

NNN Manganese Complex Catalyzed α -Alkylation of Methyl ketones using Alcohols: An Experimental and Computational study

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Supporting Information

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1. Characterization of $[(\text{NN}^{\text{H}}\text{N})\text{Mn}(\text{CO})_3]^+\text{Br}^-$ (Mn-1):

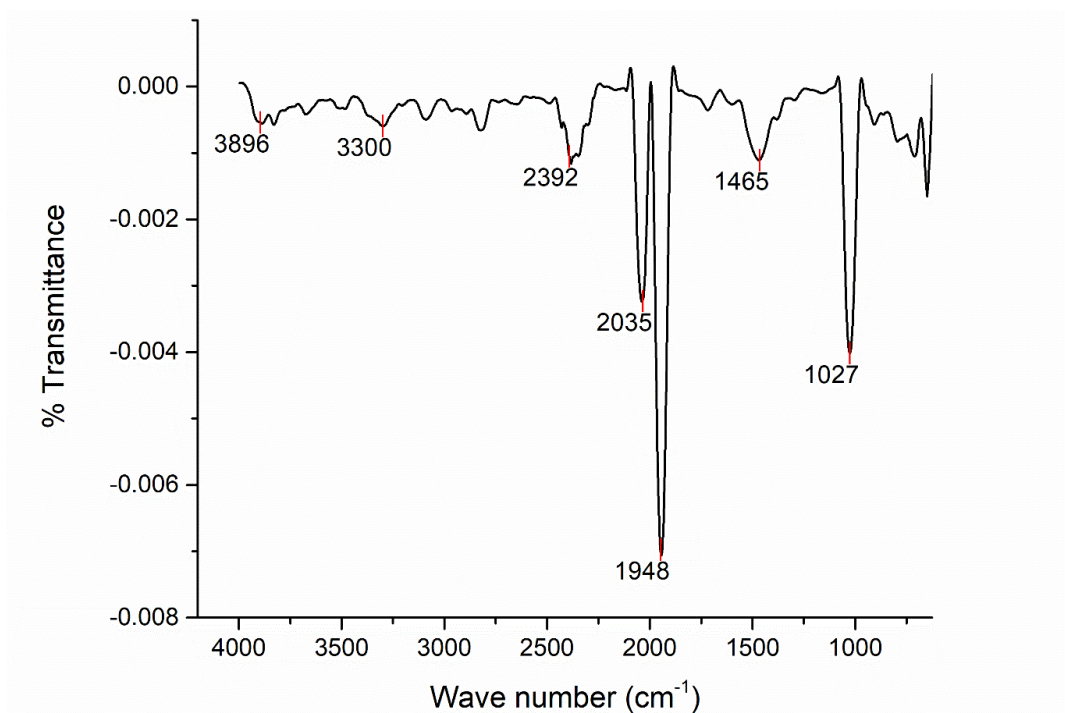


Fig. S1 FT-IR spectra of Mn-1.

2. X-Ray crystallographic studies

Single crystals of $\text{C}_{19}\text{H}_{14}\text{BrCl}_3\text{MnN}_3\text{O}_3$ $[(\text{NN}^{\text{H}}\text{NMn}(\text{CO})_3]^+\text{Br}^-$ were yellow in colour. A suitable crystal was selected and collected on Bruker D8 Venture Duo X-ray diffractometer equipped with a Microfocus X-ray source (operated at 50 W; 50 kV/1 mA) on a Bruker APEX-II CCD diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2,¹ the structure was solved with the SHELXT² structure solution program using Intrinsic Phasing and refined with the SHELXL³ refinement package using Least Squares minimisation. The structures were examined using the Adsym subroutine in PLATON to assure that no additional symmetries could be applied to the model. **CCDC number: 2295408** for $[(\text{NN}^{\text{H}}\text{NMn}(\text{CO})_3]\text{Br}$ contains the supplementary crystallographic data for this paper. The ORTEP drawing of $[(\text{NN}^{\text{H}}\text{NMn}(\text{CO})_3]\text{Br}$ at the 30% probability level.

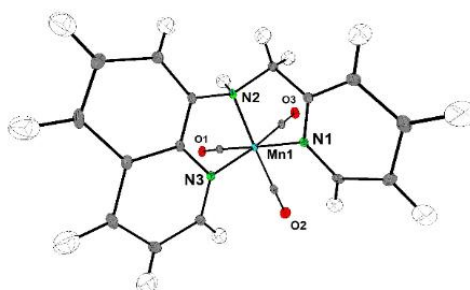


Fig. S2 Molecular structure of $[(\text{Mn}(\text{CO})_3(\text{NN}^{\text{H}}\text{N}))^+$ (Mn-1). Counter anion is omitted for clarity.

Crystal Data for $C_{19}H_{14}BrCl_3MnN_3O_3$ ($M = 573.53$ g/mol): triclinic, space group P-1 (no. 2), $a = 10.0855(9)$ Å, $b = 14.7980(11)$ Å, $c = 16.4672(13)$ Å, $\alpha = 101.388(2)^\circ$, $\beta = 106.123(2)^\circ$, $\gamma = 103.595(2)^\circ$, $V = 2202.1(3)$ Å³, $Z = 4$, $T = 296.15$ K, $\mu(\text{MoK}\alpha) = 2.804$ mm⁻¹, $D_{\text{calc}} = 1.730$ g/cm³, 64016 reflections measured ($4.32^\circ \leq 2\theta \leq 56.734^\circ$), 10957 unique ($R_{\text{int}} = 0.0754$, $R_{\text{sigma}} = 0.0551$) which were used in all calculations. The final R_1 was 0.0416 ($I > 2\sigma(I)$) and wR_2 was 0.0974 (all data).

Table S1 Crystal data and structure refinement for $[(\text{NN}^H\text{N})\text{Mn}(\text{CO})_3]^+\text{Br}^-$ (**Mn-1**)

Identification code	$[(\text{NN}^H\text{N})\text{Mn}(\text{CO})_3]^+\text{Br}^-$ (Mn-1) (2295408)
Empirical formula	$C_{19}H_{14}BrCl_3MnN_3O_3$
Formula weight	573.53
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
$a/\text{Å}$	10.0855(9)
$b/\text{Å}$	14.7980(11)
$c/\text{Å}$	16.4672(13)
$\alpha/^\circ$	101.388(2)
$\beta/^\circ$	106.123(2)
$\gamma/^\circ$	103.595(2)
Volume/Å ³	2202.1(3)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.730
μ/mm^{-1}	2.804
$F(000)$	1136.0
Crystal size/mm ³	$0.14 \times 0.12 \times 0.11$
Radiation	MoK α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	4.32 to 56.734
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 15$, $-21 \leq l \leq 21$
Reflections collected	64016
Independent reflections	10957 [$R_{\text{int}} = 0.0754$, $R_{\text{sigma}} = 0.0551$]
Data/restraints/parameters	10957/0/549
Goodness-of-fit on F^2	1.021
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0416$, $wR_2 = 0.0878$
Final R indexes [all data]	$R_1 = 0.0666$, $wR_2 = 0.0974$
Largest diff. peak/hole / $e \text{ Å}^{-3}$	0.92/-0.81

Table S2 Selected bond lengths and bond angles of $[(\text{NN}^H\text{N})\text{Mn}(\text{CO})_3]^+\text{Br}^-$ (**Mn-1**).

Bond Length [Å]			Bond Angle [deg.]	
Mn1-C1	C1	1.8123(32)	O2-C2-Mn1	179.211(278)
Mn1-C2	C2	1.8168(31)	C1-Mn1-C3	89.180(134)
Mn1-C3	C3	1.8146(29)	C1-Mn1-C2	89.773(138)
Mn1-N1	N1	2.0552(26)	C1-Mn1-N3	89.082(116)
Mn1-N2	N2	2.0675(28)	C1-Mn1-N1	173.933(118)

Mn1-N3	N3	2.0522(22)	C1-Mn1-N2	96.342(118)
N2-H2	H2	0.8786(427)	C3-Mn1-C2	89.670(137)
O1-C1	C1	1.1409(40)	C3-Mn1-N3	174.489(119)
O2-C2	C2	1.1413(38)	C3-Mn1-N1	95.260(119)
O3-C3	C3	1.1496(36)	C3-Mn1-N2	93.637(119)
			C2-Mn1-N2	173.081(125)
			N3-Mn1-N1	86.116(97)
			H2-N2-C8	141.221(2498)
			C10-N2-Mn1	110.947(177)

3. Characterisation data for the stoichiometric reaction:

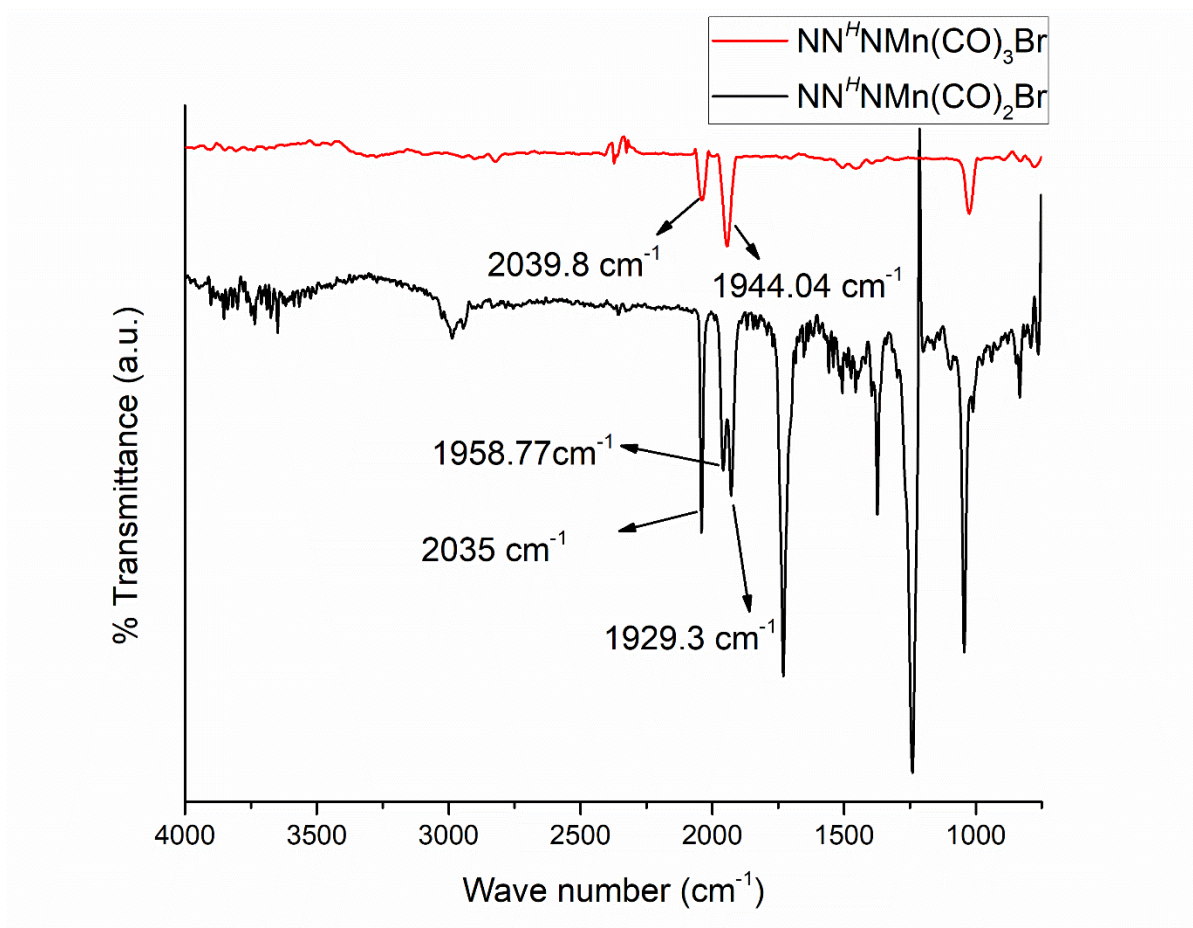


Fig. S3 IR spectra for the comparison of [(NN^HN)Mn(CO)₃]⁺Br⁻ (**Mn-1**) and (NN^HN)Mn(CO)₂Br.

¹H NMR:

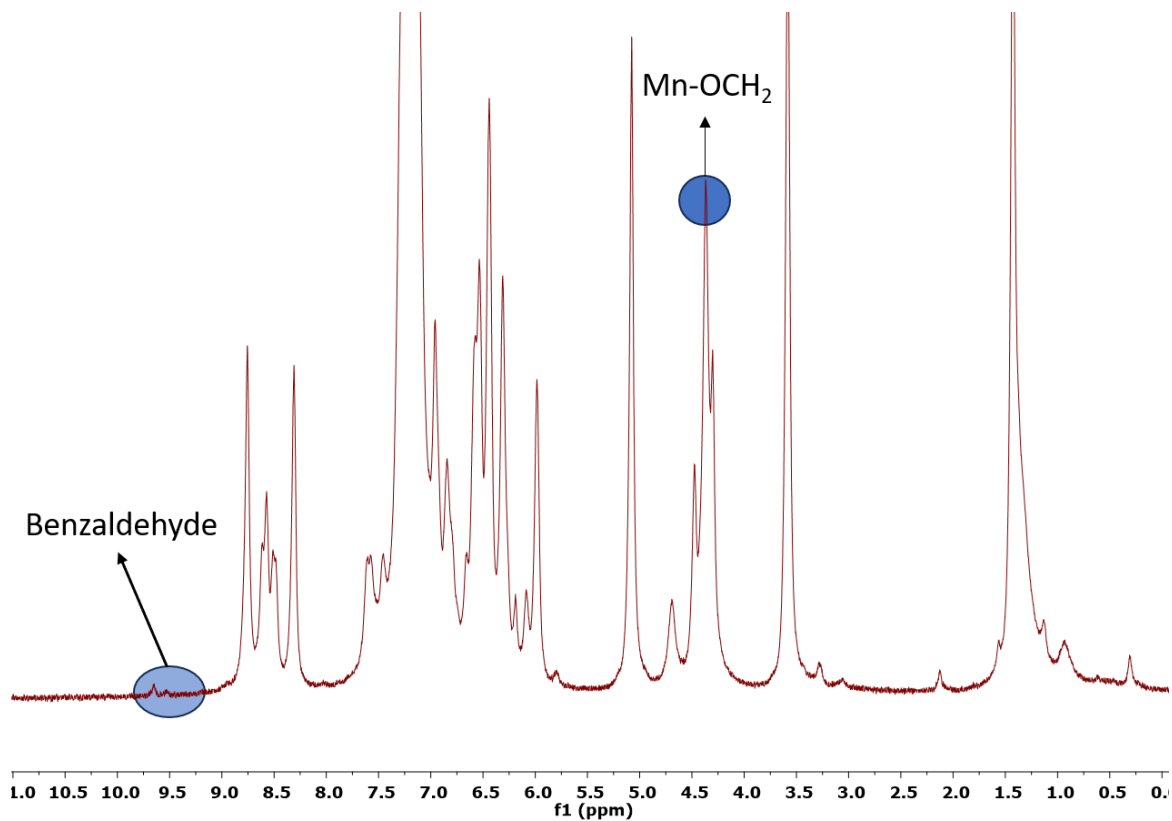
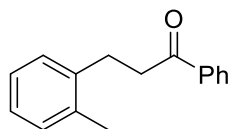


Fig. S4: ¹H NMR spectra of the reaction of **Mn-1** with benzyl alcohol and NaOH after 2 h at room temperature in tol-d₈.

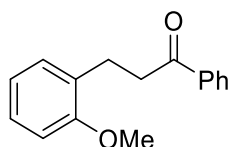
4. Analytical data of isolated products:

1-phenyl-3-(o-tolyl)propan-1-one⁶ (**3a**)



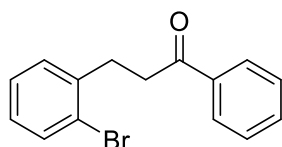
¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.99 (m, 2H), 7.60 (td, *J* = 7.2, 1.4 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.26 – 7.13 (m, 4H), 3.32 – 3.25 (m, 2H), 3.13 – 3.07 (m, 2H), 2.39 (d, *J* = 1.8 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 199.4, 139.4, 136.8, 136.0, 133.1, 130.3, 128.7, 128.6, 128.0, 126.3, 126.2, 39.1, 27.5, 19.3.

3-(2-methoxyphenyl)-1-phenylpropan-1-one⁴ (**3b**)



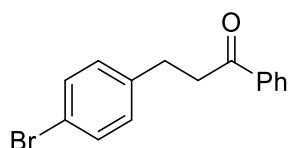
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.05 – 7.97 (m, 2H), 7.65 – 7.54 (m, 1H), 7.54 – 7.44 (m, 2H), 7.24 (ddq, $J = 7.4, 5.4, 1.7$ Hz, 2H), 6.98 – 6.85 (m, 2H), 3.86 (d, $J = 1.1$ Hz, 3H), 3.30 (td, $J = 7.6, 1.3$ Hz, 2H), 3.09 (ddd, $J = 9.1, 6.8, 1.9$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 200.0, 157.6, 137.0, 132.9, 130.2, 129.5, 128.5 (2C), 128.1 (2C), 127.5, 120.5, 110.2, 55.2, 38.9, 25.7.

3-(2-bromophenyl)-1-phenylpropan-1-one⁷ (3c)



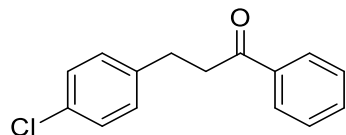
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.01 (dd, $J = 8.4, 1.5$ Hz, 2H), 7.63 – 7.55 (m, 2H), 7.48 (t, $J = 7.8$ Hz, 2H), 7.35 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.32 – 7.24 (m, 1H), 7.11 (td, $J = 7.6, 1.7$ Hz, 1H), 3.35 (dd, $J = 8.3, 6.4$ Hz, 2H), 3.21 (dd, $J = 8.7, 6.7$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 199.0, 140.5, 136.7, 132.9, 130.8, 128.6, 128.0, 127.6, 124.4, 38.6, 30.8.

3-(4-bromophenyl)-1-phenylpropan-1-one⁵ (3d)



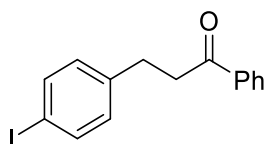
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 2H), 7.64 – 7.55 (m, 1H), 7.51 – 7.46 (m, 2H), 7.44 (dd, $J = 8.2, 1.6$ Hz, 2H), 7.19 – 7.13 (m, 2H), 3.36 – 3.27 (t, 2H), 3.06 (t, $J = 7.5$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 198.8, 140.2, 136.7, 133.2, 131.5 (2C), 130.3 (2C), 128.6 (2C), 128.0 (2C), 119.9, 40.0, 29.4.

3-(4-chlorophenyl)-1-phenylpropan-1-one⁸ (3e)



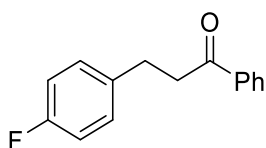
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.98 (dd, $J = 8.1, 1.4$ Hz, 2H), 7.63 – 7.55 (m, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H), 3.31 (t, $J = 7.5$ Hz, 2H), 3.07 (t, $J = 7.5$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 198.8, 139.7, 136.7, 133.2, 131.8, 129.8, 128.6, 128.6, 128.0, 40.1, 29.4.

3-(4-iodophenyl)-1-phenylpropan-1-one⁷ (3f)



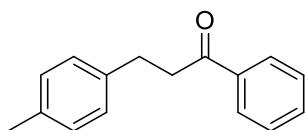
¹H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.93 (m, 2H), 7.63 (d, J = 7.9 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 3.30 (t, J = 7.6 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 198.8, 140.9 (2C), 137.5, 136.7, 133.2, 130.6 (2C), 128.6 (2C), 128.0 (2C), 91.2, 40.0, 29.5.

3-(4-fluorophenyl)-1-phenylpropan-1-one⁵ (3g)



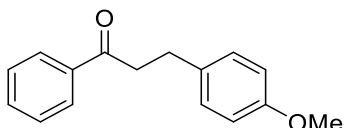
¹H NMR (500 MHz, Chloroform-*d*) δ 8.04 – 7.92 (m, 2H), 7.63 – 7.55 (m, 1H), 7.53 – 7.44 (m, 2H), 7.27 – 7.18 (m, 2H), 7.05 – 6.95 (m, 2H), 3.31 (dd, J = 8.1, 7.0 Hz, 2H), 3.07 (t, J = 7.6 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 199.0, 161.4 (d, $^1J_{CF}$ =244), 136.8, 133.1, 129.8, 128.6, 128.0, 115.1, 40.4, 29.2. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -117.24.

1-phenyl-3-(p-tolyl)propan-1-one⁵ (3h)



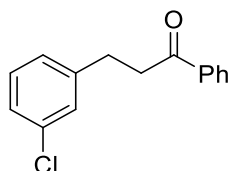
¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 (dd, J = 8.3, 1.4 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.50 (dd, J = 8.4, 7.0 Hz, 2H), 7.25 – 7.15 (m, 4H), 3.34 (dd, J = 8.5, 7.0 Hz, 2H), 3.10 (t, J = 7.7 Hz, 2H), 2.39 (s, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 199.3, 138.2, 136.9, 135.6, 133.0, 129.2, 128.6, 128.3, 128.1, 40.6, 29.7, 21.0.

3-(4-methoxyphenyl)-1-phenylpropan-1-one⁸ (3i)



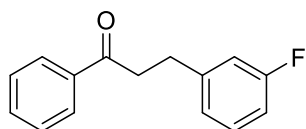
¹H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 2H), 7.56 (td, J = 7.2, 1.4 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.18 (d, J = 8.5 Hz, 2H), 6.89 – 6.81 (m, 2H), 3.79 (s, 3H), 3.28 (dd, J = 8.3, 7.0 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 199.5, 158.0, 136.9, 133.2, 130.3, 114.0, 55.3, 40.8, 29.3.

3-(3-chlorophenyl)-1-phenylpropan-1-one⁸ (3j)



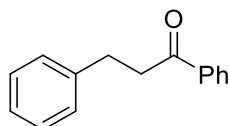
¹H NMR (500 MHz, Chloroform-*d*) δ 7.98 (dd, $J = 8.2, 1.4$ Hz, 2H), 7.66 – 7.54 (m, 1H), 7.49 (t, $J = 7.7$ Hz, 2H), 7.28 (dd, $J = 3.7, 1.9$ Hz, 1H), 7.26 – 7.19 (m, 2H), 7.16 (dt, $J = 7.3, 1.6$ Hz, 1H), 3.32 (t, $J = 7.6$ Hz, 2H), 3.08 (t, $J = 7.6$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 198.7, 143.3 (2C), 136.7, 134.2, 133.2, 129.7, 128.6, 128.5, 128.0, 126.7, 126.3, 40.0, 29.6.

3-(3-fluorophenyl)-1-phenylpropan-1-one⁷ (3k)



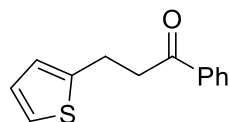
¹H NMR (500 MHz, Chloroform-*d*) δ 7.96 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.62 – 7.52 (m, 1H), 7.46 (dd, $J = 8.4, 7.2$ Hz, 2H), 7.25 (d, $J = 6.5$ Hz, 1H), 7.03 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.96 (dt, $J = 9.9, 2.2$ Hz, 1H), 6.93 – 6.84 (m, 1H), 3.31 (dd, $J = 8.3, 6.9$ Hz, 2H), 3.08 (t, $J = 7.6$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 198.9, 162.9 (d, $^1J_{CF} = 245$ Hz), 143.9, 136.8, 133.3, 128.7, 128.1, 124.2, 115.4, 113.1, 40.1, 29.8. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -113.43.

1,3-diphenylpropan-1-one⁴ (3l)



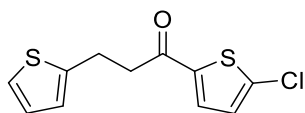
¹H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, $J = 7.0$ Hz, 1H), 7.64 – 7.54 (m, 1H), 7.48 (dd, $J = 8.4, 7.1$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.27 (m, 3H), 7.27 – 7.21 (m, 1H), 3.42 – 3.27 (m, 2H), 3.10 (dd, $J = 8.5, 7.0$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 199.2, 141.3, 136.8, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.

1-phenyl-3-(thiophen-2-yl)propan-1-one⁴ (3m)



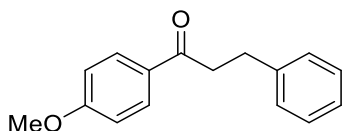
¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 7.95 (d, 2H), 7.65 – 7.55 (m, 1H), 7.49 (dd, $J = 8.4, 7.1$ Hz, 2H), 7.16 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.95 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.92 – 6.86 (m, 1H), 3.40 (t, $J = 7.9 - 6.5, 1.6$ Hz, 2H), 3.36 – 3.30 (t, 1.6 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 198.6, 143.9, 136.7, 133.1, 128.6, 128.0, 126.8, 124.7, 123.4, 40.5, 24.2.

1-(5-chlorothiophen-2-yl)-3-(thiophen-2-yl)propan-1-one (3q)



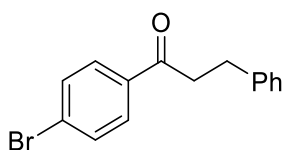
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.50 (d, $J = 4.1$ Hz, 1H), 7.15 (dd, $J = 5.2, 1.2$ Hz, 1H), 6.97 (d, $J = 4.1$ Hz, 1H), 6.94 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.88 – 6.86 (m, 1H), 3.30 (ddt, $J = 7.7, 6.5, 1.1$ Hz, 2H), 3.23 (ddd, $J = 8.3, 6.6, 1.5$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 190.6, 143.2, 142.6, 139.7, 131.4, 127.6, 126.9, 124.8, 123.5, 40.3, 24.3. HRMS: calculated: 255.9783; found: 255.9802.

1-(4-methoxyphenyl)-3-phenylpropan-1-one⁵ (3s)



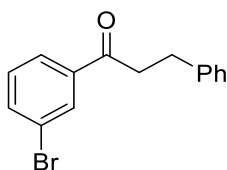
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.94 (d, $J = 9.0$ Hz, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.24 (m, 3H), 7.23 – 7.18 (m, 1H), 6.97 – 6.87 (m, 2H), 3.86 (s, 3H), 3.25 (dd, $J = 8.8, 7.0$ Hz, 2H), 3.06 (t, $J = 7.8$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 198.2, 163.8, 141.8, 130.6, 130.3, 128.8, 126.5, 114.0, 55.8, 40.4, 30.6.

1-(4-bromophenyl)-3-phenylpropan-1-one⁸ (3t)



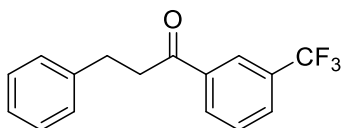
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 2H), 7.64 – 7.59 (m, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.31 – 7.20 (m, 3H), 3.34 – 3.25 (m, 2H), 3.09 (t, $J = 7.6$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 198.1, 141.0, 135.5, 131.9, 130.8, 129.6, 128.5, 128.2, 126.2, 40.4, 30.0.

1-(3-bromophenyl)-3-phenylpropan-1-one⁹ (3u)



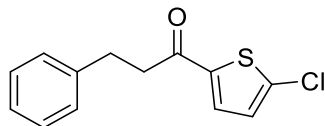
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.08 (d, $J = 2.0$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 1H), 7.36 – 7.28 (m, 3H), 7.27 – 7.19 (m, 3H), 3.28 (t, $J = 7.6$ Hz, 2H), 3.07 (t, $J = 7.6$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 197.6, 140.8, 138.4, 135.7, 131.0, 130.0, 128.4, 128.2, 126.4, 126.1, 122.8, 40.4, 29.8.

