# Supporting Information

## Domino Synthesis of 2,3-Dialkylidenetetrahydrofurans via Tandem Prins Cyclization/Skeletal Reorganization

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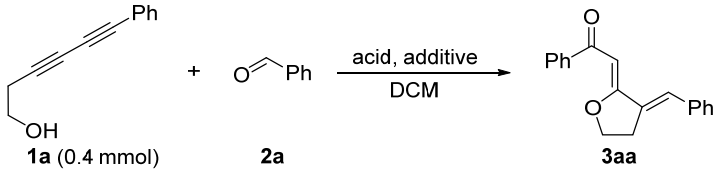
### *Evaluation of acids and additives for the formation of 3aa*

As shown in Table S-1, acids and additives were evaluated for the domino reaction of 3,5-diynol **1a** and benzaldehyde (**2a**) in dichloromethane (DCM). Initially, it turned out that the catalytic amounts of acids brought about the low conversion to the desired furans **3aa** at room tmparature (up to 15% yields, entries 1–3 and 5). Even under catalytic conditions, the reaction temperatures were rised in dichloroethane to give the complex mixture (entries 4 and 6). Also, iodine reagents such as "$IBF_4$"[1] and molecular iodine,[2] which worked well in the Prins cyclization and its related reaction, afforded the complex mixture (entries 7–9). On the other hand, when one equivalent of TMSOTf, HOTf and $HBF_4 \cdot OEt_2$ were used, the furans **3aa** were obtained in 17–25% yields at room temperature for 8 h (entries 10–12). Furthermore, the addition of methanol (1 equiv) with $HBF_4 \cdot OEt_2$ (1 equiv) showed better result, in which the yield of **3aa** was improved up to 37% (entry 15). Unfortunately, the reaction with an increased amount of methanol (2 or 5 equiv) was sluggish (entry 16 or 17). In contrast, increasing the amounts of both methanol and $HBF_4 \cdot OEt_2$ by 1 equiv led to good conversion to **3aa** (entries 18 and 19), and finally, the use of 3 equiv each afforded **3aa** in high yield (80%, entry 19). Notably, compared with other alcohols (entries 21–23) and $H_2O$ (entry 24), methanol was found out to be the best additive (entry 19). Furthermore, the present reaction could be successfully scaled up (**1a**: 5 mmol, entry 25).

**Table S-1**. Evaluation of acids and additives for the formation of **3aa**




**1a** (0.4 mmol) **2a** **3aa**

| entry | **2a** (equiv) | Acid (equiv) | Addtive (equiv) | Temp. / (h) | **3aa** (%)[a] | **1a** (%)[a] |
|---|---|---|---|---|---|---|
| 1 | 1.2 | $BF_3 \cdot OEt_2$ (0.2) | | rt / 24 | 2 | 87 |
| 2 | 1.2 | TfOH (0.2) | | rt / 24 | 6 | 56 |
| 3 | 1.2 | $HBF_4 \cdot OEt_2$ (0.2) | | rt / 24 | 4 | 93 |
| 4[b] | 1.2 | $HBF_4 \cdot OEt_2$ (0.2) | | 90 ºC / 24 | 0 | 27 |
| 5 | 2 | TMSOTf (0.2) | | rt / 24 | 15 | 48 |
| 6[b] | 2 | $Yb(OTf)_3$ (0.2) | | 60 ºC / 24 | 0 | 69 |
| 7 | 2 | $IPy_2BF_4$ (0.2) | $HBF_4 \cdot OEt_2$ (0.4) | rt / 24 | 0 | 75 |
| 8 | 2 | $I_2$ (0.2) | $AgBF_4$ (0.2) | rt / 24 | 0 | 64 |
| 9 | 2 | $I_2$ (1) | | rt / 24 | 0 | 29 |
| 10 | 2 | TMSOTf (1) | | rt / 8 | 17 | 6 |
| 11 | 2 | HOTf (1) | | rt / 8 | 21 | 6 |
| 12 | 2 | $HBF_4 \cdot OEt_2$ (1) | | rt / 8 | 25 | 27 |
| 13 | 5 | $HBF_4 \cdot OEt_2$ (1) | | rt / 24 | 25 | 12 |
| 14 | 10 | $HBF_4 \cdot OEt_2$ (1) | | rt / 24 | 21 | 0 |
| 15 | 2 | $HBF_4 \cdot OEt_2$ (1) | MeOH (1) | rt / 8 | 37 | 46 |
| 16 | 2 | $HBF_4 \cdot OEt_2$ (1) | MeOH (2) | rt / 8 | 21 | 79 |
| 17 | 2 | $HBF_4 \cdot OEt_2$ (1) | MeOH (5) | rt / 8 | 0 | 100 |
| 18 | 2 | $HBF_4 \cdot OEt_2$ (2) | MeOH (2) | rt / 8 | 66 | 25 |
| 19 | 2 | $HBF_4 \cdot OEt_2$ (3) | MeOH (3) | rt / 8 | 80[c] | 0 |
| 20 | 2 | TMSOTf (3) | MeOH (3) | rt / 8 | 10 | 55 |
| 21 | 2 | $HBF_4 \cdot OEt_2$ (3) | EtOH (3) | rt / 8 | 62[c] | 0 |
| 22 | 2 | $HBF_4 \cdot OEt_2$ (3) | *i*-PrOH (3) | rt / 8 | 57[c] | 0 |
| 23 | 2 | $HBF_4 \cdot OEt_2$ (3) | *t*-BuOH (3) | rt / 8 | trace | trace |
| 24 | 2 | $HBF_4 \cdot OEt_2$ (3) | $H_2O$ (3) | rt / 8 | 25 | 3 |
| 25[d] | 2 | $HBF_4 \cdot OEt_2$ (3) | MeOH (3) | rt / 8 | 81[c] | 0 |

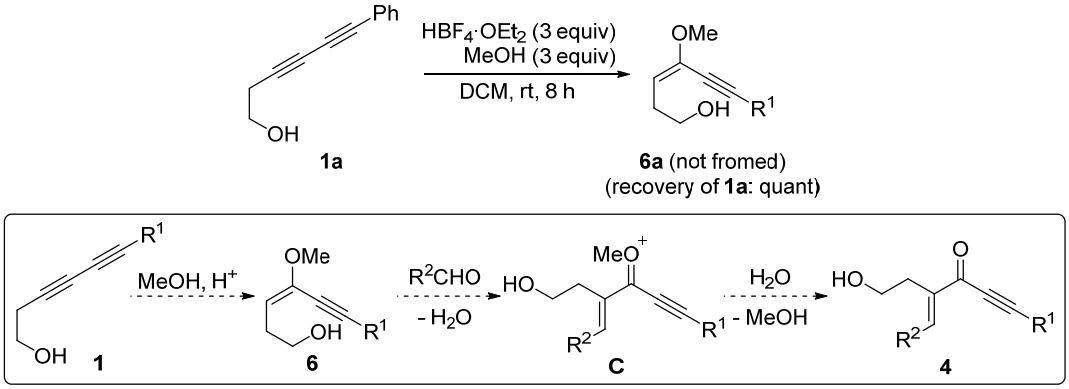
[a] Values were determined by $^1H$ NMR. [b] Solvent: 1,2-dichloroethane. [c] Isolated yield.
[d] As a example of scale-up reaction, 5 mmol of **1a** was used.

[1] K. Murai, K. Tateishi, A. Saito, *Org. Biomol. Chem.* **2016**, *14*, 10352–10356.
[2] J. S. Yadav, B. V. Subba Reddy, G. G. K. S. Narayana Kumar, T. Swamy, *Tetrahedron Lett.* **2007**, *48*, 2205–2208.

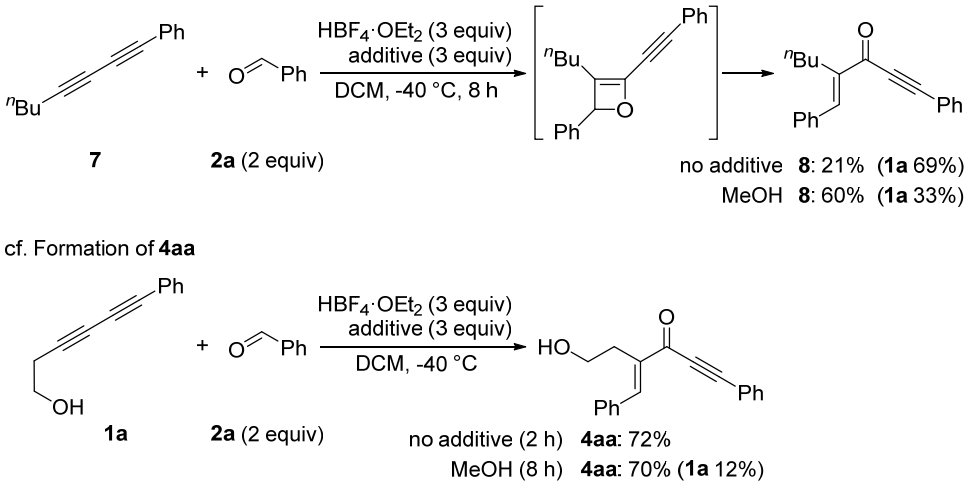
## *Other control experiments*

As the alternative formation path of 4-en-1-yn-3-ones **4**, the Aldol-type reaction of vinyl ethers **6** derived from 3,5-diynols **1** (Scheme S-1) and methanol or alkyn-carbonyl metathesis reaction[3] such as the conversion of diyne **7** with aldehyde **2a** to 4-en-1-yn-3-one **8** (Scheme S-2) would be presumed. However, since treatment of **1a** with methanol in the presence of $HBF_4{\cdot}OEt_2$ led to no conversion of **1a** under the optimum conditions, we believe that vinyl ether **6** is not involved as an intermediate. On the other hand, regardless of the presence or absence of methanol, diyne **7** having no hydroxy group was exposed with **2a** in the presence of $HBF_4{\cdot}OEt_2$ to give **8** (Scheme S-2). However, compared to **4aa**, the products **8** were obtained lower yields. Considering that hydroxyethyl group-binding alkyne site exclusively underwent the reaction with aldehydes irrespective of the type of $R^1$ group ($R^1$ = aryl or *n*-butyl, Scheme 3 in the text), the hydroxy groups in the substrates are essential for the formation of 4-en-1-yn-3-ones under the optimum conditions. Thus, 4-en-1-yn-3-ones **4** would be obtained mainly through Prins-type cyclization.

**Scheme S-1**. No conversion of **1a** to **6a** under the optimum conditions




**Scheme S-2**. No conversion of **7** and **2a** to **8** under the optimum conditions

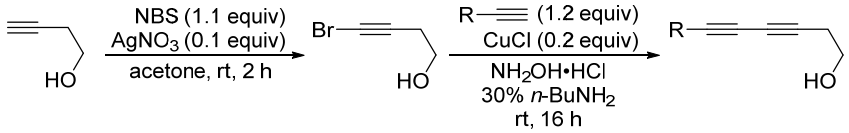



## *General information*

All reactions were carried out under an argon atmosphere. 3,5-Diynols **1a**,[4] **1b**,[4] **1f**,[5] and **1g**[6] were prepared by the method reported in the literatures. Tetrafluoroboric acid diethyl ether complex and aldehydes **2a-l** are commercially available. Dichloromethane and methanol were purchased as the "anhydrous" and used without further purification. Column chromatography was performed on silica gel 60N (63-200 μm, neutral, Kanto Kagaku Co., Ltd.). Preparative thin layer chromatography (PTLC) was carried out using Wakogel B-5F. $^1$H and $^{13}$C NMR spectra were measured at 500 (or 300) and 125 (or 75) MHz in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for $^1$H NMR and $CDCl_3$ (77.0 ppm) for $^{13}$C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). Mass spectra and HRMS were recorded on double-focusing magnetic sector by FAB methods.

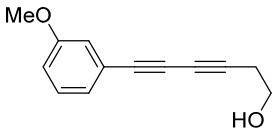
[3] Review: A. Saito, K. Tateishi, *Heterocycles* **2016**, *92*, 607–630.
[4] H. -F. Jiang, A. -Z. Wang, *Synthesis* **2007**, *11*, 1649–1654.
[5] S. Wang, Y. Li, H. Liu, J. Li, T. Li, Y. Wu, S. Okada, H. Nakanishi, *Org. Biomol. Chem.* **2015**, *13*, 5467–5474.
[6] S. H. Kang, K. S. Jang, P. Theato, R. Zentel, J. Y. Chang, *Macromolecules* **2007**, *40*, 8349–8354.

### *Preparation and Characterization of 3,5-Diynols 1c-e*

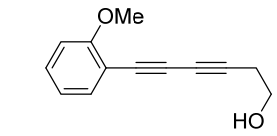



In a light-shielded flask, a solution of 3-butyn-1-ol (0.91 mL, 12 mmol), *N*-bromosuccinimide (2.35 g, 13.2 mmol) and $AgNO_3$ (0.20 g, 1.2 mmol) in acetone (40 mL) was stirred at room temperature for 2 h. After the solvent is distilled off under reduced pressure, the residue was extracted with $Et_2O$. The extraction solvent was concentrated in vacuo to give 4-bromo-3-butyn-1-ol (1.76 g, 98%).[7]

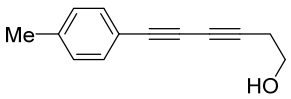
CuCl (0.20 mg, 2.0 mmol) was added to a 30% n-$BuNH_2$ (20 mL) aqueous solution at room temperature. And then, until the resulting blue solution became colorless, hydroxylamine hydrochloride were added. After the solution was cooled to 0 ºC, 3-ethynylanisole (1.32 g, 10 mmol), 2-ethynylanisole[8] (1.32 g, 10 mmol) or 4-ethynyltoluene (1.16 g, 10 mmol) was added, thereby forming in a yellow acetylide suspension. Subsequently, 4-bromo-3-butyn-1-ol (1.76 g, 11.8 mmol) was added at same temperature. After being stirred at room temperature for 16 h, the reaction mixture was extracted with $Et_2O$. The organic layer was washed with sat. $NH_4Cl$, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel column chromatography (hexane:AcOEt = 3:1) to give **1c**, **1d** or **1e**.




**6-(3-Methoxyphenyl)hexa-3,5-diyn-1-ol (1c):** 0.87 g (43%). Brown oil. IR (neat) ν $cm^{-1}$; 3370, 1228, 1042. $^1$H NMR (300 MHz) δ ppm; 1.84 (br.s, 1H), 2.64 (t, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 3.80 (t, *J* = 6.3 Hz, 2H), 6.91 (ddd, *J* = 8.1, 2.7, 1.2 Hz, 1H), 7.00 (dd, *J* = 2.7, 1.2 Hz, 1H), 7.08 (dt,, *J* = 8.1, 1.2 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 1H). $^{13}$C NMR (75 MHz) δ ppm; 23.9, 55.2, 60.8, 66.8, 73.7, 75.3, 81.0, 115.9, 117.3, 122.8, 125.2, 129.6, 159.4. HRMS(FAB): *m/z* calcd. for $C_{13}H_{13}O_2$ [M + H] 201.0916; found 201.0903.

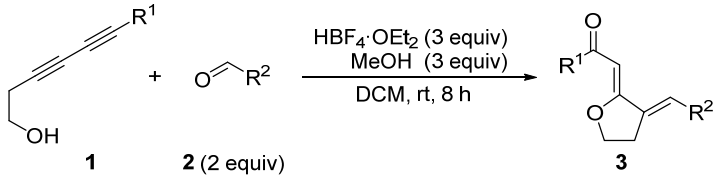



**6-(2-Methoxyphenyl)hexa-3,5-diyn-1-ol (1d):** 1.52 g (76%). Brown oil. IR (neat) ν $cm^{-1}$; 3370, 1245, 1162, 1044. $^1$H NMR (300 MHz) δ ppm; 1.87 (br.s, 1H), 2.64 (t, *J* = 6.0 Hz, 2H), 3.79 (t, *J* = 6.0Hz, 2H), 3.87 (s, 3H), 6.82-6.98 (m, 2H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (dd, *J* = 7.5, 1.5 Hz, 1H). $^{13}$C NMR (75 MHz) δ ppm; 24.0, 55.7, 60.7, 67.1, 71.8, 77.6, 81.5, 110.6, 110.9, 120.5, 130.6, 134.5, 161.6. HRMS(FAB): *m/z* calcd. for $C_{13}H_{13}O_2$ [M + H] 201.0916; found 201.0924.




