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Synthesis and Structure of Pd(II) Pincer Complexes: Catalytic Application to β-Alkylation of Secondary Alcohols Involving Sequential Dehydrogenation of Alcohols via Borrowing Hydrogen Approach

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1. Materials and methods

Chemically pure and analar grade reagents were used for all the reactions. Commercially available $[PdCl_2(PPh_3)_2]$, 4-dimethylamino-2-benzaldehyde, benzhydrazide derivatives, $CDCl_3$, DMSO-d_6 and various alcohols was used as supplied from Sigma Aldrich. The solvents were freshly distilled before use following the standard procedures.[1] Melting point was recorded in the Boeties micro heating table and is uncorrected. Infrared spectra of complexes were recorded in KBr pellets with a Perkin – Elmer 597 spectrophotometer in the range of 4000-400 cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 with Bruker 400 MHz instrument using TMS as internal reference. A Micro mass thermoscientific LTQ XL mass spectrometer was utilized for electrospray ionization mass spectrometry (ESI-MS).

2. X-ray crystallographic data collection

Single crystals of complexes **3** were grown by slow evaporation of dichloromethane in methanol solution at room temperature. A single crystal of suitable size was covered with Paratone oil, mounted on the top of glass fiber, and transferred to a Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated MoKα radiation (λ = 0.71073). Data were collected at 293 K. The structure was solved by direct methods using SIR-97 and was refined by the full matrix least-squares method on F^2 with SHELXL-97.[2] Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and collected to refine using a riding model. Frame integration and data reduction were performed using the Bruker SAINT Plus (Version 7.06a) software. The multiscan absorption corrections were applied to the data using SADABS software.[3]

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Table S1. Crystal data and structure refinement for complex 3.

CCDC	2191316
Empirical formula	$C_{37}H_{36}N_3O_3PPd$
Formula weight	708.06
Temperature/K	298(2)
Crystal system	orthorhombic
Space group	*F d d 2*
a/Å, b/Å, c/Å	23.9295(12), 52.455(3), 10.7669(6)
α/°, β/°, γ/°	90, 90, 90
Volume/Å^3	13514.8(12)
Z	16
ρcalc g/cm3	1.392
m/mm-1	0.636
F(000)	5824
Crystal size/mm	0.150 x 0.220 x 0.270
Theta range for data collection	2.11 to 30.09°
Index ranges	-33<=h<=32, -73<=k<=72, -15<=l<=14
Reflections collected	74297
Independent reflections	9273 [R(int) = 0.0641]
Data/restraints/parameters	9273 / 1 / 409
Goodness-of-fit on F^2	0.923
Final R indexes [I>2σ (I)]	R1 = 0.0340, wR2 = 0.1034
Final R indexes [all data]	R1 = 0.0541, wR2 = 0.1267
Largest diff. peak and hole / eÅ^{-3}	0.459 and -0.682

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Table S2. Selected bond lengths (Å) and bond angles (°) for complexes 3.

Complex 3	
Pd(1)- N(1)	1.974(4)
Pd(1)-O(1)	1.989(3)
Pd(1)-O(2)	1.969(3)
Pd(1)-P(1)	2.2827(12)
N(1)-Pd(1)-O(1)	80.29(16)
O(2)-Pd(1)-N(1)	94.56(16)
O(2)-Pd(1)-O(1)	174.8(2)
O(2)-Pd(1)-P(1)	90.30(15)
N(1)-Pd(1)-P(1)	172.76(11)
O(1) Pd(1) P(1)	94.82(13)

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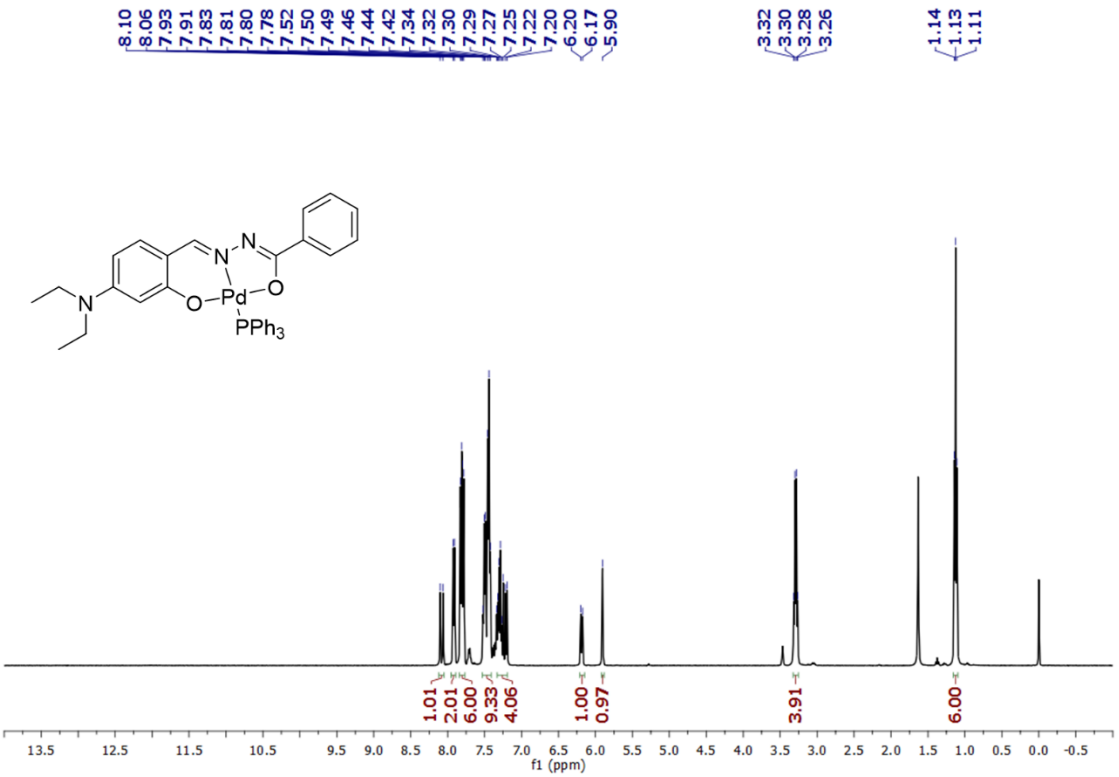

Figure S1. ^{1}H NMR spectrum of complex **1** in $CDCl_3$ (400 MHz, 293 K).

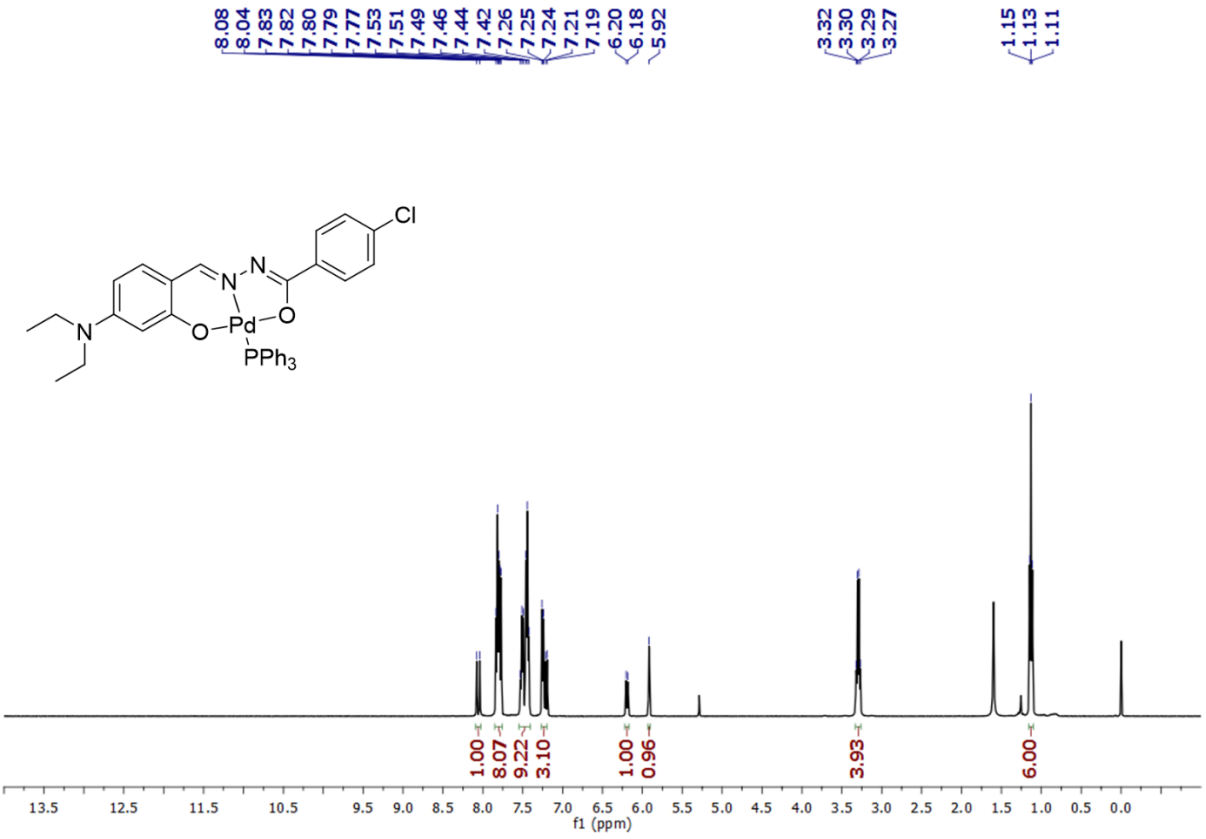

Figure S2. ^{1}H NMR spectrum of complex **2** in $CDCl_3$ (400 MHz, 293 K).

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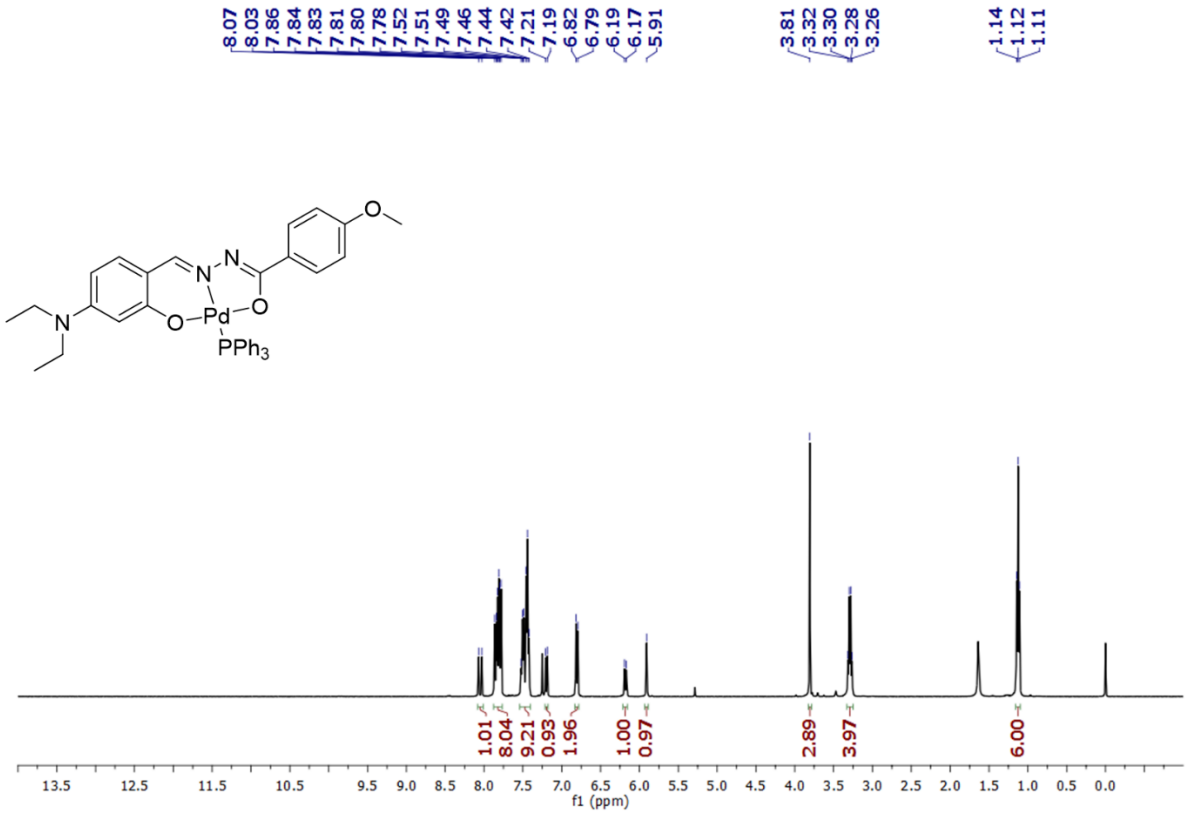

Figure S3. ^{1}H NMR spectrum of complex **3** in $CDCl_3$ (400 MHz, 293 K).

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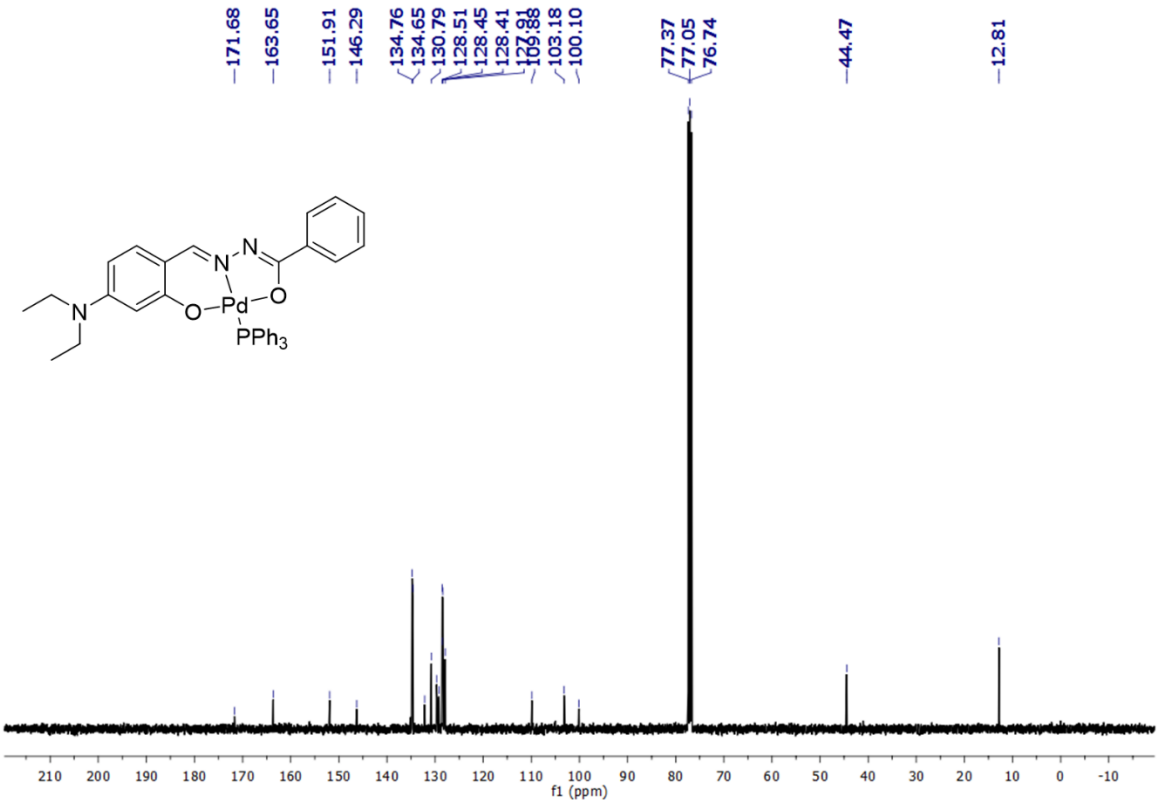

Figure S4. ^{13}C NMR spectrum of complex **1** in $CDCl_3$(100 MHz, 293 K).

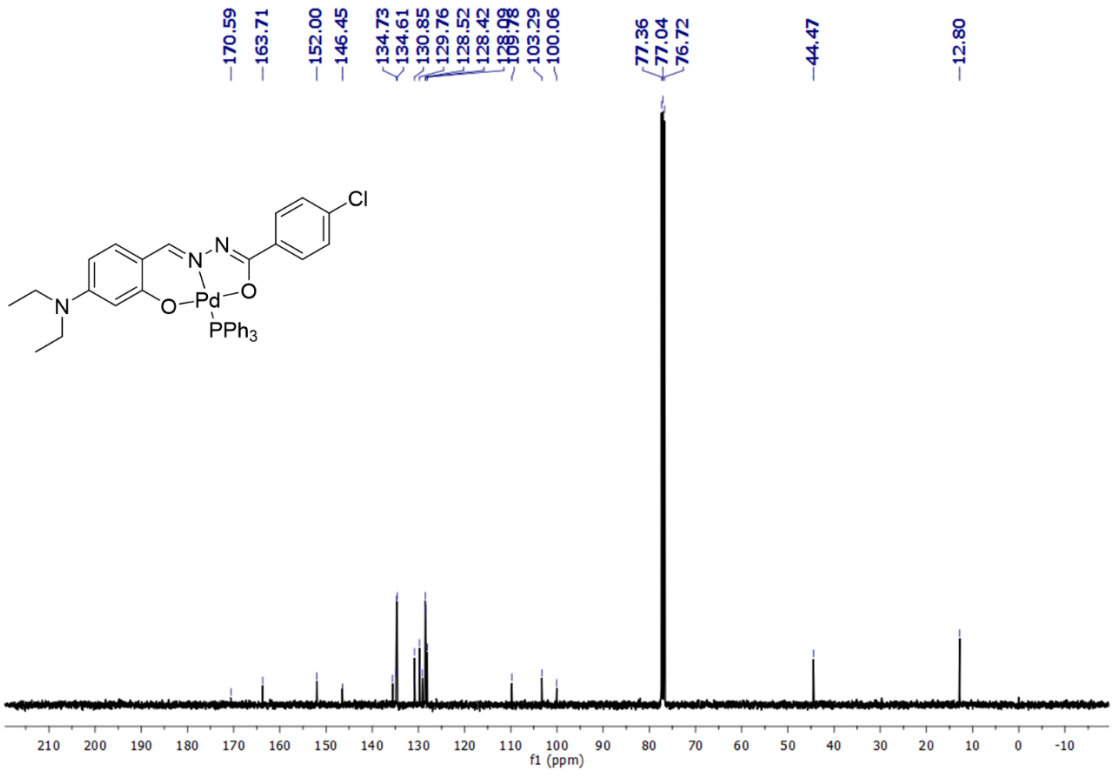

Figure S5. ^{13}C NMR spectrum of complex **2** in $CDCl_3$ (100 MHz, 293 K).

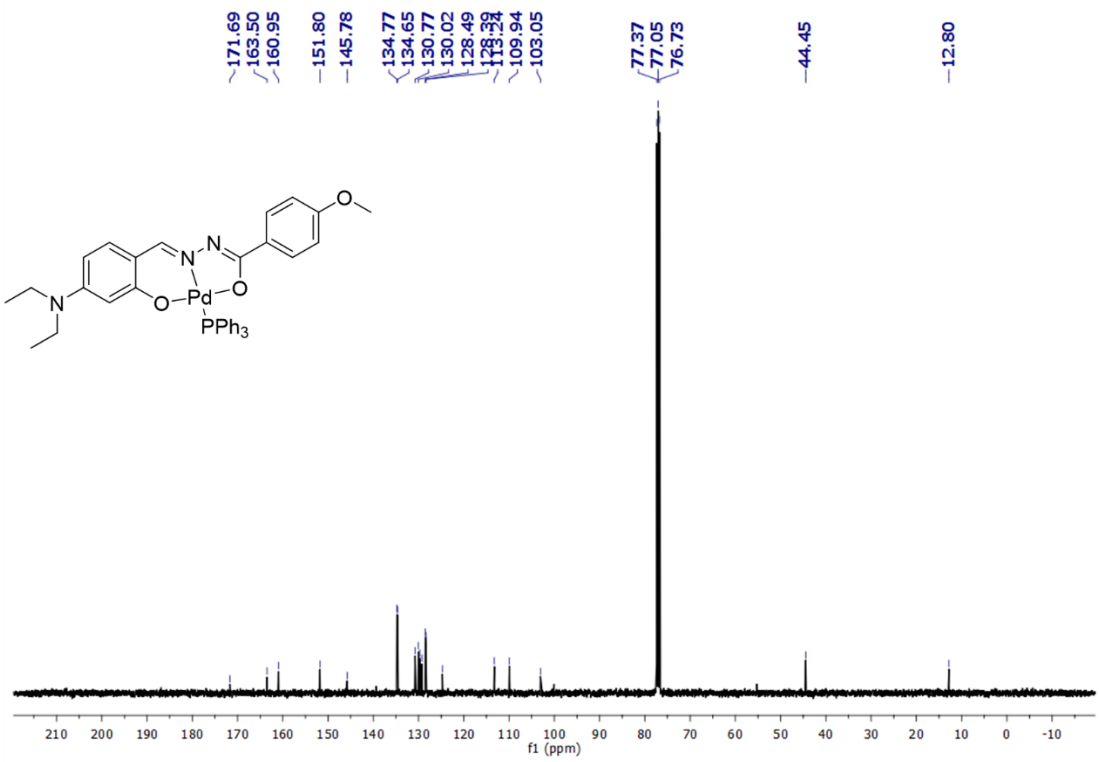

Figure S6. ^{13}C NMR spectrum of complex **3** in $CDCl_3$ (100 MHz, 293 K).

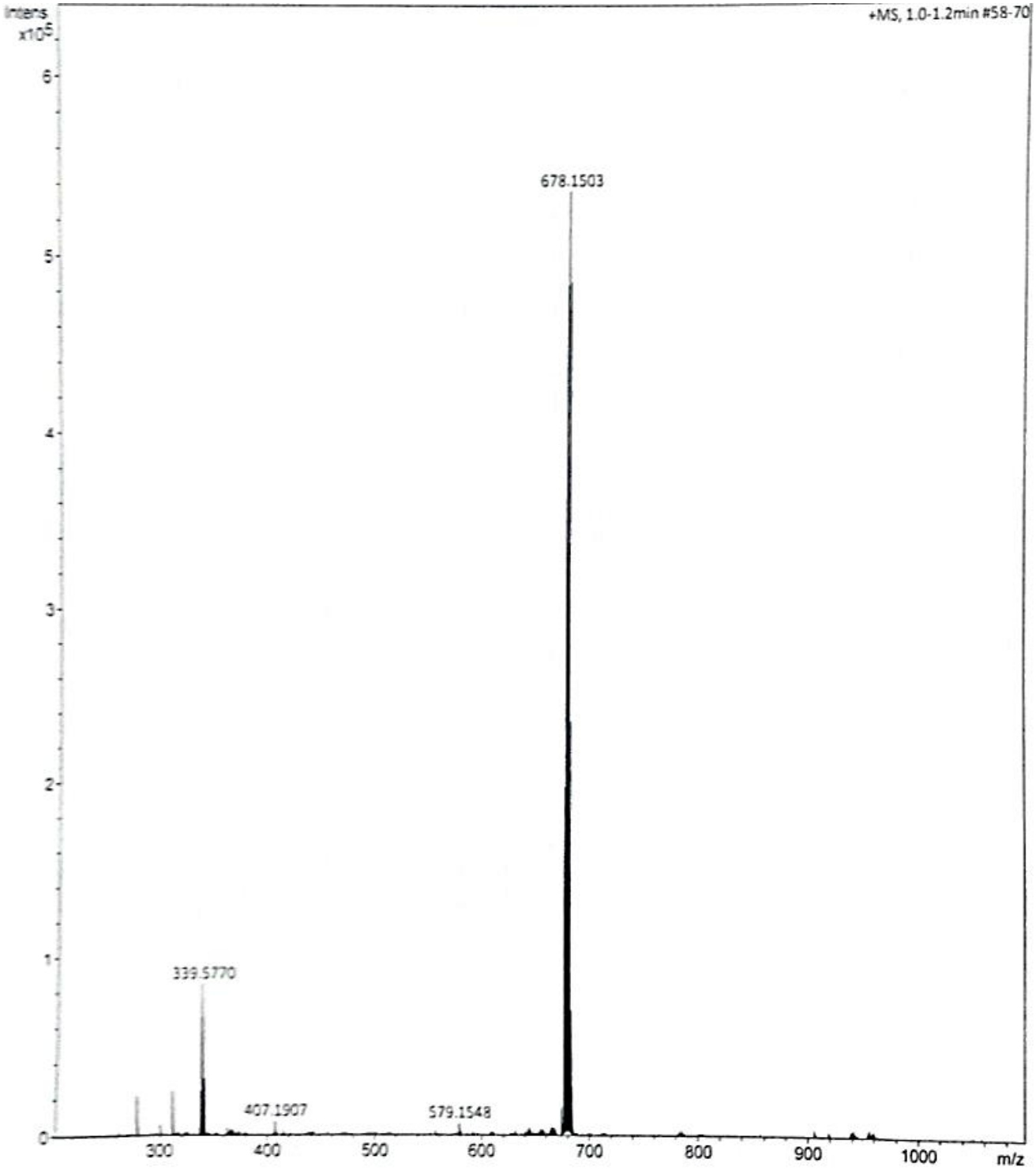

Figure S7 MS spectrum of complex **1**

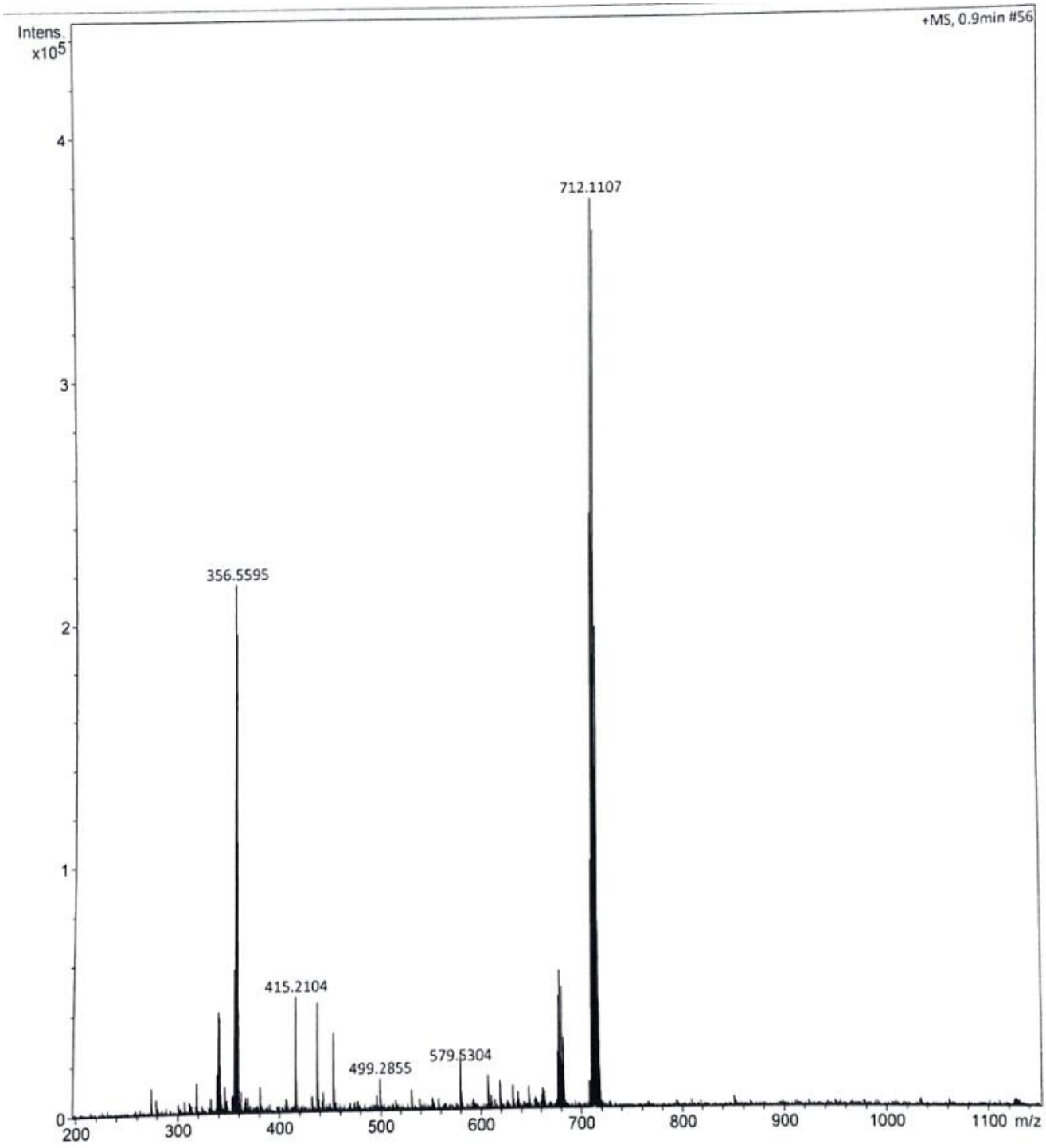

Figure S8 MS spectrum of complex **2**

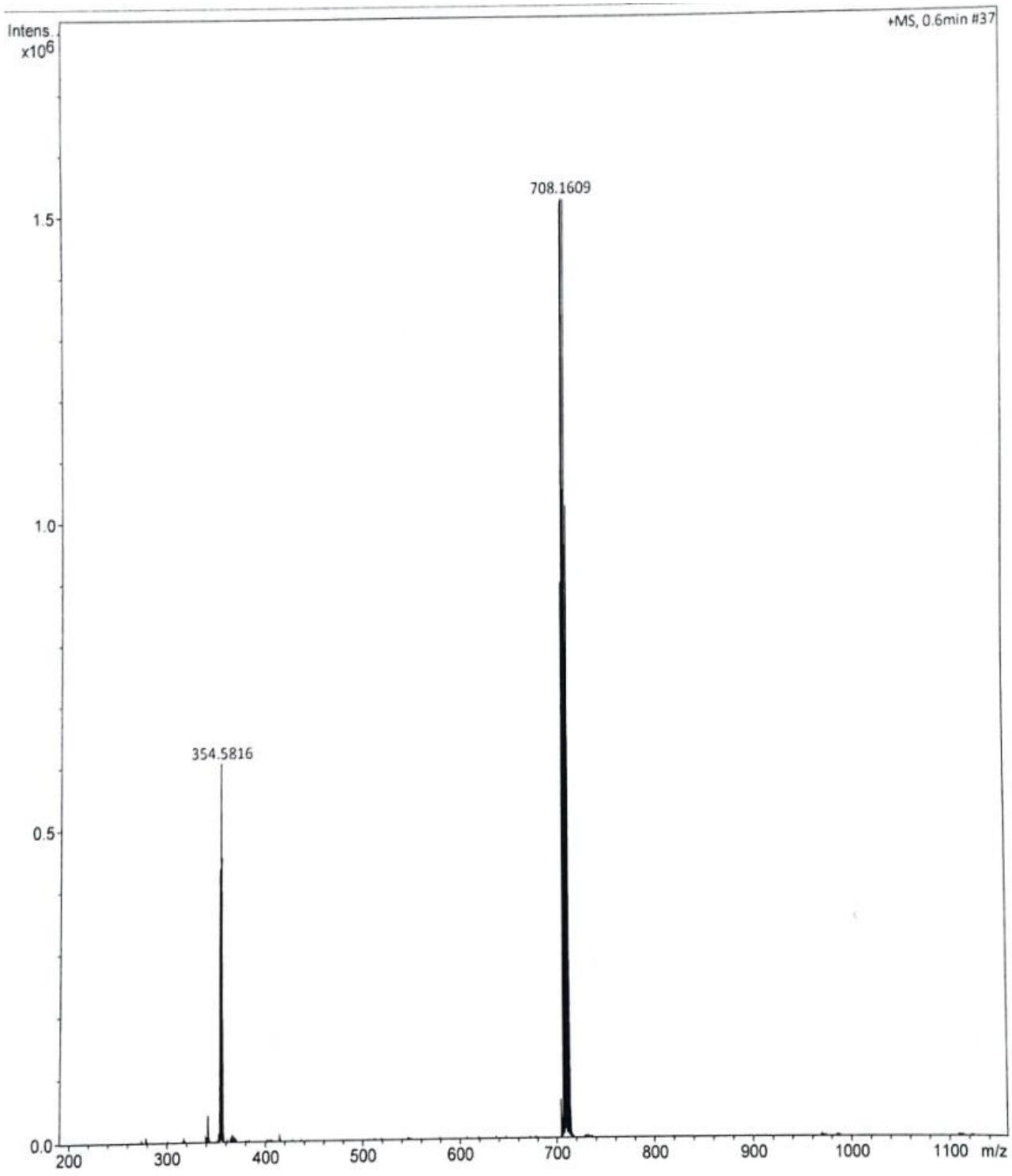

Figure S9 MS spectrum of complex **3**

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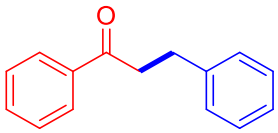
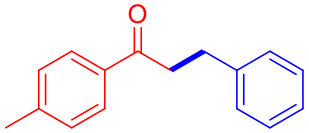
Characterization data for *α*-branched ketone products

