 3.33 (ddd, *J* = 19.5, 17.7, 6.4 Hz, 2H), 1.35 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 196.1, 174.9, 162.1, 136.5, 133.2, 130.3, 129.1, 128.5, 128.0, 115.1, 70.1, 52.1, 39.5, 39.1, 35.9, 21.8.

methyl 4-(4-((methoxycarbonyl)oxy)phenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4e - Table 1**)



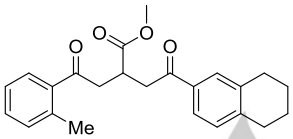
The reaction was carried out following a modified procedure of Method B using 4 equivalents of DMDC starting from 4-hydroxybenzoic acid **1e** (55.2 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as yellowish oil (46 mg, 54% yield). HRMS calcd for ($C_{25}H_{27}O_7$): 439.1757, found 439.1753. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.65 (dq, *J* = 3.7, 2.0 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.68 (s, 3H), 3.65 – 3.57 (m, 1H), 3.51 (ddd, *J* = 17.9, 8.4, 5.7 Hz, 2H), 3.32 (ddd, *J* = 17.9, 6.4, 4.1 Hz, 2H), 2.78 (p, *J* = 3.4 Hz, 4H), 1.79 (dq, *J* = 6.7, 3.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 196.5, 174.8, 154.6, 153.4, 143.5, 137.5, 134.2, 133.9, 129.8, 129.3, 128.9, 125.0, 121.1, 55.6, 52.1, 39.4, 39.3, 35.8, 29.6, 29.3, 22.9, 22.7.

methyl 4-(2-chlorophenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4f - Table 1**)



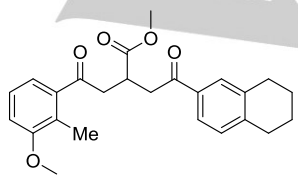
The reaction was carried out following the general method starting from 2-chlorobenzoic acid **1f** (62.6 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (43 mg, 54% yield). HRMS calcd for ($C_{23}H_{24}O_4Cl$): 399.1363, found 399.1372. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 4.2, 2.3 Hz, 2H), 7.53 (ddd, *J* = 7.4, 1.7, 0.7 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.31 (ddd, *J* = 7.5, 6.4, 2.2 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 3.70 (s, 3H), 3.63 (p, *J* = 6.4 Hz, 1H), 3.50 (ddd, *J* = 18.3, 10.6, 6.0 Hz, 2H), 3.39 – 3.23 (m, 2H), 2.80 (td, *J* = 6.1, 5.2, 3.0 Hz, 4H), 1.85 – 1.76 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 197.4, 174.5, 143.5, 138.7, 137.5, 133.9, 131.8, 130.9, 130.5, 129.3, 129.1, 128.9, 126.9, 125.1, 52.1, 43.6, 39.2, 36.1, 29.6, 29.3, 22.9, 22.7.

methyl 4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)-4-(o-tolyl)butanoate (**4g - Table 1**)



The reaction was carried out following the general method starting from 2-methylbenzoic acid **1g** (54.5 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (57 mg, 75% yield). HRMS calcd for ($C_{24}H_{27}O_4$): 379.1909, found 379.1913. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 3H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 – 7.18 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 3.69 (s, 3H), 3.65 – 3.56 (m, 1H), 3.47 (ddd, *J* = 24.4, 17.8, 6.0 Hz, 2H), 3.27 (ddd, *J* = 27.0, 17.8, 6.4 Hz, 2H), 2.78 (p, *J* = 3.5 Hz, 4H), 2.47 (s, 3H), 1.84 – 1.72 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 197.6, 174.9, 143.5, 138.2, 137.5, 137.2, 133.9, 131.9, 131.4, 129.3, 128.9, 128.6, 125.6, 125.0, 77.3, 77.0, 76.7, 52.1, 42.2, 39.4, 36.1, 29.6, 29.3, 22.9, 22.7, 21.3.

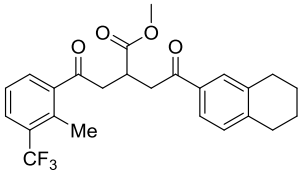
methyl 4-(3-methoxy-2-methylphenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4h - Table 1**)



The reaction was carried out following the general method starting from 3-methoxy-2-methylbenzoic acid **1h** (66.5 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a yellowish oil (56 mg, 69% yield). HRMS calcd for ($C_{25}H_{29}O_5$): 409.2015, found

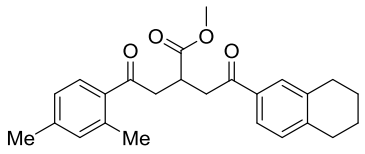
409.2020. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 4.2, 2.3 Hz, 2H), 7.19 (t, J = 7.9 Hz, 1H), 7.12 (dd, J = 8.0, 1.5 Hz, 2H), 6.93 (dd, J = 8.1, 1.2 Hz, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 3.61 (ddd, J = 12.4, 6.6, 5.5 Hz, 1H), 3.51 (dd, J = 17.7, 5.5 Hz, 1H), 3.35 (ddd, J = 31.5, 17.9, 6.8 Hz, 2H), 3.19 (dd, J = 18.0, 5.8 Hz, 1H), 2.79 (q, J = 4.5, 3.2 Hz, 4H), 1.80 (p, J = 3.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 174.8, 158.1, 143.5, 140.0, 137.5, 134.0, 129.3, 128.9, 126.2, 125.7, 125.1, 119.5, 112.6, 55.7, 52.1, 43.2, 39.3, 36.1, 29.6, 29.3, 22.9, 22.7, 12.4.

methyl 4-(2-methyl-3-(trifluoromethyl)phenyl)-4-oxo-2-(2-oxo-2-phenylethyl)butanoate (**4i - Table 1**)



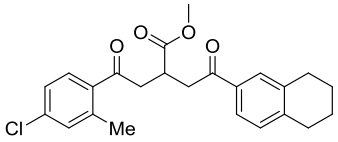
The reaction was carried out following the general method starting from 2-methyl-3-(trifluoromethyl)benzoic acid **1i** (80.0 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-phenylvinyl)oxy)silane **3a** (98.6 µL, 0.4 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (26 mg, 33% yield). HRMS calcd for ($C_{21}H_{20}O_4F_3$): 393.1314, found 393.1324. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.67 (ddt, J = 23.2, 7.7, 0.9 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 7.38 – 7.28 (m, 1H), 3.70 (s, 3H), 3.65 (ddd, J = 7.3, 5.0, 2.3 Hz, 1H), 3.55 (dd, J = 17.9, 4.9 Hz, 1H), 3.40 (ddd, J = 17.9, 14.1, 7.3 Hz, 2H), 3.16 (dd, J = 18.3, 5.2 Hz, 1H), 2.47 (q, J = 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 197.5, 174.4, 141.5, 136.3, 133.5, 130.2, 130.2, 128.7, 128.0, 128.0, 127.9, 125.6, 52.2, 43.6, 39.4, 35.9, 15.9, 15.8.

methyl 4-(2,4-dimethylphenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4j - Table 1**)



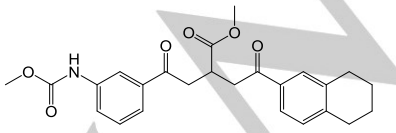
The reaction was carried out following the general method starting from 2,4-dimethylbenzoic acid **1j** (60.1 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as yellowish oil (48 mg, 61% yield). HRMS calcd for ($C_{25}H_{29}O_4$): 393.2066, found 393.2068. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 4.3, 2.3 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.07 – 7.01 (m, 2H), 3.69 (s, 3H), 3.67 – 3.55 (m, 1H), 3.47 (ddd, J = 27.5, 17.7, 6.0 Hz, 2H), 3.27 (ddd, J = 21.8, 17.7, 6.5 Hz, 2H), 2.79 (p, J = 3.6 Hz, 4H), 2.47 (s, 3H), 2.33 (s, 3H), 1.80 (dq, J = 6.7, 3.7, 3.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 197.6, 175.0, 143.4, 142.1, 138.8, 137.4, 134.2, 134.0, 132.8, 129.3, 129.2, 128.9, 126.3, 125.1, 52.0, 41.9, 39.4, 36.2, 29.6, 29.3, 22.9, 22.7, 21.5, 21.3.

methyl 4-(4-chloro-2-methylphenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4k - Table 1**)



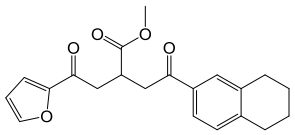
The reaction was carried out following the general method starting from 4-chloro-2-methylbenzoic acid **1k** (68.2 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (51 mg, 62% yield). HRMS calcd for ($C_{24}H_{26}O_4Cl$): 413.1520, found 413.1516. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 3H), 7.24 – 7.18 (m, 2H), 7.13 (d, J = 8.5 Hz, 1H), 3.69 (s, 3H), 3.60 (tt, J = 7.0, 5.3 Hz, 1H), 3.49 (dd, J = 17.8, 5.1 Hz, 1H), 3.37 (ddd, J = 42.2, 17.8, 7.1 Hz, 2H), 3.19 (dd, J = 17.8, 5.6 Hz, 1H), 2.79 (qd, J = 4.3, 2.8, 2.2 Hz, 4H), 1.80 (dq, J = 6.7, 3.7, 3.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 197.5, 174.8, 143.6, 140.6, 137.5, 137.4, 135.4, 133.9, 131.9, 130.1, 129.4, 128.9, 125.8, 125.0, 77.3, 77.0, 76.7, 52.1, 42.1, 39.3, 36.1, 29.6, 29.3, 22.9, 22.7, 21.2.

methyl 4-(3-((methoxycarbonyl)amino)phenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4l - Table 1**)



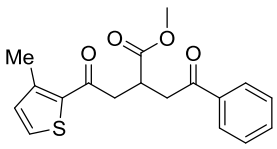
The reaction was carried out following a modified procedure of Method B using 4 equivalents of DMDC starting from 3-aminobenzoic acid **1l** (54.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a yellowish oil (45 mg, 53% yield). HRMS calcd for ($C_{25}H_{28}NO_6$): 438.1917, found 438.1913. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, J = 2.0 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.66 – 7.61 (m, 3H), 7.38 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 3.66 – 3.57 (m, 1H), 3.50 (ddd, J = 17.9, 6.9, 5.8 Hz, 2H), 3.36 – 3.26 (m, 2H), 2.82 – 2.74 (m, 4H), 1.78 (tt, J = 3.7, 2.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 197.5, 174.9, 153.9, 143.5, 138.4, 137.4, 137.2, 133.9, 129.4, 129.3, 129.3, 128.9, 125.0, 123.3, 123.0, 117.9, 52.4, 52.1, 39.6, 39.3, 35.8, 29.6, 29.3, 22.9, 22.7.

methyl 4-(furan-2-yl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4m - Table 1**)



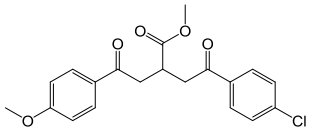
The reaction was carried out following the general method starting from 2-furoic acid **1m** (44.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a yellowish oil (42 mg, 59% yield). HRMS calcd for ($C_{21}H_{23}O_5$): 399.1363, found 355.1548. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, J = 3.9, 1.9 Hz, 2H), 7.55 (dd, J = 1.6, 0.8 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.11 (d, J = 8.4 Hz, 1H), 6.51 (dd, J = 3.7, 1.7 Hz, 1H), 3.68 (s, 3H), 3.58 (p, J = 6.2 Hz, 1H), 3.48 (dd, J = 17.8, 5.8 Hz, 1H), 3.43 – 3.26 (m, 2H), 3.18 (dd, J = 17.5, 6.5 Hz, 1H), 2.78 (p, J = 3.3 Hz, 4H), 1.79 (p, J = 3.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 186.9, 174.6, 152.3, 146.4, 143.5, 137.4, 133.9, 129.3, 128.9, 125.0, 117.3, 112.2, 77.3, 52.1, 39.2, 39.1, 35.6, 29.6, 29.3, 22.9, 22.7.

methyl 4-(3-methylthiophen-2-yl)-4-oxo-2-(2-oxo-2-phenylethyl)butanoate (**4n - Table 1**)



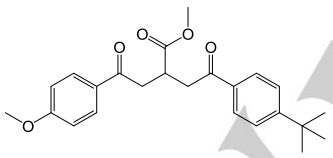
The reaction was carried out following a the general method starting from 3-methyl-2-thiophenecarboxylic acid **1n** (59.0 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-phenylvinyl)oxy)silane **3a** (98.6 µL, 0.4 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a yellowish oil (38 mg, 57% yield). HRMS calcd for ($C_{18}H_{19}O_4S$): 331.1004, found 331.1008. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.58 – 7.53 (m, 1H), 7.45 (ddt, J = 7.9, 6.7, 1.2 Hz, 2H), 7.40 (d, J = 4.9 Hz, 1H), 6.93 (d, J = 5.0 Hz, 1H), 3.71 (s, 3H), 3.63 (p, J = 6.0 Hz, 1H), 3.57 (dd, J = 17.7, 6.0 Hz, 1H), 3.44 – 3.30 (m, 2H), 3.25 (dd, J = 17.5, 6.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 191.1, 174.7, 145.5, 136.5, 135.2, 133.2, 132.6, 129.9, 128.6, 128.0, 52.1, 42.2, 39.4, 35.9, 16.9.

methyl 4-(4-chlorophenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-oxobutanoate (**4o - Table 1**)



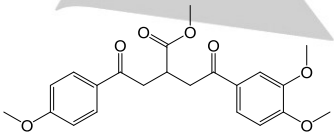
The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyl((1-(4-chlorophenyl)vinyl)oxy)dimethylsilane **3c** (53.8 mg, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (35 mg, 46% yield). HRMS calcd for ($C_{20}H_{20}O_5Cl$): 375.0999, found 375.1001. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 4H), 7.45 – 7.40 (m, 2H), 6.94 (t, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.70 (s, 3H), 3.62 (qd, J = 6.2, 5.2 Hz, 1H), 3.57 – 3.46 (m, 2H), 3.32 (ddd, J = 17.9, 11.3, 6.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 196.1, 174.8, 163.7, 139.7, 134.8, 132.3, 130.3, 129.5, 128.9, 113.7, 113.7, 55.4, 55.4, 52.1, 39.4, 39.1, 35.9.

methyl 4-(4-(tert-butyl)phenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-oxobutanoate (**4p - Table 1**)



The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyl((1-(4-(tert-butyl)phenyl)vinyl)oxy)dimethylsilane **3d** (58.1 mg, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a yellowish oil (48 mg, 61% yield). HRMS calcd for ($C_{24}H_{29}O_5$): 397.2015, found 397.2022. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 17.6, 8.7 Hz, 4H), 7.47 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 3.70 (s, 3H), 3.63 (p, J = 6.1 Hz, 1H), 3.52 (ddd, J = 17.6, 13.9, 5.7 Hz, 2H), 3.33 (ddd, J = 19.7, 17.7, 6.5 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 196.3, 175.0, 163.6, 157.0, 133.9, 132.8, 130.3, 129.6, 128.0, 125.5, 114.1, 113.7, 55.4, 52.1, 39.4, 39.1, 36.0, 35.1, 31.0.

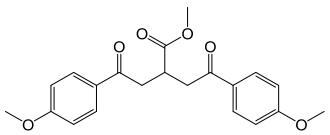
methyl 4-(3,4-dimethoxyphenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-oxobutanoate (**4q - Table 1**)



The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyl((1-(3,4-dimethoxyphenyl)vinyl)oxy)dimethylsilane **3e** (58.9 mg, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a yellowish oil (28 mg, 34% yield). HRMS calcd for ($C_{22}H_{25}O_7$): 401.1600, found

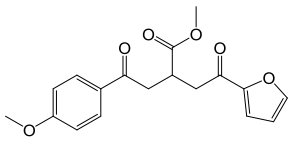
401.1600. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 9.0 Hz, 2H), 7.59 (dd, J = 8.4, 2.0 Hz, 1H), 7.50 (d, J = 2.0 Hz, 1H), 6.88 (dd, J = 18.8, 8.7 Hz, 3H), 3.92 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 3.69 (s, 3H), 3.59 (q, J = 6.1 Hz, 1H), 3.49 (ddd, J = 17.7, 5.7, 0.9 Hz, 2H), 3.31 (ddd, J = 17.7, 8.4, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 196.3, 175.0, 163.6, 153.4, 148.9, 130.3, 129.7, 129.56, 122.8, 113.8, 110.0, 109.97, 56.0, 55.9, 55.4, 52.1, 39.1, 39.0, 36.1.

methyl 4-(4-methoxyphenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-oxobutanoate (**4r - Table 1**)



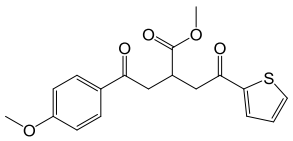
The reaction was carried out following the general method starting *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyl((1-(4-methoxyphenyl)vinyl)oxy)dimethylsilane **3f** (58.9 mg, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (47 mg, 63% yield). HRMS calcd for ($C_{21}H_{23}O_6$): 371.1495, found 371.1502. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 4H), 6.94 – 6.89 (m, 4H), 3.86 (s, 6H), 3.70 (s, 3H), 3.61 (p, J = 6.2 Hz, 1H), 3.50 (dd, J = 17.7, 5.8 Hz, 2H), 3.31 (dd, J = 17.7, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 175.1, 163.6, 130.3, 129.6, 113.7, 55.4, 52.1, 39.1, 36.0.

methyl 4-(furan-2-yl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-oxobutanoate (**4s - Table 1**)



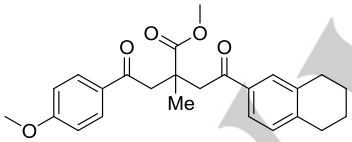
The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(furan-2-yl)vinyl)oxy)silane **3g** (44.9 mg, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a colorless oil (33 mg, 50% yield). HRMS calcd for $C_{18}H_{19}O_5S$): 347.0953, found 347.0950. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.57 (dd, J = 1.7, 0.7 Hz, 1H), 7.22 (dd, J = 3.6, 0.8 Hz, 1H), 6.93 (dd, J = 9.0, 2.1 Hz, 2H), 6.53 (dd, J = 3.6, 1.7 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 3.60 (p, J = 6.2 Hz, 1H), 3.45 (ddd, J = 34.0, 17.6, 6.0 Hz, 2H), 3.32 (dd, J = 17.7, 6.4 Hz, 1H), 3.20 (dd, J = 17.6, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 186.9, 174.7, 163.6, 152.3, 146.4, 132.3, 130.3, 129.5, 117.3, 113.7, 112.2, 77.3, 77.1, 76.9, 76.6, 55.4, 52.1, 39.2, 39.0, 35.6, 29.6.

methyl 4-(4-methoxyphenyl)-4-oxo-2-(2-oxo-2-(thiophen-2-yl)ethyl)butanoate (**4t - Table 1**)



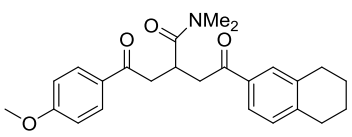
The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (36 µL, 0.4 mmol) and tert-butyldimethyl((1-(thiophen-2-yl)vinyl)oxy)silane **3h** (48.1 mg, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a colorless oil (28 mg, 40% yield). HRMS calcd for ($C_{18}H_{19}O_6$): 331.1182, found 331.1186. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.75 (dd, J = 3.8, 1.1 Hz, 1H), 7.64 (dd, J = 4.9, 1.1 Hz, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 6.95 – 6.90 (m, 2H), 3.87 (s, 3H), 3.70 (s, 3H), 3.64 – 3.58 (m, 1H), 3.50 (ddd, J = 17.4, 5.8, 1.9 Hz, 2H), 3.32 (td, J = 17.3, 6.5 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 190.8, 174.7, 163.6, 143.7, 133.8, 132.1, 130.3, 129.5, 128.1, 113.7, 55.4, 52.1, 40.0, 39.0, 36.1.

methyl 4-(4-methoxyphenyl)-2-methyl-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4u - Table 2**)



The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), methyl methacrylate **2b** (43 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a yellowish oil (34 mg, 41% yield). HRMS calcd for ($C_{25}H_{29}O_5$): 409.2015, found 409.2009. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.65 (dq, J = 4.5, 2.0 Hz, 2H), 7.13 (d, J = 8.5 Hz, 1H), 6.95 – 6.89 (m, 2H), 3.87 (s, 3H), 3.78 – 3.68 (m, 1H), 3.41 (ddd, J = 17.7, 7.1, 5.4 Hz, 2H), 3.17 (ddd, J = 17.7, 7.2, 6.0 Hz, 2H), 2.80 (ddt, J = 7.2, 5.2, 2.5 Hz, 4H), 2.40 (s, 3H), 1.86 – 1.76 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 196.3, 163.6, 143.5, 137.5, 130.3, 129.5, 129.3, 129.0, 125.1, 113.7, 55.4, 42.5, 40.0, 39.8, 29.6, 29.6, 29.3, 22.9, 22.7.

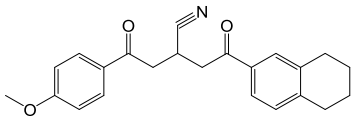
4-(4-methoxyphenyl)-N,N-dimethyl-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanamide (**4v - Table 2**)



The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), N,N-dimethylacrylamide **2c** (41 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column

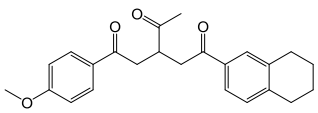
chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a yellowish oil (37 mg, 45% yield). HRMS calcd for ($C_{25}H_{30}NO_4$): 408.2175, found 408.2178. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.65 (d, J = 6.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 1H), 6.95 – 6.88 (m, 2H), 4.00 (dq, J = 13.5, 6.8, 6.3 Hz, 1H), 3.86 (s, 3H), 3.43 (ddd, J = 17.6, 7.8, 3.8 Hz, 2H), 3.29 (s, 3H), 3.14 (ddd, J = 17.3, 15.7, 5.8 Hz, 2H), 2.94 (s, 3H), 2.79 (tt, J = 4.9, 2.7 Hz, 4H), 1.80 (p, J = 3.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2, 196.8, 163.5, 143.3, 137.4, 134.1, 130.3, 129.7, 129.3, 129.0, 125.1, 113.6, 55.4, 41.3, 41.0, 37.7, 35.9, 32.3, 29.6, 29.3, 22.9, 22.8.

4-(4-methoxyphenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanenitrile (**4w - Table 2**)



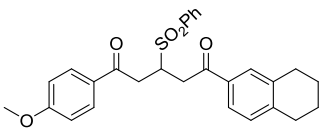
The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), acrylonitrile **2d** (27 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a colorless oil (38 mg, 52% yield). HRMS calcd for ($C_{23}H_{24}NO_3$): 362.1756, found 362.1758. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.65 (dq, J = 3.4, 2.0 Hz, 2H), 7.17 – 7.11 (m, 1H), 6.94 (dd, J = 9.0, 2.3 Hz, 2H), 3.87 (s, 3H), 3.82 (p, J = 6.4 Hz, 1H), 3.45 (ddd, J = 12.1, 6.5, 2.0 Hz, 4H), 2.80 (ddt, J = 7.0, 5.1, 2.4 Hz, 4H), 1.81 (dq, J = 6.7, 3.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 193.7, 164.0, 144.1, 137.7, 133.3, 132.3, 130.4, 129.5, 128.9, 128.9, 125.0, 121.6, 113.9, 113.7, 55.5, 55.4, 39.6, 39.3, 29.6, 29.3, 22.8, 22.7, 21.8.

1-(4-methoxyphenyl)-3-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)pentane-1,4-dione (**4x - Table 2**)



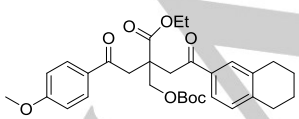
The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), but-3-en-2-one **2e** (33 µL, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (36 mg, 47% yield). HRMS calcd for ($C_{24}H_{27}O_4$): 379.1909, found 379.1910. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.67 – 7.62 (m, 2H), 7.15 – 7.10 (m, 1H), 6.93 – 6.90 (m, 2H), 3.86 (s, 3H), 3.79 – 3.68 (m, 1H), 3.41 (ddd, J = 17.7, 7.1, 5.6 Hz, 2H), 3.17 (ddd, J = 17.7, 7.4, 6.1 Hz, 2H), 2.80 (dt, J = 6.2, 3.4 Hz, 4H), 2.40 (s, 3H), 1.81 (p, J = 3.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0, 197.8, 196.4, 163.6, 143.5, 137.5, 133.8, 132.2, 130.3, 129.4, 129.3, 128.9, 125.0, 113.7, 113.7, 55.4, 55.4, 42.4, 40.0, 39.83, 29.6, 29.6, 29.3, 22.9, 22.7.

1-(4-methoxyphenyl)-3-(phenylsulfonyl)-5-(5,6,7,8-tetrahydronaphthalen-2-yl)pentane-1,5-dione (**4y - Table 2**)



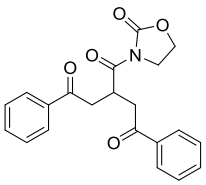
The reaction was carried out following the general method starting from *p*-anisic acid **1b** (60.8 mg, 0.4 mmol), (vinylsulfonyl)benzene **2f** (67.2 mg, 0.4 mmol) (added together with **1b** and $Ir(ppy)_3$ before closing the vial) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 50:50 pentane/ethyl acetate) afforded the title compound as a colorless oil (63 mg, 66% yield). HRMS calcd for ($C_{28}H_{29}O_5S$): 477.1736, found 477.1737. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.86 – 7.81 (m, 2H), 7.64 – 7.59 (m, 1H), 7.59 – 7.53 (m, 3H), 7.53 – 7.47 (m, 2H), 7.12 – 7.07 (m, 1H), 6.92 – 6.88 (m, 2H), 4.72 (tt, J = 7.2, 5.1 Hz, 1H), 3.86 (s, 3H), 3.70 (dd, J = 17.4, 5.2 Hz, 2H), 3.27 (ddd, J = 18.0, 17.4, 7.2 Hz, 2H), 2.84 – 2.72 (m, 4H), 1.85 – 1.73 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 193.4, 163.8, 143.7, 137.5, 133.9, 133.6, 130.4, 130.4, 129.4, 129.2, 129.1, 129.0, 128.9, 127.9, 125.1, 113.8, 56.3, 55.5, 37.1, 36.8, 29.6, 29.3, 22.9, 22.7.

ethyl 2-(((tert-butoxycarbonyl)oxy)methyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)-4-phenylbutanoate (**4z - Table 2**)



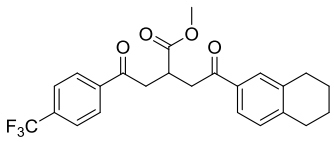
The reaction was carried out following the general method starting from *p*-anisic acid **1c** (60.8 mg, 0.4 mmol), ethyl 2-(((tert-butoxycarbonyl)oxy)methyl)acrylate **2g** (92 mg, 0.4 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (63 mg, 62% yield). HRMS calcd for ($C_{30}H_{37}O_7$): 509.2539, found 509.2544. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.68 – 7.61 (m, 2H), 7.57 – 7.48 (m, 1H), 7.47 – 7.37 (m, 2H), 7.09 (d, J = 8.6 Hz, 1H), 4.56 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.80 – 3.58 (m, 4H), 2.82 – 2.73 (m, 4H), 1.78 (p, J = 3.4 Hz, 4H), 1.39 (s, 9H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 197.9, 197.7, 173.2, 152.9, 143.3, 137.3, 137.0, 134.5, 133.1, 129.2, 128.9, 128.4, 128.0, 125.1, 82.2, 68.5, 61.2, 46.7, 39.6, 39.5, 30.9, 29.6, 29.3, 27.6, 22.9, 22.7, 13.9.

