Electronic Supplementary Material (ESI) for ChemComm.

# Supporting Information

## Palladium-Catalysed Mono-α-Alkenylation of Ketones with Alkenyl Tosylates

Yong Wu, ‡[a] Wai Chung Fu, ‡[c] Chien-Wei Chiang,[a] Pui Ying Choy,[c] Fuk Yee Kwong*[c]
and Aiwen Lei*[ab]

[a]College of Chemistry and Molecular Sciences, the Institute for Advanced Studies (IAS), Wuhan
University, Wuhan 430072, Hubei (P.R. China)

[b]National Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang
330022, P. R. China

*Email:* aiwenlei@whu.edu.cn;

[c]State Key Laboratory of Chirosciences and Department of Applied Biology and Chemical
Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
*E-mail:* fuk-yee.kwong@polyu.edu.hk

### *Table of Content*

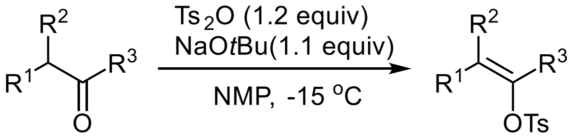
## 1. General considerations

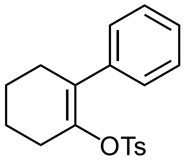
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All arylation reactions were performed in resealable screw-capped Schlenk tube (approx. 20 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4 mm × 10 mm). Tertiary butanol (*t*-BuOH) and $CH_3CN$ was distilled under calcium hydride under reduced pressure. Toluene, Dioxane and tetrahydrofuran (THF) were distilled from sodium under nitrogen. LiO*t*-Bu, NaO*t*-Bu, and $K_3PO_4$ were purchased from Aldrich. $LiOH\cdot H_2O$ and $Li_2CO_3$ were purchased from Merck. $Pd(dba)_2$ and $Pd(OAc)_2$ were purchased from Strem. $[PdCl(cinnamyl)]_2$, $PdCl_2(CH_3CN)_2$, $PdCl_2(allyl)_2$ and $Pd(cod)Cl_2$ were purchased from Aldrich. **CM-Phos** and **PhMezole-Phos** were prepared according to reported literature procedures.[1] **BrettPhos**, **XPhos**, **SPhos**, **DavePhos**, **cataCXium A**, **NiXantPhos** and **SIMes-HBF$_4$** were purchased from Strem. **DPPE**, **Mor-DalPhos** and **XantPhos** were purchased from Aldrich. $PPh_3$ was purchased from Acros, Thin layer chromatography was performed on Merck precoated silica gel 60 $F_{254}$ plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. $^1H$ NMR spectra were recorded on ADVANCE III (400 MHz). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. $^{13}C$ NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz).

## 2. Preparation of alkenyl tosylates substrates

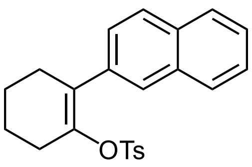
Alkenyl tosylates **1a**, **1e-1k** were prepared from their corresponding species according to the literature method[2-4] without modifications. Spectral data for the alkenyl tosylates **1a**,[2] **1e**,[2] **1f**,[2] **1g**,[3] **1h**,[3] **1i**,[4] **1j**,[2] and **1k**[2] showed good agreement with the literature data.

Alkenyl tosylate **1b-1d** were synthesized from corresponding ketones according to the literature method. A round bottom flask was charged with ketone (20 mmol) and purged with nitrogen. NMP (40 ml) was added and was cooled to -15°C. Solid NaOtBu (22 mmol) was added and the solution was stirred at room temperature for 2h. The solution was cooled to -20 °C and p-toluenesulfonic anhydride (24 mmol) was added in a single portion. The reaction mixture was stirred at -20 °C to r.t. for overnight. The tan solution was combined MTBE (300ml) and washed with aq $NaHCO_3$ (200ml) and water. The organic phase was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

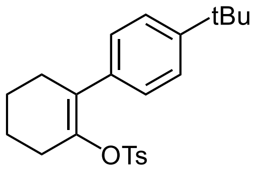




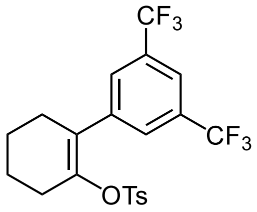
**1a**



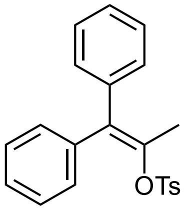
**1b**



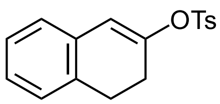
**1c**



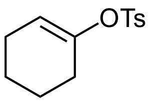
**1d**



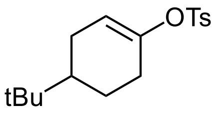
**1e**



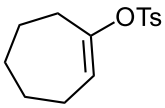
**1f**



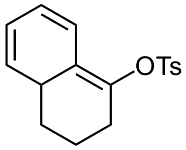
**1g**



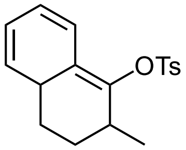
**1h**



**1i**



**1j**



**1k**

2-(Naphthalen-2-yl) cyclohex-1-en-1-yl 4-methylbenzenesulfonate (**1b**): White solid (71%

yield, eluent: Hexane/EA 20:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.74 (m, 1H), 7.61 (m, 2H), 7.51 – 7.44 (m, 2H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.11 (m, 3H), 6.62 (d, *J* = 8.1 Hz, 2H), 2.67 (m, 2H), 2.44 (m, 2H), 2.12 (s, 3H), 1.92 – 1.84 (m, 2H), 1.83 – 1.74 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.8, 135.6, 133.0, 132.9, 132.1, 128.7, 128.3, 127.8, 127.4, 127.3, 127.3, 127.0, 126.7, 126.6, 125.7, 125.7, 30.5, 29.2, 23.0, 22.4, 21.4.

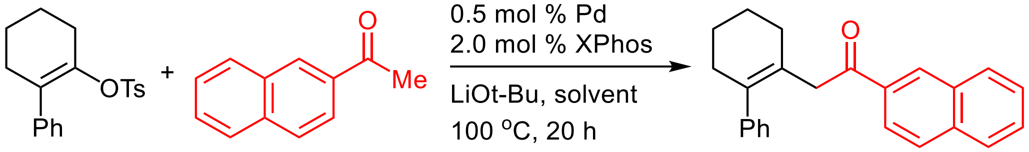
4'-(Tert-butyl)-3, 4, 5, 6-tetrahydro-[1, 1’-biphenyl]-2-yl 4-methylbenzenesulfonate (**1c**): Colorless oil (82% yield, eluent: Hexane/EA 20:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.18 – 7.11 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.84 (m, 2H), 2.61 (m, 2H), 2.37 (s, 3H), 2.31 (m, 2H), 1.86 – 1.77 (m, 2H), 1.77 – 1.68 (m, 2H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.5, 143.8, 143.0, 135.1, 133.1, 129.0, 128.4, 127.8, 127.7, 124.5, 34.4, 31.4, 30.5, 28.9, 23.1, 22.5, 21.6.

3', 5’-Bis (trifluoromethyl)-3, 4, 5, 6-tetrahydro-[1, 1’-biphenyl]-2-yl 4-methylbenzenesulfonate (**1d**): Colorless oil (69% yield, eluent: Hexane/EA 20:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.47 (d, *J* = 1.6 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 2.64 (m, 2H), 2.40 – 2.29 (m, 5H), 1.84 (m, 2H), 1.77 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.8, 144.9, 140.3, 133.0, 131.0 (d, $J_{C\text{-}F}$ = 33 Hz), 129.3, 128.3, 128.3, 127.5, 125.6, 123.1 (d, $J_{C\text{-}F}$ = 271 Hz), 120.4, 30.1, 29.1, 22.7, 22.1, 21.3.

## 3. General procedures for ligand and reaction condition screenings

*General procedure for screening:* A Schlenk tube equipped with a Teflon-coated stir bar was carefully evacuated and backfilled with nitrogen for three cycles. Pd source (0.0125 mmol) and ligand with corresponding ratio in 5 mL DCM (1.00 mol% Pd per 1.00 mL stock solution) was then prepared under $N_2$ with stirring until all of the solids are dissolved (usually within 1 min). The corresponding volume of stock solution was then immediately added to the Schlenk tube by syringe (In case of 0.25 mol% Pd, additional 0.25 mL of DCM was added). The palladium complex solution was stirred and placed in a preheated oil bath (40 °C) for 2 minutes. The solvent was then evaporated under high vacuum. Alkenyl tosylates (0.375 mmol) and base (0.375 mmol) were loaded into the tube, and the system was further evacuated and filled with nitrogen for three cycles. Solvent (0.5 mL) and subsequently 2-Acetonaphthone (0.25 mmol) were added with stirring (250 rpm) at room temperature. After that, the tube was further stirred (1000 rpm) at room temperature for 5 minutes. The tube was then placed into a preheated oil bath (100 °C) and stirred for 24 h. Ethyl acetate (~3 mL), dodecane (57 µL, internal standard), water (~2 mL) were added. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

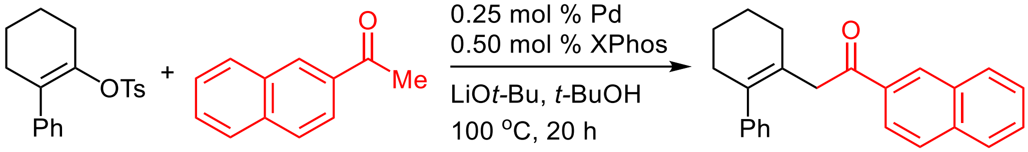
**Table S1.** Screening of solvent[a]



| Entry | Solvent | Yield (%) |
|---|---|---|
| 1 | *t*-BuOH | 87 |
| 2 | toluene | 24 |
| 3 | dioxane | 67 |
| 4 | DMF | 58 |
| 5 | THF | 66 |
| 6 | $CH_3CN$ | 24 |
| 7 | *i*-PrOH | trace |
| 8 | MeOH | trace |

[a] Reaction conditions: Alkenyl tosylates (0.375 mmol), LiO*t*-Bu (0.375 mmol), ketone (0.25 mmol), solvent (0.5 mL), Pd/XPhos = 1:4 at 100 °C for 20 h under $N_2$; Calibrated GC yields were reported using dodecane as the internal standard.

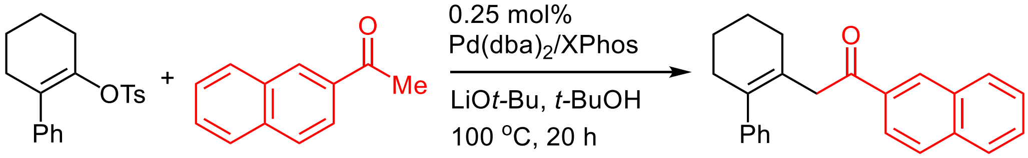
**Table S2.** Screening of Pd source[a]



| Entry | Pd (mol%) | Yield (%) |
|---|---|---|
| 1 | $Pd(OAc)_2$ | 71 |
| 2 | $Pd(TFA)_2$ | 67 |
| 3 | $Pd(dba)_2$ | 81 |
| 4 | $Pd_2(dba)_3$ | 71 |
| 5 | $PdCl_2(cod)$ | 70 |
| 6 | $[PdCl(cinnamyl)]_2$ | 60 |
| 7 | $PdCl_2(allyl)_2$ | 63 |
| 8 | $PdCl_2(CH_3CN)_2$ | 69 |

[a] Reaction conditions: Alkenyl tosylates (0.375 mmol), LiO*t*-Bu (0.375 mmol), ketone (0.25 mmol), *t*-BuOH (0.5 mL), Pd/XPhos = 1:4 at 100 °C for 20 h under $N_2$; Calibrated GC yields were reported using dodecane as the internal standard.

**Table S3.** Optimization of metal-to-ligand ratio[a]



| Entry | Pd: XPhos | Yield (%) |
|---|---|---|
| 1 | 1:1 | 80 |
| 2 | 1:2 | 81 |
| 3 | 1:3 | 80 |
| 4 | 1:4 | 81 |

[a] Reaction conditions: Alkenyl tosylates (0.375 mmol), LiO*t*-Bu (0.375 mmol), ketone (0.25 mmol), *t*-BuOH (0.5 mL), $Pd(dba)_2$ (0.06 mmol) at 100 °C for 20 h under $N_2$; Calibrated GC yields were reported using dodecane as the internal standard.

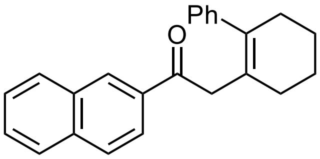
## 4. General procedures for alkelyation of ketones

*General procedure for $\alpha$-alkenylation of aryl ketones with alkenyl tosylates:* A Schlenk tube equipped with a Teflon-coated stir bar was carefully evacuated and backfilled with nitrogen for three cycles. Pd source (14.4 mg, 0.025 mmol) and **L2** (24 mg, 0.05 mmol) in 5 mL DCM (1.00 mol% Pd per 1.00 mL stock solution) was then prepared under $N_2$ until all of the solids are dissolved (usually within 1 min). The corresponding volume of stock solution was then immediately added to the Schlenk tube by syringe (In case of 0.25 mol% Pd, additional 0.25 mL of DCM was added). The palladium complex solution was stirred and placed in a preheated oil bath (40 °C) for 2 minutes. The solvent was then evaporated under high vacuum. Alkenyl tosylates (0.75 mmol) and LiO-*t*Bu (0.75 mmol) or $LiOH\cdot H_2O$ (0.75 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three cycles. *t*-BuOH (1 mL) and subsequently aryl ketone (0.5 mmol) were added with stirring (250 rpm) at room temperature. After that, the tube was further stirred (1000 rpm) at room temperature for 5 minutes. The tube was then placed into a preheated oil bath (100 °C) and stirred for 24 h. Ethyl acetate (~3 mL), water (~2 mL) were added. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

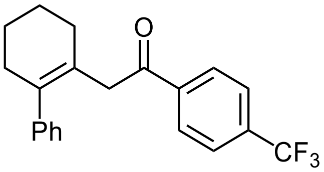
*General procedure for $\alpha$-alkenylation of aliphatic ketones with alkenyl tosylates:* A Schlenk tube equipped with a Teflon-coated stir bar was carefully evacuated and backfilled with nitrogen for three cycles. Pd source (7.2 mg, 0.0125 mmol) and **L1** (12 mg, 0.025 mmol) in 5 mL DCM (1.00 mol% Pd per 1.00 mL stock solution) was then prepared under $N_2$ until all of the solids are dissolved (usually within 1 min). The corresponding volume of stock solution was then immediately added to the Schlenk tube by syringe (In case of 0.25 mol% Pd, additional 0.25 mL of DCM was added). The palladium complex solution was stirred and placed in a preheated oil bath (40 °C) for 2 minutes. The solvent was then evaporated under high vacuum. Alkenyl tosylates (0.25 mmol) and LiO-*t*Bu (0.375 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three cycles. *t*-BuOH (0.5 mL) and subsequently aliphatic ketone (2.5 mmol) were added with stirring (250 rpm) at room temperature. After that, the tube was further stirred (1000 rpm) at room temperature for 5 minutes. The tube was then placed into a preheated oil bath (100 °C) and stirred for 24 h. Ethyl acetate (~3 mL), water (~2 mL) were added.

The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

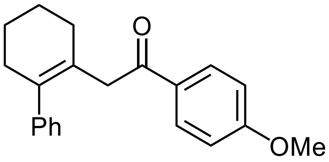
## 5. Characterization data for coupling products



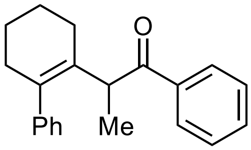
1-(Naphthalen-2-yl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (**3a**): isolated yield 90%; colorless oil; Hexane:EA=100:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (s, 1H), 7.83 – 7.76 (m, 1H), 7.68 (t, *J* = 6.3 Hz, 3H), 7.39 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.10 (t, *J* = 8.2 Hz, 3H), 3.61 (s, 2H), 2.23 (s, 2H), 2.04 (s, 2H), 1.62 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.9, 143.6, 136.6, 135.4, 134.1, 132.3, 129.8, 129.4, 128.2, 128.2, 128.1, 127.6, 127.3, 126.5, 123.9, 44.6, 32.2, 29.7, 23.1, 22.8. HRMS: (EI+) m/z calcd. for $C_{24}H_{22}O$ : 326.1671, found 326.1655.



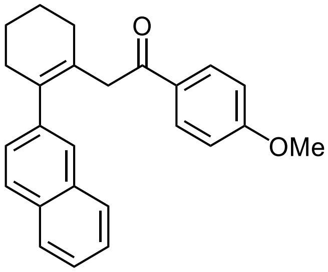
2-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**3b**): isolated yield 72%; colorless oil; Hexane:DCM=50:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 3.63 (s, 2H), 2.36 (s, 2H), 2.14 (s, 2H), 1.77 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.1, 143.4, 139.6, 137.3, 134.1 (q, *J* = 33 Hz), 128.4, 128.3, 128.2, 127.9, 126.6, 125.4 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 271 Hz), 44.9, 32.3, 29.8, 23.1, 22.8. $^{19}$F NMR (377 MHz, CDCl$_3$) δ -63.11. HRMS: (ESI+) m/z calcd. for $C_{21}H_{19}F_3OH^+$ : 345.1461, found 291.1456.



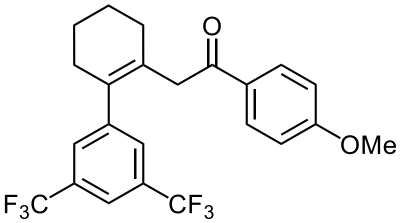
1-(4-Methoxyphenyl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (**3c**): isolated yield 65%; colorless oil; Hexane:EA=20:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.20 (m, 2H), 7.15 – 7.04 (m, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.75 (d, *J* = 6.8 Hz, 3H), 3.46 (s, 2H), 2.25 (s, 2H), 2.03 (s, 2H), 1.65 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.6, 163.2, 143.7, 136.4, 130.4, 130.1, 128.2, 128.1, 127.6, 126.4, 113.5, 55.4, 44.2, 32.2, 29.8, 23.2, 22.8. HRMS: (EI+) m/z calcd. for $C_{21}H_{22}O_2$ : 306.1620, found 306.1614.



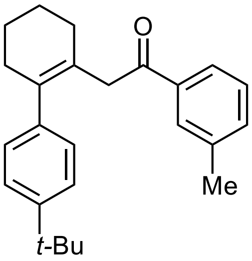
1-Phenyl-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)propan-1-one (**3d**): isolated yield 84%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.35 (m, 3H), 7.25 (d, *J* = 7.1 Hz, 2H), 4.23 (q, *J* = 6.7 Hz, 1H), 2.34 (m, 1H), 2.20 (m, 2H), 1.78 – 1.67 (m, 2H), 1.59 (m, 3H), 1.33 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.3, 143.8, 136.8, 135.7, 132.8, 132.5, 128.4, 128.2, 128.1, 126.7, 45.6, 32.8, 24.4, 23.0, 22.8, 15.7. HRMS: (ESI+) m/z calcd. for $C_{21}H_{23}OH^+$ : 291.1743, found 291.1755



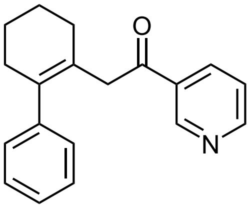
1-(4-Methoxyphenyl)-2-(2-(naphthalen-2-yl)cyclohex-1-en-1-yl)ethan-1-one (**3e**): isolated yield 72%; white solid; Hexane:EA=20:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 5H), 7.62 (s, 1H), 7.48 – 7.40 (m, 2H), 7.33 (m, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.62 (d, *J* = 12.0 Hz, 2H), 2.44 (s, 2H), 2.16 (d, *J* = 22.5 Hz, 2H), 1.89 – 1.75 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 163.2, 141.1, 136.3, 133.4, 132.2, 130.3, 130.1, 128.1, 127.8, 127.7, 127.5, 126.8, 126.5, 125.9, 125.5, 113.4, 55.3, 44.3, 32.3, 29.9, 23.3, 22.9. HRMS: (ESI+) m/z calcd. for $C_{25}H_{24}O_2H^+$ : 357.1849, found 357.1850



2-(3',5'-Bis(trifluoromethyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)-1-(4-methoxyphenyl)ethan-1-one (**3f**): isolated yield 69%; colorless oil; Hexane:DCM=20:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.71 (s, 1H), 7.64 (s, 2H), 6.92 – 6.81 (m, 2H), 3.85 (s, 3H), 3.47 (s, 2H), 2.35 (d, *J* = 5.4 Hz, 2H), 2.17 (m, 2H), 1.80 (d, *J* = 6.1 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.5, 145.7, 134.0, 131.5 (q, *J* = 33 Hz ), 130.7, 130.2, 129.9, 128.4, 123.3 (q, *J* = 271 Hz ) 120.4, 113.6, 55.4, 43.7, 32.0, 30.3, 22.9, 22.6. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -62.88. HRMS: (ESI+) m/z calcd. for $C_{23}H_{20}F_6O_2H^+$ : 443.1440, found 443.1433

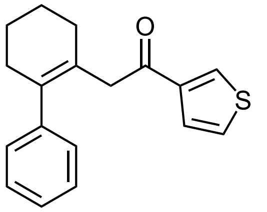


2-(4'-(Tert-butyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)-1-(m-tolyl)ethan-1-one (**3g**): isolated yield 85%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.35 (m, 2H), 7.25 – 7.15 (m, 4H), 7.01 (d, *J* = 8.2 Hz, 2H), 3.52 (s, 2H), 2.26 (d, *J* = 12.0 Hz, 5H), 2.02 (s, 2H), 1.69 – 1.60 (m, 4H), 1.22 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.5, 149.2, 140.5, 138.1, 137.1, 136.4, 133.5, 128.7, 128.2, 127.7, 127.1, 125.4, 125.1, 44.8, 34.4, 32.3, 31.4, 29.8, 23.3, 22.9, 21.3. HRMS: (ESI+) m/z calcd. for $C_{25}H_{30}OH^+$ : 347.2369, found 347.2365

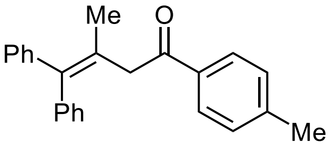


1-(Pyridin-3-yl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (**3h**): isolated yield 85%; colorless oil; Hexane:EA=8:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 1.4 Hz, 1H), 8.64 (m, 1H), 7.96 (m, 1H), 7.24 (m, 3H), 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 3.51

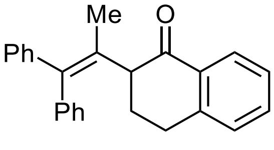
(s, 2H), 2.25 (s, 2H), 2.03 (s, 2H), 1.71 – 1.62 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.8, 152.9, 149.4, 143.3, 137.5, 135.5, 132.2, 128.3, 127.9, 126.7, 126.4, 123.5, 44.9, 32.3, 29.8, 23.1, 22.8. HRMS: (EI+) m/z calcd. for $C_{19}H_{19}NO$ : 277.1467, found 277.1472.



2-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)-1-(thiophen-3-yl)ethan-1-one (**3i**): isolated yield 65%; colorless oil; Hexane: EA=50:1; $^{1}$H NMR (400 MHz, CDCl3) δ 7.68 (d, *J* = 2.8 Hz, 1H), 7.35 (d, *J* = 5.1 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.07 (d, *J* = 7.4 Hz, 2H), 3.42 (s, 2H), 2.25 (d, *J* = 5.3 Hz, 2H), 2.05 (d, *J* = 4.7 Hz, 2H), 1.66 (dt, *J* = 7.8, 4.4 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.3, 143.6, 142.2, 136.7, 131.9, 128.2, 128.1, 127.2, 127.0, 126.5, 125.9, 45.7, 32.3, 29.8, 23.2, 22.8. HRMS: (EI+) m/z calcd. for $C_{18}H_{18}SO$ : 282.1078, found 282.1075.

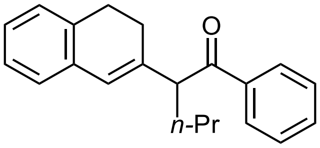


3-Methyl-4,4-diphenyl-1-(p-tolyl)but-3-en-1-one (**3j**): isolated yield 73%; white solid; Hexane:EA=50:1; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.21 (m, 11H), 3.84 (s, 2H), 2.43 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.2, 143.8, 142.6, 142.5, 140.8, 134.4, 129.7, 129.3, 129.1, 128.8, 128.3, 128.2, 127.9, 126.7, 126.4, 45.9, 21.6, 20.7. HRMS: (EI+) m/z calcd. for $C_{24}H_{22}O$ : 326.1671, found 326.1654.

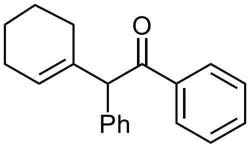


2-(1,1-Diphenylprop-1-en-2-yl)-3,4-dihydronaphthalen-1(2H)-one (**3k**): isolated yield 60%; white solid; Hexane:EA=25:1; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.24 (t, *J* = 7.7 Hz, 3H), 7.21 – 7.12 (m, 9H), 3.55 (m, 1H), 2.91 – 2.82 (m, 2H), 2.42 – 2.26 (m, 1H), 2.14 – 2.01 (m, 1H), 1.69 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.4, 144.1, 142.8, 142.6, 141.2, 133.2, 132.9, 132.7, 129.7, 129.1, 128.6, 128.2, 127.9, 127.4, 126.6, 126.6, 126.4, 54.2, 29.5, 29.0, 16.8. HRMS: (EI+) m/z calcd. for

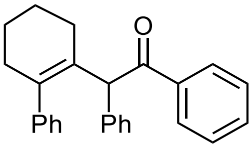
$C_{25}H_{22}O$ : 338.1671, found 338.1649.



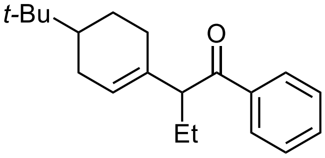
2-(3,4-Dihydronaphthalen-2-yl)-1-phenylpentan-1-one (**3l**): isolated yield 74%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.03 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.43 (s, 1H), 4.21 (t, *J* = 7.1 Hz, 1H), 2.83 – 2.66 (m, 2H), 2.43 – 2.22 (m, 2H), 2.08 – 1.91 (m, 1H), 1.77 (m, 1H), 1.47 – 1.30 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.0, 139.2, 137.3, 134.7, 134.3, 132.8, 128.5, 128.4, 127.2, 126.8, 126.4, 126.3, 125.9, 54.8, 32.4, 28.1, 24.8, 20.9, 14.1. HRMS: (EI+) m/z calcd. for $C_{21}H_{22}O$ : 290.1671, found 290.1654.