1,3-diphenylpropan-1-one (**3a**).[4]



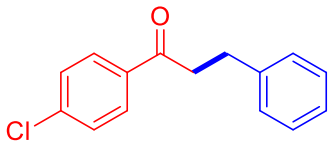
White solid (88%, 185 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8 Hz, 2H), 7.43 (t, J = 8 Hz, 1H), 7.33 (t, J = 8 Hz, 2H), 7.21 – 7.09 (m, 5H), 3.18 (t, J = 8 Hz, 2H), 2.96 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.27, 141.37, 136.91, 133.15, 128.68, 128.61, 128.52, 128.12, 126.22, 40.51, 30.19.

3-phenyl-1-(p-tolyl)propan-1-one (**3b**).[4]



White solid (91%, 204 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8 Hz, 2H), 7.15 – 7.07 (m, 7H), 3.10 (t, J = 8 Hz, 2H), 2.91 (t, J = 8 Hz, 2H), 2.23 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.69, 142.68, 140.31, 133.29, 128.18, 127.41, 127.34, 127.29, 127.07, 125.00, 39.19, 29.09, 20.52.

1-(4-chlorophenyl)-3-phenylpropan-1-one (**3c**).[4]



White solid (84%, 206 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8 Hz, 1H), 7.25 (d, J = 8 Hz, 2H), 7.16 – 7.10 (m, 6H), 3.11 (t, J = 8 Hz, 2H), 2.94 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.98, 141.16, 139.52, 135.22, 129.55, 128.98, 128.52, 128.12, 126.31, 40.47, 30.10.

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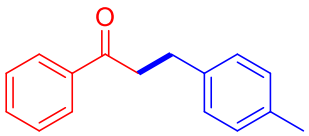
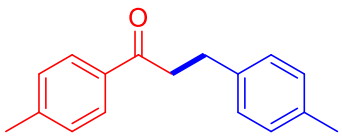
1-phenyl-3-(p-tolyl)propan-1-one (**3d**).[4]



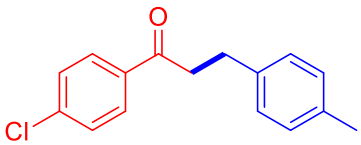
White solid (90%, 202 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8 Hz, 2H), 7.45 (t, J = 8 Hz, 1H), 7.35 (t, J = 8 Hz, 2H),7.05 – 7.01 (m, 4H), 6.93 (s, 1H), 3.19 (t, J = 8 Hz, 2H), 2.94 (t, J = 8 Hz, 2H), 2.23 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 199.41, 138.24, 136.92, 135.67, 133.09, 129.27, 129.11, 128.95, 128.65, 128.36, 128.10, 40.66, 29.76, 21.07.

1,3-di-p-tolylpropan-1-one (**3e**).[5]



White solid (92%, 220 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 7.15-7.09 (m, 4H), 3.24 (t, J = 8 Hz, 2H), 3.01 (t, J = 8 Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 199.02, 143.81, 138.35, 135.60, 134.47, 129.37, 129.23, 128.34, 128.21, 40.54, 29.84, 21.66, 21.05.

1-(4-chlorophenyl)-3-(p-tolyl)propan-1-one (**3f**).[5]



White solid (85%, 220 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.06-7.01 (m, 4H), 3.16 (t, J = 8 Hz, 2H), 2.94 (t, J = 8 Hz, 2H), 2.24 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 198.15, 139.50, 137.98, 135.76, 135.21, 129.49, 129.27, 128.94, 128.31, 40.61, 29.66, 21.04.

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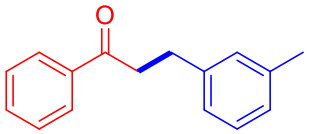
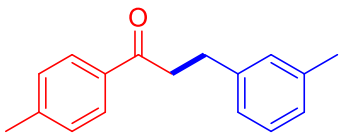
1-phenyl-3-(m-tolyl)propan-1-one (**3g**).[6]



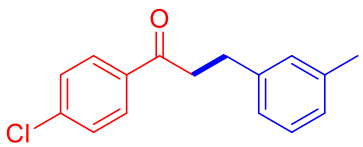
White solid (87%, 195 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8 Hz, 2H), 7.44 (t, J = 8 Hz, 1H), 7.34 (t, J = 8 Hz, 2H), 7.09 (t, J = 8 Hz, 1H), 6.97-6.92 (m, 3H), 3.19 (t, J = 8 Hz, 2H), 2.93 (t, J = 8 Hz, 2H), 2.24 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 198.24, 140.18, 137.04, 135.80, 131.99, 128.19, 127.54, 127.39, 126.99, 125.83, 124.35, 39.47, 29.00, 20.35.

3-(m-tolyl)-1-(p-tolyl)propan-1-one (**3h**).



White solid (89%, 212 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8 Hz, 2H), 7.14 (d, J = 8 Hz, 2H), 7.09 (t, J = 8 Hz, 1H), 6.97-6.91 (m, 3H), 3.16 (t, J = 8 Hz, 2H), 2.92 (t, J = 8 Hz, 2H), 2.30 (s, 3H) , 2.23 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.98, 143.83, 141.39, 138.11, 134.46, 129.31, 129.28, 128.47, 128.22, 126.89, 125.44, 40.46, 30.20, 21.66, 21.45.

1-(4-chlorophenyl)-3-(m-tolyl)propan-1-one (**3i**).



White solid (80%, 207 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8 Hz, 2H), 7.42 (d, J = 8 Hz, 2H), 7.19 (t, J = 8 Hz, 1H), 7.04 (t, J = 8 Hz, 3H), 3.26 (t, J = 8 Hz, 2H), 3.02 (t, J = 8 Hz, 2H), 2.33 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.12, 141.01, 139.52, 138.02, 135.19, 129.49, 129.24, 128.94, 128.50, 126.99, 125.39, 40.54, 30.00, 21.42.

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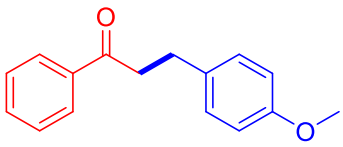
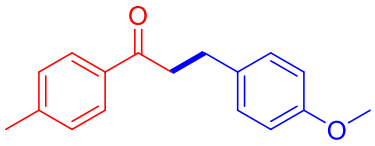
3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3j**).[4]



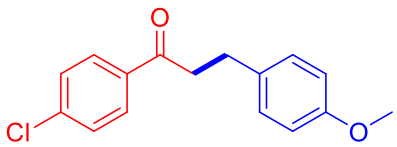
White solid (86%, 207 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8 Hz, 2H), 7.47 (t, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 6.76 (d, J = 8 Hz, 2H), 3.70 (s, 3H), 3.18 (t, J = 8 Hz, 2H), 2.93 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.45, 158.02, 136.93, 133.35, 133.07, 129.39, 128.63, 128.08, 113.97, 55.30, 40.74, 29.31.

3-(4-methoxyphenyl)-1-(p-tolyl)propan-1-one (**3k**).[5]



White solid (95%, 242 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 6.84 (d, J = 8 Hz, 2H), 3.78 (s, 3H), 3.24 (t, J = 8 Hz, 2H), 3.00 (t, J = 8 Hz, 2H), 2.40 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.09, 157.98, 143.80, 134.45, 133.44, 129.35, 128.18, 113.93, 55.29, 40.62, 29.38, 21.63.

1-(4-chlorophenyl)-3-(4-methoxyphenyl)propan-1-one (**3l**).[5]



White solid (83%, 228 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 2H), 7.42 (d, J = 8 Hz, 2H), 7.16(d, J = 8 Hz, 2H), 6.84 (d, J = 8 Hz, 2H), 3.79 (s, 3H), 3.21 (t, J = 8 Hz, 2H), 3.00 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.22, 158.07, 139.50, 135.22, 133.09, 129.49, 129.37, 128.94, 113.91, 55.30, 40.71, 29.22.

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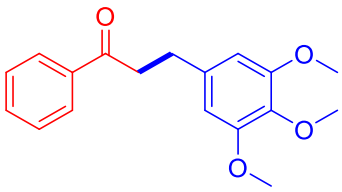
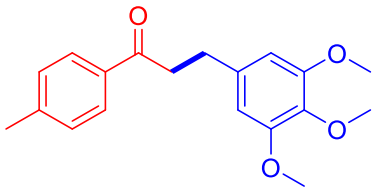
1-phenyl-3-(3,4,5-trimethoxyphenyl)propan-1-one (**3m**).[7]



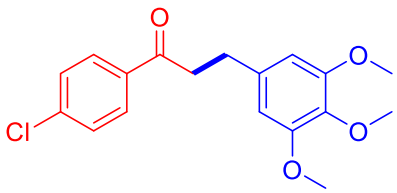
White solid (76%, 228 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 7.37 (t, J = 8 Hz, 2H), 7.24 – 7.15 (m, 2H), 6.99 (t, J = 8 Hz, 1H), 3.23 (t, J = 8 Hz, 2H), 3.10 (t, J = 8 Hz, 2H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 197.91, 139.52, 135.70, 132.09, 131.85, 129.77, 127.57, 127.04, 126.95, 126.60, 123.32, 37.56, 29.75.

1-(p-tolyl)-3-(3,4,5-trimethoxyphenyl)propan-1-one (**3n**).



White solid (81%, 255 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 6.46 (s, 2H), 3.83 (d, J = 8 Hz, 9H), 3.27 (t, J = 8 Hz, 2H), 3.00 (t, J = 8 Hz, 2H), 2.41 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.93, 153.22, 143.92, 137.23, 136.33, 134.43, 129.31, 128.17, 105.40, 60.85, 56.10, 40.48, 30.71, 21.64.

1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)propan-1-one (**3o**).



White solid (65%, 218 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8 Hz, 1H), 7.56 (d, J = 8 Hz, 1H), 7.46 (t, J = 8 Hz, 2H), 6.47 (s, 2H), 3.83 (d, J = 8 Hz, 9H), 3.30 (t, J = 8 Hz, 2H), 3.02 (t, J = 8 Hz, 2H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 199.32, 153.24, 137.14, 136.33, 133.16, 128.65, 128.06, 105.39, 60.88, 56.11, 40.61, 30.63.

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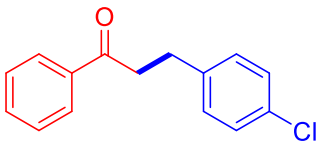
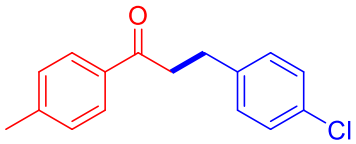
3-(4-chlorophenyl)-1-phenylpropan-1-one (**3p**).



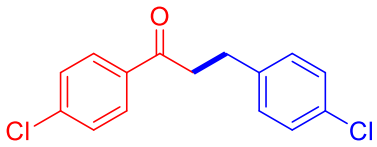
White solid (79%, 193 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8 Hz, 2H), 7.47 (t, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 6.76 (d, J = 8 Hz, 2H), 3.70 (s, 3H), 3.18 (t, J = 8 Hz, 2H), 2.93 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.45, 158.02, 136.93, 133.35, 133.07, 129.39, 128.63, 128.08, 113.97, 55.30, 40.74, 29.31.

3-(4-chlorophenyl)-1-(p-tolyl)propan-1-one (**3q**).[5]



White solid (78%, 202 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.22-7.08 (m, 6H), 3.17 (t, J = 8 Hz, 2H), 2.96 (t, J = 8 Hz, 2H), 2.32 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 197.87, 142.80, 140.36, 138.80, 133.34, 128.79, 128.24, 127.47, 127.39, 127.13, 125.06, 39.30, 29.17, 20.59.

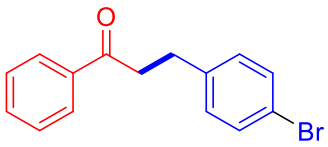
1,3-bis(4-chlorophenyl)propan-1-one (**3r**).[5]



White solid (63%, 176 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 3.17 (t, J = 8 Hz, 2H), 2.96 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.64, 139.67, 139.52, 135.06, 131.99, 129.83, 129.45, 128.99, 128.66, 40.14, 29.30.

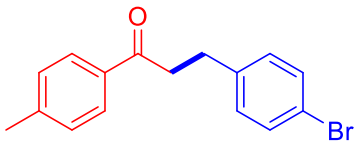
Supporting Information

3-(4-bromophenyl)-1-phenylpropan-1-one (**3s**).[8]



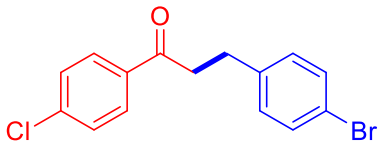
White solid (77%, 223 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8 Hz, 2H), 7.56 (t, J = 8 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.13 (d, J = 8 Hz, 2H), 3.28 (t, J = 8 Hz, 2H), 3.02 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.87, 140.29, 136.75, 133.22, 131.58, 130.27, 128.68, 128.04, 119.92, 40.09, 29.45.

3-(4-bromophenyl)-1-(p-tolyl)propan-1-one (**3t**).



White solid (82%, 249 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H),7.12 (d, J = 8 Hz, 2H), 3.24 (t, J = 8 Hz, 3H), 3.01 (t, J = 8 Hz, 3H), 2.40 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 198.47, 143.99, 140.40, 134.30, 131.55, 130.26, 129.33, 129.29, 128.53, 128.44, 128.18, 128.15, 126.11, 119.86, 39.95, 29.53, 21.65.

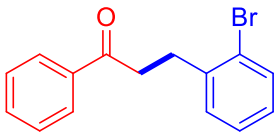
3-(4-bromophenyl)-1-(4-chlorophenyl)propan-1-one (**3u**).



White solid (62%, 201 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 2H), 7.42 (t, J = 8 Hz, 4H), 7.12 (d, J = 8 Hz, 2H), 3.25(t, J = 8 Hz, 2H), 3.02 (t, J = 8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.60, 140.05, 139.68, 135.04, 131.62, 130.71, 130.24, 129.45, 129.00, 120.01, 40.08, 29.35.

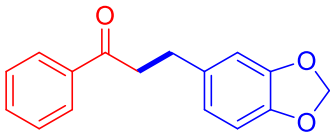
Supporting Information

3-(2-bromophenyl)-1-phenylpropan-1-one (**3v**).



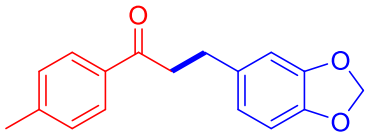
White solid (72%, 208 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 7.37 (t, J = 8 Hz, 2H), 7.24 – 7.15 (m, 2H), 6.99 (t, J = 8 Hz, 1H), 3.23 (t, J = 8 Hz, 2H), 3.10 (t, J = 8 Hz, 2H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 197.91, 139.52, 135.70, 132.09, 131.85, 129.77, 127.57, 127.04, 126.95, 126.60, 123.32, 37.56, 29.75.

3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-one (**3w**).[4]



White solid (64%, 163 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 2H), 7.48 (d, J = 8 Hz, 1H), 7.39 (d, J = 8 Hz, 2H), 6.67 - 6.61 (m, 3H), 5.85 (s, 1H), 3.19 (t, J = 8 Hz, 2H), 2.92 (t, J = 8 Hz, 2H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 198.21, 157.17, 146.62, 144.81, 135.82, 134.05, 132.06, 127.59, 127.01, 120.15, 107.91, 107.26, 99.80, 39.65, 28.85.

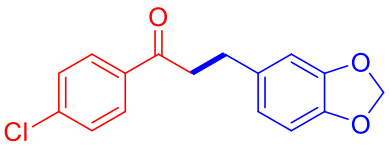
3-(benzo[d][1,3]dioxol-5-yl)-1-(p-tolyl)propan-1-one (**3x**).



White solid (68%, 183 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 6.74-6.68 (m, 3H), 5.91 (s, 2H), 3.32 (t, J = 8 Hz, 2H), 2.97 (t, J = 8 Hz, 2H), 2.40 (s, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 198.87, 147.65, 145.83, 143.86, 135.21, 134.41, 129.29, 128.17, 121.17, 108.94, 108.28, 100.83, 40.57, 29.98, 21.63.

Supporting Information

3-(benzo[d][1,3]dioxol-5-yl)-1-(4-chlorophenyl)propan-1-one (**3y**).



White solid (60%, 173 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 6.66 - 6.61 (m, 3H), 5.83 (s, 2H), 3.13 (t, J = 8 Hz, 2H), 2.89 (t, J = 8 Hz, 2H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 196.92, 146.64, 144.86, 138.47, 134.10, 133.78, 128.41, 127.88, 127.57, 126.99, 120.13, 107.86, 107.27, 99.82, 39.60, 28.74.

Supporting Information

NMR spectrum of the catalytic isolated products

(i) Intermediate-benzaldehyde

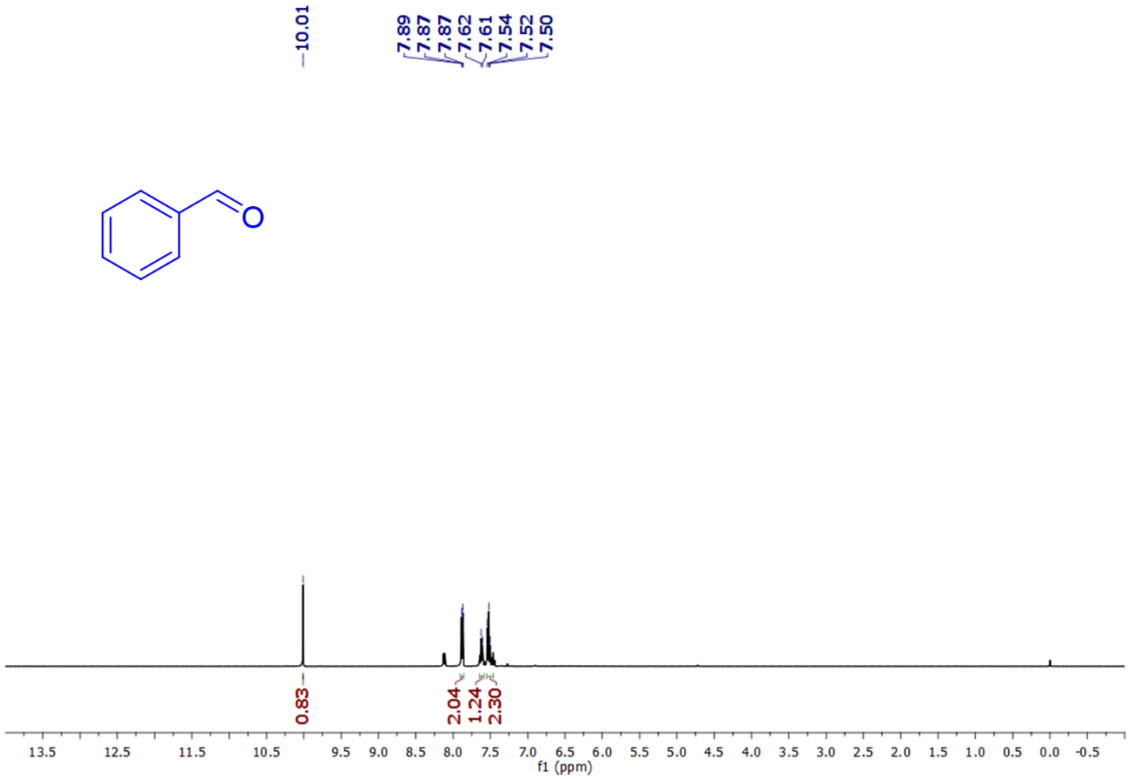


Figure S10. ^{1}H NMR spectrum of benzaldehyde **2a'** in $CDCl_3$ (400 MHz, 293 K).

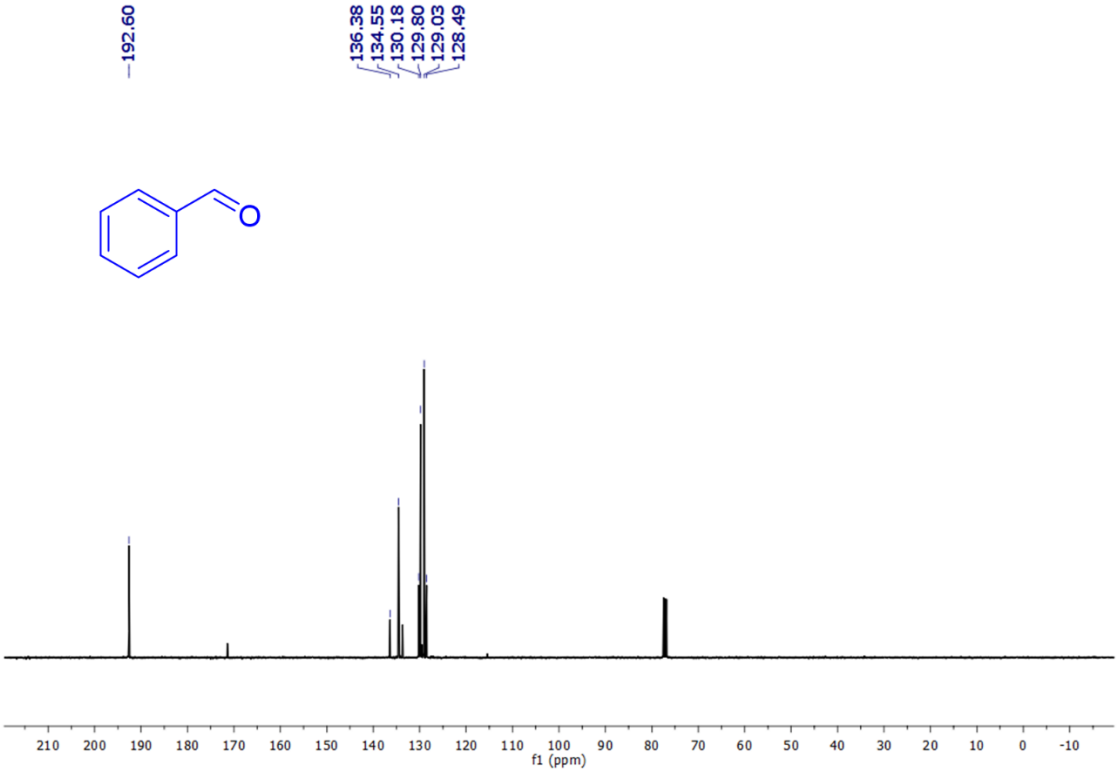


Figure S11. ^{13}C NMR spectrum of benzaldehyde **2a'** in $CDCl_3$ (100 MHz, 293 K).

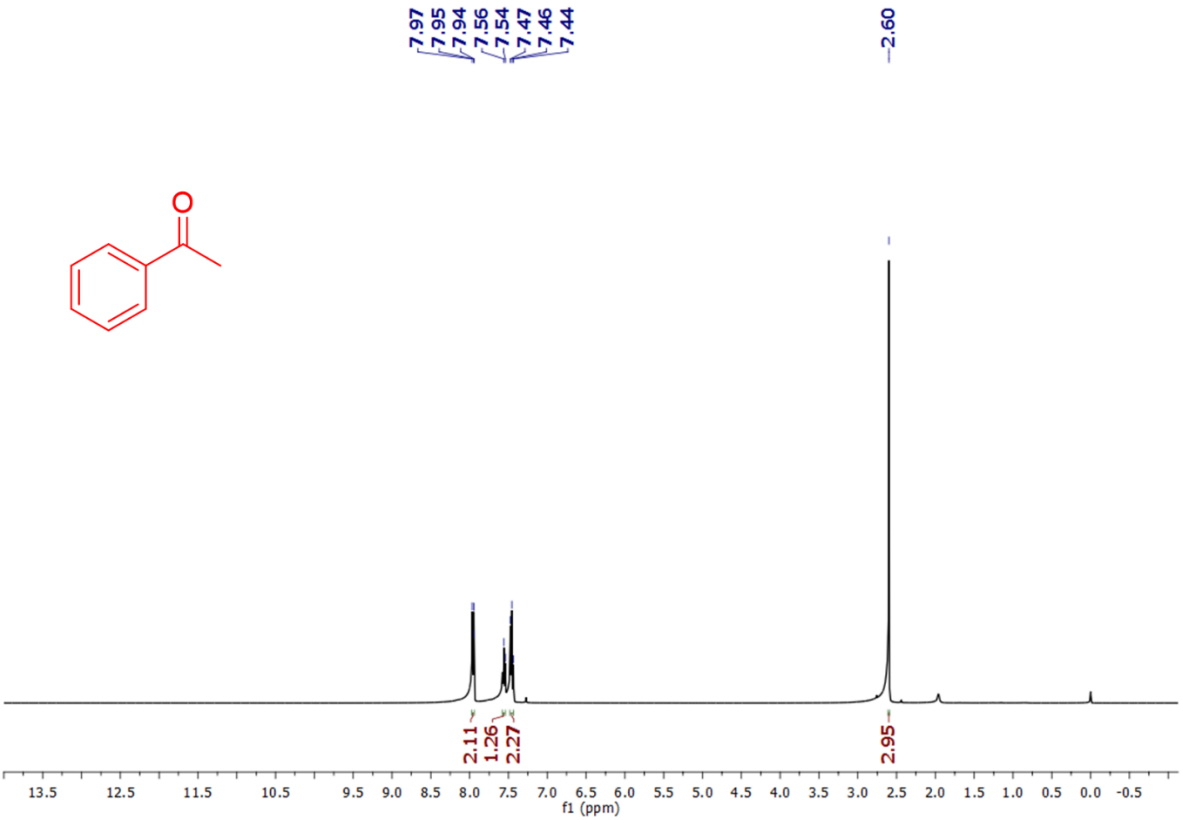


Figure S12. ^{1}H NMR spectrum of acetophenone **2a'** in $CDCl_3$ (400 MHz, 293 K).