3-(2-oxooxazolidine-3-carbonyl)-1,5-diphenylpentane-1,5-dione (**4aa - Table 2**)



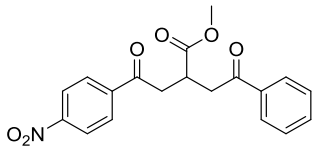
The reaction was carried out following a modified procedure of the general method starting from benzoic acid **1a** (48.8 mg, 0.4 mmol), 1-(oxazolidin-3-yl)pro*p*-2-en-1-one **2h** (28.2 mg, 0.2 mmol) and tert-butyldimethyl((1-phenylvinyl)oxy)silane **3a** (98.6 µL, 0.4 mmol) using 2 mol% of *fac*-Ir(ppy)$_3$. Purification by flash column chromatography (CH_2Cl_2) afforded the title compound as yellowish oil (35 mg, 66% yield). HRMS calcd for ($C_{21}H_{20}NO_5$): 366.1341, found 366.1346. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 4H), 7.55 (ddt, *J* = 8.0, 6.8, 1.3 Hz, 2H), 7.48 – 7.40 (m, 4H), 4.77 (tt, *J* = 7.3, 6.5 Hz, 1H), 4.52 – 4.38 (m, 2H), 4.07 (dd, *J* = 8.8, 7.5 Hz, 2H), 3.55 (dd, *J* = 17.5, 7.3 Hz, 2H), 3.30 (dd, *J* = 17.5, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 175.3, 153.3, 136.3, 133.3, 128.6, 128.1, 62.1, 42.9, 40.1, 34.9.

methyl 4-oxo-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-(5,6,7,8-tetrahydronaphthalen-2-yl)butanoate (4ab)



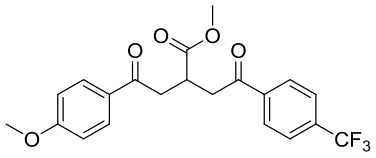
The reaction was carried out following the general method starting from 4-trifluoromethylbenzoic acid **4o** (76 mg, 0.4 mmol), methyl acrylate **2a** (18 µL, 0.2 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (58 µL, 0.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) using 2,5-dimethylfuran as internal standard indicated ca 10% yield while major product formed was identified as the methyl ester (see NMR spectra).

methyl 4-oxo-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-(5,6,7,8-tetrahydronaphthalen-2-yl)butanoate (4ac)



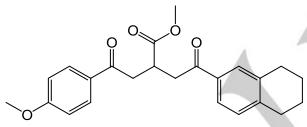
The reaction was carried out following the general method starting from 4-nitrobenzoic acid **4p** (69 mg, 0.4 mmol), methyl acrylate **2a** (18 µL, 0.2 mmol) and tert-butyldimethyl((1-phenylvinyl)oxy)silane **3a** (98.6 µL, 0.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) using 2,5-dimethylfuran as internal standard indicated no desired product while major product formed was identified as the methyl ester (see NMR spectra).

methyl 4-(4-methoxyphenyl)-4-oxo-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)butanoate (4ad)



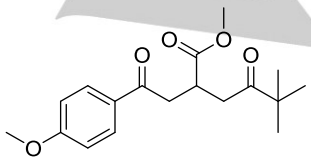
The reaction was carried out following the general method starting from *p*-anisic acid **1c** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (18 µL, 0.2 mmol) and tert-butyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)dimethylsilane **3i** (60.5 mg, 0.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) using 2,5-dimethylfuran as internal standard indicated no desired product.

methyl 4-(4-methoxyphenyl)-4-oxo-2-(2-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)butanoate (**4c**, Scale up reaction)



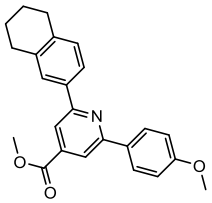
The reaction was carried out following a scaled up procedure of Method A starting from *fac*-Ir(ppy)$_3$ (15 mg, 2 mol%), 2,6-lutidine (58 µL, 0.5 mmol), dimethyl dicarbonate (DMDC) (0.32 mL, 3.0 mmol), *p*-anisic acid **1c** (0.304 g, 2.0 mmol), methyl acrylate **2a** (0.18 mL, 2.0 mmol) and tert-butyldimethyl((1-(5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)oxy)silane **3b** (0.29 mL, 1.0 mmol) in 5 mL DMF in a 25 mL vial. Purification by flash column chromatography (gradient eluent from pentane to 80:20 pentane/ethyl acetate) afforded the title compound as a colorless oil (348 mg, 87% yield). ^{1}H and ^{13}C NMR spectra corresponds to those of **4c**.

methyl 2-(2-(4-methoxyphenyl)-2-oxoethyl)-5,5-dimethyl-4-oxohexanoate (4ae)



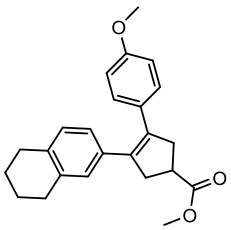
The reaction was carried out following the general method starting from *p*-anisic acid **1c** (60.8 mg, 0.4 mmol), methyl acrylate **2a** (18 µL, 0.2 mmol) and tert-butyl((3,3-dimethylbut-1-en-2-yl)oxy)dimethylsilane **3j** (42.9 mg, 0.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) using 2,5-dimethylfuran as internal standard indicated no desired product.

methyl 2-(4-methoxyphenyl)-6-(5,6,7,8-tetrahydronaphthalen-2-yl)isonicotinate (**5a**)



The reaction was carried out following a modified procedure from Boivin *et al*. [2]: A solution of compound **4c** (0.079 g, 0.2 mmol) in AcOH (1.2 mL), containing NH_4OAc (0.12 g, 1.67 mmol) was placed into a 10 mL vial equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with nitrogen. The solution was then heated at 120°C for 5 h after which the solvent was evaporated under reduced pressure and the residue was taken up in Et_2O. The organic layer was washed successively with 2 N aq NaOH and brine, then dried ($MgSO_4$). The residue was chromatographed over silica gel (gradient eluent from pentane to 80:20 pentane/ethyl acetate) to yield the title compound **5a** (34 mg, 46% yield) as a yellowish oil. HRMS calcd for ($C_{24}H_{24}NO_3$): 374.1756, found 374.1754 ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 4H), 7.91 – 7.85 (m, 2H), 7.21 – 7.15 (m, 1H), 7.05 – 6.98 (m, 2H), 3.99 (s, 3H), 3.87 (s, 3H), 2.91 – 2.78 (m, 4H), 1.84 (p, J = 3.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 160.7, 157.8, 157.3, 138.7, 137.5, 135.9, 131.4, 129.5, 128.4, 127.6, 124.1, 116.7, 116.6, 114.0, 55.3, 52.6, 29.6, 29.3, 23.2, 23.1.

methyl 3-(4-methoxyphenyl)-4-(5,6,7,8-tetrahydronaphthalen-2-yl)cyclopent-3-ene-1-carboxylate (**5b**)



The reaction was carried out following a modified procedure from Duan *et al*. [3]. Zinc powder (0.08 g, 1.2 mmol) and 2 mL dried THF was placed into a 10 mL vial equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with nitrogen. The mixture was cooled to −5 to 0 °C, and $TiCl_4$ (0.065 mL, 0.6 mmol) was slowly added by a syringe with the temperature kept under 10 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at 65 °C for 2.5 h. The mixture was again cooled to −5 to 0 °C, charged with pyridine (0.025 mL, 0.3 mmol) and stirred for 10 min. A solution of **4c** (0.025 g, 0.06 mmol) in 1 mL THF was added slowly. After addition, the reaction mixture was heated at 65 °C **4c** was consumed (monitored by TLC). The reaction was quenched with 10% K_2CO_3 aqueous solution and taken up with CH_2Cl_2. The organic layer was collected and concentrated. The residue was chromatographed over silica gel (gradient eluent from pentane to 80:20 pentane/ethyl acetate) to yield the title compound **5b** (10 mg, 48%) as a colorless oil. HRMS calcd for ($C_{24}H_{27}O_3$): 363.1960, found 363.1957. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.90 (t, J = 1.2 Hz, 1H), 6.87 (d, J = 1.3 Hz, 2H), 6.78 – 6.70 (m, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.35 – 3.24 (m, 1H), 3.24 – 3.14 (m, 2H), 3.14 – 3.04 (m, 2H), 2.75 – 2.57 (m, 4H), 1.84 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 158.3, 136.7, 135.7, 134.6, 134.0, 133.8, 129.9, 129.2, 128.7, 128.5, 125.3, 113.4, 55.1, 51.8, 42.0, 41.8, 40.1, 29.3, 29.1, 23.1.

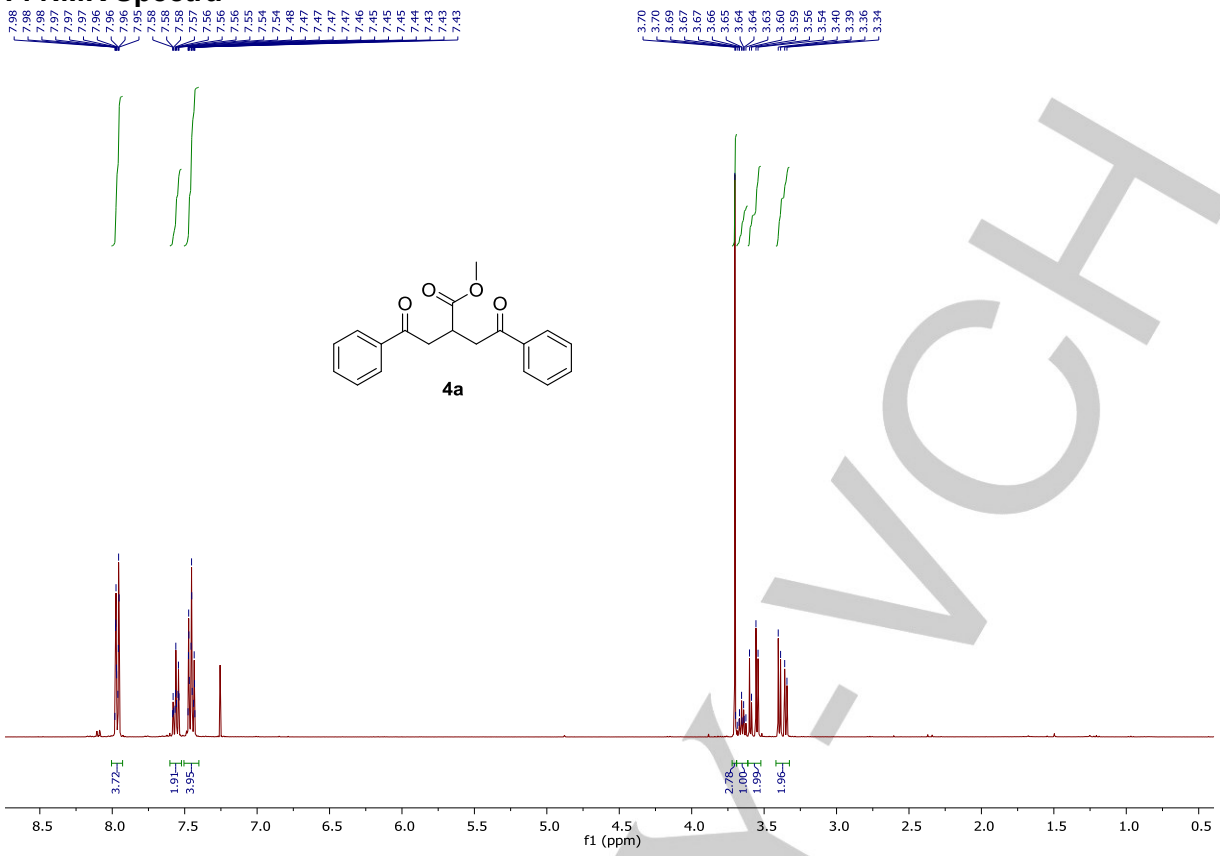
E. References

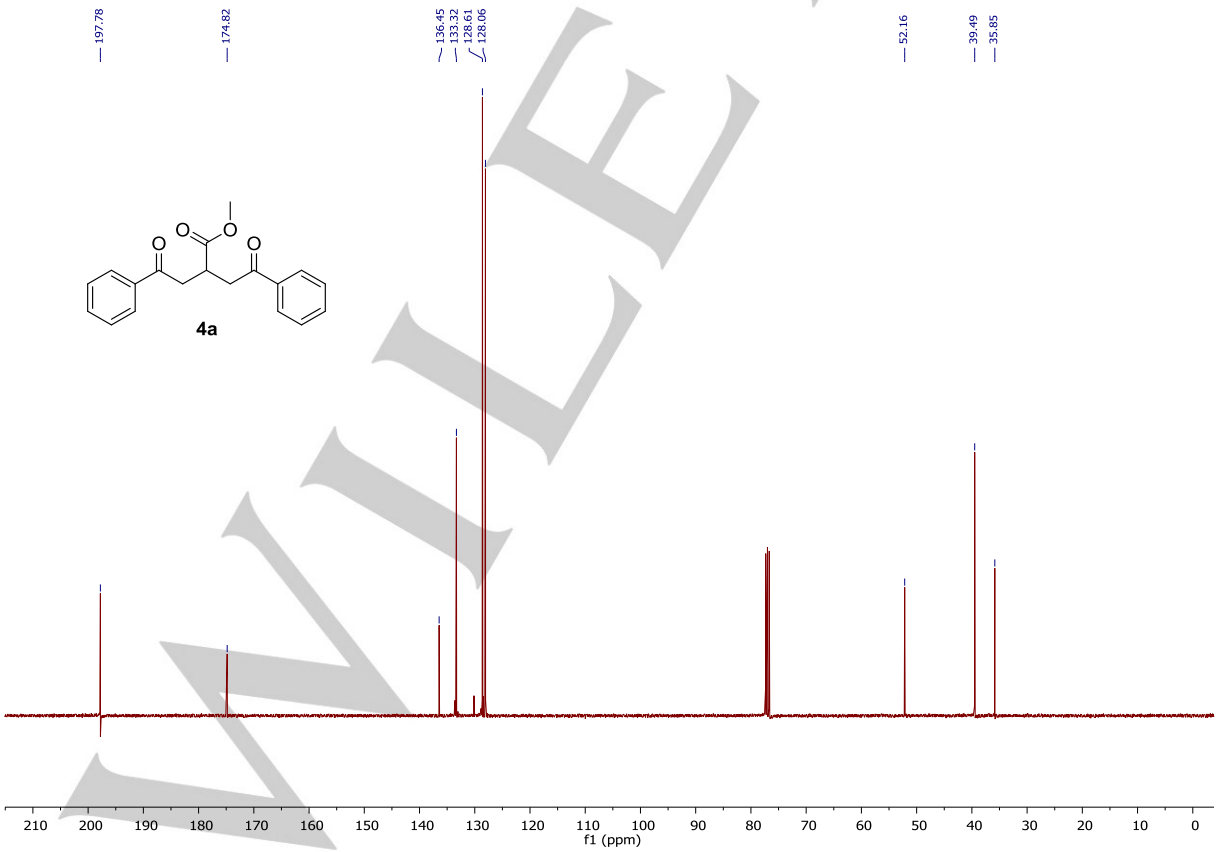
[1] N. S. Y. Loy, S. Choi, S. Kim, C.-M. Park, *Chemical Communications* 2016, *52*, 7336-7339.

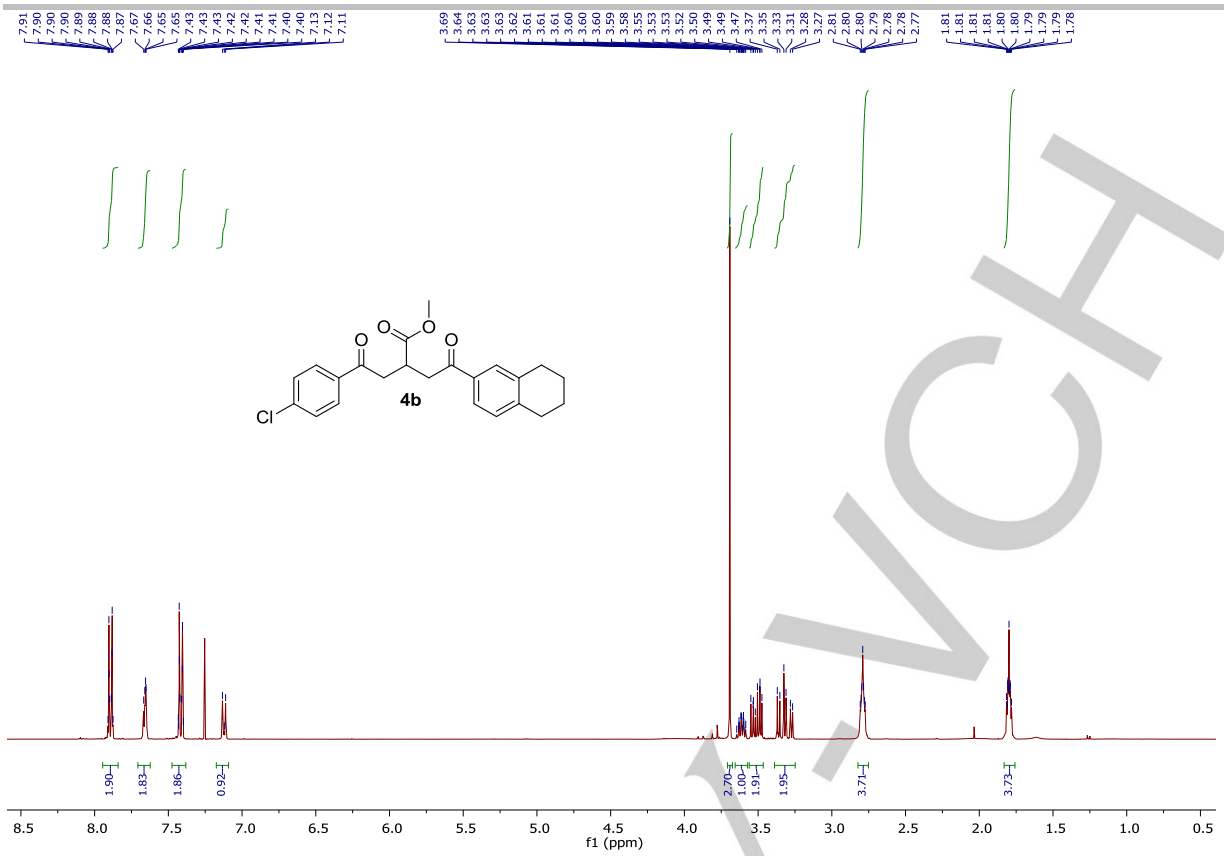
[2] J. Boivin, F. Carpentier, R. Jrad, *Synthesis* 2006, *2006*, 1664-1672.

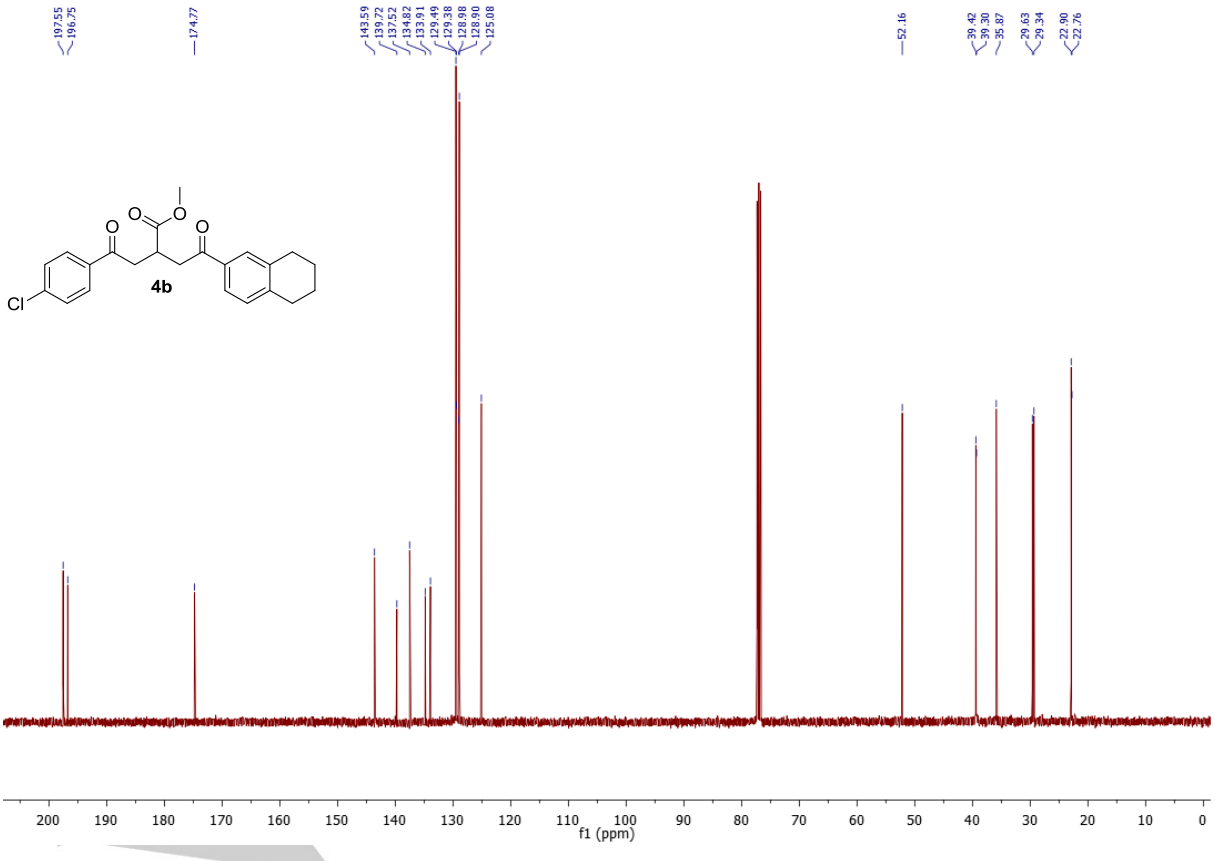
[3] X.-F. Duan, J. Zeng, J.-W. Lü, Z.-B. Zhang, *The Journal of Organic Chemistry* 2006, *71*, 9873-9876.

