Supplementary Information (SI) for ChemComm.


# Designing NNO-Manganese Complex Overcoming Steric Constraints in (De)hydrogenative Coupling

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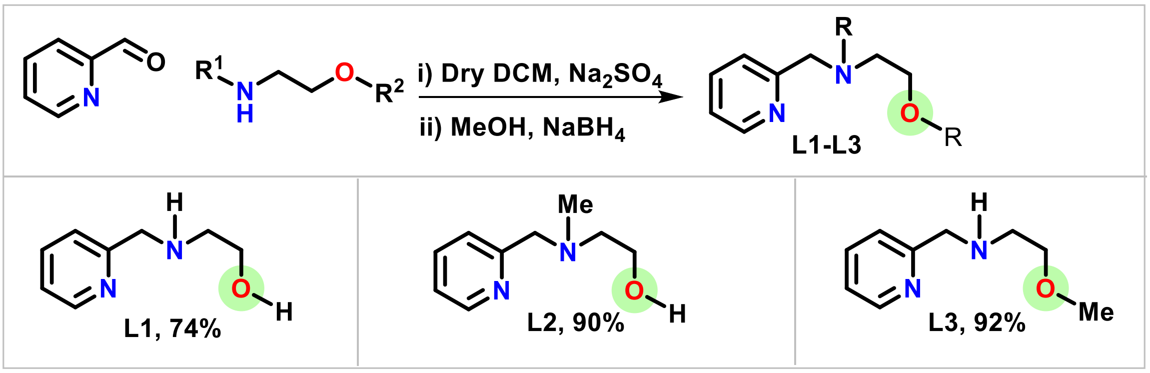
## 1. General Information:

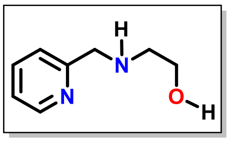
Unless otherwise mentioned, all chemicals were purchased from common commercial available sources and used as received. In the catalytic reaction, racemic terpineol derivatives such as citronellol, nerol, geraniol, and farnesol are used. All solvents were dried by using standard procedure. The preparation of catalyst was carried out under argon atmosphere with freshly distilled dry THF. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques, JACOMAX glove box filled with argon. DRX-400 Varian spectrometer and Bruker Advance III 400 MHz, 500 MHz and 600 MHz spectrometers were used to record $^{1}H$ and $^{13}C$ NMR spectra using DMSO-$d_6$, $CDCl_3$, $C_6D_6$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (*J*) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet and brs = broad singlet. ATIR data was collected on PerkinElmer IR spectrometer. Q-TOF ESI-MS instrument (Agilent: 6546 LC/Q-TOF) was used for recording mass spectra. PerkinElmer clarus-590 GC instrument using Elite Plot-Q is used for GC analysis. Single crystal X-RAY diffractometer (BRUKER D8QUEST) is used for single crystal data collection. SRL silica gel (100-200 mesh) was used for column chromatography.

## 2. Synthesis and characterization of NNO Ligands:

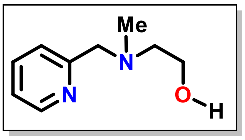



Pyridine-2-carboxaldehyde (5 mmol) and amino-ethanol derivatives (5 mmol) were dissolved in dry $CH_2Cl_2$ (15 mL) and then $Na_2SO_4$ (12.5 mmol) was added to it. The resulting suspension was stirred for 12 h at room temperature. Then, it was filtered and the filter residue was washed thoroughly with $CH_2Cl_2$ and the combined solvent was removed under reduced pressure. The residue obtained was directly used for the next step without further purification. The residue was dissolved in methanol (20 mL) and $NaBH_4$ (10 mmol) was added portion wise in stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 30 mL of water was added. After that, it was extracted by $CH_2Cl_2$ and the combined organic phase was dried over $Na_2SO_4$. Then the solvent was evaporated to get the crude product, which was purified further by silica gel (100-200 mess) column chromatography using 20-40 % ethyl acetate in hexane.

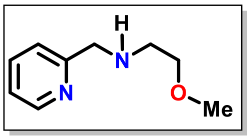
**2-((pyridin-2-ylmethyl)amino)ethan-1-ol (L1):**[1] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/ petroleum ether 20% to 50%) afforded the title compound in 74% yield (563 mg, 3.7 mmol) as yellow liquid. **$^1$H NMR (600 MHz, Chloroform-*d*) δ** 8.54 (s, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.16 (m, 1H), 3.97 (s, 2H), 3.95 (brs, 2H), 3.70 – 3.68 (m, 2H), 2.82 – 2.84 (m, 2H). **$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 159.0, 149.2, 136.7, 122.5, 122.2, 60.6, 54.2, 51.1.

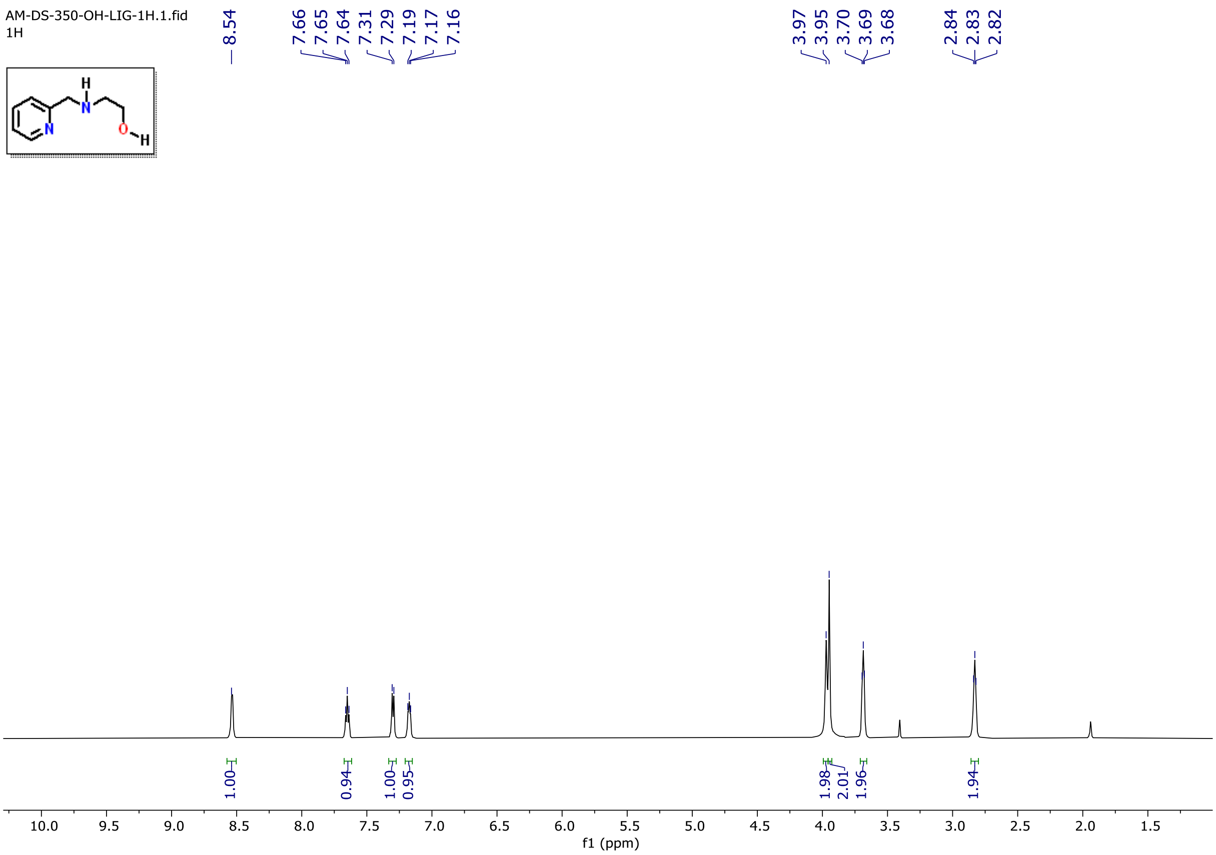



**2-(methyl (pyridin-2-ylmethyl) amino) ethan-1-ol (L2):**[2] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/ petroleum ether 20% to 50%) afforded the title compound in 90% yield (751 mg, 4.53 mmol) as yellow liquid. **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.48 (d, *J* = 4.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.04 (m, 1H), 3.69 (s, 2H), 3.60 – 3.57 (m, 2H), 2.67 – 2.45 (m, 2H), 2.28 (s, 3H), 1.93 (brs, 1H). **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 158.9, 149.3, 136.7, 123.2, 122.5, 63.4, 59.0, 58.9, 42.6.




**2-methoxy-N-(pyridin-2-ylmethyl) ethan-1-amine (L3):**[2] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/ petroleum ether 20% to 50%) afforded the title compound in 92% yield (764 mg, 4.6 mmol) as brown liquid. **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.56 (d, *J* = 4.2 Hz, 1H), 7.64 (t, *J* = 7.6, Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.07 (m, 1H), 3.88 (s, 2H), 3.60 – 3.46 (m, 2H), 3.29 (s, 3H), 2.79 – 2.77 (m, 2H), 2.23 (brs, 1H). **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 159.9, 149.4, 136.5, 122.3, 122.0, 72.2, 58.9, 55.3, 49.0.




AM-DS-350-OH-LIG-1H.1.fid
1H
8.54
7.66
7.65
7.64
7.31
7.29
7.19
7.17
7.16
3.97
3.95
3.70
3.69
3.68
2.84
2.83
2.82
1.00
0.94
1.00
0.95
1.98
2.01
1.96
1.94
f1 (ppm)

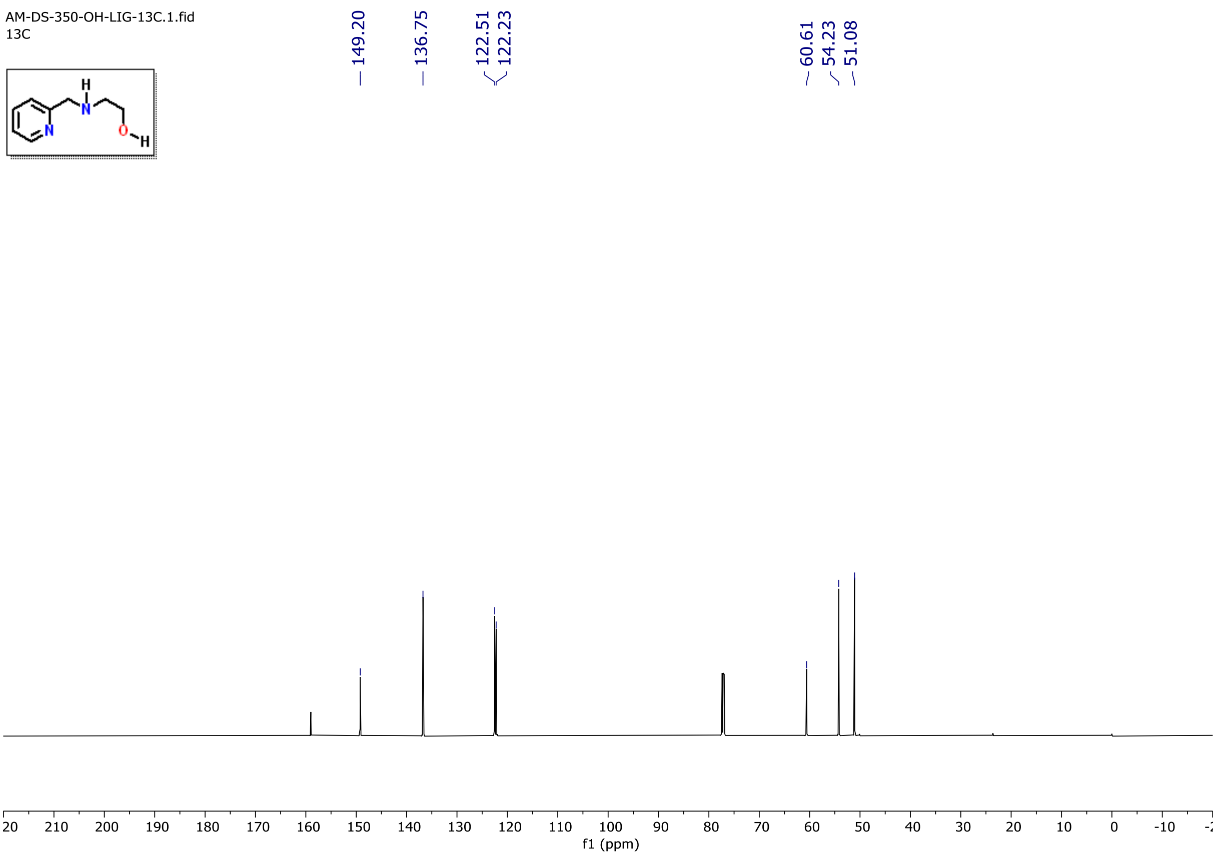
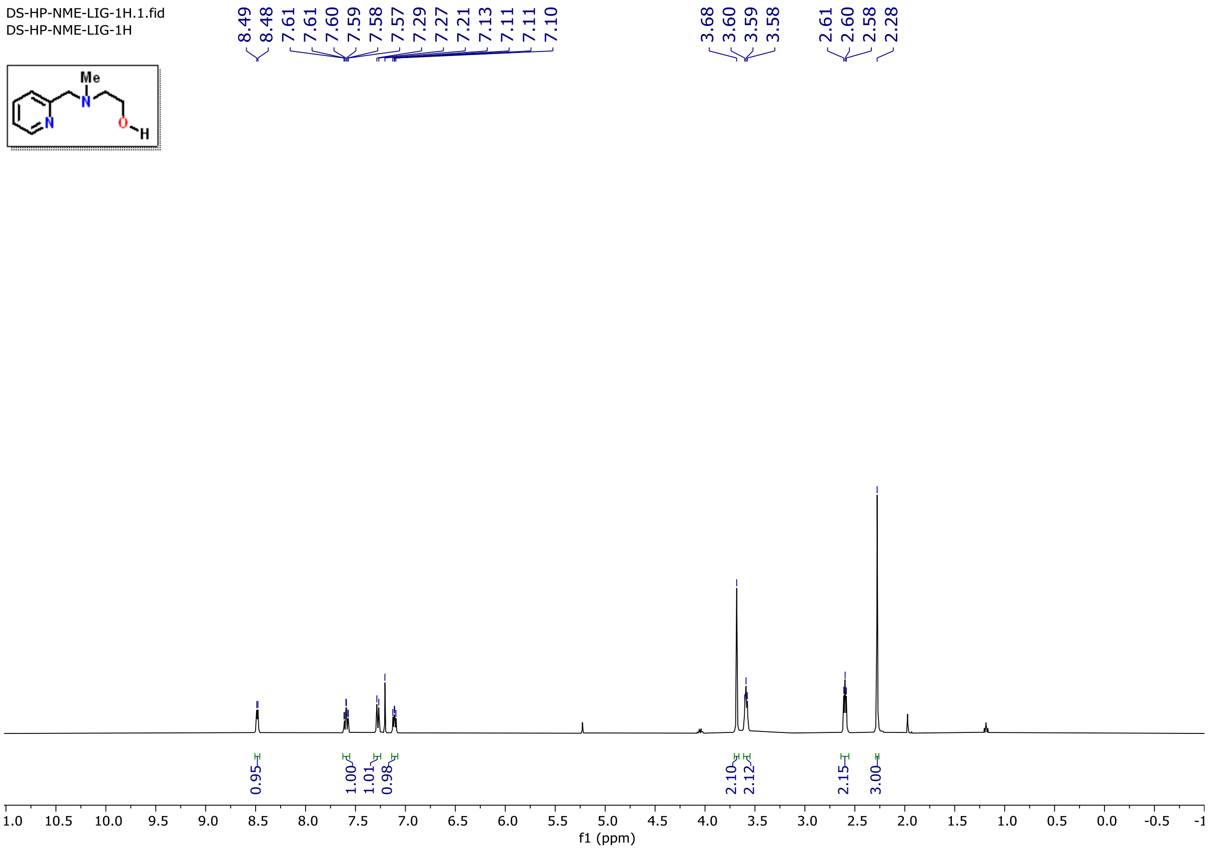

AM-DS-350-OH-LIG-13C.1.fid
13C
149.20
136.75
122.51
122.23
60.61
54.23
51.08
f1 (ppm)

**Figure S1.** $^{1}H$ (600 MHz) and $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectrum of **L1** in $CDCl_3$.



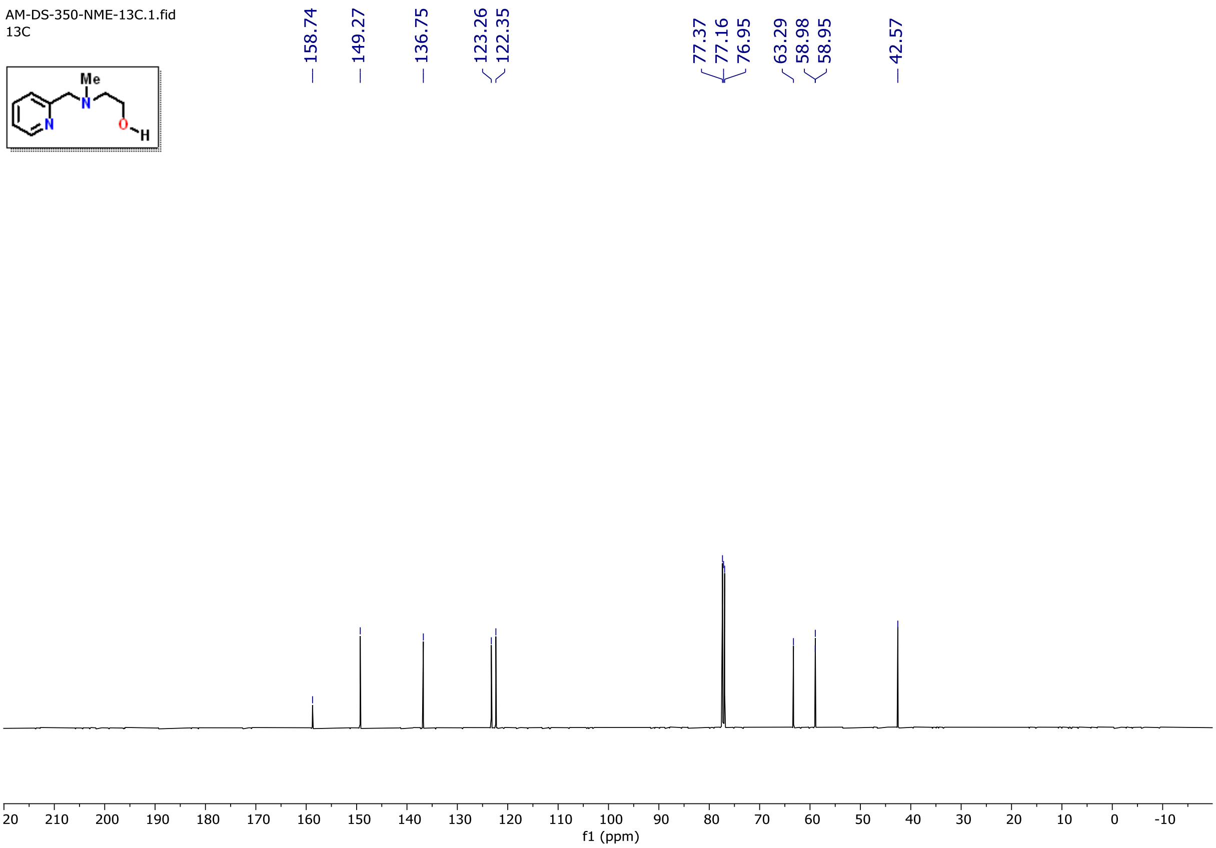
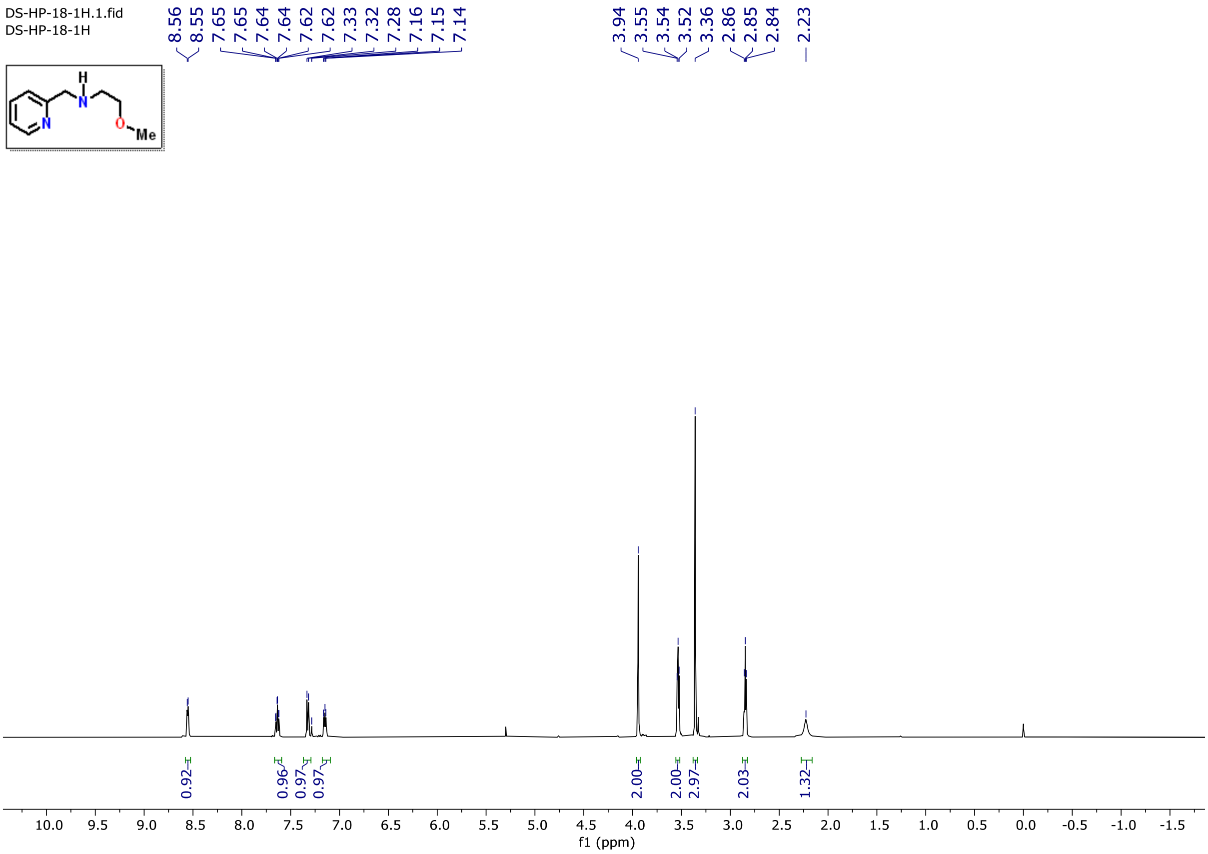



**Figure S2.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **L2** in $CDCl_3$.



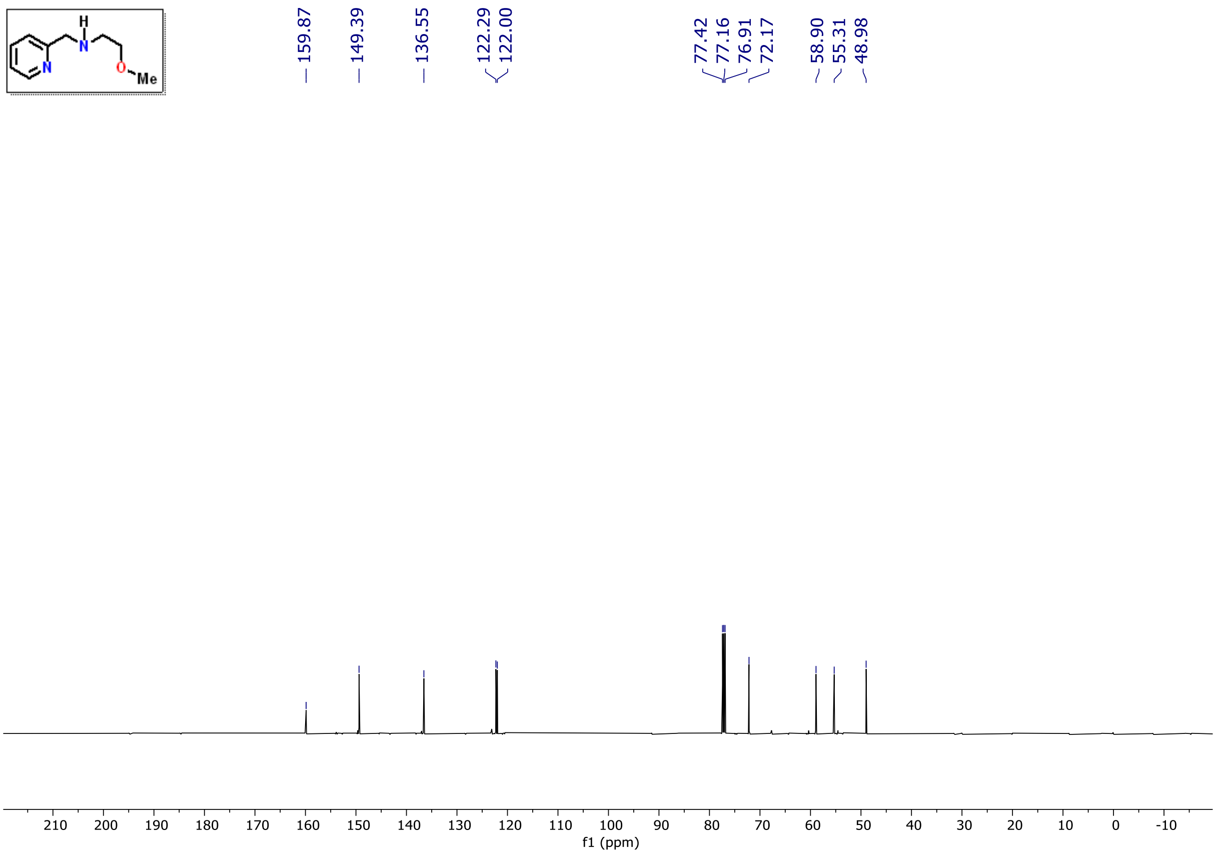
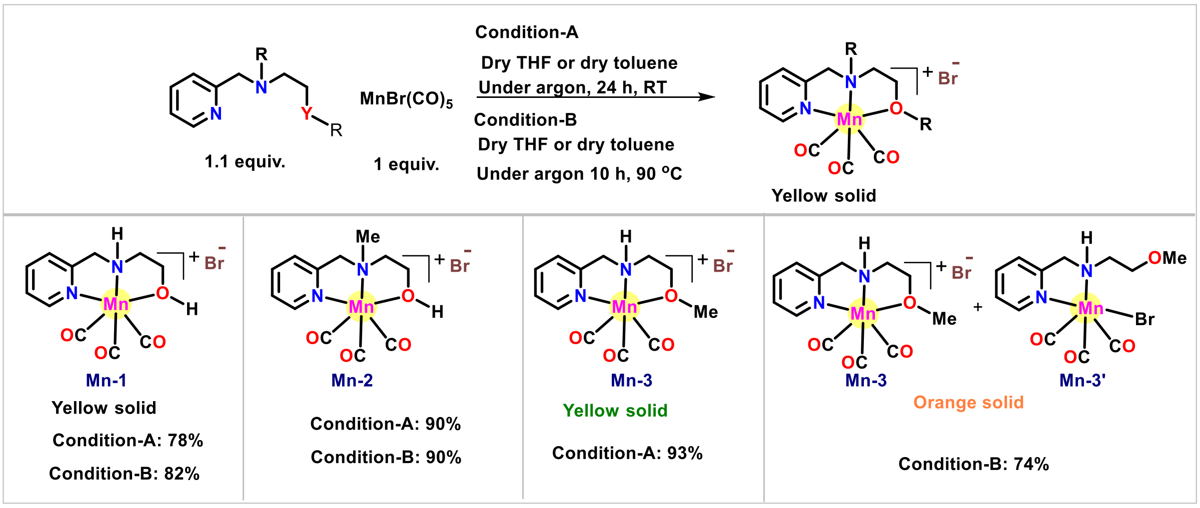



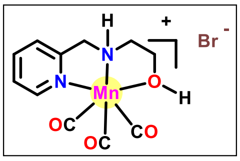
**Figure S3.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **L3** in $CDCl_3$.

## 3. Preparation of Mn-NNO complexes:

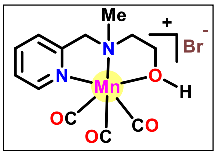



2 mL colorless THF solution of NNO ligands (1.1 mmol) was added drop wise to the orange-yellow suspension of [$MnBr(CO)_5$] (1.0 mmol) in 3 mL degassed dry THF. Afterward, the resulting mixture was stirred at 90 °C for 12 h or for 24 h at RT under argon atmosphere. After the completion of the reaction, the reaction mixture was cooled down to the room temperature, then the solvent was evaporated to obtain the residue, which was further washed with hexane and diethyl ether, and dried under vacuum to a get yellow solid of Mn-complexes.

**NNO-Manganese (I) complex (Mn-1):** Purification by washing using diethyl ether (10×4 mL) and hexane (10×2 mL afforded the title complex in 91% yield (304 mg, 0.82 mmol) as yellow crystalline solid. **$^{1}$H NMR (500 MHz, DMSO-d$_6$) δ** 8.88 (d, $J$ = 5.2 Hz, 1H), 8.08 (t, $J$ = 7.5 Hz, 1H), 7.64 (d, $J$ = 7.8 Hz, 1H), 7.60 (t, $J$ = 6.5 Hz, 1H), 7.46 (brs, 1H), 4.73 – 4.68 (m, 2H), 4.40 – 4.36 (m, 1H), 2.88 (m, 2H), 2.75 – 2.73 (m, 1H), 2.46 – 2.41 (m, 1H). **$^{13}$C NMR (125 MHz, CDCl$_3$) δ** 219.9, 216.7, 216.6, 160.2, 151.3, 138.2, 123.7, 120.2, 58.9, 57.8, 51.4. **IR** (ATIR, in cm$^{-1}$)**:** $\gamma_{CO}$2031, 1921(2CO). **HRMS: (ESI):** Calc'd for. **$C_{18}H_{13}MnN_3O_3$ [M-Br]$^+$: 291.0178**; found = 291.0182. **Crystallization:** Methanolic saturated solution of **Mn-1** in 5 mL glass vial kept at room temperature.

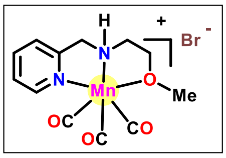


**NNO-Manganese (I) complex (Mn-2):** Purification by washing using diethyl ether (10×4 mL) and hexane (10×2 mL afforded the title complex in 94% yield (361 mg, 0.94 mmol) as yellow crystalline solid. **$^{1}$H NMR (500 MHz, DMSO-d6) δ** 8.72 (s, 1H), 8.70 – 8.69 (m, 1H), 7.95 – 7.93 (m, 1H), 7.50 (d, $J$ = 6.6 Hz, 1H), 7.47 – 7.45 (m, 1H), 4.59 – 4.56 (m, 2H), 4.33 – 4.30 (m, 2H), 3.08 (s, 3H), 2.77 – 2.70 (m, 2H). **$^{13}$C NMR (150 MHz, CDCl$_3$) δ** 221.4, 218.2, 217.7, 159.2, 155.3, 140.2, 126.0, 123.0, 70.1, 63.3, 62.7,



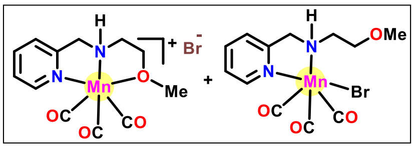
55.3. **IR** (ATIR, in cm$^{-1}$): $\gamma_{CO}$2035, 1918 (2CO). **HRMS: (ESI):** Calc'd for.**$C_{15}H_{22}BrMnN_2O_4$ [M-Br]$^+$: 305.0334**; found = **305.0330. Crystallization:** Methanolic saturated solution of **Mn-2** in 5 mL glass vial kept at room temperature.

**NNO-Manganese (I) complex (Mn-3):** Purification by washing using diethyl ether (10×4 mL) and



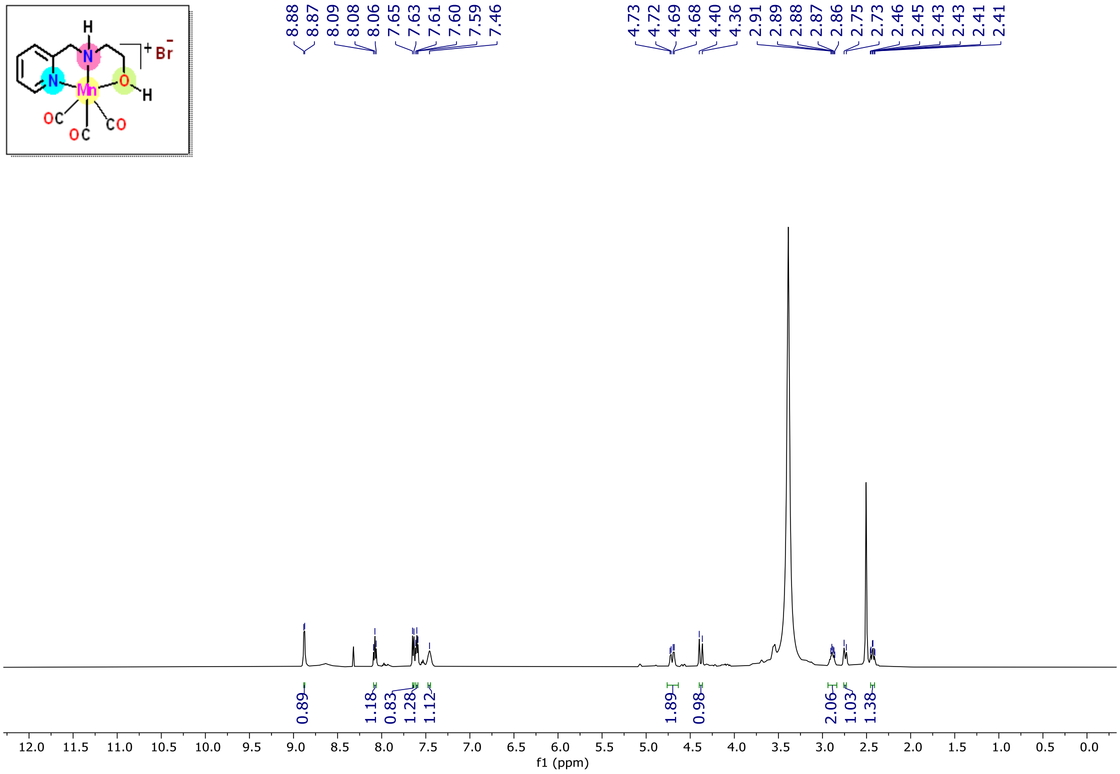

hexane (10×2 mL afforded the title complex in 91% yield (350 mg, 0.91 mmol) as yellow crystalline solid.**$^1$H NMR (500 MHz, Chloroform-d) δ** 8.99 (s, 1H), 7.78 (s, 1H), 7.37 – 7.34 (m, 2H), 4.52 – 4.50 (m, 1H), 4.10 – 4.05 (m, 2H), 3.79 (brs, 1H), 3.69 – 3.63 (m, 2H), 3.42 (s, 3H), 3.22 (s, 1H).**$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 222.5, 221.0, 158.8, 153.6, 138.1, 124.6, 121.1, 69.1, 58.7, 58.3, 55.4. **IR** (ATIR, in cm$^{-1}$): $\gamma_{CO}$2015, 1894 (2CO). **HRMS: (ESI):** Calc'd for. **$C_{15}H_{22}BrMnN_2O_4$ [M-Br]$^+$: 305.0334**; found = **305.0332**. **Crystallization:** several combinations of solvents and techniques were applied to get the single-crystal of **Mn-3** but it formed poly crystals which are not suitable for analysis.

**NNO-Manganese (I) complex (Mn-3+Mn-3´):**Purification by washing using diethyl ether (10×4 mL)




and hexane (10×2 mL afforded the title complex in 74% yield (284 mg, 0.74 mmol) as orange crystalline solid.**$^1$H NMR (600 MHz, DMSO-d6) δ** 8.94 (s, 2H), 8.05–7.98 (m, 2H), 7.66 – 7.65 (m, 1H), 7.61 –7.58 (m, 2H), 7.54 – 7.52 (m, 1H), 6.00 (brs, 1H), 4.65–4.63 (m, 1H), 4.30–4.16 (m, 4H), 3.81–3.78 (m, 2H), 3.69 (s, 3H), 3.71–3.67 (m, 4H), 3.48 – 3.45 (m, 1H), 3.39 (s, 3H), 3.31–3.24 (m, 4H).**$^{13}$C NMR (150 MHz, DMSO-d6) δ** 222.9, 222.8, 222.4, 222.3, 221.9, 221.9, 162.3, 160.6, 153.5, 152.7, 139.2, 139.1, 125.3, 124.4, 122.3, 122.2, 70.3, 69.2, 58.7, 58.6, 57.8, 56.5, 55.7, 53.2, 40.2. **IR** (ATIR, in cm$^{-1}$): $\gamma_{CO}$2032, 1944 & 1925. **HRMS: (ESI):** Calc'd for. **$C_{15}H_{22}BrMnN_2O_4$ [M-Br]$^+$: 305.0334**; found = **305.0330**.

**Crystallization:** Methanolic saturated solution of **Mn-4** in 5 mL glass vial kept at room temperature.



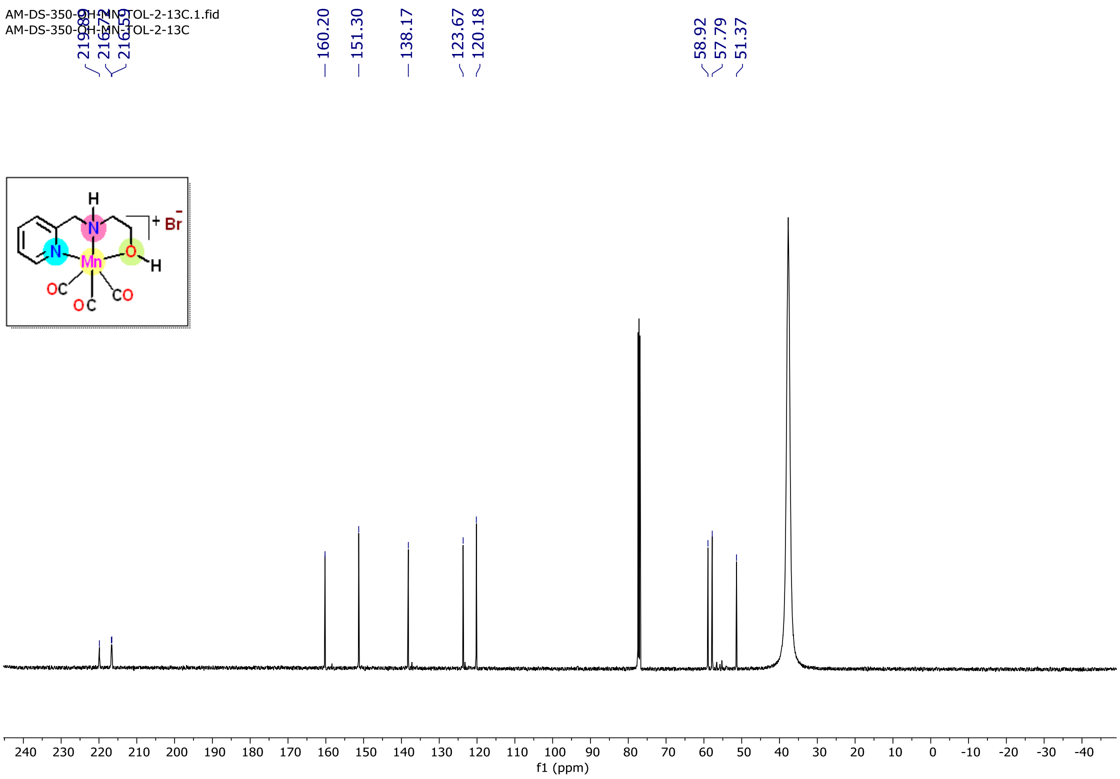
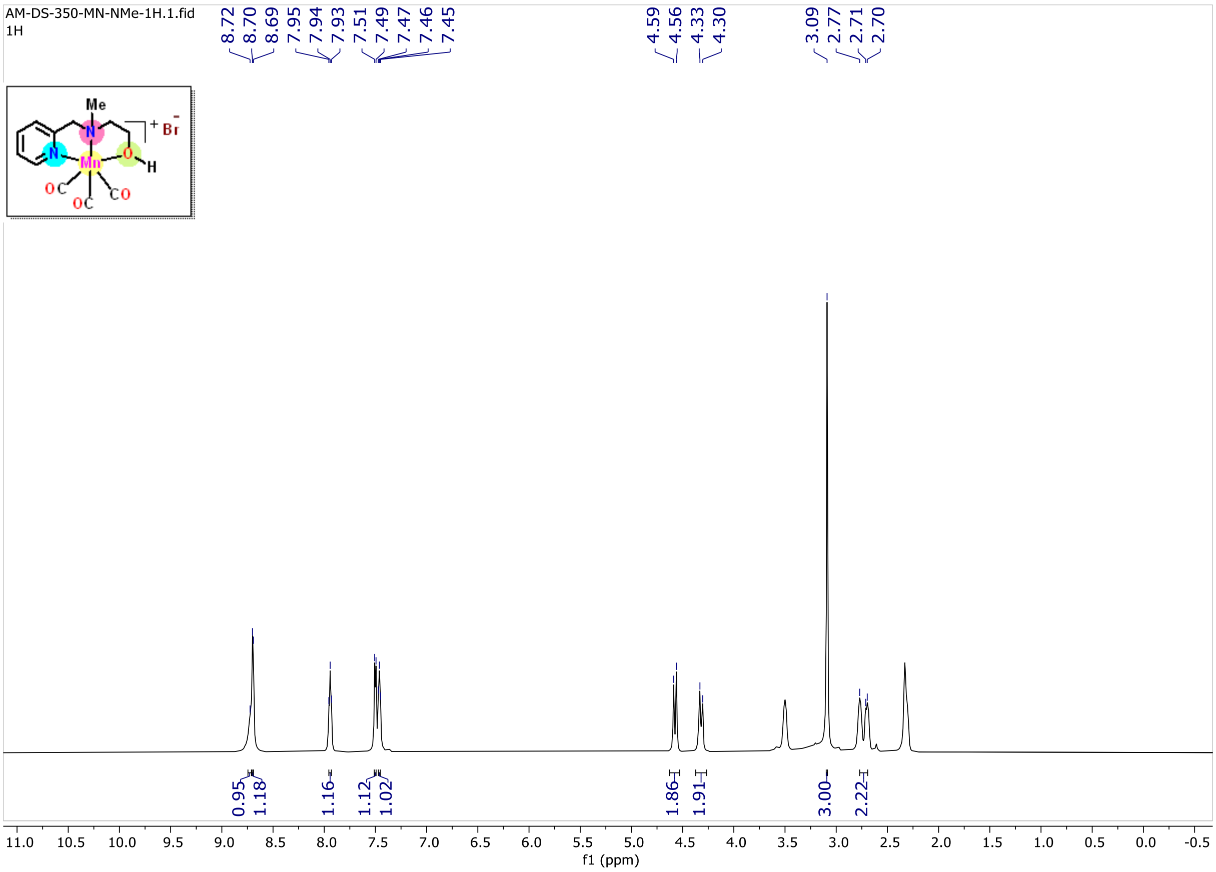


**Figure S4.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **Mn-1** in DMSO-d6+$CDCl_3$.


AM-DS-350-MN-NMe-1H.1.fid
1H
8.72
8.70
8.69
7.95
7.94
7.93
7.51
7.49
7.47
7.46
7.45
4.59
4.56
4.33
4.30
3.09
2.77
2.71
2.70
Me
N
N
Mn
O
H
+ Br⁻
OC
OC
CO
0.95
1.18
1.16
1.12
1.02
1.86
1.91
3.00
2.22
f1 (ppm)

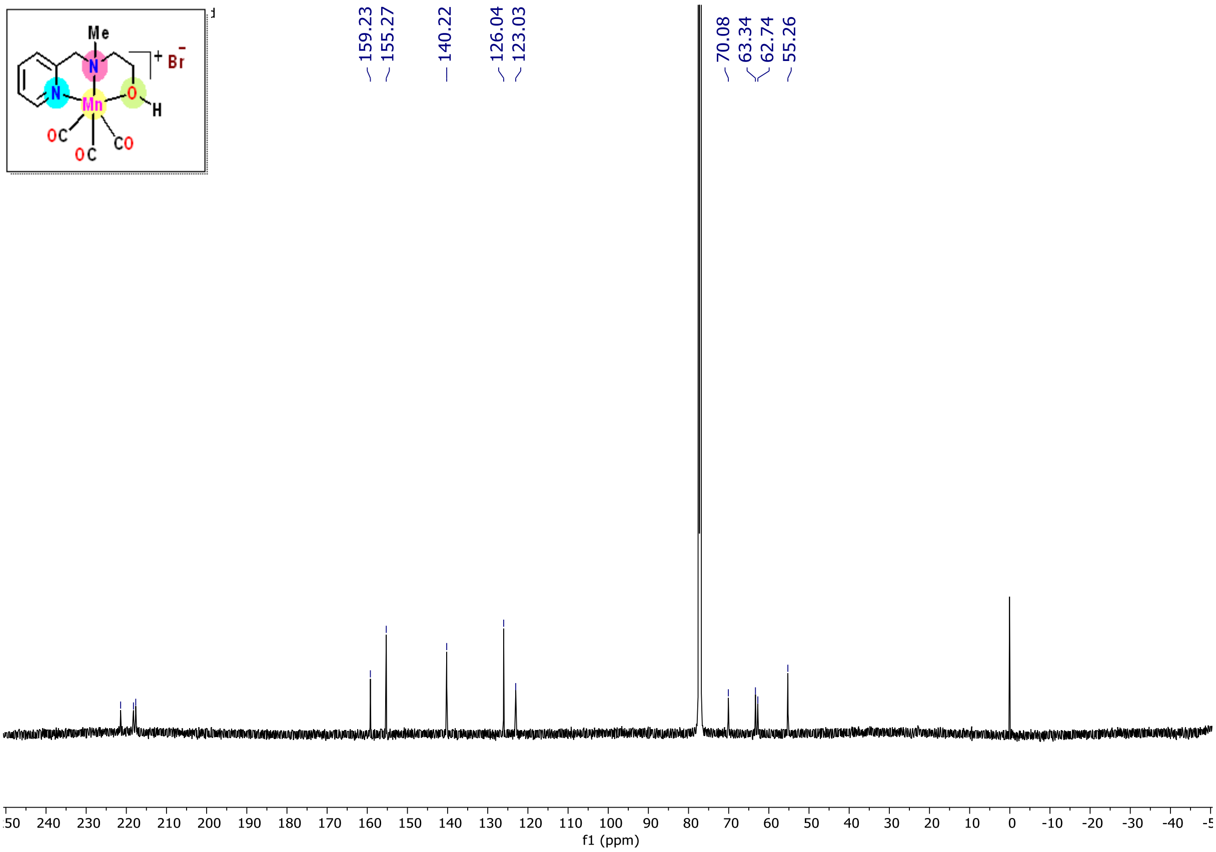
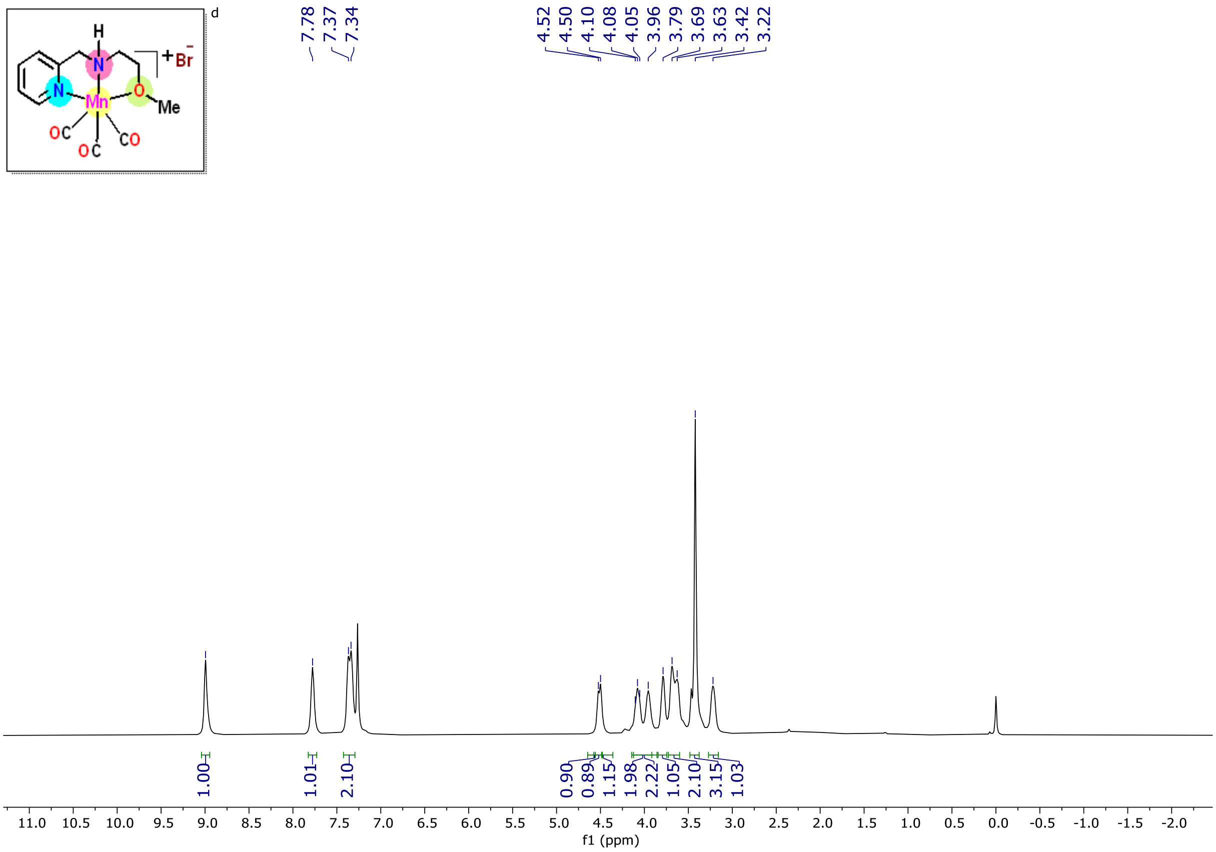

159.23
155.27
140.22
126.04
123.03
70.08
63.34
62.74
55.26
Me
N
N
Mn
O
H
+ Br⁻
OC
OC
CO
f1 (ppm)

**Figure S5.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **(Mn-2)** in DMSO-d6 and CDCl$_3$.



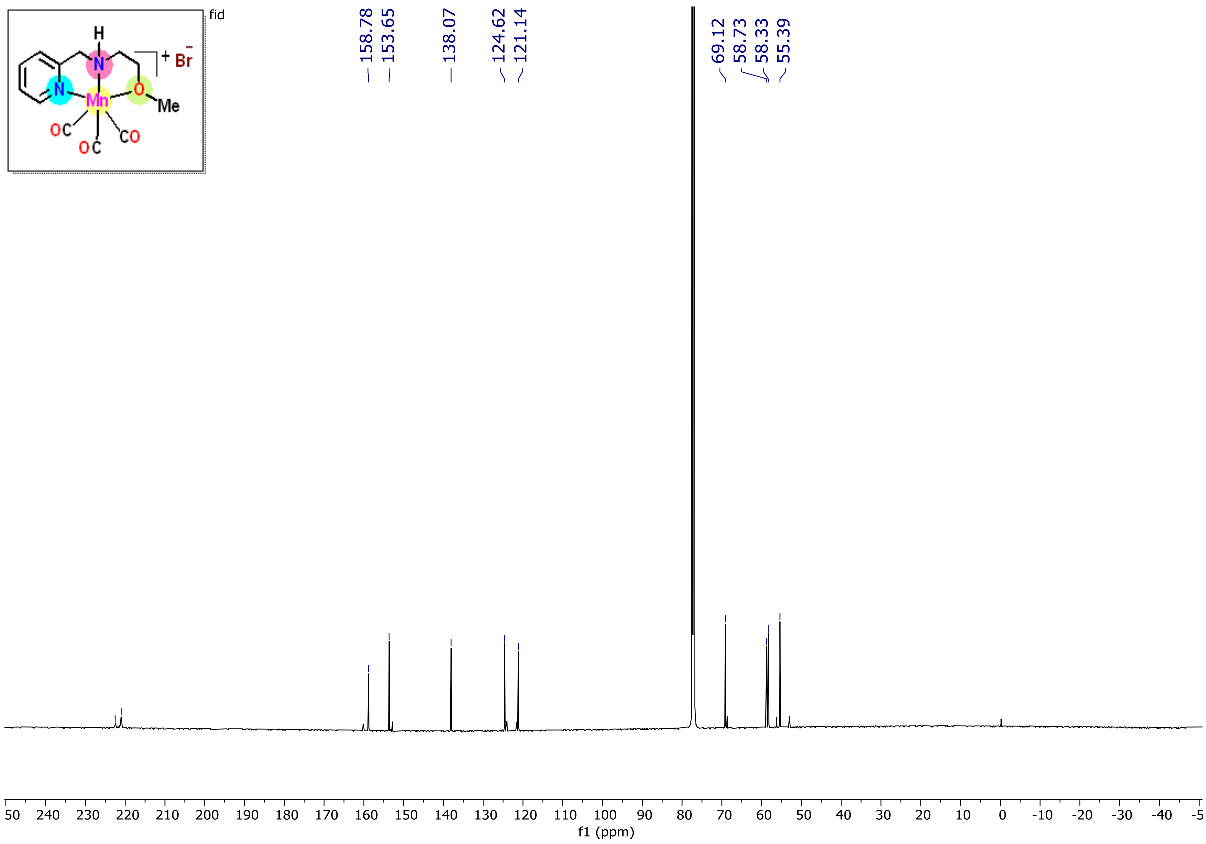
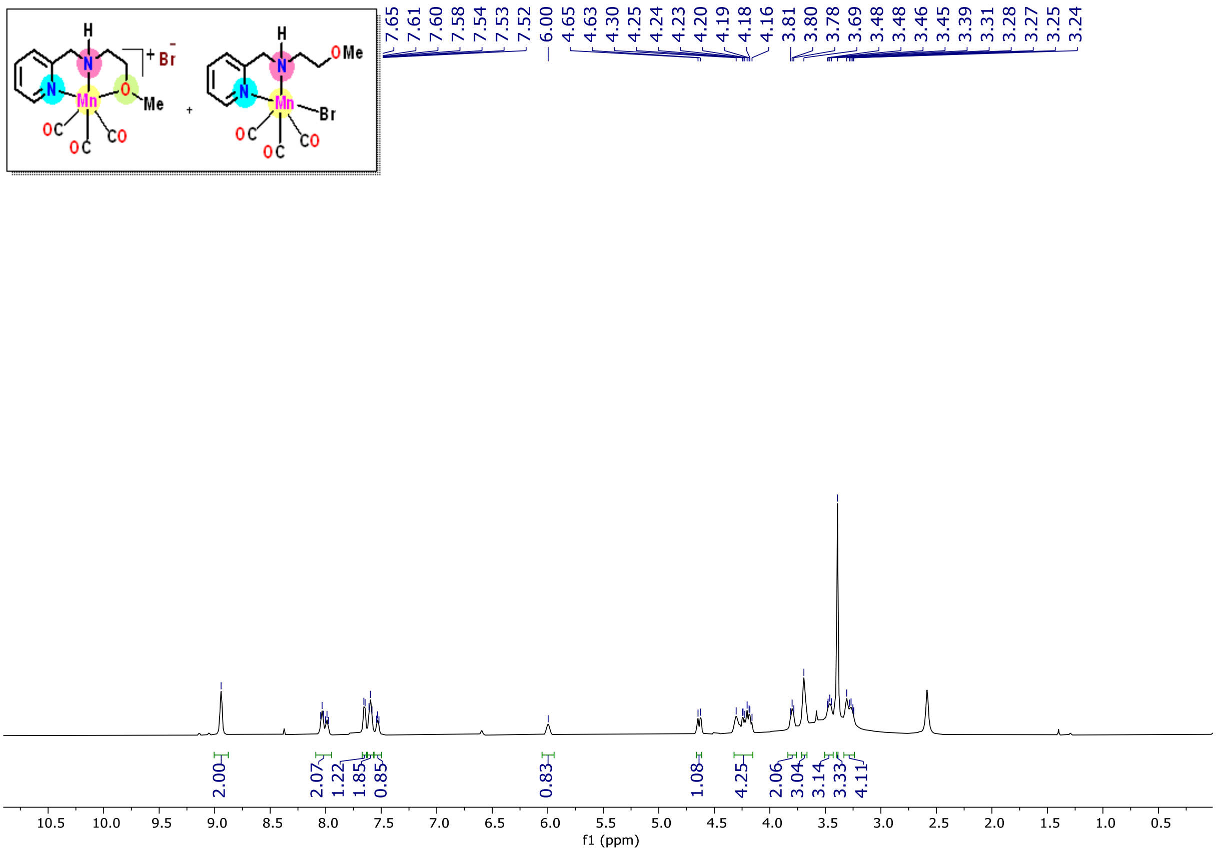



**Figure S6.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **Mn-3** in $CDCl_3$.



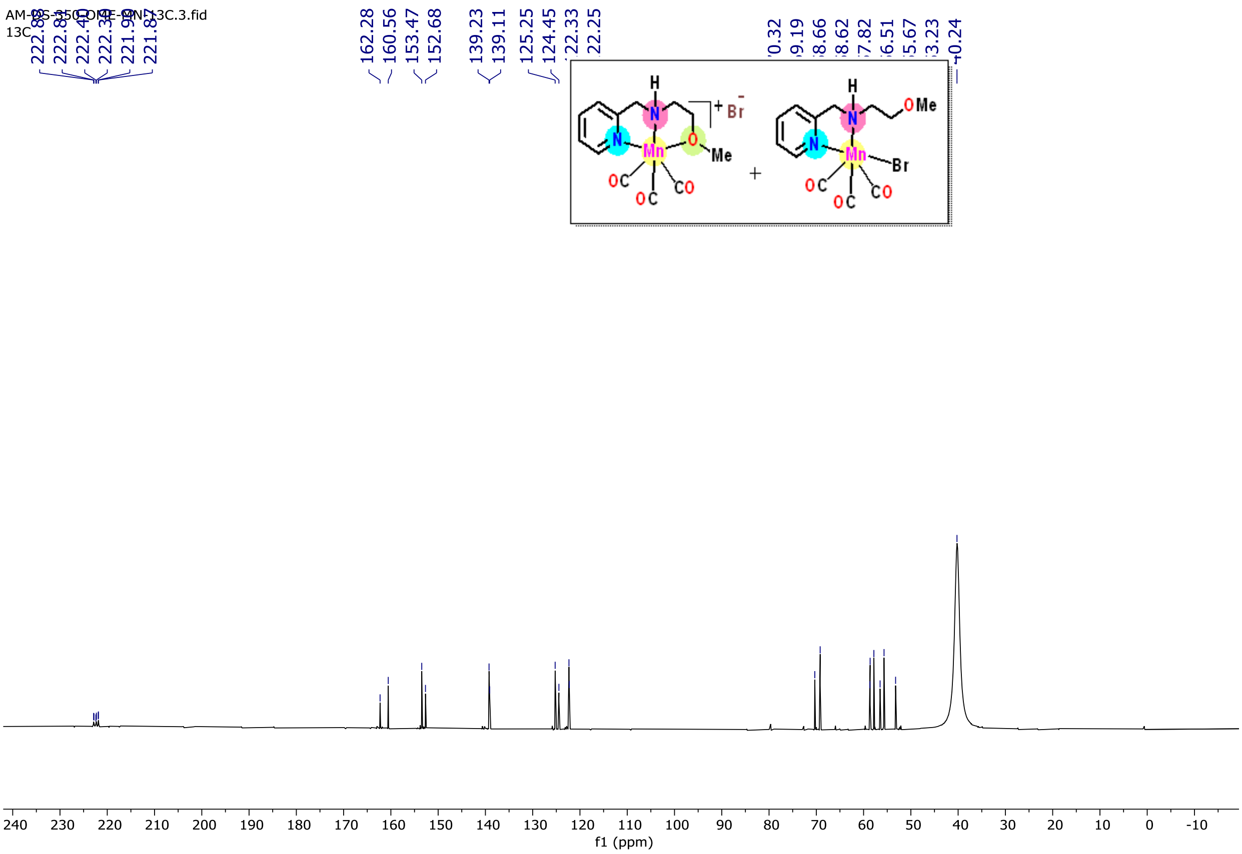
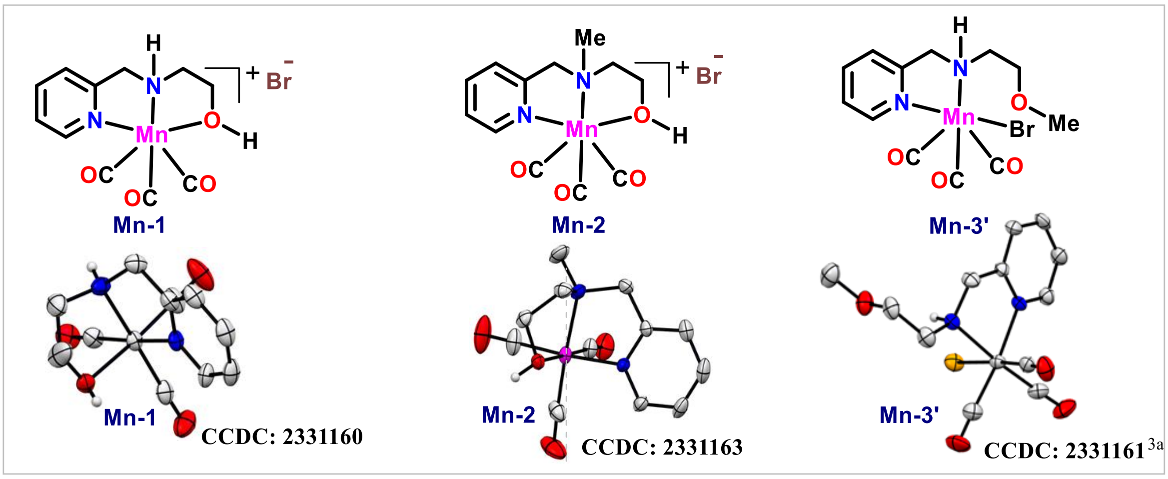




**Figure S7.** $^{1}$H (500 MHz) and$^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **(Mn-3+Mn-3´)** in DMSO-d6.



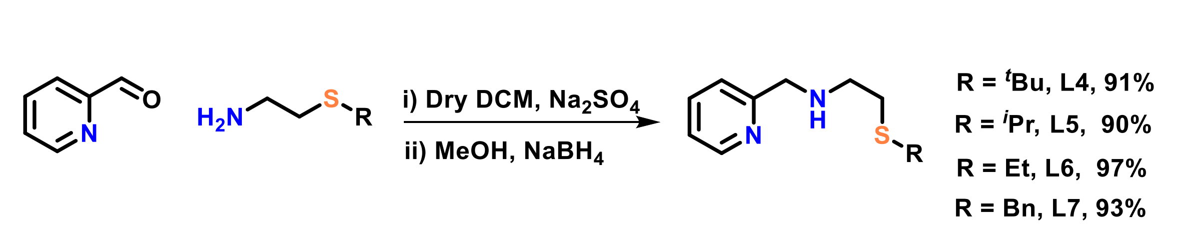

| | **Mn-1** | **Mn-2** |
|---|---|---|
| **Empirical formula** | $C_{11} H_{12} Mn N_2 O_4$, Br | $C_{12} H_{14} Mn N_2 O_4$, Br |
| Formula weight | 371.08 | 385.10 |
| Temperature, T | 296 K | 296 K |
| Crystal system | monoclinic | triclinic |
| Space group | P 21/n | P -1 |
| Unit cell dimensions | a=7.963(5)Å, α=90°<br>b=21.994(12)Å,<br>β=98.60(2) °<br>c= 8.314(5)Å, γ=90° | a=7.3733(5)Å,<br>α=79.837(3)°<br>b=8.8785(8)Å,<br>β=75.722(2)°<br>c=12.8155(14)Å,<br>γ=71.616(4)° |
| Volume, V (Å3 ) | 1439.8(15) | 767.09(12) |
| Z | 4 | 2 |
| Density (calculated), | 1.712 | 1.667 |
| Absorption coefficient, μ (mm–1 ) | 3.701 | 3.477 |
| F(000) | 736.0 | 384.0 |
| Crystal size, mm3 | 0.39 0.35 0.31 | 0.22 0.15 0.10 |
| Theta range for data collection | 2.64 to 26.50 | 2.43 to 27.29 |

| | | |
|---|---|---|
| Index ranges | -9 ≤ h ≤ 9, -26 ≤ k ≤ 26, -9 ≤ l ≤ 9 | -8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15 |
| Reflections collected | 7574 | 3242 |
| Independent reflections | 2535 | 2542 |
| Completeness to theta | 0.999 | 0.941 |
| Absorption correction | Multi-scan | Multi-scan |
| Refinement method | SHELXL-'2019/1'(Sheldrick,2018)' | SHELXL-'2019/1'(Sheldrick,2018)' |
| Data / restraints / parameters | 2535/0/176 | 2544/0/ 186 |
| Goodness-of-fit on F2 | 1.030 | 1.051 |
| Final R indices [I>2sigma(I)] | R1 = 0.0676 ( 2100),wR2= 0.1630( 2535) | R1=0.0413(2123), wR2(reflections)= 0.1130( 2542) |
| R indices (all data) | $R_1$= 0.0809, $WR_2$=0.1522 | $R_1$= 0.0508, $wR_2$=0.1070 |

| | **Mn-3´ [3a]** |
|---|---|
| Empirical formula | $C_{12}H_{14}BrMnN_2O_4$ |
| Formula weight | 385.10 |
| Temperature, T | 298 K |
| Crystal system | 'triclinic' |
| Space group | P -1 |
| Unit cell dimensions | a= 8.6784(14), b= 13.536(2), c=13.691(2)<br>α= 105.774(4) β= 91.146(4), γ= 90.908(4) |
| Volume, V (Å$^3$) | 1547.1(4) |
| Z | 4 |
| Density (calculated), g cm$^{-3}$ | 1.653 |
| Absorption coefficient, μ (mm$^{-1}$) | 3.448 |
| F (000) | 768.0 |
| Crystal size, mm$^3$ | 0.39 0.35 0.31 |
| Theta range for data collection | 2.48 to 24.02 |
| Index ranges | -10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16 |

| | |
|---|---|
| Reflections collected | 9946 |
| Independent reflections | 5440 |
| Completeness to theta | 1 |
| Absorption correction | multi-scan |
| Max. and min. transmission | SHELXL-'2019/1'(Sheldrick,2018)' |
| Refinement method | 5440/0/371 |
| Data / restraints / parameters | 1.090 |
| Goodness-of-fit on $F^2$ | R1 = 0.0529( 3993), wR2= 0.1343( 5440) |
| Final R indices [I>2sigma(I)] | R1= 0.0841, WR2= 0.1149 |

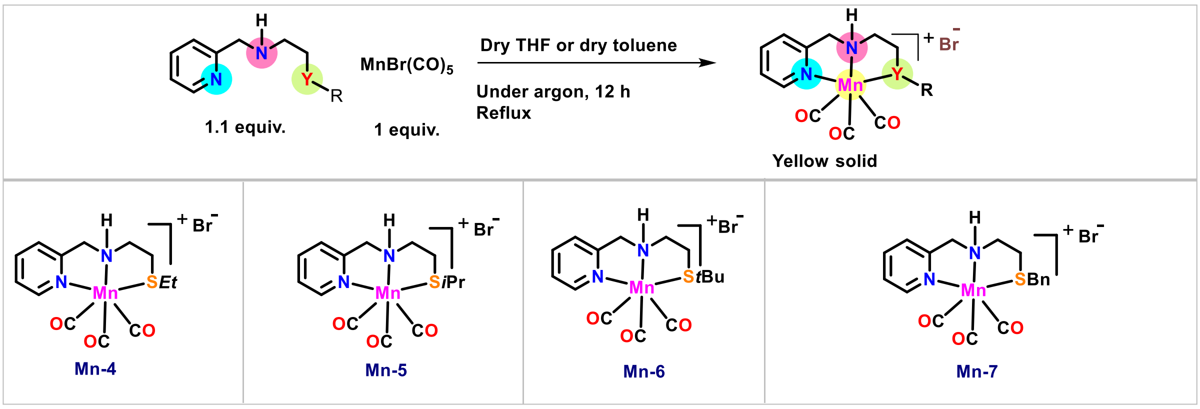
**4. Synthesis of NNS Ligands (L4-L7):**




All four ligands (**L4-L7**) were prepared according to previous reported literature methods.[3b] Pyridine-2-carboxaldehyde (5 mmol) and amino-thiol compound (5 mmol,) were dissolved in dry $CH_2Cl_2$ (15 mL) and then $Na_2SO_4$ (12.5 mmol) was added to it. The resulting suspension was stirred for 12 hrs at room temperature. Then, it was filtered and the filter residue was washed thoroughly with $CH_2Cl_2$ and the combined solvent was removed under reduced pressure. The residue obtained was directly used for the next step without further purification. The residue was dissolved in methanol (20 mL) and $NaBH_4$ (10 mmol) was added portion wise in stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 30 mL of water was added. After that, it was extracted by $CH_2Cl_2$ and the combined organic phase was dried over $Na_2SO_4$. Then the solvent was evaporated to get the crude product, which was purified further by silica gel (100-200 mess) column chromatography using 20-40 % ethyl acetate in hexane.

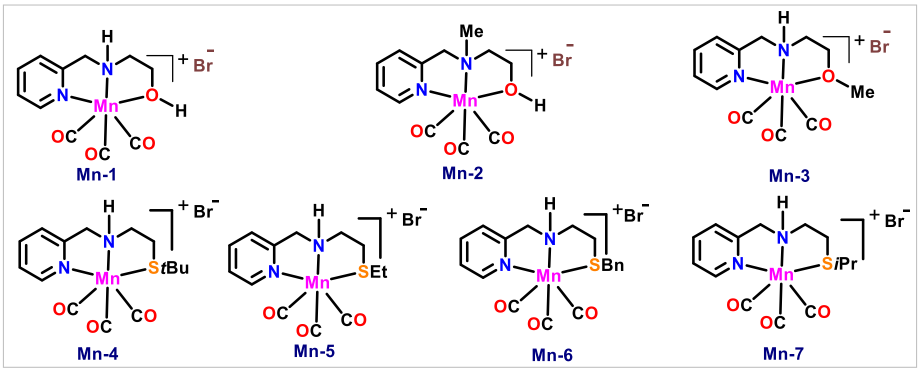
**5. Preparation of NNS-complexes (Mn4-Mn7):**

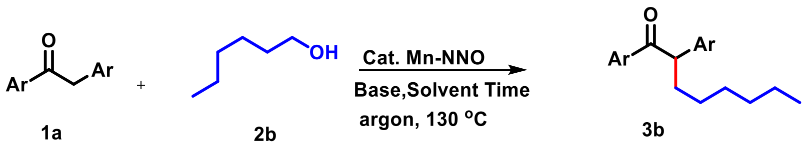
All four complexes were prepared according to previous reported literature methods.[3] Ligand [($PyCH_2$) HN ($CH_2CH_2SR$), R= Et, $^t$Bu, $^i$Pr, Bn] (0.25 mmol) was taken in 2 mL dry THF and was added dropwise to the orange-yellow suspension of [$MnBr(CO)_5$] (0.2 mmol) in 3 mL degassed dry THF. Afterward, the suspension was refluxed for overnight under argon atmosphere. After the completion of the reaction, the reaction mixture was cooled down to the room temperature, then the solvent was evaporated to obtain the residue, which was further washed with hexane and diethyl ether, and dried under vacuum to a get yellow solid of Mn-complexes.




**6. Table 1. Manganese catalysed *α*-functionalization of *α*-branched ketones using primary alcohols:**

**Reaction optimization:** At the onset, we initiated the reaction of desoxyanisoin (**1a**) and 1-hexanol (**2b**) as model substrates to examine the activity pattern of our designed catalysts. Reaction of 1-hexanol, **2b** (2 mmol), with desoxyanisoin, **1a** (1 mmol), using our **Mn-1** complex (5 mol %) and *t*BuOK (50 mol %) in toluene under an argon atmosphere 40% **3b** was isolated at 130 °C after 24 h (Table 1, entry 1). Subsequently, increasing the base loading from 0.5 to 1 equivalent while maintaining other parameters constant enhanced the yield of the desired product (**3b**) (Table 1, entry 2). Switching the base from KO*t*Bu to NaO*t*Bu proved less effective in this transformation (Table 1, entry 3). Pleasingly, employing KOH led to an improved yield of 67% for the *α*-alkylated branched product (Table 1, entry 4). Encouraged by this promising result, we subsequently increased both the base and alcohol concentrations. Gratifyingly, both cases produced the targeted alkylated product in similar yields (Table 1, entries 5 & 6). Notably, lower base loading (0.8 equiv.) and catalyst loading (3 mol %) also effectively delivered the desired product (**3b**) with comparable yield, but further reducing the catalyst loading to 2 mol % and the base to 0.6 equiv. proved detrimental (Table 1, entries 7-10).





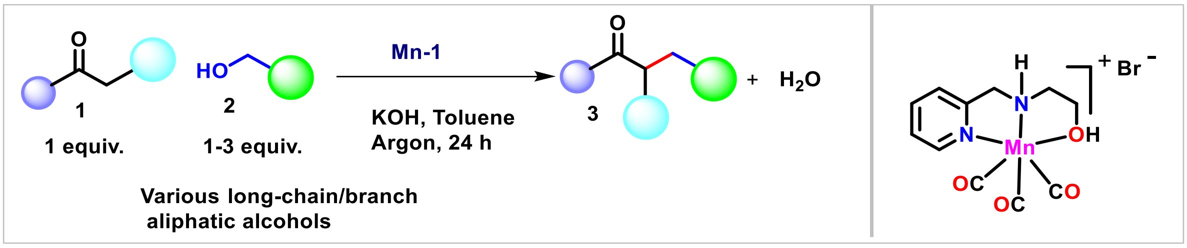

| Entry | 1a : | 2b | Base (equiv.) | Solvent (1 mL) | Cat. (mol%) | Time (h) | 3b (%) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 2 | KO$^t$Bu (0.5) | Toluene | Mn1 (5) | 24 | 40% |
| 2 | 1 | 2 | KO$^t$Bu (1) | Toluene | Mn1 (5) | 24 | 61% |
| 3 | 1 | 2 | NaO$^t$Bu (1) | Toluene | Mn1 (5) | 24 | 28% |
| 4 | 1 | 2 | KOH (1) | Toluene | Mn1 (5) | 24 | 67% |
| 5 | 1 | 2 | KOH (1.5) | Toluene | Mn1 (5) | 24 | 70% |
| 6 | 1 | 2.2 | KOH (1) | Toluene | Mn1 (5) | 24 | 68% |
| 7 | 1 | 2 | KOH (0.8) | Toluene | Mn1 (5) | 24 | 67% |
| 8 | 1 | 2 | KOH (0.8) | Toluene | Mn1 (3) | 24 | 67% |
| 9 | 1 | 2 | KOH (0.8) | Toluene | Mn1 (2) | 24 | 54% |
| 10 | 1 | 2 | KOH (0.6) | Toluene | Mn1 (2) | 24 | 53% |
| 11 | 1 | 2 | KOH (0.8) | Toluene | Mn1 (6) | 24 | 70% |
| 12 | 1 | 1 | KOH (0.8) | Toluene | Mn1 (3) | 36 | 69% |
| 13 | 1 | 2 | NaOH (0.8) | Toluene | Mn1 (3) | 24 | 21% |
| 14 | 1 | 2 | CsOH.$H_2O$ (0.8) | Toluene | Mn1 (3) | 24 | 30% |
| 15 | 1 | 2 | $Na_2CO_3$ (0.8) | Toluene | Mn1 (3) | 24 | SMR |
| 16 | 1 | 2 | $K_2CO_3$ (0.8) | Toluene | Mn1 (3) | 24 | SMR |
| 17 | 1 | 2 | $Cs_2CO_3$ (0.8) | Toluene | Mn1 (3) | 24 | SMR |
| 18 | 1 | 2 | KOH(0.8) | Xylene | Mn1 (3) | 24 | 57% |
| 19* | 1 | 2 | KOH (0.8) | Toluene | Mn1 (3) | 24 | 21% |
| 20 | 1 | 2 | KOH (0.8) | Toluene | Mn2 (3) | 24 | 63% |
| 21 | 1 | 2 | KOH (0.8) | Toluene | Mn3 (3) | 24 | 21% |
| 22 | 1 | 2 | KOH (0.8) | Toluene | Mn4-Mn7 | 24 | SMR |
| 23 | 1 | 2 | KOH (0.8) | Toluene | Mn1 (3) | 12 | 37% |
| 24 | 1 | 2 | KOH (0.8) | Toluene | ... | 24 | .... |
| 25 | 1 | 2 | ... | Toluene | Mn1 (3) | 24 | .... |
| 26 | 1 | 2 | KOH (0.8) | Toluene | RuMACHO | 24 | Trace |
| 27 | 1 | 2 | KOH (0.8) | Toluene | $MnBr(CO)_5$ | 24 | SMR |
| 28[c] | 1 | 2 | KOH (0.8) | Toluene | Mn1 (3) | 24 | 66% |
| 29 | 1 | 2 | TBAOH (0.8) | Toluene | Mn1 (3) | 24 | Trace |

[a]**Reaction conditions: 1a** (1 mmol), **2b** (1-2.2 mmol), Base (0.5-1.5 mmol), **Mn-1** (2-5 mol%), Solvents (1 mL), Temperature 130 °C, Time: 12 h -36 h, [b]Isolated yields, [c]Reaction carried out in 10 mL round-bottom flask instead of 100 seal tube, SMR=starting materials recovered.

Increasing the catalyst loading to 6 mol % and reaction time to 36 h also yielded similar product amounts (Table 1, entries 11 & 12). Other bases were showed the detrimental effect for *α, α′*-branched product formation, with NaOH and CsOH·$H_2$ O providing poor yields of 21% and 30%, respectively (Table 1, entries 13-17). Moreover, employing the higher-boiling solvent xylene under the same conditions afforded a 57% product yield (Table 1, entry 18). Lowering the reaction temperature to 100 °C while keeping other parameters constant resulted in a significantly reduced yield of 21% for the target product

(Table 1, entry 19). We then evaluated the reactivity and selectivity of another catalyst for the selective synthesis of *α, α′*-disubstituted branched ketones. Catalyst **Mn-2** exhibited similar activity, while **Mn-3** showed poor performance, indicating the importance of a less hindered hydroxyl arm in the catalyst (Table 1, entries 21 & 22). Conversely, our previously developed NNS-Mn catalysts (**Mn-4-Mn-7**) failed to produce the desired products (Table 1, entry 23). Reducing the reaction time by 12 h led to the formation of only 37% desired product (Table 1, entry 23). Control experiments revealed the necessity of both the catalyst and a suitable amount of base for the formation of the branched ketone using long-chain alcohols (Table 1, entries 24 & 25). Only metal salt $MnBr(CO)_5$ completely silent in this transformation (Table 1, entry 27). Moreover, less coordinating tetrabutylammonium hydroxide (TBAOH) gave only trace amount of product, which also underpins that chelation, plays an important role for the process.

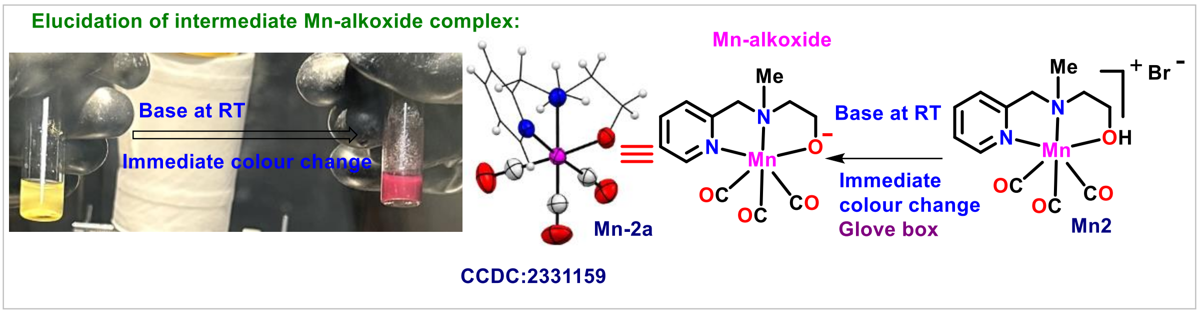
**7. General synthetic procedure of one-pot *α, α*-branch ketones:** In an oven dried 100 mL seal tube, equipped with a stirring bar was charged with *α*-branch ketone derivatives **1** (1.0 mmol), primary alcohols, **2** (1.0-3.0 mmol), KOH (0.2-1.7 equiv.) Then the seal tube was closed with a rubber septum, evacuated and refilled with Ar (x 3).