**6-(4-Methylphenyl)hexa-3,5-diyn-1-ol (1e):** 1.58 g (86%). Brown oil. IR (neat) ν $cm^{-1}$; 3369, 1044, 816. $^1$H NMR (300 MHz) δ ppm; 2.19 (br.s, 1H), 2.34 (s, 3H), 2.63 (t, *J* = 6.3 Hz, 2H), 3.79 (t, *J* = 6.3 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H). $^{13}$C NMR (75 MHz) δ ppm; 21.4, 23.8, 60.7, 66.8, 73.3, 75.6, 80.6, 118.5, 129.2, 132.5, 139.5. HRMS(FAB): *m/z* calcd. for $C_{13}H_{13}O$ [M + H] 185.0966; found 185.0943.

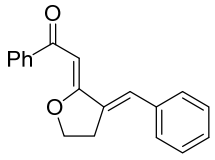
### *Domino Synthesis of 2,3-Dialkylidenetetrahydrofurans 3 and Characterization of 3 and 4da*



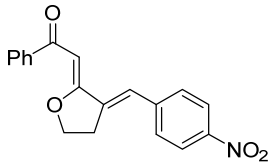

To a solution of 3,5-diynol **1** (0.4 mmol), aldehyde **2** (0.8 mmol) and methanol (48.6 μL, 1.2 mmol) in dichloromethane (DCM, 2.5 mL) was added $HBF_4 \cdot OEt_2$ (163.3 μL, 1.2 mmol) at 0 ºC. After being stirred at room temperature for 8 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 1:1) to give **3**.

**Scale-up preparation of 3aa**: According to the above procedure, **3aa** was prepared from **1a** (851 mg, 5 mmol), benzaldehyde (**2a**, 1.0 mL, 10 mmol), methanol (0.61 mL, 15 mmol) and $HBF_4 \cdot OEt_2$ (2.0 mL, 15 mmol) in DCM (31 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 3:1), **3aa** was obtained in the 81% yield (1.12 g, 4.05 mmol).

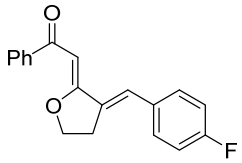
[7] A. H. Cherney, S. H. Reisman, *J. Am. Chem. Soc.* **2014**, *136*, 14365–14368.
[8] M. Tsuji, *J. Org. Chem.* **2003**, *68*, 9589–9597.



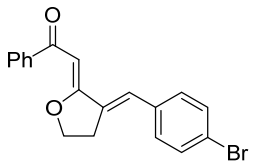
**(2*Z*)-2-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3aa):** $R_f$ = 0.25. 88.1 mg (80%). Yellow solid. MP: 116-118 ºC. IR (KBr) ν $cm^{-1}$; 3054, 1580, 1248, 1011. $^1$H NMR (500 MHz) δ ppm; 3.11 (td, *J* = 7.5, 2.5 Hz, 2H), 4.62 (t, *J* = 7.5 Hz, 2H), 6.58 (s, 1H), 7.31 (t, *J* = 2.5 Hz, 1H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.39-7.53 (m, 7H), 7.98 (d, *J* = 7.0 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.0, 72.1, 90.4, 127.5, 127.6, 128.2, 128.76, 128.81, 129.4, 131.5, 134.2, 135.5, 140.3, 168.8, 188.3. HRMS(FAB): *m/z* calcd. for $C_{19}H_{17}O_2$ [M + H] 277.1229; found 277.1241.



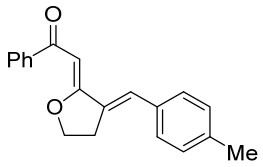
**(2*Z*)-2-[(*E*)-3-(4-Nitrobenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ab):** $R_f$ = 0.27. 91.8 mg (71%). Yellow solid. MP: 172-174 ºC. IR (KBr) ν $cm^{-1}$; 3063, 1561, 1520, 1344, 1009. $^1$H NMR (500 MHz) δ ppm; 3.15 (td, *J* = 7.5, 2.5 Hz, 2H), 4.66 (t, *J* = 7.5 Hz, 2H), 6.62 (s, 1H), 7.34 (t, *J* = 2.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.52 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.97 (dt, *J* = 7.5, 2.0 Hz, 2H), 8.29 (d, *J* = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.3, 72.0, 91.7, 124.1, 124.6, 127.7, 128.4, 129.8, 131.9, 138.8, 139.9, 141.8, 147.2, 167.3, 188.4. HRMS(FAB): *m/z* calcd. for $C_{19}H_{16}NO_4$ [M + H] 322.1079; found 322.1056.



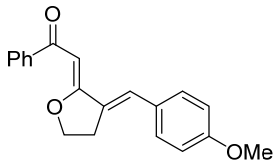
**(2*Z*)-2-[(*E*)-3-(4-Fluorobenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ac):** $R_f$ = 0.19. 95.9 mg (81%). Yellow solid. MP: 114-116 ºC. IR (KBr) ν $cm^{-1}$; 3066, 1557, 1252, 1232, 1012. $^1$H NMR (500 MHz) δ ppm; 3.08 (td, *J* = 7.5, 3.0 Hz, 2H), 4.63 (t, *J* = 7.5 Hz, 2H), 6.56 (s, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 3.0 Hz, 1H), 7.42-7.48 (m, 4H), 7.50 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.97 (dt, *J* = 7.5, 1.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 28.9, 72.1, 90.4, 115.9 (d, *J* = 22.6 Hz), 126.3, 127.7, 128.3, 131.2 (d, *J* = 8.3 Hz), 131.6, 131.8 (d, *J* = 3.6 Hz), 133.8, 140.3, 162.7 (d, *J* = 249.3 Hz), 168.6, 188.3. HRMS(FAB): *m/z* calcd. for $C_{19}H_{16}FO_2$ [M + H] 295.1134; found 295.1145.



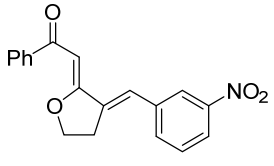
**(2*Z*)-2-[(*E*)-3-(4-Bromobenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ad):** $R_f$ = 0.24. 112.1 mg (79%). Yellow solid. MP: 125-127 ºC. IR (KBr) ν $cm^{-1}$; 3057, 1561, 1249, 1008. $^1$H NMR (500 MHz) δ ppm; 3.06 (td, *J* = 7.5, 2.5 Hz, 2H), 4.62 (t, *J* = 7.5 Hz, 2H), 6.56 (s, 1H), 7.22 (t, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.50 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.55 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.0, 72.1, 90.7, 123.0, 126.1, 127.7, 128.3, 130.7, 131.6, 132.0, 134.4, 135.0, 140.2, 168.4, 188.3. HRMS(FAB): *m/z* calcd. for $C_{19}H_{16}BrO_2$ [M + H] 355.0334; found 355.0338.



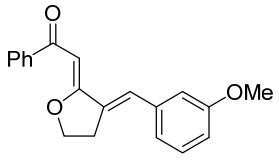
**(2*Z*)-2-[(*E*)-3-(4-Methylbenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ae):** $R_f$ = 0.21. 87.8 mg (75%). Yellow solid. MP: 121-123 ºC. IR (KBr) ν $cm^{-1}$; 3022, 2919, 1557, 1252, 1011. $^1$H NMR (500 MHz) δ ppm; 2.40 (s, 3H), 3.12 (td, *J* = 7.5, 2.0 Hz, 2H), 4.64 (t, *J* = 7.5 Hz, 2H), 6.56 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.50 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.98 (dt, *J* = 7.5, 2.0 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 21.3, 28.9, 72.1, 90.1, 127.5, 127.6, 128.2, 129.4, 129.5, 131.4, 132.7, 133.0, 139.1, 140.3, 169.1, 188.2. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_2$ [M + H] 291.1385; found 291.1400.



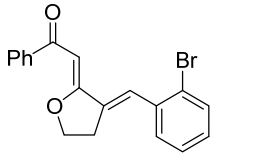
**(2*Z*)-2-[(*E*)-3-(4-Methoxybenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3af):** $R_f$ = 0.11. 29.4 mg (24%). Yellow amorphous. IR (neat) ν $cm^{-1}$; 2968, 1511, 1252, 1173, 1028, 1010. $^1$H NMR (300 MHz) δ ppm; 3.09 (td, *J* = 7.5, 2.4 Hz, 2H), 3.85 (s, 3H), 4.64 (t, *J* = 7.5 Hz, 2H), 6.54 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = 2.4 Hz, 1H), 7.39-7.55 (m, 5H), 7.98 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR (75 MHz) δ ppm; 28.9, 55.3, 72.2, 89.9, 114.3, 127.4, 127.7, 128.31, 128.34, 131.2, 131.5, 131.6, 140.6, 160.2, 169.6, 188.4. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_3$ [M + H] 307.1334; found 307.1348.



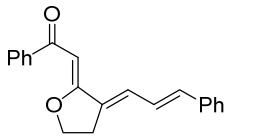
**(2*Z*)-2-[(*E*)-3-(3-Nitrobenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ag):** $R_f$ = 0.12. 91.4 mg (71%). Yellow solid. MP: 142-144 ºC. IR (KBr) ν $cm^{-1}$; 3070, 1565, 1526, 1353, 1011. $^1$H NMR (500 MHz) δ ppm; 3.18 (td, *J* = 7.5, 3.0 Hz, 2H), 4.68 (t, *J* = 7.5 Hz, 2H), 6.62 (s, 1H), 7.35 (t, *J* = 3.0 Hz, 1H), 7.45-7.50 (m, 2H), 7.51-7.56 (m, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.21 (dd, *J* = 8.0, 2.1 Hz, 1H), 8.34 (s, 1H). $^{13}$C NMR (125 MHz) δ ppm; 28.9, 72.0, 91.2, 123.0, 123.5, 124.5, 127.6, 128.2, 129.7, 131.7, 134.8, 137.1, 137.4, 139.8, 148.3, 167.5, 188.2. HRMS(FAB): *m/z* calcd. for $C_{19}H_{16}NO_4$ [M + H] 322.1079; found 322.1062.



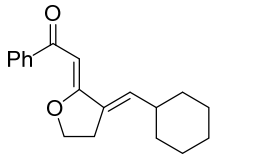
**(2*Z*)-2-[(*E*)-3-(3-Methoxybenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ah):** $R_f$ = 0.18. 76.0 mg (62%). Brown amorphous. IR (neat) ν $cm^{-1}$; 2973, 1562, 1280, 1238, 1033, 1011. $^1$H NMR (500 MHz) δ ppm; 3.13 (td, *J* = 7.5, 2.0 Hz, 2H), 3.85 (s, 3H), 4.64 (t, *J* = 7.5 Hz, 2H), 6.58 (s, 1H), 6.93 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.00 (t, *J* = 2.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 2.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 2H), 7.51 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.99 (dt, *J* = 7.5, 1.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.1, 55.3, 72.2, 90.5, 114.3, 114.9, 121.9, 127.4, 127.7, 128.3, 129.8, 131.6, 134.5, 136.8, 140.3, 159.7, 168.7, 188.3. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_3$ [M + H] 307.1334; found 307.1320.



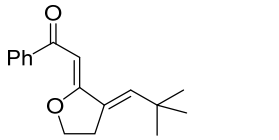
**(2*Z*)-2-[(*E*)-3-(2-Bromobenzylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ai):** $R_f$ = 0.15. 98.2 mg (69%). Yellow solid. MP: 113-114 ºC. IR (KBr) ν $cm^{-1}$; 30557, 1554, 1246, 1009. $^1$H NMR (500 MHz) δ ppm; 3.02 (td, *J* = 7.5, 2.5 Hz, 2H), 4.60 (t, *J* = 7.5 Hz, 2H), 6.62 (s, 1H), 7.22 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 (t, *J* = 2.5 Hz, 1H), 7.42-7.49 (m, 3H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.66 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.99 (dt, *J* = 7.0, 1.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 28.8, 72.0, 91.2, 125.1, 126.3, 127.4, 127.7, 128.3, 129.5, 130.0, 131.7, 133.2, 135.4, 136.6, 140.1, 167.9, 188.4. HRMS(FAB): *m/z* calcd. for $C_{19}H_{16}BrO_2$ [M + H] 355.0334; found 355.0338.



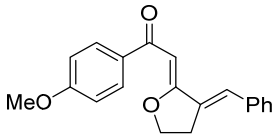
**(2*Z*)-2-{(*E*)-3-[(*E*)-3-Phenylallylidene]dihydrofuran-2(3*H*)-ylidene}1-phenylethanone (3aj):** $R_f$ = 0.24. 51.3 mg (42%). Yellow amorphous. IR (KBr) ν $cm^{-1}$; 2974, 1556, 1233, 1017. $^1$H NMR (500 MHz) δ ppm; 3.00 (td, *J* = 7.5, 2.5 Hz, 2H), 4.64 (t, *J* = 7.5 Hz, 2H), 6.50 (s, 1H), 6.84-6.96 (m, 2H), 7.05 (dt, *J* = 10.0, 2.5 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.46-7.52 (m, 3H), 7.96 (d, *J* = 7.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 27.2, 71.9, 90.5, 124.8, 127.0, 127.1, 127.6, 128.2, 128.8, 131.5, 134.8, 136.4, 138.3, 140.3, 167.8, 188.1. HRMS(FAB): *m/z* calcd. for $C_{21}H_{19}O_2$ [M + H] 303.1385; found 303.1379.



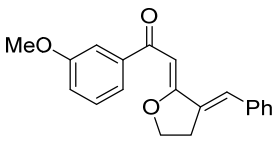
**(2*Z*)-2-[(*E*)-3-(cyclohexylmethylene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3ak):** $R_f$ = 0.30. 14.3 mg (13%). Yellow amorphous. IR (neat) ν $cm^{-1}$; 2926, 1584, 1228, 1016. $^1$H NMR (500 MHz) δ ppm; 1.15-1.37 (m, 6H), 1.65-1.84 (m, 4H), 2.16-2.27 (m, 1H), 2.77 (td, *J* = 7.5, 2.5 Hz, 2H), 4.56 (t, *J* = 7.5 Hz, 2H), 6.25 (dt, *J* = 10.0, 2.5 Hz, 1H), 6.36 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 3H), 7.47 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.93 (dt, *J* = 7.5, 2.4 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 25.6, 25.8, 26.4, 32.0, 39.9, 72.3, 89.7, 127.6, 128.2, 131.4, 132.5, 135.6, 140.4, 168.2, 188.3. HRMS(FAB): *m/z* calcd. for $C_{19}H_{23}O_2$ [M + H] 283.1698; found 283.1663.



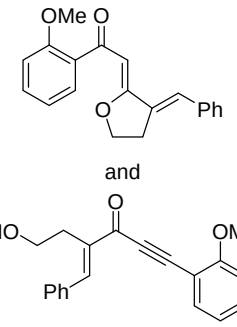
**(2*Z*)-2-[(*E*)-3-(2,2-Dimethylpropylidene)dihydrofuran-2(3*H*)-ylidene]-1-phenylethanone (3al):** $R_f$ = 0.36. 61.9 mg (60%). Yellow amorphous. IR (neat) ν $cm^{-1}$; 2960, 1567, 1242, 1020. $^1$H NMR (500 MHz) δ ppm; 1.20 (s, 9H), 2.89 (td, *J* = 7.5, 2.5 Hz, 2H), 4.54 (t, *J* = 7.5 Hz, 2H), 6.35 (s, 1H), 6.42 (t, *J* = 2.5 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.93 (d, *J* = 7.0 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 26.7, 29.8, 33.7, 72.2, 89.4, 127.6, 128.2, 131.2, 131.3, 139.9, 140.5, 169.7, 188.3. HRMS(FAB): *m/z* calcd. for $C_{17}H_{21}O_2$ [M + H] 257.1542; found 257.1579.



**(2*Z*)-2-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]-1-(4-methoxyphenyl)ethanone (3ba):** $R_f$ = 0.19. 92.0 mg (75%). Brown amorphous. IR (neat) ν $cm^{-1}$; 2973, 1649, 1600, 1509, 1248, 1172, 1023. $^1$H NMR (500 MHz) δ ppm; 3.11 (td, *J* = 7.5, 2.5 Hz, 2H), 3.86 (s, 3H), 4.61 (t, *J* = 7.5 Hz, 2H), 6.56 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 2.5 Hz, 1H), 7.36 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.41-7.49 (m, 4H), 7.99 (d, *J* = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.1, 55.4, 72.0, 90.3, 113.4, 127.1, 128.7, 128.8, 129.4, 129.8, 133.1, 134.3, 135.6, 162.4, 168.2, 187.1. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_3$ [M + H] 307.1334; found 307.1370.