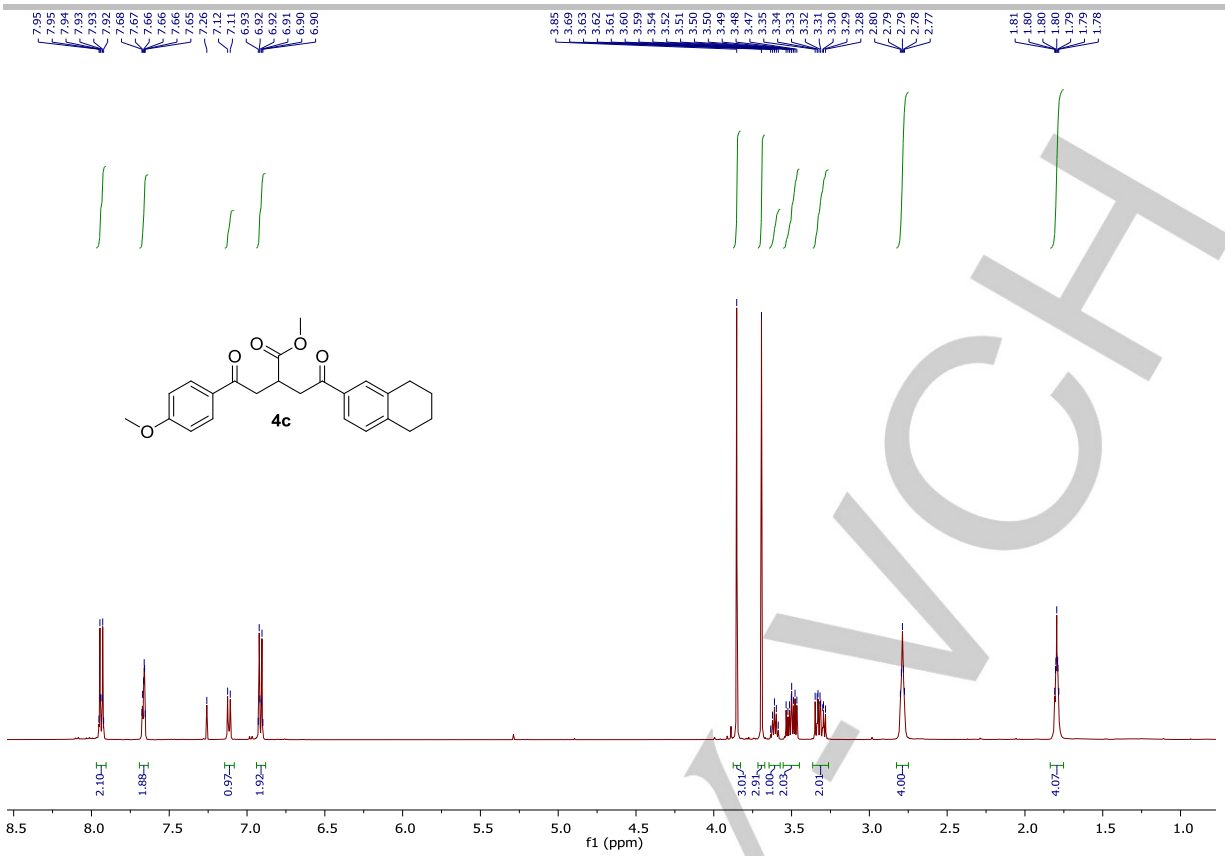
F. NMR Spectra







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1.78
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1.92
3.01
2.91
1.00
2.03
2.01
4.00
4.07
8.5
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7.5
7.0
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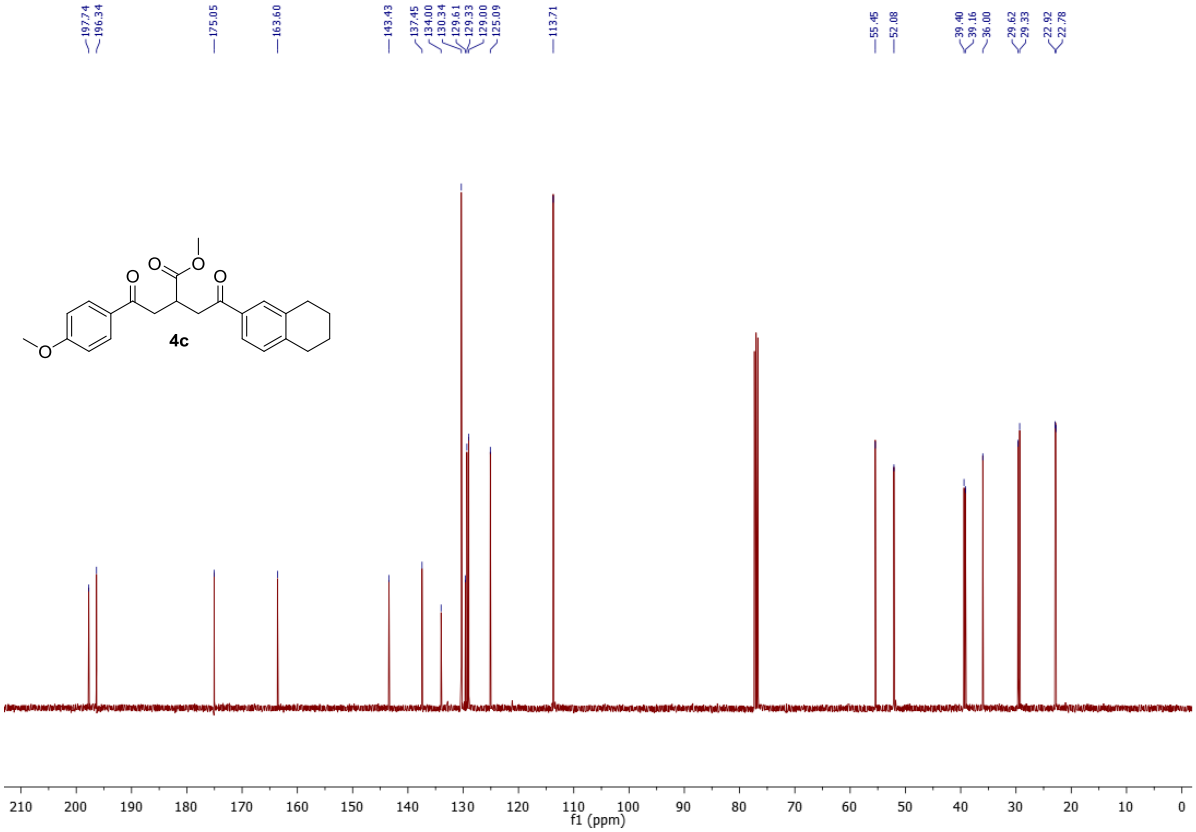
f1 (ppm)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39.16
36.60
29.62
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22.92
22.78
4c
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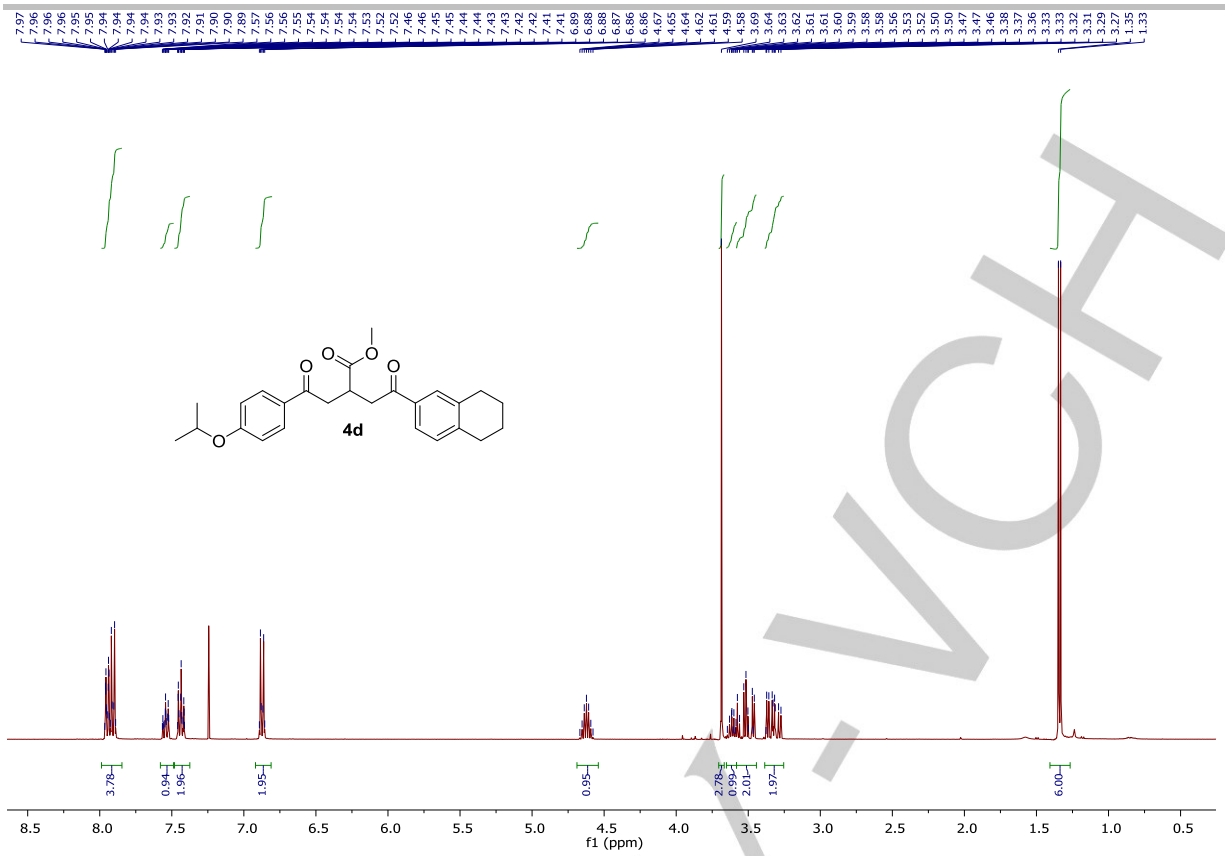
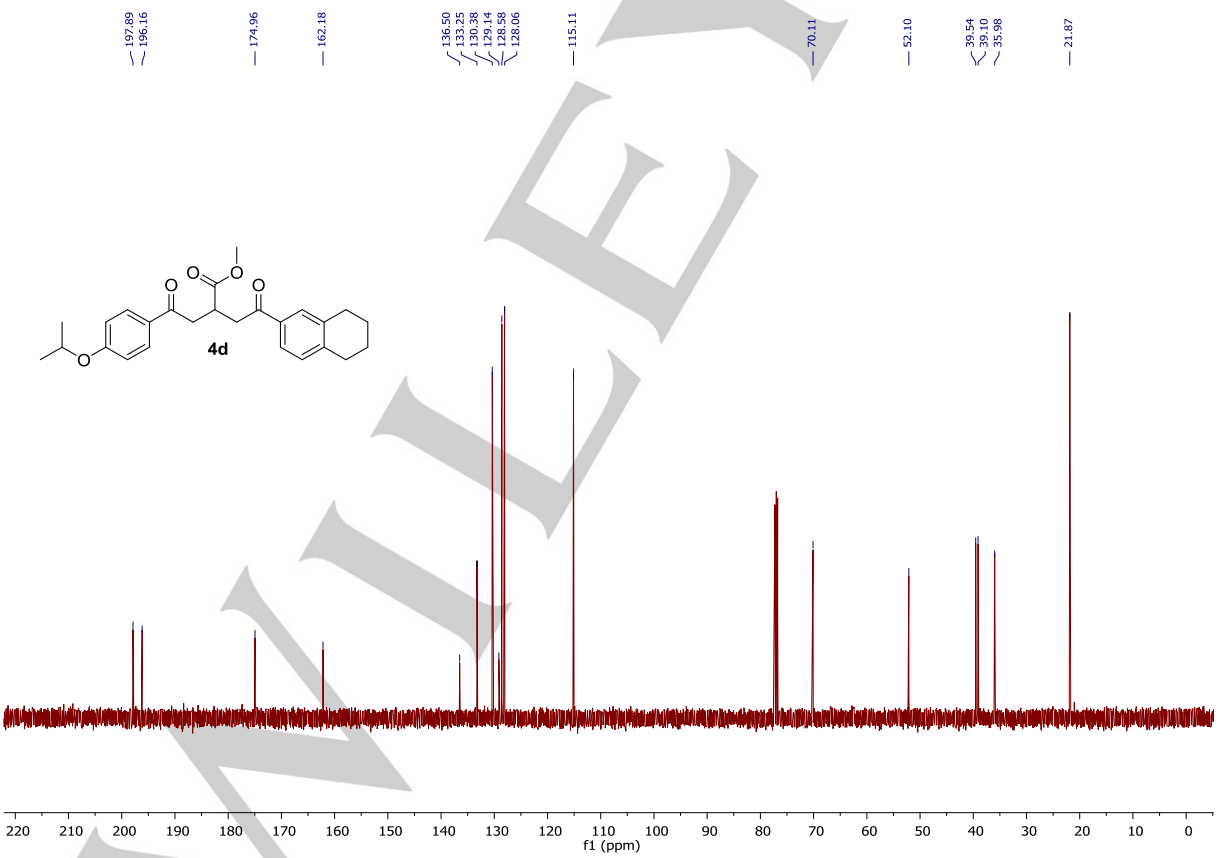
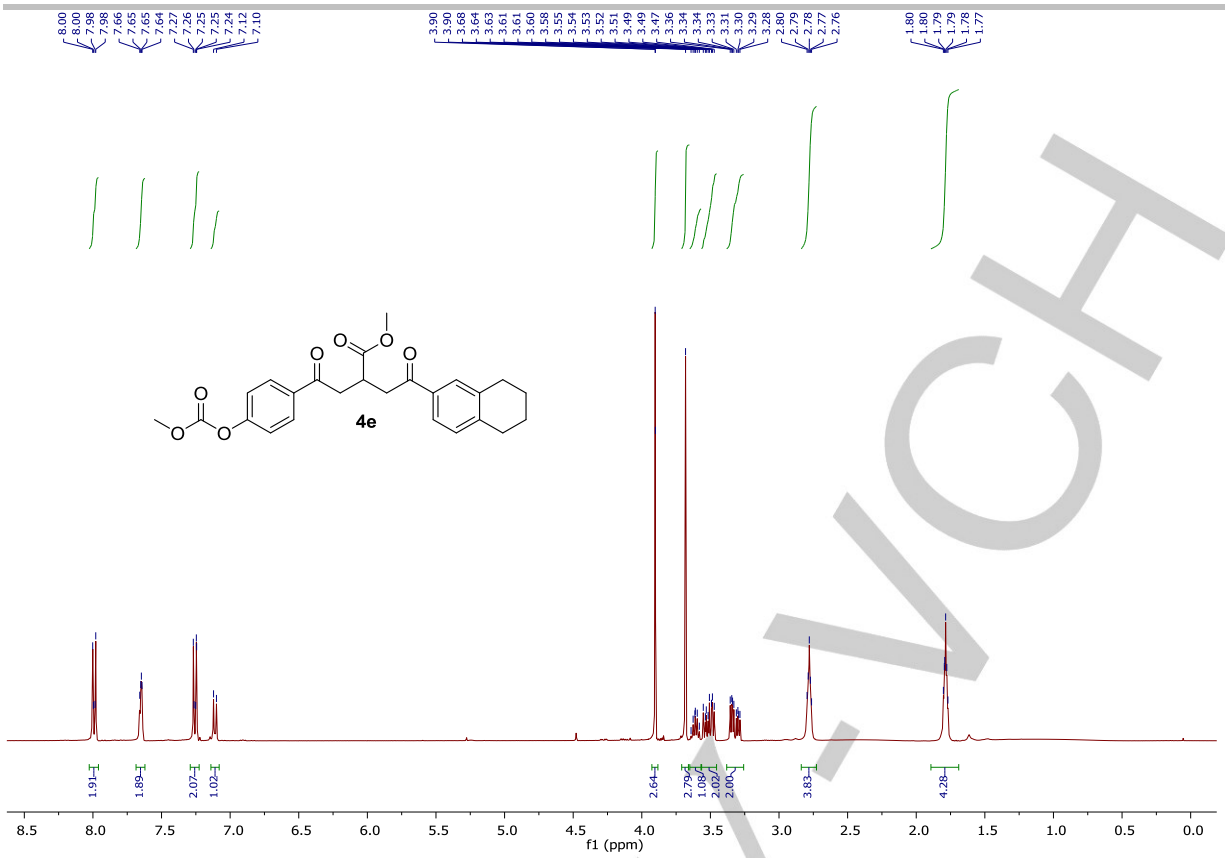
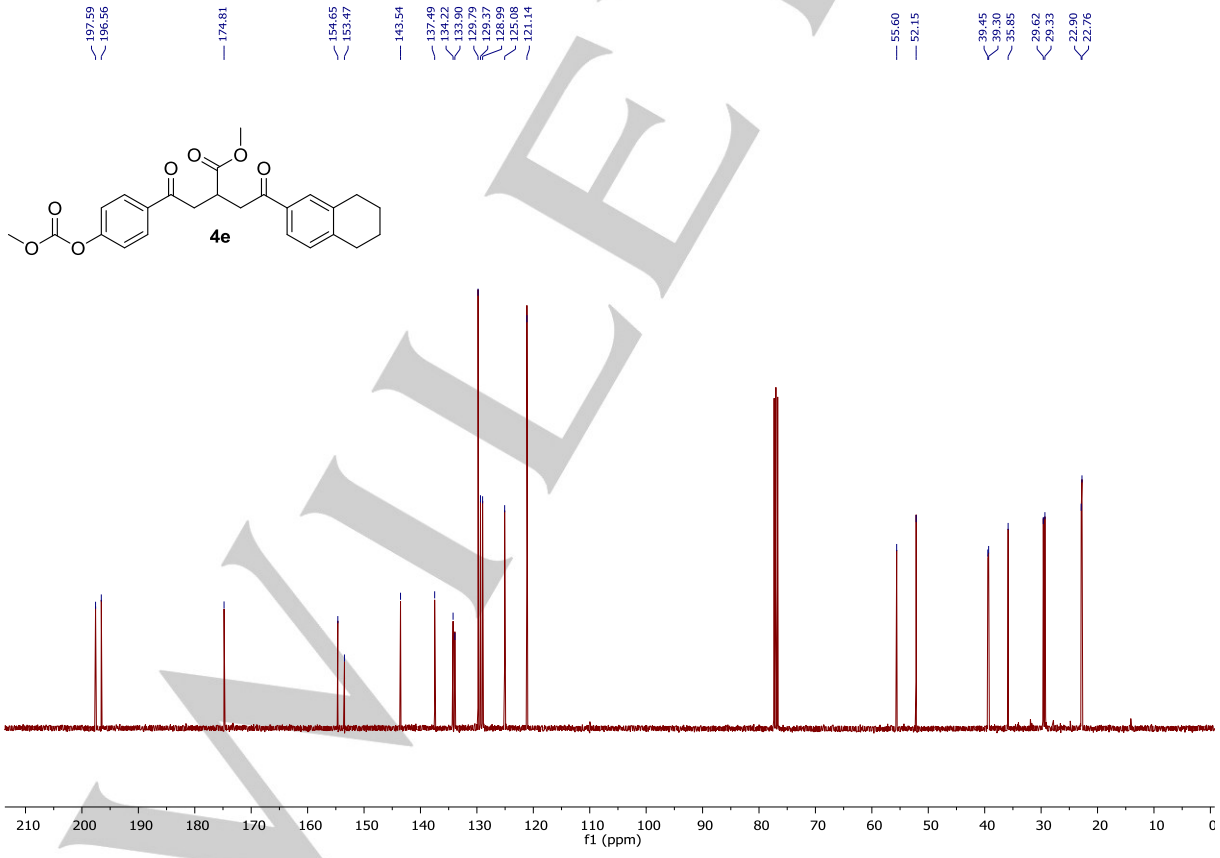
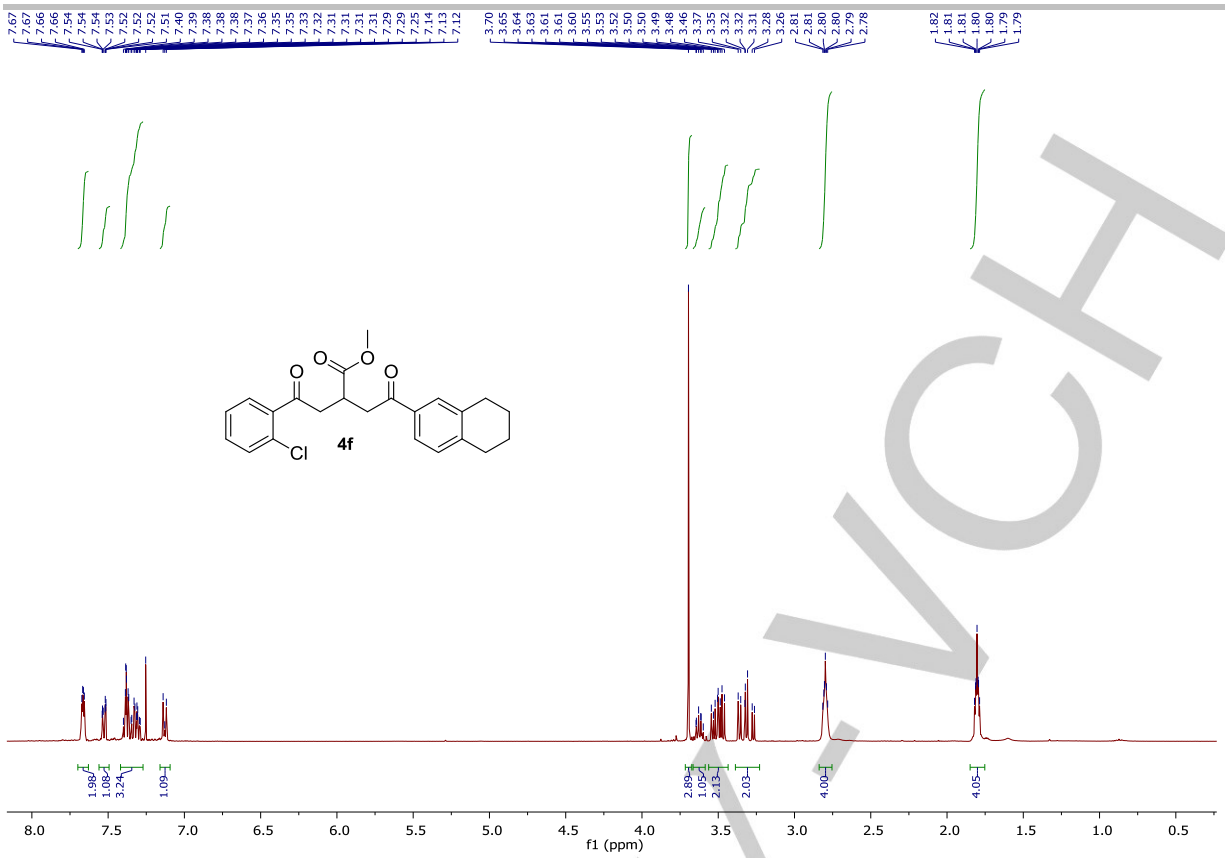
f1 (ppm)