3-phenyl-1-(3-(trifluoromethyl)phenyl)propan-1-one⁵ (3v)



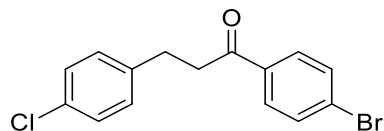
¹H NMR (500 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.16 (d, $J = 7.8$ Hz, 1H), 7.89 – 7.81 (m, 1H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.30 (d, $J = 1.6$ Hz, 1H), 7.28 (d, $J = 1.4$ Hz, 1H), 7.27 – 7.23 (m, 1H), 3.36 (dd, $J = 8.3, 7.0$ Hz, 2H), 3.12 (t, $J = 7.6$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 197.8, 140.9, 137.3, 129.4, 128.6, 128.4, 128.1, 126.3, 124.9, 122.6, 40.6, 29.9. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -62.79.

1-(5-chlorothiophen-2-yl)-3-phenylpropan-1-one⁵ (3w)



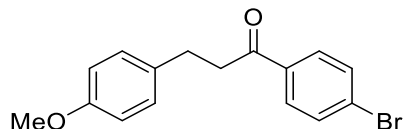
¹H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, $J = 4.1$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.26 (td, $J = 7.3, 5.7$ Hz, 3H), 6.96 (d, $J = 4.0$ Hz, 1H), 3.18 (dd, $J = 8.2, 6.5$ Hz, 2H), 3.11 – 3.04 (m, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 191.3, 142.7, 140.7, 139.5, 131.3, 128.6, 128.4, 127.6, 126.3, 40.3, 30.3.

1-(4-bromophenyl)-3-(4-chlorophenyl)propan-1-one⁸ (3x)



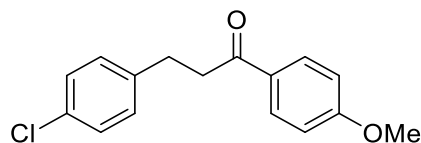
¹H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, $J = 8.5$ Hz, 2H), 7.62 (d, $J = 8.6$ Hz, 2H), 7.32 – 7.25 (m, 2H), 7.19 (d, $J = 8.5$ Hz, 2H), 3.26 (t, $J = 7.5$ Hz, 2H), 3.06 (t, $J = 7.5$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 197.8, 139.4, 135.4, 131.9, 129.8, 129.5, 128.6, 128.3, 40.1, 29.2.

1-(4-bromophenyl)-3-(4-methoxyphenyl)propan-1-one⁸ (3y)



¹H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.6$ Hz, 2H), 6.92 – 6.81 (m, 2H), 3.81 (s, 3H), 3.25 (dd, $J = 8.2, 6.9$ Hz, 2H), 3.02 (t, $J = 7.6$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 198.3, 158.0, 135.6, 133.0, 131.9, 131.4, 129.8, 129.5, 129.3, 128.2, 113.9, 55.2, 40.6, 29.2.

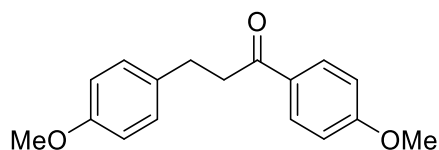
3-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one⁸ (3z)



¹H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, $J = 8.9$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H), 3.24 (dd, $J = 8.2, 6.9$ Hz, 2H), 3.05

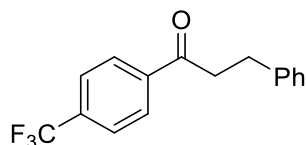
(t, $J = 7.6$ Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 197.4, 163.5, 139.9, 131.8, 130.3, 129.8, 128.5, 113.7, 55.4, 39.7, 29.5.

1,3-bis(4-methoxyphenyl)propan-1-one⁸ (3aa)



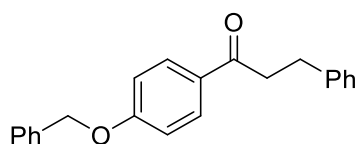
^1H NMR (500 MHz, Chloroform- d) δ 7.96 (d, $J = 8.9$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 3.24 (dd, $J = 8.5, 6.9$ Hz, 2H), 3.02 (dd, $J = 8.5, 6.9$ Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 198.0, 163.4, 157.9, 133.5, 130.6, 130.3, 130.0, 129.3, 113.8, 55.4, 55.2, 40.3, 29.5.

3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one⁵ (3ab)



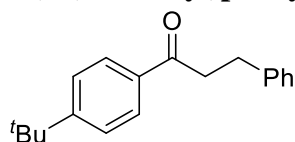
^1H NMR (500 MHz, Chloroform- d) δ 8.04 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 3.31 (dd, $J = 8.0, 1.7$ Hz, 2H), 3.09 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 198.2, 146.1, 140.9 (2C), 139.5, 134.5, 129.60, 128.6, 128.41, 126.32, 125.69, 40.75, 29.94. ^{19}F NMR (471 MHz, Chloroform- d) δ -63.11.

1-(4-(benzyloxy)phenyl)-3-phenylpropan-1-one⁸ (3ac)



^1H NMR (500 MHz, Chloroform- d) δ 7.97 (d, $J = 8.9$ Hz, 2H), 7.48 – 7.40 (m, 4H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.29 (s, 3H), 7.25 – 7.18 (m, 1H), 7.03 (d, $J = 8.8$ Hz, 2H), 5.16 (s, 2H), 3.28 (dd, $J = 8.6, 6.9$ Hz, 2H), 3.14 – 3.04 (m, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 197.8, 162.6, 141.4, 136.1, 130.3, 128.7, 128.5, 128.4, 128.2, 127.4, 126.1, 114.6, 70.1, 40.1, 30.3.

1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-one⁸ (3ag)



^1H NMR (500 MHz, Chloroform- d) δ 8.03 – 7.99 (m, 1H), 7.95 – 7.91 (m, 3H), 7.50 (dd, $J = 8.6, 6.7$ Hz, 3H), 7.32 (d, $J = 7.3$ Hz, 2H), 3.31 (dd, $J = 8.5, 7.0$ Hz, 2H), 3.10 (dd, $J = 8.6, 6.9$ Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, Chloroform- d) δ 198.9, 156.8, 144.4, 141.45, 134.3, 130.4, 128.9, 128.5, 128.3, 128.0, 126.1, 40.3, 31.1, 30.2.

Computational Studies:

The Electronic structure calculations were performed using M06-L/BS1 level of theory where BS1 includes double zeta basis set, SDD¹² with effective core potential¹¹ for Mn and 6-31G(d,p) basis sets for all other atoms. Calculations were done using CPCM model with toluene solvent (Refractive index=1.497 and the dielectric constant=2.4) and the Gibbs free energy were calculated at 298.15K and 1 atm using ORCA version 5.0.3.¹⁰ The stationary states were characterized by vibrational modes analysis and the transition states were confirmed by the intrinsic reaction coordinate (IRC), which is the minimum energy pathway that leads to forward and backward minima. Fig. 2. represents the potential energy diagram where Gibbs free energies are relative to the reactants and H₂ energy added wherever necessary. The computed electronic energy, final Gibbs free energy and frequencies along with the coordinates of the identified stationary states are provided below. The cartesian coordinates are given in Angstrom units and the energies provided are in hartree.

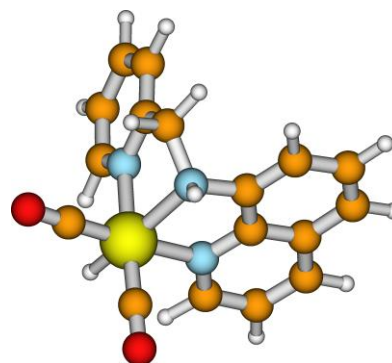
Cartesian coordinates of the stationary states:

1. Mn-1a

Final Gibbs free energy = -1073.86461842 Eh

Total Energy = -1074.09948332 Eh

C	-3.551667	-0.095857	1.122032
C	-2.791350	-0.798919	0.166814
C	-1.419258	-0.863802	0.278055
C	-0.764964	-0.224244	1.355101
C	-1.530929	0.479773	2.328045
C	-2.935954	0.531804	2.181622
N	0.599136	-0.325339	1.428432
C	1.216452	0.254738	2.450823
C	0.538164	0.964029	3.457699
C	-0.829977	1.083443	3.398463
N	-0.577325	-1.561311	-0.672455
C	-0.650251	-0.972099	-2.030833
C	0.131259	0.304566	-2.054155
C	-0.210777	1.392587	-2.848708
C	0.599973	2.522355	-2.831418
C	1.723320	2.527920	-2.009238
C	1.993685	1.408944	-1.235845



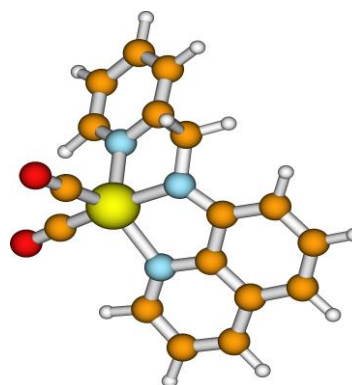
N	1.219585	0.310418	-1.255837
Mn	1.512343	-1.403769	-0.087582
C	2.215103	-2.290466	-1.415005
O	2.671503	-2.894823	-2.323373
C	1.727722	-2.788505	0.948314
O	1.888386	-3.717820	1.660786
H	-4.631280	-0.055946	1.018907
H	-3.289016	-1.299083	-0.660152
H	-3.518591	1.070538	2.923740
H	2.296358	0.142642	2.463662
H	1.106713	1.412562	4.264803
H	-1.380921	1.626140	4.161463
H	-0.871544	-2.531547	-0.730544
H	-1.683720	-0.799438	-2.359355
H	-0.197506	-1.697399	-2.716748
H	-1.102185	1.350817	-3.466820
H	0.354132	3.384965	-3.442560
H	2.381376	3.388471	-1.962985
H	2.853791	1.358739	-0.575208
H	2.939158	-0.802978	0.372838

2. Mn-1b

Final Gibbs free energy = -1072.70300127 Eh

Total Energy = -1072.91640701 Eh

C	-3.072803	1.964798	1.362851
C	-2.624956	0.928698	0.526319
C	-1.337602	0.396030	0.672050
C	-0.508855	0.970891	1.696378
C	-0.974340	2.012191	2.542737
C	-2.288418	2.504841	2.363540
N	0.762848	0.481163	1.767084
C	1.602529	0.988065	2.670690
C	1.213772	1.982619	3.577135
C	-0.065251	2.493799	3.509470
N	-0.747585	-0.615513	-0.005406
C	-1.227587	-1.067093	-1.288879
C	-0.072354	-1.045693	-2.248286
C	-0.210163	-1.062215	-3.628878
C	0.923002	-1.059962	-4.434683
C	2.173998	-1.031178	-3.825521
C	2.247368	-1.010146	-2.443698
N	1.152092	-1.042559	-1.654040
Mn	1.130558	-1.033276	0.343380
C	2.868907	-1.097614	0.619261
O	4.030930	-1.104618	0.818273
C	1.027787	-2.748417	0.504461
O	0.910011	-3.915035	0.622881

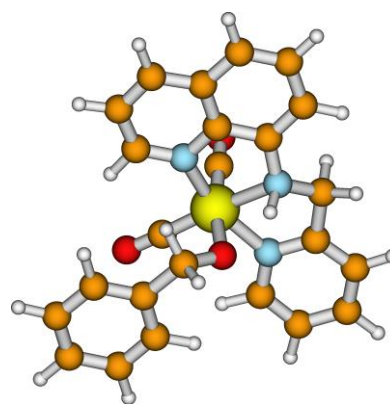


H	-4.081118	2.343950	1.217608
H	-3.298429	0.525362	-0.224054
H	-2.655250	3.299648	3.005205
H	2.610384	0.582865	2.674240
H	1.928345	2.351525	4.304403
H	-0.384038	3.278611	4.191478
H	-1.595214	-2.106229	-1.231405
H	-2.067294	-0.474274	-1.674620
H	-1.206391	-1.077354	-4.060067
H	0.831598	-1.073651	-5.516028
H	3.086692	-1.017247	-4.410160
H	3.199511	-0.991387	-1.923957

3. Mn-1c

Final Gibbs free energy = -1419.27328934 Eh
 Total Energy = -1419.69537429 Eh

C	-0.870197	3.546037	2.050974
C	-0.928727	3.226973	0.678308
C	-0.142192	2.218780	0.168397
C	0.719215	1.486622	1.021508
C	0.829313	1.851947	2.392516
C	0.003035	2.890142	2.886432
N	1.422218	0.433245	0.488300
C	2.270003	-0.217989	1.280153
C	2.480265	0.118020	2.624446
C	1.751764	1.138140	3.190008
N	-0.076181	1.884583	-1.236110
C	-1.363063	1.810590	-1.959630
C	-1.236769	0.894297	-3.143669
C	-2.080928	1.003045	-4.242851
C	-1.969849	0.091929	-5.287273
C	-0.997334	-0.899281	-5.205117
C	-0.174969	-0.936590	-4.089695
N	-0.284187	-0.065899	-3.071179
Mn	0.822307	-0.047654	-1.361165
O	-0.968317	-0.470477	-0.524226
C	-1.229603	-1.754457	-0.089927
C	1.456293	-1.670282	-1.446057
O	1.907671	-2.754292	-1.556448
C	2.291405	0.509332	-2.165585
O	3.274919	0.861126	-2.710054
C	-0.573792	-2.082832	1.234258
C	0.356124	-3.114794	1.369869
C	0.950925	-3.385781	2.603112
C	0.616102	-2.626622	3.721213
C	-0.307955	-1.587806	3.596237
C	-0.889991	-1.317966	2.363763



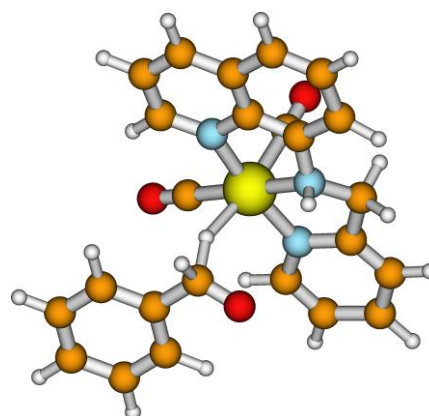
H	-1.507222	4.334213	2.439865
H	-1.588005	3.785278	0.019772
H	0.069301	3.155212	3.938147
H	2.790137	-1.055375	0.824151
H	3.183381	-0.465660	3.208078
H	1.860731	1.394797	4.240155
H	0.522647	2.564116	-1.699325
H	-2.086398	1.380906	-1.263075
H	-1.720183	2.799016	-2.273616
H	-2.818822	1.799369	-4.270030
H	-2.625652	0.156690	-6.149610
H	-0.868652	-1.635759	-5.990057
H	0.602123	-1.687198	-3.981761
H	-2.324258	-1.887374	0.040908
H	-0.926192	-2.532213	-0.825255
H	0.620993	-3.703487	0.493978
H	1.676519	-4.190902	2.690831
H	1.076008	-2.835131	4.683827
H	-0.569107	-0.985510	4.463812
H	-1.599176	-0.497581	2.256884

4. Mn-1d

Final Gibbs free energy = -1419.31533916 Eh

Total Energy = -1419.65525932 Eh

C	-0.802192	3.670522	2.030198
C	-0.852371	3.313116	0.668279
C	-0.108290	2.253403	0.206980
C	0.734668	1.535282	1.085234
C	0.810213	1.912672	2.455259
C	0.009589	2.988440	2.906179
N	1.466949	0.487311	0.574397
C	2.274465	-0.174013	1.403181
C	2.424097	0.154770	2.757335
C	1.690553	1.188424	3.289618
N	-0.094534	1.821317	-1.175227
C	-1.426456	1.553035	-1.781452
C	-1.251981	0.676890	-2.978476
C	-2.162778	0.653484	-4.028805
C	-1.980116	-0.240325	-5.076472
C	-0.872584	-1.082847	-5.051435
C	0.004621	-1.000677	-3.983243
N	-0.169965	-0.145433	-2.956923
Mn	1.003740	0.021262	-1.313598
O	-2.050560	0.108005	0.681279
C	-1.413628	-0.951015	0.294035
C	1.729232	-1.566112	-1.363816
O	2.225083	-2.632738	-1.413189



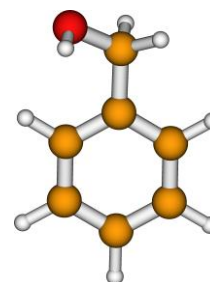
C	2.406231	0.684593	-2.116941
O	3.362696	1.109671	-2.652820
C	-0.738855	-1.789514	1.366097
C	-0.055573	-2.967482	1.054585
C	0.563821	-3.712891	2.052687
C	0.494388	-3.291069	3.381883
C	-0.199085	-2.125272	3.700108
C	-0.811655	-1.379146	2.695209
H	-1.408375	4.499136	2.381993
H	-1.494168	3.863253	-0.013699
H	0.053417	3.268444	3.954954
H	2.820192	-1.004953	0.966424
H	3.098342	-0.434505	3.368600
H	1.769076	1.454478	4.340043
H	0.373251	2.535122	-1.729715
H	-2.008695	1.033453	-0.992217
H	-1.953426	2.477249	-2.044663
H	-3.012056	1.329145	-4.010578
H	-2.685323	-0.274900	-5.900587
H	-0.686246	-1.797627	-5.844538
H	0.885914	-1.631558	-3.925512
H	-1.943191	-1.637696	-0.425286
H	-0.480528	-0.706280	-0.456866
H	-0.005631	-3.297509	0.017887
H	1.102626	-4.621419	1.795835
H	0.977905	-3.870624	4.163980
H	-0.257093	-1.795037	4.734942
H	-1.355713	-0.461831	2.908855

5. Benzyl alcohol (BA)

Final Gibbs free energy = -346.63702690 Eh

Total Energy = -346.73975707 Eh

C	-2.353972	3.352255	0.058449
C	-3.590684	2.744165	-0.175551
C	-1.228646	2.545434	0.232339
C	-1.337539	1.157814	0.176391
C	-3.703377	1.358587	-0.224153
C	-2.574744	0.559624	-0.049197
C	-2.254872	4.853246	0.143403
O	-0.955129	5.365019	-0.069317
H	-2.536618	5.186268	1.149949
H	-4.471656	3.366223	-0.325113
H	-0.265134	3.016079	0.407684
H	-4.672142	0.901254	-0.405801
H	-0.452349	0.541570	0.309467
H	-2.659006	-0.522405	-0.094390
H	-0.691345	5.106116	-0.959325



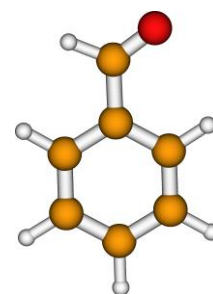
H -2.989527 5.305551 -0.542723

7. Benzaldehyde (BD)

Final Gibbs free energy = -345.46160406 Eh

Total Energy = -345.53824234 Eh

C	-1.661743	2.833383	0.000007
C	-2.752098	1.976599	-0.000001
C	-0.362814	2.308293	0.000012
C	-0.168732	0.923125	0.000007
C	-2.552014	0.593679	-0.000005
C	-1.262422	0.064964	-0.000000
C	0.803829	3.200306	0.000023
H	1.784345	2.665642	-0.000024
O	0.751888	4.417369	-0.000023
H	-1.785468	3.912731	0.000011
H	0.846631	0.531044	0.000011
H	-1.113927	-1.010531	-0.000003
H	-3.409650	-0.072942	-0.000011
H	-3.761625	2.376539	-0.000004



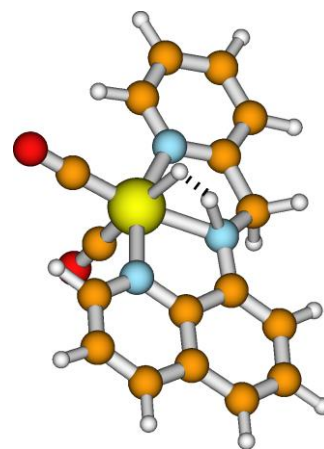
6. TS1

Final Gibbs free energy = -1073.85501577 Eh

Total Energy = -1074.08345283 Eh

Imaginary frequency = -1409.70 cm⁻¹

C	-3.914014	-0.167232	1.096334
C	-2.979518	0.030590	0.063726
C	-1.629386	-0.193417	0.298604
C	-1.204410	-0.573875	1.607484
C	-2.158207	-0.804151	2.634224
C	-3.528592	-0.593727	2.349780
N	0.152898	-0.673914	1.819422
C	0.571178	-1.051450	3.026777
C	-0.307570	-1.336055	4.083038
C	-1.664485	-1.206412	3.896984
N	-0.609282	-0.106631	-0.619848
C	-0.731205	0.559101	-1.890254
C	0.641587	0.689032	-2.498677
C	0.810609	1.060264	-3.827701
C	2.090814	1.203629	-4.347784
C	3.177124	0.958675	-3.512979
C	2.941329	0.580849	-2.201768
N	1.701989	0.447740	-1.685510
Mn	1.288689	-0.095584	0.235745
H	1.018098	-1.712717	-0.431497



C	2.882778	-0.504081	0.825704
O	3.954805	-0.804543	1.210899
H	-4.965883	0.011356	0.890214
H	-3.311491	0.344891	-0.921761
H	-4.260390	-0.755888	3.135798
H	1.646986	-1.118094	3.158396
H	0.102396	-1.641986	5.039563
H	-2.363817	-1.400769	4.706014
H	0.098954	-1.125301	-0.646062
H	-1.166561	1.563280	-1.752060
H	-1.397783	0.031731	-2.591867
H	-0.067538	1.233926	-4.442695
H	2.237146	1.497067	-5.382490
H	4.197644	1.051532	-3.867579
H	3.756993	0.371993	-1.516628
C	1.439084	1.566335	0.829327
O	1.549034	2.663838	1.229126

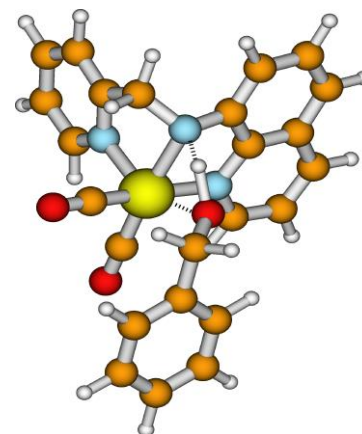
7. TS2

Final Gibbs free energy = -1419.33428688 Eh

Total Energy = -1419.67251939 Eh

Imaginary frequency = -1374.68 cm⁻¹

C	0.332641	-2.461258	2.854922
C	-0.747922	-2.877195	2.068976
C	-0.794521	-4.203718	1.638325
C	0.212002	-5.102246	1.990064
C	1.281310	-4.679354	2.775038
C	1.339452	-3.353432	3.205748
C	-1.817965	-1.890541	1.687039
O	-1.251662	-0.678351	1.258923
Mn	-0.104516	-0.630188	-0.489488
C	1.270890	-1.695317	-0.337014
O	2.238334	-2.364721	-0.253881
N	0.871691	0.934462	0.501432
C	0.149603	2.096511	0.568887
C	0.653835	3.271020	1.195540
C	1.919804	3.182503	1.817408
C	2.613822	1.995697	1.773325
C	2.060349	0.897683	1.093036
C	-0.117315	4.454360	1.144076
C	-1.332092	4.453682	0.493694
C	-1.844045	3.280728	-0.092960
C	-1.131637	2.094205	-0.043714
N	-1.600904	0.856394	-0.533250
C	-2.053878	0.857585	-1.917683
C	-0.832708	0.869865	-2.806329
C	-0.778906	1.497557	-4.042493



C	0.393776	1.446336	-4.791556
C	1.488929	0.766752	-4.268434
C	1.374581	0.166423	-3.023056
N	0.242122	0.205800	-2.296579
C	-0.996448	-1.955401	-1.235369
O	-1.558942	-2.860287	-1.731682
H	-1.919786	5.366059	0.445868
H	-2.821024	3.299562	-0.568761
H	0.266998	5.355982	1.613007
H	2.602324	-0.042340	1.024085
H	3.585960	1.891768	2.242756
H	2.330168	4.055152	2.319391
H	-2.632301	-0.057703	-2.096657
H	-2.711385	1.701646	-2.168306
H	-1.655614	2.025114	-4.406420
H	0.451587	1.931523	-5.760954
H	2.426065	0.701426	-4.810400
H	2.201515	-0.377394	-2.574938
H	-2.464191	-1.690823	2.559703
H	-2.467092	-2.343243	0.916551
H	-1.620472	-4.528480	1.007375
H	0.165582	-6.130597	1.641080
H	2.070680	-5.376090	3.044039
H	2.175894	-3.015649	3.812772
H	0.381104	-1.421375	3.171369
H	-1.845691	0.079909	0.385492

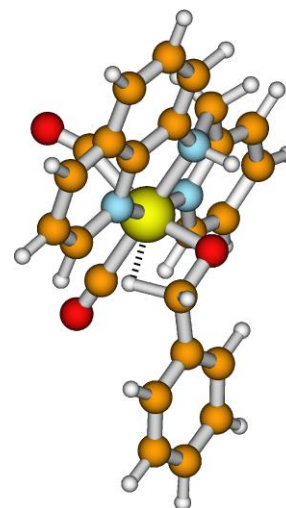
8. TS3

Final Gibbs free energy = -1419.30159934 Eh

Total Energy = -1419.64204846 Eh

Imaginary frequency = -368.77 cm⁻¹

C	-0.767320	3.950865	1.929137
C	-0.868211	3.485573	0.600816
C	-0.157675	2.379644	0.198110
C	0.679907	1.699907	1.111662
C	0.803995	2.180878	2.442553
C	0.056870	3.319326	2.830000
N	1.355013	0.584155	0.676450
C	2.142372	-0.052615	1.537347
C	2.333112	0.369845	2.862324
C	1.664665	1.480852	3.317601
N	-0.161373	1.880063	-1.158146
C	-1.488966	1.611040	-1.768566
C	-1.285580	0.752604	-2.968074
C	-2.125865	0.781453	-4.077405
C	-1.916688	-0.111563	-5.119909
C	-0.857426	-1.012325	-5.031584

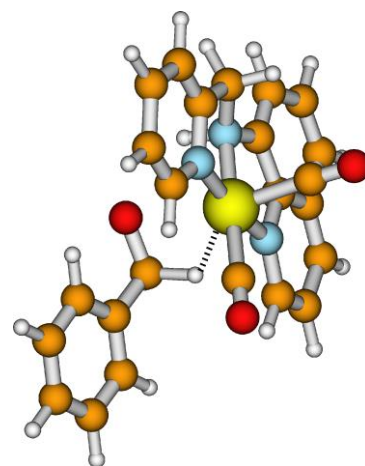


C	-0.051187	-0.983675	-3.906056
N	-0.251354	-0.125963	-2.886761
Mn	0.858738	0.021790	-1.182358
O	-1.512600	0.010477	0.489132
C	-1.297430	-1.274867	0.182823
C	1.664722	-1.540945	-1.205519
O	2.250954	-2.557005	-1.249666
C	2.255164	0.680734	-1.952100
O	3.209997	1.115841	-2.482279
C	-0.643618	-2.105273	1.279675
C	-0.111842	-3.373220	1.025755
C	0.494799	-4.108934	2.039453
C	0.568786	-3.587108	3.332732
C	0.033868	-2.328017	3.596150
C	-0.563073	-1.592233	2.573513
H	-1.341410	4.821087	2.231911
H	-1.514095	3.999082	-0.106160
H	0.146339	3.679636	3.851269
H	2.635063	-0.946421	1.163762
H	2.988159	-0.204017	3.508194
H	1.780266	1.827622	4.341246
H	0.331958	2.552126	-1.744121
H	-2.009006	1.019068	-0.979153
H	-2.037268	2.527456	-2.014434
H	-2.936170	1.503153	-4.109163
H	-2.565215	-0.102183	-5.990504
H	-0.652804	-1.726994	-5.820657
H	0.789213	-1.662142	-3.792701
H	-2.211099	-1.851630	-0.142243
H	-0.640029	-1.453163	-0.737935
H	-0.162081	-3.778516	0.014614
H	0.915035	-5.088627	1.823647
H	1.043523	-4.159297	4.125996
H	0.093229	-1.912443	4.600591
H	-0.966363	-0.595103	2.739033