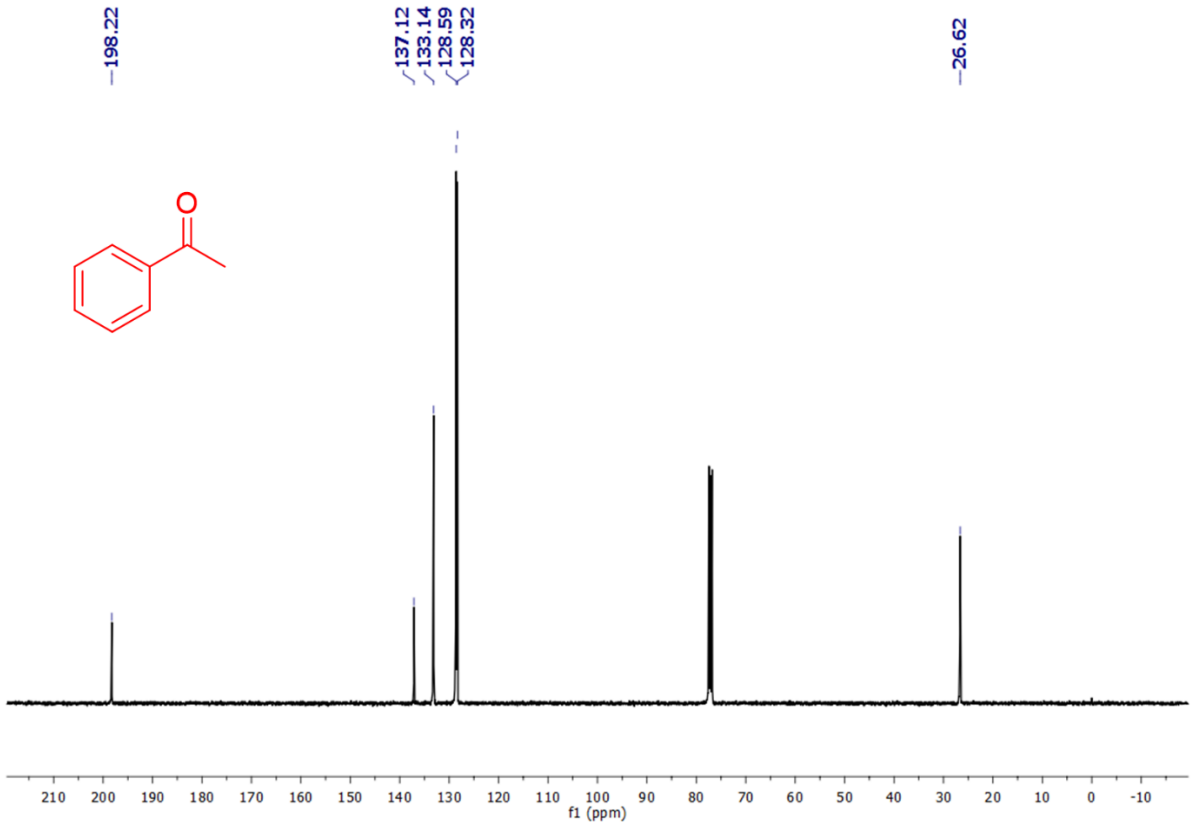


Figure S13. ^{13}C NMR spectrum of acetophenone **2a'** in $CDCl_3$ (100 MHz, 293 K).

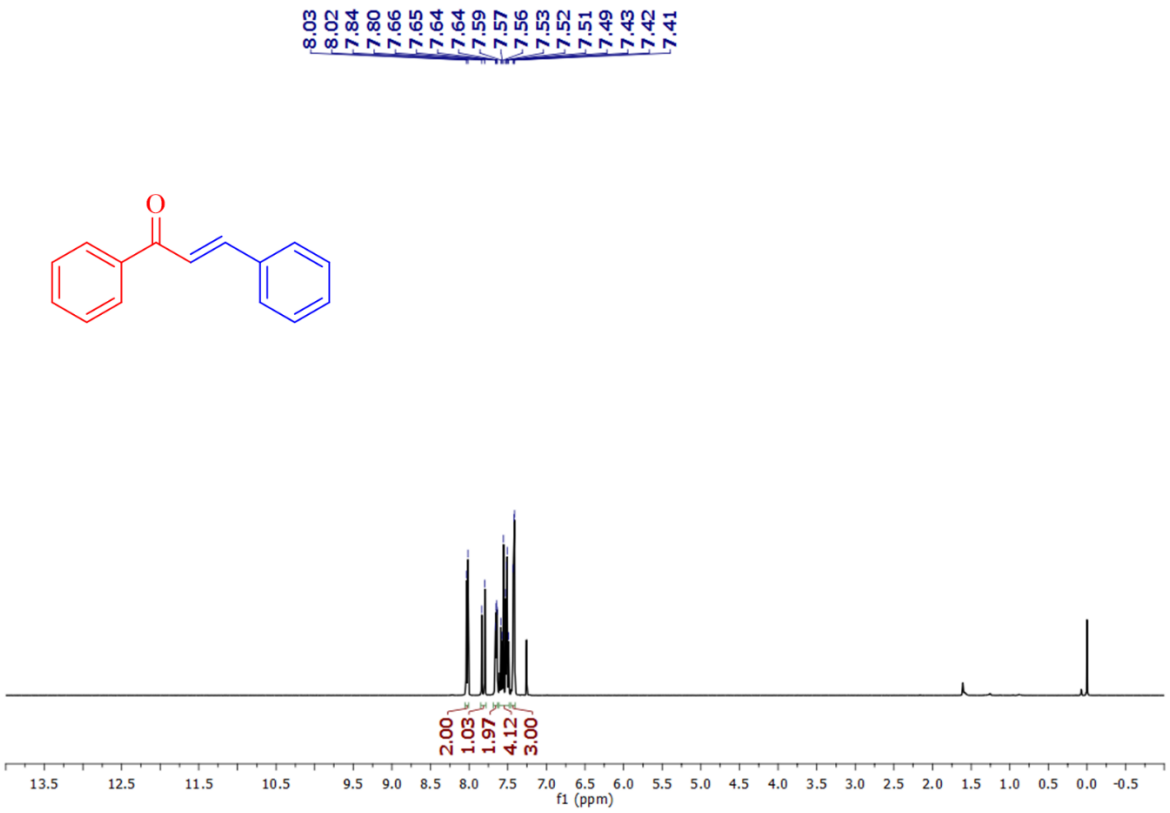


Figure S14. ^{1}H NMR spectrum of intermediate **3a'** in $CDCl_3$ (400 MHz, 293 K).

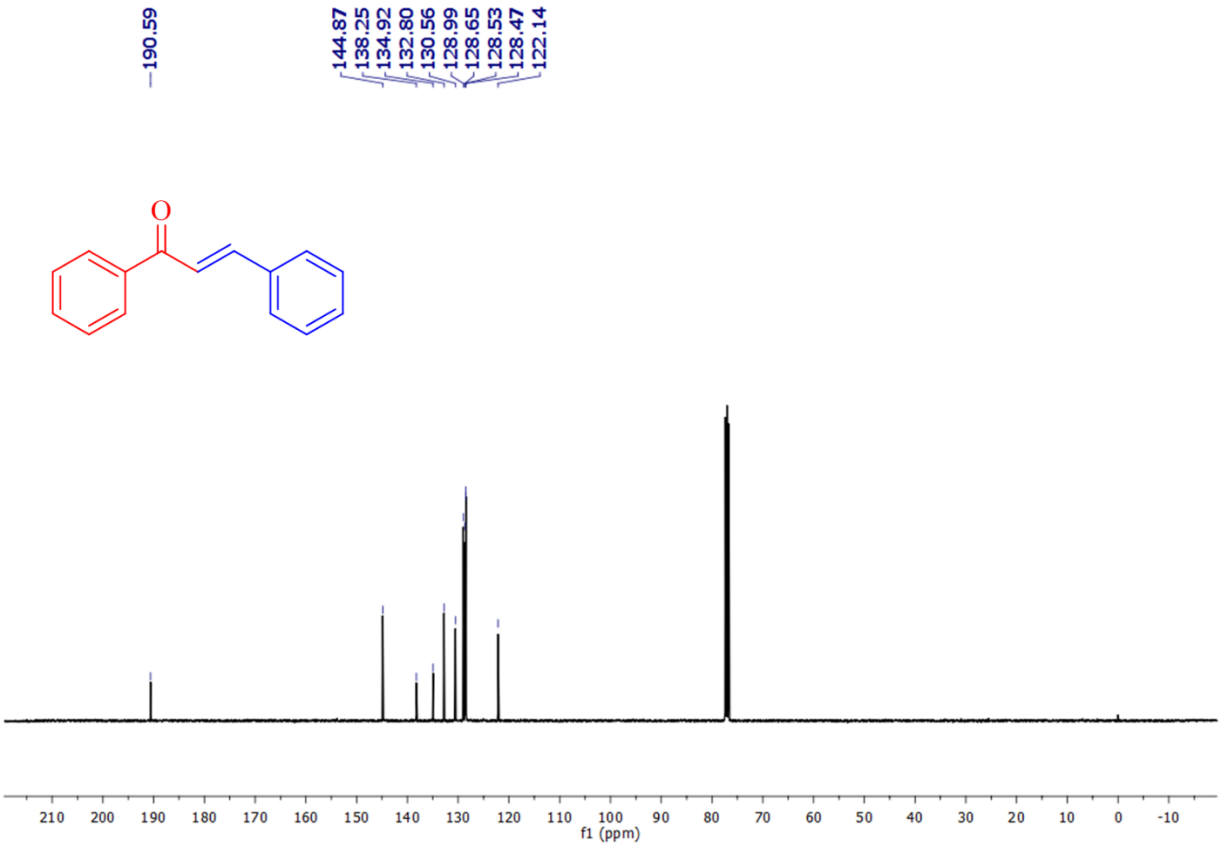


Figure S15. ^{13}C NMR spectrum of intermediate **3a'** in $CDCl_3$ (100 MHz, 293 K).

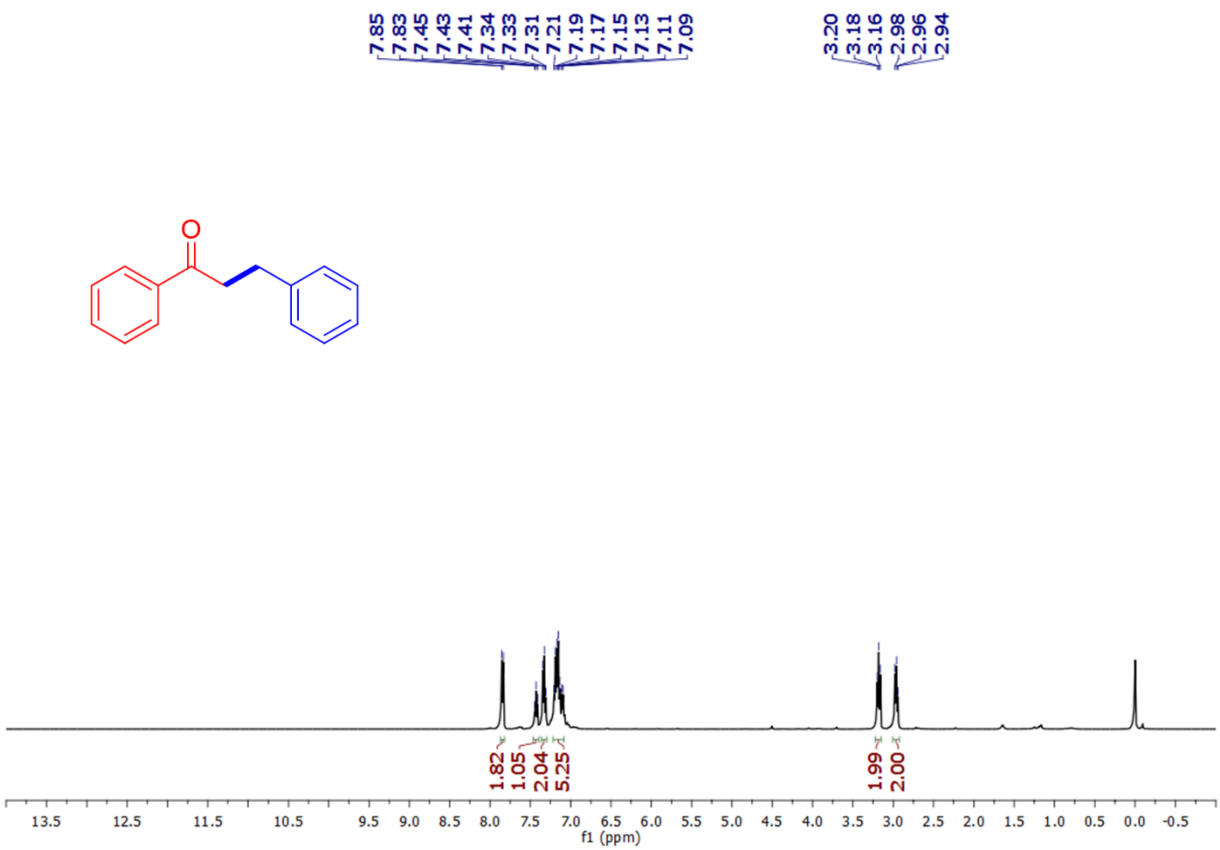


Figure S16. ^{1}H NMR spectrum of compound **3a** in $CDCl_3$ (400 MHz, 293 K). [8]

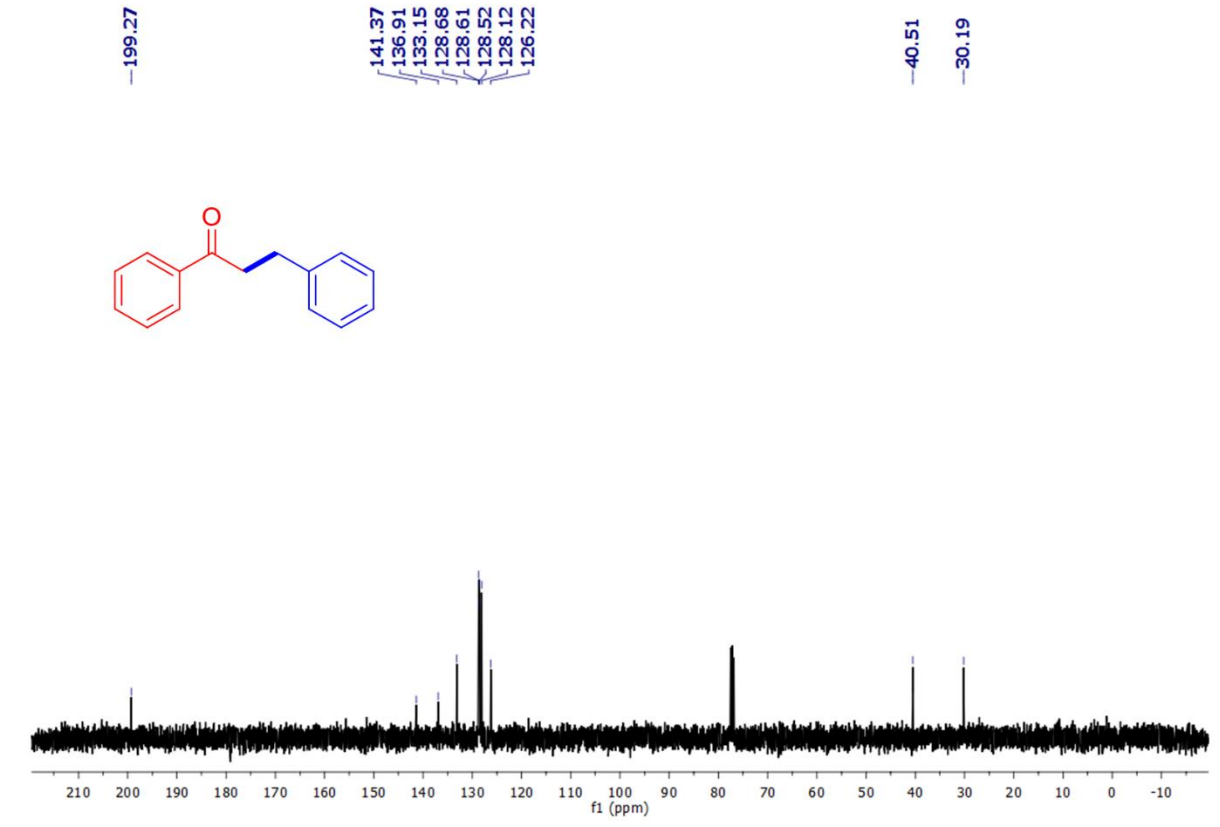


Figure S17. ^{13}C NMR spectrum of compound **3a** in $CDCl_3$ (100 MHz, 293 K). [8]

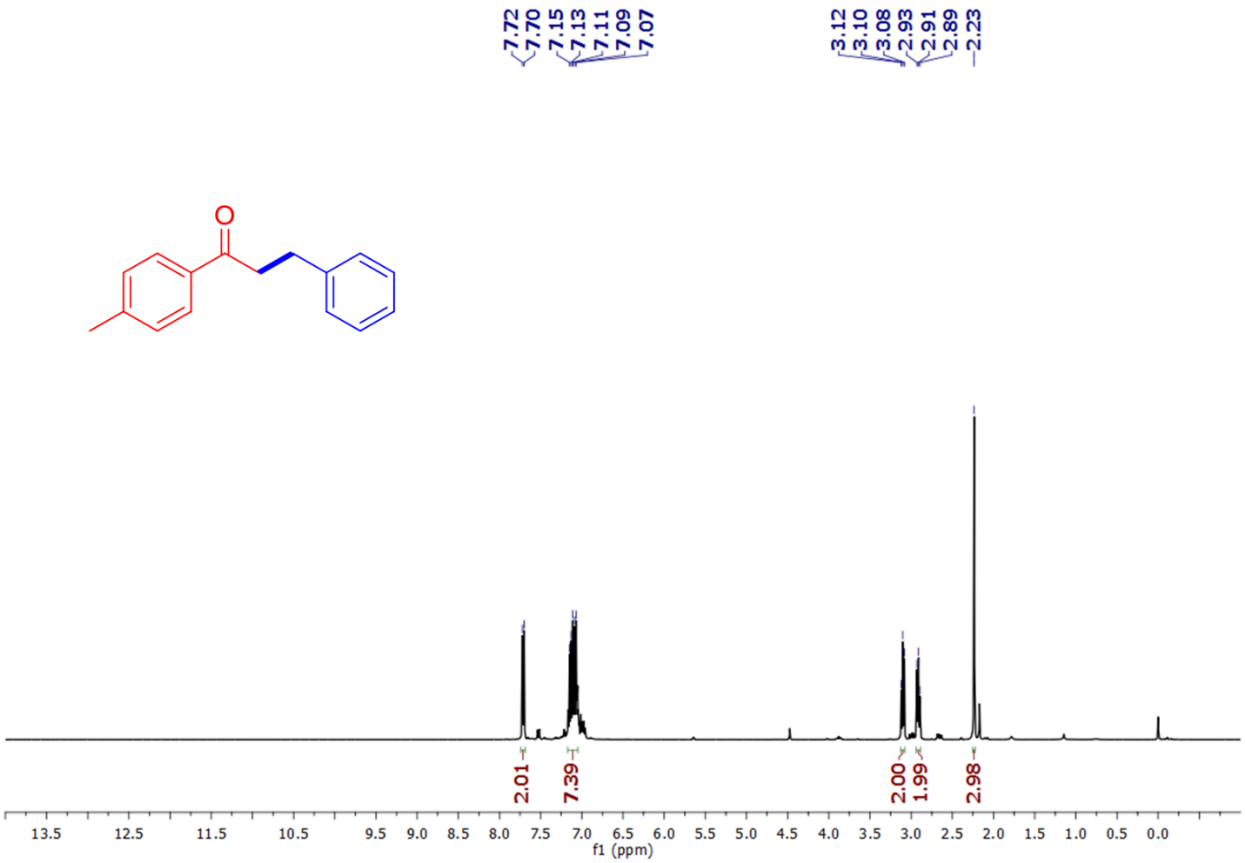


Figure S18. ^{1}H NMR spectrum of compound **3b** in $CDCl_3$ (400 MHz, 293 K). [8]

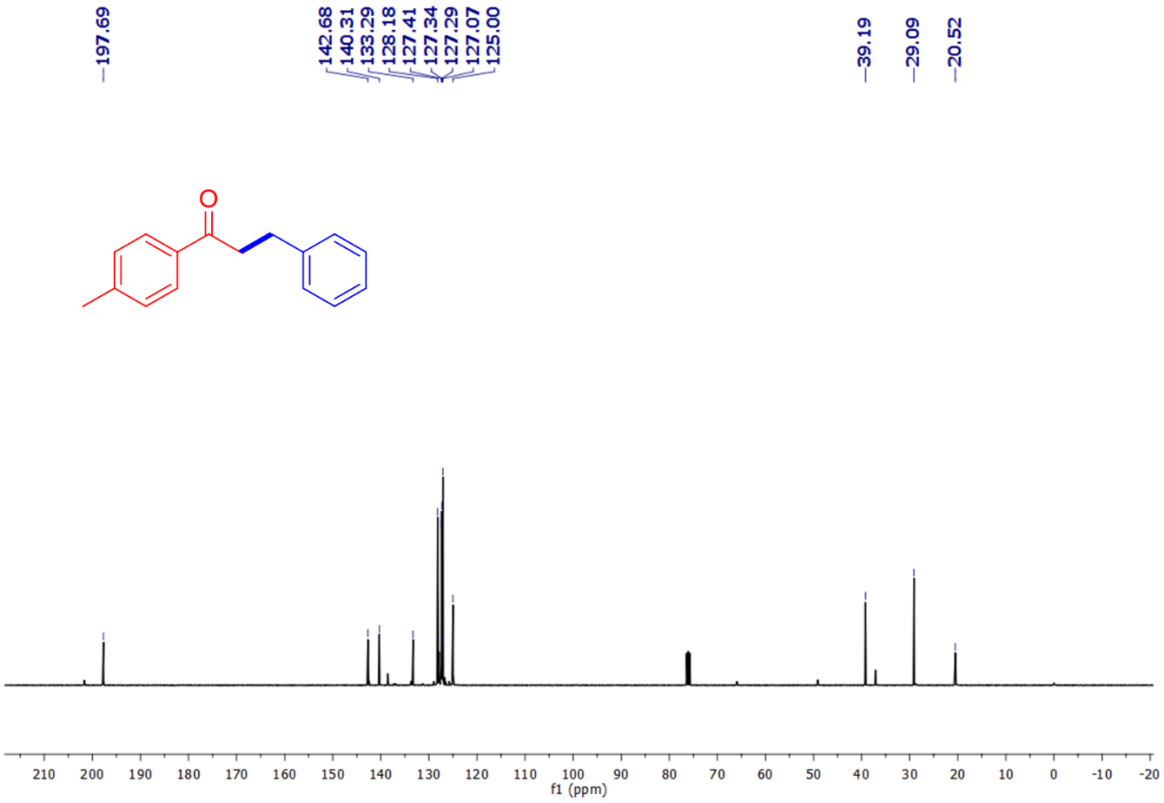


Figure S19. ^{13}C NMR spectrum of compound **3b** in $CDCl_3$ (100 MHz, 293 K). [8]

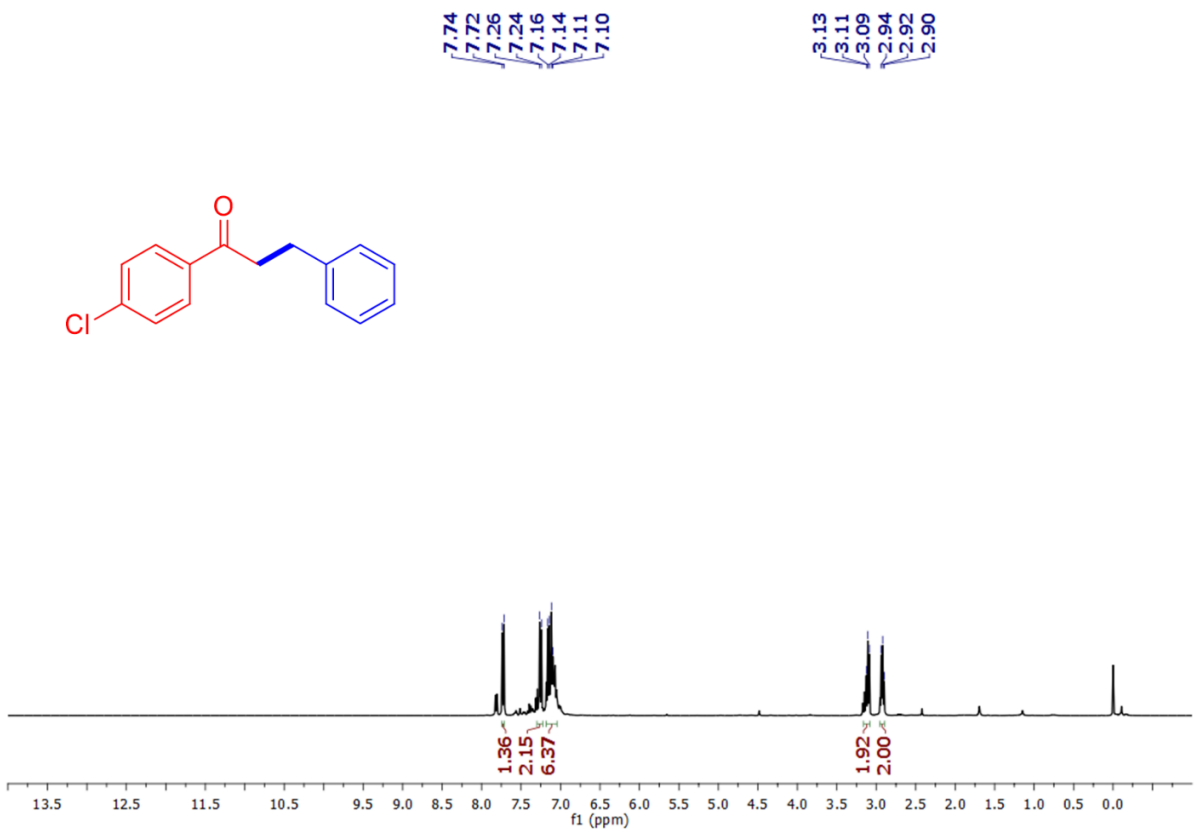


Figure S20. ^{1}H MR spectrum of compound **3c** in $CDCl_3$ (400 MHz, 293 K). [8]