**(2*Z*)-2-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]-1-(3-methoxyphenyl)ethanone (3ca):** $R_f$ = 0.19. 68.9 mg (56%). Brown amorphous. IR (neat) ν $cm^{-1}$; 2971, 1650, 1562, 1259, 1020. $^1$H NMR (500 MHz) δ ppm; 3.12 (td, *J* = 7.5, 2.5 Hz, 2H), 3.87 (s, 3H), 4.63 (t, *J* = 7.5 Hz, 2H), 6.56 (s, 1H), 7.05 (ddd, *J* = 8.5, 3.0, 1.0 Hz, 1H), 7.31 (t, *J* = 2.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.41-7.49 (m, 4H), 7.53 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.56 (dt, *J* = 8.5, 1.0 Hz, 1H). $^{13}$C NMR (125 MHz) δ ppm; 29.1, 55.4, 72.2, 90.5, 112.5, 117.7, 120.1, 127.6, 128.8, 128.9, 129.2, 129.4, 134.2, 135.5, 141.8, 159.6, 168.9, 188.0. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_3$ [M + H] 307.1334; found 307.1344.

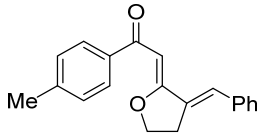


**(2*Z*)-2-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]-1-(3-methoxyphenyl)ethanone (3da):** $R_f$ = 0.20. 46.1 mg (38%). Brown amorphous. IR (neat) ν $cm^{-1}$; 2973, 1598, 1243, 1023. $^1$H NMR (500 MHz) δ ppm; 3.09 (td, *J* = 7.5, 2.5 Hz, 2H), 3.90 (s, 3H), 4.58 (t, *J* = 7.5 Hz, 2H), 6.53 (s, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 7.00 (td, *J* = 7.5, 1.5 Hz, 1H), 7.22 (t, *J* = 2.5 Hz, 1H), 7.31-7.36 (m, 1H), 7.37-7.46 (m, 5H), 7.63 (dd, *J* = 7.5, 1.5 Hz, 1H). $^{13}$C NMR (125 MHz) δ ppm; 29.0, 55.8, 72.0, 95.4, 111.4, 120.7, 127.2, 128.65, 128.70, 129.3, 129.9, 131.6, 131.8, 134.3, 135.6, 157.2, 167.3, 189.7. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_3$ [M + H] 307.1334; found 307.1341.

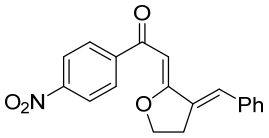
and



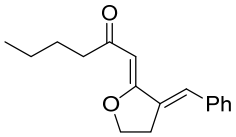
**(*E*)-4-Benzylidene-6-hydroxy-1-(2-methoxyphenyl)hex-1-yn-3-one (4da):** $R_f$ = 0.25. 14.6 mg (25%). Yellow oil. IR (neat) ν $cm^{-1}$; 3430, 2971, 2197, 1614, 1277, 1044. $^1$H NMR (500 MHz) δ ppm; 2.06 (t, *J* = 6.3 Hz, 1H), 2.95 (t, *J* = 6.3 Hz, 2H), 3.87 (td, *J* = 6.3, 6.3 Hz, 2H), 3.94 (s, 3H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.38-7.48 (m, 4H), 7.56-7.60 (m, 3H), 8.45 (s, 1H). $^{13}$C NMR (125 MHz) δ ppm; 29.4, 55.9, 61.8, 90.2, 90.4, 109.4, 110.7, 120.7, 128.8, 129.5, 129.7, 132.4, 134.8, 135.2, 139.4, 148.5, 161.7, 181.6. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_3$ [M + H] 307.1334; found 307.1341.



**(2*Z*)-2-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]-1-(*p*-tolyl)ethanone (3ea):** $R_f$ = 0.21. 76.1 mg (65%). Yellow amorphous. IR (neat) ν $cm^{-1}$; 2974, 1607, 1251, 1181. $^1$H NMR (500 MHz) δ ppm; 2.41 (s, 3H), 3.12 (td, *J* = 7.5, 3.0 Hz, 2H), 4.62 (t, *J* = 7.5 Hz, 2H), 6.58 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 3.0 Hz, 1H), 7.34-7.41 (m, 1H), 7.42-7.49 (m, 4H), 7.90 (d, *J* = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 21.6, 29.1, 72.1, 90.5, 126.4, 127.3, 127.8, 128.8, 129.0, 129.4, 134.3, 135.6, 137.7, 142.2, 168.5, 188.1. HRMS(FAB): *m/z* calcd. for $C_{20}H_{19}O_2$ [M + H] 291.1385; found 291.1355.

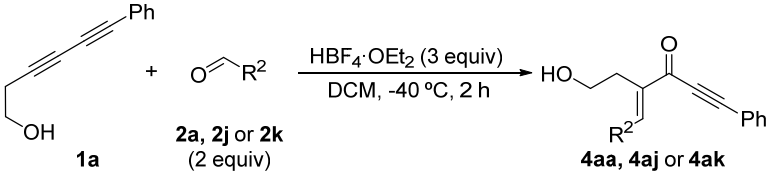


**(2*Z*)-2-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]-1-(4-nitrophenyl)ethanone (3fa):** $R_f$ = 0.25. 29.7 mg (23%). Yellow solid. MP: 195-196 ºC. IR (KBr) ν $cm^{-1}$; 3068, 1556, 1520, 1345, 1025. $^1$H NMR (500 MHz) δ ppm; 3.16 (td, *J* = 7.5, 2.5 Hz, 2H), 4.67 (t, *J* = 7.5 Hz, 2H), 6.51 (s, 1H), 7.36 (t, *J* = 2.5 Hz, 1H), 7.39 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.43-7.51 (m, 4H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.29 (d, *J* = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.0, 72.7 90.2, 123.6, 128.6, 128.87, 128.92, 129.3, 129.6, 133.7, 135.2, 145.5, 149.4, 170.7, 186.3. HRMS(FAB): *m/z* calcd. for $C_{19}H_{16}NO_4$ [M + H] 322.1079; found 322.1111.

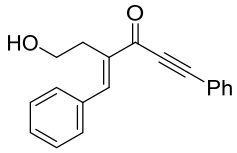


**(2*Z*)-1-[(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-ylidene]hexan-2-one (3ga):** $R_f$ = 0.43. 67.0 mg (65%). Colorless amorphous. IR (neat) ν $cm^{-1}$; 2956, 1618, 1399, 1033. $^1$H NMR (500 MHz) δ ppm; 0.93 (t, *J* = 7.5 Hz, 3H), 1.37 (sext, *J* = 7.5 Hz, 2H), 1.63 (quint, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 3.09 (td, *J* = 7.5, 3.0 Hz, 2H), 4.52 (t, *J* = 7.5 Hz, 2H), 5.76 (s, 1H), 7.14 (t, *J* = 3.0 Hz, 1H), 7.32-7.37 (m, 1H), 7.39-7.43 (m, 4H), 7.42-7.49 (m, 4H). $^{13}$C NMR (125 MHz) δ ppm; 13.9, 22.5, 27.0, 29.1, 43.1, 71.5, 95.7, 127.2, 128.6, 128.7, 129.2, 133.5, 135.6, 166.3, 199.7. HRMS(FAB): *m/z* calcd. for $C_{17}H_{21}O_2$ [M + H] 257.1542; found 257.1530.

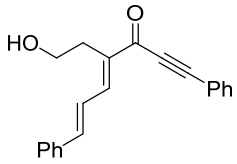
## *Preparation and Characterization of 4-En-1-yn-3-ones 4aa, 4aj or 4ak*



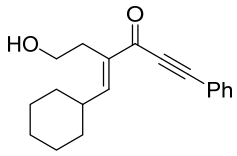

To a solution of 3,5-diynol **1a** (68.1 mg, 0.4 mmol) and aldehyde **2** (**2a**: 81.6 μL, 0.80 mmol; **2j**: 100.7 μL, 0.80 mmol; **2k**: 96.5 μL, 0.80 mmol) in dichloromethane (DCM, 2.5 mL) was added $HBF_4$·$OEt_2$ (163.3 μL, 1.2 mmol) at -40 ºC. After being stirred at same temperature for 2 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 2:1) to give **4aa**, **4aj** or **4ak**.



**(*E*)-4-Benzylidene-6-hydroxy-1-phenylhex-1-yn-3-one (4aa):** $R_f$ = 0.30. 79.6 mg (72%). Yellow oil. IR (neat) ν $cm^{-1}$; 3429, 2973, 2876, 1617, 1277. $^1$H NMR (500 MHz) δ ppm; 2.07 (br.s, 1H), 2.94 (t, *J* = 6.5 Hz, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 7.38-7.48 (m, 6H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.64 (dd, *J* = 8.5, 1.5 Hz, 2H), 8.26 (s, 1H). $^{13}$C NMR (125 MHz) δ ppm; 29.4, 61.7, 86.0, 92.9, 120.2, 128.7, 128.8, 129.6, 129.7, 130.6, 132.8, 134.8, 139.4, 148.3, 181.4. HRMS(FAB): *m/z* calcd. for $C_{19}H_{15}O$ [M − OH] 259.1123; found 259.1135.

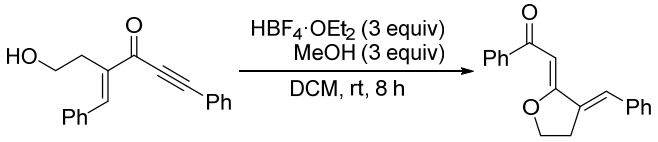


**(4*E*,6*E*)-4-(2-Hydroxyethyl)-1,7-diphenylhepta-4,6-dien-1-yn-3-one (4aj):** $R_f$ = 0.26. 68.2 mg (56%). Yellow solid. MP: 86-88 ºC. IR (KBr) ν $cm^{-1}$; 3345, 2882, 1604. $^1$H NMR (500 MHz) δ ppm; 1.85 (t, *J* = 5.2 Hz, 1H), 2.89 (t, *J* = 6.3 Hz, 2H), 3.77 (td, *J* = 6.3, 5.2 Hz, 2H), 7.11 (d, *J* = 15.0 Hz, 1H), 7.27 (dd, *J* = 15.0, 11.0 Hz, 1H), 7.33-7.45 (m, 5H), 7.48 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.65 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.89 (d, *J* = 11.0 Hz, 1H). $^{13}$C NMR (125 MHz) δ ppm; 29.0, 61.9, 86.2, 92.0, 120.3, 123.7, 127.5, 128.6, 128.8, 129.5, 130.4, 132.7, 135.9, 138.2, 143.0, 147.4, 180.1. HRMS(FAB): *m/z* calcd. for $C_{21}H_{19}O_2$ [M + H] 303.1385; found 303.1394.



**(*E*)-4-(Cyclohexylmethylene)-6-hydroxy-1-phenylhex-1-yn-3-one (4ak):** $R_f$ = 0.46. 67.1 mg (61%). Yellow oil. IR (neat) ν $cm^{-1}$; 3437, 2927, 2202, 1626. $^1$H NMR (500 MHz) δ ppm; 1.20-1.42 (m, 6H), 1.69-1.85 (m, 5H), 2.48-2.58 (m, 1H), 2.67 (t, *J* = 6.5 Hz, 2H), 3.68 (t, *J* = 6.5 Hz, 2H), 7.16 (d, *J* = 10.2 Hz, 1H), 7.40 (td, *J* = 7.5, 1.5 Hz, 2H), 7.46 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.59 (dt, *J* = 7.5, 1.5Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 25.3, 25.7, 28.9, 32.1, 38.5, 62.0, 86.0, 91.9, 120.3, 128.6, 130.4, 132.7, 137.4, 157.9, 181.3. HRMS(FAB): *m/z* calcd. for $C_{19}H_{21}O$ [M − OH] 265.1592; found 265.1609.

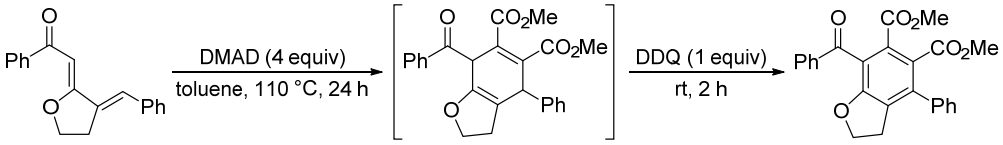
### *Preparation of 2,3-Dialkylidenetetrahydrofuran 3aa from 4-En-1-yn-3-one 4aa*




**4aa** **3aa**

To a solution of 4-en-2-ynone **4aa** (110.5 mg, 0.4 mmol) and methanol (48.6 μL, 1.2 mmol) in dichloromethane (DCM, 2.5 mL) was added $HBF_4$·$OEt_2$ (163.3 μL, 1.2 mmol) at 0 ºC. After being stirred at room temperature for 8 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 1:1, $R_f$ = 0.25) to give **3aa** (83.0 mg, 75%).

### *Preparation and Characterization of Dihydrobenzofuran 5*

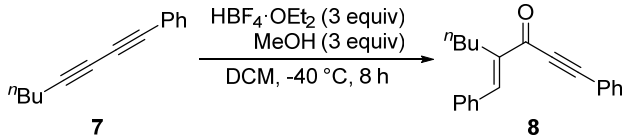



**3aa** **5**

A solution of 2,3-dialkylidenetetrahydrofuran **3aa** (27.6 mg, 0.1 mmol) and dimethyl acetylenedicarboxylate (DMAD, 49 μL, 0.4 mmol) in toluene (1 mL) was stirred at 110 ºC for 24 h. After the reaction mixture was cooled to room temperature, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 22.7 mg, 0.1 mmol) was added. After being stirred at same temperature for 2 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 2:1) to give **5** (17.9 mg, 43%).

**Dimethyl 7-benzoyl-2,3-dihydro-4-phenylbenzofuran-5,6-dicarboxylate (5):** $R_f$ = 0.34. Yellow amorphous. IR (neat) ν $cm^{-1}$; 2975, 1736, 1671, 1246, 1035. $^1$H NMR (500 MHz) δ ppm; 3.10 (t, *J* = 9.0 Hz, 2H), 3.52 (s, 3H), 3.53 (s, 3H), 4.59 (t, *J* = 9.0 Hz, 2H), 7.30 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.39 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.41-7.49 (m, 4H), 7.58 (tt, *J* = 7.5, 1.5Hz, 1H), 7.88 (dt, *J* = 7.5, 1.5 Hz, 2H). $^{13}$C NMR (125 MHz) δ ppm; 29.0, 52.1, 52.3, 72.5, 121.1, 127.5, 128.0, 128.1, 128.4, 128.5, 129.2, 130.0, 131.3, 133.4, 136.8, 136.9, 139.0, 157.8, 166.1, 168.1, 193.2. HRMS(FAB): *m/z* calcd. for $C_{25}H_{20}O_6$ [M] 416.1260; found 416.1272.

### *Preparation and Characterization of 4-En-1-yn-3-one 8*




**7** **8**

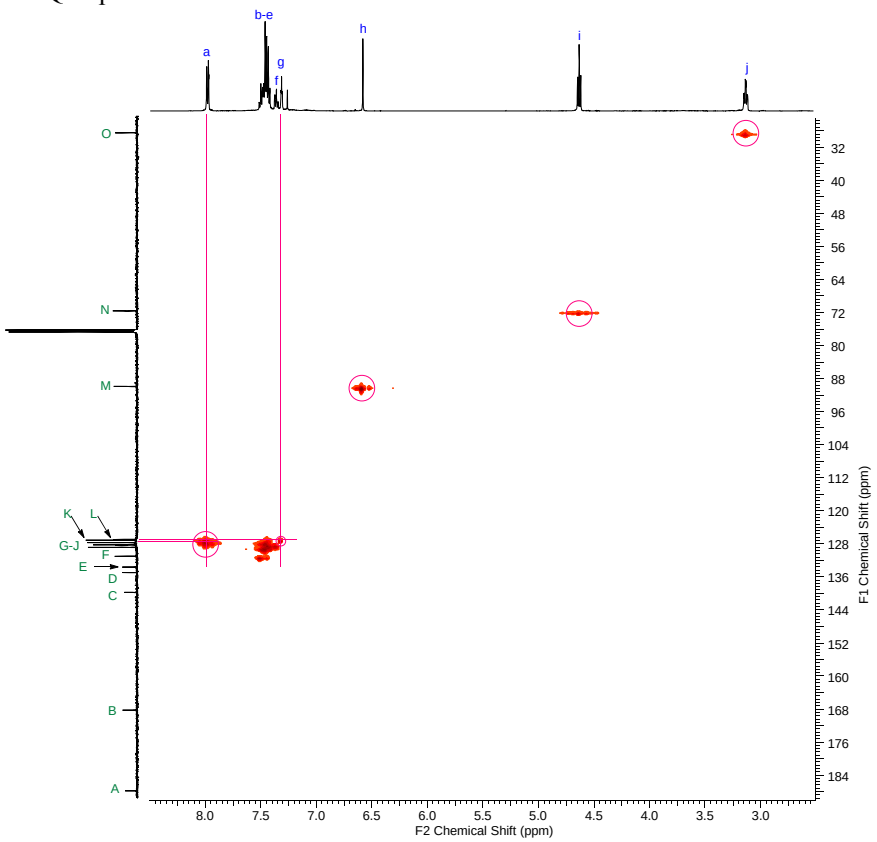
To a solution of diyne **7**[9] (72.9 mg, 0.4 mmol), benzaldehyde (**2a**: 81.6 μL, 0.80 mmol) and methanol (48.6 μL, 1.2 mmol) in dichloromethane (DCM, 2.5 mL) was added $HBF_4 \cdot OEt_2$ (163.3 μL, 1.2 mmol) at -40 ºC. After being stirred at same temperature for 8 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by medium-pressure liquid chromatography (MPLC, hexane:AcOEt = 99:1, flow rate 20 mL/min) to give **8** (69.4 mg, 60%).