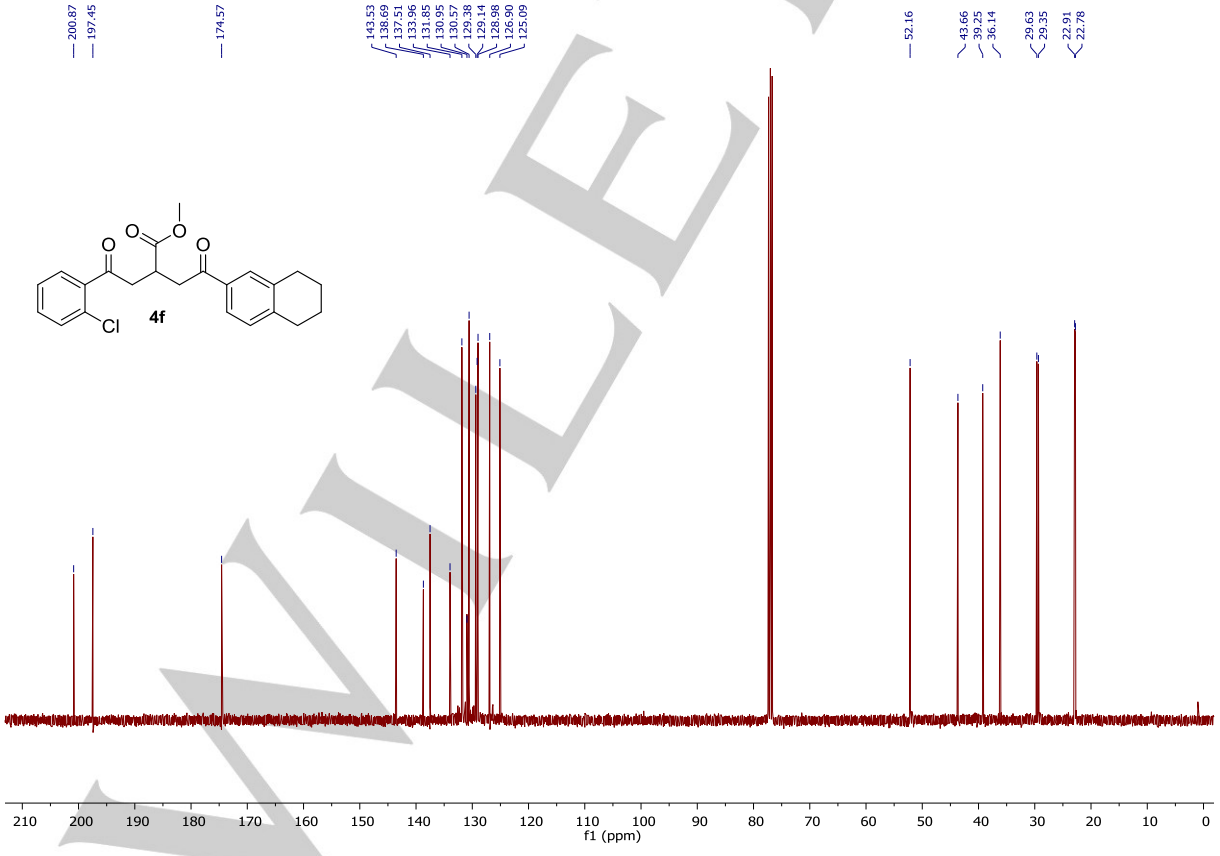


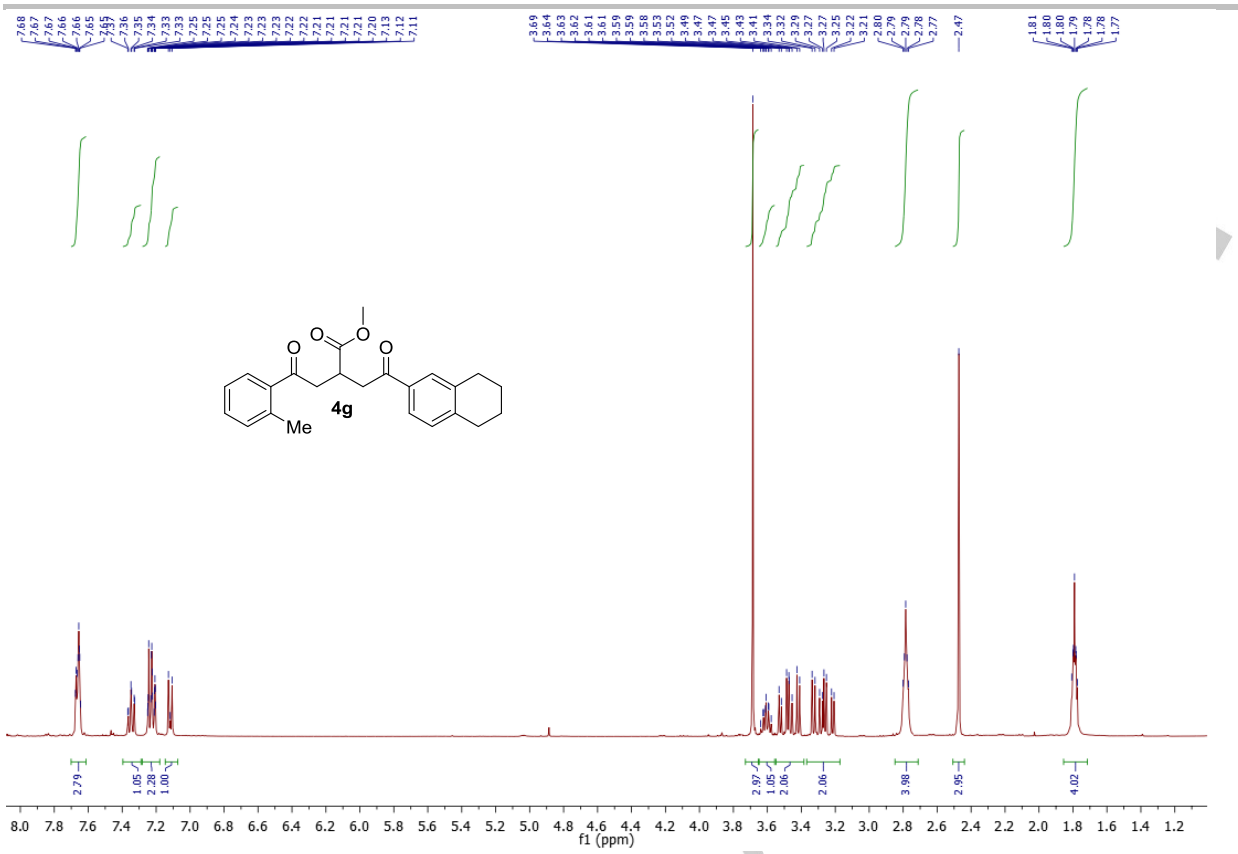


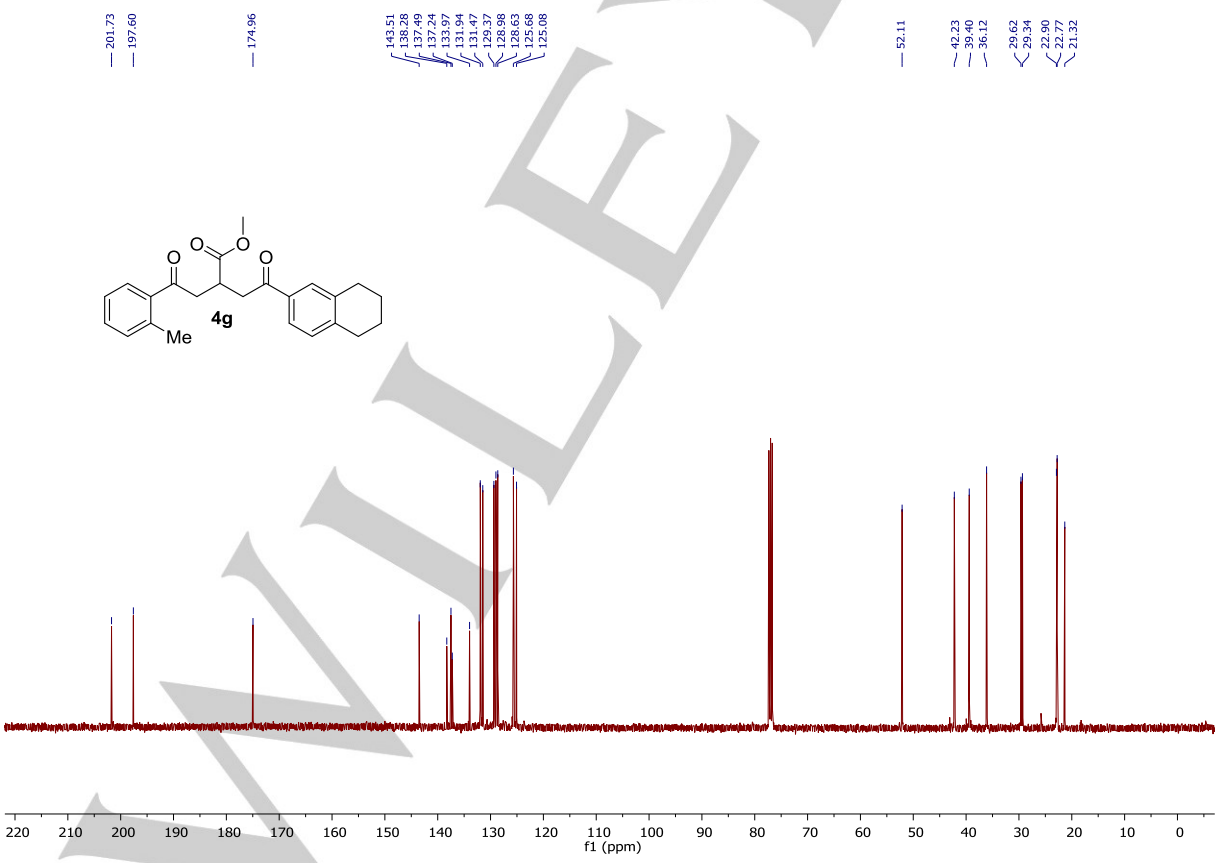


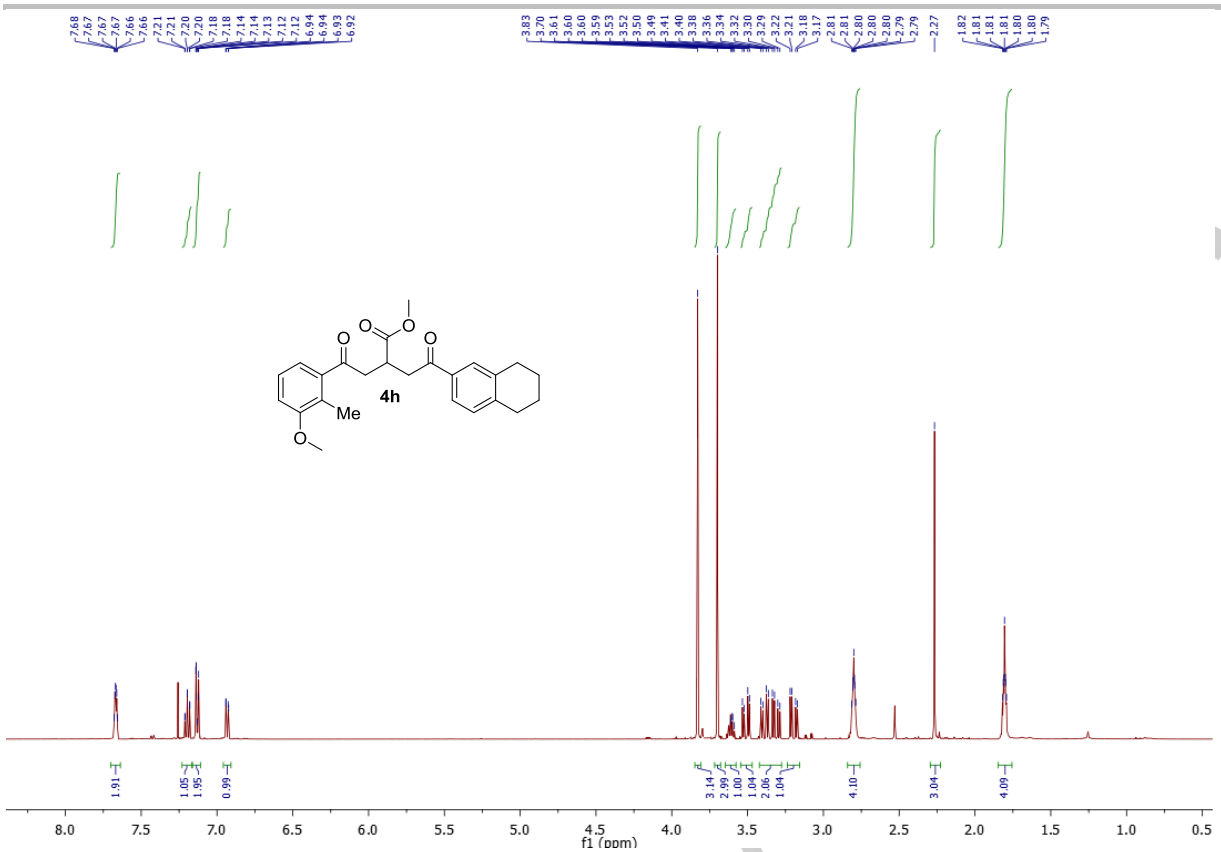








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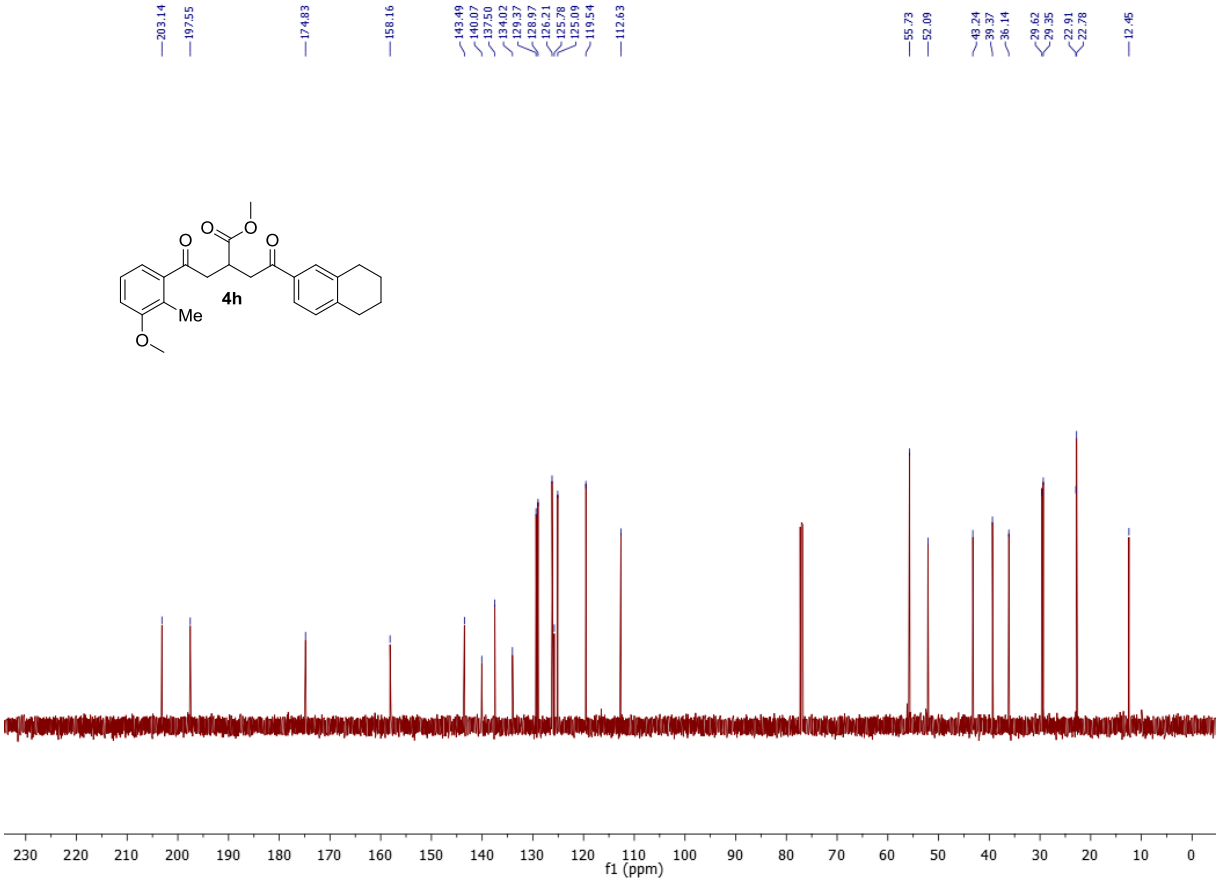
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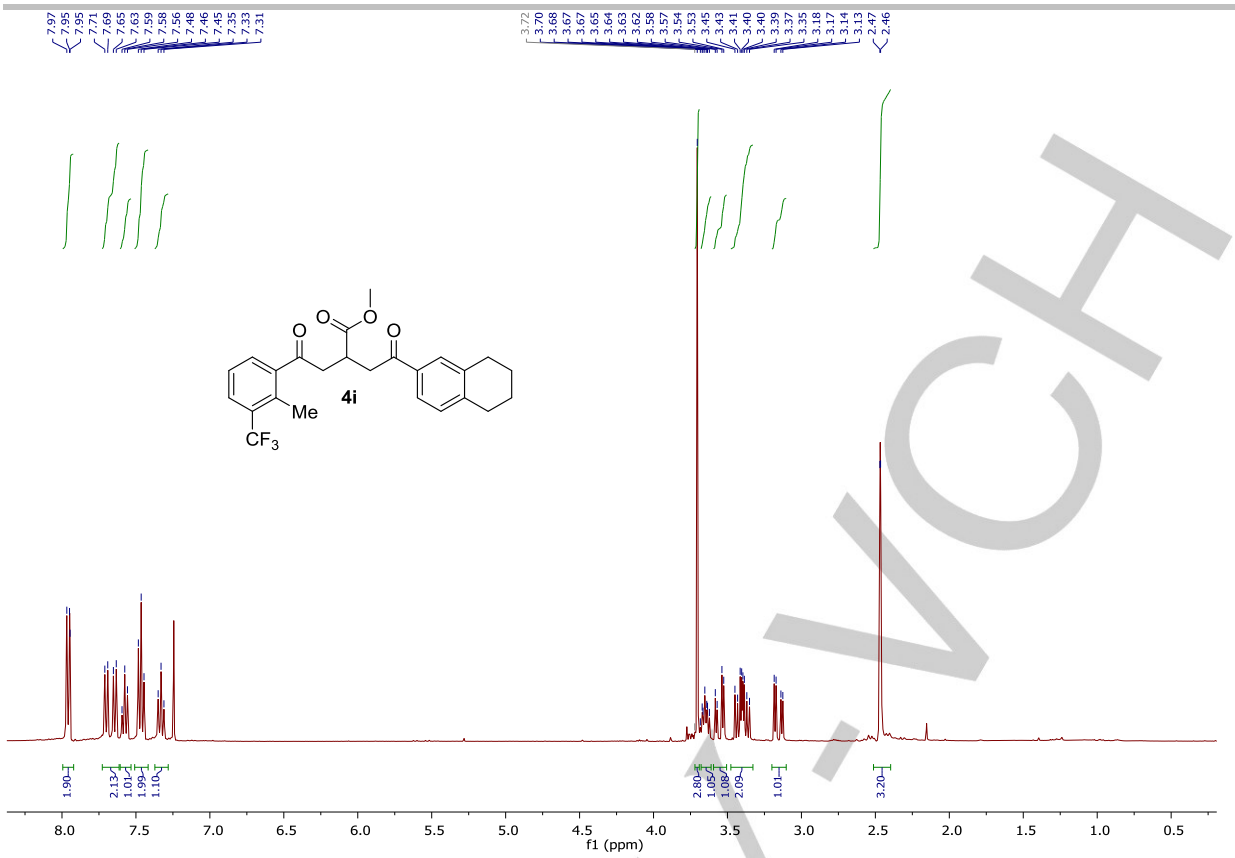
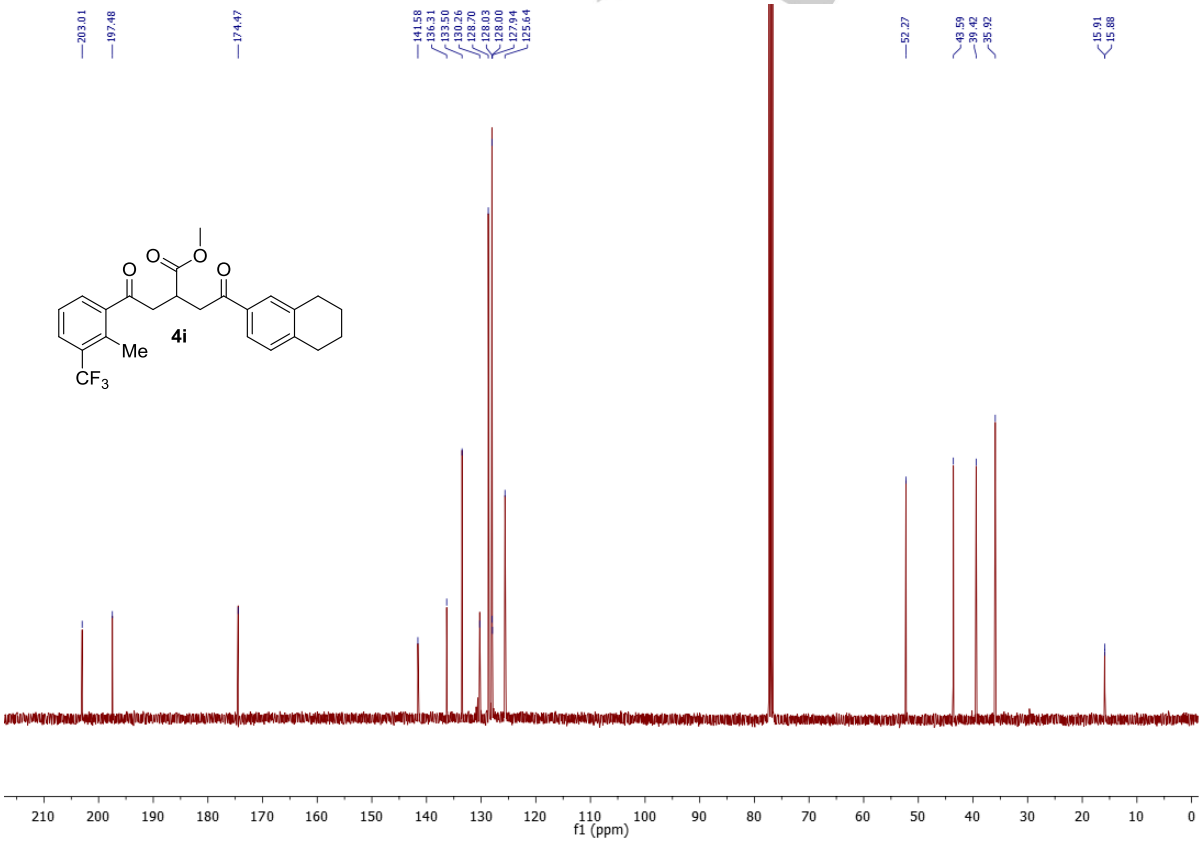
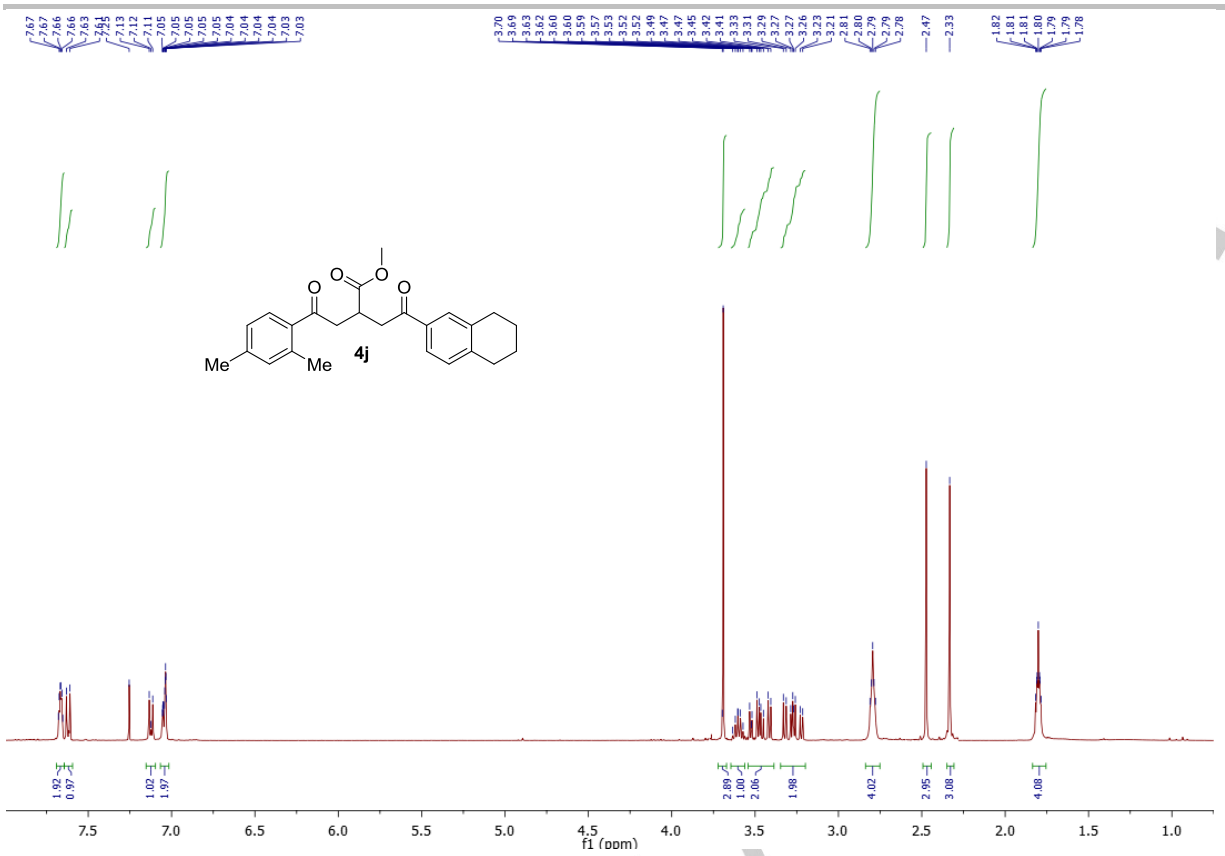
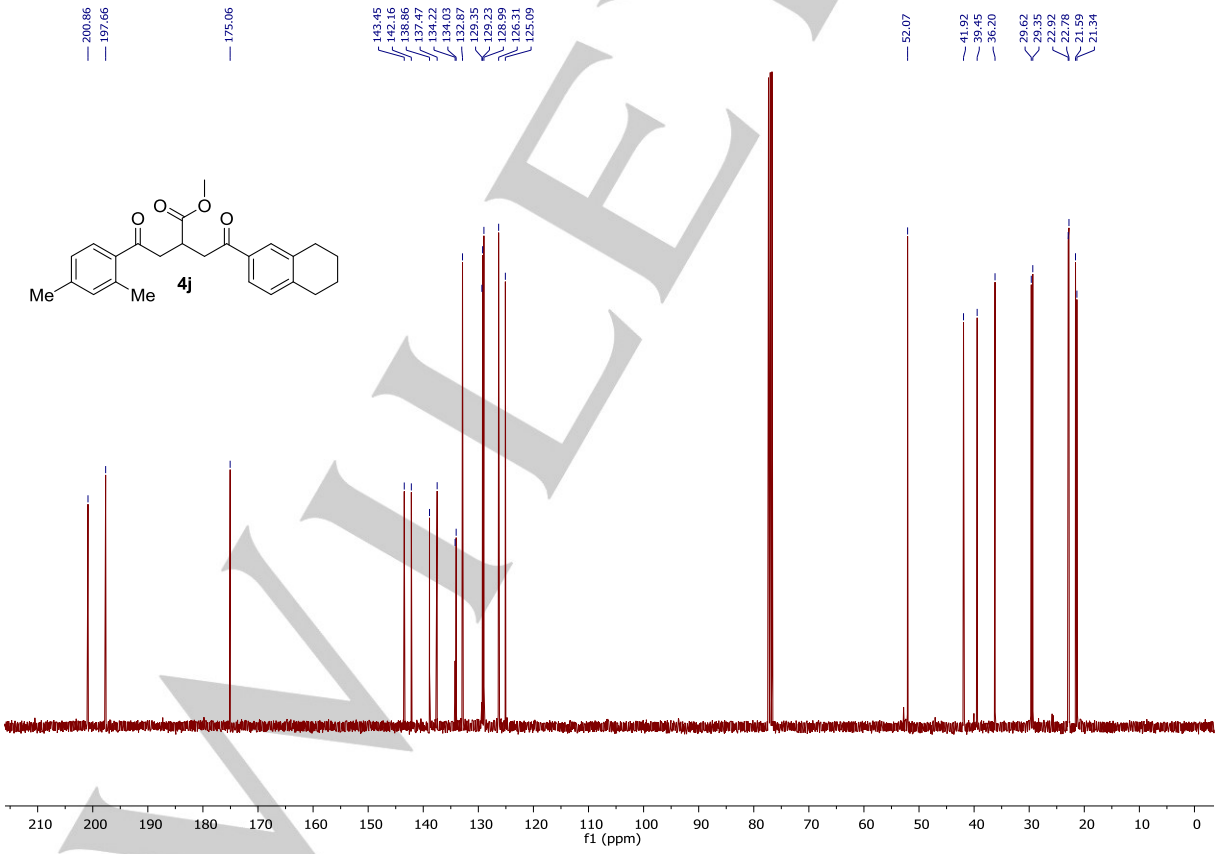
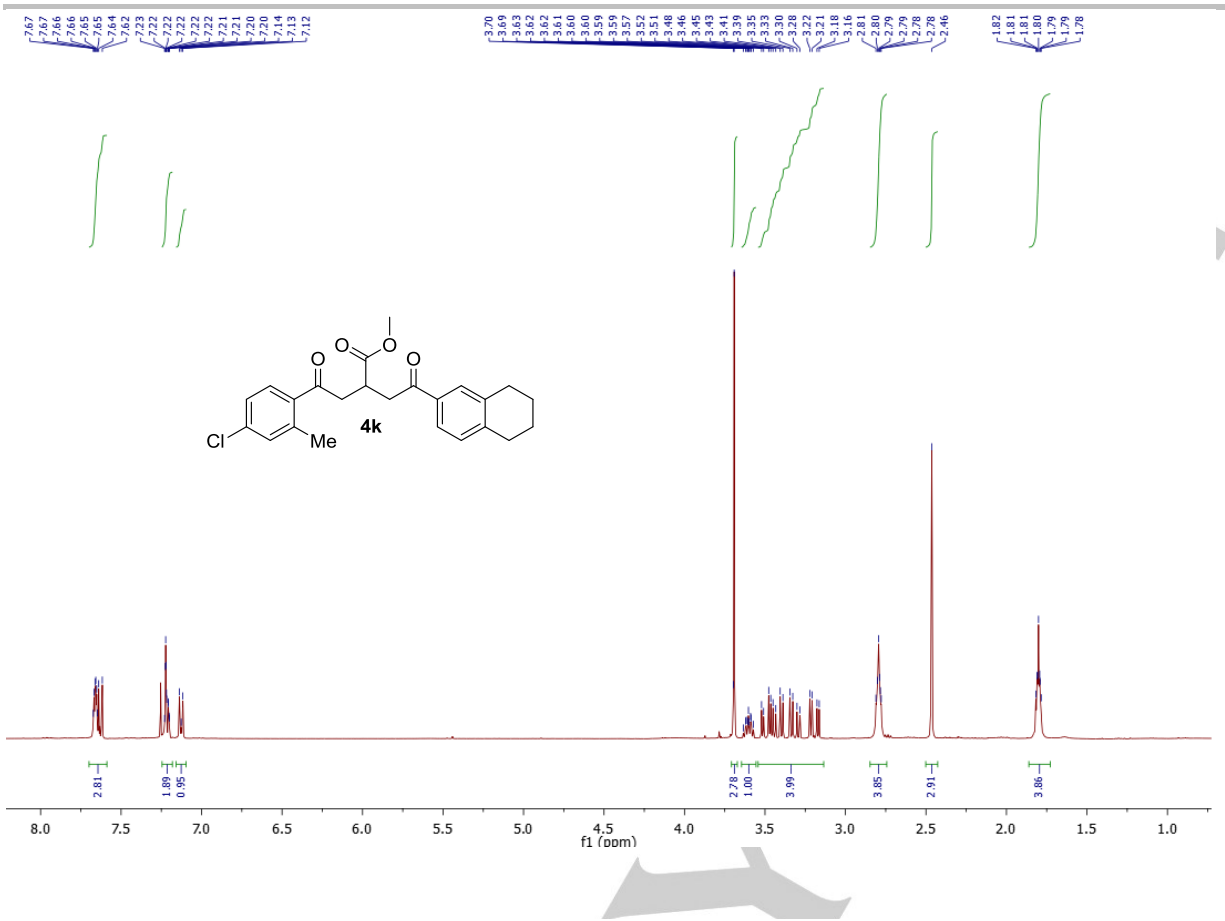
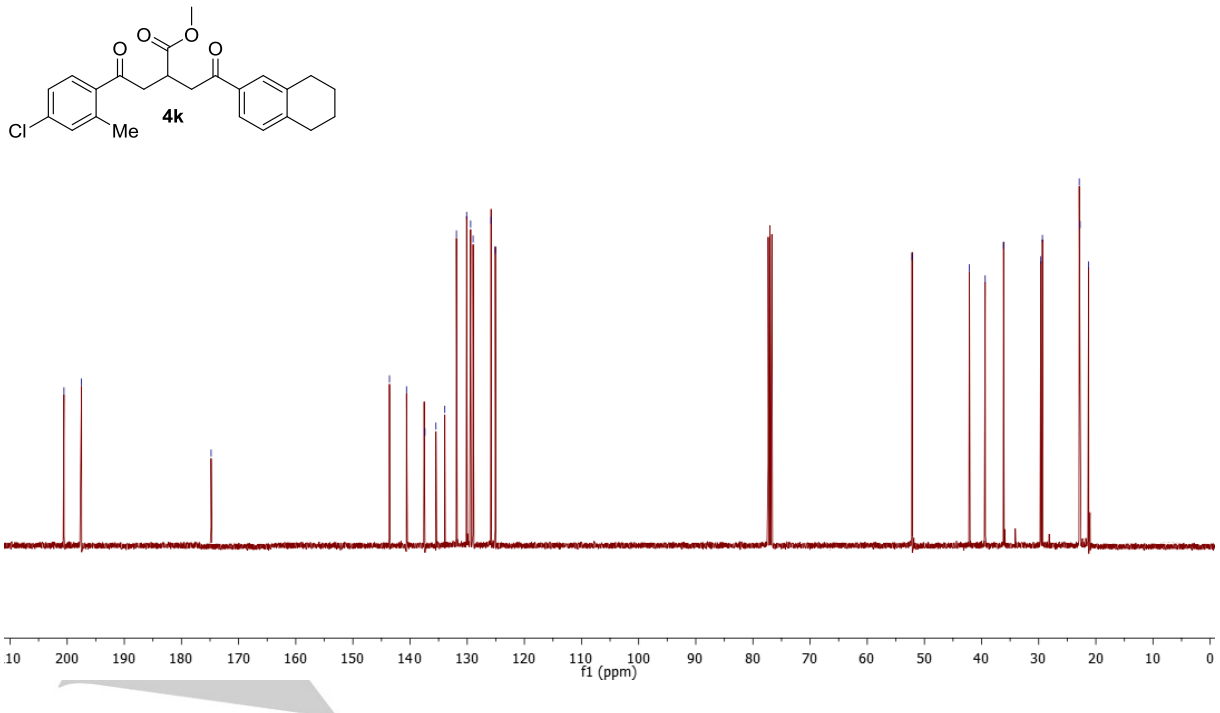









4k
Cl
Me
f1 (ppm)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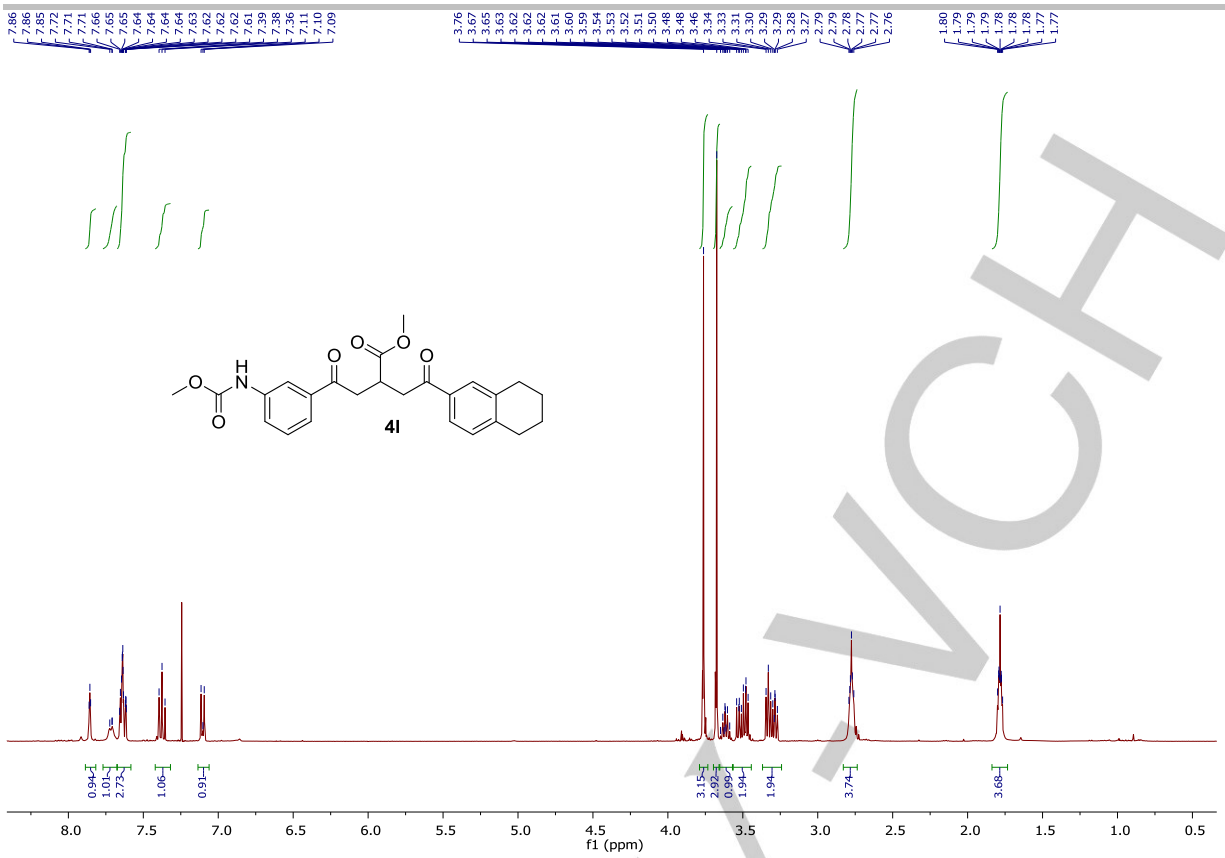