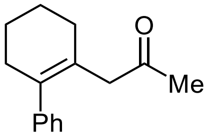
2-(Cyclohex-1-en-1-yl)-1,2-diphenylethan-1-one (**3m**): isolated yield 54%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 (m, 3H), 5.48 (s, 1H), 5.21 (s, 1H), 2.05 (d, *J* = 3.9 Hz, 4H), 1.66 – 1.58 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.6, 137.8, 137.3, 136.3, 132.7, 129.4, 128.6, 128.5, 128.4, 127.0, 126.3, 61.1, 28.6, 25.4, 23.0, 22.1. HRMS: (ESI+) m/z calcd. for $C_{20}H_{20}OH^+$ : 277.1587, found 277.1584.



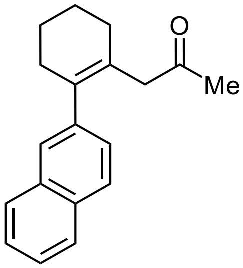
1,2-Diphenyl-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (**3n**): isolated yield 90%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.16 (m, 8H), 7.01 (m, 4H), 5.45 (s, 1H), 2.29 – 2.17 (m, 3H), 1.85 – 1.73 (m, 1H), 1.61 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.1, 143.7, 139.0, 137.3, 136.9, 132.6, 131.3, 129.0, 128.5, 128.4, 128.2, 128.0, 126.6, 126.5, 56.4, 33.0, 26.7, 23.0, 22.9. HRMS: (EI+) m/z calcd. for $C_{26}H_{24}O$ : 352.1827, found 352.1828.



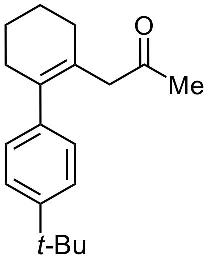
2-(4-(Tert-butyl)cyclohex-1-en-1-yl)-1-phenylpropan-1-one (**3o**): isolated yield 82%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (dq, *J* = 7.1, 1.6 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.44 (m, 2H), 5.65 (m, 1H), 3.84 (m, 1H), 2.13 – 2.03 (m, 2H), 1.95 – 1.69 (m, 5H), 1.18 – 1.04 (m, 2H), 0.91 – 0.88 (m, 3H), 0.83 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.7, 200.6, 137.6, 137.5, 135.6, 135.4, 132.5, 132.5, 128.4, 128.4, 128.3, 126.2, 126.2, 77.3, 77.0, 76.7, 56.8, 56.4, 43.9, 43.8, 32.1, 27.7, 27.6, 27.1, 27.1, 24.3, 24.2, 23.6, 23.3, 12.3, 12.3. HRMS: (ESI+) m/z calcd. for $C_{19}H_{28}OH^+$ : 285.2213, found 285.2209.



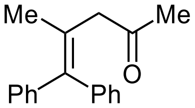
1-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)propan-2-one (**4a**): isolated yield 72%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (t, *J* = 7.4 Hz, 2H), 7.16 (q, *J* = 7.4 Hz, 1H), 7.05 – 7.00 (m, 2H), 2.93 (s, 2H), 2.22 (s, 2H), 1.97 (s, 2H), 1.91 (s, 3H), 1.65 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.8, 143.7, 137.0, 128.2, 127.9, 126.9, 126.4, 49.6, 32.3, 29.7, 29.4, 23.1, 22.8. HRMS: (EI+) m/z calcd. for $C_{15}H_{18}O$ : 214.1358, found 214.1341.



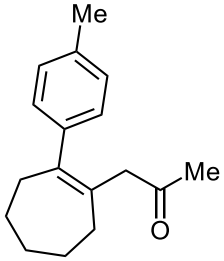
1-(2-(Naphthalen-2-yl)cyclohex-1-en-1-yl)propan-2-one (**4b**): isolated yield 72%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 – 7.68 (m, 3H), 7.48 (s, 1H), 7.38 (m, 2H), 7.18 (m, 1H), 2.97 (s, 2H), 2.31 (s, 2H), 2.02 (s, 2H), 1.91 (s, 3H), 1.74 – 1.67 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.7, 141.1, 137.0, 133.4, 132.2, 127.9, 127.8, 127.6, 127.5, 126.7, 126.3, 126.0, 125.6, 49.6, 32.3, 29.8, 29.6, 23.2, 22.9. HRMS: (EI+) m/z calcd. for $C_{19}H_{20}O$ : 264.1514, found 264.1484.



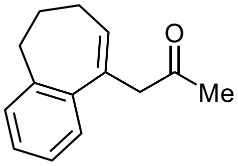
1-(4'-(Tert-butyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)propan-2-one (**4c**): isolated yield 70%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.04 (s, 2H), 2.30 (s, 2H), 2.05 (s, 2H), 2.02 (s, 3H), 1.73 (m, 4H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 208.1, 149.2, 140.5, 136.9, 127.5, 126.8, 125.1, 49.7, 34.4, 32.3, 31.4, 29.8, 29.5, 23.2, 22.8. HRMS: (EI+) m/z calcd. for $C_{19}H_{26}O$ : 270.1984, found 270.1990.



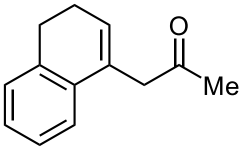
4-Methyl-5,5-diphenylpent-4-en-2-one (**4d**): isolated yield 62%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (tt, *J* = 5.3, 2.5 Hz, 4H), 7.16 – 7.08 (m, 4H), 7.07 – 6.98 (m, 2H), 3.17 (s, 2H), 2.00 (s, 3H), 1.72 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.1, 142.7, 142.2, 141.2, 129.5, 129.0, 128.2, 128.0, 126.7, 126.5, 50.7, 29.7, 20.7. HRMS: (EI+) m/z calcd. for $C_{18}H_{18}O$ : 250.1358, found 250.1366.



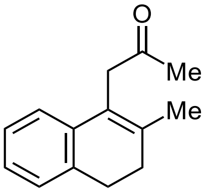
1-(2-(P-tolyl)cyclohept-1-en-1-yl)propan-2-one (**4e**): isolated yield 70%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.11 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 3.10 (s, 2H), 2.53 – 2.47 (m, 2H), 2.34 (s, 3H), 2.28 – 2.24 (m, 2H), 2.03 (s, 3H), 1.82 (m, 2H), 1.63 – 1.57 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 208.1, 142.8, 142.3, 135.8, 132.8, 128.9, 127.4, 51.6, 36.4, 34.1, 32.5, 29.6, 26.7, 26.0, 21.1. HRMS: (EI+) m/z calcd. for $C_{17}H_{22}O$ : 242.1671, found 242.1668.



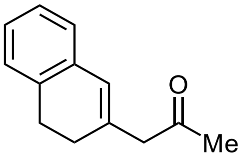
1-(6,7-Dihydro-5H-benzo[7]annulen-9-yl)propan-2-one (**4f**): isolated yield 50%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 3H), 7.16 – 7.12 (m, 1H), 6.28 (d, *J* = 1.6 Hz, 1H), 2.98 (s, 2H), 2.76 (t, *J* = 5.8 Hz, 2H), 2.30 (s, 3H), 1.80 – 1.75 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.7, 162.9, 143.0, 139.8, 129.0, 128.5, 126.9, 126.3, 124.9, 33.8, 32.1, 31.5, 26.9, 26.2. HRMS: (ESI+) m/z calcd. for $C_{14}H_{16}OH^+$ : 201.1474, found 201.1474.



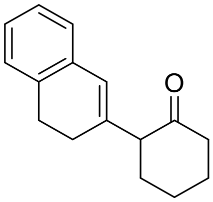
1-(3,4-Dihydronaphthalen-1-yl)propan-2-one (**4g**): isolated yield 46%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 3H), 7.13 – 7.07 (m, 1H), 6.01 (t, *J* = 4.6 Hz, 1H), 3.49 (s, 2H), 2.82 (t, *J* = 8.1 Hz, 2H), 2.36 (m, 2H), 2.16 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.9, 136.3, 134.1, 131.0, 129.6, 127.7, 127.2, 126.6, 122.8, 49.1, 28.5, 28.0, 23.3. HRMS: (EI+) m/z calcd. for $C_{13}H_{14}O$ : 186.1045, found 186.1055.



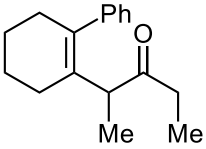
1-(2-Methyl-3,4-dihydronaphthalen-1-yl)propan-2-one (**4h**): isolated yield 46%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.09 (m, 3H), 7.06 (d, *J* = 7.7 Hz, 1H), 3.60 (s, 2H), 2.78 (t, *J* = 7.9 Hz, 2H), 2.33 (t, *J* = 7.9 Hz, 2H), 2.13 (s, 3H), 1.96 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.8, 136.4, 135.6, 135.4, 127.3, 126.5, 126.1, 124.1, 122.4, 44.2, 30.6, 28.7, 28.2, 20.7. HRMS: (EI+) m/z calcd. for $C_{14}H_{16}O$ : 200.1201, found 200.1190.



1-(3,4-Dihydronaphthalen-2-yl)propan-2-one (**4i**): isolated yield 47%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.19 – 7.10 (m, 3H), 7.02 (d, *J* = 6.8 Hz, 1H), 6.36 (s, 1H), 3.30 (s, 2H), 2.85 (t, *J* = 8.1 Hz, 2H), 2.29 (t, *J* = 8.1 Hz, 2H), 2.22 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 206.5, 134.4, 134.4, 134.1, 127.3, 126.9, 126.6, 126.5, 125.8, 52.6, 29.2, 27.9, 27.3. HRMS: (EI+) m/z calcd. for $C_{13}H_{14}O$ : 186.1045, found 186.1038.



2-(3,4-Dihydronaphthalen-2-yl)cyclohexan-1-one (**4j**): isolated yield 80%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.08 (m, 3H), 7.00 (d, *J* = 6.8 Hz, 1H), 6.25 (s, 1H), 3.20 (m, 1H), 2.84 (m, 2H), 2.51 – 2.34 (m, 2H), 2.28 – 2.22 (m, 2H), 2.11 (m, 2H), 1.98 (m, 2H), 1.76 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.6, 139.4, 135.1, 134.3, 127.1, 126.5, 126.3, 125.7, 124.3, 58.4, 42.2, 31.8, 28.0, 27.6, 26.4, 24.8. HRMS: (EI+) m/z calcd. for $C_{16}H_{18}O$ : 226.1358, found 226.1341.



2-(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)pentan-3-one (**4k**): isolated yield 71%; colorless oil; Hexane:DCM=10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.18 (m, 1H), 7.11 – 7.03 (m, 2H), 3.30 (q, *J* = 6.8 Hz, 1H), 2.32 (m, 2H), 2.17 – 1.97 (m, 3H), 1.63 – 1.56 (m, 4H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 212.8, 144.1, 136.8, 132.4, 128.4, 127.9, 126.4, 49.9, 33.7, 32.8, 24.4, 23.2, 22.9, 13.7, 7.9. HRMS: (EI+) m/z calcd. for $C_{17}H_{22}O$ : 242.1671, found 242.1668.

## 6. References

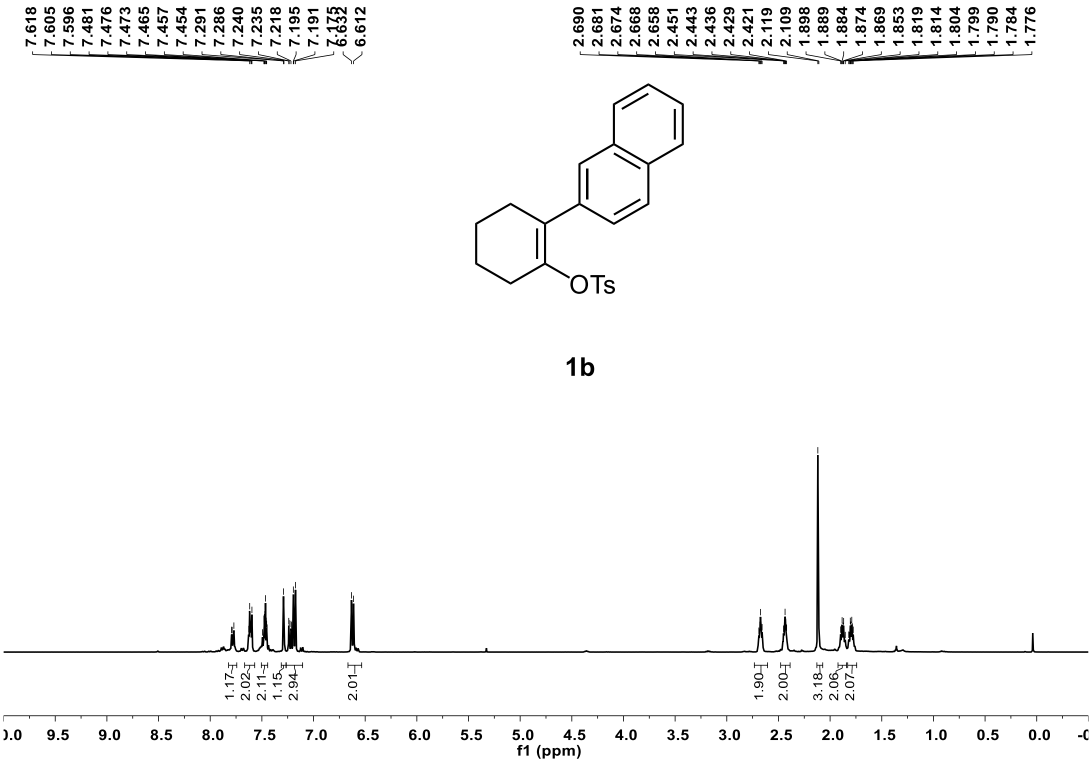
(1) (a) C. M. So, C. P. Lau and F. Y. Kwong, *Angew. Chem. Int. Ed.*, 2008, **47**, 8059. (b) K. H. Chung, C. M. So, S. M. Wong, C. H. Luk, Z. Zhou, C. P. Lau and F. Y. Kwong, *Chem. Commun.*, 2012, **48**, 1967.

(2) A. Klapars, K. R. Campos, C. Y. Chen and R. P. Volante, *Org. Lett.*, 2005, **7**, 1185.

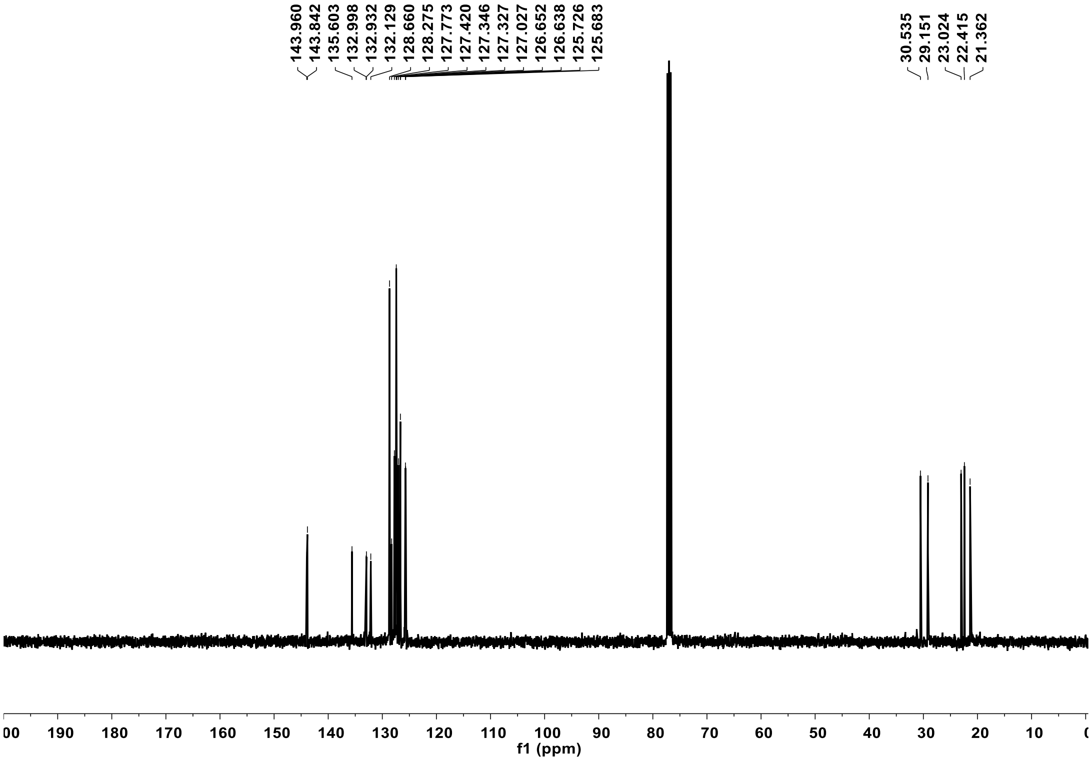
(3) T. Ueda, H. Konishi and K. Manabe, *Tetrahedron Lett.*, 2012, **53**, 5171.

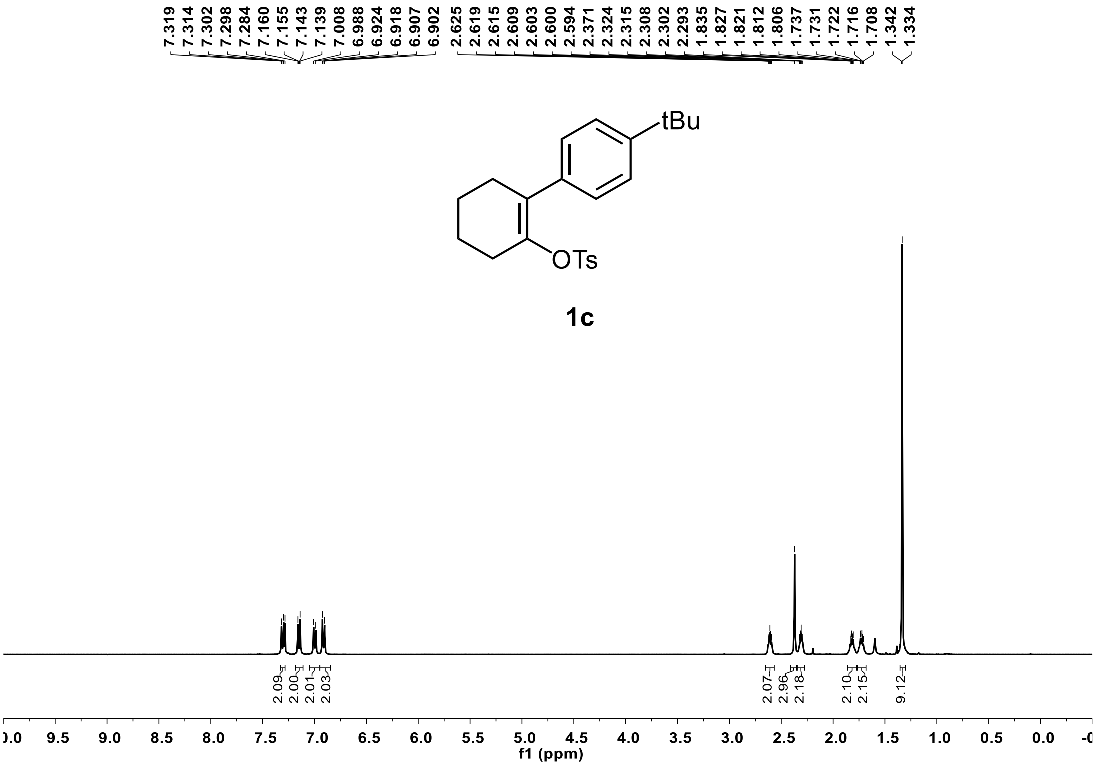
(4) D. C. Reeves, S. Rodriguez, H. Lee, N. Haddad, D. Krishnamurthy and C. H. Senanayake, *Tetrahedron Lett.*, 2009, **50**, 2870.