Then 1 mL dry toluene and **Mn-1** (0.5-5.0 mol %) was added under argon flow. The reaction mixture was refluxed in a preheated oil bath at 130 °C for 24 h. After completion of the reaction mixture was cooled to room temperature and ethyl acetate was added and filtered through celite pad. Filtrate mixture was evaporated in reduced pressure and purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure products.

## 8. Mechanistic investigation:

### 8.1. Elucidation of catalytically active Mn-alkoxide complex:



After addition of base to the **Mn-1** and **Mn-2** there is color change of the solution from yellow to dark pink which prompted us to investigate the catalytically active species after addition of base. KOH (9 mg, 0.16 mmol) in the THF solution was added dropwise to the THF solution of **Mn-2**, 0.2 mmol. After stirring the mixture for 30 minutes at room temperature inside the glove box. The resulting mixture was filtered through a celite pad. Then, the crystal has been grown by layering the filtrate THF part with pentane and keeping it at -10 °C inside the argon-filled glove box.

| | **Mn-2a** |
|---|---|
| Empirical formula | $C_{12}$ $H_{13}$ Mn $N_2$ $O_4$ |
| Formula weight | 304.18 |
| Temperature, T | 297 K |
| Crystal system | 'monoclinic' |
| Space group | C 1 2/c 1 |
| Unit cell dimensions | a=13.0025(11), b=14.8905(12) c=14.8729(12), α=90, β=92.647(2), γ=90 |
| Volume, V (Å$^3$ ) | 2876.5(4) |
| Z | 8 |
| Density (calculated), g cm$^{-3}$ | 1.405 |
| Absorption coefficient, μ (mm$^{-1}$) | 0.928 |
| F (000) | 1248.0 |
| Crystal size, mm$^3$ | 0.36 0.33 0.30 |
| Theta range for data collection | 2.45 to 25.00 |
| Index ranges | -15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17 |
| Reflections collected | 9214 |
| Independent reflections | 2541 |
| Completeness to theta | 0.997 |
| Absorption correction | multi-scan |
| Max. and min. transmission | 'SHELXT 2018/2 (Sheldrick, 2018) |
| Refinement method | 2541/0/173 |
| Data / restraints / parameters | 1.027 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | R1 = 0.0359( 2230), wR2=0.0988( 2541) |
| Final R indices [I>2sigma(I)] | R1= 0.0431, WR2= 0.0914 |

## 8.2 IR study:

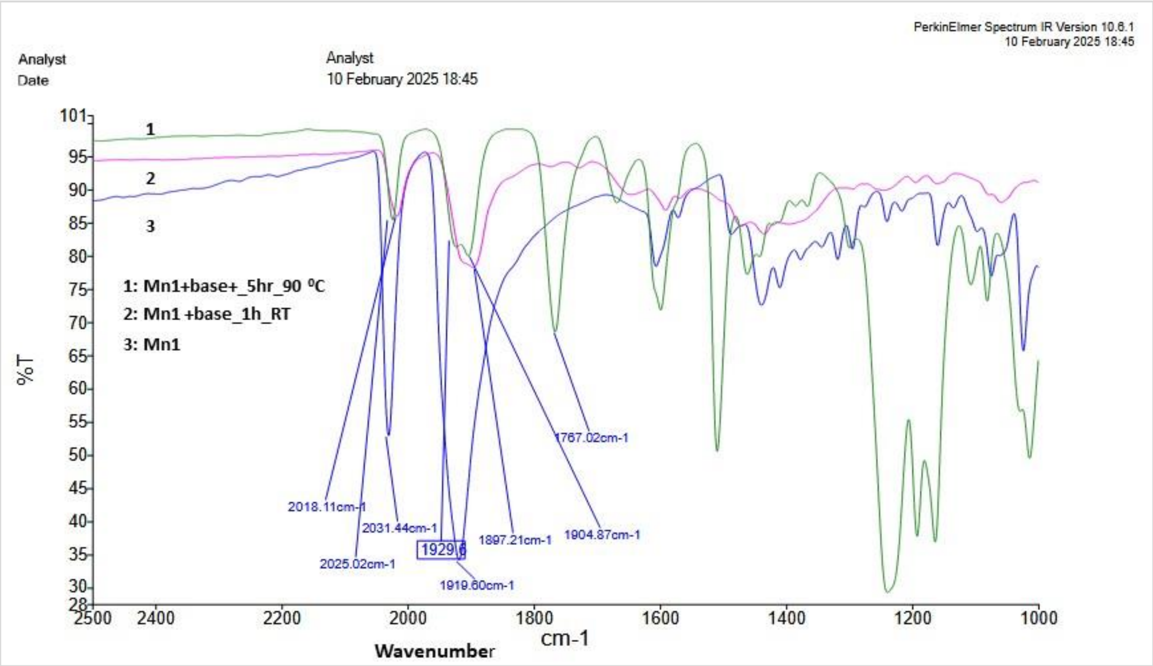
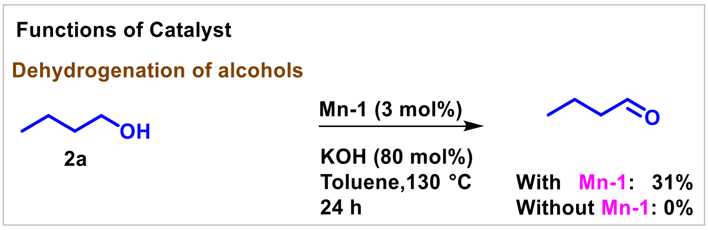



**Figure S8.** IR study of Mn1.

**8.3. Dehydrogenation of alcohol:** To an oven-dried 100 mL seal tube, **Mn-1** (3 mol%), 1-butanol, **2a** (1.0 mmol), toluene (2 mL) were added under argon. The reaction mixture was kept for heating at 130 °C for 24 h. Then, the reaction mixture was submitted for crude NMR analysis.




**8.4. Aldol condensation of ketone and aldehyde:** Deoxyanisoin **1a** (1.0 mmol), KOH (45 mg, 0.8 mmol), butanal (3 mmol) and **Mn-1** (1 mol%) were charged in 100 mL seal tube with stirring magnetic bar in dry toluene (1 mL) under argon. The flask was then placed in a preheated oil bath at 100 °C. After 24 h, the crude reaction mixture was diluted by ethyl acetate and filter through celite. The filtrate was concentrated under vacuum and resultant residue was purified by column chromatography using 100-200 mesh size silica with hexane/ethyl acetate as an eluent, 53% product (**3a´**) was isolated. The same reaction was conducted in presence of $MnBr_2$, $MnBr(CO)_5$, Ru-MACHO instead of **Mn-1** and also only KOH, KO$^t$Bu (in absence of any catalysts or metal salts) keeping other parameters constant. The results of all the reaction was shown in the bar diagram.

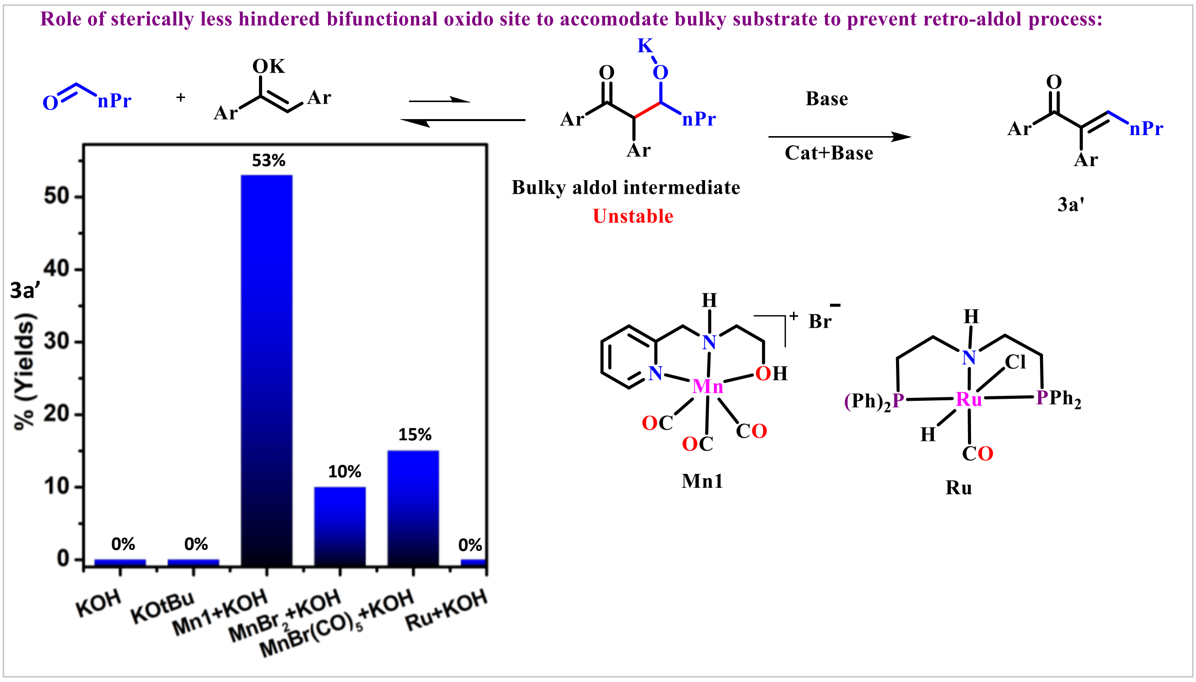
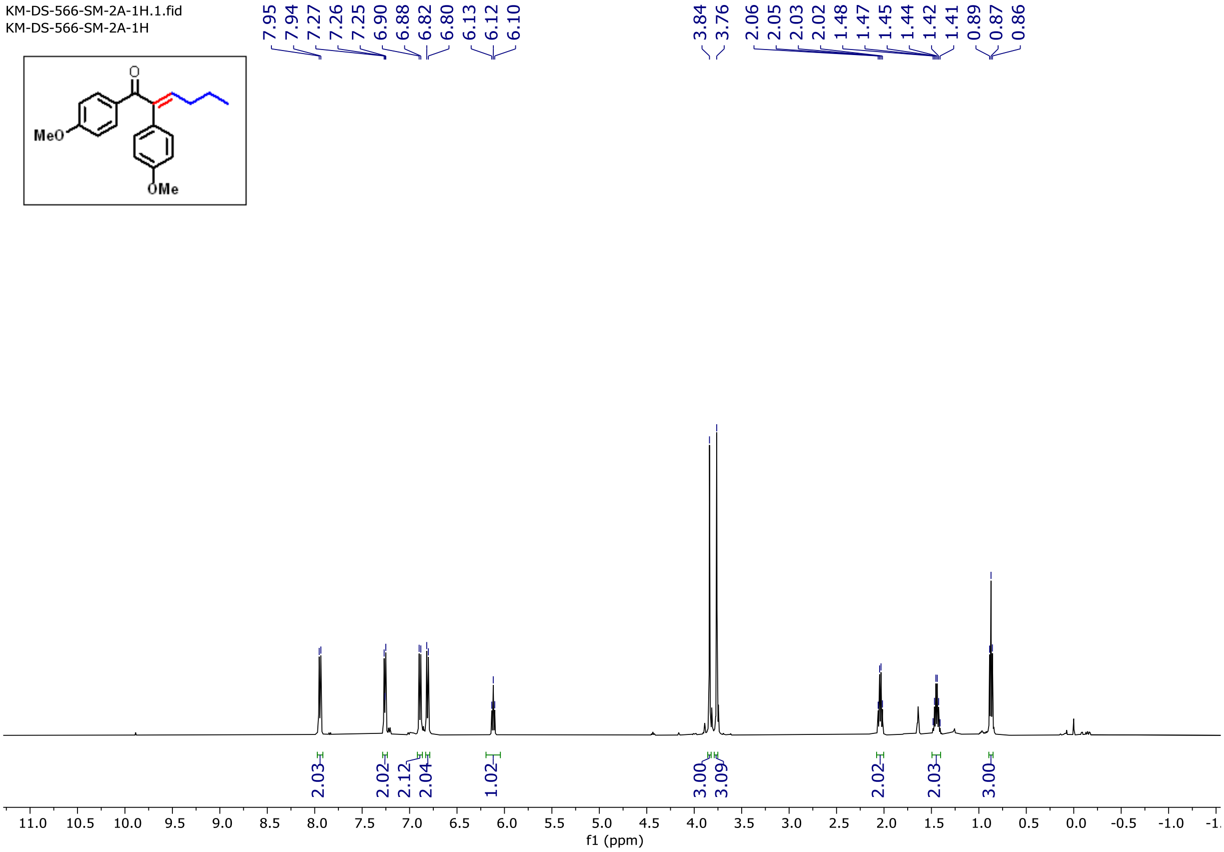



**Figure S9.** Experimental study of aldol condensation step in different catalytic systems.


KM-DS-566-SM-2A-1H.1.fid
KM-DS-566-SM-2A-1H
7.95
7.94
7.27
7.26
7.25
6.90
6.88
6.82
6.80
6.13
6.12
6.10
3.84
3.76
2.06
2.05
2.03
2.02
1.48
1.47
1.45
1.44
1.42
1.41
0.89
0.87
0.86
MeO
OMe
O
2.03
2.02
2.12
2.04
1.02
3.00
3.09
2.02
2.03
3.00
f1 (ppm)

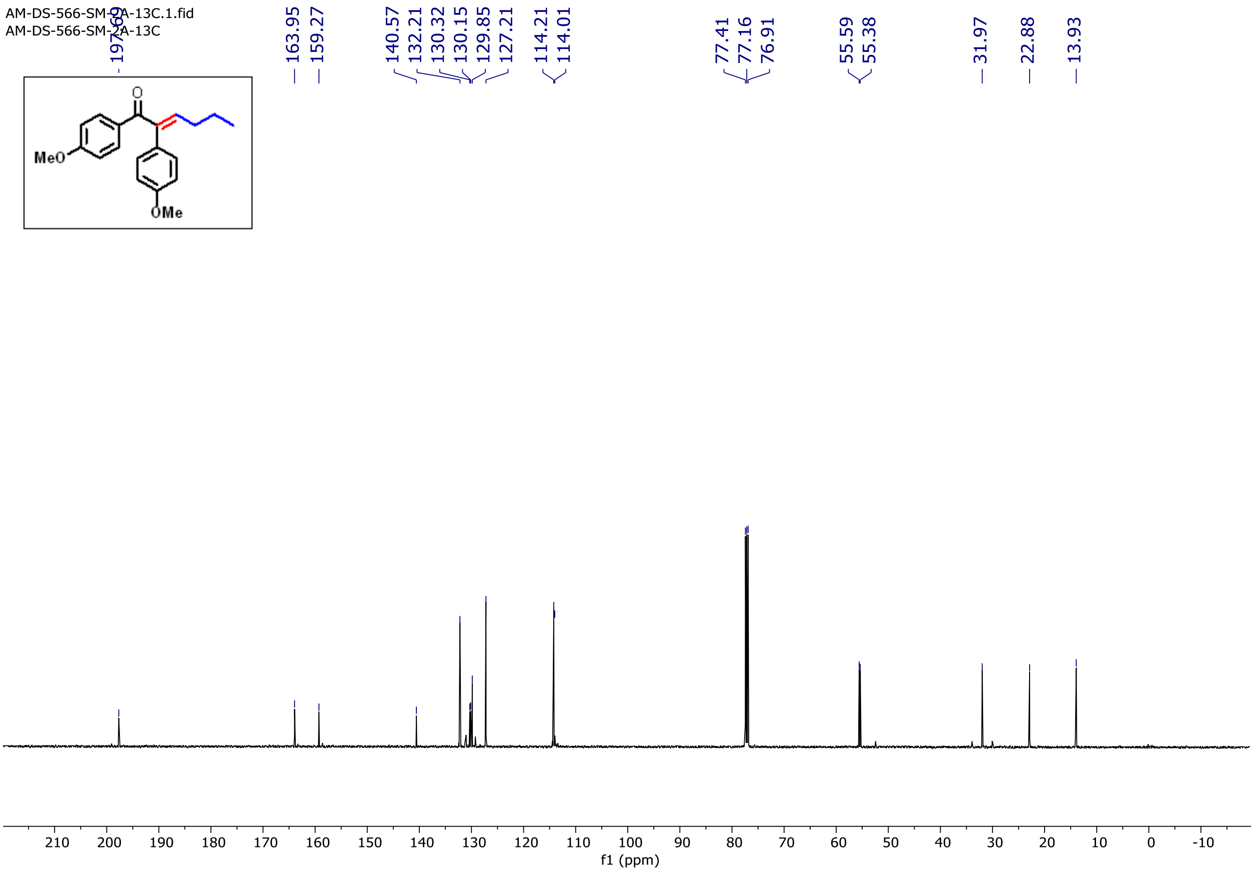
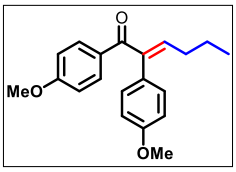
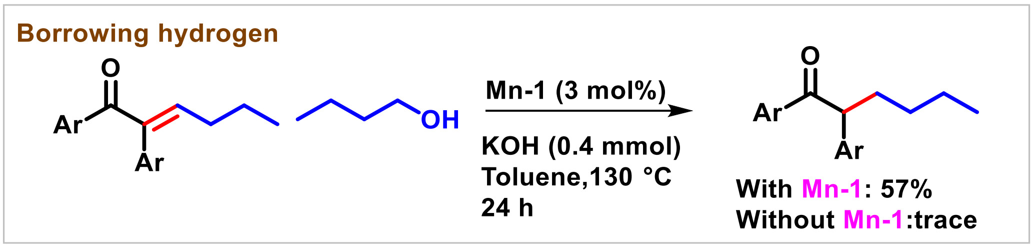

AM-DS-566-SM-2A-13C.1.fid
AM-DS-566-SM-2A-13C
197.60
163.95
159.27
140.57
132.21
130.32
130.15
129.85
127.21
114.21
114.01
77.41
77.16
76.91
55.59
55.38
31.97
22.88
13.93
MeO
OMe
O
f1 (ppm)

**Figure S10.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3a´** in $CDCl_3$.

**(E)-1,2-bis(4-methoxyphenyl)hex-2-en-1-one (3a´):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 10%) afforded the title compound in 53% yield (164 mg, 0.53 mmol) as yellow liquid. **$^{1}$H NMR (500 MHz, Chloroform-*d*) δ** 7.94 (d, $J$ = 8.8 Hz, 2H), 7.26 – 7.25 (m, 2H), 6.88 (d, $J$ = 8.8 Hz, 2H), 6.80 (d, $J$ = 8.7 Hz, 2H), 6.11 (t, $J$ = 7.7 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 2.06 – 2.02 (m, 2H), 1.48 – 1.40 (m, 2H), 0.87 (t, $J$ = 7.3 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 197.7, 163.9, 159.3, 140.6, 132.2, 130.3, 130.1, 129.8, 127.2, 114.2, 114.0, 55.6, 55.4, 32.0, 22.9, 13.9. **HRMS: (ESI):** Calc'd for. **$C_{20}H_{22}O_3$ $[M+H]^+$: 311.1647**; **found = 311.1654.**

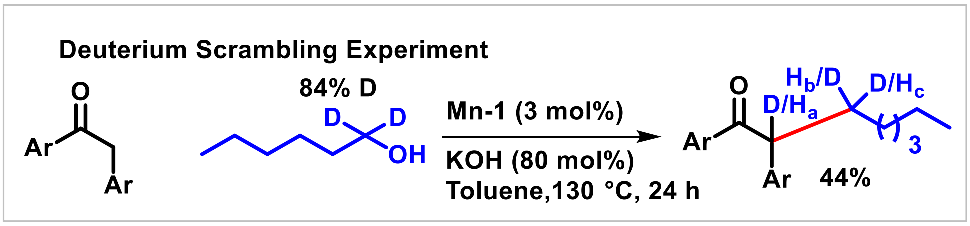



**10.4. Transfer hydrogenation of intermediate *α, β*-unsaturated ketone:** In an oven dried 100 mL seal tube *α, β*-unsaturated ketone, **3a´** (0.5 mmol), butanol, **2a** (1.5 mmol), KOH (0.4 mmol) were taken with stirring magnetic bar. Then the mixture was connected with high vacuum for 10 mins, next 1 mL dry toluene and **Mn-1** (3 mol%) were added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C under an argon atmosphere and continued for 24 h. After completion, the reaction cooled to room temperature, after that ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture (0–2%) as eluent, 57% of **3a** was obtained.




## 8.5. Deuterium scrambling experiments:

In an oven dried 100 mL seal tube, equipped with a stirring bar was charged with the deoxyanisoin, **1a** (1 mmol), deuterated 1-hexanol, **2b–d2** (3.0 mmol), KOH (0.8 mmol). Then the seal tube was closed with a rubber septum, evacuated and refilled with Ar (x 3). Then, dry toluene (1 mL) and **Mn-1** (3 mol%) were added. The resulting mixture was then placed into the pre heated oil bath at 130 °C under an argon atmosphere and continued for 24 h. After completion, the reaction cooled to room temperature, after that ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl-acetate mixture (0–2%) as eluent, 44% of '**3b-d2**' was obtained with 60% (at *α*-position), 65% (at *β*-position) deuterium incorporation respectively. The percentage of deuterium incorporation was analysed using $^{1}$H NMR spectroscopy.



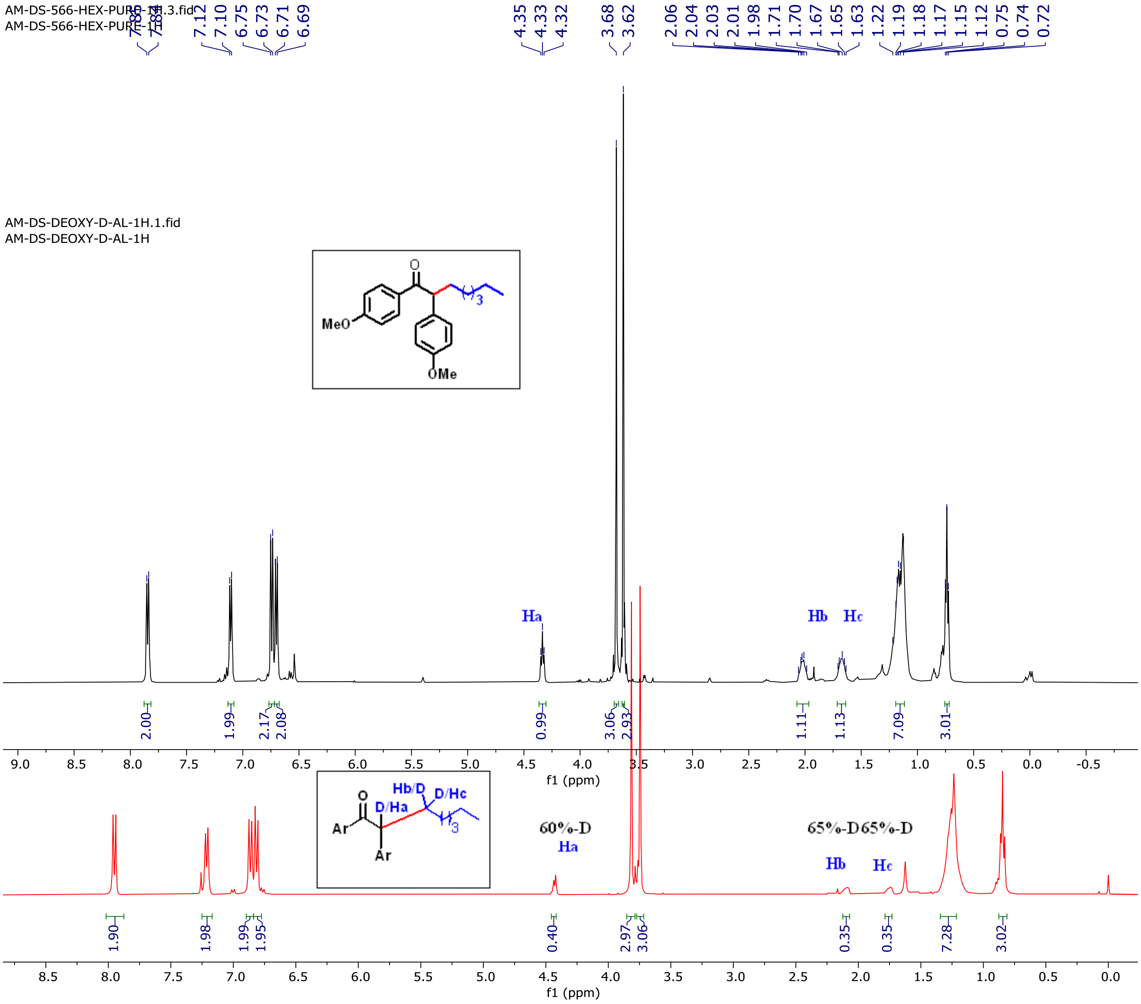
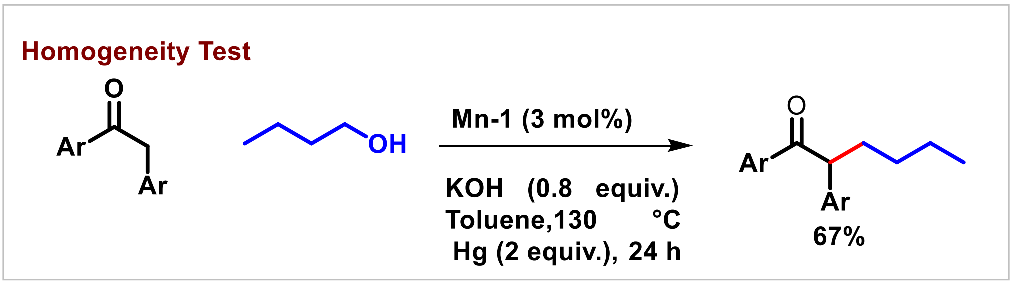
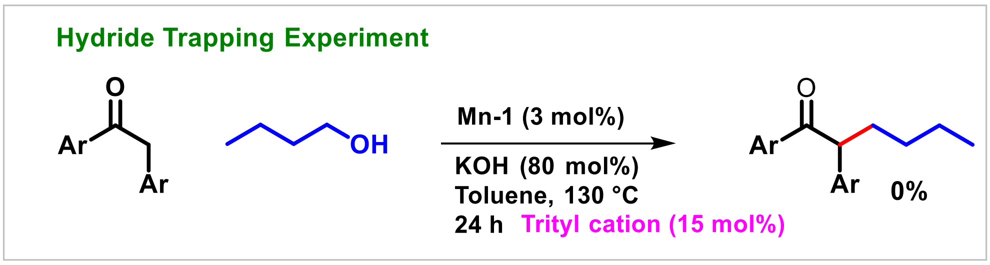




**Figure S11.** $^{1}$H (500 MHz) NMR Spectrum of **3a** in $CDCl_3$.

**8.6. Hg-dropping experiment:** In an oven dried 100 mL seal tube deoxyanisoin, **1a** (1 mmol, 150 mg), 1-butanol, **2a** (3 mmol, 108 mg), KOH (0.8 mmol), and 2.0 equiv. metallic Hg were taken together and connected with high vacuum for 10 minutes. Then 1 mL dry toluene and **Mn-1** (3 mol%) are added to the mixture tube under argon. The reaction mixture is heated at 130 °C. After stirring for 24 h, the mixture is cooled down to room temperature. Then, reaction tube was taken out from hot oil bath and cooled to room temperature. Then purified the crude reaction mixture using 5% petroleum ether and ethyl acetate as an eluent.

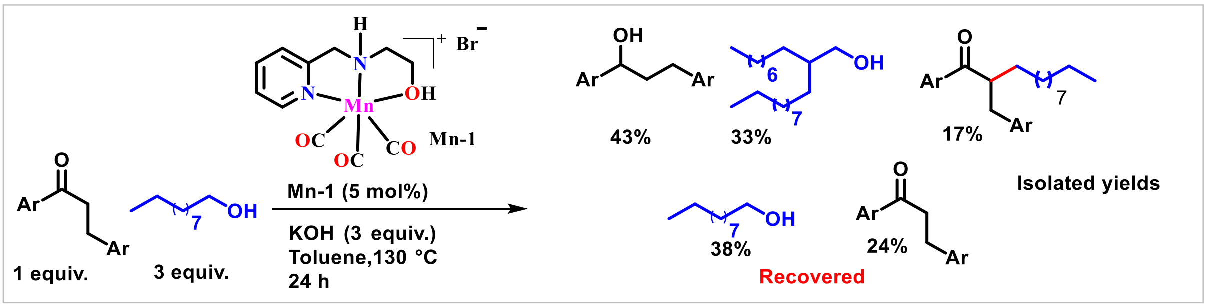



**8.7. Hydride trapping experiment:** In an oven dried 100 mL seal tube deoxyanisoin, **1a** (1 mmol), 1-butanol, **2a** (3 mmol), KOH (0.8 mmol) 1 mL dry toluene and **Mn-1** (3 mol%) are added sequentially inside the argon filled glove box. Then reaction mixture is stirred at room temperature. After stirring for 0.5 h, 10 mol% tritylium tetrafluoroborate is added to the previous reaction mixture. Then, the tube was sealed and placed in a preheated oil bath at 130 °C (oil bath temperature) for 24 h. After completion of the reaction, the tube was allowed to cool at room temperature. Then, analysed the $^{1}$H nmr of crude reaction mixture which indicated that no product was formed.




**9. Reaction with excess amount of alcohols and base in presence of Mn-1 catalyst:**

In a 100 mL seal tube, *α*-branch ketone (0.5 mmol), 1-decanol, **2n** (1.5 mmol), KOH (1.5 mmol) were taken with a magnetic bar. Then the seal tube was closed with a rubber septum, evacuated and refilled with Ar (x 3) for 10 mins. Then 1 mL dry toluene and **Mn-1** (5 mol%) was added under argon atmosphere. The reaction mixture was refluxed in an oil bath at 130 °C for 24 h. After completion of the reaction mixture was cooled to room temperature and ethyl acetate was added and filtered through celite pad. The filtrate was evaporated under reduced pressure. Then the crude residue was characterized by $^{1}$H-NMR spectroscopy and subsequently purified by column chromatography using a gradient of hexane and ethyl acetate as the eluent.



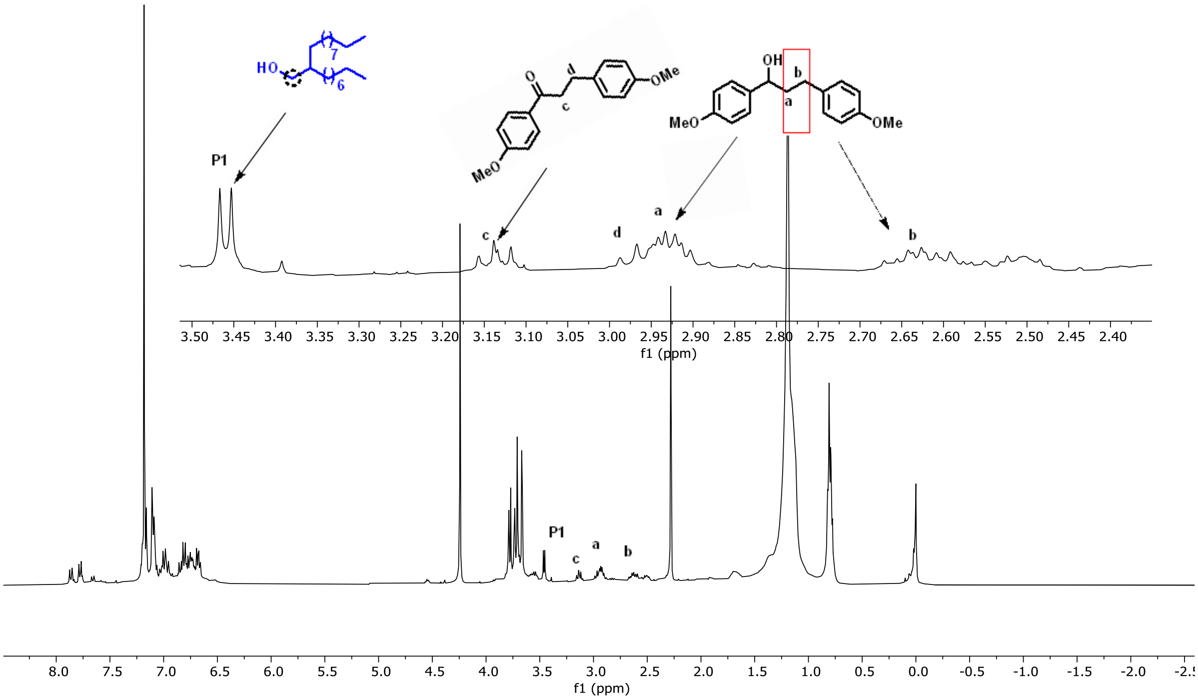
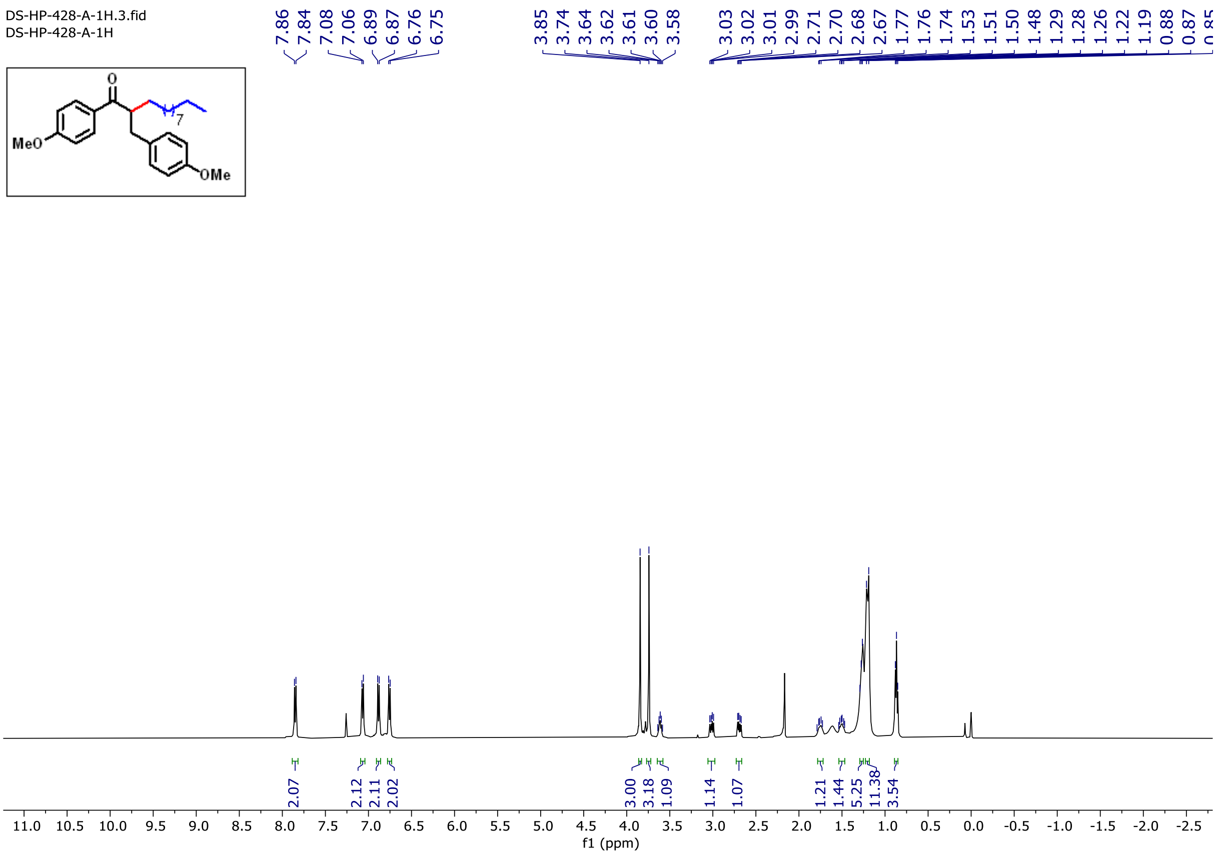



**Figure S12.** $^{1}H$ (500 MHz) NMR Spectrum of crude reaction mixture in $CDCl_3$.



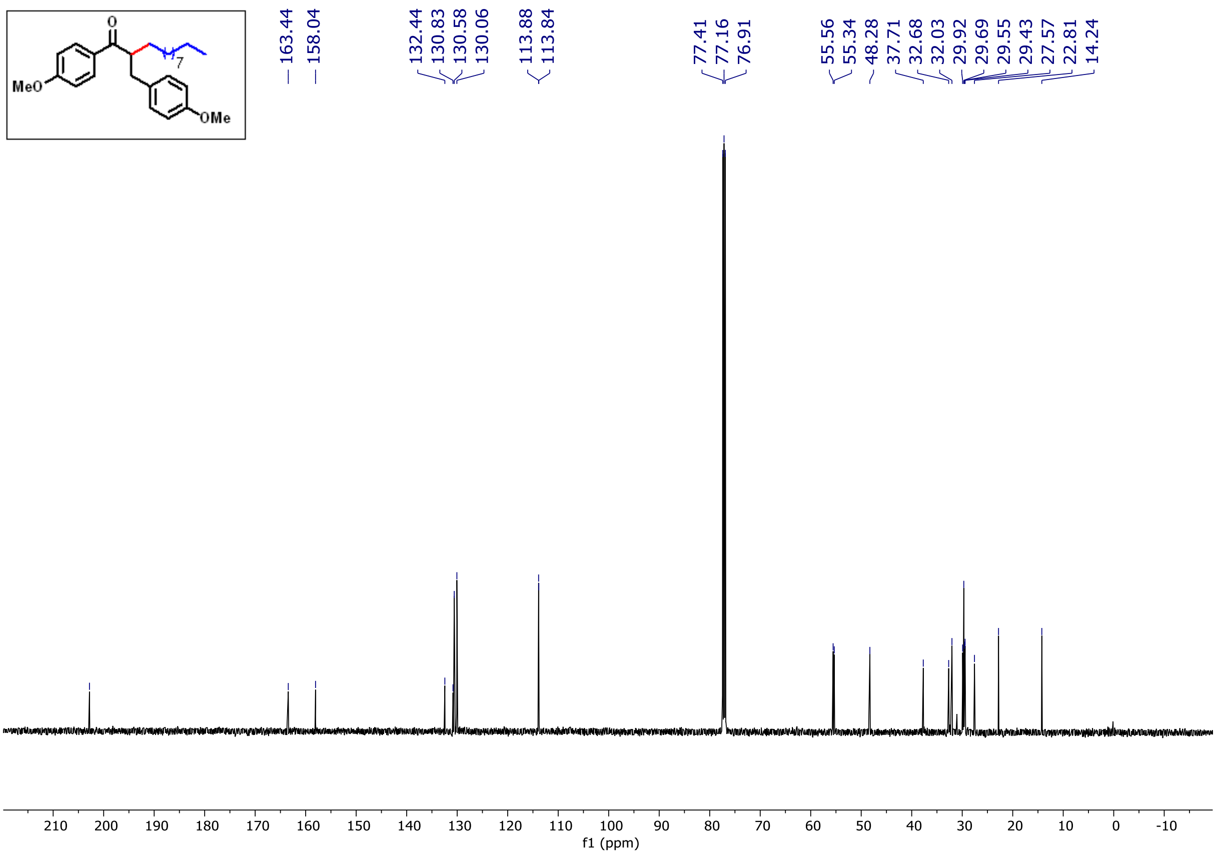
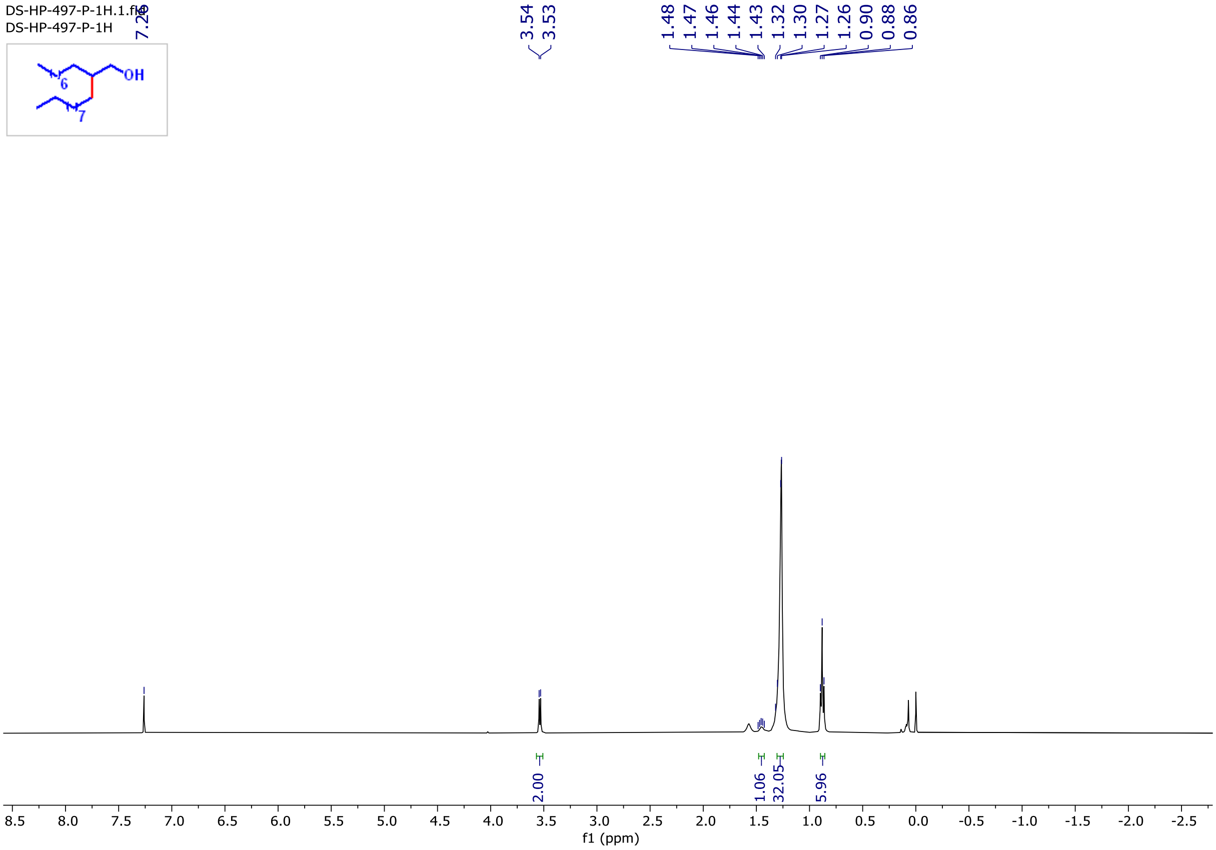




**Figure S13.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3ah** in $CDCl_3$.


DS-HP-497-P-1H.1.fid
DS-HP-497-P-1H
7.26
3.54
3.53
1.48
1.47
1.46
1.44
1.43
1.32
1.30
1.27
1.26
0.90
0.88
0.86
OH
6
7
2.00
1.06
32.05
5.96
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)

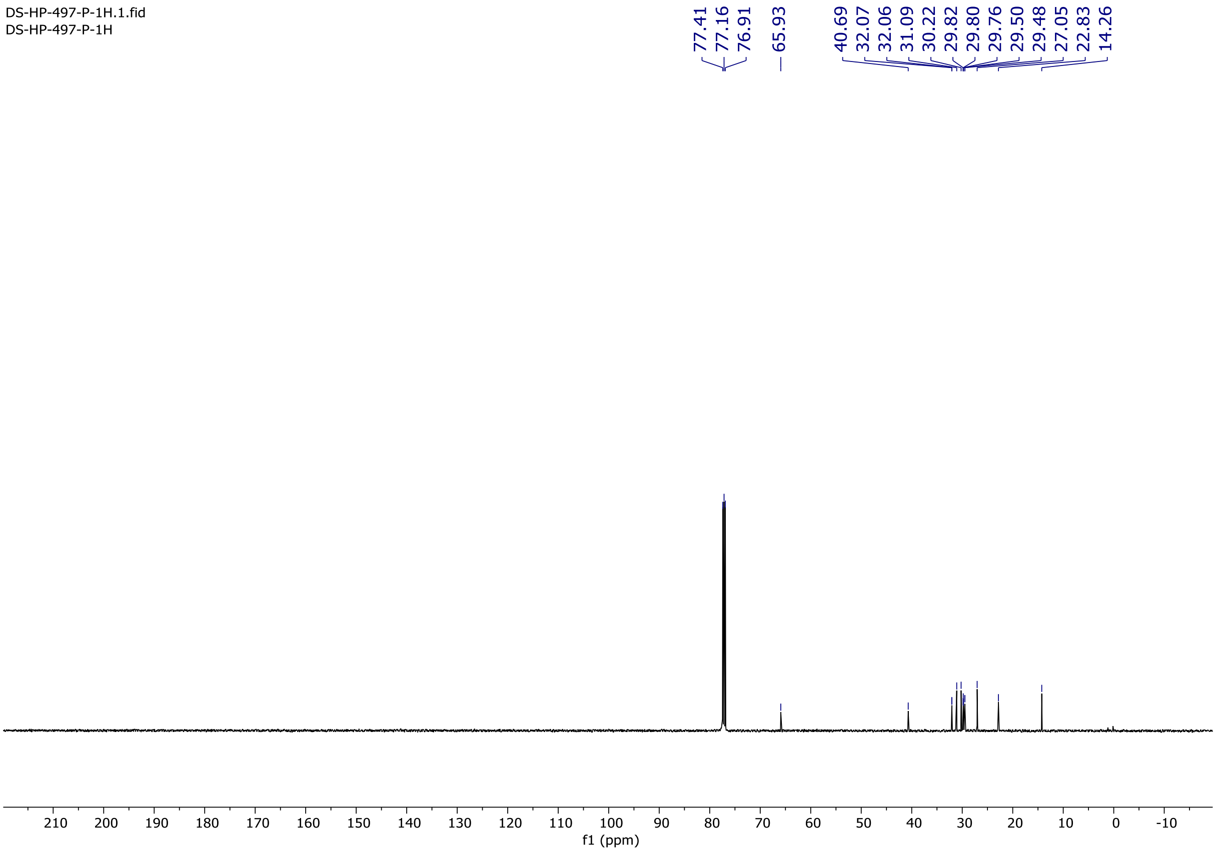

DS-HP-497-P-1H.1.fid
DS-HP-497-P-1H
77.41
77.16
76.91
65.93
40.69
32.07
32.06
31.09
30.22
29.82
29.80
29.76
29.50
29.48
27.05
22.83
14.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

**Figure S14.** $^1$H (500 MHz) and $^{13}$C{$^1$H} (125 MHz) NMR Spectrum of **3ah** in $CDCl_3$.

## 10. Kinetic experiments:

**Experimental procedure:** To an oven dried 10 mL 2-neck round bottomed flask, deoxyanisoin, **1a** (1 mmol), 1-hexanol, **2b** (2 mmol), KOH (0.8 mmol, 80 mol%) and **Mn-1** (3 mol%), mesitylene (1.0 mmol, 1 equiv.) as an internal standard and toluene as a solvent were added under argon to make up the total volume of the reaction mixture 2 mL. Afterwards, the reaction mixture was kept in a preheated oil bath for stirring at 130 °C. At regular intervals (1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, 12 h, 14 h, 15 h) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of the product (mmolar) *vs* time (h) plot **(Figure S14)**.

### 10.1. Monitoring the kinetics of the reaction with respect to hexanol:

| Time (h) | Concentration of Deoxyanisoin (mmolar) | Concentration of Hexanol (mmolar) | Concentration of Single bonded product (mmolar) | Concentration of Double bonded product (mmolar) |
|---|---|---|---|---|
| 0 | 1 | 2 | 0 | 0 |
| 1 | 0.965 | 1.943 | 0.035 | 0.102 |
| 3 | 0.921 | 1.864 | 0.067 | 0.183 |
| 5 | 0.885 | 1.795 | 0.097 | 0.156 |
| 7 | 0.842 | 1.732 | 0.138 | 0.122 |
| 9 | 0.794 | 1.655 | 0.189 | 0.093 |
| 11 | 0.742 | 1.564 | 0.235 | 0.082 |
| 12 | 0.674 | 1.476 | 0.296 | 0.075 |
| 13 | 0.602 | 1.375 | 0.358 | 0.07 |
| 14 | 0.524 | 1.278 | 0.429 | 0.067 |
| 15 | 0.443 | 1.179 | 0.498 | 0.065 |
| 16 | 0.364 | 1.082 | 0.566 | 0.063 |
| 18 | 0.283 | 0.979 | 0.634 | 0.061 |
| 20 | 0.202 | 0.886 | 0.687 | 0.058 |
| 22 | 0.134 | 0.793 | 0.735 | 0.055 |
| 24 | 0.063 | 0.709 | 0.787 | 0.051 |

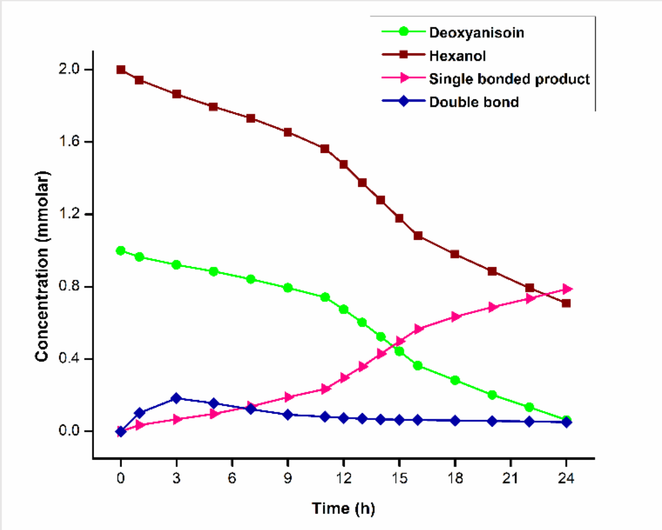



**Figure S15.** Full reaction kinetics of single bond with respect to hexanol.

## 10.2. Rate order determination:

The initial rate method was used to determine the rate order of the deoxyanisoin, **1a** (1 mmol) and 1-hexanol, **2b** (2 mmol), KOH (0.8 mmol, 80 mol%) and **Mn-1** (3 mol%), mesitylene (1.0 mmol, 1 equiv.) for the *α, α´*-branched ketone synthesis **3b** synthesis reaction with respect to various components of the reaction. The data of the concentration (mM) *vs* time (h) plot was fitted to linear using origin pro 9. The slope of the linear fitted curve represents the initial rate of the reaction. The order of the reaction was determined by plotting log(rate) *vs* log(concentration) of that particular component.

## 10.3. Rate order determination with respect to hexanol:

To an oven dried 10 mL 2-neck round bottomed flask, deoxyanisoin, **1a** (0.5 mmol, 1equiv.), KOH (0.8 mmol, 80 mol%) and **Mn-1** (3 mol%), mesitylene (1.0 mmol, 1 equiv.) as an internal standard, specific amount of benzyl alcohol **2a** and toluene as a solvent were added under argon to make up the total volume of the reaction mixture 2 mL. Afterwards, the reaction mixture was kept in an oil bath of 130 °C for stirring. At regular intervals (3 h, 4 h, 5 h, 6 h, 7 h, 8 h) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of the product (mM) *vs* time (h) plot **(Figure S15)**. The rate of the reaction at different initial concentration of benzyl alcohol **2a** was given below and used to plot the log(rate) *vs* log (concentration of benzyl alcohol **2a)** to determine the order of the reaction with respect to benzyl alcohol **2a (Figure S16)**.

| Time (h) | Concentration of Single bonded product formed at initial concentration of Hexanol 0.34 mM | Concentration of Single bonded product formed at initial concentration of Hexanol 0.37 mM | Concentration of Single bonded product formed at initial concentration of Hexanol 0.4 mM | Concentration of Single bonded product formed at initial concentration of Hexanol 0.43 mM |
|---|---|---|---|---|
| 13 | 0.1088 | 0.1221 | 0.14 | 0.1548 |
| 14 | 0.1258 | 0.1406 | 0.16 | 0.1763 |
| 15 | 0.1428 | 0.1591 | 0.18 | 0.1978 |
| 16 | 0.1632 | 0.1813 | 0.204 | 0.2236 |
| 17 | 0.1836 | 0.2035 | 0.228 | 0.2494 |
| 18 | 0.204 | 0.2257 | 0.252 | 0.2752 |

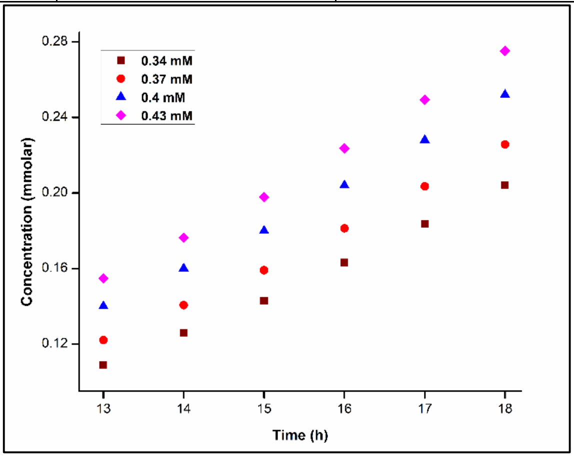



**Figure S16.** Order calculation with respect to hexanol.

| log(concentration of hexanol) | log(rate) |
|---|---|
| -0.4685 | -1.7181 |
| -0.4318 | -1.6813 |
| -0.3979 | -1.6476 |
| -0.3665 | -1.6162 |
| | |

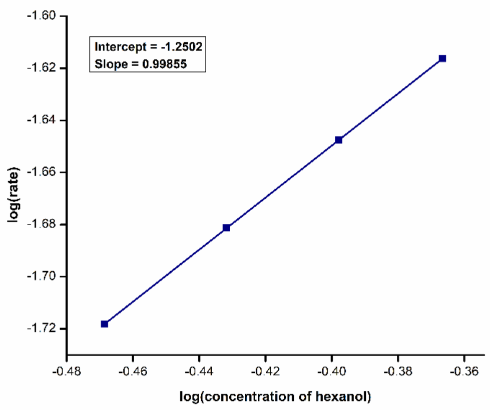
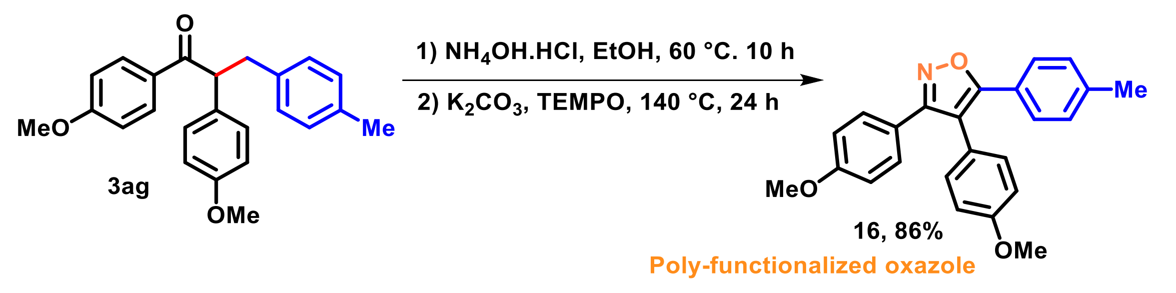



**Figure S17.** Order data with respect to hexanol.

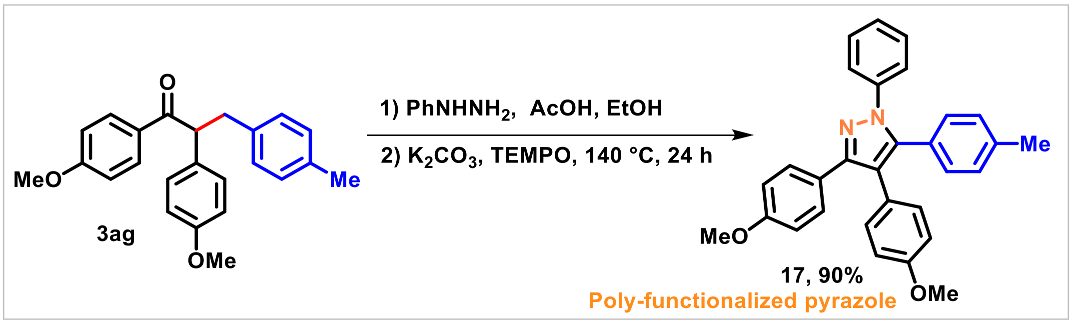
## 11. Synthetic applications:

**11.1. Synthesis highly substituted oxazole unit via oxime formation**: This was prepared by previously reported procedures.[15] To a solution of **3ag** (0.5 mmol, 1 equiv) in EtOH (2 mL) was added hydroxylamine hydrochloride (0.75 mmol, 1.5 equiv) and pyridine (2.25 mmol 2.5 equiv) under a argon atmosphere. The reaction mixture was then stirred at 60 °C for 12 h. The solvent was evaporated, and the residue was diluted with water and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with 1 N aqueous HCl and brine, dried over $Na_2SO_4$, and concentrated. The white solid product was used for the next step without further purification. To a DMF (2 mL) solution of crude product, TEMPO (117.4 mg, 0.752 mmol) and $K_2CO_3$ (69.2 mg, 0.501 mmol) were added. The reaction mixture was then stirred for 24 h at 140 ºC under a argon atmosphere. The resulting mixture was cooled to room temperature and diluted with water and EtOAc. The aqueous layer was extracted with EtOAc for three times. The combined organic extracts were washed with brine, dried over MgSO4, and concentrated. Purification of the crude product by flash column chromatography (silica gel; hexane: ethyl acetate = 99:1) afforded **16** (160 mg, 0.43 mmol) in 86% yield as a white solid.

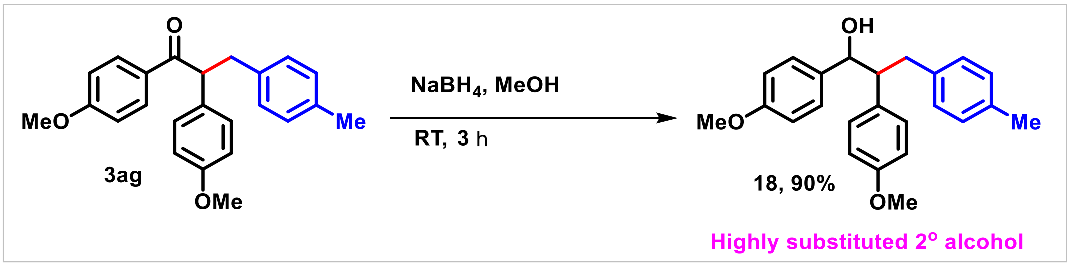



**11.2. Synthesis of poly functionalized pyrazole:**[15]

To a solution of ketone, **3ag** (1.0 equiv) in EtOH (2 mL) was added phenylhydrazine (2.0 equiv) and acetic acid (0.2 equiv) under argon atmosphere. The reaction mixture was stirred at 75 °C until the ketone was consumed. The reaction mixture was evaporated to remove the solvent and the crude product was further used for the next step. The crude product was dissolved in DMF (2 mL), then TEMPO (1.5 mmol, 3 equiv) and $K_2CO_3$ (1 mmol, 2 equiv.) was added. Then the reaction mixture was stirred for 24 h at 140 °C under argon atmosphere. The resulting mixture was cooled to room temperature and diluted with water and EtOAc. The aqueous layer was extracted with EtOAc for three times. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, and concentrated. Purification of the crude product by silica gel column chromatography (100-200 mesh size) using petroleum ether and ethyl acetate as eluent afforded the **17** in 90% yield.



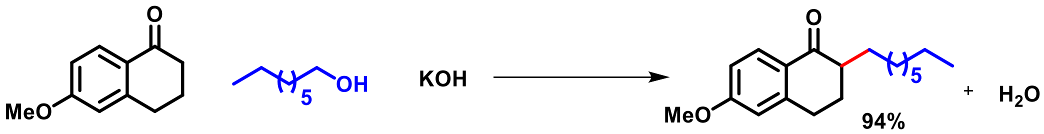

**11.3. Synthesis of *β*, *β*′-disubstituted secondary alcohol (18):** This was prepared by the reduction **3ag** with $NaBH_4$ following standard procedures (90% yield).




## 12. Gram scale synthesis and green chemistry matric calculations:

In a 50 mL oven-dried round bottom flask, *α*-branch ketone derivatives **1** (5.0 mmol), primary alcohols, **2** (5.0 mmol), KOH (0.20 mmol) were added. Then connected with high vacuum for 10 mins, then 4 mL dry toluene and **Mn-1** (0.5 mol %) was added under an argon atmosphere. Then the reaction mixture was refluxed in preheated oil bath at 130 °C for 24 h. After completion of the reaction mixture was cooled to room temperature and ethyl acetate was added and filtered through celite pad. Filtrate mixture was evaporated in reduced pressure and purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product **3**. Green chemistry matric of all the products are calculated using standard methods and all values are highlighted in above table.

## 12.1. One representative calculation procedure for green chemistry matrics:




| $C_{11}H_{12}O_2$ | $C_8H_{18}O$ | | $C_{19}H_{28}O_2$ | |
|---|---|---|---|---|
| 176.2150 | 130.2310 | 56.1053 | 288.2089 | 18.01 |

- Weight taken (5 mmol)

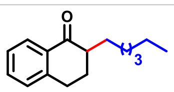
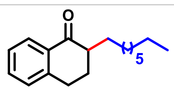
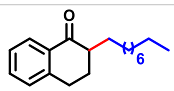
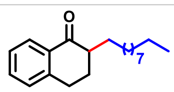
| | | | |
|---|---|---|---|
| 881.075 mg | 651.155 mg | 84 mg | 1354.58 mg |
| 0.88107g | 0.6515 g | 0.084 g | 1.3546 g |

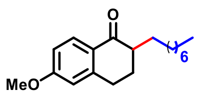
- Toluene used: 4 mL: 3.464
- Recovered: 3 mL: 2.601 g

- E-factor = [(0.88107+0.6515+0.084+3.464)-(1.3546+2.601)]/1.3546
  = (5.08057-3.9956)/1.3546
  = 0.80kg waste/kg product

- Atom economy = (product mass/reactant mass) 100
  = (288.2089/306.446)100
  = 94%
- Carbon efficiency: 100%

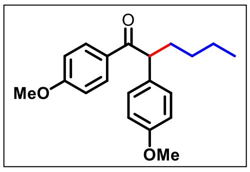
- Reaction mass efficiency = (1.3546/1.5325)100
  = 88%
- Atom efficiency: 88%

| Compounds / Parameters |  0.979 g, 85% 3k |  1.176 g, 91% 3l |  1.226 g, 90% 3m |  1.332 g, 93% 3n |
|---|---|---|---|---|
| E-factor | 1.20 kg waste/1kg waste | 0.98 kg waste/1kg waste | 0.94 kg waste/1kg waste | 0.83 kg waste/1kg waste |
| Atom economy | 93% | 94% | 94% | 94.1% |
| Atom efficiency | 78.7% | 85.5% | 84.6% | 87.5% |
| Carbon efficiency | 100% | 100% | 100% | 100% |
| Reaction mass efficiency | 87% | 84% | 84.4% | 87.5% |

| Compounds / Parameters |  1.3546 g, 94%, 3r |
|---|---|
| E-factor | 0.80 kg waste/1kg waste |
| Atom economy | 94% |
| Atom efficiency | 88% |
| Carbon efficiency | 100% |
| Reaction mass efficiency | 88% |

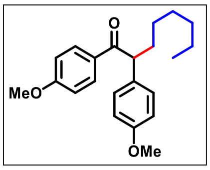
**13. Analytical data of compounds:**

**1,2-bis(4-methoxyphenyl)hexan-1-one (3a)**[16] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 63% yield (197 mg, 0.63 mmol) as Yellowish liquid.



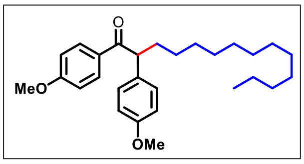

**$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.95 (d, *J* = 8.9 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.43 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.16 -2.09 (m, 1H), 1.81 – 1.74 (m, 1H), 1.35 – 1.18 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H).**$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 199.0, 163.3, 158.6, 132.5, 131.0, 130.1, 129.3, 114.3, 113.8, 55.5, 55.3, 52.5, 33.9, 30.1, 22.9, 14.1.

**1,2-bis(4-methoxyphenyl)octan-1-one (3b)**, Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 67% yield (228 mg, 0.67 mmol) as Yellowish liquid.



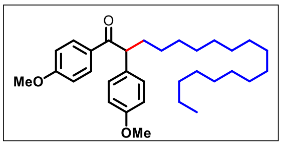

**$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.85 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 4.33 (t, *J* = 7.3 Hz, 1H), 3.68 (s, 3H), 3.62 (s, 3H), 2.06 – 1.98 (m, 1H), 1.70 – 1.64 (m, 1H), 1.22 – 1.12 (m, 8H), 0.74 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 199.0, 163.3, 158.5, 132.4, 131.0, 130.1, 129.2, 114.3, 113.7, 55.4, 55.2, 52.4, 34.2, 31.8, 29.4, 27.8, 22.7, 14.1. **HRMS: (ESI):** Calc'd for. **$C_{22}H_{29}O_3$: 342.2150; Found: 342.2158.**

**1,2-bis(4-methoxyphenyl)tetradecan-1-one (3c):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 71% yield (301 mg, 0.70 mmol) as white solid.



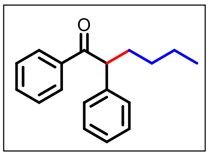

**$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.86 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.07 – 2.00 (m, 1H), 1.73 – 1.64 (m, 1H), 1.22 – 1.11 (m, 20H), 0.79 (t, *J* = 6.6 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 199.0, 163.3, 158.6, 132.5, 131.0, 130.2, 129.2, 114.3, 113.8, 55.5, 55.3, 52.5, 34.2, 32.0, 29.77, 29.76, 29.75, 29.71, 29.6, 29.5, 27.8, 22.8, 14.2.
**HRMS: (ESI):** Calc'd for. **$C_{28}H_{42}O_3$: 426.3134; Found: 426.3094.**

**1,2-bis(4-methoxyphenyl)octadecan-1-one (3d):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 73% yield (351 mg, 0.73 mmol) as white solid.

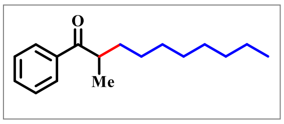



**$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.94 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 4.43 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.15 – 2.09 (m, 1H), 1.80 – 1.74 (m, 1H), 1.27 – 1.20 (m, 28H), 0.87 (t, *J* = 6.4 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 199.0, 163.3, 158.6, 132.5, 131.0, 130.2, 129.3, 114.3, 113.8, 55.5, 55.3, 52.5, 34.2, 32.1, 29.83, 29.79, 29.77, 29.73, 29.6, 29.5, 27.9, 22.8, 14.2. **HRMS: (ESI):** Calc'd for. **$C_{32}H_{48}O_3$ $[M+H]^+$: 481.3682; Found: 481.3683.**

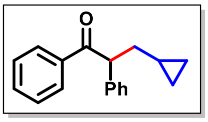
**1,2-diphenylhexan-1-one (3e):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 76% yield (192 mg, 0.76 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.88 (d, *J* = 8.1 Hz, 2H), 7.39–7.37 (m, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.23–7.18 (m, 4H), 7.12–7.08 (m, 1H), 4.45 (t, *J* = 7.2 Hz, 1H), 2.14 –2.07 (m, 1H), 1.78–1.71 (m, 1H), 1.31–1.17 (m, 4H), 0.78 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.3, 140.0, 137.2, 132.9, 129.0, 128.7, 128.6, 128.3, 127.0, 53.8, 33.9, 30.0, 22.8, 14.1. **HRMS: (ESI):** Calc'd for.**$C_{18}H_{20}O$ $[M+H]^+$: 253.1592**; found = **253.1597.**



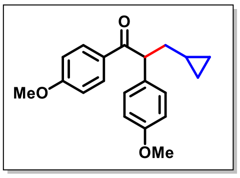
**1-(4-methoxyphenyl)-2-methyldecan-1-one (3f)**:[17] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 61% yield (150 mg, 0.61 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.96 – 7.94 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 3.49 – 3.42 (m, 1H), 1.83 – 1.76 (m, 1H), 1.46 – 1.39 (m, 2H), 1.30 – 1.23 (m, 11H), 1.18 (d, *J* = 6.9 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H).**$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 204.7, 136.9, 132.9, 128.7, 128.4, 40.7, 33.7, 32.0, 29.9, 29.6, 29.4, 27.5, 22.8, 17.3, 14.2.



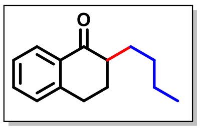

**3-cyclopropyl-1,2-diphenylpropan-1-one (3g):**[18] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 77% yield (193 mg, 0.77 mmol) as Yellowish liquid.**$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.99 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.32 (m, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.17 (m, 1H), 4.68 (t, *J* = 7.1 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.78 – 1.73 (m, 1H), 0.67 – 0.59 (m, 1H), 0.43 – 0.32 (m, 2H), 0.07 – 0.06 (m, 1H), 0.05 – 0.01 (m, 1H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.3, 140.0, 137.1, 132.9, 128.9, 128.8, 128.6, 128.3, 127.0, 54.2, 39.3, 9.6, 4.8, 4.8.




**3-cyclopropyl-1,2-bis(4-methoxyphenyl)propan-1-one (3h).** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 86% yield (267 mg, 0.86 mmol) as Yellowish liquid. **$^1$H NMR (600 MHz, $CDCl_3$) δ** 8.00 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 2.05 – 2.00 (m, 1H), 1.76 – 1.71 (m, 1H), 0.67 – 0.62 (m, 1H), 0.44 – 0.40 (m, 1H), 0.39 – 0.35 (m, 1H), 0.12 – 0.08 (m, 1H), 0.06 – 0.02 (m, 1H). **$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 199.0, 163.3, 158.5, 132.5, 131.1, 130.1, 129.3, 114.3, 113.7, 55.5, 55.3, 52.9, 39.3, 9.5, 4.8, 4.7.

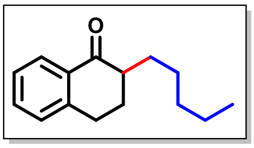



**2-butyl-3,4-dihydronaphthalen-1(2H)-one (3i):**[19] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 79% yield (160 mg, 0.79 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.01 – 2.95 (m, 2H), 2.49 – 2.44 (m, 1H), 2.26 – 2.21 (m, 1H), 1.97 – 1.87 (m, 2H), 1.64 – 1.62 (m, 1H), 1.53 – 1.46 (m, 1H), 1.39 – 1.34 (m, 3H), 0.92 (t, *J* = 6.5 Hz,

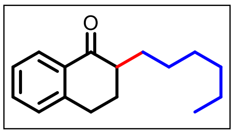


3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.7, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 29.4, 29.2, 28.4, 28.3, 23.0, 14.2.

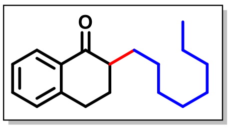
**2-pentyl-3,4-dihydronaphthalen-1(2H)-one (3j):**[20] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 83% yield (179 mg, 0.83 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.02 – 2.93 (m, 2H), 2.49 – 2.44 (m, 1H), 2.25 – 2.21 (m, 1H), 1.96 – 1.85 (m, 2H), 1.63 – 1.62 (m, 1H), 1.53 – 1.46 (m, 1H), 1.42 – 1.40 (m, 1H), 1.36 – 1.30 (m, 4H), 0.91 – 0.86 (t, *J* = 6.6 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.7, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 32.1, 29.5, 28.4, 28.3, 26.8, 22.7, 14.2.



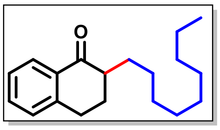
**2-hexyl-3,4-dihydronaphthalen-1(2H)-one (3k):**[20] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 84% yield (193 mg, 0.70 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.49 – 2.43 (m, 1H), 2.26 – 2.20 (m, 1H), 1.97 – 1.85 (m, 2H), 1.52 – 1.48 (m, 1H), 1.45 – 1.40 (m, 1H), 1.36 – 1.26 (m, 7H), 0.88 (t, *J* = 6.4 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.6, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 31.9, 29.6, 29.5, 28.4, 28.3, 27.1, 22.8, 14.2.



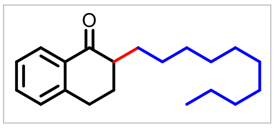
**2-octyl-3,4-dihydronaphthalen-1(2H)-one (3l):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 90% yield (257 mg, 0.90 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.49 – 2.44 (m, 1H), 2.26 – 2.20 (m, 1H), 1.97 – 1.85 (m, 2H), 1.52 – 1.39 (m, 3H), 1.33 – 1.26 (m, 10H), 0.87 (t, *J* = 6.7 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.7, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 32.0, 29.9, 29.7, 29.5, 29.45, 28.4, 28.3, 27.2, 22.8, 14.3. **HRMS: (ESI):** Calc'd for.**$C_{18}H_{26}O$ [M+H]$^+$: 259.2062**; found = **259.2063**.



**2-nonyl-3,4-dihydronaphthalen-1(2H)-one (3m):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 89% yield (242 mg, 0.89 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.07 – 2.91 (m, 2H), 2.49 – 2.44 (m, 1H), 2.26 – 2.20 (m, 1H), 2.00 – 1.82 (m, 2H), 1.51 – 1.46 (m, 1H), 1.45 – 1.37 (m, 2H), 1.32 – 1.23 (m, 12H), 0.87 (t, *J* = 6.5 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.7, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 32.0, 29.9, 29.7, 29.7, 29.5, 29.5, 28.4, 28.3, 27.2, 22.8, 14.3. **HRMS: (ESI):** Calc'd for.**$C_{19}H_{28}O$ [M+H]$^+$: 273.2218**; found = **273.2223**.

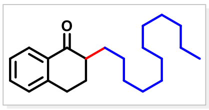


**2-decyl-3,4-dihydronaphthalen-1(2H)-one (3n):**[21] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 89% yield



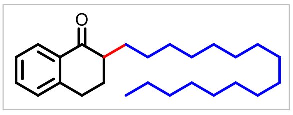
(254 mg, 0.89 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, $J$ = 7.8 Hz, 1H), 7.44 (t, $J$ = 7.4 Hz, 1H), 7.29 (t, $J$ = 7.6 Hz, 1H), 7.22 (d, $J$ = 7.7 Hz, 1H), 3.04 – 2.91 (m, 2H), 2.49 – 2.44 (m, 1H), 2.26 – 2.20 (m, 1H), 1.97 – 1.85 (m, 2H), 1.52 – 1.41 (m, 2H), 1.33 – 1.23 (m, 15H), 0.88 (t, $J$= 6.5 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.6, 144.1, 133.1, 132.7, 128.7, 127.6, 126.6, 47.6, 32.0, 29.9, 29.79, 29.77, 29.72, 29.5, 29.4, 28.4, 28.3, 27.1, 22.8, 14.2. **HRMS: (ESI):** Calc'd for.**$C_{20}H_{30}O$[M+H]$^+$: 287.2375**; found = **287.2373.**

**2-dodecyl-3,4-dihydronaphthalen-1(2H)-one (3o):** Purification by column chromatography ($SiO_2$,



100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 94% yield (295 mg, 0.94 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.02 (d, $J$ = 7.8 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.28 (t, $J$ = 7.5 Hz, 1H), 7.22 (d, $J$ = 7.6 Hz, 1H), 3.03 – 2.92 (m, 2H), 2.49 – 2.43 (m, 1H), 2.25 – 2.20 (m, 1H), 1.97 – 1.84 (m, 2H), 1.54 – 1.44 (m, 2H), 1.31 – 1.25 (m, 19H), 0.87 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 200.6, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 32.1, 29.9, 29.82, 29.80, 29.78, 29.71, 29.55, 29.49, 28.4, 28.3, 27.2, 22.8, 14.2. **HRMS: (ESI):** Calc'd for. **$C_{22}H_{34}O$ [M+H]$^+$: 315.2688**; found = **315.2689.**

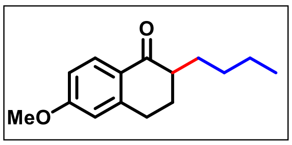
**2-hexadecyl-3,4-dihydronaphthalen-1(2H)-one (3p):**[22] **Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in**



**95% yield (352 mg, 0.95 mmol) as white solid. $^1$H NMR (600 MHz, Chloroform-*d*) δ** 8.02 (d, $J$ = 8.0 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.28 (t, $J$ = 7.5 Hz, 1H), 7.22 (d, $J$ = 7.6 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.48 – 2.44 (m, 1H), 2.25 – 2.20 (m, 1H), 1.96 – 1.85 (m, 2H), 1.51 – 1.45 (m, 1H), 1.44 – 1.39 (m, 1H), 1.33 – 1.23 (m, 27H), 0.87 (t, $J$ = 6.8 Hz, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 200.6, 144.1, 133.2, 132.7, 128.8, 127.6, 126.7, 47.6, 32.1, 29.9, 29.84, 29.83, 29.81, 29.81, 29.80, 29.79, 29.72 29.54, 29.51, 28.4, 28.3, 27.2, 22.8, 14.3.

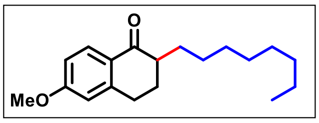
**HRMS: (ESI):** Calc'd for. **$C_{26}H_{42}O$ [M+H]$^+$: 371.3314**; found = **371.3316**.

**2-butyl-6-methoxy-3,4-dihydronaphthalen-1(2H)-one** (**3q**):[23] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title

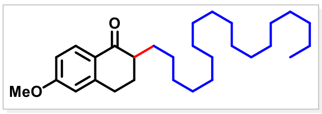



compound in 78% yield (181 mg, 0.78 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.00 (d, $J$ = 8.8 Hz, 1H), 6.82 – 6.80 (m, 1H), 6.67 (s, 1H), 3.84 (s, 3H), 2.99 – 2.88 (m, 2H), 2.44 – 2.39 (m, 1H), 2.23 – 2.18 (m, 1H), 1.97 – 1.83 (m, 2H), 1.51 – 1.44 (m, 1H), 1.42 – 1.33 (m, 4H), 0.92 (t, $J$ = 6.8 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 199.4, 163.5, 146.5, 130.0, 126.4, 113.2, 112.5, 55.5, 47.3, 29.4, 29.3, 28.8, 28.3, 23.0, 14.1.

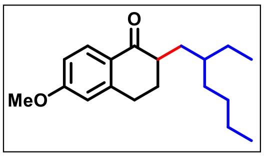
**6-methoxy-2-octyl-3,4-dihydronaphthalen-1(2H)-one (3r):**[24] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 83% yield (239 mg, 0.83 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.99 (d, *J* = 8.7 Hz, 1H), 6.80 – 6.79 (m, 1H), 6.69 – 6.67 (m, 1H), 3.84 (s, 3H), 2.98 – 2.88 (m, 2H), 2.44 – 2.38 (m, 1H), 2.23 – 2.17 (m, 1H), 1.95 – 1.82 (m, 2H), 1.74 – 1.64 (m, 1H), 1.50 – 1.39 (m, 3H), 1.32 – 1.27 (m, 9H), 0.88 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 199.4, 163.4, 146.5, 130.0, 126.3, 113.1, 112.5, 55.5, 47.3, 32.0, 29.9, 29.67, 29.64, 29.4, 28.7, 28.3, 27.2, 22.7, 14.2.