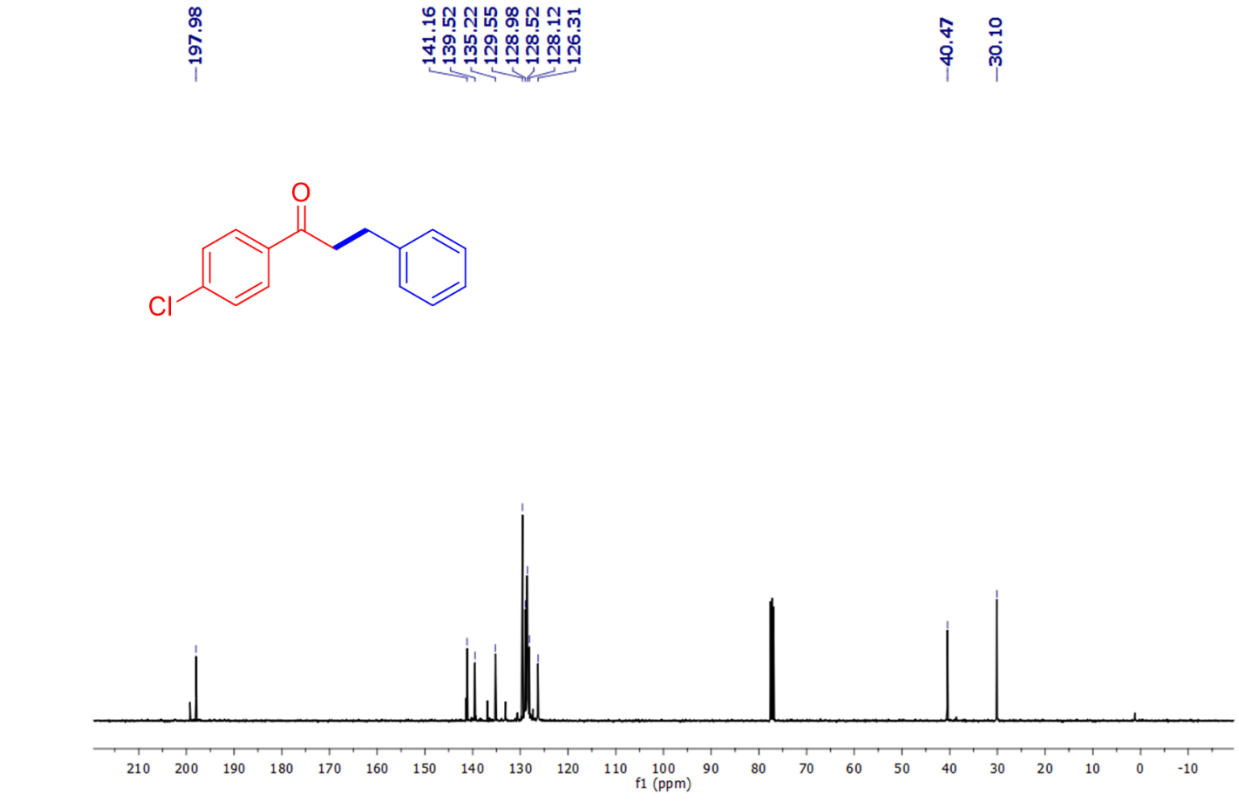


Figure S21. ^{13}C NMR spectrum of compound **3c** in $CDCl_3$ (100 MHz, 293 K). [8]

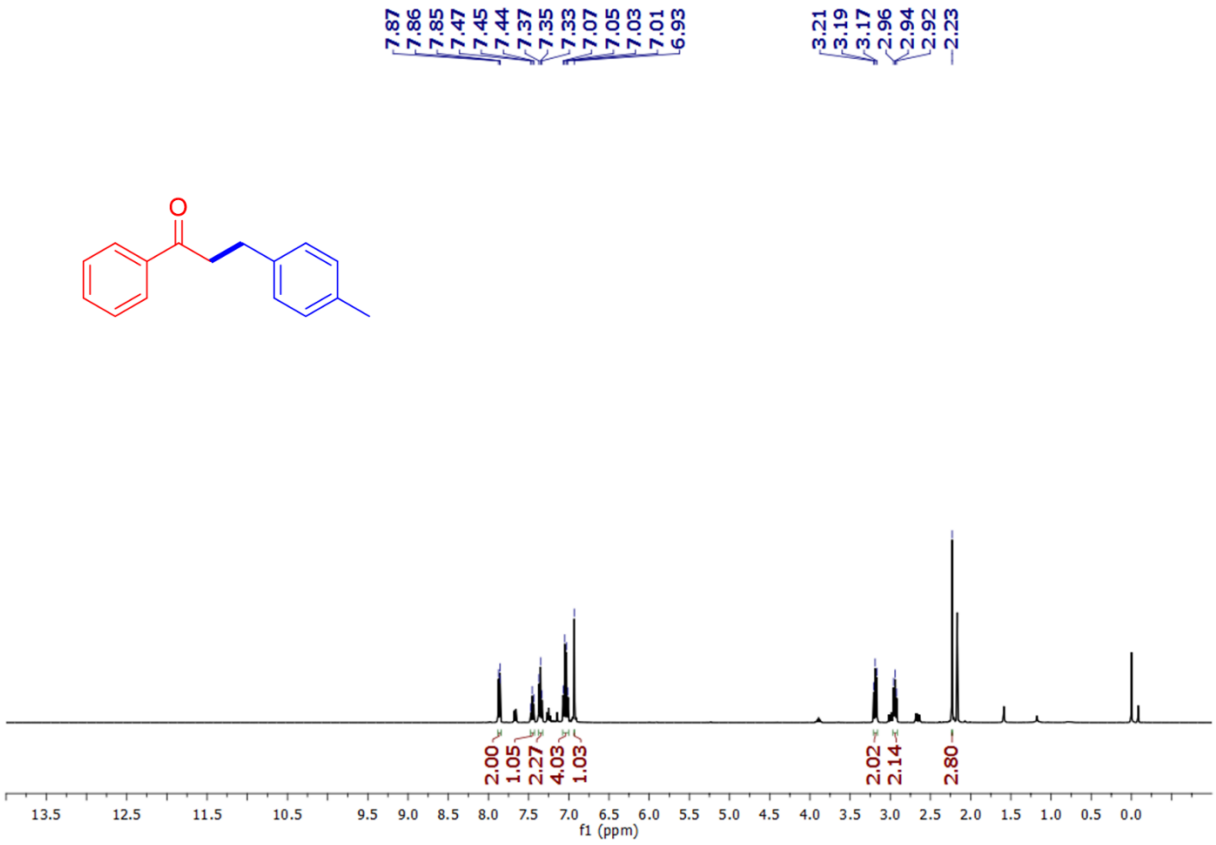


Figure S22. ^{1}H NMR spectrum of compound **3d** in $CDCl_3$ (400 MHz, 293 K). [8]

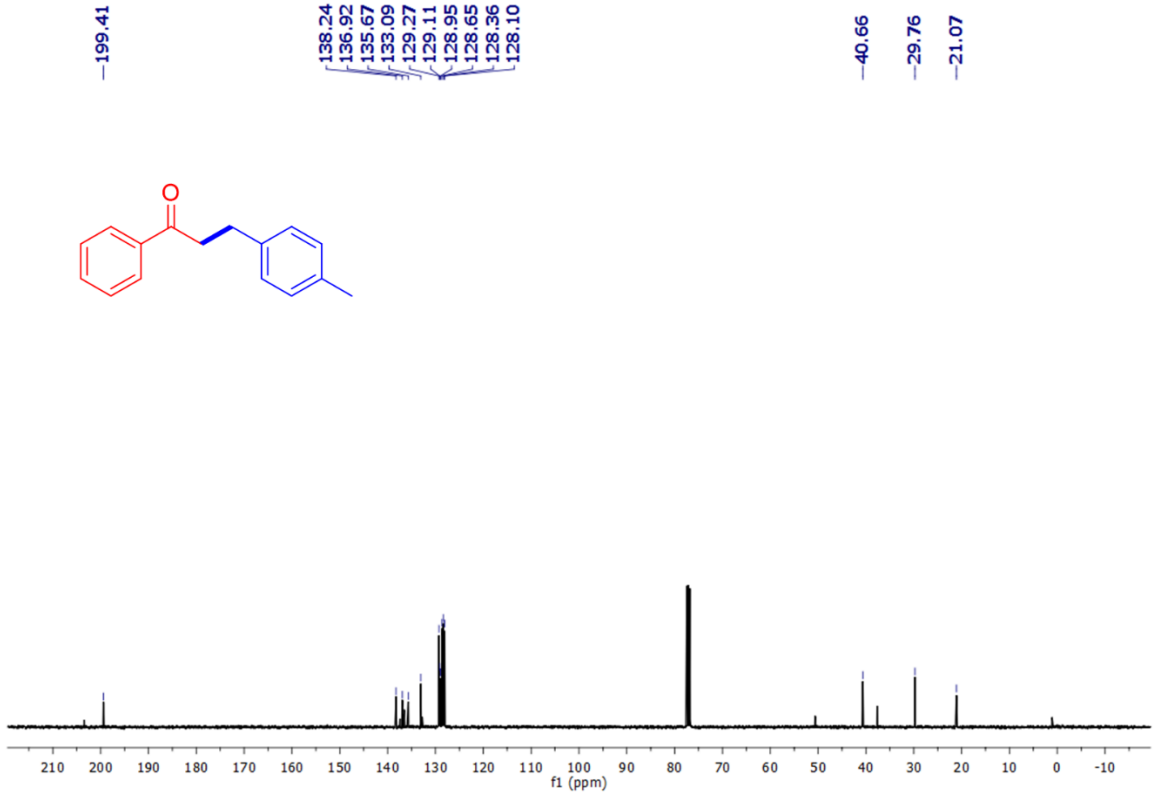


Figure S23. ^{13}C NMR spectrum of compound **3d** in $CDCl_3$ (100 MHz, 293 K). [8]

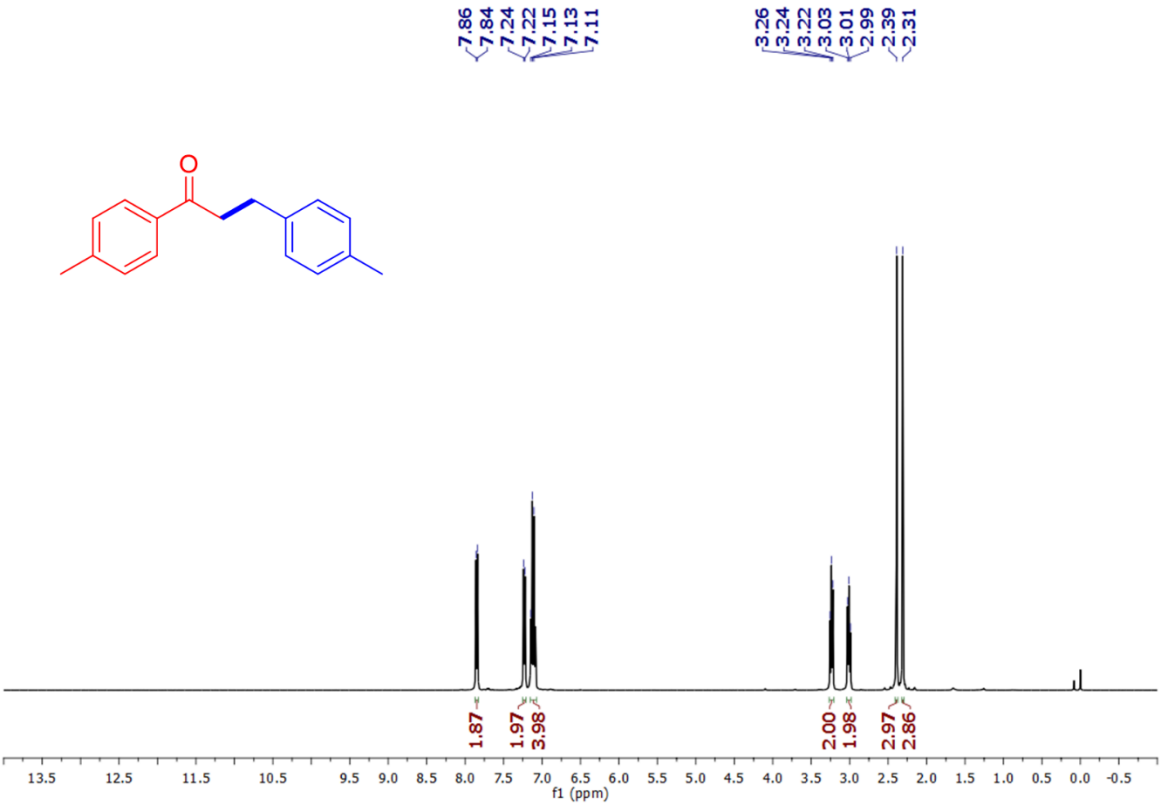


Figure S24. ^{1}H NMR spectrum of compound **3e** in $CDCl_3$ (400 MHz, 293 K). [22]

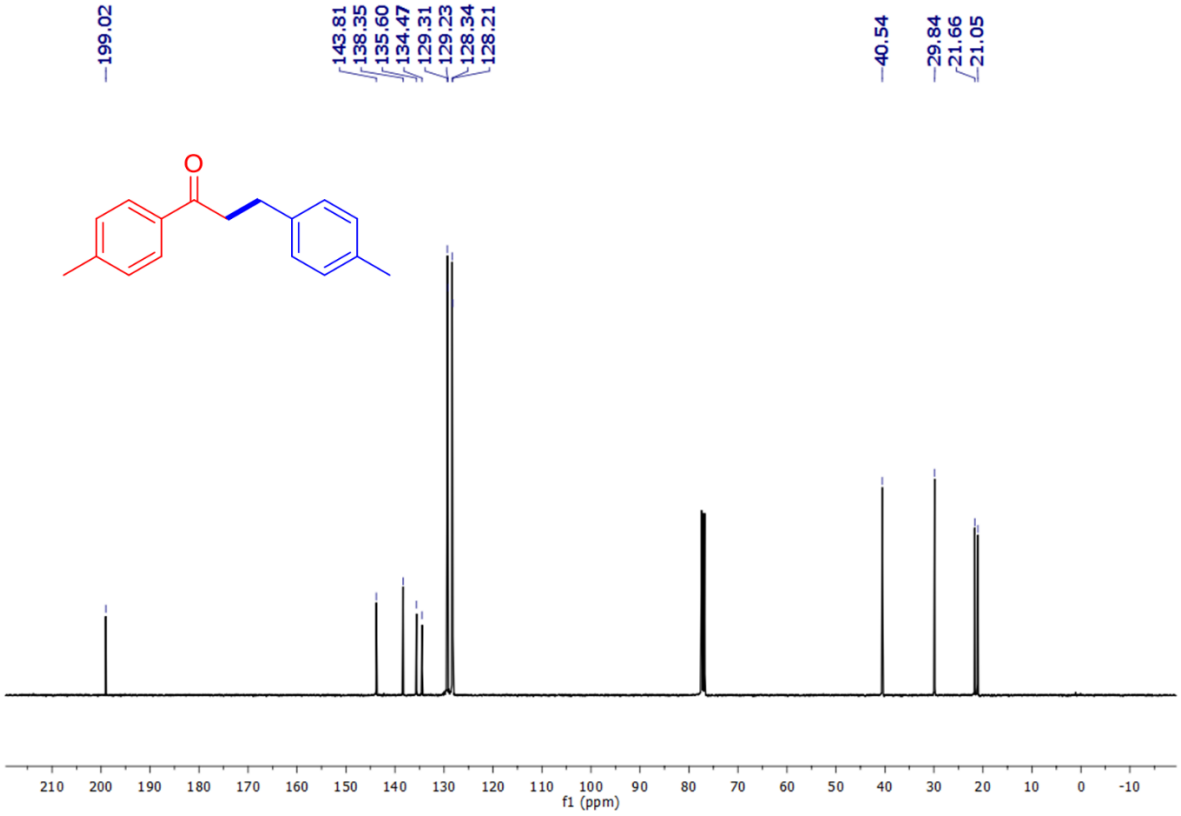


Figure S25. ^{13}C NMR spectrum of compound **3e** in $CDCl_3$ (100 MHz, 293 K). [22]

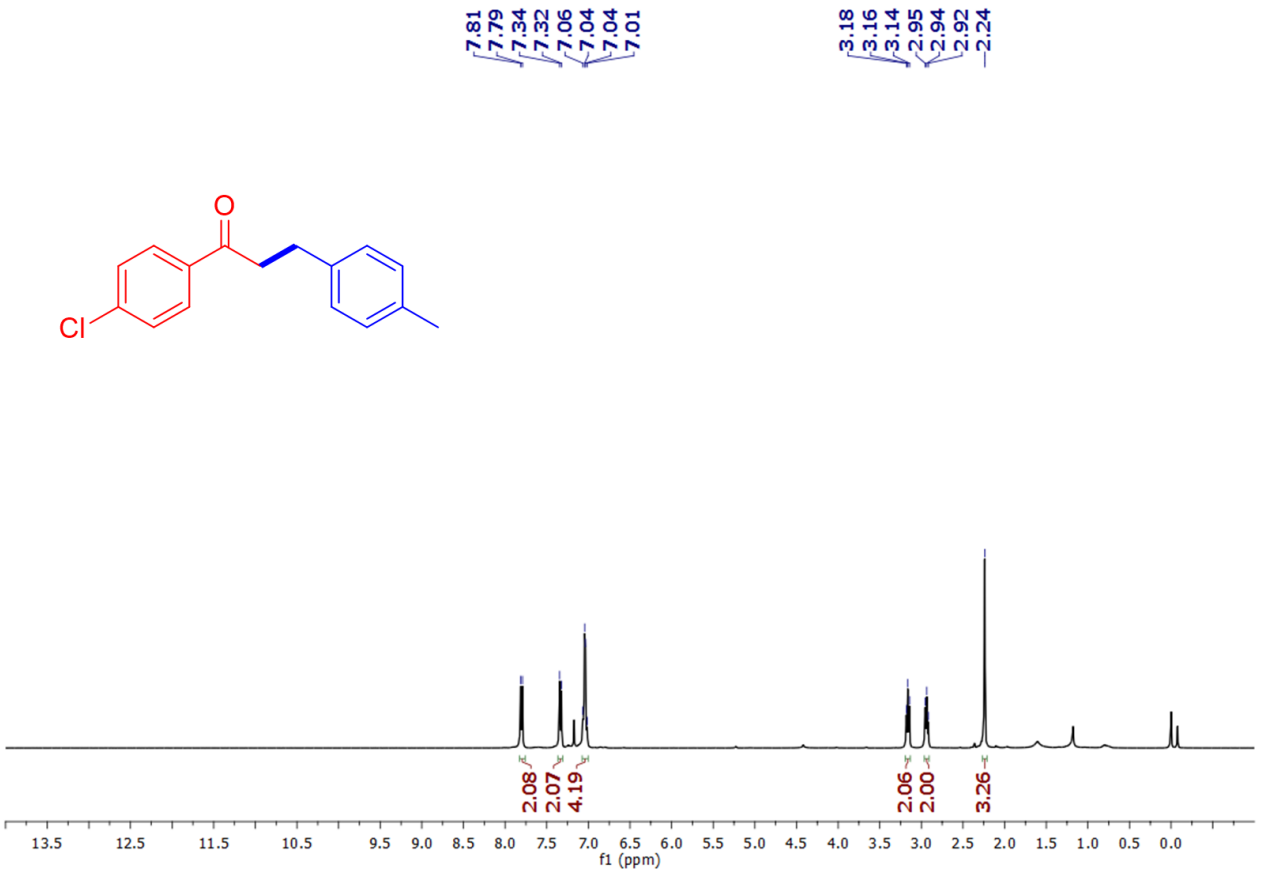


Figure S26. ^{1}H NMR spectrum of compound **3f** in $CDCl_3$ (400 MHz, 293 K). [22]

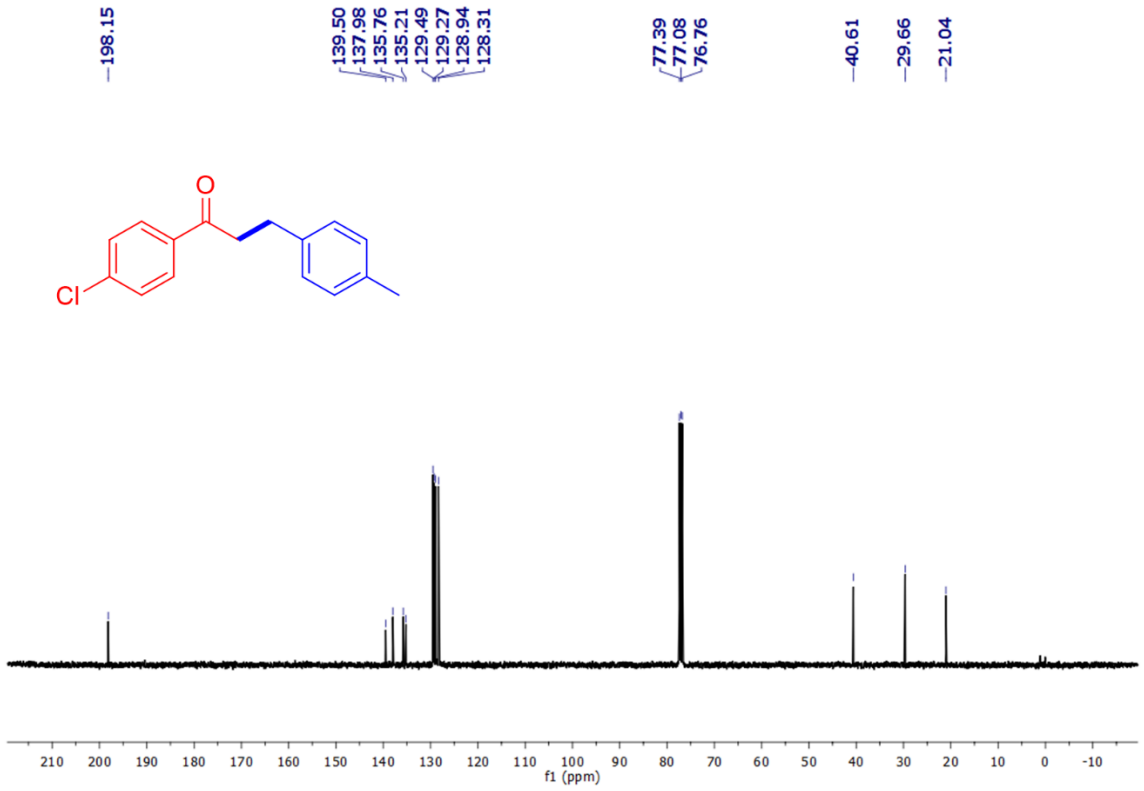


Figure S27. ^{13}C NMR spectrum of compound **3f** in $CDCl_3$ (100 MHz, 293 K). [22]

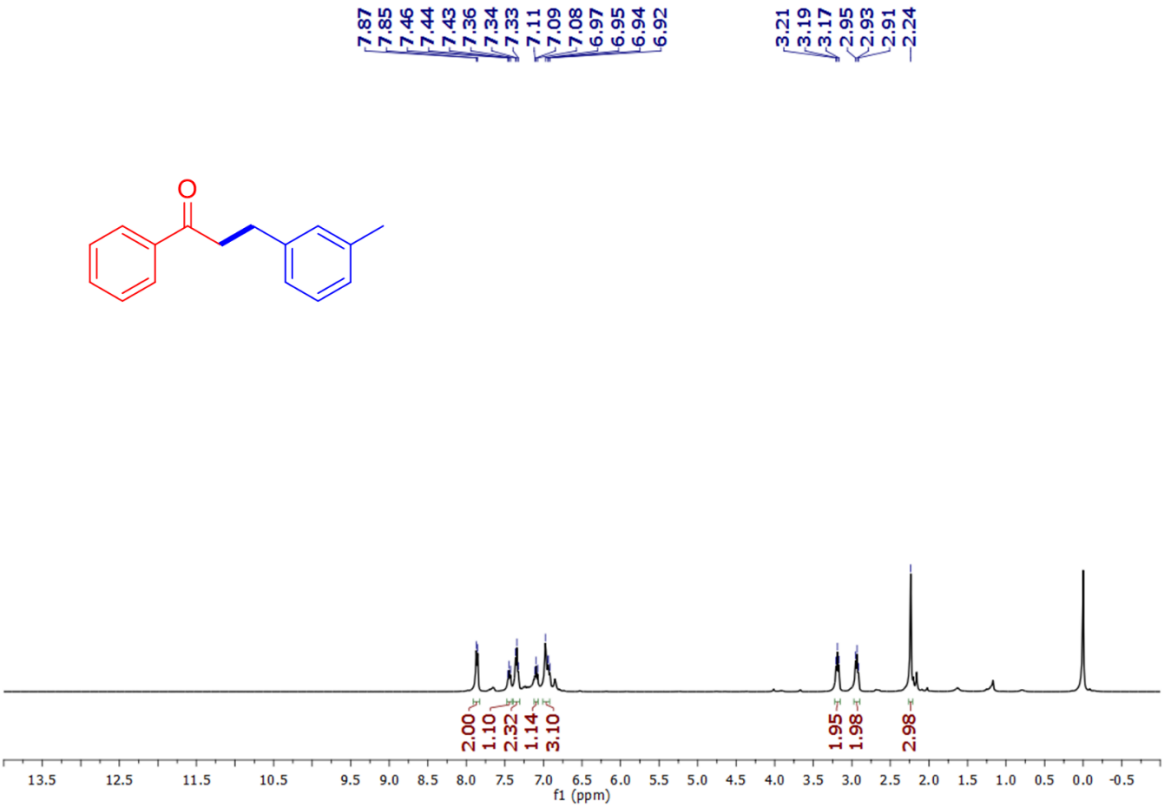


Figure S28. ^{1}H NMR spectrum of compound **3g** in $CDCl_3$ (400 MHz, 293 K). [12]

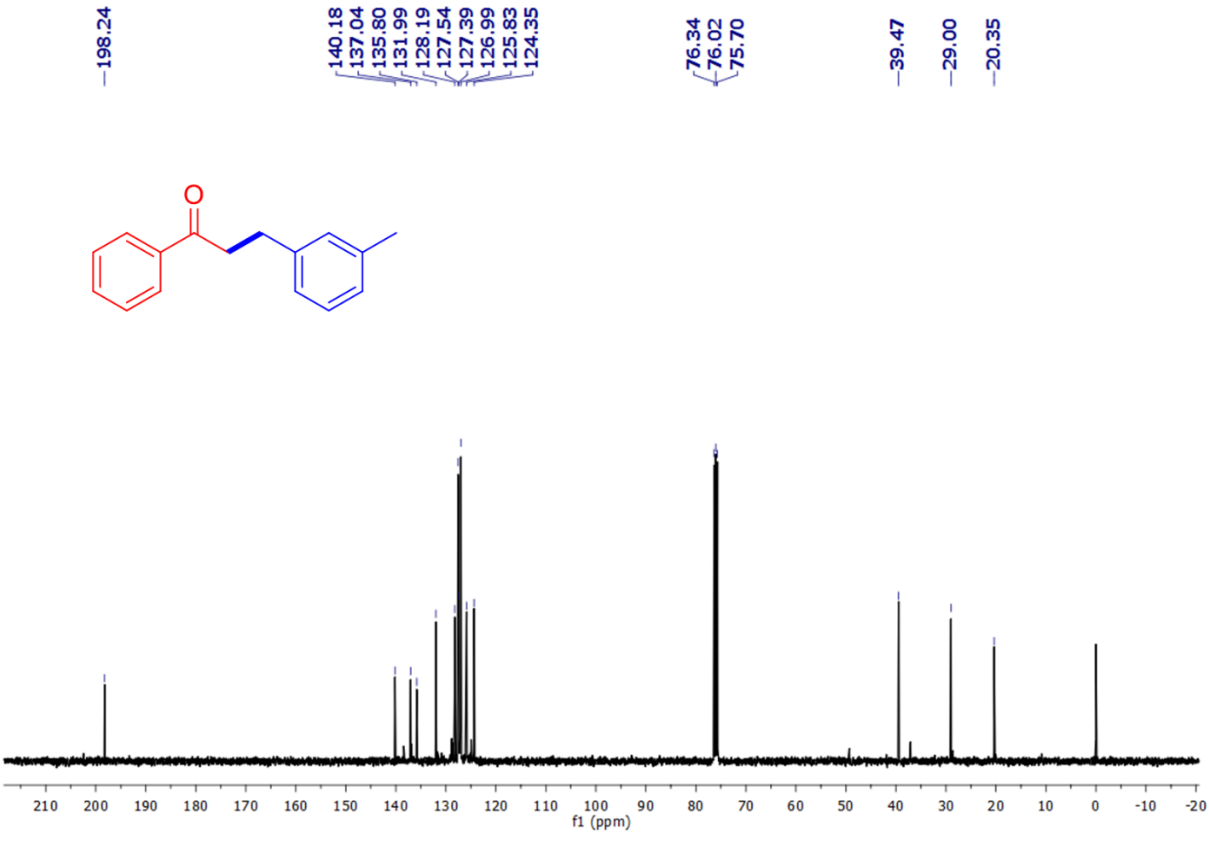


Figure S29. ^{13}C NMR spectrum of compound **3g** in $CDCl_3$ (100 MHz, 293 K). [12]

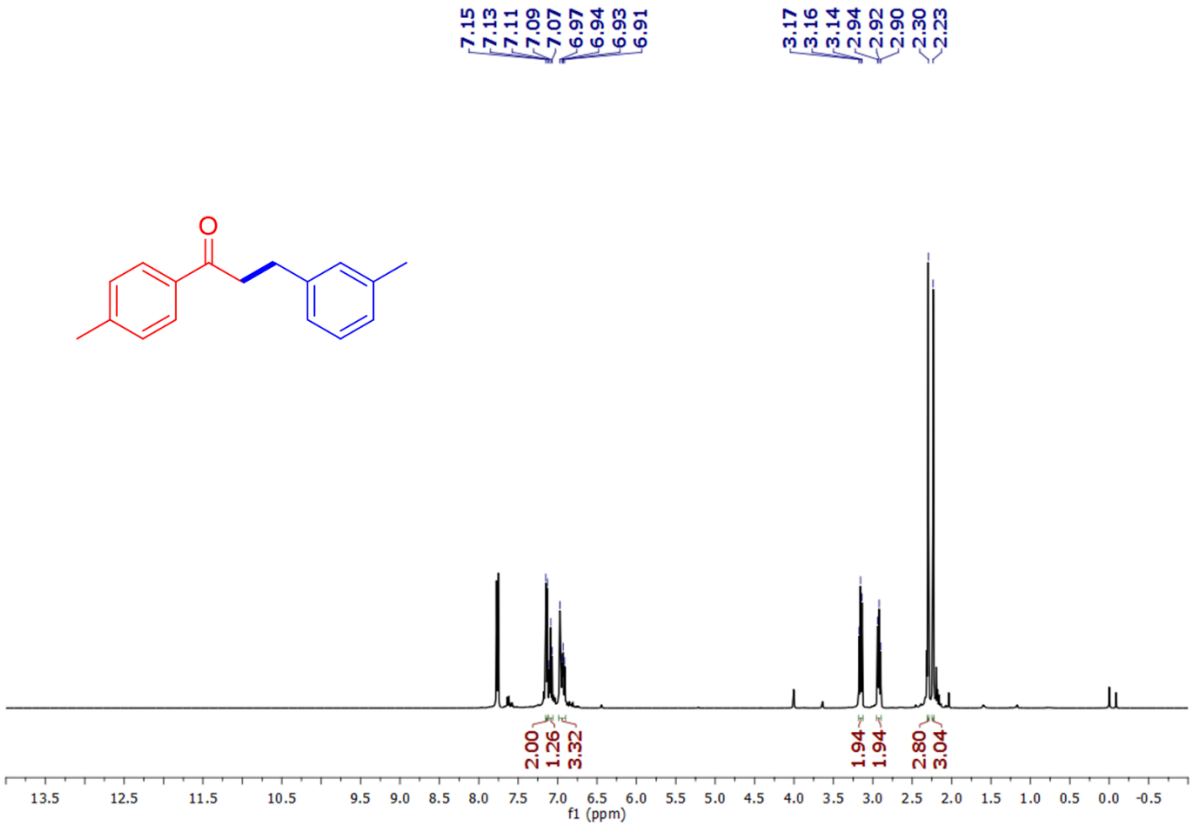


Figure S30. ^{1}H NMR spectrum of compound **3h** in $CDCl_3$ (400 MHz, 293 K).