# 7. $^1$H and $^{13}$C NMR spectra

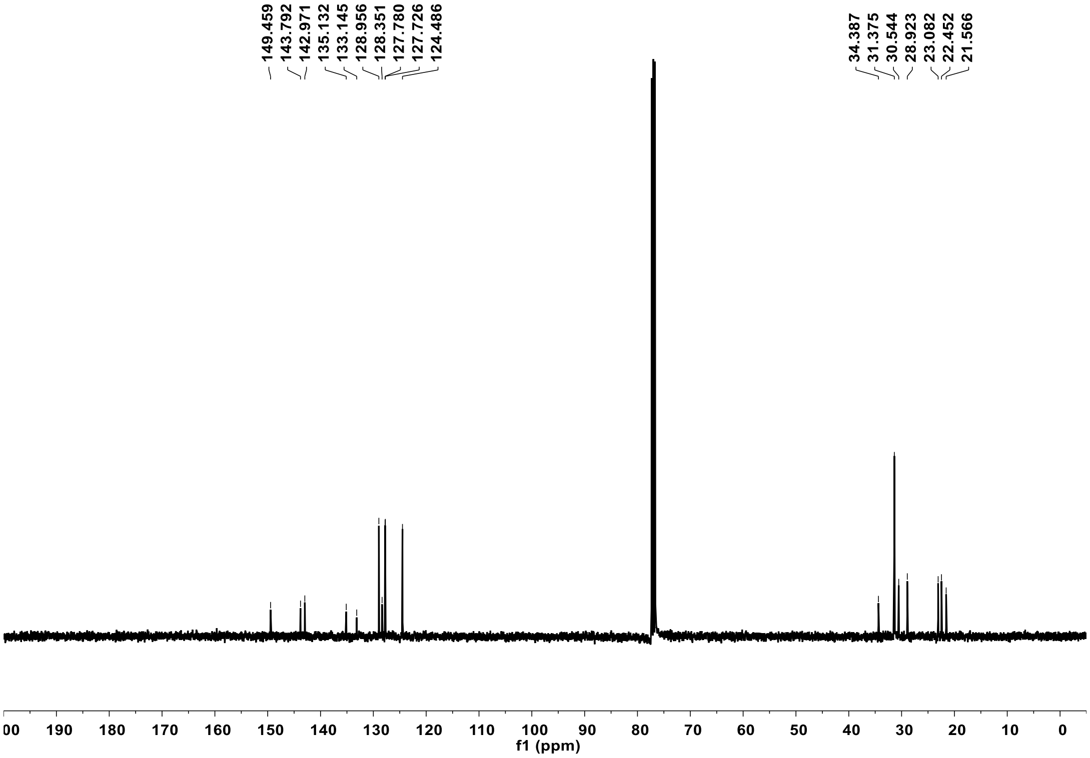


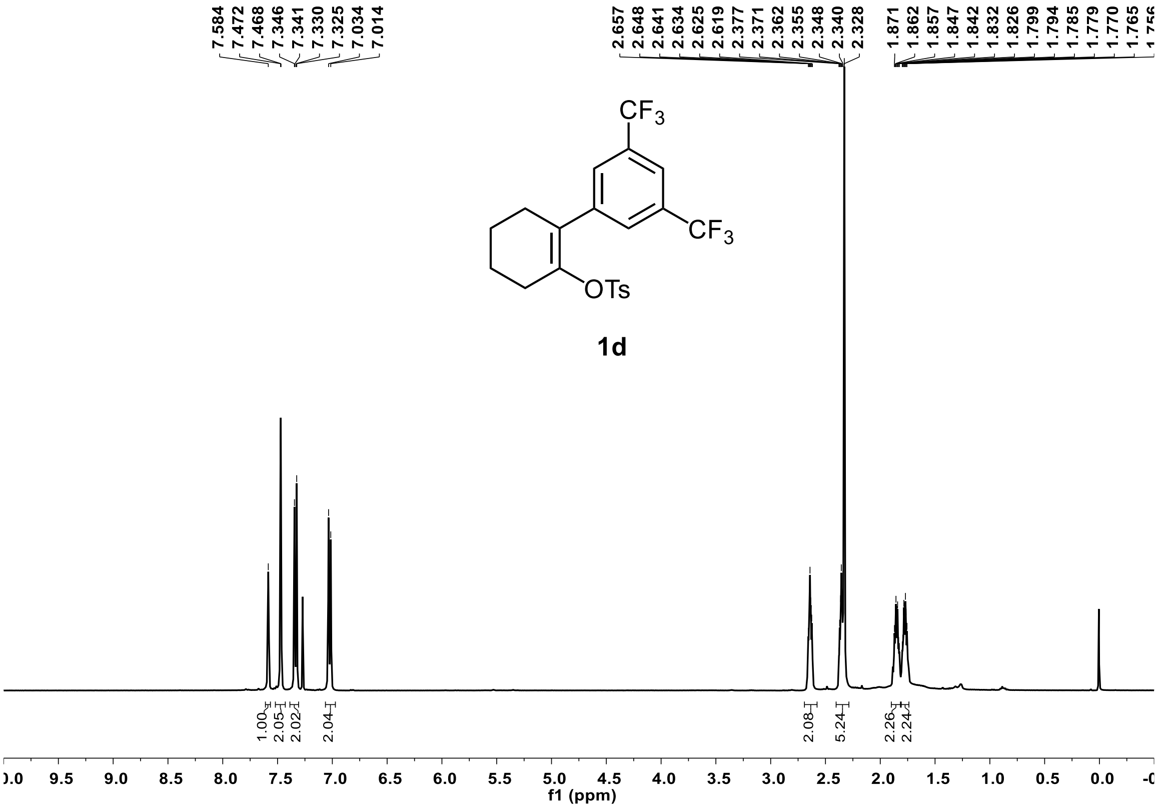
**1b**

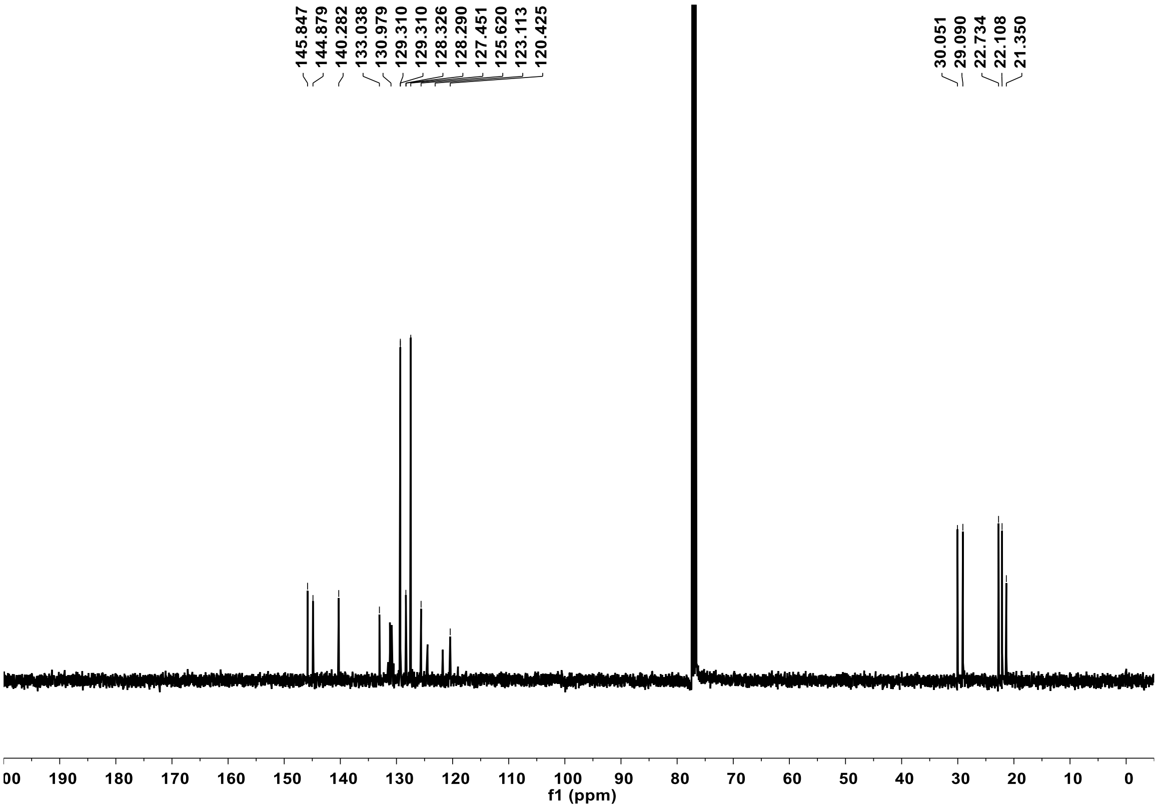


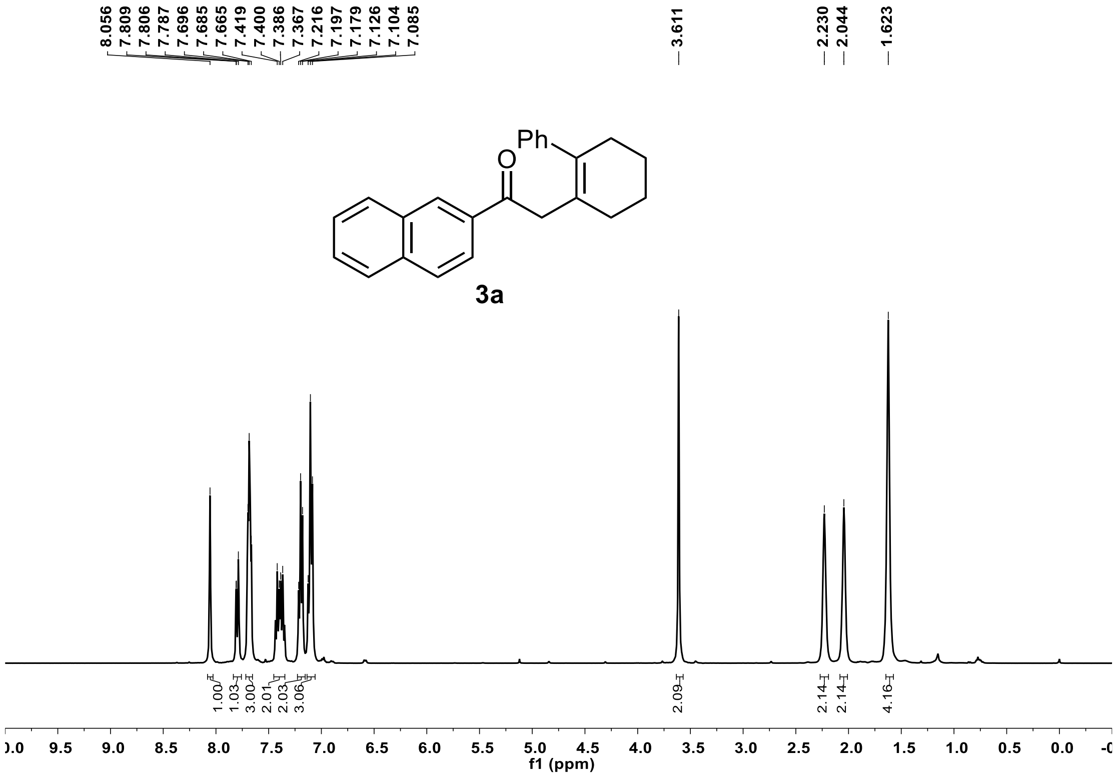

7.319
7.314
7.302
7.298
7.284
7.160
7.155
7.143
7.139
7.008
6.988
6.924
6.918
6.907
6.902
2.625
2.619
2.615
2.609
2.603
2.600
2.594
2.371
2.324
2.315
2.308
2.302
2.293
1.835
1.827
1.821
1.812
1.806
1.737
1.731
1.722
1.716
1.708
1.342
1.334
tBu
OTs
2.09
2.00
2.01
2.03
2.07
2.96
2.18
2.10
2.15
9.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

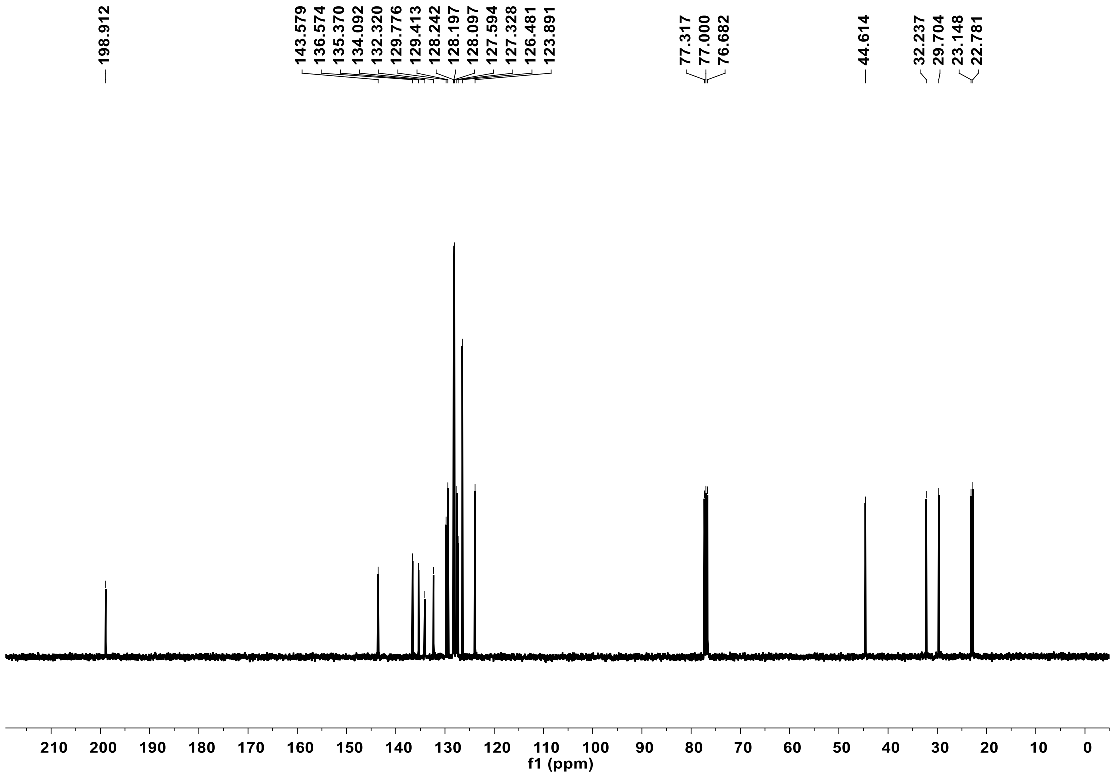
**1c**

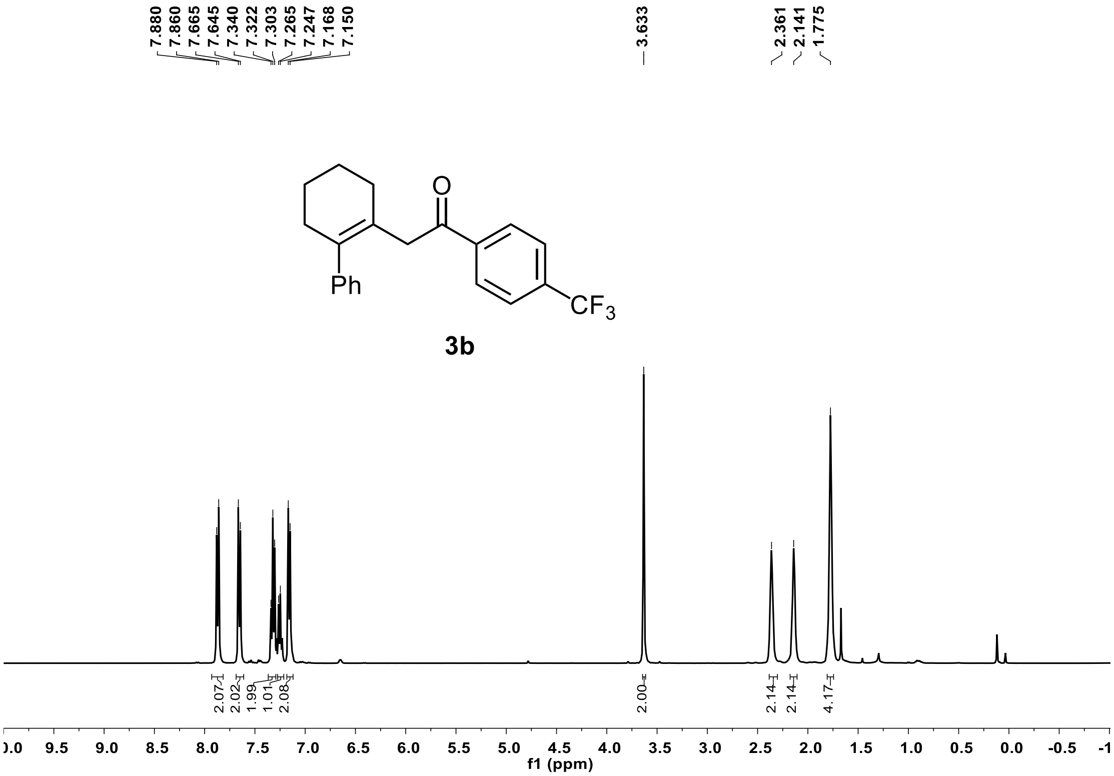

149.459
143.792
142.971
135.132
133.145
128.956
128.351
127.780
127.726
124.486
34.387
31.375
30.544
28.923
23.082
22.452
21.566
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.584
7.472
7.468
7.346
7.341
7.330
7.325
7.034
7.014
2.657
2.648
2.641
2.634
2.625
2.619
2.377
2.371
2.362
2.355
2.348
2.340
2.328
1.871
1.862
1.857
1.847
1.842
1.832
1.826
1.799
1.794
1.785
1.779
1.770
1.765
CF3
CF3
OTs
1d
1.00
2.05
2.02
2.04
2.08
5.24
2.26
2.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

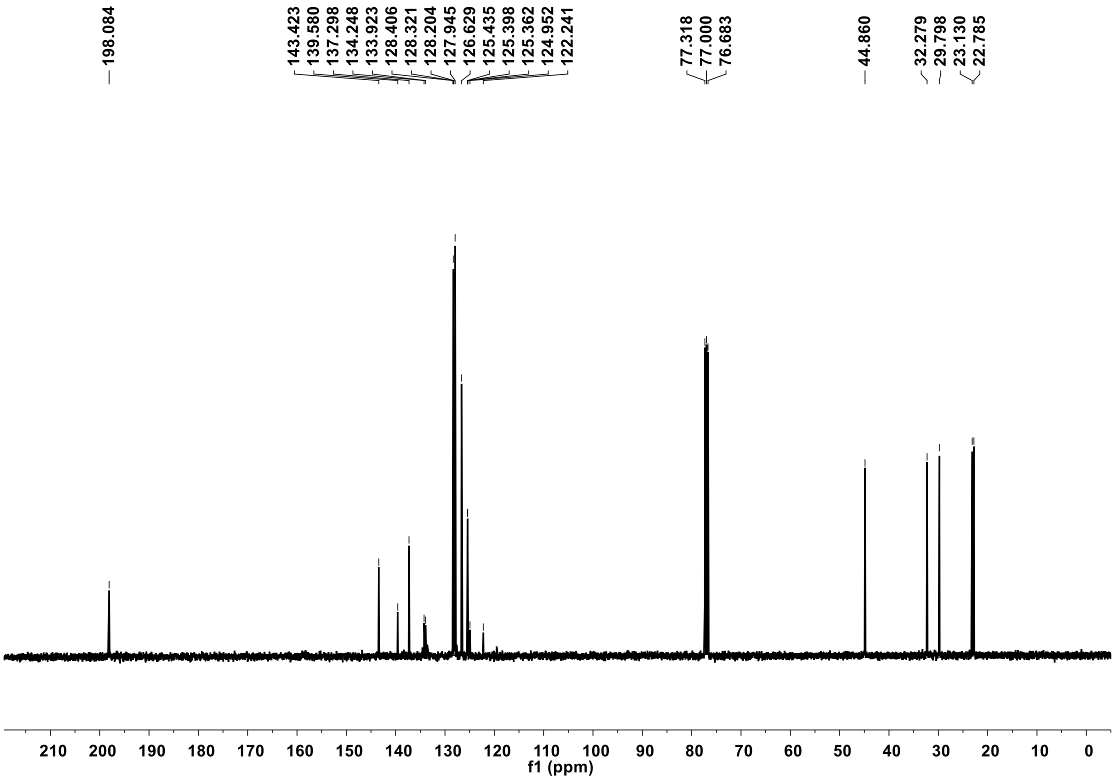

145.847
144.879
140.282
133.038
130.979
129.310
129.310
128.326
128.290
127.451
125.620
123.113
120.425
30.051
29.090
22.734
22.108
21.350
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

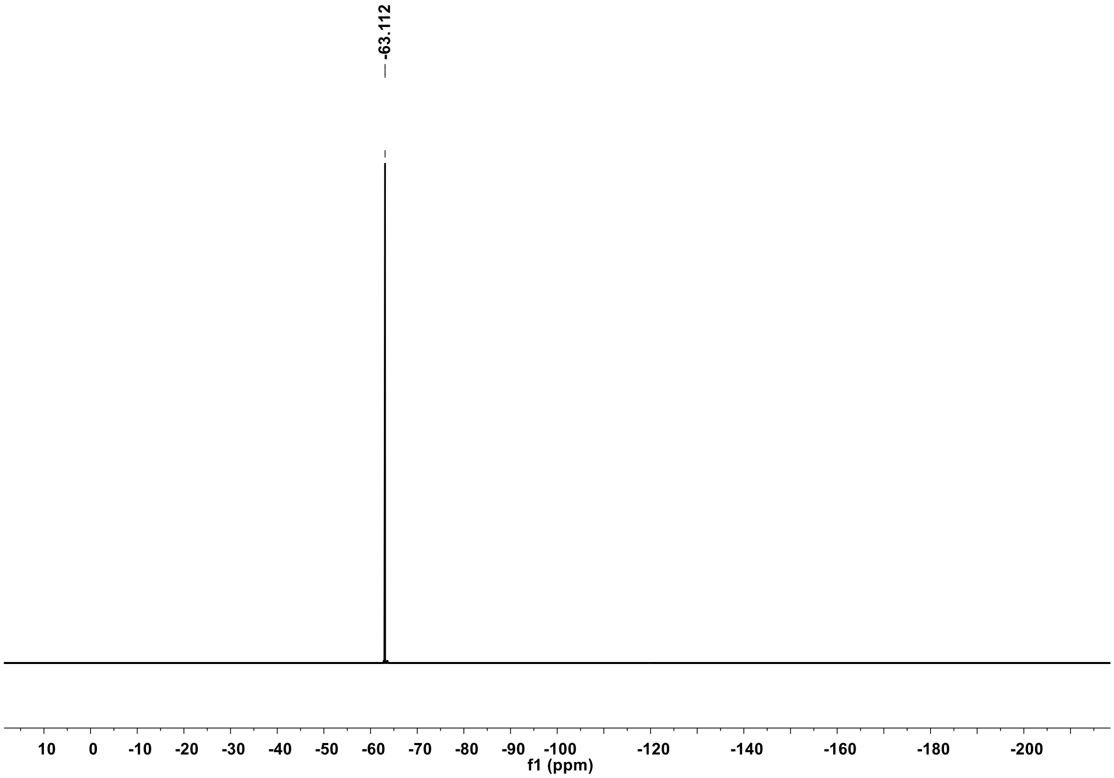

8.056
7.809
7.806
7.787
7.696
7.685
7.665
7.419
7.400
7.386
7.367
7.216
7.197
7.179
7.126
7.104
7.085
3.611
2.230
2.044
1.623
Ph
O
3a
1.00
1.03
3.00
2.01
2.03
3.06
2.09
2.14
2.14
4.16
f1 (ppm)

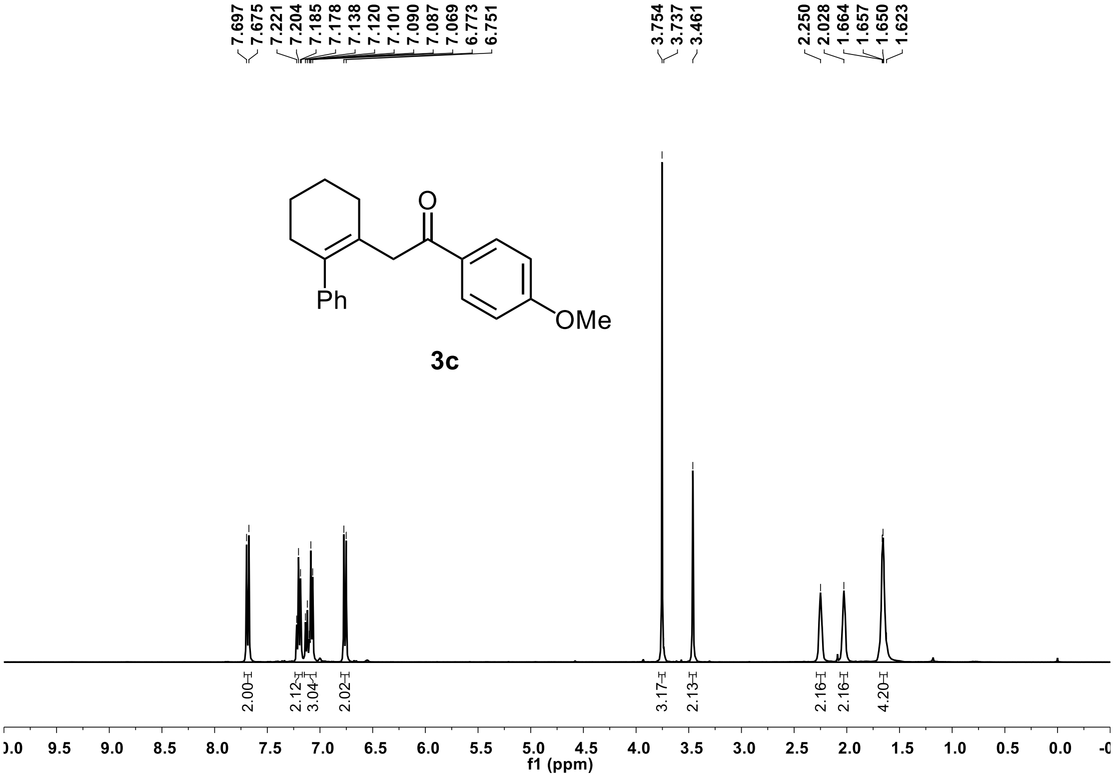

198.912
143.579
136.574
135.370
134.092
132.320
129.776
129.413
128.242
128.197
128.097
127.594
127.328
126.481
123.891
77.317
77.000
76.682
44.614
32.237
29.704
23.148
22.781
f1 (ppm)


7.880
7.860
7.665
7.645
7.340
7.322
7.303
7.265
7.247
7.168
7.150
3.633
2.361
2.141
1.775
O
Ph
CF3
2.07
2.02
1.99
1.01
2.08
2.00
2.14
2.14
4.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

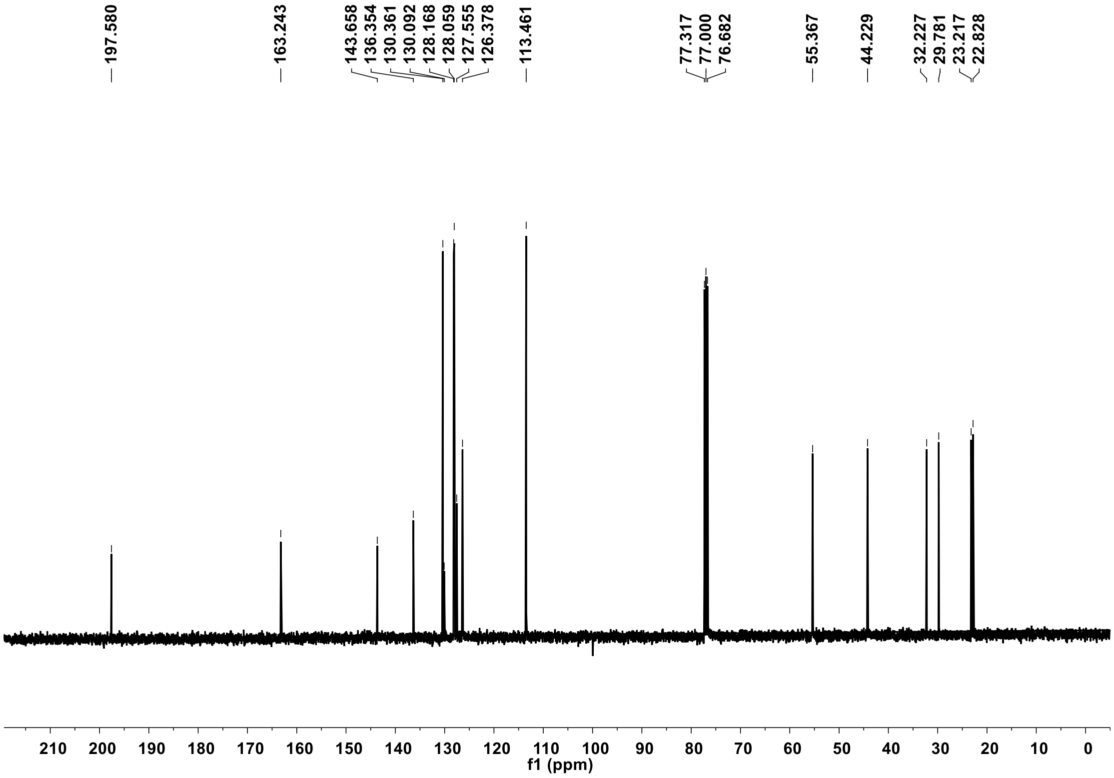
**3b**

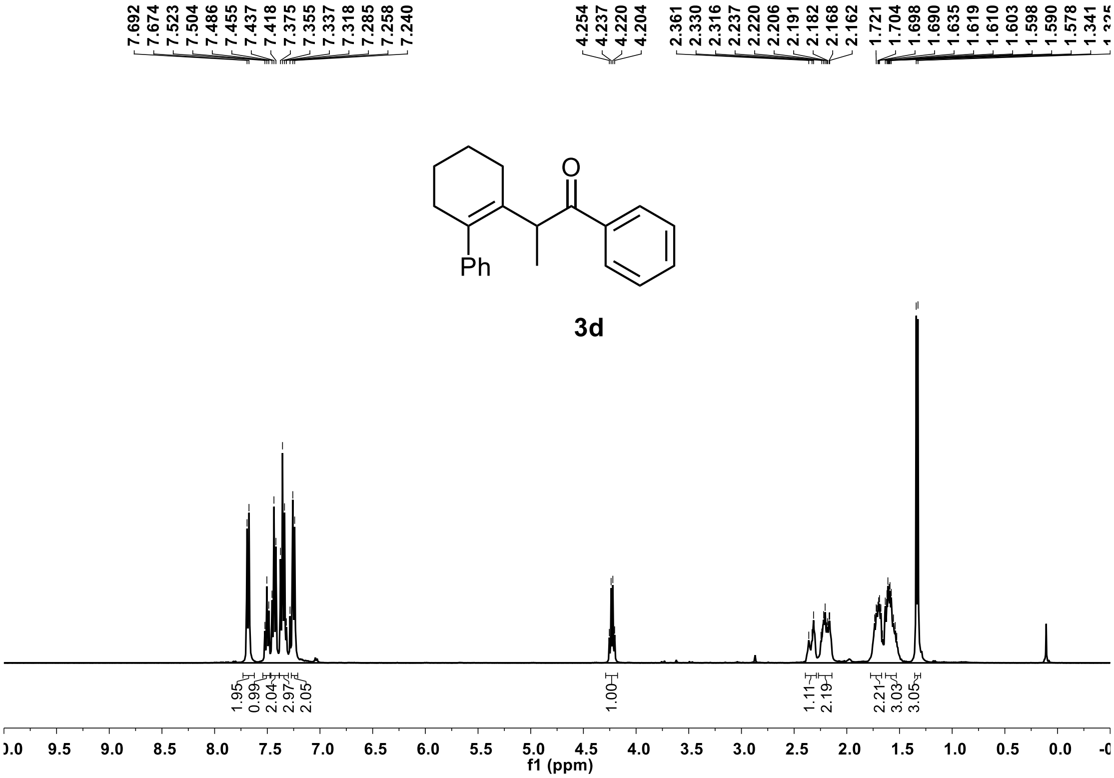

198.084
143.423
139.580
137.298
134.248
133.923
128.406
128.321
128.204
127.945
126.629
125.435
125.398
125.362
124.952
122.241
77.318
77.000
76.683
44.860
32.279
29.798
23.130
22.785
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.112
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