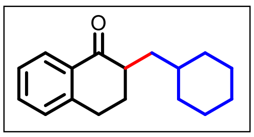

**2-octadecyl-3,4-dihydronaphthalen-1(2H)-one (3s):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 96% yield (411 mg, 0.96 mmol) as white solid. **$^1$H NMR (600 MHz, Chloroform-*d*) δ** 8.02 (d, *J* = 8.7 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.70 (s, 1H), 3.87 (s, 3H), 3.03 – 2.89 (m, 2H), 2.46 – 2.41 (m, 1H), 2.25 – 2.20 (m, 1H), 1.96 – 1.85 (m, 2H), 1.52 – 1.47 (m, 1H), 1.45 – 1.41 (m, 1H), 1.34 – 1.27 (m, 31H), 0.90 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 199.4, 163.4, 146.5, 130.0, 126.3, 113.1, 112.5, 55.5, 47.3, 32.1, 29.9, 29.84, 29.82, 29.81, 29.80, 29.7, 29.6, 29.5, 28.8, 28.3, 27.2, 22.8, 14.2. **HRMS: (ESI):** Calc'd for.**$C_{29}H_{48}O_2$ [M+H]$^+$: 429.3733**; **found: 429.3733.**



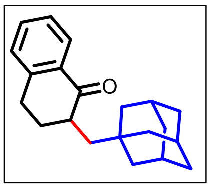

**2-(2-ethylhexyl)-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (3t):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 72% yield (207 mg, 0.72 mmol) as white solid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.51 – 7.50 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.04 – 7.02 (m, 1H), 3.82 (s, 3H), 2.97 – 2.85 (m, 2H), 2.54 – 2.48 (m, 1H), 2.23 – 2.18 (m, 1H), 1.93 – 1.88 (m, 1H), 1.86 – 1.78 (m, 1H), 1.46 – 1.25 (m, 10H), 0.90 – 0.85 (m, 6H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 201.0, 158.5, 136.6, 133.5, 130.0, 121.6, 109.6, 55.6, 45.2, 36.2, 33.5, 33.3, 29.1, 28.8, 27.4, 25.4, 23.2, 14.3, 10.4. **HRMS: (ESI):** Calc'd for. **$C_{19}H_{28}O_2$ [M+H]$^+$: 289.2168**; **found =289.2177.**



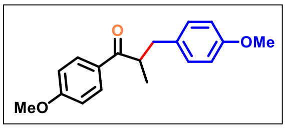

**2-(cyclohexylmethyl)-3,4-dihydronaphthalen-1(2H)-one (3u)**:[25] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 2%) afforded the title compound in 78% yield (189 mg, 0.78 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.92 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 2.93 – 2.82 (m, 2H), 2.50 – 2.45 (m, 1H), 2.15 – 2.09 (m, 1H), 1.79 – 1.72 (m, 2H), 1.66 – 1.57 (m, 5H), 1.36 – 1.27 (m, 1H), 1.23 – 1.07 (m, 4H), 0.91 – 0.76 (m, 2H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 201.1, 143.9, 133.1, 132.7, 128.7, 127.5, 126.6, 44.7, 37.0, 34.9, 34.2, 32.7, 28.5, 28.2, 26.7, 26.5, 26.4.



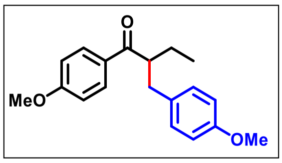
**2-(((3r,5r,7r)-adamantan-1-yl)methyl)-3,4-dihydronaphthalen-1(2H)-one (3v):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 70% yield (206 mg, 0.70 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 8.00 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 3.05 – 2.92 (m, 2H), 2.54 – 2.51 (m, 1H), 2.20 – 2.15 (m, 1H), 2.10 – 2.07 (m, 1H), 1.96 – 1.94 (m, 2H), 1.7 – 1.68 (m, 4H), 1.65 – 1.60 (m, 4H), 1.55 -1.51 (m, 6H), 0.96 – 0.92 (m, 1H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 201.1, 144.0, 133.0, 132.9, 128.7, 127.7, 126.6, 43.5, 42.8, 42.7, 39.5, 39.1, 37.2, 37.1, 36.7, 32.9, 32.1, 28.8, 28.2, 28.1. **HRMS: (ESI):** Calc'd for. **$C_{21}H_{26}O$ [M+H]$^+$: 295.2062**; **found =295.2061.**



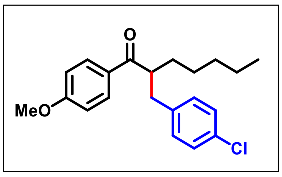

**1,3-bis(4-methoxyphenyl)-2-methylpropan-1-one (3w):**[26] Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 88% yield (250 mg, 0.88 mmol) as Yellowish liquid **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.91 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 3.76 (s, 3H), 3.69 – 3.62 (m, 1H), 3.08 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.62 (dd, *J* = 13.8, 7.7 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 202.5, 163.5, 158.1, 132.3, 130.7, 130.1, 129.6, 113.9, 55.6, 55.3, 42.7, 38.8, 17.6.



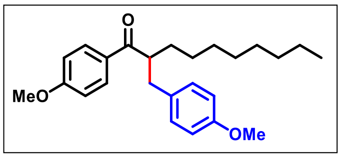

**2-(4-methoxybenzyl)-1-(4-methoxyphenyl)butan-1-one (3x).** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 76% yield (226 mg, 0.76 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.66 (s, 3H), 3.52 – 3.46 (m, 1H), 2.94 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.62 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.75 – 1.66 (m, 1H), 1.54 – 1.46 (m, 1H), 0.78 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 201.5, 162.3, 156.9, 131.2, 129.7, 129.4, 128.9, 112.7, 112.7, 54.4, 54.2, 48.5, 36.1, 24.4, 10.7. **HRMS: (ESI):** Calc'd for. **$C_{19}H_{22}O_3$ [M+H]$^+$: 299.1647, Found: 299.1633**.




**2-(4-chlorobenzyl)-1-(4-methoxyphenyl)heptan-1-one (3y).** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 51% yield **(176 mg, 0.51 mmol) as Yellowish liquid.** $^1$**H NMR (400 MHz, Chloroform-*d*) δ** 7.76 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 3.59 – 3.52 (m, 1H), 2.98 (dd, *J* = 13.6, 8.2 Hz, 1H), 2.66 (dd, *J* = 13.7, 6.0 Hz, 1H), 1.71 – 1.65 (m, 1H), 1.46 – 1.39 (m, 1H), 1.26 – 1.12 (m, 6H), 0.75 (t, *J* = 6.3 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 202.1, 163.4, 138.7, 131.8, 130.4, 130.3, 128.4, 113.8, 55.5, 47.8, 37.6, 32.7, 31.9, 27.0, 22.4, 14.0. **HRMS: (ESI):** Calc'd for. **$C_{21}H_{25}ClO_2$ [M+H]$^+$: 345.1621, Found: 345.1625.**

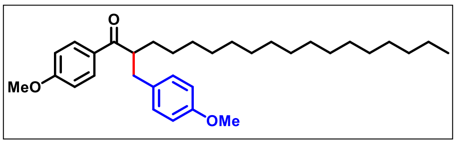


**2-(4-methoxybenzyl)-1-(4-methoxyphenyl)decan-1-one (3z).** Purification by column

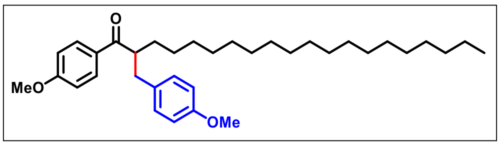


chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 44% yield (169 mg, 0.44 mmol) as Yellowish liquid. **$^1$H NMR (400 MHz, Chloroform-*d*) δ** 7.78 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.58 – 3.51 (m, 1H), 2.94 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.62 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.70 – 1.65 (m, 1H), 1.46 – 1.39 (m, 1H), 1.23 – 1.07 (m, 12H), 0.78 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 202.8, 163.4, 158.0, 132.4, 130.8, 130.6, 130.0, 113.9, 113.8, 55.5, 55.3, 48.3, 37.7, 32.7, 29.9, 29.5, 29.3, 27.6, 22.7, 14.2. **HRMS: (ESI):** Calc'd for. **$C_{25}H_{34}O_3$ [M+H]$^+$: 383.2586,** Found: 383.2592.

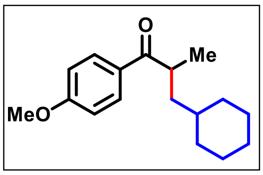
**2-(4-methoxybenzyl)-1-(4-methoxyphenyl)octadecan-1-one (3aa).** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 33% yield (164 mg, 0.33 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.78 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.67 (s, 3H), 3.57 – 3.51 (m, 1H), 2.94 (dd, *J* = 13.7, 7.7 Hz, 1H), 2.62 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.45 – 1.41 (m, 1H), 1.18 – 1.12 (m, 28H), 0.81 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 202.7, 163.3, 157.9, 132.3, 130.7, 130.4, 129.9, 113.7, 113.6, 55.4, 55.2, 48.1, 37.6, 32.5, 31.9, 29.79, 29.70, 29.66, 29.61, 29.56, 29.43, 29.37, 27.4, 22.7, 14.1. **HRMS: (ESI):** Calc'd for. **$C_{25}H_{34}O_3$ [M+H]$^+$: 383.2586;** Found: 495.3838.



**2-(4-methoxybenzyl)-1-(4-methoxyphenyl)icosan-1-one (3ab)**. Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 31% yield (162 mg, 0.31 mmol) as Yellowish liquid. **$^1$H NMR (400 MHz, Chloroform-*d*) δ** 7.78 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.67 (s, 3H), 3.57 – 3.51 (m, 1H), 2.94 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.62 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.68 – 1.65 (m, 1H), 1.46 – 1.42 (m, 1H), 1.17 (d, *J* = 10.2 Hz, 32H), 0.81 (t, *J* = 6.7 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 202.8, 163.4, 158.0, 132.4, 130.8, 130.6, 130.1, 113.9, 55.6, 55.3, 48.3, 37.7, 32.7, 32.1, 29.9, 29.84, 29.82, 29.81, 29.80, 29.75, 29.70, 29.6, 29.5, 27.6, 22.8, 14.3 **HRMS: (ESI):** Calc'd for. **$C_{35}H_{54}O_3$ [M+H]$^+$: 523.4151,** Found: 523.4141.

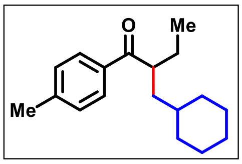


**3-cyclohexyl-1-(4-methoxyphenyl)-2-methylpropan-1-one (3ac):** Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 78% yield (203 mg, 0.78 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.95 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 3.57 – 3.50 (m, 1H), 1.78 – 1.76 (m, 1H), 1.73 – 1.63 (m, 6H), 1.31 – 1.23 (m, 3H), 1.21 – 1.18 (m, 1H), 1.16 (d, *J* = 6.7 Hz, 3H), 0.92 – 0.85 (m, 2H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 203.2, 163.4, 130.6, 129.8, 113.9, 55.5, 41.6, 37.5,



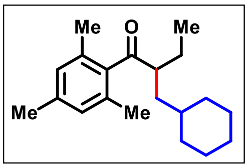
35.6, 34.0, 33.3, 26.7, 26.4, 26.3, 17.9. **HRMS: (ESI):** Calc'd for.**$C_{17}H_{24}O_2$[M+H]$^+$: 261.1855**; found = **261.1854.**

**2-(cyclohexylmethyl)-1-(p-tolyl)butan-1-one (3ad):** Purification by column chromatography ($SiO_2$,



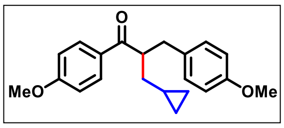
100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 52% yield (134 mg, 0.52 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.86 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.24 (m, 2H), 3.46 -3.41 (m, 1H), 2.93 – 2.90 (m, 1H), 2.41 (s, 3H), 1.78 –1.63 (m, 7H), 1.55 – 1.48 (m, 1H), 1.34 –1.28 (m, 1H), 1.25 – 1.20 (m, 1H), 1.18 – 1.06 (m, 3H), 1.01 – 0.98 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 204.4, 143.6, 135.4, 129.4, 128.4, 44.8, 39.7, 35.9, 33.8, 33.76, 26.7, 26.4, 26.1, 21.7, 14.1, 12.2. **HRMS: (ESI):** Calc'd for. $C_{18}H_{26}O$ **[M+H]$^+$**: 259.2062, Found: 259.2070.

**2-(cyclohexylmethyl)-1-mesitylbutan-1-one (3ae):** Purification by column chromatography ($SiO_2$,



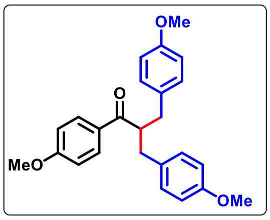
100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the title compound in 48% yield (138 mg, 0.48 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 6.82 (s, 2H), 3.46 – 3.44 (m, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.27 (s, 3H), 2.18 (s, 6H), 2.07 (s, 1H), 1.77 – 1.65 (m, 6H), 1.60 – 1.59 (m, 1H), 1.52 – 1.43 (m, 1H), 1.28 – 1.08 (m, 4H), 1.00 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 210.9, 140.0, 138.3, 132.6, 128.6, 68.3, 46.9, 40.4, 32.1, 29.9, 26.8, 26.1, 25.7, 21.1, 19.2, 17.0, 14.0. **HRMS: (ESI):** Calc'd for. $C_{20}H_{30}O$ **[M+H]$^+$**: 287.2375; Found: 287.2381.

**3-cyclopropyl-2-(4-methoxybenzyl)-1-(4-methoxyphenyl)propan-1-one** (**3af**). Purification by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 1% to 5%) afforded the



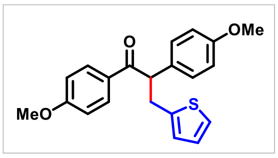
title compound in 87% yield (282 mg, 0.87 mmol) as Yellowish liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.98 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.93 (s, 3H), 3.89 – 3.84 (m, 1H), 3.82 (s, 3H), 3.12 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.83 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.83 – 1.76 (m, 1H), 1.51 – 1.45 (m, 1H), 0.74 – 0.64 (m, 1H), 0.46 – 0.36 (m, 2H), 0.09 – 0.02 (m, 2H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 203.0, 163.4, 158.0, 132.3, 131.0, 130.6, 130.0, 113.8, 113.8, 55.5, 55.3, 48.7, 38.0, 37.7, 9.5, 5.2, 4.9. **HRMS: (ESI):** Calc'd for. **$C_{21}H_{24}O_3$ [M+H]$^+$: 325.1804,** Found: 325.1804.

**2-(4-methoxybenzyl)-1,3-bis(4-methoxyphenyl)propan-1-one (3ah) : Purification by column**



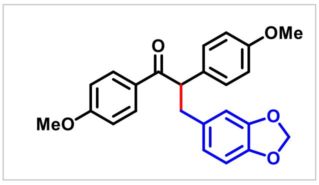
**chromatography (SiO2, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 15%) afforded the title compound in 91% yield (355 mg, 0.91) as yellow gel. $^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 4H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 4H), 3.89 – 3.85 (m, 1H), 3.80 (s, 3H), 3.73 (s, 6H), 3.03 (dd, *J* = 13.8 Hz, *J* = 7.9 Hz, 2H), 2.72 (dd, *J* = 13.8 Hz, *J* = 6.2 Hz, 2H). **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 202.1, 163.3, 158.1, 131.9, 130.6, 130.5, 130.0, 113.9, 113.7, 55.5, 55.3, 50.6, 37.5. **HRMS: (ESI):** Calc'd for. **$C_{25}H_{26}O_4$ [M+H]$^+$: 391.1909**; found = **391.1928.**

**1,2-bis(4-methoxyphenyl)-3-(thiophen-2-yl)propan-1-one (3ai): Purification by column**



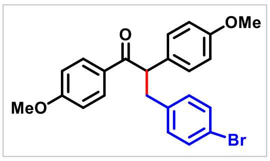

**chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 15%) afforded the title compound in 87% yield (320 mg, 0.87) as Yellow solid, $^1$H NMR (600 MHz, $CDCl_3$) δ** 7.96 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 5.1 Hz, 1H), 6.88 – 6.83 (m, 5H), 6.71 – 6.70 (m, 1H), 4.78 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.79 – 3.75 (m, 4H), 3.27 (dd, *J* = 14.9, 6.8 Hz, 1H). **$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 197.6, 163.4, 158.9, 142.5, 131.2, 131.1, 129.7, 129.4, 126.7, 125.7, 123.6, 114.4, 113.8, 55.5, 55.3, 54.9, 34.3. **HRMS: (ESI):** Calc'd for.**$C_{22}H_{24}O_3S$ [M+H]$^+$: 369.1524**; **Found: 369.1520.**

**3-(benzo[d][1,3]dioxol-5-yl)-1,2-bis(4-methoxyphenyl)propan-1-one (3aj)**: **Purification**




**by column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 20%) afforded the title compound in 79% yield (308 mg, 0.79) as white solid, $^1$H NMR (400 MHz, $CDCl_3$) δ** 7.89 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.58 – 6.57 (m, 1H), 6.53 – 6.51 (m, 1H), 5.87 (s, 2H), 4.65 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.43 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.93 (dd, *J* = 13.8, 7.1 Hz, 1H). **$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 198.1, 163.4, 158.7, 147.4, 145.9, 134.0, 131.6, 131.1, 129.8, 129.3, 122.2, 114.4, 113.8, 109.7, 108.1, 100.8, 55.5, 55.3, 54.9, 40.0. **HRMS: (ESI):** Calc'd for.**$C_{23}H_{23}O_5$ [M+H]$^+$: 391.1545**; **Found: 425.0732.**

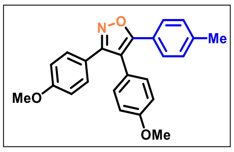
**3-(4-bromophenyl)-1,2-bis(4-methoxyphenyl)propan-1-one (3ak)**: **Purification by**




**column chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 15%) afforded the title compound in 71% yield (301 mg, 0.71) as white solid, $^1$H NMR (400 MHz, $CDCl_3$) δ** 7.88 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.64 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.44 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.97 (dd, *J* = 13.7, 7.3 Hz, 1H).

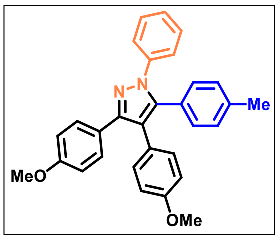
**$^{13}$C NMR (150 MHz, $CDCl_3$) δ** 197.7, 163.4, 158.8, 139.2, 131.3, 131.2, 131.1, 131.1, 129.3, 120.0, 114.5, 113.8, 113.8, 55.5, 55.3, 54.6, 39.6. **HRMS: (ESI):** Calc'd for.**$C_{23}H_{22}BrO_3$ [M+H]$^+$: 425.0752**; **Found: 425.0732.**

**3,4-bis(4-methoxyphenyl)-5-(p-tolyl)isoxazole (16).** Purification by column chromatography



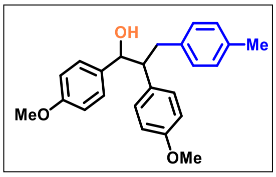

($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 30%) afforded the title compound in 86% yield (160 mg, 0.43 mmol, reaction conducted in 0.5 mmol scale) as white solid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.37 (d, *J* = 8.4 Hz, 3H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 3H), 7.06 (d, *J* = 8.2 Hz, 3H), 6.85 (d, *J* = 8.7 Hz, 3H), 6.76 (d, *J* = 8.8 Hz, 3H), 3.79 (s, 3H), 3.72 (s, 3H), 2.27 (s, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 165.4, 161.8, 160.4, 159.4, 139.8, 131.7, 129.7, 129.3, 126.8, 125.3, 123.0, 121.7, 114.5, 113.9, 55.2, 55.2, 21.4. **HRMS: (ESI):** Calc'd for.**$C_{24}H_{21}NO_3$ [M+H]$^+$: 372.1600**; **Found: 372.1610.**

**3,4-bis(4-methoxyphenyl)-1-phenyl-5-(p-tolyl)-1H-pyrazole (17).** Purification by column



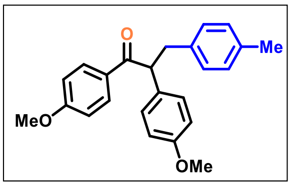

chromatography ($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 30%) afforded the title compound in 90% yield (201 mg, 0.45 mmol, reaction conducted in 0.5 mmol scale) as pale yellow solid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.40 – 7.37 (m, 2H), 7.26 – 7.20 (m, 4H), 7.18 – 7.16 (m, 1H), 6.97 – 6.91 (m, 4H), 6.88 – 6.84 (m, 1H), 6.76 – 6.73 (m, 2H), 6.73 – 6.68 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.22 (s, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2, 158.3, 150.0, 141.3, 140.2, 137.8, 131.8, 130.3, 129.6, 129.0, 128.7, 127.3, 127.0, 126.0, 126.0, 125.3, 119.9, 113.7, 113.7, 55.3, 55.2, 21.4. **HRMS: (ESI):** Calc'd for.**$C_{30}H_{26}N_2O_2$[M+H]$^+$: 447.2073**; **Found: 449.2141.**

**1,2-bis(4-methoxyphenyl)-3-(p-tolyl)propan-1-ol (18).** Purification by column chromatography




($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 30%) afforded the title compound in 90% yield (325 mg, 0.92 mmol, reaction conducted in 1 mmol scale) as yellow liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.09 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 6.4 Hz, 2H), 6.82 (m, 2H), 6.78 – 6.74 (m, 2H), 6.70 – 6.66 (m, 4H), 4.64 (d, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.98 – 2.93 (m, 1H), 2.76 – 2.72 (m, 1H), 2.66 – 2.60 (m, 1H), 2.13 (s, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2, 158.5, 137.2, 137.1, 135.1, 135.0, 135.0, 132.3, 130.1, 128.9, 128.8, 128.1, 113.82, 113.7, 55.5, 55.3, 55.2, 38.4, 21.1. **HRMS: (ESI):** Calc'd for.**$C_{24}H_{26}O_3$[M+Na]$^+$: 385.1780**; Found: 385.1752.

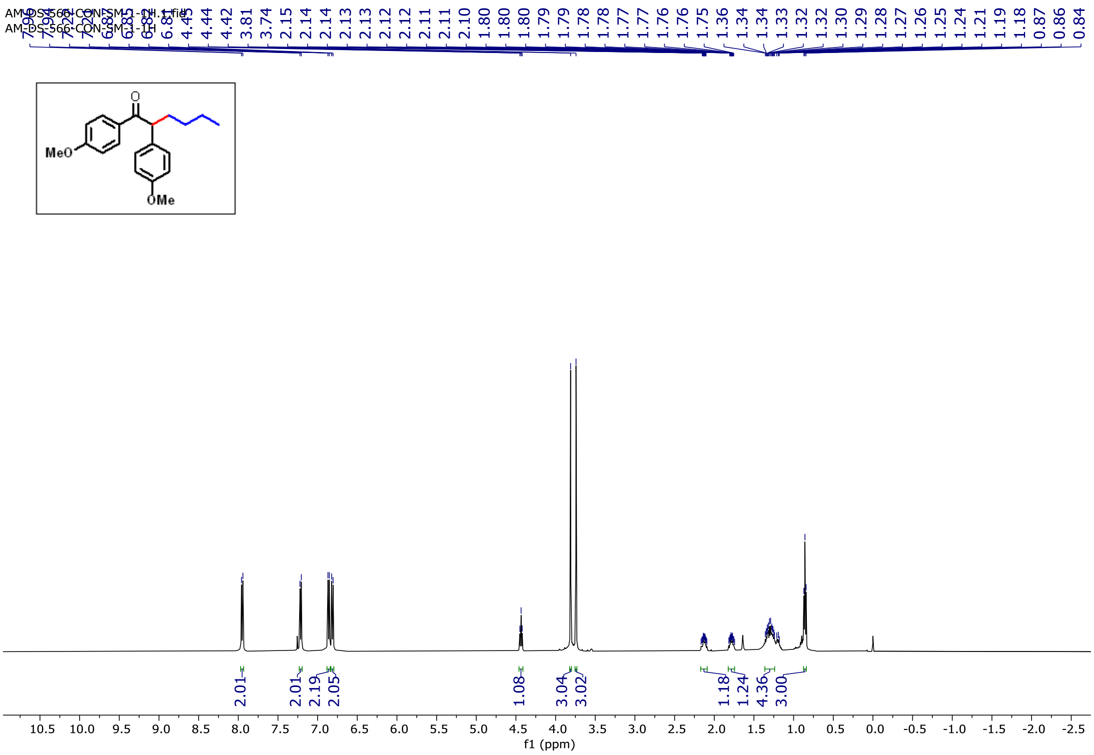
**1,2-bis(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (3ag).** Purification by column chromatography




($SiO_2$, 100–200 mesh, eluent: AcOEt/petroleum ether 5% to 10%) afforded the title compound in 82% yield (427 mg, 1.64 mmol, reaction conducted in 2 mmol scale) as gummy liquid. **$^1$H NMR (500 MHz, Chloroform-*d*) δ** 7.82 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.94 – 6.86 (m, 4H), 6.74 (d, *J* = 8.8 Hz, 2H), 6. 70 (d, *J* = 8.8 Hz, 2H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.40 (dd, *J*

= 13.8, 7.4 Hz, 1H), 2.90 (dd, $J$ = 13.8, 7.1 Hz, 1H), 2.18 (s, 3H). **$^{13}$C NMR (125 MHz, CDCl$_3$) δ** 198.1, 163.2, 158.5, 137.0, 135.4, 131.7, 131.0, 129.8, 129.3, 129.0, 128.9, 114.2, 113.6, 55.4, 55.2, 54.6, 39.7, 21.0. **HRMS: (ESI):** Calc'd for.**$C_{24}H_{24}O_3$[M+H]$^+$: 361.1804**; Found: 361.1734.

## 14. $^1$H and $^{13}$C copies of synthesized compounds:



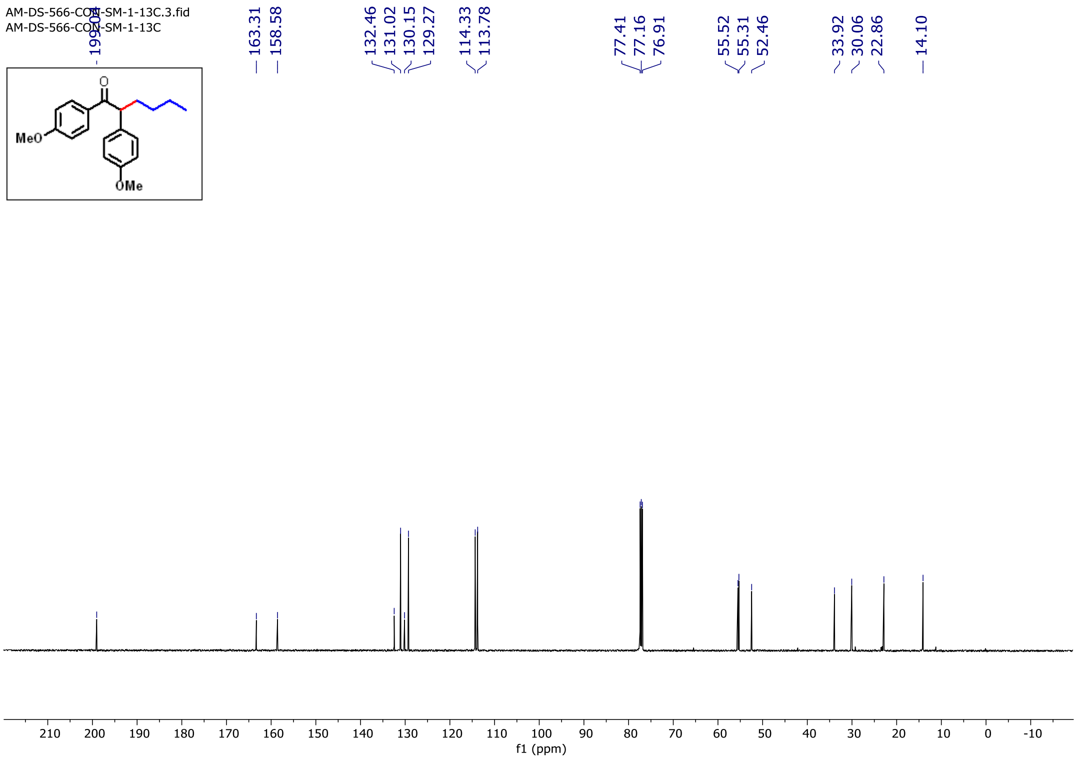
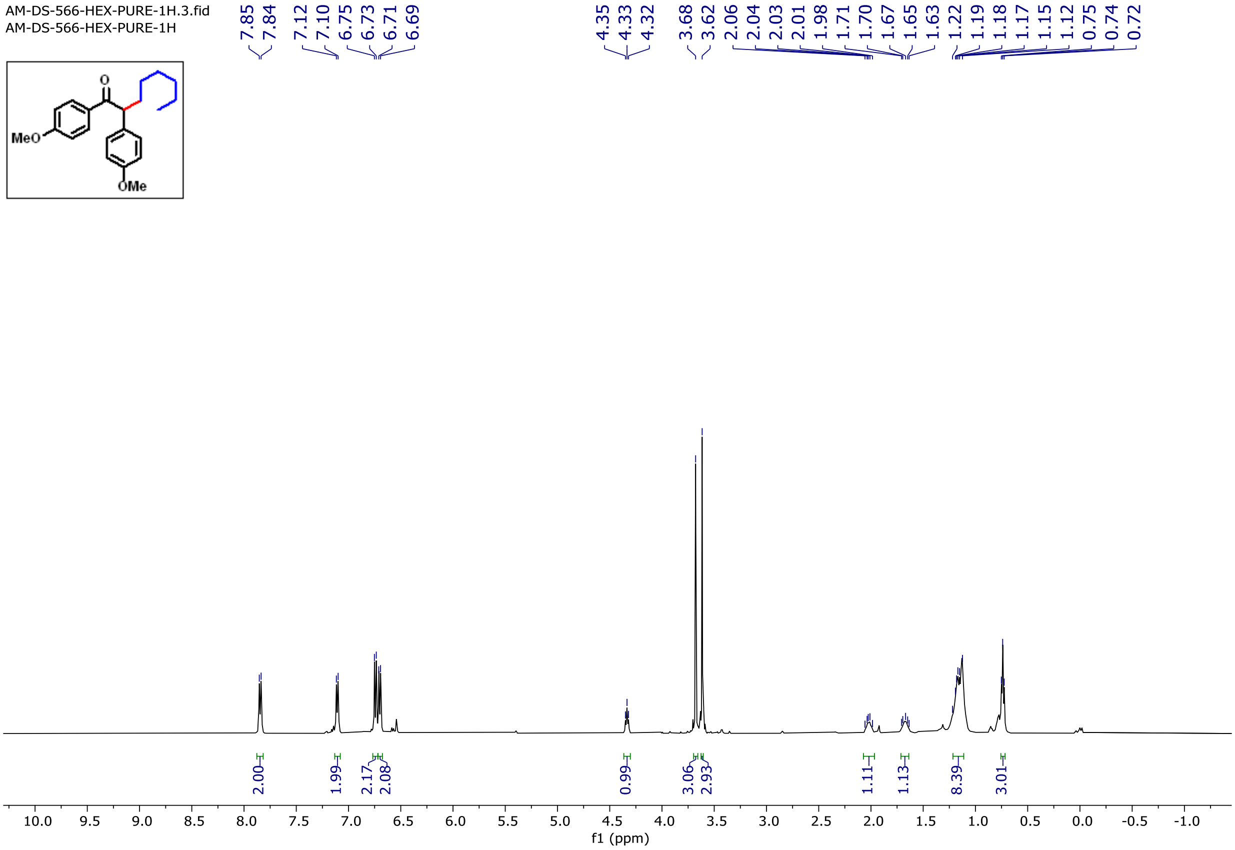




**Figure S18.** $^1$H (500 MHz) and $^{13}$C{$^1$H} (125 MHz) NMR Spectrum of **3a** in $CDCl_3$.



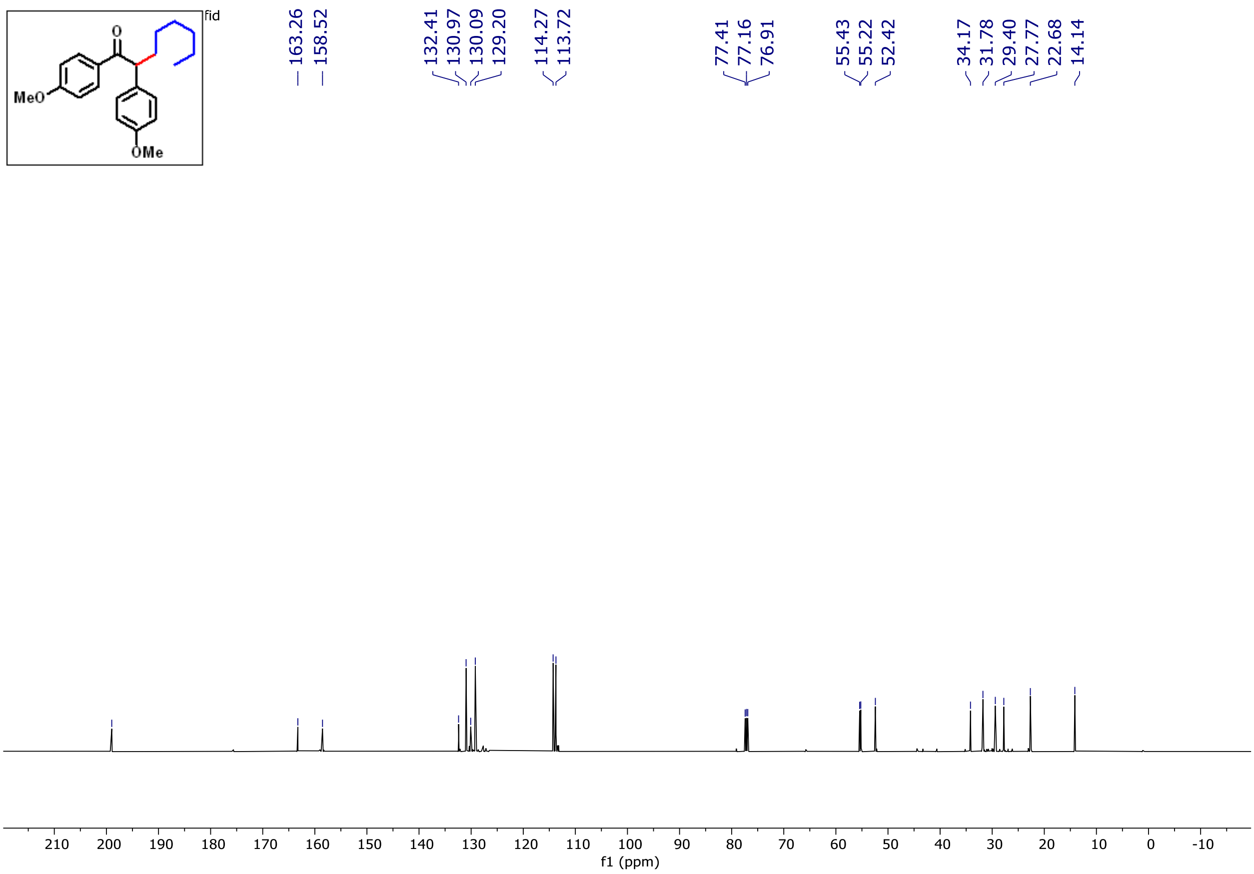
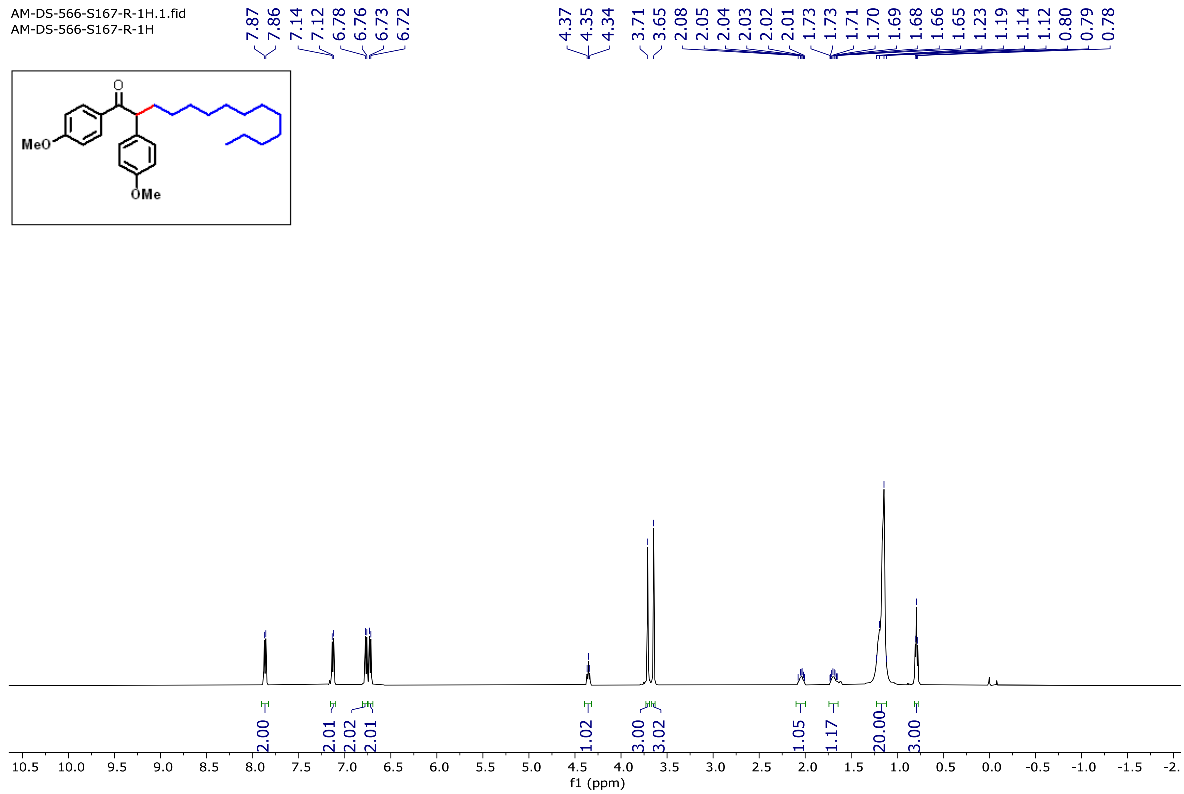




**Figure S19.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3b** in $CDCl_3$.



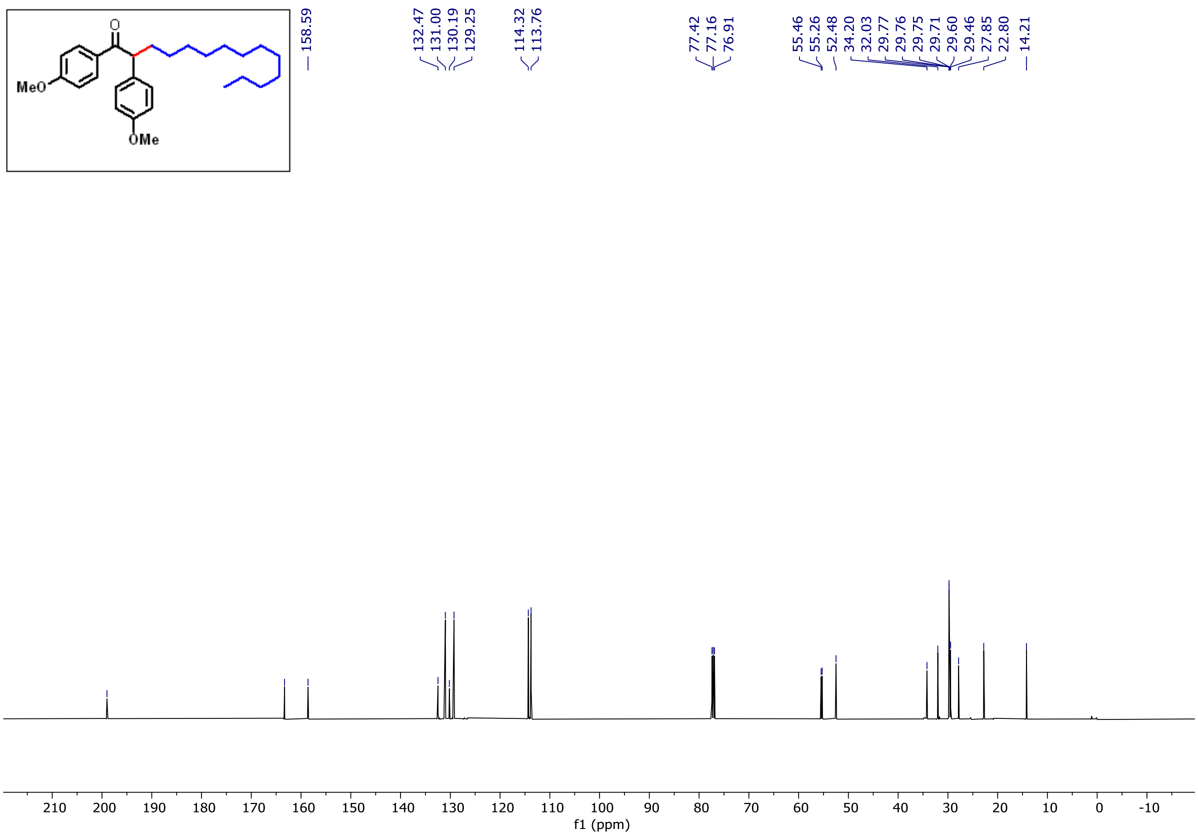
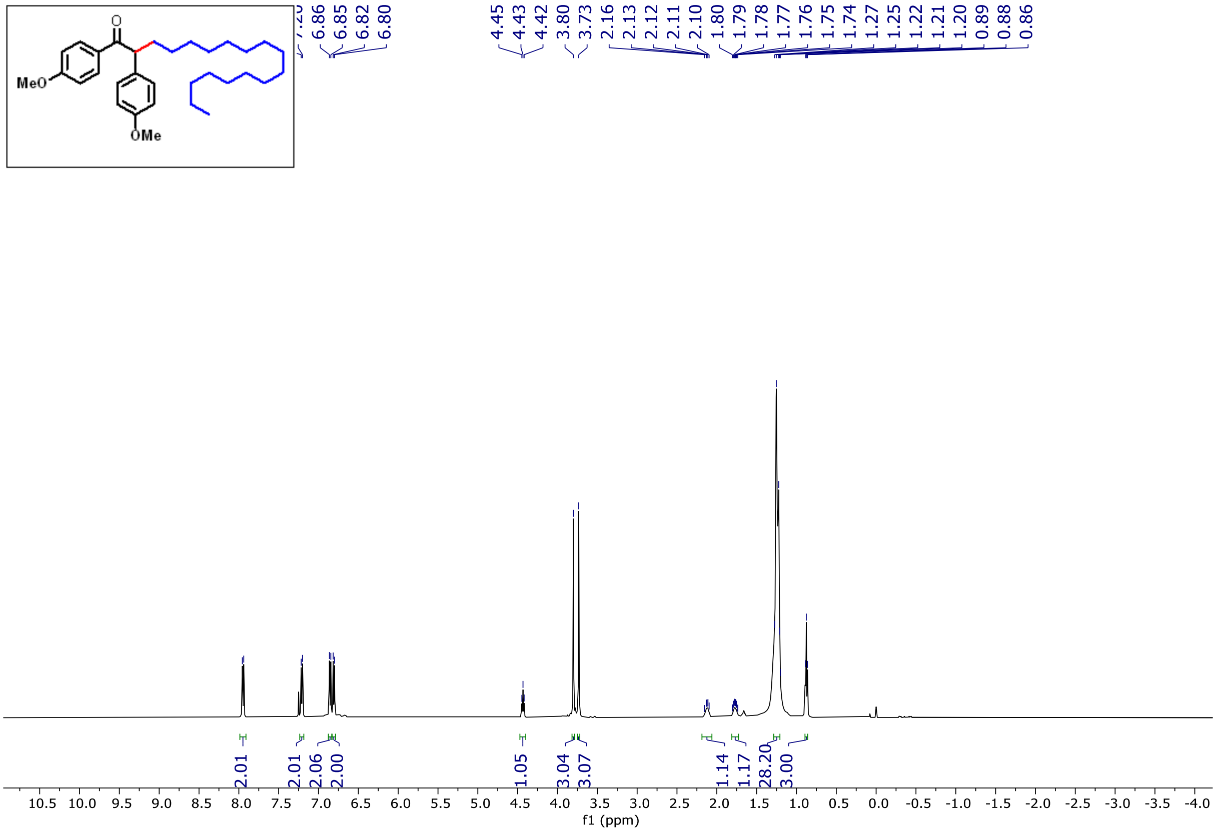




**Figure S20.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3c** in $CDCl_3$.



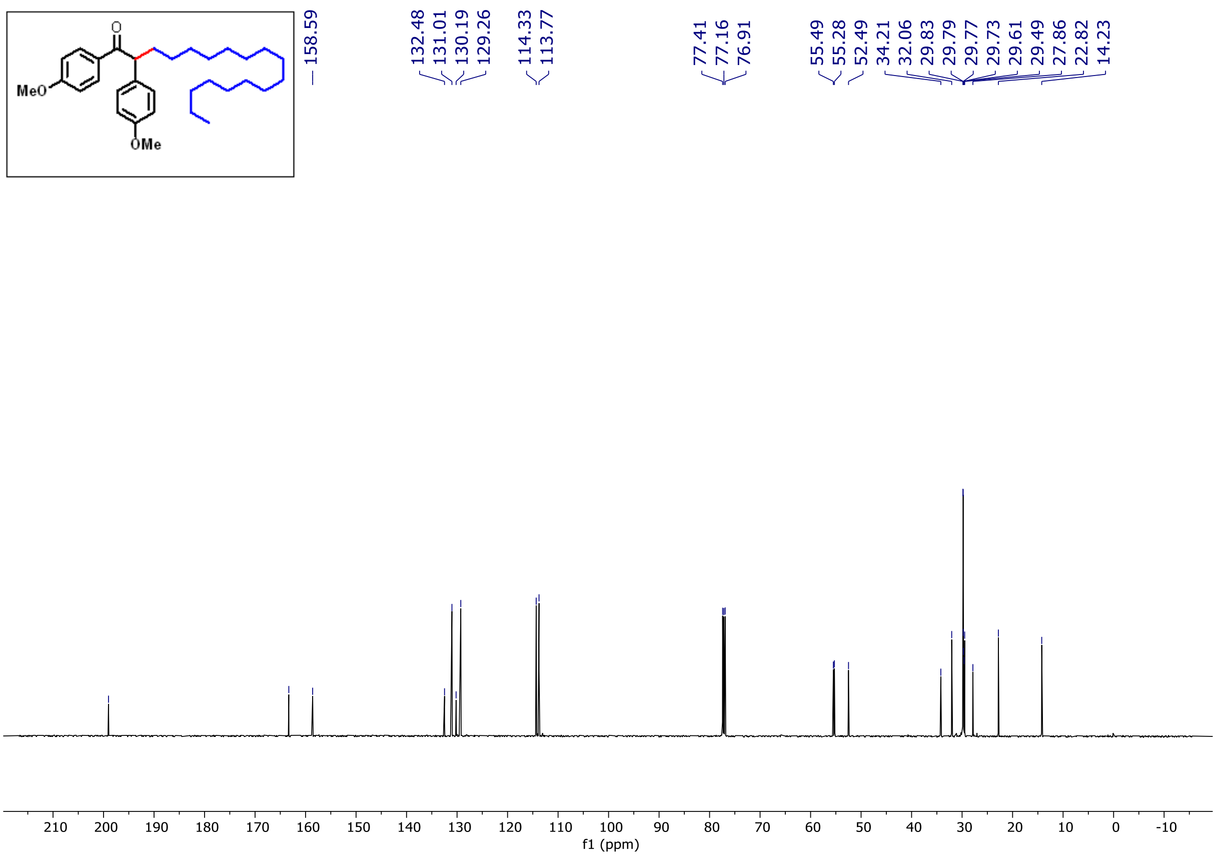
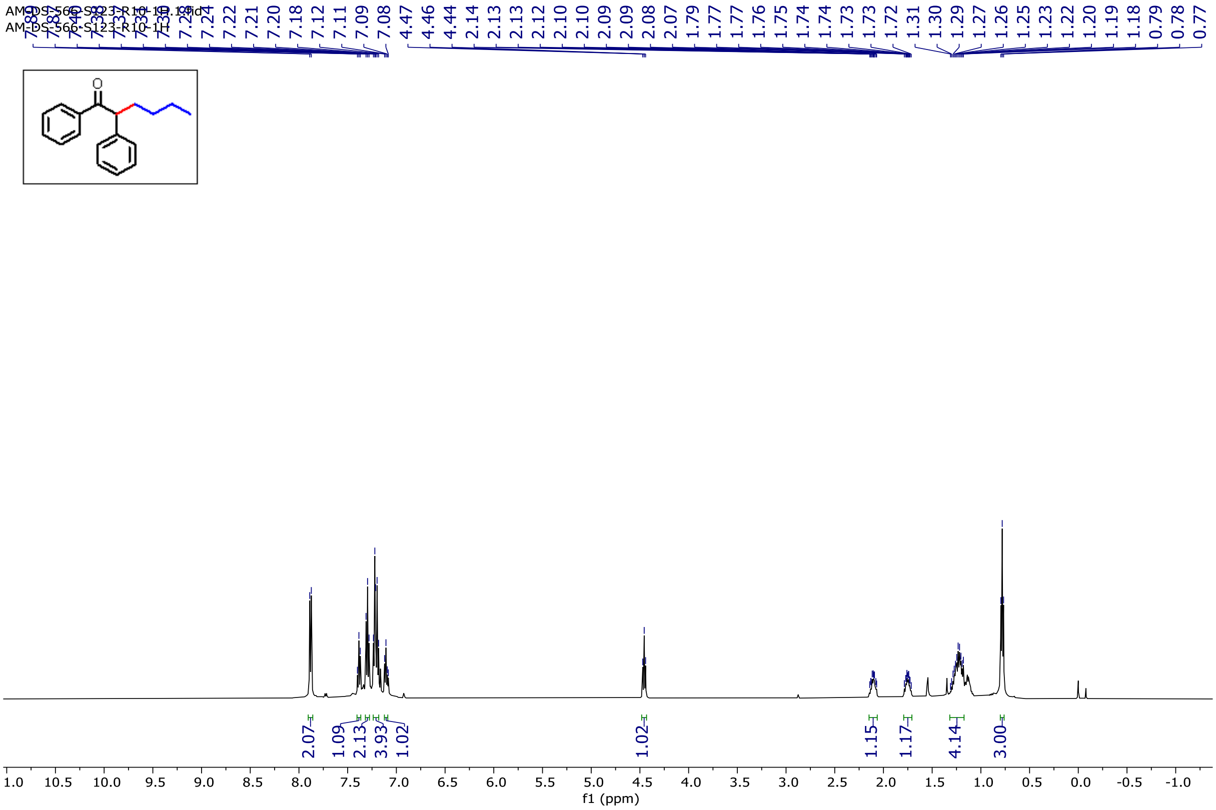


**Figure S21.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3d** in $CDCl_3$.



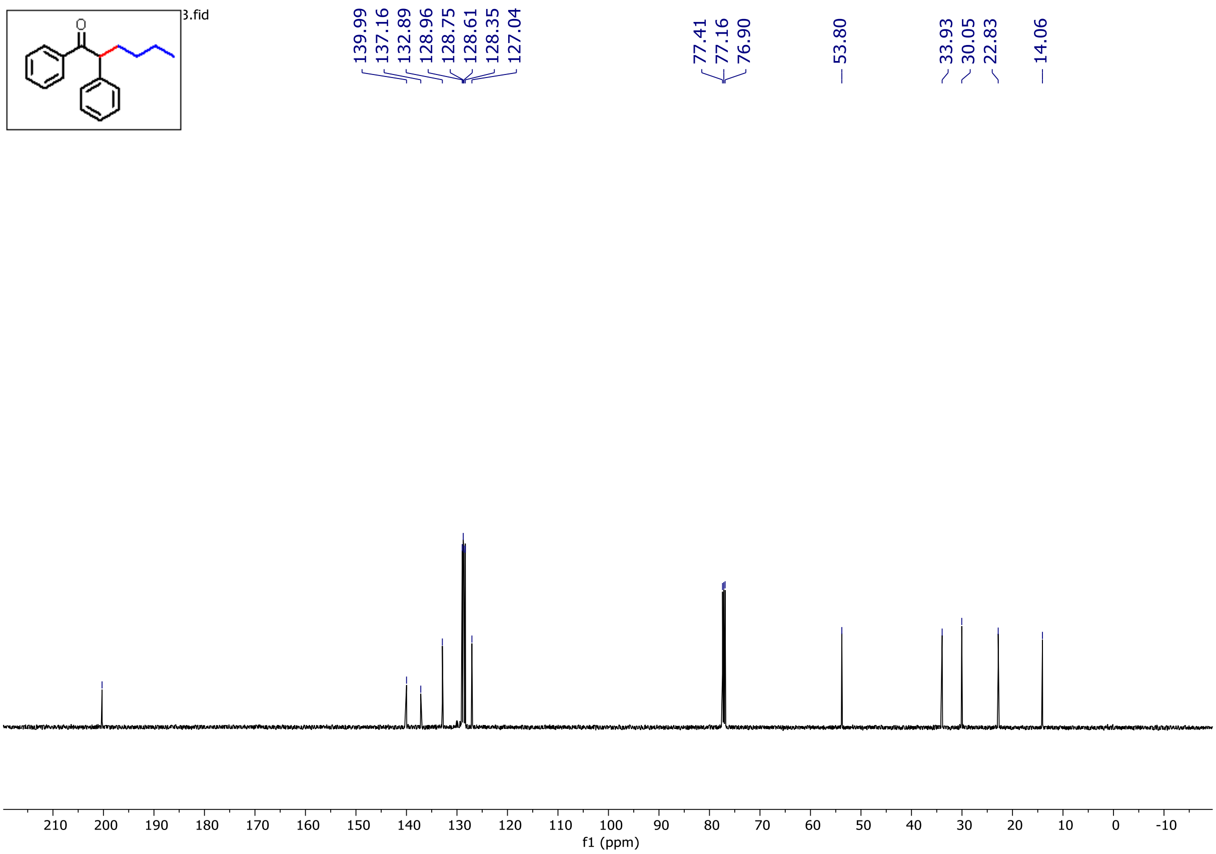
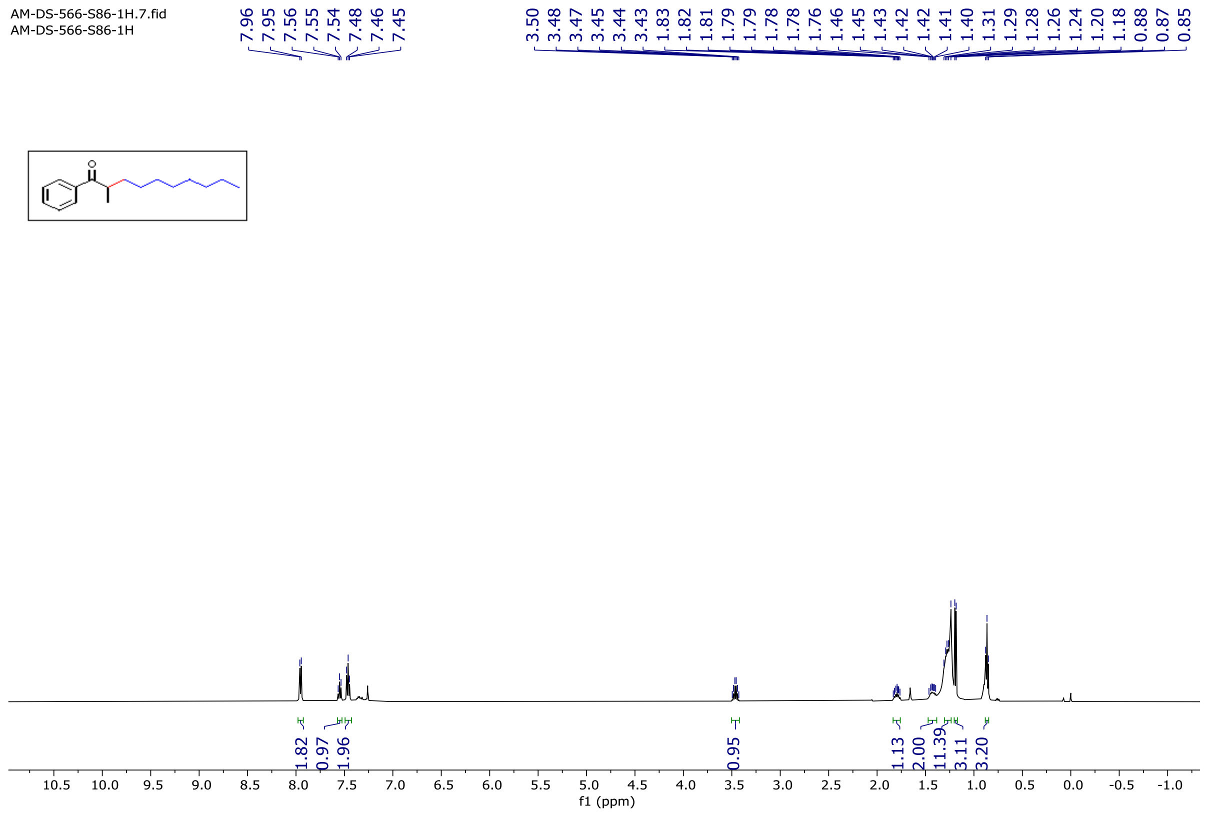


**Figure S22.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3e** in $CDCl_3$.



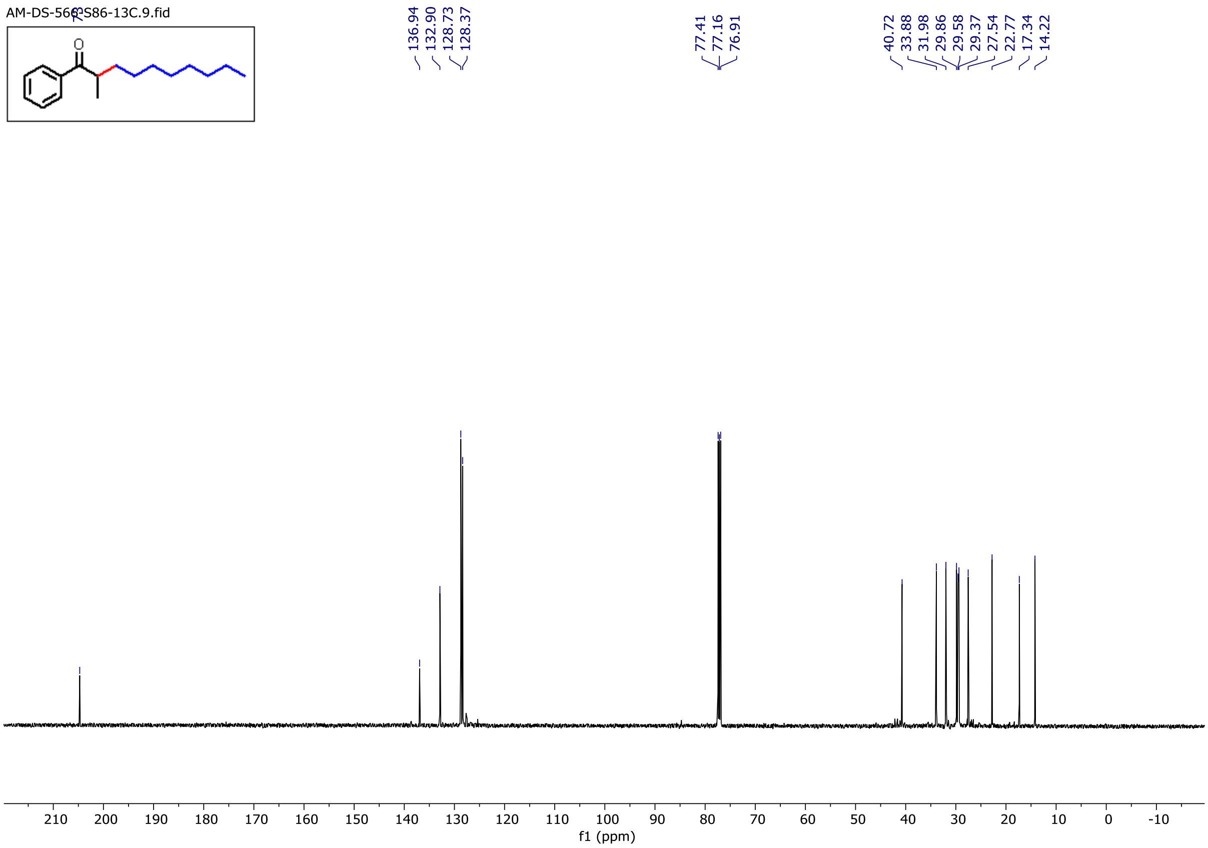
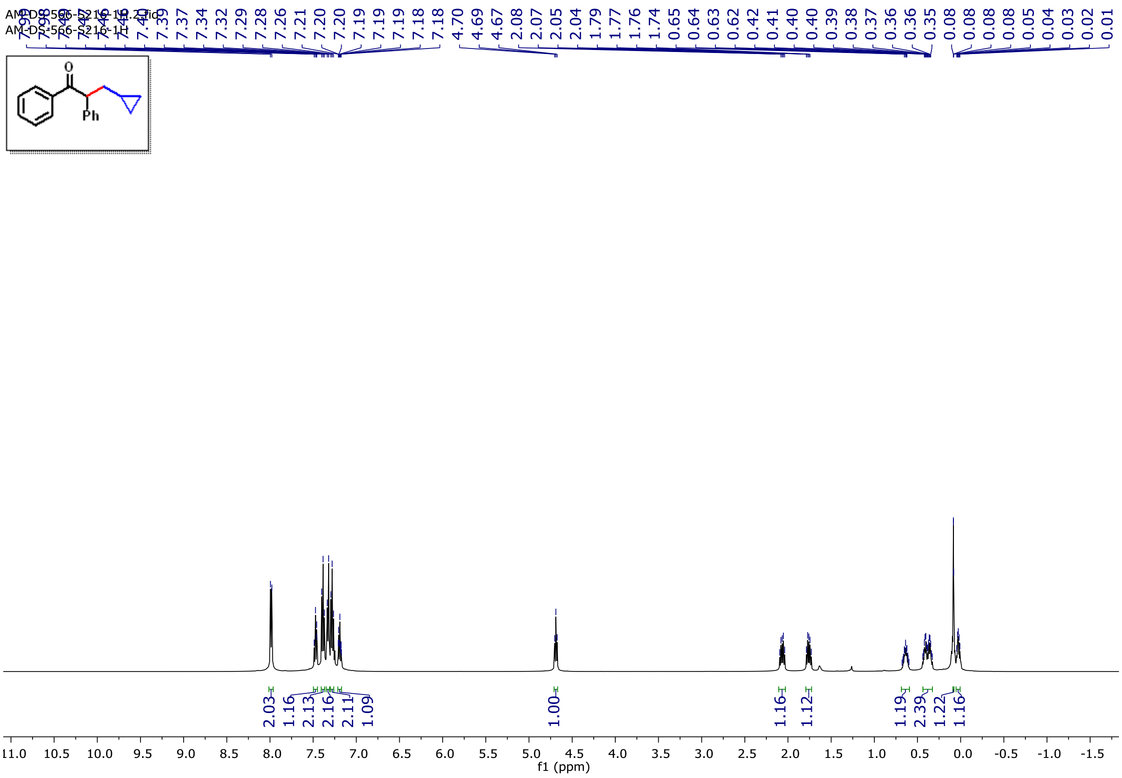




**Figure S23.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3f** in $CDCl_3$.



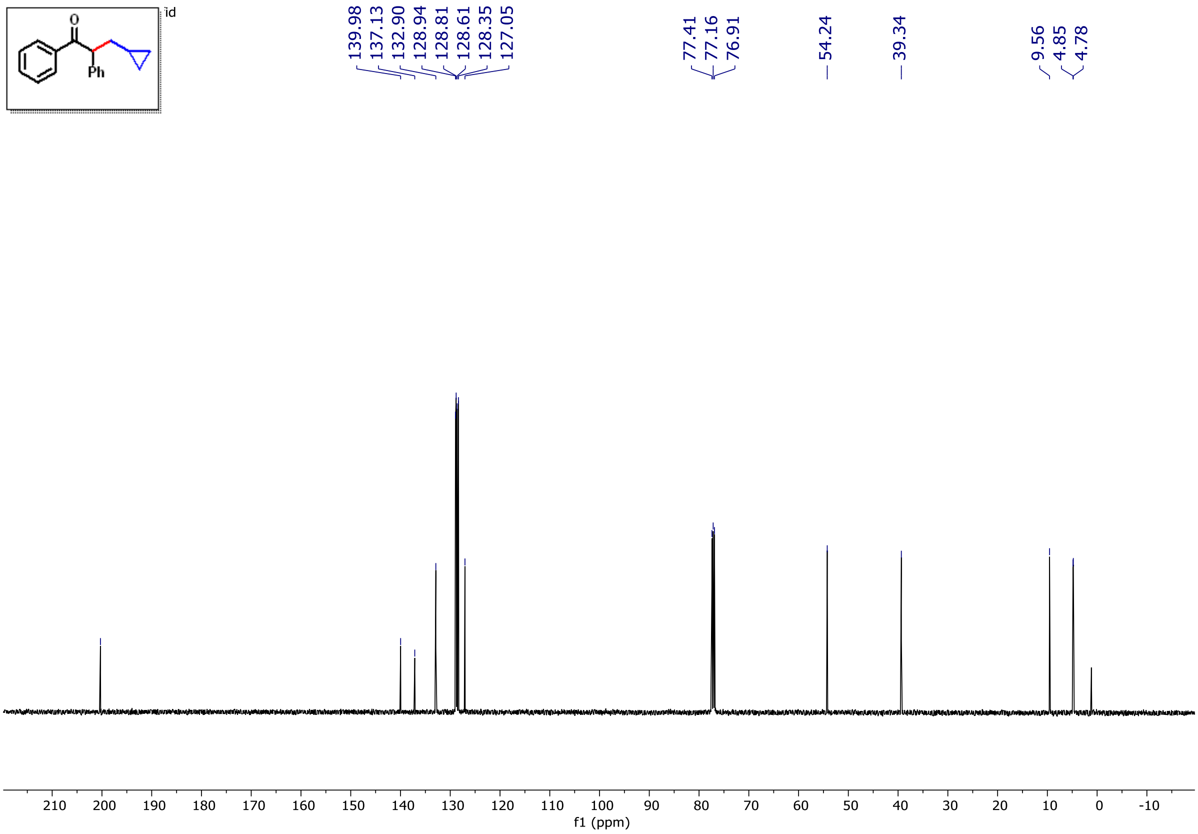
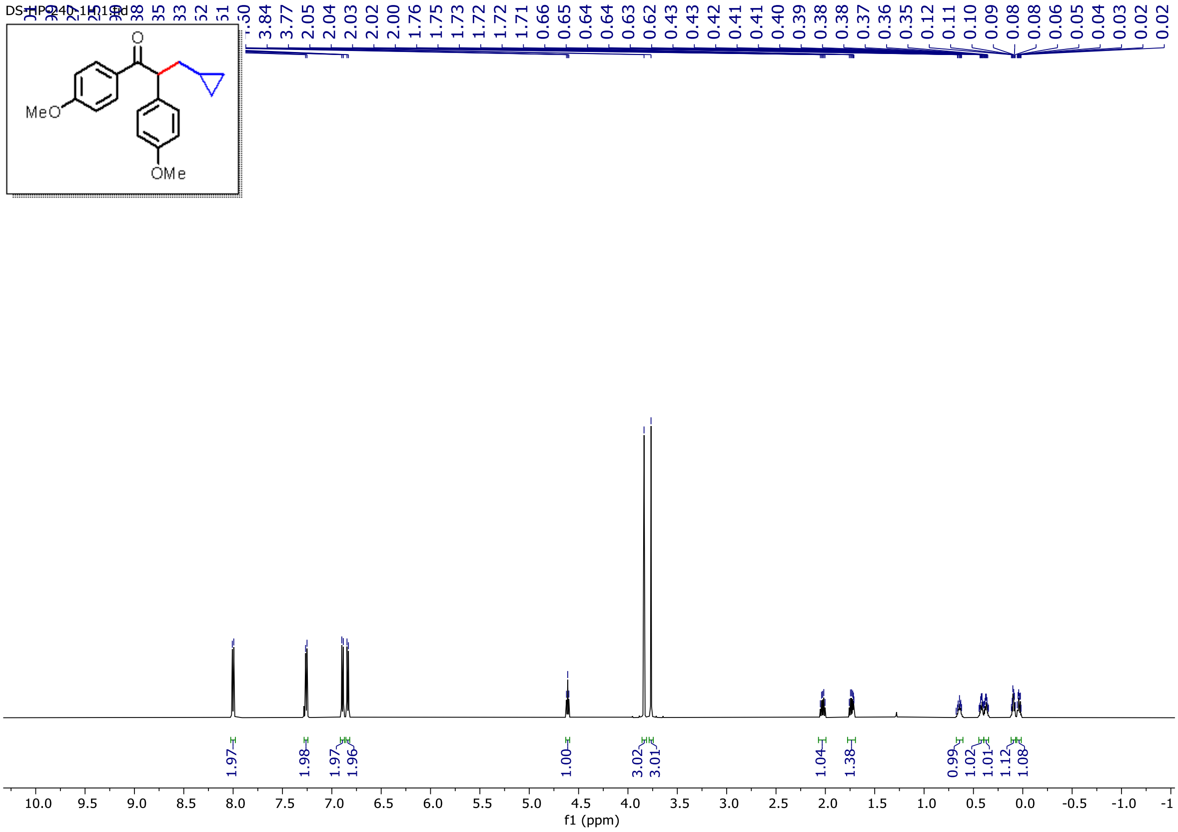


**Figure S24.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3g** in $CDCl_3$.



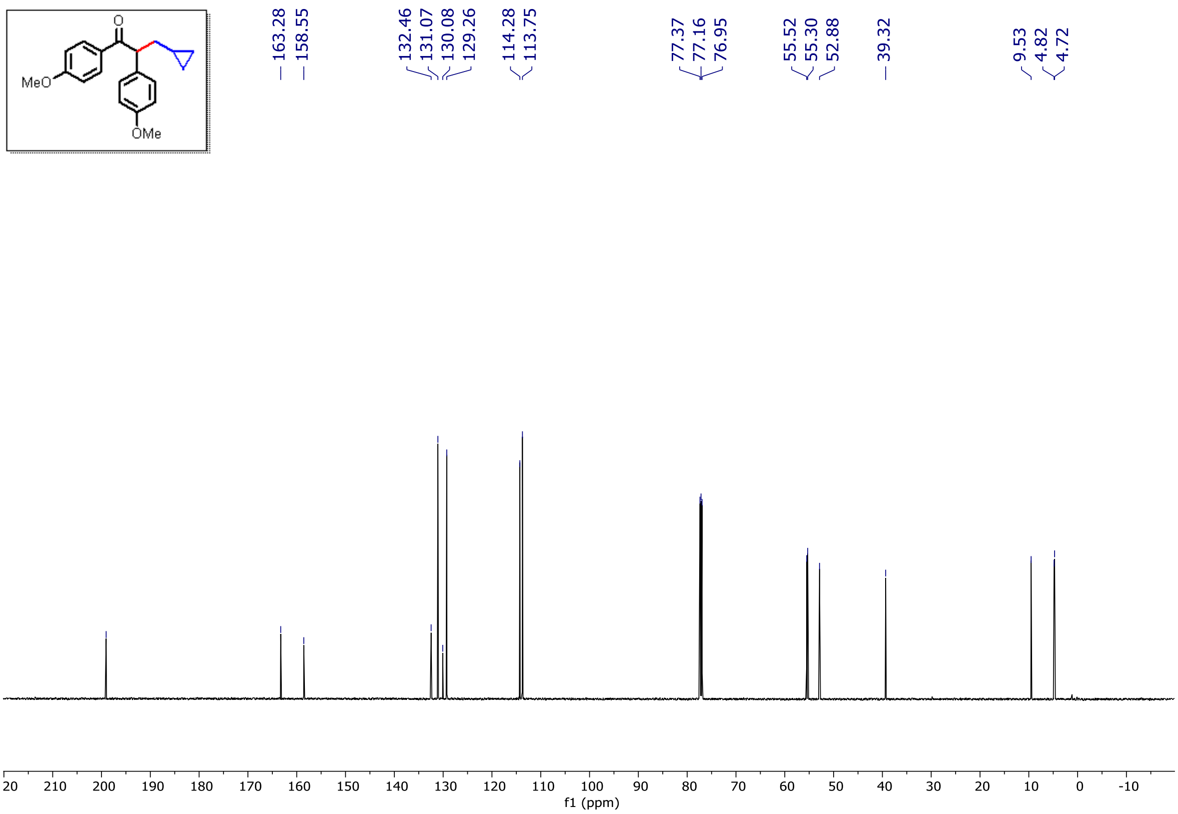
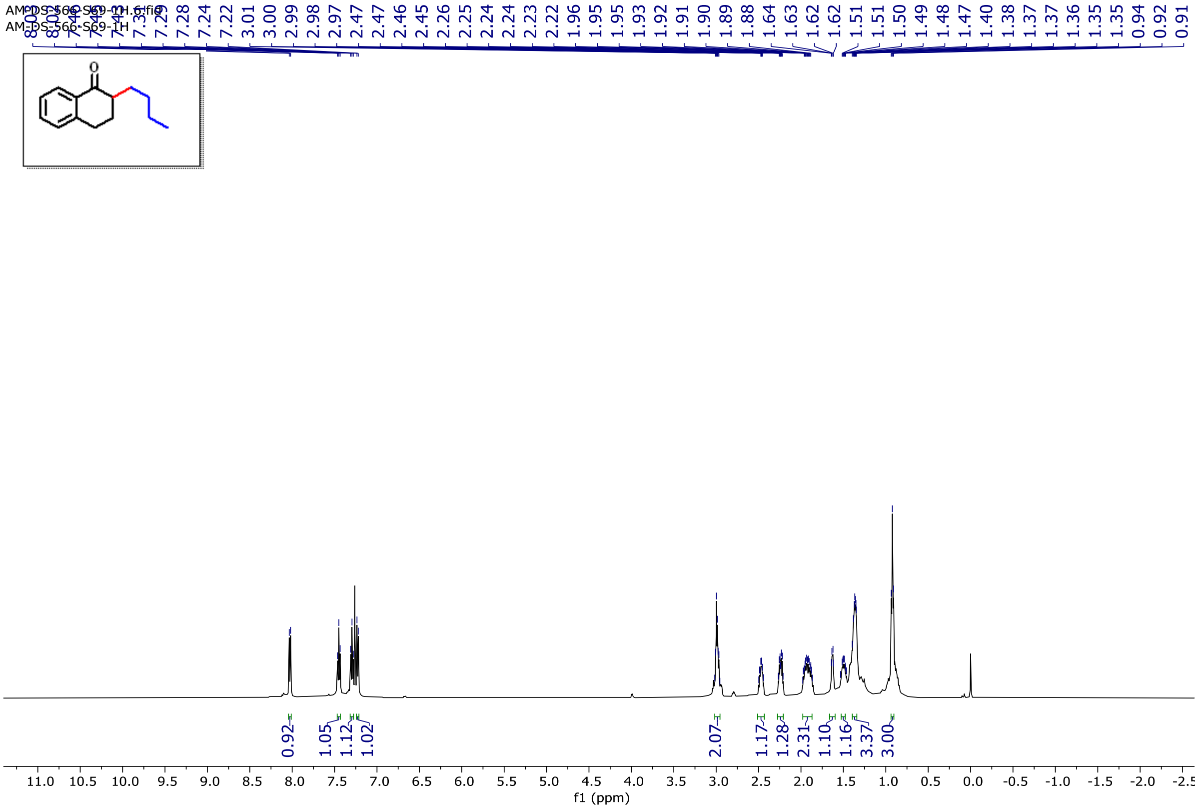


**Figure S25.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3h** in $CDCl_3$.



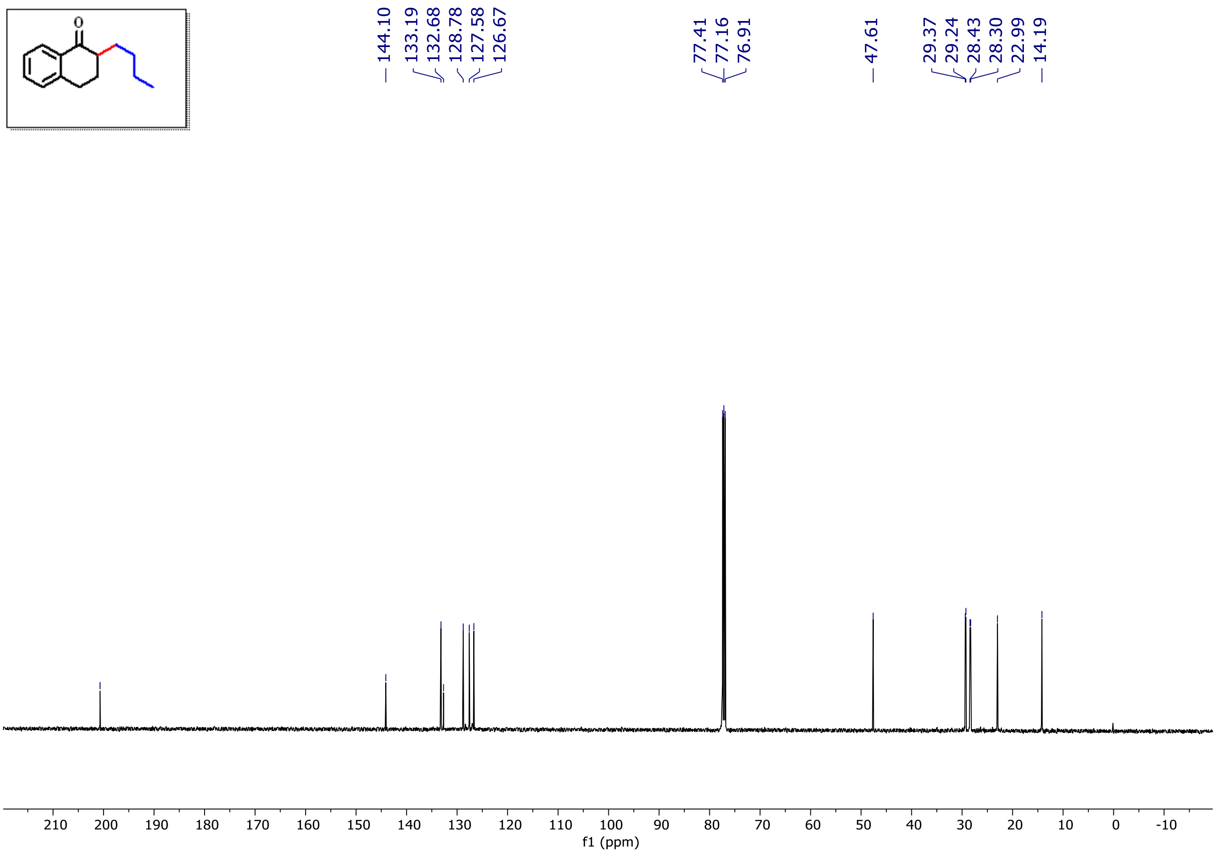




**Figure S26.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3i** in $CDCl_3$.

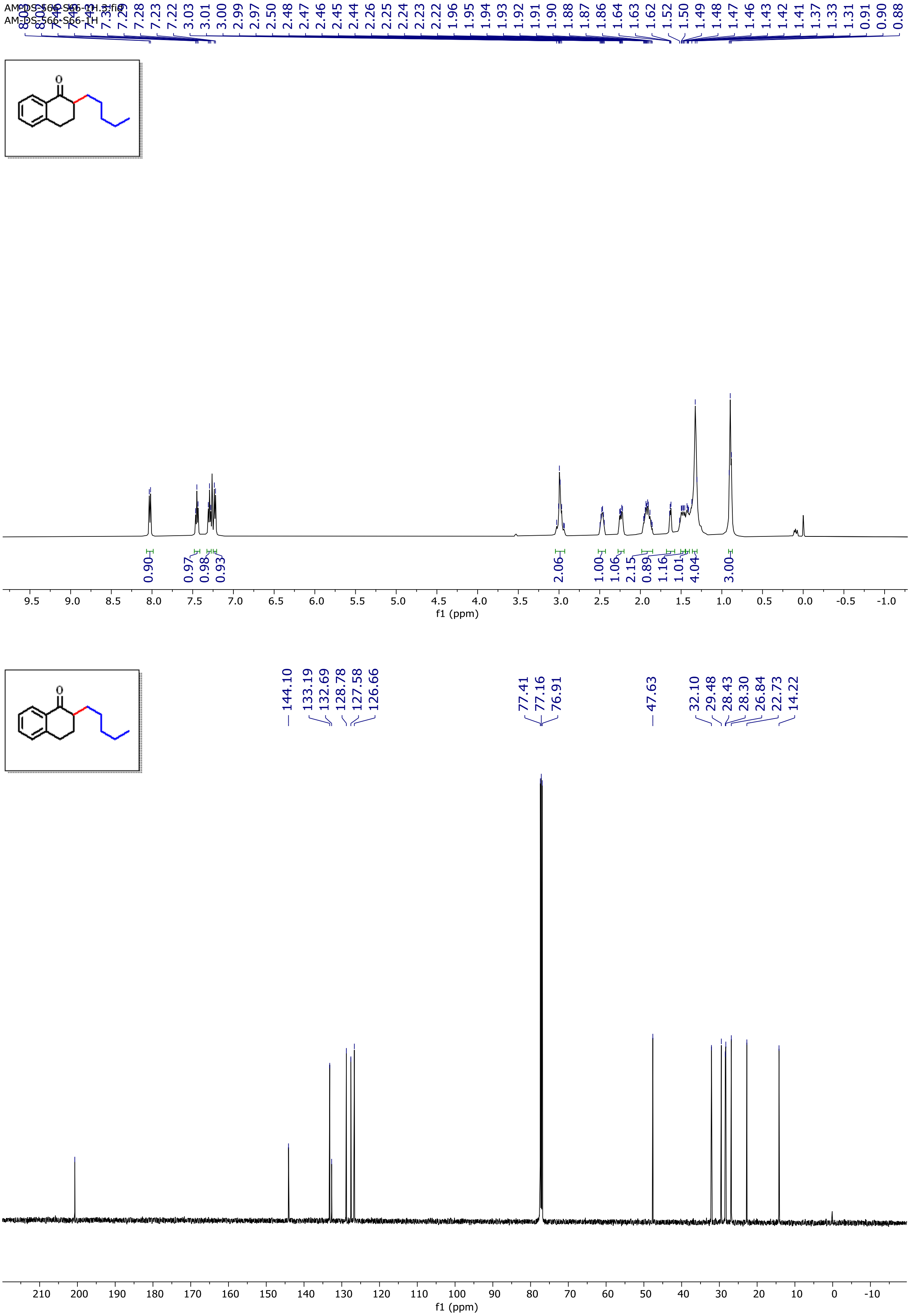
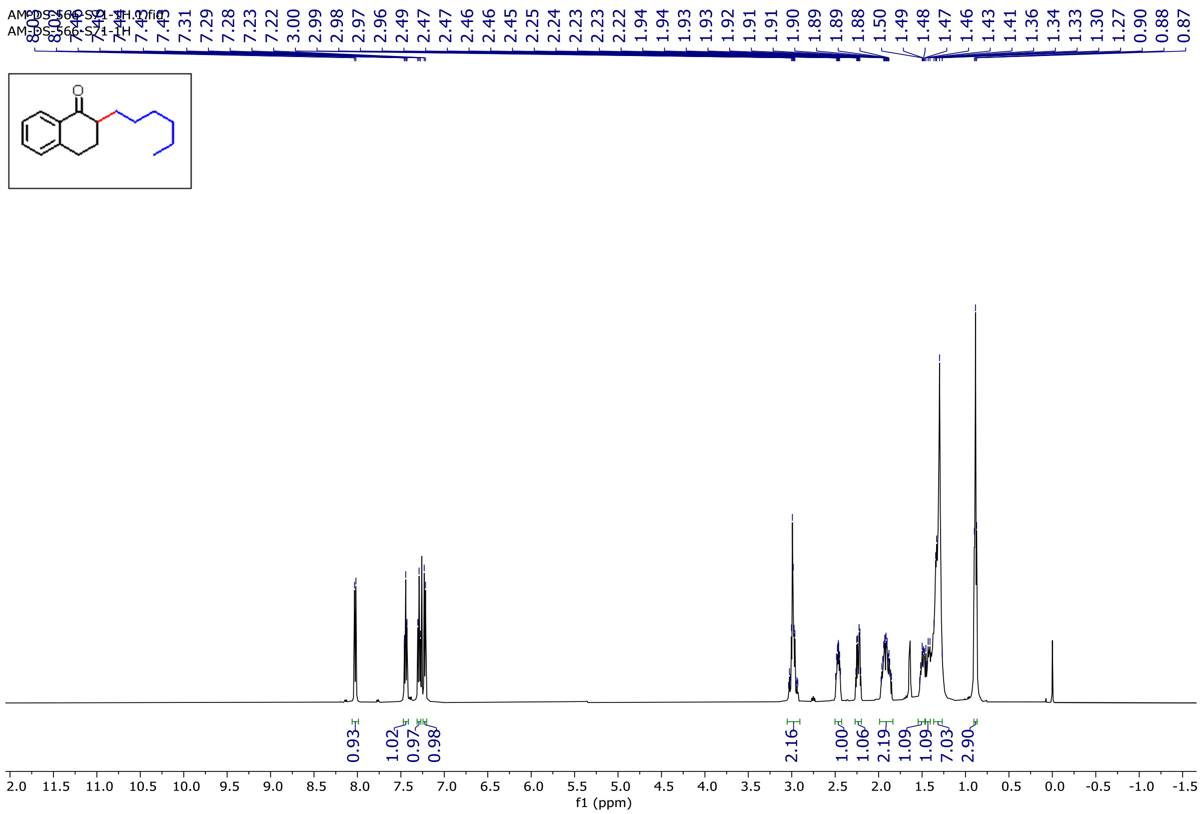