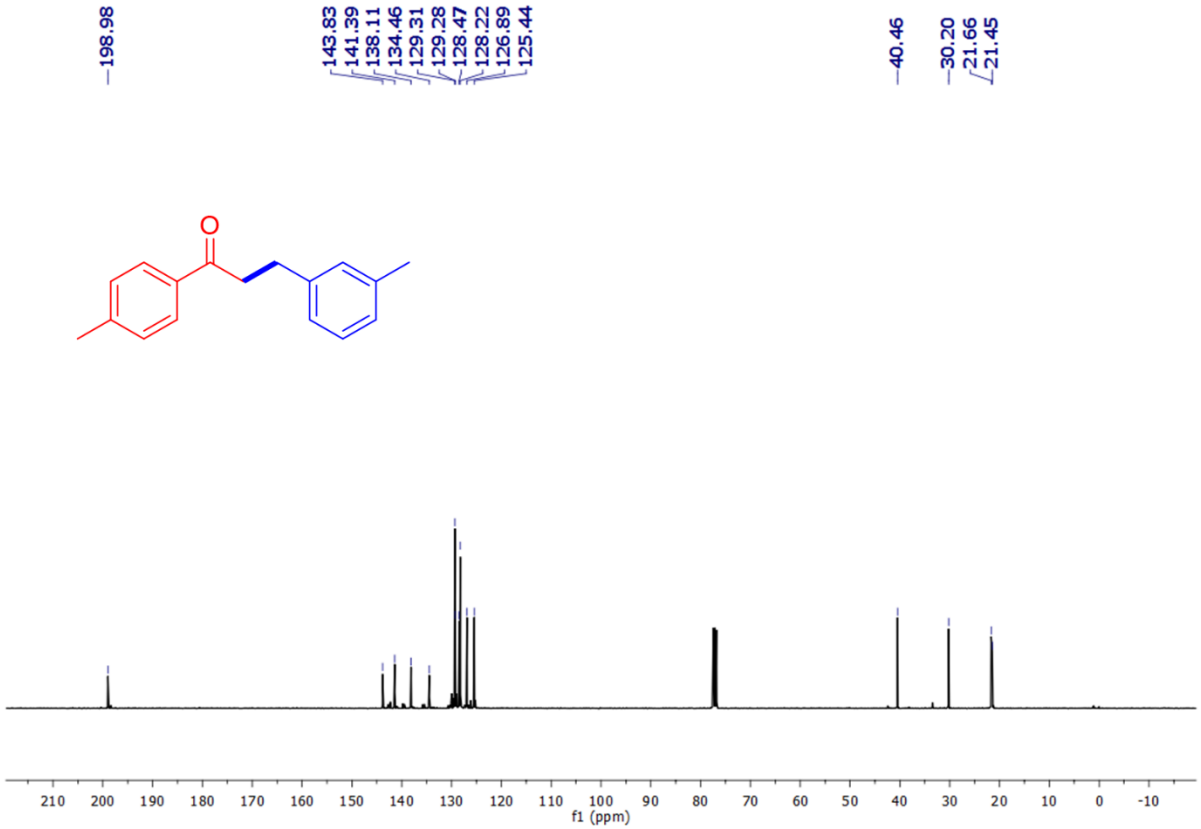


Figure S31. ^{13}C NMR spectrum of compound **3h** in $CDCl_3$ (100 MHz, 293 K).

Supporting Information

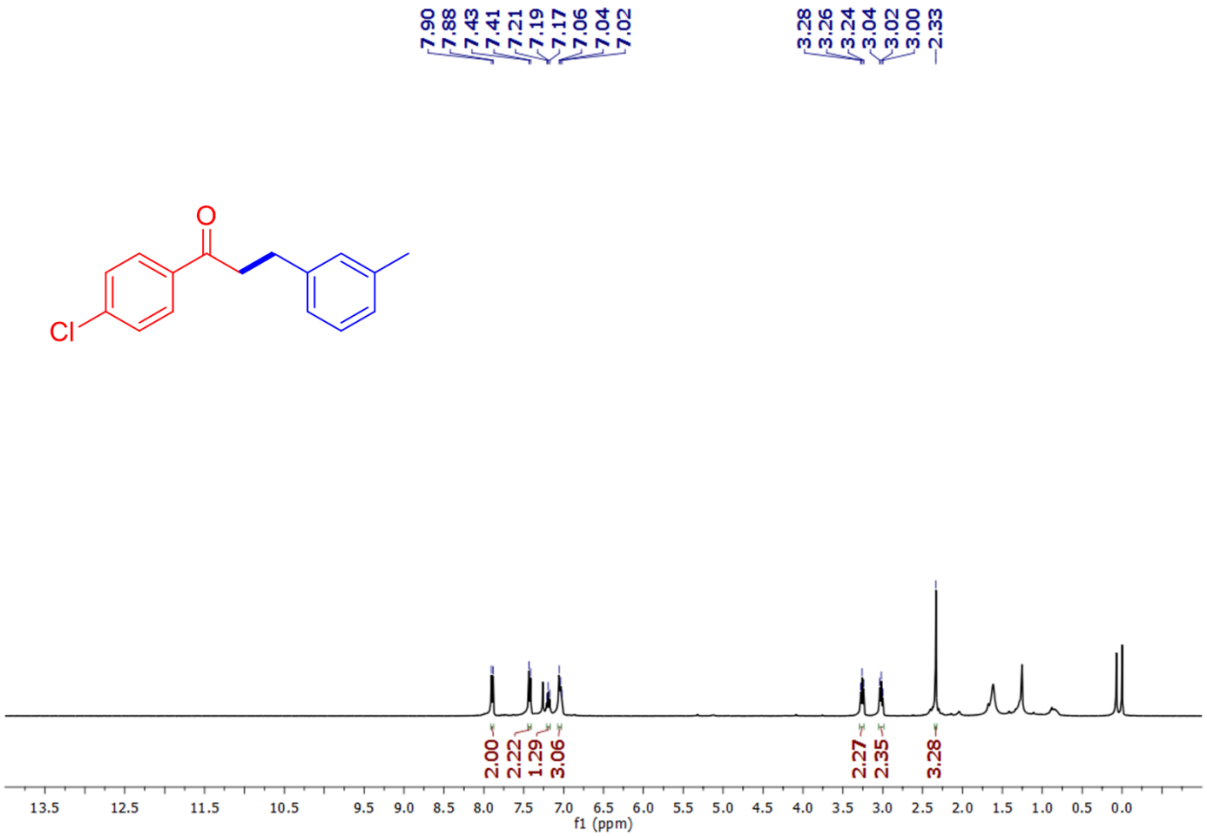


Figure S32. ^{1}H NMR spectrum of compound **3i** in $CDCl_3$ (400 MHz, 293 K).

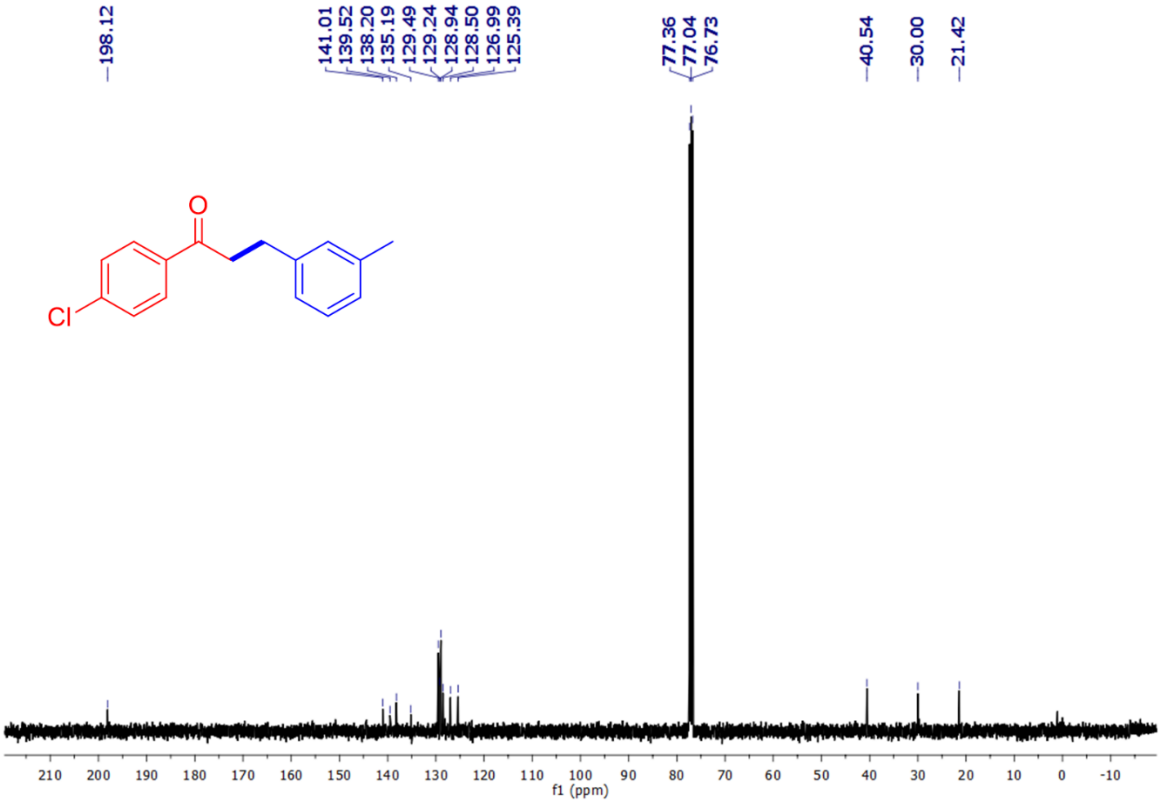


Figure S33. ^{13}C NMR spectrum of compound **3i** in $CDCl_3$ (100 MHz, 293 K).

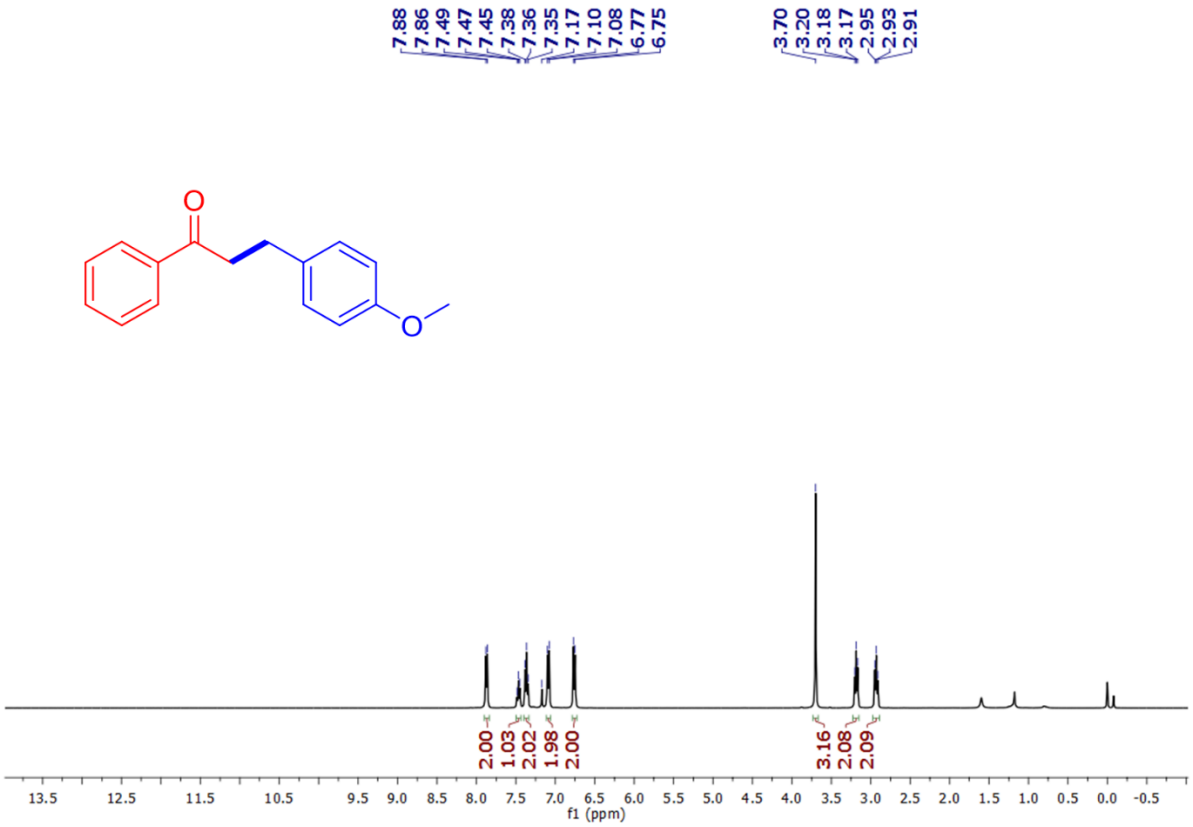


Figure S34. ^{1}H NMR spectrum of compound **3j** in $CDCl_3$ (400 MHz, 293 K). [8]

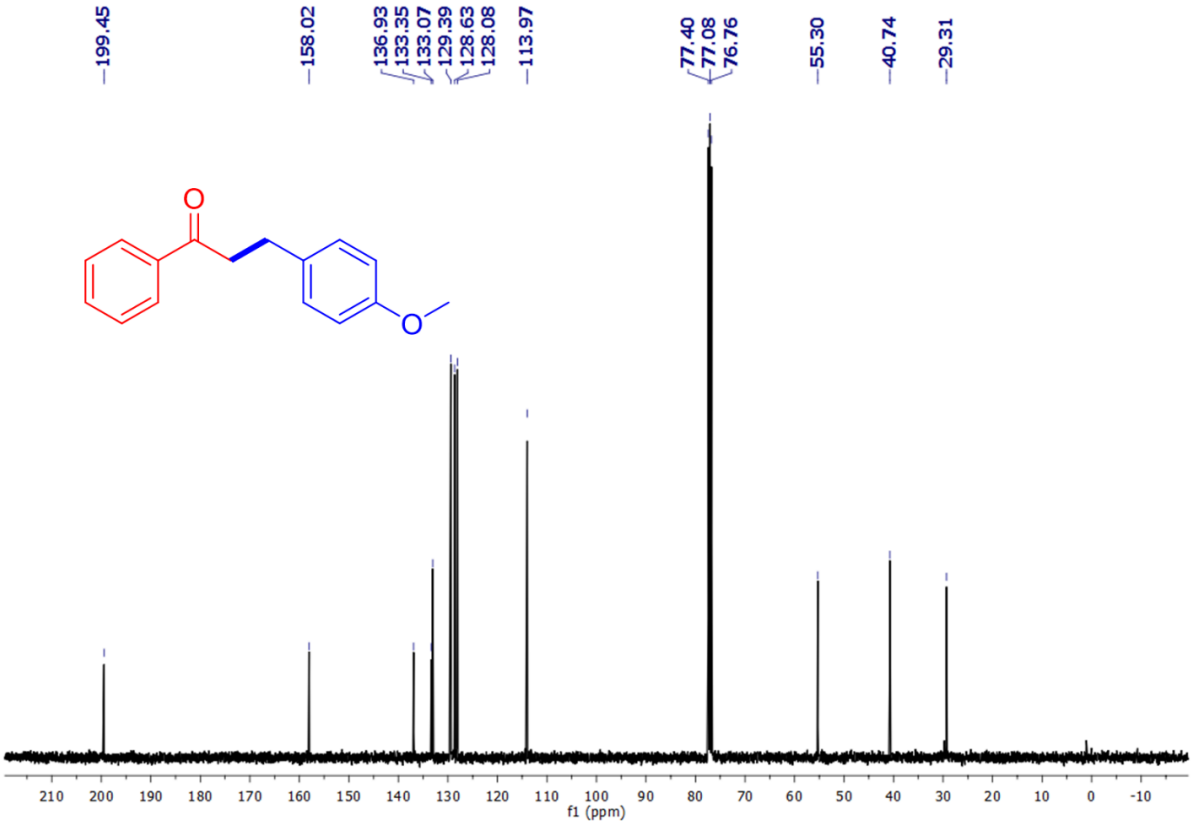


Figure S35. ^{13}C NMR spectrum of compound **3j** in $CDCl_3$ (100 MHz, 293 K). [8]

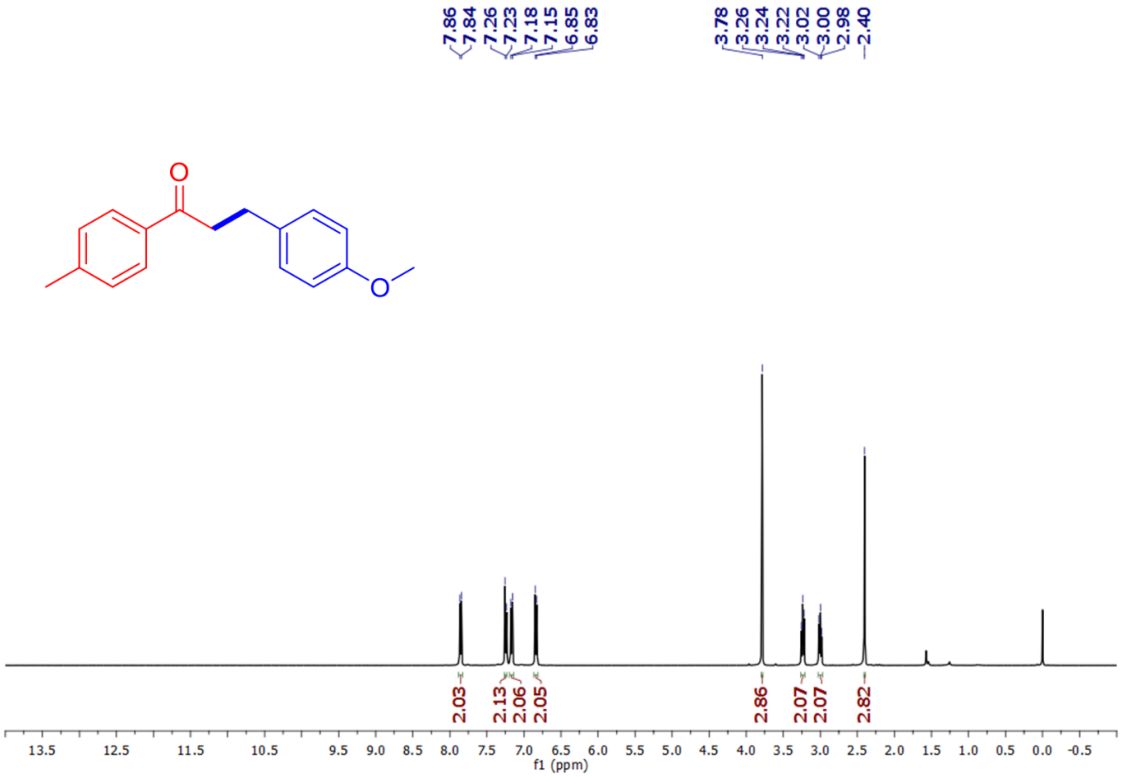


Figure S36. ^{1}H NMR spectrum of compound **3k** in $CDCl_3$ (400 MHz, 293 K). [22]

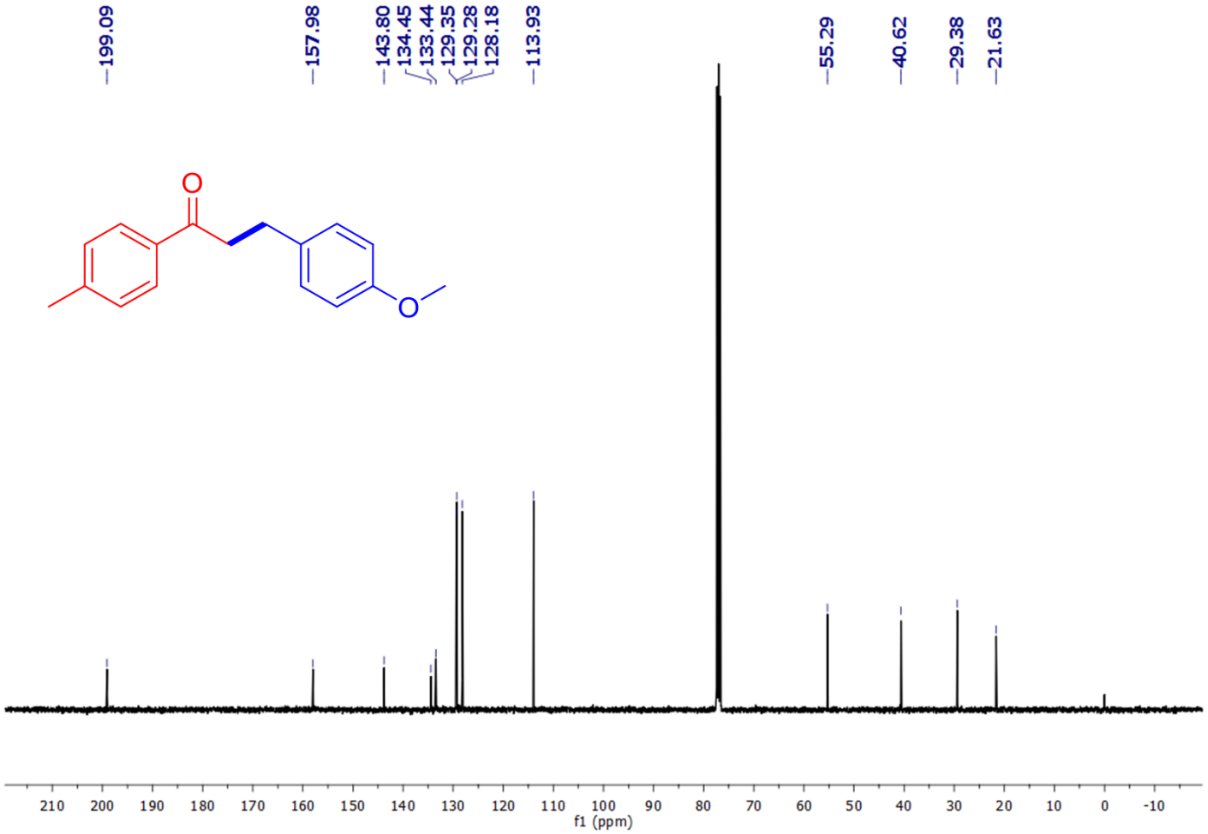


Figure S37. ^{13}C NMR spectrum of compound **3k** in $CDCl_3$ (100 MHz, 293 K). [22]

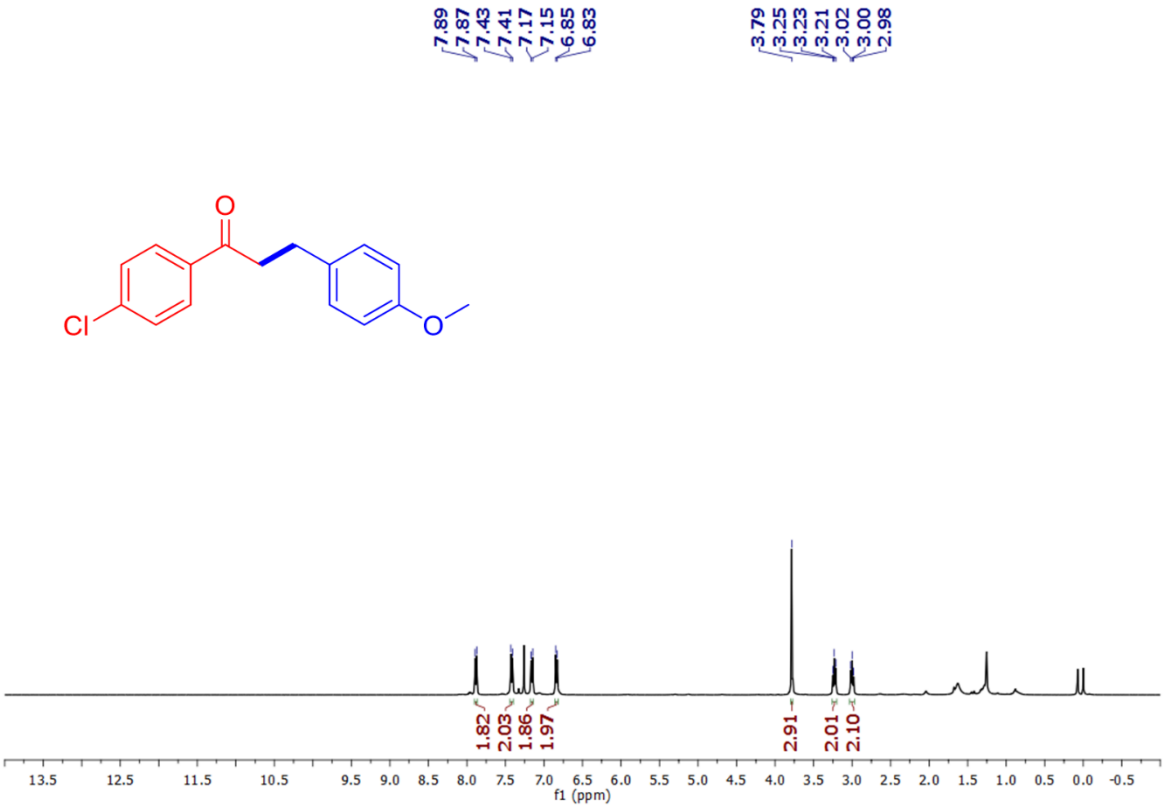


Figure S38. ^{1}H NMR spectrum of compound **3l** in $CDCl_3$ (400 MHz, 293 K). [22]