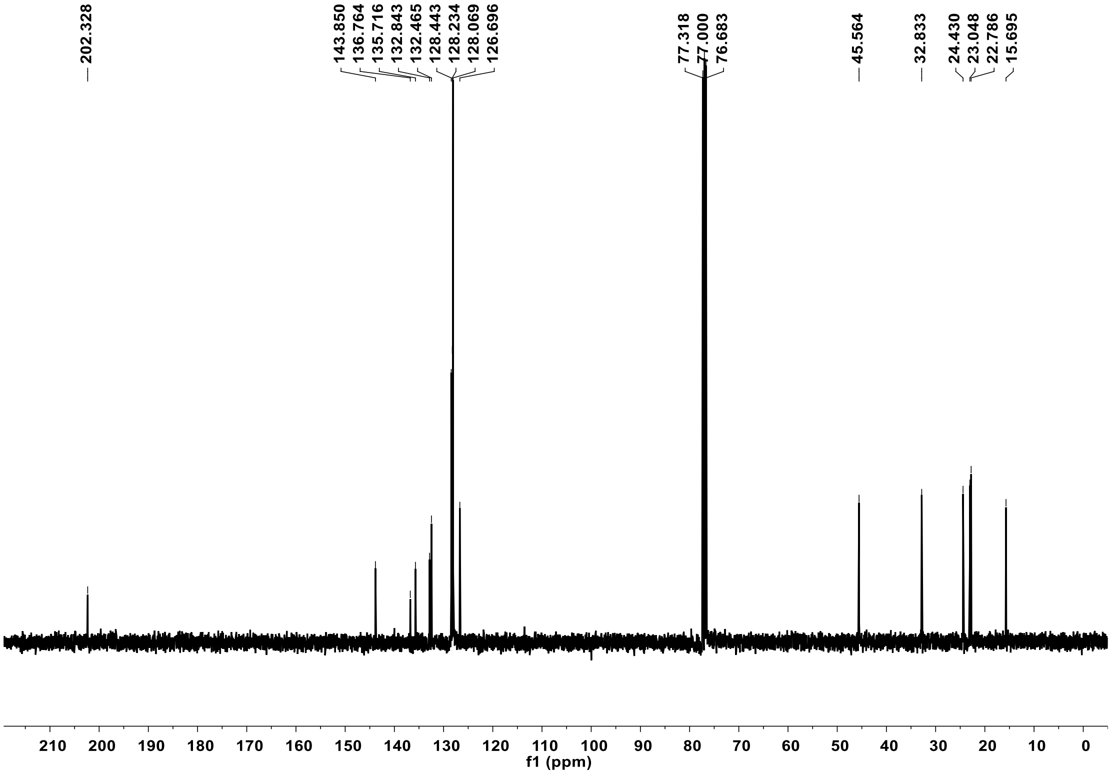

7.697
7.675
7.221
7.204
7.185
7.178
7.138
7.120
7.101
7.090
7.087
7.069
6.773
6.751
3.754
3.737
3.461
2.250
2.028
1.664
1.657
1.650
1.623
O
Ph
OMe
2.00
2.12
3.04
2.02
3.17
2.13
2.16
2.16
4.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

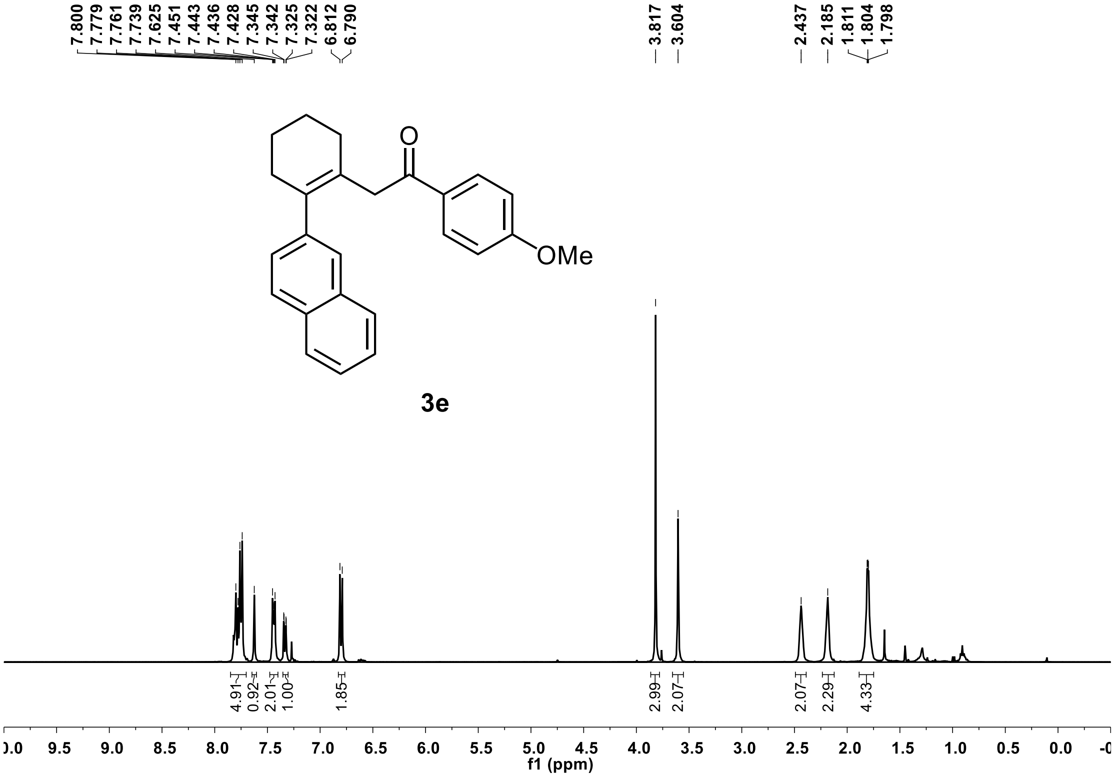
**3c**


197.580
163.243
143.658
136.354
130.361
130.092
128.168
128.059
127.555
126.378
113.461
77.317
77.000
76.682
55.367
44.229
32.227
29.781
23.217
22.828
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

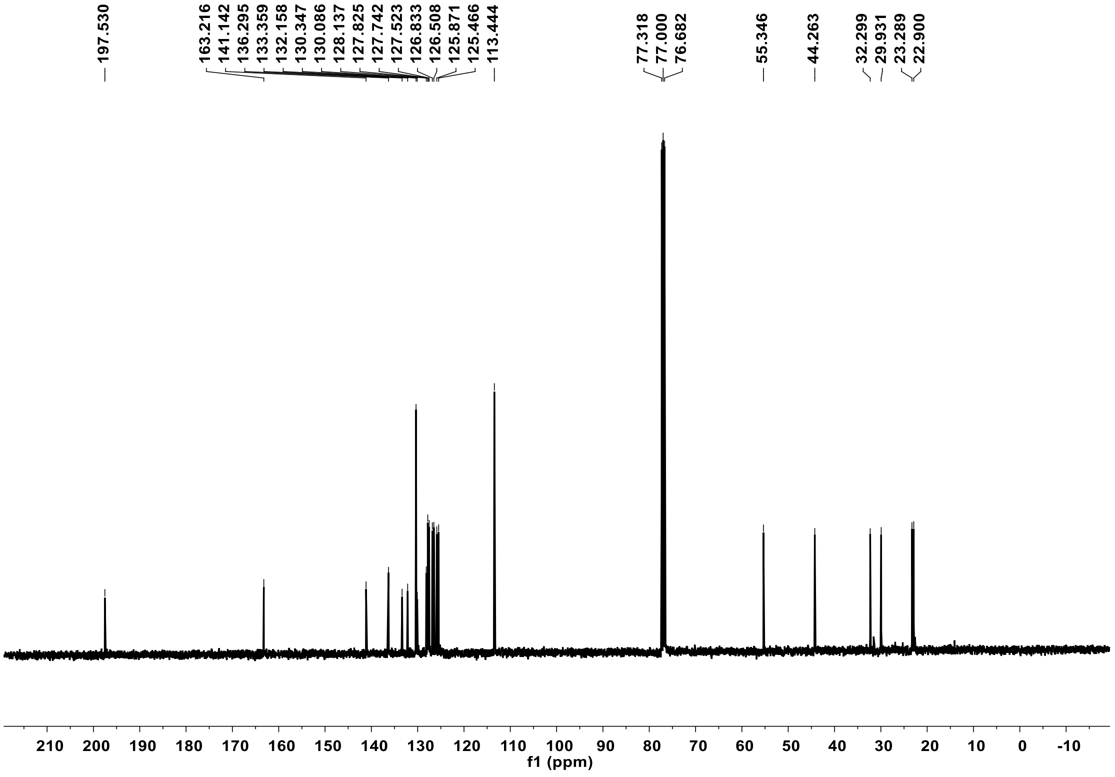

7.692
7.674
7.523
7.504
7.486
7.455
7.437
7.418
7.375
7.355
7.337
7.318
7.285
7.258
7.240
4.254
4.237
4.220
4.204
2.361
2.330
2.316
2.237
2.220
2.206
2.191
2.182
2.168
2.162
1.721
1.704
1.698
1.690
1.635
1.619
1.610
1.603
1.598
1.590
1.578
1.341
O
Ph
1.95
0.99
2.04
2.97
2.05
1.00
1.11
2.19
2.21
3.03
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

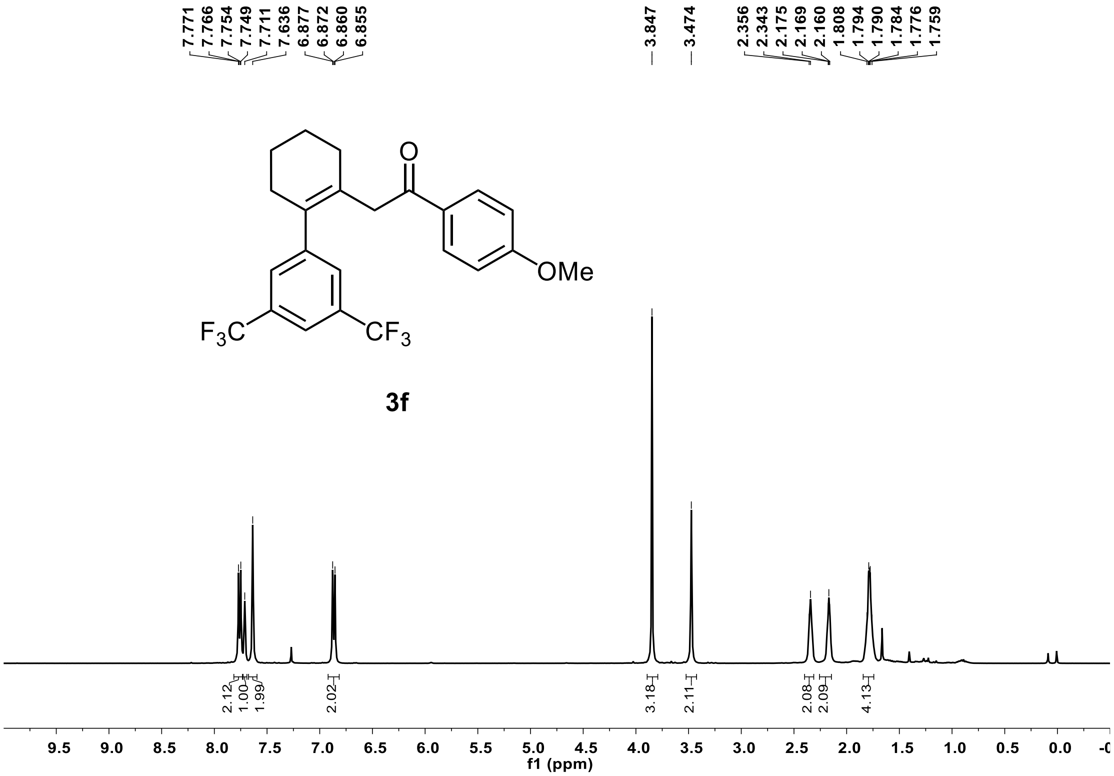
**3d**

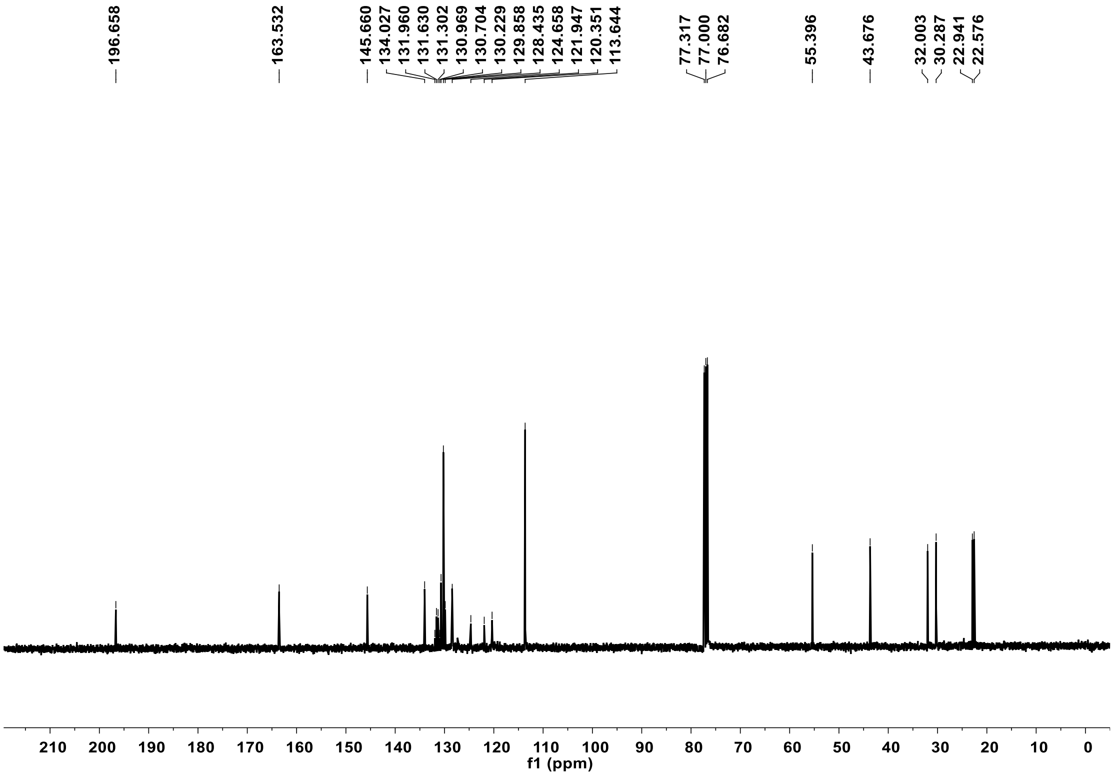

202.328
143.850
136.764
135.716
132.843
132.465
128.443
128.234
128.069
126.696
77.318
77.000
76.683
45.564
32.833
24.430
23.048
22.786
15.695
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

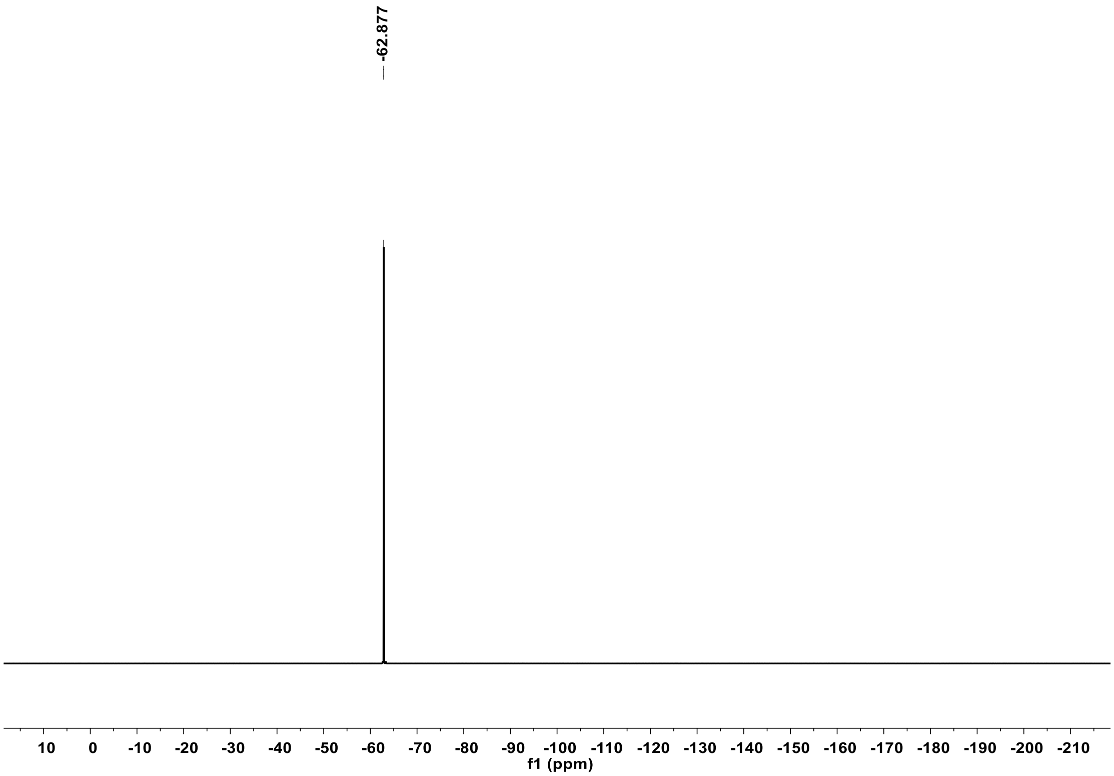

7.800
7.779
7.761
7.739
7.625
7.451
7.443
7.436
7.428
7.345
7.342
7.325
7.322
6.812
6.790
3.817
3.604
2.437
2.185
1.811
1.804
1.798
O
OMe
4.91
0.92
2.01
1.00
1.85
2.99
2.07
2.07
2.29
4.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

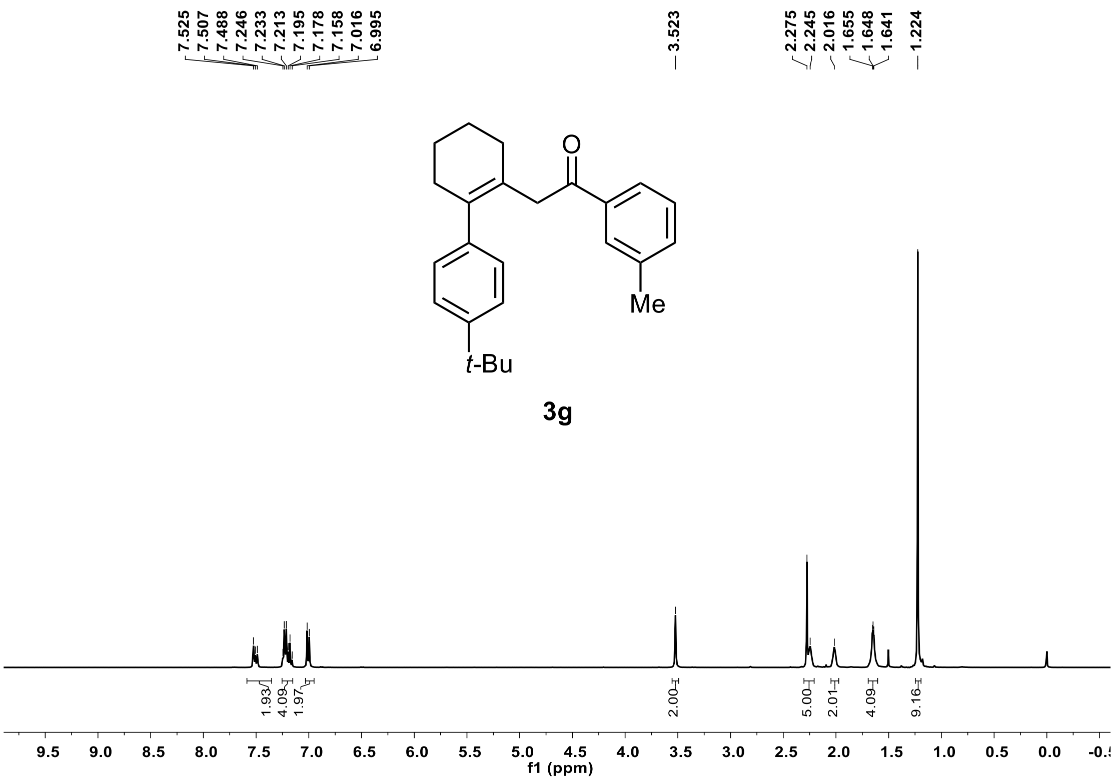
**3e**


197.530
163.216
141.142
136.295
133.359
132.158
130.347
130.086
128.137
127.825
127.742
127.523
126.833
126.508
125.871
125.466
113.444
77.318
77.000
76.682
55.346
44.263
32.299
29.931
23.289
22.900
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)

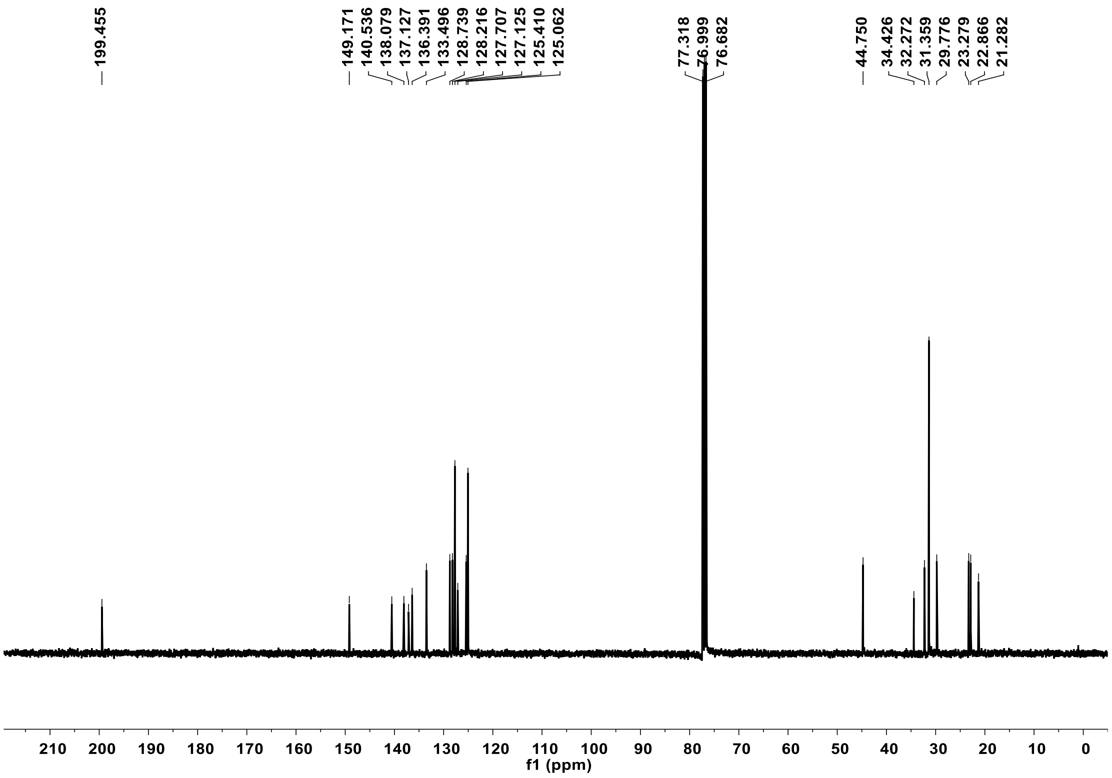

7.771
7.766
7.754
7.749
7.711
7.636
6.877
6.872
6.860
6.855
3.847
3.474
2.356
2.343
2.175
2.169
2.160
1.808
1.794
1.790
1.784
1.776
1.759
O
OMe
$F_3C$
$CF_3$
3f
2.12
1.00
1.99
2.02
3.18
2.11
2.08
2.09
4.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

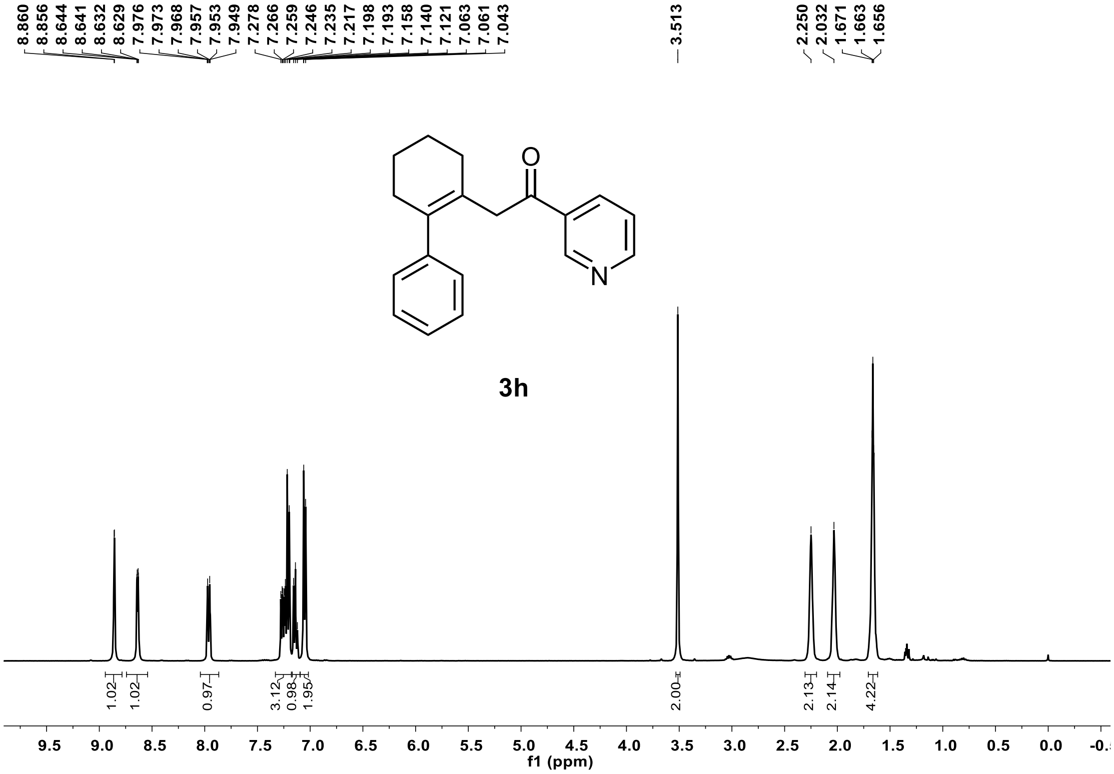

196.658
163.532
145.660
134.027
131.960
131.630
131.302
130.969
130.704
130.229
129.858
128.435
124.658
121.947
120.351
113.644
77.317
77.000
76.682
55.396
43.676
32.003
30.287
22.941
22.576
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