**Figure S27.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3j** in $CDCl_3$.



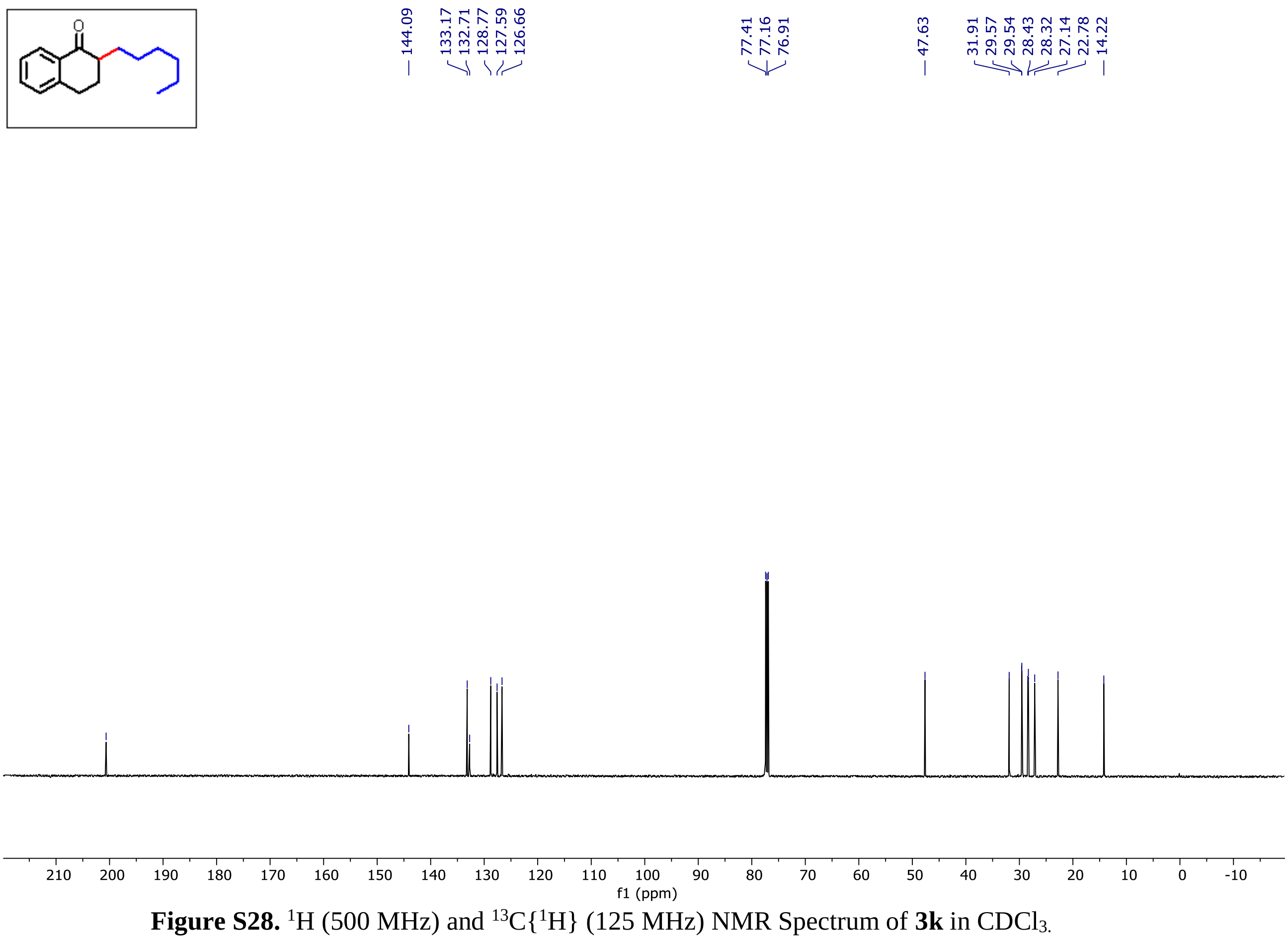
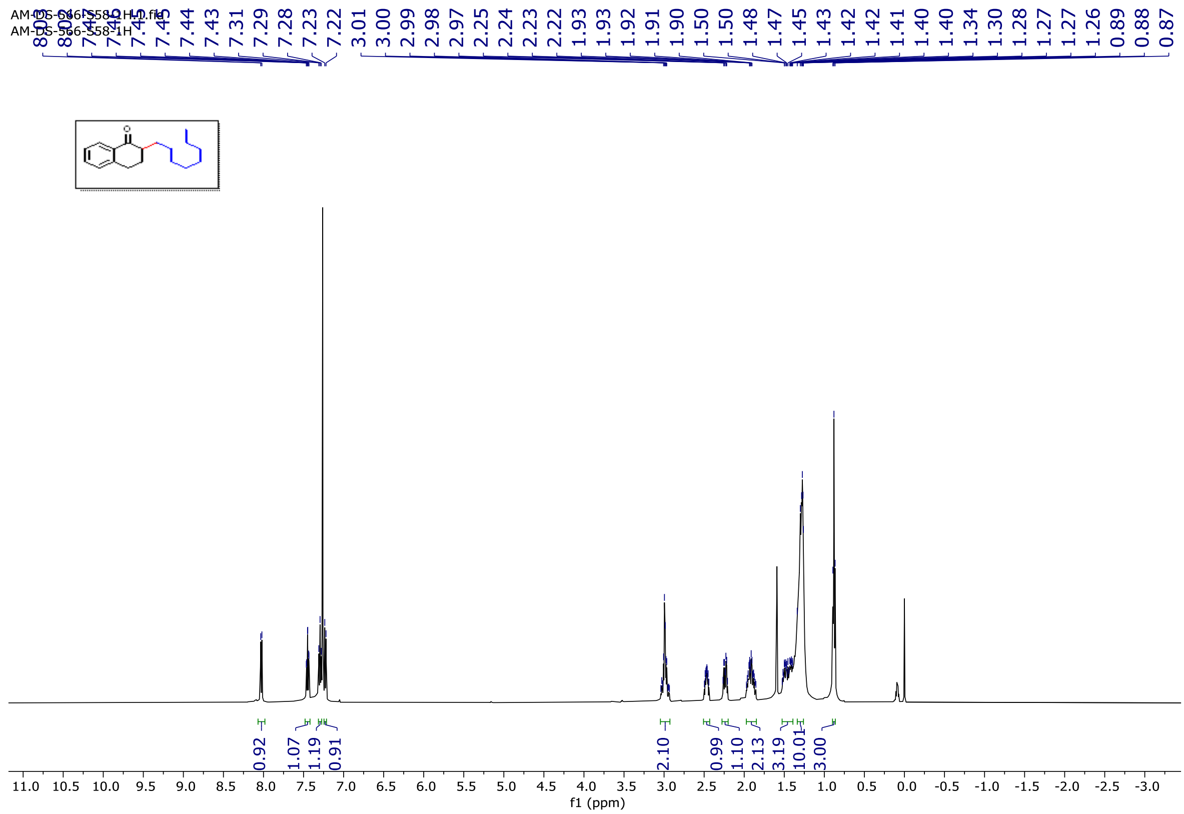


**Figure S28.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3k** in $CDCl_3$.



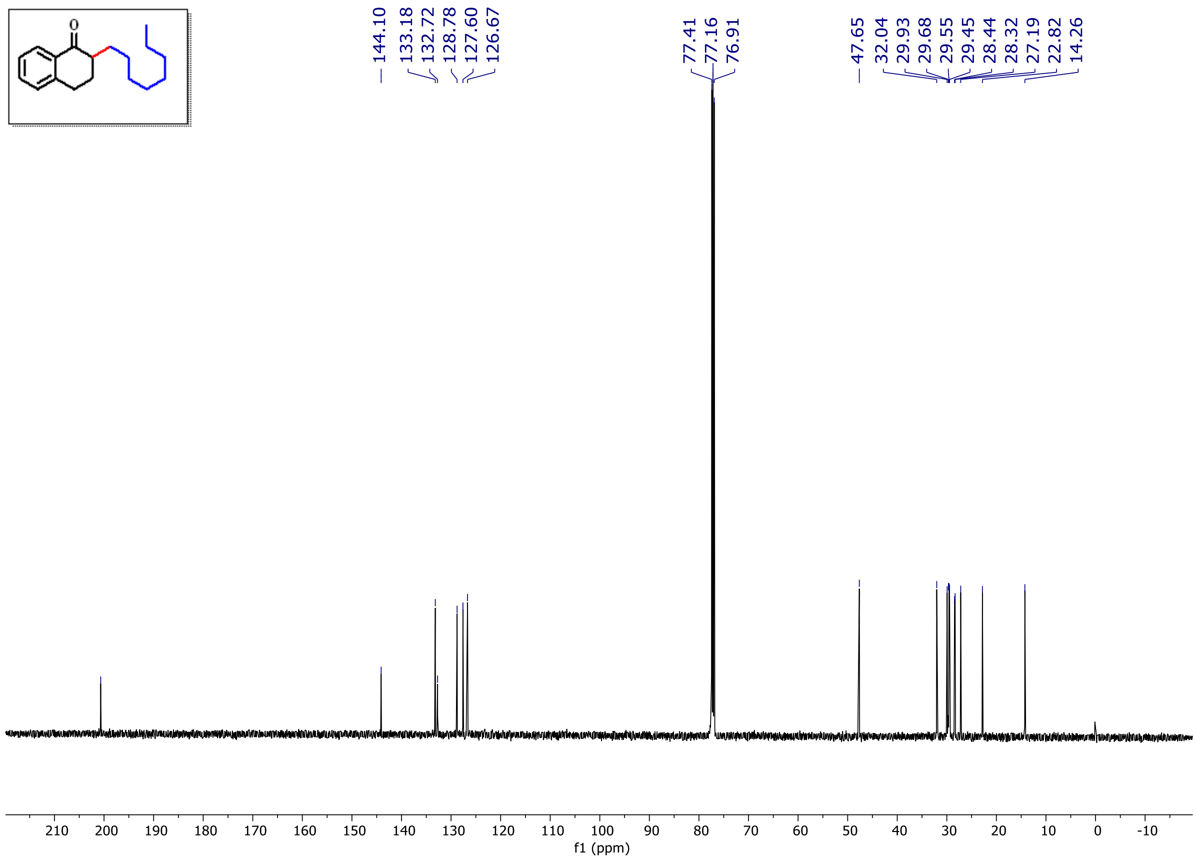
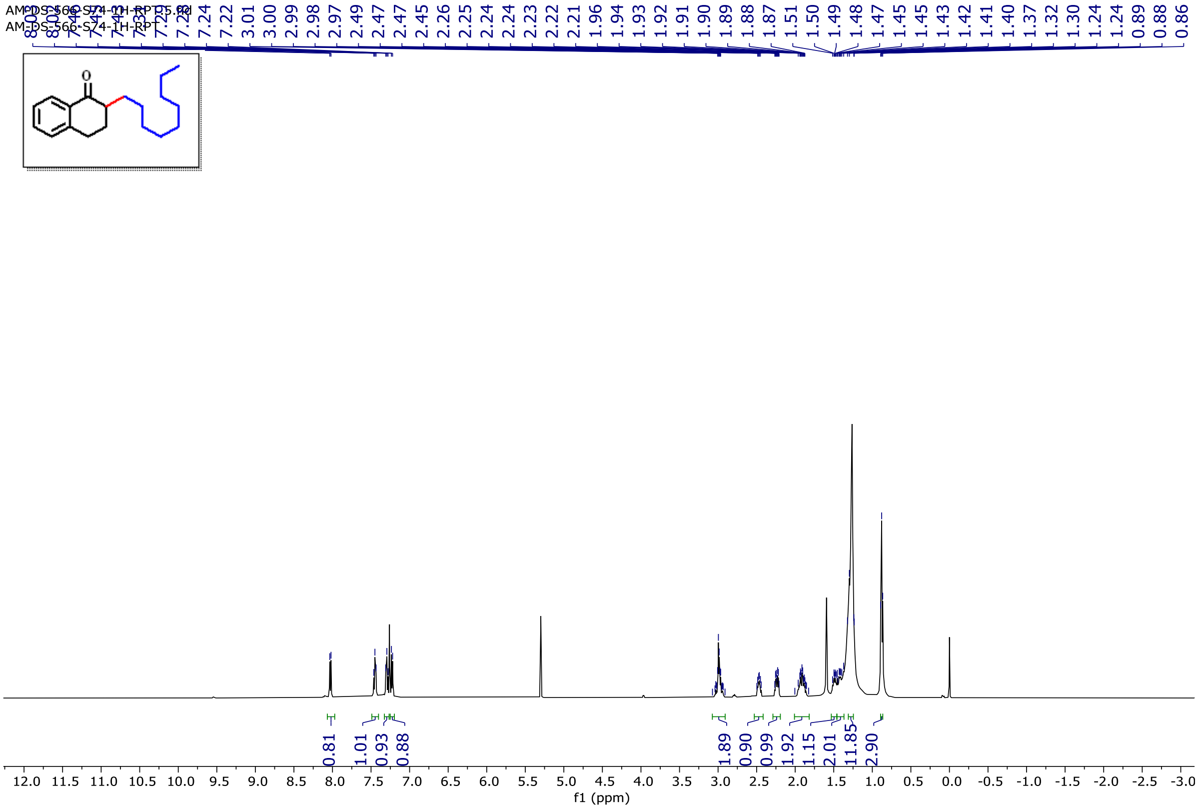




**Figure S29.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3l** in $CDCl_3$.



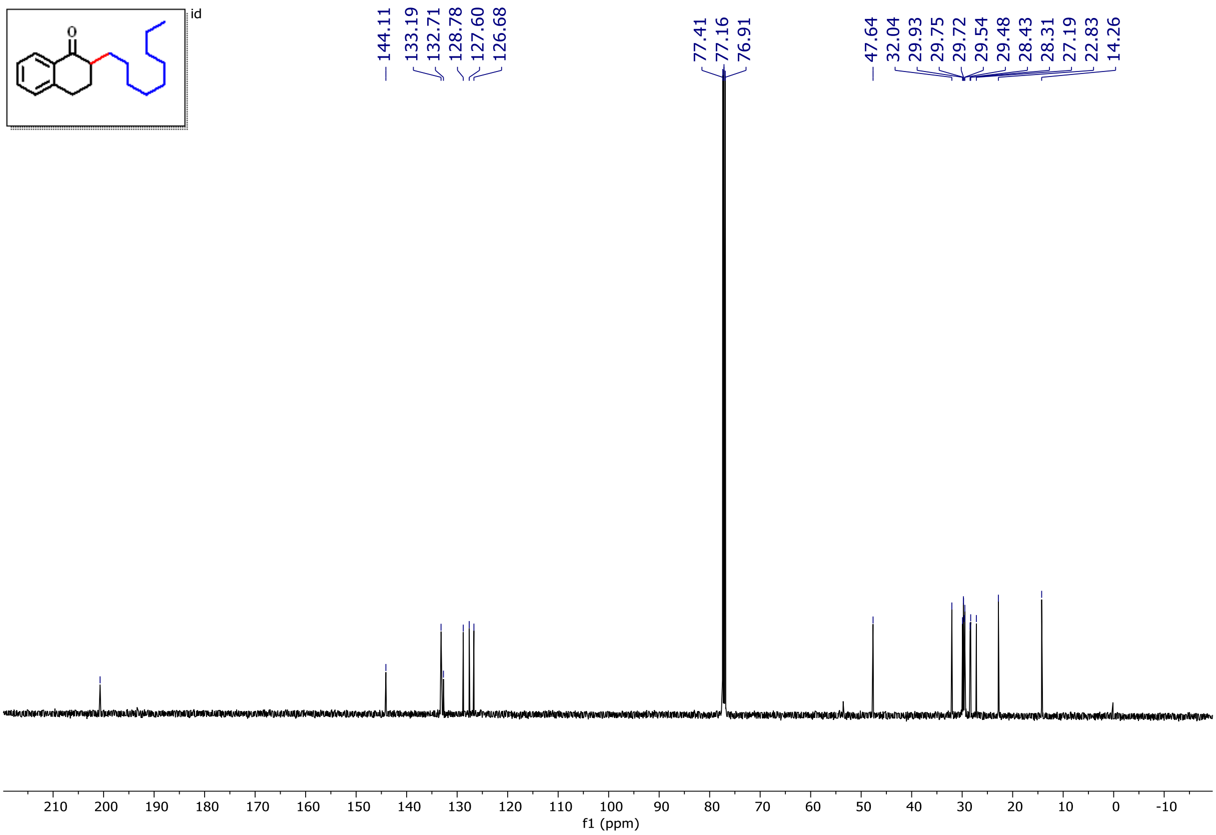
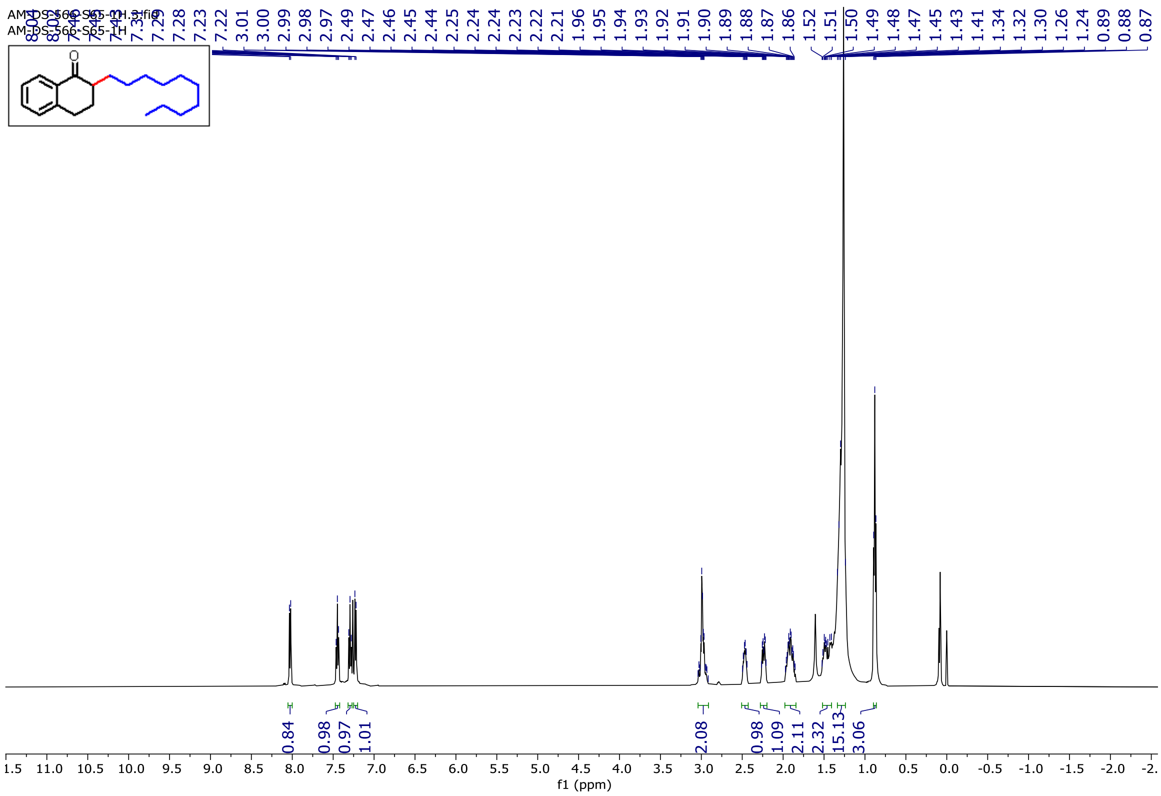




**Figure S30.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3m** in $CDCl_3$.



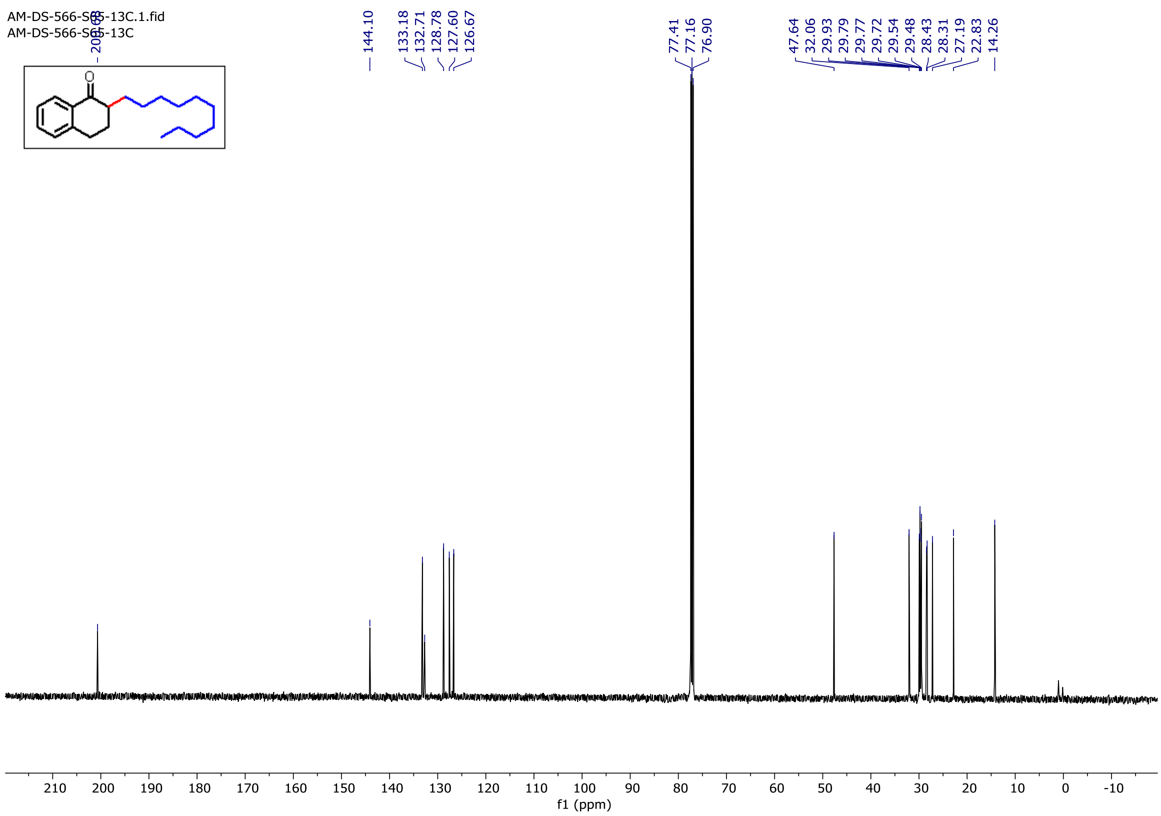
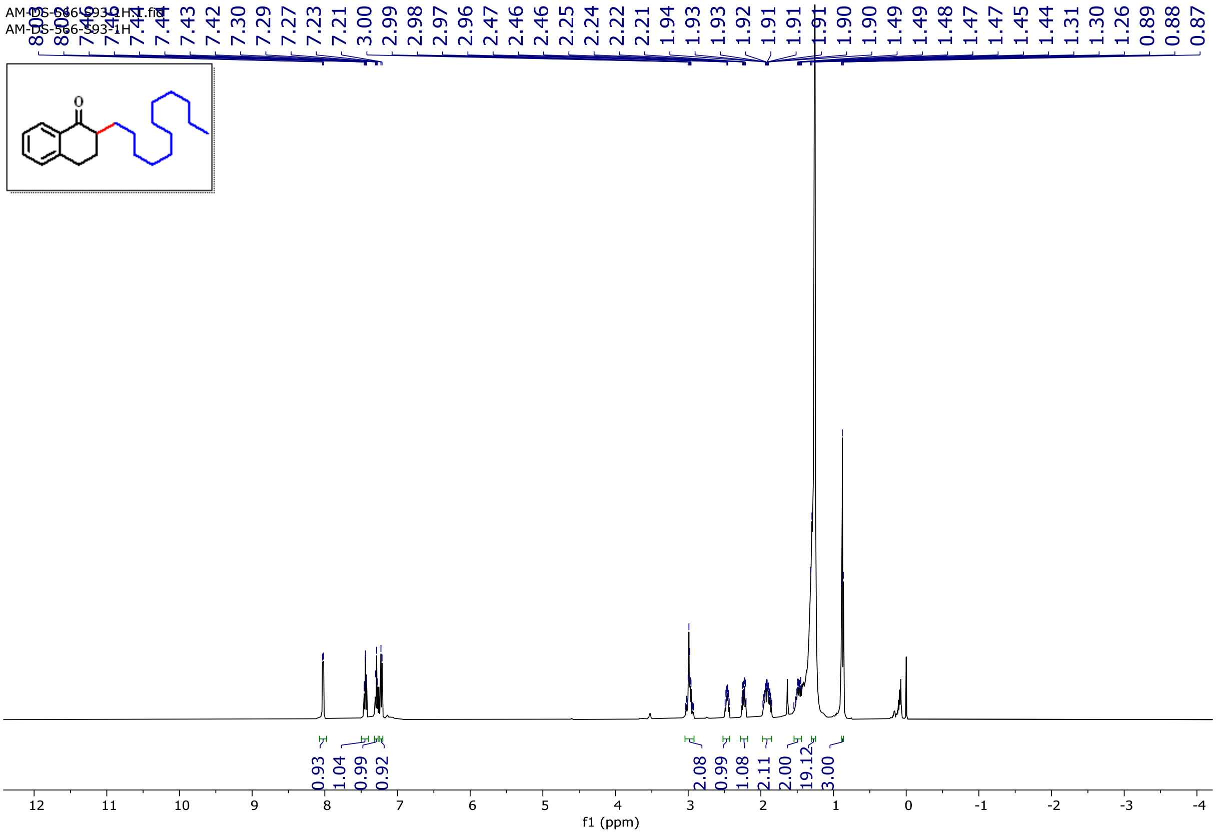


**Figure S31.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3n** in $CDCl_3$.



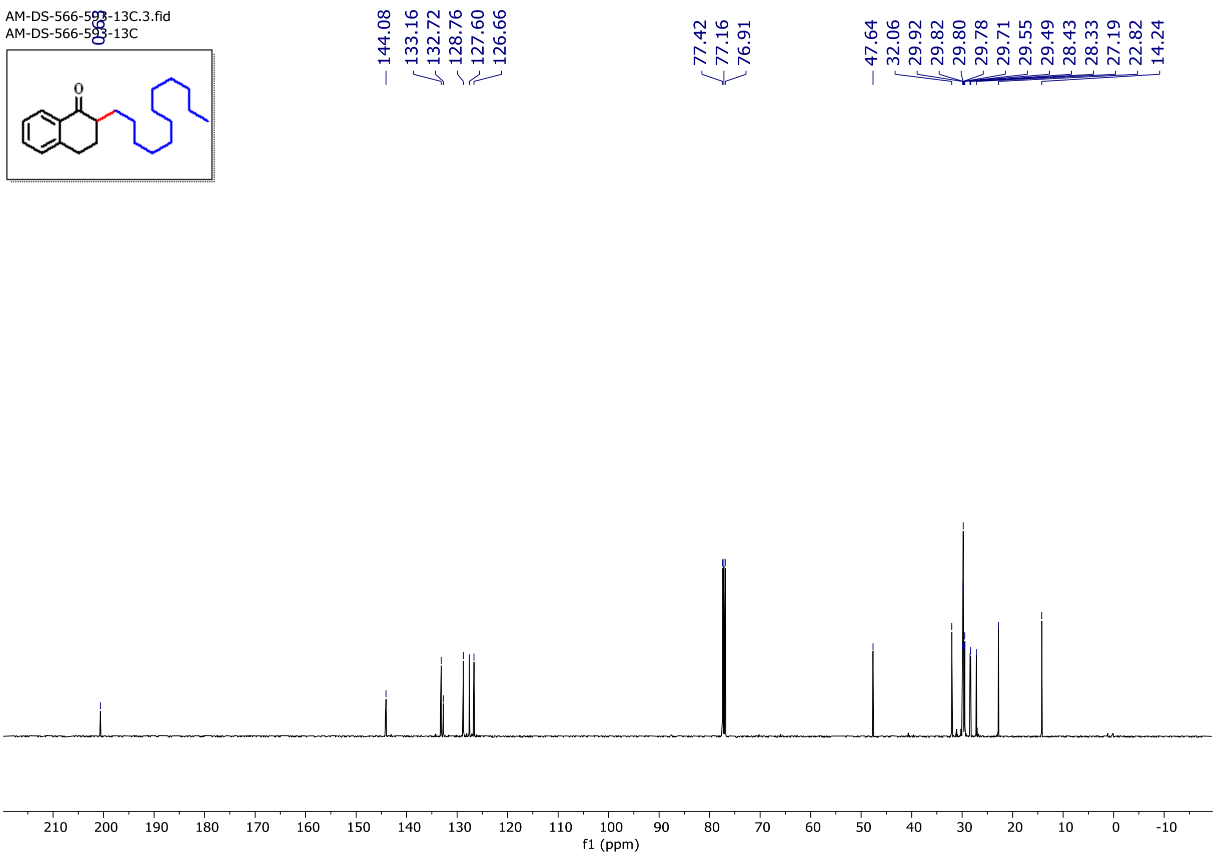
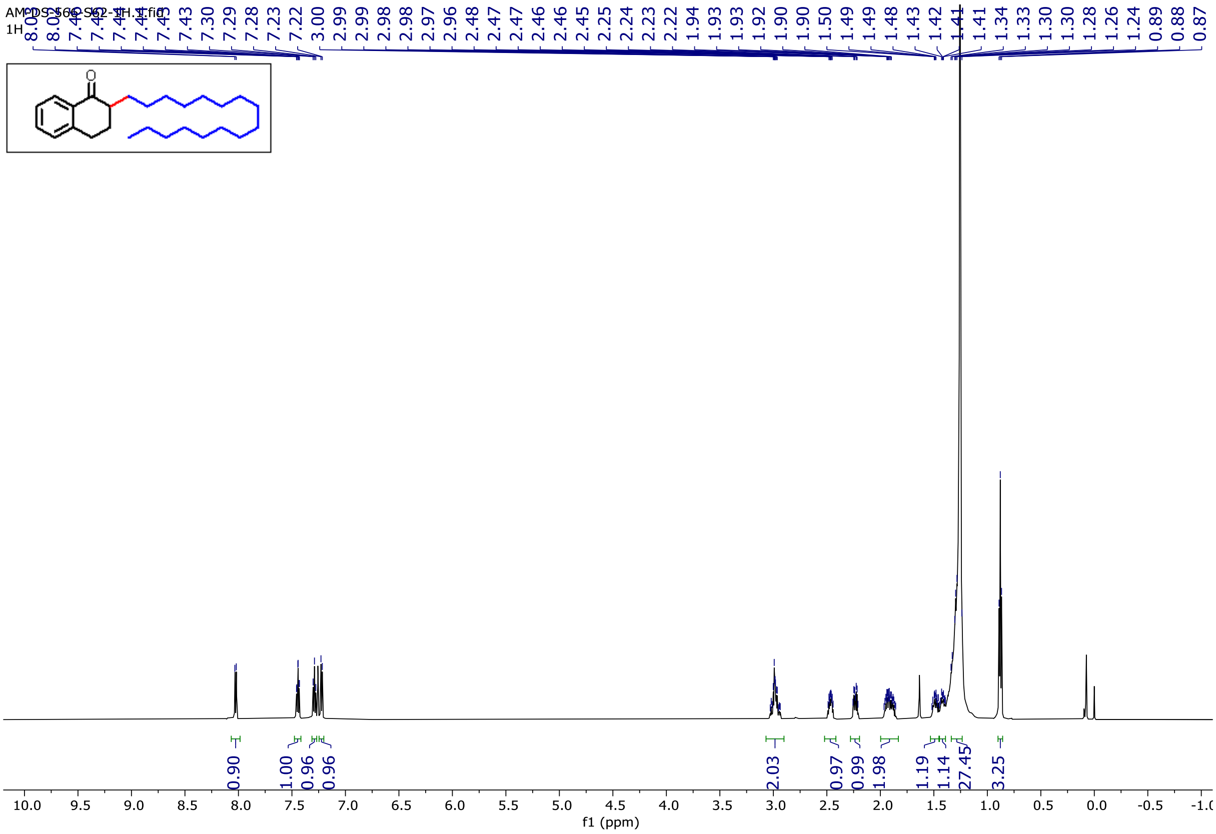


**Figure S32.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3o** in $CDCl_3$.



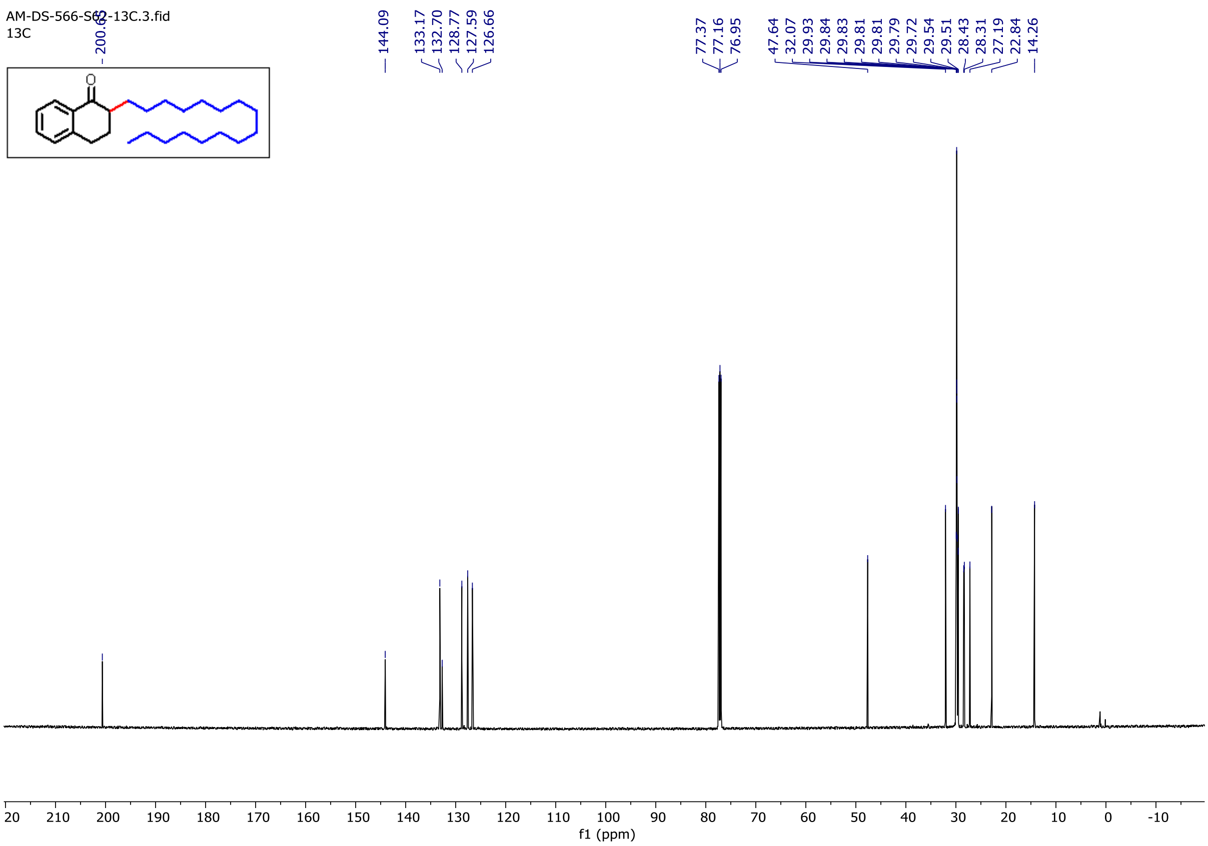
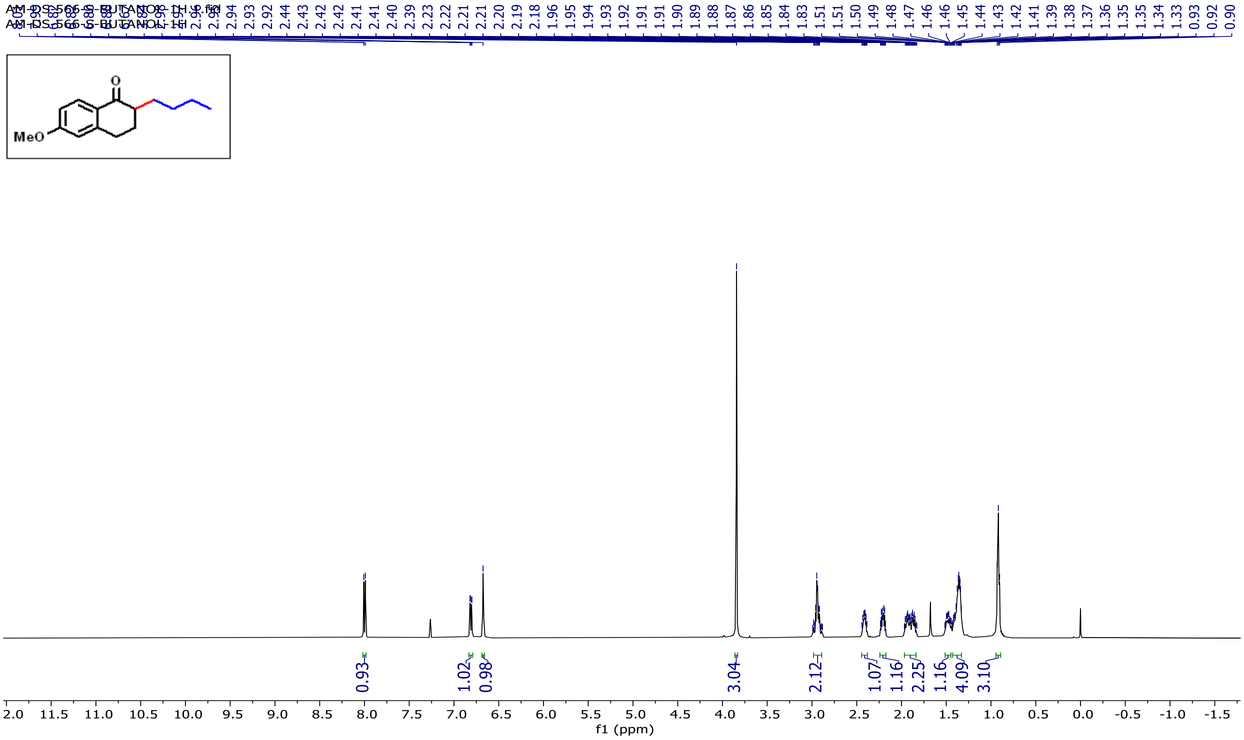


**Figure S33.** $^{1}$H (600 MHz) and $^{13}$C{$^{1}$H} (150 MHz) NMR Spectrum of **3p** in $CDCl_3$.



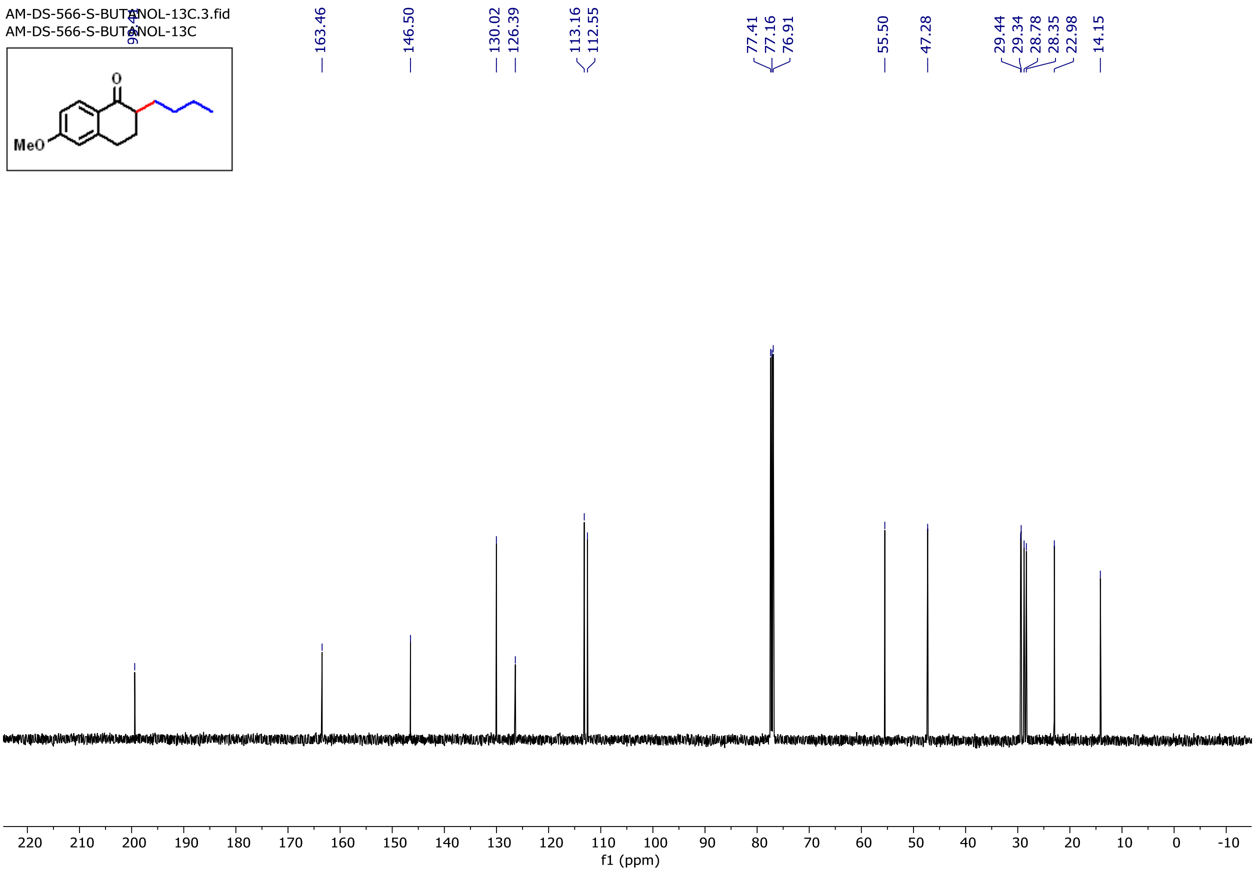
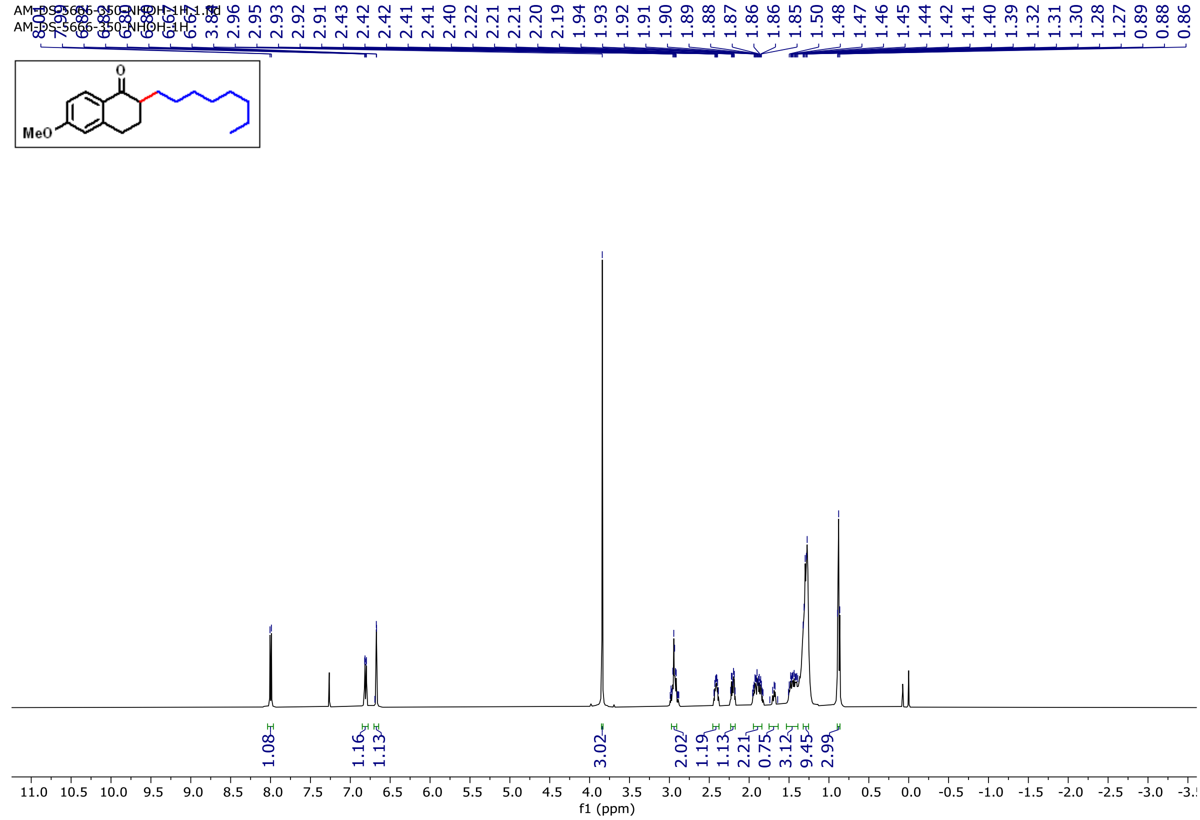




**Figure S34.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3q** in $CDCl_3$.



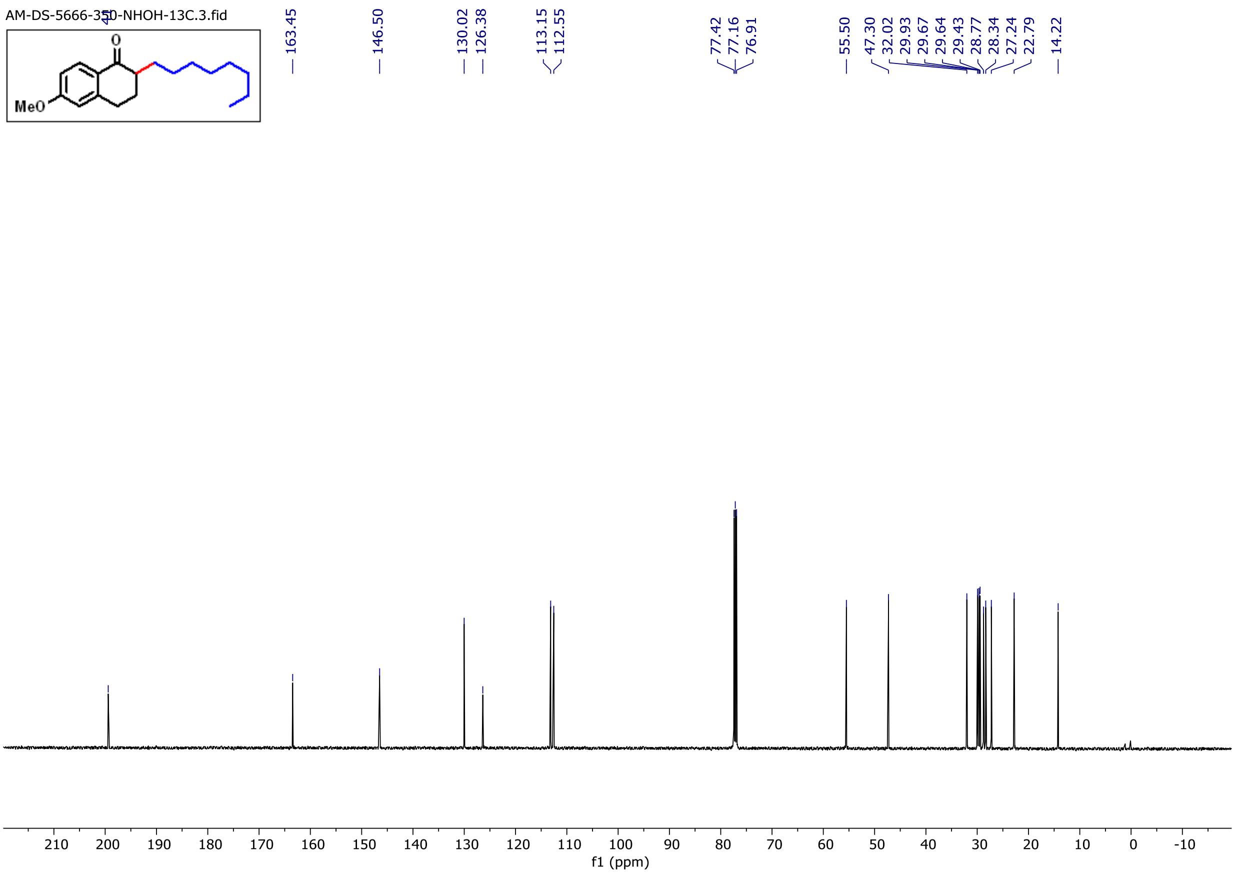
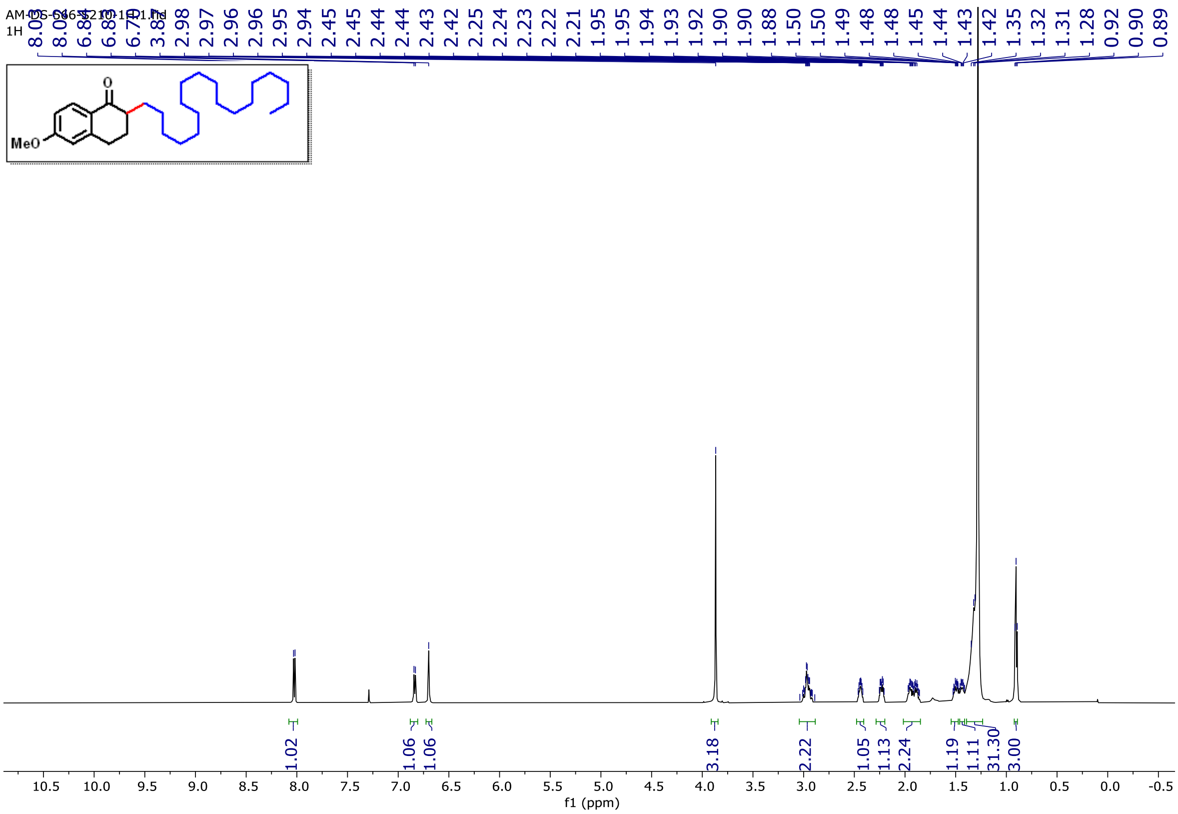




**Figure S35.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3r** in $CDCl_3$.



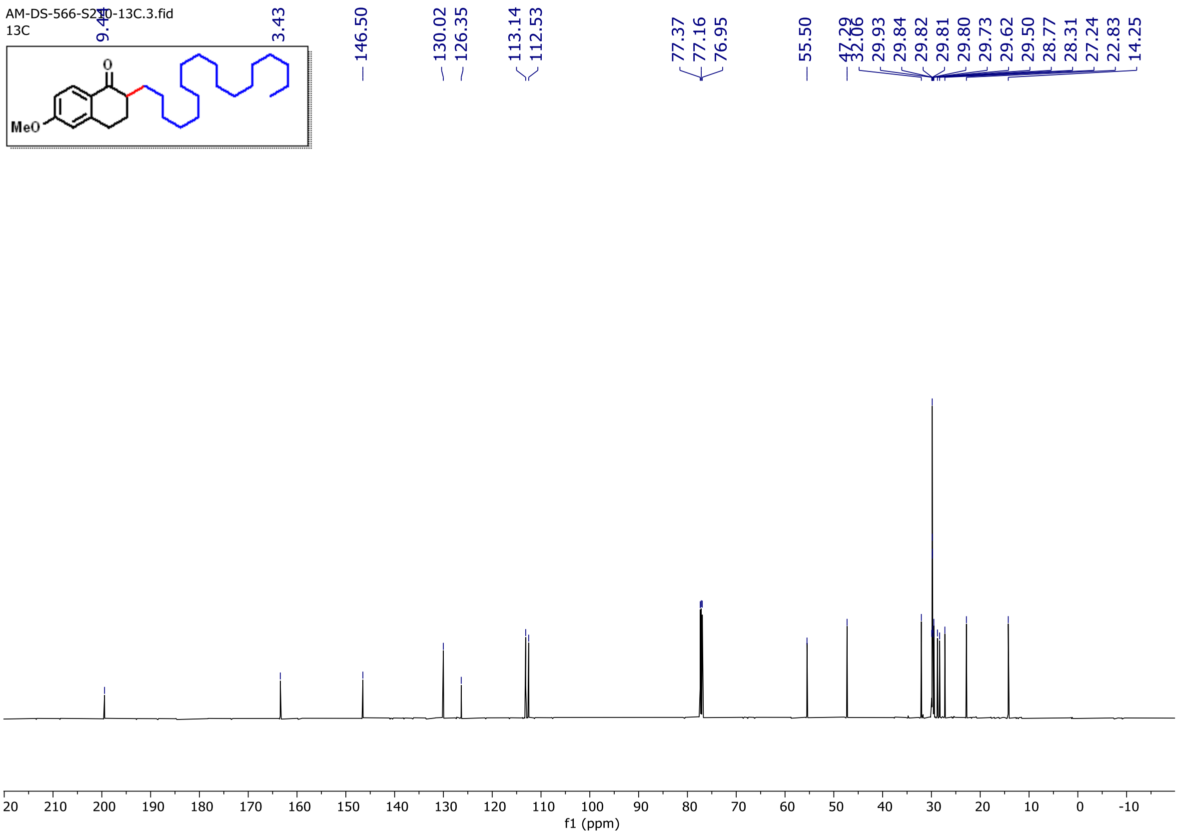
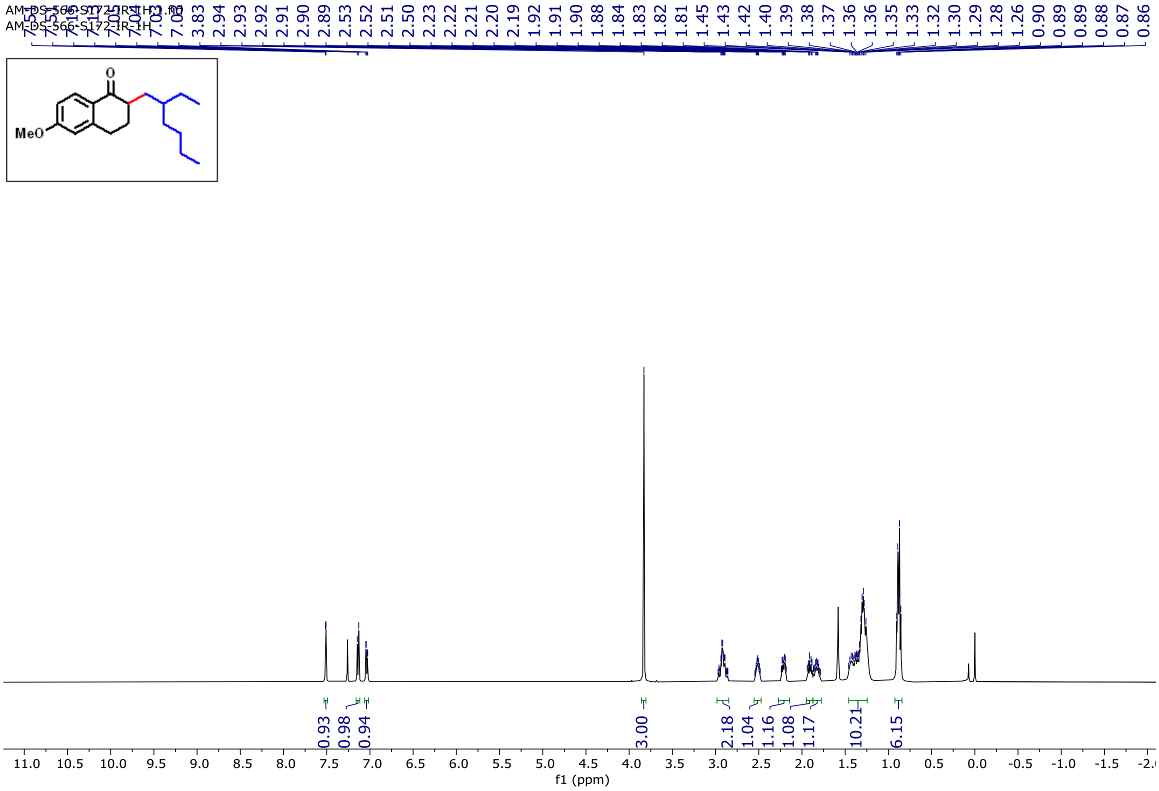


**Figure S36.** $^{1}H$ (600 MHz) and $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectrum of **3s** in $CDCl_3$.



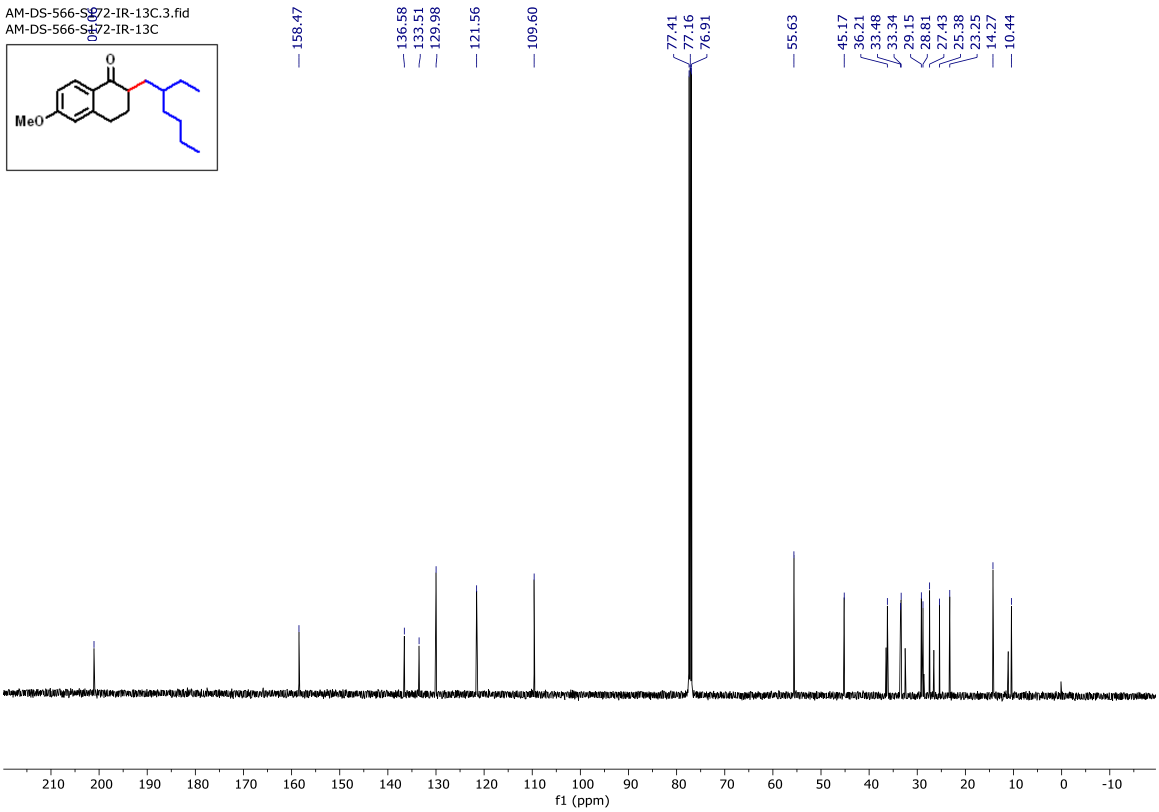
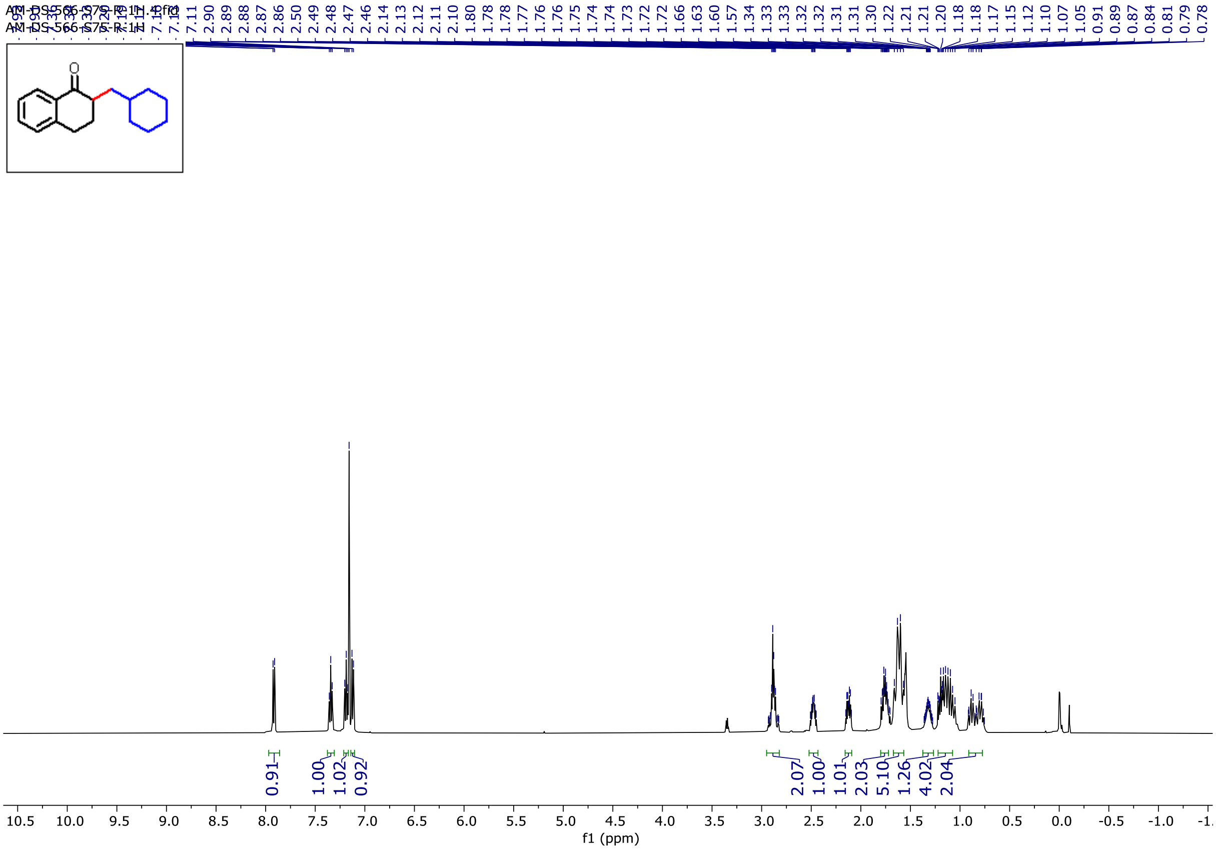




**Figure S37.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3t** in $CDCl_3$.



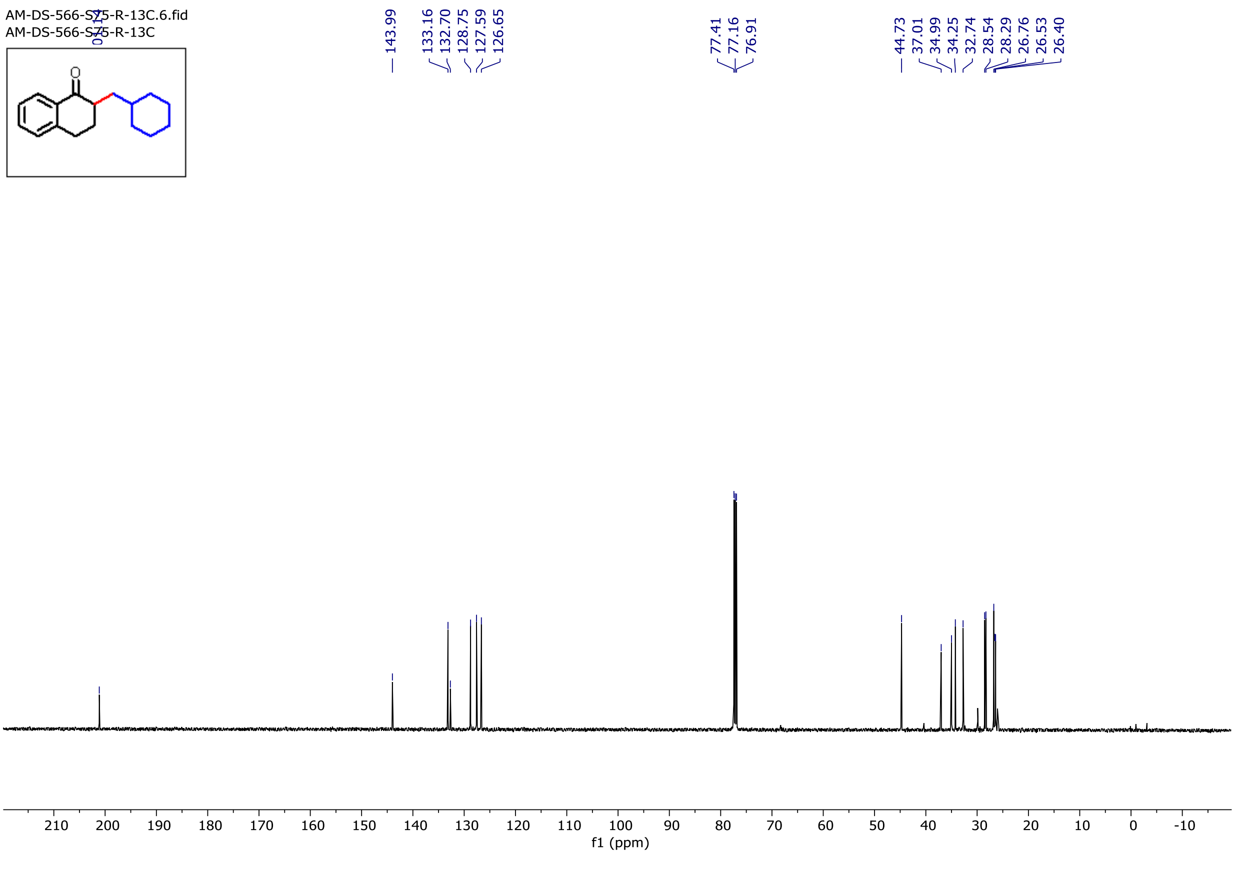
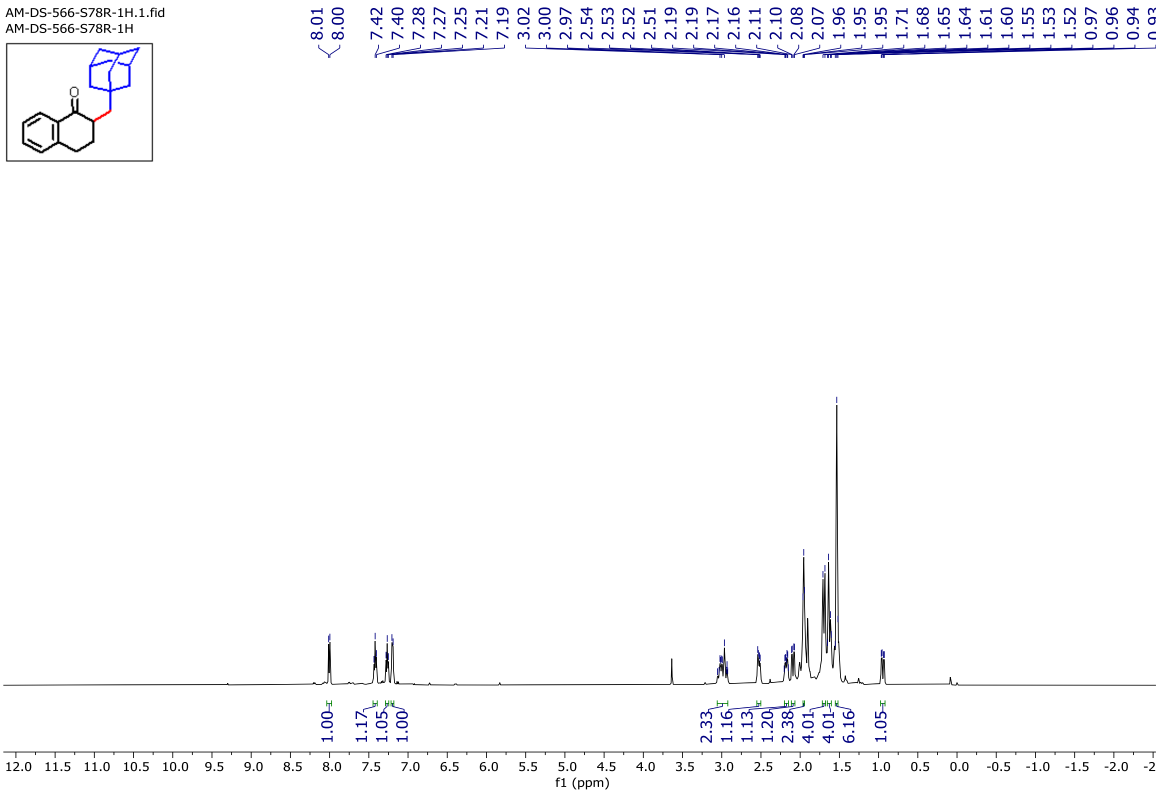




**Figure S38.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3u** in $CDCl_3$.



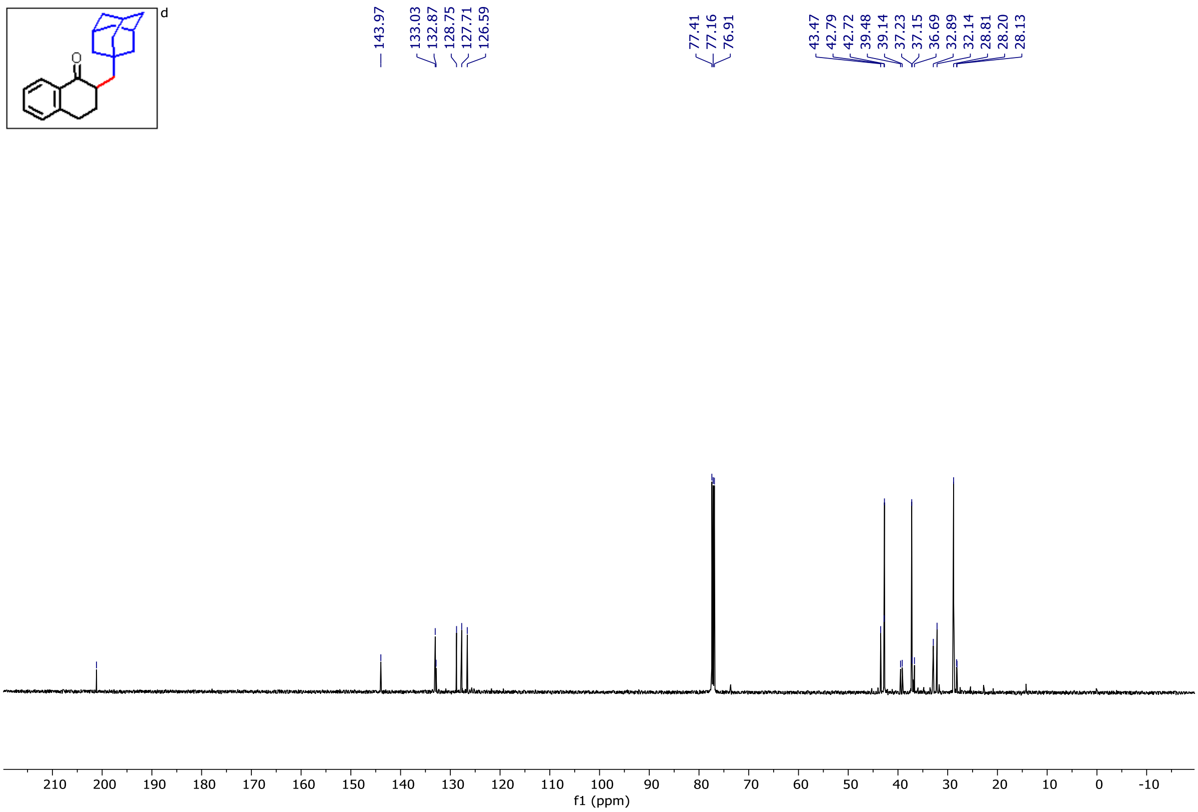
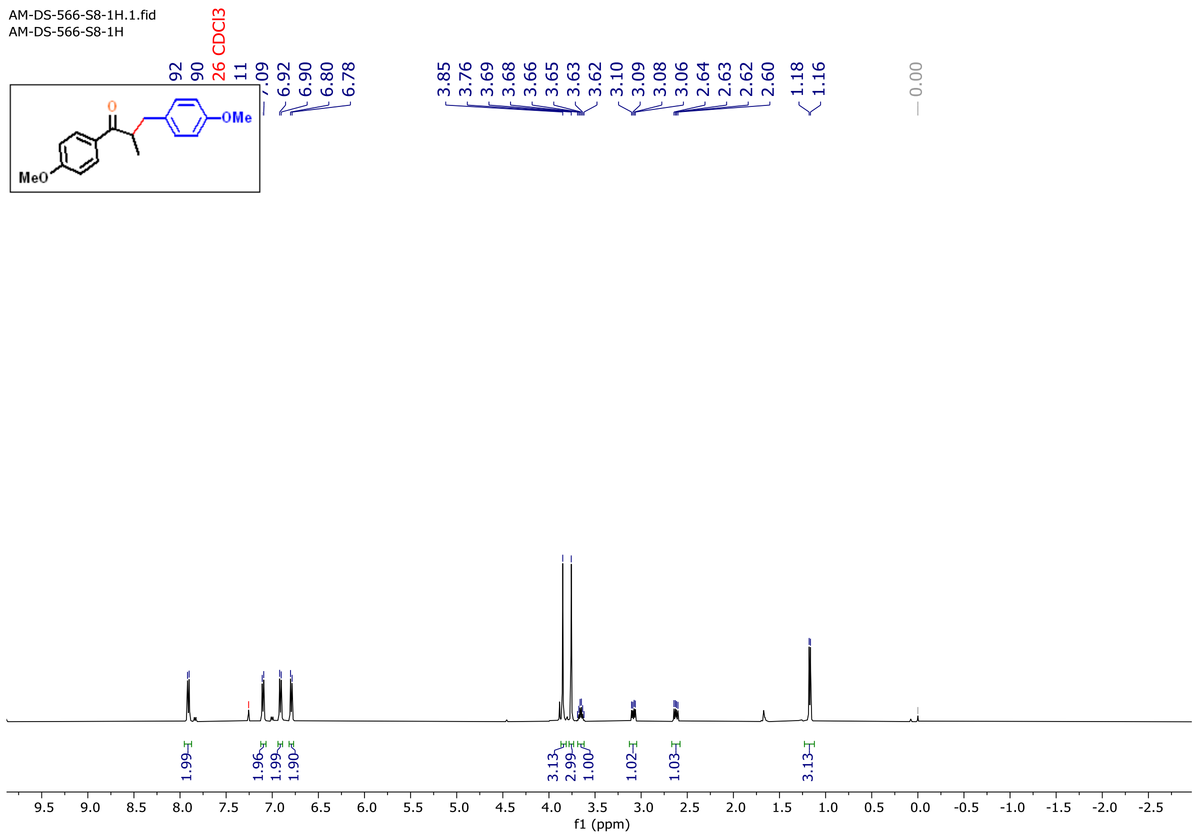