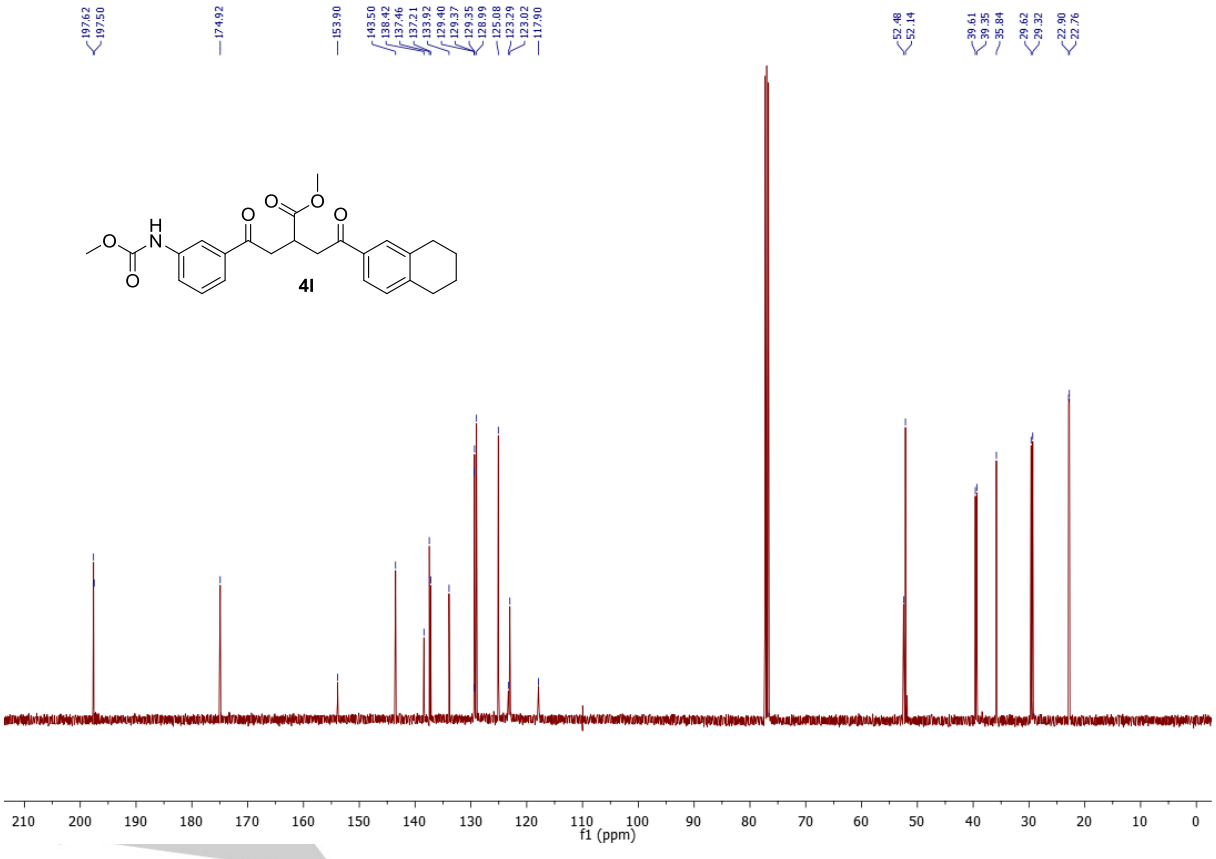

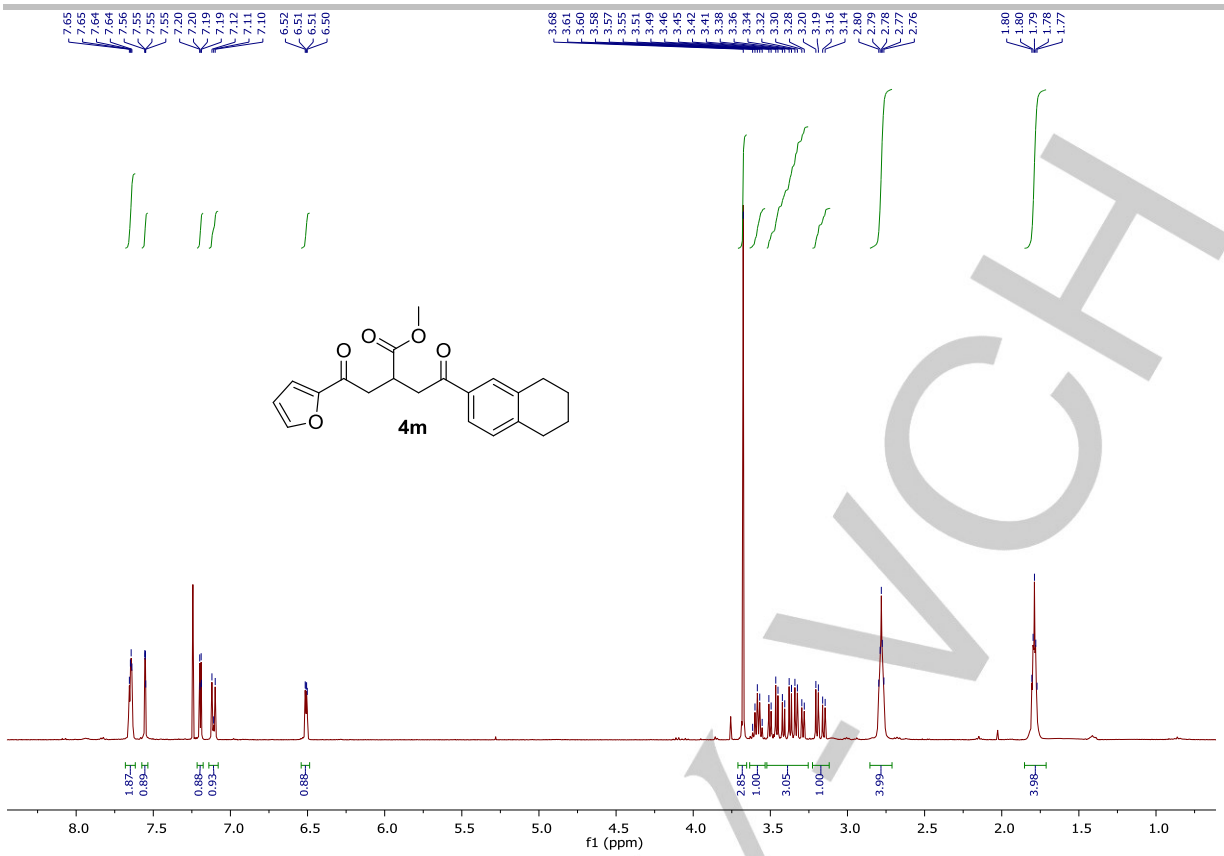
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1.80 1.80 1.79 1.78 1.77
4m
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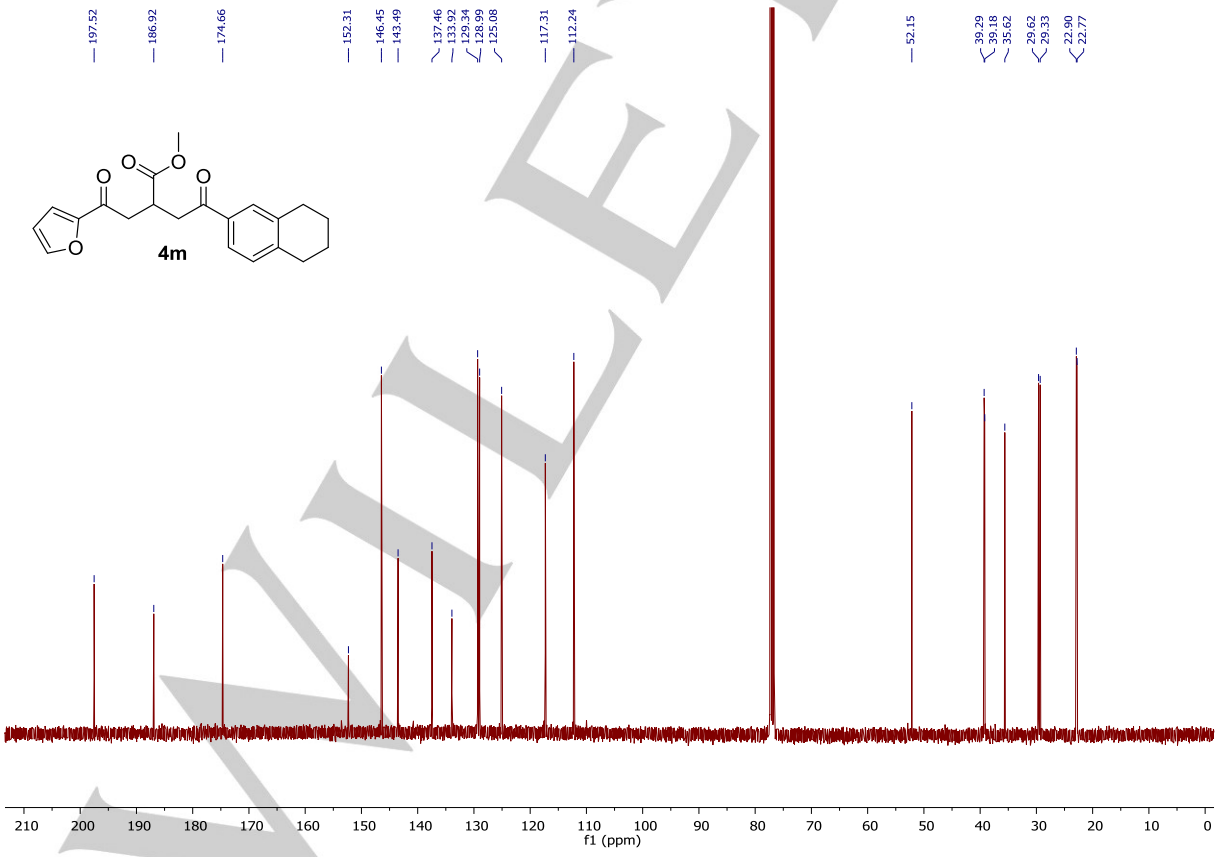
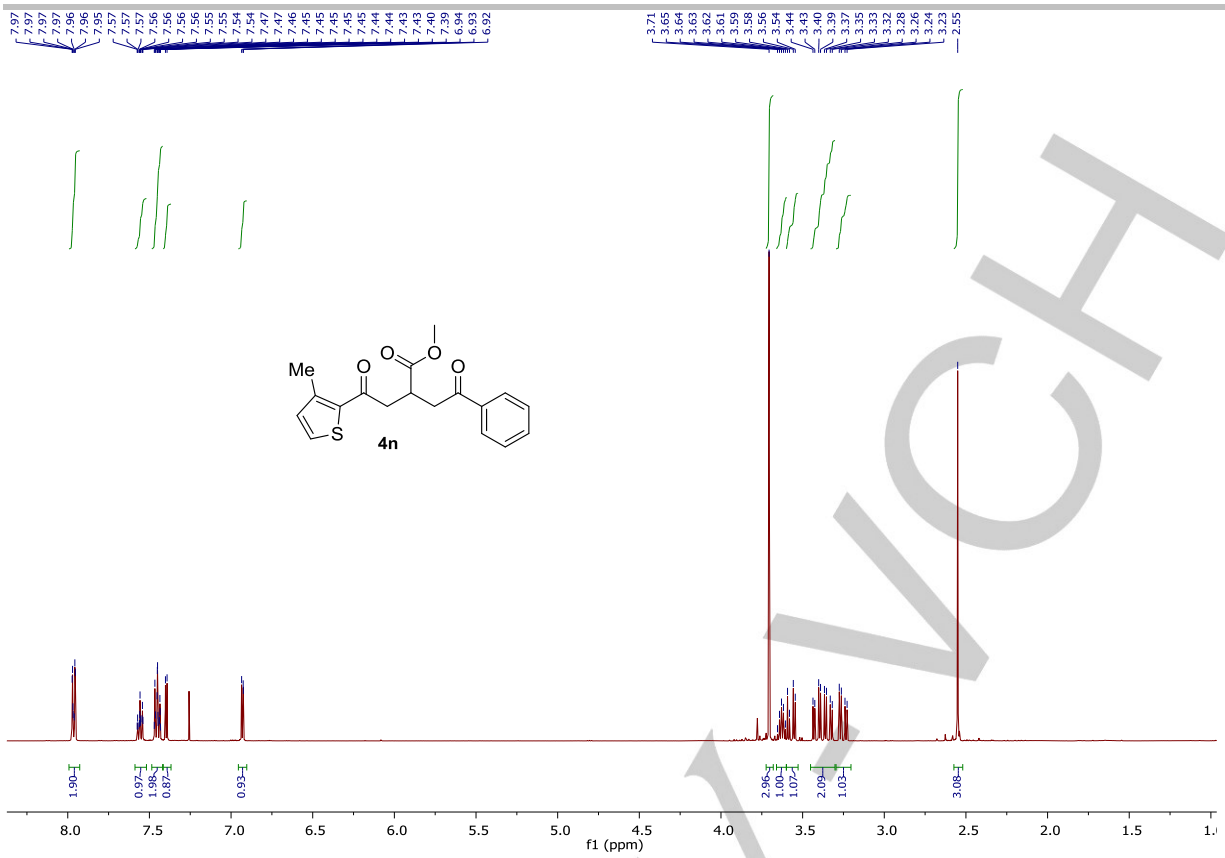
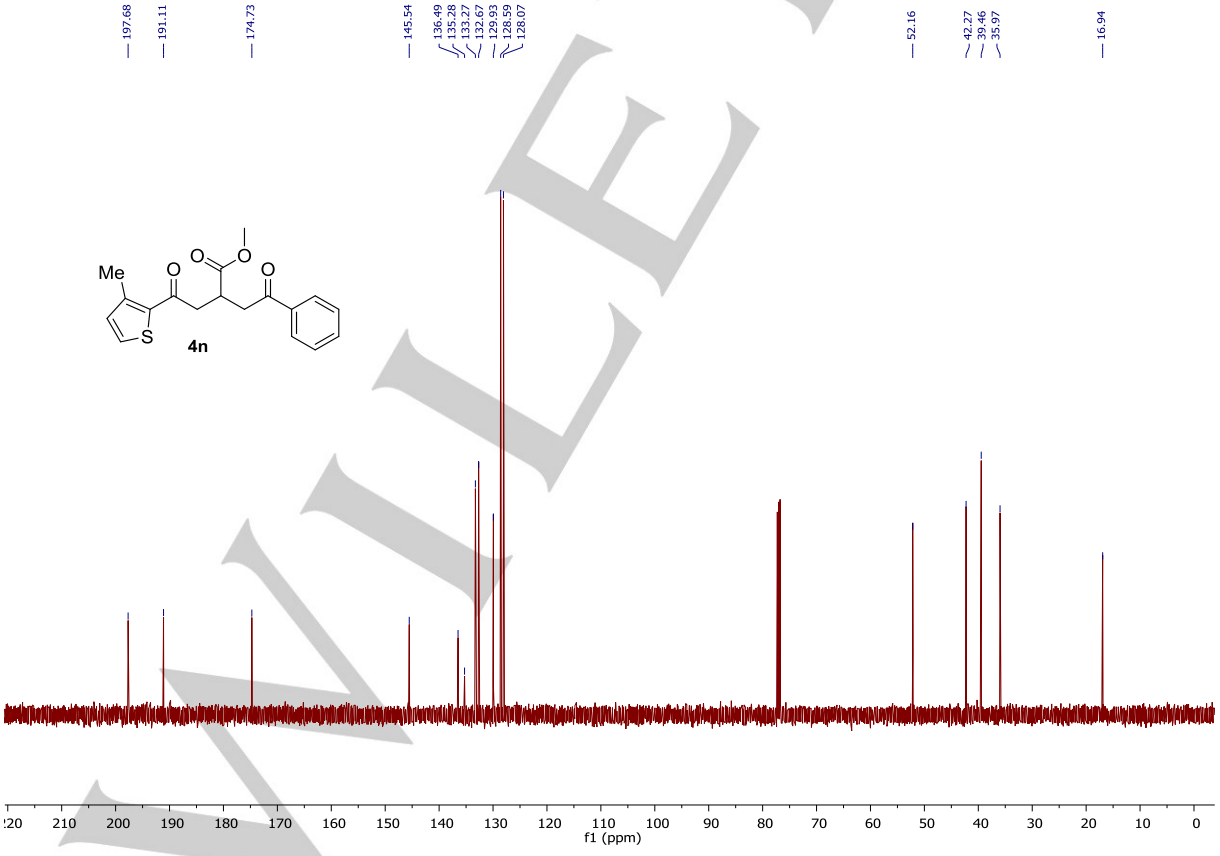
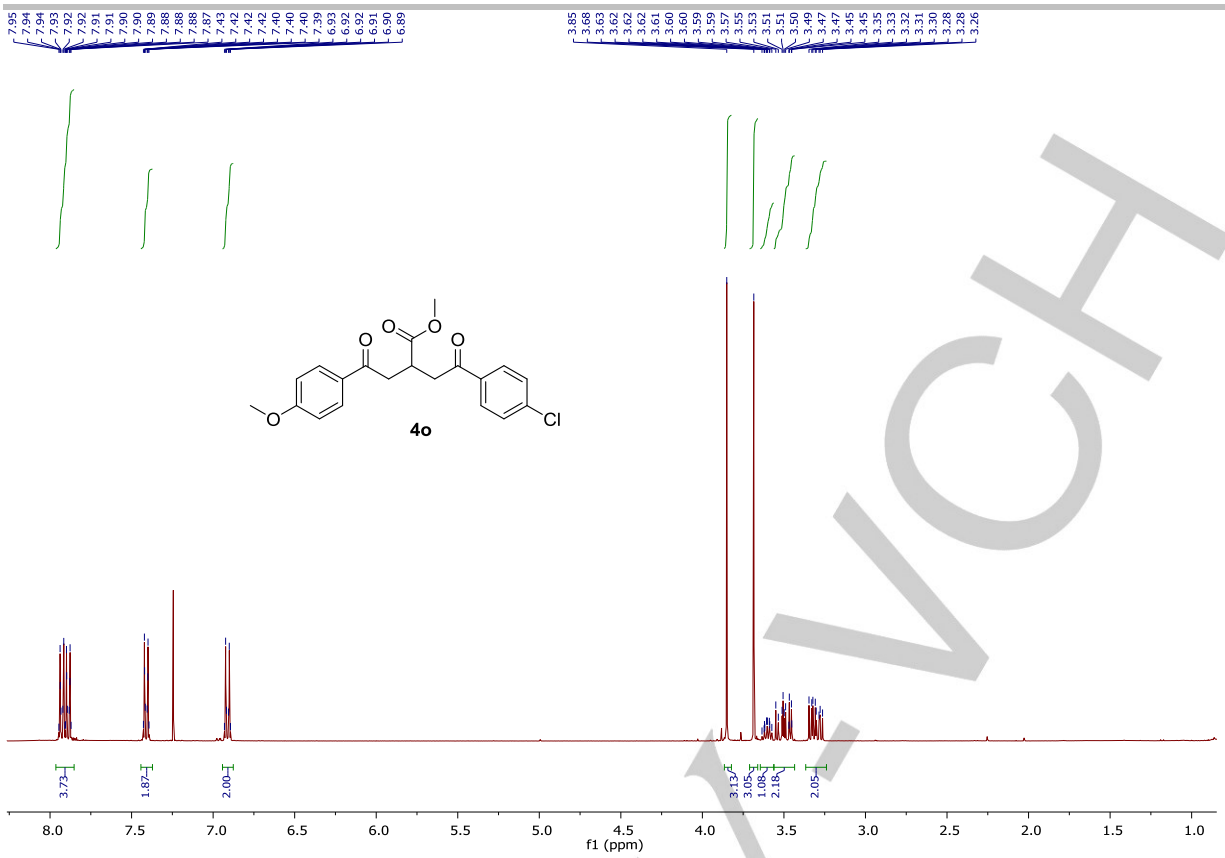
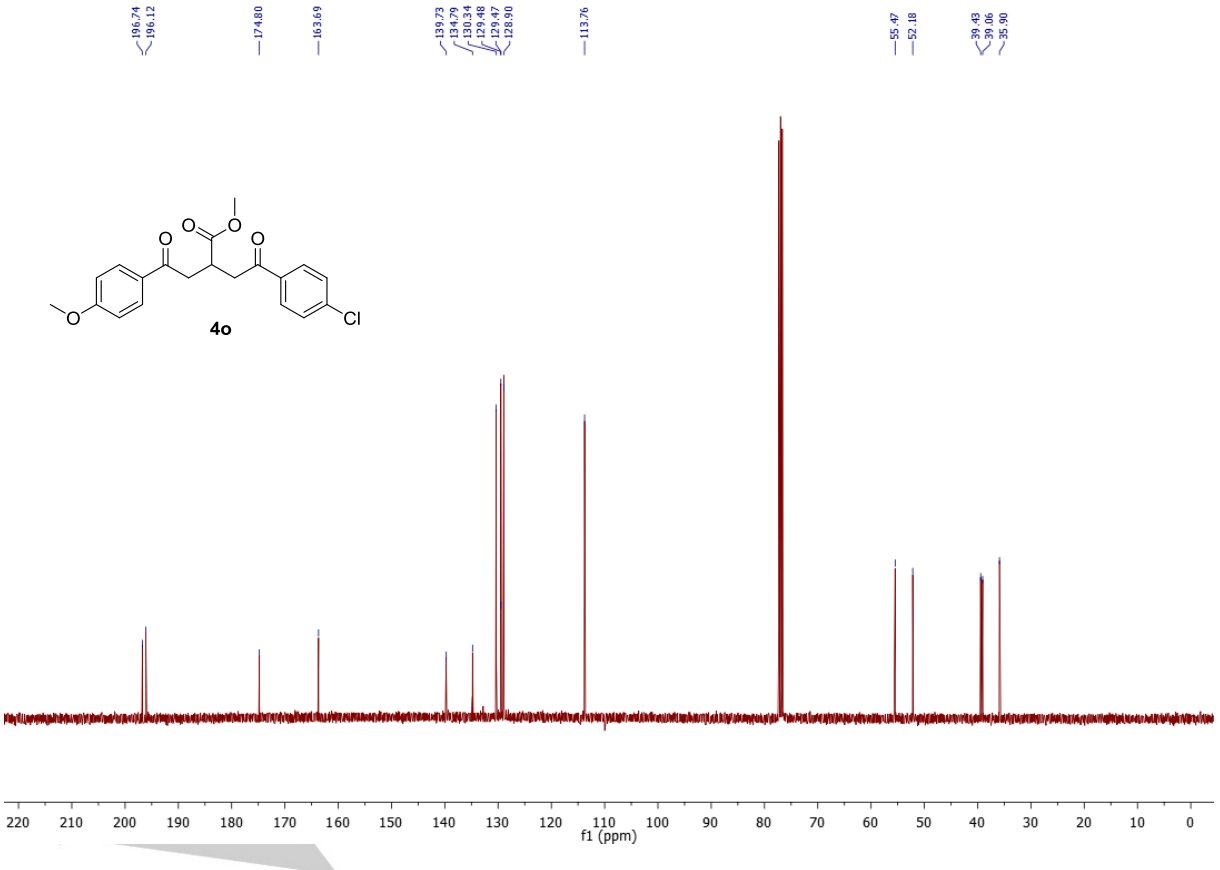
f1 (ppm)

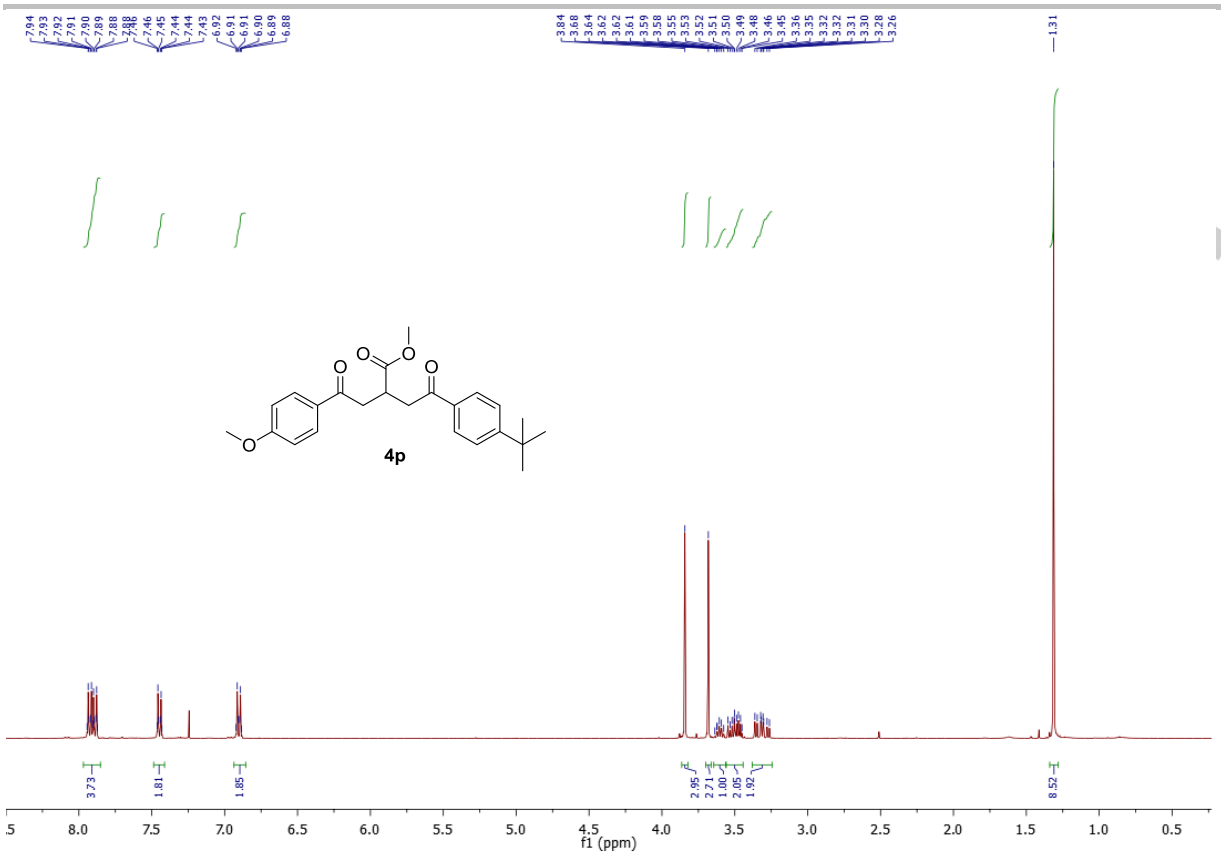

197.52 186.92 174.66 152.31 146.45 143.49 137.46 133.92 129.34 128.99 125.08 117.31 112.24 52.15 39.29 39.18 35.62 29.62 29.33 22.90 22.77
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