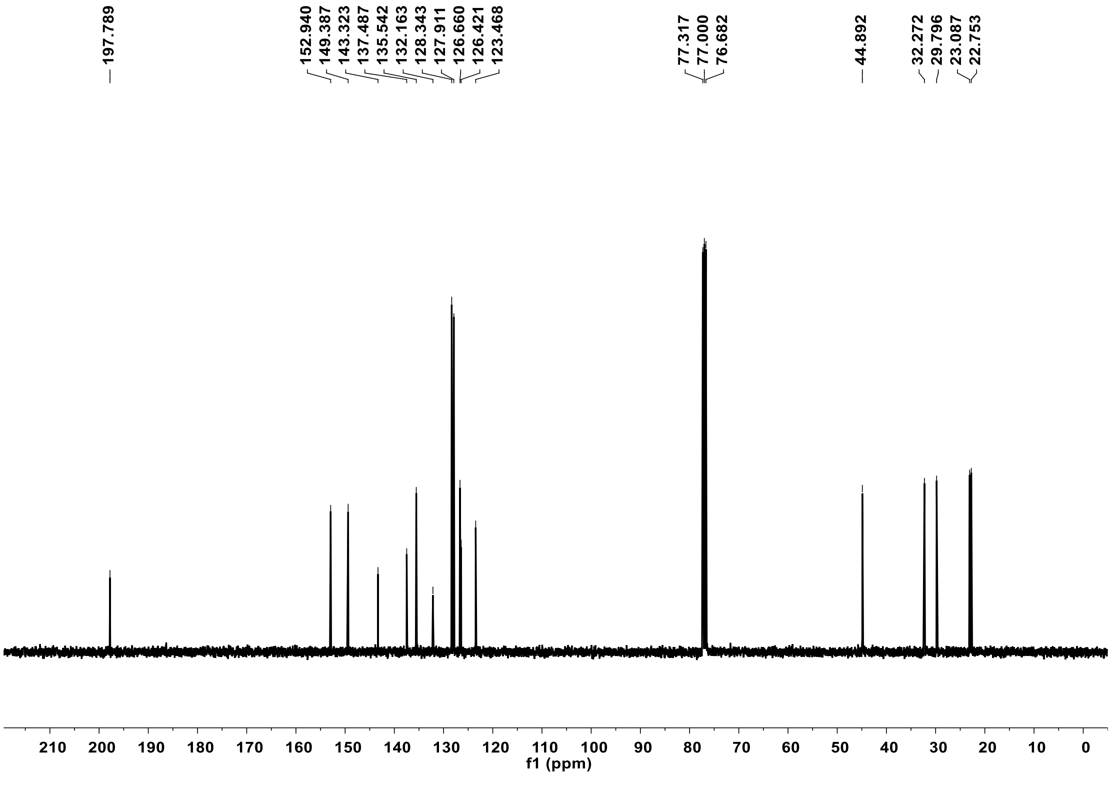

-62.877
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

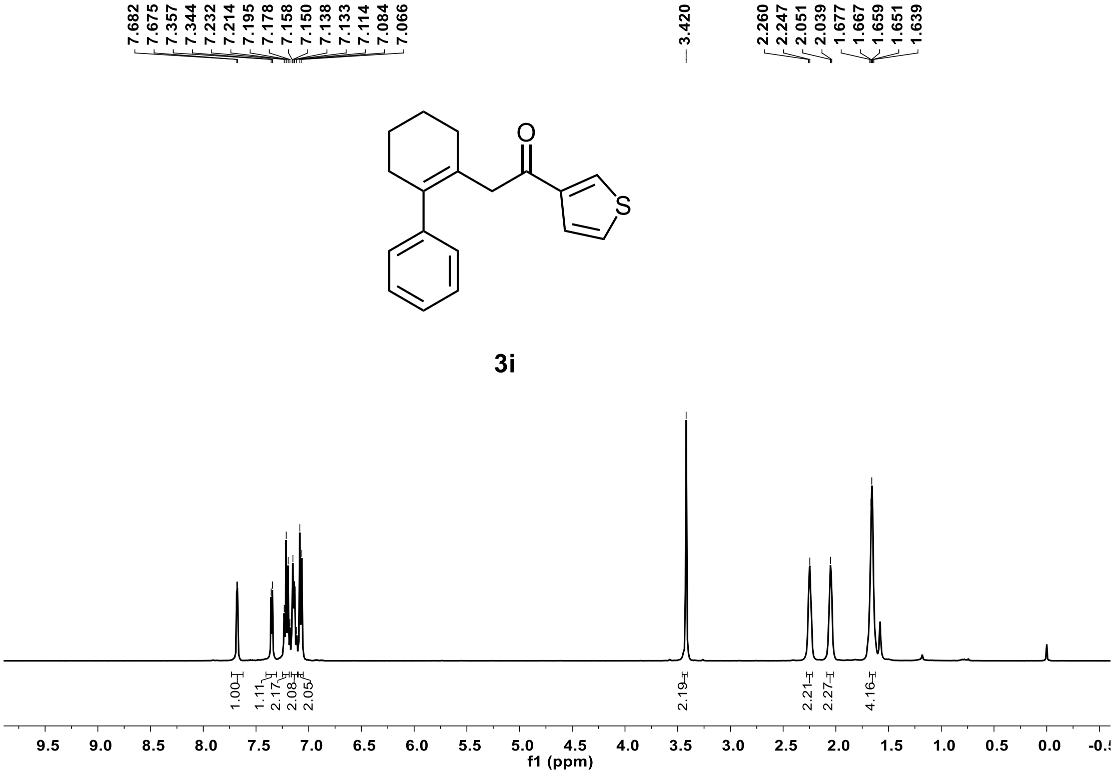

7.525
7.507
7.488
7.246
7.233
7.213
7.195
7.178
7.158
7.016
6.995
3.523
2.275
2.245
2.016
1.655
1.648
1.641
1.224
O
Me
t-Bu
1.93
4.09
1.97
2.00
5.00
2.01
4.09
9.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

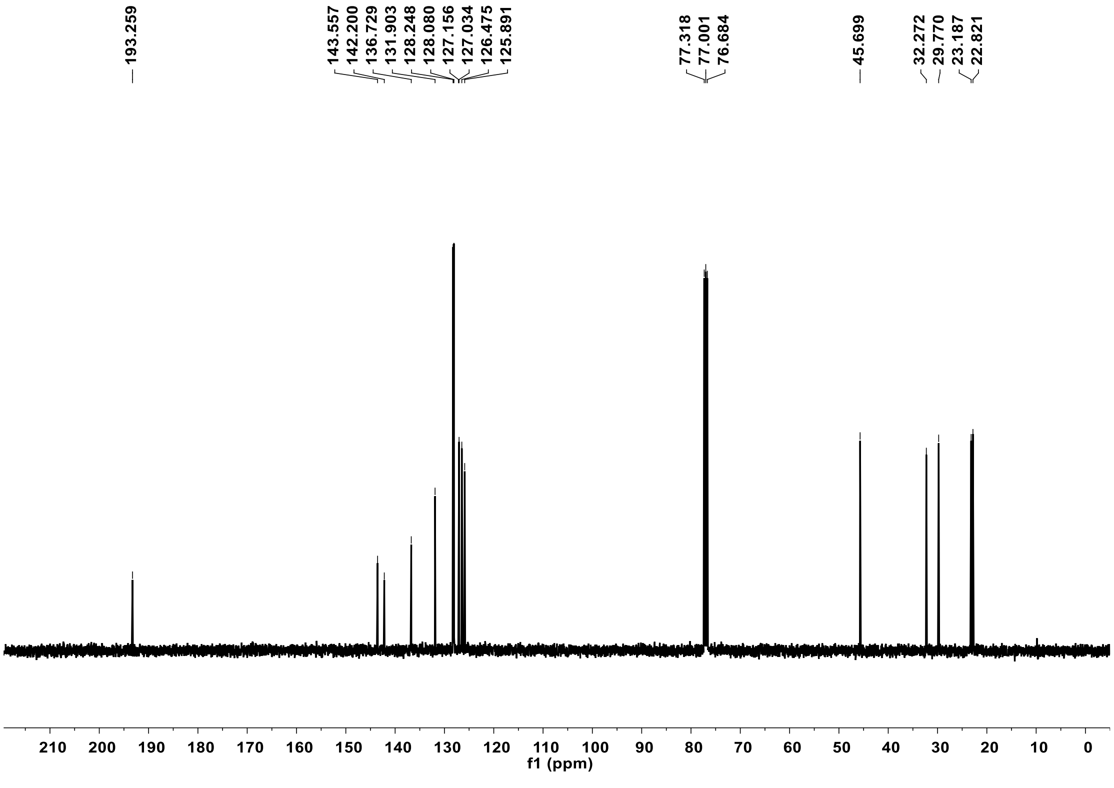
**3g**

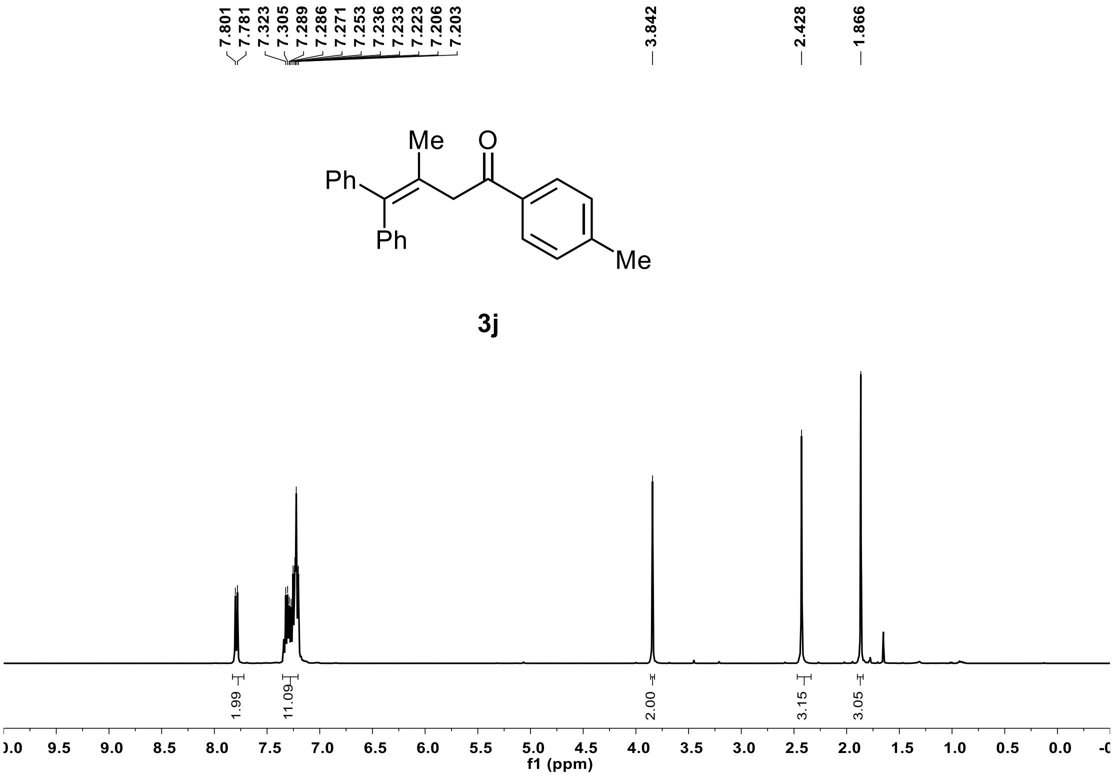

199.455
149.171
140.536
138.079
137.127
136.391
133.496
128.739
128.216
127.707
127.125
125.410
125.062
77.318
76.999
76.682
44.750
34.426
32.272
31.359
29.776
23.279
22.866
21.282
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.860
8.856
8.644
8.641
8.632
8.629
7.976
7.973
7.968
7.957
7.953
7.949
7.278
7.266
7.259
7.246
7.235
7.217
7.198
7.193
7.158
7.140
7.121
7.063
7.061
7.043
3.513
2.250
2.032
1.671
1.663
1.656
O
N
3h
1.02
1.02
0.97
3.12
0.98
1.95
2.00
2.13
2.14
4.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

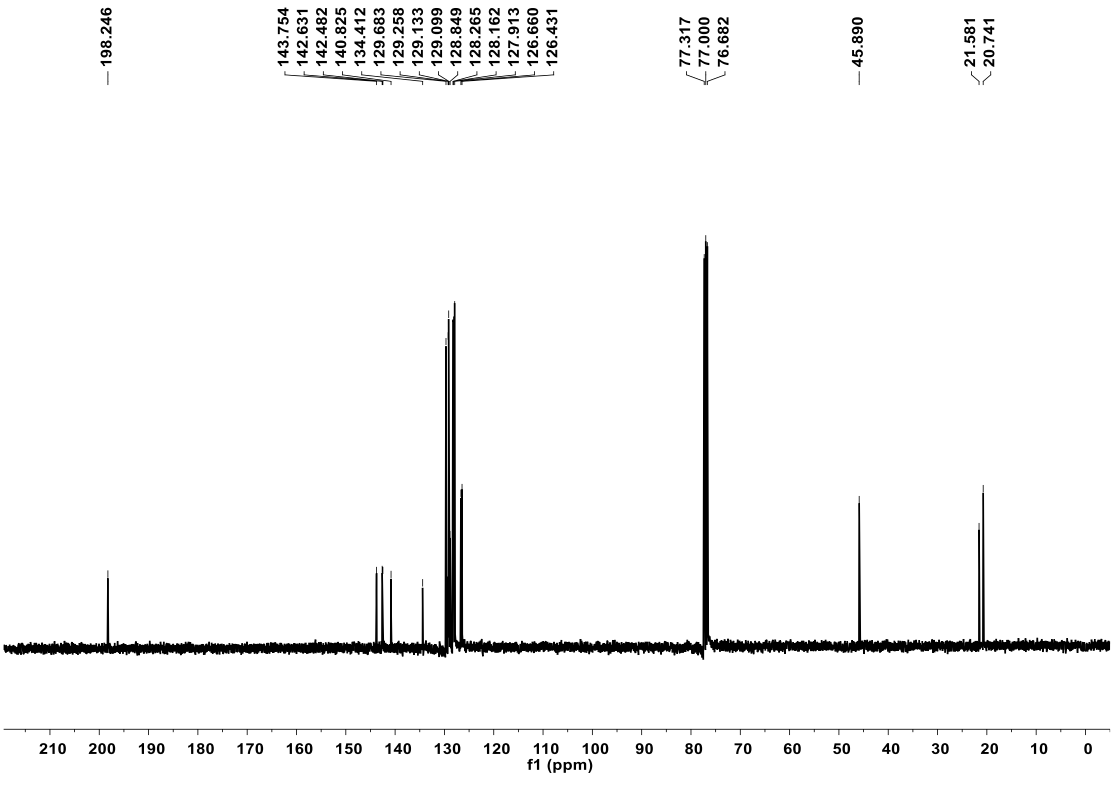

197.789
152.940
149.387
143.323
137.487
135.542
132.163
128.343
127.911
126.660
126.421
123.468
77.317
77.000
76.682
44.892
32.272
29.796
23.087
22.753
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

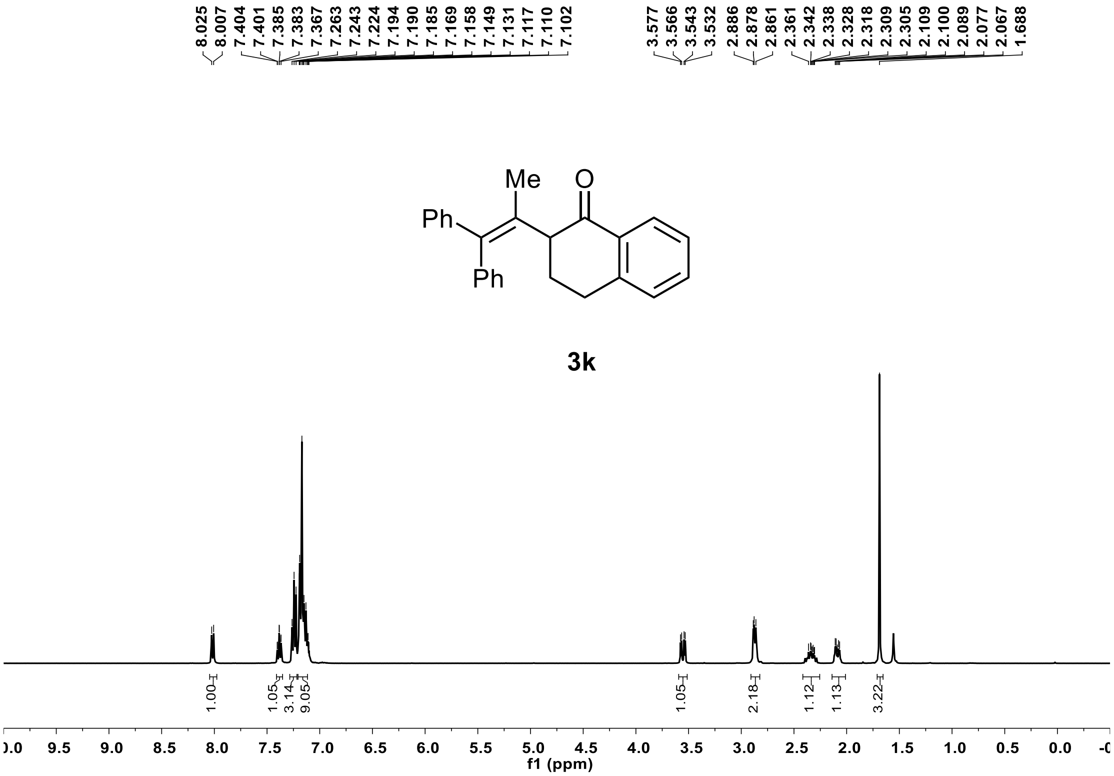

7.682
7.675
7.357
7.344
7.232
7.214
7.195
7.178
7.158
7.150
7.138
7.133
7.114
7.084
7.066
3.420
2.260
2.247
2.051
2.039
1.677
1.667
1.659
1.651
1.639
O
S
3i
1.00
1.11
2.17
2.08
2.05
2.19
2.21
2.27
4.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


193.259
143.557
142.200
136.729
131.903
128.248
128.080
127.156
127.034
126.475
125.891
77.318
77.001
76.684
45.699
32.272
29.770
23.187
22.821
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

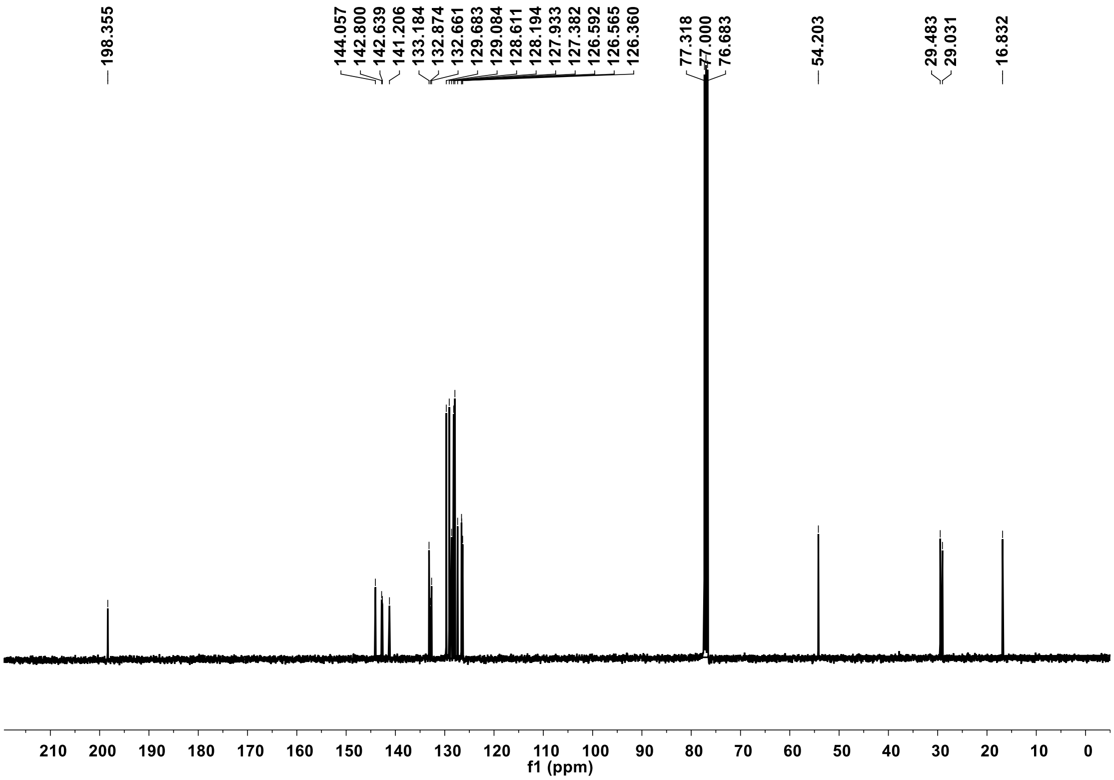

7.801
7.781
7.323
7.305
7.289
7.286
7.271
7.253
7.236
7.233
7.223
7.206
7.203
3.842
2.428
1.866
Me
O
Ph
Ph
Me
1.99
11.09
2.00
3.15
3.05
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

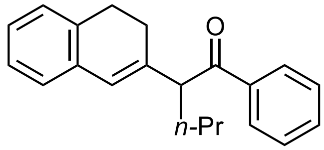
**3j**


198.246
143.754
142.631
142.482
140.825
134.412
129.683
129.258
129.133
129.099
128.849
128.265
128.162
127.913
126.660
126.431
77.317
77.000
76.682
45.890
21.581
20.741
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

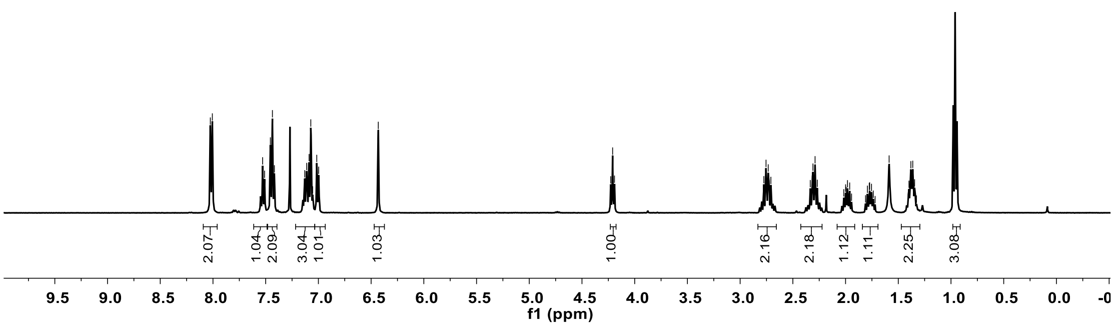

8.025
8.007
7.404
7.401
7.385
7.383
7.367
7.263
7.243
7.224
7.194
7.190
7.185
7.169
7.158
7.149
7.131
7.117
7.110
7.102
3.577
3.566
3.543
3.532
2.886
2.878
2.861
2.361
2.342
2.338
2.328
2.318
2.309
2.305
2.109
2.100
2.089
2.077
2.067
1.688
Me
O
Ph
Ph
1.00
1.05
3.14
9.05
1.05
2.18
1.12
1.13
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

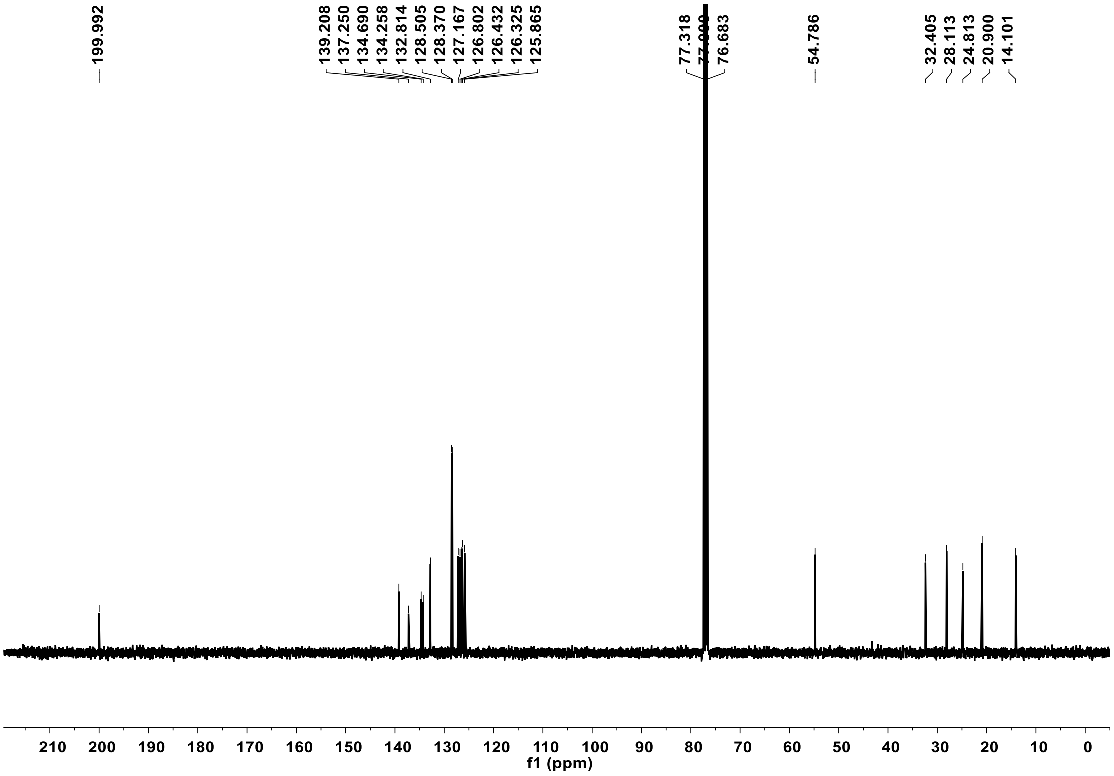
**3k**

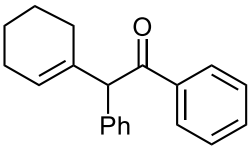

198.355
144.057
142.800
142.639
141.206
133.184
132.874
132.661
129.683
129.084
128.611
128.194
127.933
127.382
126.592
126.565
126.360
77.318
77.000
76.683
54.203
29.483
29.031
16.832
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
n-Pr