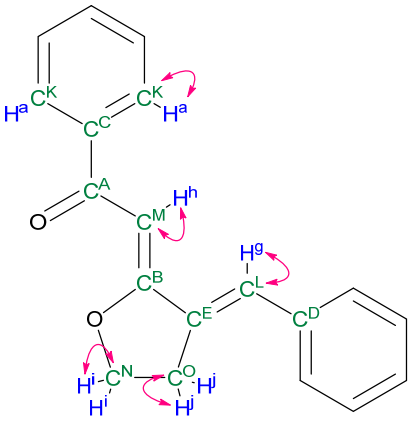
**(*E*)-4-Benzylidene-1-phenyloct-1-yn-3-one (8):** Colorless oil. IR (neat) ν $cm^{-1}$; 2200, 1622. $^1H$ NMR (500 MHz) δ ppm; 0.95 (t, *J* = 7.3 Hz, 3H), 1.44 (sextet, *J* = 7.3 Hz, 2H), 1.50-1.58 (m, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 7.37-7.48 (m, 6H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.64 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.09 (s, 1H). $^{13}C$ NMR (125 MHz) δ ppm; 13.8, 22.9, 25.6, 30.8, 86.4, 91.6, 120.4, 128.55, 128.61, 129.14, 129.6, 130.3, 132.7, 135.4, 143.1, 145.2, 180.6. HRMS(FAB): *m/z* calcd. for $C_{21}H_{21}O$ [M+H] 289.1592; found 289.1605.

[9] Y. Matsuda, S. Naoe, S. Oishi, N. Fujii, H. Ohno, *Chem. Eur. J.* **2015**, *21*, 1463–1467.

## *2D NMR spectra of Product 3aa, 4aa and 8*

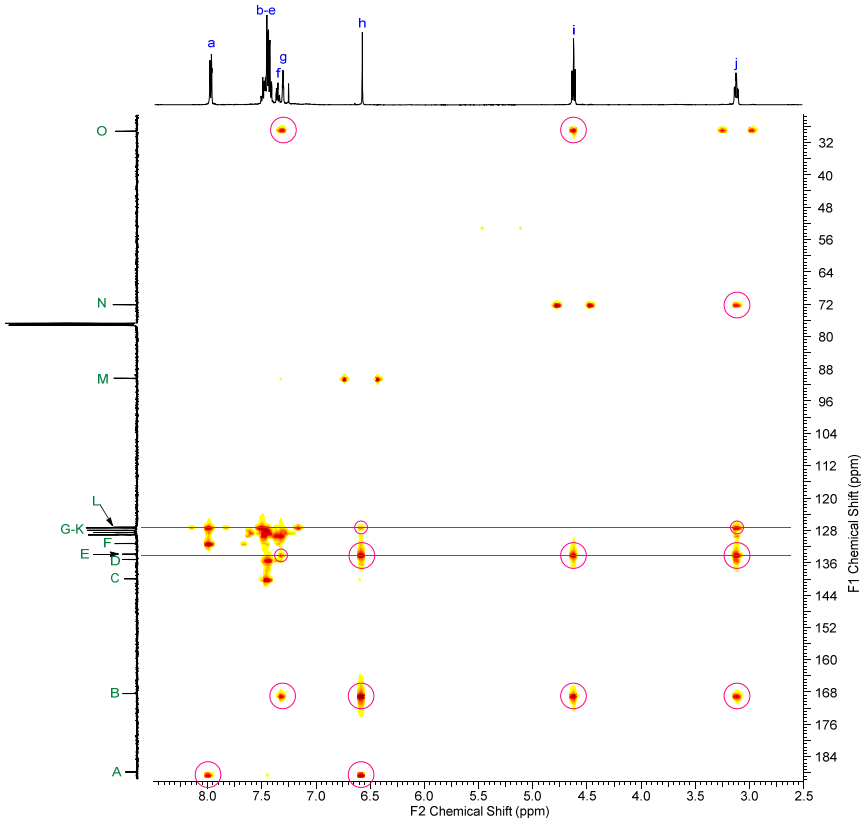
HMQC spectra of **3aa**

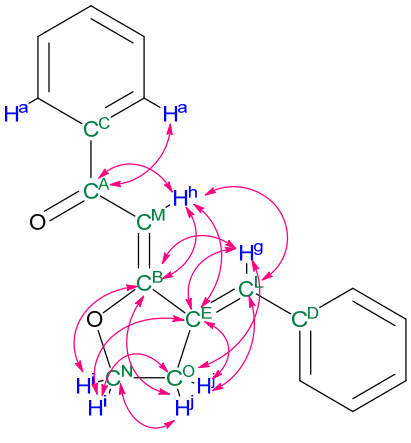


**3aa**

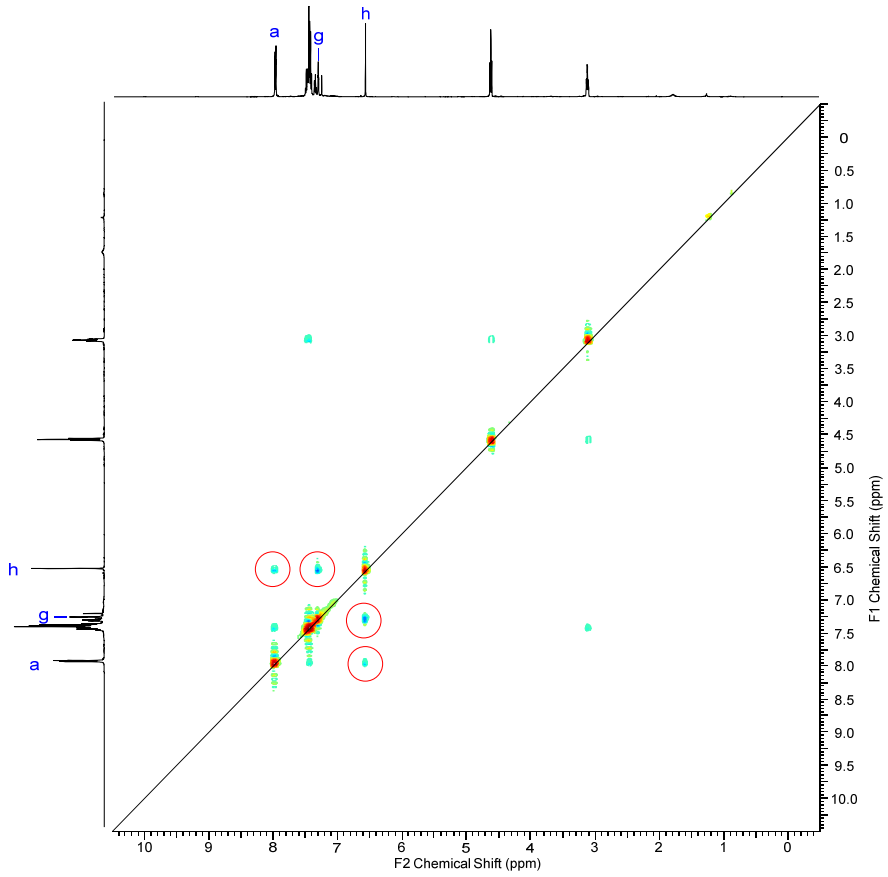
HMBC spectra of **3aa**

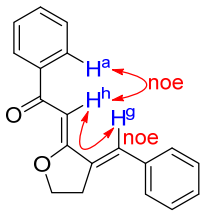


**3aa**

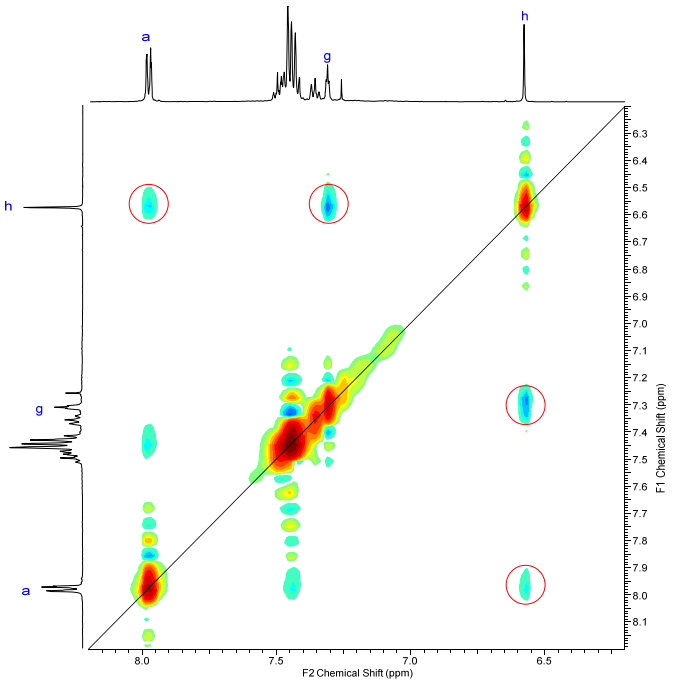
NOESY spectra of **3aa**



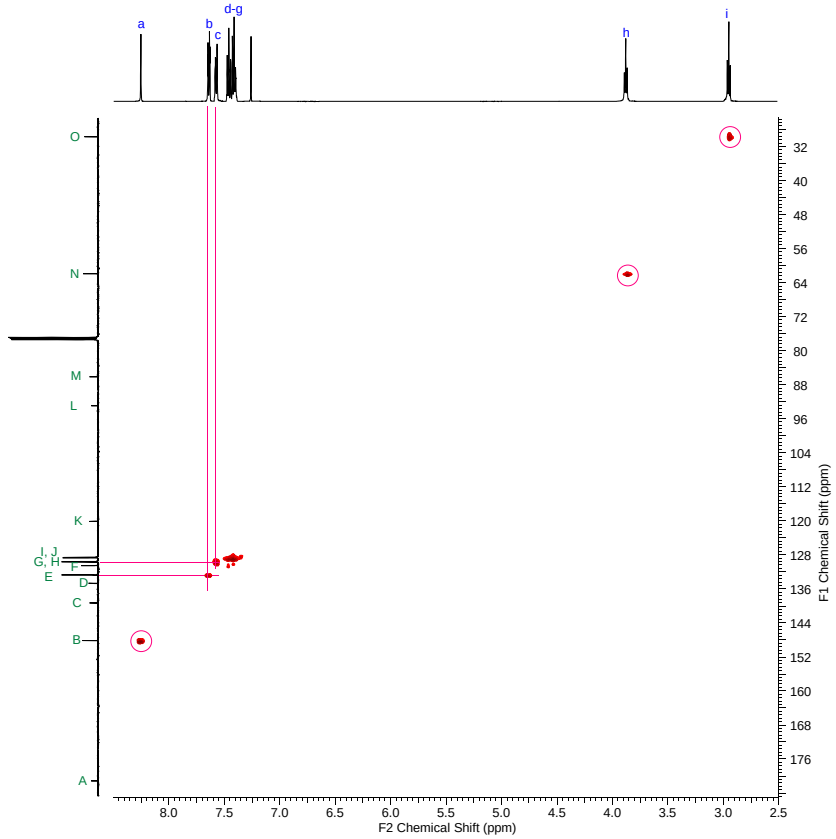



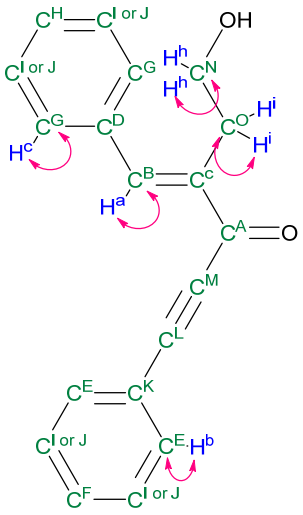

**3aa**

The chart on the right is an enlarged view (6.2–8.2 ppm) of the above NOESY spectrum of **3aa**. As shown in the enlarged view, NOE is not observed between $H^a$ and $H^g$ but between $H^a$ and $H^h$ or between $H^g$ and $H^h$. Since $H^a$, $H^g$ and $H^h$ are assigned as each proton in the structure of **3aa** on the upper right, the stereochemistry of **3aa** was determined as the illustrated structure.