**Figure S39.** $^1$H (500 MHz) and $^{13}$C{$^1$H} (125 MHz) NMR Spectrum of **3v** in $CDCl_3$.



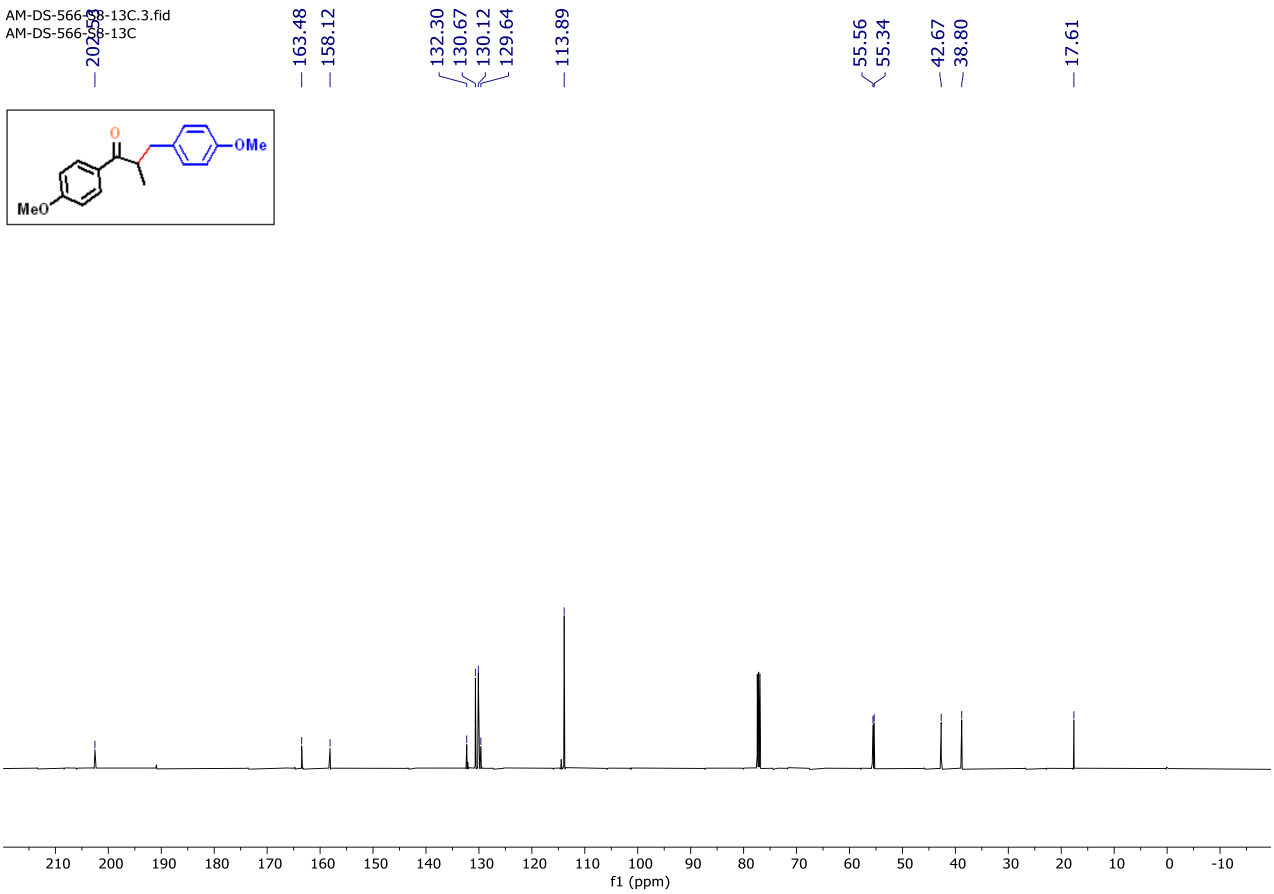
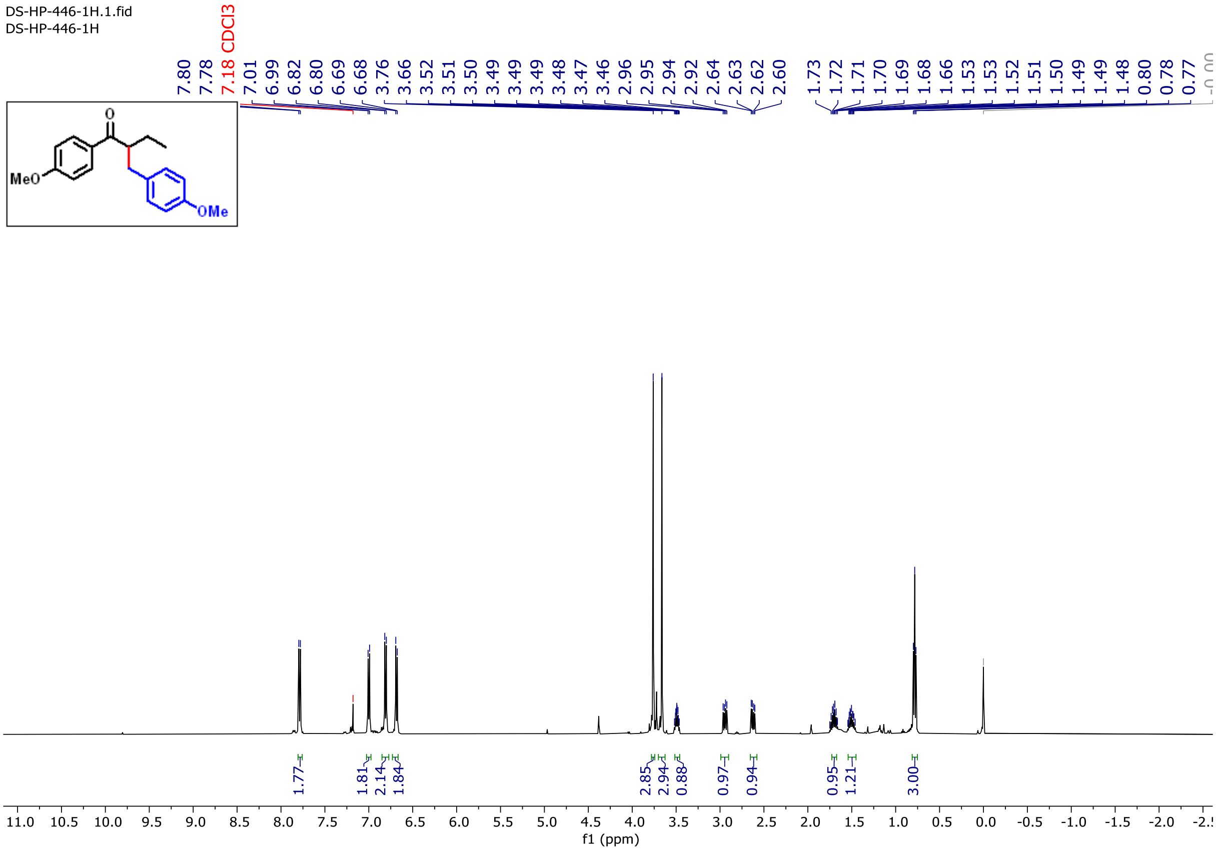


**Figure S40.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3w** in $CDCl_3$.

DS-HP-446-1H.1.fid
DS-HP-446-1H




DS-HP-446-13C.3.fid
DS-HP-446-13C

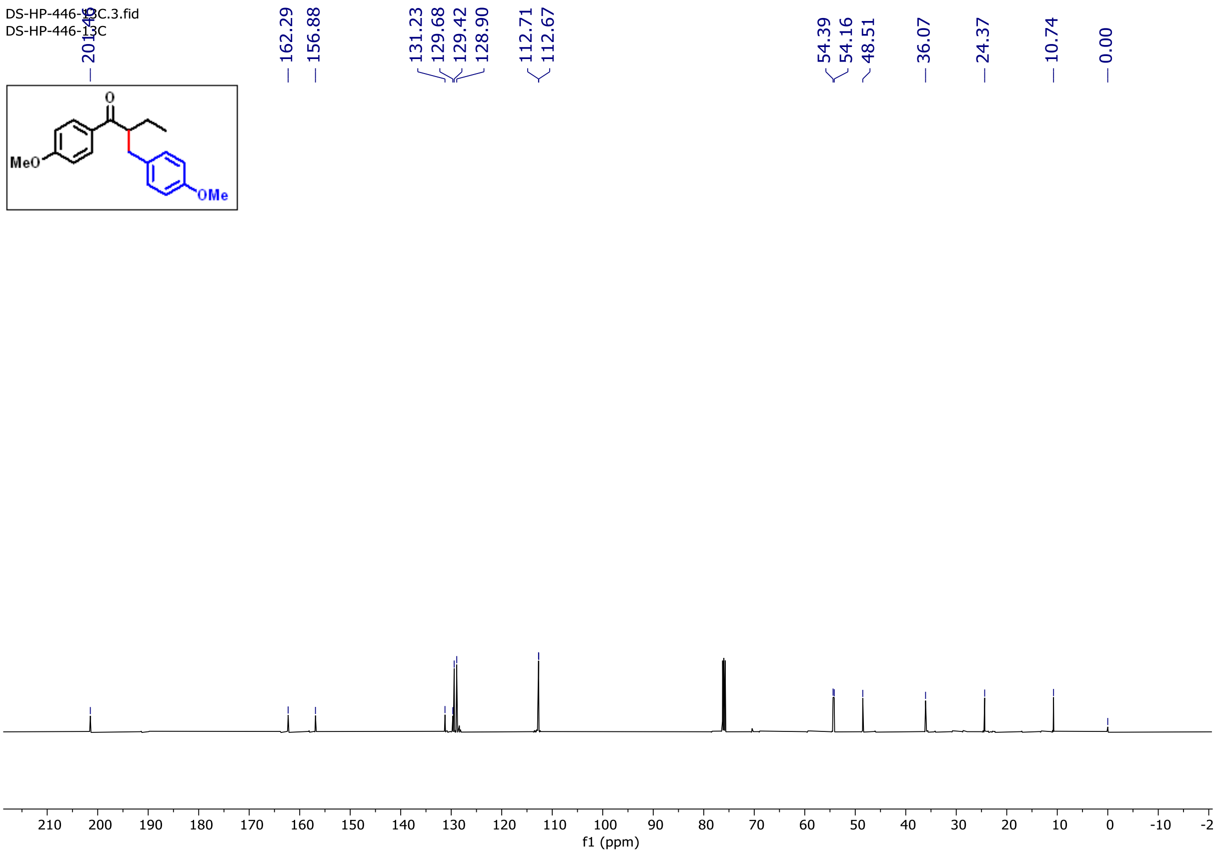
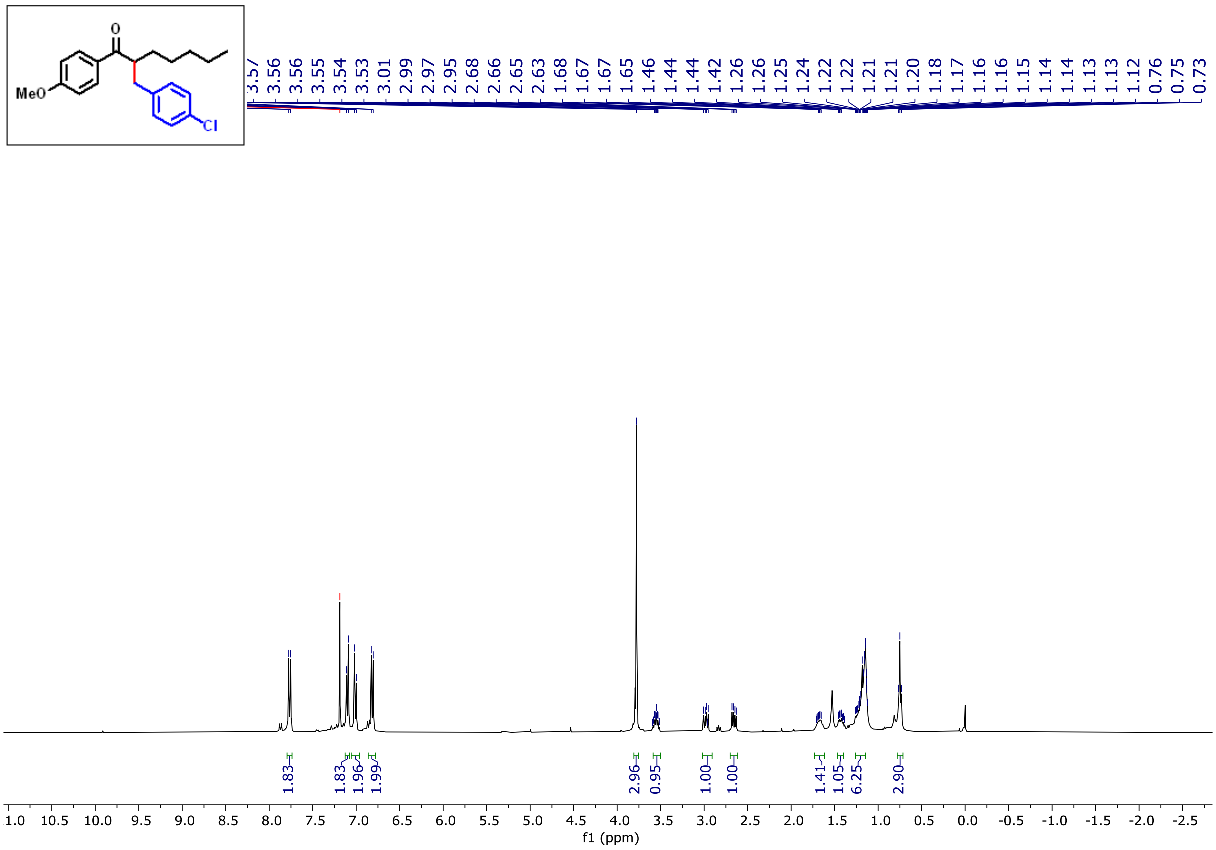


**Figure S41.** $^1$H (500 MHz) and $^{13}$C{$^1$H} (125 MHz) NMR Spectrum of **3x** in $CDCl_3$.



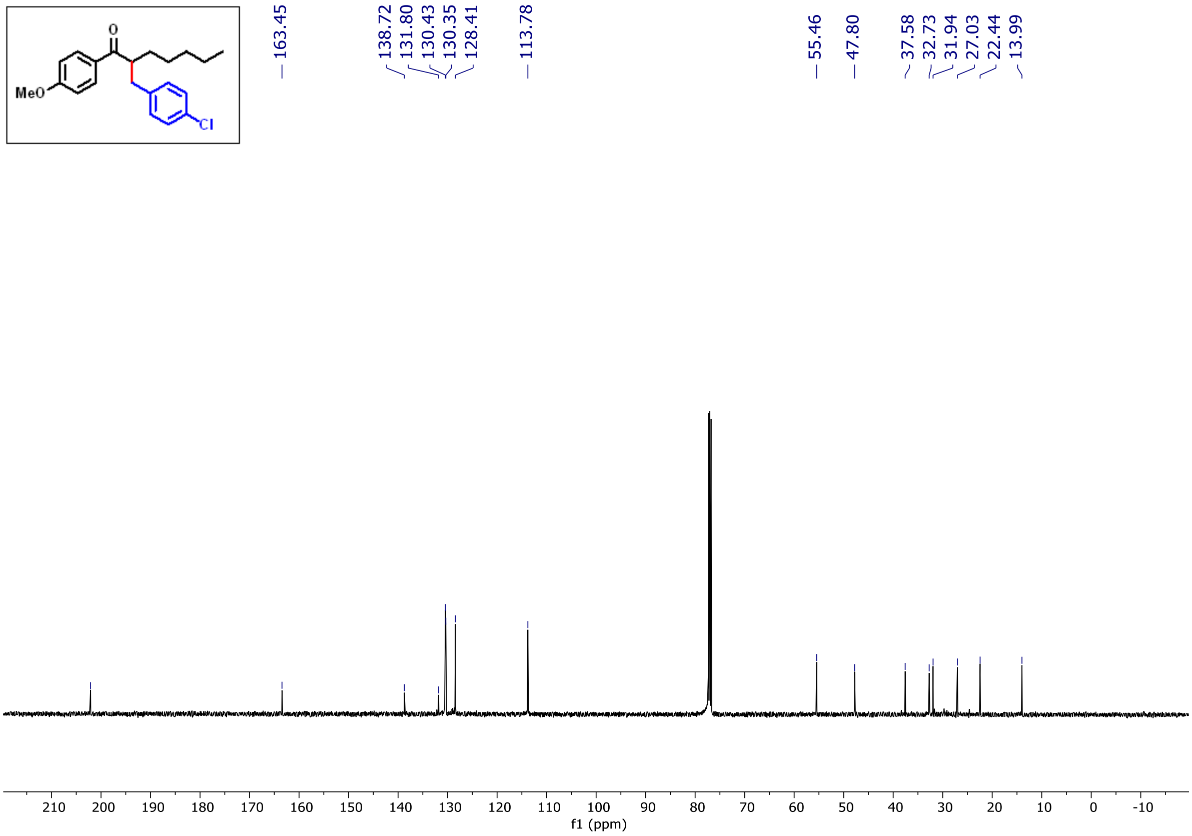
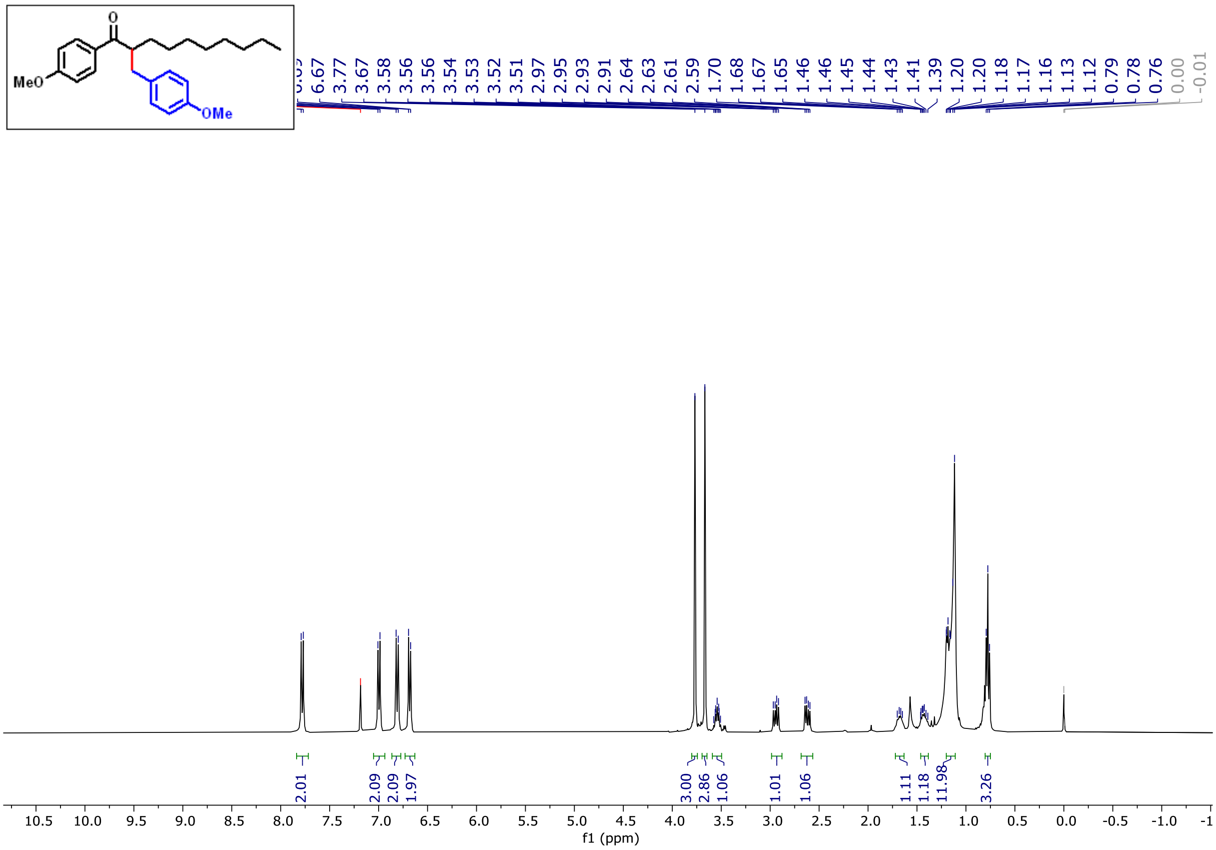


**Figure S42.** $^1$H (400 MHz) and $^{13}$C{$^1$H} (125 MHz) NMR Spectrum of **3y** in $CDCl_3$.



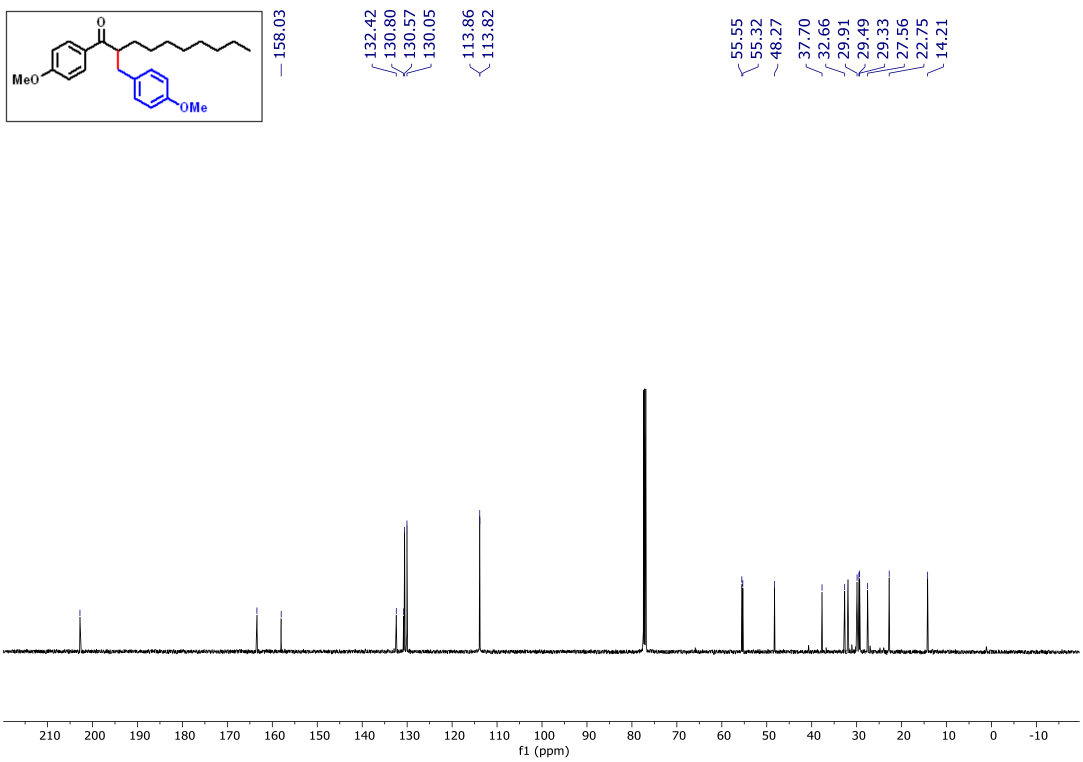
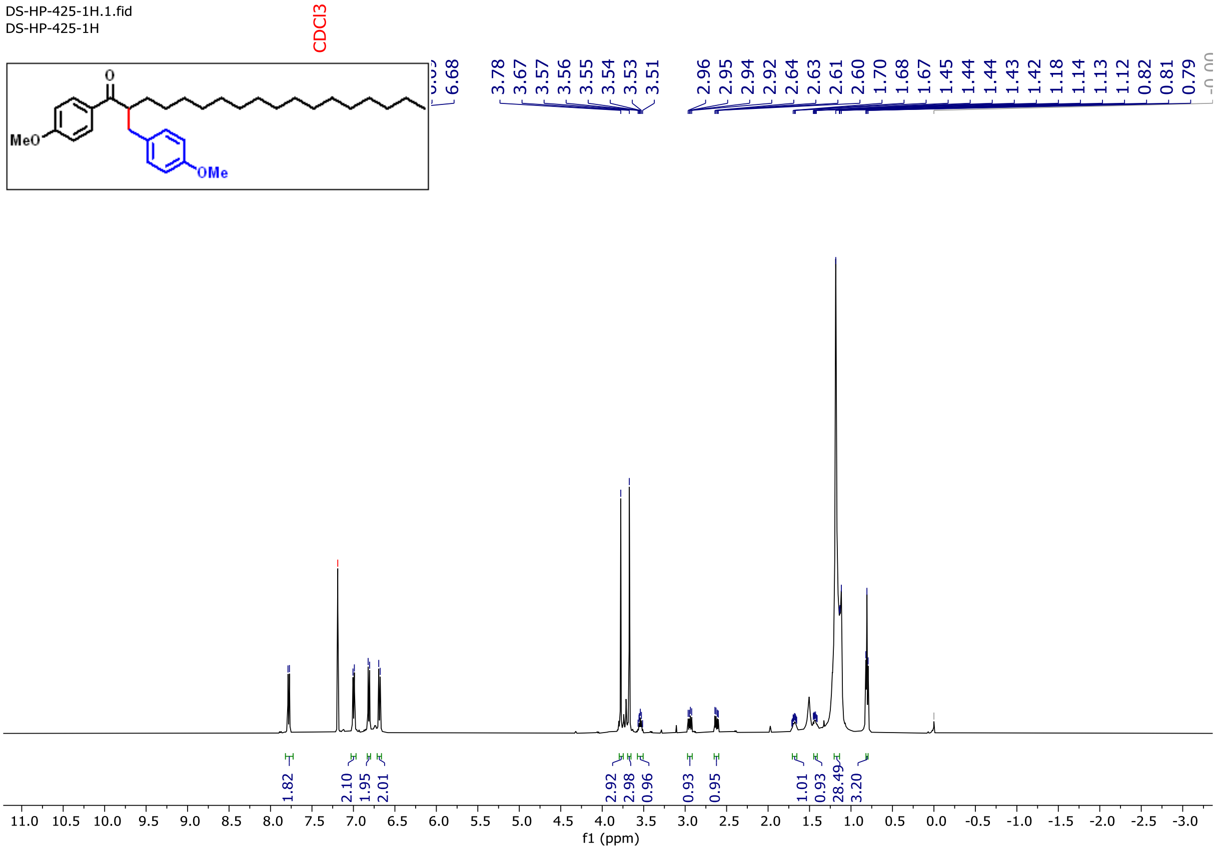


**Figure S43.** $^{1}H$ (400 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3z** in $CDCl_3$.



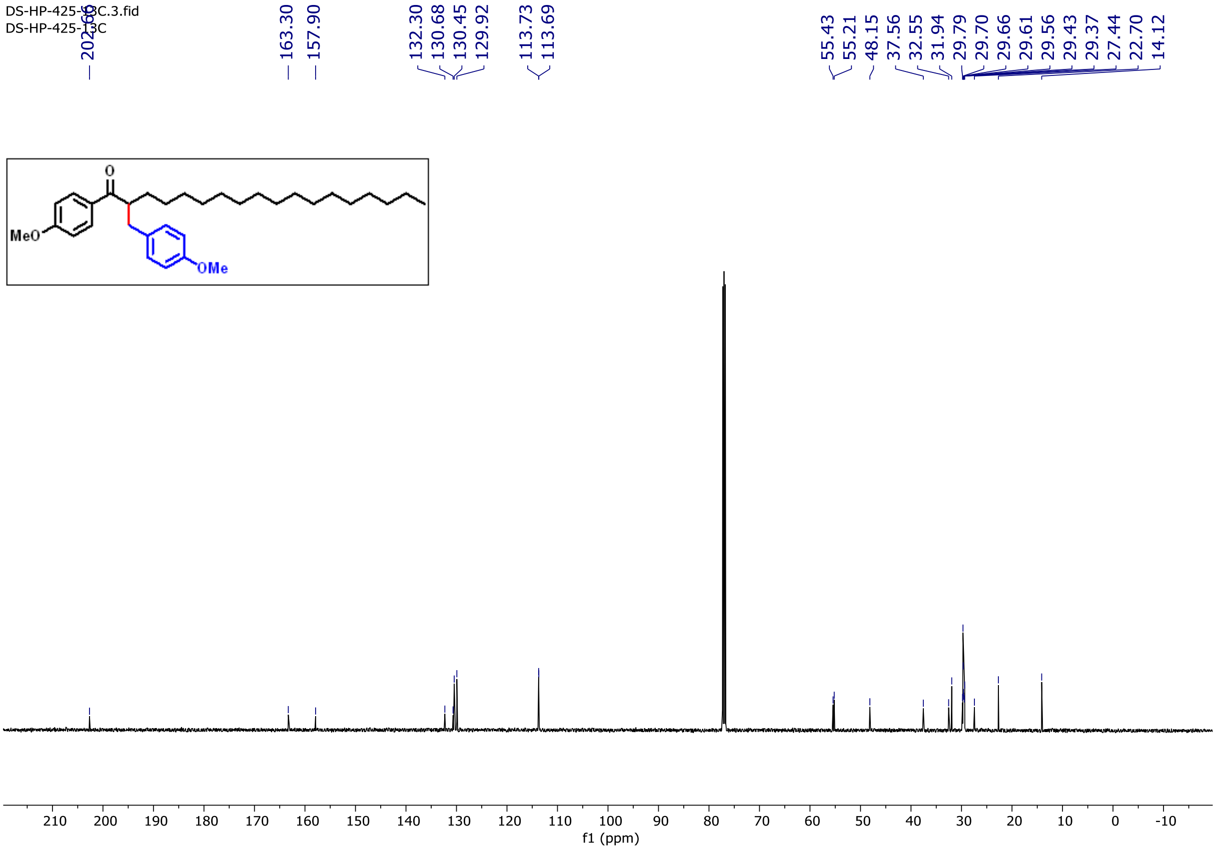
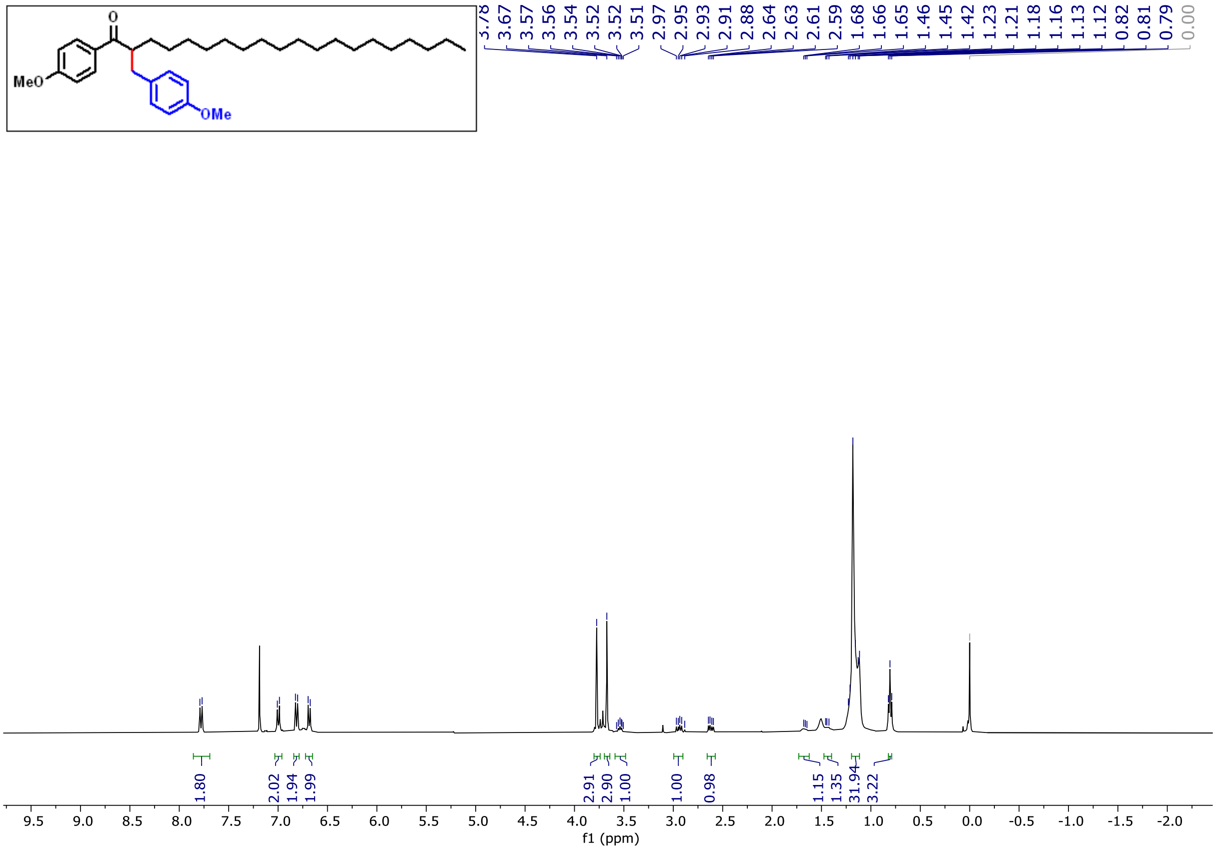


**Figure S44.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3aa** in $CDCl_3$.



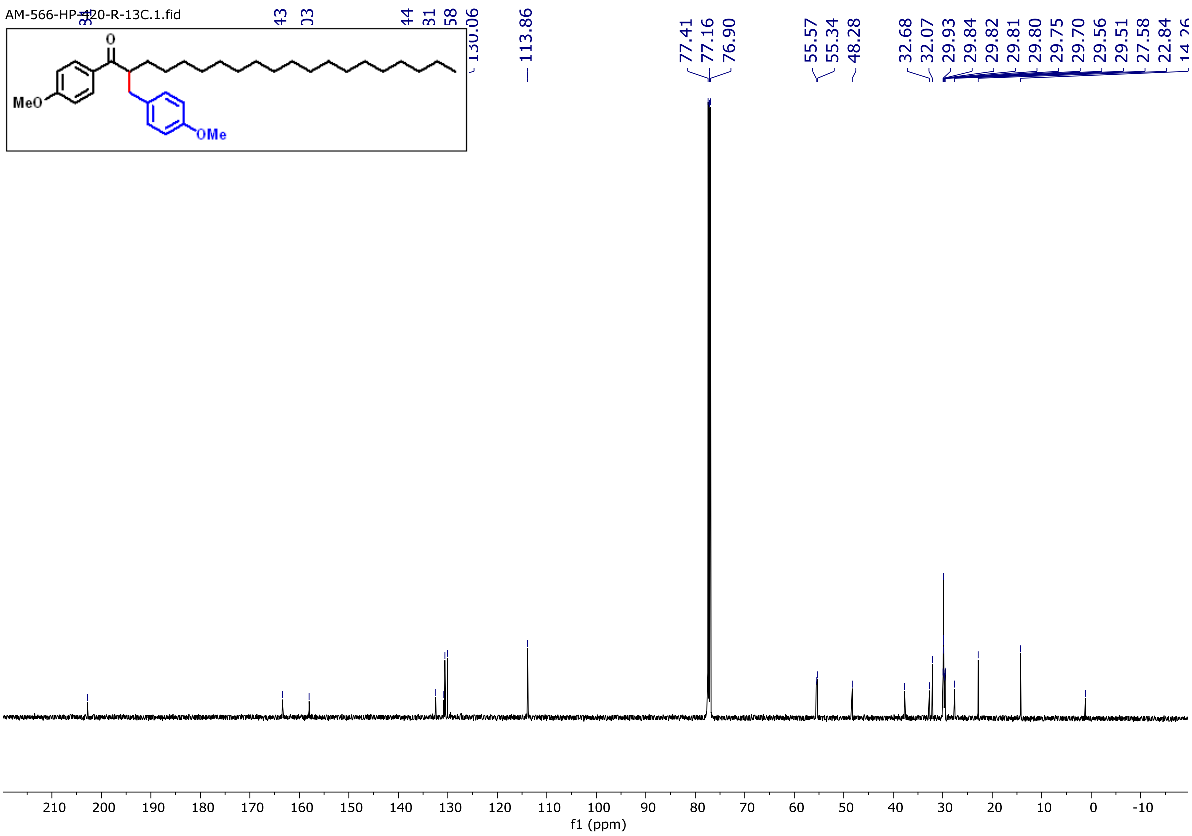


**Figure S45.** $^{1}H$ (400 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3ab** in $CDCl_3$.

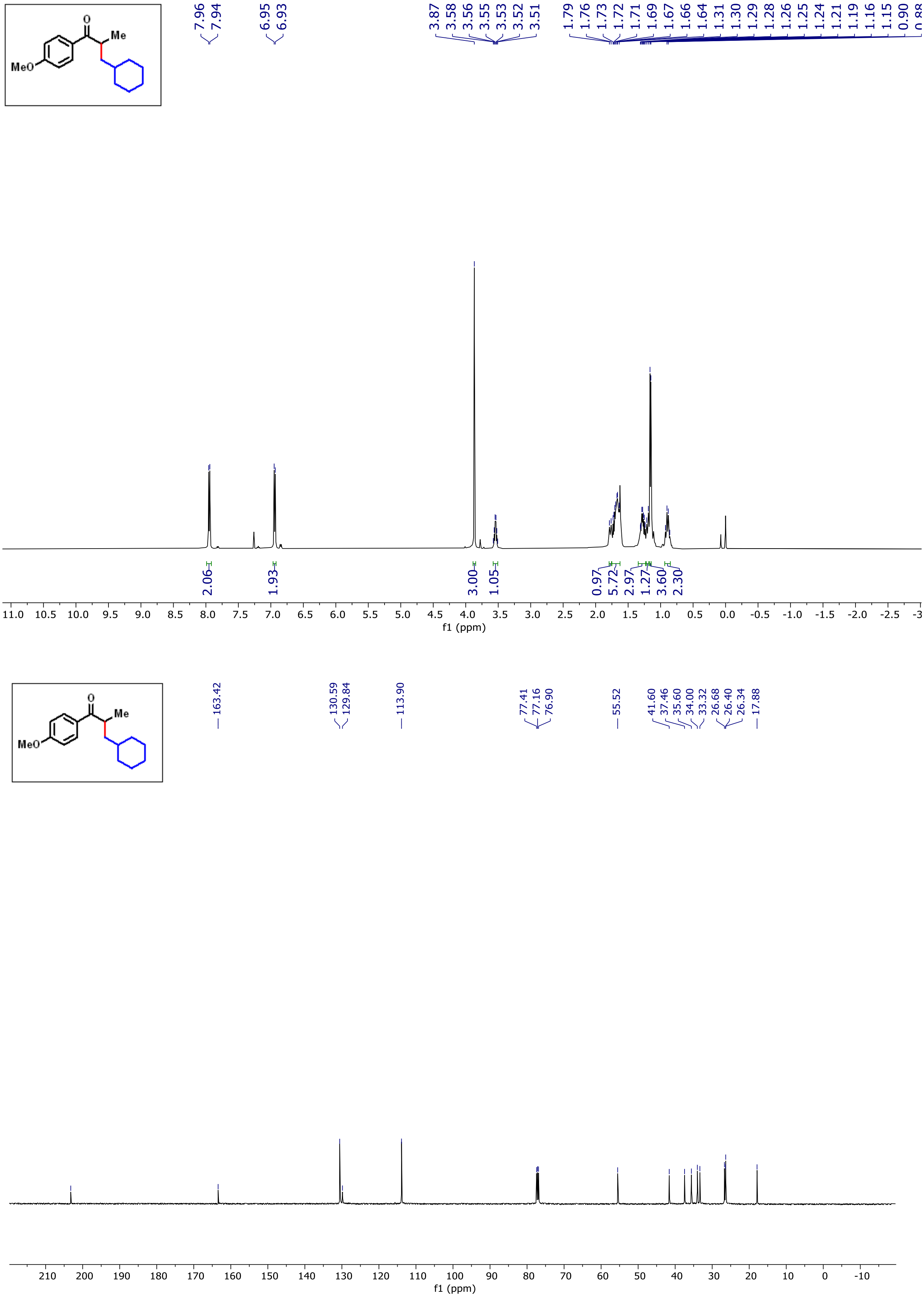
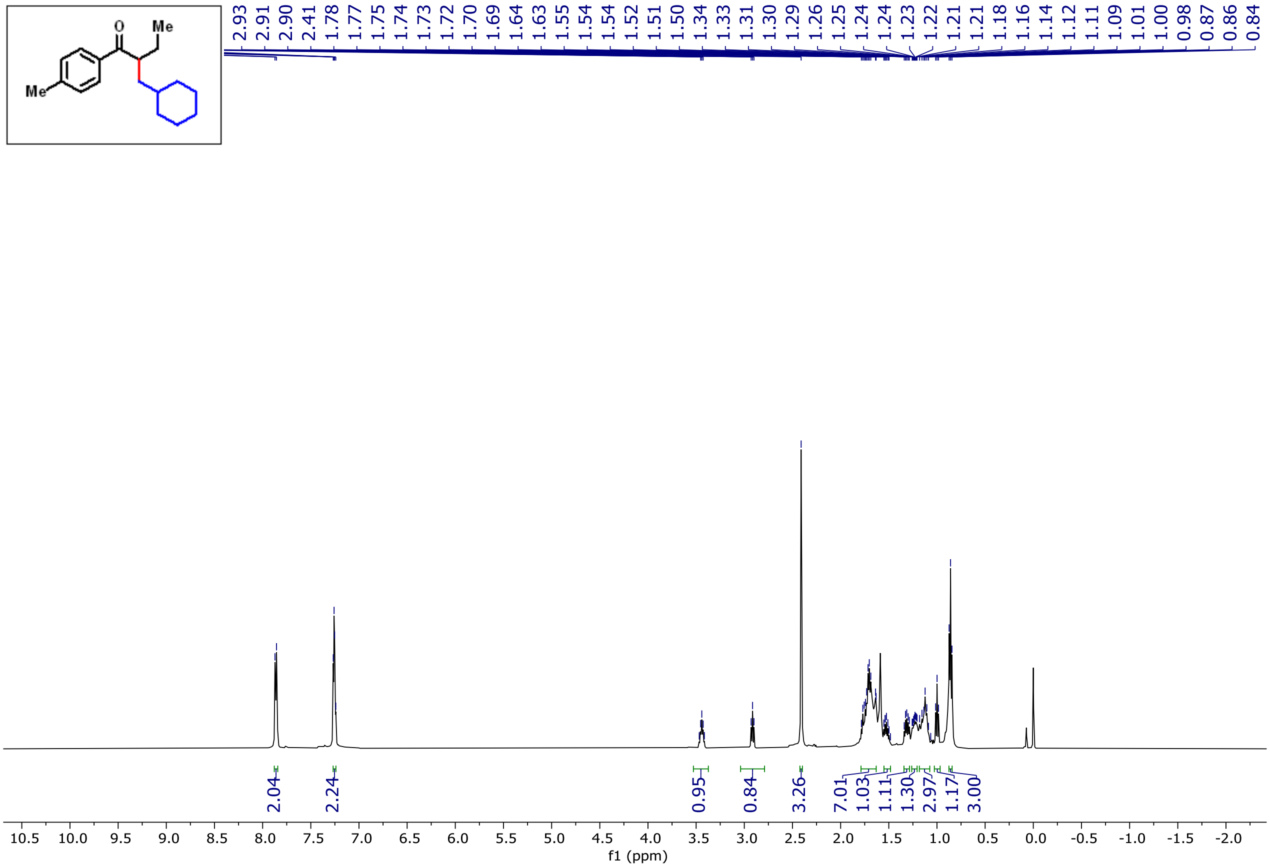



**Figure S46.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3ac** in $CDCl_3$.



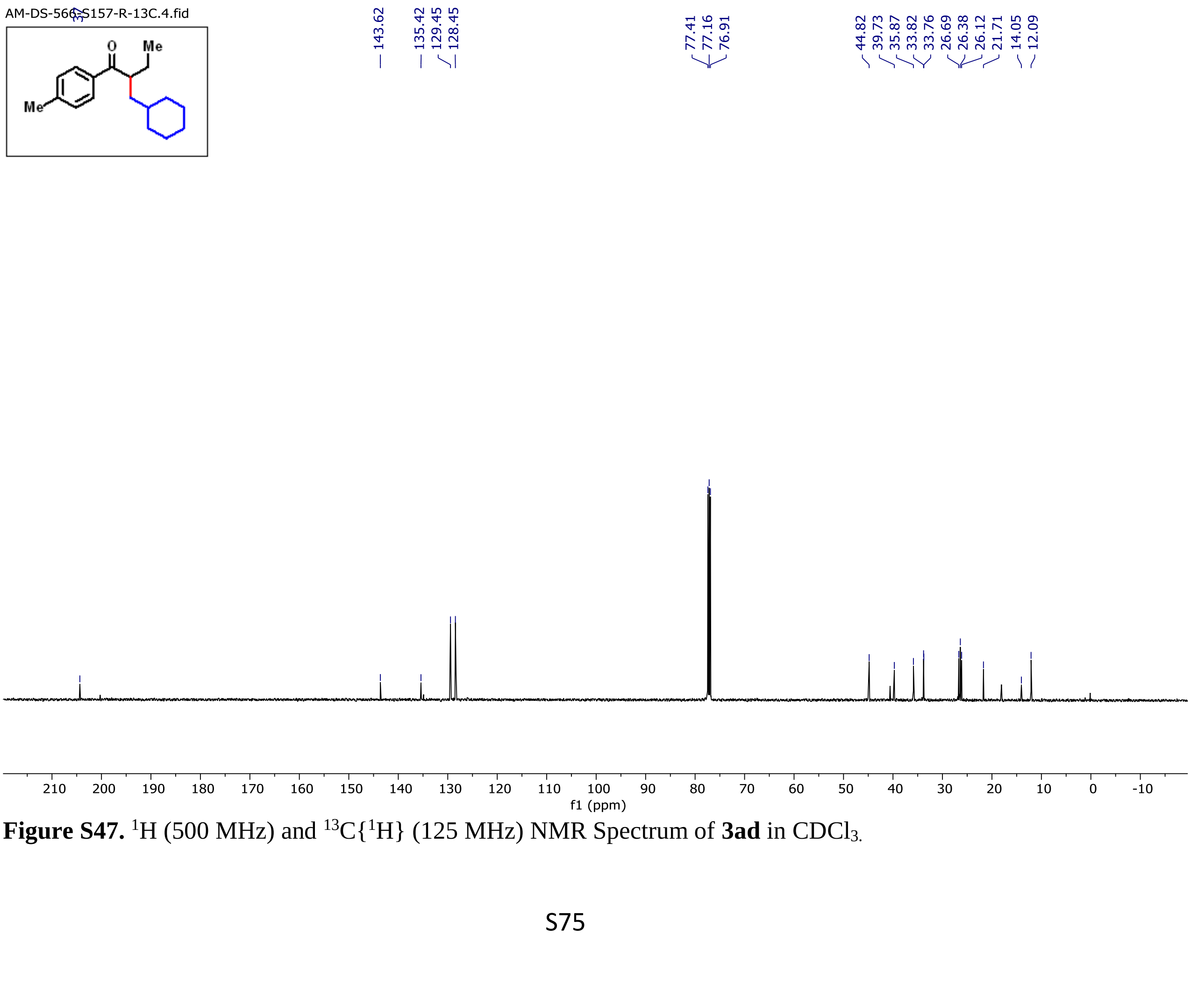
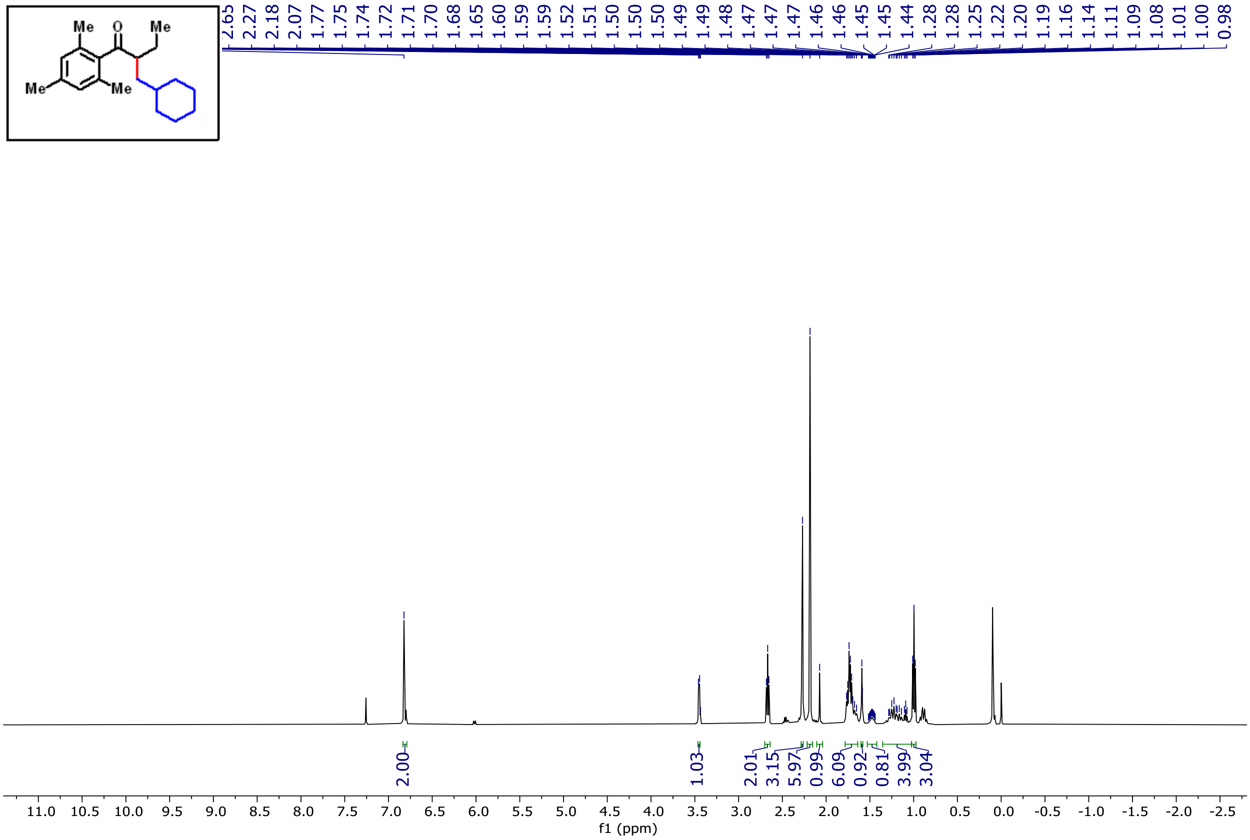




**Figure S47.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3ad** in $CDCl_3$.



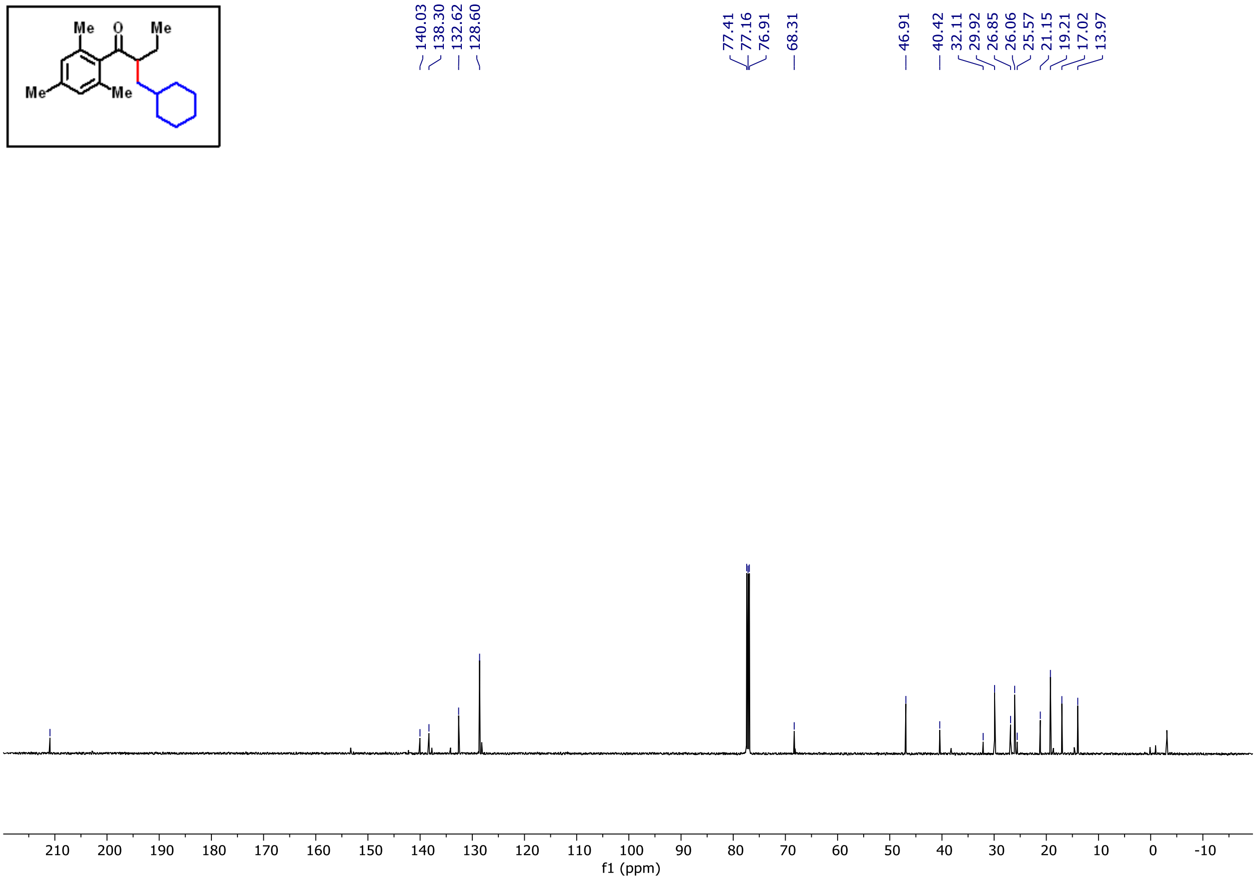
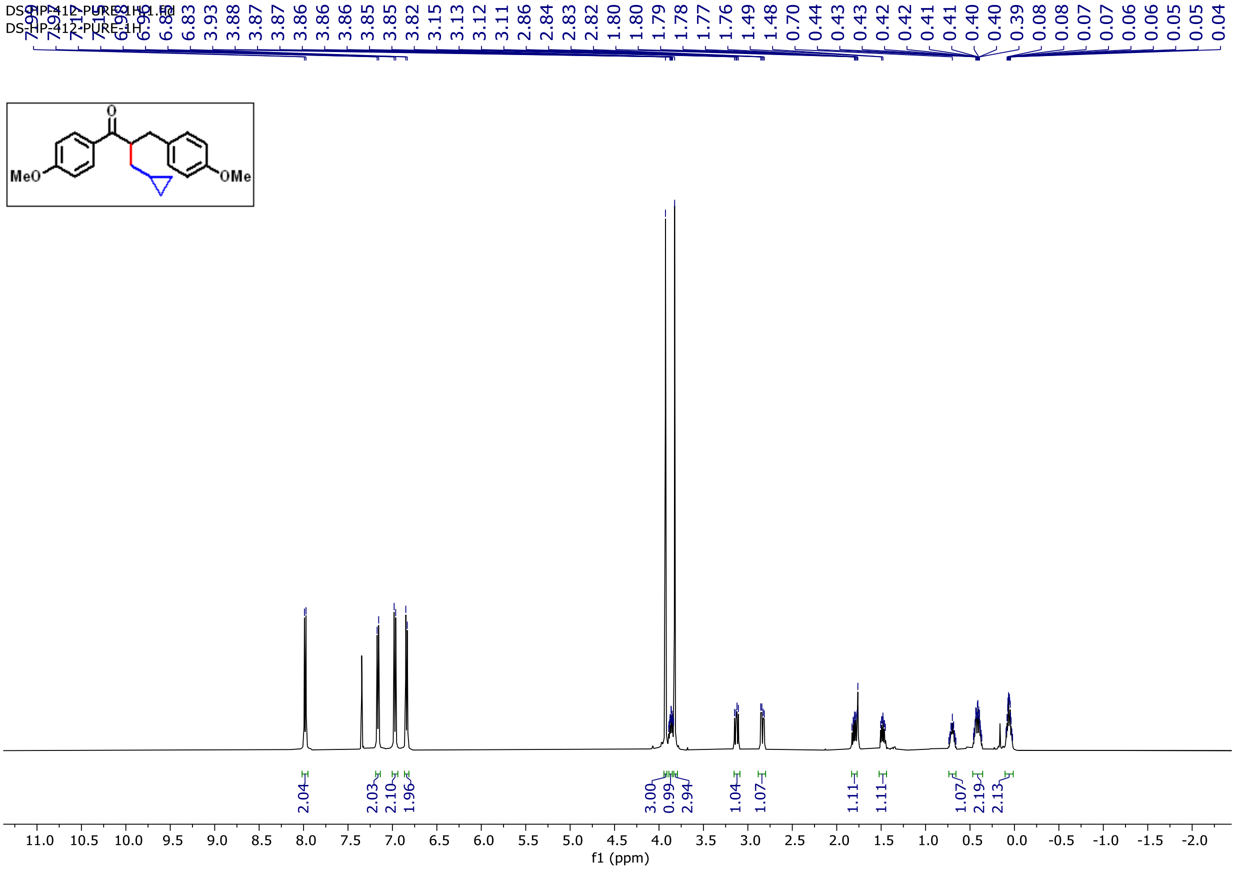




**Figure S48.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3ae** in $CDCl_3$.



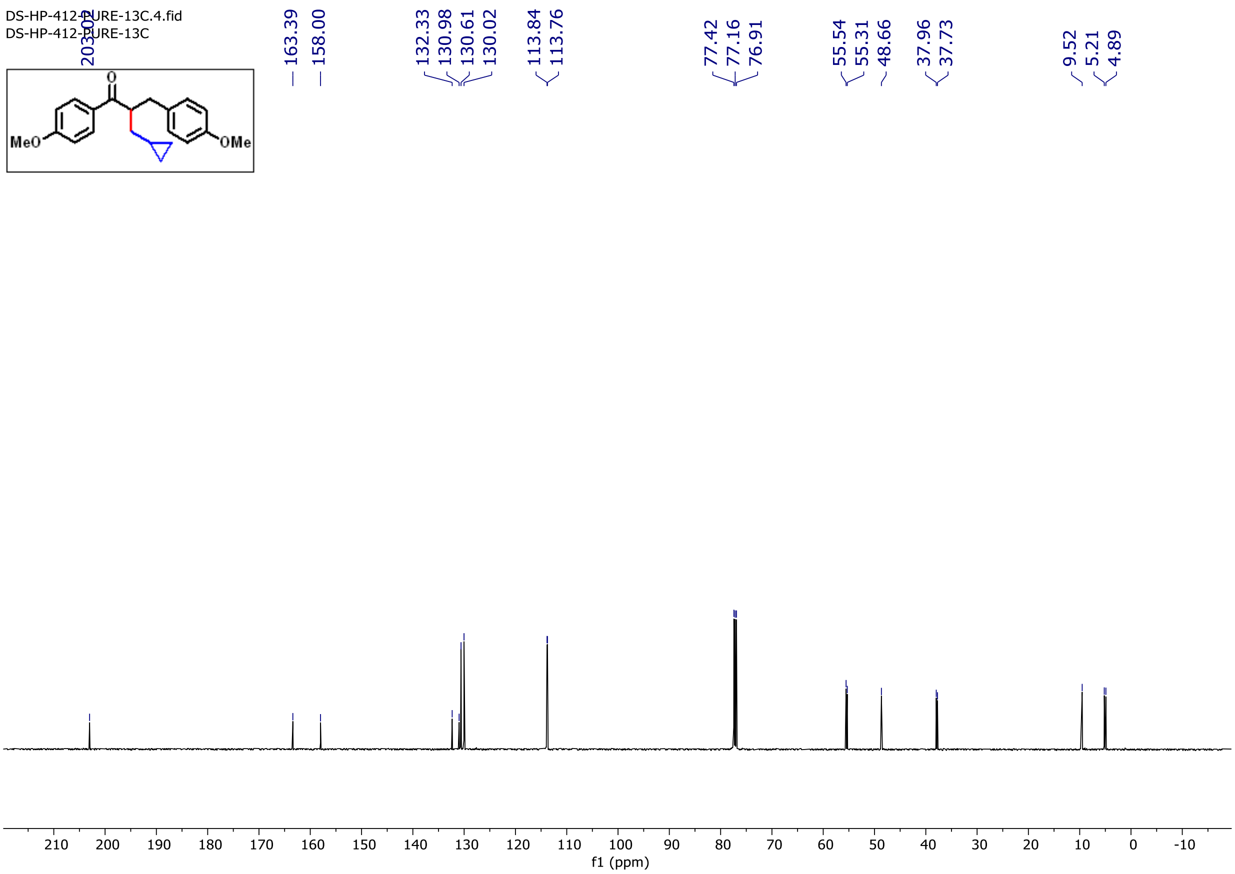
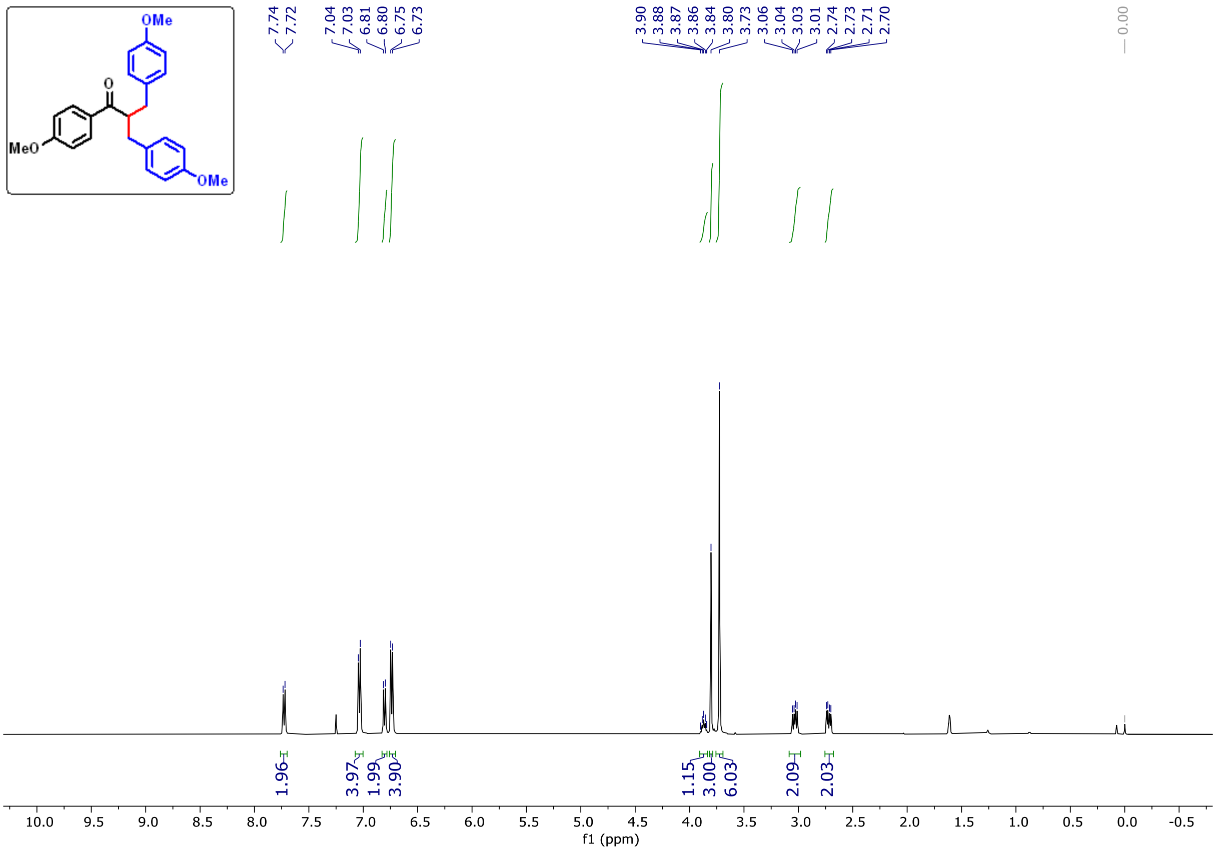




**Figure S49.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3af** in $CDCl_3$.



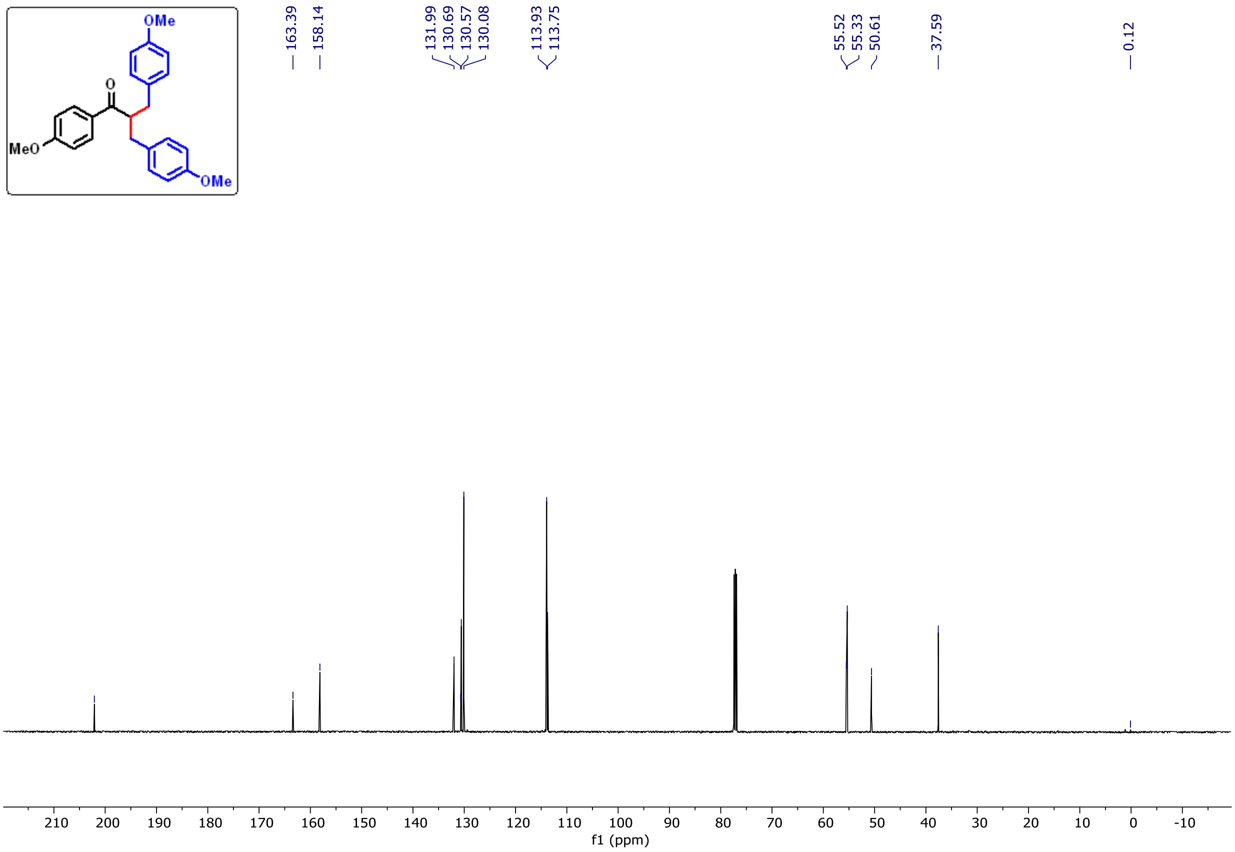
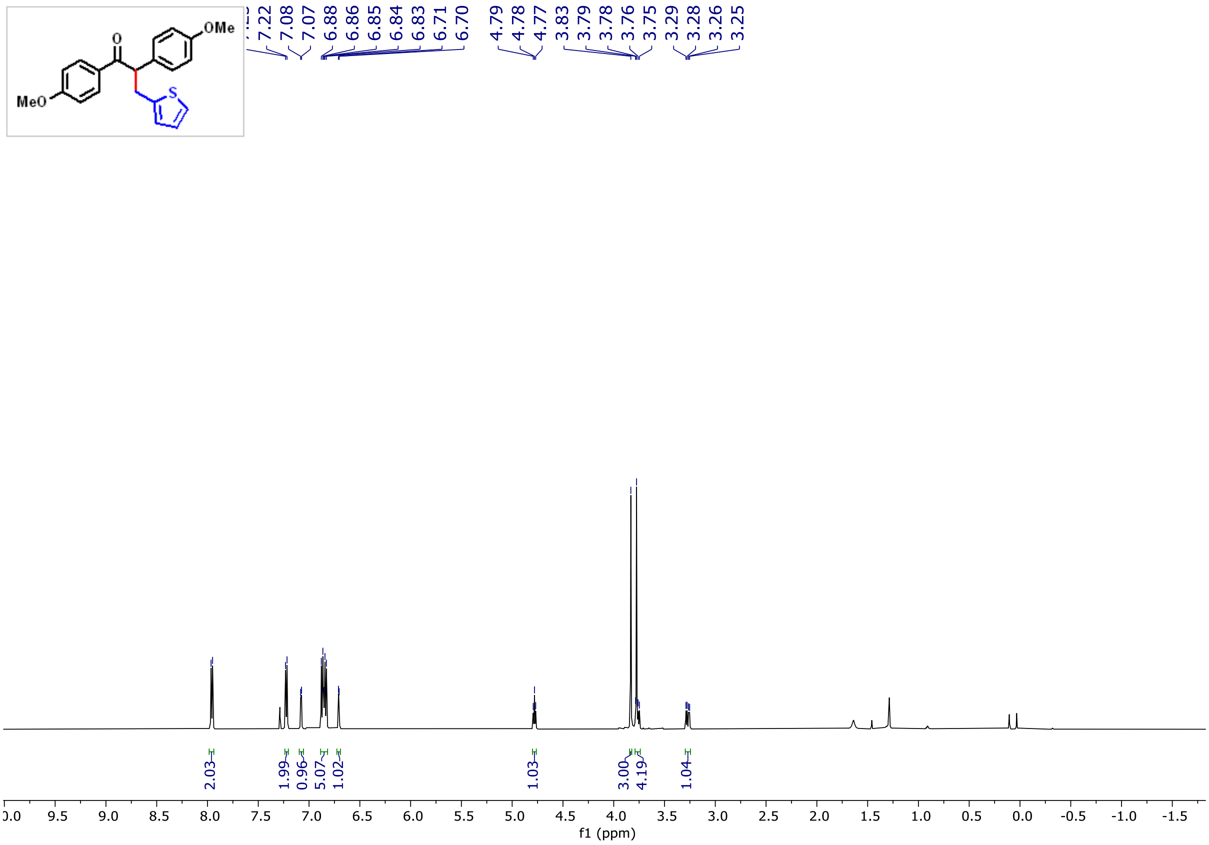




**Figure S50.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3ah** in $CDCl_3$.


OMe
O
MeO
S
7.22
7.08
7.07
6.88
6.86
6.85
6.84
6.83
6.71
6.70
4.79
4.78
4.77
3.83
3.79
3.78
3.76
3.75
3.29
3.28
3.26
3.25
2.03
1.99
0.96
5.07
1.02
1.03
3.00
4.19
1.04
f1 (ppm)

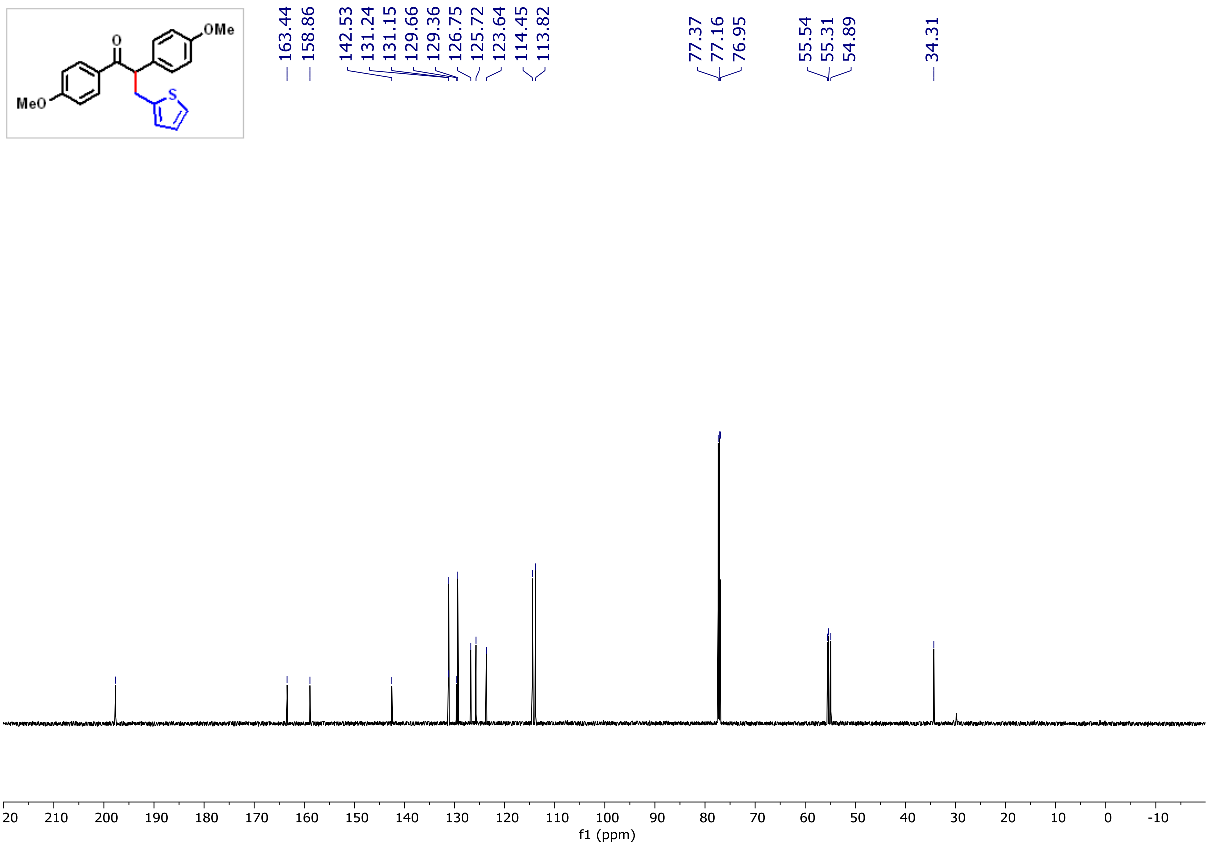
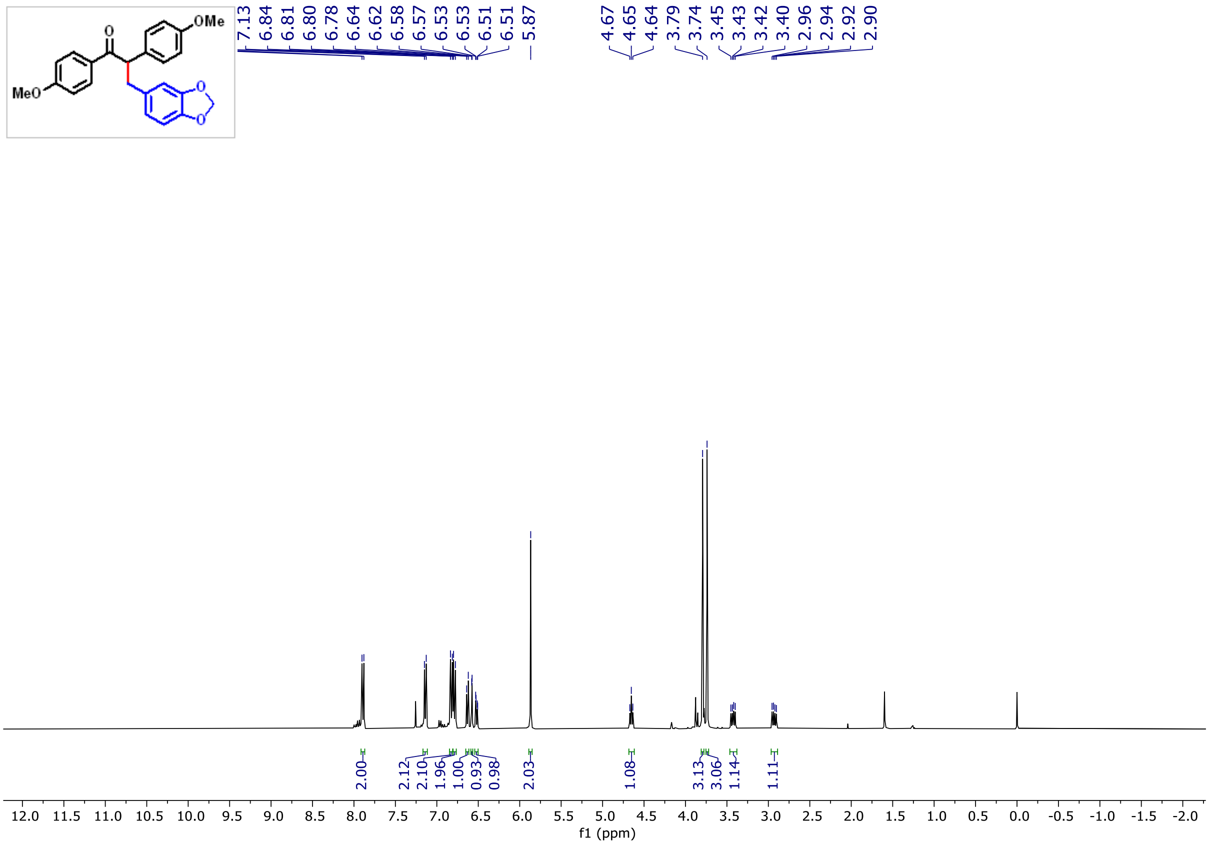

OMe
O
MeO
S
163.44
158.86
142.53
131.24
131.15
129.66
129.36
126.75
125.72
123.64
114.45
113.82
77.37
77.16
76.95
55.54
55.31
54.89
34.31
f1 (ppm)

**Figure S51.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **3ai** in $CDCl_3$.



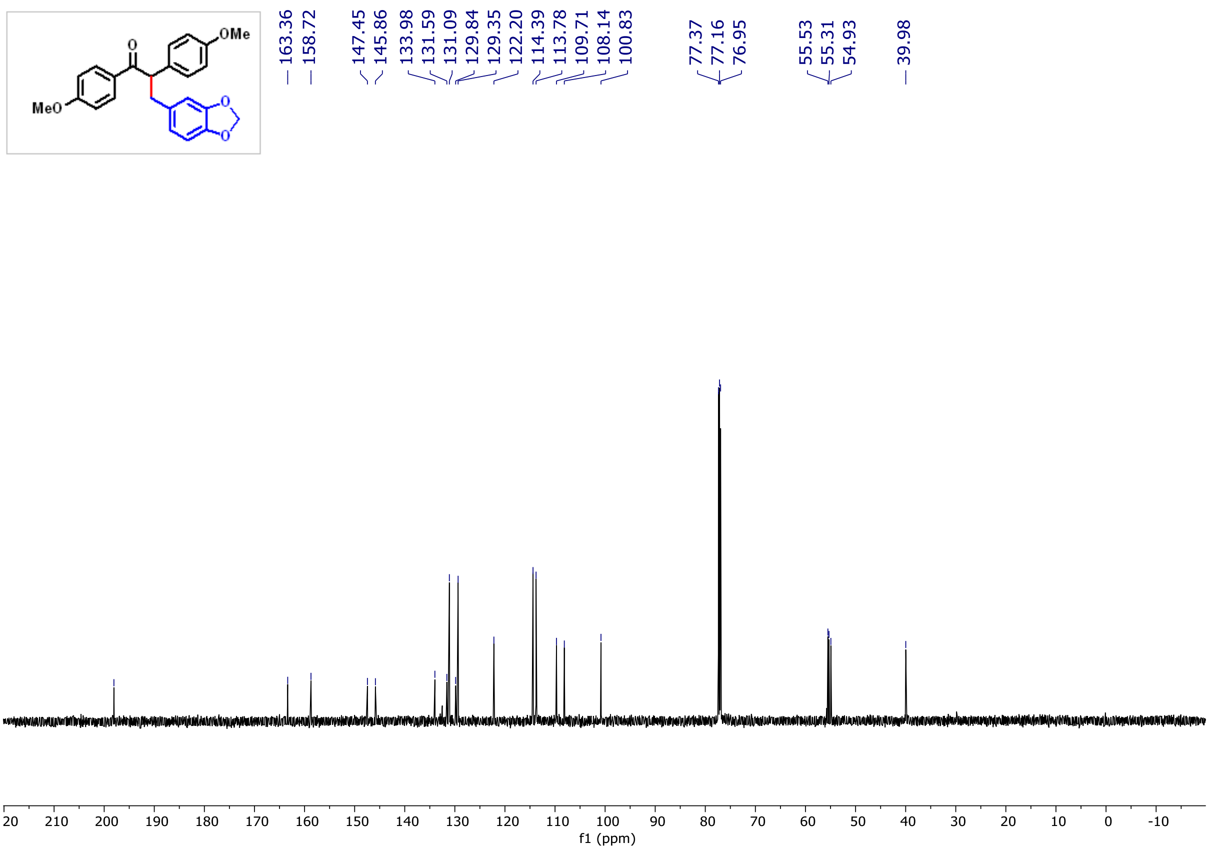
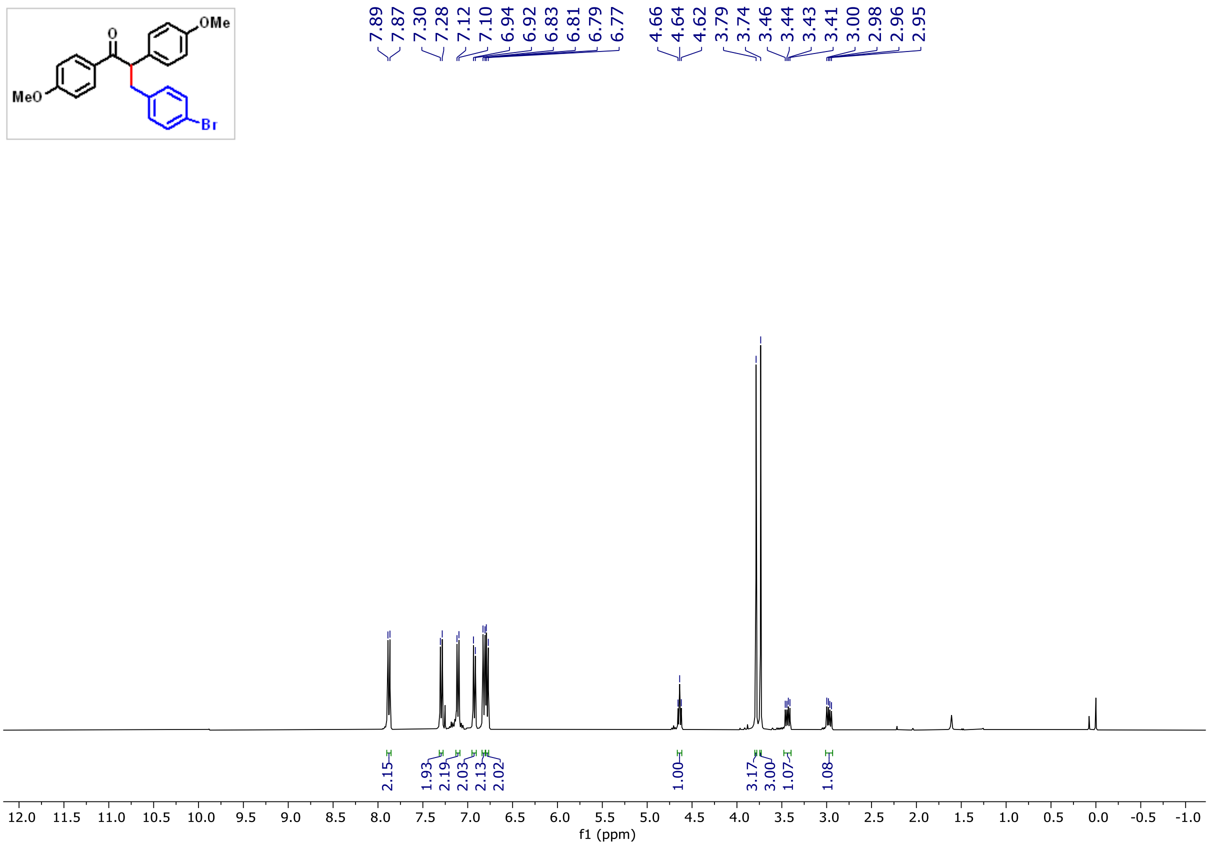



**Figure S52.** $^{1}H$ (400 MHz) and $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectrum of **3aj** in $CDCl_3$.