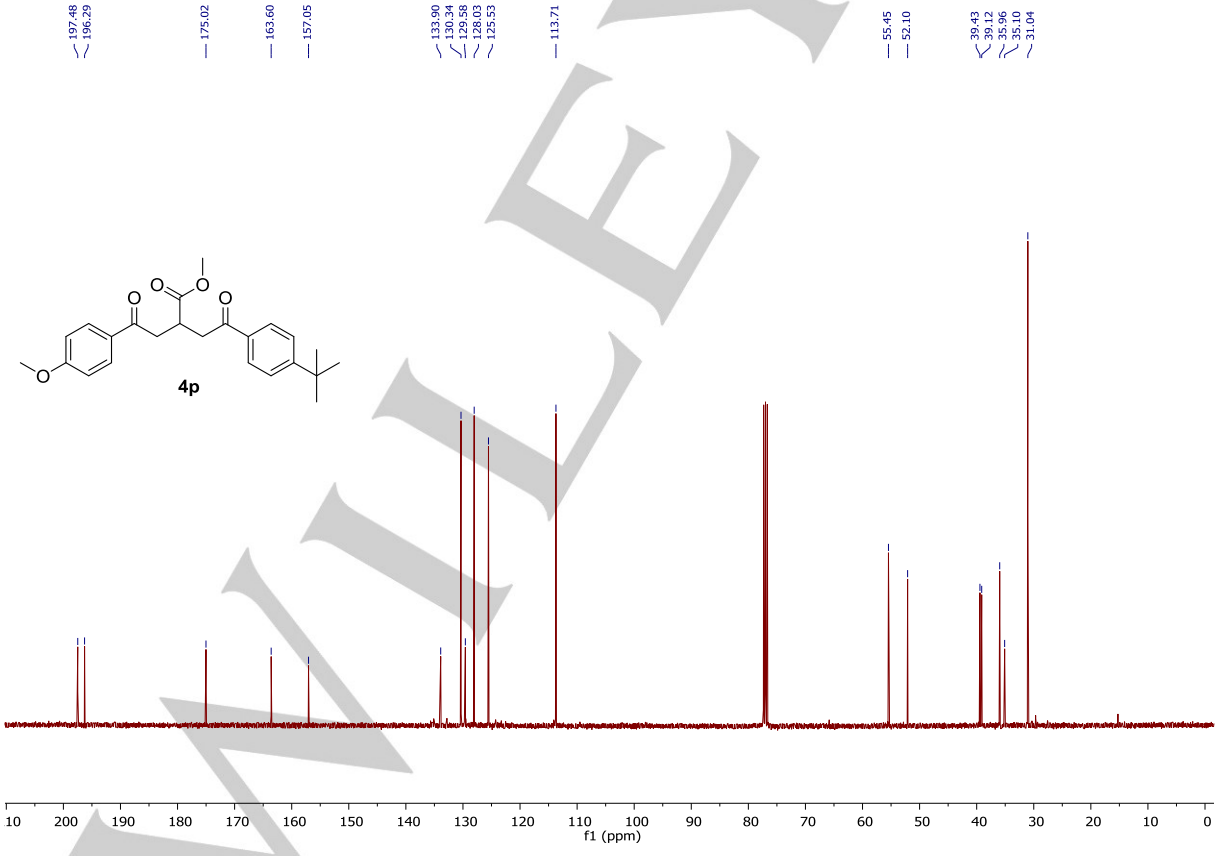


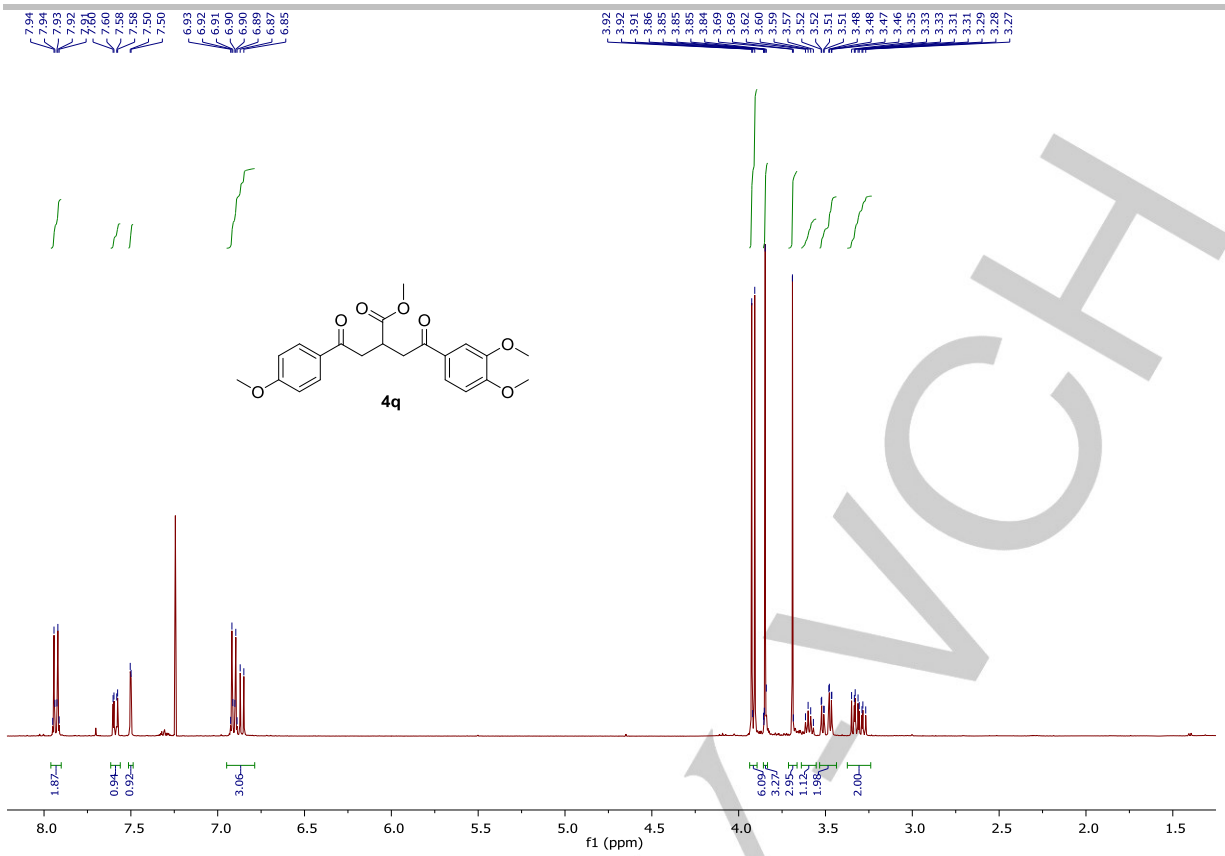


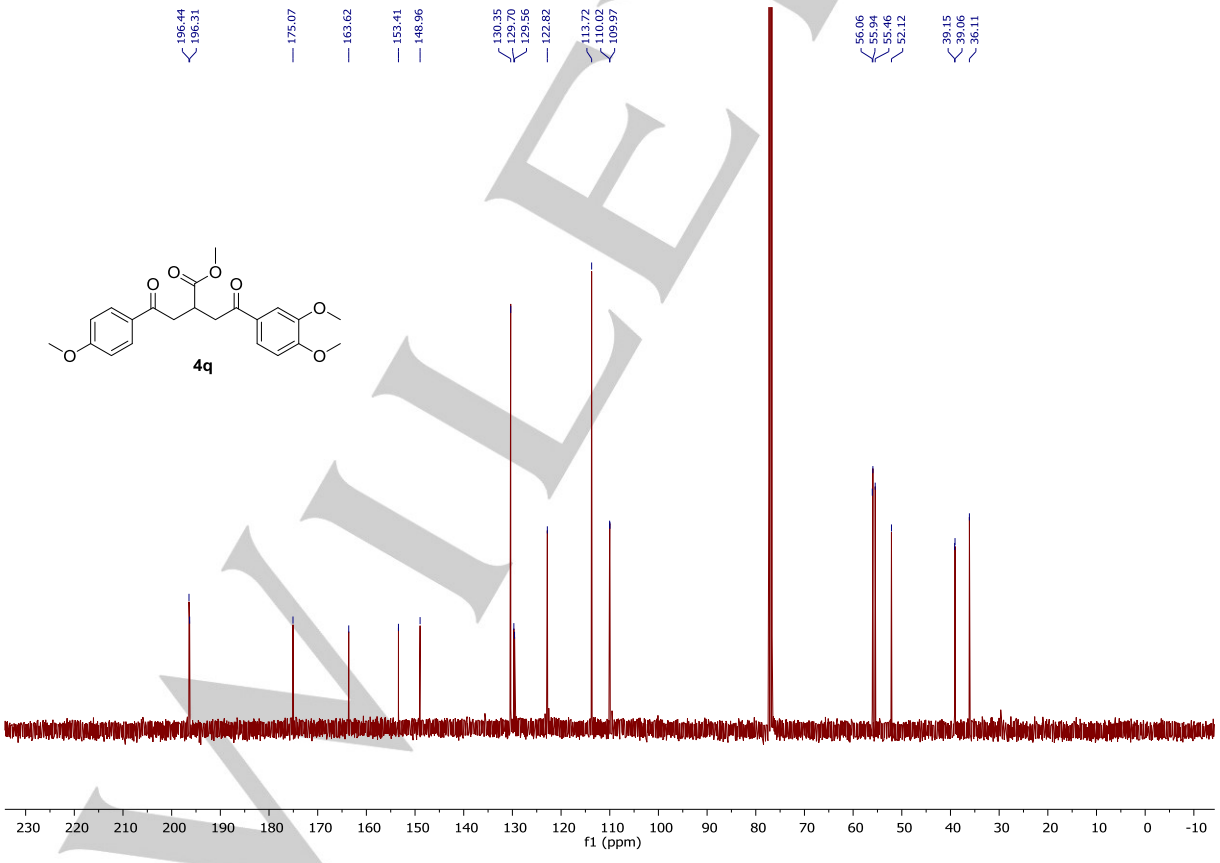


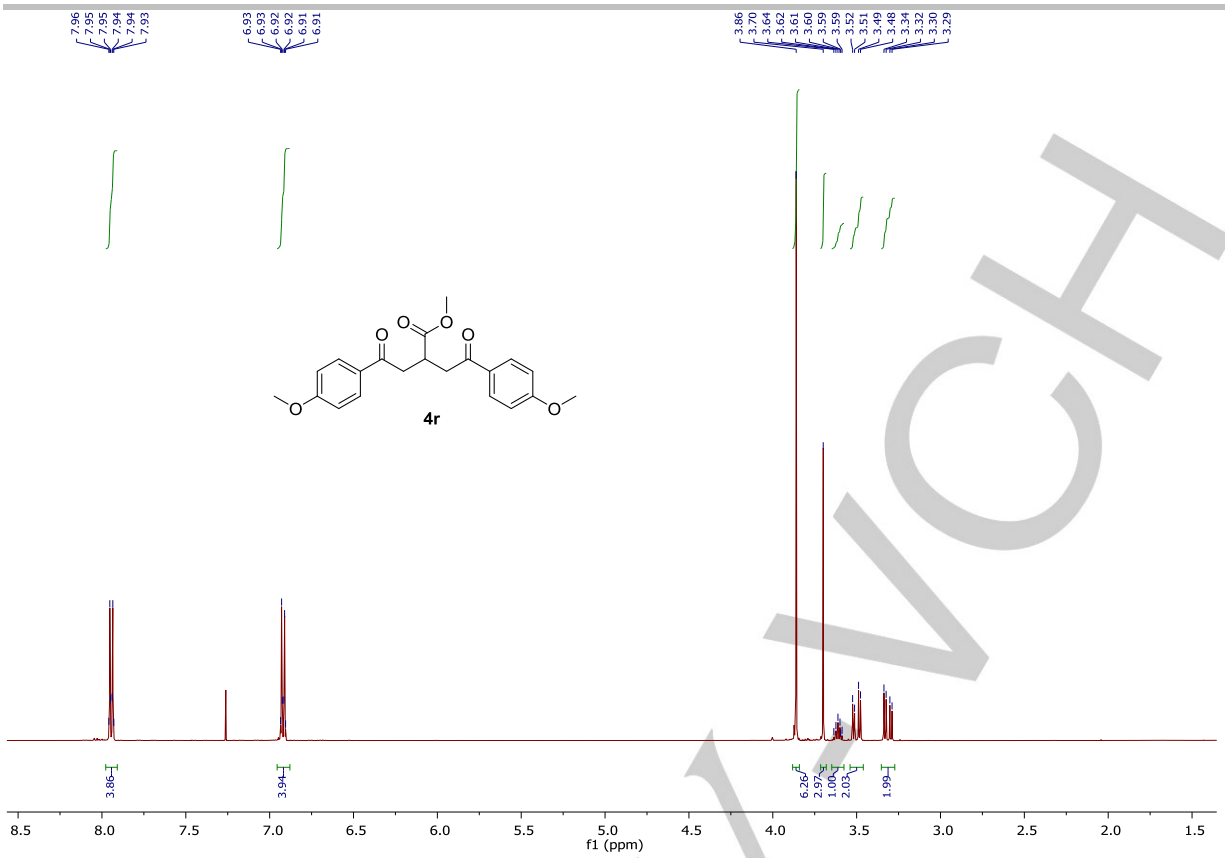


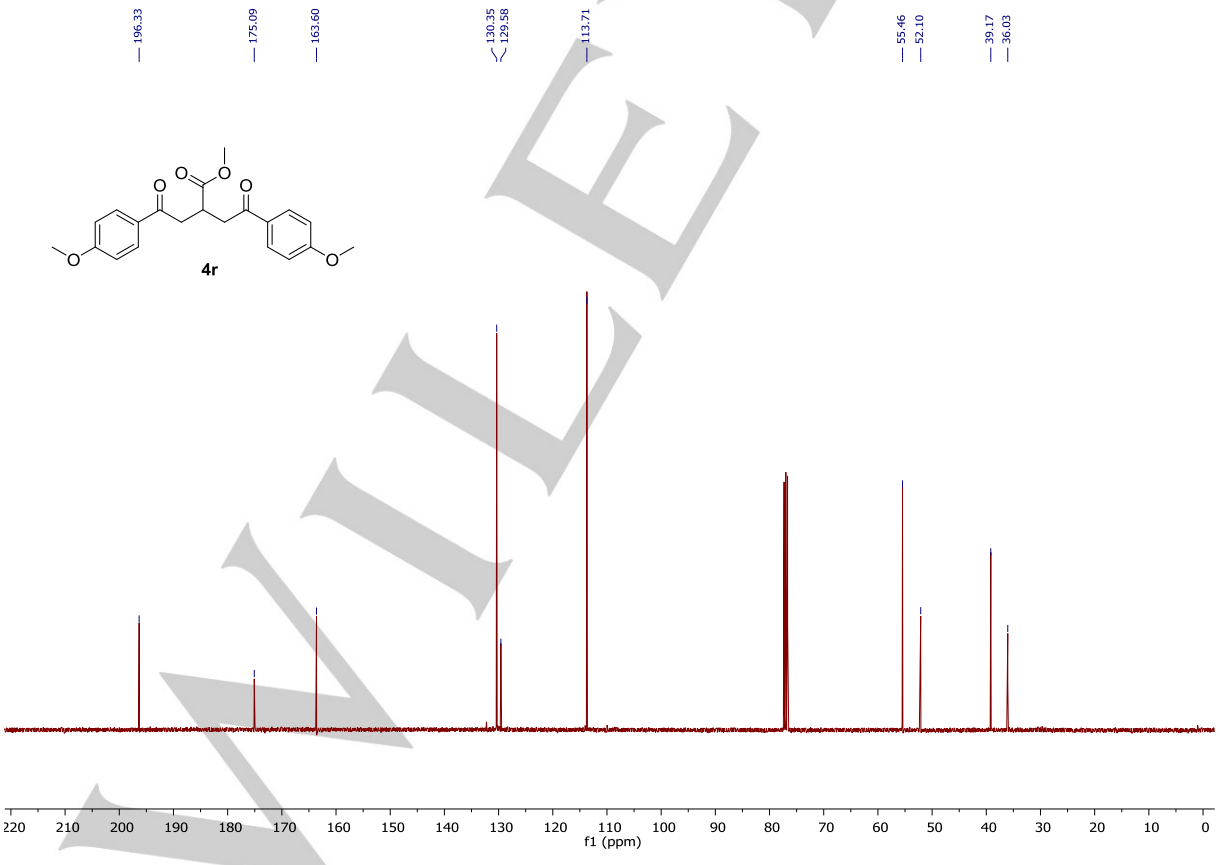


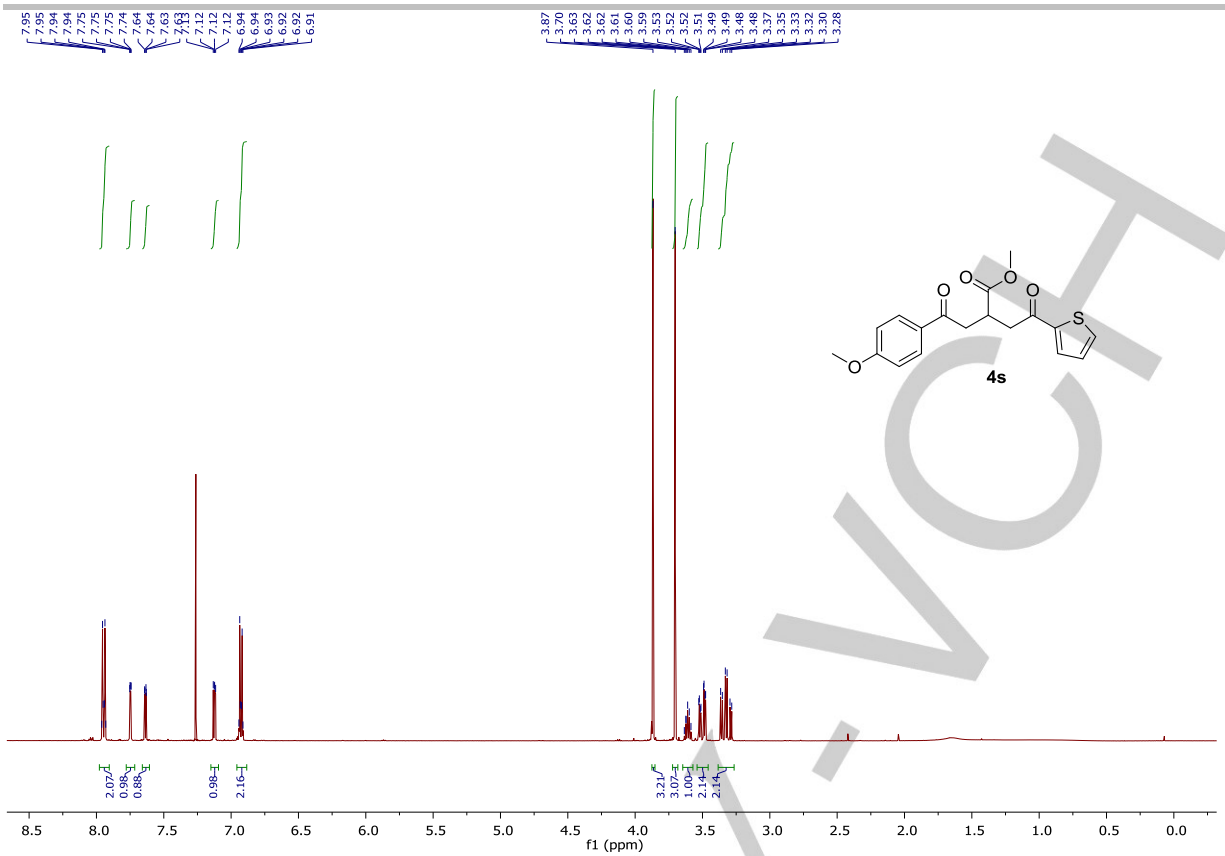


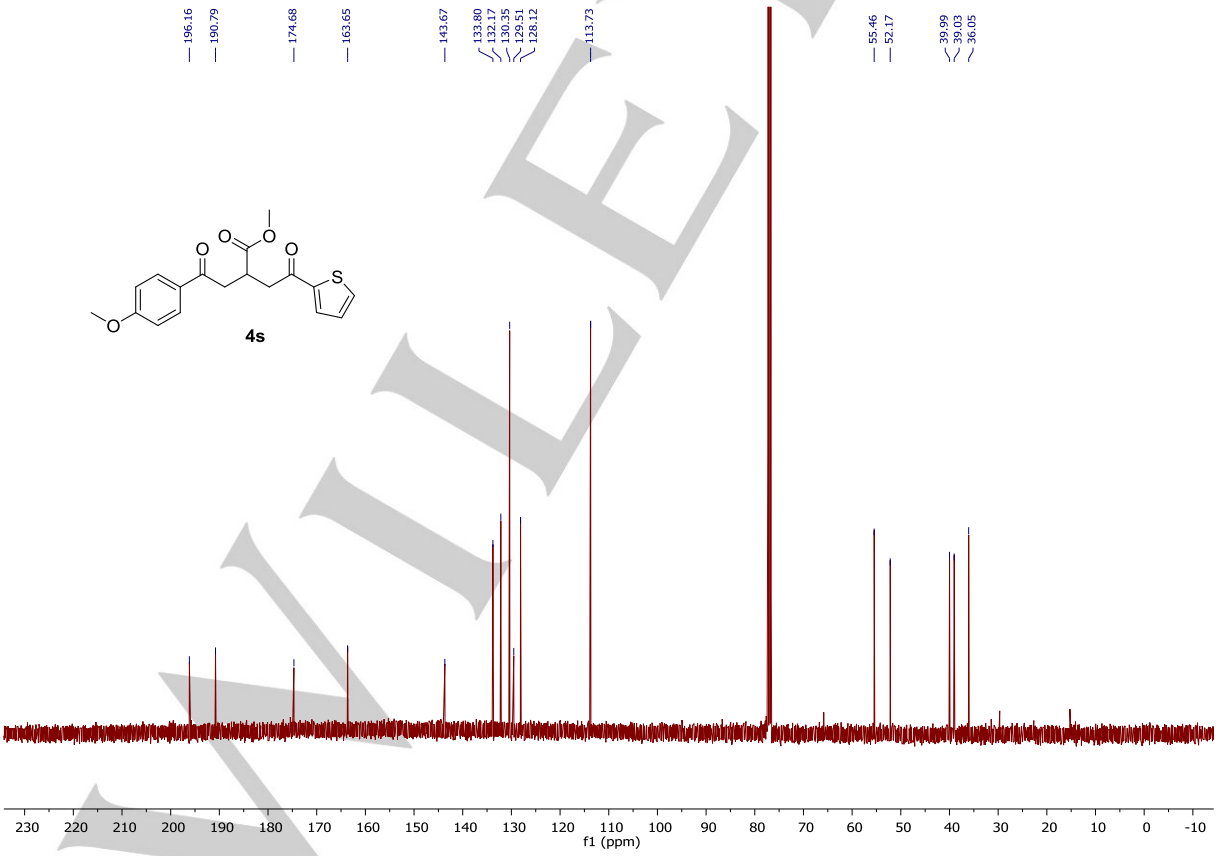


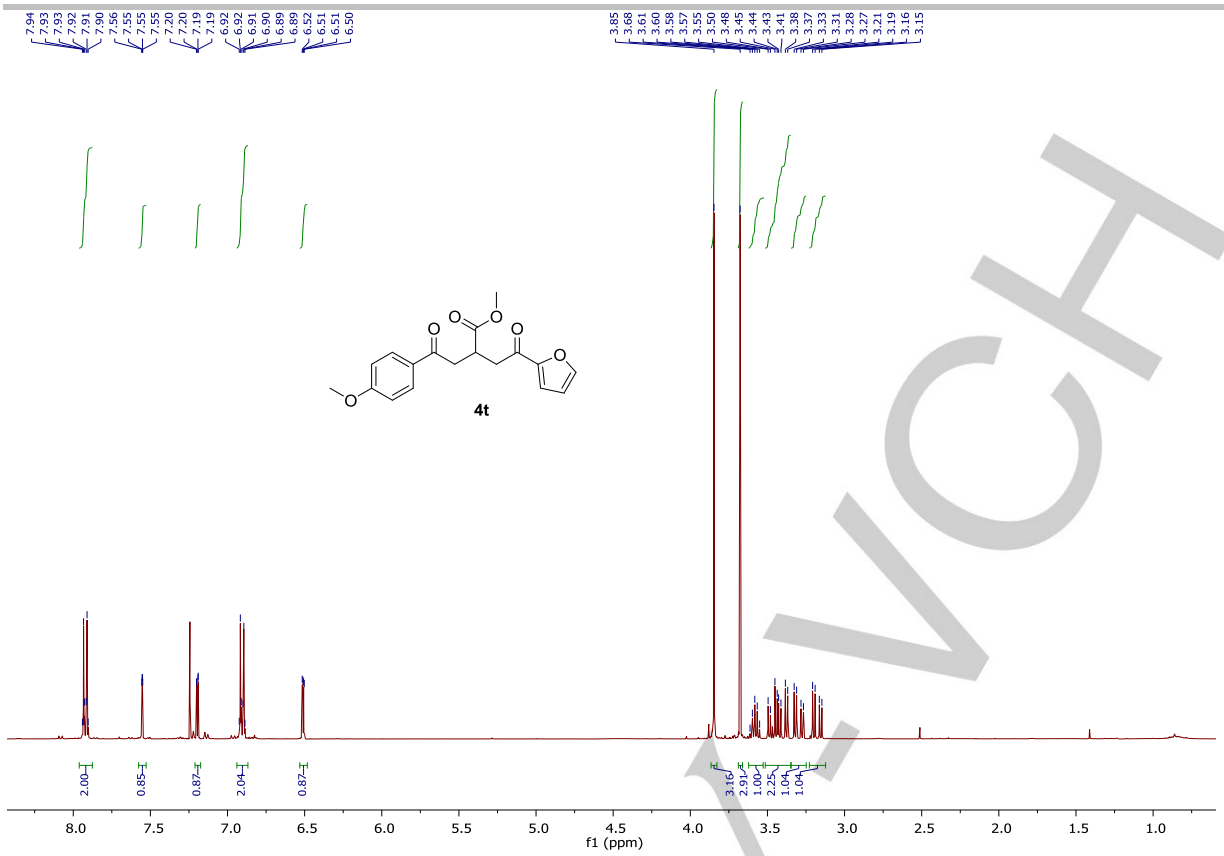


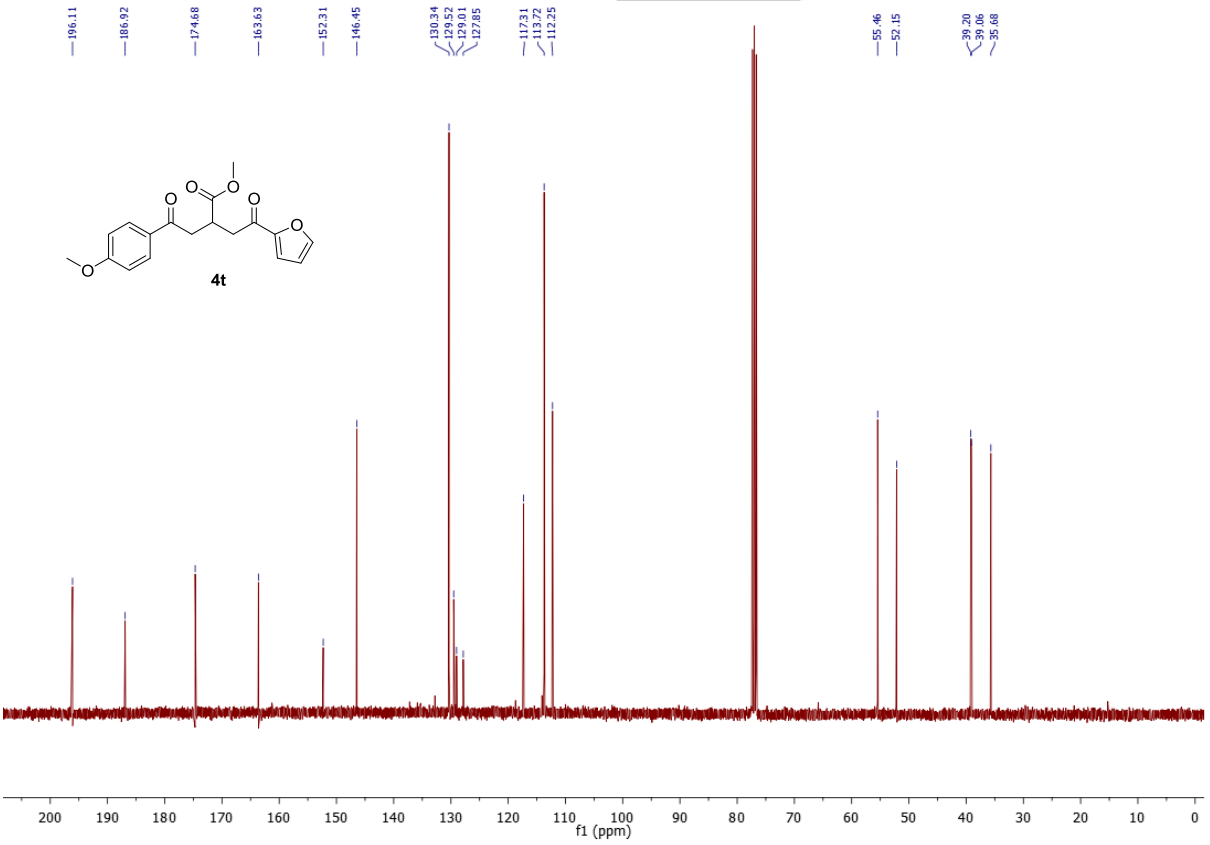

7.96
7.95
7.95
7.94
7.94
7.93
6.93
6.93
6.92
6.92
6.91
6.91
3.86
3.70
3.64
3.62
3.61
3.60
3.59
3.59
3.52
3.51
3.49
3.46
3.34
3.32
3.30
3.29
4r
3.86
3.94
6.26
2.97
1.00
2.03
1.99
f1 (ppm)

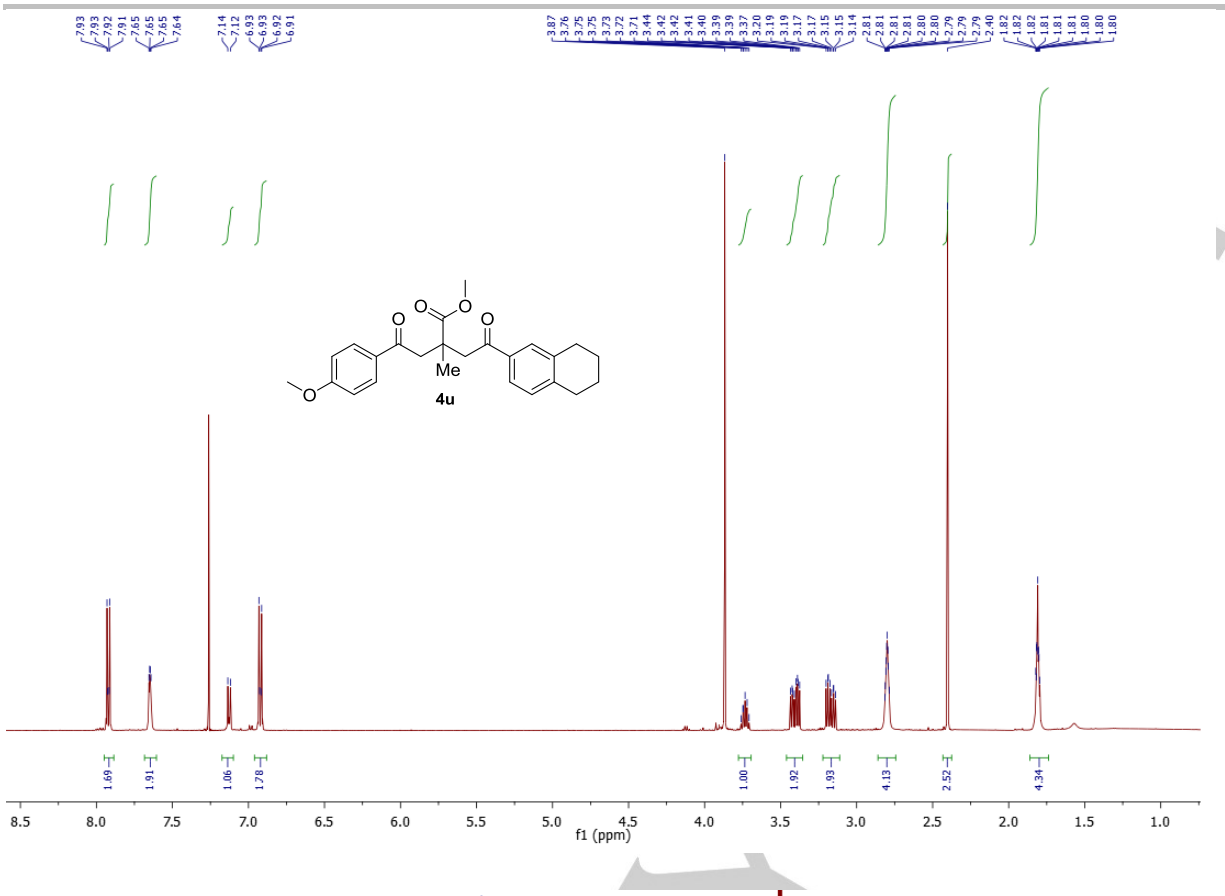

196.33
175.09
163.60
130.35
129.58
113.71
55.46
52.10
39.17
36.03
4r
f1 (ppm)

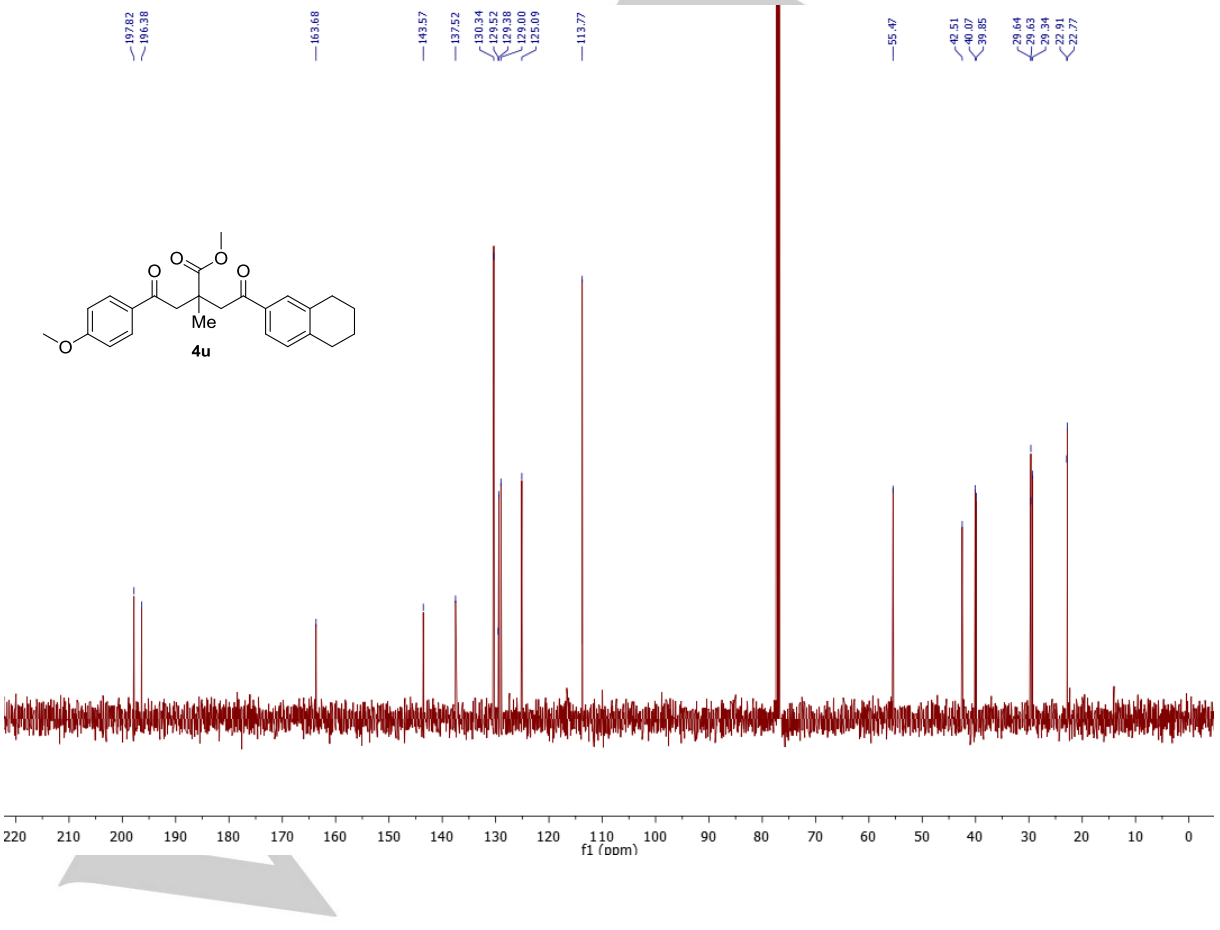

7.95
7.95
7.94
7.94
7.75
7.75
7.75
7.74
7.64
7.64
7.63
7.63
7.12
7.12
7.12
6.94
6.94
6.93
6.92
6.92
6.91
3.87
3.70
3.63
3.62
3.62
3.61
3.60
3.59
3.53
3.52
3.52
3.51
3.49
3.49
3.48
3.37
3.35
3.33
3.32
3.30
3.28
2.07
0.98
0.88
0.98
2.16
3.21
3.07
1.00
2.14
2.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4s

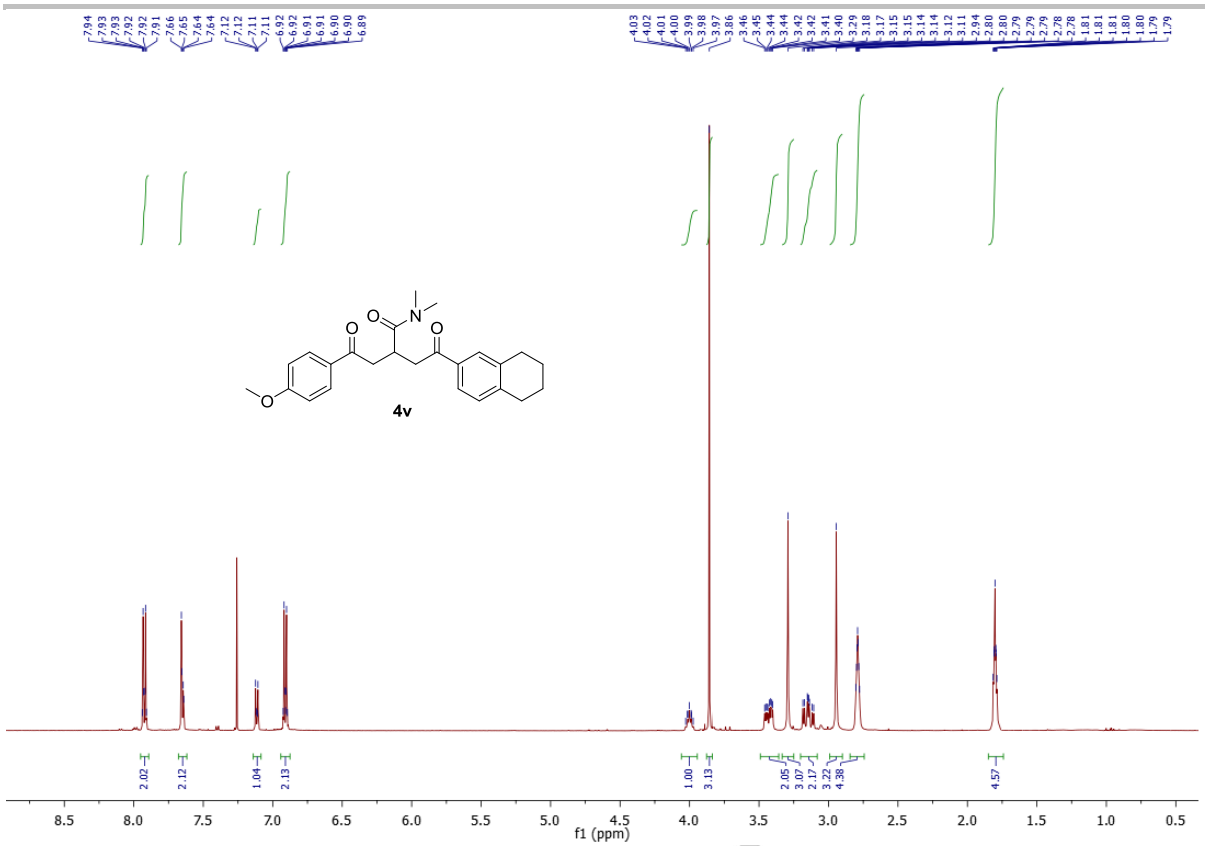

196.16
190.79
174.68
163.65
143.67
133.80
132.17
130.35
129.51
128.12
113.73
55.46
52.17
39.99
39.03
36.05
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4s