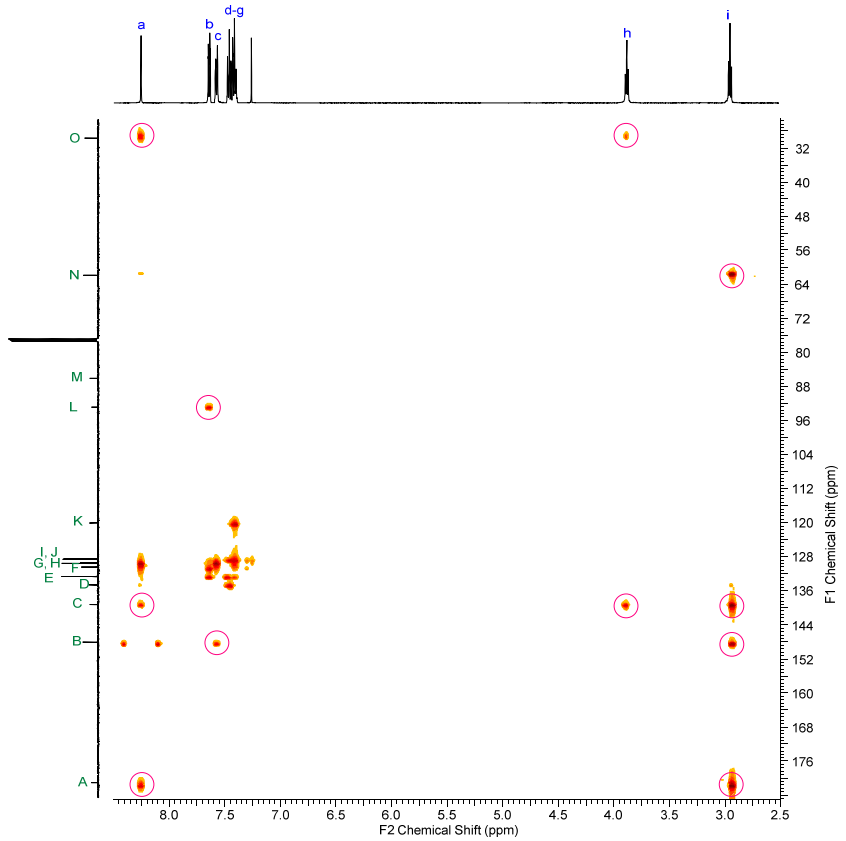


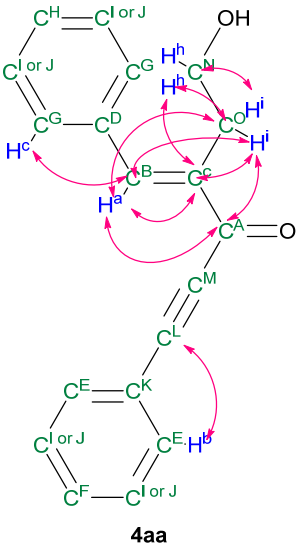
HMQC spectra of **4aa**



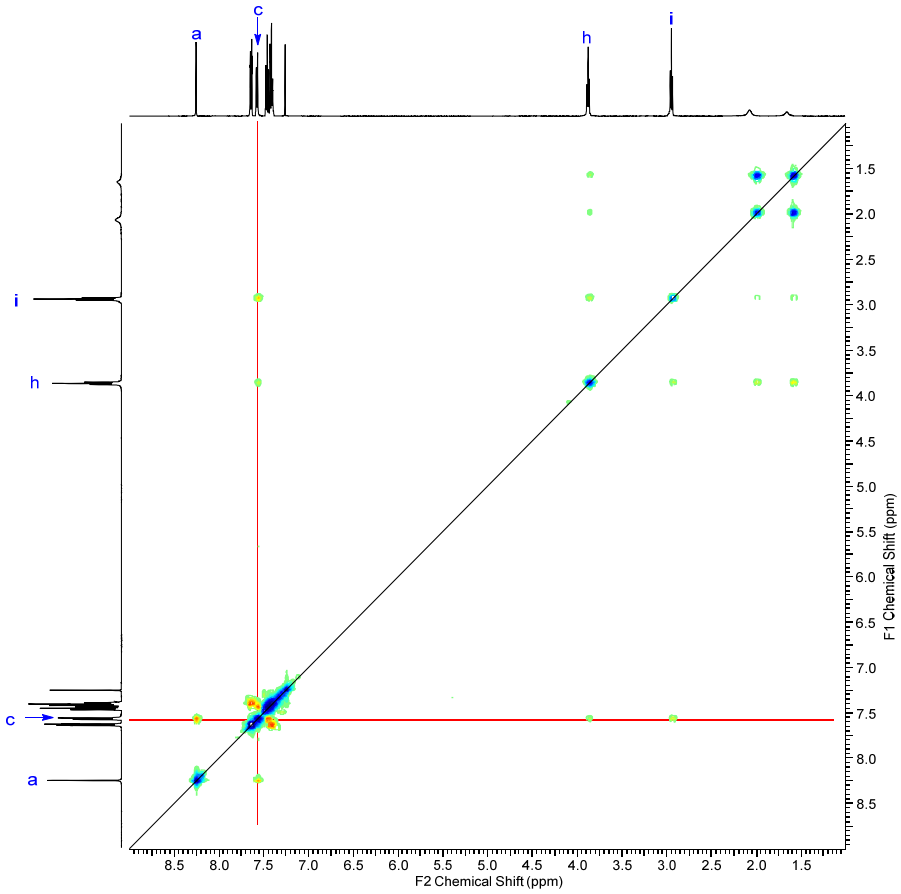



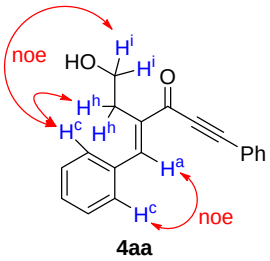

HMBC spectra of **4aa**



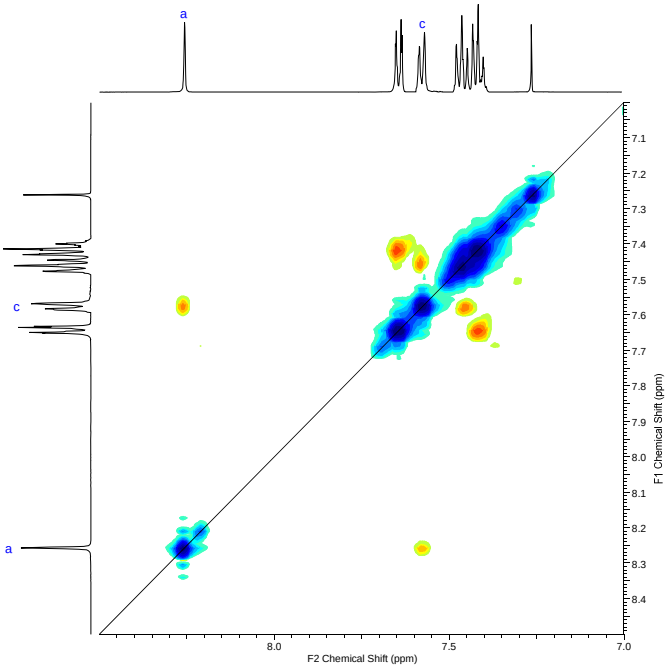
NOESY spectra of **4aa**



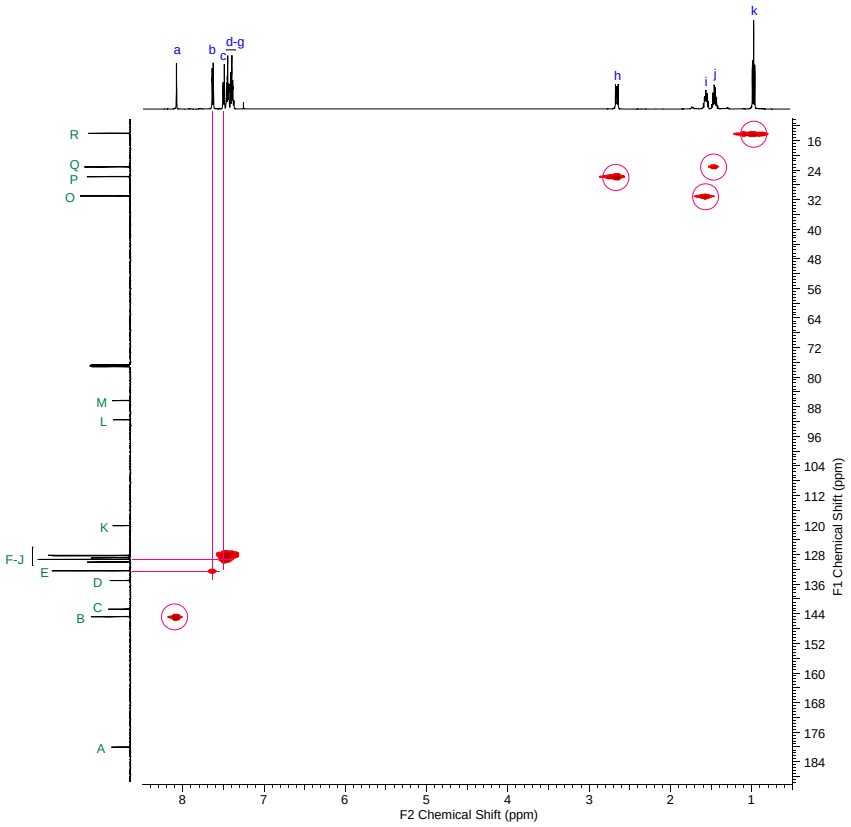



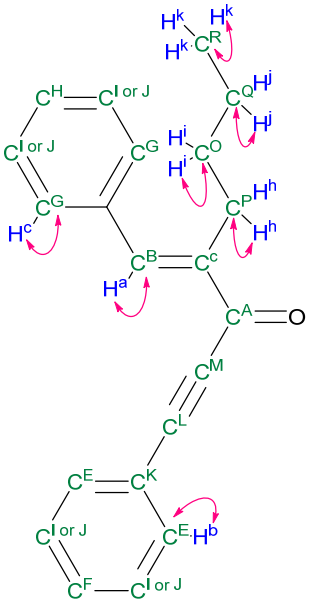

**4aa**

The chart on the right is an enlarged view (7.0–8.5 ppm) of the above NOESY spectrum of **4aa**. As shown in the enlarged view and above NOESY spectrum (red lines), NOE is observed between $H^a$ and $H^c$, between $H^c$ and $H^h$ or between $H^c$ and $H^i$. On the other hand, NOE is not observed between $H^a$ and $H^h$ or between $H^a$ and $H^i$. Since $H^a$, $H^c$, $H^h$ and $H^i$ are assigned as each proton in the structure of **4aa** on the upper right, the stereochemistry of **4aa** was determined as the illustrated structure.



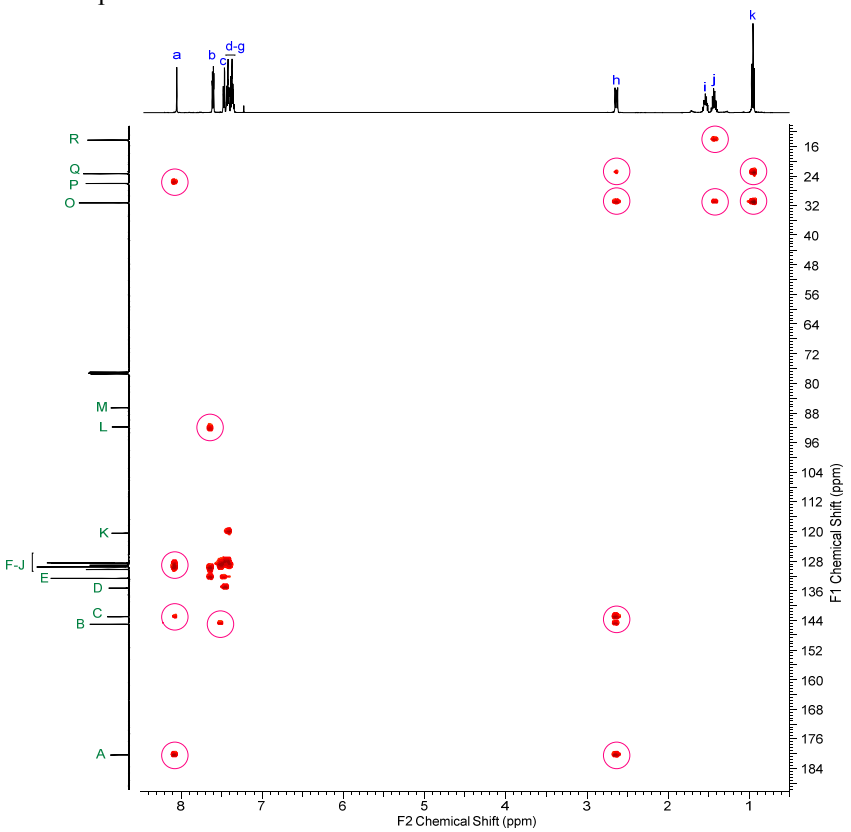
HMQC spectra of **8**

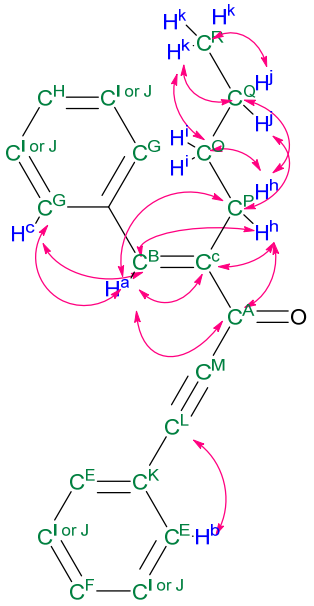


**8**

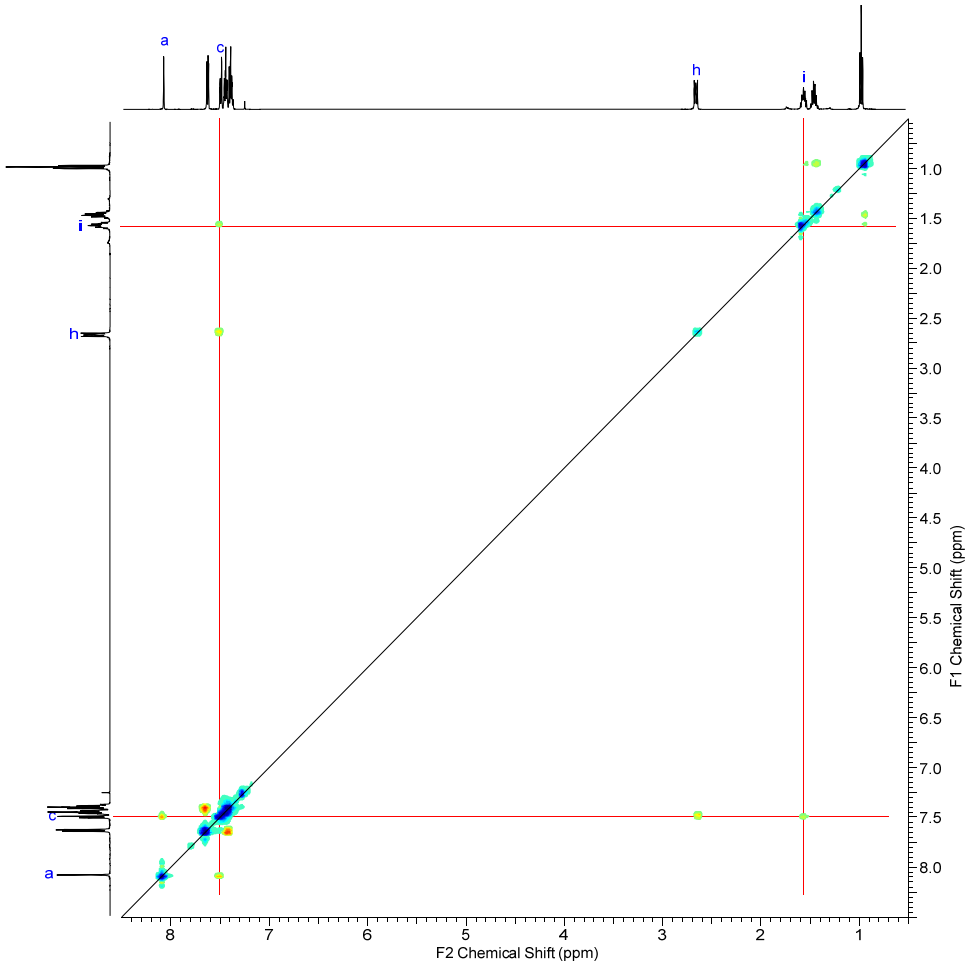
HMBC spectra of **8**

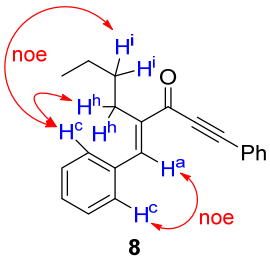


**8**

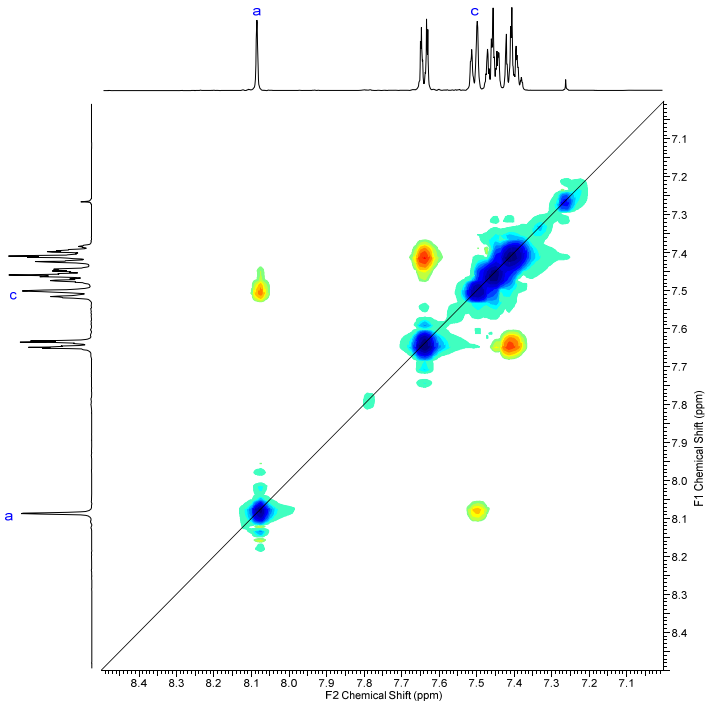
NOESY spectra of **8**



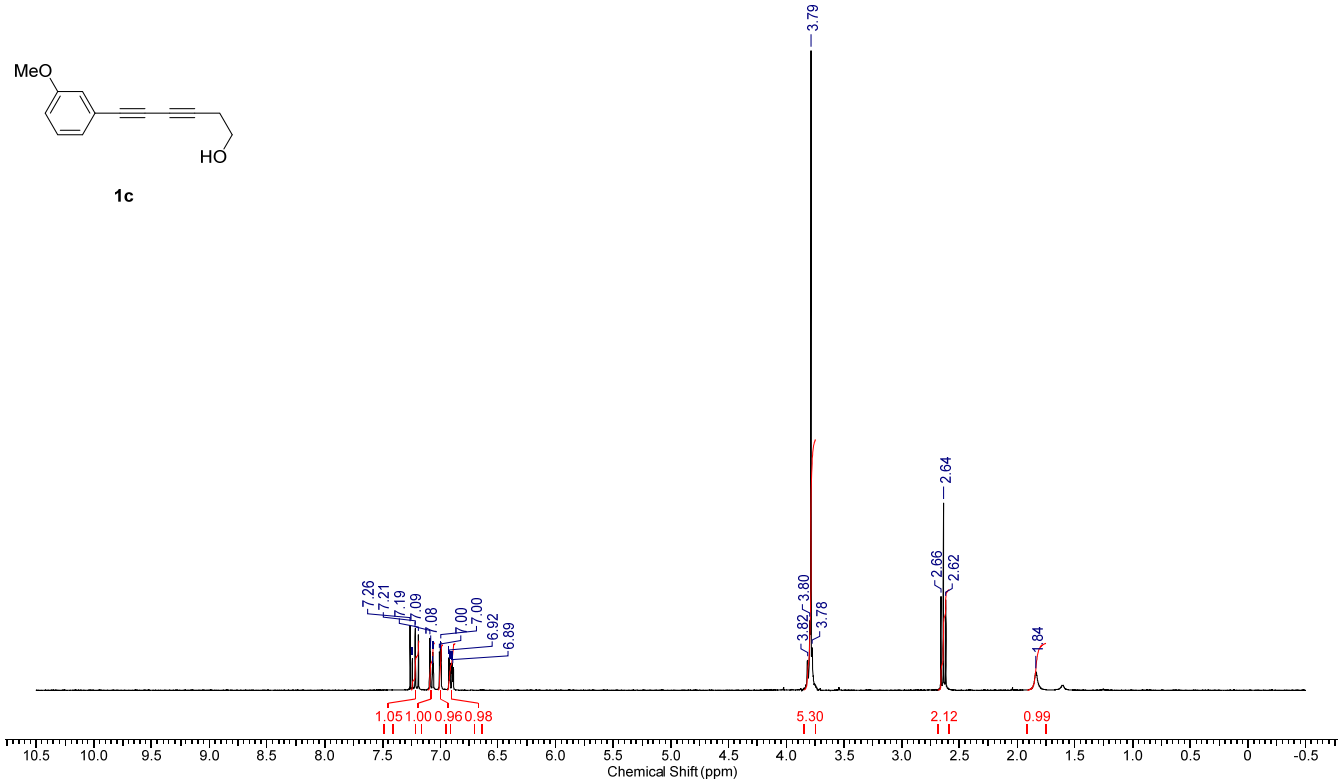

**8**

The chart on the right is an enlarged view (7.0–8.5 ppm) of the above NOESY spectrum of **8**. As shown in the enlarged view and above NOESY spectrum (red lines), NOE is observed between $H^a$ and $H^c$, between $H^c$ and $H^h$ or between $H^c$ and $H^i$. On the other hand, NOE is not observed between $H^a$ and $H^h$ or between $H^a$ and $H^i$. Since $H^a$, $H^c$, $H^h$ and $H^i$ are assigned as each proton in the structure of **8** on the upper right, the stereochemistry of **8** was determined as the illustrated structure.