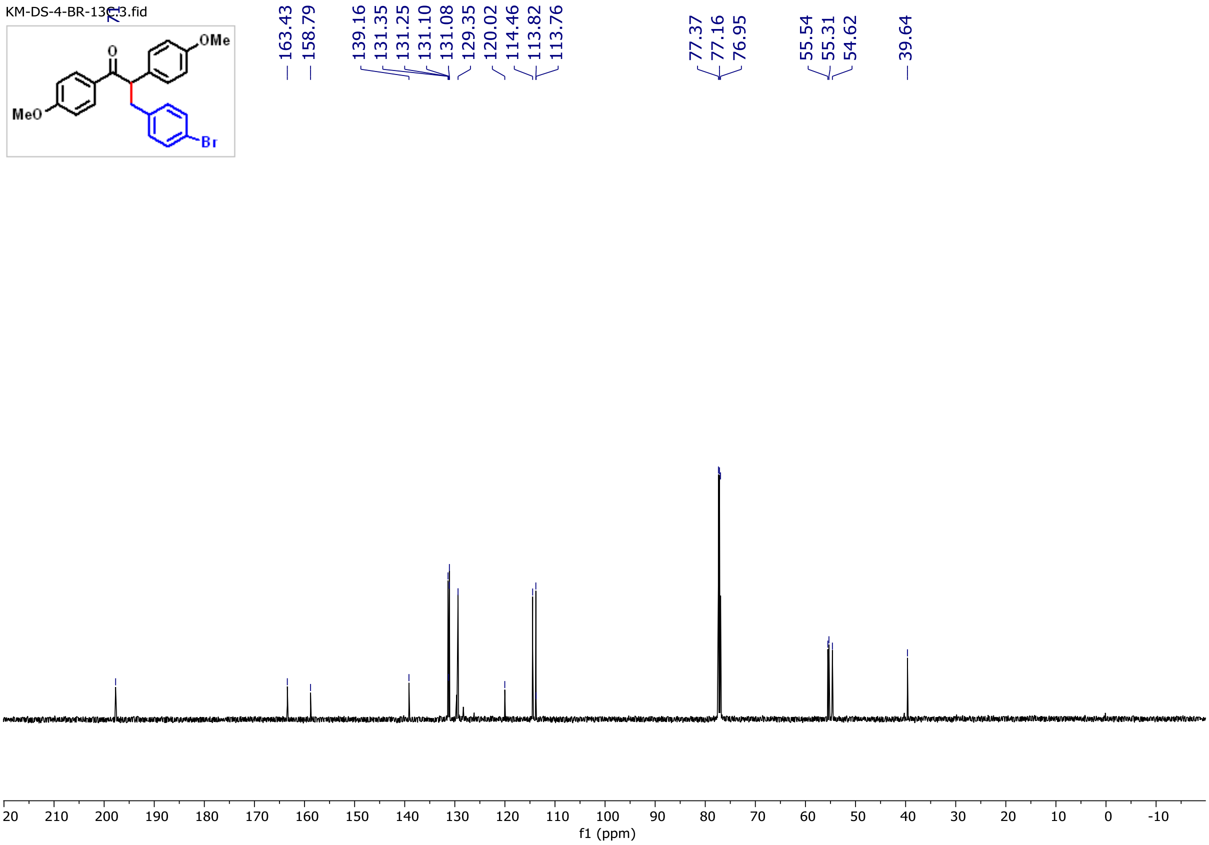
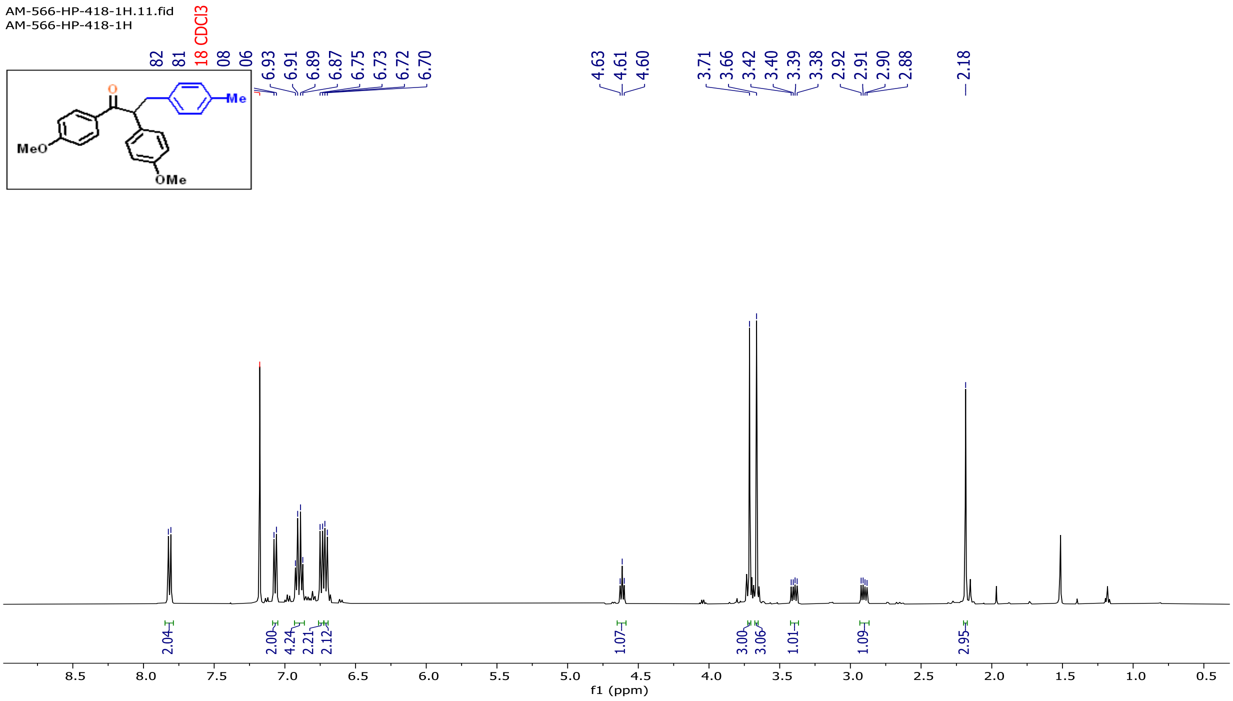



**Figure S53.** $^{1}$H (400 MHz) and $^{13}$C{$^{1}$H} (150 MHz) NMR Spectrum of **3ak** in $CDCl_3$.



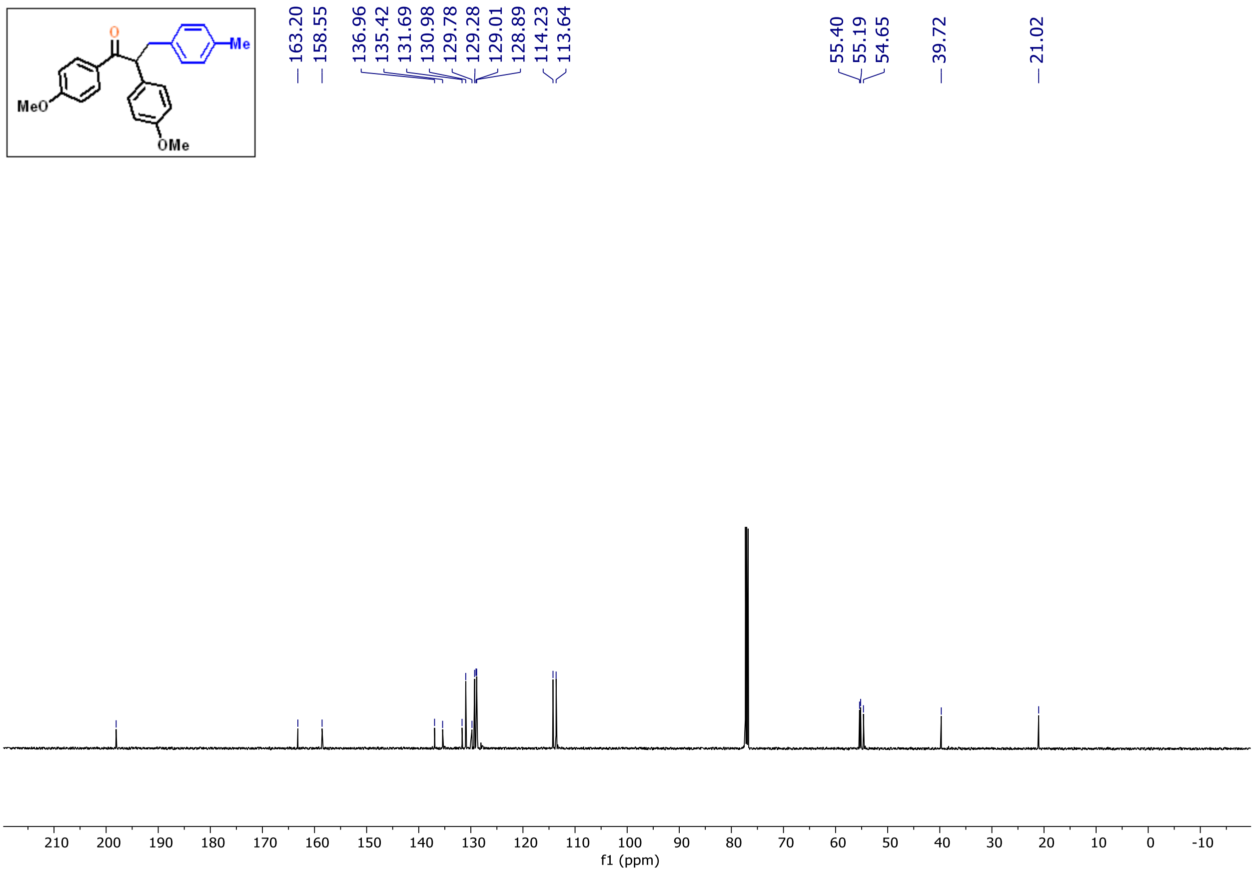
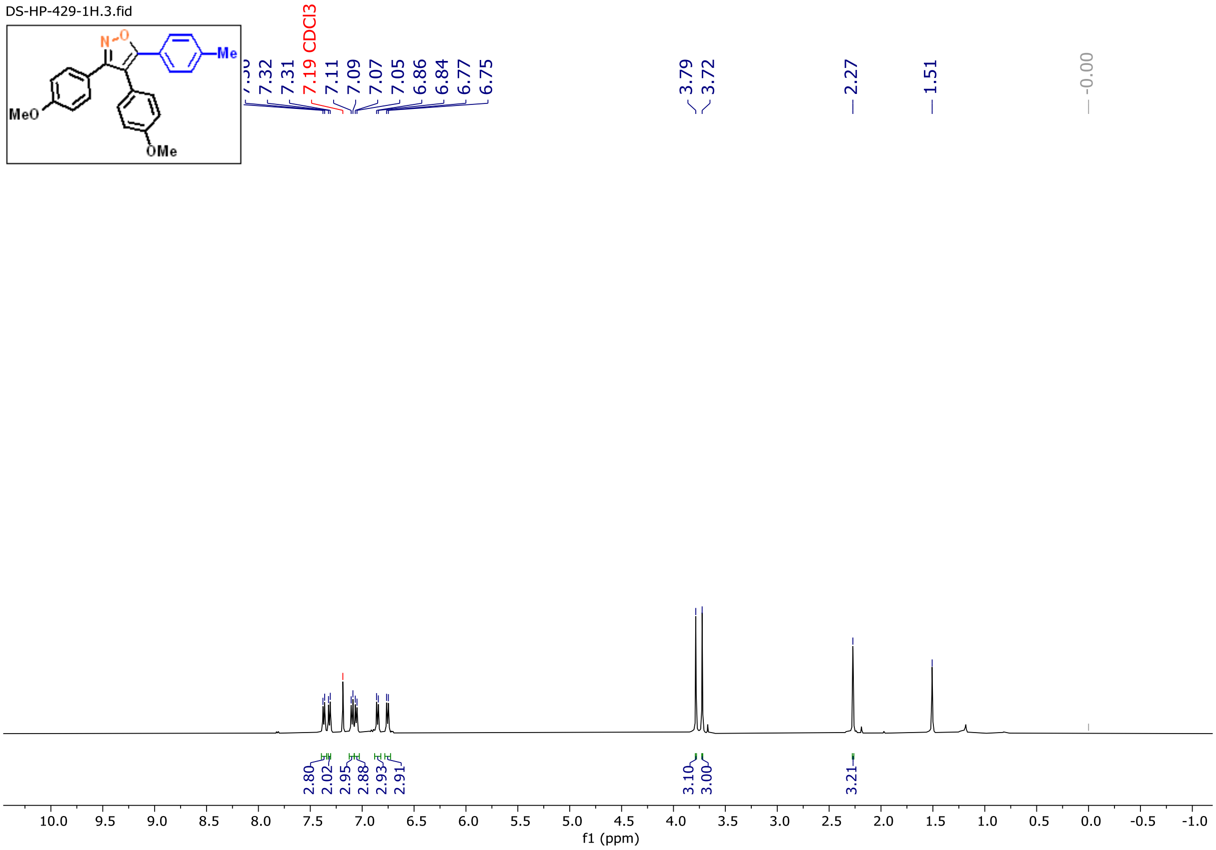




**Figure S54.** $^{1}$H (500 MHz) and $^{13}$C{$^{1}$H} (125 MHz) NMR Spectrum of **3ai** in $CDCl_3$.



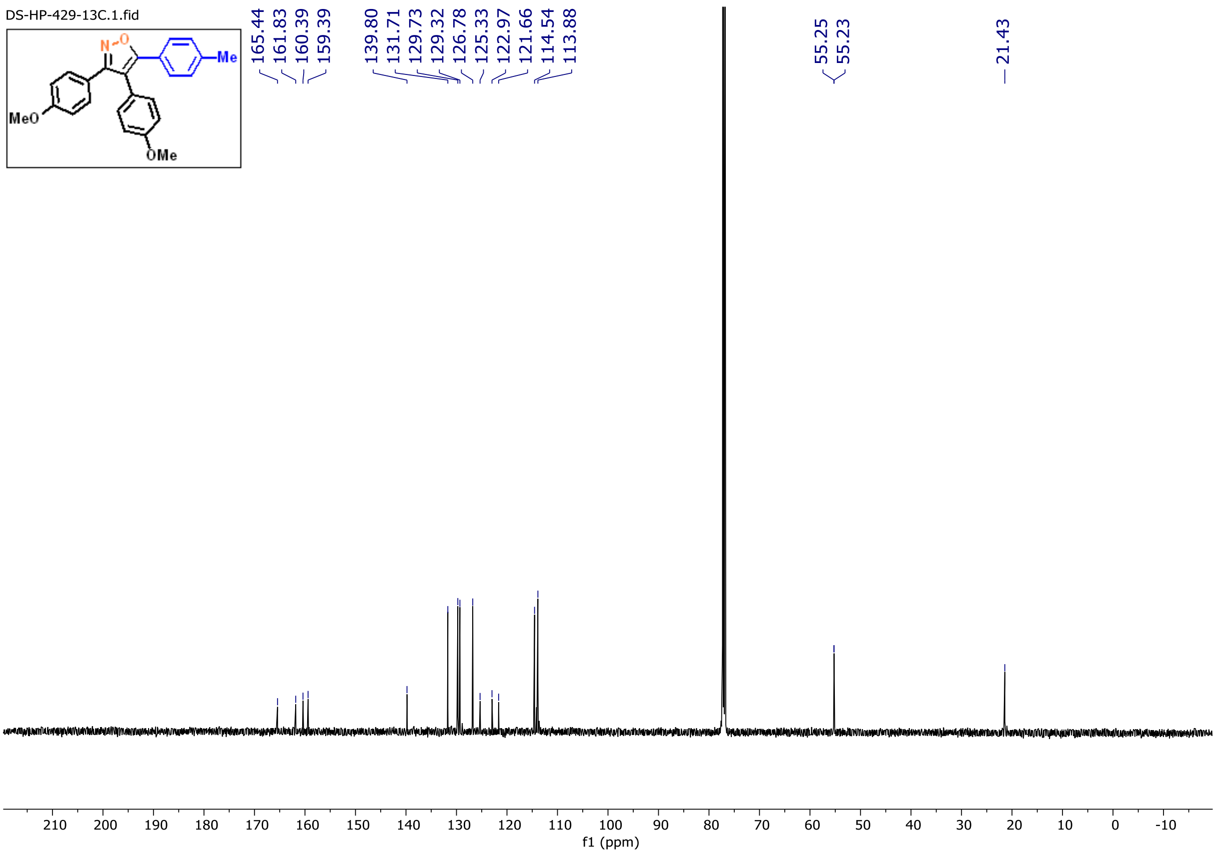
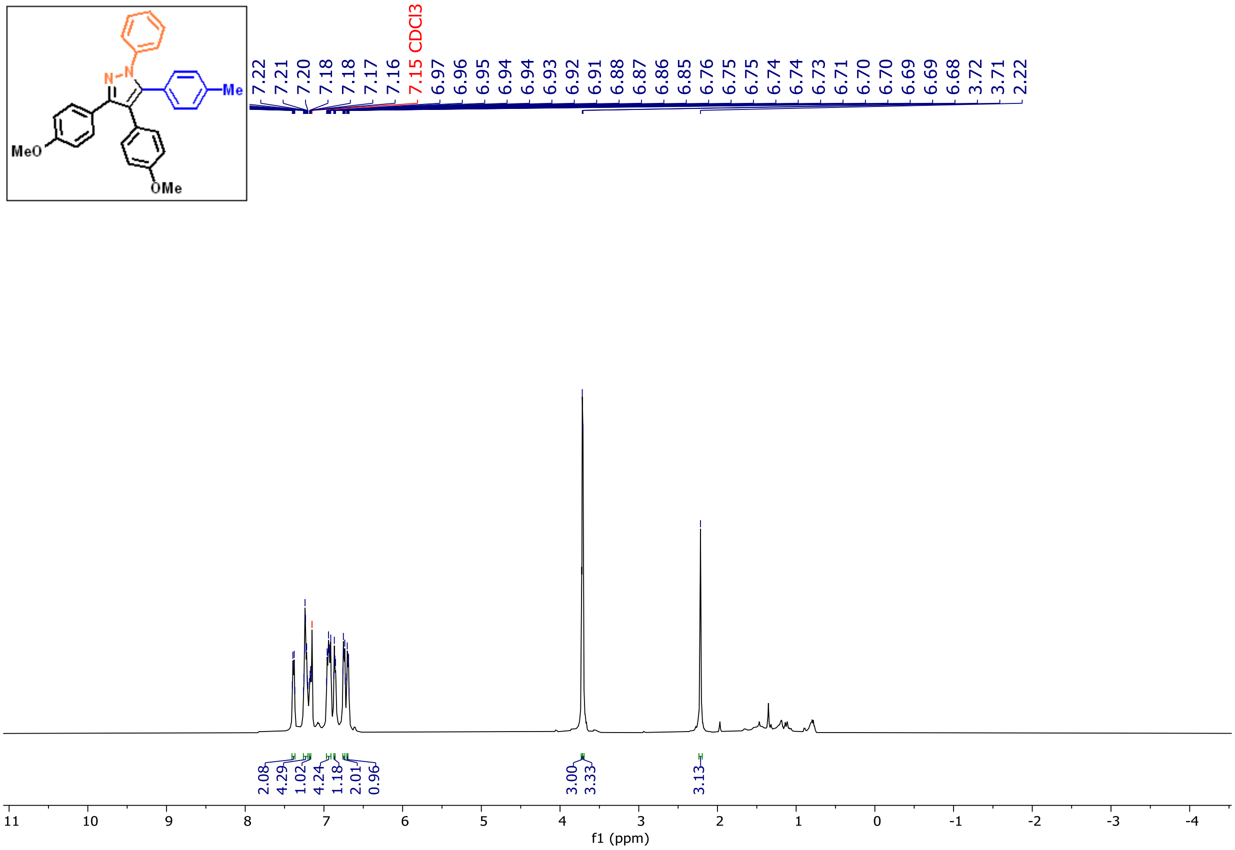




**Figure S55.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **16** in $CDCl_3$.



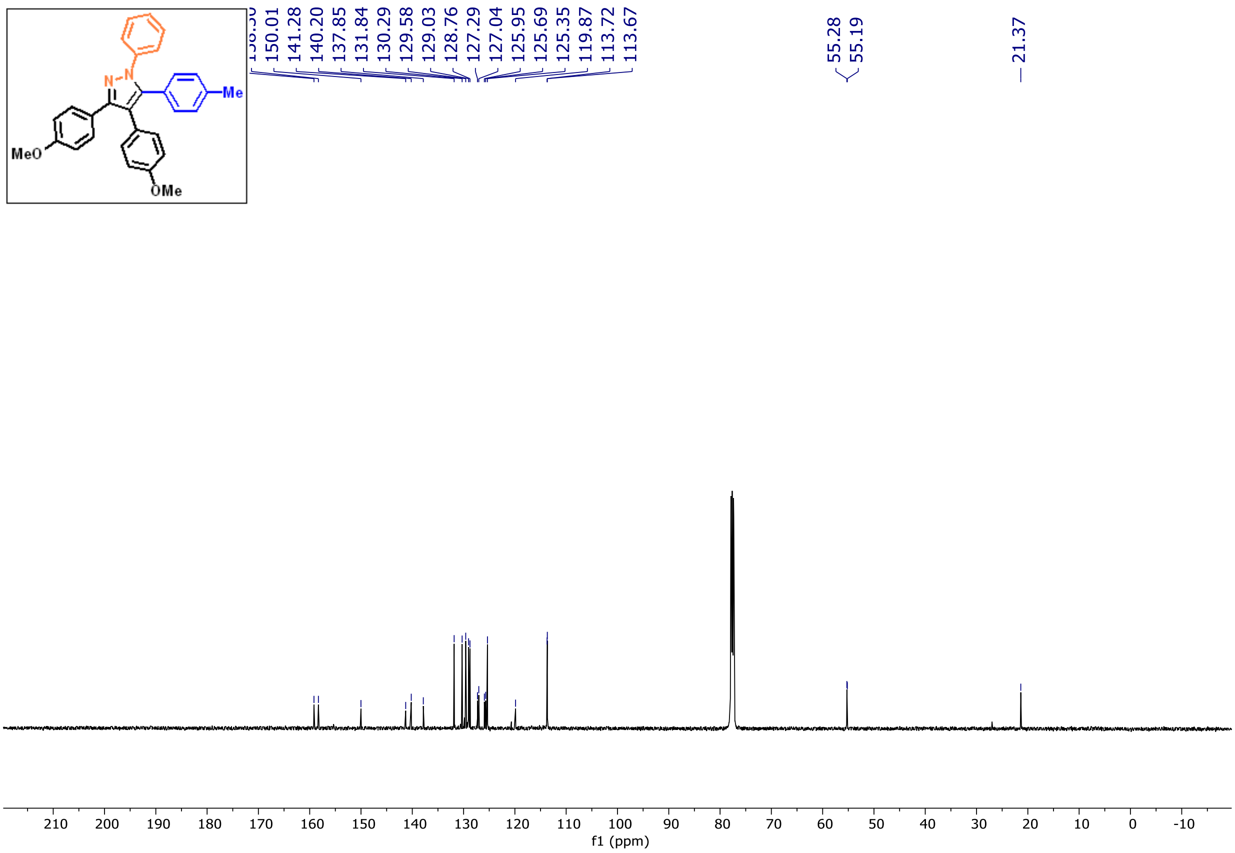
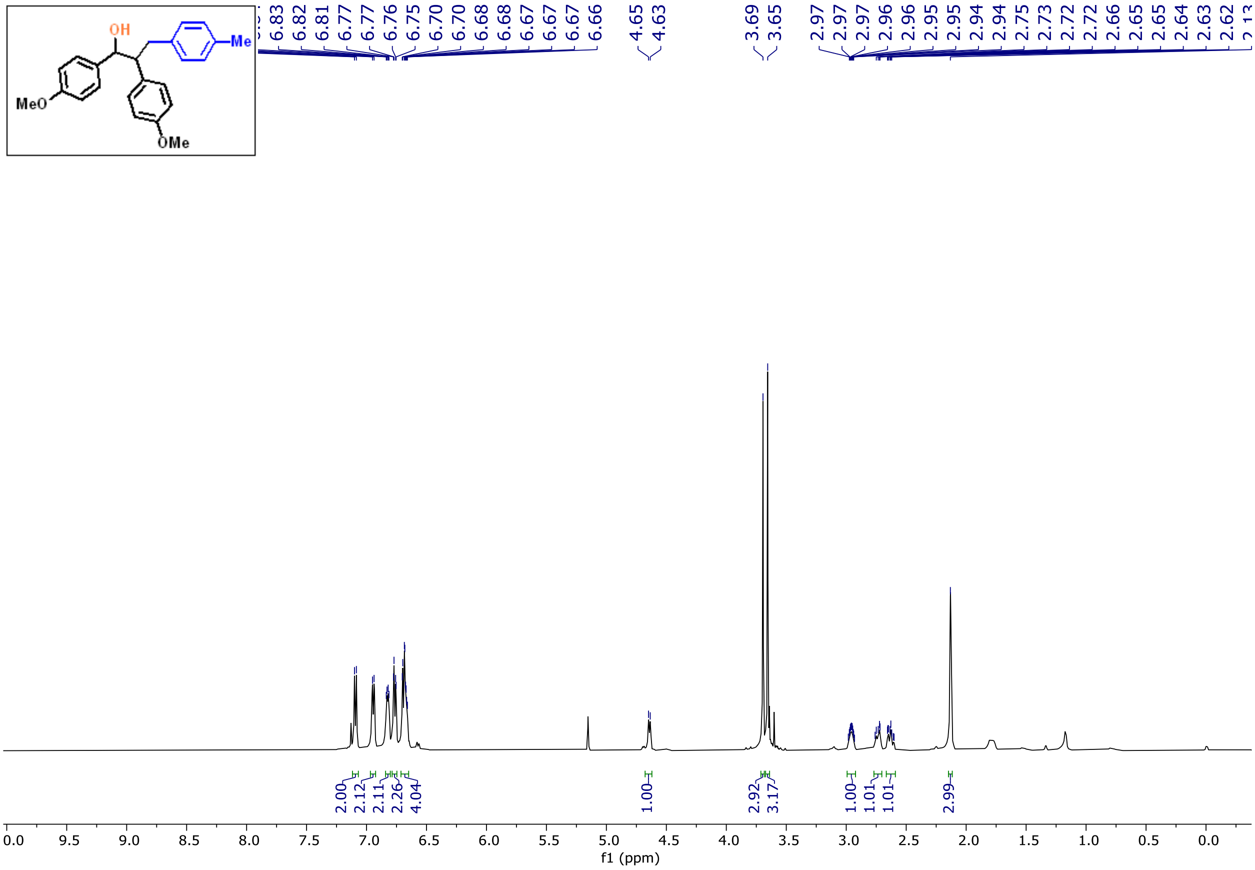


**Figure S56.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **17** in $CDCl_3$.



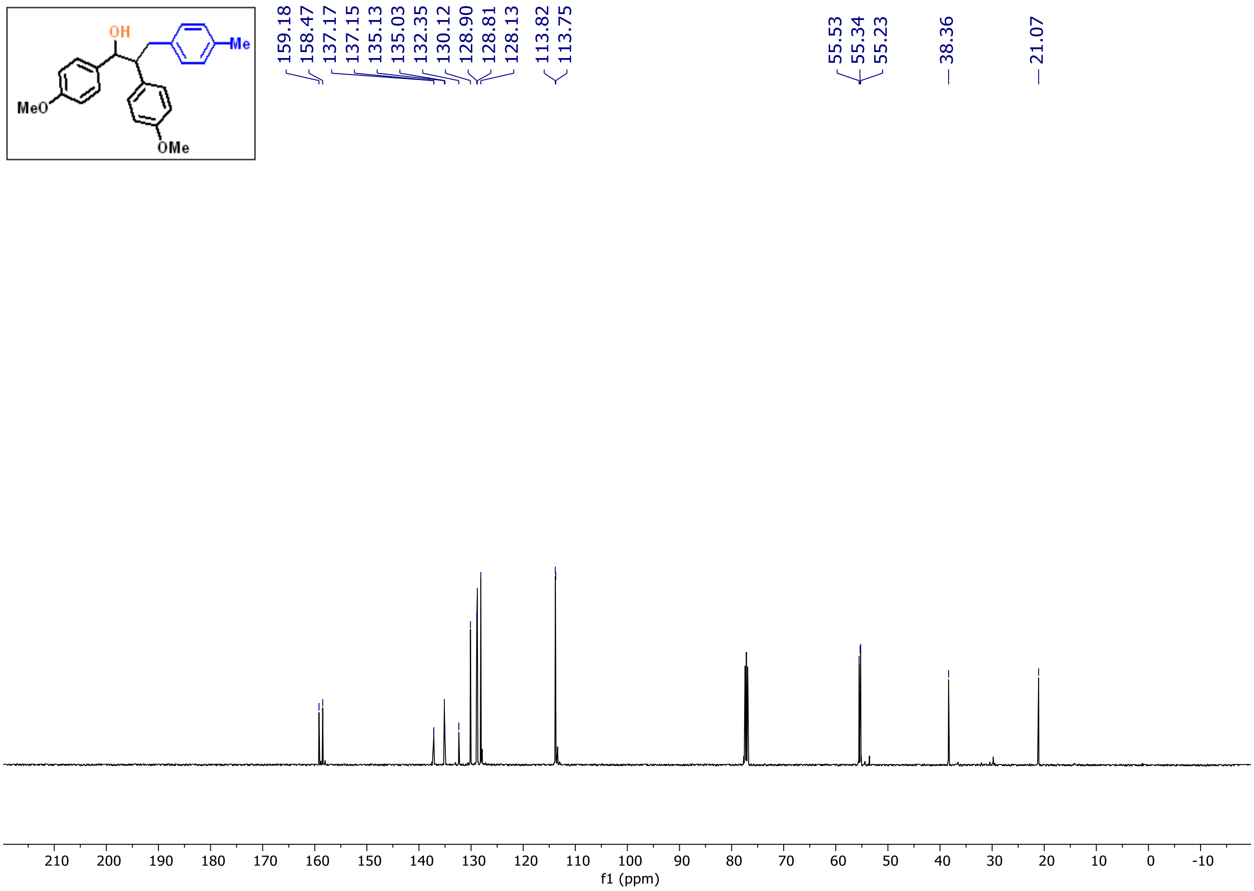
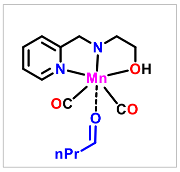


**Figure S57.** $^{1}H$ (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectrum of **18** in $CDCl_3$.

## 15. Computational Details:

All the structures were fully optimized without any symmetry constraints at PBE0 using def2-TZVP basis set for all atoms. Harmonic frequency calculations were also performed at the same level of theory to understand the nature of the transition states. All the intermediates were characterized by real values of the Hessian matrix while the transition states were characterized by one imaginary value of the Hessian matrix. The transition states were further characterized by intrinsic reaction coordinate (IRC) analysis. All calculations were performed in toluene medium using polarizable continuum model (PCM). All energies were zero point corrected. All these calculations were performed using Gaussian 16 suite of program.[27]

### 15.1. Buried Volume Plot-Mn-1n:




| V Free | V Buried | V Total | V Exact |
|---|---|---|---|
| 22.2 | 157.3 | 179.5 | 179.6 |

| %V_Free | **%V_Bur** | % Tot/Ex |
|---|---|---|
| 12.4 | **87.6** | 100.0 |

| Quadrant | V_f | V_b | V_t | %V_f | **%V_b** |
|---|---|---|---|---|---|
| SW | 4.4 | 40.4 | 44.9 | 9.9 | **90.1** |
| NW | 4.2 | 40.6 | 44.9 | 9.5 | **90.5** |
| NE | 6.4 | 38.4 | 44.8 | 14.4 | **85.6** |
| SE | 7.1 | 37.8 | 44.9 | 15.8 | **84.2** |

**Figure S58.** Percentage of buried volume (%V Bur) data.

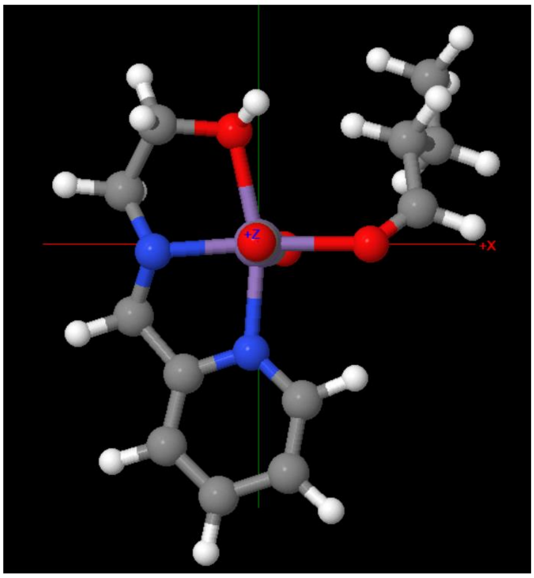



**Figure S59.** The orientation of the catalyst for buried volume analysis.

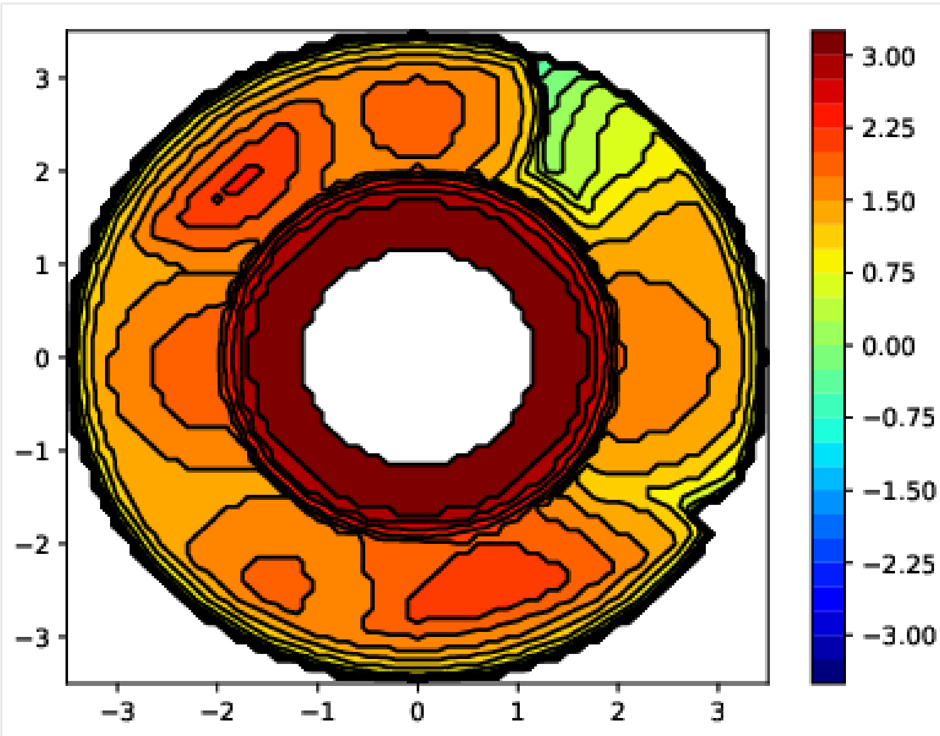
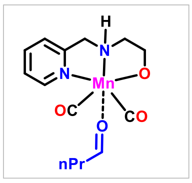



**Figure S60**. Steric map of the catalyst **Mn-1** on the basis of the DFT optimized structure of **Mn-1n**. The steric map is viewed down the z-axis. The red and blue zones indicate the more-hindered and less-hindered zones in the catalytic pocket, respectively.

### 15.2. Buried Volume Plot-Mn-1o:




| V Free | V Buried | V Total | V Exact |
|---|---|---|---|
| 21.3 | 158.2 | 179.5 | 179.6 |

| %V_Free | **%V_Bur** | % Tot/Ex |
|---|---|---|
| 11.9 | **88.1** | 100.0 |

| Quadrant | V_f | V_b | V_t | %V_f | **%V_b** |
|---|---|---|---|---|---|
| SW | 4.9 | 39.9 | 44.9 | 11.0 | **89.0** |
| NW | 3.5 | 41.4 | 44.9 | 7.7 | **92.3** |
| NE | 4.5 | 40.4 | 44.8 | 10.0 | **90.0** |
| SE | 8.4 | 36.5 | 44.9 | 18.7 | **81.3** |

**Figure S61**. **A.** %V Bur, percentage of buried volume data for **Mn-1o**.

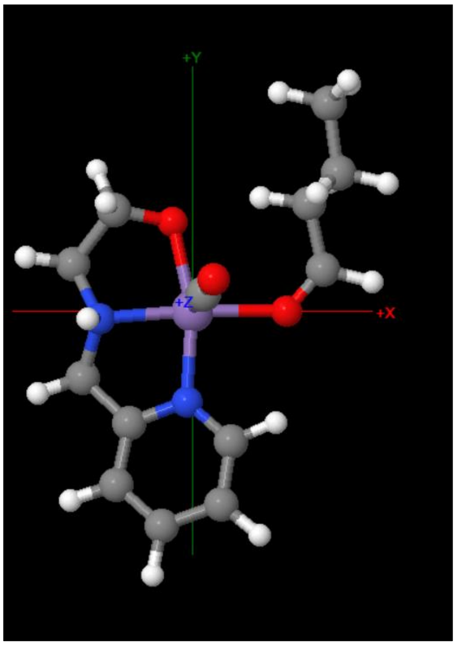



**Figure S62**. The orientation of the catalyst **Mn-1o**.

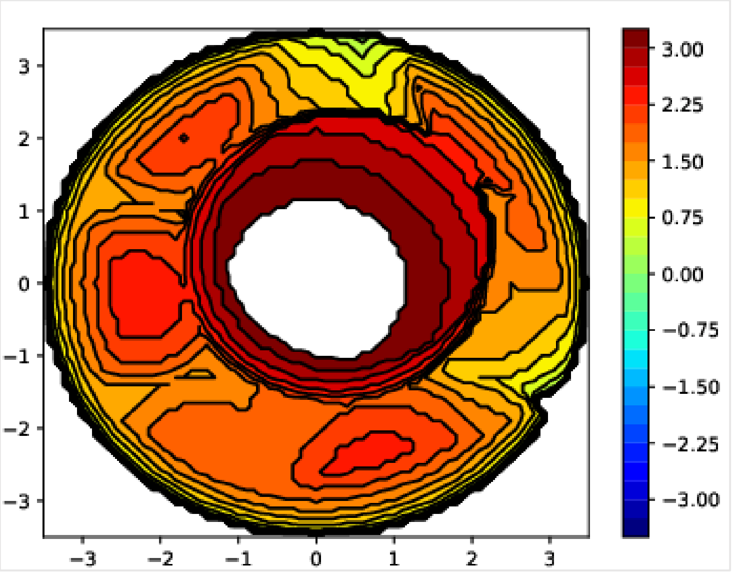
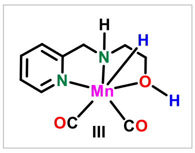



**Figure S63**. Steric map of the catalyst **Mn-1** on the basis of the DFT optimized structure of **Mn-1o**. The steric map is viewed down the z-axis. The red and blue zones indicate the more-hindered and less-hindered zones in the catalytic pocket, respectively.

**Explanation:** Steric maps depict the steric environment around the metal center by partitioning the spatial influence into quadrants and visualizing them with colored contours, typically viewed along the metal-carbonyl bond. These maps provide insight into the ligand's steric profile. The Mn-1o complex exhibits significant steric congestion in all quadrants, as evidenced by the prominent red and orange regions. Conversely, the Mn-1n complex displays a less congested region in the first quadrant, indicated by the green hue in the buried volume plot. But for both the complex enolate binding may preferentially occur in the less hindered oxygen site of the complex.

**15.3. Buried Volume Plot (I)-Mn-III-opt:**



| V Free | V Buried | V Total | V Exact |
|---|---|---|---|
| 170.5 | 211.3 | 381.8 | 381.7 |

| %V_Free | **%V_Bur** | % Tot/Ex |
|---|---|---|
| 44.7 | **55.3** | 100.0 |

| Quadrant | V_f | V_b | V_t | %V_f | **%V_b** |
|---|---|---|---|---|---|
| SW | 45.9 | 49.5 | 95.5 | 48.1 | **51.9** |
| NW | 36.2 | 59.3 | 95.4 | 37.9 | **62.1** |
| NE | 40.3 | 55.1 | 95.4 | 42.2 | **57.8** |
| SE | 48.2 | 47.3 | 95.4 | 50.5 | **49.5** |

**Figure S64**. %V Bur, percentage of buried volume data for **Mn-III**.

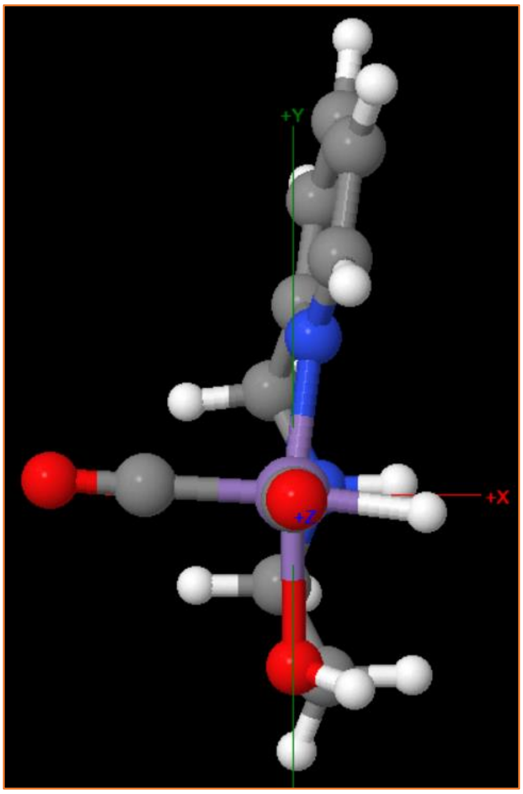



**Figure S65**. The orientation of the catalyst **Mn-III**.

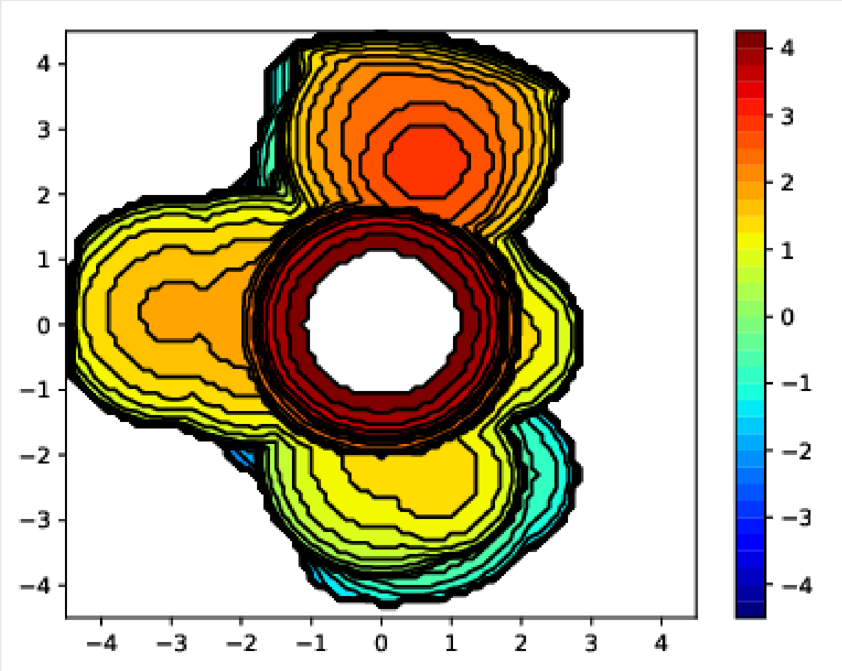



**Figure S66**. Steric map of the catalyst **Mn-1** on the basis of the DFT optimized structure of **III**. The steric map is viewed down the z-axis. The red and blue zones indicate the more-hindered and less-hindered zones in the catalytic pocket, respectively.

**15.4. Gibbs-free energies of cis-enolate pathway for the aldol condensation step to form of bulky *β*-hydroxy ketone.**

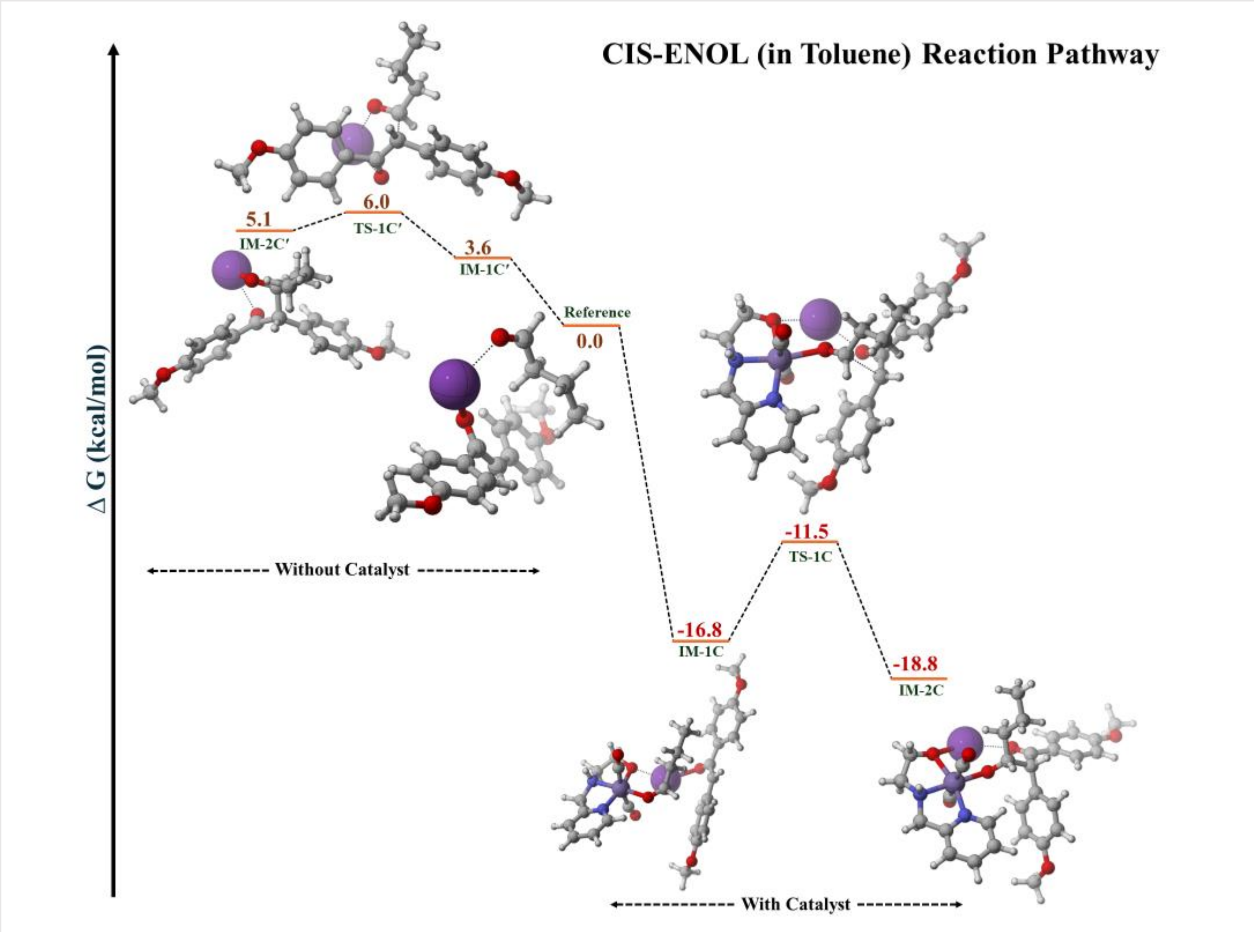



**Figure S67.** Gibbs-free energies of cis-enolate pathway**.**

**15.5. Gibbs-free energies of trans-enolate pathway for the aldol condensation step to form of bulky *β*-hydroxy ketone.**

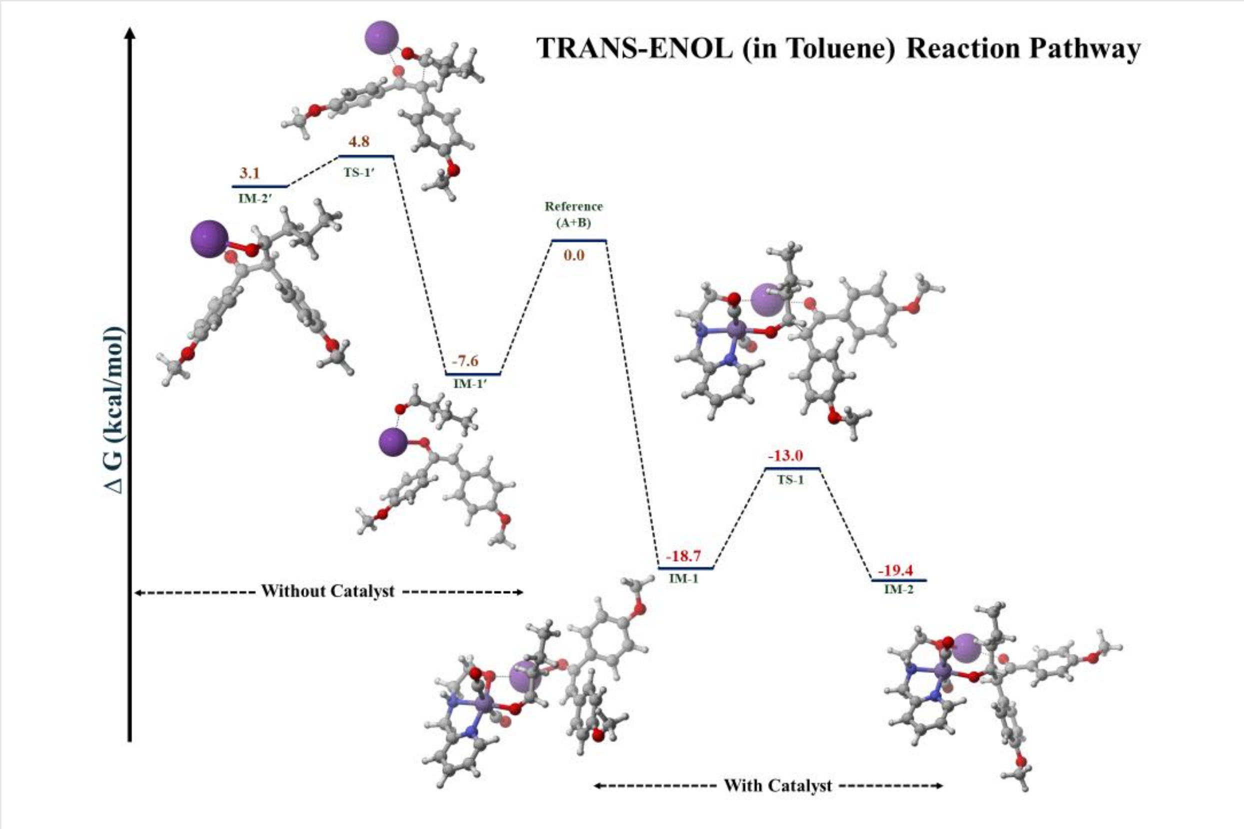



**Figure S68. Gibbs-free energies of trans-enolate pathway.**

### 15.6. Combined Gibbs-free energies of both cis and trans-enolate in one figure:

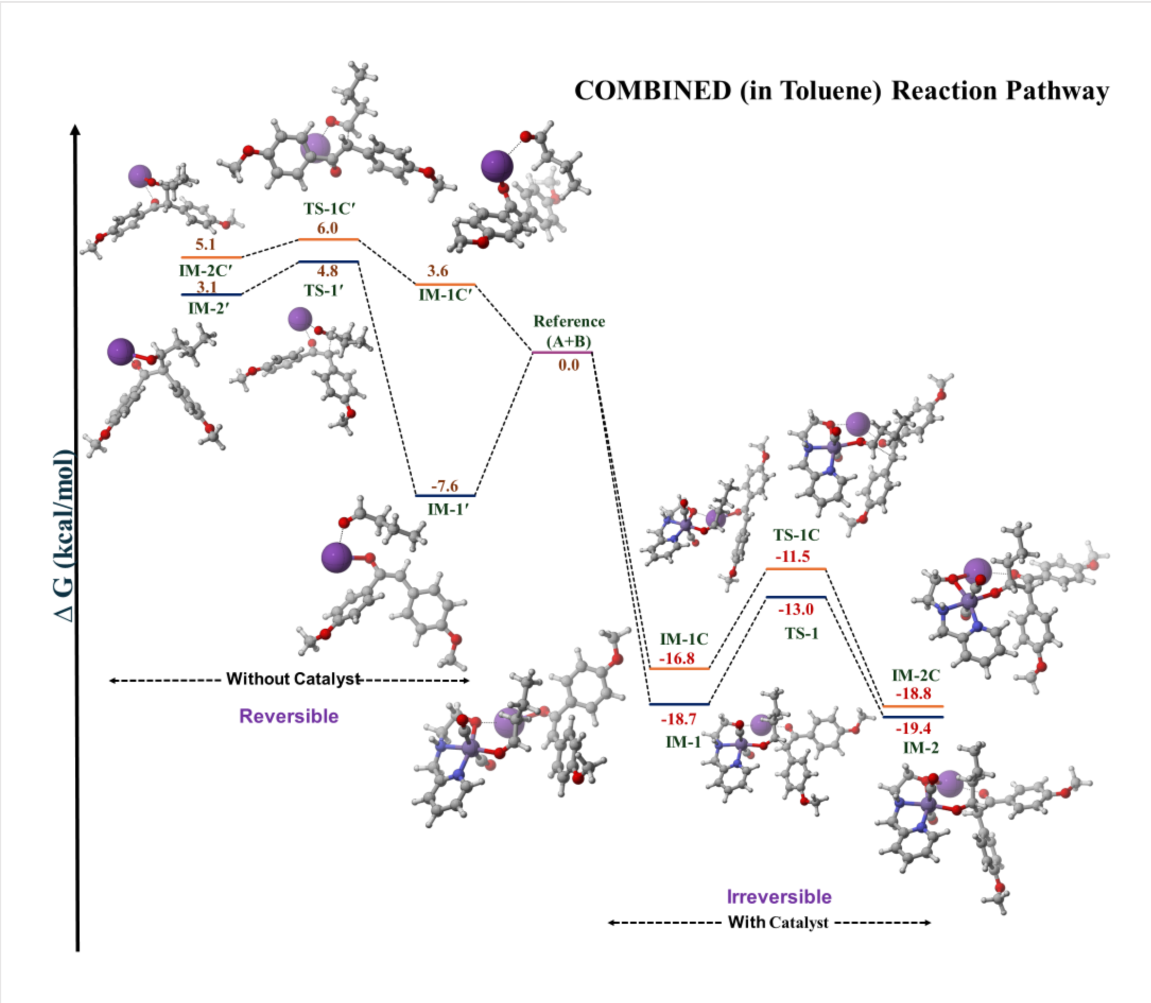
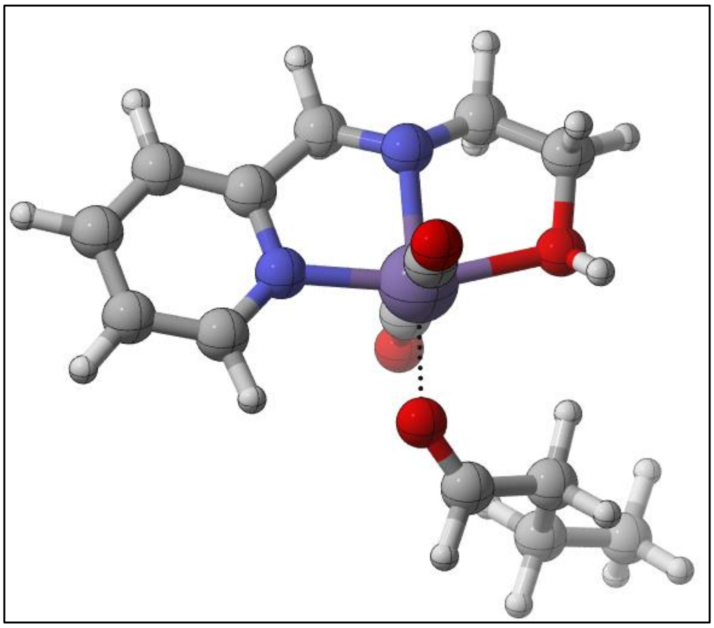



**Figure S69.** Combined Gibbs-free energies of both cis and trans-enolate pathway for comparative study.

## 15.7. Coordinate File:

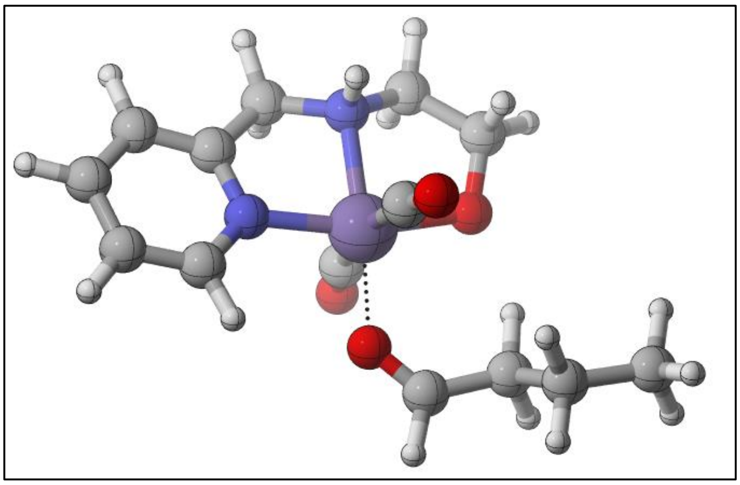
- **Mn-1n:**



| | | | |
|---|---|---|---|
| C | 3.653031000000 | 1.791377000000 | -0.419976000000 |
| C | 2.568053000000 | 0.916815000000 | -0.340553000000 |
| C | 1.382965000000 | 2.456189000000 | 0.946941000000 |
| C | 2.422499000000 | 3.378079000000 | 0.895550000000 |
| C | 3.583361000000 | 3.037183000000 | 0.199595000000 |
| H | 4.540544000000 | 1.486334000000 | -0.965406000000 |
| H | 0.460106000000 | 2.659504000000 | 1.480520000000 |
| H | 2.321808000000 | 4.335301000000 | 1.396261000000 |
| H | 4.419855000000 | 3.727706000000 | 0.145021000000 |
| C | 2.509440000000 | -0.429478000000 | -1.021477000000 |
| H | 2.105602000000 | -0.233894000000 | -2.050136000000 |
| H | 3.537301000000 | -0.807705000000 | -1.178280000000 |
| N | 1.659476000000 | -1.309526000000 | -0.268543000000 |
| C | 1.185199000000 | -2.427240000000 | -1.031515000000 |
| H | 1.974624000000 | -3.158432000000 | -1.296532000000 |
| H | 0.709341000000 | -2.125995000000 | -1.997629000000 |
| C | 0.148088000000 | -3.166443000000 | -0.202654000000 |
| H | -0.321536000000 | -3.987309000000 | -0.756889000000 |
| H | 0.616376000000 | -3.553628000000 | 0.709671000000 |
| O | -0.888445000000 | -2.205859000000 | 0.174391000000 |
| N | 1.448899000000 | 1.254669000000 | 0.346047000000 |
| Mn | 0.090944000000 | -0.259698000000 | 0.395107000000 |

| | | | |
|---|---|---|---|
| C | 0.661508000000 | -0.674586000000 | 2.125224000000 |
| C | -0.586563000000 | 0.253616000000 | -1.265795000000 |
| O | 1.058252000000 | -0.929111000000 | 3.180803000000 |
| O | -1.176083000000 | 0.699083000000 | -2.163038000000 |
| C | -5.450599000000 | -0.304696000000 | -1.183502000000 |
| H | -4.947042000000 | -1.162497000000 | -1.641996000000 |
| H | -6.141752000000 | -0.688208000000 | -0.424244000000 |
| H | -6.045415000000 | 0.185878000000 | -1.960136000000 |
| C | -4.436703000000 | 0.668044000000 | -0.574430000000 |
| H | -3.775050000000 | 1.054629000000 | -1.356932000000 |
| H | -4.963171000000 | 1.531868000000 | -0.147400000000 |
| C | -3.571464000000 | 0.002205000000 | 0.519153000000 |
| H | -4.240155000000 | -0.413205000000 | 1.289625000000 |
| H | -2.977428000000 | -0.815761000000 | 0.100915000000 |
| C | -2.660913000000 | 0.985908000000 | 1.192325000000 |
| H | -3.146831000000 | 1.843189000000 | 1.692739000000 |
| O | -1.430995000000 | 0.924531000000 | 1.218751000000 |
| H | -1.290206000000 | -2.509000000000 | 0.996991000000 |

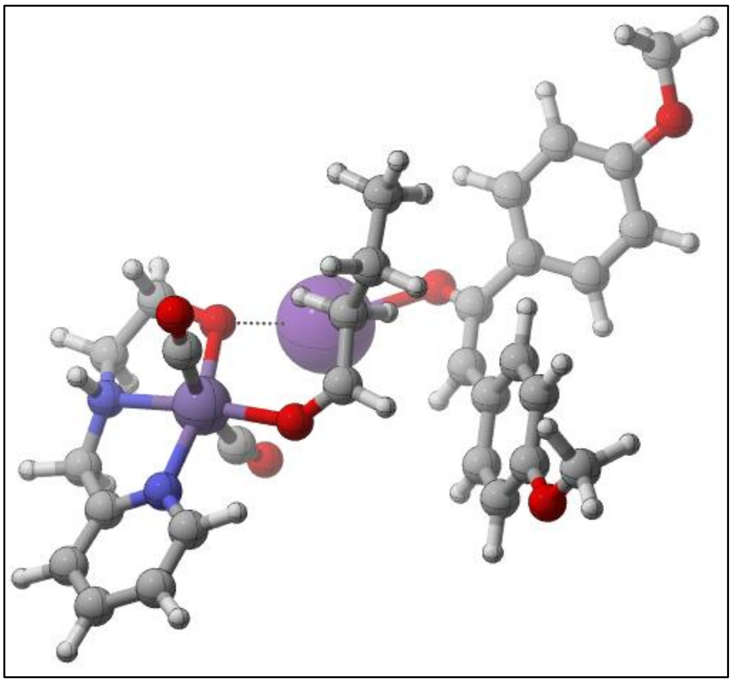
- **<u>Mn-1o:</u>**



| | | | |
|---|---|---|---|
| C | 4.215123000000 | -0.057976000000 | 0.182249000000 |
| C | 2.876349000000 | -0.399354000000 | 0.009680000000 |
| C | 2.248466000000 | 1.836390000000 | 0.055465000000 |
| C | 3.567043000000 | 2.249865000000 | 0.212889000000 |
| C | 4.573898000000 | 1.286821000000 | 0.283492000000 |
| H | 4.965391000000 | -0.841325000000 | 0.232696000000 |

| | | | |
|---|---|---|---|
| H | 1.428106000000 | 2.543887000000 | -0.001116000000 |
| H | 3.792940000000 | 3.308729000000 | 0.284183000000 |
| H | 5.612295000000 | 1.573466000000 | 0.416652000000 |
| C | 2.411364000000 | -1.829130000000 | -0.180263000000 |
| H | 2.359264000000 | -2.045251000000 | -1.255132000000 |
| H | 3.126375000000 | -2.535834000000 | 0.264178000000 |
| N | 1.045033000000 | -1.964833000000 | 0.351024000000 |
| H | 1.092298000000 | -1.991385000000 | 1.367374000000 |
| C | 0.215269000000 | -3.110748000000 | -0.100979000000 |
| H | 0.512967000000 | -4.048916000000 | 0.391929000000 |
| H | 0.362949000000 | -3.218099000000 | -1.180581000000 |
| C | -1.252794000000 | -2.721424000000 | 0.181031000000 |
| H | -1.894160000000 | -3.549577000000 | -0.177210000000 |
| H | -1.364698000000 | -2.710513000000 | 1.294875000000 |
| O | -1.579034000000 | -1.520553000000 | -0.406860000000 |
| N | 1.894727000000 | 0.539307000000 | -0.041138000000 |
| Mn | 0.020420000000 | -0.239069000000 | -0.184561000000 |
| C | -0.493352000000 | 0.127845000000 | 1.547225000000 |
| C | 0.114893000000 | -0.565568000000 | -2.030527000000 |
| O | -0.908738000000 | 0.422220000000 | 2.591409000000 |
| O | 0.004904000000 | -0.732762000000 | -3.168899000000 |
| C | -5.381122000000 | 0.700898000000 | 0.685369000000 |
| H | -6.002644000000 | 0.790793000000 | -0.212759000000 |
| H | -5.148859000000 | -0.359501000000 | 0.825866000000 |
| H | -5.977556000000 | 1.033404000000 | 1.541149000000 |
| C | -4.097764000000 | 1.526510000000 | 0.555745000000 |
| H | -4.351011000000 | 2.589237000000 | 0.437412000000 |
| H | -3.512138000000 | 1.443119000000 | 1.478659000000 |
| C | -3.227313000000 | 1.049527000000 | -0.631622000000 |
| H | -2.896651000000 | 0.010945000000 | -0.499028000000 |
| H | -3.825373000000 | 1.124995000000 | -1.553355000000 |
| C | -2.038091000000 | 1.934408000000 | -0.809661000000 |
| H | -2.235272000000 | 2.997375000000 | -1.047280000000 |
| O | -0.859511000000 | 1.598456000000 | -0.693008000000 |

- **IM-1:**

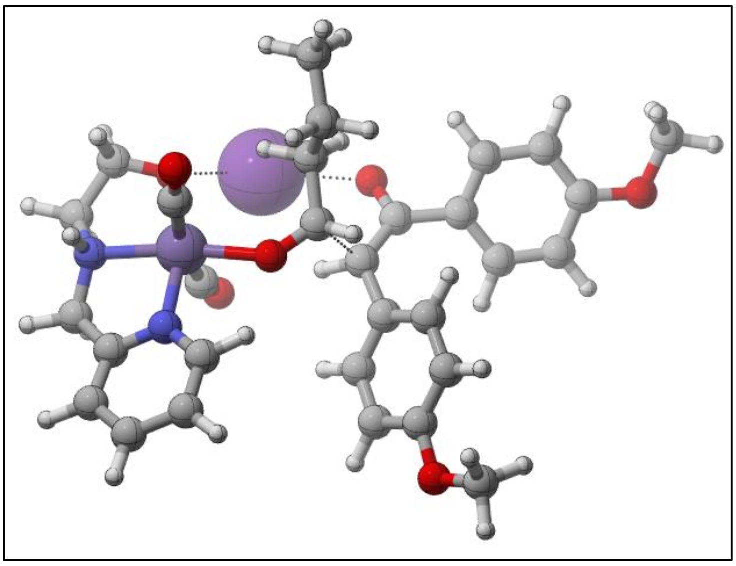


| | | | |
|---|---|---|---|
| C | 3.033758000000 | 1.465375000000 | 2.198949000000 |
| C | 2.207081000000 | 0.709628000000 | 1.371414000000 |
| C | 0.919162000000 | 2.575428000000 | 0.864254000000 |
| C | 1.712866000000 | 3.394237000000 | 1.661801000000 |
| C | 2.788302000000 | 2.830798000000 | 2.347469000000 |
| H | 3.860758000000 | 0.986876000000 | 2.714521000000 |
| H | 0.072825000000 | 2.960402000000 | 0.306105000000 |
| H | 1.483591000000 | 4.451488000000 | 1.741389000000 |
| H | 3.422084000000 | 3.438652000000 | 2.985446000000 |
| C | 2.447476000000 | -0.760555000000 | 1.092791000000 |
| H | 3.062675000000 | -0.854785000000 | 0.188829000000 |
| H | 2.997522000000 | -1.232046000000 | 1.918876000000 |
| N | 1.156364000000 | -1.409760000000 | 0.806779000000 |
| H | 0.654089000000 | -1.521603000000 | 1.685337000000 |
| C | 1.158884000000 | -2.720477000000 | 0.114004000000 |
| H | 1.440023000000 | -3.541682000000 | 0.790243000000 |
| H | 1.896466000000 | -2.665310000000 | -0.693796000000 |
| C | -0.251646000000 | -2.903971000000 | -0.482524000000 |
| H | -0.269043000000 | -3.880200000000 | -1.005832000000 |
| H | -0.952817000000 | -3.011358000000 | 0.376632000000 |
| O | -0.594463000000 | -1.854966000000 | -1.319761000000 |
| N | 1.151758000000 | 1.257448000000 | 0.718395000000 |

| | | | |
|---|---|---|---|
| Mn | 0.063999000000 | -0.088726000000 | -0.371952000000 |
| C | -1.395436000000 | -0.140402000000 | 0.782683000000 |
| C | 1.213933000000 | -0.127539000000 | -1.813992000000 |
| O | -2.356902000000 | -0.129972000000 | 1.427210000000 |
| O | 1.742841000000 | -0.246335000000 | -2.844070000000 |
| C | -5.307311000000 | -0.551243000000 | -2.373310000000 |
| H | -5.257647000000 | -0.683332000000 | -3.459686000000 |
| H | -5.010321000000 | -1.496526000000 | -1.904702000000 |
| H | -6.351620000000 | -0.361560000000 | -2.105305000000 |
| C | -4.405891000000 | 0.599123000000 | -1.914223000000 |
| H | -4.731157000000 | 1.534272000000 | -2.384939000000 |
| H | -4.500879000000 | 0.733999000000 | -0.829567000000 |
| C | -2.926176000000 | 0.346715000000 | -2.268997000000 |
| H | -2.529143000000 | -0.547482000000 | -1.774298000000 |
| H | -2.850739000000 | 0.213278000000 | -3.363400000000 |
| C | -2.050132000000 | 1.515300000000 | -1.963837000000 |
| H | -2.384701000000 | 2.501320000000 | -2.321743000000 |
| O | -0.974686000000 | 1.459169000000 | -1.357651000000 |
| C | -1.217807000000 | 2.949418000000 | -5.121325000000 |
| C | -2.203765000000 | 1.954253000000 | -5.372630000000 |
| C | -3.539220000000 | 2.364941000000 | -5.138311000000 |
| C | -3.868485000000 | 3.658985000000 | -4.722421000000 |
| C | -2.867163000000 | 4.609931000000 | -4.497424000000 |
| C | -1.531892000000 | 4.233662000000 | -4.698153000000 |
| H | -0.171815000000 | 2.692348000000 | -5.274181000000 |
| H | -4.348669000000 | 1.660042000000 | -5.287459000000 |
| H | -4.914701000000 | 3.907085000000 | -4.577381000000 |
| H | -0.752406000000 | 4.970288000000 | -4.525630000000 |
| O | -3.080931000000 | 5.906621000000 | -4.086154000000 |
| C | -4.419167000000 | 6.326989000000 | -3.916324000000 |
| H | -4.935015000000 | 5.752545000000 | -3.133302000000 |
| H | -4.375946000000 | 7.376053000000 | -3.615783000000 |
| C | -1.761270000000 | 0.618611000000 | -5.740024000000 |
| H | -0.678472000000 | 0.488498000000 | -5.665419000000 |
| C | -2.422757000000 | -0.531916000000 | -6.210034000000 |
| C | -3.820931000000 | -0.496985000000 | -6.778246000000 |
| C | -4.677715000000 | -1.580008000000 | -6.553162000000 |

| | | | |
|---|---|---|---|
| C | -4.265948000000 | 0.519003000000 | -7.641793000000 |
| C | -5.953831000000 | -1.641921000000 | -7.118665000000 |
| H | -4.319881000000 | -2.399412000000 | -5.937310000000 |
| C | -5.523841000000 | 0.466579000000 | -8.229376000000 |
| H | -3.607944000000 | 1.354389000000 | -7.858536000000 |
| C | -6.381439000000 | -0.611055000000 | -7.963640000000 |
| H | -6.590646000000 | -2.494074000000 | -6.909453000000 |
| H | -5.864096000000 | 1.244087000000 | -8.906311000000 |
| O | -7.603209000000 | -0.566133000000 | -8.581254000000 |
| C | -8.495090000000 | -1.645444000000 | -8.372166000000 |
| H | -9.390998000000 | -1.416284000000 | -8.952414000000 |
| H | -8.073484000000 | -2.597015000000 | -8.722694000000 |
| H | -8.770123000000 | -1.749252000000 | -7.313767000000 |
| O | -1.865336000000 | -1.686681000000 | -6.206049000000 |
| K | -0.700659000000 | -1.752989000000 | -3.937647000000 |
| H | -4.996651000000 | 6.244201000000 | -4.847526000000 |

➢ **TS-1:**

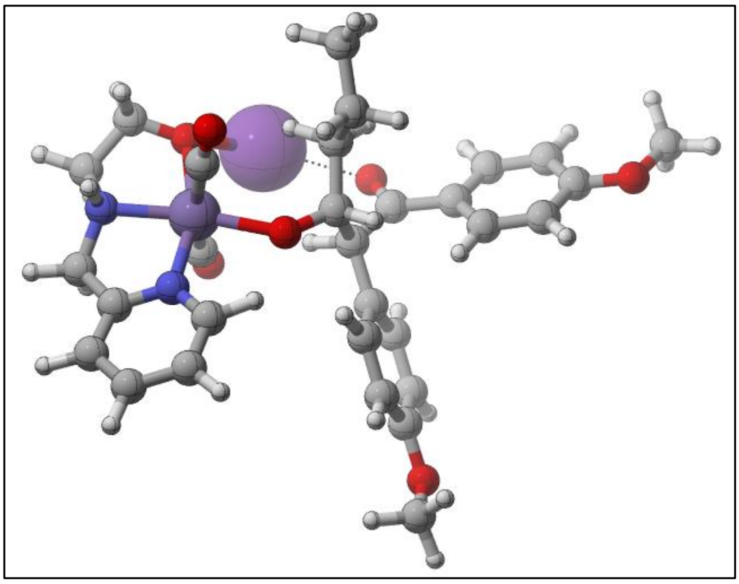


| | | | |
|---|---|---|---|
| C | 2.221119000000 | 2.536930000000 | 1.107070000000 |
| C | 1.674875000000 | 1.379048000000 | 0.559371000000 |
| C | -0.206011000000 | 2.539051000000 | -0.168264000000 |
| C | 0.288375000000 | 3.736761000000 | 0.341196000000 |
| C | 1.519202000000 | 3.738459000000 | 0.996926000000 |
| H | 3.184858000000 | 2.494946000000 | 1.605748000000 |

| | | | |
|---|---|---|---|
| H | -1.148791000000 | 2.459484000000 | -0.699959000000 |
| H | -0.288156000000 | 4.648077000000 | 0.222142000000 |
| H | 1.926951000000 | 4.654329000000 | 1.413792000000 |
| C | 2.398033000000 | 0.047197000000 | 0.550106000000 |
| H | 2.956960000000 | -0.044826000000 | -0.390080000000 |
| H | 3.121388000000 | -0.014503000000 | 1.375808000000 |
| N | 1.402160000000 | -1.037035000000 | 0.564054000000 |
| H | 1.007595000000 | -1.097500000000 | 1.500802000000 |
| C | 1.826797000000 | -2.395012000000 | 0.159369000000 |
| H | 2.427506000000 | -2.890484000000 | 0.938413000000 |
| H | 2.438120000000 | -2.293491000000 | -0.743813000000 |
| C | 0.538743000000 | -3.176284000000 | -0.173207000000 |
| H | 0.839201000000 | -4.201827000000 | -0.469415000000 |
| H | -0.017969000000 | -3.294577000000 | 0.786558000000 |
| O | -0.208724000000 | -2.544821000000 | -1.147541000000 |
| N | 0.468373000000 | 1.379314000000 | -0.057252000000 |
| Mn | -0.148255000000 | -0.453491000000 | -0.712919000000 |
| C | -1.451272000000 | -0.702444000000 | 0.607850000000 |
| C | 0.824660000000 | -0.433451000000 | -2.248853000000 |
| O | -2.324138000000 | -0.850088000000 | 1.352910000000 |
| O | 1.294796000000 | -0.594557000000 | -3.310952000000 |
| C | -5.163592000000 | -2.628611000000 | -1.087508000000 |
| H | -5.397328000000 | -3.154828000000 | -2.021155000000 |
| H | -4.438698000000 | -3.236908000000 | -0.534596000000 |
| H | -6.082040000000 | -2.584048000000 | -0.492301000000 |
| C | -4.607070000000 | -1.228281000000 | -1.363699000000 |
| H | -5.367762000000 | -0.625993000000 | -1.878261000000 |
| H | -4.400168000000 | -0.723504000000 | -0.413218000000 |
| C | -3.324356000000 | -1.259246000000 | -2.217679000000 |
| H | -2.565493000000 | -1.859846000000 | -1.699254000000 |
| H | -3.557900000000 | -1.741939000000 | -3.173096000000 |
| C | -2.757050000000 | 0.149137000000 | -2.412000000000 |
| H | -3.550893000000 | 0.905746000000 | -2.510485000000 |
| O | -1.743637000000 | 0.524694000000 | -1.704912000000 |
| C | -1.001005000000 | 2.647379000000 | -4.468860000000 |
| C | -2.209702000000 | 1.922717000000 | -4.448610000000 |
| C | -3.394773000000 | 2.675619000000 | -4.402904000000 |

| | | | |
|---|---|---|---|
| C | -3.388996000000 | 4.073197000000 | -4.416414000000 |
| C | -2.172989000000 | 4.763694000000 | -4.452483000000 |
| C | -0.975428000000 | 4.037116000000 | -4.473388000000 |
| H | -0.061291000000 | 2.101398000000 | -4.481224000000 |
| H | -4.352345000000 | 2.165291000000 | -4.368351000000 |
| H | -4.333494000000 | 4.604594000000 | -4.389630000000 |
| H | -0.036852000000 | 4.582421000000 | -4.495205000000 |
| O | -2.047802000000 | 6.129900000000 | -4.464599000000 |
| C | -3.232752000000 | 6.903559000000 | -4.454621000000 |
| H | -3.827884000000 | 6.729505000000 | -3.547705000000 |
| H | -2.915144000000 | 7.947895000000 | -4.477319000000 |
| C | -2.173316000000 | 0.438610000000 | -4.355896000000 |
| H | -1.160978000000 | 0.086649000000 | -4.170026000000 |
| C | -2.850791000000 | -0.486535000000 | -5.245151000000 |
| C | -3.984127000000 | -0.113099000000 | -6.159075000000 |
| C | -5.062992000000 | -0.998589000000 | -6.277924000000 |
| C | -3.960688000000 | 1.013083000000 | -7.001723000000 |
| C | -6.115711000000 | -0.759661000000 | -7.160912000000 |
| H | -5.068171000000 | -1.895113000000 | -5.666425000000 |
| C | -4.986394000000 | 1.250052000000 | -7.907173000000 |
| H | -3.123926000000 | 1.699941000000 | -6.959668000000 |
| C | -6.078756000000 | 0.373367000000 | -7.984076000000 |
| H | -6.942266000000 | -1.459087000000 | -7.208198000000 |
| H | -4.964699000000 | 2.109428000000 | -8.569533000000 |
| O | -7.043339000000 | 0.705283000000 | -8.891371000000 |
| C | -8.164225000000 | -0.153029000000 | -9.023955000000 |
| H | -8.798269000000 | 0.294439000000 | -9.791219000000 |
| H | -7.868674000000 | -1.160768000000 | -9.343686000000 |
| H | -8.731516000000 | -0.228322000000 | -8.087097000000 |
| O | -2.544464000000 | -1.710643000000 | -5.221852000000 |
| K | -0.781200000000 | -2.743357000000 | -3.625333000000 |
| H | -3.861010000000 | 6.700522000000 | -5.332512000000 |