9. TS4

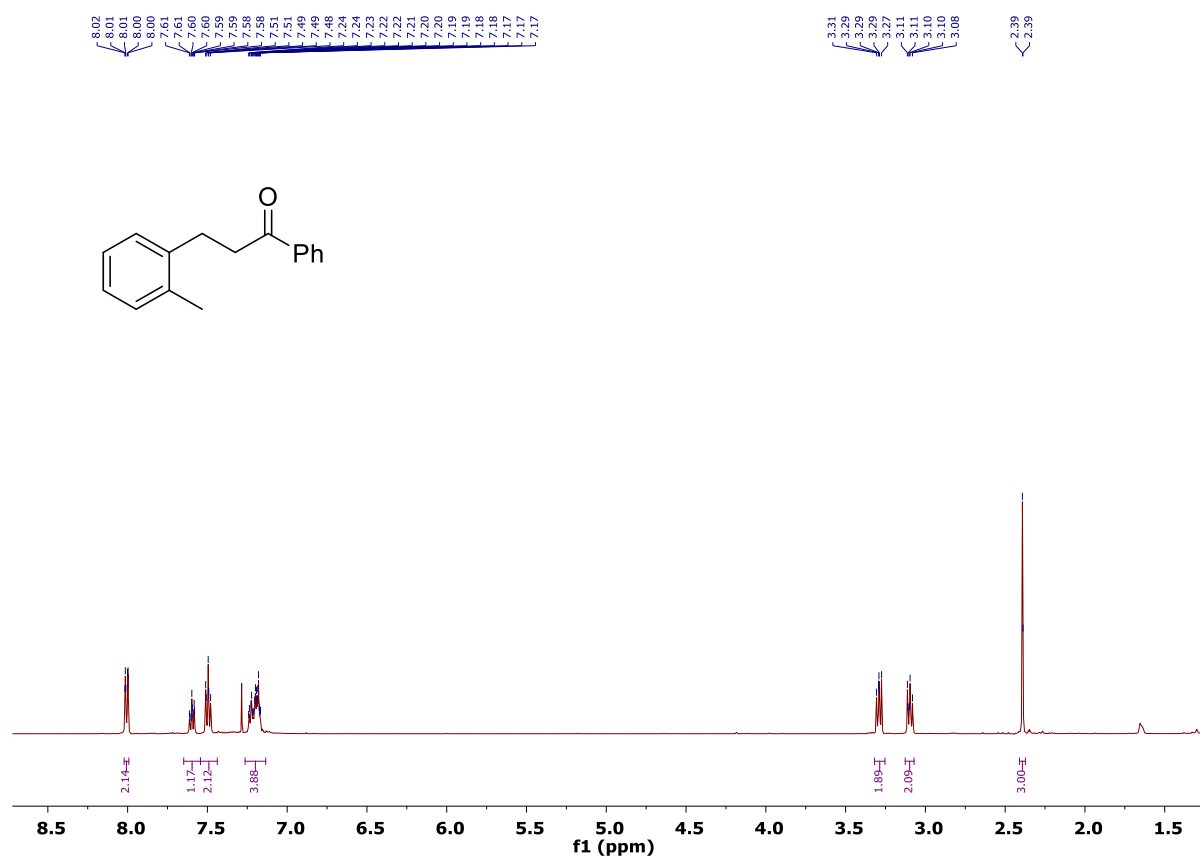
Final Gibbs free energy = -1419.31279770Eh
Total Energy = -1419.65051153 Eh
Imaginary frequency = -356.37 cm⁻¹

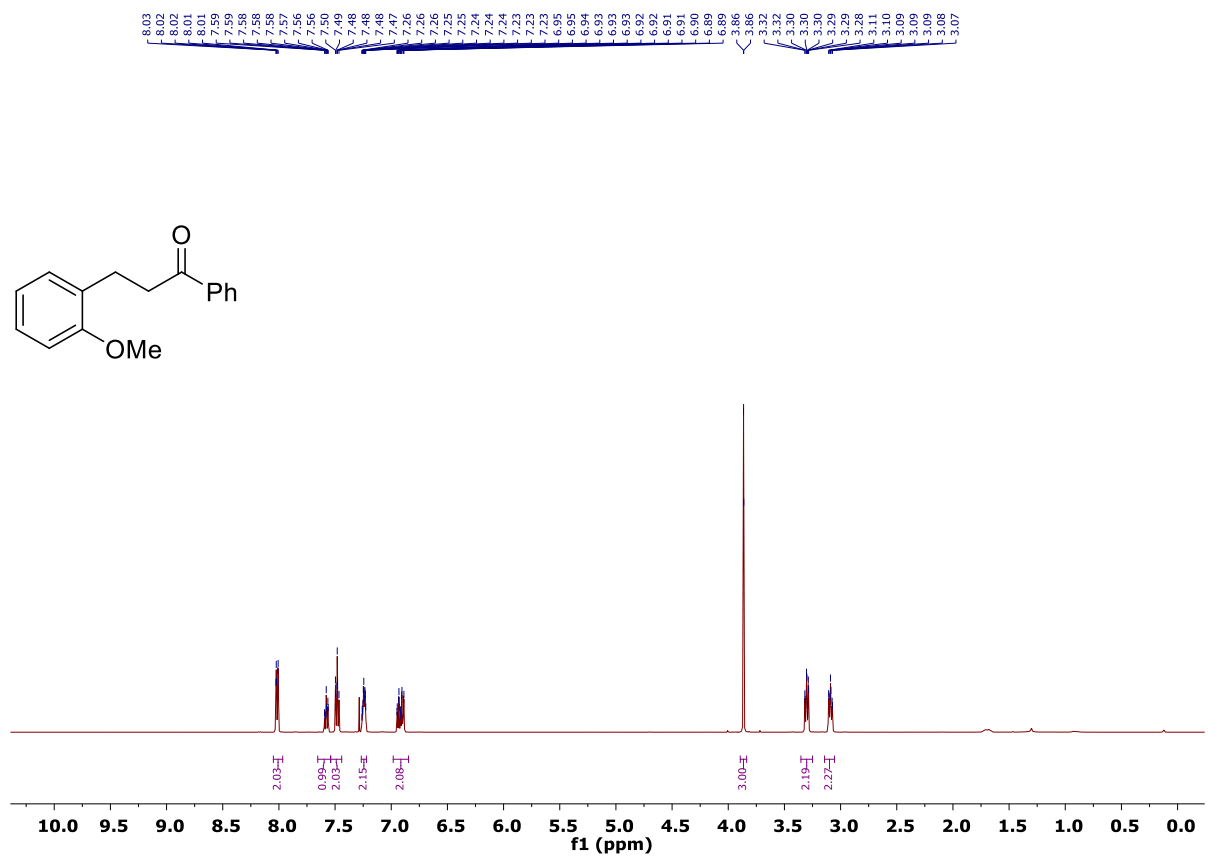
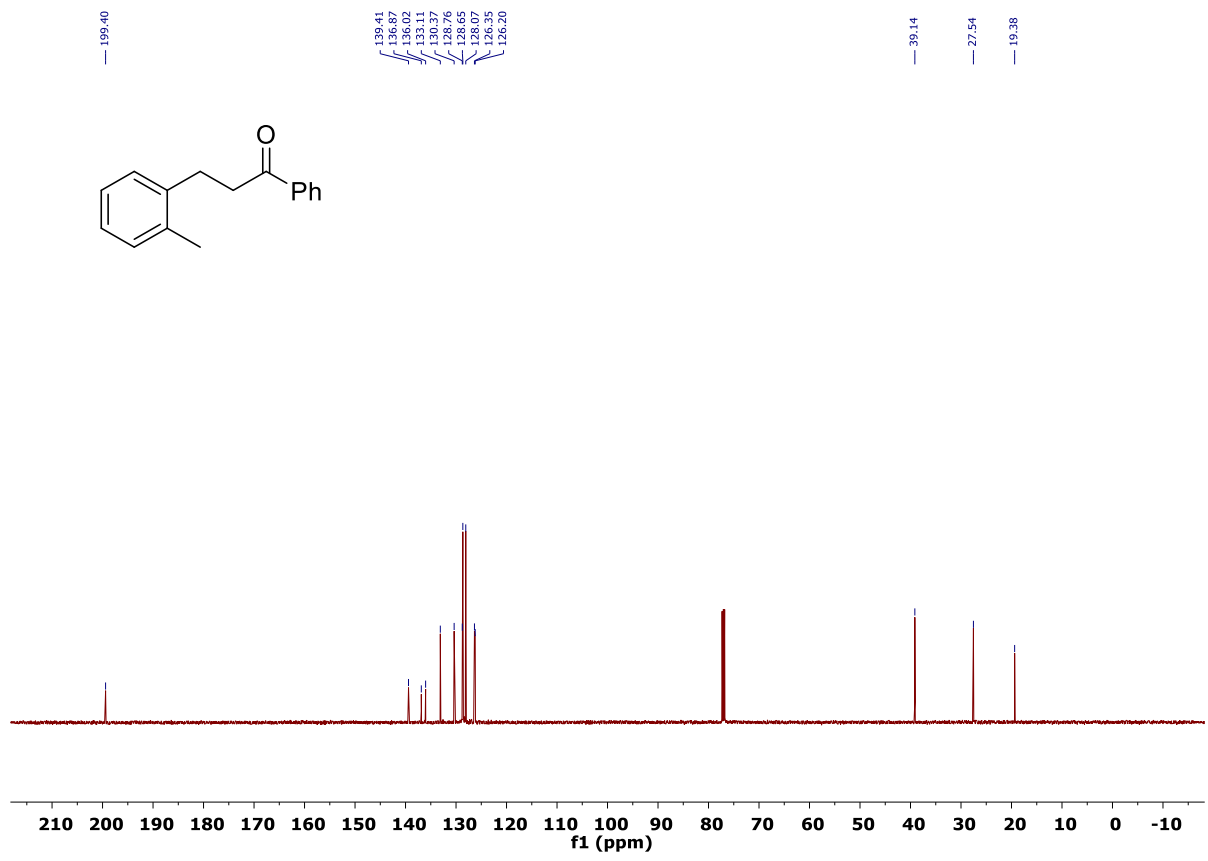
C	-0.897012	3.612753	2.028134
C	-0.941142	3.249829	0.668435
C	-0.158221	2.216913	0.204792
C	0.699588	1.518597	1.083253
C	0.780008	1.912657	2.447517
C	-0.048278	2.966044	2.898000
N	1.435416	0.469697	0.575182
C	2.260021	-0.166021	1.406212
C	2.426252	0.189908	2.753359
C	1.686337	1.220178	3.282529
N	-0.125135	1.793573	-1.177140
C	-1.439802	1.511103	-1.798941
C	-1.224757	0.679722	-3.025402
C	-2.083262	0.718731	-4.116443
C	-1.858606	-0.126214	-5.198074
C	-0.760127	-0.979916	-5.155434
C	0.065689	-0.957618	-4.042878
N	-0.150261	-0.150559	-2.984800
Mn	0.969242	-0.024548	-1.302802
O	-2.231010	0.032524	0.844159
C	-1.662252	-1.026483	0.516517
C	1.644251	-1.628866	-1.313382
O	2.087627	-2.722381	-1.313840
C	2.411313	0.632276	-2.089747
O	3.391388	1.019582	-2.614897
C	-0.835047	-1.802301	1.488652
C	-0.225760	-3.003843	1.117749
C	0.525064	-3.724573	2.038578
C	0.659076	-3.255595	3.347425
C	0.041824	-2.064864	3.725726
C	-0.699123	-1.338621	2.797455
H	-1.530661	4.419107	2.384248
H	-1.600198	3.778269	-0.014943
H	0.000438	3.256242	3.944254
H	2.807400	-1.002064	0.980195
H	3.121969	-0.377600	3.362063
H	1.775689	1.504210	4.327647
H	0.343173	2.511933	-1.725368
H	-2.024334	0.954822	-1.052102
H	-1.993351	2.426910	-2.041909
H	-2.922264	1.408067	-4.106298
H	-2.522250	-0.113008	-6.056833
H	-0.536177	-1.655920	-5.973300
H	0.938137	-1.599794	-3.970125
H	-2.057563	-1.646797	-0.320997
H	-0.421397	-0.704279	-0.535814

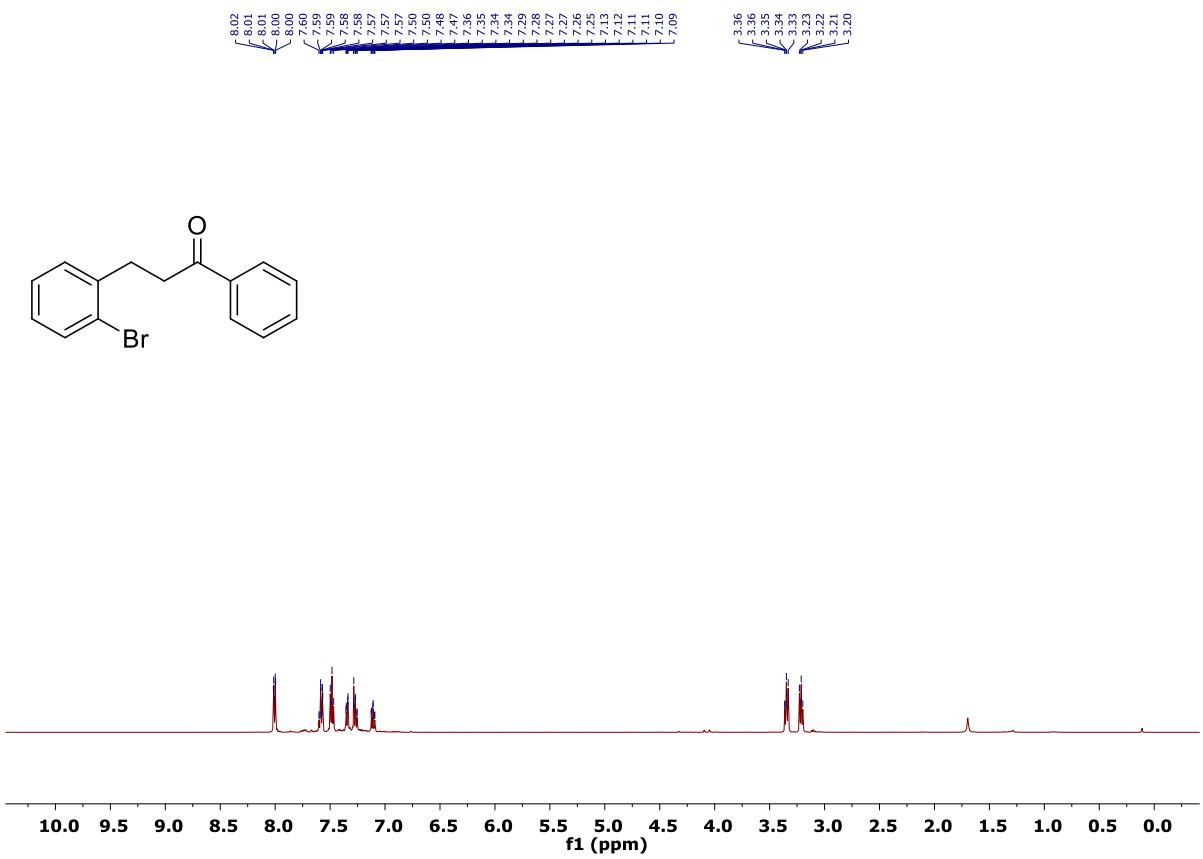
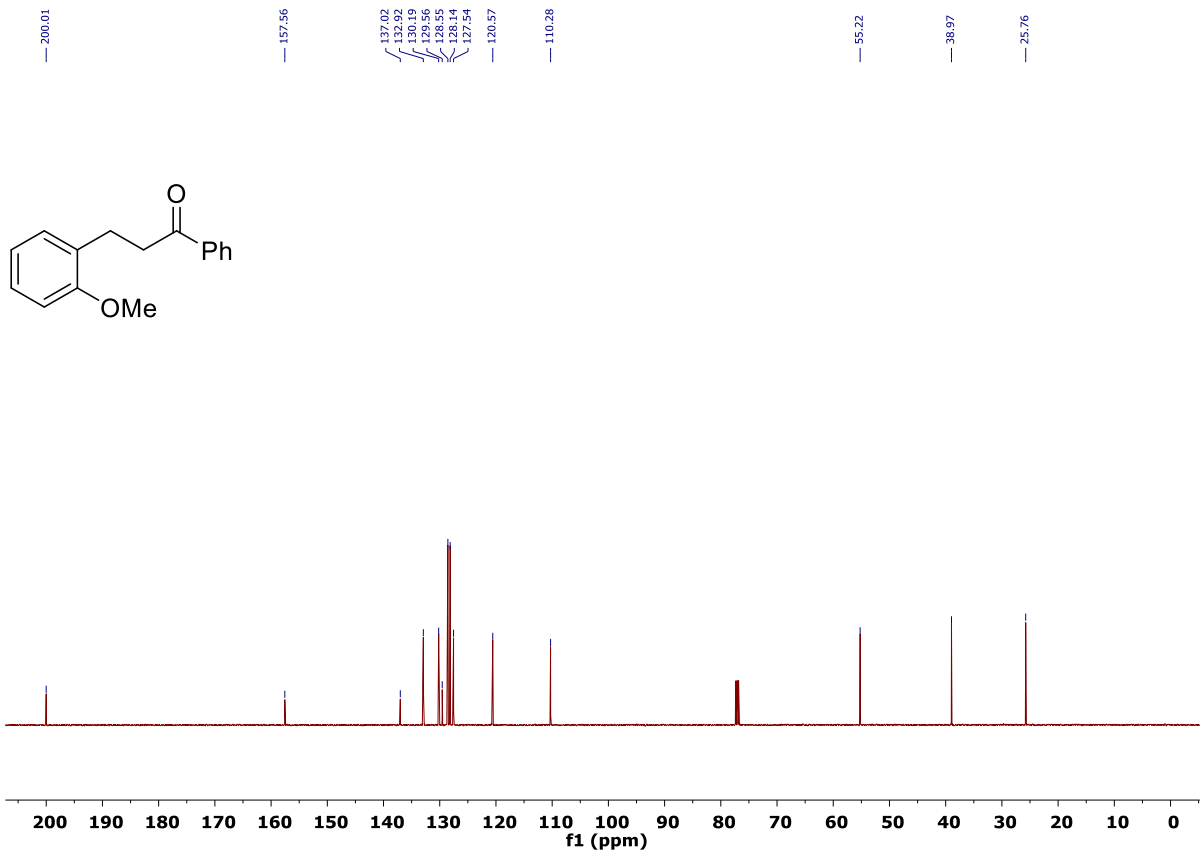


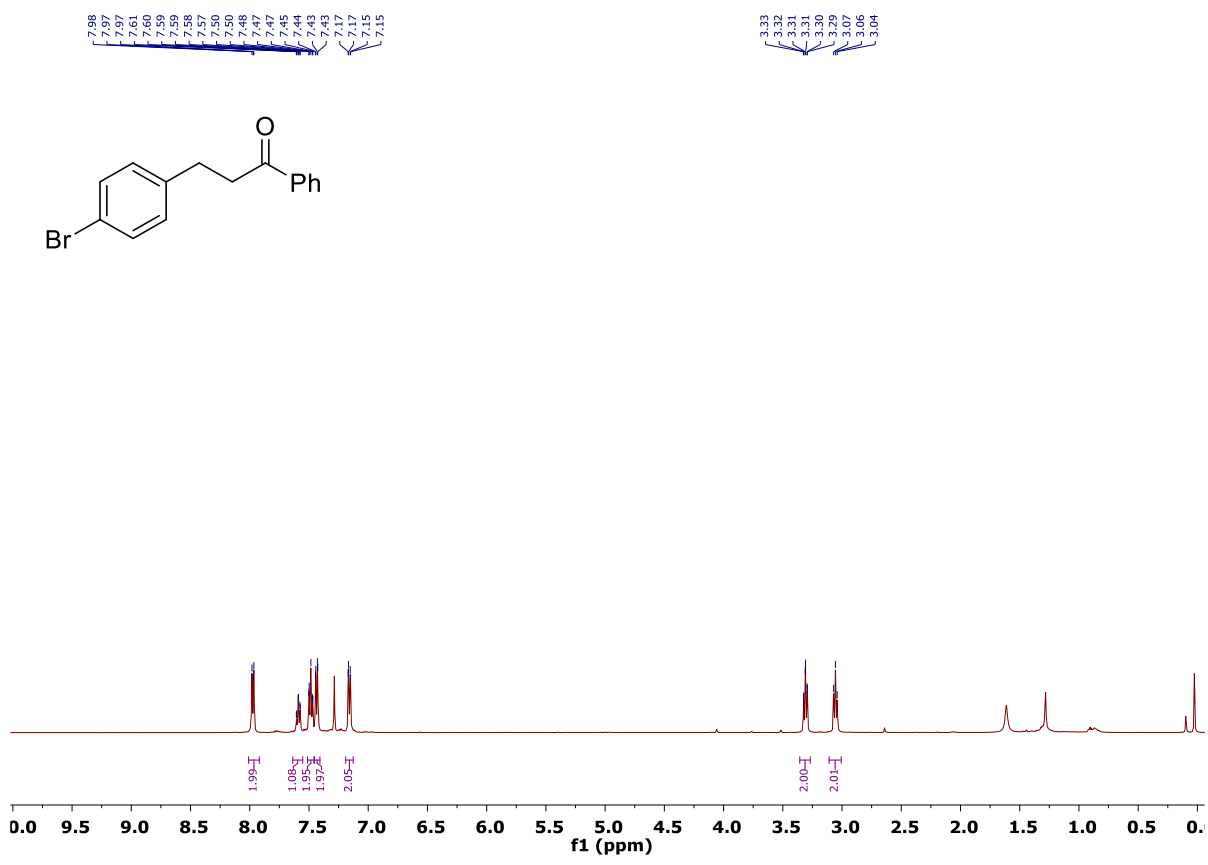
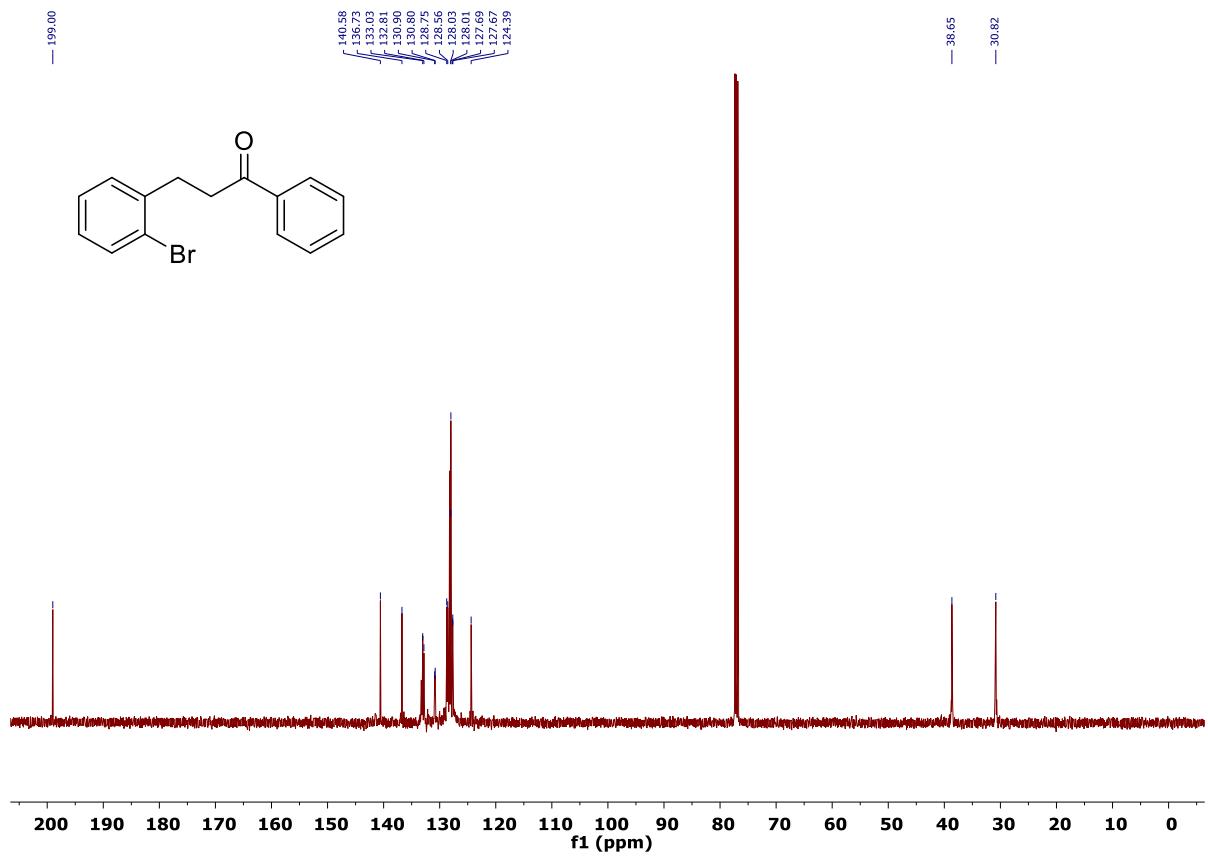
H	-0.327995	-3.356217	0.092624
H	1.007216	-4.651617	1.739410
H	1.242347	-3.821074	4.069577
H	0.145046	-1.698599	4.744633
H	-1.188525	-0.404275	3.063143