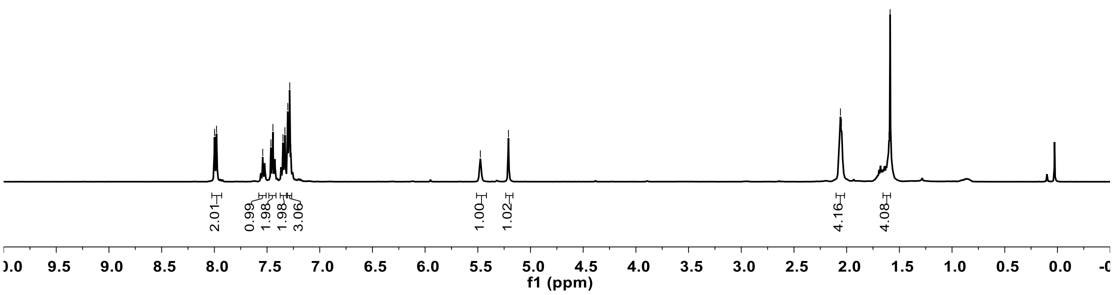
**3l**

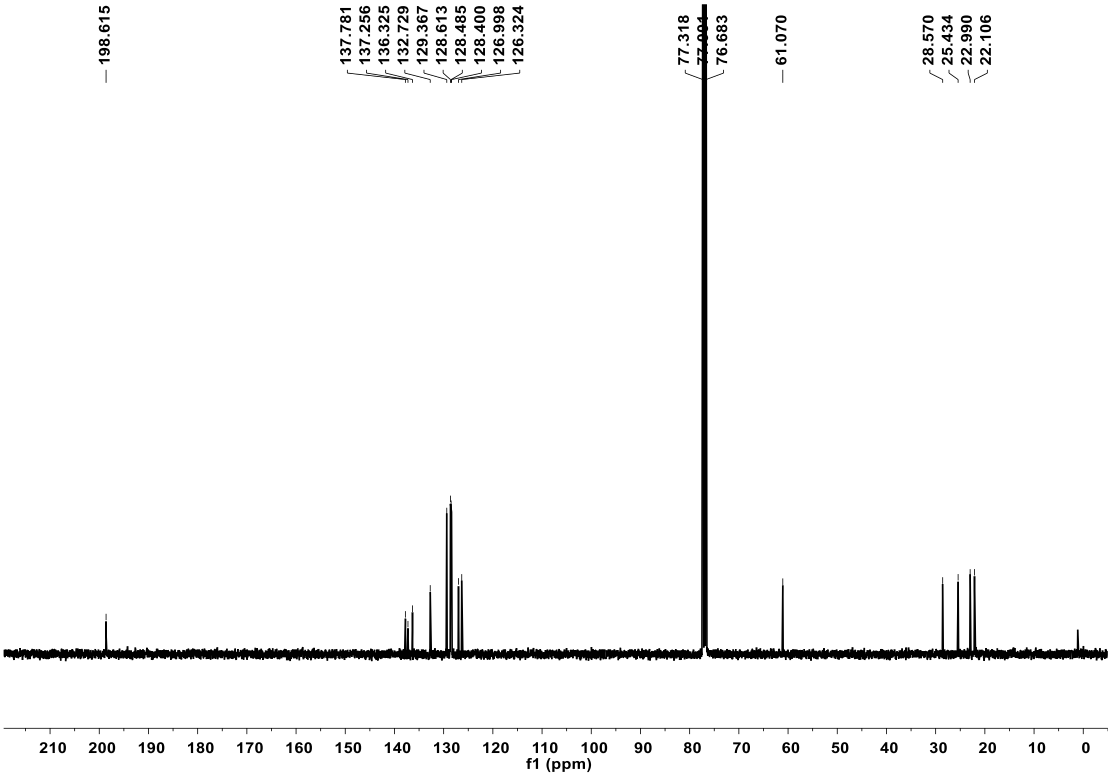

8.025
8.006
7.529
7.511
7.455
7.436
7.417
7.129
7.111
7.088
7.072
7.055
7.015
6.997
6.432
4.227
4.210
4.192
2.775
2.754
2.734
2.708
2.335
2.309
2.289
2.268
2.000
1.982
1.961
1.793
1.775
1.772
1.754
1.587
1.398
1.381
1.363
1.34
2.07
1.04
2.09
3.04
1.01
1.03
1.00
2.16
2.18
1.12
1.11
2.25
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

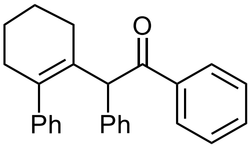

199.992
139.208
137.250
134.690
134.258
132.814
128.505
128.370
127.167
126.802
126.432
126.325
125.865
77.318
77.000
76.683
54.786
32.405
28.113
24.813
20.900
14.101
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Ph

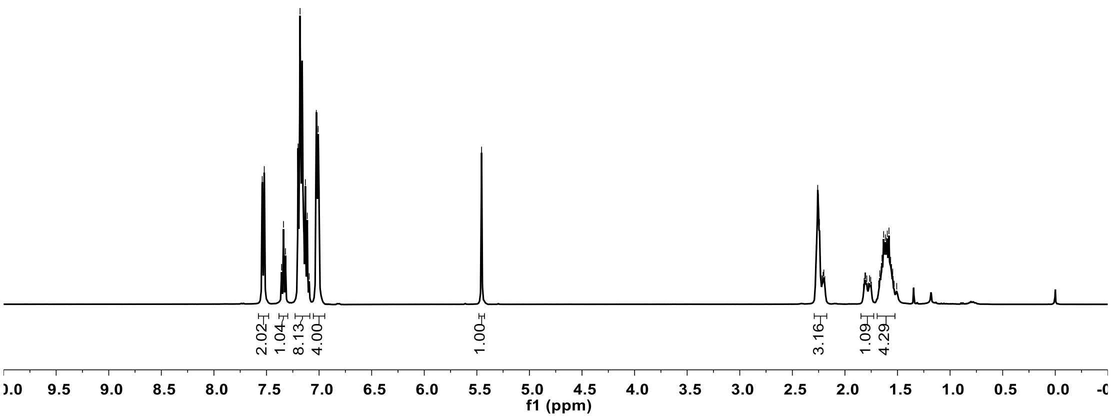
**3m**

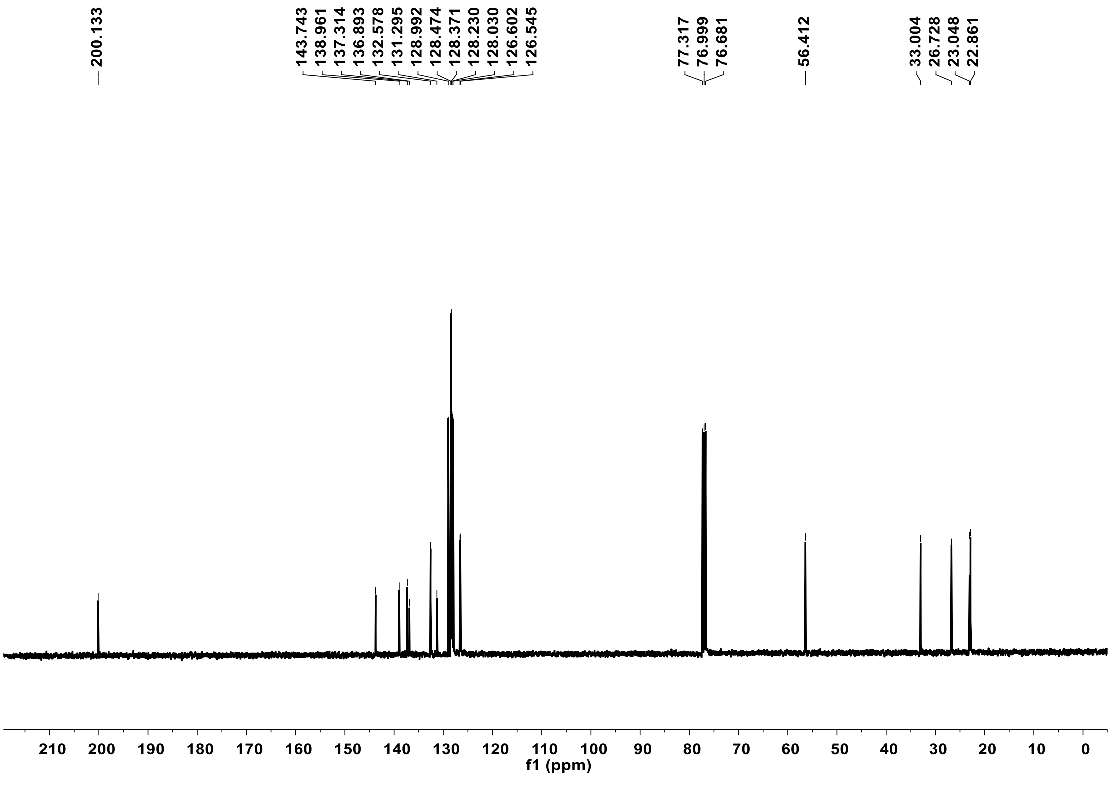

7.998
7.979
7.541
7.464
7.445
7.349
7.331
7.303
7.295
7.285
7.275
5.476
5.210
2.059
2.049
1.598
1.587
2.01
0.99
1.98
1.98
3.06
1.00
1.02
4.16
4.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

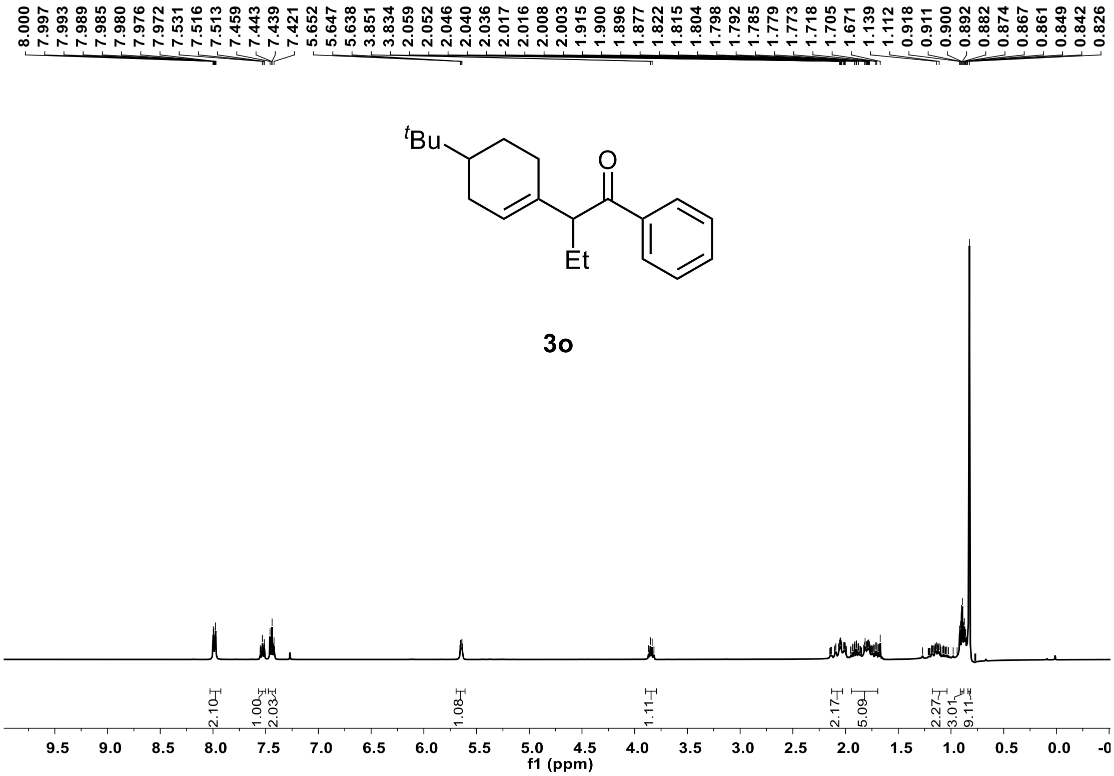

198.615
137.781
137.256
136.325
132.729
129.367
128.613
128.485
128.400
126.998
126.324
77.318
77.004
76.683
61.070
28.570
25.434
22.990
22.106
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



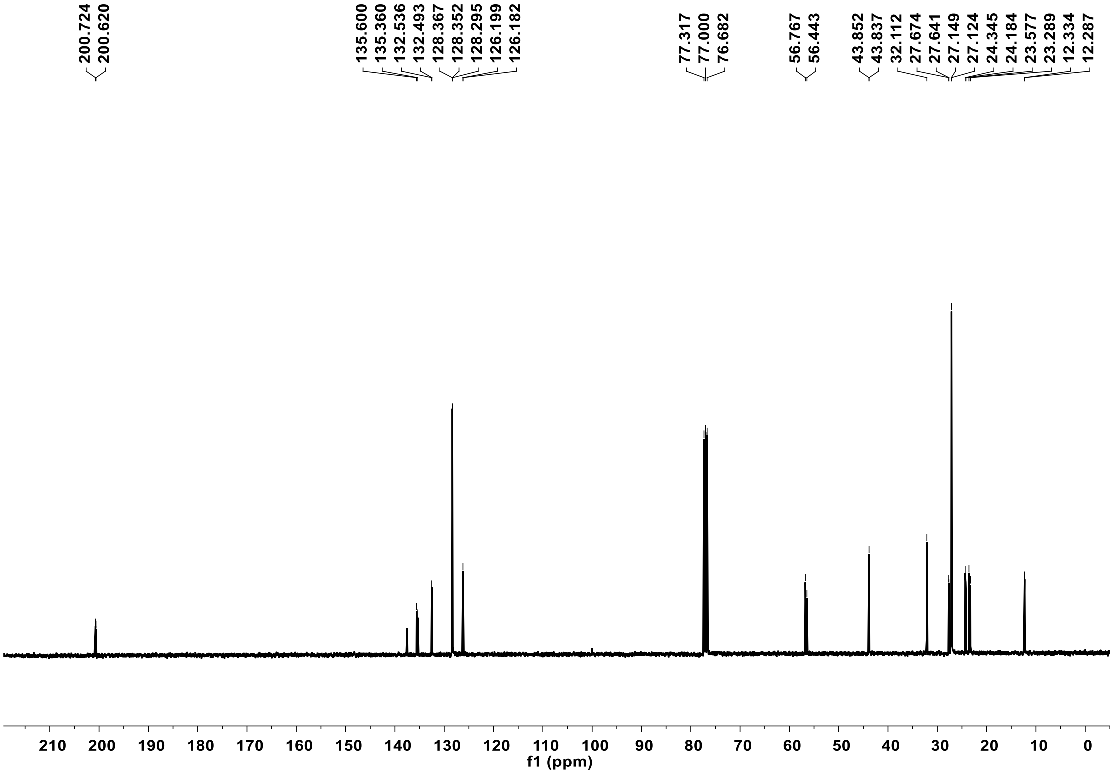
**3n**

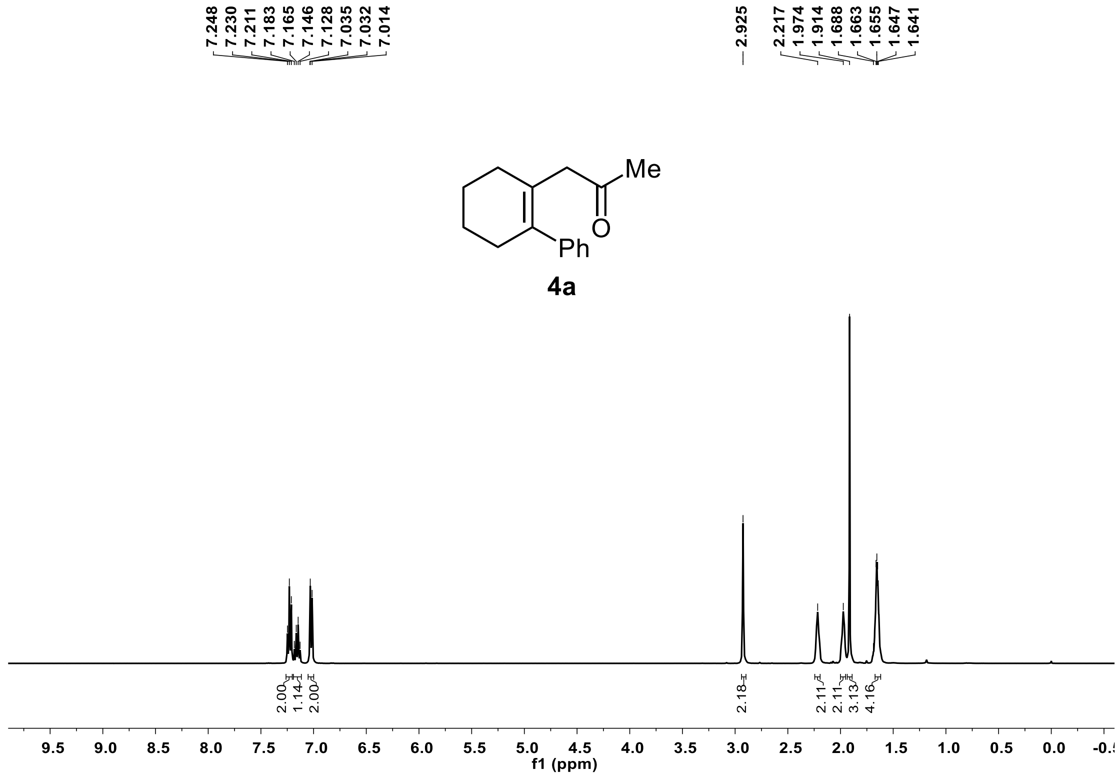

7.541
7.521
7.357
7.338
7.320
7.199
7.181
7.162
7.156
7.147
7.130
7.112
7.105
7.094
7.026
7.020
7.008
7.002
5.455
2.273
2.259
2.253
2.243
2.217
2.207
2.201
2.192
1.810
1.804
1.669
1.656
1.647
1.632
1.616
1.605
1.597
1.581
1.565
1.557
1.54
2.02
1.04
8.13
4.00
1.00
3.16
1.09
4.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

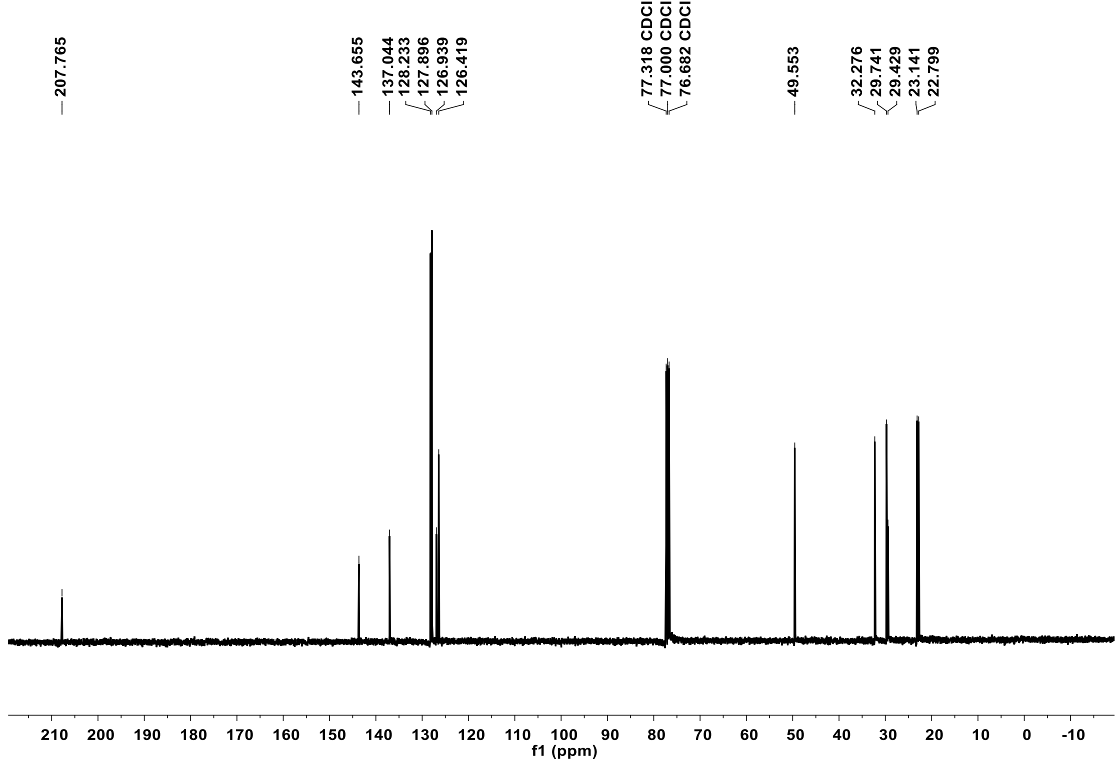

200.133
143.743
138.961
137.314
136.893
132.578
131.295
128.992
128.474
128.371
128.230
128.030
126.602
126.545
77.317
76.999
76.681
56.412
33.004
26.728
23.048
22.861
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

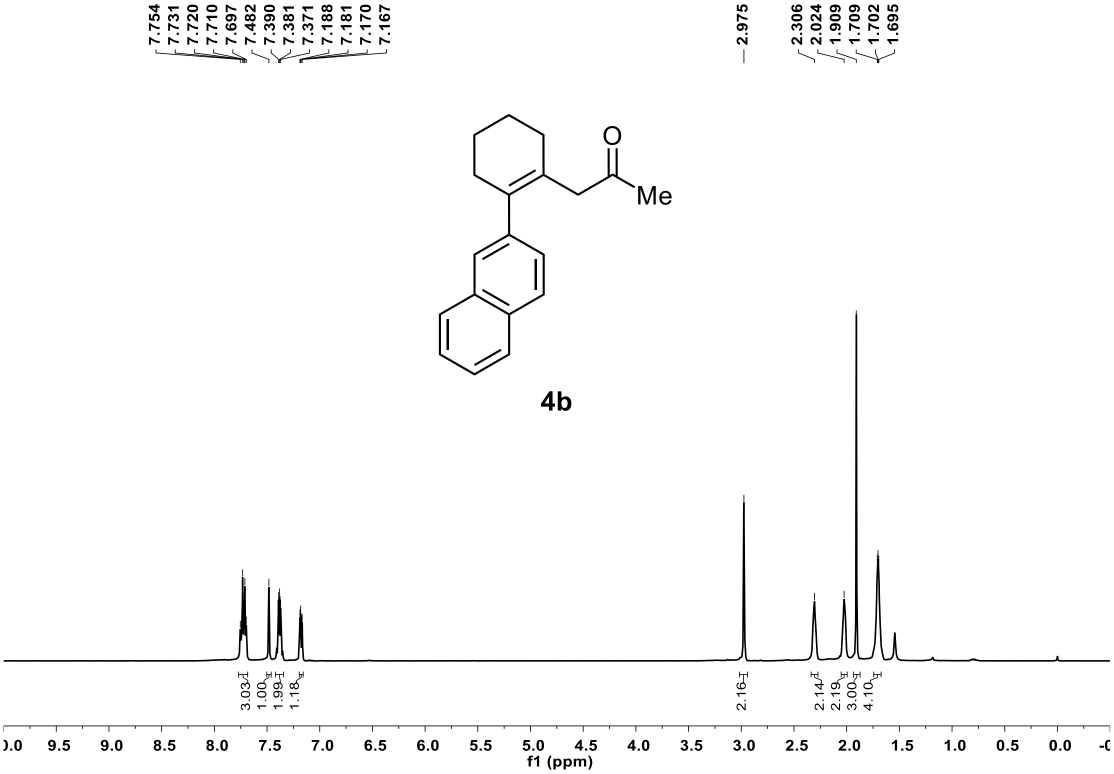

8.000
7.997
7.993
7.989
7.985
7.980
7.976
7.972
7.531
7.516
7.513
7.459
7.443
7.439
7.421
5.652
5.647
5.638
3.851
3.834
2.059
2.052
2.046
2.040
2.036
2.017
2.016
2.008
2.003
1.915
1.900
1.896
1.877
1.822
1.815
1.804
1.798
1.792
1.785
1.779
1.773
1.718
1.705
1.671
1.139
1.112
0.918
0.911
0.900
0.892
0.882
0.874
0.867
0.861
0.849
0.842
0.826
$^t$Bu
O
Et
2.10
1.00
2.03
1.08
1.11
2.17
5.09
2.27
3.01
9.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

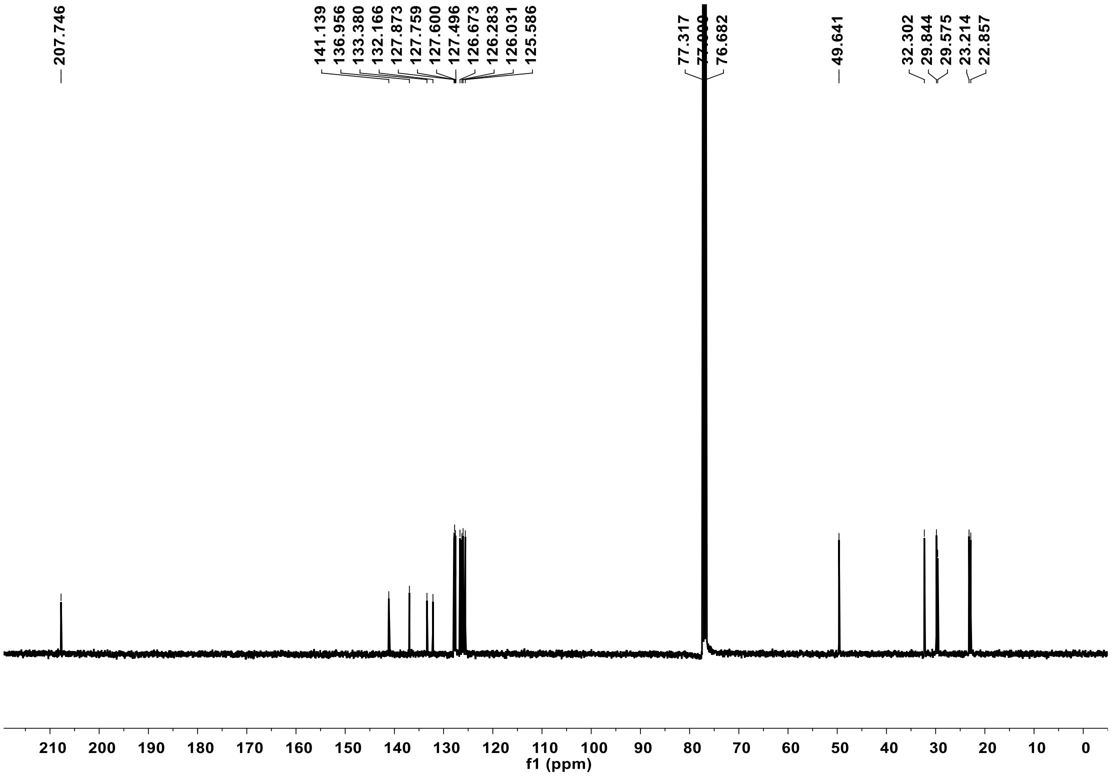
**3o**

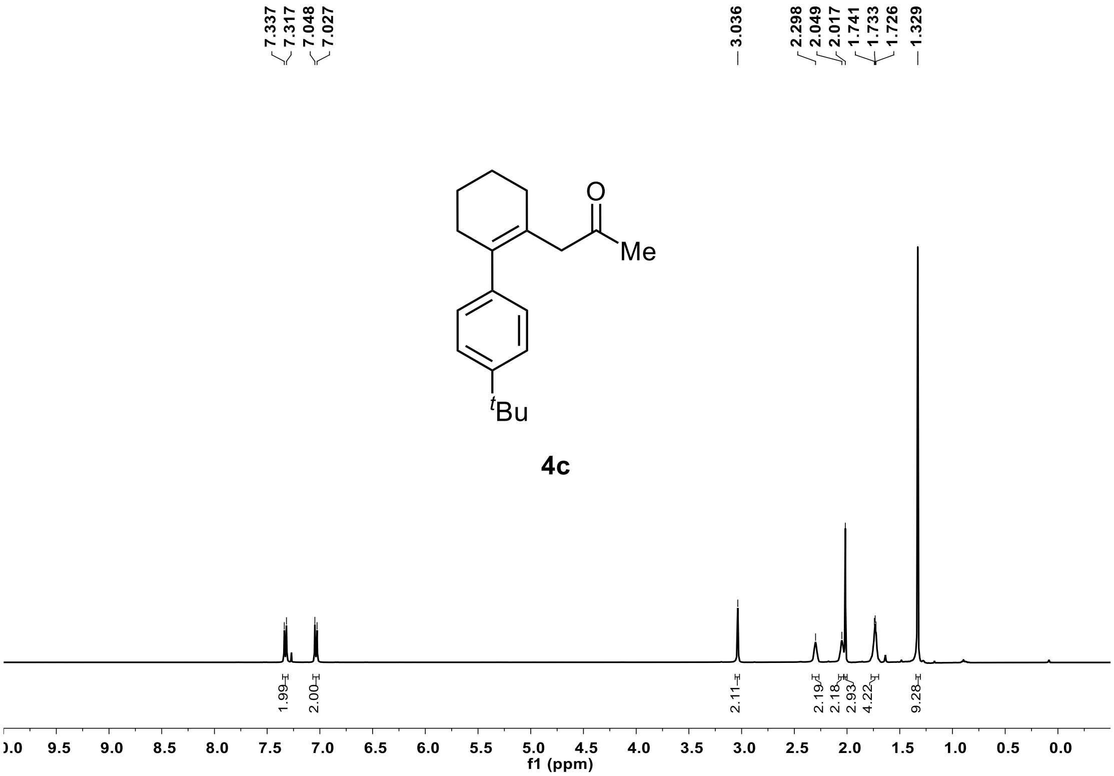

200.724
200.620
135.600
135.360
132.536
132.493
128.367
128.352
128.295
126.199
126.182
77.317
77.000
76.682
56.767
56.443
43.852
43.837
32.112
27.674
27.641
27.149
27.124
24.345
24.184
23.577
23.289
12.334
12.287
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