- **IM-2:**

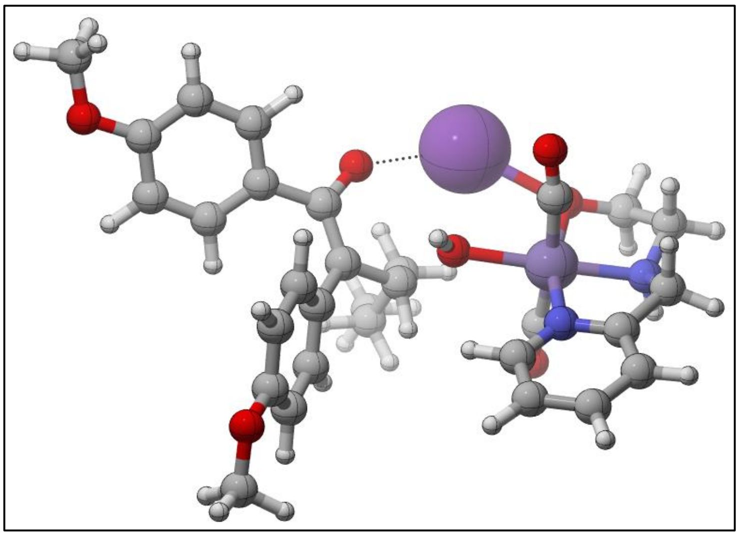


| | | | |
|---|---|---|---|
| C | 3.334394000000 | 2.235199000000 | 4.402049000000 |
| C | 2.958505000000 | 1.090780000000 | 3.703403000000 |
| C | 0.971273000000 | 2.087038000000 | 3.019338000000 |
| C | 1.288834000000 | 3.266795000000 | 3.686603000000 |
| C | 2.490627000000 | 3.347158000000 | 4.390602000000 |
| H | 4.274595000000 | 2.250817000000 | 4.945308000000 |
| H | 0.058148000000 | 1.934140000000 | 2.452282000000 |
| H | 0.598720000000 | 4.103860000000 | 3.656185000000 |
| H | 2.763310000000 | 4.251009000000 | 4.926985000000 |
| C | 3.817098000000 | -0.153481000000 | 3.617931000000 |
| H | 4.413870000000 | -0.116770000000 | 2.697580000000 |
| H | 4.511972000000 | -0.211810000000 | 4.468502000000 |
| N | 2.928111000000 | -1.321575000000 | 3.505656000000 |
| H | 2.479367000000 | -1.470723000000 | 4.407692000000 |
| C | 3.501189000000 | -2.608480000000 | 3.061395000000 |
| H | 4.095289000000 | -3.094065000000 | 3.852268000000 |
| H | 4.156094000000 | -2.401374000000 | 2.208147000000 |
| C | 2.313336000000 | -3.479317000000 | 2.603074000000 |
| H | 2.724761000000 | -4.458295000000 | 2.279858000000 |
| H | 1.710180000000 | -3.699569000000 | 3.515820000000 |
| O | 1.576583000000 | -2.863175000000 | 1.612388000000 |
| N | 1.790227000000 | 1.019069000000 | 3.020971000000 |
| Mn | 1.409096000000 | -0.785506000000 | 2.152608000000 |
| C | 0.043670000000 | -1.258519000000 | 3.346593000000 |

| | | | |
|---|---|---|---|
| C | 2.494604000000 | -0.595192000000 | 0.715700000000 |
| O | -0.846067000000 | -1.552990000000 | 4.024729000000 |
| O | 3.096500000000 | -0.695656000000 | -0.289557000000 |
| C | -3.226379000000 | -3.166473000000 | 1.676669000000 |
| H | -3.443144000000 | -3.785015000000 | 0.796316000000 |
| H | -2.427773000000 | -3.659161000000 | 2.242539000000 |
| H | -4.123580000000 | -3.161362000000 | 2.305438000000 |
| C | -2.814647000000 | -1.747555000000 | 1.273883000000 |
| H | -3.652242000000 | -1.253443000000 | 0.762309000000 |
| H | -2.605015000000 | -1.157052000000 | 2.170847000000 |
| C | -1.584284000000 | -1.710617000000 | 0.354202000000 |
| H | -0.779066000000 | -2.298844000000 | 0.815731000000 |
| H | -1.862271000000 | -2.192389000000 | -0.593578000000 |
| C | -1.054375000000 | -0.261835000000 | 0.157380000000 |
| H | -1.959057000000 | 0.380590000000 | 0.099734000000 |
| O | -0.249297000000 | 0.158762000000 | 1.176379000000 |
| C | 0.237323000000 | 1.800726000000 | -2.943653000000 |
| C | -0.193661000000 | 1.449276000000 | -1.651140000000 |
| C | -0.440554000000 | 2.490468000000 | -0.751111000000 |
| C | -0.294829000000 | 3.831766000000 | -1.122696000000 |
| C | 0.117630000000 | 4.156681000000 | -2.418171000000 |
| C | 0.388967000000 | 3.126573000000 | -3.328823000000 |
| H | 0.459456000000 | 1.020013000000 | -3.667353000000 |
| H | -0.718666000000 | 2.244261000000 | 0.266239000000 |
| H | -0.497892000000 | 4.606068000000 | -0.391525000000 |
| H | 0.716904000000 | 3.389292000000 | -4.329592000000 |
| O | 0.290832000000 | 5.430941000000 | -2.888910000000 |
| C | 0.037543000000 | 6.506554000000 | -2.003599000000 |
| H | 0.700660000000 | 6.479358000000 | -1.128497000000 |
| H | 0.231707000000 | 7.418999000000 | -2.570528000000 |
| C | -0.323543000000 | -0.024750000000 | -1.267072000000 |
| H | 0.694831000000 | -0.386280000000 | -1.106392000000 |
| C | -0.873745000000 | -0.893158000000 | -2.381770000000 |
| C | -2.187570000000 | -0.617952000000 | -3.024263000000 |
| C | -2.622562000000 | -1.481802000000 | -4.041852000000 |
| C | -3.035022000000 | 0.444357000000 | -2.649349000000 |
| C | -3.849874000000 | -1.309728000000 | -4.672830000000 |

| | | | |
|---|---|---|---|
| H | -1.971416000000 | -2.300843000000 | -4.327914000000 |
| C | -4.264547000000 | 0.623418000000 | -3.263098000000 |
| H | -2.725724000000 | 1.140652000000 | -1.879920000000 |
| C | -4.681985000000 | -0.249464000000 | -4.280949000000 |
| H | -4.150446000000 | -1.995550000000 | -5.456060000000 |
| H | -4.922534000000 | 1.437737000000 | -2.978711000000 |
| O | -5.899902000000 | 0.016113000000 | -4.822885000000 |
| C | -6.379964000000 | -0.826049000000 | -5.861296000000 |
| H | -7.357536000000 | -0.430464000000 | -6.140319000000 |
| H | -5.718389000000 | -0.805144000000 | -6.736303000000 |
| H | -6.493586000000 | -1.862700000000 | -5.520390000000 |
| O | -0.239911000000 | -1.910266000000 | -2.721067000000 |
| K | 1.318820000000 | -3.021874000000 | -0.894941000000 |
| H | -1.004838000000 | 6.513613000000 | -1.657658000000 |

➢ **α,β-unsaturated intermediate:**

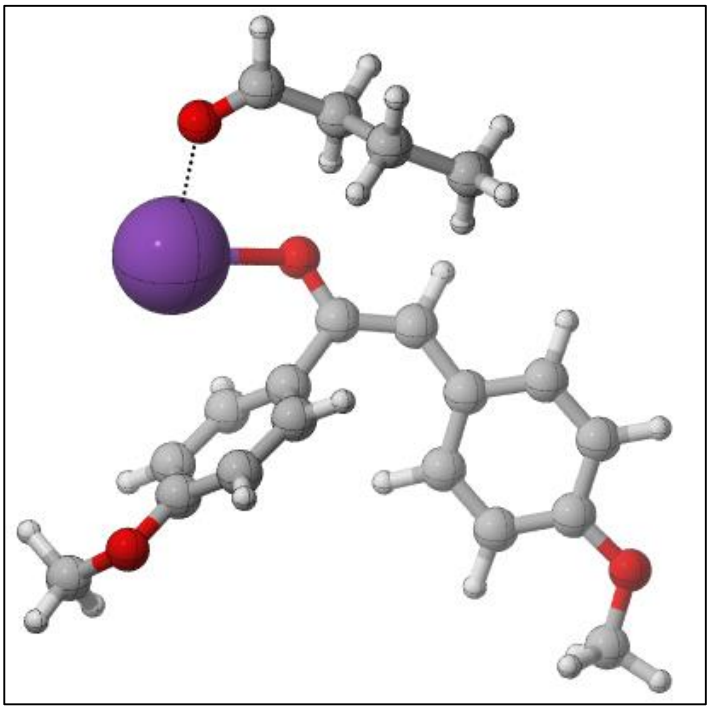


| | | | |
|---|---|---|---|
| C | 4.695725000000 | 1.942043000000 | 2.993754000000 |
| C | 3.968994000000 | 0.766397000000 | 2.824584000000 |
| C | 2.256847000000 | 1.919518000000 | 1.757242000000 |
| C | 2.936055000000 | 3.128059000000 | 1.876175000000 |
| C | 4.178135000000 | 3.144219000000 | 2.509535000000 |
| H | 5.657792000000 | 1.910417000000 | 3.496165000000 |
| H | 1.284821000000 | 1.863150000000 | 1.278610000000 |
| H | 2.489035000000 | 4.033429000000 | 1.480021000000 |
| H | 4.731314000000 | 4.070567000000 | 2.627971000000 |

| | | | |
|---|---|---|---|
| C | 4.493647000000 | -0.589896000000 | 3.254782000000 |
| H | 5.010560000000 | -1.056037000000 | 2.406400000000 |
| H | 5.223669000000 | -0.485608000000 | 4.069615000000 |
| N | 3.356780000000 | -1.462635000000 | 3.598615000000 |
| H | 3.008296000000 | -1.190859000000 | 4.515984000000 |
| C | 3.564154000000 | -2.932233000000 | 3.605951000000 |
| H | 4.111886000000 | -3.263748000000 | 4.501378000000 |
| H | 4.154095000000 | -3.185972000000 | 2.719214000000 |
| C | 2.166019000000 | -3.579638000000 | 3.500819000000 |
| H | 2.309403000000 | -4.677687000000 | 3.497404000000 |
| H | 1.637521000000 | -3.346410000000 | 4.455941000000 |
| O | 1.473465000000 | -3.138255000000 | 2.391161000000 |
| N | 2.753733000000 | 0.754520000000 | 2.217959000000 |
| Mn | 1.875182000000 | -1.087430000000 | 2.194074000000 |
| C | 0.665232000000 | -0.626119000000 | 3.525806000000 |
| C | 2.861334000000 | -1.706258000000 | 0.756273000000 |
| O | -0.079860000000 | -0.307052000000 | 4.354497000000 |
| O | 3.293421000000 | -2.205205000000 | -0.201784000000 |
| C | -4.150288000000 | -1.556119000000 | 2.729655000000 |
| H | -4.506844000000 | -2.297348000000 | 2.004973000000 |
| H | -3.642348000000 | -2.096772000000 | 3.537057000000 |
| H | -5.028839000000 | -1.064986000000 | 3.161082000000 |
| C | -3.212554000000 | -0.542754000000 | 2.065926000000 |
| H | -3.752874000000 | -0.001490000000 | 1.279369000000 |
| H | -2.901437000000 | 0.205721000000 | 2.807706000000 |
| C | -1.969309000000 | -1.198800000000 | 1.451027000000 |
| H | -1.399764000000 | -1.693095000000 | 2.248781000000 |
| H | -2.282452000000 | -1.958022000000 | 0.728107000000 |
| C | -1.076245000000 | -0.176413000000 | 0.734174000000 |
| H | -1.000343000000 | 0.713223000000 | 1.367785000000 |
| O | 0.346169000000 | -0.735544000000 | 0.704020000000 |
| C | -0.759849000000 | 2.137207000000 | -2.159878000000 |
| C | -1.397539000000 | 1.655748000000 | -0.989420000000 |
| C | -1.913236000000 | 2.642287000000 | -0.125219000000 |
| C | -1.806256000000 | 4.012545000000 | -0.390430000000 |
| C | -1.184357000000 | 4.446062000000 | -1.563648000000 |
| C | -0.664998000000 | 3.490868000000 | -2.449423000000 |

| | | | |
|---|---|---|---|
| H | -0.330825000000 | 1.421395000000 | -2.854177000000 |
| H | -2.438568000000 | 2.336693000000 | 0.775798000000 |
| H | -2.229778000000 | 4.720529000000 | 0.313524000000 |
| H | -0.173996000000 | 3.836407000000 | -3.354284000000 |
| O | -1.026140000000 | 5.759742000000 | -1.932880000000 |
| C | -1.573118000000 | 6.752275000000 | -1.087478000000 |
| H | -1.117601000000 | 6.736616000000 | -0.087158000000 |
| H | -1.356466000000 | 7.711691000000 | -1.561672000000 |
| C | -1.454302000000 | 0.212231000000 | -0.659010000000 |
| H | 0.683788000000 | -0.379489000000 | -0.130693000000 |
| C | -1.648856000000 | -0.828533000000 | -1.599364000000 |
| C | -2.287813000000 | -0.572311000000 | -2.942130000000 |
| C | -1.924343000000 | -1.381037000000 | -4.024697000000 |
| C | -3.314917000000 | 0.366911000000 | -3.145942000000 |
| C | -2.522133000000 | -1.248804000000 | -5.279695000000 |
| H | -1.159609000000 | -2.134745000000 | -3.866370000000 |
| C | -3.933729000000 | 0.501287000000 | -4.381595000000 |
| H | -3.637747000000 | 0.991044000000 | -2.319837000000 |
| C | -3.535236000000 | -0.300255000000 | -5.461504000000 |
| H | -2.200912000000 | -1.887317000000 | -6.094921000000 |
| H | -4.733602000000 | 1.218498000000 | -4.536955000000 |
| O | -4.199005000000 | -0.084945000000 | -6.639544000000 |
| C | -3.843570000000 | -0.875738000000 | -7.758752000000 |
| H | -4.484232000000 | -0.546716000000 | -8.579176000000 |
| H | -2.792763000000 | -0.731100000000 | -8.043637000000 |
| H | -4.016117000000 | -1.944687000000 | -7.574641000000 |
| O | -1.339940000000 | -2.049932000000 | -1.365426000000 |
| K | 0.062584000000 | -3.439391000000 | 0.258998000000 |
| H | -2.660880000000 | 6.643298000000 | -0.978696000000 |

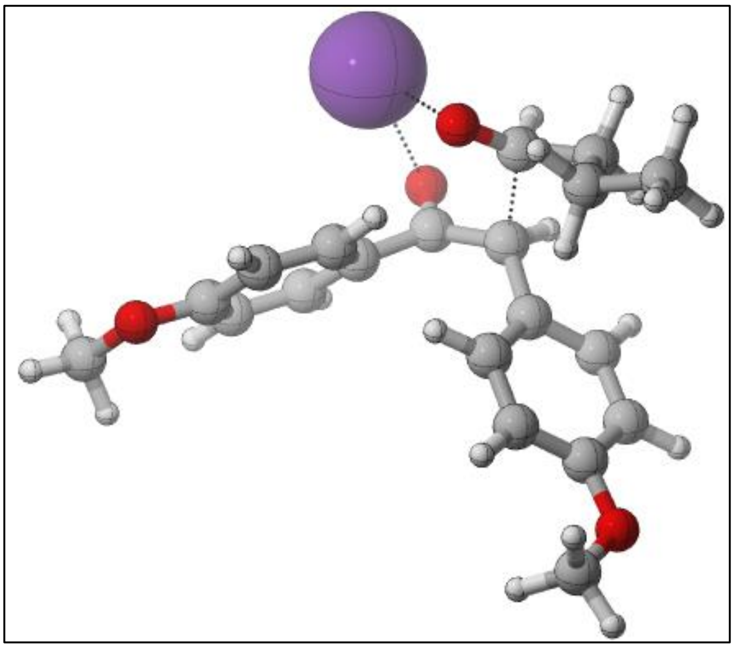
➢ <u>**IM-1′:**</u>



| | | | |
|---|---|---|---|
| C | -0.629193000000 | -0.545965000000 | -0.310395000000 |
| C | -0.739310000000 | 0.369782000000 | -1.366814000000 |
| C | -1.828614000000 | 0.274904000000 | -2.246777000000 |
| C | -2.785633000000 | -0.722393000000 | -2.075330000000 |
| C | -2.703358000000 | -1.649123000000 | -1.018346000000 |
| C | -1.610617000000 | -1.533152000000 | -0.146416000000 |
| H | 0.214535000000 | -0.514160000000 | 0.370356000000 |
| H | -1.895305000000 | 0.985896000000 | -3.064854000000 |
| H | -3.613472000000 | -0.799829000000 | -2.774606000000 |
| H | -1.519362000000 | -2.240160000000 | 0.675012000000 |
| C | -3.855765000000 | -2.580307000000 | -0.688315000000 |
| C | -4.258181000000 | -3.595496000000 | -1.527633000000 |
| H | -5.156008000000 | -4.113650000000 | -1.192338000000 |
| C | -3.672774000000 | -4.108068000000 | -2.763896000000 |
| C | -4.481017000000 | -4.899844000000 | -3.618819000000 |
| C | -2.339000000000 | -3.925292000000 | -3.185279000000 |
| C | -4.009710000000 | -5.438566000000 | -4.806777000000 |
| H | -5.512745000000 | -5.088211000000 | -3.330270000000 |
| C | -1.853201000000 | -4.452402000000 | -4.385527000000 |
| H | -1.648574000000 | -3.374114000000 | -2.557226000000 |

| | | | |
|---|---|---|---|
| C | -2.687163000000 | -5.211937000000 | -5.210060000000 |
| H | -4.651621000000 | -6.039673000000 | -5.444239000000 |
| H | -0.816614000000 | -4.275964000000 | -4.652164000000 |
| C | -7.524810000000 | -1.161419000000 | 0.189579000000 |
| H | -8.291804000000 | -1.854225000000 | 0.562568000000 |
| H | -6.537329000000 | -1.641118000000 | 0.264971000000 |
| C | -7.853266000000 | -0.816327000000 | -1.287474000000 |
| H | -8.831624000000 | -0.320145000000 | -1.345646000000 |
| H | -7.114562000000 | -0.091704000000 | -1.653425000000 |
| C | -7.837320000000 | -2.058724000000 | -2.182507000000 |
| H | -8.078895000000 | -1.793113000000 | -3.216800000000 |
| H | -6.850239000000 | -2.531170000000 | -2.170460000000 |
| H | -8.573917000000 | -2.796581000000 | -1.845274000000 |
| C | -7.575969000000 | 0.084186000000 | 1.020075000000 |
| H | -8.591024000000 | 0.480687000000 | 1.241992000000 |
| O | -4.442453000000 | -2.257893000000 | 0.427736000000 |
| O | -2.312717000000 | -5.779575000000 | -6.407480000000 |
| O | 0.149026000000 | 1.379283000000 | -1.620462000000 |
| O | -6.602262000000 | 0.707444000000 | 1.421411000000 |
| K | -4.013014000000 | 0.100234000000 | 1.199984000000 |
| C | 1.309484000000 | 1.468326000000 | -0.811928000000 |
| H | 1.914841000000 | 0.554394000000 | -0.867610000000 |
| H | 1.888291000000 | 2.306345000000 | -1.203551000000 |
| H | 1.060985000000 | 1.665993000000 | 0.240174000000 |
| C | -0.981187000000 | -5.585839000000 | -6.836043000000 |
| H | -0.887632000000 | -6.104407000000 | -7.792842000000 |
| H | -0.746559000000 | -4.521702000000 | -6.981558000000 |
| H | -0.255227000000 | -6.009353000000 | -6.127500000000 |

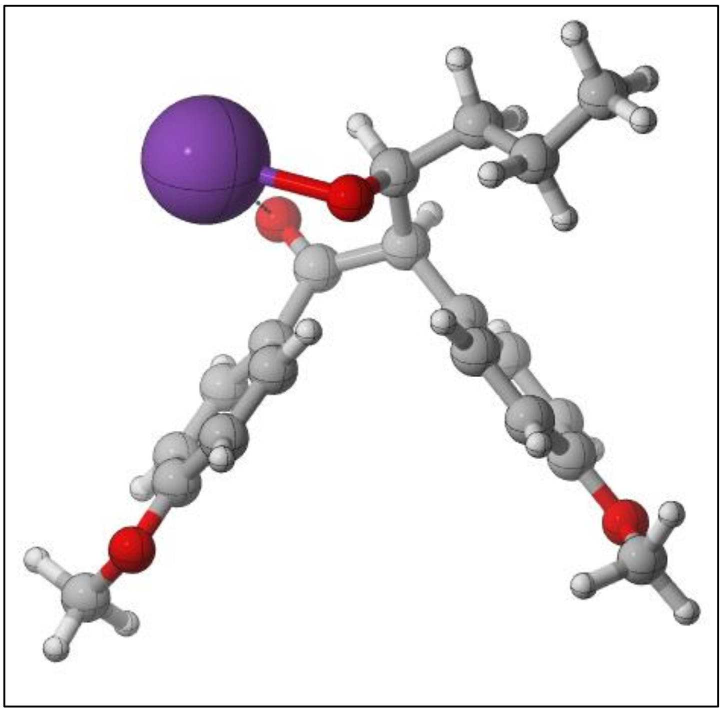
➢ **TS-1′:**



| | | | |
|---|---|---|---|
| C | -0.150440000000 | -0.529932000000 | 0.054582000000 |
| C | -0.412967000000 | 0.509140000000 | -0.849516000000 |
| C | -1.693038000000 | 0.633559000000 | -1.411097000000 |
| C | -2.690517000000 | -0.287477000000 | -1.104250000000 |
| C | -2.436886000000 | -1.338118000000 | -0.201629000000 |
| C | -1.168407000000 | -1.425479000000 | 0.385890000000 |
| H | 0.828555000000 | -0.645221000000 | 0.504863000000 |
| H | -1.878262000000 | 1.454024000000 | -2.097838000000 |
| H | -3.697199000000 | -0.179016000000 | -1.505647000000 |
| H | -0.975358000000 | -2.213353000000 | 1.107907000000 |
| C | -3.521658000000 | -2.265909000000 | 0.280962000000 |
| C | -4.459615000000 | -2.956551000000 | -0.607957000000 |
| H | -4.915983000000 | -3.744960000000 | -0.006773000000 |
| C | -4.061561000000 | -3.535350000000 | -1.933345000000 |
| C | -4.370426000000 | -4.893770000000 | -2.166131000000 |
| C | -3.432659000000 | -2.856480000000 | -2.988247000000 |
| C | -4.071357000000 | -5.533936000000 | -3.361098000000 |
| H | -4.855875000000 | -5.463935000000 | -1.377563000000 |
| C | -3.115296000000 | -3.486147000000 | -4.196434000000 |
| H | -3.182783000000 | -1.808987000000 | -2.889350000000 |
| C | -3.434035000000 | -4.832488000000 | -4.392055000000 |
| H | -4.317454000000 | -6.579843000000 | -3.516049000000 |

| | | | |
|---|---|---|---|
| H | -2.628164000000 | -2.909017000000 | -4.974233000000 |
| C | -6.971349000000 | -2.324920000000 | -1.559343000000 |
| H | -7.955376000000 | -2.075947000000 | -1.129439000000 |
| H | -6.927178000000 | -3.420515000000 | -1.605921000000 |
| C | -6.893896000000 | -1.714060000000 | -2.960989000000 |
| H | -6.842212000000 | -0.625966000000 | -2.849043000000 |
| H | -5.961910000000 | -2.020062000000 | -3.446707000000 |
| C | -8.082171000000 | -2.105915000000 | -3.845243000000 |
| H | -8.011777000000 | -1.647211000000 | -4.838164000000 |
| H | -8.135353000000 | -3.191948000000 | -3.987637000000 |
| H | -9.033308000000 | -1.787132000000 | -3.400654000000 |
| C | -5.932765000000 | -1.773609000000 | -0.558625000000 |
| H | -6.207306000000 | -2.128048000000 | 0.468948000000 |
| O | -3.687564000000 | -2.308389000000 | 1.521754000000 |
| O | -3.171962000000 | -5.544839000000 | -5.533492000000 |
| O | 0.499315000000 | 1.447795000000 | -1.236158000000 |
| O | -5.637552000000 | -0.508194000000 | -0.653436000000 |
| K | -4.723602000000 | 0.178074000000 | 1.609469000000 |
| C | 1.820900000000 | 1.351697000000 | -0.729257000000 |
| H | 2.293603000000 | 0.401204000000 | -1.007656000000 |
| H | 2.377481000000 | 2.174792000000 | -1.180115000000 |
| H | 1.846340000000 | 1.456565000000 | 0.363436000000 |
| C | -2.538409000000 | -4.869952000000 | -6.604109000000 |
| H | -2.425840000000 | -5.604967000000 | -7.403489000000 |
| H | -3.142541000000 | -4.029467000000 | -6.971743000000 |
| H | -1.546070000000 | -4.493868000000 | -6.320162000000 |

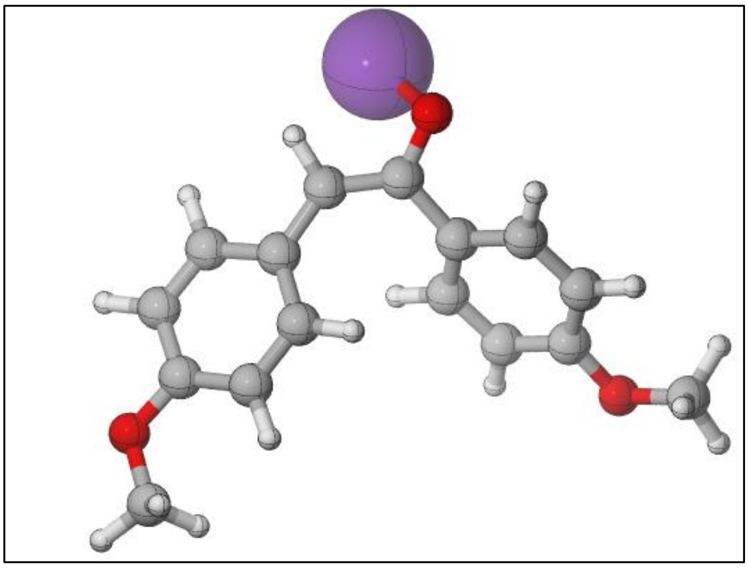
➢ **IM-2′ :**



| | | | |
|---|---|---|---|
| C | -0.075039000000 | -0.804640000000 | 0.201193000000 |
| C | -0.103469000000 | 0.077296000000 | -0.888655000000 |
| C | -1.287987000000 | 0.235994000000 | -1.626049000000 |
| C | -2.419724000000 | -0.505113000000 | -1.308358000000 |
| C | -2.400452000000 | -1.396857000000 | -0.219001000000 |
| C | -1.227798000000 | -1.514303000000 | 0.537982000000 |
| H | 0.825484000000 | -0.939205000000 | 0.788714000000 |
| H | -1.289680000000 | 0.938333000000 | -2.453961000000 |
| H | -3.358893000000 | -0.369645000000 | -1.839308000000 |
| H | -1.218852000000 | -2.179157000000 | 1.396489000000 |
| C | -3.630488000000 | -2.124232000000 | 0.240133000000 |
| C | -4.592530000000 | -2.819960000000 | -0.706492000000 |
| H | -4.973745000000 | -3.664077000000 | -0.118715000000 |
| C | -3.987131000000 | -3.364628000000 | -1.986364000000 |
| C | -3.442943000000 | -4.661281000000 | -1.988195000000 |
| C | -3.936091000000 | -2.646286000000 | -3.186511000000 |
| C | -2.868585000000 | -5.214681000000 | -3.126435000000 |
| H | -3.473601000000 | -5.252515000000 | -1.075312000000 |
| C | -3.367181000000 | -3.187768000000 | -4.343413000000 |
| H | -4.380219000000 | -1.657430000000 | -3.213896000000 |
| C | -2.824431000000 | -4.476556000000 | -4.316520000000 |

| | | | |
|---|---|---|---|
| H | -2.452245000000 | -6.217145000000 | -3.119791000000 |
| H | -3.358344000000 | -2.597299000000 | -5.252540000000 |
| C | -7.107230000000 | -2.429273000000 | -1.488654000000 |
| H | -7.966005000000 | -1.902062000000 | -1.045206000000 |
| H | -7.205770000000 | -3.480262000000 | -1.178798000000 |
| C | -7.231933000000 | -2.298276000000 | -3.009227000000 |
| H | -6.957490000000 | -1.270461000000 | -3.272515000000 |
| H | -6.513742000000 | -2.954917000000 | -3.510157000000 |
| C | -8.642985000000 | -2.617217000000 | -3.516415000000 |
| H | -8.713299000000 | -2.510236000000 | -4.605123000000 |
| H | -8.937657000000 | -3.644148000000 | -3.267282000000 |
| H | -9.387782000000 | -1.947041000000 | -3.069212000000 |
| C | -5.847036000000 | -1.785419000000 | -0.826164000000 |
| H | -6.138866000000 | -1.765033000000 | 0.269803000000 |
| O | -3.904605000000 | -2.069599000000 | 1.447383000000 |
| O | -2.238762000000 | -5.101470000000 | -5.385786000000 |
| O | 0.956334000000 | 0.829154000000 | -1.301629000000 |
| O | -5.490503000000 | -0.581752000000 | -1.315347000000 |
| K | -4.956300000000 | 0.542907000000 | 0.859795000000 |
| C | 2.191571000000 | 0.688567000000 | -0.617186000000 |
| H | 2.568528000000 | -0.340607000000 | -0.670072000000 |
| H | 2.893194000000 | 1.354308000000 | -1.122090000000 |
| H | 2.108488000000 | 0.985605000000 | 0.436460000000 |
| C | -2.185486000000 | -4.402377000000 | -6.615957000000 |
| H | -1.690645000000 | -5.070163000000 | -7.323801000000 |
| H | -3.188670000000 | -4.160285000000 | -6.991584000000 |
| H | -1.605386000000 | -3.473434000000 | -6.532921000000 |

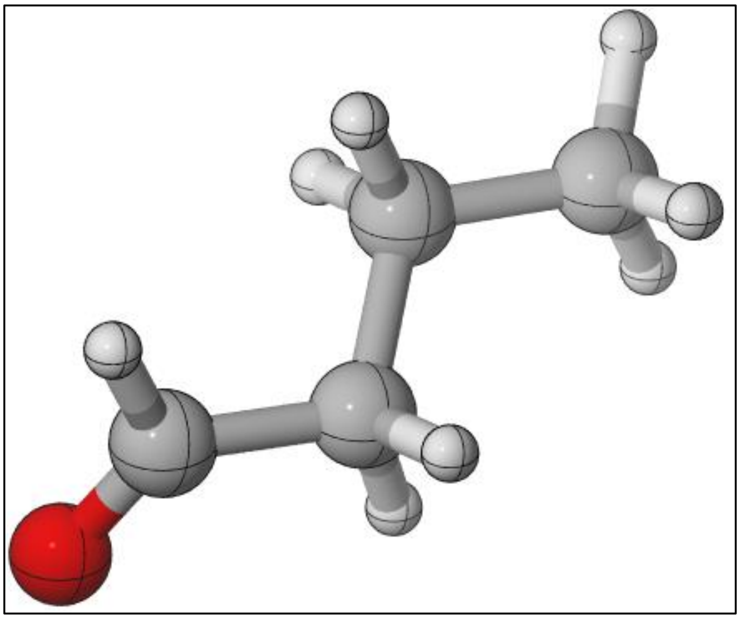
- **B:**



| | | | |
|---|---|---|---|
| C | 10.024811000000 | 0.673251000000 | 0.773247000000 |
| C | 10.299684000000 | 1.764022000000 | -0.059801000000 |
| C | 9.277376000000 | 2.296853000000 | -0.858435000000 |
| C | 8.006851000000 | 1.733355000000 | -0.835391000000 |
| C | 7.710031000000 | 0.631270000000 | -0.012796000000 |
| C | 8.736424000000 | 0.134536000000 | 0.799440000000 |
| H | 10.793887000000 | 0.246253000000 | 1.407025000000 |
| H | 9.504505000000 | 3.151284000000 | -1.488642000000 |
| H | 7.232415000000 | 2.149562000000 | -1.472039000000 |
| H | 8.501782000000 | -0.684613000000 | 1.471154000000 |
| C | 6.323206000000 | 0.050251000000 | 0.148571000000 |
| C | 5.392710000000 | -0.015350000000 | -0.894775000000 |
| H | 4.440142000000 | -0.462321000000 | -0.590390000000 |
| C | 5.536950000000 | 0.093340000000 | -2.351208000000 |
| C | 4.396844000000 | 0.384821000000 | -3.138981000000 |
| C | 6.727923000000 | -0.142060000000 | -3.066474000000 |
| C | 4.442712000000 | 0.462216000000 | -4.524082000000 |
| H | 3.444542000000 | 0.551816000000 | -2.637546000000 |
| C | 6.796135000000 | -0.049826000000 | -4.459233000000 |
| H | 7.625343000000 | -0.418733000000 | -2.524934000000 |
| C | 5.651721000000 | 0.256434000000 | -5.201274000000 |
| H | 3.553168000000 | 0.687412000000 | -5.105151000000 |
| H | 7.744317000000 | -0.241038000000 | -4.949686000000 |

| | | | |
|---|---|---|---|
| O | 6.019677000000 | -0.276907000000 | 1.359626000000 |
| O | 5.604139000000 | 0.368081000000 | -6.570956000000 |
| O | 11.517904000000 | 2.382473000000 | -0.160210000000 |
| K | 4.231220000000 | 1.445606000000 | 1.482796000000 |
| C | 12.587248000000 | 1.875959000000 | 0.617636000000 |
| H | 12.814457000000 | 0.831112000000 | 0.367519000000 |
| H | 13.454353000000 | 2.496266000000 | 0.382836000000 |
| H | 12.377904000000 | 1.944103000000 | 1.693771000000 |
| C | 6.802102000000 | 0.150941000000 | -7.289533000000 |
| H | 6.555522000000 | 0.288075000000 | -8.344546000000 |
| H | 7.585057000000 | 0.868956000000 | -7.008220000000 |
| H | 7.190305000000 | -0.866405000000 | -7.141945000000 |

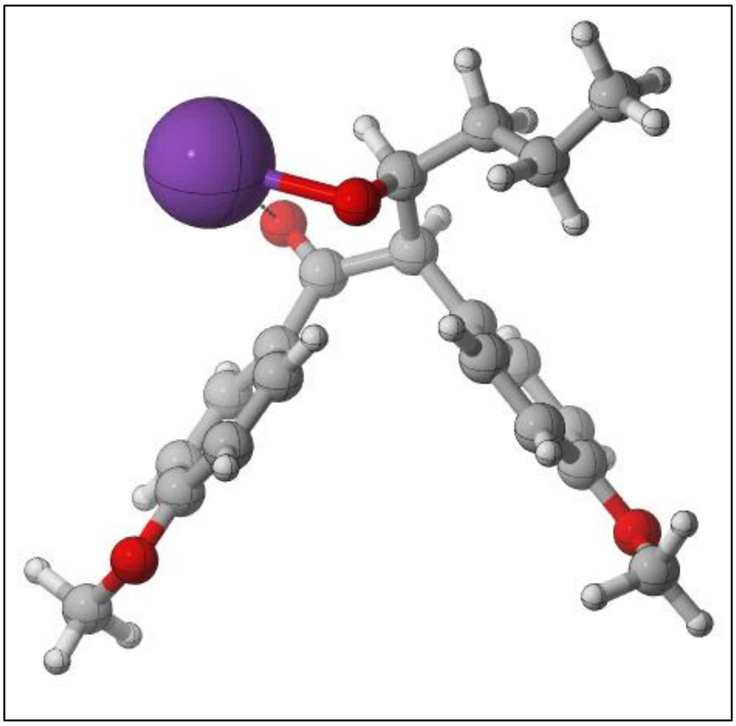
- **A′ :**



| | | | |
|---|---|---|---|
| C | -1.463486000000 | 0.236293000000 | 0.271513000000 |
| H | -1.506026000000 | 1.148364000000 | 0.913306000000 |
| C | -0.118954000000 | -0.452786000000 | 0.251807000000 |
| H | 0.072742000000 | -0.830717000000 | 1.267894000000 |
| H | -0.179412000000 | -1.313328000000 | -0.421771000000 |
| C | 1.020856000000 | 0.502866000000 | -0.147824000000 |
| H | 1.000303000000 | 1.385250000000 | 0.505347000000 |
| H | 0.841660000000 | 0.869840000000 | -1.165912000000 |
| C | 2.399509000000 | -0.158973000000 | -0.073097000000 |
| H | 2.457919000000 | -1.028370000000 | -0.736625000000 |

| | | | |
|---|---|---|---|
| H | 3.188748000000 | 0.539461000000 | -0.368092000000 |
| H | 2.619237000000 | -0.502299000000 | 0.943932000000 |
| O | -2.440340000000 | -0.129075000000 | -0.344060000000 |

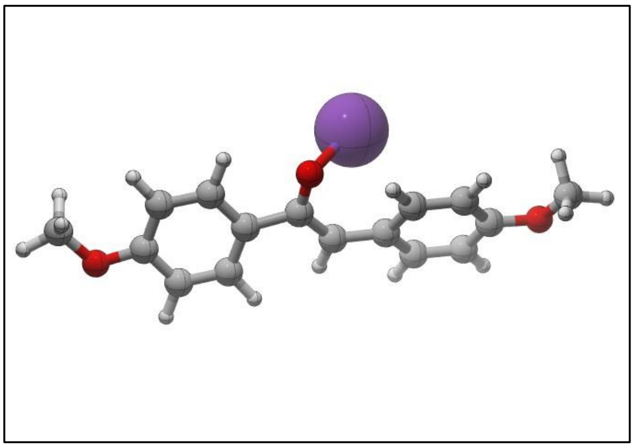
- **Alpha :**



| | | | |
|---|---|---|---|
| C | 9.682062000000 | 0.402628000000 | -0.004614000000 |
| C | 10.132367000000 | 1.726597000000 | -0.067438000000 |
| C | 9.201243000000 | 2.775935000000 | -0.052146000000 |
| C | 7.838393000000 | 2.508170000000 | 0.002087000000 |
| C | 7.369771000000 | 1.183064000000 | 0.051299000000 |
| C | 8.310746000000 | 0.146304000000 | 0.064961000000 |
| H | 10.379197000000 | -0.427265000000 | -0.006950000000 |
| H | 9.572972000000 | 3.795809000000 | -0.076632000000 |
| H | 7.105767000000 | 3.305848000000 | 0.064394000000 |
| H | 7.962415000000 | -0.880322000000 | 0.124153000000 |
| C | 5.910489000000 | 0.792662000000 | 0.124684000000 |
| C | 4.929827000000 | 1.133289000000 | -1.027628000000 |
| H | 4.013938000000 | 0.598593000000 | -0.746653000000 |
| C | 5.348956000000 | 0.652443000000 | -2.402464000000 |
| C | 4.692285000000 | -0.439342000000 | -2.998667000000 |
| C | 6.387397000000 | 1.247450000000 | -3.130343000000 |
| C | 5.046985000000 | -0.912521000000 | -4.256051000000 |

| | | | |
|---|---|---|---|
| H | 3.882183000000 | -0.926489000000 | -2.461080000000 |
| C | 6.759129000000 | 0.786985000000 | -4.397001000000 |
| H | 6.928328000000 | 2.087194000000 | -2.707230000000 |
| C | 6.087117000000 | -0.299174000000 | -4.966992000000 |
| H | 4.532677000000 | -1.754057000000 | -4.709511000000 |
| H | 7.568490000000 | 1.281160000000 | -4.922045000000 |
| C | 3.281214000000 | 3.146232000000 | -1.071861000000 |
| H | 3.209099000000 | 4.164814000000 | -0.664372000000 |
| H | 2.567886000000 | 2.534726000000 | -0.497005000000 |
| C | 2.882373000000 | 3.157949000000 | -2.553108000000 |
| H | 3.623603000000 | 3.735274000000 | -3.122315000000 |
| H | 2.922623000000 | 2.139641000000 | -2.958648000000 |
| C | 1.487327000000 | 3.745949000000 | -2.793728000000 |
| H | 1.226974000000 | 3.747167000000 | -3.857999000000 |
| H | 0.717882000000 | 3.170126000000 | -2.265368000000 |
| H | 1.425881000000 | 4.780252000000 | -2.434648000000 |
| C | 4.701932000000 | 2.646938000000 | -0.753015000000 |
| H | 5.395392000000 | 3.226599000000 | -1.405379000000 |
| O | 5.579925000000 | -0.033501000000 | 0.993962000000 |
| O | 6.365306000000 | -0.832002000000 | -6.197629000000 |
| O | 11.446785000000 | 2.098106000000 | -0.132818000000 |
| O | 5.018773000000 | 2.775560000000 | 0.591500000000 |
| K | 4.901560000000 | 1.735297000000 | 2.786402000000 |
| C | 12.429944000000 | 1.077834000000 | -0.156528000000 |
| H | 12.312805000000 | 0.419875000000 | -1.027602000000 |
| H | 13.393396000000 | 1.586809000000 | -0.219570000000 |
| H | 12.405452000000 | 0.466773000000 | 0.755618000000 |
| C | 7.403643000000 | -0.241884000000 | -6.958459000000 |
| H | 7.456200000000 | -0.807395000000 | -7.890732000000 |
| H | 7.193151000000 | 0.811166000000 | -7.188425000000 |
| H | 8.372466000000 | -0.305045000000 | -6.444981000000 |

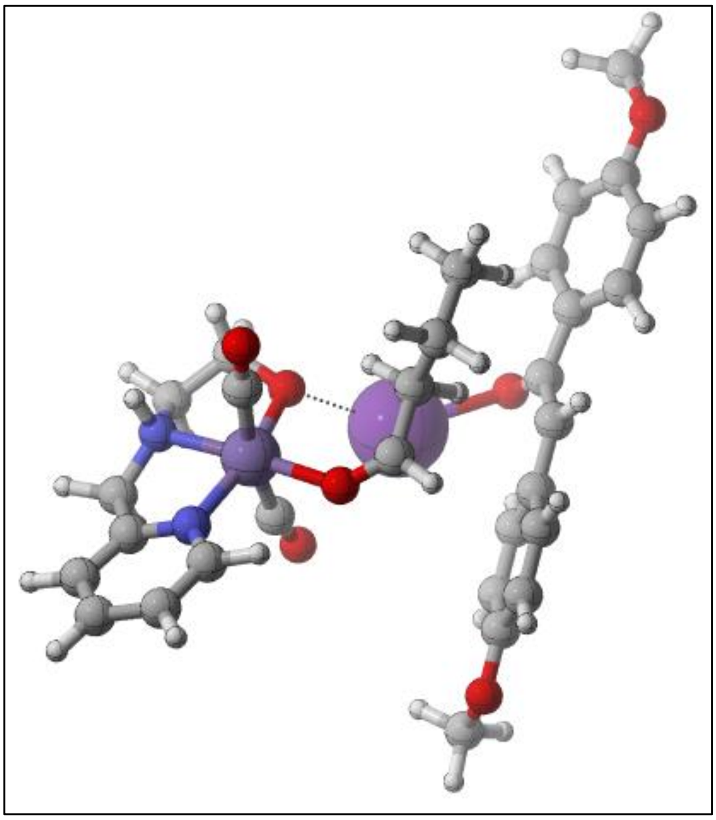
➢ **Bc:**



| | | | |
|---|---|---|---|
| C | -3.411944000000 | -0.856014000000 | 0.377294000000 |
| C | -3.725059000000 | 0.504293000000 | 0.247760000000 |
| C | -2.792655000000 | 1.398510000000 | -0.285651000000 |
| C | -1.535191000000 | 0.909232000000 | -0.674724000000 |
| C | -1.230409000000 | -0.436648000000 | -0.544923000000 |
| C | -2.155478000000 | -1.384172000000 | -0.022266000000 |
| H | -4.127470000000 | -1.534393000000 | 0.831271000000 |
| H | -4.694032000000 | 0.851000000000 | 0.592277000000 |
| H | -0.808182000000 | 1.611175000000 | -1.073039000000 |
| H | -0.244296000000 | -0.783806000000 | -0.846521000000 |
| C | -1.787202000000 | -2.786762000000 | 0.065082000000 |
| H | -0.729439000000 | -2.992770000000 | -0.061332000000 |
| C | -2.650253000000 | -3.861269000000 | 0.319774000000 |
| C | -2.063847000000 | -5.239567000000 | 0.515995000000 |
| C | -0.704959000000 | -5.499161000000 | 0.777349000000 |
| C | -2.927968000000 | -6.339636000000 | 0.458137000000 |
| C | -0.234039000000 | -6.794869000000 | 0.941543000000 |
| H | -0.006336000000 | -4.675221000000 | 0.880015000000 |
| C | -2.473976000000 | -7.650232000000 | 0.620943000000 |
| H | -3.981990000000 | -6.138252000000 | 0.296768000000 |
| C | -1.115154000000 | -7.883620000000 | 0.859093000000 |
| H | 0.813046000000 | -6.991929000000 | 1.149959000000 |
| H | -3.180981000000 | -8.470799000000 | 0.568836000000 |
| O | -2.999925000000 | 2.745715000000 | -0.469580000000 |
| O | -0.552657000000 | -9.119801000000 | 1.035003000000 |
| O | -3.935519000000 | -3.776860000000 | 0.321842000000 |

| | | | |
|---|---|---|---|
| C | -4.213875000000 | 3.294223000000 | 0.003505000000 |
| H | -4.167110000000 | 4.365562000000 | -0.201805000000 |
| H | -5.086623000000 | 2.870216000000 | -0.514123000000 |
| H | -4.338831000000 | 3.139954000000 | 1.083996000000 |
| C | -1.404705000000 | -10.249852000000 | 0.996743000000 |
| H | -0.765673000000 | -11.118485000000 | 1.166642000000 |
| H | -2.172001000000 | -10.208830000000 | 1.781305000000 |
| H | -1.900846000000 | -10.354591000000 | 0.022285000000 |
| K | -4.065353000000 | -2.661503000000 | -1.955185000000 |

- **IM-1C:**

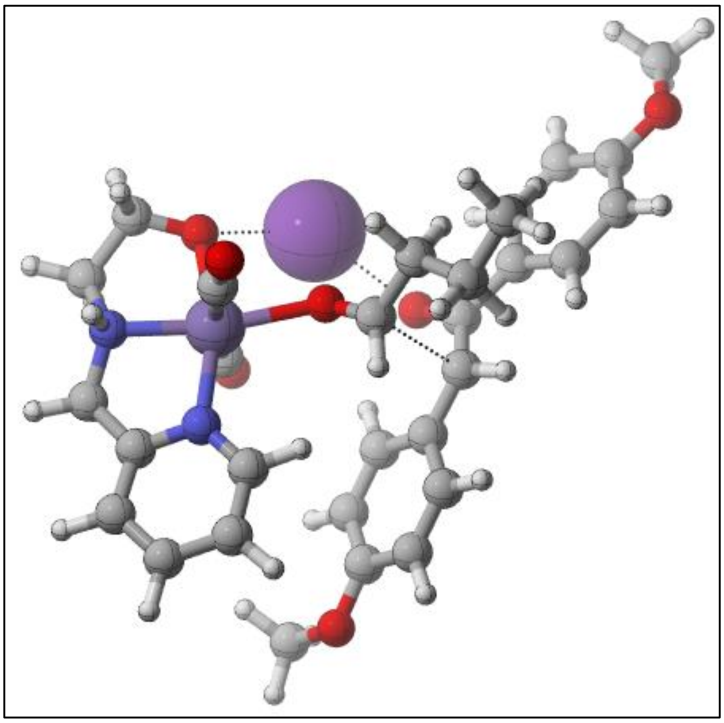


| | | | |
|---|---|---|---|
| C | 2.744264000000 | 0.503016000000 | 2.871451000000 |
| C | 1.937730000000 | 0.012399000000 | 1.847639000000 |
| C | 1.336755000000 | 2.166482000000 | 1.218040000000 |
| C | 2.135747000000 | 2.726931000000 | 2.209874000000 |
| C | 2.850435000000 | 1.881695000000 | 3.057889000000 |
| H | 3.284164000000 | -0.190159000000 | 3.509210000000 |
| H | 0.761259000000 | 2.776011000000 | 0.529871000000 |
| H | 2.188483000000 | 3.805603000000 | 2.311788000000 |

| | | | |
|---|---|---|---|
| H | 3.475634000000 | 2.284659000000 | 3.848383000000 |
| C | 1.827748000000 | -1.465107000000 | 1.526279000000 |
| H | 2.573323000000 | -1.718559000000 | 0.761900000000 |
| H | 2.042938000000 | -2.076470000000 | 2.413504000000 |
| N | 0.501560000000 | -1.731035000000 | 0.942470000000 |
| H | -0.186002000000 | -1.718826000000 | 1.693259000000 |
| C | 0.301894000000 | -2.978528000000 | 0.164681000000 |
| H | 0.207448000000 | -3.858231000000 | 0.818713000000 |
| H | 1.179631000000 | -3.112040000000 | -0.476500000000 |
| C | -0.949807000000 | -2.755221000000 | -0.709125000000 |
| H | -1.114796000000 | -3.675890000000 | -1.300965000000 |
| H | -1.817865000000 | -2.682659000000 | -0.014165000000 |
| O | -0.819452000000 | -1.634325000000 | -1.512305000000 |
| N | 1.230224000000 | 0.837029000000 | 1.034803000000 |
| Mn | 0.071111000000 | -0.146234000000 | -0.333003000000 |
| C | -1.534174000000 | 0.203903000000 | 0.540309000000 |
| C | 1.467224000000 | -0.481244000000 | -1.498282000000 |
| O | -2.543164000000 | 0.488953000000 | 1.031971000000 |
| O | 2.183527000000 | -0.726484000000 | -2.380616000000 |
| C | -4.918835000000 | 0.959542000000 | -2.873270000000 |
| H | -4.833933000000 | 0.795786000000 | -3.952270000000 |
| H | -4.949620000000 | -0.022376000000 | -2.388555000000 |
| H | -5.874387000000 | 1.456989000000 | -2.679096000000 |
| C | -3.750701000000 | 1.795947000000 | -2.341582000000 |
| H | -3.763659000000 | 2.789577000000 | -2.808461000000 |
| H | -3.867353000000 | 1.952726000000 | -1.262343000000 |
| C | -2.388283000000 | 1.119881000000 | -2.617197000000 |
| H | -2.319485000000 | 0.134495000000 | -2.141732000000 |
| H | -2.302968000000 | 0.992532000000 | -3.717224000000 |
| C | -1.239903000000 | 1.961939000000 | -2.180573000000 |
| H | -1.216239000000 | 3.000392000000 | -2.548499000000 |
| O | -0.315418000000 | 1.604945000000 | -1.440282000000 |
| C | -0.393178000000 | 2.775114000000 | -5.430938000000 |
| C | -0.570548000000 | 1.456968000000 | -5.937843000000 |
| C | 0.624327000000 | 0.747232000000 | -6.225397000000 |
| C | 1.890876000000 | 1.299186000000 | -6.002173000000 |
| C | 2.021686000000 | 2.591323000000 | -5.482557000000 |

| | | | |
|---|---|---|---|
| C | 0.860556000000 | 3.328674000000 | -5.211360000000 |
| H | -1.276405000000 | 3.380865000000 | -5.235899000000 |
| H | 0.534772000000 | -0.234417000000 | -6.679215000000 |
| H | 2.767200000000 | 0.713222000000 | -6.259125000000 |
| H | 0.967396000000 | 4.341560000000 | -4.833351000000 |
| O | 3.215060000000 | 3.221262000000 | -5.214798000000 |
| C | 4.407027000000 | 2.524515000000 | -5.518109000000 |
| H | 4.481535000000 | 2.285995000000 | -6.588216000000 |
| H | 5.228798000000 | 3.189494000000 | -5.244098000000 |
| C | -1.907674000000 | 0.934257000000 | -6.135760000000 |
| H | -2.700980000000 | 1.673442000000 | -6.086863000000 |
| C | -2.254316000000 | -0.390665000000 | -6.446988000000 |
| C | -3.701065000000 | -0.709149000000 | -6.749733000000 |
| C | -4.099456000000 | -2.051345000000 | -6.733861000000 |
| C | -4.679272000000 | 0.249776000000 | -7.076727000000 |
| C | -5.414595000000 | -2.439110000000 | -6.997471000000 |
| H | -3.339211000000 | -2.795575000000 | -6.520828000000 |
| C | -5.992848000000 | -0.116049000000 | -7.342140000000 |
| H | -4.406973000000 | 1.297414000000 | -7.154229000000 |
| C | -6.373227000000 | -1.465435000000 | -7.298838000000 |
| H | -5.675952000000 | -3.491195000000 | -6.971692000000 |
| H | -6.742884000000 | 0.624802000000 | -7.601561000000 |
| O | -7.690000000000 | -1.722730000000 | -7.574889000000 |
| C | -8.118262000000 | -3.072155000000 | -7.571975000000 |
| H | -9.181554000000 | -3.054305000000 | -7.818907000000 |
| H | -7.584982000000 | -3.671091000000 | -8.322285000000 |
| H | -7.986306000000 | -3.540481000000 | -6.587189000000 |
| O | -1.439248000000 | -1.380301000000 | -6.434511000000 |
| K | -0.409924000000 | -1.262509000000 | -4.071025000000 |
| H | 4.494367000000 | 1.591664000000 | -4.943284000000 |

- **<u>TS-1C:</u>**

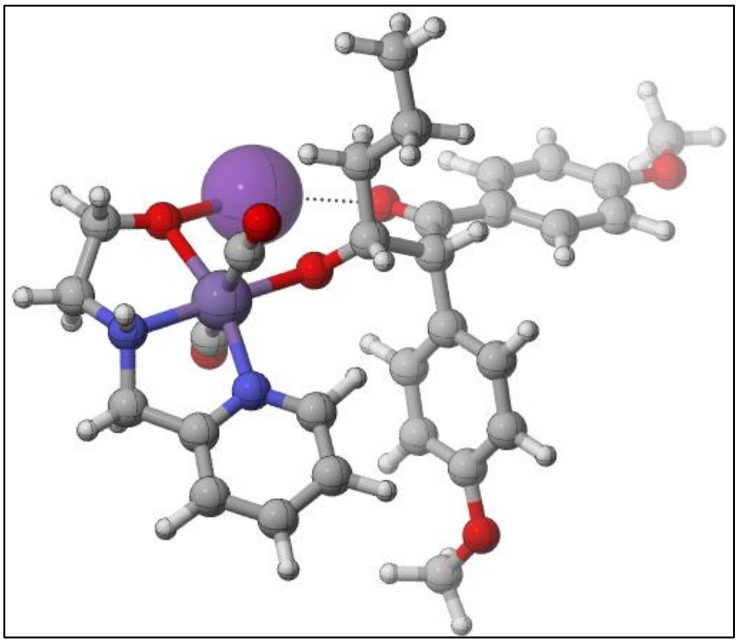


| | | | |
|---|---|---|---|
| C | 3.183957000000 | 1.239739000000 | 0.612403000000 |
| C | 2.316980000000 | 0.241422000000 | 0.176028000000 |
| C | 1.001041000000 | 1.795009000000 | -0.932875000000 |
| C | 1.837139000000 | 2.841585000000 | -0.553173000000 |
| C | 2.944206000000 | 2.564556000000 | 0.245564000000 |
| H | 4.041871000000 | 0.974753000000 | 1.223156000000 |
| H | 0.140225000000 | 1.970840000000 | -1.566325000000 |
| H | 1.620209000000 | 3.846630000000 | -0.896027000000 |
| H | 3.611529000000 | 3.357312000000 | 0.569076000000 |
| C | 2.585213000000 | -1.227374000000 | 0.434862000000 |
| H | 3.171940000000 | -1.628694000000 | -0.401304000000 |
| H | 3.181847000000 | -1.361722000000 | 1.348316000000 |
| N | 1.311614000000 | -1.961870000000 | 0.458260000000 |
| H | 0.858251000000 | -1.791081000000 | 1.353540000000 |
| C | 1.342670000000 | -3.428025000000 | 0.237805000000 |
| H | 1.718330000000 | -3.966523000000 | 1.121798000000 |
| H | 2.015753000000 | -3.620260000000 | -0.604248000000 |
| C | -0.092361000000 | -3.845751000000 | -0.145208000000 |
| H | -0.085390000000 | -4.939902000000 | -0.319180000000 |
| H | -0.721383000000 | -3.688591000000 | 0.764612000000 |
| O | -0.550911000000 | -3.142138000000 | -1.237005000000 |

| | | | |
|---|---|---|---|
| N | 1.216459000000 | 0.516082000000 | -0.571209000000 |
| Mn | 0.085043000000 | -1.152360000000 | -1.014689000000 |
| C | -1.247285000000 | -0.758568000000 | 0.225400000000 |
| C | 1.202833000000 | -1.590384000000 | -2.419054000000 |
| O | -2.126456000000 | -0.466233000000 | 0.921877000000 |
| O | 1.797365000000 | -1.957454000000 | -3.348244000000 |
| C | -6.016364000000 | 1.489980000000 | -2.314840000000 |
| H | -6.414041000000 | 0.937485000000 | -3.173282000000 |
| H | -6.271563000000 | 0.927489000000 | -1.409416000000 |
| H | -6.536483000000 | 2.452268000000 | -2.265784000000 |
| C | -4.501641000000 | 1.680766000000 | -2.439905000000 |
| H | -4.277556000000 | 2.263846000000 | -3.340202000000 |
| H | -4.135254000000 | 2.275618000000 | -1.592432000000 |
| C | -3.740436000000 | 0.351905000000 | -2.485470000000 |
| H | -3.927828000000 | -0.203103000000 | -1.553351000000 |
| H | -4.113708000000 | -0.281364000000 | -3.298359000000 |
| C | -2.229968000000 | 0.491867000000 | -2.577431000000 |
| H | -1.826615000000 | 1.492771000000 | -2.362854000000 |
| O | -1.500470000000 | -0.519909000000 | -2.412325000000 |
| C | -0.460160000000 | 3.160788000000 | -4.332604000000 |
| C | -0.575107000000 | 1.790111000000 | -4.668575000000 |
| C | 0.628877000000 | 1.066133000000 | -4.776223000000 |
| C | 1.871866000000 | 1.669792000000 | -4.564020000000 |
| C | 1.951842000000 | 3.024899000000 | -4.227221000000 |
| C | 0.769696000000 | 3.769942000000 | -4.118377000000 |
| H | -1.363739000000 | 3.762316000000 | -4.254819000000 |
| H | 0.575690000000 | 0.019774000000 | -5.044872000000 |
| H | 2.766930000000 | 1.065606000000 | -4.663124000000 |
| H | 0.839632000000 | 4.826754000000 | -3.877173000000 |
| O | 3.118538000000 | 3.710024000000 | -3.980570000000 |
| C | 4.336317000000 | 3.002034000000 | -4.109412000000 |
| H | 4.474876000000 | 2.607134000000 | -5.124884000000 |
| H | 5.131289000000 | 3.719418000000 | -3.894655000000 |
| C | -1.907664000000 | 1.220032000000 | -4.866049000000 |
| H | -2.684425000000 | 1.972902000000 | -4.949375000000 |
| C | -2.193120000000 | -0.047906000000 | -5.433856000000 |
| C | -3.577163000000 | -0.316513000000 | -5.990132000000 |

| | | | |
|---|---|---|---|
| C | -3.824014000000 | -1.579502000000 | -6.547434000000 |
| C | -4.639340000000 | 0.609726000000 | -6.019945000000 |
| C | -5.061169000000 | -1.931510000000 | -7.089138000000 |
| H | -2.998148000000 | -2.282839000000 | -6.577831000000 |
| C | -5.879851000000 | 0.278008000000 | -6.547918000000 |
| H | -4.503989000000 | 1.612497000000 | -5.631495000000 |
| C | -6.104713000000 | -0.998753000000 | -7.085045000000 |
| H | -5.195452000000 | -2.918387000000 | -7.517574000000 |
| H | -6.692636000000 | 0.997135000000 | -6.566848000000 |
| O | -7.356172000000 | -1.223826000000 | -7.581982000000 |
| C | -7.632028000000 | -2.491708000000 | -8.153327000000 |
| H | -8.671589000000 | -2.455172000000 | -8.483160000000 |
| H | -6.986956000000 | -2.696802000000 | -9.017571000000 |
| H | -7.515216000000 | -3.301471000000 | -7.420942000000 |
| O | -1.374365000000 | -1.015597000000 | -5.463121000000 |
| K | -1.389874000000 | -2.865913000000 | -3.630853000000 |
| H | 4.402364000000 | 2.168555000000 | -3.396233000000 |

- **IM-2C:**

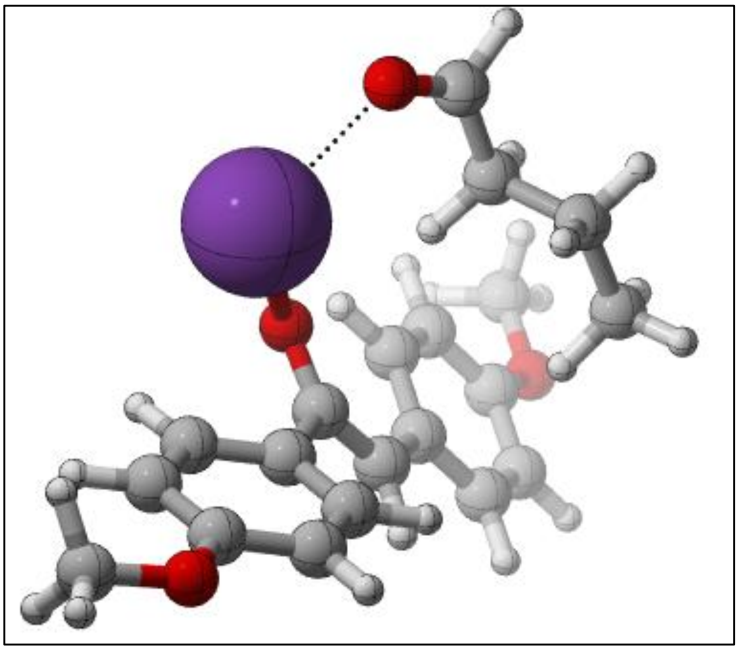


| | | | |
|---|---|---|---|
| C | 3.330859000000 | 1.535819000000 | 0.370774000000 |
| C | 2.460147000000 | 0.458620000000 | 0.229529000000 |
| C | 1.078506000000 | 1.689272000000 | -1.177525000000 |
| C | 1.914212000000 | 2.799423000000 | -1.095524000000 |

| | | | |
|---|---|---|---|
| C | 3.058395000000 | 2.729098000000 | -0.301074000000 |
| H | 4.213341000000 | 1.434470000000 | 0.995756000000 |
| H | 0.184145000000 | 1.684561000000 | -1.788666000000 |
| H | 1.664231000000 | 3.696552000000 | -1.651755000000 |
| H | 3.725271000000 | 3.580623000000 | -0.206102000000 |
| C | 2.727281000000 | -0.901825000000 | 0.842964000000 |
| H | 3.256181000000 | -1.520631000000 | 0.106446000000 |
| H | 3.375648000000 | -0.813070000000 | 1.726944000000 |
| N | 1.446082000000 | -1.571405000000 | 1.118741000000 |
| H | 1.039627000000 | -1.164083000000 | 1.958493000000 |
| C | 1.435222000000 | -3.044150000000 | 1.271928000000 |
| H | 1.848094000000 | -3.361622000000 | 2.243222000000 |
| H | 2.055606000000 | -3.461717000000 | 0.471672000000 |
| C | -0.027692000000 | -3.502232000000 | 1.079933000000 |
| H | -0.045144000000 | -4.604561000000 | 1.201772000000 |
| H | -0.598541000000 | -3.095195000000 | 1.951023000000 |
| O | -0.541029000000 | -3.095364000000 | -0.129577000000 |
| N | 1.333129000000 | 0.539689000000 | -0.523320000000 |
| Mn | 0.173986000000 | -1.128423000000 | -0.481467000000 |
| C | -1.067487000000 | -0.333090000000 | 0.628188000000 |
| C | 1.173142000000 | -1.960589000000 | -1.790929000000 |
| O | -1.838969000000 | 0.224462000000 | 1.296115000000 |
| O | 1.586493000000 | -2.539752000000 | -2.714403000000 |
| C | -5.813263000000 | -0.316948000000 | -0.629749000000 |
| H | -6.241643000000 | -1.083496000000 | -1.286991000000 |
| H | -5.516223000000 | -0.809385000000 | 0.303173000000 |
| H | -6.609437000000 | 0.396700000000 | -0.390743000000 |
| C | -4.614610000000 | 0.374339000000 | -1.289674000000 |
| H | -4.957103000000 | 0.891496000000 | -2.196611000000 |
| H | -4.230809000000 | 1.152903000000 | -0.617715000000 |
| C | -3.473287000000 | -0.594980000000 | -1.626451000000 |
| H | -3.165361000000 | -1.102362000000 | -0.705125000000 |
| H | -3.853330000000 | -1.372192000000 | -2.305521000000 |
| C | -2.188015000000 | 0.057505000000 | -2.229288000000 |
| H | -2.065572000000 | 1.020067000000 | -1.678288000000 |
| O | -1.069511000000 | -0.729799000000 | -2.157688000000 |
| C | -1.242379000000 | 2.692162000000 | -4.293259000000 |

| | | | |
|---|---|---|---|
| C | -1.246300000000 | 1.288188000000 | -4.256912000000 |
| C | -0.084615000000 | 0.623089000000 | -4.665678000000 |
| C | 1.040632000000 | 1.323806000000 | -5.107969000000 |
| C | 1.022970000000 | 2.723229000000 | -5.138675000000 |
| C | -0.128638000000 | 3.406530000000 | -4.724117000000 |
| H | -2.125331000000 | 3.238774000000 | -3.968244000000 |
| H | -0.047525000000 | -0.458143000000 | -4.612880000000 |
| H | 1.920514000000 | 0.769409000000 | -5.412869000000 |
| H | -0.129993000000 | 4.491608000000 | -4.753809000000 |
| O | 2.065663000000 | 3.508162000000 | -5.550439000000 |
| C | 3.256819000000 | 2.865940000000 | -5.971660000000 |
| H | 3.084189000000 | 2.216699000000 | -6.840092000000 |
| H | 3.947345000000 | 3.663033000000 | -6.253191000000 |
| C | -2.448712000000 | 0.529454000000 | -3.715378000000 |
| H | -3.287650000000 | 1.235643000000 | -3.685423000000 |
| C | -2.860165000000 | -0.586899000000 | -4.686744000000 |
| C | -3.608289000000 | -0.224155000000 | -5.931788000000 |
| C | -4.055538000000 | -1.263954000000 | -6.761235000000 |
| C | -3.896492000000 | 1.098764000000 | -6.321255000000 |
| C | -4.769727000000 | -1.016286000000 | -7.928898000000 |
| H | -3.830632000000 | -2.283309000000 | -6.466461000000 |
| C | -4.603308000000 | 1.363655000000 | -7.483682000000 |
| H | -3.547943000000 | 1.933047000000 | -5.724904000000 |
| C | -5.049156000000 | 0.308716000000 | -8.296542000000 |
| H | -5.101482000000 | -1.847234000000 | -8.540129000000 |
| H | -4.822717000000 | 2.380769000000 | -7.790833000000 |
| O | -5.736341000000 | 0.672656000000 | -9.410846000000 |
| C | -6.210455000000 | -0.346580000000 | -10.280081000000 |
| H | -6.722287000000 | 0.168178000000 | -11.094259000000 |
| H | -5.385759000000 | -0.942305000000 | -10.690645000000 |
| H | -6.918519000000 | -1.012985000000 | -9.771952000000 |
| O | -2.608098000000 | -1.776188000000 | -4.476373000000 |
| K | -1.594911000000 | -3.230212000000 | -2.438114000000 |
| H | 3.704226000000 | 2.269275000000 | -5.165769000000 |

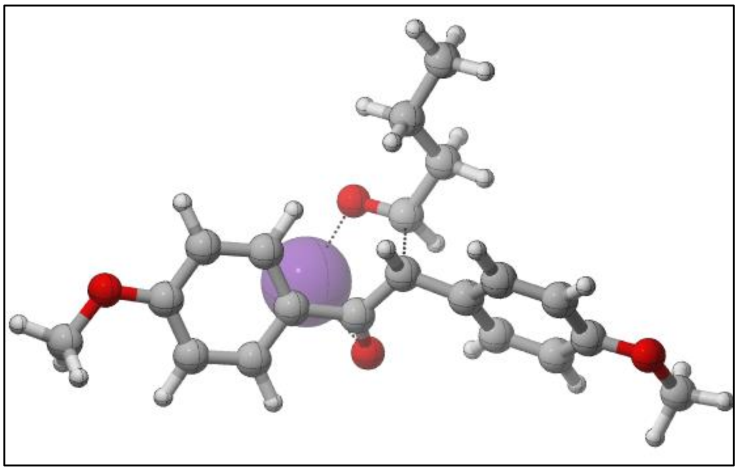
- **<u>IM-1C´:</u>**



| | | | |
|---|---|---|---|
| C | -0.764580000000 | -0.524629000000 | -0.124839000000 |
| C | -0.628725000000 | 0.190013000000 | -1.322005000000 |
| C | -1.556847000000 | -0.018001000000 | -2.353424000000 |
| C | -2.599179000000 | -0.923623000000 | -2.190767000000 |
| C | -2.762708000000 | -1.656617000000 | -0.998211000000 |
| C | -1.825634000000 | -1.426699000000 | 0.022838000000 |
| H | -0.045192000000 | -0.409632000000 | 0.678883000000 |
| H | -1.440548000000 | 0.547383000000 | -3.273168000000 |
| H | -3.313863000000 | -1.067848000000 | -2.995757000000 |
| H | -1.910267000000 | -2.010639000000 | 0.937140000000 |
| C | -3.918570000000 | -2.600640000000 | -0.751382000000 |
| C | -4.292363000000 | -3.436216000000 | -1.787339000000 |
| H | -3.716607000000 | -3.376248000000 | -2.707252000000 |
| C | -5.333447000000 | -4.451505000000 | -1.761119000000 |
| C | -5.638164000000 | -5.174857000000 | -2.940978000000 |
| C | -6.083629000000 | -4.785276000000 | -0.611306000000 |
| C | -6.625395000000 | -6.148583000000 | -2.978394000000 |
| H | -5.078522000000 | -4.958051000000 | -3.848674000000 |
| C | -7.079030000000 | -5.766307000000 | -0.639563000000 |
| H | -5.854786000000 | -4.262304000000 | 0.309546000000 |
| C | -7.360739000000 | -6.453380000000 | -1.824500000000 |
| H | -6.845323000000 | -6.692233000000 | -3.892607000000 |
| H | -7.620691000000 | -5.990192000000 | 0.273812000000 |

| | | | |
|---|---|---|---|
| C | -7.676643000000 | -1.288947000000 | -0.183941000000 |
| H | -8.427999000000 | -2.079865000000 | -0.059501000000 |
| H | -6.682316000000 | -1.742431000000 | -0.085833000000 |
| C | -7.864543000000 | -0.645515000000 | -1.583843000000 |
| H | -8.858415000000 | -0.181400000000 | -1.643617000000 |
| H | -7.136232000000 | 0.168045000000 | -1.699721000000 |
| C | -7.686634000000 | -1.662023000000 | -2.714895000000 |
| H | -7.830455000000 | -1.180621000000 | -3.687943000000 |
| H | -6.686425000000 | -2.103055000000 | -2.687143000000 |
| H | -8.410500000000 | -2.478934000000 | -2.631423000000 |
| C | -7.888518000000 | -0.253099000000 | 0.876355000000 |
| H | -8.940832000000 | 0.059157000000 | 1.051149000000 |
| O | -4.446744000000 | -2.534622000000 | 0.434683000000 |
| O | -8.320977000000 | -7.431435000000 | -1.962678000000 |
| O | 0.355924000000 | 1.106185000000 | -1.578393000000 |
| O | -6.997878000000 | 0.295289000000 | 1.512067000000 |
| K | -4.387380000000 | -0.242942000000 | 1.456076000000 |
| C | 1.354755000000 | 1.305302000000 | -0.594401000000 |
| H | 1.906016000000 | 0.380161000000 | -0.380537000000 |
| H | 2.043405000000 | 2.045315000000 | -1.005655000000 |
| H | 0.933303000000 | 1.691837000000 | 0.344096000000 |
| C | -9.056898000000 | -7.794935000000 | -0.813943000000 |
| H | -9.745838000000 | -8.582879000000 | -1.126592000000 |
| H | -8.408441000000 | -8.182275000000 | -0.015460000000 |
| H | -9.637715000000 | -6.951894000000 | -0.412539000000 |

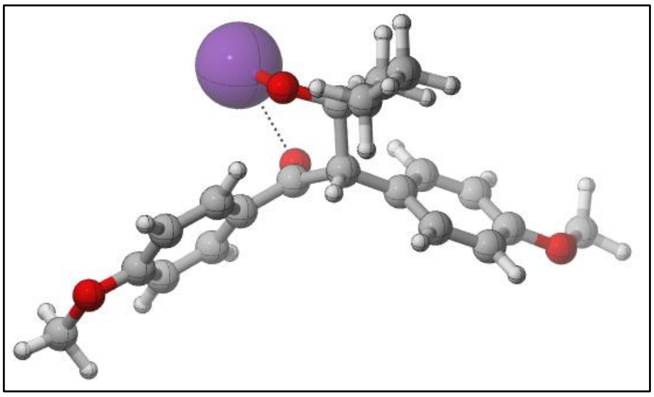
- **TS-1C´:**



| | | | |
|---|---|---|---|
| C | -0.344262000000 | -0.389545000000 | 0.137533000000 |
| C | -0.581169000000 | 0.421917000000 | -0.982218000000 |
| C | -1.797393000000 | 0.311853000000 | -1.674852000000 |
| C | -2.753285000000 | -0.615856000000 | -1.279027000000 |
| C | -2.527303000000 | -1.444271000000 | -0.161383000000 |
| C | -1.322093000000 | -1.298860000000 | 0.542475000000 |
| H | 0.588273000000 | -0.327208000000 | 0.686400000000 |
| H | -1.967496000000 | 0.964779000000 | -2.525130000000 |
| H | -3.709064000000 | -0.657652000000 | -1.787691000000 |
| H | -1.151896000000 | -1.928066000000 | 1.411086000000 |
| C | -3.545221000000 | -2.418235000000 | 0.360547000000 |
| C | -4.501147000000 | -3.012541000000 | -0.573751000000 |
| H | -4.176058000000 | -2.886707000000 | -1.606447000000 |
| C | -4.952865000000 | -4.415419000000 | -0.331869000000 |
| C | -5.085343000000 | -5.297053000000 | -1.424082000000 |
| C | -5.301738000000 | -4.913328000000 | 0.933200000000 |
| C | -5.537063000000 | -6.600332000000 | -1.267054000000 |
| H | -4.823695000000 | -4.948023000000 | -2.420316000000 |
| C | -5.751884000000 | -6.226600000000 | 1.108123000000 |
| H | -5.187443000000 | -4.272608000000 | 1.798305000000 |
| C | -5.875619000000 | -7.077465000000 | 0.006643000000 |
| H | -5.632073000000 | -7.270167000000 | -2.116028000000 |
| H | -6.000886000000 | -6.568086000000 | 2.106696000000 |
| C | -6.924179000000 | -2.228521000000 | -1.537206000000 |
| H | -7.908312000000 | -1.838613000000 | -1.234111000000 |
| H | -7.035329000000 | -3.314799000000 | -1.629834000000 |
| C | -6.549522000000 | -1.597546000000 | -2.880515000000 |
| H | -6.383742000000 | -0.527683000000 | -2.714043000000 |
| H | -5.592153000000 | -2.009070000000 | -3.230424000000 |
| C | -7.610714000000 | -1.810760000000 | -3.964965000000 |
| H | -7.318171000000 | -1.345097000000 | -4.913057000000 |
| H | -7.778975000000 | -2.877044000000 | -4.157525000000 |
| H | -8.572821000000 | -1.377549000000 | -3.666310000000 |
| C | -5.965069000000 | -1.866700000000 | -0.384145000000 |
| H | -6.314268000000 | -2.365301000000 | 0.554595000000 |
| O | -3.595839000000 | -2.580007000000 | 1.600490000000 |

| | | | |
|---|---|---|---|
| O | -6.309218000000 | -8.377880000000 | 0.063011000000 |
| O | 0.295864000000 | 1.346418000000 | -1.466616000000 |
| O | -5.643305000000 | -0.606728000000 | -0.290942000000 |
| K | -4.484175000000 | 0.011359000000 | 1.843911000000 |
| C | 1.558364000000 | 1.477693000000 | -0.832102000000 |
| H | 2.127817000000 | 0.540295000000 | -0.865695000000 |
| H | 2.097226000000 | 2.245374000000 | -1.389383000000 |
| H | 1.456675000000 | 1.797198000000 | 0.213451000000 |
| C | -6.662118000000 | -8.903426000000 | 1.328117000000 |
| H | -6.976266000000 | -9.934386000000 | 1.153263000000 |
| H | -5.811999000000 | -8.900700000000 | 2.024023000000 |
| H | -7.492787000000 | -8.347906000000 | 1.784596000000 |

- **IM-2C´:**



| | | | |
|---|---|---|---|
| C | -0.351301000000 | -0.615350000000 | 0.197068000000 |
| C | -0.460605000000 | 0.204108000000 | -0.935537000000 |
| C | -1.683535000000 | 0.289164000000 | -1.622729000000 |
| C | -2.775113000000 | -0.459768000000 | -1.207643000000 |
| C | -2.673961000000 | -1.293796000000 | -0.077220000000 |
| C | -1.463155000000 | -1.341990000000 | 0.624632000000 |
| H | 0.581822000000 | -0.694329000000 | 0.742418000000 |
| H | -1.747579000000 | 0.952079000000 | -2.479836000000 |
| H | -3.746710000000 | -0.360659000000 | -1.683893000000 |
| H | -1.391819000000 | -1.972714000000 | 1.505783000000 |
| C | -3.839938000000 | -2.083586000000 | 0.425130000000 |
| C | -4.802669000000 | -2.721456000000 | -0.564749000000 |
| H | -4.399858000000 | -2.583072000000 | -1.571173000000 |
| C | -5.027171000000 | -4.201533000000 | -0.343013000000 |
| C | -4.879628000000 | -5.099632000000 | -1.415447000000 |

| | | | |
|---|---|---|---|
| C | -5.432329000000 | -4.733819000000 | 0.888069000000 |
| C | -5.125099000000 | -6.459498000000 | -1.271555000000 |
| H | -4.567136000000 | -4.720793000000 | -2.385600000000 |
| C | -5.678802000000 | -6.100702000000 | 1.052559000000 |
| H | -5.533824000000 | -4.072616000000 | 1.740429000000 |
| C | -5.528595000000 | -6.971467000000 | -0.031226000000 |
| H | -5.009160000000 | -7.145496000000 | -2.104765000000 |
| H | -5.985185000000 | -6.468846000000 | 2.025221000000 |
| C | -7.171217000000 | -2.148719000000 | -1.520911000000 |
| H | -8.094469000000 | -1.629129000000 | -1.224955000000 |
| H | -7.396000000000 | -3.224501000000 | -1.505997000000 |
| C | -6.798239000000 | -1.695188000000 | -2.935384000000 |
| H | -6.493587000000 | -0.644827000000 | -2.874614000000 |
| H | -5.921460000000 | -2.254609000000 | -3.291186000000 |
| C | -7.937463000000 | -1.864958000000 | -3.945783000000 |
| H | -7.645222000000 | -1.526192000000 | -4.946618000000 |
| H | -8.247496000000 | -2.913753000000 | -4.028986000000 |
| H | -8.820138000000 | -1.287182000000 | -3.645634000000 |
| C | -6.111804000000 | -1.796002000000 | -0.447035000000 |
| H | -6.556314000000 | -2.148881000000 | 0.529966000000 |
| O | -4.004649000000 | -2.186225000000 | 1.649123000000 |
| O | -5.745339000000 | -8.324075000000 | 0.015279000000 |
| O | 0.554295000000 | 0.960558000000 | -1.441467000000 |
| O | -5.741774000000 | -0.491288000000 | -0.449547000000 |
| K | -5.311534000000 | 0.188936000000 | 1.876243000000 |
| C | 1.820665000000 | 0.906384000000 | -0.803836000000 |
| H | 2.236146000000 | -0.109288000000 | -0.813921000000 |
| H | 2.474307000000 | 1.567113000000 | -1.375357000000 |
| H | 1.768354000000 | 1.261141000000 | 0.233790000000 |
| C | -6.158952000000 | -8.888509000000 | 1.245432000000 |
| H | -6.276749000000 | -9.958746000000 | 1.064904000000 |
| H | -5.411341000000 | -8.738327000000 | 2.036163000000 |
| H | -7.118410000000 | -8.473812000000 | 1.583154000000 |

**15.8. DFT calculation to understand more favourable bifunctional site of Mn-1 complex:**

During the catalytic screening with Mn(NH)OH (Mn-1), Mn(NMe)OH (**Mn-2**) and Mn(NH)OMe (Mn-3) indicate that OH functionality[28] is crucial for the success of the reaction and the presence of both free amine and hydroxyl functionality at ligand framework enhanced the catalytic activity. Amido complexes are well known for their MLC[29] and here we observed the formation of Mn-alkoxide complexes (figure 2, main manuscript). Thus complex having dual bifunctional sites can choose the appropriate MLC mode when confronting different catalytic stages during the catalysis. Therefore, computational calculations were performed to understand which bifunctional site could be the most appropriate and energetically most favorable. We compared Gibbs free energy in this current transformation for both bifunctional sites separately employing symmetry constraints using PBE0 functional along with the def2-TZVP basis set for all atoms. At first, under the standard conditions, hexacoordinate tricarbonyl cationic bromide complex (**Mn-1**) converted to pentacoordinated dicarbonyl either amido or Mn-alkoxide complex. But pentacoordinate dicarbonyl Mn-alkoxide complex (Mn-1a) is energetically lower by 3.0 kcal/mol compared to amido complex (Mn-1b) which indicates that deprotonation of the hydroxyl arm is very fast and energetically favorable. Next, the dehydrogenation of alcohol to aldehyde can go via MLC using amido/ Mn-alkoxide arm to form Mn-H intermediate III. The activation barrier through amido assisted path-way required 12.3 kcal/mol whereas only 7.7 kcal/mol energy is involved to reach oxide six-member transition state. Comparing these two transition state, amido assisted transition state (TSIIb-III) 13.5 kcal/mol higher in energy. The formation of Mn-H and elimination of aldehyde showed endothermic process by 23.5 kcal/mol (TSIIb-III→III) and 10 kcal/mol (TSIIa-III→III). At this stage, the formed aldehyde undergoes catalytic aldol condensation (detailed described in figure 4) with the bulky enolate to result in highly branched α, β-unsaturated ketone upon removal of $H_2O$. Next, in the transfer hydrogenation step, the in situ formed α, β-unsaturated ketone undergoes hydrogenation through the transfer of hydride from the Mn−H and followed by proton transfer from the O-H or N−H sites of the complex [PyN(NH)(OH)-MnH$(CO)_2$] to the C=C double bond of the α, β-unsaturated ketone. Energy calculation and buried volume plot (see SI, S150-S151) of III recommended that reduction of α, β-unsaturated ketone via "H−O−Mn−H" is more feasible than "H−N−Mn−H" pathway to deliver desired hydrogenated product. The comparative energy profile of both routes indicate that once α, β-unsaturated ketone intermediate was formed, the subsequent hydride and proton are transferred at β-carbon and carbonyl oxygen of α, β-unsaturated ketone from "H−O−Mn−H" occurred via TSIIIA & Int-a with a free-energy barrier of 12.1 kcal/mol, whereas 18.2 kcal/mol energy is required and proceeds via TSIIIB pathway. This result underpins that the proton transfer from hydroxyl site is more kinetically as well as thermodynamically favorable and irreversible in nature than that of bulky “N-H” end.