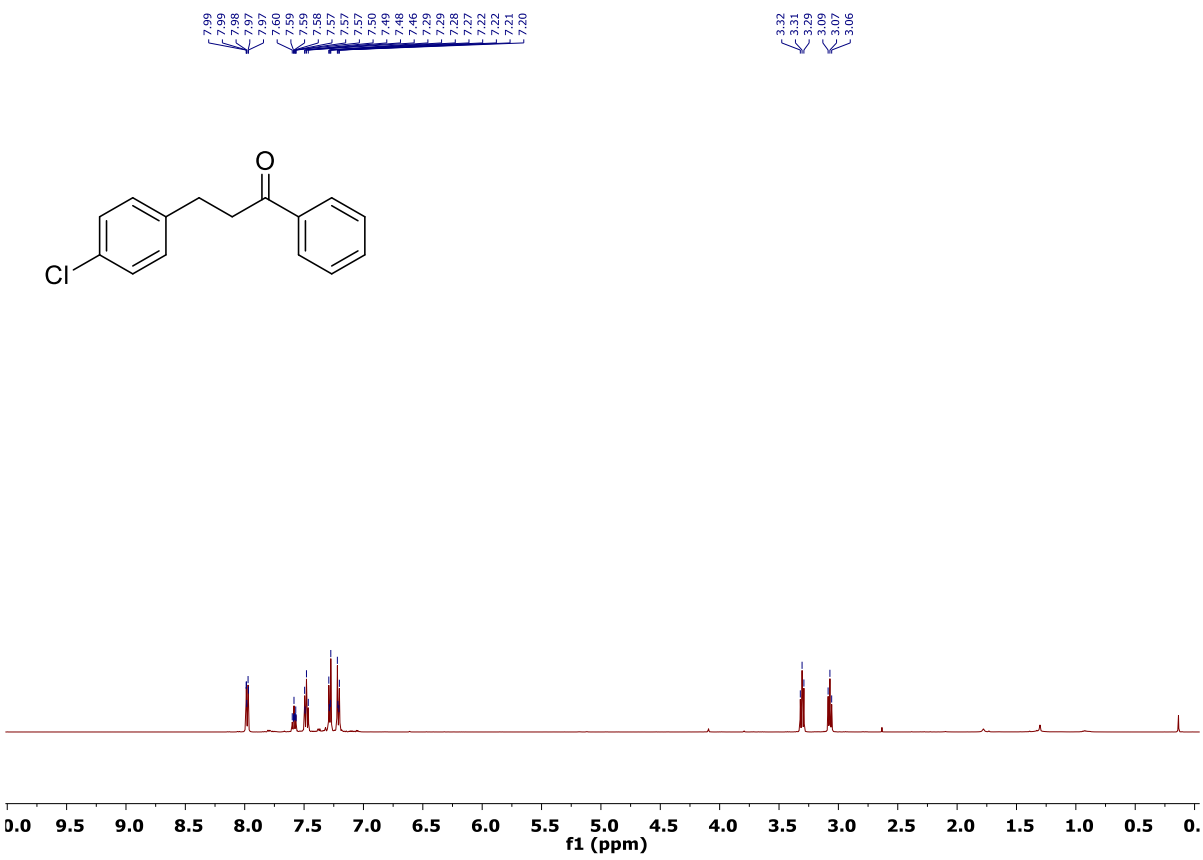
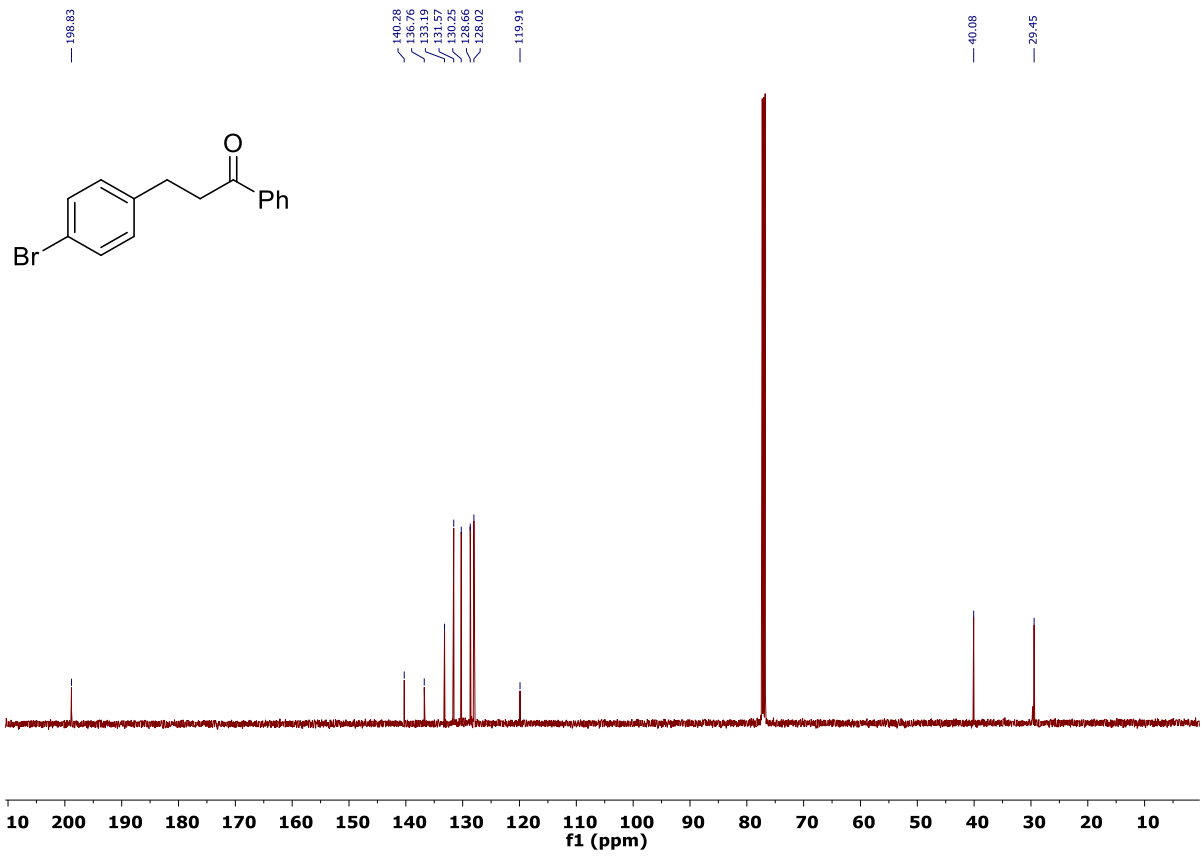
^1H and ^{13}C and ^{19}F NMR data of isolated products:

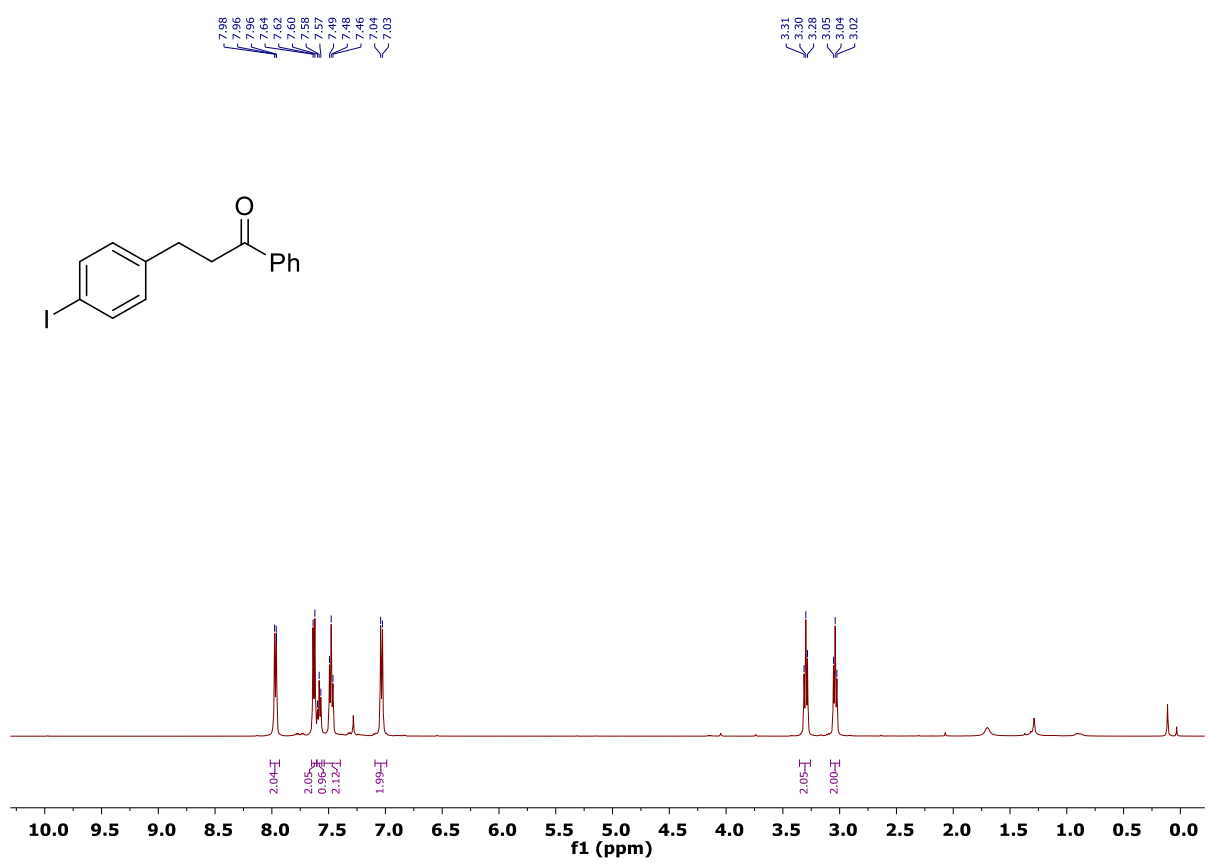
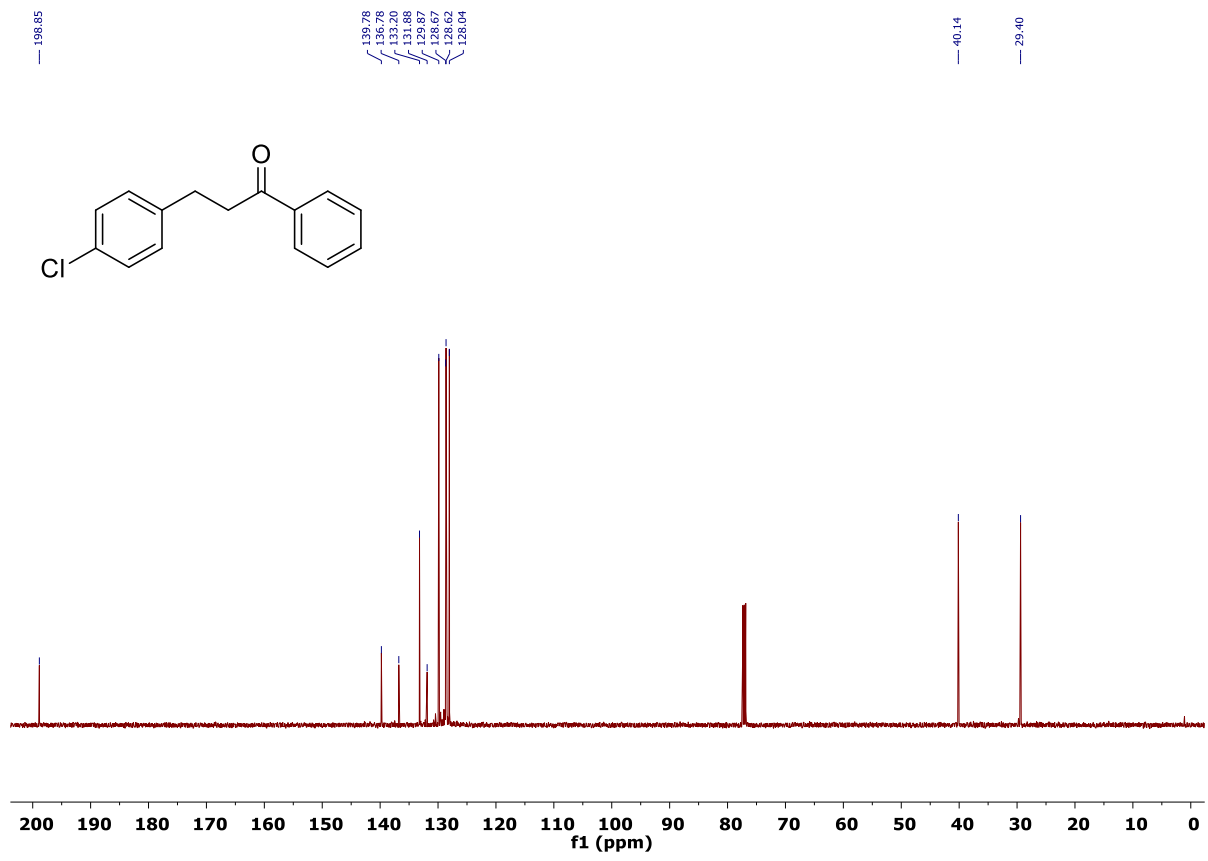


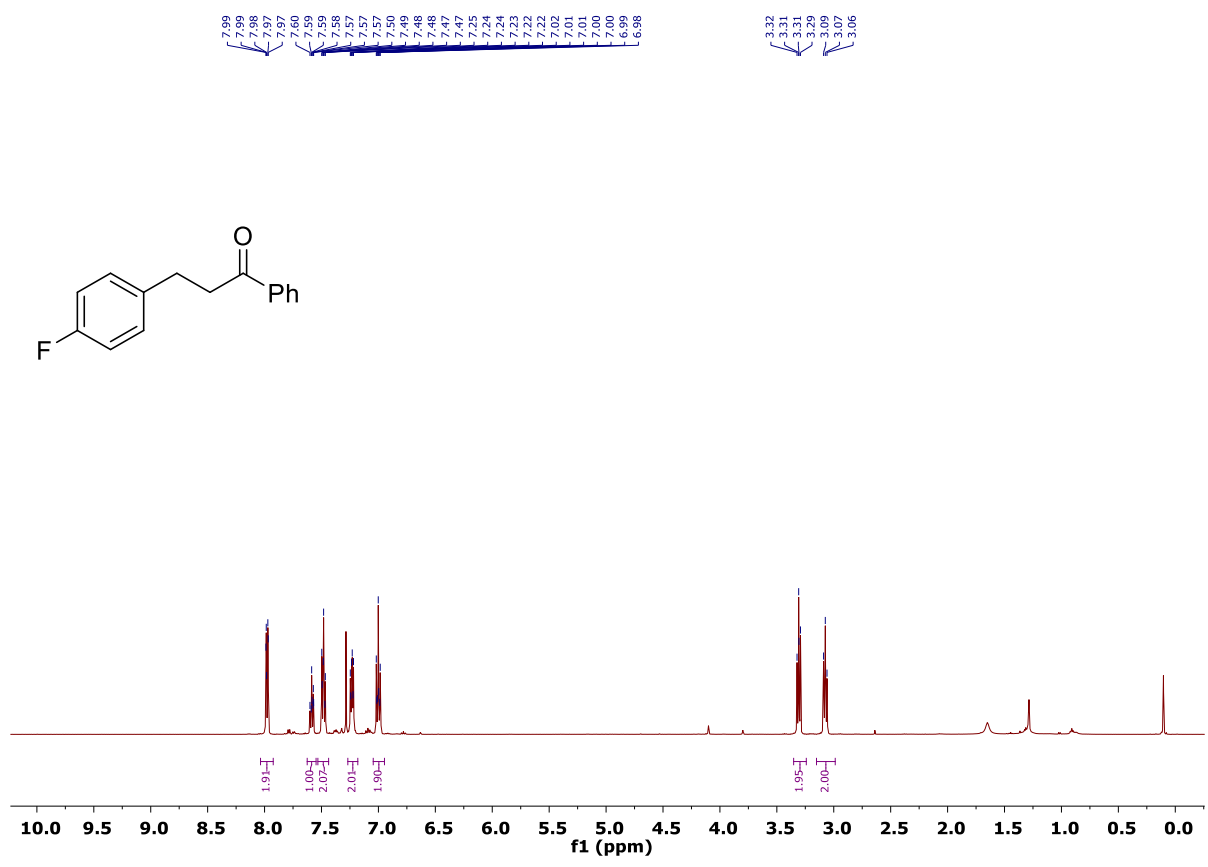
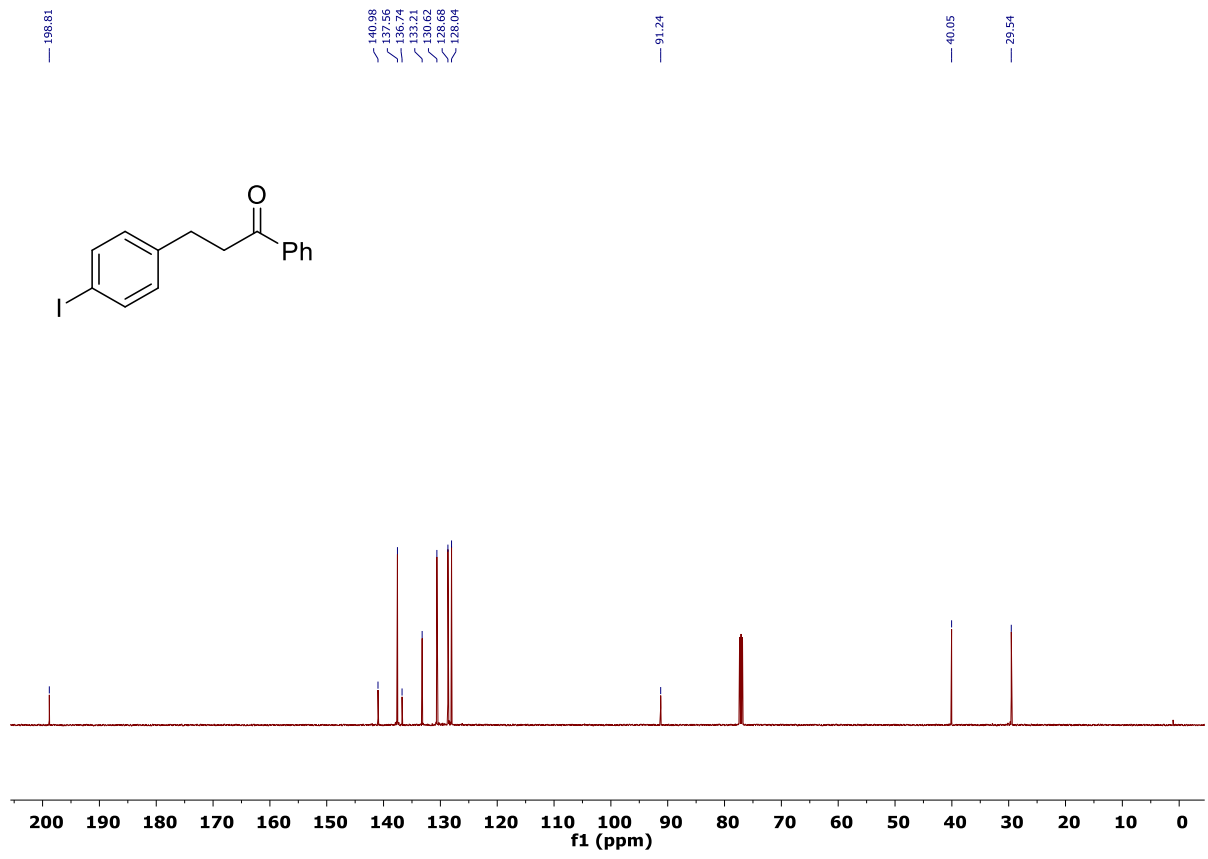


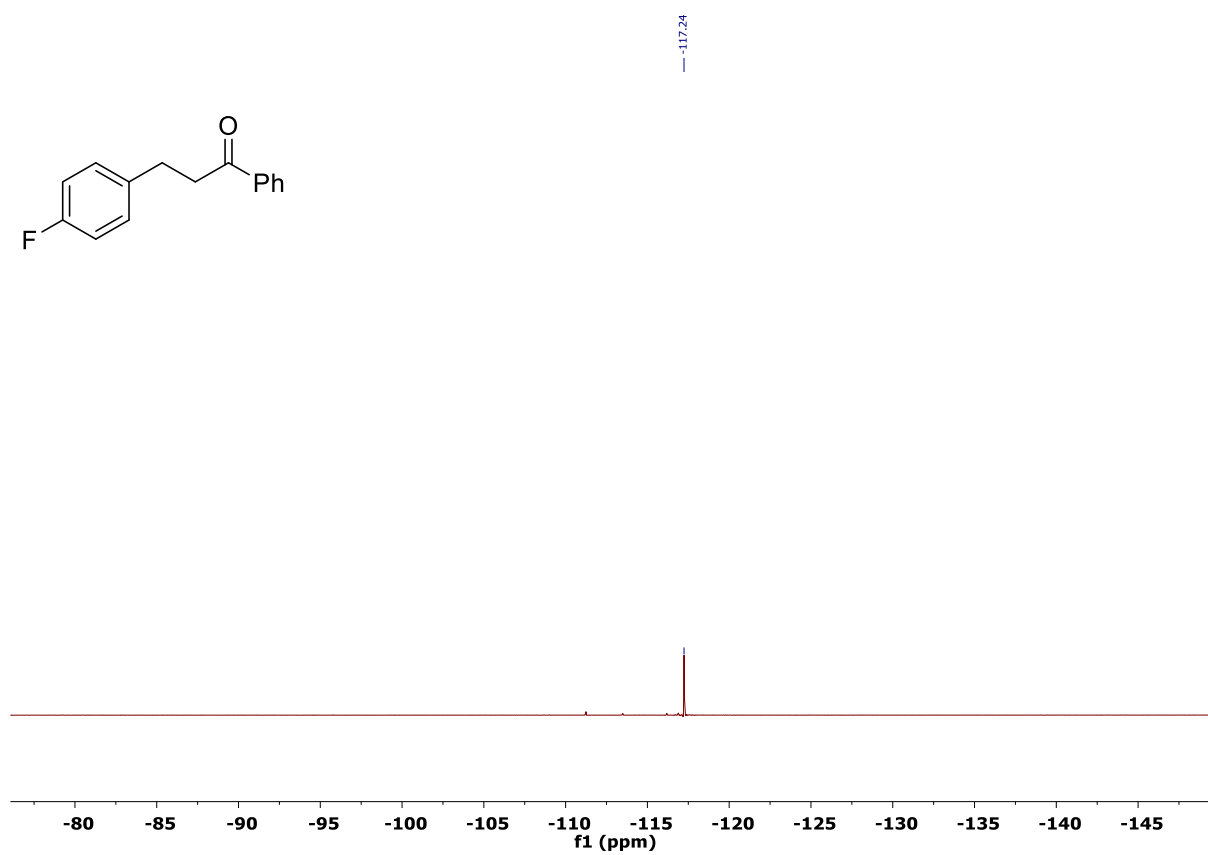
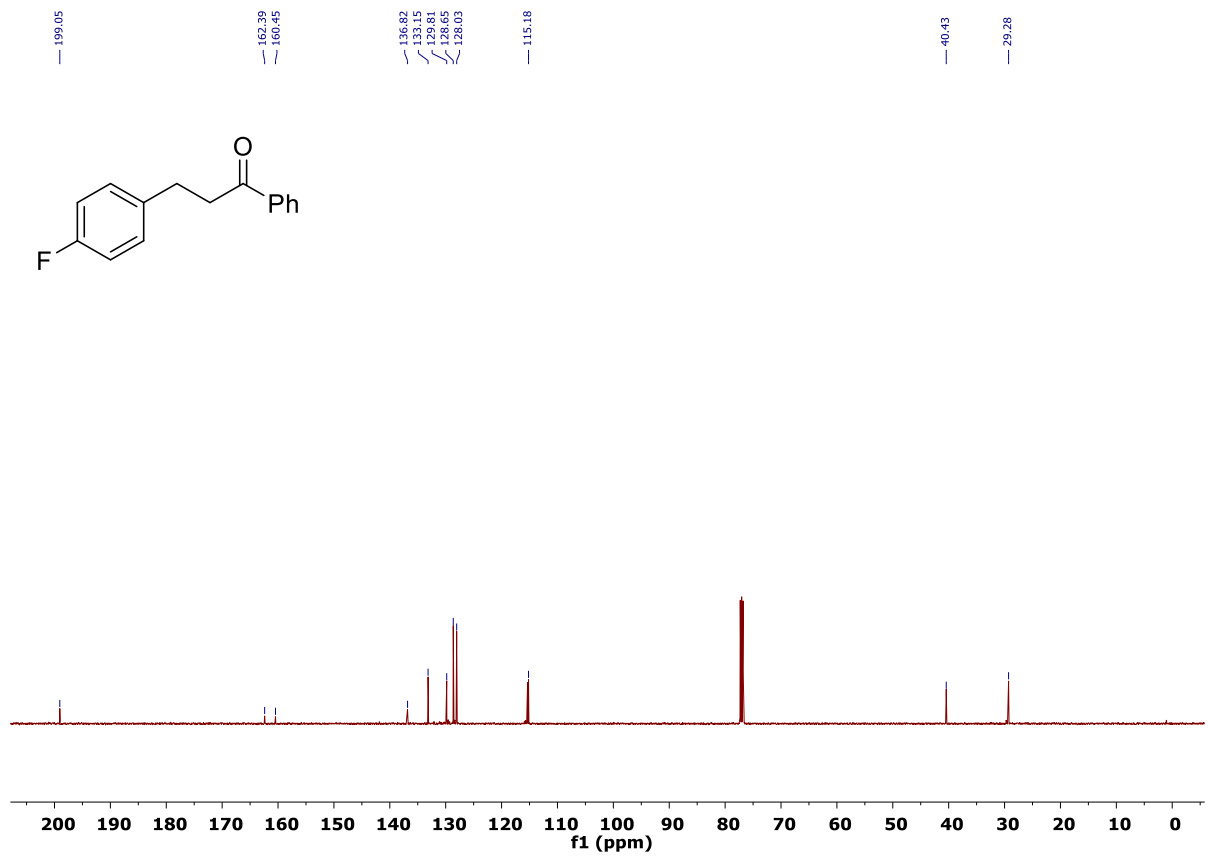