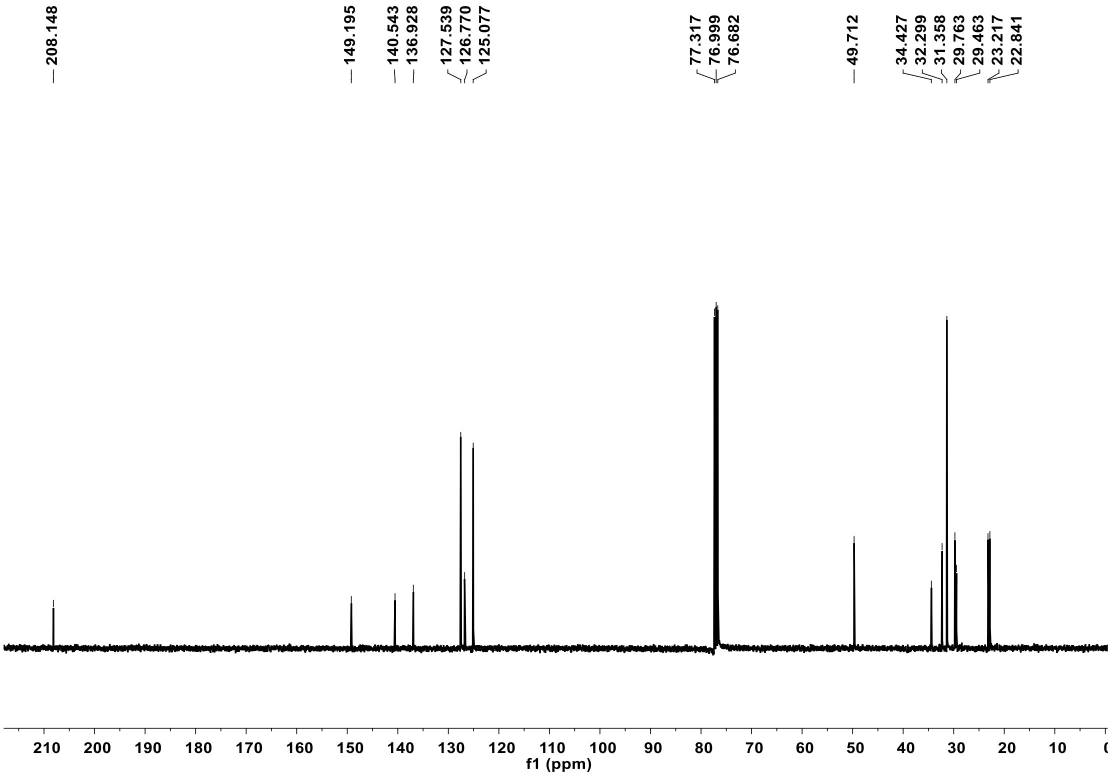

7.248
7.230
7.211
7.183
7.165
7.146
7.128
7.035
7.032
7.014
2.925
2.217
1.974
1.914
1.688
1.663
1.655
1.647
1.641
Me
O
Ph
4a
2.00
1.14
2.00
2.18
2.11
2.11
3.13
4.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

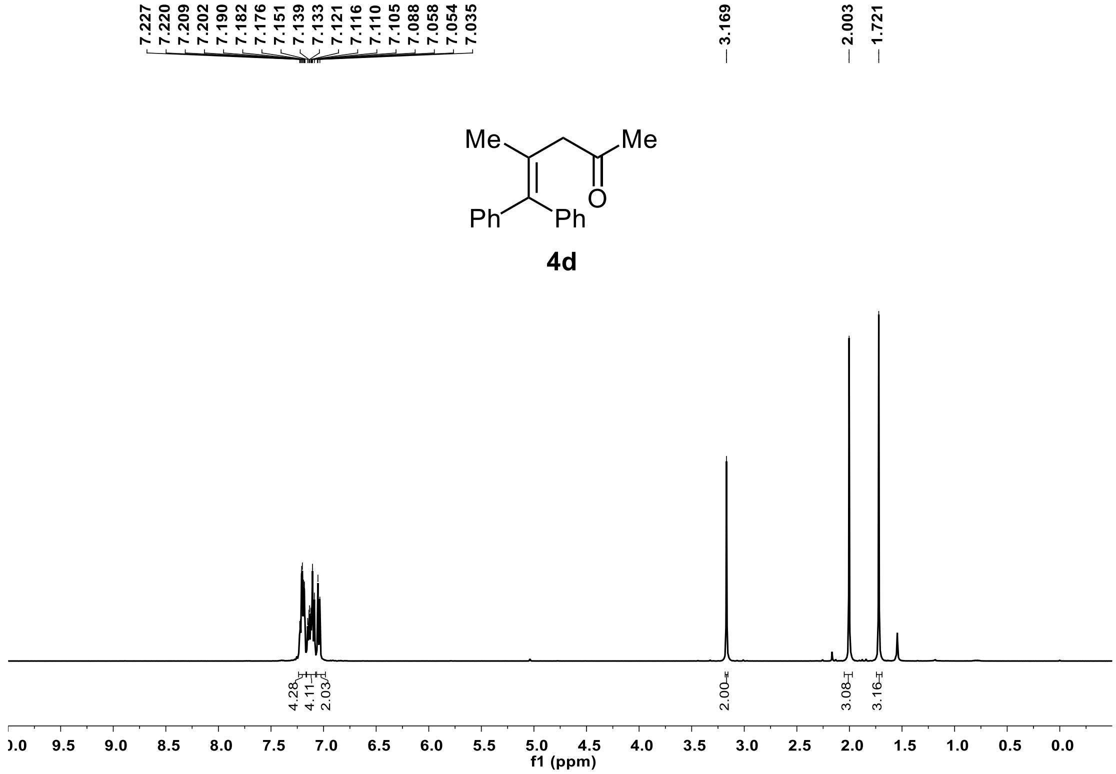

207.765
143.655
137.044
128.233
127.896
126.939
126.419
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
49.553
32.276
29.741
29.429
23.141
22.799
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

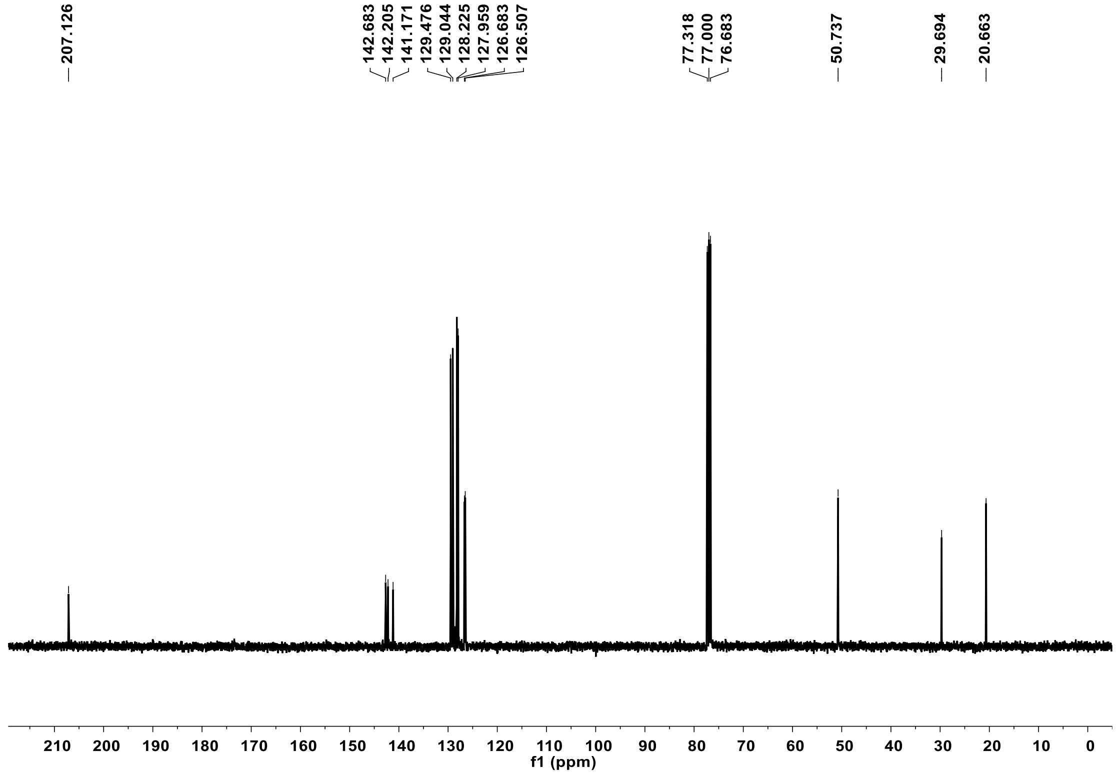

7.754
7.731
7.720
7.710
7.697
7.482
7.390
7.381
7.371
7.188
7.181
7.170
7.167
2.975
2.306
2.024
1.909
1.709
1.702
1.695
O
Me
4b
3.03
1.00
1.99
1.18
2.16
2.14
2.19
3.00
4.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

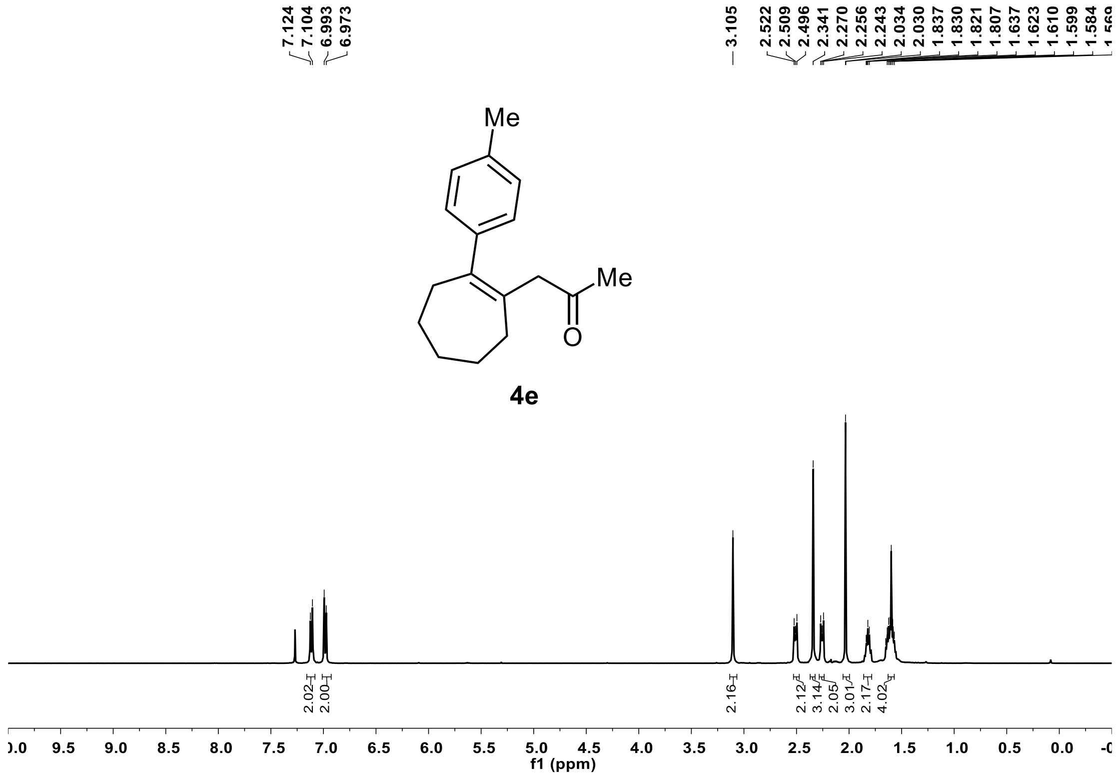

207.746
141.139
136.956
133.380
132.166
127.873
127.759
127.600
127.496
126.673
126.283
126.031
125.586
77.317
77.000
76.682
49.641
32.302
29.844
29.575
23.214
22.857
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

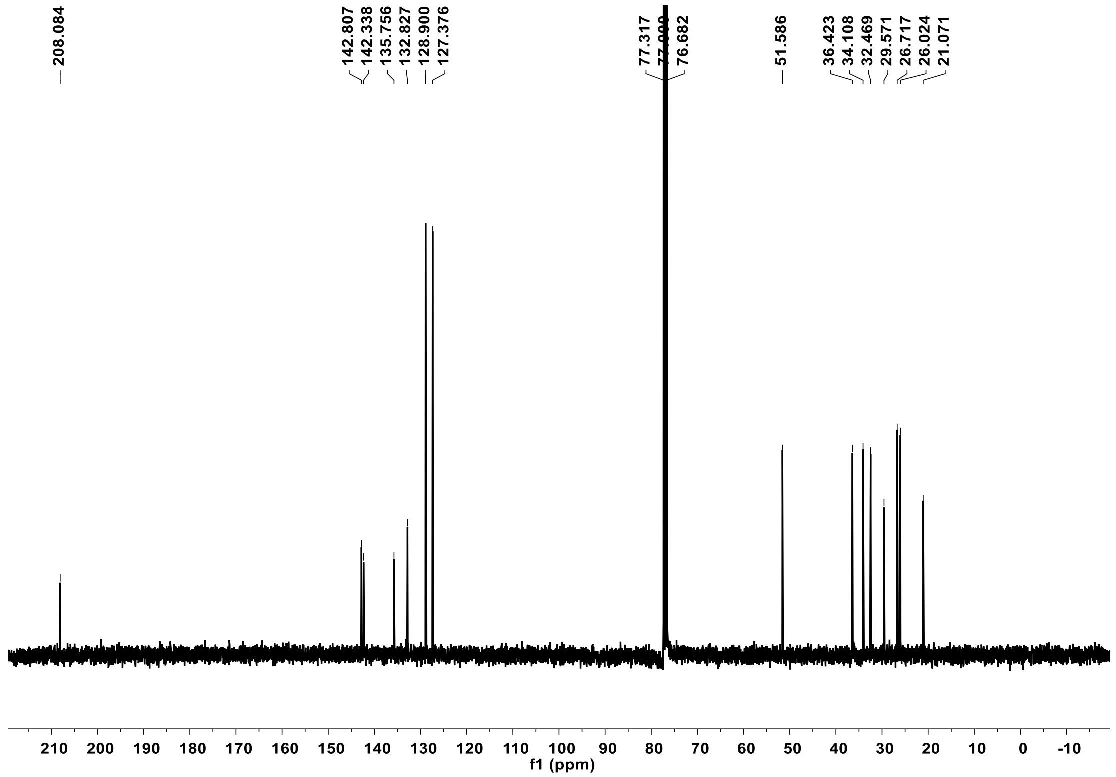

7.337
7.317
7.048
7.027
3.036
2.298
2.049
2.017
1.741
1.733
1.726
1.329
O
Me
tBu
4c
1.99
2.00
2.11
2.19
2.18
2.93
4.22
9.28
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

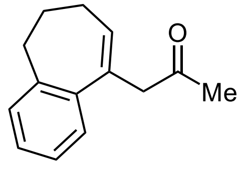

208.148
149.195
140.543
136.928
127.539
126.770
125.077
77.317
76.999
76.682
49.712
34.427
32.299
31.358
29.763
29.463
23.217
22.841
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.227
7.220
7.209
7.202
7.190
7.182
7.176
7.151
7.139
7.133
7.121
7.116
7.110
7.105
7.088
7.058
7.054
7.035
3.169
2.003
1.721
Me
Me
O
Ph
Ph
4d
4.28
4.11
2.03
2.00
3.08
3.16
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

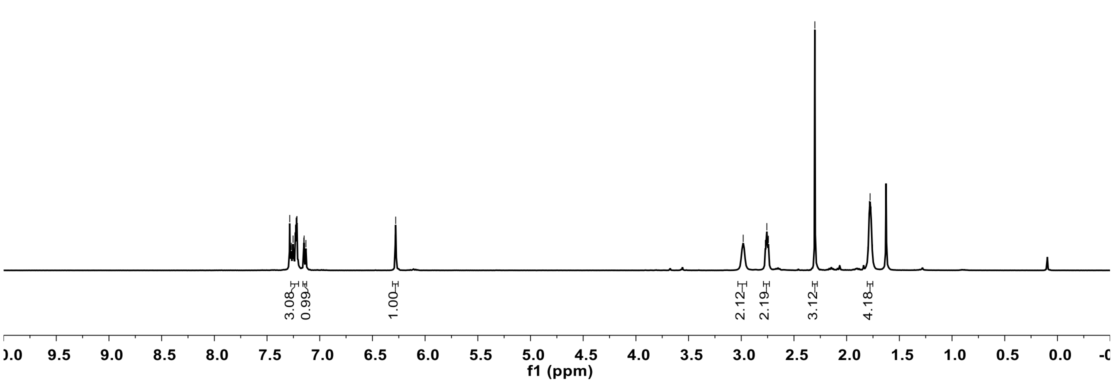

207.126
142.683
142.205
141.171
129.476
129.044
128.225
127.959
126.683
126.507
77.318
77.000
76.683
50.737
29.694
20.663
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

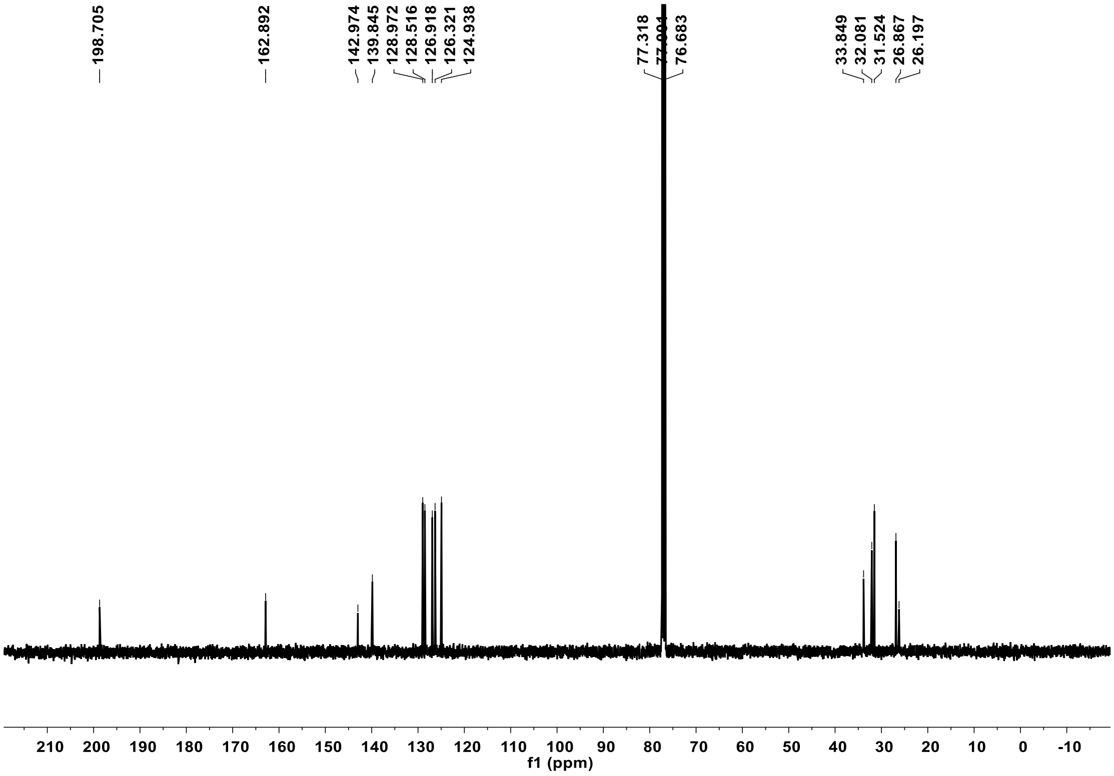

7.124
7.104
6.993
6.973
3.105
2.522
2.509
2.496
2.341
2.270
2.256
2.243
2.034
2.030
1.837
1.830
1.821
1.807
1.637
1.623
1.610
1.599
1.584
Me
Me
O
4e
2.02
2.00
2.16
2.12
3.14
2.05
3.01
2.17
4.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

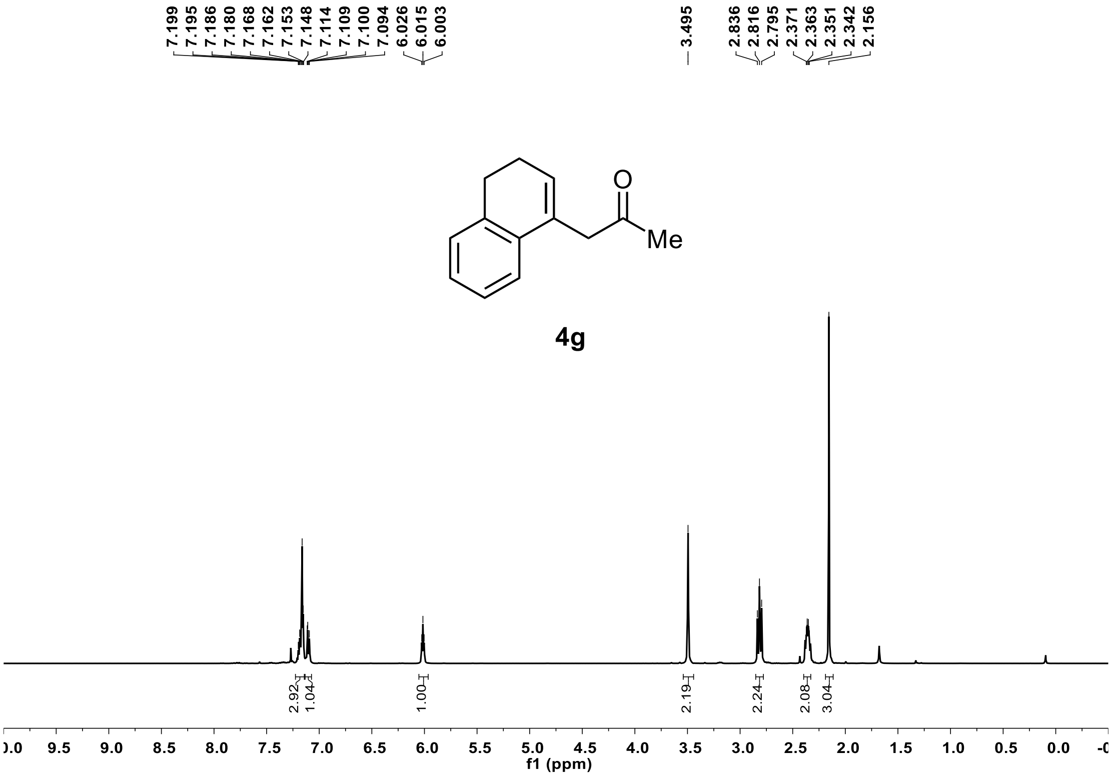

208.084
142.807
142.338
135.756
132.827
128.900
127.376
77.317
77.000
76.682
51.586
36.423
34.108
32.469
29.571
26.717
26.024
21.071
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