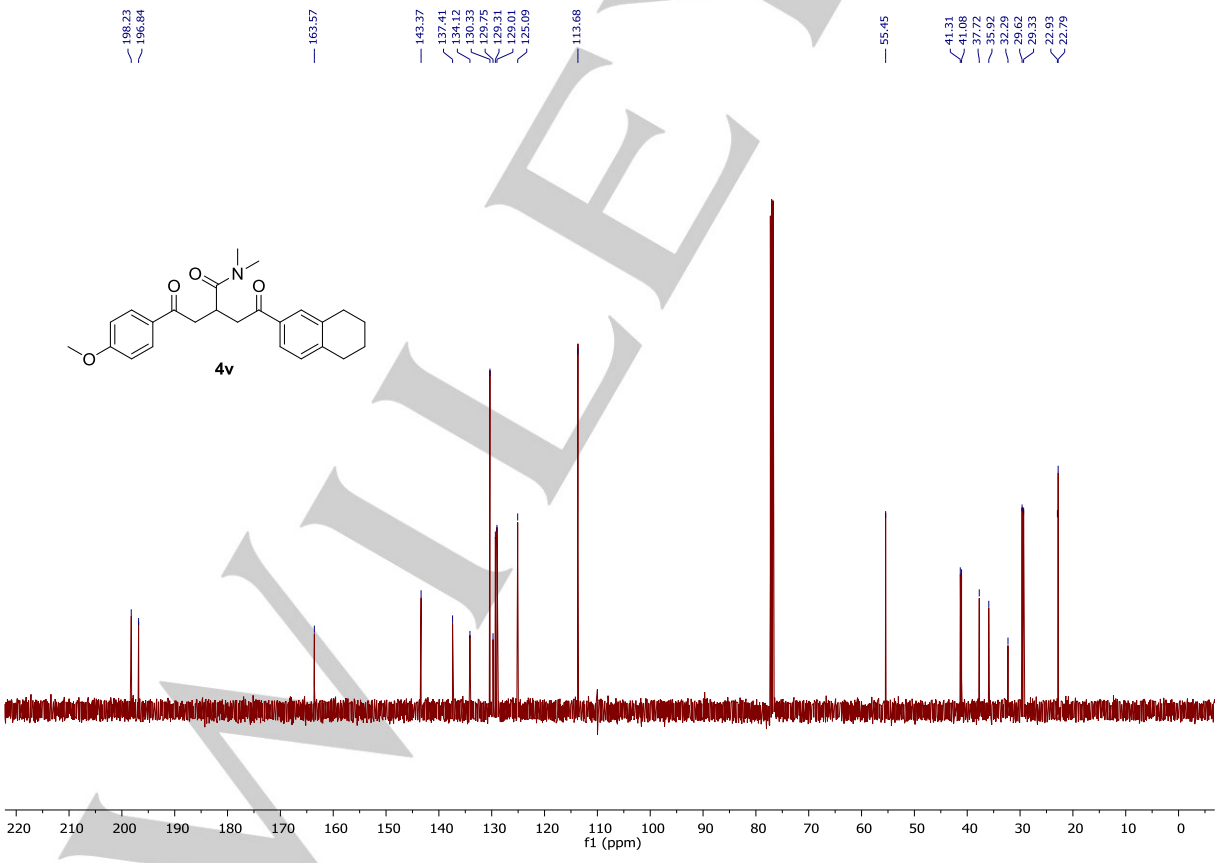

7.94 7.93 7.93 7.92 7.91 7.90 7.56 7.55 7.55 7.55 7.20 7.20 7.19 7.19 6.92 6.92 6.91 6.90 6.89 6.89 6.52 6.51 6.51 6.50
3.85 3.68 3.61 3.60 3.58 3.57 3.55 3.50 3.48 3.45 3.44 3.43 3.41 3.38 3.37 3.33 3.31 3.28 3.27 3.21 3.19 3.16 3.15
4t
2.00 0.85 0.87 2.04 0.87 3.16 2.91 1.00 2.25 1.04 1.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

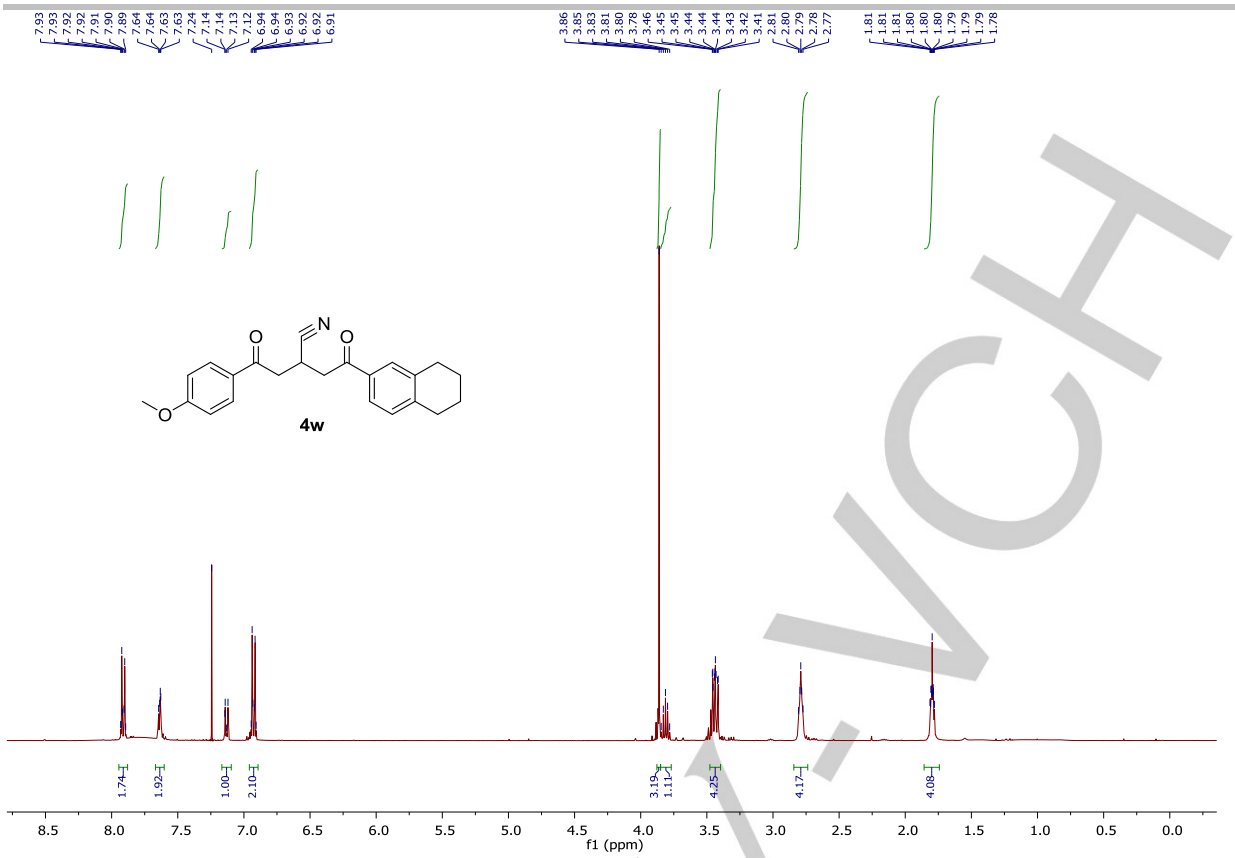

196.11 186.92 174.68 163.63 152.31 146.45 130.34 129.52 129.01 127.85 117.31 113.72 112.25 55.46 52.15 39.20 39.06 35.68
4t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

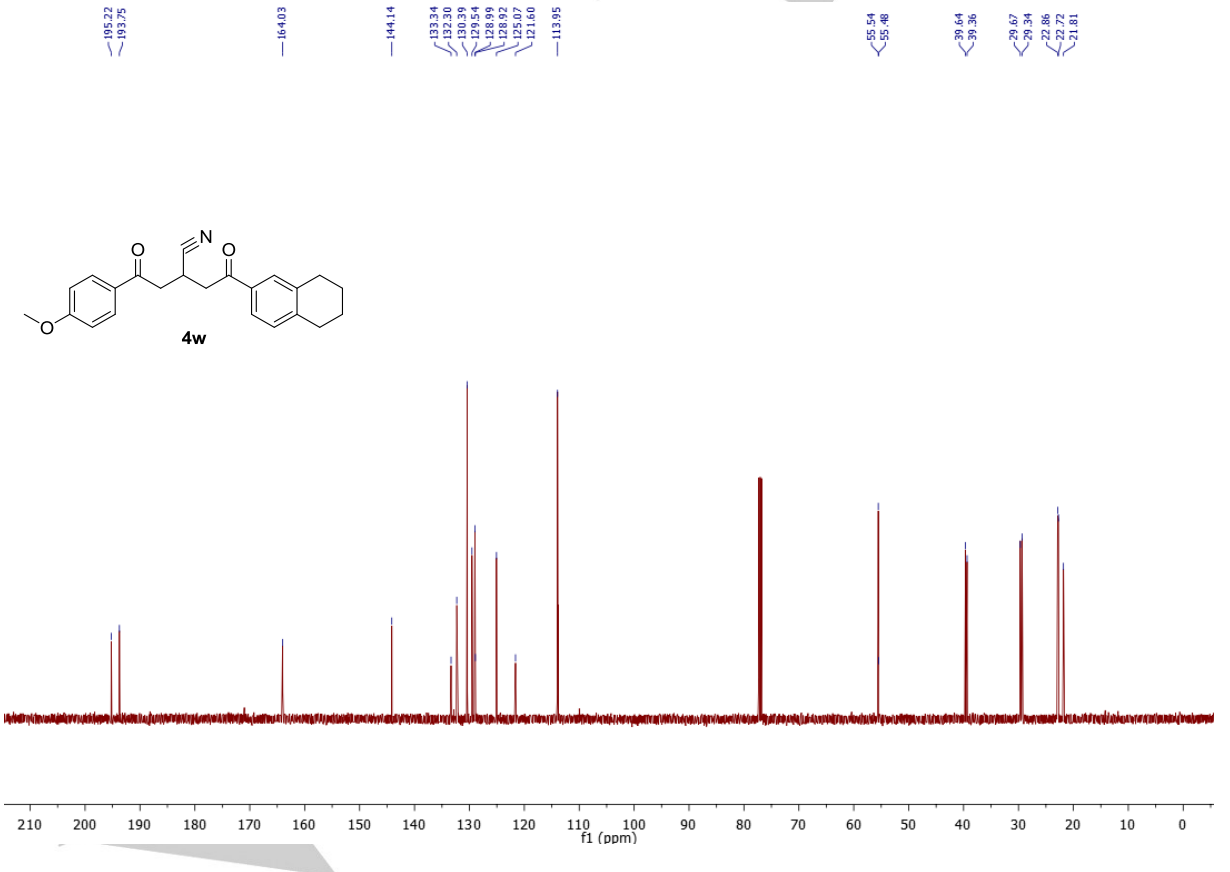

4u
f1 (ppm)

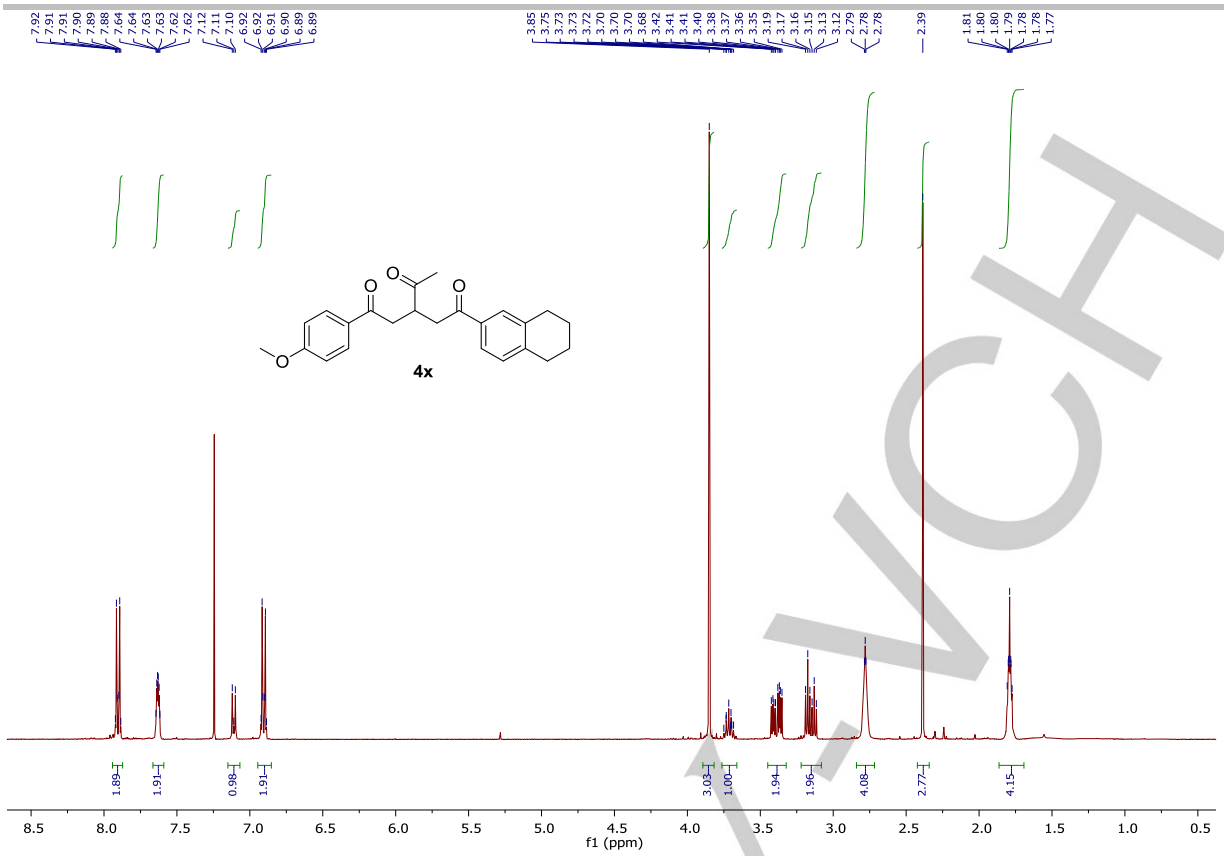

4u
f1 (ppm)