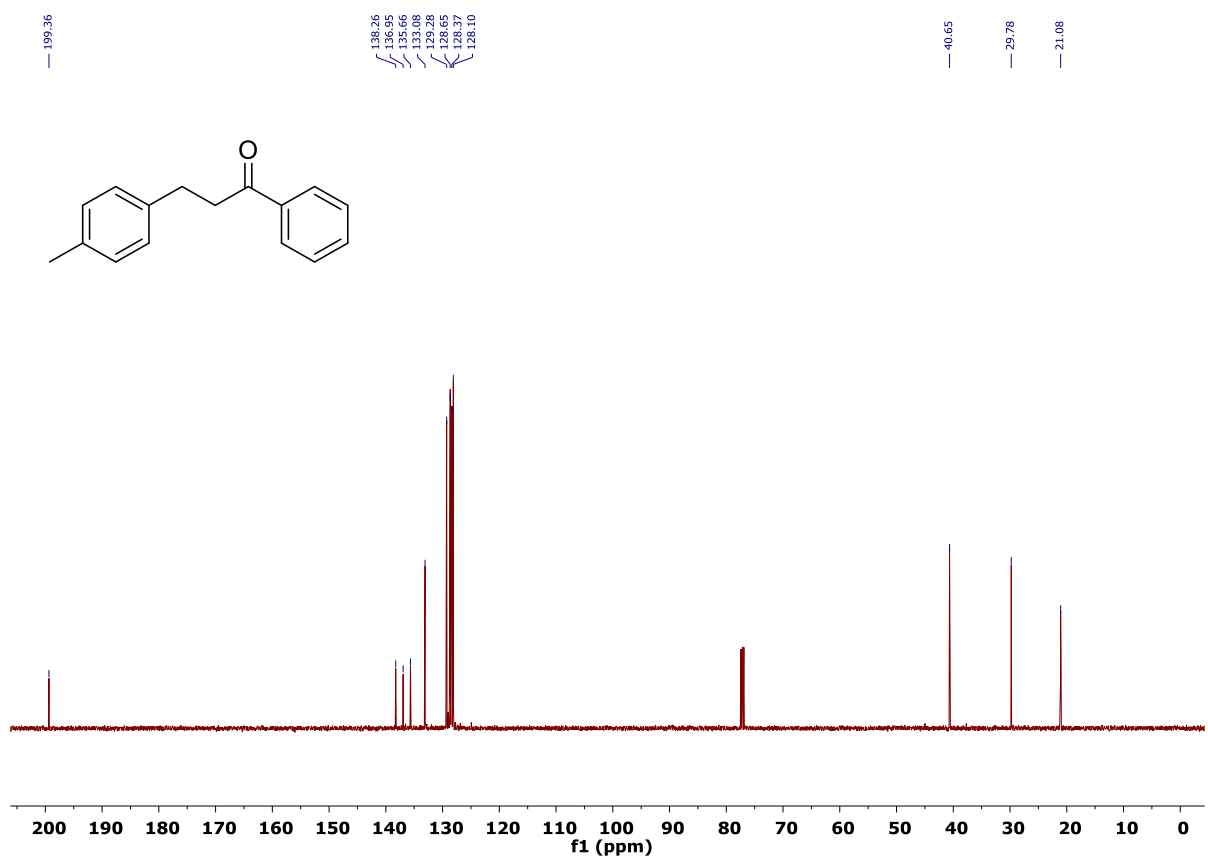
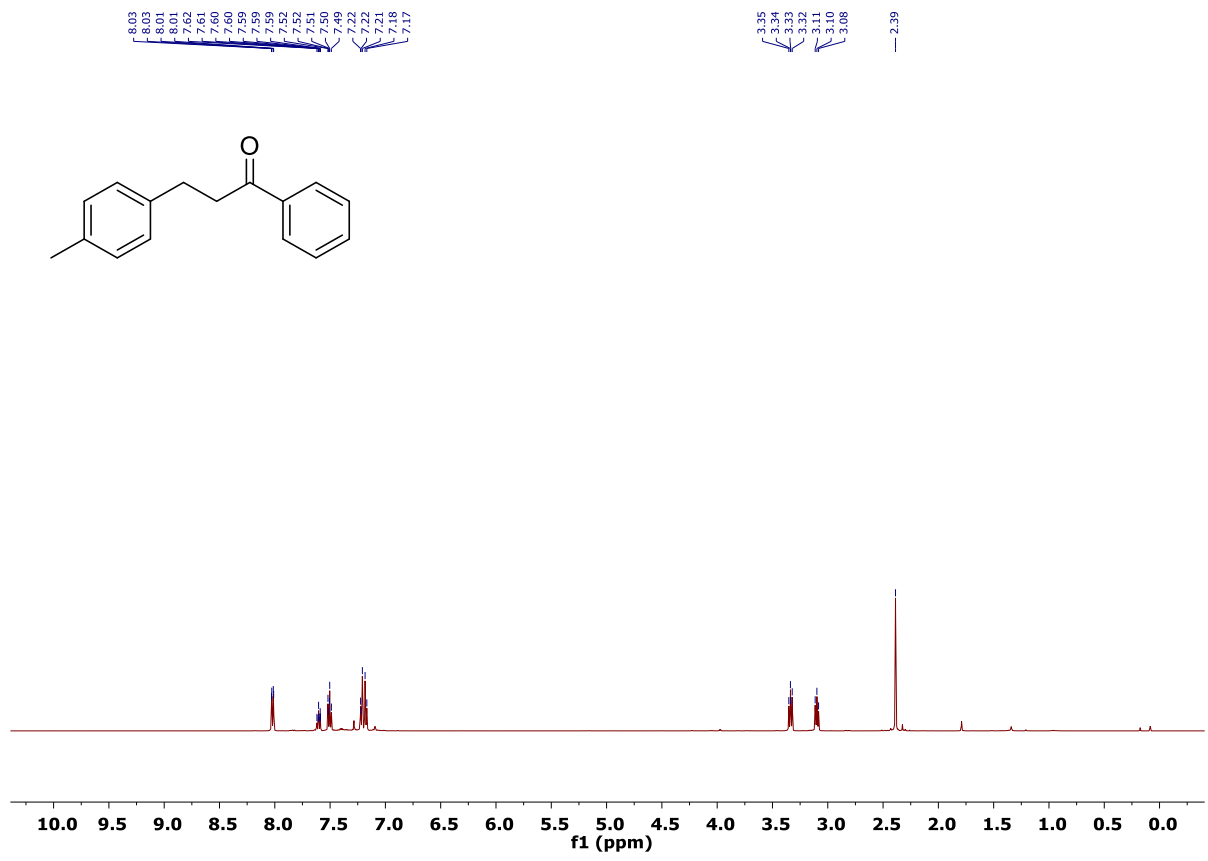


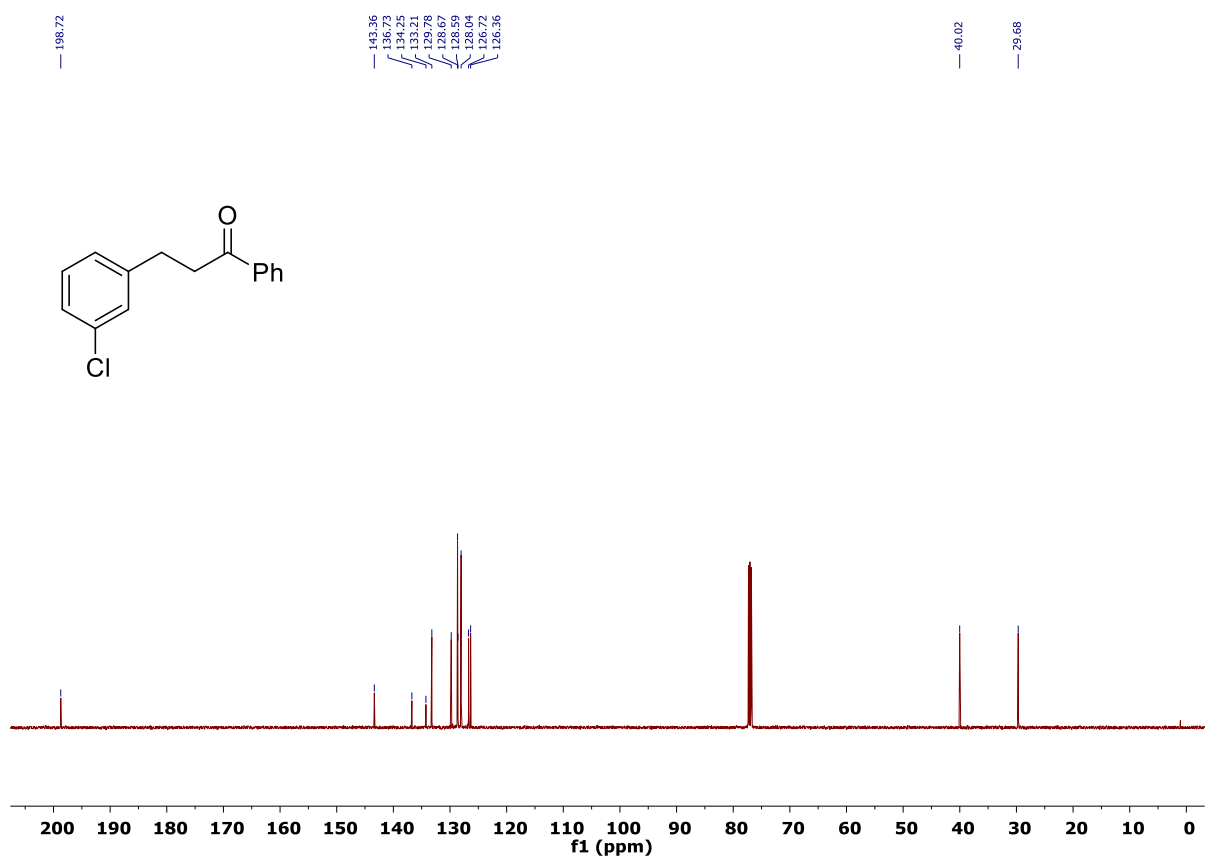
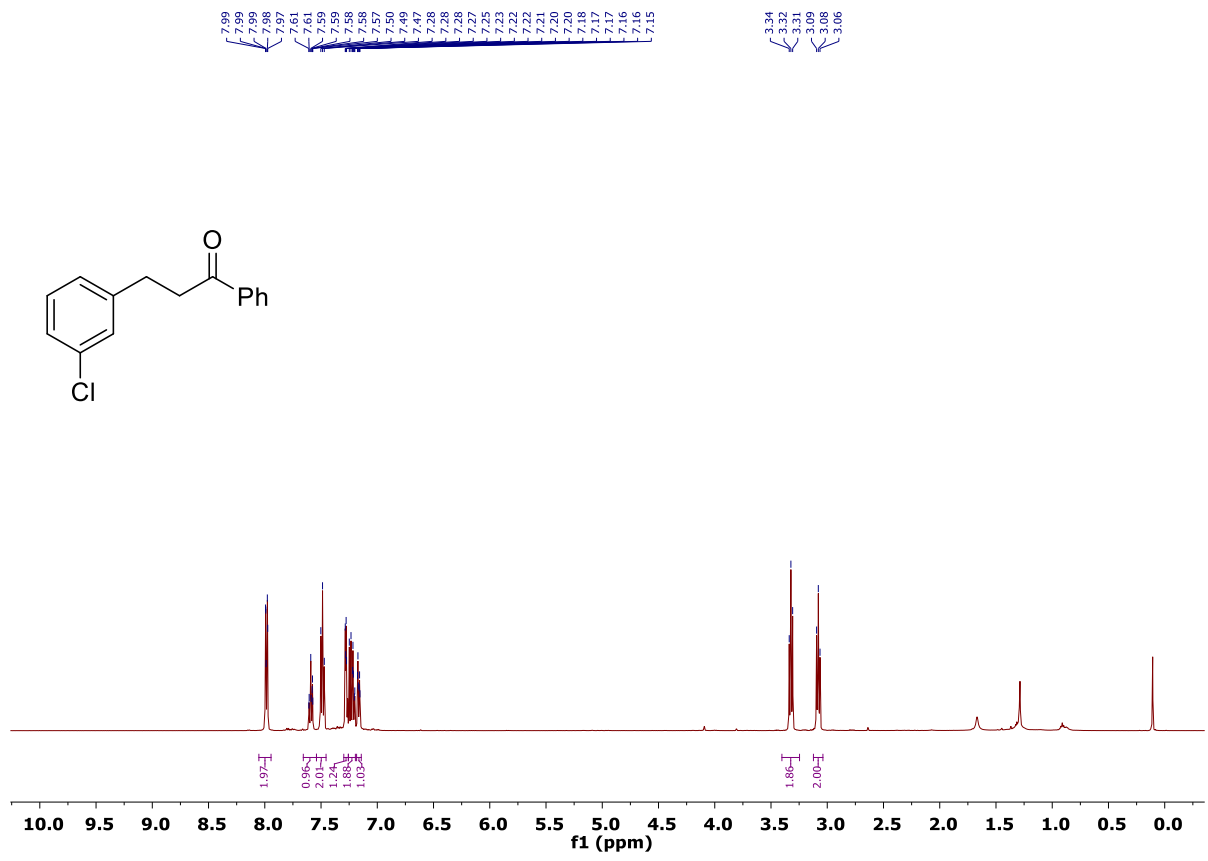


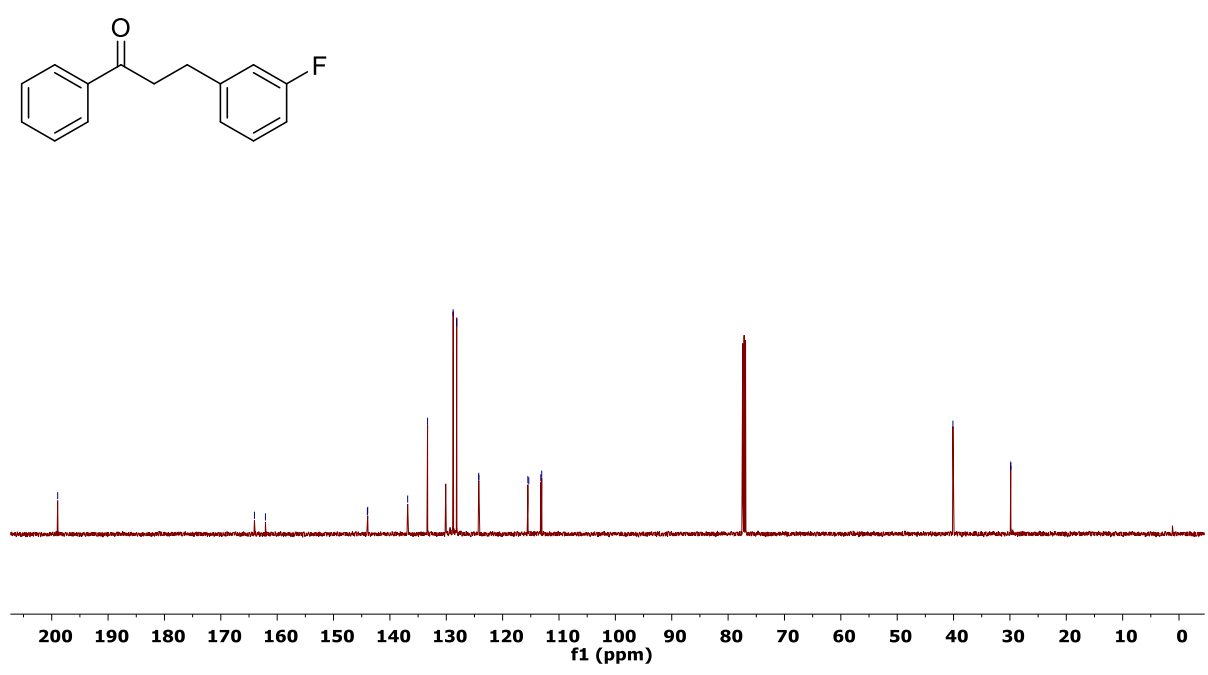
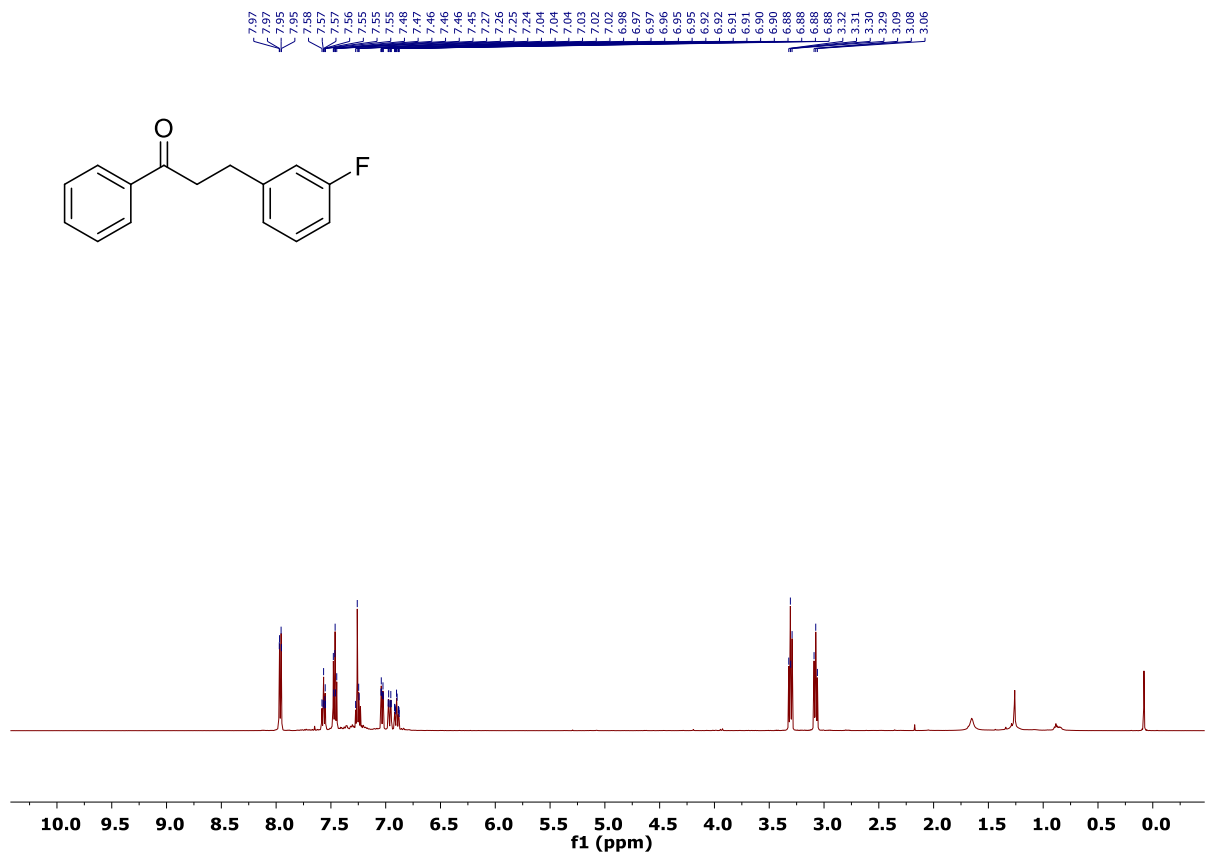


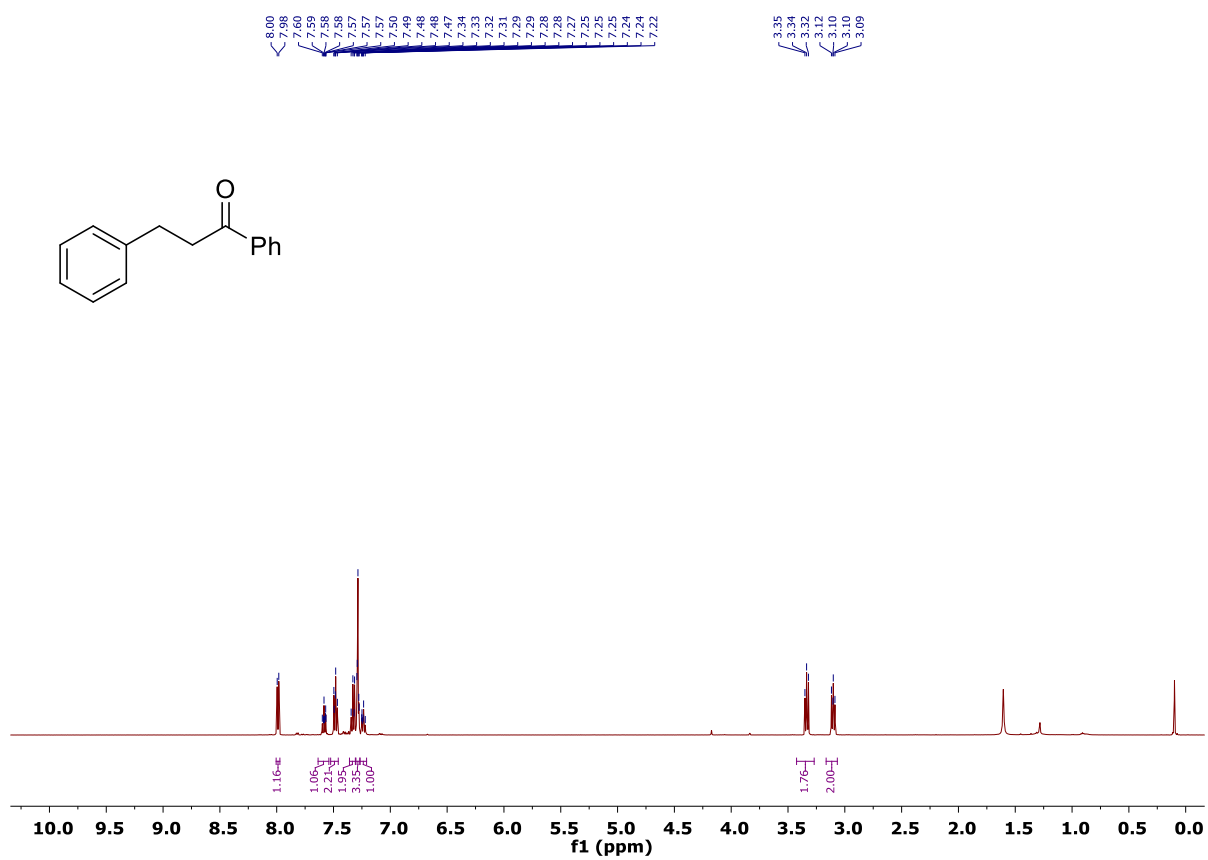
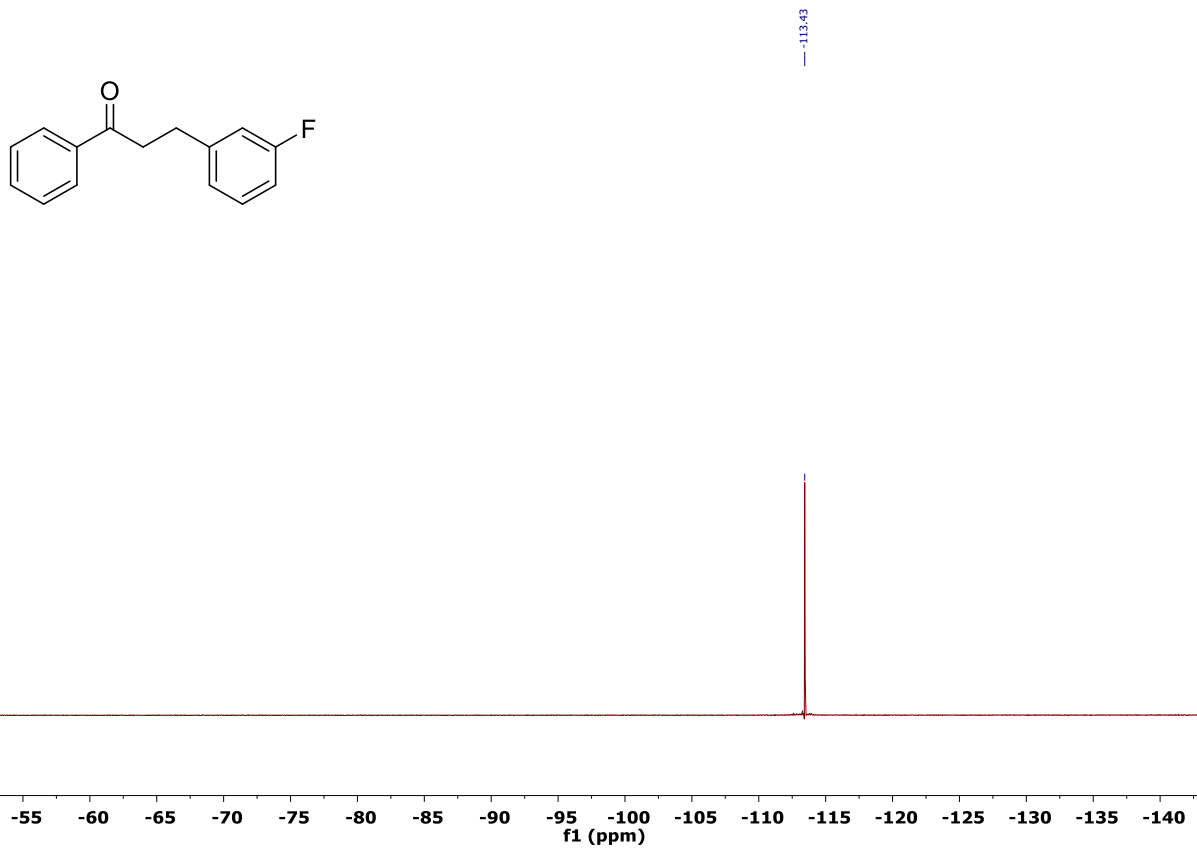


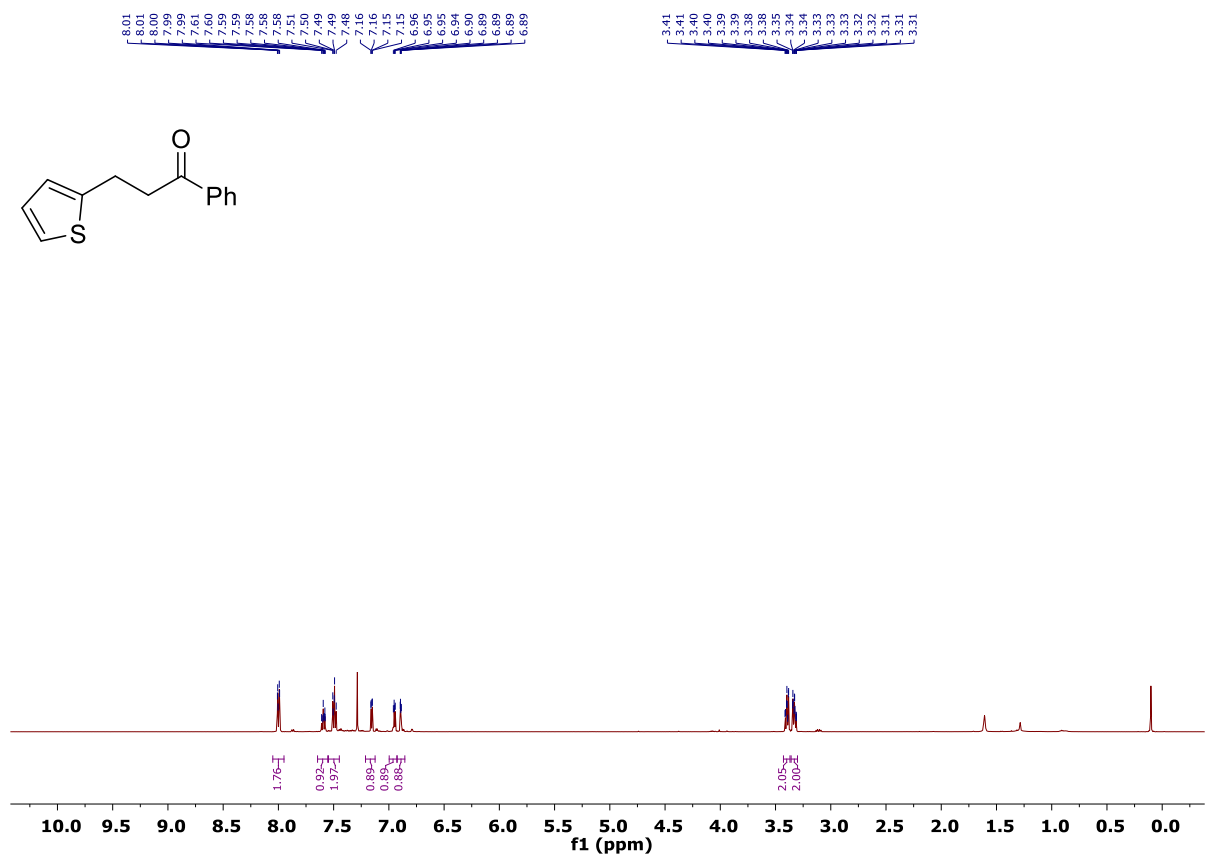
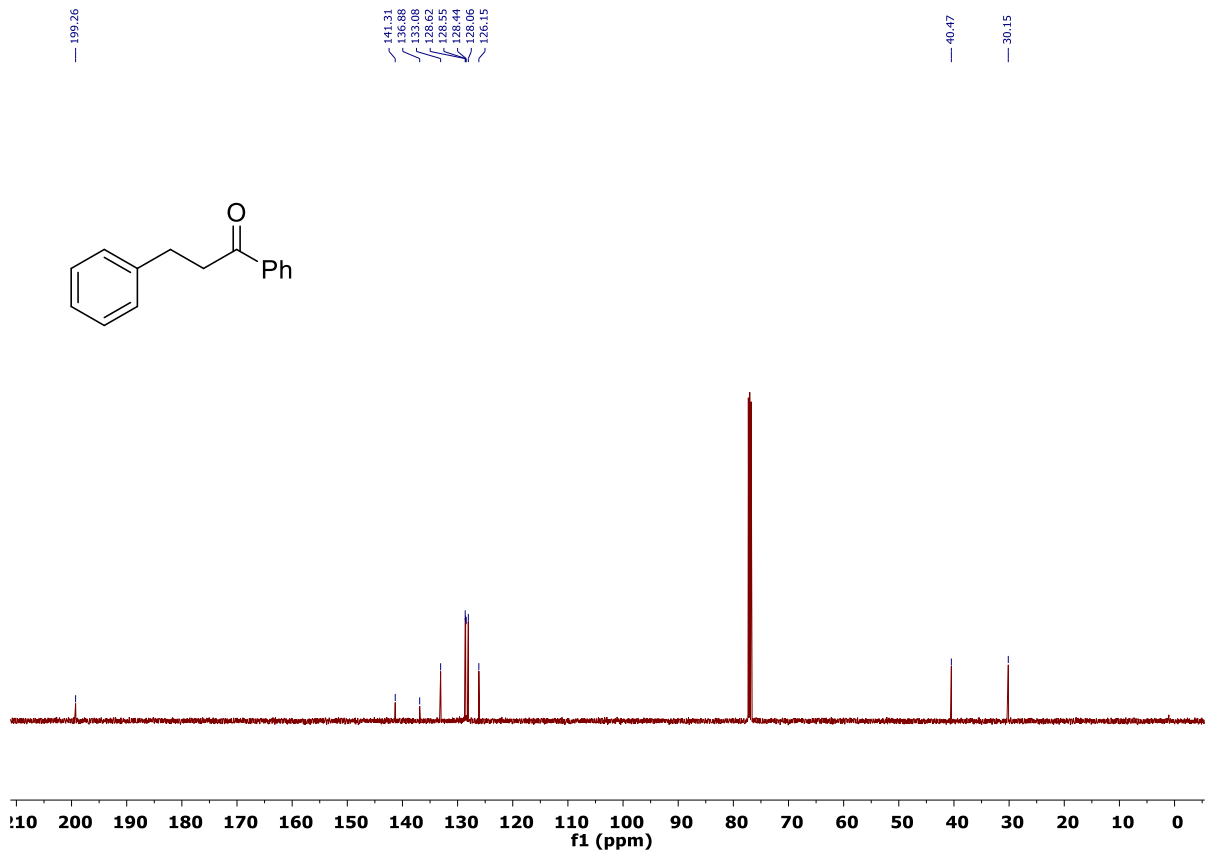