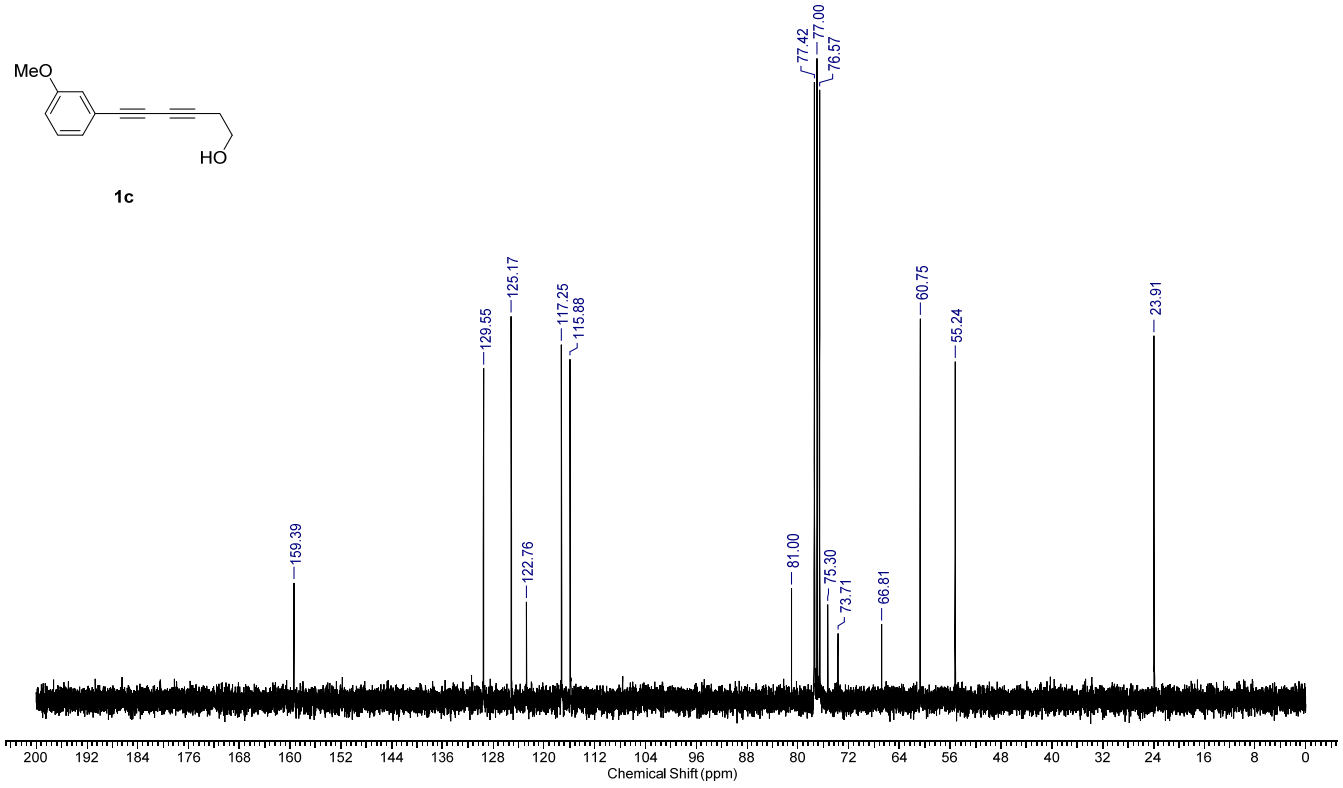


## *[1]H and [13]C NMR spectra of new compounds*

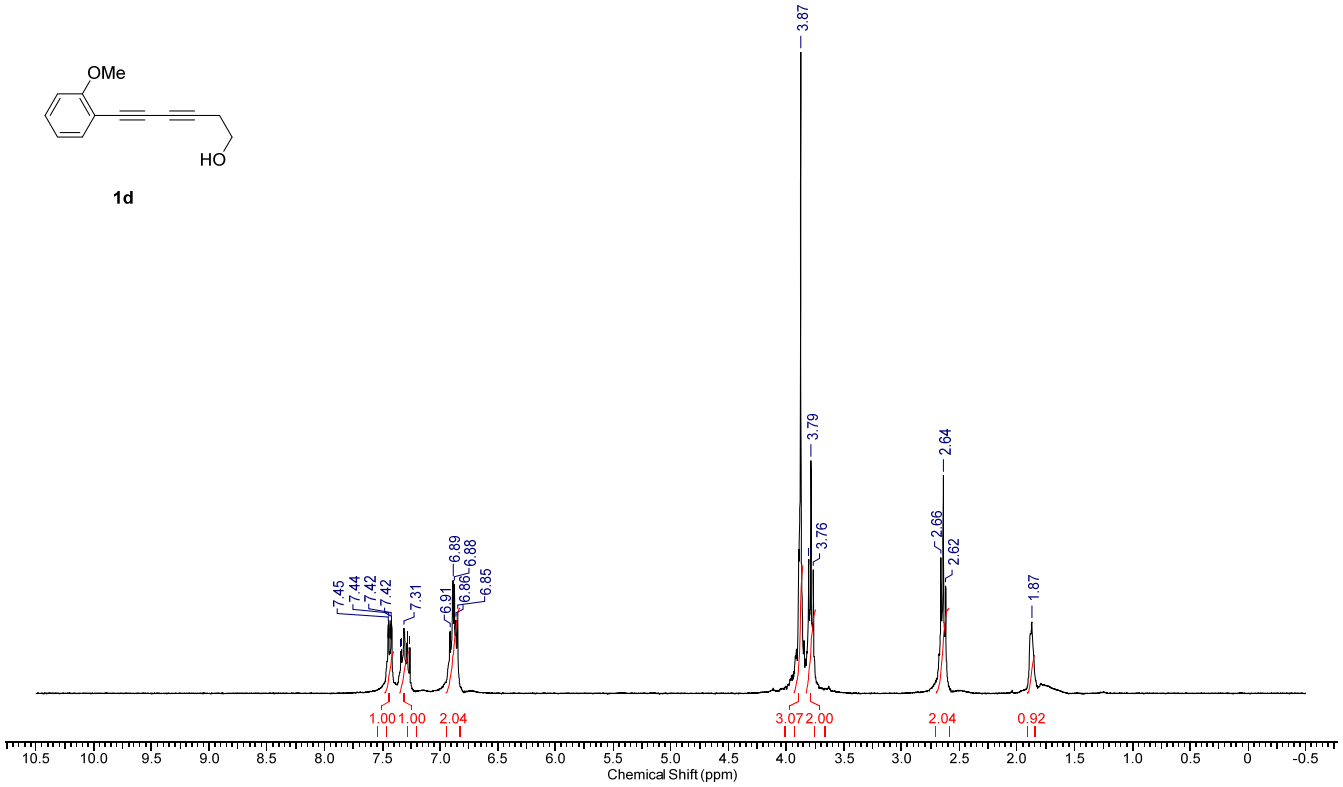
[1]H NMR of **1c**



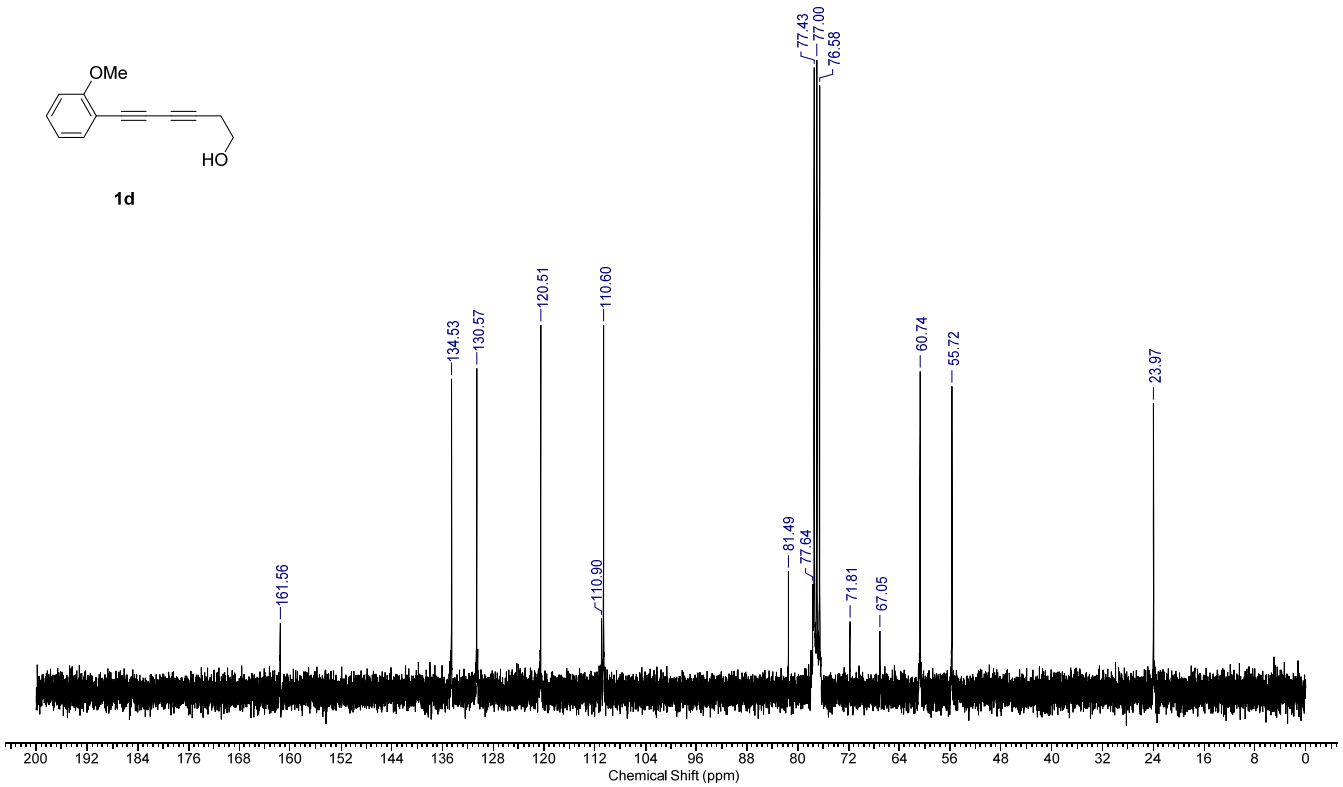

[13]C NMR of **1c**



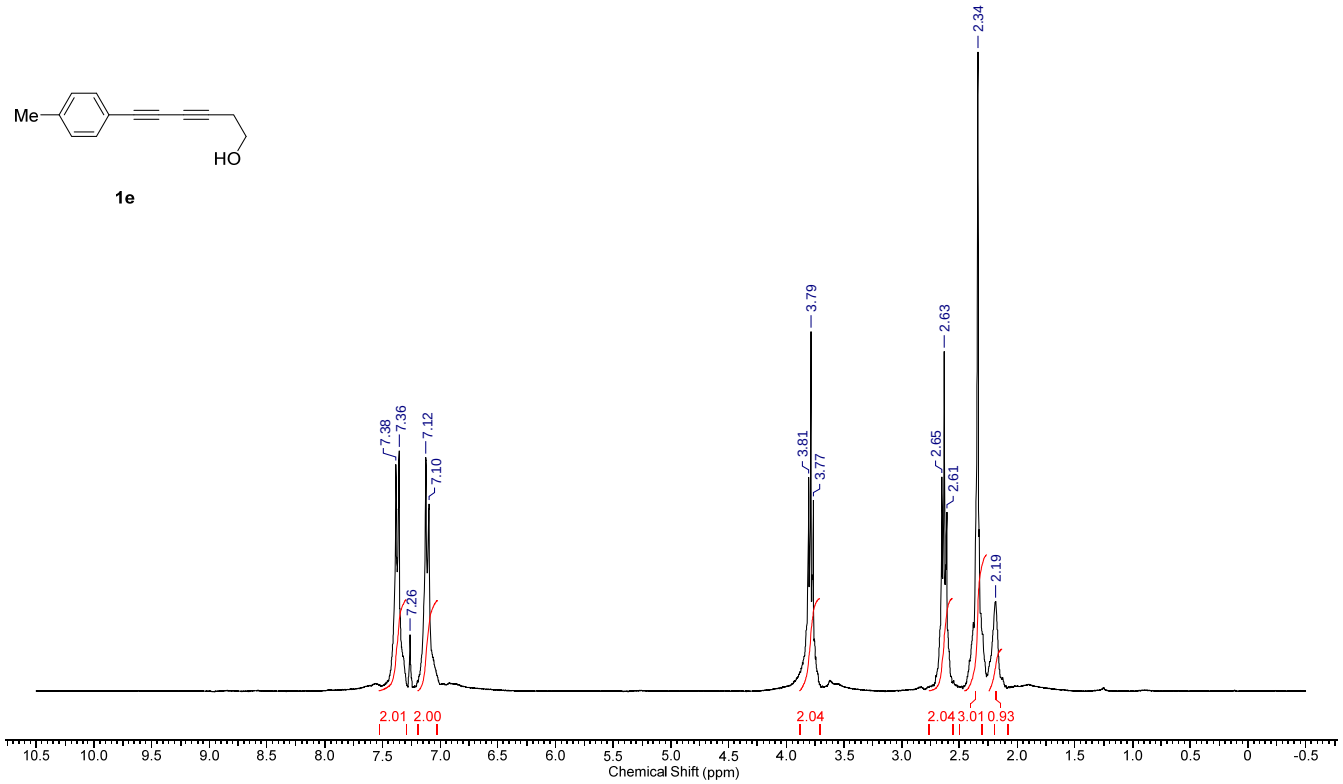
$^{1}$H NMR of **1d**



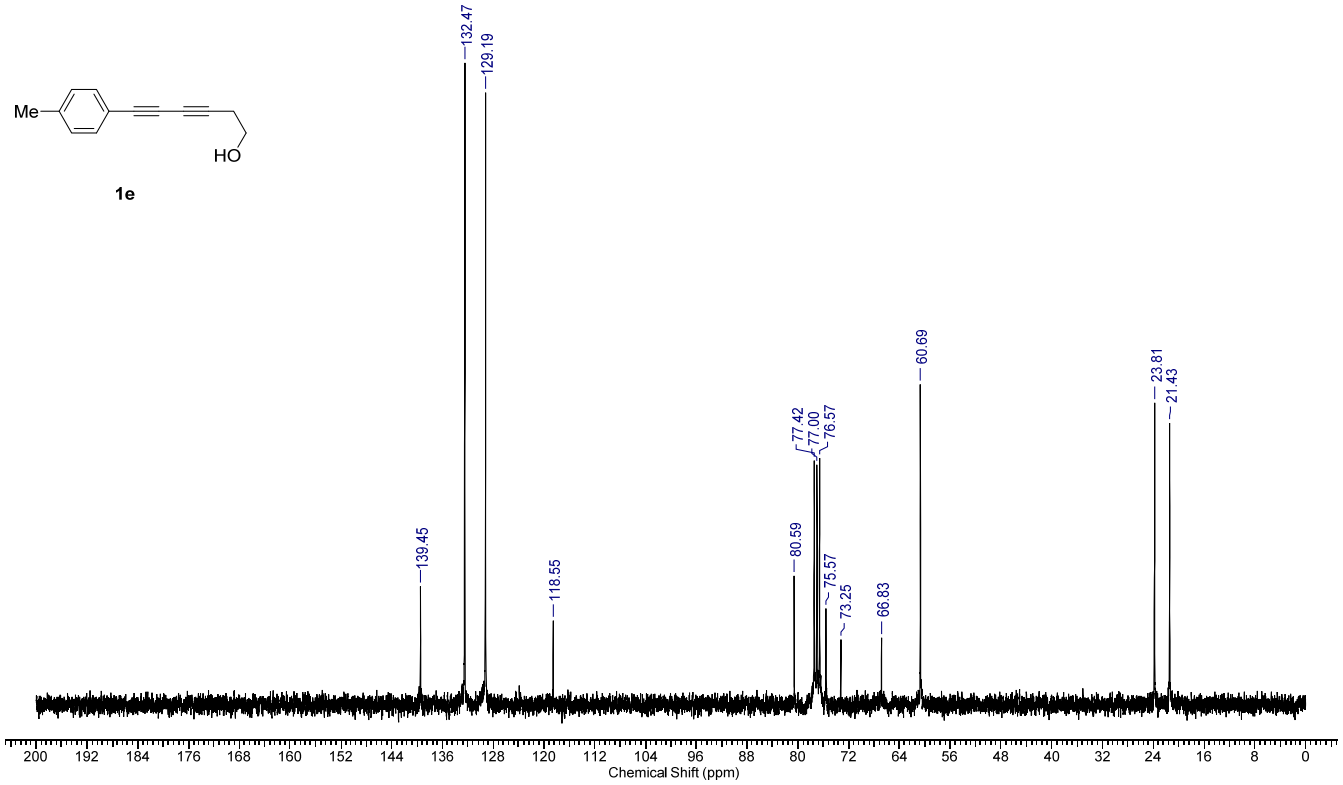