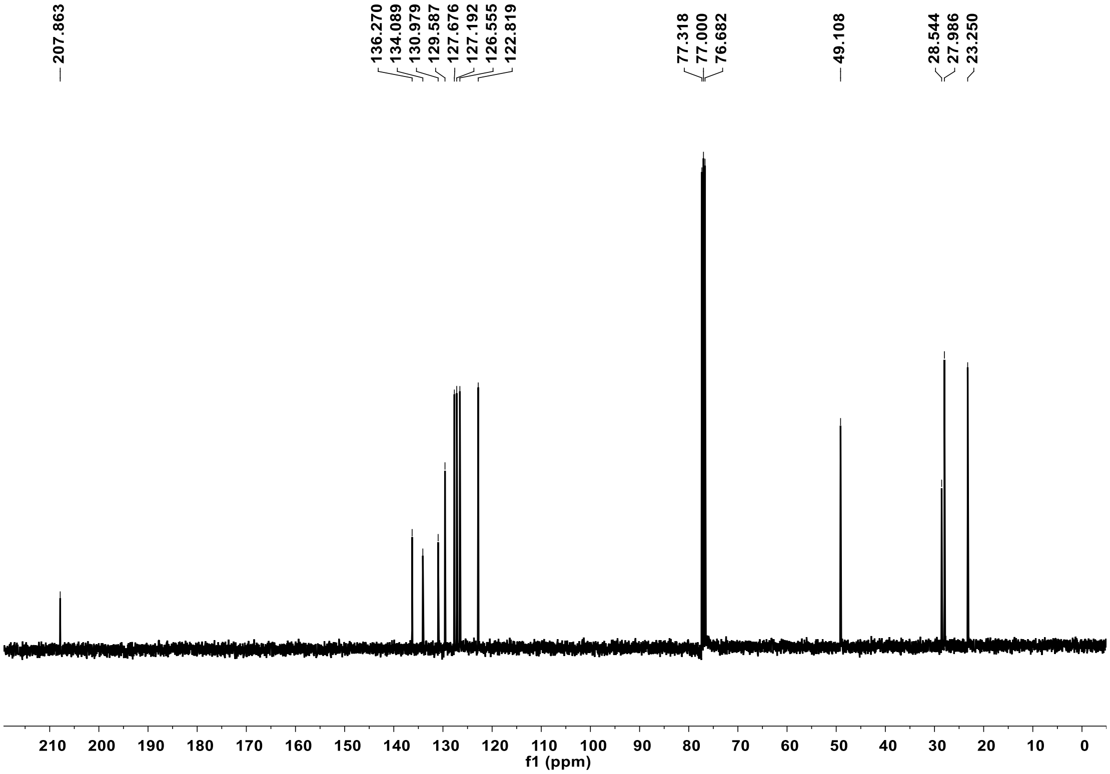

O
Me

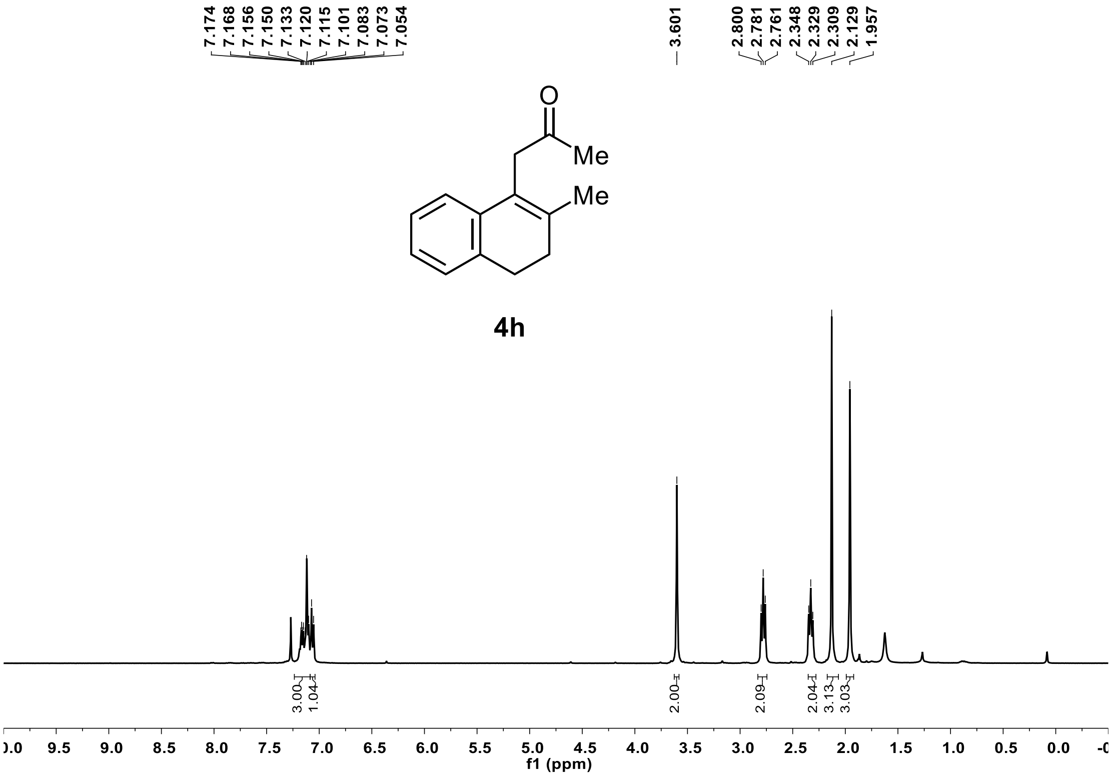
**4f**


7.285
7.277
7.270
7.261
7.253
7.248
7.234
7.230
7.224
7.218
7.216
7.151
7.148
7.131
6.283
6.279
2.982
2.772
2.758
2.743
2.302
1.800
1.792
1.785
1.777
1.768
1.755
3.08
0.99
1.00
2.12
2.19
3.12
4.18
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)

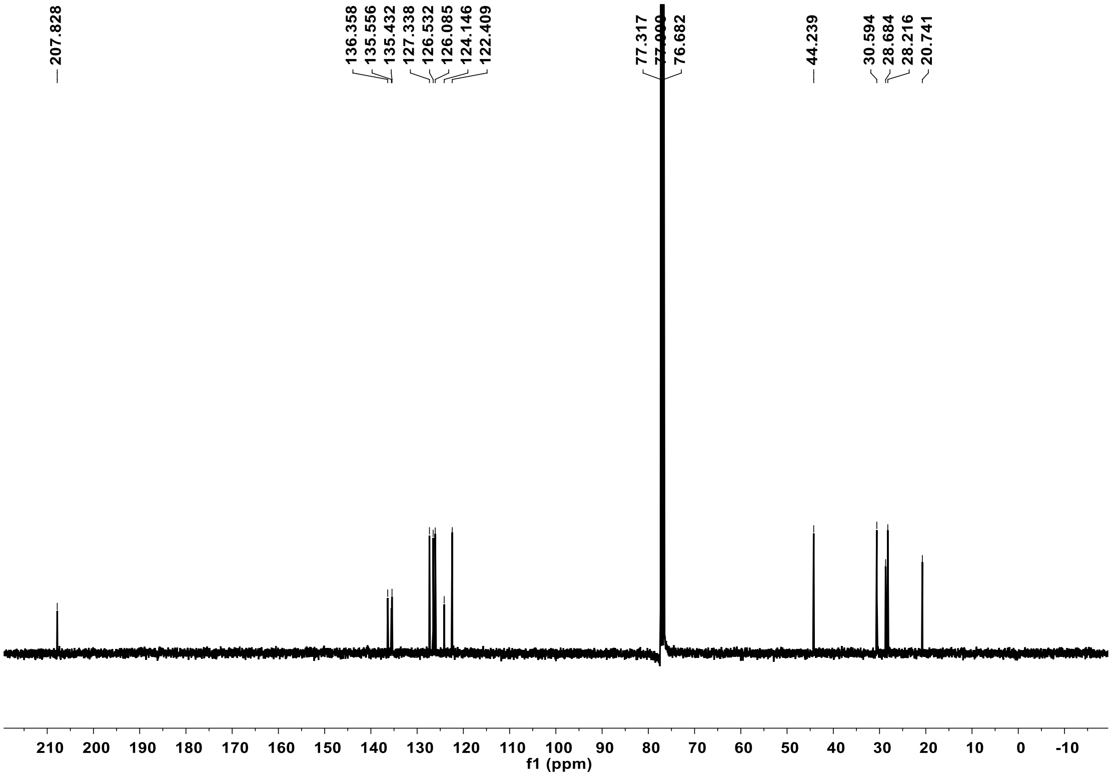

198.705
162.892
142.974
139.845
128.972
128.516
126.918
126.321
124.938
77.318
77.001
76.683
33.849
32.081
31.524
26.867
26.197
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

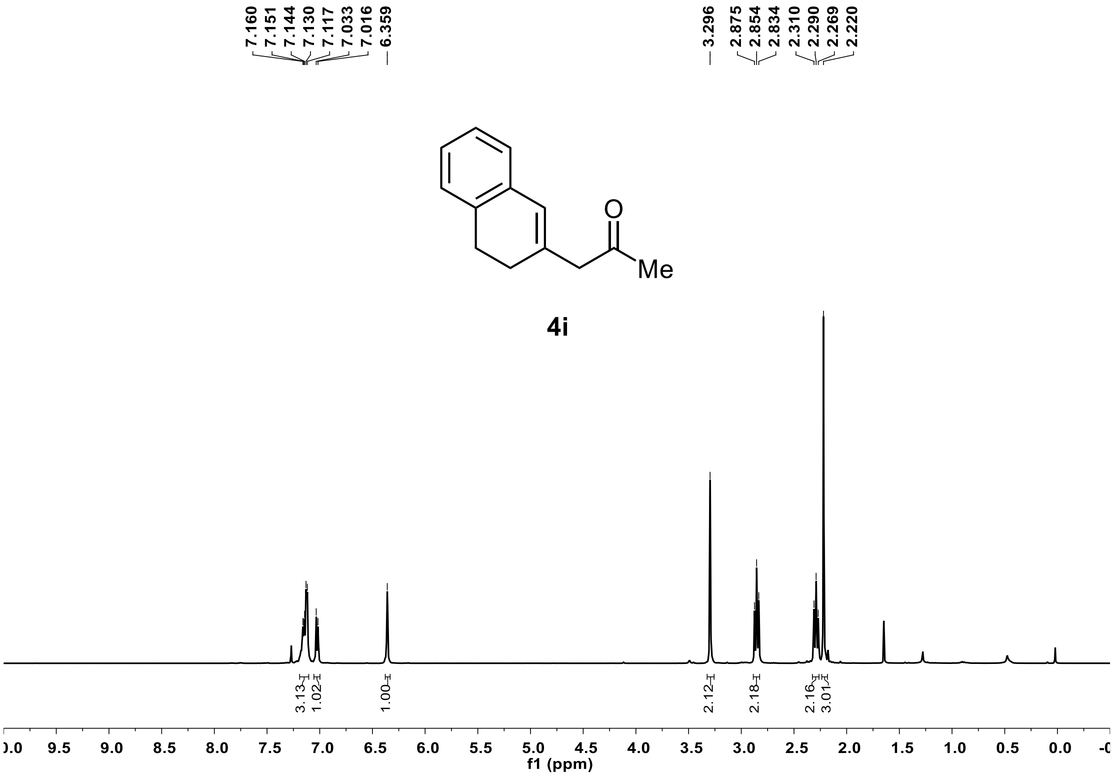

7.199
7.195
7.186
7.180
7.168
7.162
7.153
7.148
7.114
7.109
7.100
7.094
6.026
6.015
6.003
3.495
2.836
2.816
2.795
2.371
2.363
2.351
2.342
2.156
O
Me
4g
2.92
1.04
1.00
2.19
2.24
2.08
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.863
136.270
134.089
130.979
129.587
127.676
127.192
126.555
122.819
77.318
77.000
76.682
49.108
28.544
27.986
23.250
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

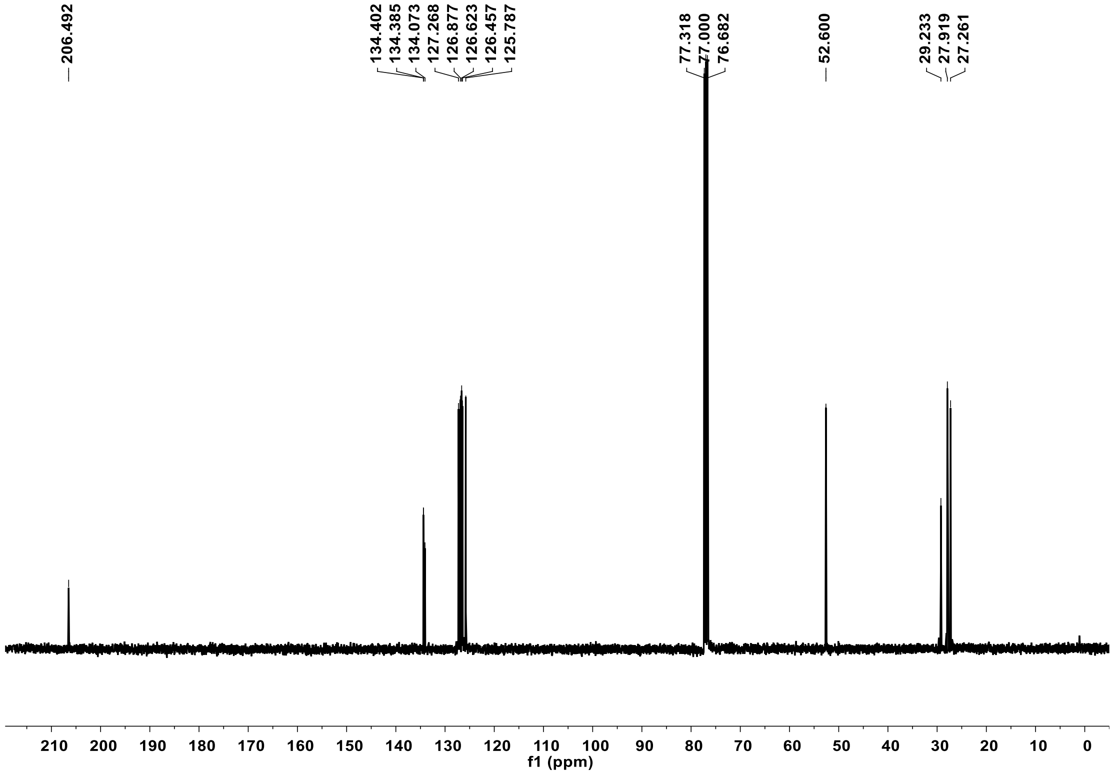

7.174
7.168
7.156
7.150
7.133
7.120
7.115
7.101
7.083
7.073
7.054
3.601
2.800
2.781
2.761
2.348
2.329
2.309
2.129
1.957
O
Me
Me
3.00
1.04
2.00
2.09
2.04
3.13
3.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

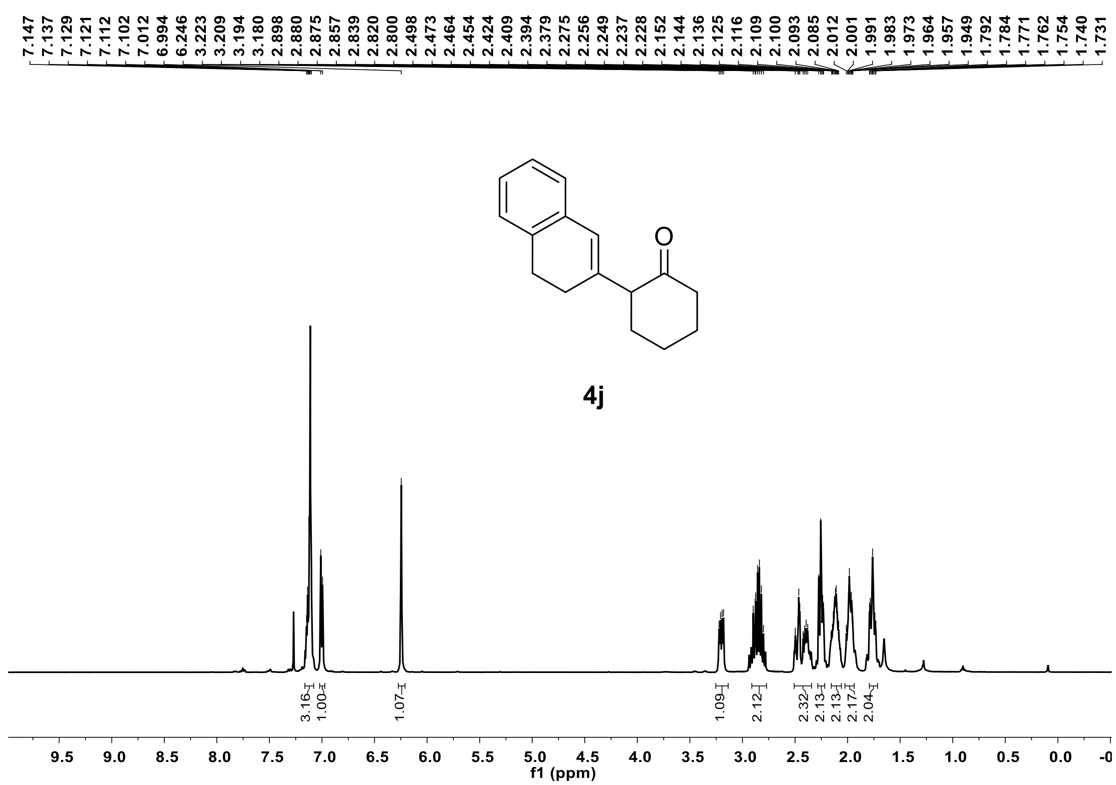
**4h**


207.828
136.358
135.556
135.432
127.338
126.532
126.085
124.146
122.409
77.317
77.000
76.682
44.239
30.594
28.684
28.216
20.741
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)

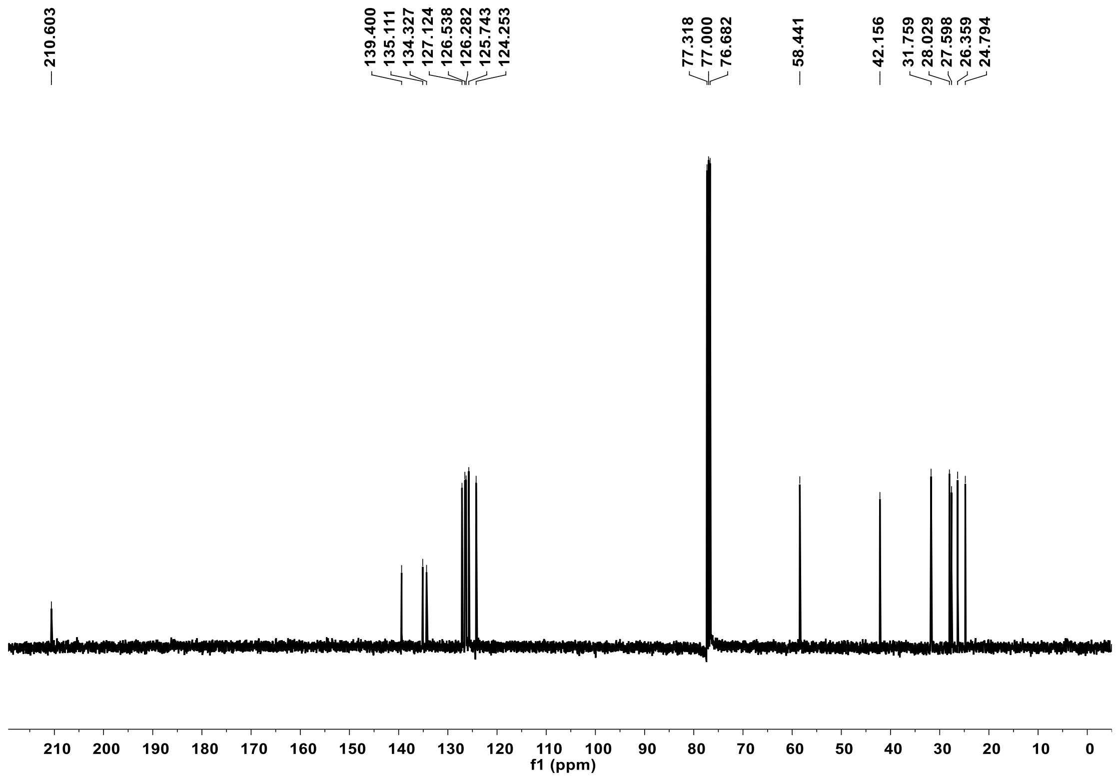

7.160
7.151
7.144
7.130
7.117
7.033
7.016
6.359
3.296
2.875
2.854
2.834
2.310
2.290
2.269
2.220
O
Me
3.13
1.02
1.00
2.12
2.18
2.16
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

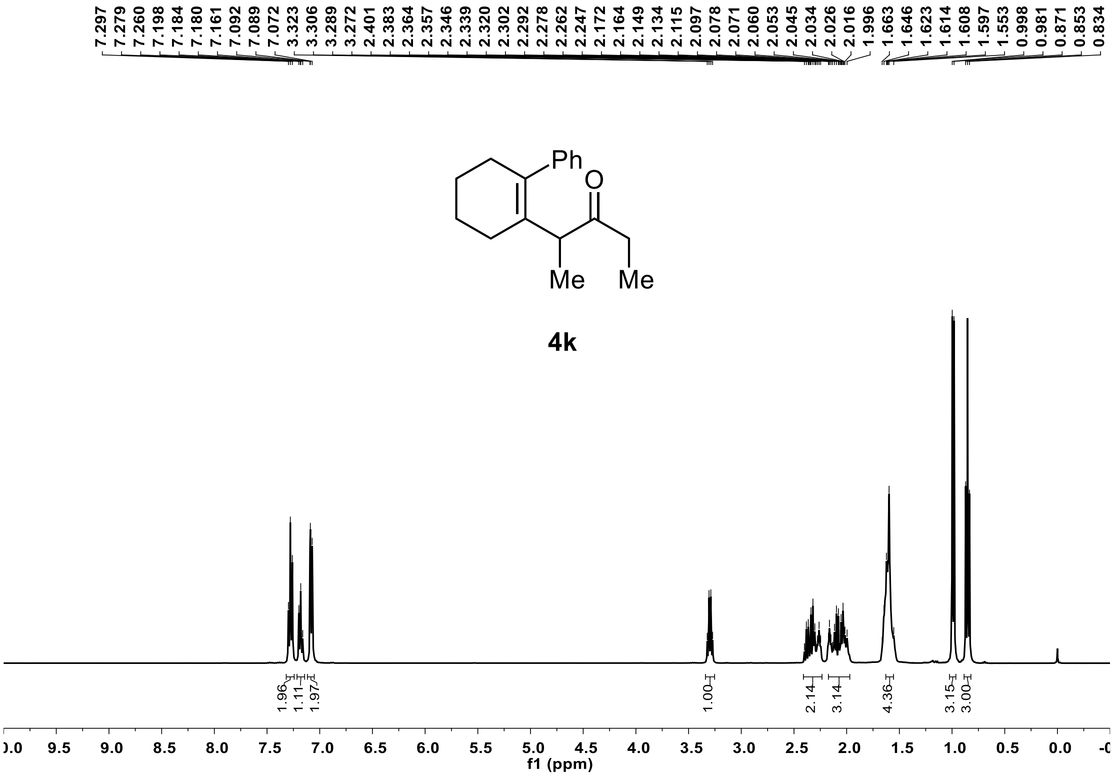
**4i**

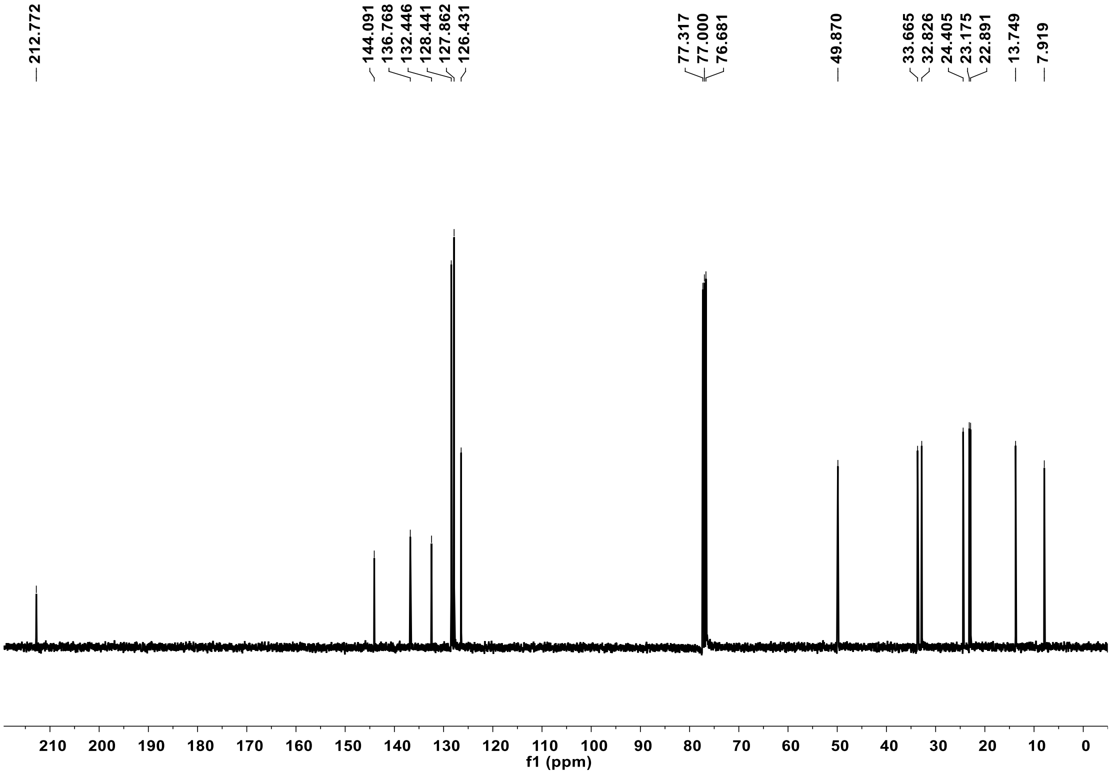

206.492
134.402
134.385
134.073
127.268
126.877
126.623
126.457
125.787
77.318
77.000
76.682
52.600
29.233
27.919
27.261
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.147
7.137
7.129
7.121
7.112
7.102
7.012
6.994
6.246
3.223
3.209
3.194
3.180
2.898
2.880
2.875
2.857
2.839
2.820
2.800
2.498
2.473
2.464
2.454
2.424
2.409
2.394
2.379
2.275
2.256
2.249
2.237
2.228
2.152
2.144
2.136
2.125
2.116
2.109
2.100
2.093
2.085
2.012
2.001
1.991
1.983
1.973
1.964
1.957
1.949
1.792
1.784
1.771
1.762
1.754
1.740
1.731
O
3.16
1.00
1.07
1.09
2.12
2.32
2.13
2.13
2.17
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

**4j**


210.603
139.400
135.111
134.327
127.124
126.538
126.282
125.743
124.253
77.318
77.000
76.682
58.441
42.156
31.759
28.029
27.598
26.359
24.794
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.297
7.279
7.260
7.198
7.184
7.180
7.161
7.092
7.089
7.072
3.323
3.306
3.289
3.272
2.401
2.383
2.364
2.357
2.346
2.339
2.320
2.302
2.292
2.278
2.262
2.247
2.172
2.164
2.149
2.134
2.115
2.097
2.078
2.071
2.060
2.053
2.045
2.034
2.026
2.016
1.996
1.663
1.646
1.623
1.614
1.608
1.597
1.553
0.998
0.981
0.871
0.853
0.834
Ph
O
Me
Me
4k
1.96
1.11
1.97
1.00
2.14
3.14
4.36
3.15
3.00
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


212.772
144.091
136.768
132.446
128.441
127.862
126.431
77.317
77.000
76.681
49.870
33.665
32.826
24.405
23.175
22.891
13.749
7.919
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)