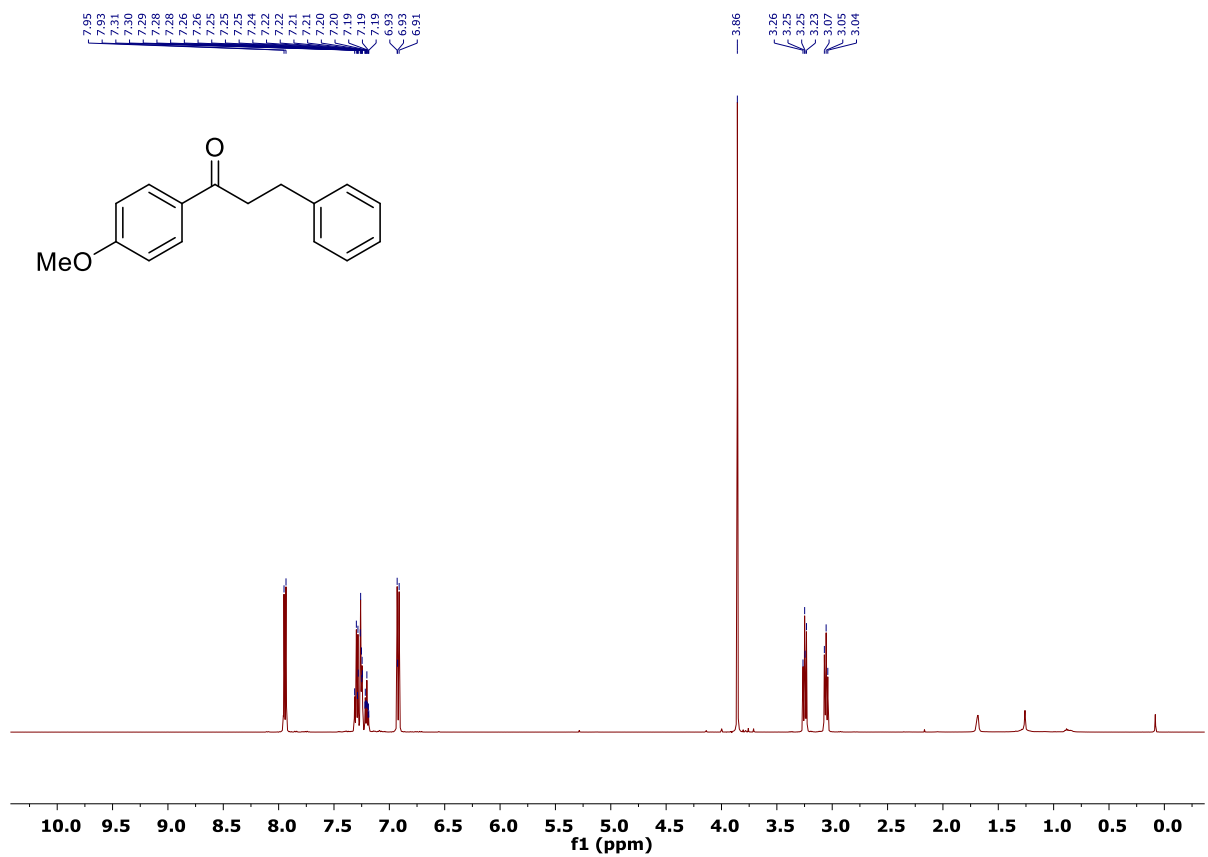
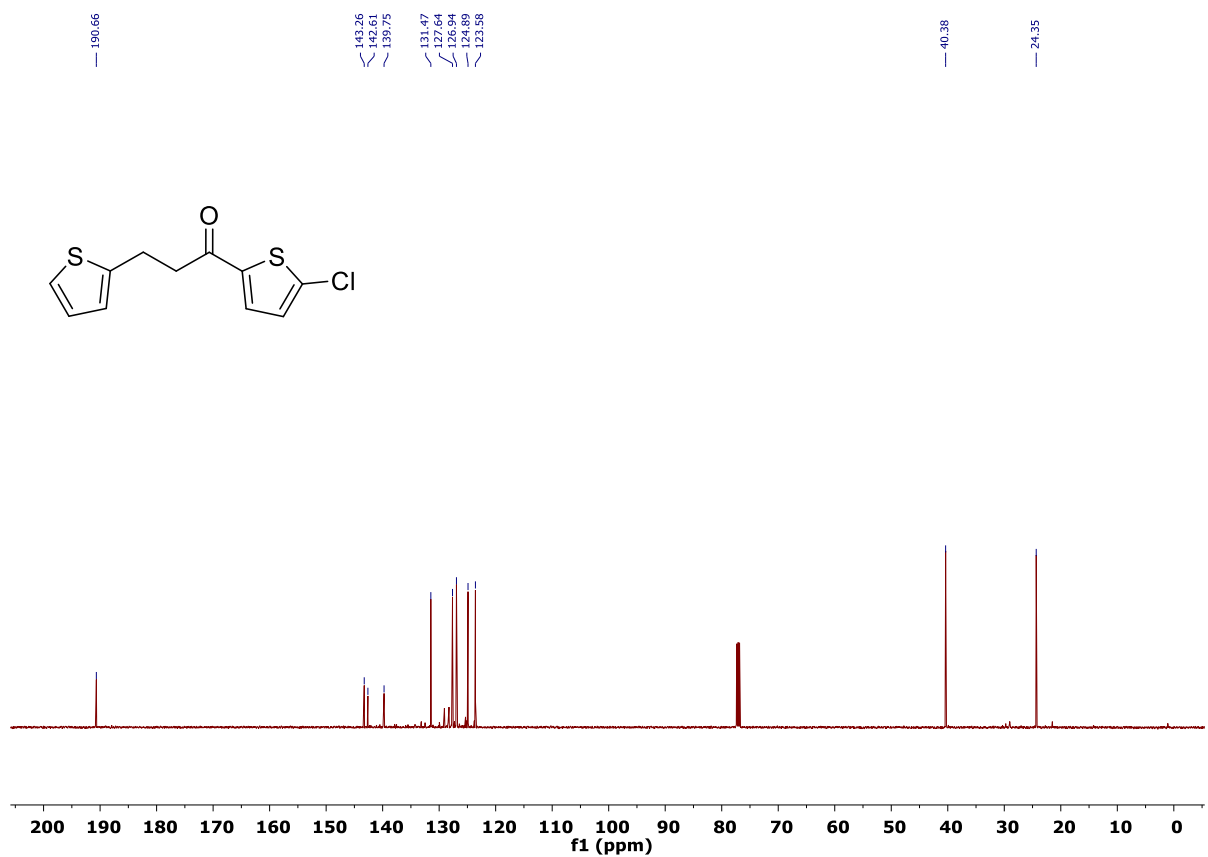


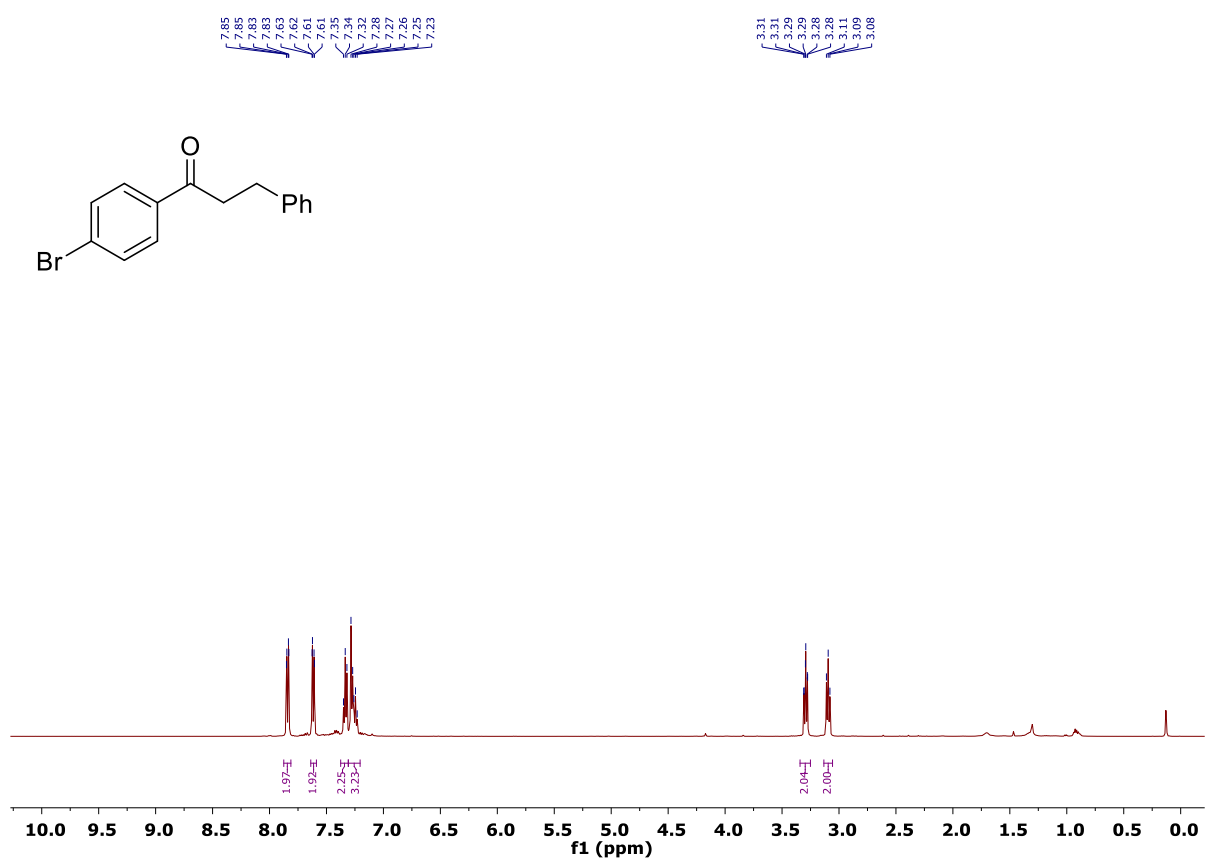
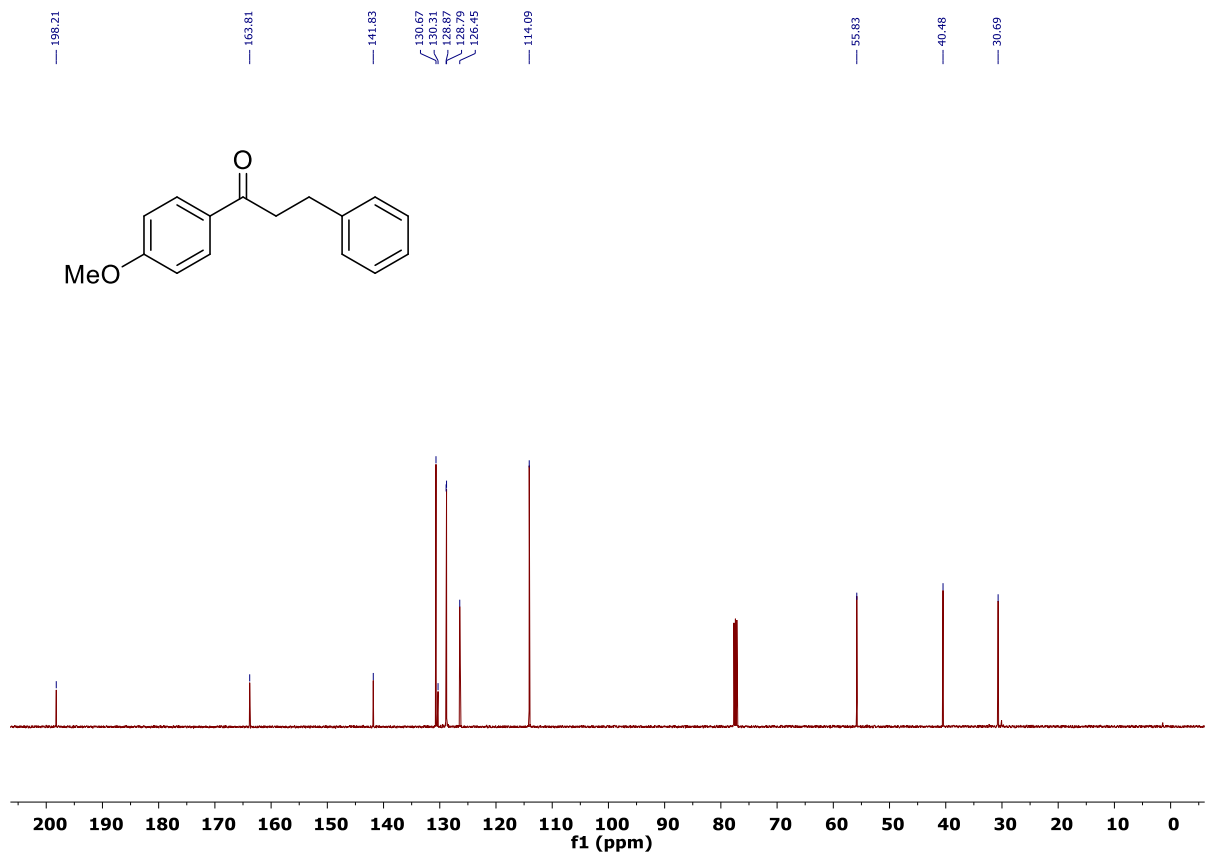


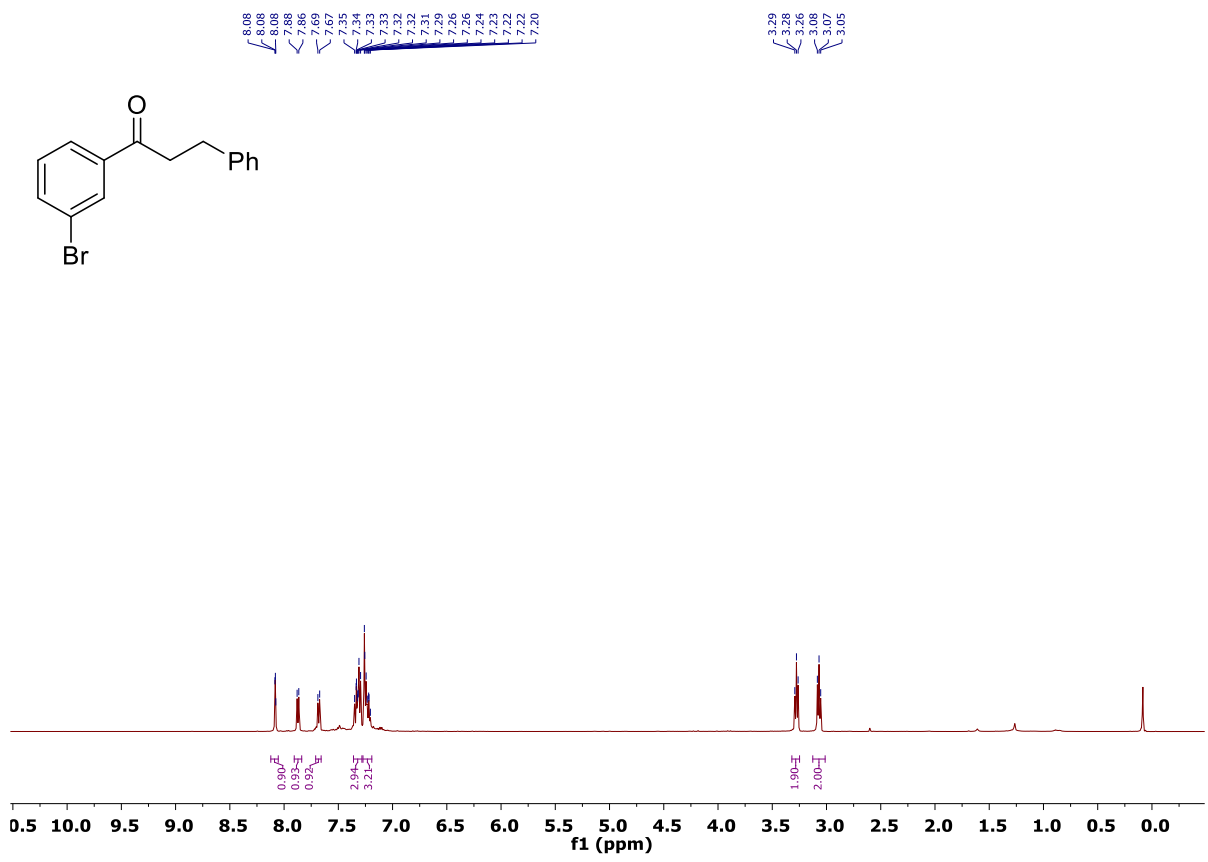
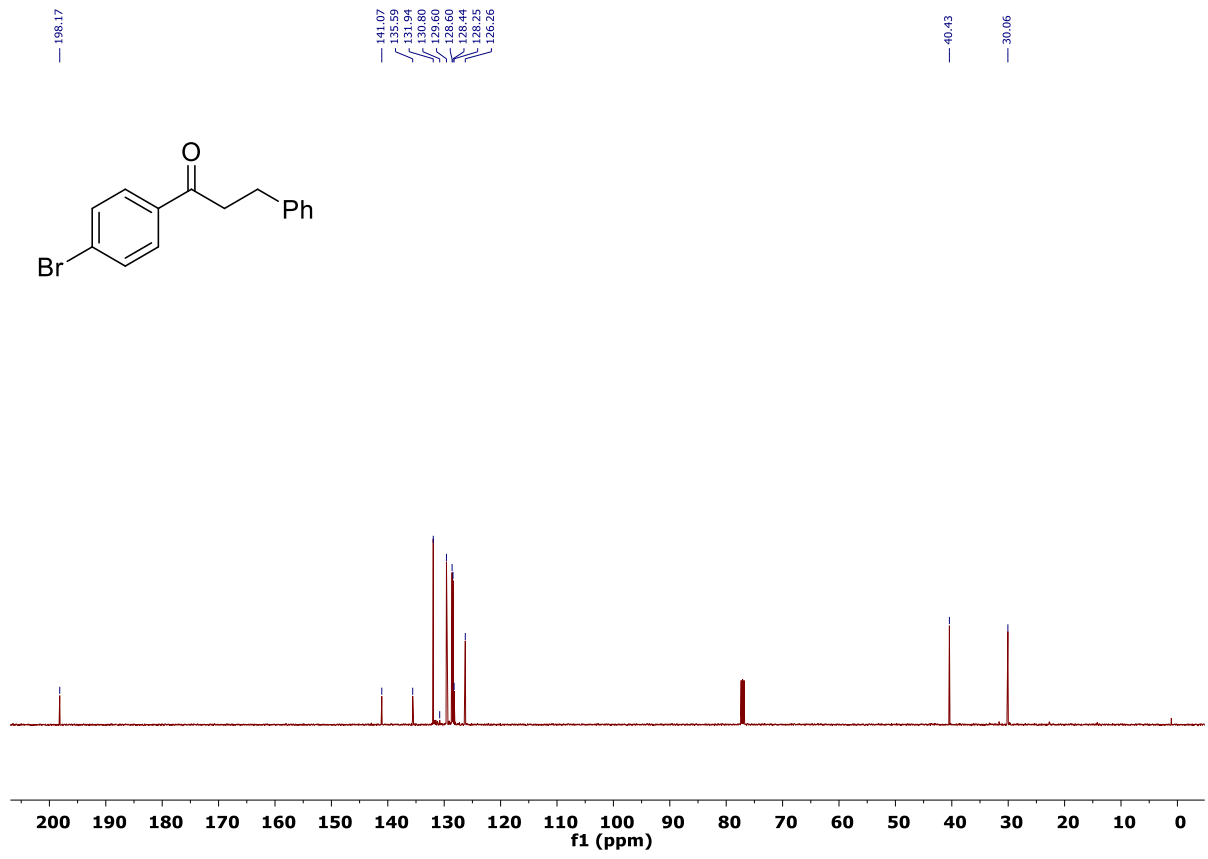


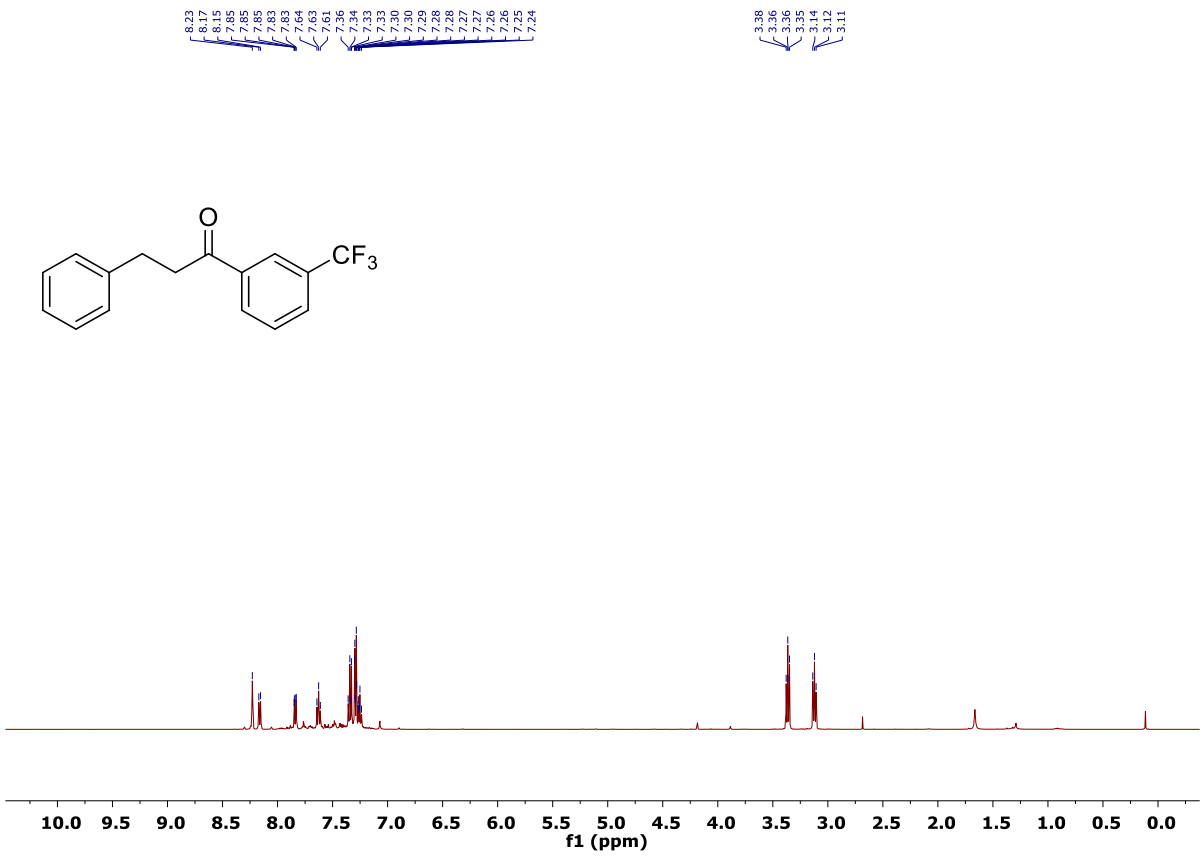
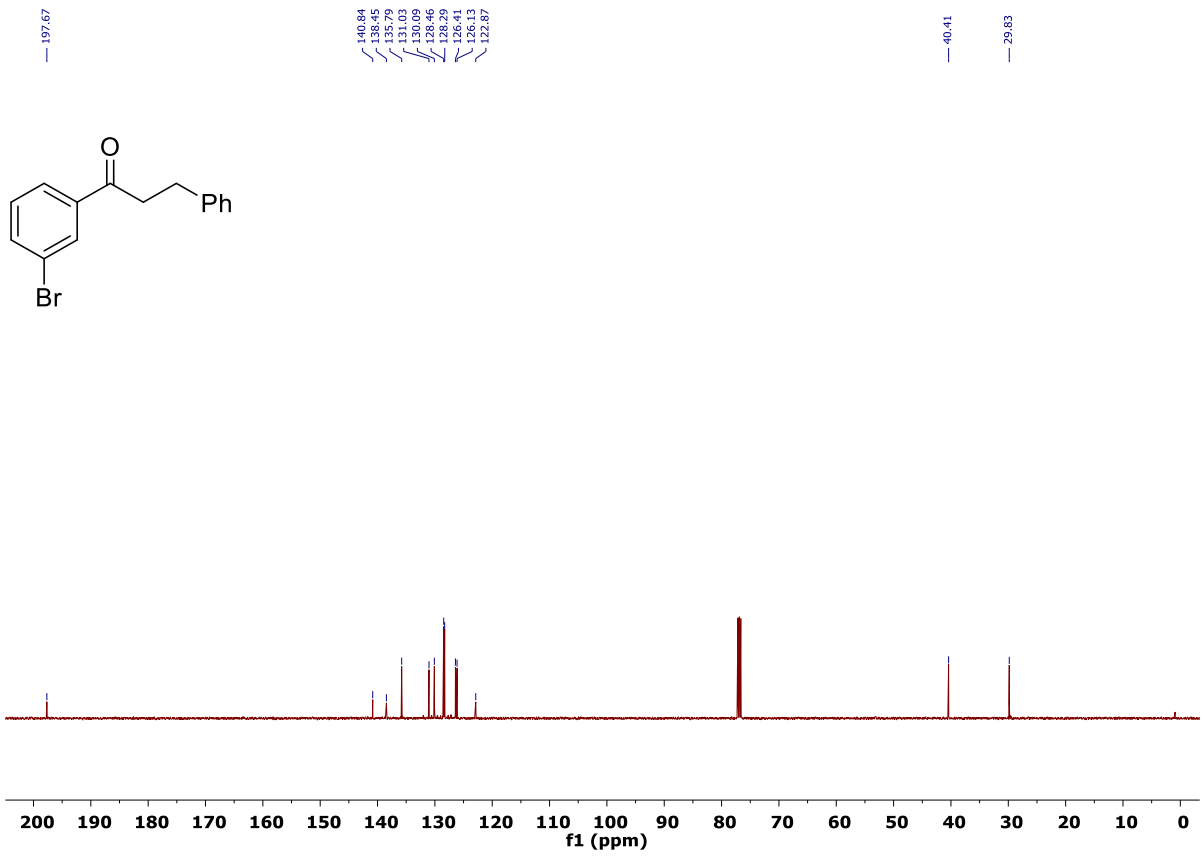