$^{13}$C NMR of **1d**



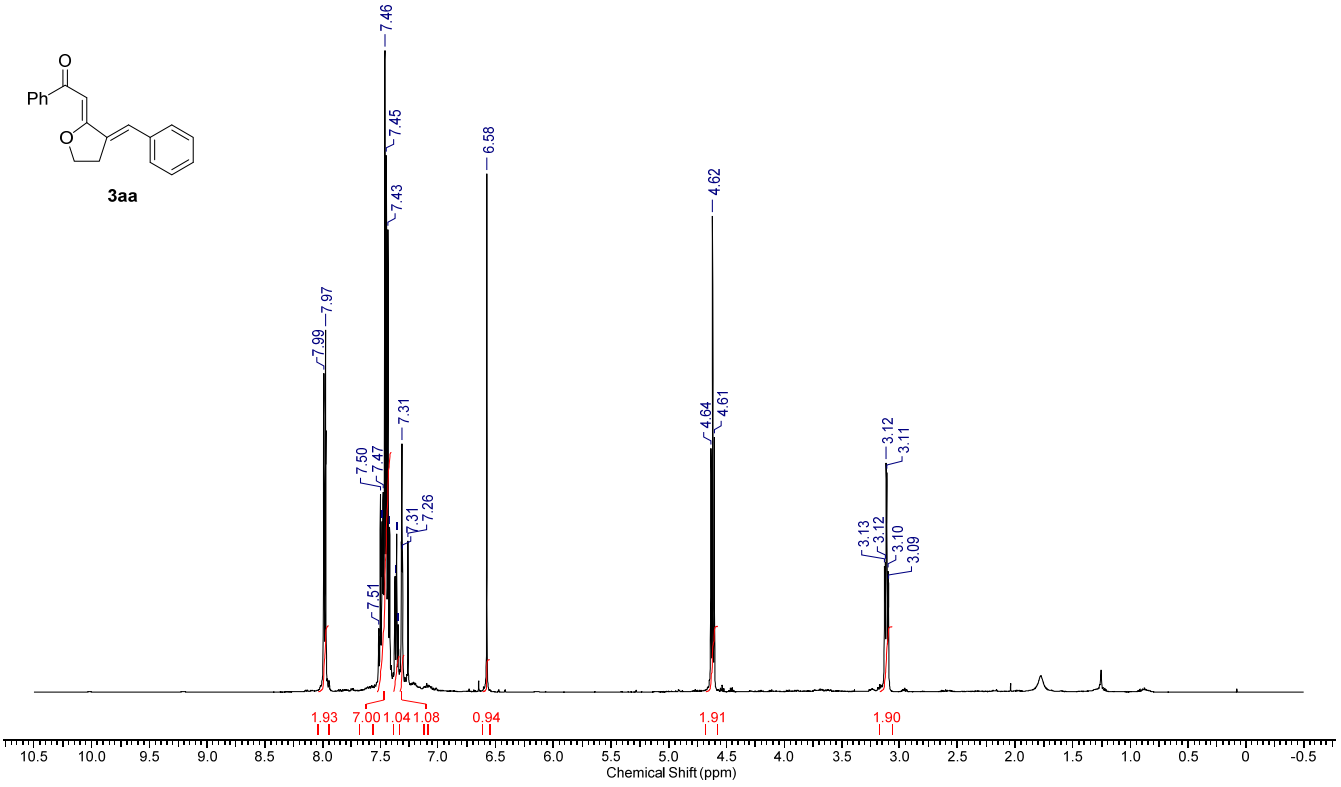
$^{1}$H NMR of **1e**



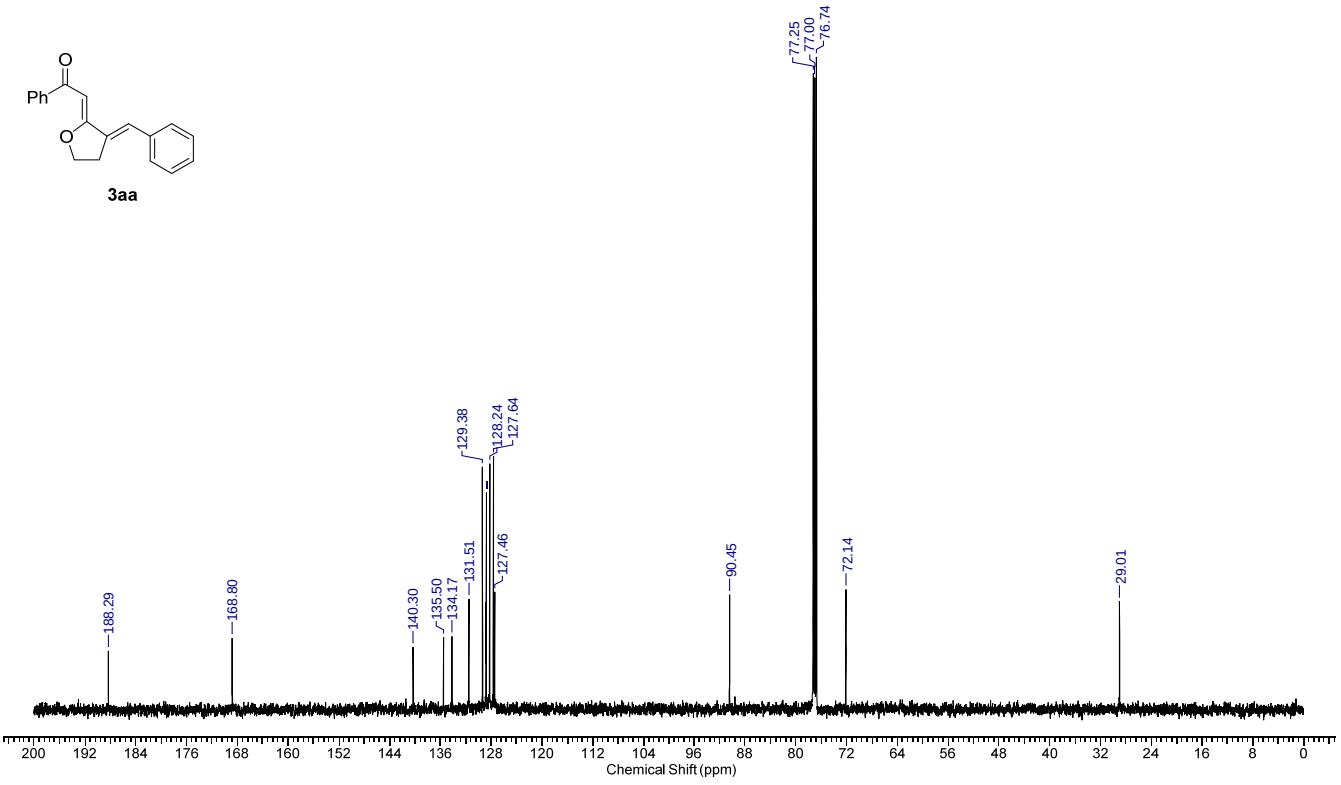

$^{13}$C NMR of **1e**



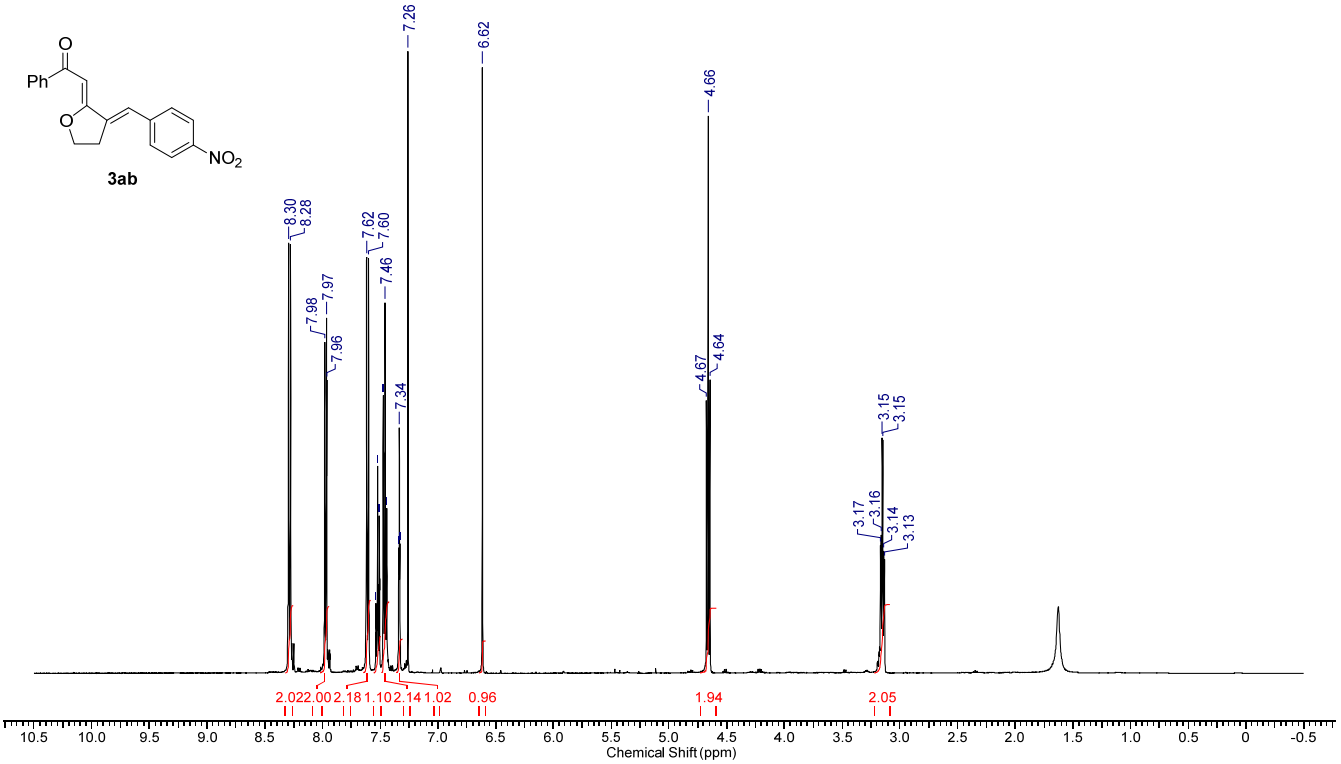
$^{1}$H NMR of **3aa**



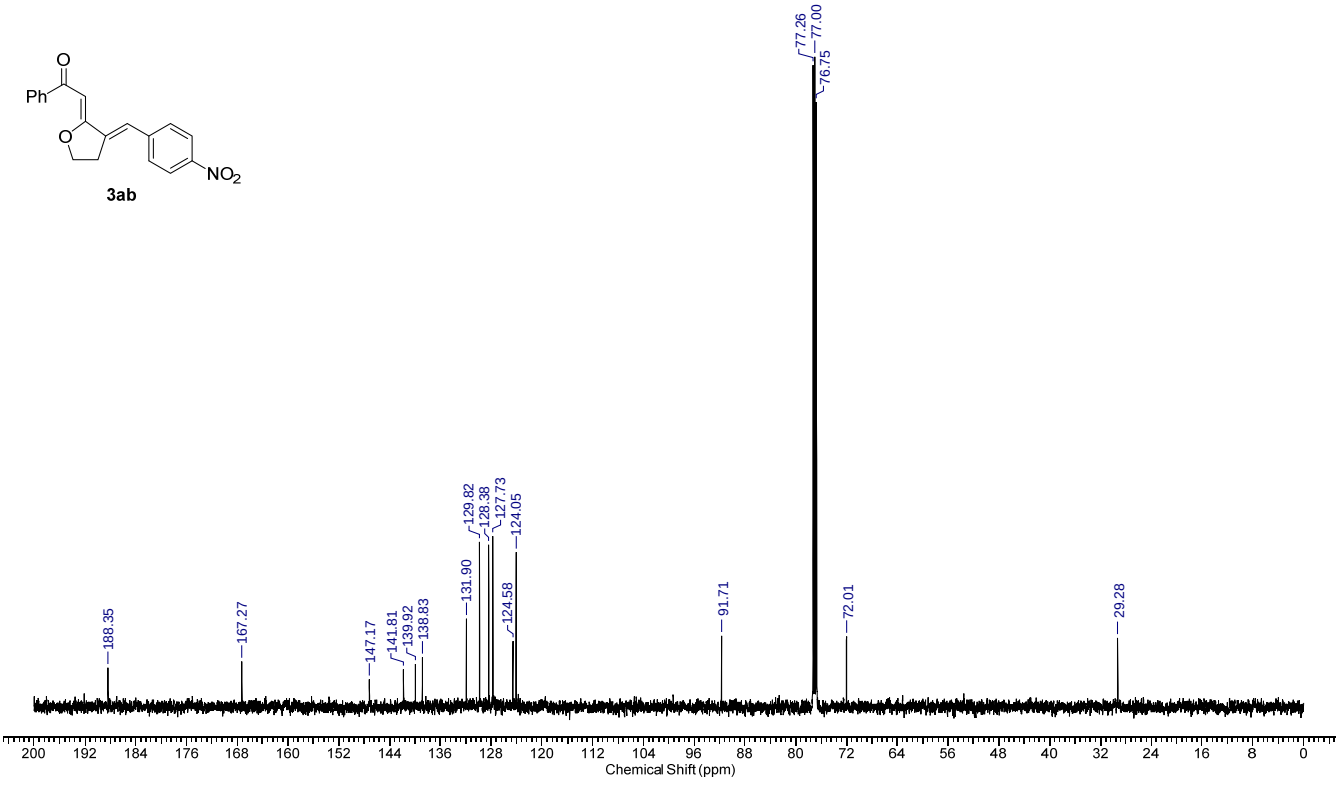

$^{13}$C NMR of **3aa**