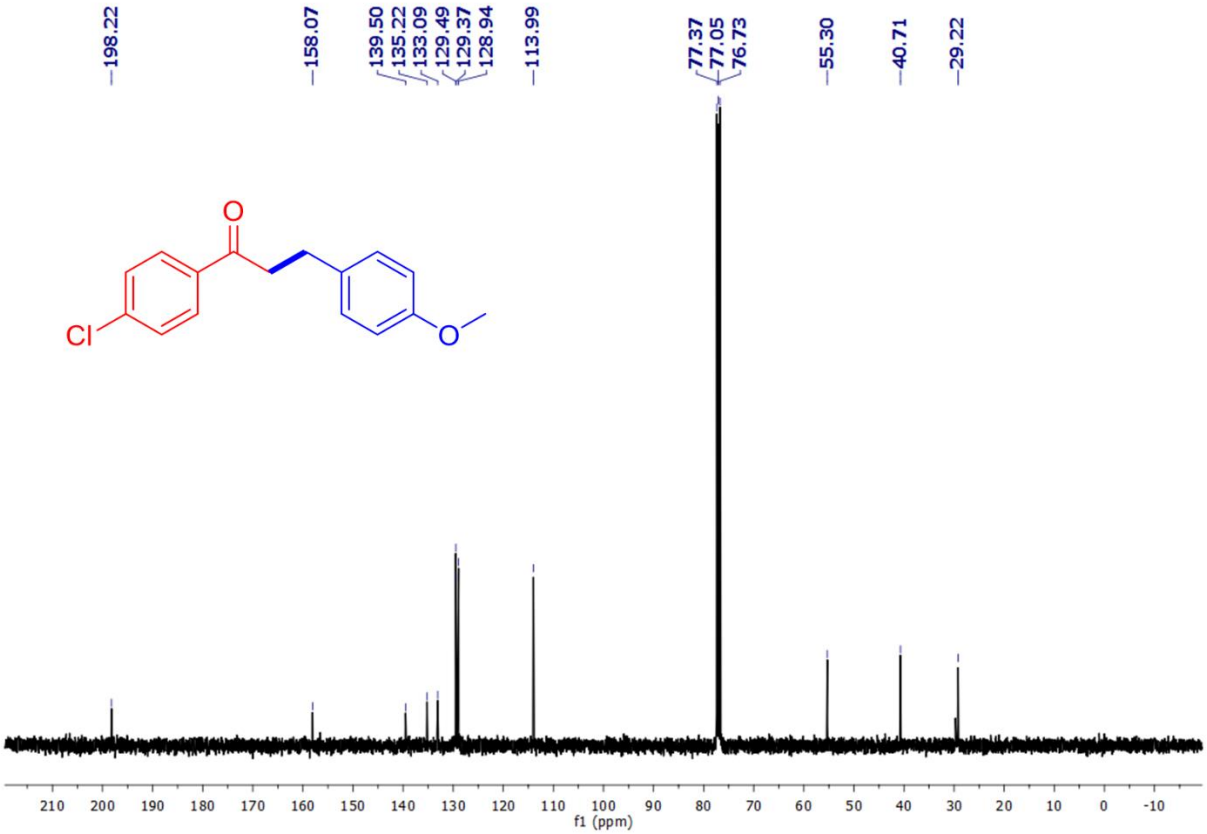


Figure S39. ^{13}C NMR spectrum of compound **3l** in $CDCl_3$ (100 MHz, 293 K). [22]

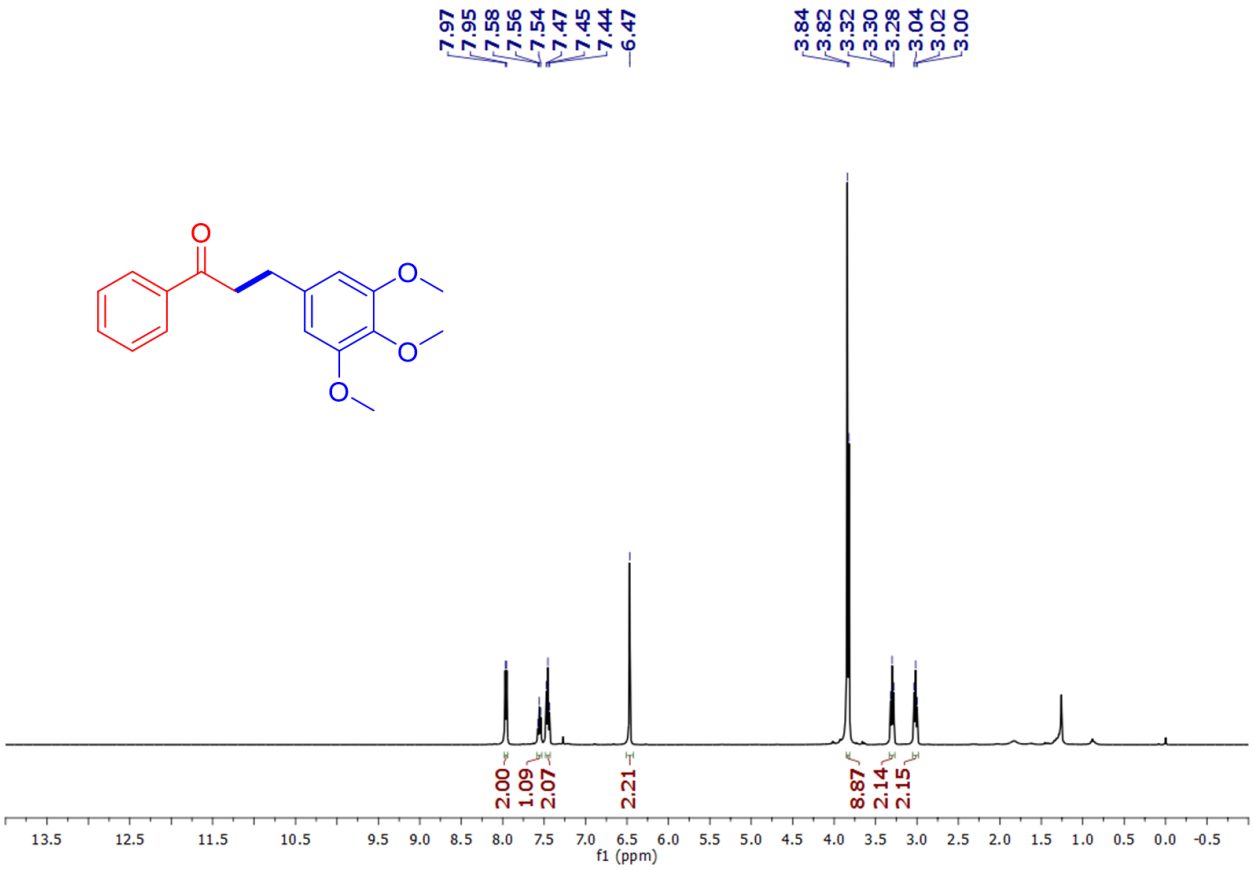


Figure S40. ^{1}H NMR spectrum of compound **3m** in $CDCl_3$ (400 MHz, 293 K). [23]

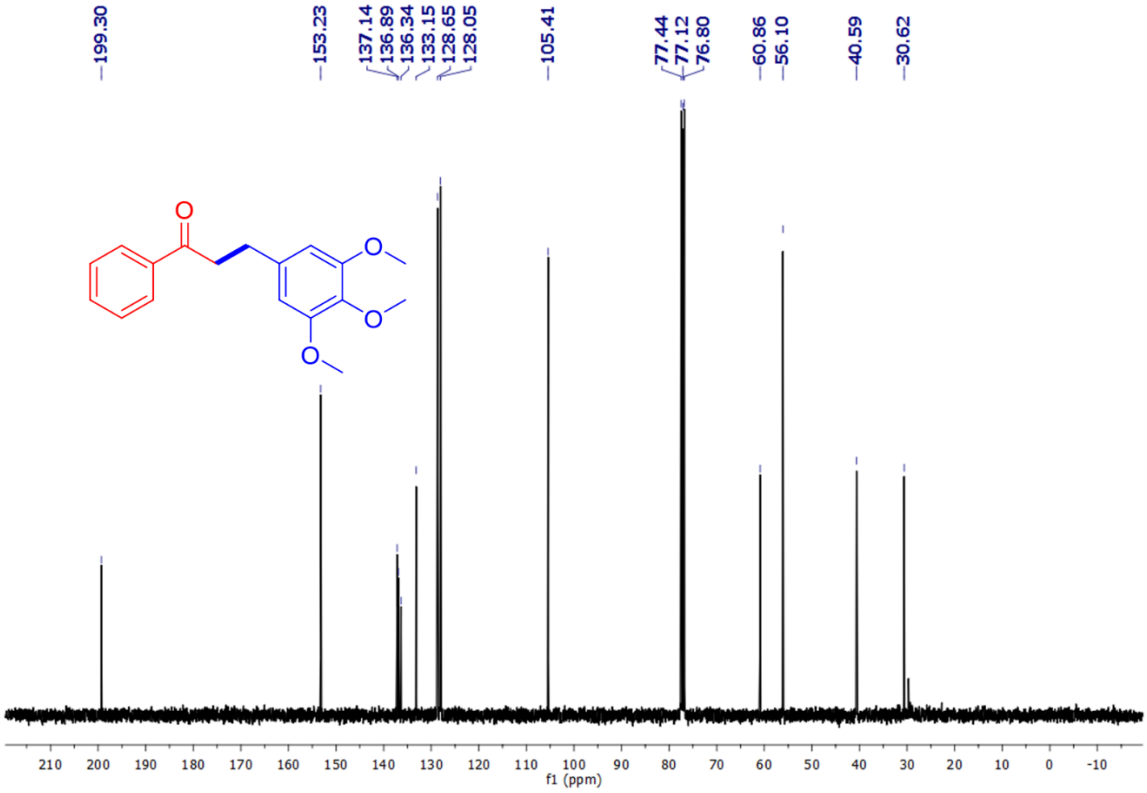


Figure S41. ^{13}C NMR spectrum of compound **3m** in $CDCl_3$ (100 MHz, 293 K). [23]

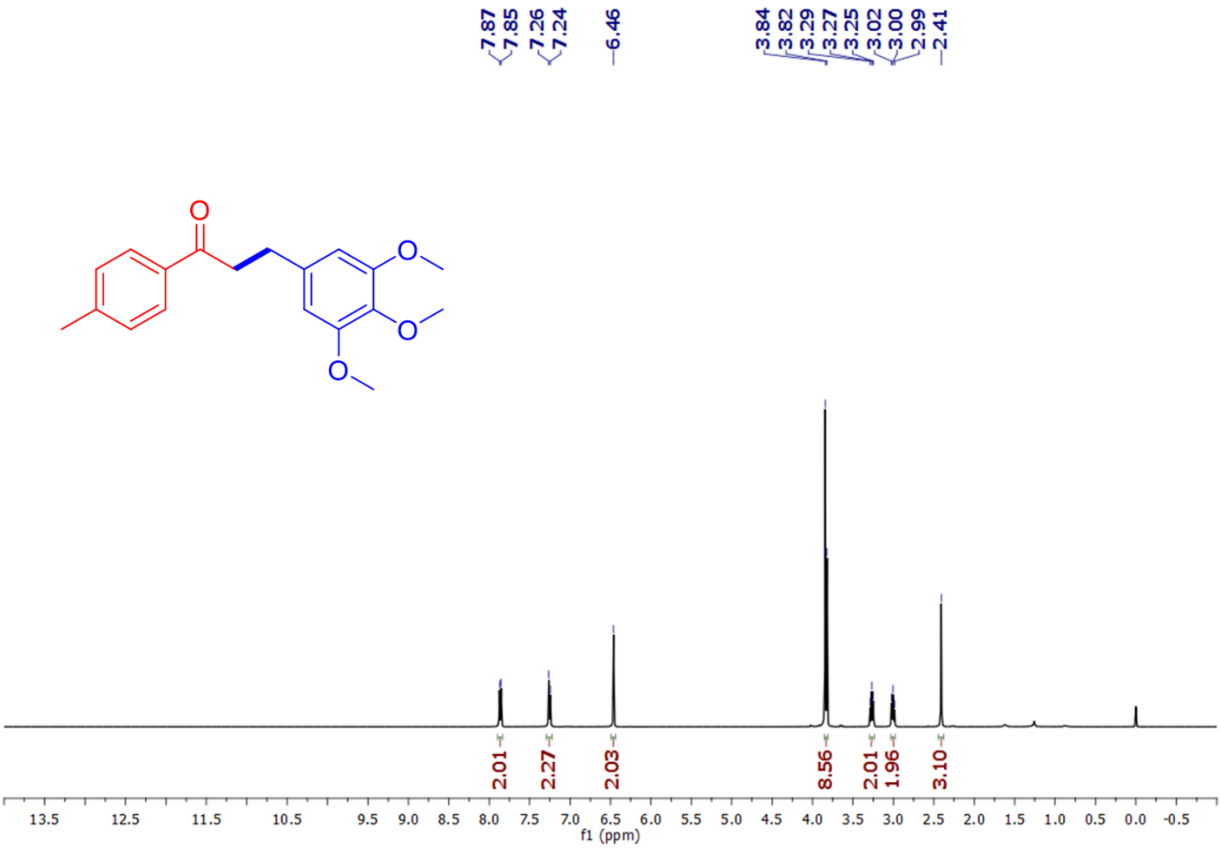


Figure S42. ^{1}H NMR spectrum of compound **3n** in $CDCl_3$ (400 MHz, 293 K).

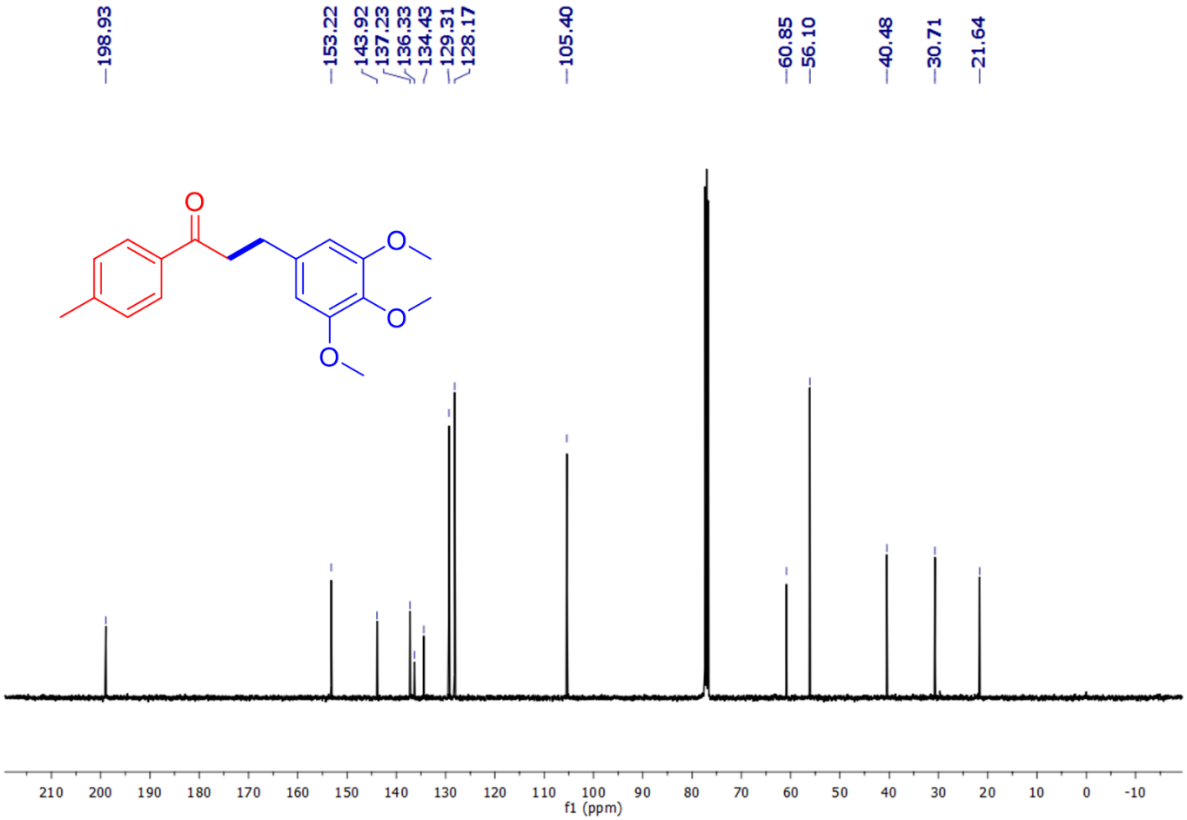


Figure S43. ^{13}C NMR spectrum of compound **3n** in $CDCl_3$ (100 MHz, 293 K).

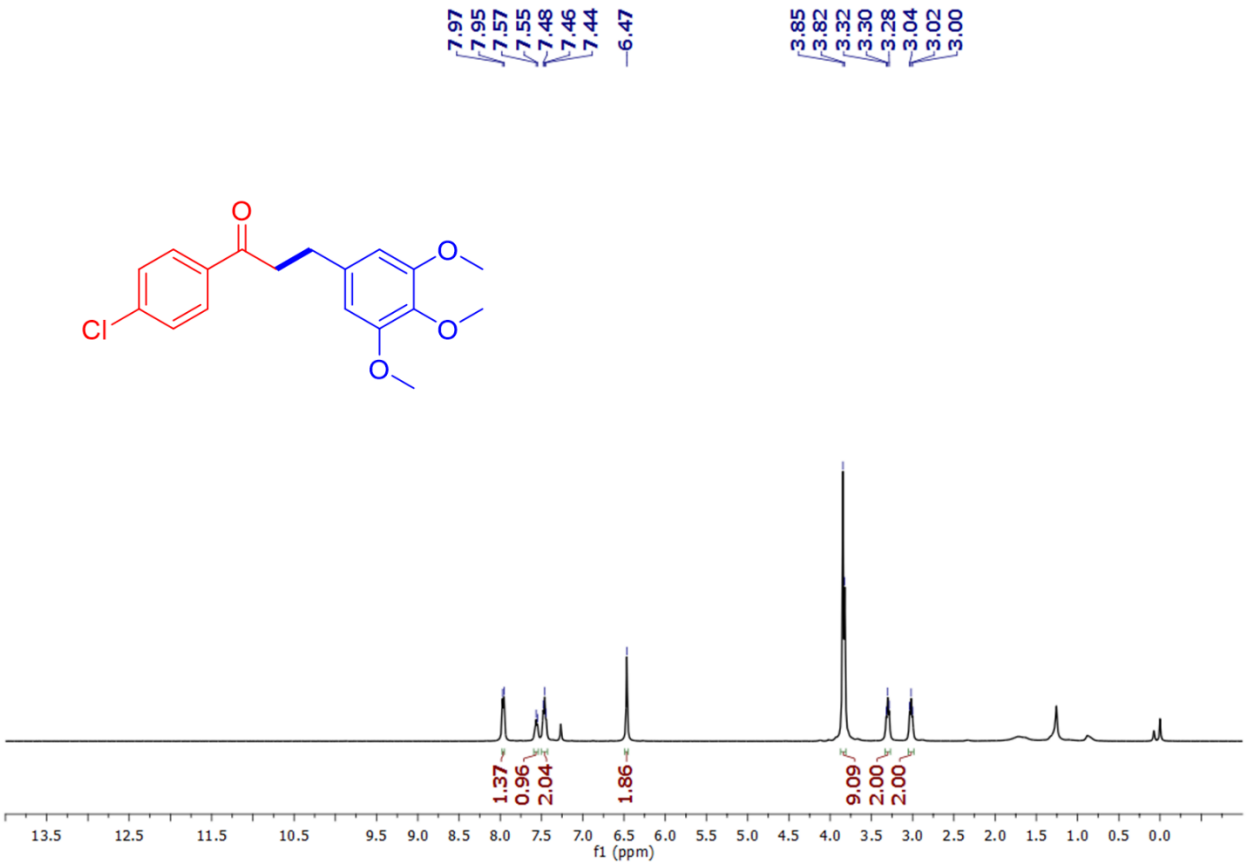


Figure S44. ^{1}H NMR spectrum of compound **3o** in $CDCl_3$ (400 MHz, 293 K).

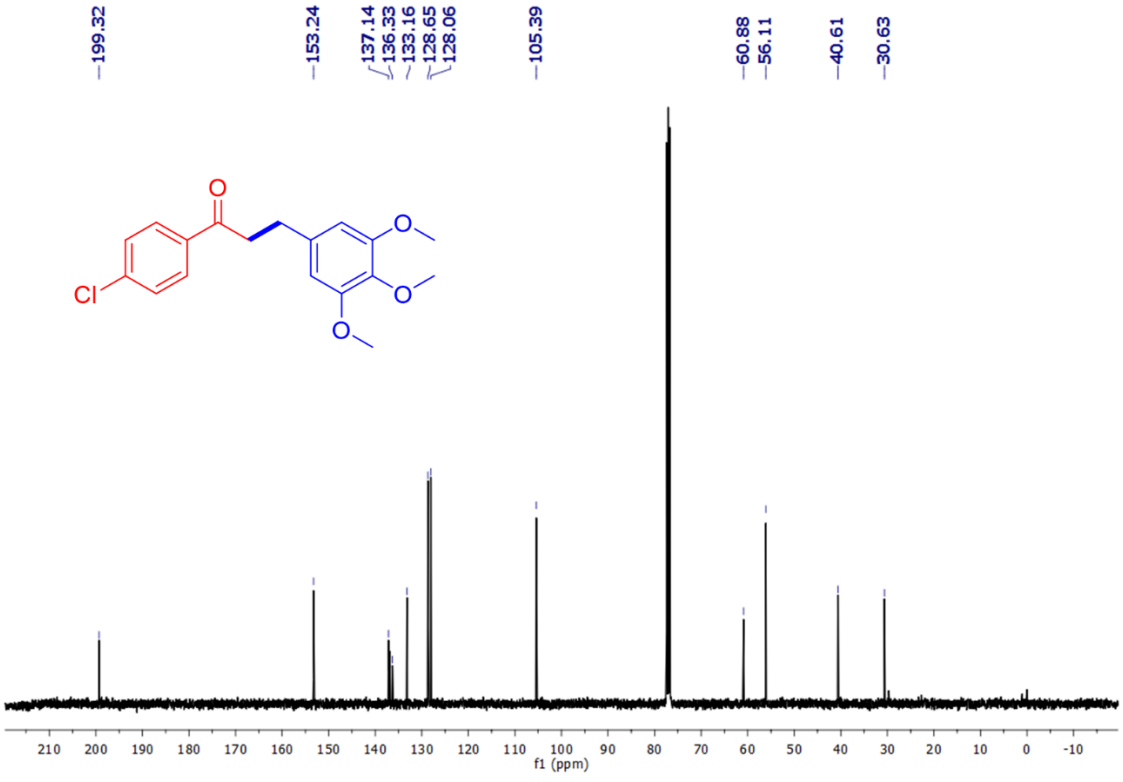


Figure S45. ^{13}C NMR spectrum of compound **3o** in $CDCl_3$ (100 MHz, 293 K).

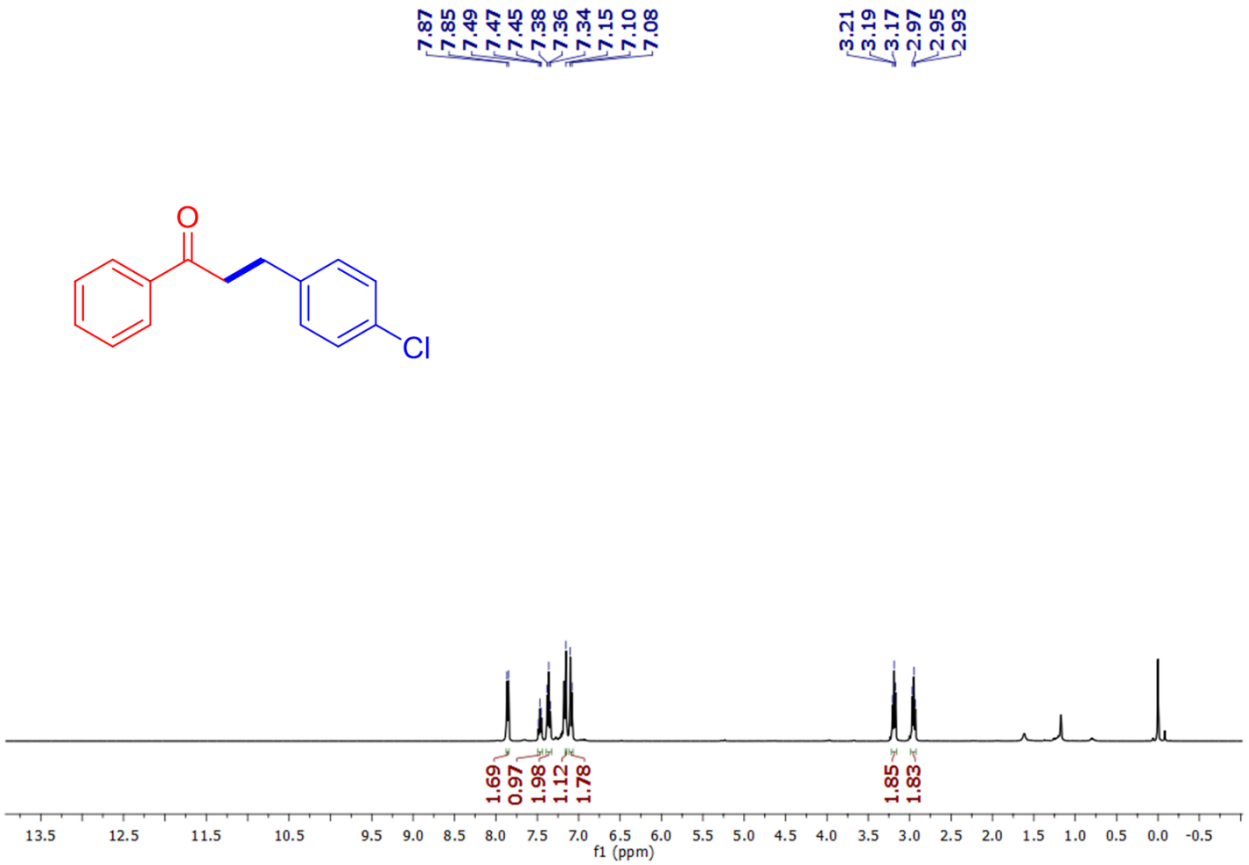


Figure S46. ^{1}H NMR spectrum of compound **3p** in $CDCl_3$ (400 MHz, 293 K). [8]

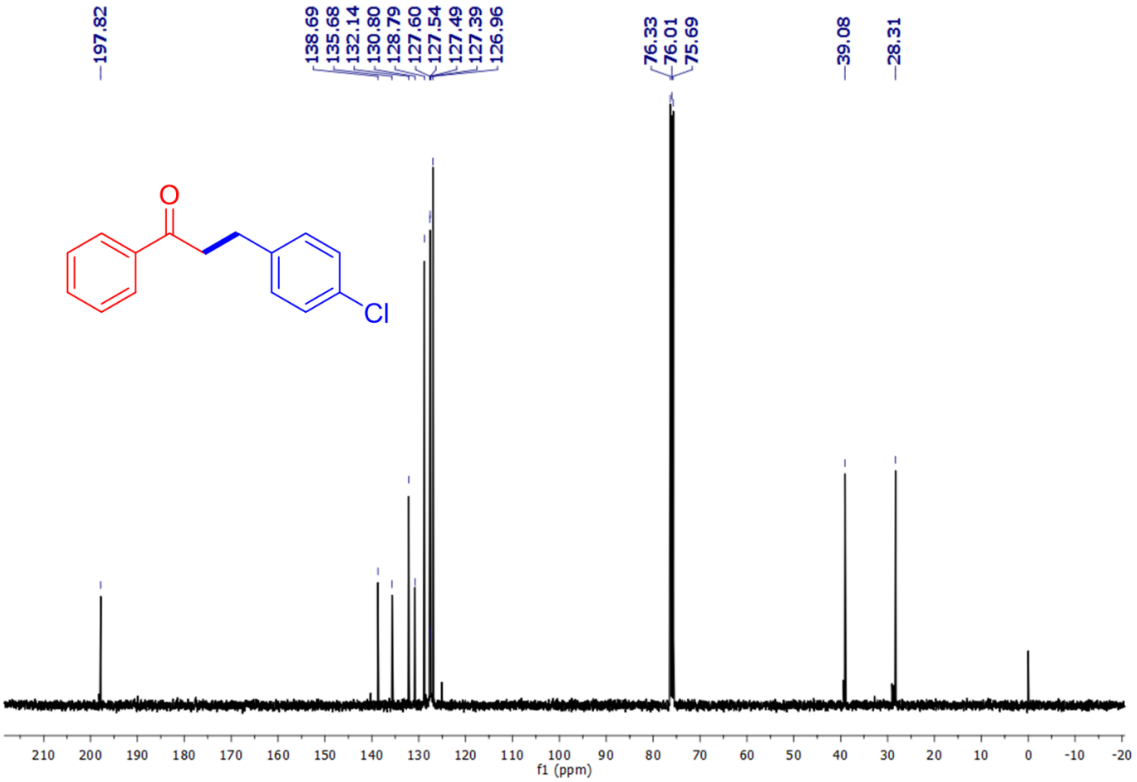


Figure S47. ^{13}C NMR spectrum of compound **3p** in $CDCl_3$ (100 MHz, 293 K). [8]