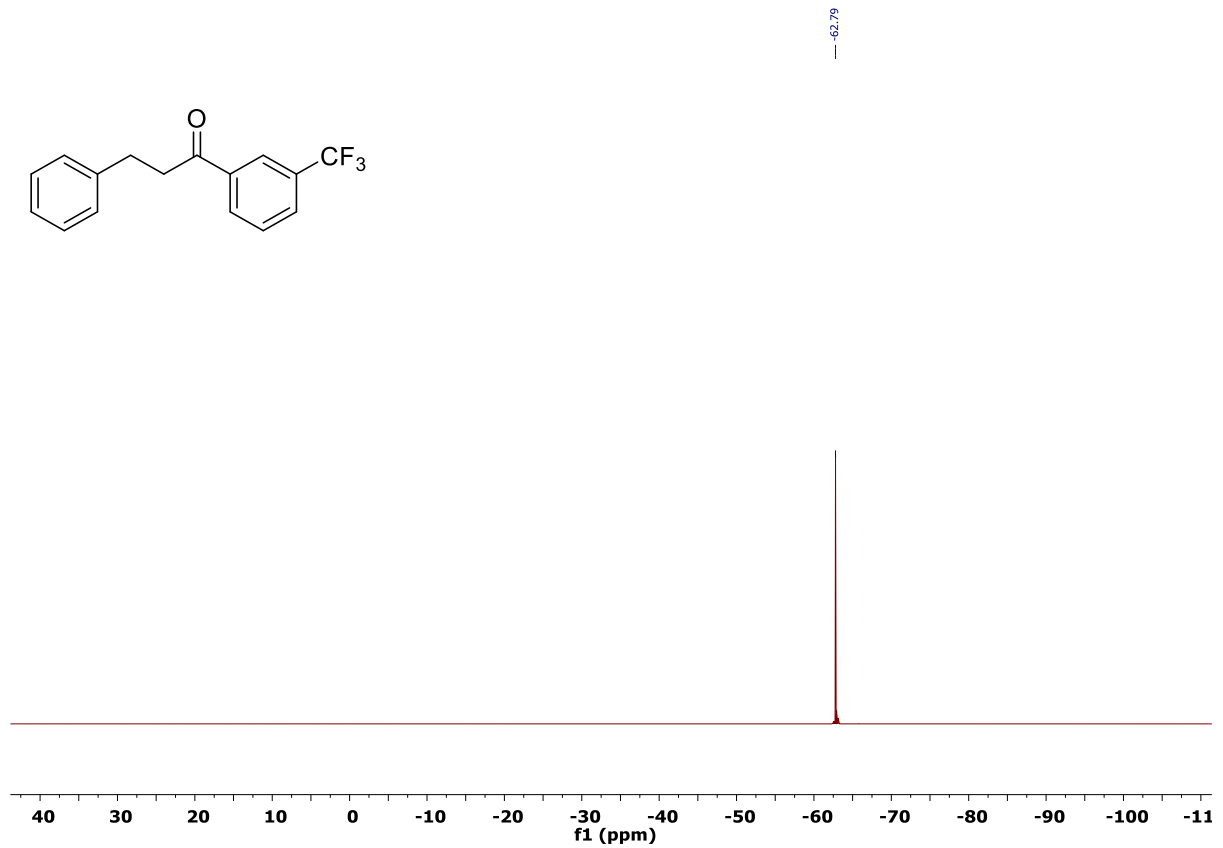
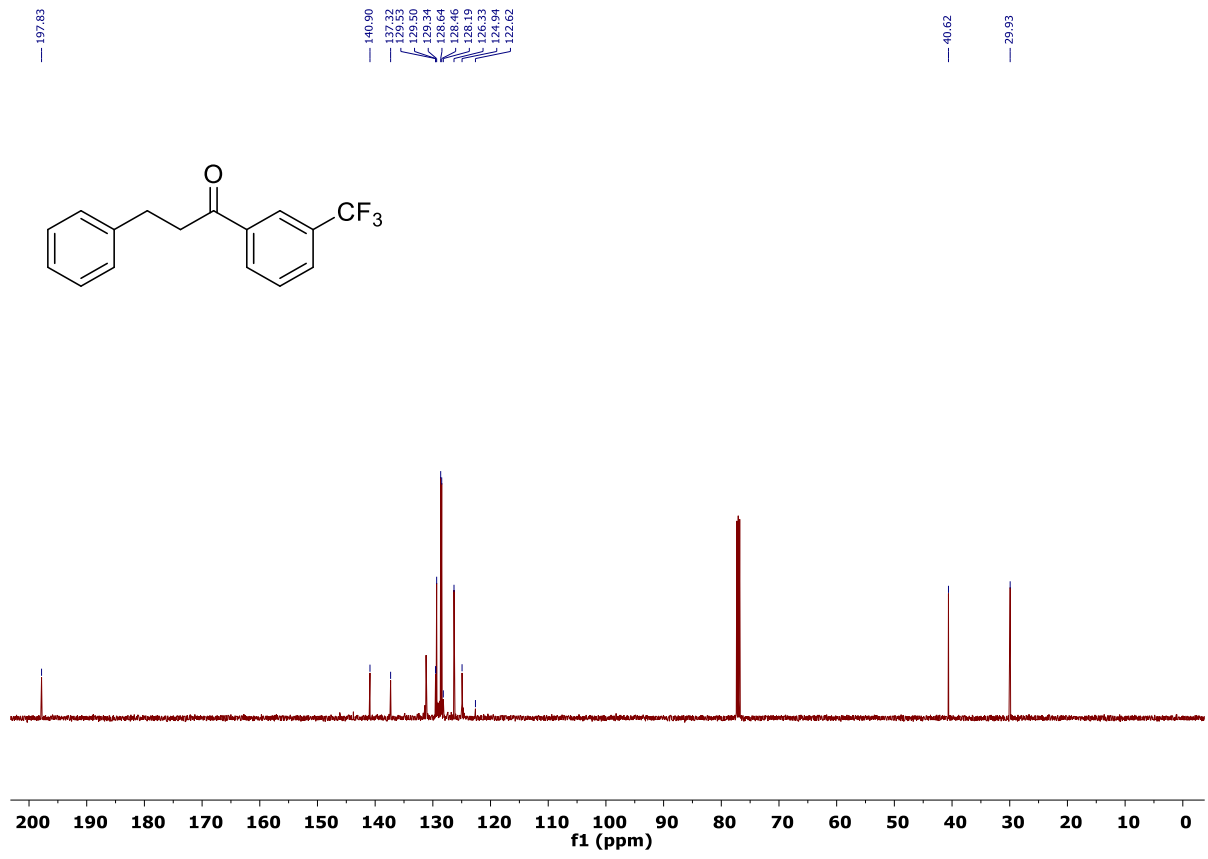


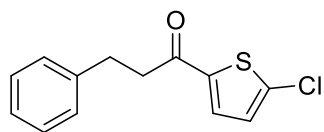






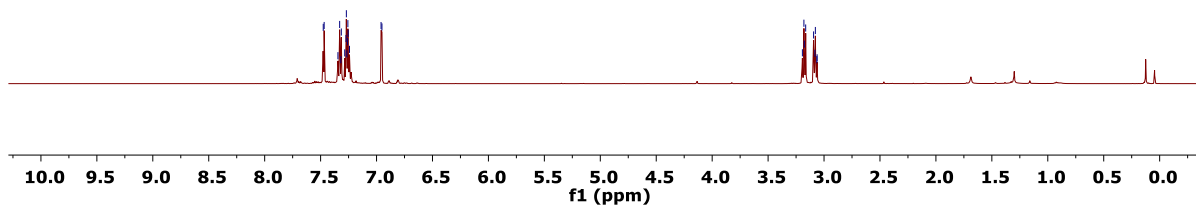






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3.06
3.06

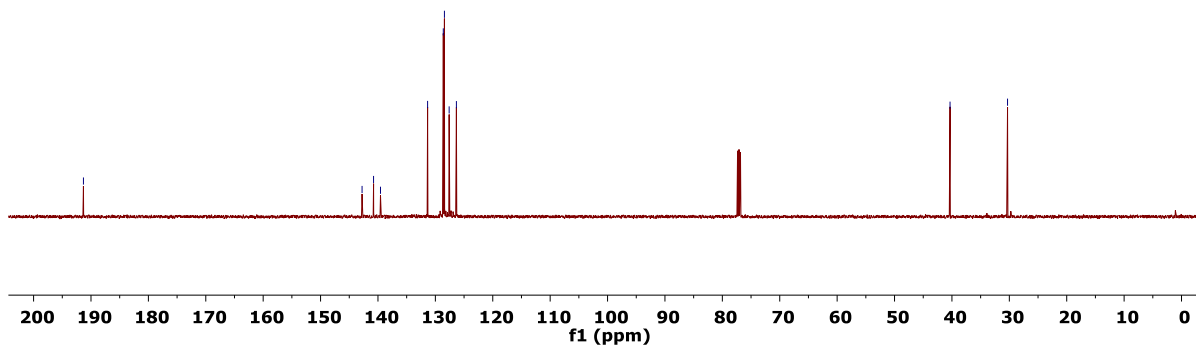
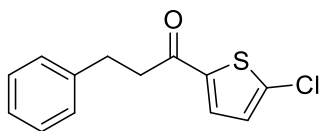


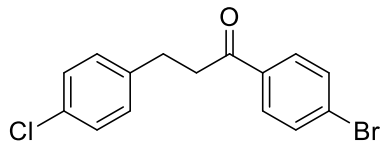
191.31

142.77
140.77
139.56
131.35
128.62
128.42
127.60
126.33

40.33

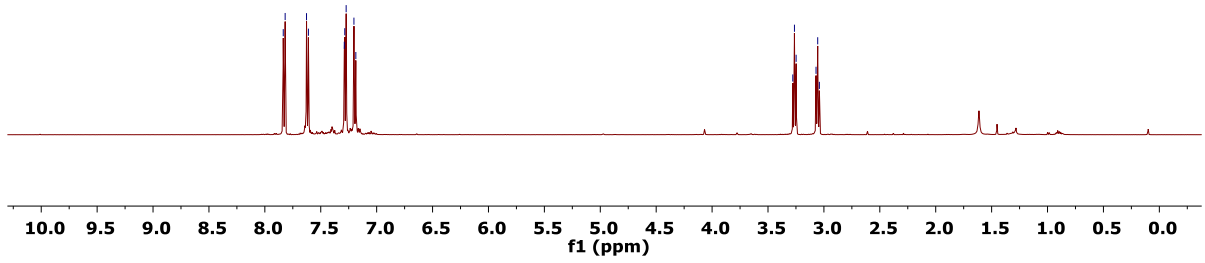
30.31





7.84
7.82
7.63
7.61
7.29
7.27
7.20
7.19

3.28
3.25
3.07
3.06
3.04

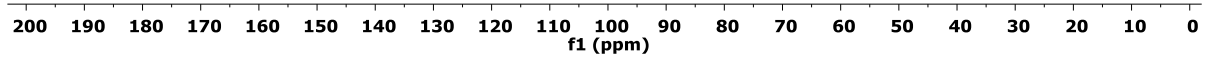
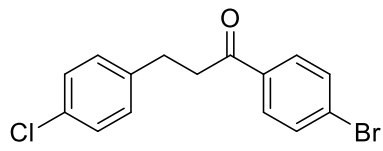


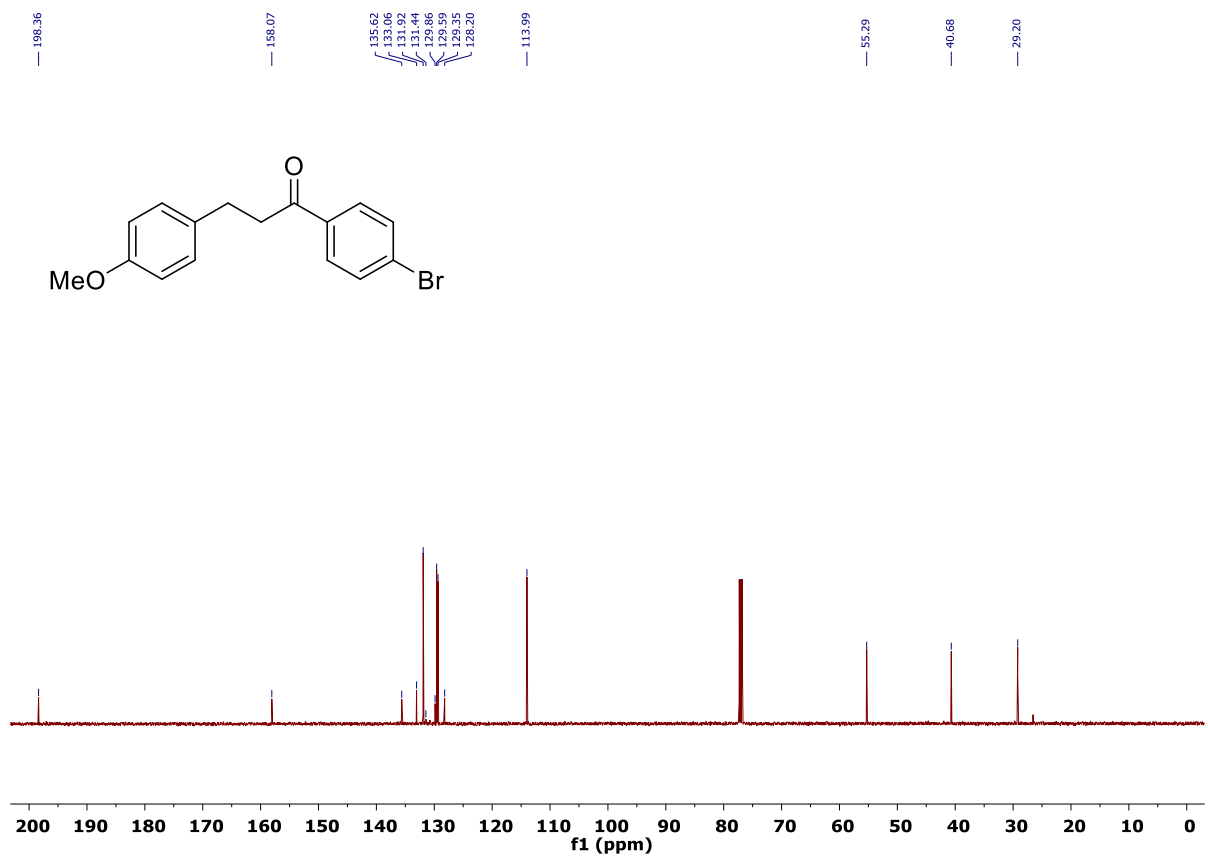
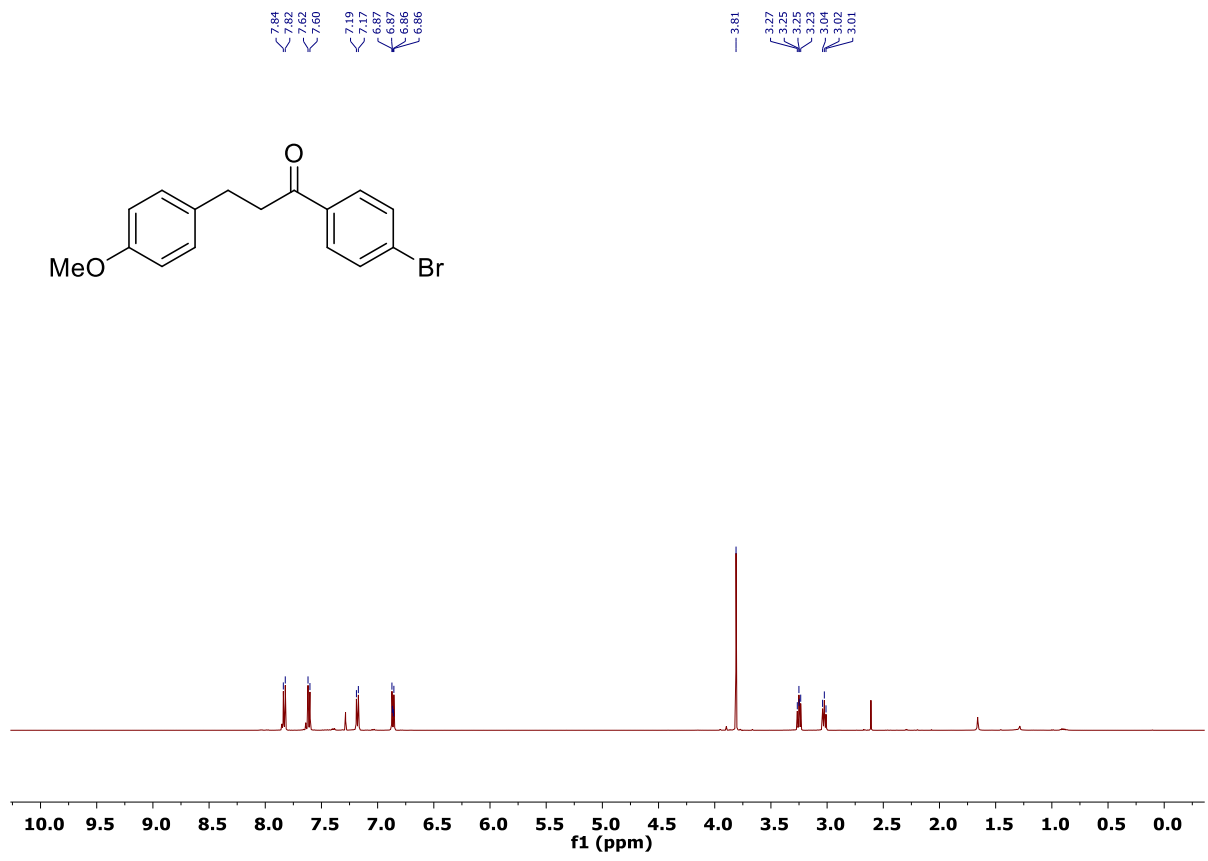
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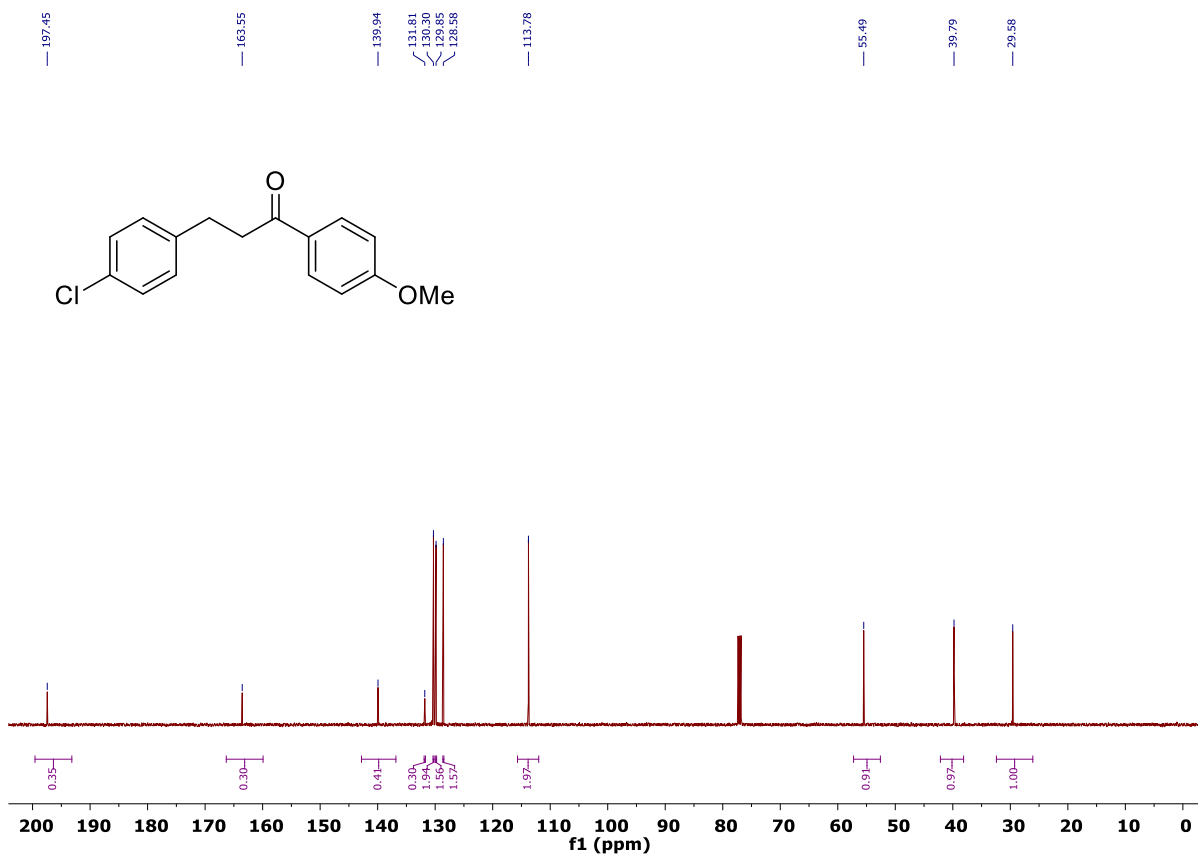
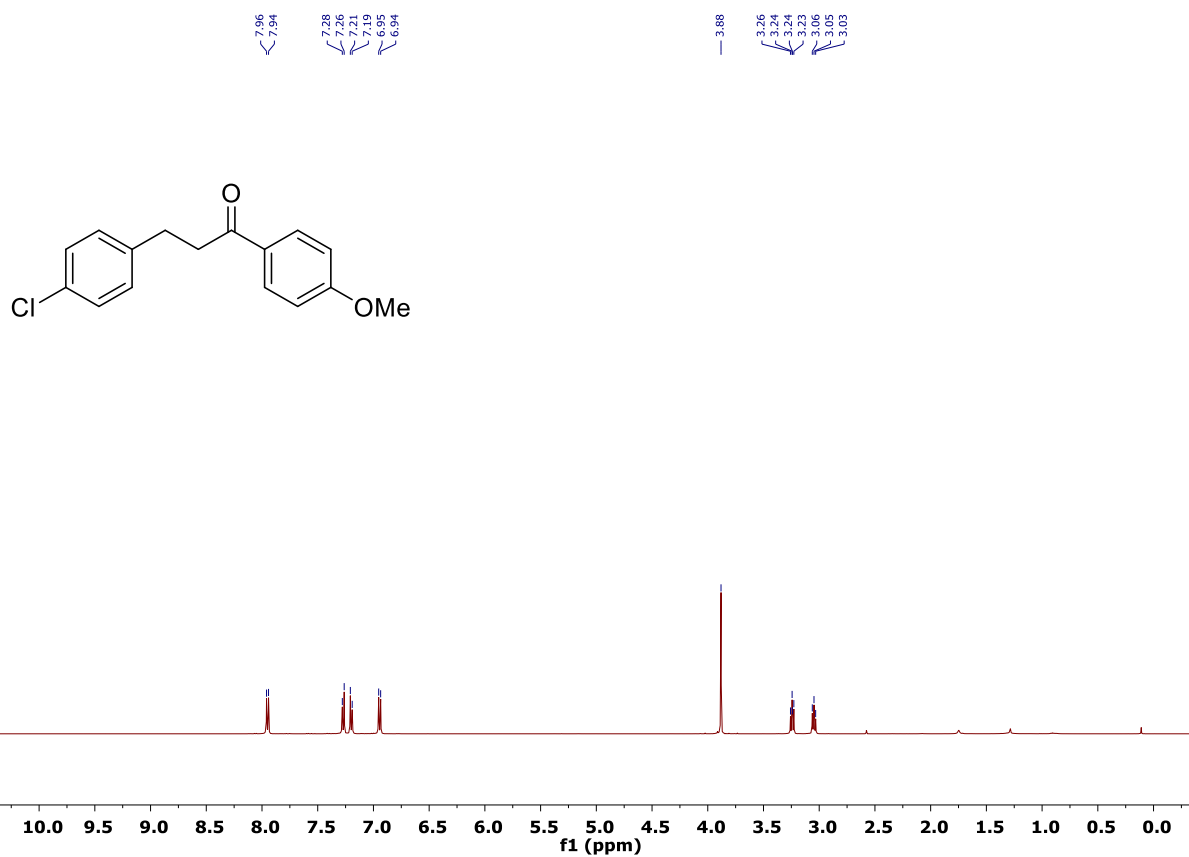
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128.66
126.38