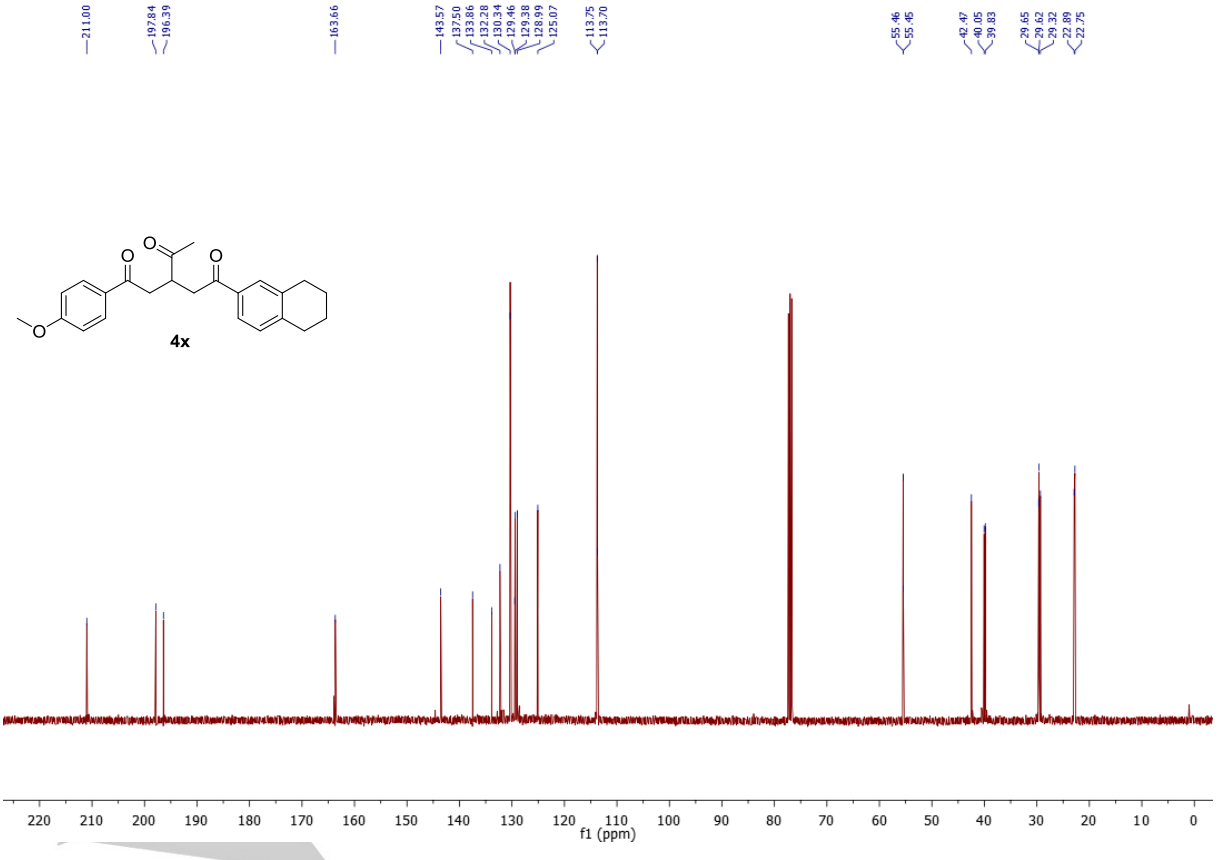


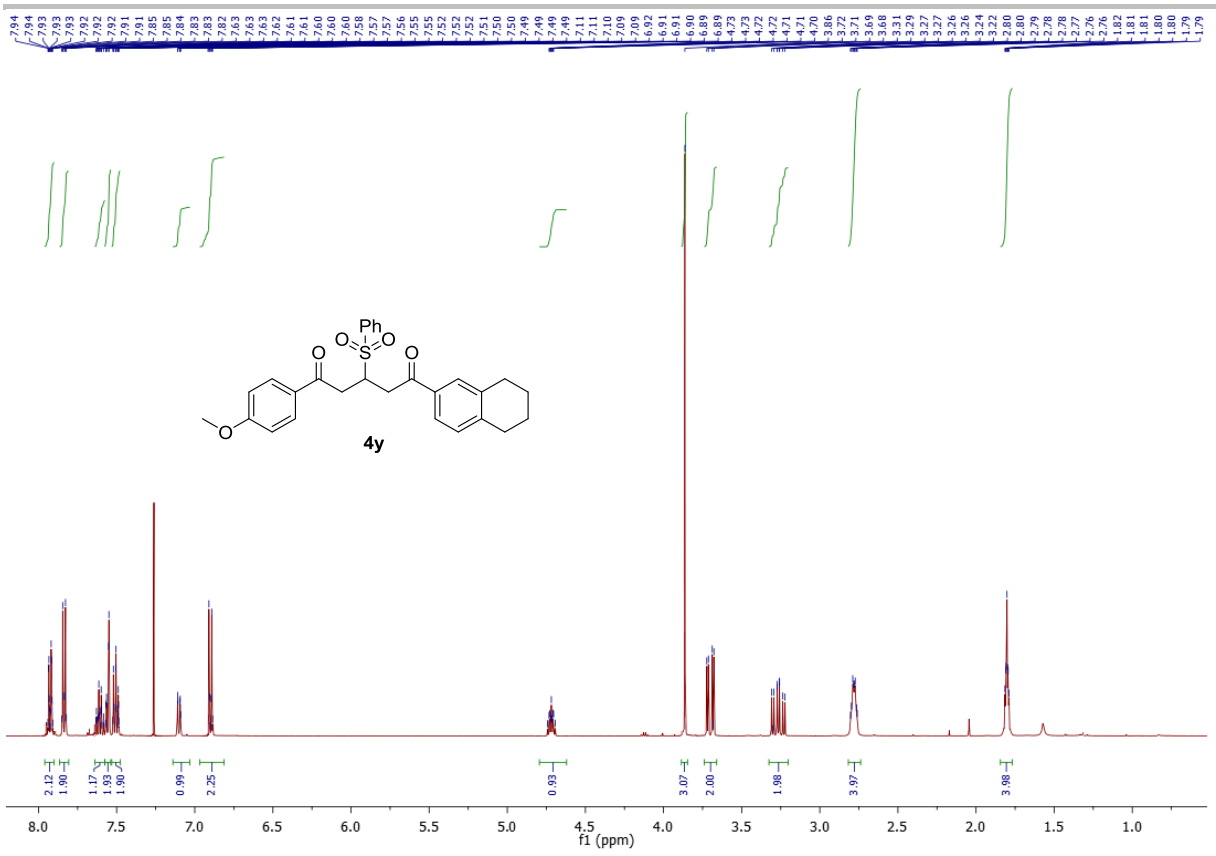


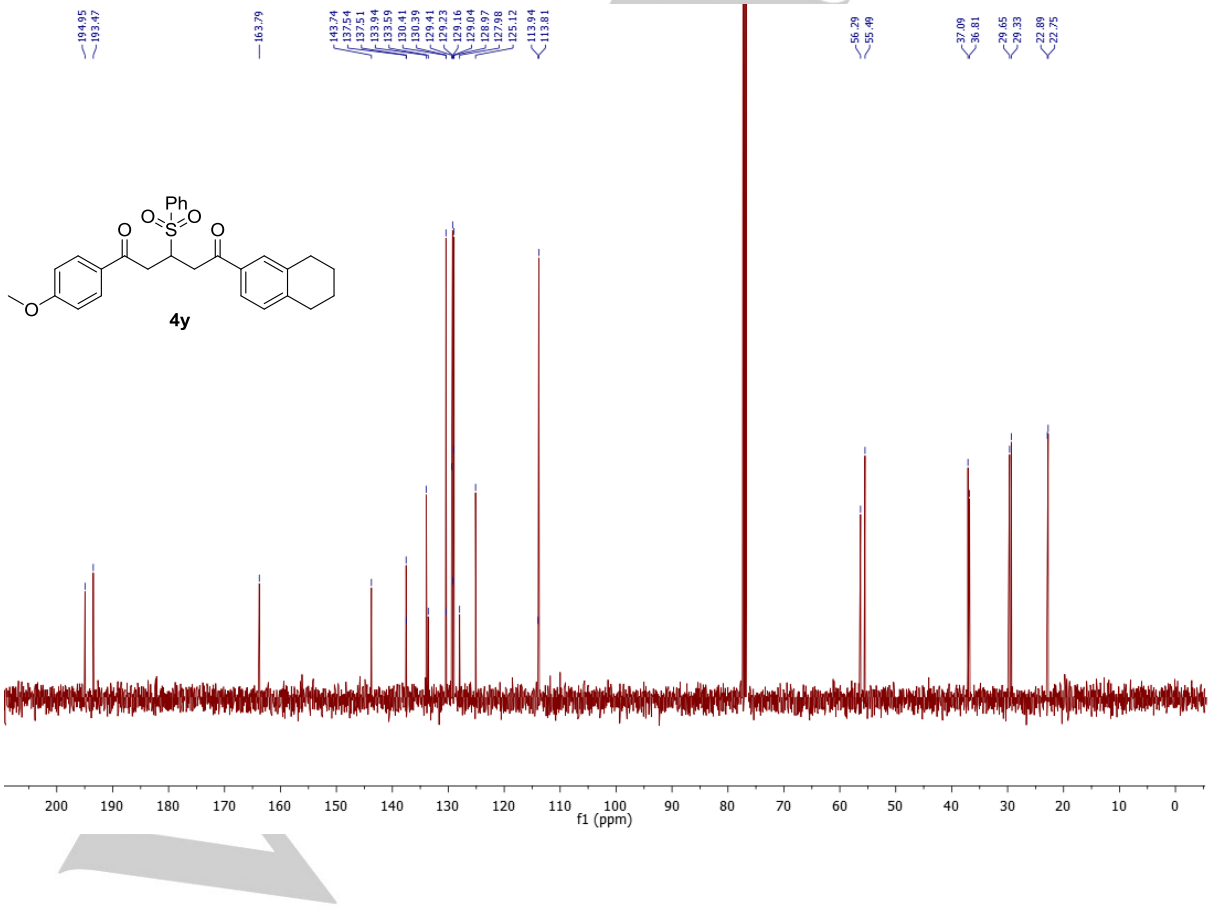


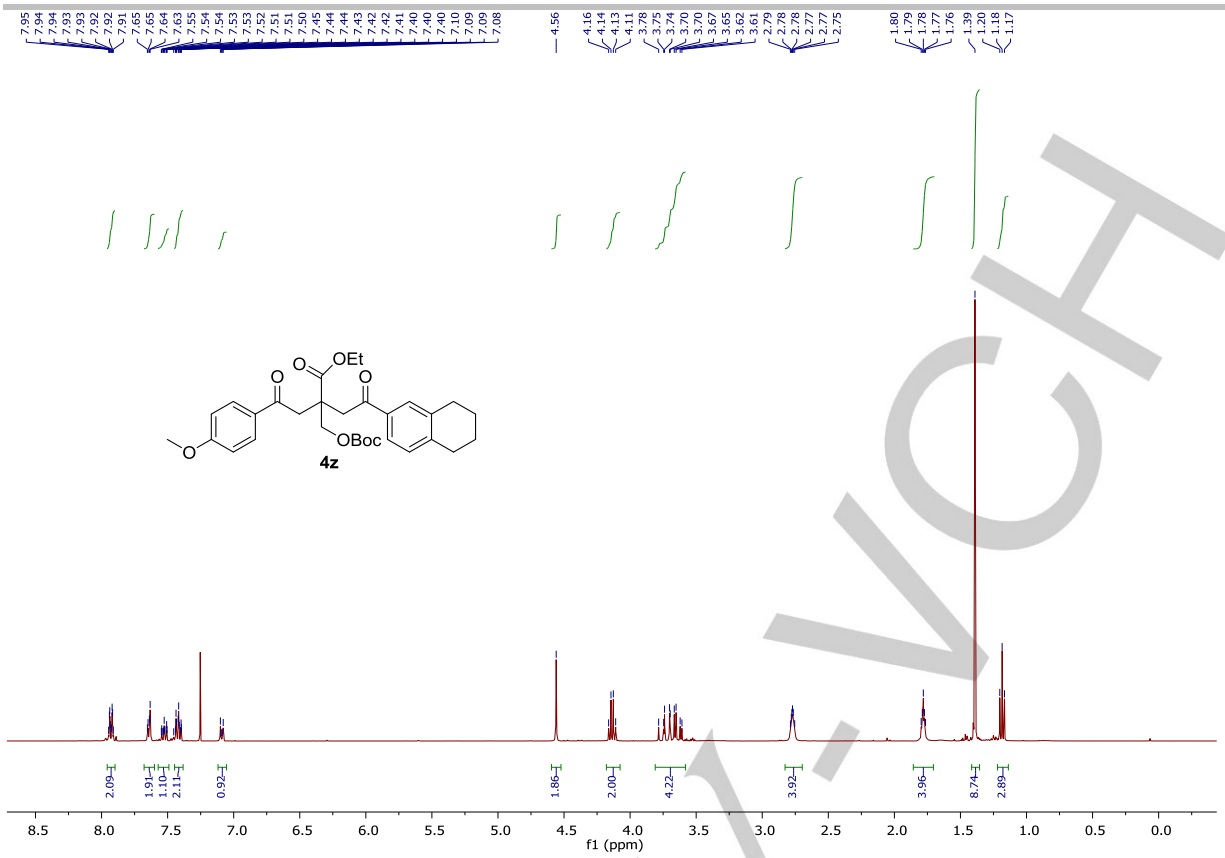


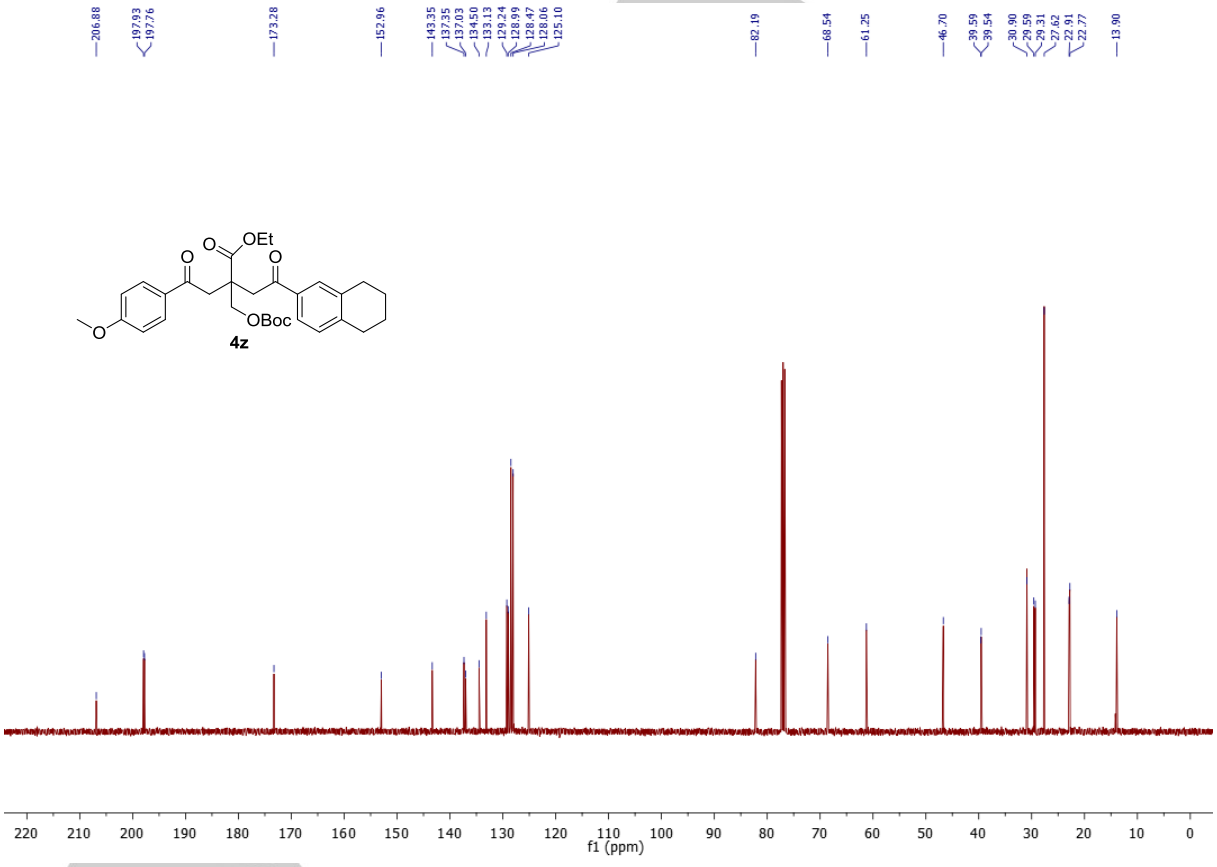


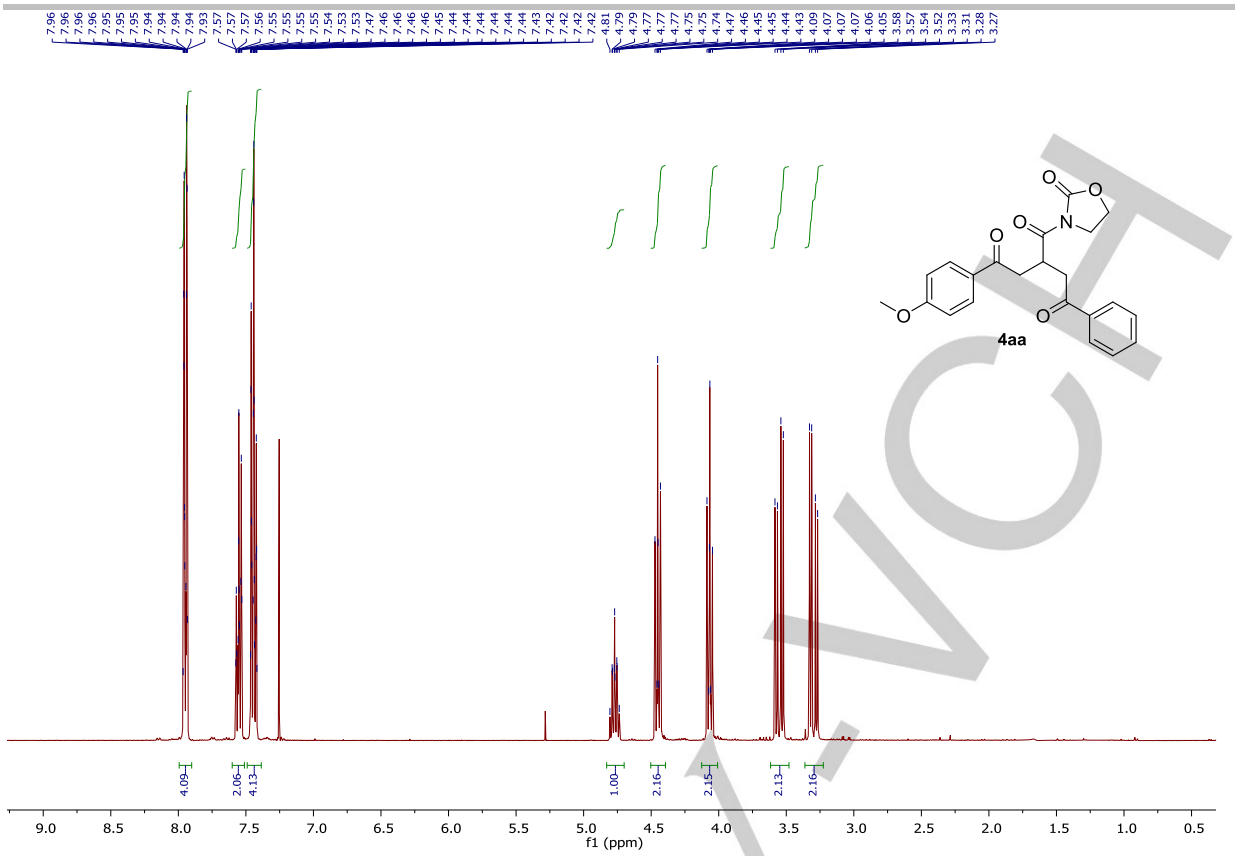


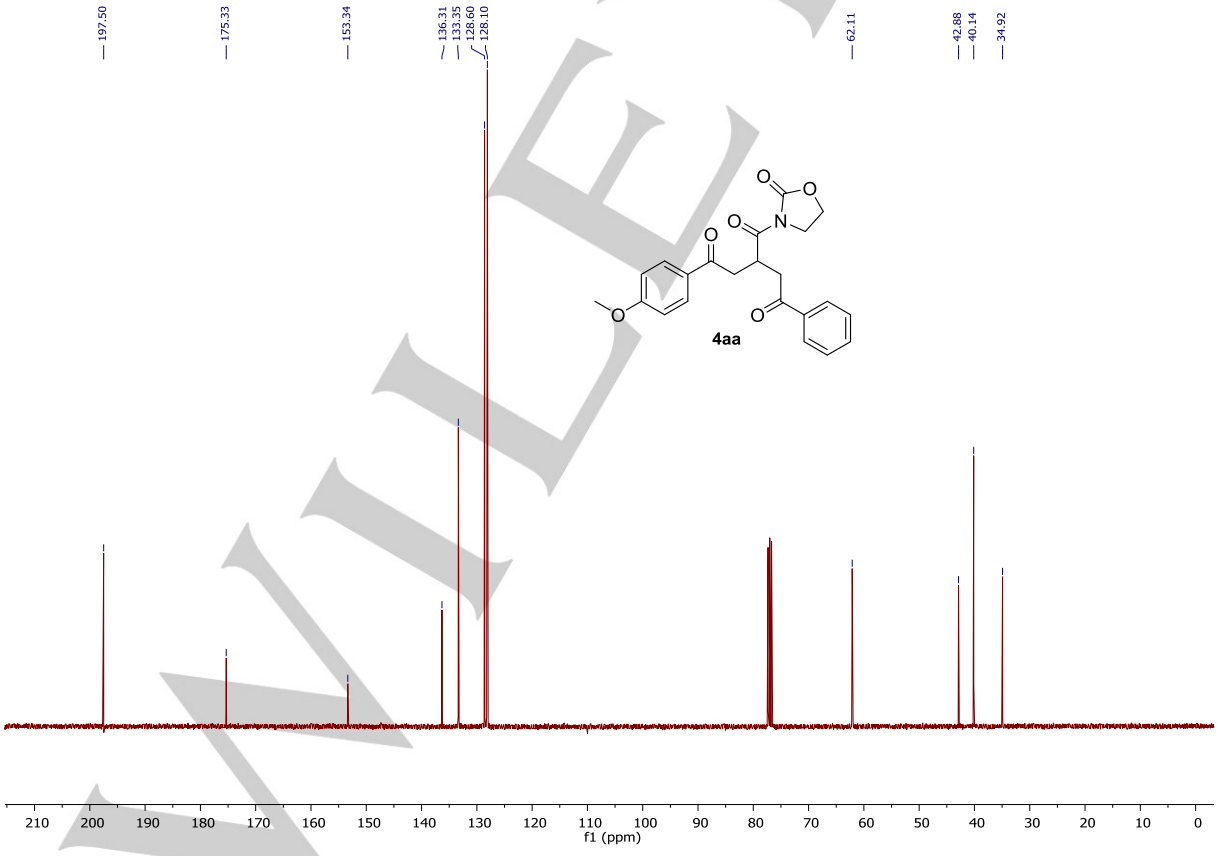

Ph
O
S
O
O
O
O
4y
2.12
1.90
1.17
1.93
1.90
0.99
2.25
0.93
3.07
2.00
1.98
3.97
3.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

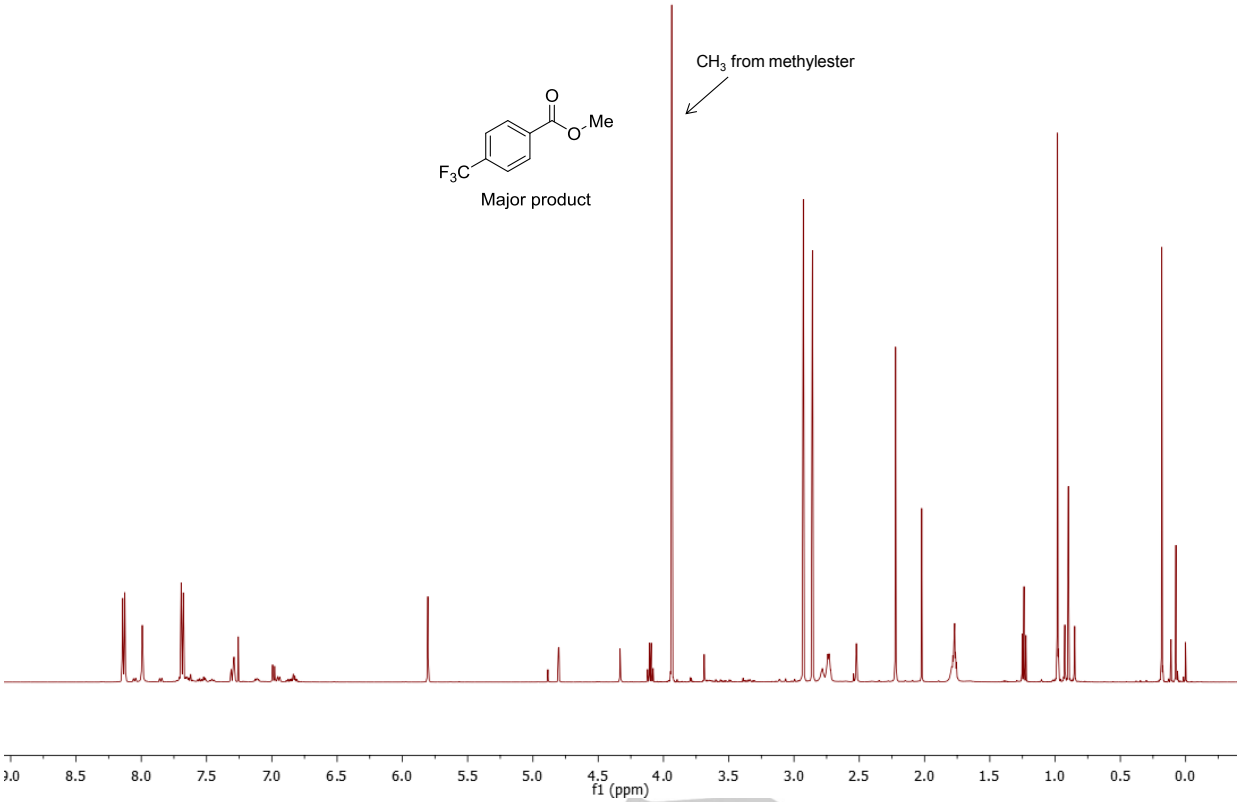

194.95
193.47
163.79
143.74
137.54
137.51
133.94
133.59
130.41
130.39
129.41
129.23
129.16
129.04
128.97
127.98
125.12
113.94
113.81
56.29
55.49
37.09
36.81
29.65
29.33
22.89
22.75
Ph
O
S
O
O
O
O
4y
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OEt
O
O
O
OBoc
O
4z
f1 (ppm)

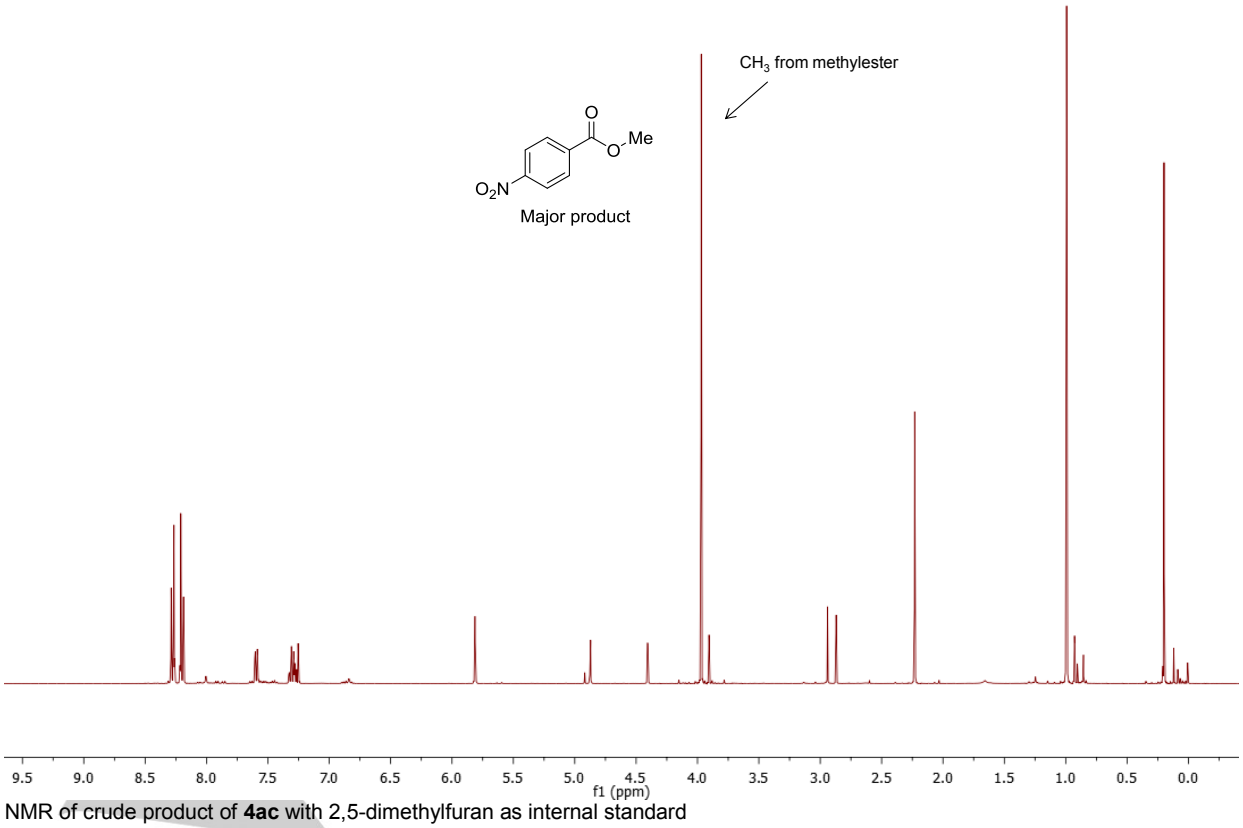

OEt
O
O
O
OBoc
O
4z
f1 (ppm)


4aa
4.09
2.06
4.13
1.00
2.16
2.15
2.13
2.16
f1 (ppm)

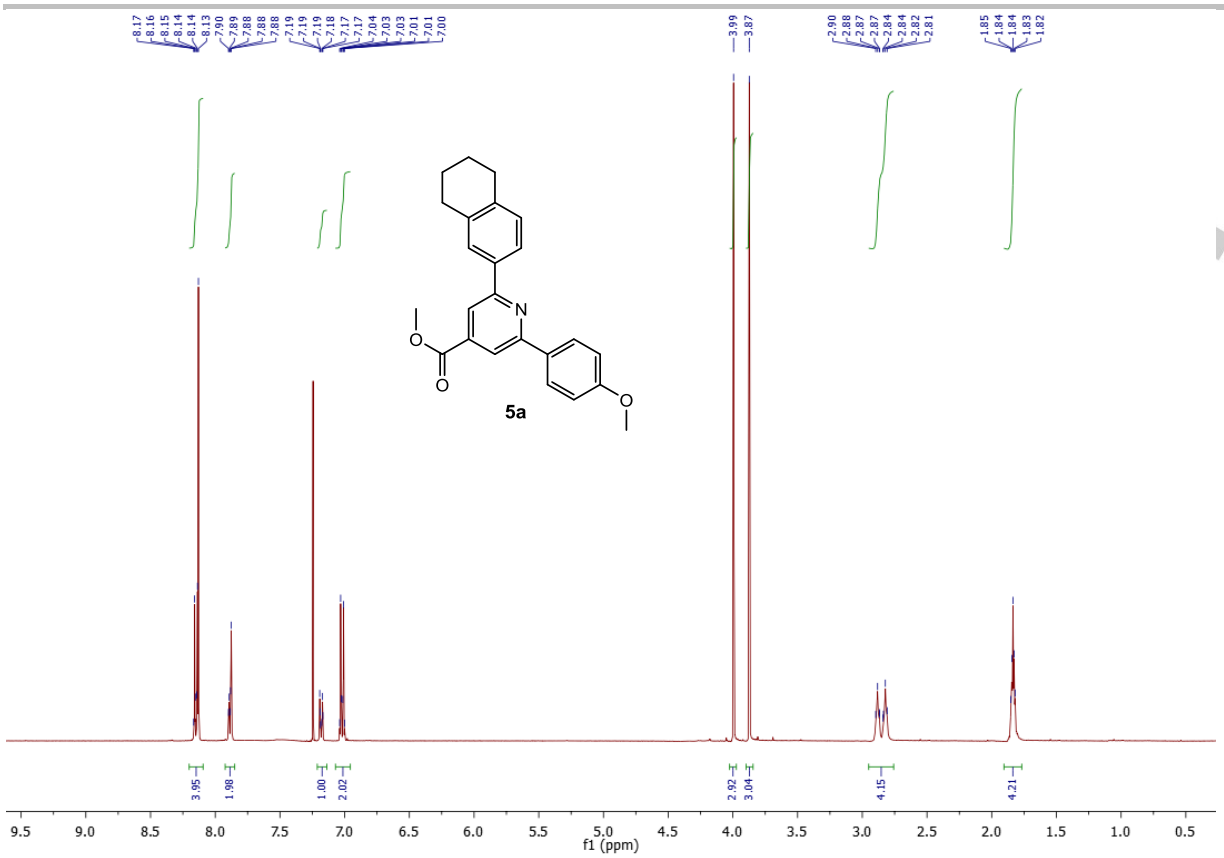

197.50
175.33
153.34
136.31
133.35
128.60
128.10
62.11
42.88
40.14
34.92
4aa
f1 (ppm)

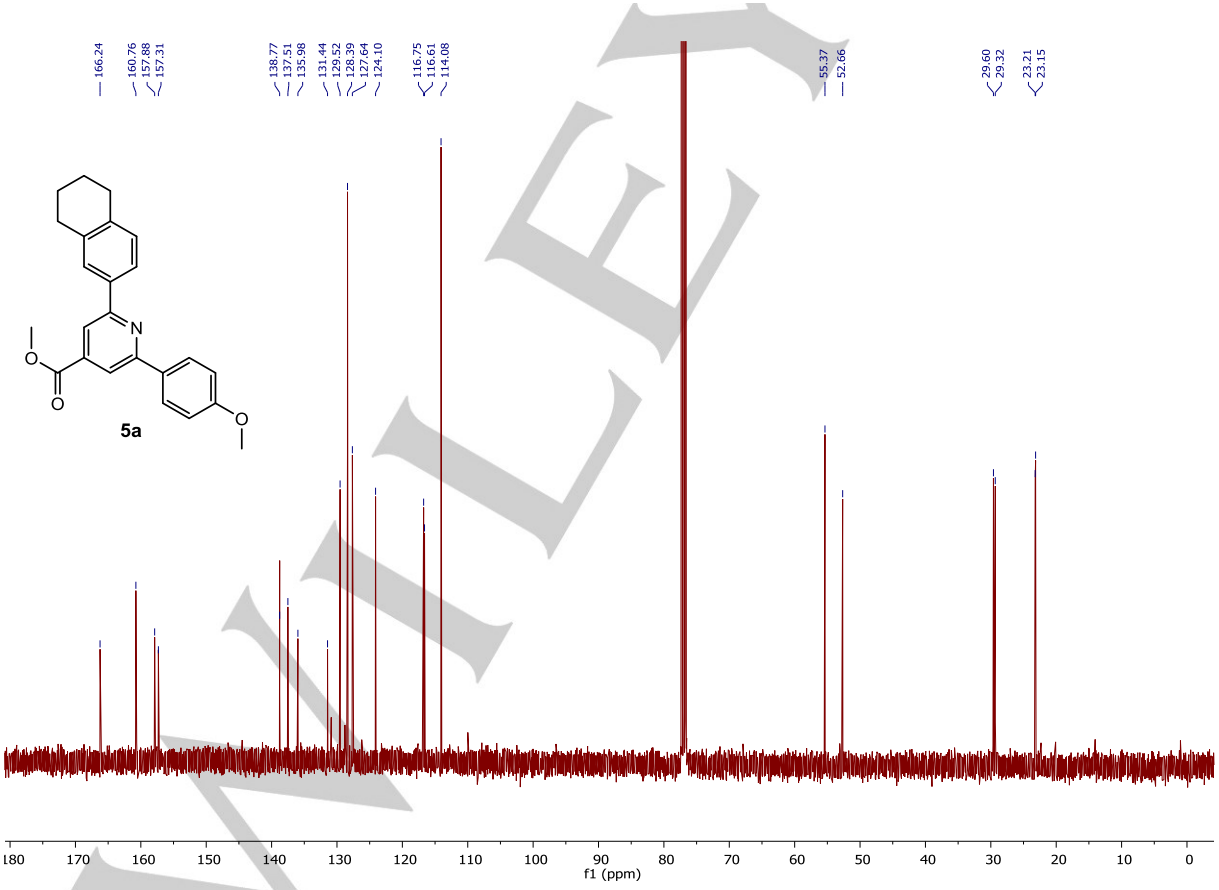


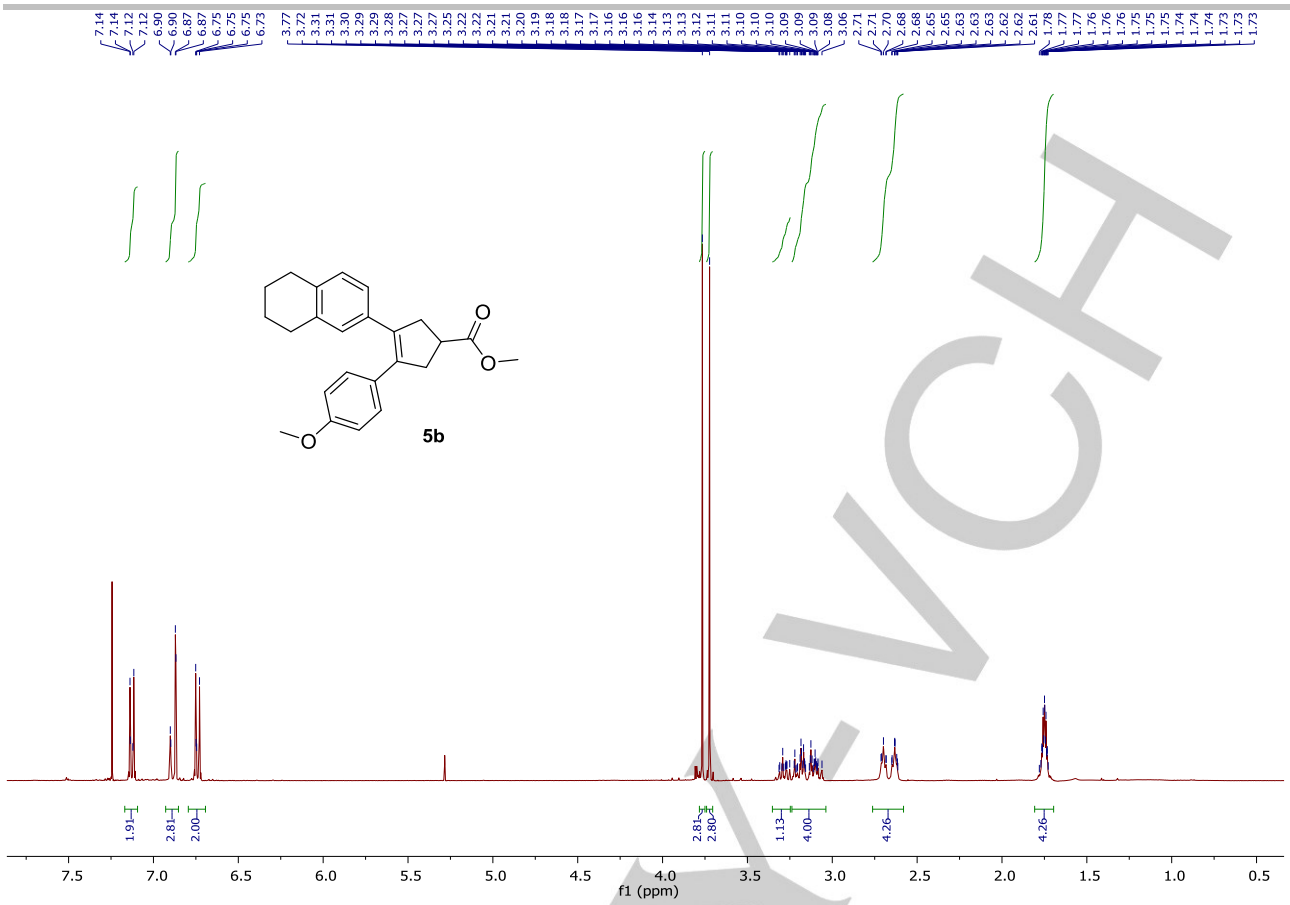
NMR of crude product of **4ab** with 2,5-dimethylfuran as internal standard

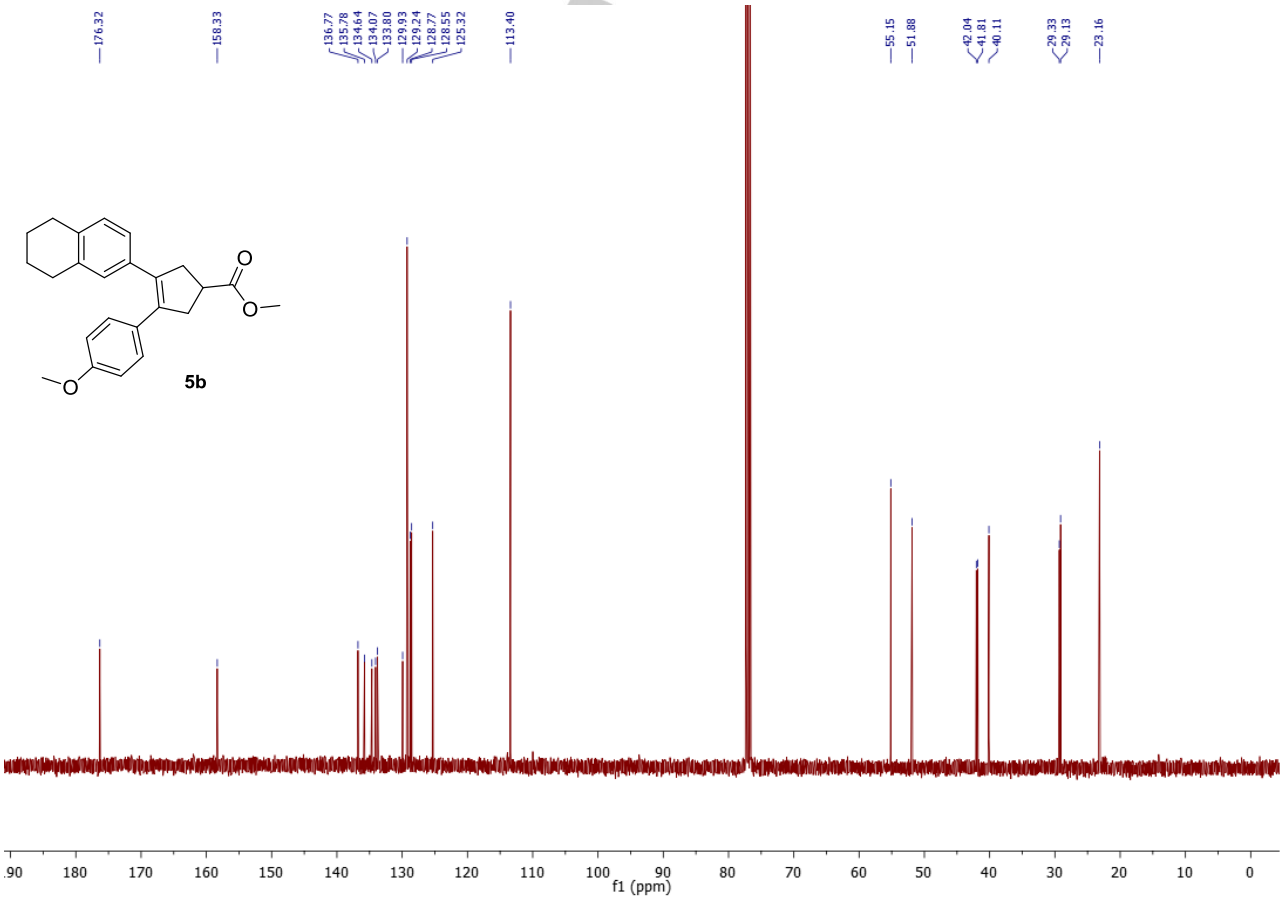


NMR of crude product of **4ac** with 2,5-dimethylfuran as internal standard


8.17
8.16
8.15
8.14
8.14
8.13
7.90
7.89
7.88
7.88
7.88
7.19
7.19
7.19
7.18
7.17
7.17
7.04
7.03
7.03
7.01
7.01
7.00
3.99
3.87
2.90
2.88
2.87
2.87
2.84
2.84
2.82
2.81
1.85
1.84
1.84
1.83
1.82
N
O
O
O
5a
3.95
1.98
1.00
2.02
2.92
3.04
4.15
4.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.24
160.76
157.88
157.31
138.77
137.51
135.98
131.44
129.52
128.39
127.64
124.10
116.75
116.61
114.08
55.37
52.66
29.60
29.32
23.21
23.15
N
O
O
O
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5b
f1 (ppm)


5b
f1 (ppm)