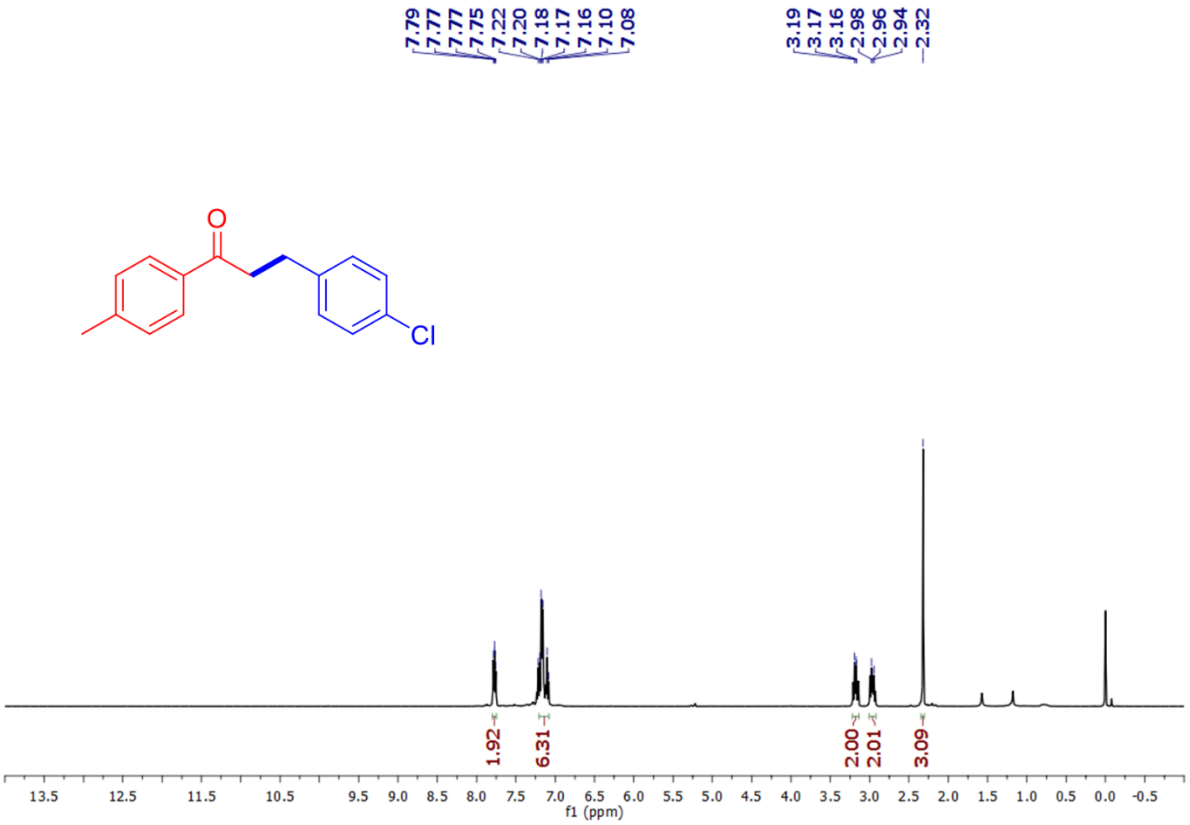


Figure S48. ^{1}H NMR spectrum of compound **3q** in $CDCl_3$ (400 MHz, 293 K). [22]

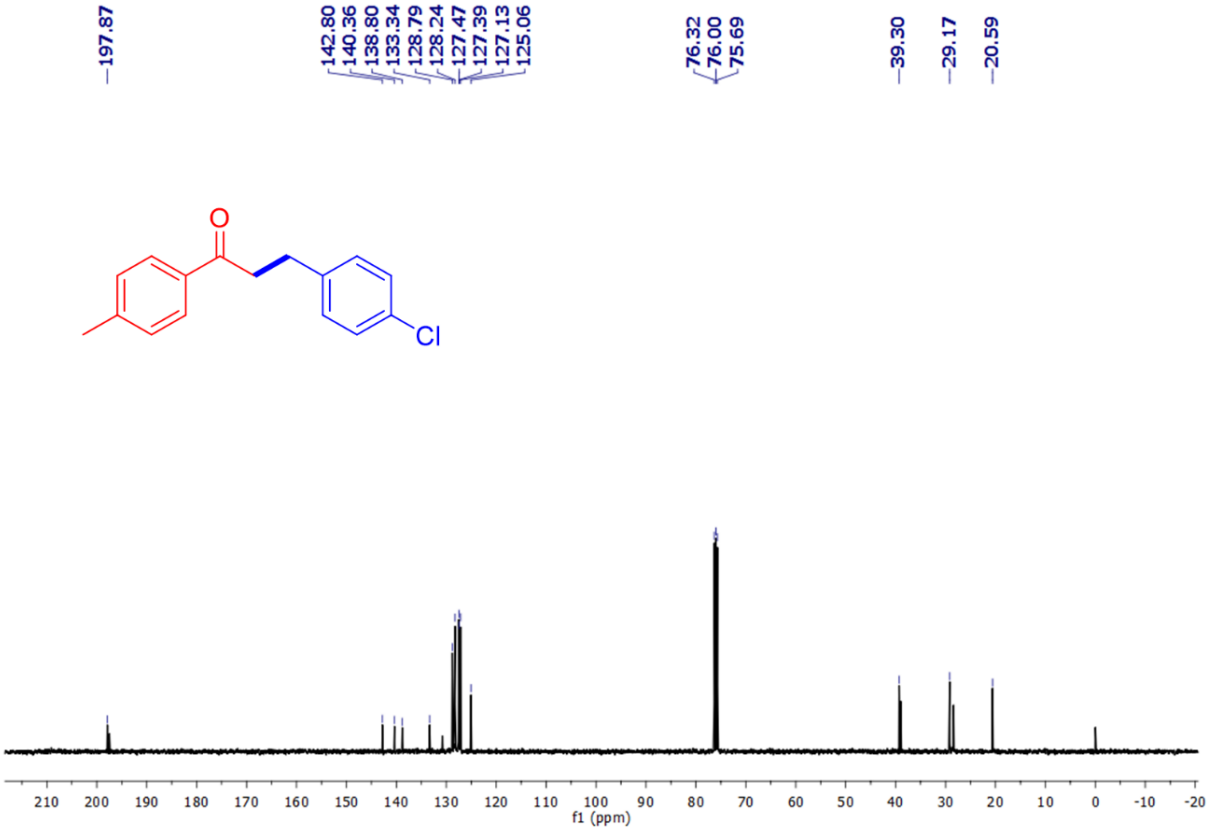


Figure S49. ^{13}C NMR spectrum of compound **3q** in $CDCl_3$ (100 MHz, 293 K). [22]

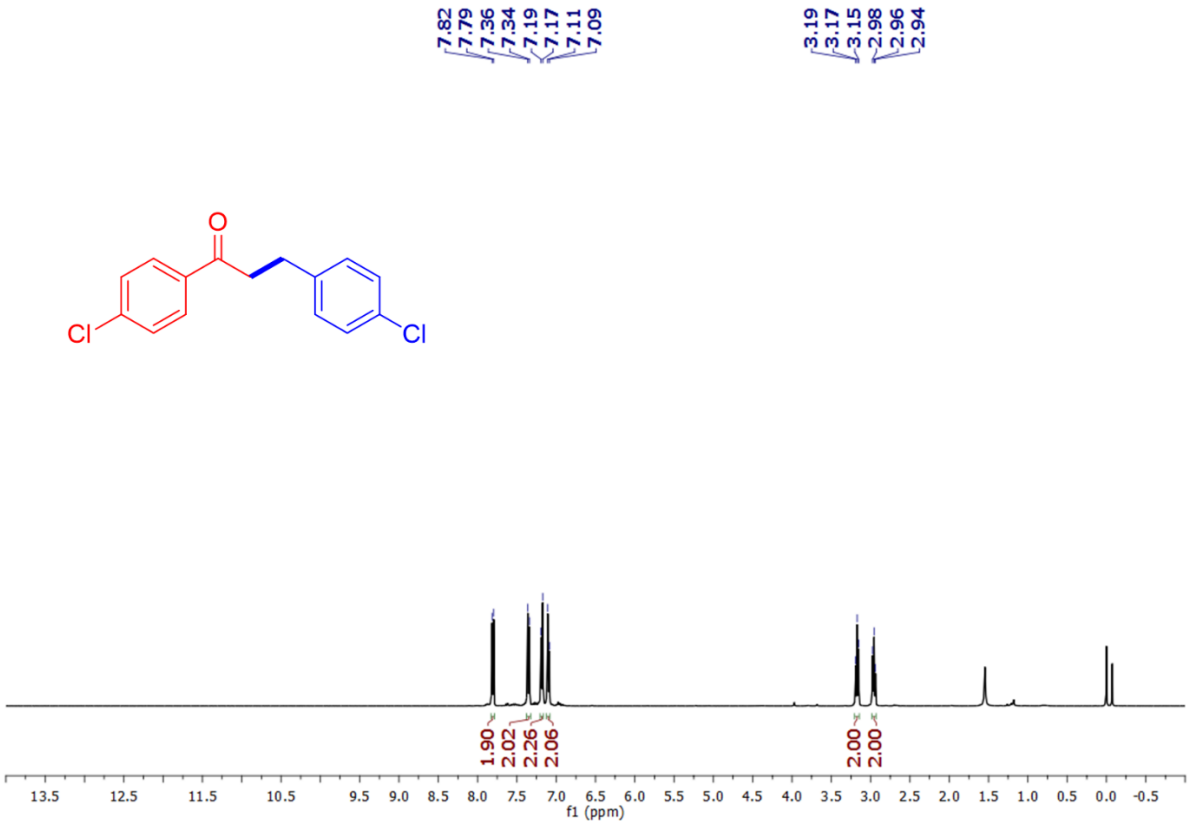


Figure S50. ^{1}H NMR spectrum of compound **3r** in $CDCl_3$ (400 MHz, 293 K). [22]

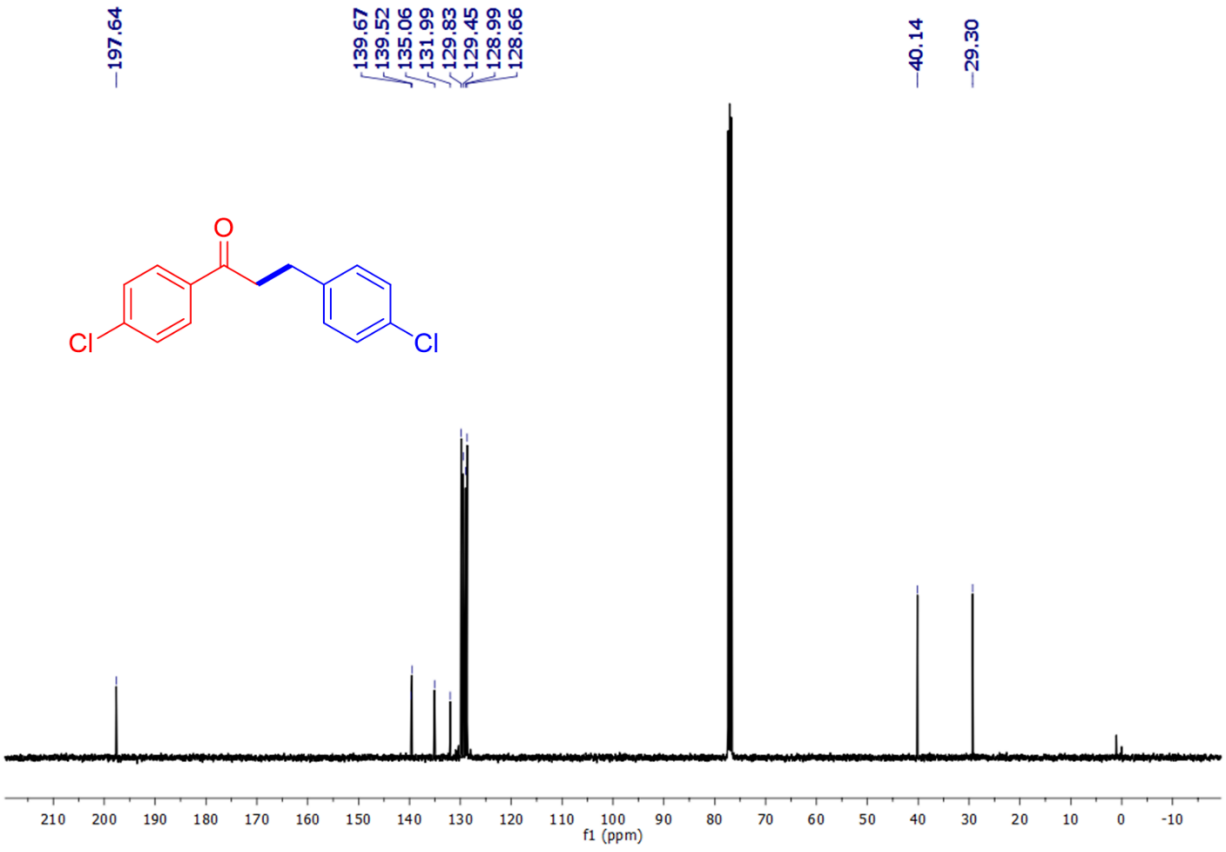


Figure S51. ^{13}C NMR spectrum of compound **3r** in $CDCl_3$ (100 MHz, 293 K). [22]

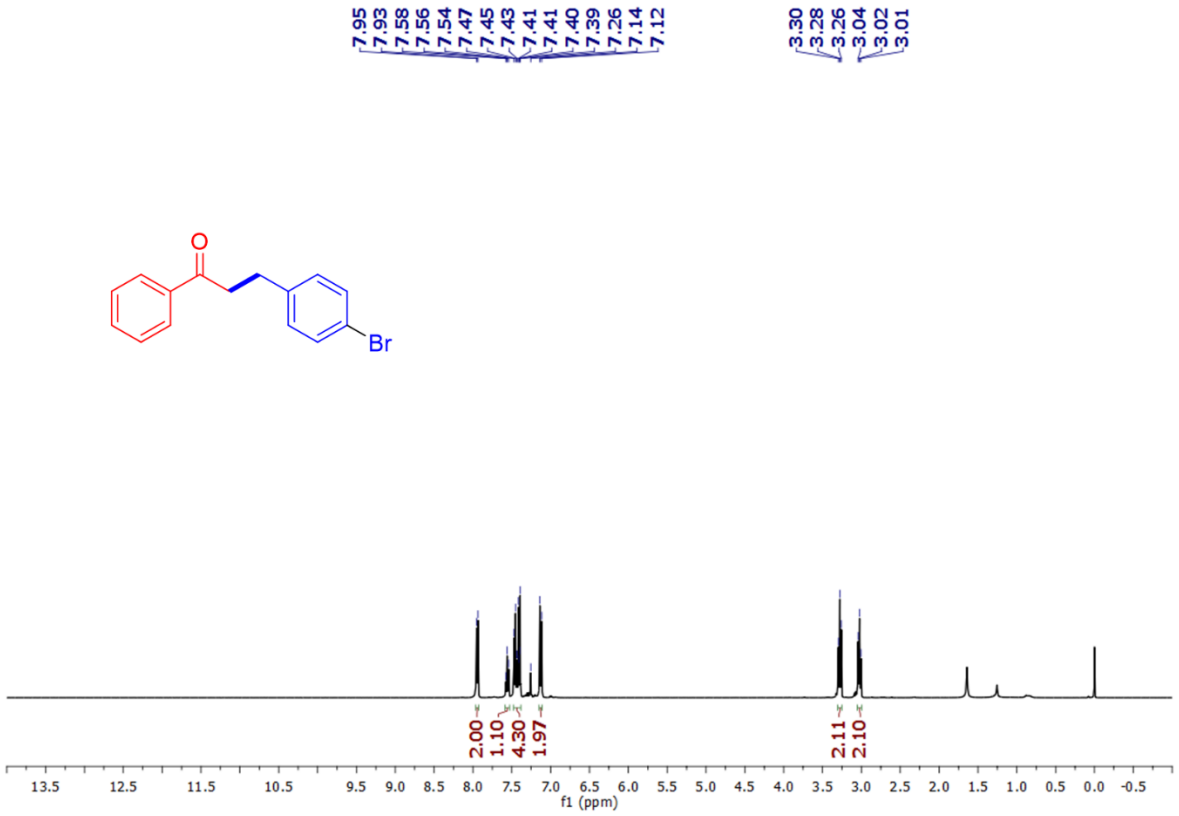


Figure S52. ^{1}H NMR spectrum of compound **3s** in $CDCl_3$ (400 MHz, 293 K). [9]

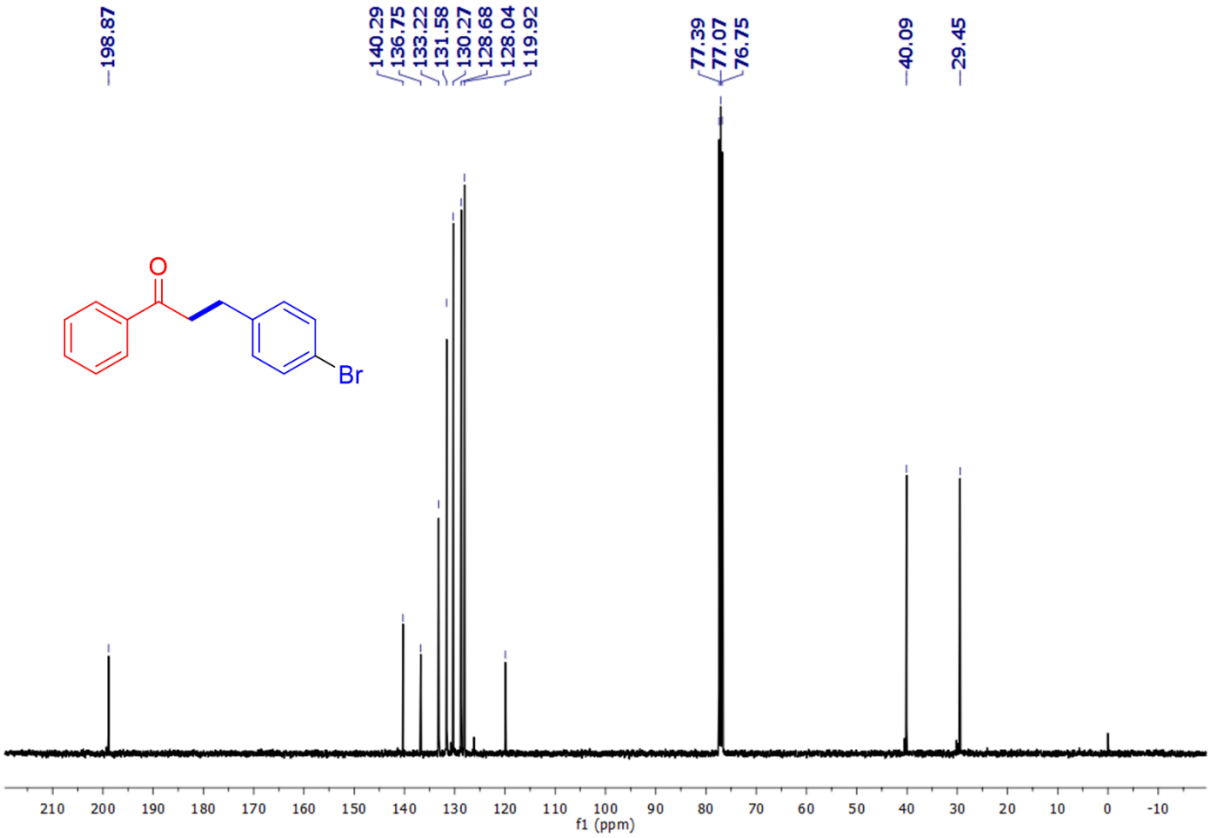


Figure S53. ^{13}C NMR spectrum of compound **3s** in $CDCl_3$ (100 MHz, 293 K). [9]

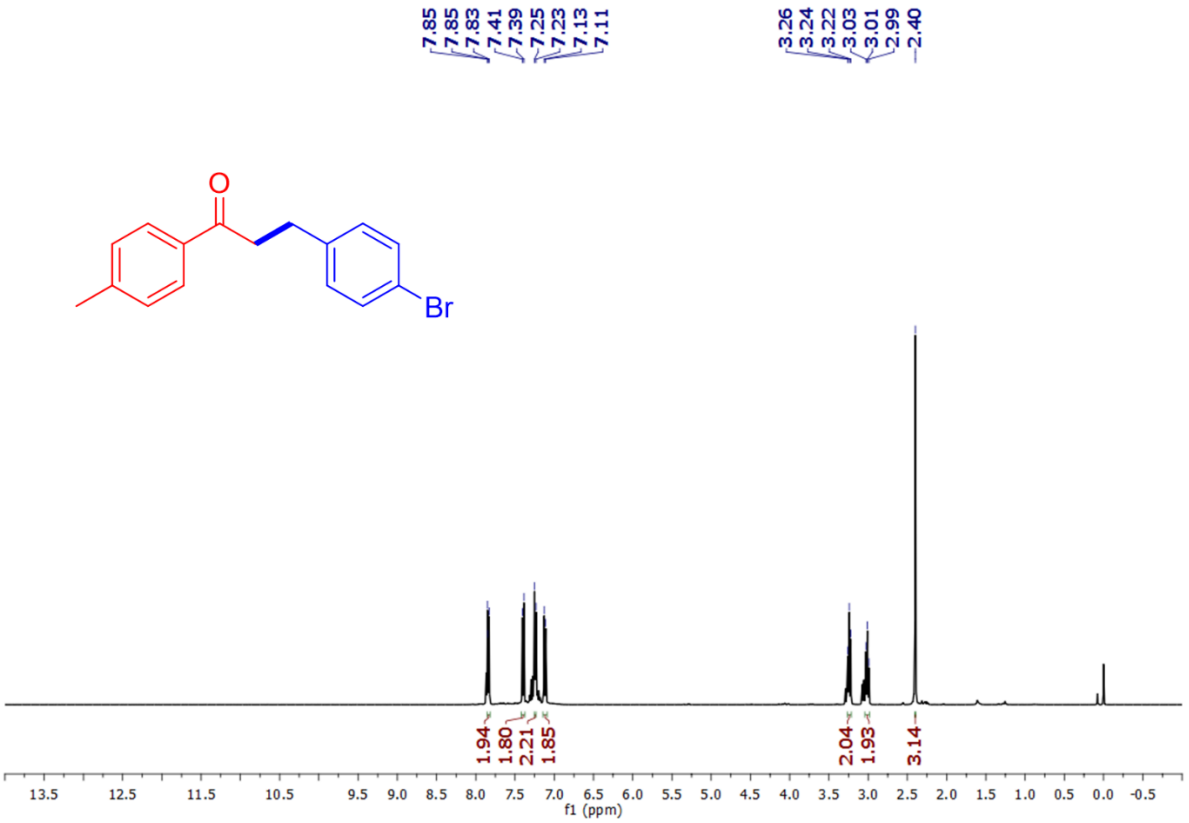


Figure S54. ^{1}H NMR spectrum of compound **3t** in $CDCl_3$ (400 MHz, 293 K).

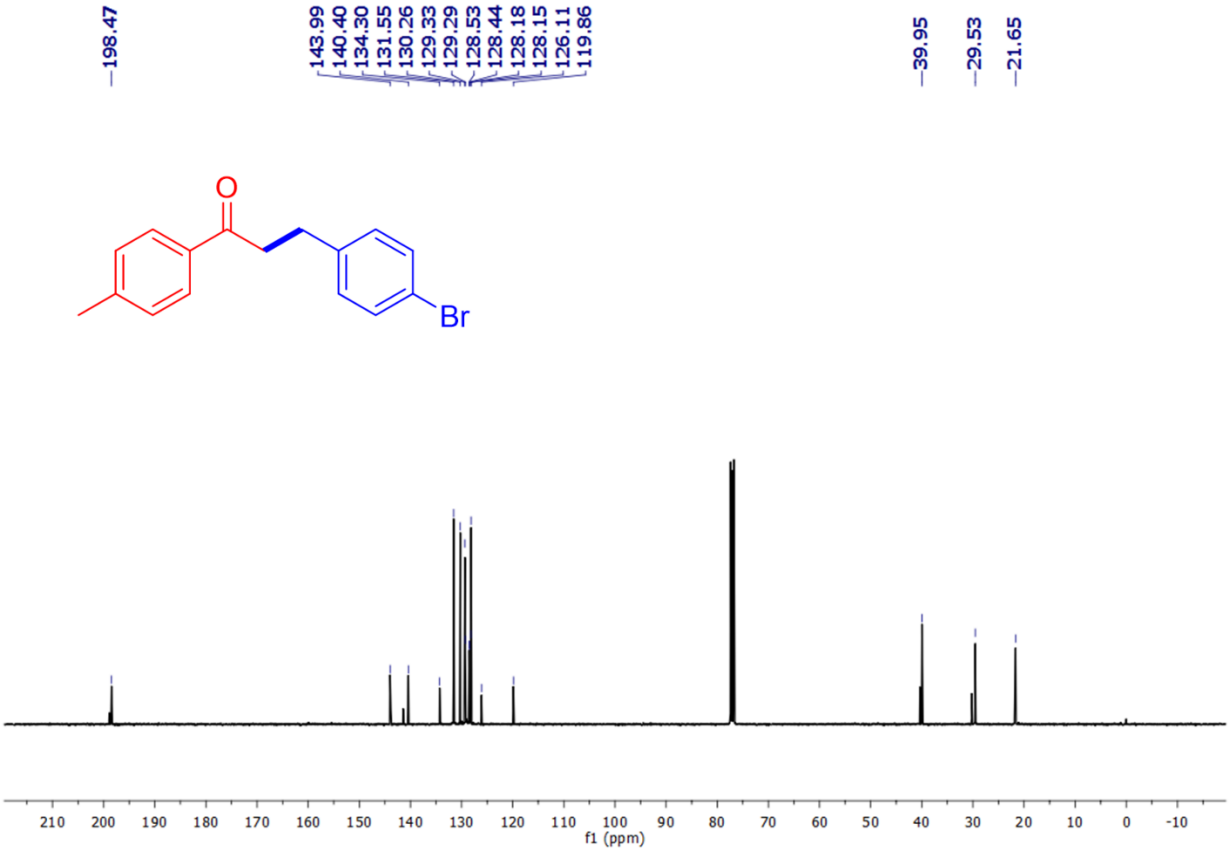


Figure S55. ^{13}C NMR spectrum of compound **3t** in $CDCl_3$ (100 MHz, 293 K).

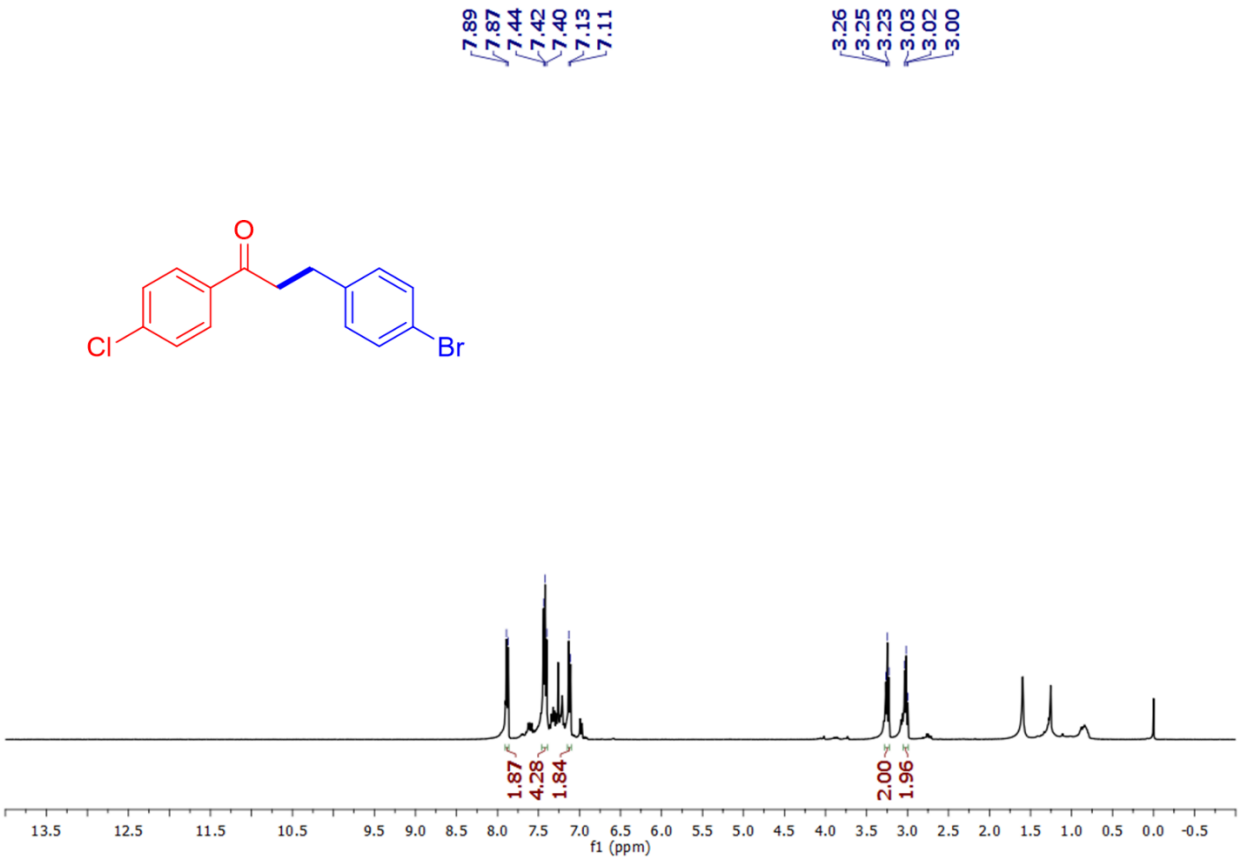


Figure S56. ^{1}H NMR spectrum of compound **3u** in $CDCl_3$ (400 MHz, 293 K).