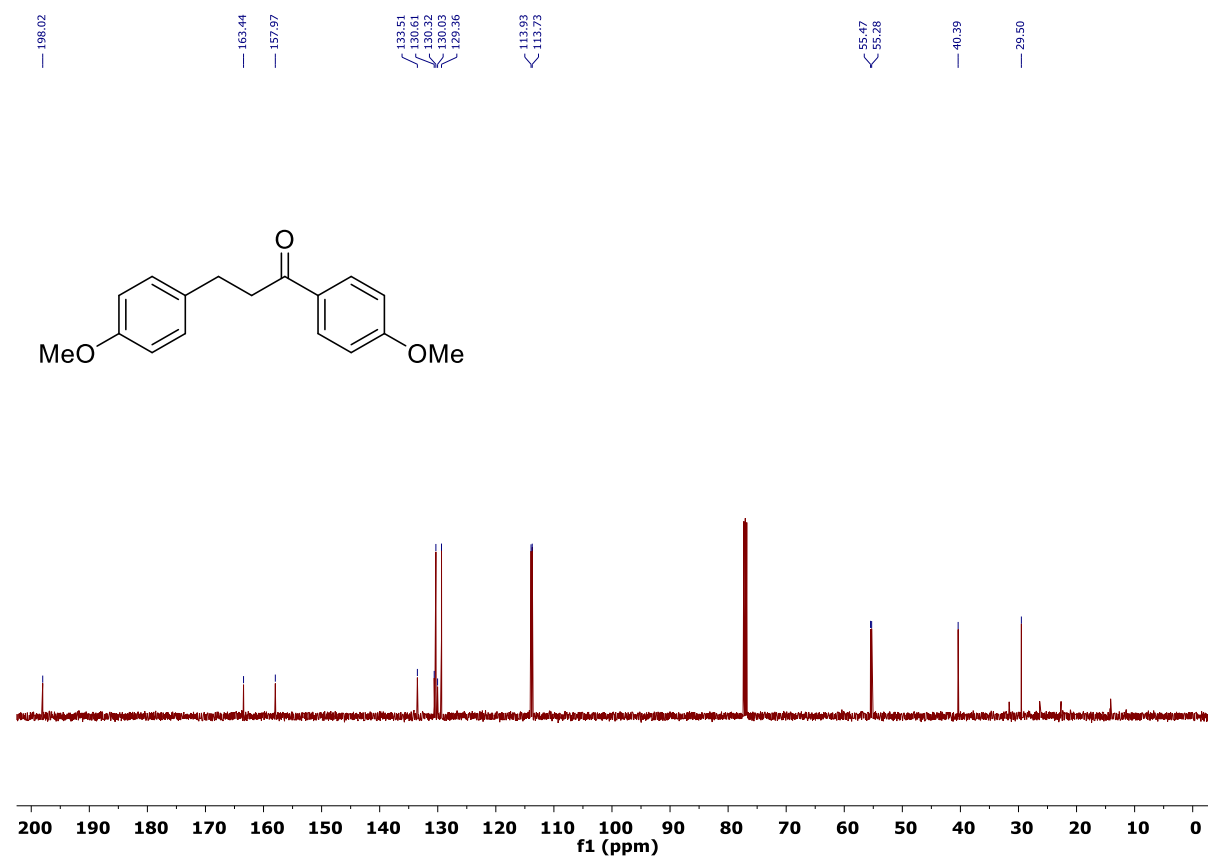
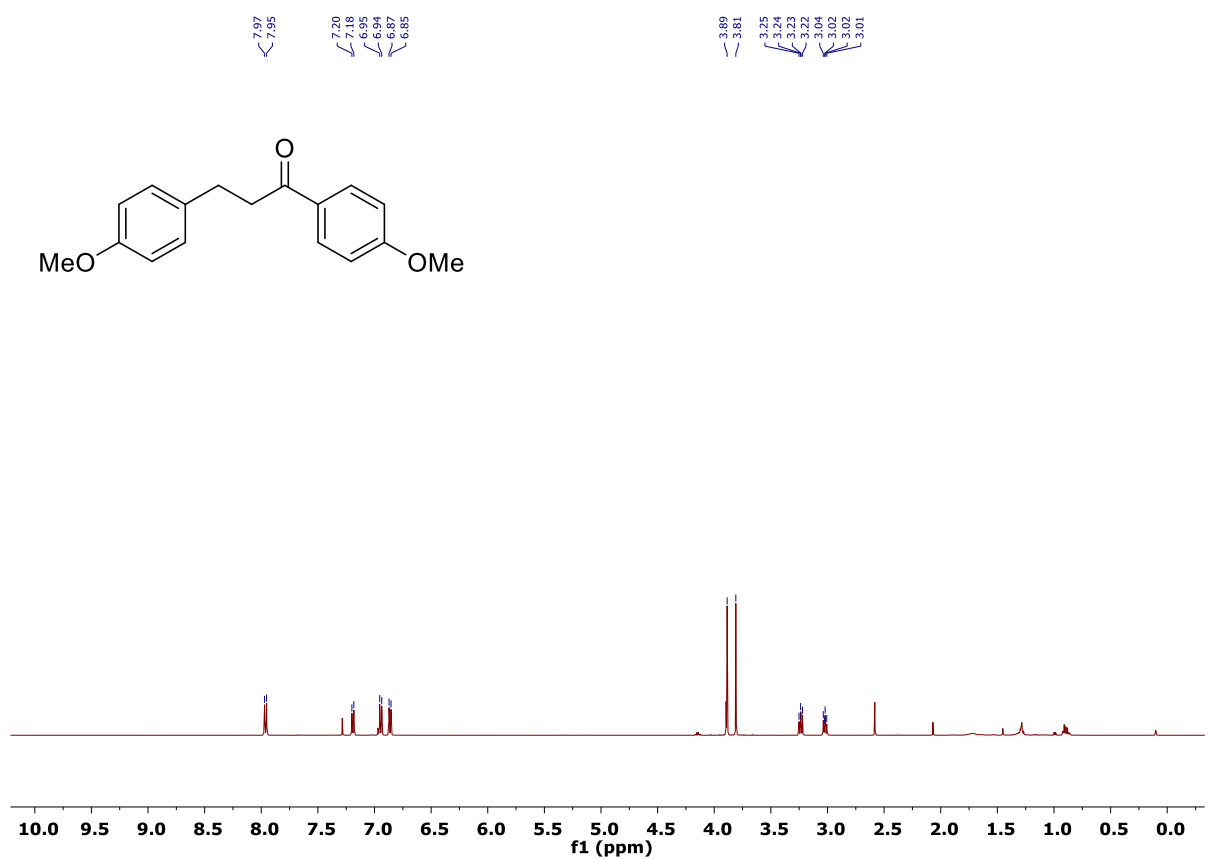
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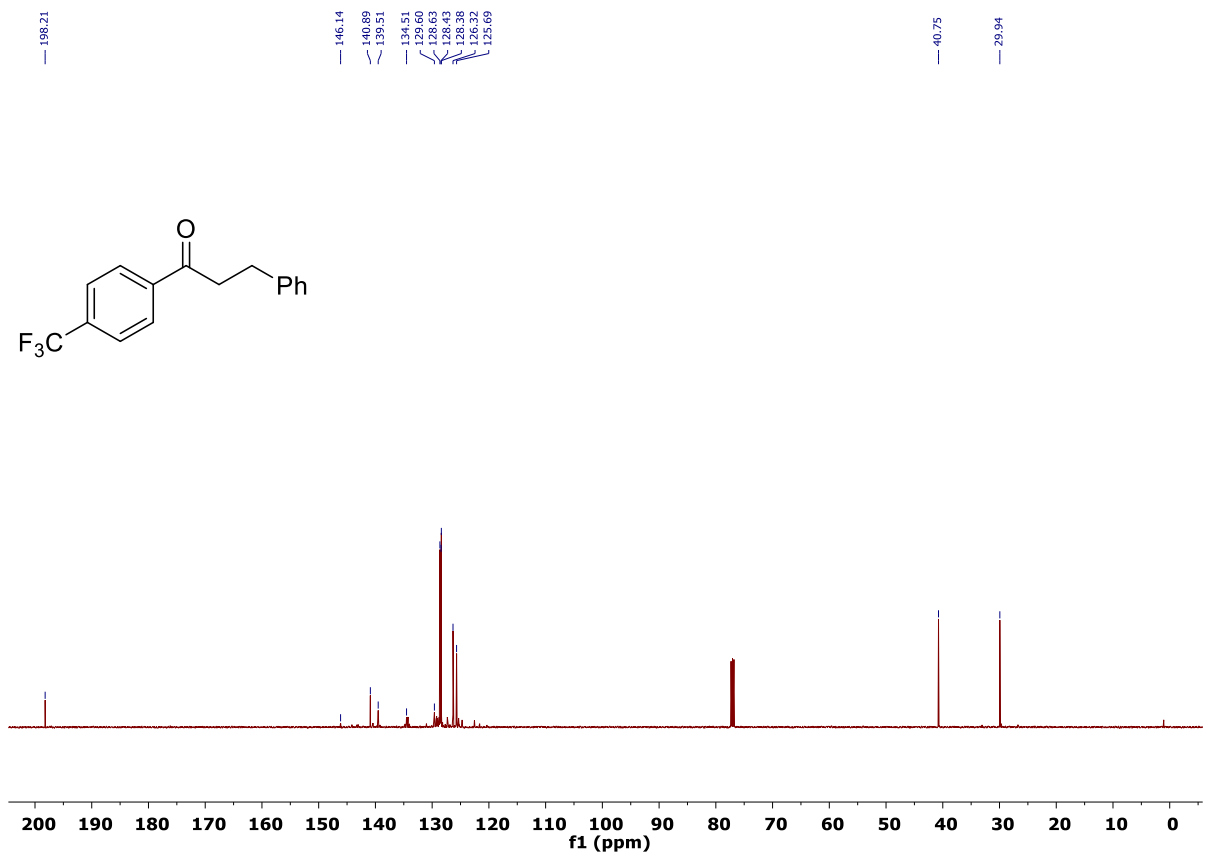
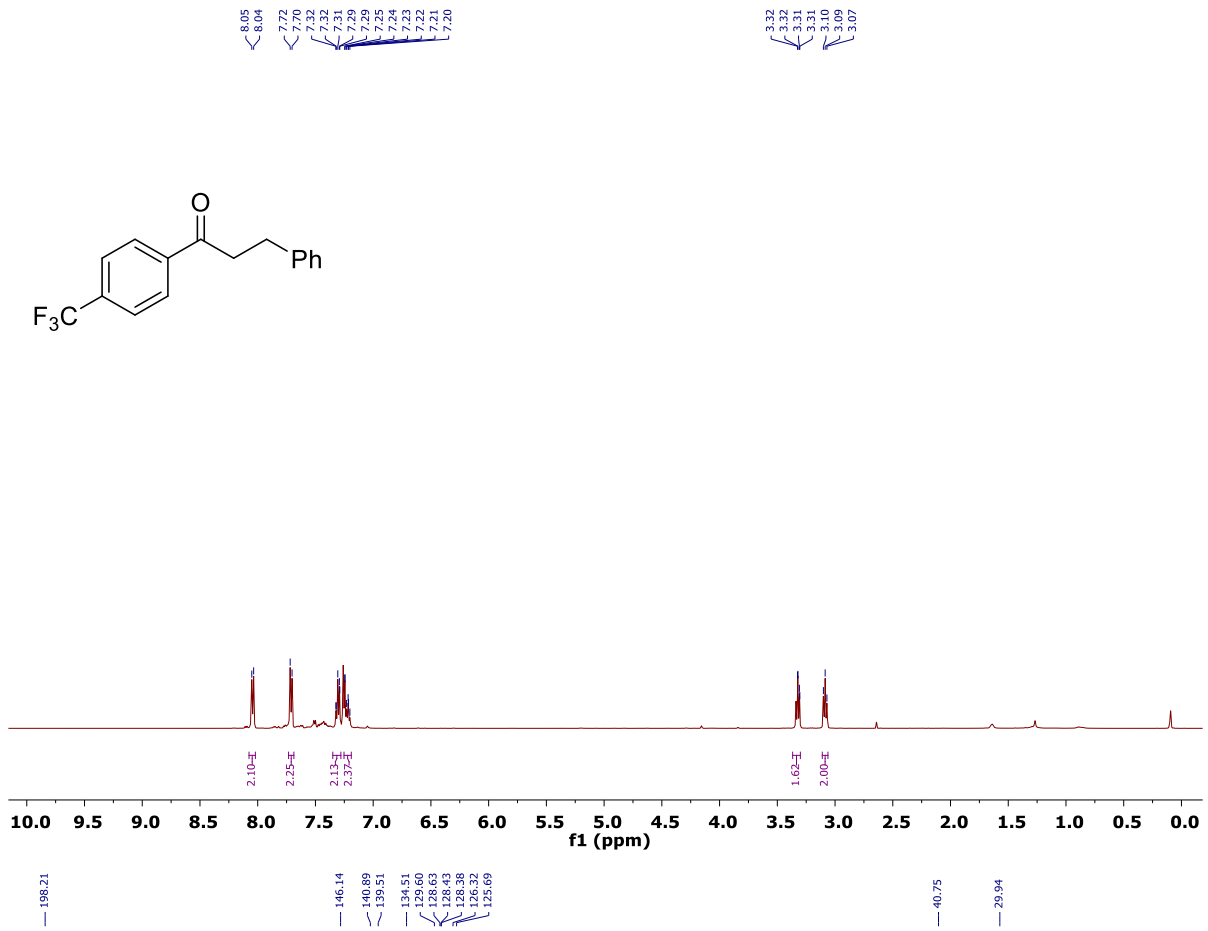
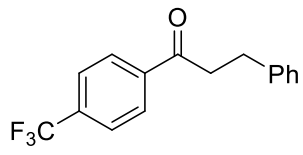
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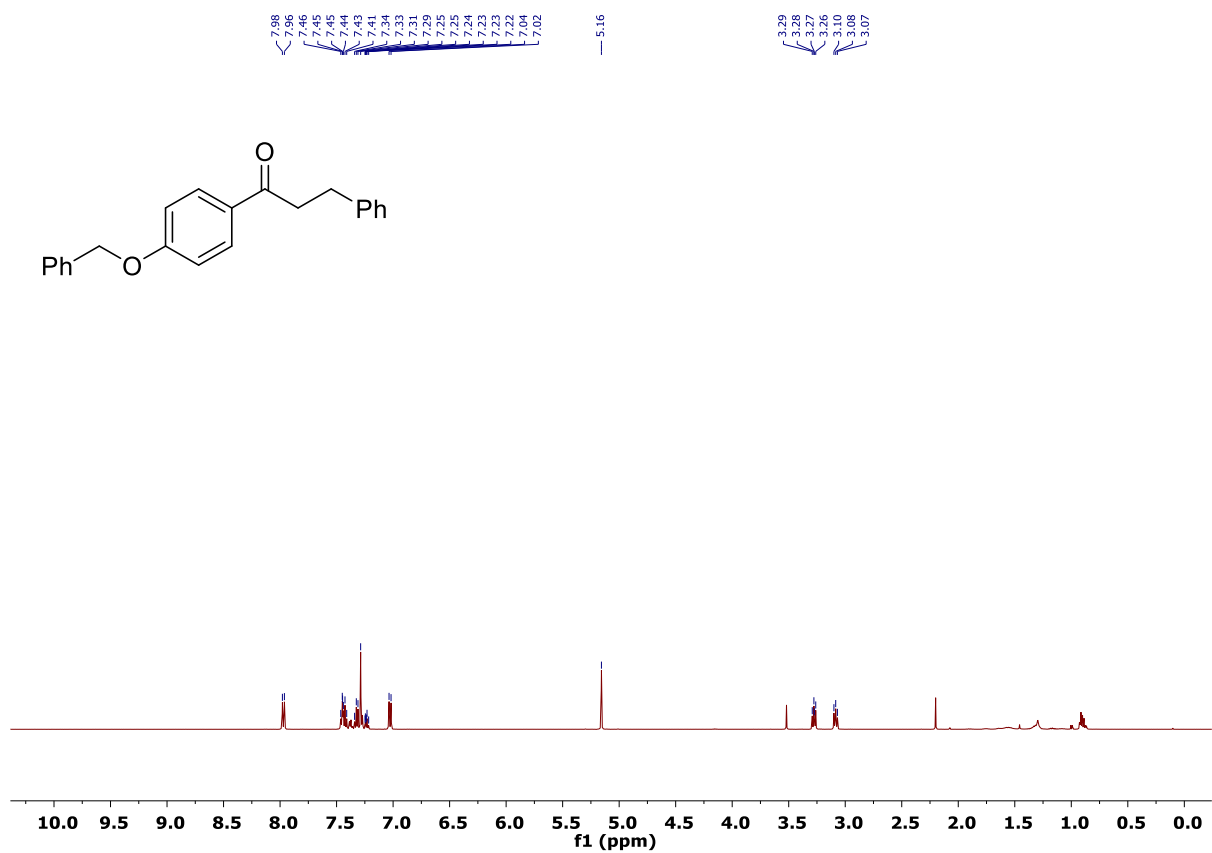
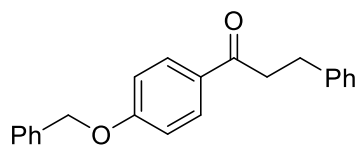
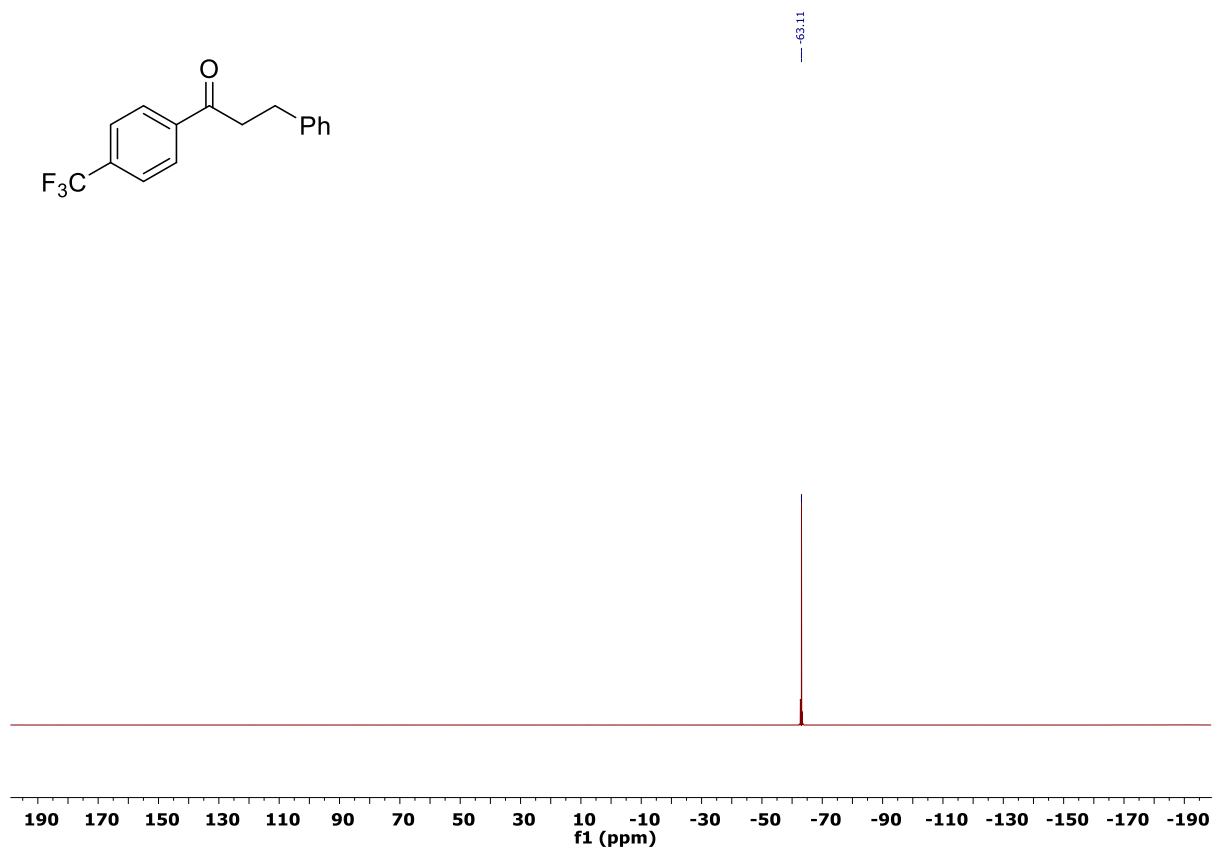
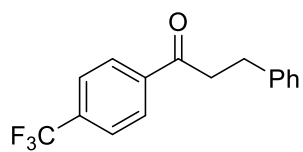


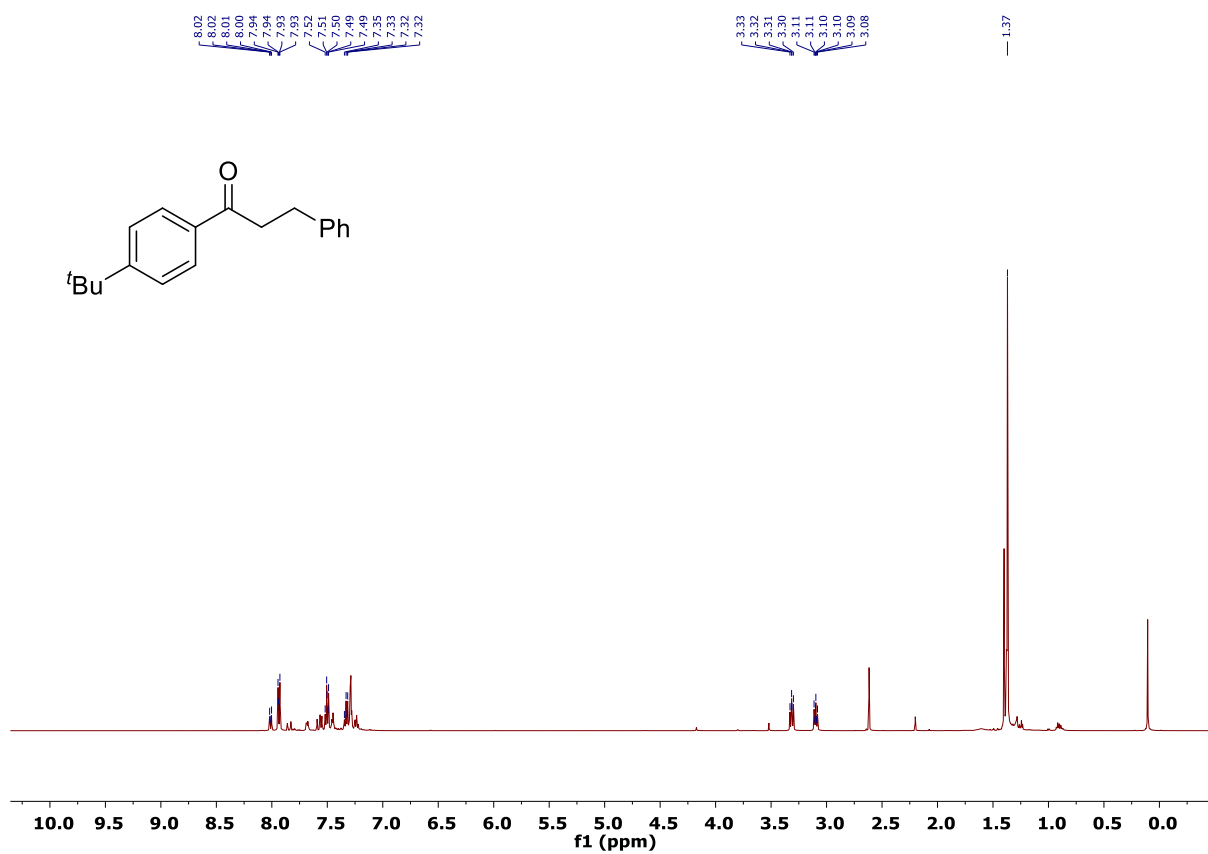
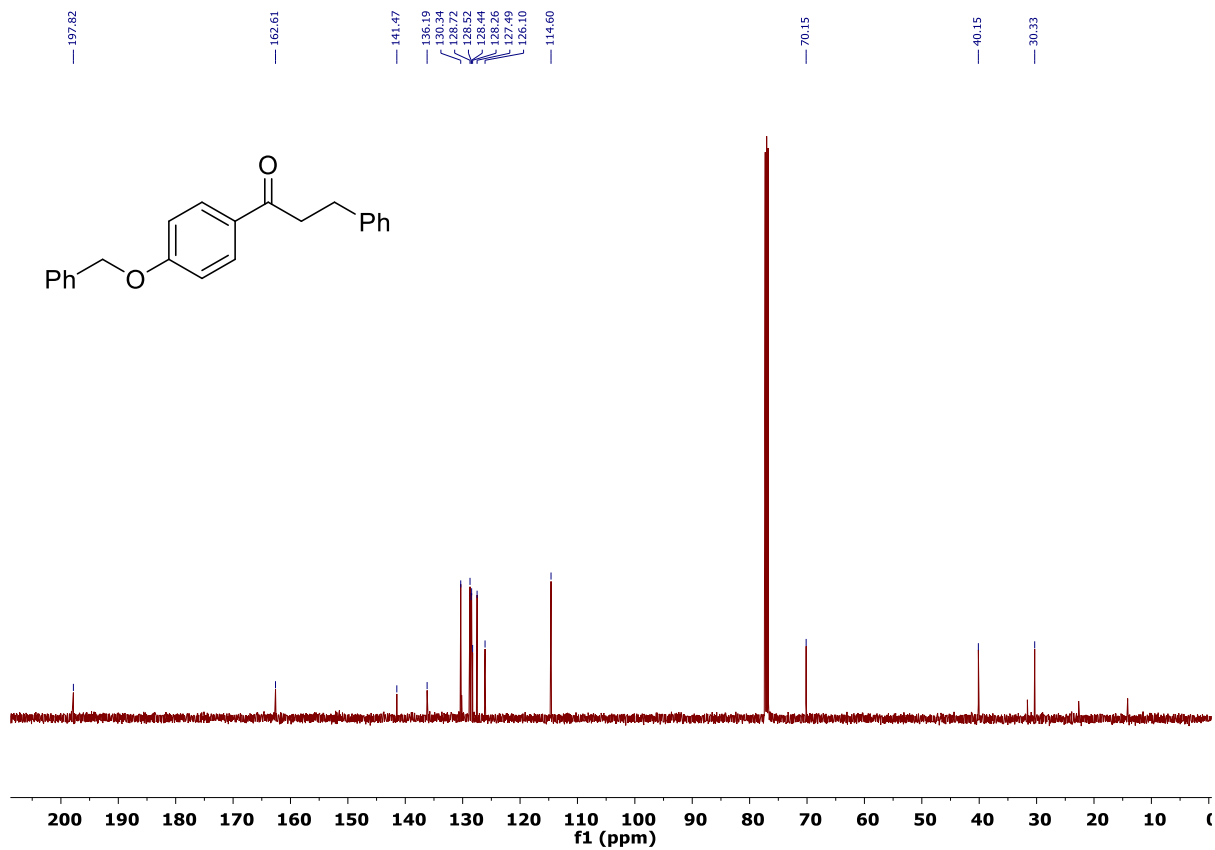


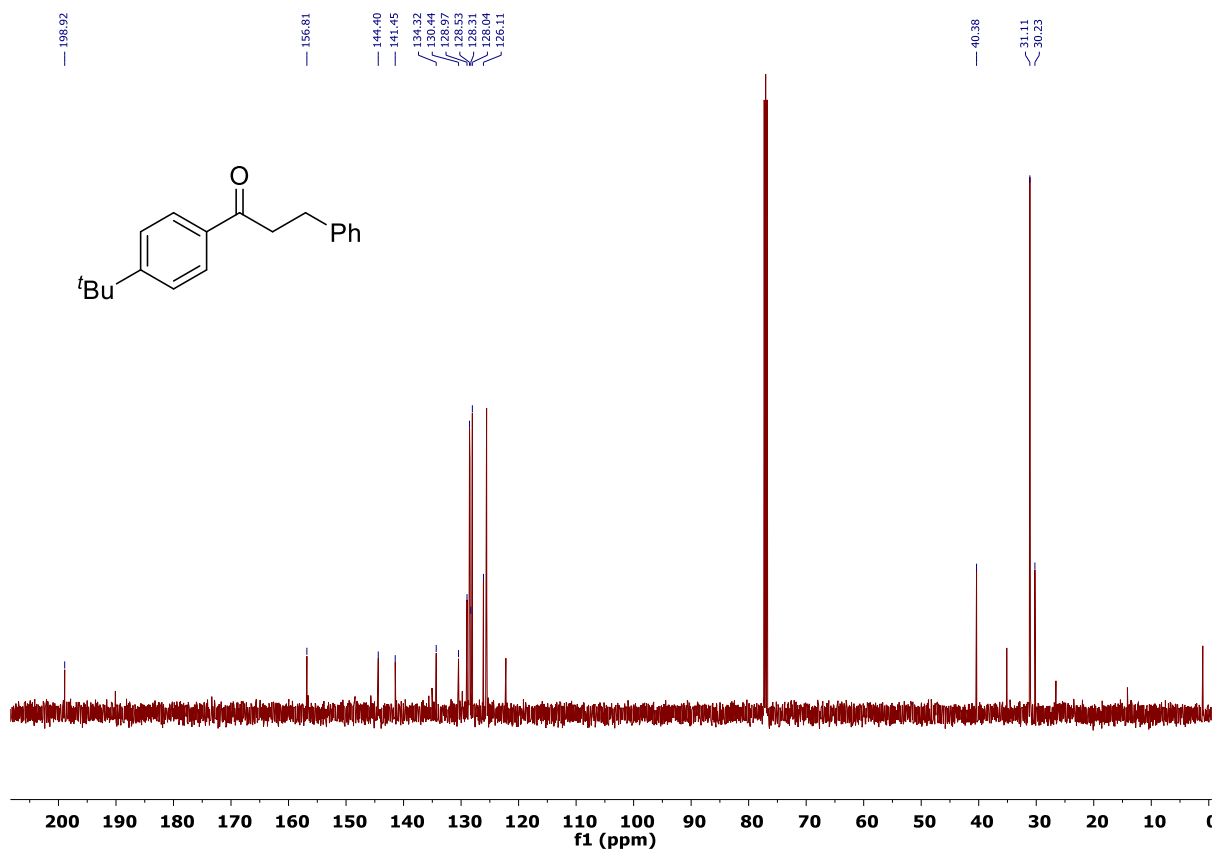












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