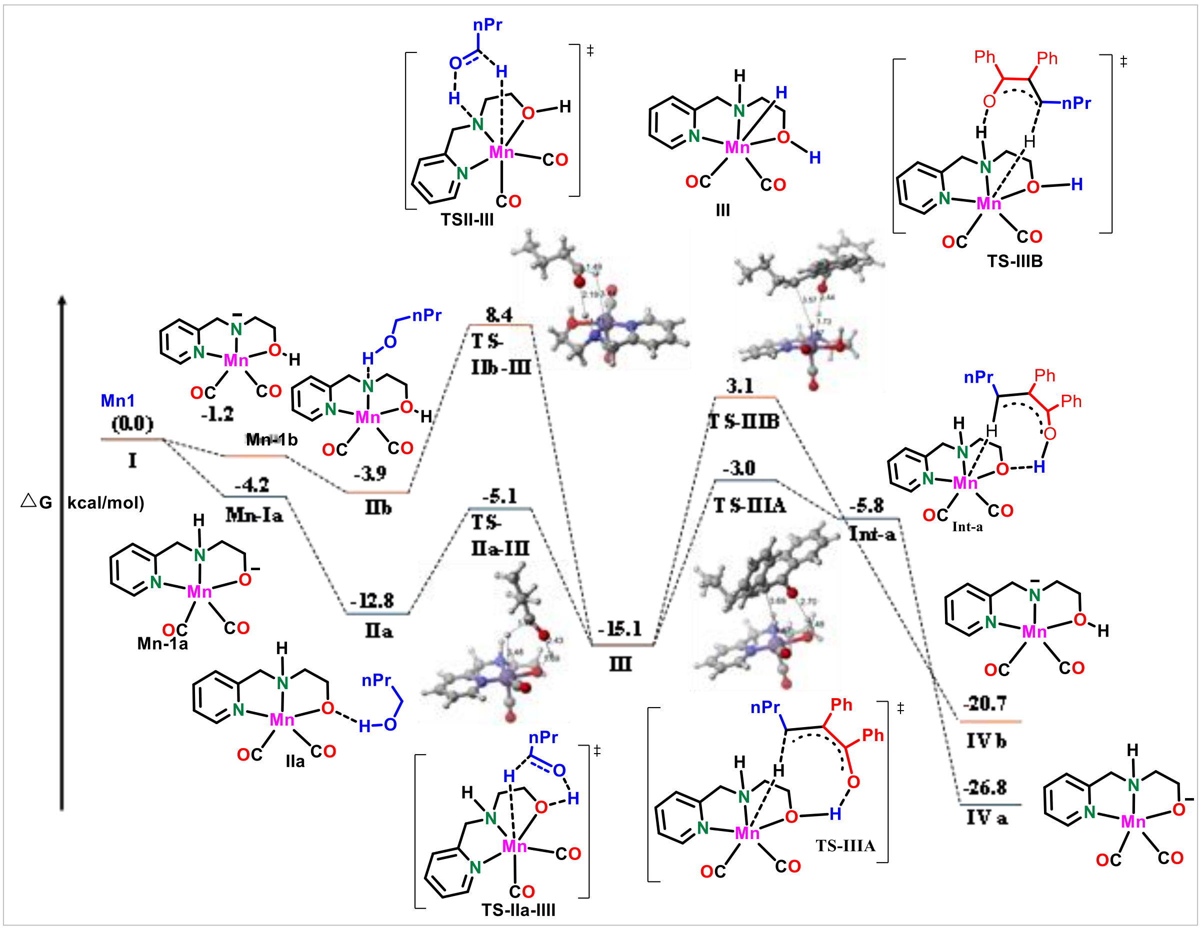


**Figure 70.** Energy profile diagram of our Mn-catalyzed C(sp$^3$)-C(sp$^3$) coupling of two bulky partners.

## 15.9. Plausible Reaction mechanism:

Accounting all experimental results and theoretical calculations it is anticipated that the Mn-alkoxide site not only plays a key role in facilitating the chelation-assisted aldol reaction but also demonstrates superior bifunctional activity compared to the manganese-amido site. The hydroxyl bifunctional site's lower acidity and reduced steric hindrance enhance its participation in metal-ligand cooperation, which is also reflected by computational analysis. As a result, the dehydrogenation and transfer-hydrogenation processes are most likely to proceed via pathway-I, ultimately yielding the desired branched products (figure 5).

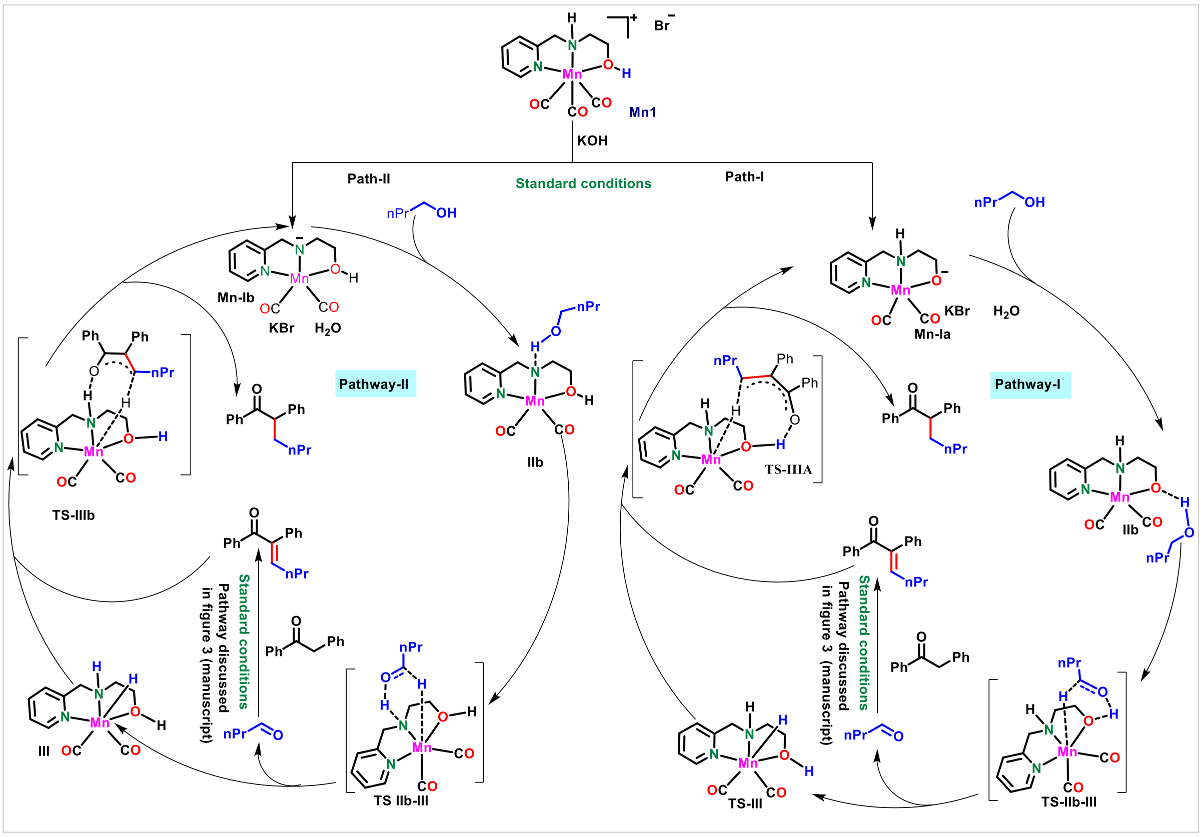
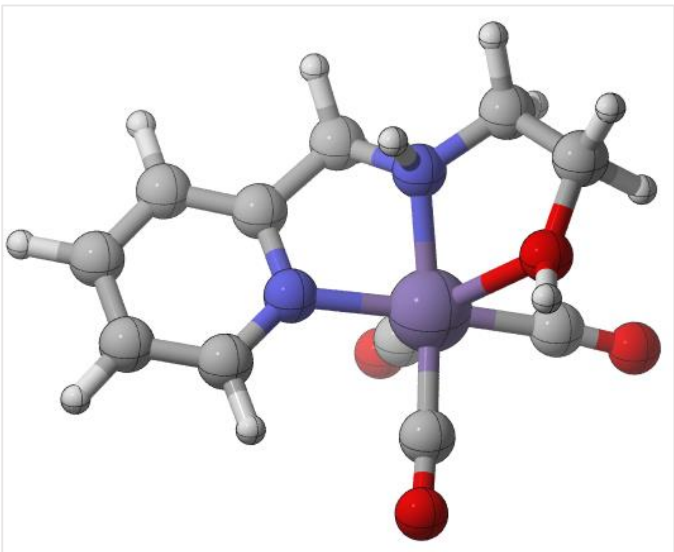


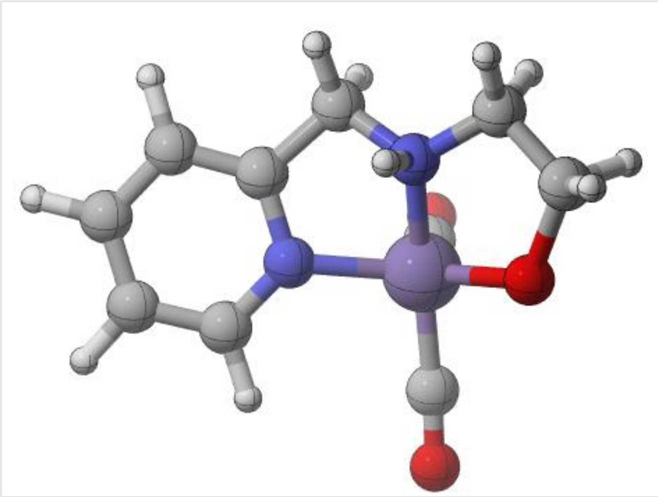

**Figure71.** Plausible catalytic pathways via metal-ligand cooperativity through Mn-amido and Mn-alkoxide arm.



## Structure I

| | | | |
|---|---|---|---|
| C | -1.811418000 | -1.075366000 | 0.193328000 |
| C | -3.168317000 | -1.400734000 | 0.236872000 |

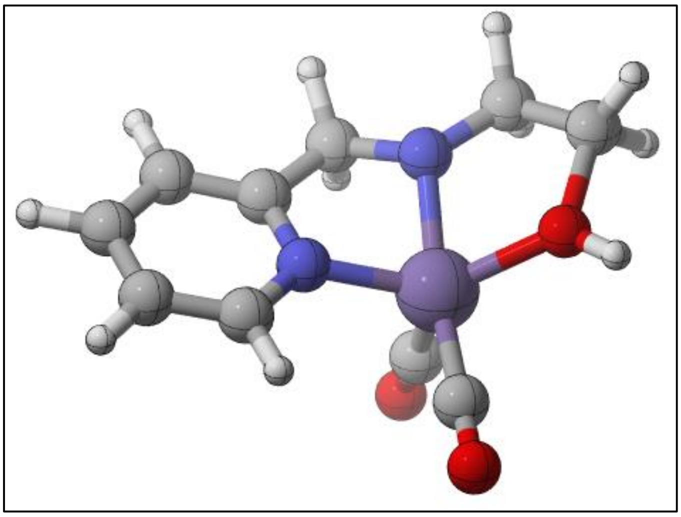
| | | | |
|---|---|---|---|
| C | -4.099877000 | -0.492815000 | -0.286941000 |
| C | -3.650746000 | 0.703022000 | -0.844531000 |
| C | -2.272785000 | 0.986735000 | -0.860056000 |
| H | -3.507670000 | -2.342680000 | 0.676360000 |
| H | -5.169952000 | -0.728833000 | -0.257397000 |
| H | -4.355939000 | 1.427567000 | -1.265339000 |
| H | -1.904205000 | 1.927736000 | -1.303607000 |
| N | -1.360359000 | 0.114739000 | -0.353203000 |
| C | -0.715062000 | -1.992530000 | 0.706596000 |
| H | -0.989954000 | -3.066599000 | 0.565492000 |
| N | 0.495484000 | -1.577926000 | -0.082402000 |
| Mn | 0.569539000 | 0.400883000 | 0.019031000 |
| C | 0.508110000 | 2.154879000 | -0.540148000 |
| O | 0.425564000 | 3.194629000 | -1.034678000 |
| C | 2.331795000 | 0.746611000 | 0.442669000 |
| O | 3.406744000 | 1.063547000 | 0.730295000 |
| O | 2.301346184 | -0.362159130 | -1.099632223 |
| C | 1.753323000 | -2.366151000 | 0.074201000 |
| H | 1.615253000 | -3.434492000 | -0.233617000 |
| C | 2.810862000 | -1.696581000 | -0.825537000 |
| H | -0.547064000 | -1.870095000 | 1.804725000 |
| H | 2.074063000 | -2.423116000 | 1.141579000 |
| H | 3.631145000 | -1.216249000 | -0.252437000 |
| H | 3.286547000 | -2.404165000 | -1.536116000 |
| C | 0.020465000 | 0.885008000 | 1.675165000 |
| O | -0.368253000 | 1.129679000 | 2.737450000 |
| H | 2.330959882 | 0.194402403 | -1.926955917 |
| H | 0.208524426 | -2.025641652 | -1.004525644 |



**Mn-Ia**

| | | | |
|---|---|---|---|
| C | -1.811418000 | -1.075366000 | 0.193328000 |
| C | -3.168317000 | -1.400734000 | 0.236872000 |
| C | -4.099877000 | -0.492815000 | -0.286941000 |
| C | -3.650746000 | 0.703022000 | -0.844531000 |
| C | -2.272785000 | 0.986735000 | -0.860056000 |
| H | -3.507670000 | -2.342680000 | 0.676360000 |
| H | -5.169952000 | -0.728833000 | -0.257397000 |
| H | -4.355939000 | 1.427567000 | -1.265339000 |
| H | -1.904205000 | 1.927736000 | -1.303607000 |
| N | -1.360359000 | 0.114739000 | -0.353203000 |
| C | -0.715062000 | -1.992530000 | 0.706596000 |
| H | -0.989954000 | -3.066599000 | 0.565492000 |
| N | 0.495484000 | -1.577926000 | -0.082402000 |
| Mn | 0.569539000 | 0.400883000 | 0.019031000 |
| C | 0.747434969 | 2.178548379 | -0.429539473 |
| O | 0.814497152 | 3.247586225 | -0.859788905 |
| O | 2.279217695 | -0.130401906 | -0.966711783 |
| C | 1.753323000 | -2.366151000 | 0.074201000 |
| H | 1.615253000 | -3.434492000 | -0.233617000 |
| C | 2.810862000 | -1.696581000 | -0.825537000 |
| H | -0.547064000 | -1.870095000 | 1.804725000 |

| | | | |
|---|---|---|---|
| H | 2.074063000 | -2.423116000 | 1.141579000 |
| H | 3.654162316 | -1.686873911 | -0.103888200 |
| H | 3.284065566 | -2.160315299 | -1.715987862 |
| C | 0.468730398 | 0.872789103 | 1.764247707 |
| O | 0.364317749 | 1.112029322 | 2.891756962 |
| H | 0.208524426 | -2.025641652 | -1.004525644 |

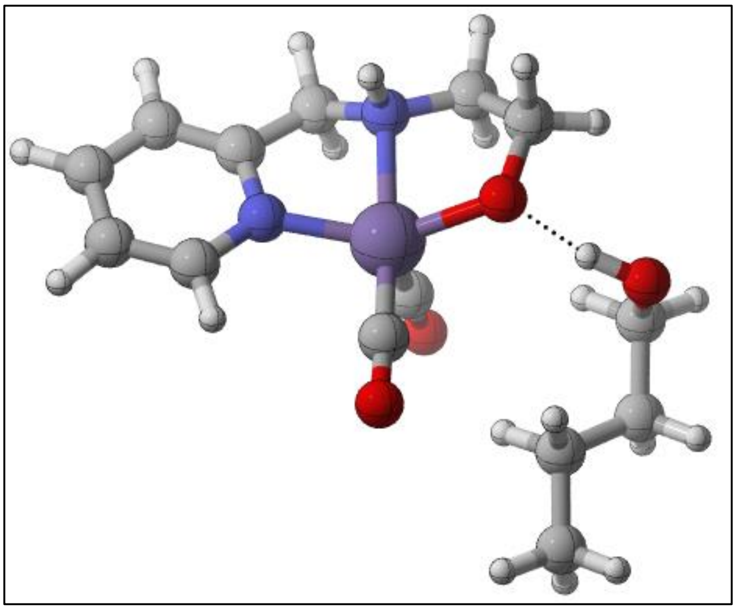


**Mn-Ib**

| | | | |
|---|---|---|---|
| C | -1.811418000 | -1.075366000 | 0.193328000 |
| C | -3.168317000 | -1.400734000 | 0.236872000 |
| C | -4.099877000 | -0.492815000 | -0.286941000 |
| C | -3.650746000 | 0.703022000 | -0.844531000 |
| C | -2.272785000 | 0.986735000 | -0.860056000 |
| H | -3.507670000 | -2.342680000 | 0.676360000 |
| H | -5.169952000 | -0.728833000 | -0.257397000 |
| H | -4.355939000 | 1.427567000 | -1.265339000 |
| H | -1.904205000 | 1.927736000 | -1.303607000 |
| N | -1.360359000 | 0.114739000 | -0.353203000 |
| C | -0.715062000 | -1.992530000 | 0.706596000 |
| H | -0.989954000 | -3.066599000 | 0.565492000 |
| N | 0.495484000 | -1.577926000 | -0.082402000 |
| Mn | 0.569539000 | 0.400883000 | 0.019031000 |

| | | | |
|---|---|---|---|
| C | 0.747434969 | 2.178548379 | -0.429539473 |
| O | 0.814497152 | 3.247586225 | -0.859788905 |
| O | 2.279217695 | -0.130401906 | -0.966711783 |
| C | 1.753323000 | -2.366151000 | 0.074201000 |
| H | 1.615253000 | -3.434492000 | -0.233617000 |
| C | 2.810862000 | -1.696581000 | -0.825537000 |
| H | -0.547064000 | -1.870095000 | 1.804725000 |
| H | 2.074063000 | -2.423116000 | 1.141579000 |
| H | 3.654162316 | -1.686873911 | -0.103888200 |
| H | 3.284065566 | -2.160315299 | -1.715987862 |
| C | 0.468730398 | 0.872789103 | 1.764247707 |
| O | 0.364317749 | 1.112029322 | 2.891756962 |
| H | 2.904250991 | 0.388136723 | -1.478621023 |

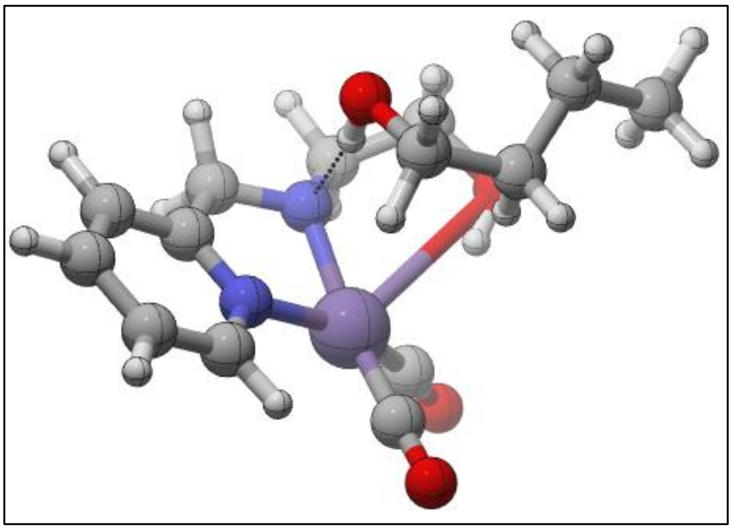
- **IIa:**



| | | | |
|---|---|---|---|
| C | -2.856081000000 | 0.158660000000 | 0.010093000000 |
| C | -4.144657000000 | 0.639021000000 | 0.125149000000 |
| C | -4.469481000000 | 1.931920000000 | -0.326158000000 |
| C | -3.410531000000 | 2.691441000000 | -0.876875000000 |
| C | -2.148354000000 | 2.151692000000 | -0.988900000000 |
| H | -4.898872000000 | 0.002440000000 | 0.584312000000 |
| H | -5.476368000000 | 2.327122000000 | -0.244801000000 |

| | | | |
|---|---|---|---|
| H | -3.577858000000 | 3.705499000000 | -1.231885000000 |
| H | -1.328149000000 | 2.713177000000 | -1.421988000000 |
| N | -1.820209000000 | 0.875445000000 | -0.586011000000 |
| C | -2.405019000000 | -1.168552000000 | 0.555931000000 |
| H | -3.245737000000 | -1.867965000000 | 0.688634000000 |
| N | -1.368534000000 | -1.657638000000 | -0.359418000000 |
| Mn | -0.059357000000 | -0.049265000000 | -0.634934000000 |
| C | 0.920933000000 | 1.291199000000 | -1.269977000000 |
| O | 1.546010000000 | 2.195530000000 | -1.680908000000 |
| C | 0.556392000000 | 0.196756000000 | 0.992599000000 |
| O | 1.007989000000 | 0.378519000000 | 2.066328000000 |
| O | 1.032907000000 | -1.555572000000 | -1.388821000000 |
| C | -0.517478000000 | -2.798767000000 | -0.008923000000 |
| H | -1.076578000000 | -3.748002000000 | 0.065086000000 |
| C | 0.558215000000 | -2.832617000000 | -1.112336000000 |
| H | -1.907022000000 | -1.029745000000 | 1.528265000000 |
| H | -0.062287000000 | -2.575329000000 | 0.960814000000 |
| H | 1.373270000000 | -3.511288000000 | -0.801855000000 |
| H | 0.092549000000 | -3.299654000000 | -2.010834000000 |
| H | 2.613198000000 | -1.697877000000 | -1.152435000000 |
| O | 3.542626000000 | -1.980951000000 | -0.900478000000 |
| C | 3.733105000000 | -1.669996000000 | 0.460147000000 |
| C | 4.658478000000 | -0.458228000000 | 0.642313000000 |
| H | 5.615720000000 | -0.679795000000 | 0.146709000000 |
| C | 4.060019000000 | 0.822966000000 | 0.058321000000 |
| C | 5.009512000000 | 2.022251000000 | 0.100842000000 |
| H | 5.930557000000 | 1.821402000000 | -0.462223000000 |
| H | 4.538137000000 | 2.911375000000 | -0.332656000000 |
| H | 5.302724000000 | 2.265411000000 | 1.130862000000 |
| H | 3.760316000000 | 0.623161000000 | -0.974820000000 |
| H | 3.139280000000 | 1.064894000000 | 0.599024000000 |
| H | 4.876746000000 | -0.321155000000 | 1.713346000000 |
| H | 4.181461000000 | -2.539941000000 | 0.973281000000 |
| H | -1.786219000000 | -1.821428000000 | -1.277698000000 |
| H | 2.773365000000 | -1.461388000000 | 0.957225000000 |

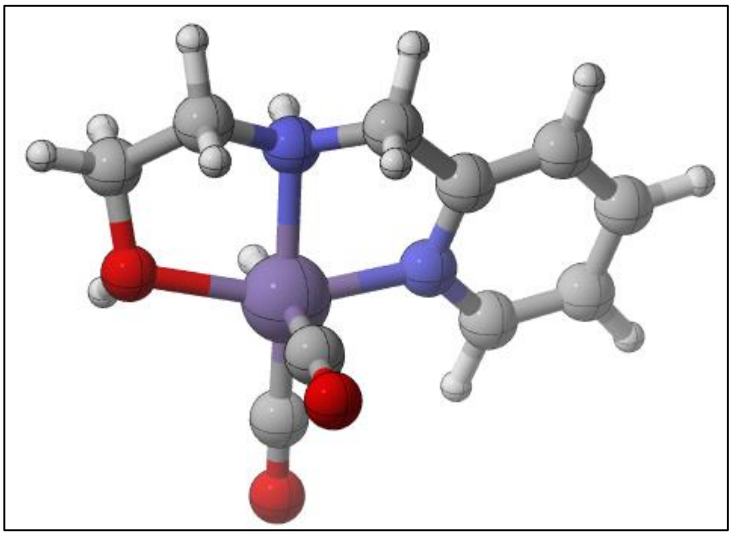
➢ **IIb:**



| | | | |
|---|---|---|---|
| C | -0.368480000000 | 2.010632000000 | -0.935337000000 |
| C | -0.282408000000 | 3.392758000000 | -1.118348000000 |
| C | 0.297565000000 | 4.183307000000 | -0.131927000000 |
| C | 0.780618000000 | 3.557263000000 | 1.025111000000 |
| C | 0.661050000000 | 2.181468000000 | 1.141710000000 |
| H | -0.661594000000 | 3.829011000000 | -2.037952000000 |
| H | 0.379105000000 | 5.259377000000 | -0.258770000000 |
| H | 1.245666000000 | 4.126136000000 | 1.824144000000 |
| H | 1.016869000000 | 1.646945000000 | 2.014851000000 |
| N | 0.097048000000 | 1.406689000000 | 0.184617000000 |
| C | -0.987339000000 | 1.080597000000 | -1.939365000000 |
| H | -0.699206000000 | 1.420515000000 | -2.954904000000 |
| N | -0.587996000000 | -0.280983000000 | -1.657812000000 |
| Mn | -0.257855000000 | -0.614575000000 | 0.279599000000 |
| C | 0.463406000000 | -0.802606000000 | 1.898390000000 |
| O | 0.977159000000 | -0.912039000000 | 2.961918000000 |
| C | -1.086777000000 | -2.166405000000 | 0.556463000000 |
| O | -1.727750000000 | -3.115096000000 | 0.850053000000 |
| O | 0.131014000000 | -3.264907000000 | -2.014155000000 |
| C | -1.136596000000 | -1.214756000000 | -2.634664000000 |
| H | -1.394973000000 | -0.689623000000 | -3.573146000000 |
| C | -0.140911000000 | -2.312526000000 | -3.031083000000 |
| H | -2.088801000000 | 1.224231000000 | -1.886806000000 |
| H | -2.064137000000 | -1.693792000000 | -2.274549000000 |

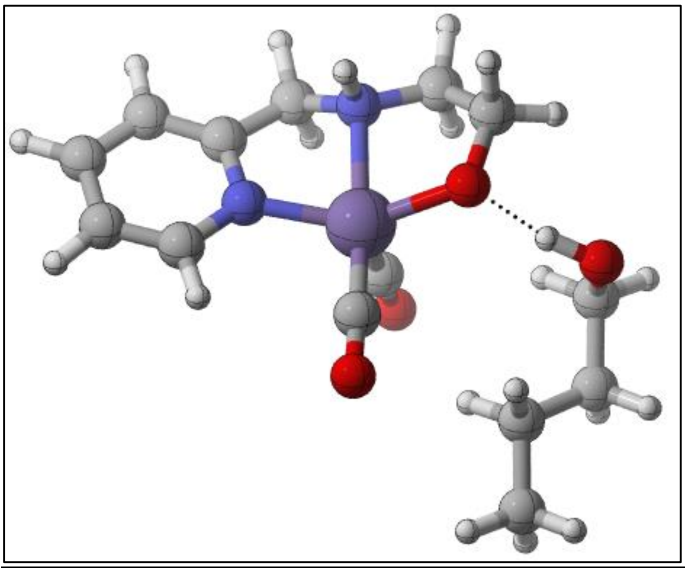
| | | | |
|---|---|---|---|
| H | -0.548290000000 | -2.875261000000 | -3.883644000000 |
| H | 0.785930000000 | -1.820577000000 | -3.365090000000 |
| H | 0.086442000000 | -2.799229000000 | -1.157171000000 |
| O | 2.052130000000 | 0.346646000000 | -2.387355000000 |
| C | 2.935318000000 | 0.048572000000 | -1.322449000000 |
| C | 3.117781000000 | -1.459367000000 | -1.113317000000 |
| H | 2.137267000000 | -1.885897000000 | -0.868125000000 |
| C | 3.690553000000 | -2.176739000000 | -2.339725000000 |
| C | 3.573963000000 | -3.701124000000 | -2.240851000000 |
| H | 2.519324000000 | -3.984677000000 | -2.159901000000 |
| H | 4.002174000000 | -4.199778000000 | -3.119738000000 |
| H | 4.097609000000 | -4.082115000000 | -1.354325000000 |
| H | 3.149617000000 | -1.820773000000 | -3.223518000000 |
| H | 4.741212000000 | -1.878864000000 | -2.480510000000 |
| H | 3.755065000000 | -1.633431000000 | -0.233758000000 |
| H | 2.583204000000 | 0.492518000000 | -0.376781000000 |
| H | 1.148052000000 | 0.028873000000 | -2.107673000000 |
| H | 3.901693000000 | 0.515800000000 | -1.566270000000 |

- **<u>III:</u>**



| | | | |
|---|---|---|---|
| C | -1.606173000000 | -1.084461000000 | 0.096854000000 |
| C | -2.926613000000 | -1.479238000000 | 0.116500000000 |
| C | -3.916654000000 | -0.547057000000 | -0.136528000000 |
| C | -3.533103000000 | 0.750545000000 | -0.415485000000 |
| C | -2.191209000000 | 1.068591000000 | -0.434173000000 |

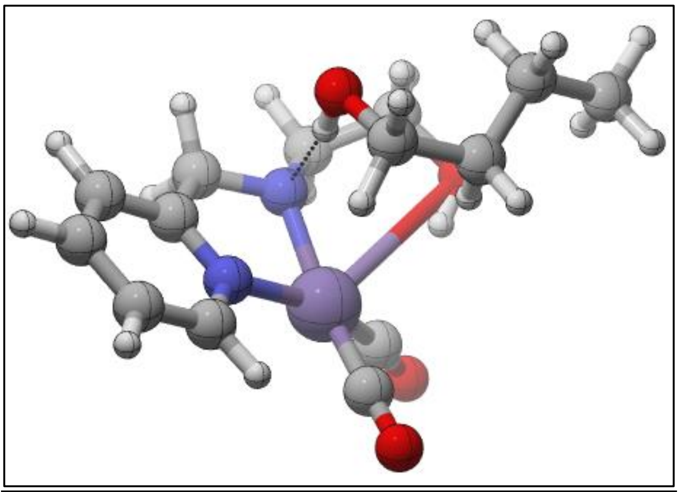
| | | | |
|---|---|---|---|
| H | -3.170736000000 | -2.509323000000 | 0.333015000000 |
| H | -4.958969000000 | -0.829339000000 | -0.120693000000 |
| H | -4.260954000000 | 1.519593000000 | -0.625095000000 |
| H | -1.855073000000 | 2.068928000000 | -0.658363000000 |
| N | -1.230037000000 | 0.177501000000 | -0.180072000000 |
| C | -0.473543000000 | -2.013275000000 | 0.404531000000 |
| H | -0.761055000000 | -3.054188000000 | 0.228364000000 |
| N | 0.663950000000 | -1.583724000000 | -0.383672000000 |
| Mn | 0.715509000000 | 0.479344000000 | -0.205009000000 |
| C | 0.703262000000 | 2.227336000000 | -0.345653000000 |
| O | 0.659044000000 | 3.376522000000 | -0.457524000000 |
| C | 0.840555000000 | 0.614332000000 | 1.580665000000 |
| O | 0.914791000000 | 0.815825000000 | 2.716126000000 |
| O | 2.798265000000 | 0.088181000000 | -0.470014000000 |
| C | 1.974957000000 | -2.088409000000 | -0.028552000000 |
| H | 2.104121000000 | -3.153724000000 | -0.246316000000 |
| C | 2.986421000000 | -1.279390000000 | -0.800430000000 |
| H | -0.200112000000 | -1.904788000000 | 1.457097000000 |
| H | 2.115997000000 | -1.932634000000 | 1.040900000000 |
| H | 4.001872000000 | -1.584836000000 | -0.546334000000 |
| H | 2.832404000000 | -1.426351000000 | -1.872086000000 |
| H | 2.922638000000 | 0.623562000000 | -1.255282000000 |
| H | 0.696893000000 | 0.523934000000 | -1.832409000000 |
| H | 0.483653000000 | -1.738942000000 | -1.366454000000 |



**IIA**

| | | | |
|---|---|---|---|
| C | -2.030478000 | 0.974566000 | -1.191101000 |
| C | -2.793829000 | 2.022229000 | -1.695612000 |
| C | -2.857905000 | 3.244026000 | -1.006267000 |
| C | -2.129259000 | 3.369719000 | 0.180251000 |
| C | -1.362598000 | 2.304174000 | 0.656075000 |
| H | -3.356576000 | 1.871529000 | -2.613922000 |
| H | -3.464621000 | 4.064491000 | -1.378381000 |
| H | -2.164269000 | 4.291312000 | 0.758671000 |
| H | -0.818891000 | 2.406617000 | 1.598289000 |
| N | -1.299512000 | 1.088807000 | -0.006617000 |
| C | -2.010590000 | -0.375890000 | -1.868625000 |
| H | -1.768735000 | -0.262428000 | -2.947048000 |
| N | -1.000413000 | -1.260773000 | -1.180862000 |
| Mn | -0.540126000 | -0.440264000 | 0.543118000 |
| C | 0.423501000 | 0.230599000 | 1.886273000 |
| O | 1.206362000 | 0.583399000 | 2.689793000 |
| C | -2.047860000 | -0.886785000 | 1.536839000 |
| O | -2.981715000 | -1.110283000 | 2.196691000 |
| O | 0.115567000 | -2.541842000 | 0.951606000 |
| C | -1.497105000 | -2.657713000 | -0.929520000 |

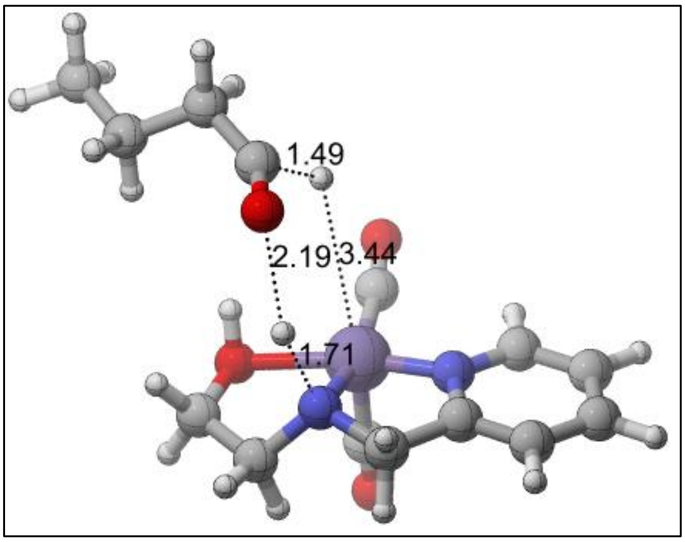
| | | | |
|---|---|---|---|
| H | -1.678040000 | -3.238252000 | -1.865443000 |
| C | -0.472437000 | -3.403548000 | -0.056203000 |
| H | -3.028278000 | -0.798928000 | -1.819072000 |
| H | -2.473625000 | -2.619931000 | -0.401848000 |
| H | -0.974512000 | -4.189808000 | 0.550473000 |
| H | 0.326212000 | -3.853414000 | -0.660831000 |
| H | 1.788019941 | -2.755545063 | 0.779077632 |
| O | 3.573423271 | -3.541384881 | 0.452125155 |
| C | 3.927022077 | -4.948017928 | 0.449355971 |
| C | 4.769066774 | -6.066935118 | -0.099830234 |
| H | 4.472450191 | -6.142002961 | -1.182310680 |
| C | 6.258369009 | -5.742863785 | 0.033331946 |
| C | 7.058368429 | -6.702029343 | -0.836448848 |
| H | 6.780867466 | -6.618729799 | -1.892529442 |
| H | 8.135669556 | -6.536532619 | -0.759218634 |
| H | 6.898105580 | -7.747181596 | -0.553396470 |
| H | 6.392162812 | -4.712457758 | -0.341418144 |
| H | 6.655514330 | -5.754237600 | 1.089028017 |
| H | 4.560553832 | -7.090324133 | 0.290249305 |
| H | 3.028312778 | -5.712736281 | 0.959747980 |
| H | 0.042920840 | -1.323335975 | -2.050145865 |



**IIB**

| | | | |
|---|---|---|---|
| C | -2.030478000 | 0.974566000 | -1.191101000 |
| C | -2.793829000 | 2.022229000 | -1.695612000 |
| C | -2.857905000 | 3.244026000 | -1.006267000 |
| C | -2.129259000 | 3.369719000 | 0.180251000 |
| C | -1.362598000 | 2.304174000 | 0.656075000 |
| H | -3.356576000 | 1.871529000 | -2.613922000 |
| H | -3.464621000 | 4.064491000 | -1.378381000 |
| H | -2.164269000 | 4.291312000 | 0.758671000 |
| H | -0.818891000 | 2.406617000 | 1.598289000 |
| N | -1.299512000 | 1.088807000 | -0.006617000 |
| C | -2.010590000 | -0.375890000 | -1.868625000 |
| H | -1.768735000 | -0.262428000 | -2.947048000 |
| N | -1.000413000 | -1.260773000 | -1.180862000 |
| Mn | -0.540126000 | -0.440264000 | 0.543118000 |
| C | 0.423501000 | 0.230599000 | 1.886273000 |
| O | 1.206362000 | 0.583399000 | 2.689793000 |
| C | -2.047860000 | -0.886785000 | 1.536839000 |
| O | -2.981715000 | -1.110283000 | 2.196691000 |
| O | 0.115567000 | -2.541842000 | 0.951606000 |
| C | -1.497105000 | -2.657713000 | -0.929520000 |
| H | -1.678040000 | -3.238252000 | -1.865443000 |
| C | -0.472437000 | -3.403548000 | -0.056203000 |
| H | -3.028278000 | -0.798928000 | -1.819072000 |
| H | -2.473625000 | -2.619931000 | -0.401848000 |
| H | -0.974512000 | -4.189808000 | 0.550473000 |
| H | 0.326212000 | -3.853414000 | -0.660831000 |
| H | 1.788019941 | -2.755545063 | 0.779077632 |
| O | 1.663030389 | -2.039045073 | -3.619475993 |

| | | | |
|---|---|---|---|
| C | 2.260214461 | -2.766352486 | -4.723129663 |
| C | 2.790679982 | -2.770386708 | -6.130684456 |
| H | 1.897433945 | -2.534876504 | -6.772577714 |
| C | 3.878888916 | -1.709163451 | -6.304988948 |
| C | 4.133789519 | -1.493791552 | -7.789966018 |
| H | 3.232873150 | -1.151949003 | -8.310297824 |
| H | 4.925444733 | -0.764118866 | -7.976489962 |
| H | 4.453713568 | -2.412747288 | -8.291279311 |
| H | 3.484363017 | -0.776689629 | -5.863495031 |
| H | 4.848936124 | -1.930239095 | -5.773498651 |
| H | 3.139101730 | -3.749968478 | -6.533160061 |
| H | 2.121910879 | -4.042040255 | -4.642721947 |
| H | 0.042920840 | -1.323335975 | -2.050145865 |

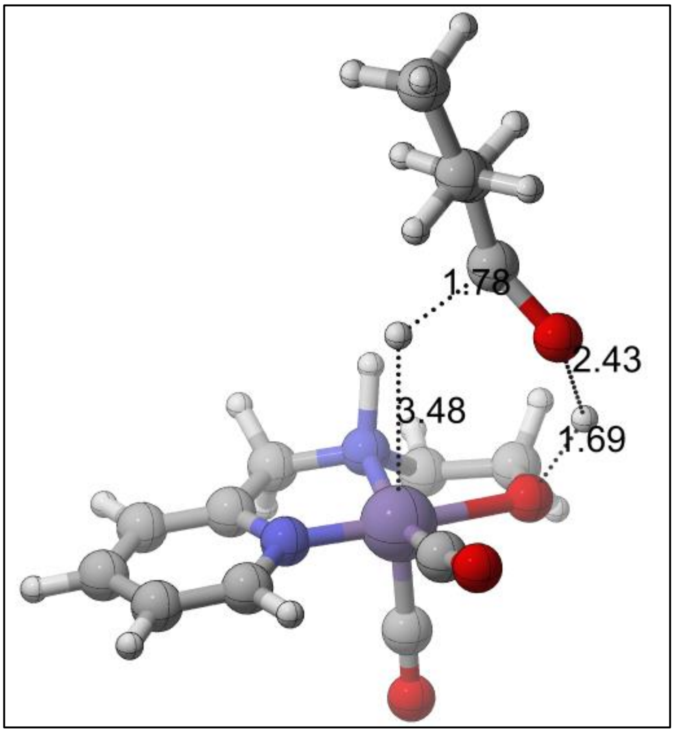



**TS-IIB-III**

| | | | |
|---|---|---|---|
| C | -2.030478000 | 0.974566000 | -1.191101000 |
| C | -2.793829000 | 2.022229000 | -1.695612000 |
| C | -2.857905000 | 3.244026000 | -1.006267000 |
| C | -2.129259000 | 3.369719000 | 0.180251000 |
| C | -1.362598000 | 2.304174000 | 0.656075000 |

| | | | |
|---|---|---|---|
| H | -3.356576000 | 1.871529000 | -2.613922000 |
| H | -3.464621000 | 4.064491000 | -1.378381000 |
| H | -2.164269000 | 4.291312000 | 0.758671000 |
| H | -0.818891000 | 2.406617000 | 1.598289000 |
| N | -1.299512000 | 1.088807000 | -0.006617000 |
| C | -2.010590000 | -0.375890000 | -1.868625000 |
| H | -1.768735000 | -0.262428000 | -2.947048000 |
| N | -1.000413000 | -1.260773000 | -1.180862000 |
| Mn | -0.540126000 | -0.440264000 | 0.543118000 |
| C | 0.423501000 | 0.230599000 | 1.886273000 |
| O | 1.206362000 | 0.583399000 | 2.689793000 |
| C | -2.047860000 | -0.886785000 | 1.536839000 |
| O | -2.981715000 | -1.110283000 | 2.196691000 |
| O | 0.115567000 | -2.541842000 | 0.951606000 |
| C | -1.497105000 | -2.657713000 | -0.929520000 |
| H | -1.678040000 | -3.238252000 | -1.865443000 |
| C | -0.472437000 | -3.403548000 | -0.056203000 |
| H | -3.028278000 | -0.798928000 | -1.819072000 |
| H | -2.473625000 | -2.619931000 | -0.401848000 |
| H | -0.974512000 | -4.189808000 | 0.550473000 |
| H | 0.326212000 | -3.853414000 | -0.660831000 |
| H | 1.038200000 | -2.283039000 | 0.638852000 |
| O | 2.617499000 | -0.946469000 | -2.300983000 |
| C | 3.390946000 | -0.800274000 | -1.362808000 |
| C | 4.632243789 | -1.345157672 | -0.710962910 |
| H | 4.765922996 | -0.835621761 | 0.282960387 |
| C | 4.611745124 | -2.865693253 | -0.542656970 |
| C | 5.794492151 | -3.367565850 | 0.273277854 |
| H | 5.776101696 | -2.976737962 | 1.296100992 |
| H | 5.828862760 | -4.458113886 | 0.332057368 |

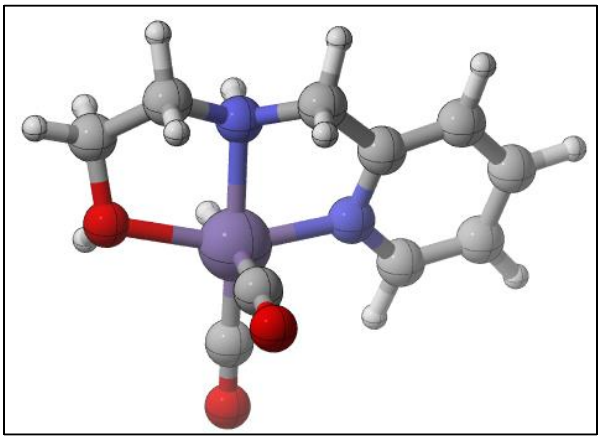
| | | | |
|---|---|---|---|
| H | 6.752938536 | -3.063803754 | -0.159452059 |
| H | 3.672697520 | -3.129346573 | -0.024244472 |
| H | 4.582686123 | -3.385889614 | -1.543106511 |
| H | 5.539174045 | -1.032051173 | -1.278771506 |
| H | 2.726545537 | 0.105028631 | -0.386056573 |
| H | 0.490373031 | -1.364832055 | -2.003599714 |




**TS-IIA-III**

| | | | |
|---|---|---|---|
| C | -2.030478000 | 0.974566000 | -1.191101000 |
| C | -2.793829000 | 2.022229000 | -1.695612000 |
| C | -2.857905000 | 3.244026000 | -1.006267000 |
| C | -2.129259000 | 3.369719000 | 0.180251000 |
| C | -1.362598000 | 2.304174000 | 0.656075000 |
| H | -3.356576000 | 1.871529000 | -2.613922000 |
| H | -3.464621000 | 4.064491000 | -1.378381000 |
| H | -2.164269000 | 4.291312000 | 0.758671000 |
| H | -0.818891000 | 2.406617000 | 1.598289000 |
| N | -1.299512000 | 1.088807000 | -0.006617000 |
| C | -2.010590000 | -0.375890000 | -1.868625000 |

| | | | |
|---|---|---|---|
| H | -1.768735000 | -0.262428000 | -2.947048000 |
| N | -1.000413000 | -1.260773000 | -1.180862000 |
| Mn | -0.540126000 | -0.440264000 | 0.543118000 |
| C | 0.423501000 | 0.230599000 | 1.886273000 |
| O | 1.206362000 | 0.583399000 | 2.689793000 |
| C | -2.047860000 | -0.886785000 | 1.536839000 |
| O | -2.981715000 | -1.110283000 | 2.196691000 |
| O | 0.115567000 | -2.541842000 | 0.951606000 |
| C | -1.497105000 | -2.657713000 | -0.929520000 |
| H | -1.678040000 | -3.238252000 | -1.865443000 |
| C | -0.472437000 | -3.403548000 | -0.056203000 |
| H | -3.028278000 | -0.798928000 | -1.819072000 |
| H | -2.473625000 | -2.619931000 | -0.401848000 |
| H | -0.974512000 | -4.189808000 | 0.550473000 |
| H | 0.326212000 | -3.853414000 | -0.660831000 |
| H | 1.788019941 | -2.755545063 | 0.779077632 |
| O | 3.607942938 | -1.180568008 | 0.443569317 |
| C | 3.825025726 | -0.641384965 | -0.900930936 |
| C | 4.860235240 | -0.120367403 | -1.859837814 |
| H | 4.339071386 | 0.219354399 | -2.797045277 |
| C | 5.715746803 | 1.005816174 | -1.276240302 |
| C | 6.630925300 | 1.629606976 | -2.320198934 |
| H | 6.061630299 | 2.105082338 | -3.125852831 |
| H | 7.299680084 | 2.381278043 | -1.893948967 |
| H | 7.282091563 | 0.888217144 | -2.793981243 |
| H | 5.027726795 | 1.777089610 | -0.886572818 |
| H | 6.321904337 | 0.643013085 | -0.396868409 |
| H | 5.510144389 | -0.951570050 | -2.219955889 |
| H | 2.504332502 | 0.546469103 | -0.826605532 |
| H | 0.042920840 | -1.323335975 | -2.050145865 |



**TSIII**

| | | | |
|---|---|---|---|
| C | 2.770771813 | 1.958091134 | -0.173240526 |
| C | 3.035384212 | 3.293194518 | -0.460151074 |
| C | 3.315868171 | 3.689314745 | -1.777916180 |
| C | 3.308439776 | 2.710034961 | -2.775665597 |
| C | 3.027972077 | 1.379375443 | -2.459048769 |
| H | 3.046024544 | 4.016165376 | 0.352183533 |
| H | 3.542666743 | 4.724990299 | -2.013874438 |
| H | 3.539388115 | 2.967034754 | -3.808013455 |
| H | 3.051265031 | 0.619565931 | -3.243920522 |
| N | 2.761580308 | 0.971604529 | -1.161735185 |
| C | 2.547999988 | 1.492357766 | 1.246841196 |
| H | 1.766083736 | 2.110947374 | 1.737060443 |
| N | 2.153003952 | 0.036224054 | 1.234831899 |
| Mn | 2.577160217 | -0.699200094 | -0.536171233 |
| C | 2.393189649 | -1.531598462 | -2.103324520 |
| O | 2.114196916 | -2.156254646 | -3.059854325 |
| C | 4.420497006 | -0.895231517 | -0.381888007 |
| O | 5.579606701 | -1.009523341 | -0.352895473 |
| O | 2.469487691 | -2.604582367 | 0.634874929 |
| C | 2.858389054 | -0.786767976 | 2.277152474 |
| H | 2.584810224 | -0.506386968 | 3.322262247 |
| C | 2.533046434 | -2.273181342 | 2.045582687 |

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|---|---|---|---|
| H | 3.480111558 | 1.660372844 | 1.812567655 |
| H | 3.955420386 | -0.632523984 | 2.198473695 |
| H | 3.361775166 | -2.917079414 | 2.415645036 |
| H | 1.591391557 | -2.563597145 | 2.530083169 |
| H | 1.440600889 | -3.141594995 | 0.361089347 |
| O | -1.620039352 | -2.340977194 | 0.958419021 |
| C | -2.678881711 | -1.753397075 | 0.775757367 |
| C | -2.781203828 | -0.390565788 | 1.404125103 |
| C | -2.193289034 | 0.848373692 | 0.489063716 |
| C | -2.410284178 | 2.404285295 | 0.562456724 |
| H | -1.919835083 | 2.737307949 | -0.358308632 |
| H | -1.955396018 | 2.971377604 | 1.380762647 |
| H | -2.863787149 | 0.766173916 | -0.384865538 |
| H | 0.605193611 | -0.652729888 | -0.548945884 |
| H | 0.548185457 | -0.086667712 | 1.282448900 |
| C | -3.796353908 | -2.227893717 | -0.171715659 |
| C | -3.512957094 | -2.587853292 | -1.500040879 |
| C | -5.128302097 | -2.313170236 | 0.267573545 |
| C | -4.524163455 | -3.017359709 | -2.357834105 |
| C | -6.139942096 | -2.742601089 | -0.589744385 |
| C | -5.842641152 | -3.096785046 | -1.906703146 |
| H | -2.490852838 | -2.529763980 | -1.861138305 |
| H | -5.370485469 | -2.040090269 | 1.289943828 |
| H | -4.281296041 | -3.290500815 | -3.380779813 |
| H | -7.162553229 | -2.800551941 | -0.227921749 |
| H | -6.630678594 | -3.431397754 | -2.574856877 |
| C | -3.112125580 | 0.132511223 | 2.814261319 |
| C | -2.037567003 | 0.810556789 | 3.414187261 |
| C | -4.248447029 | -0.131616676 | 3.597422279 |
| C | -2.096848401 | 1.209943874 | 4.748279804 |
| C | -4.308322072 | 0.267517679 | 4.931562187 |
| C | -3.232660620 | 0.940286475 | 5.513411043 |

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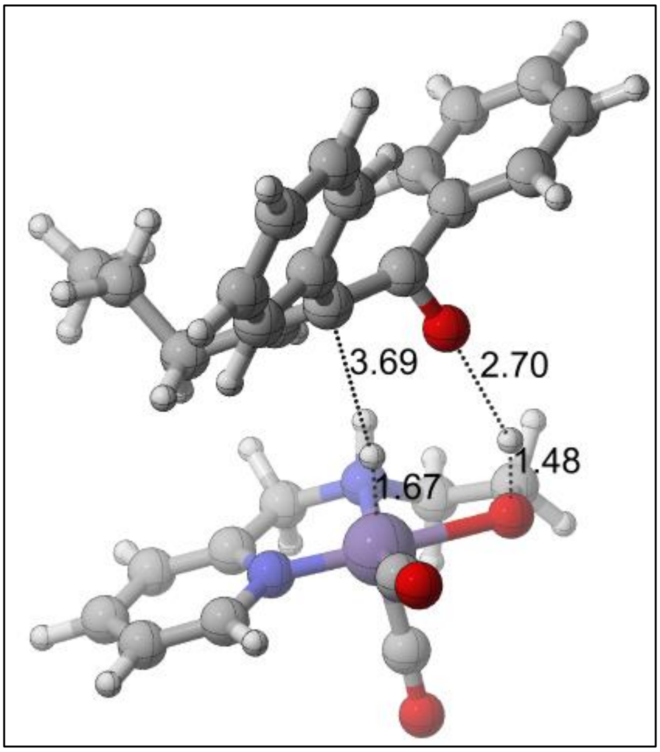
| H | -1.149398345 | 1.025325404 | 2.828105822 |
| H | -5.090676162 | -0.654263183 | 3.154752173 |
| H | -1.253800101 | 1.732900913 | 5.190765091 |
| H | -5.197299619 | 0.052365502 | 5.517595176 |
| H | -3.279079948 | 1.251365331 | 6.552869481 |
| C | -3.253021159 | 3.470771748 | -0.161424187 |
| H | -2.702422717 | 3.913291264 | -0.999352769 |
| H | -4.178258060 | 3.042761731 | -0.563734838 |
| C | -3.647075977 | 4.615257589 | 0.790664331 |
| H | -4.141132093 | 5.431118856 | 0.250865087 |
| H | -4.337439236 | 4.267994247 | 1.567783831 |
| H | -2.768958218 | 5.036279163 | 1.293415890 |




**TSIIIA**

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|---|---|---|---|
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| C | 4.069399000 | 1.124145000 | -2.657722000 |
| C | 4.629462000 | 0.014657000 | -3.311522000 |
| C | 4.479274000 | -1.243206000 | -2.720107000 |

| | | | |
|---|---|---|---|
| C | 3.789344000 | -1.380196000 | -1.513959000 |
| H | 4.174778000 | 2.124684000 | -3.070644000 |
| H | 5.173076000 | 0.131536000 | -4.244560000 |
| H | 4.913420000 | -2.128978000 | -3.180601000 |
| H | 3.701844000 | -2.365136000 | -1.049078000 |
| N | 3.242120000 | -0.293222000 | -0.851165000 |
| C | 2.858037000 | 2.144693000 | -0.686564000 |
| H | 2.226121000 | 2.774779000 | -1.348407000 |
| N | 2.068697000 | 1.651849000 | 0.501097000 |
| Mn | 2.503628000 | -0.242572000 | 0.782541000 |
| C | 2.306133000 | -1.999683000 | 1.019729000 |
| O | 1.994151000 | -3.116187000 | 1.217387000 |
| C | 4.174575000 | -0.084401000 | 1.584439000 |
| O | 5.237183000 | -0.046467000 | 2.060742000 |
| O | 1.696007000 | 0.252599000 | 2.811328000 |
| C | 2.359329000 | 2.404127000 | 1.770320000 |
| H | 2.036668000 | 3.472024000 | 1.735677000 |
| C | 1.657510000 | 1.696580000 | 2.943233000 |
| H | 3.712456000 | 2.771766000 | -0.380207000 |
| H | 3.454623000 | 2.423451000 | 1.953120000 |
| H | 2.208559000 | 1.874704000 | 3.893474000 |
| H | 0.614955000 | 2.024210000 | 3.050634000 |
| H | 0.315464000 | -0.165849000 | 2.483241000 |
| O | -1.652975090 | -1.242494159 | 0.972368546 |
| C | -2.489274788 | -1.420346316 | 0.095593473 |
| C | -1.996013637 | -2.286903636 | -1.030637192 |
| C | -1.171173743 | -1.099693488 | -1.692656675 |
| C | -0.351416016 | -1.003047925 | -2.971395823 |
| H | 0.108809221 | -1.962215784 | -3.231093191 |
| H | 0.464781153 | -0.278873548 | -2.884589160 |

| | | | |
|---|---|---|---|
| H | -0.805822381 | -0.147776268 | -1.267863781 |
| H | 0.910002000 | -0.468820000 | 0.330151000 |
| H | 1.053031000 | 1.719842000 | 0.302306000 |
| C | -3.448328460 | -0.397087428 | 0.731796443 |
| C | -4.280500887 | -0.757064240 | 1.805219869 |
| C | -3.516057840 | 0.923039558 | 0.255339691 |
| C | -5.148640498 | 0.168862814 | 2.381256157 |
| C | -4.383991709 | 1.849415705 | 0.830957569 |
| C | -5.204521248 | 1.476680854 | 1.896797186 |
| H | -4.244980052 | -1.771633496 | 2.189733208 |
| H | -2.882225269 | 1.223441971 | -0.573201924 |
| H | -5.782679387 | -0.132241322 | 3.210316280 |
| H | -4.419156594 | 2.864523883 | 0.445823787 |
| H | -5.880841539 | 2.198278934 | 2.345444267 |
| C | -2.807886075 | -3.516846022 | -1.477522006 |
| C | -4.176020734 | -3.627572230 | -1.177054177 |
| C | -2.201550988 | -4.560202734 | -2.197311748 |
| C | -4.911109945 | -4.740666775 | -1.581391776 |
| C | -2.936109754 | -5.673546827 | -2.601923063 |
| C | -4.294565603 | -5.769083770 | -2.295845203 |
| H | -4.665386880 | -2.833392273 | -0.621842237 |
| H | -1.145550869 | -4.495967155 | -2.440628246 |
| H | -5.967772139 | -4.804461915 | -1.337664006 |
| H | -2.445951156 | -6.467973130 | -3.157475254 |
| H | -4.867093820 | -6.636434001 | -2.610985851 |
| C | -1.192025661 | -0.541295741 | -4.176286001 |
| H | -1.029155108 | -1.186419576 | -5.047145297 |
| H | -2.263424571 | -0.561300817 | -3.946472452 |
| C | -0.833549827 | 0.897678540 | -4.591554927 |
| H | -1.341409569 | 1.183361558 | -5.519762815 |

| | | | |
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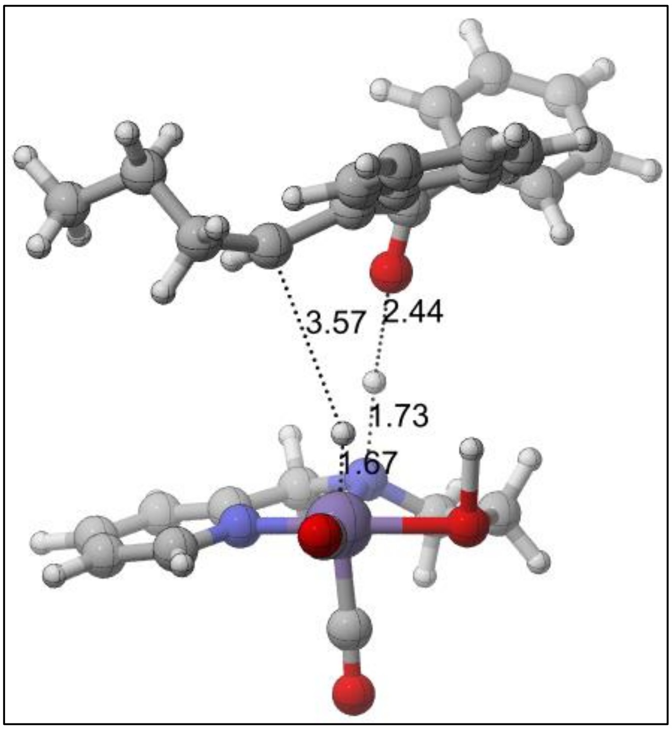
| H | -1.124699817 | 1.619819918 | -3.820288464 |
| H | 0.244107458 | 1.008385266 | -4.757404753 |




**TSIIIB**

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|---|---|---|---|
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| C | 4.069399000 | 1.124145000 | -2.657722000 |
| C | 4.629462000 | 0.014657000 | -3.311522000 |
| C | 4.479274000 | -1.243206000 | -2.720107000 |
| C | 3.789344000 | -1.380196000 | -1.513959000 |
| H | 4.174778000 | 2.124684000 | -3.070644000 |
| H | 5.173076000 | 0.131536000 | -4.244560000 |
| H | 4.913420000 | -2.128978000 | -3.180601000 |
| H | 3.701844000 | -2.365136000 | -1.049078000 |
| N | 3.242120000 | -0.293222000 | -0.851165000 |
| C | 2.858037000 | 2.144693000 | -0.686564000 |
| H | 2.226121000 | 2.774779000 | -1.348407000 |
| N | 2.068697000 | 1.651849000 | 0.501097000 |
| Mn | 2.503628000 | -0.242572000 | 0.782541000 |

| | | | |
|---|---|---|---|
| C | 2.306133000 | -1.999683000 | 1.019729000 |
| O | 1.994151000 | -3.116187000 | 1.217387000 |
| C | 4.174575000 | -0.084401000 | 1.584439000 |
| O | 5.237183000 | -0.046467000 | 2.060742000 |
| O | 1.696007000 | 0.252599000 | 2.811328000 |
| C | 2.359329000 | 2.404127000 | 1.770320000 |
| H | 2.036668000 | 3.472024000 | 1.735677000 |
| C | 1.657510000 | 1.696580000 | 2.943233000 |
| H | 3.712456000 | 2.771766000 | -0.380207000 |
| H | 3.454623000 | 2.423451000 | 1.953120000 |
| H | 2.208559000 | 1.874704000 | 3.893474000 |
| H | 0.614955000 | 2.024210000 | 3.050634000 |
| H | 0.315464000 | -0.165849000 | 2.483241000 |
| O | -1.731784516 | 0.914888230 | -0.224444603 |
| C | -2.947502628 | 0.906065083 | -0.371803785 |
| C | -2.841194038 | -0.486683365 | -0.929991842 |
| C | -1.793438012 | -1.227059023 | -1.869220131 |
| C | -1.711842705 | -2.471110622 | -2.742257776 |
| H | -2.216115216 | -3.325392678 | -2.278399632 |
| H | -0.677755946 | -2.780508452 | -2.924134935 |
| H | -1.162358406 | -0.642158763 | -2.561829134 |
| H | 0.910002000 | -0.468820000 | 0.330151000 |
| H | 0.463487340 | 1.959786774 | -0.054361093 |
| C | -3.717923015 | 2.179369337 | 0.024107342 |
| C | -3.823747959 | 2.570879636 | 1.369415066 |
| C | -4.335000377 | 2.982633591 | -0.949707647 |
| C | -4.520984532 | 3.723293174 | 1.728064337 |
| 6 | -5.032374364 | 4.135154700 | -0.591681775 |
| C | -5.128695329 | 4.511014875 | 0.749088706 |
| H | -3.354826178 | 1.965405994 | 2.138815511 |

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| H | -4.266222269 | 2.699425038 | -1.995427032 |
| H | -4.589514371 | 4.006246633 | 2.774606597 |
| H | -5.501424673 | 4.740680668 | -1.361966997 |
| H | -5.671992599 | 5.408943496 | 1.028282898 |
| C | -3.681817409 | -1.451193463 | -0.072860705 |
| C | -4.410625779 | -0.985501262 | 1.034524860 |
| C | -3.741785704 | -2.821906932 | -0.375979700 |
| C | -5.171562079 | -1.858232067 | 1.810502564 |
| C | -4.502542083 | -3.695130079 | 0.399618801 |
| C | -5.221144508 | -3.217378423 | 1.496695447 |
| H | -4.379018060 | 0.069732215 | 1.287397532 |
| H | -3.186693745 | -3.203979135 | -1.227072604 |
| H | -5.726833123 | -1.475407758 | 2.662046841 |
| H | -4.533836135 | -4.750964023 | 0.146158345 |
| H | -5.813947547 | -3.897546951 | 2.101140598 |
| C | -2.333400727 | -2.255209753 | -4.134612773 |
| H | -3.019225141 | -3.069109501 | -4.395992889 |
| H | -2.901076779 | -1.318710665 | -4.177314677 |
| C | -1.250916984 | -2.191661604 | -5.228134955 |
| H | -1.696217378 | -2.160093545 | -6.229043145 |
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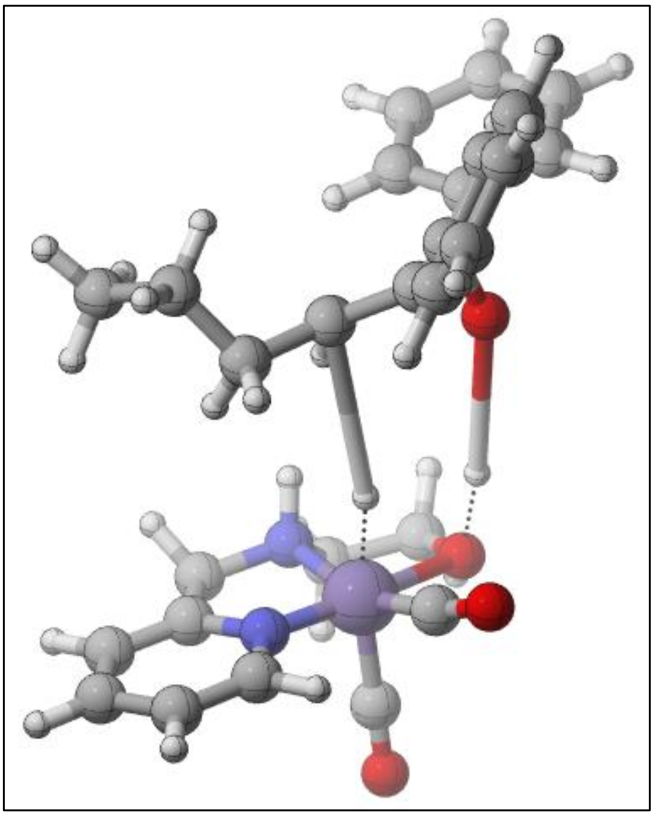

**Int-A**

| | | | |
|---|---|---|---|
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| C | 4.069399000 | 1.124145000 | -2.657722000 |
| C | 4.629462000 | 0.014657000 | -3.311522000 |
| C | 4.479274000 | -1.243206000 | -2.720107000 |
| C | 3.789344000 | -1.380196000 | -1.513959000 |
| H | 4.174778000 | 2.124684000 | -3.070644000 |
| H | 5.173076000 | 0.131536000 | -4.244560000 |
| H | 4.913420000 | -2.128978000 | -3.180601000 |
| H | 3.701844000 | -2.365136000 | -1.049078000 |
| N | 3.242120000 | -0.293222000 | -0.851165000 |
| C | 2.858037000 | 2.144693000 | -0.686564000 |
| H | 2.226121000 | 2.774779000 | -1.348407000 |
| N | 2.068697000 | 1.651849000 | 0.501097000 |
| Mn | 2.503628000 | -0.242572000 | 0.782541000 |
| C | 2.306133000 | -1.999683000 | 1.019729000 |
| O | 1.994151000 | -3.116187000 | 1.217387000 |

| | | | |
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| C | 4.174575000 | -0.084401000 | 1.584439000 |
| O | 5.237183000 | -0.046467000 | 2.060742000 |
| O | 1.696007000 | 0.252599000 | 2.811328000 |
| C | 2.359329000 | 2.404127000 | 1.770320000 |
| H | 2.036668000 | 3.472024000 | 1.735677000 |
| C | 1.657510000 | 1.696580000 | 2.943233000 |
| H | 3.712456000 | 2.771766000 | -0.380207000 |
| H | 3.454623000 | 2.423451000 | 1.953120000 |
| H | 2.208559000 | 1.874704000 | 3.893474000 |
| H | 0.614955000 | 2.024210000 | 3.050634000 |
| H | 0.315464000 | -0.165849000 | 2.483241000 |
| O | -2.225638865 | -1.268407374 | 1.259368107 |
| C | -3.061938563 | -1.446259531 | 0.382593034 |
| C | -2.568677412 | -2.312816851 | -0.743637631 |
| C | -1.743837518 | -1.125606703 | -1.405657114 |
| C | -0.924079791 | -1.028961140 | -2.684396262 |
| H | -0.463854554 | -1.988128999 | -2.944093630 |
| H | -0.107882622 | -0.304786763 | -2.597589599 |
| H | -1.157675233 | -0.349064260 | -0.882711014 |
| H | 0.910002000 | -0.468820000 | 0.330151000 |
| H | 1.053031000 | 1.719842000 | 0.302306000 |
| C | -4.020992235 | -0.423000643 | 1.018796004 |
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| C | -4.088721615 | 0.897126343 | 0.542339252 |
| C | -5.721304273 | 0.142949599 | 2.668255718 |
| C | -4.956655484 | 1.823502490 | 1.117957130 |
| C | -5.777185023 | 1.450767639 | 2.183796747 |
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| H | -3.454889044 | 1.197528756 | -0.286202363 |
| H | -6.355343162 | -0.158154537 | 3.497315841 |

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| H | -6.453505314 | 2.172365719 | 2.632443828 |
| C | -3.380549850 | -3.542759237 | -1.190522445 |
| C | -4.748684509 | -3.653485445 | -0.890054616 |
| C | -2.774214763 | -4.586115949 | -1.910312187 |
| C | -5.483773720 | -4.766579990 | -1.294392215 |
| C | -3.508773529 | -5.699460042 | -2.314923502 |
| C | -4.867229378 | -5.794996985 | -2.008845642 |
| H | -5.238050655 | -2.859305488 | -0.334842676 |
| H | -1.718214644 | -4.521880370 | -2.153628685 |
| H | -6.540435914 | -4.830375130 | -1.050664445 |
| H | -3.018614931 | -6.493886345 | -2.870475693 |
| H | -5.439757595 | -6.662347216 | -2.323986290 |
| C | -1.764689436 | -0.567208956 | -3.889286440 |
| H | -1.601818883 | -1.212332791 | -4.760145736 |
| H | -2.836088346 | -0.587214032 | -3.659472891 |
| C | -1.406213602 | 0.871765325 | -4.304555366 |
| H | -1.914073344 | 1.157448343 | -5.232763254 |
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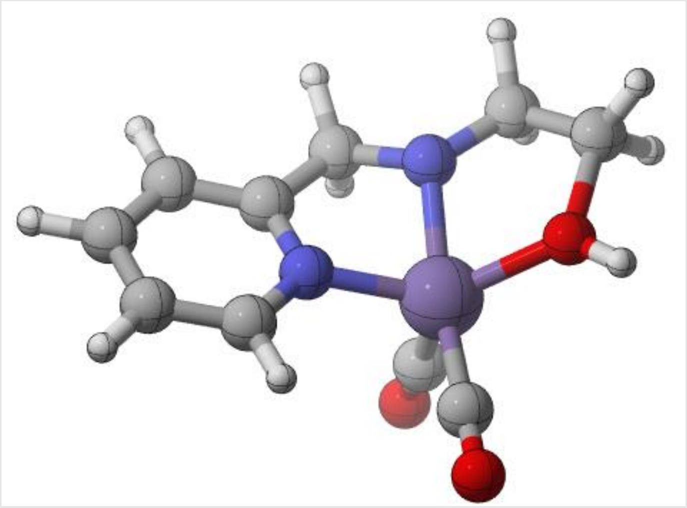

**IVB**

Coordinates

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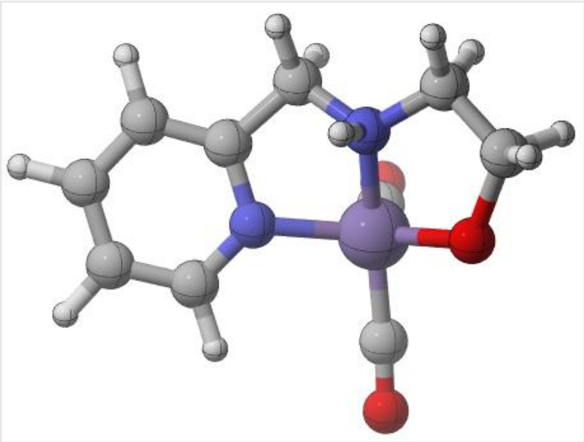
| C | 4.069399000 | 1.124145000 | -2.657722000 |
| C | 4.629462000 | 0.014657000 | -3.311522000 |
| C | 4.479274000 | -1.243206000 | -2.720107000 |
| C | 3.789344000 | -1.380196000 | -1.513959000 |
| H | 4.174778000 | 2.124684000 | -3.070644000 |
| H | 5.173076000 | 0.131536000 | -4.244560000 |
| H | 4.913420000 | -2.128978000 | -3.180601000 |
| H | 3.701844000 | -2.365136000 | -1.049078000 |
| N | 3.242120000 | -0.293222000 | -0.851165000 |
| C | 2.858037000 | 2.144693000 | -0.686564000 |
| H | 2.226121000 | 2.774779000 | -1.348407000 |
| N | 2.161715521 | 1.757262974 | 0.518218876 |
| Mn | 2.503628000 | -0.242572000 | 0.782541000 |
| C | 2.306133000 | -1.999683000 | 1.019729000 |
| O | 2.192701505 | -3.146244936 | 1.255338122 |
| C | 4.174575000 | -0.084401000 | 1.584439000 |
| O | 5.237183000 | -0.046467000 | 2.060742000 |
| O | 1.696007000 | 0.252599000 | 2.811328000 |
| C | 2.359329000 | 2.404127000 | 1.770320000 |
| H | 2.036668000 | 3.472024000 | 1.735677000 |

| | | | |
|---|---|---|---|
| C | 1.657510000 | 1.696580000 | 2.943233000 |
| H | 3.712456000 | 2.771766000 | -0.380207000 |
| H | 3.454623000 | 2.423451000 | 1.953120000 |
| H | 2.208559000 | 1.874704000 | 3.893474000 |
| H | 0.614955000 | 2.024210000 | 3.050634000 |
| H | 0.802447814 | -0.367365884 | 2.679042501 |



**IVA**

**Coordinates**

| | | | |
|---|---|---|---|
| C | 3.434670983 | 0.942137317 | -1.393852131 |
| C | 4.134335748 | 1.098425644 | -2.585859541 |
| C | 4.706949465 | -0.016585565 | -3.219067374 |
| C | 4.540900197 | -1.270033754 | -2.622541815 |
| C | 3.823463251 | -1.397394178 | -1.431480854 |
| H | 4.251027639 | 2.095878167 | -3.003183240 |
| H | 5.271860688 | 0.092826239 | -4.140284590 |
| H | 4.983672096 | -2.159764456 | -3.066908592 |
| H | 3.723494989 | -2.378918857 | -0.961913981 |
| N | 3.263436776 | -0.304856884 | -0.788833922 |
| C | 2.880471729 | 2.134829235 | -0.649865586 |
| H | 2.264995950 | 2.761430514 | -1.330249858 |
| N | 1.997184940 | 1.803880637 | 0.563327945 |
| Mn | 2.393734793 | -0.346423515 | 0.873800252 |

| | | | |
|---|---|---|---|
| C | 2.281831116 | -1.996583441 | 1.072035969 |
| O | 2.160834544 | -3.141273752 | 1.312922992 |
| C | 4.140688689 | -0.080777089 | 1.665847872 |
| O | 5.192266433 | -0.041438859 | 2.165923916 |
| O | 1.815577713 | 0.252186296 | 2.799766614 |
| C | 2.326548279 | 2.412237270 | 1.793187474 |
| H | 2.006843778 | 3.480444904 | 1.743834219 |
| C | 1.596866992 | 1.714124776 | 2.954695862 |
| H | 3.728928254 | 2.762483076 | -0.328494823 |
| H | 3.417439318 | 2.430866237 | 2.000715557 |
| H | 2.126518690 | 1.897863366 | 3.915971227 |
| H | 0.552781544 | 2.044364325 | 3.036088348 |
| H | 1.050570277 | 2.144095575 | 0.328044286 |

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