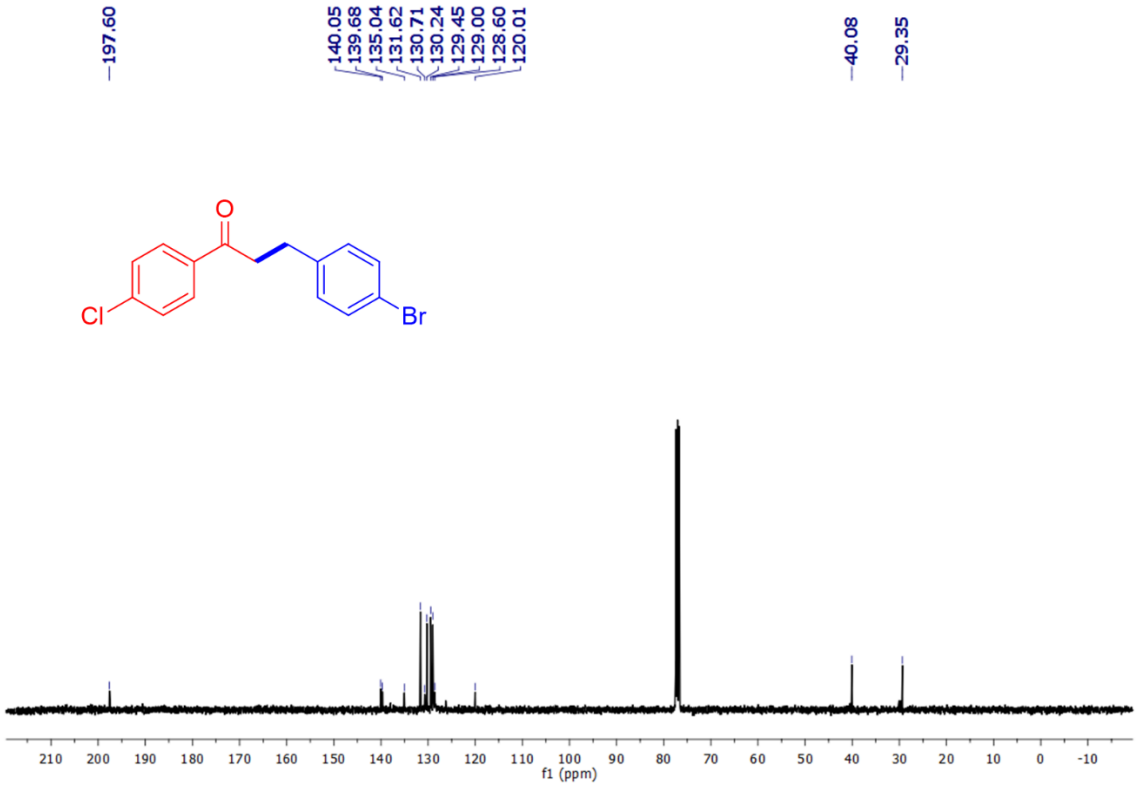


Figure S57. ^{13}C NMR spectrum of compound **3u** in $CDCl_3$ (100 MHz, 293 K).

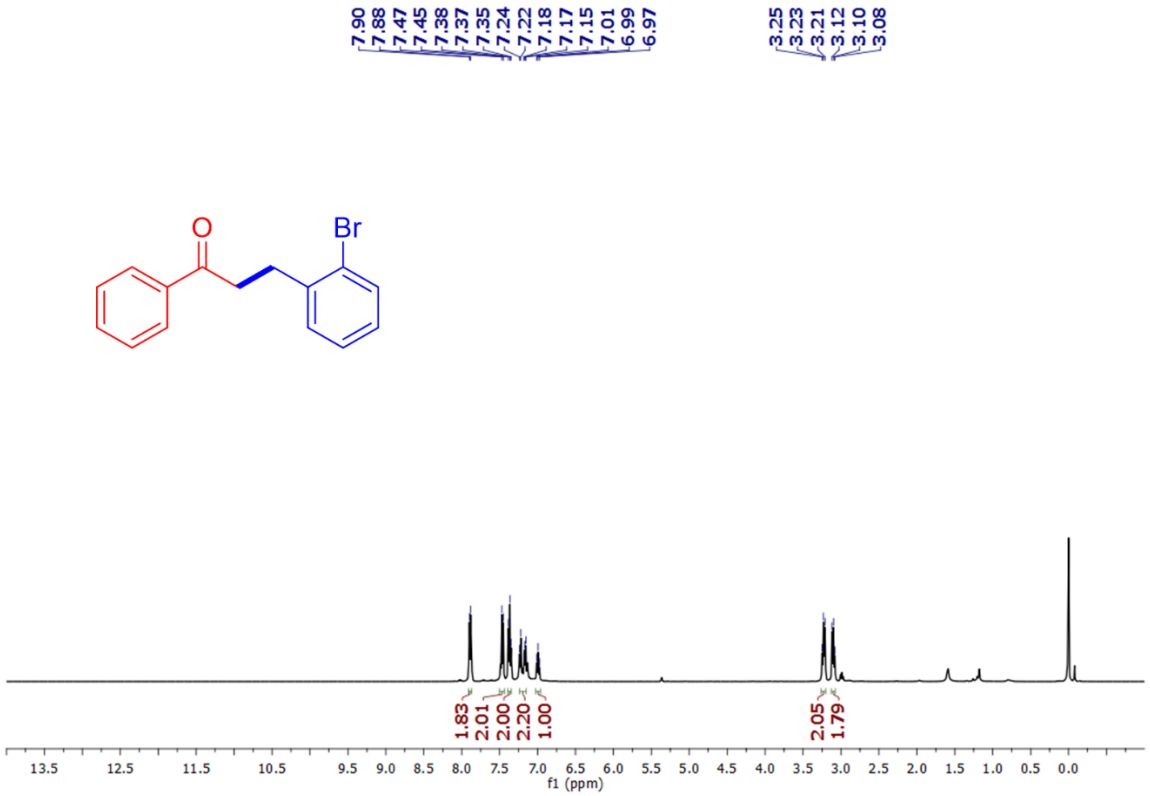


Figure S58. ^{1}H NMR spectrum of compound **3v** in $CDCl_3$ (400 MHz, 293 K).

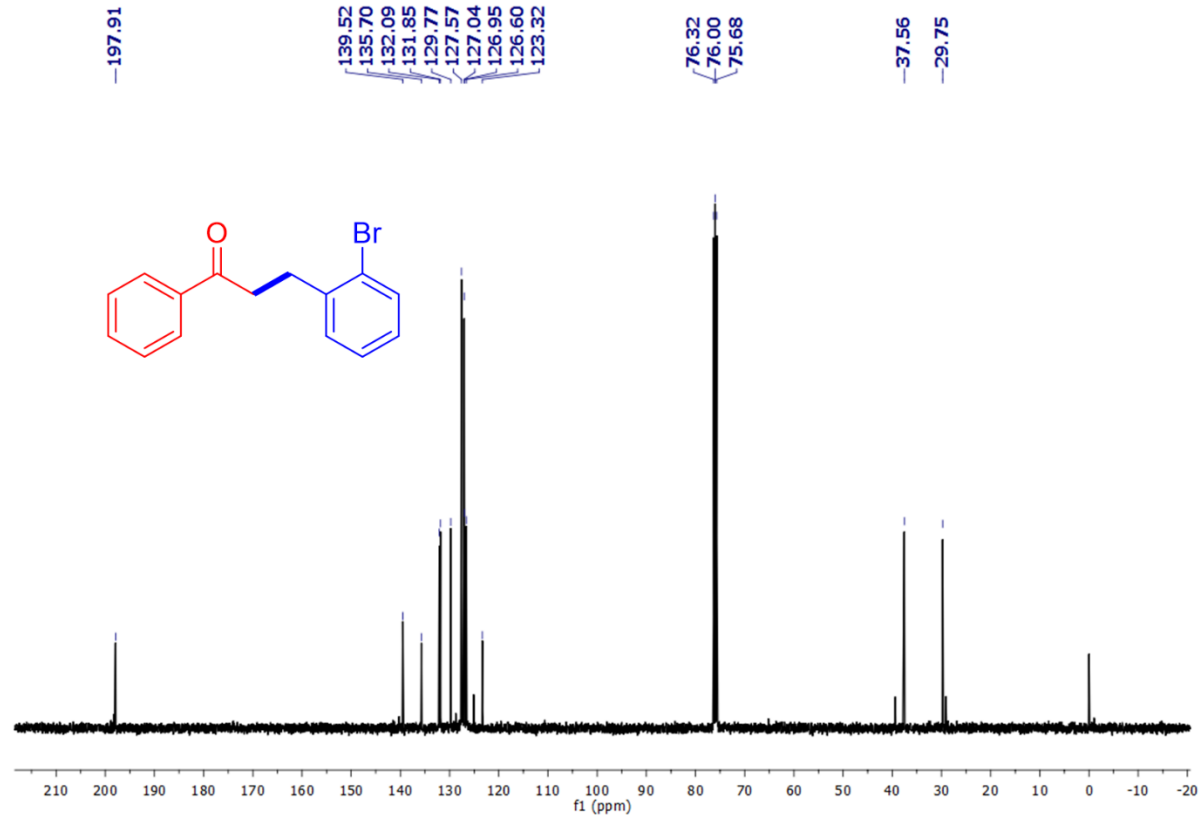


Figure S59. ^{13}C NMR spectrum of compound **3v** in $CDCl_3$ (100 MHz, 293 K).

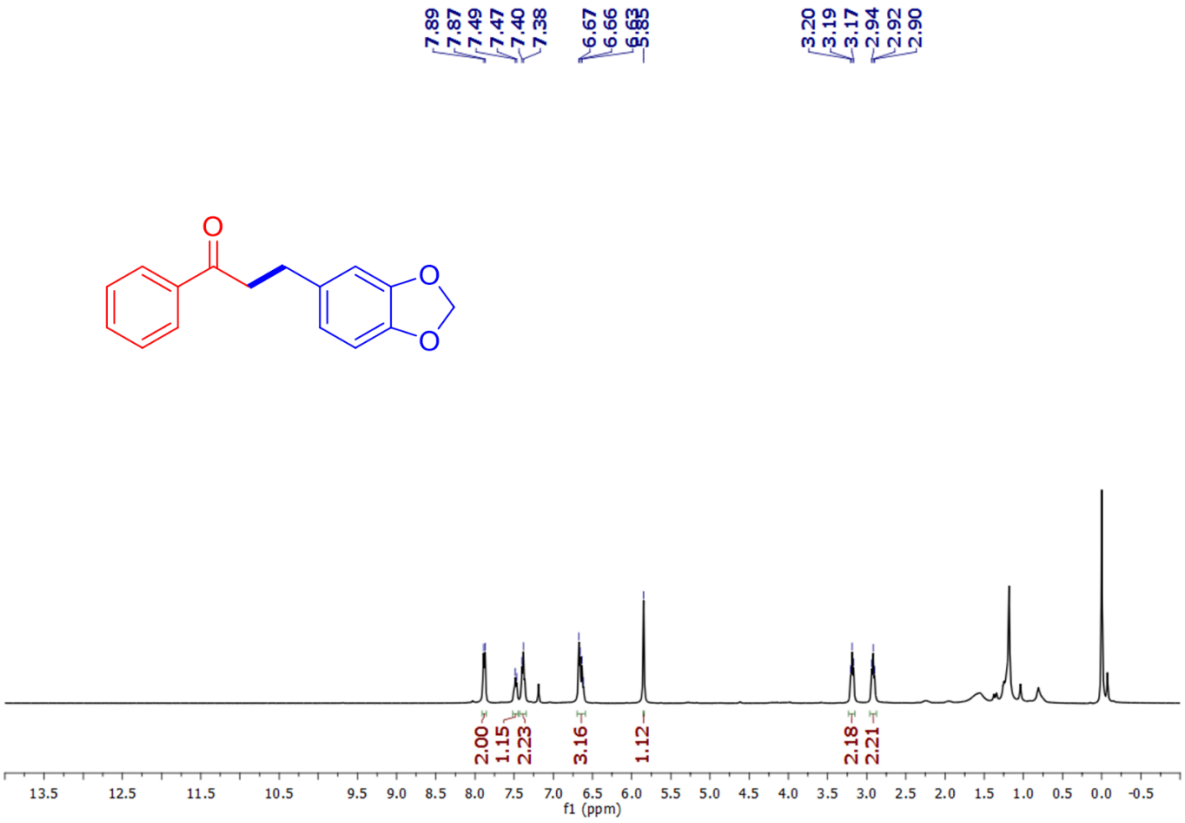


Figure S60. ^{1}H NMR spectrum of compound **3w** in $CDCl_3$ (400 MHz, 293 K). [8]

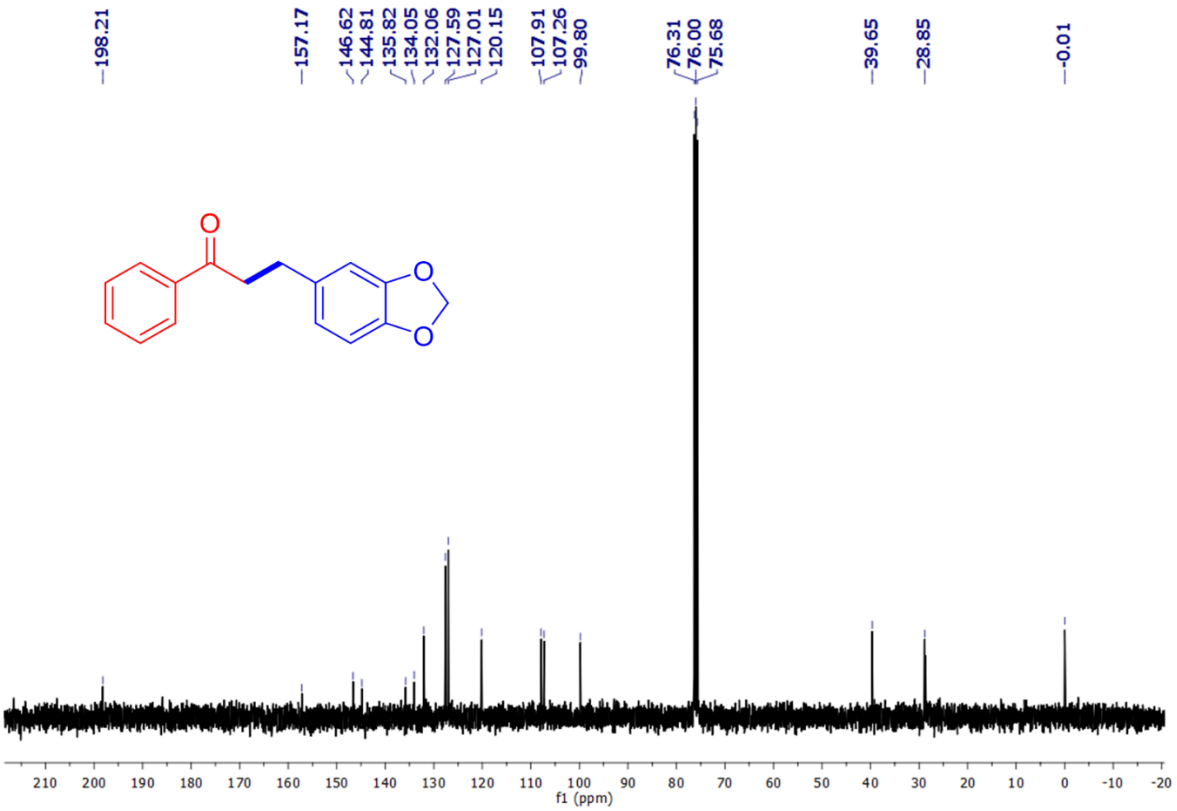


Figure S61. ^{13}C NMR spectrum of compound **3w** in $CDCl_3$ (100 MHz, 293 K). [8]

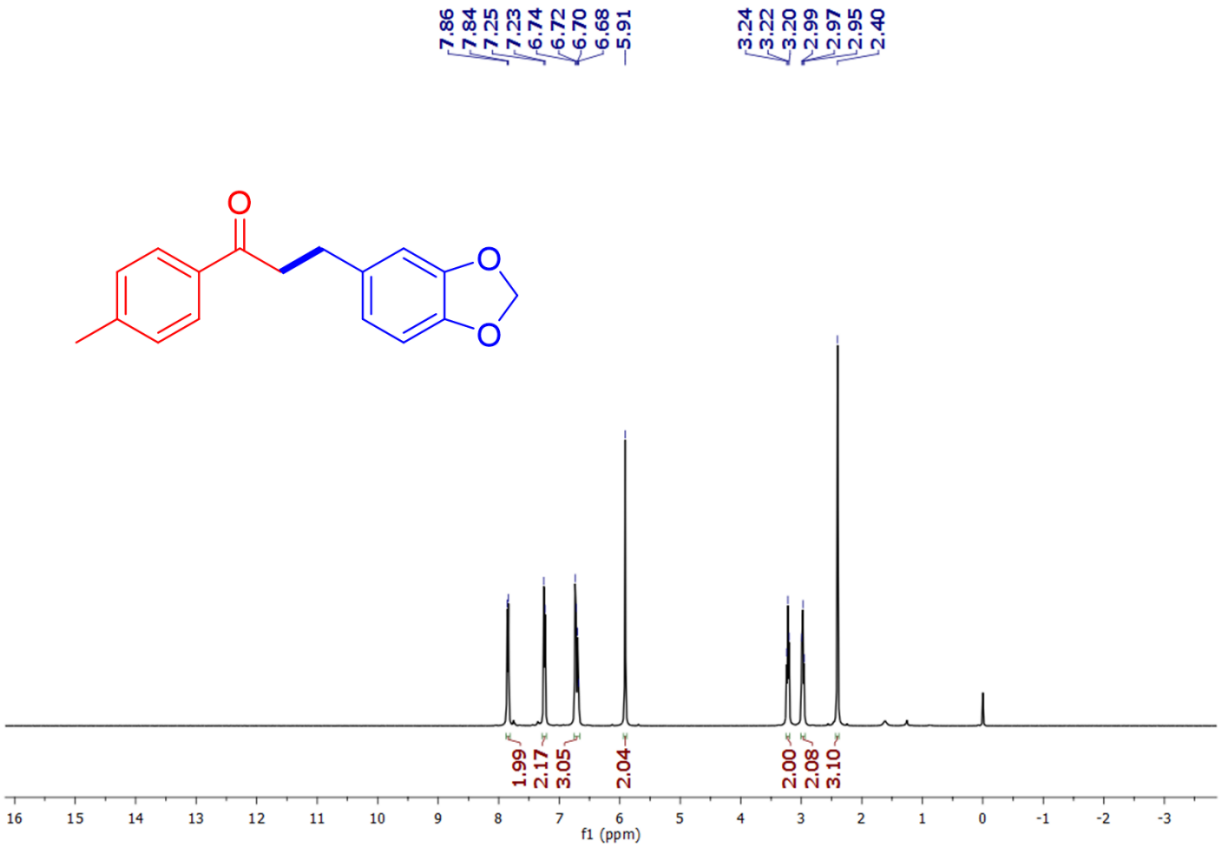


Figure S62. ^{1}H NMR spectrum of compound **3x** in $CDCl_3$ (400 MHz, 293 K).

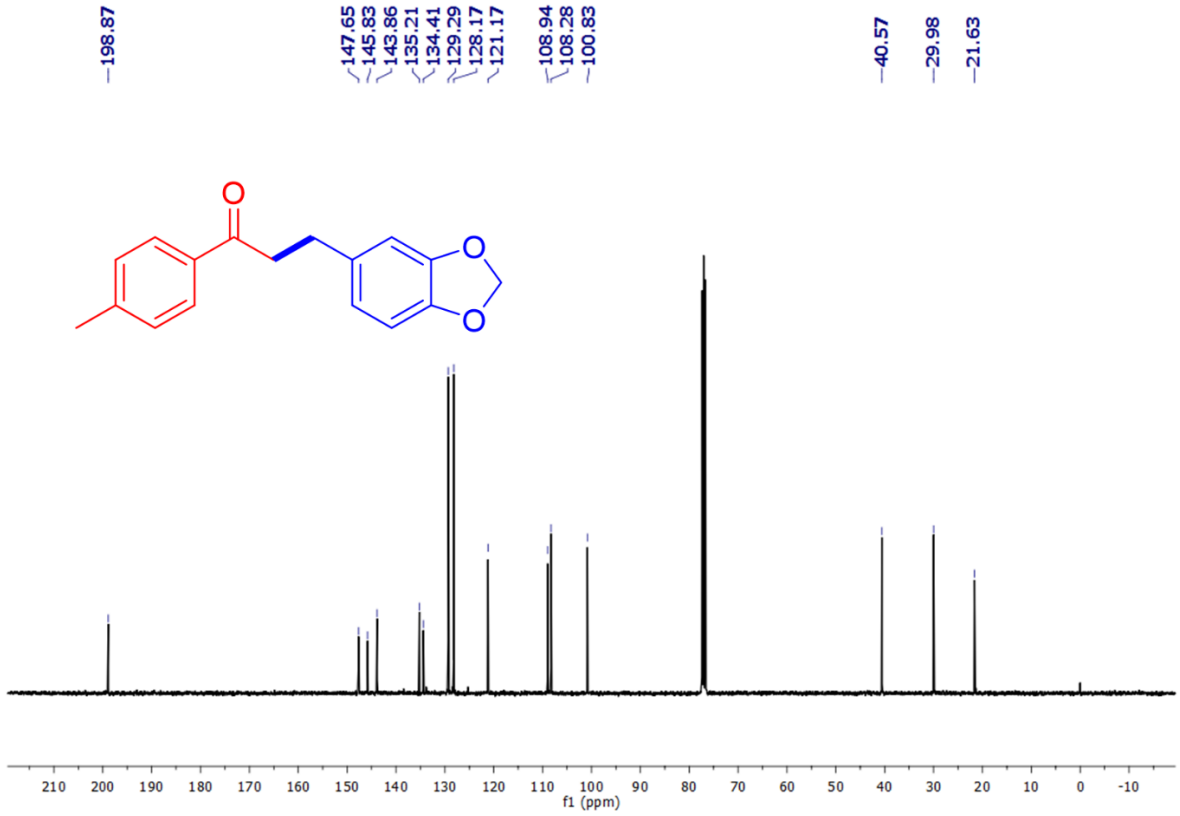


Figure S63. ^{13}C NMR spectrum of compound **3x** in $CDCl_3$ (100 MHz, 293 K).

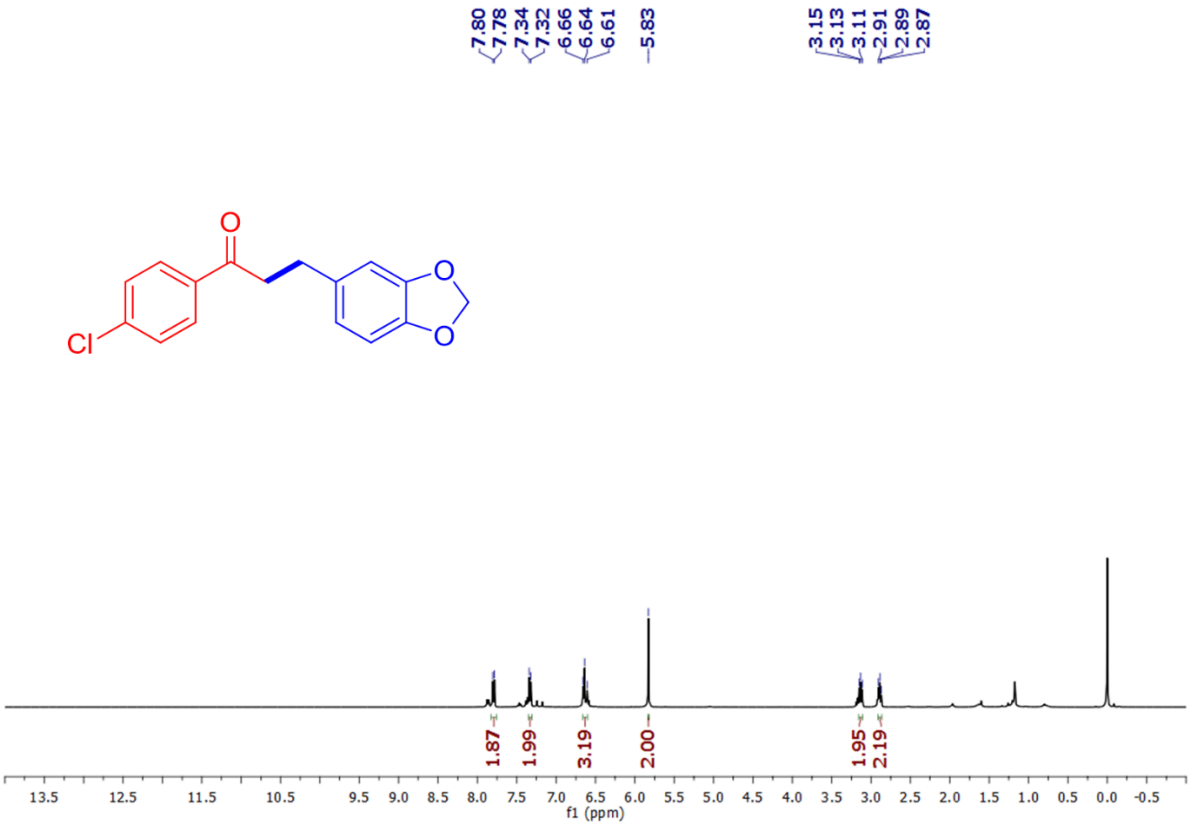


Figure S64. ^{1}H NMR spectrum of compound **3y** in $CDCl_3$ (400 MHz, 293 K).

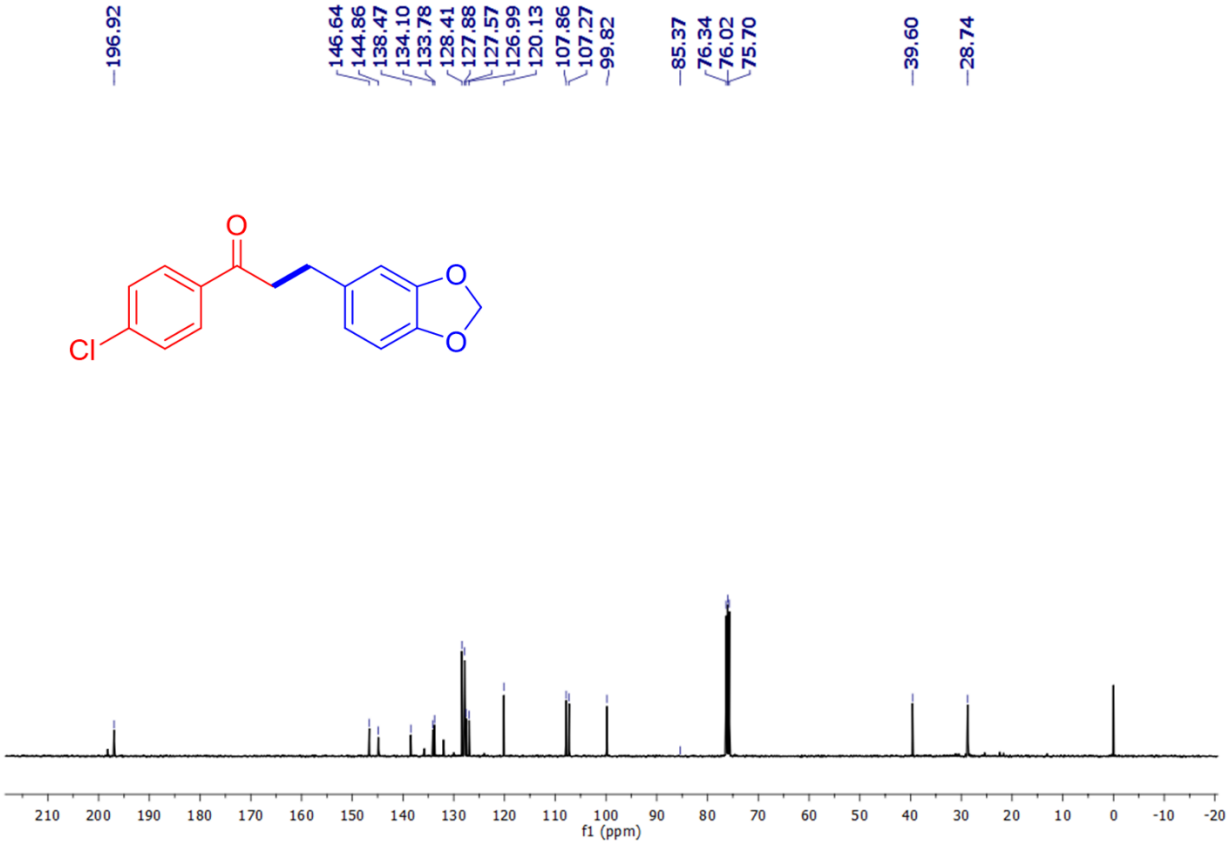


Figure S65. ^{13}C NMR spectrum of compound **3y** in $CDCl_3$ (100 MHz, 293 K)

Supporting Information

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