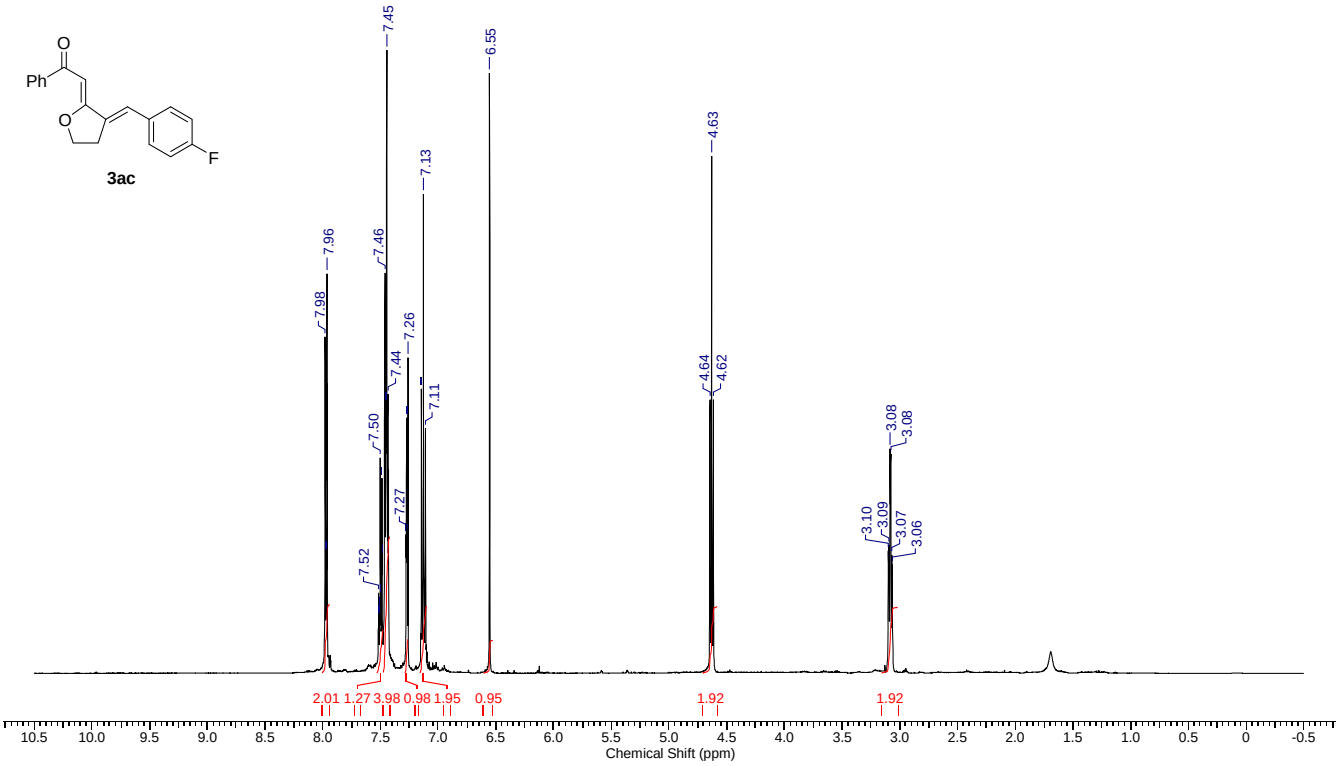
$^{1}$H NMR of **3ab**



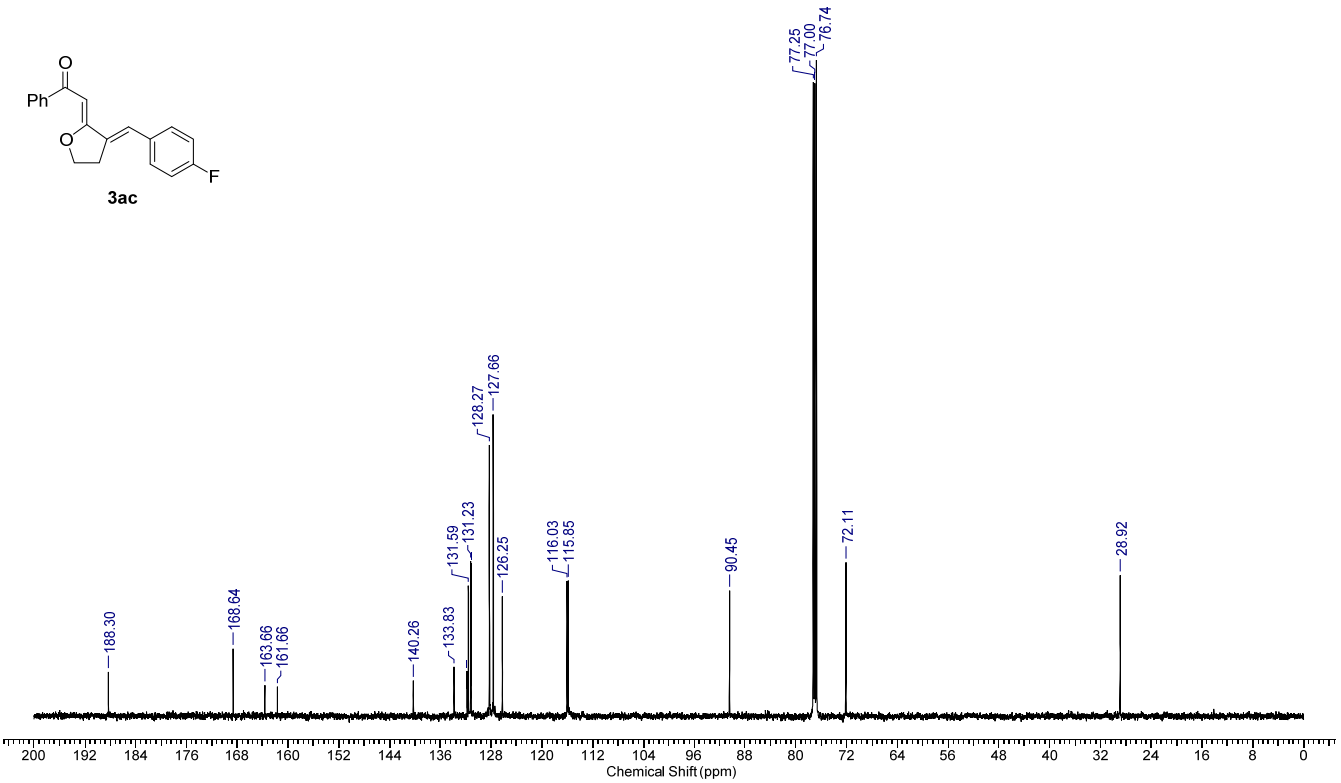

$^{13}$C NMR of **3ab**



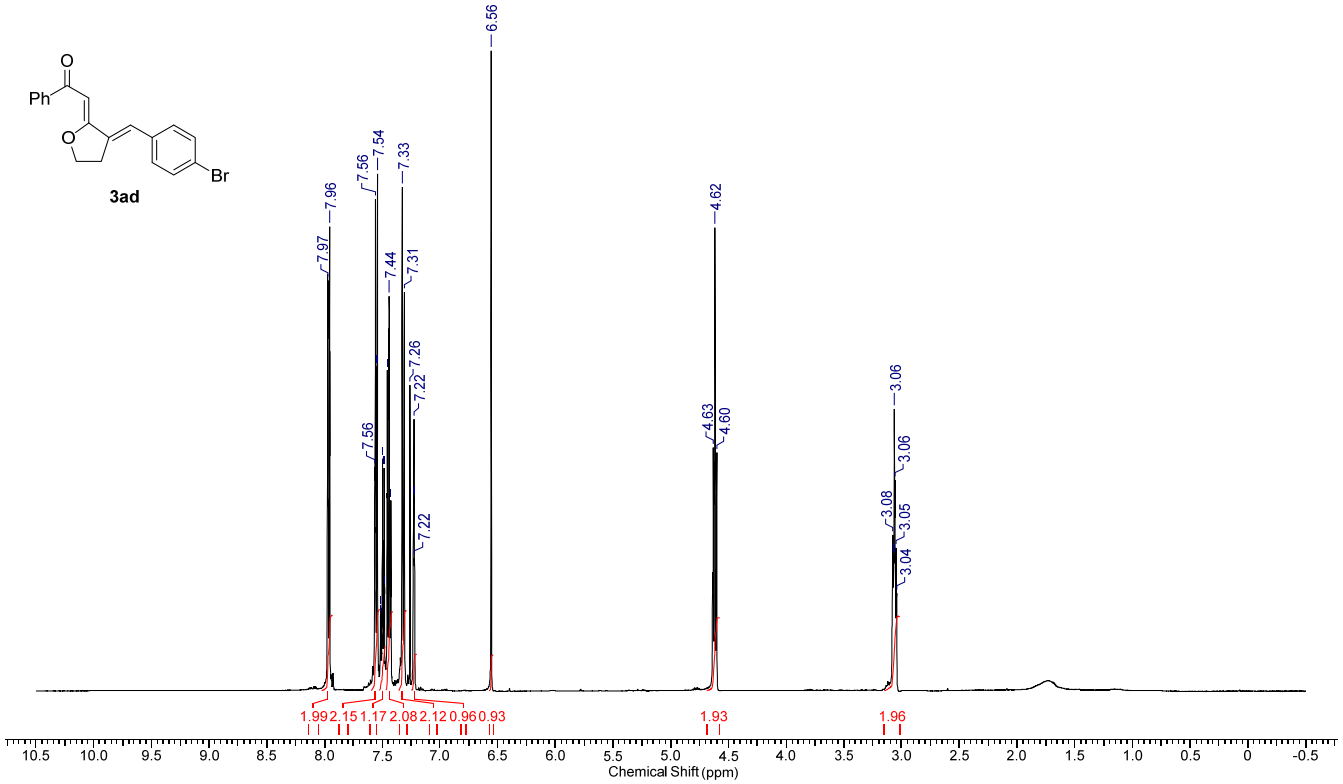
$^{1}$H NMR of **3ac**



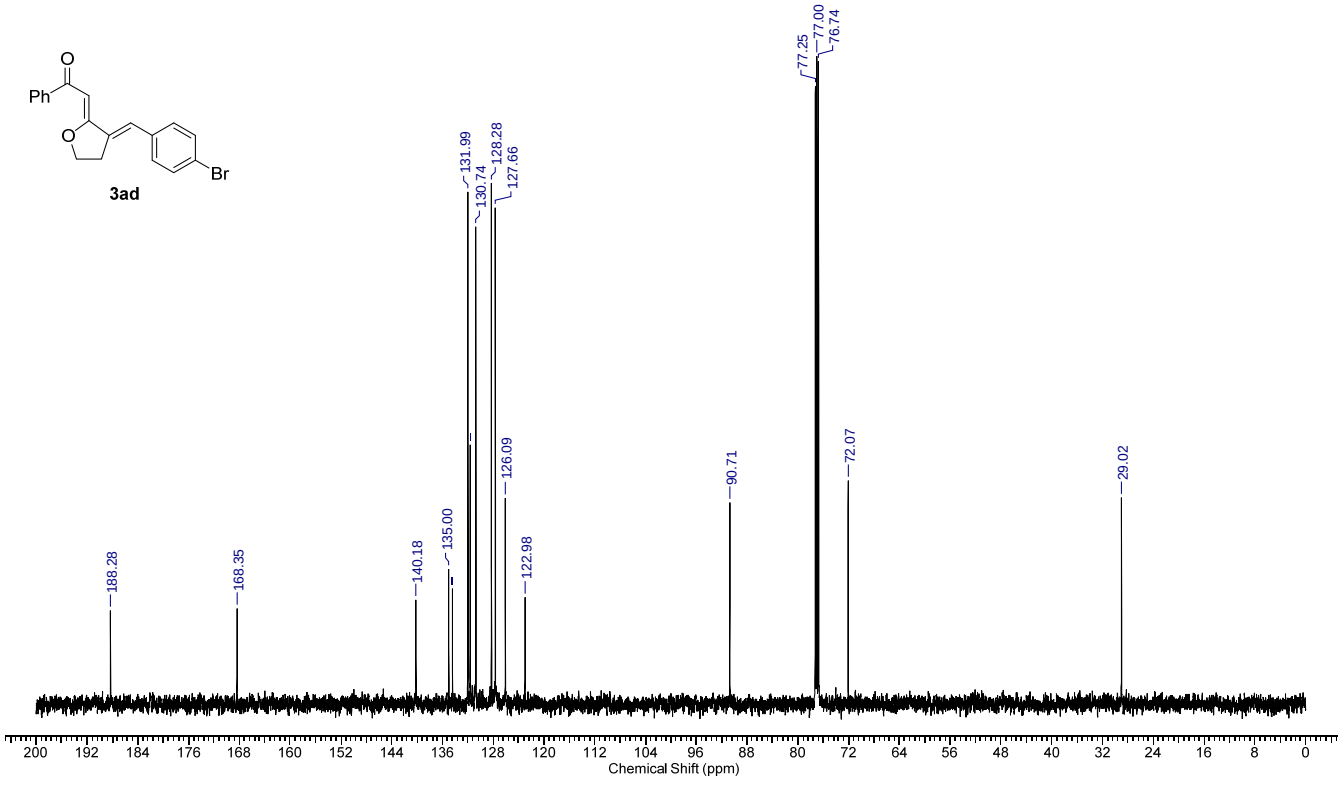

$^{13}$C NMR of **3ac**



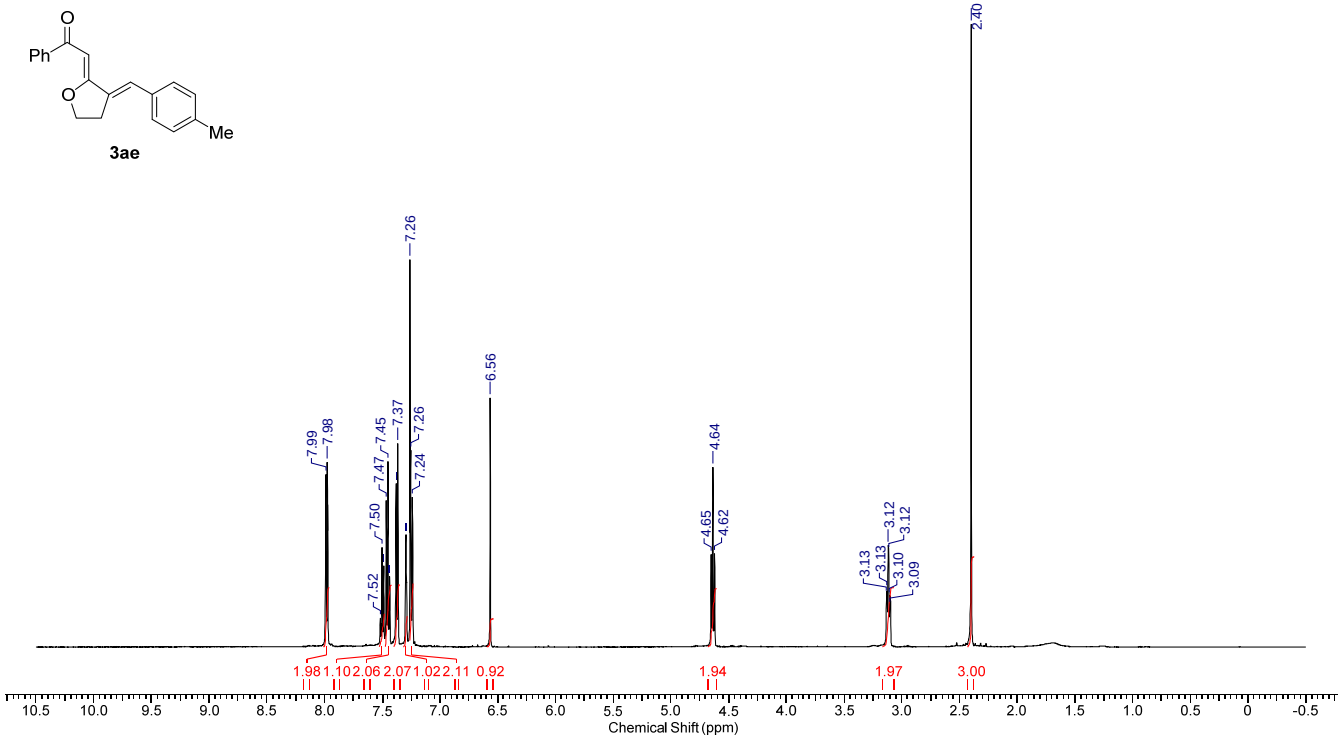
$^{1}$H NMR of **3ad**



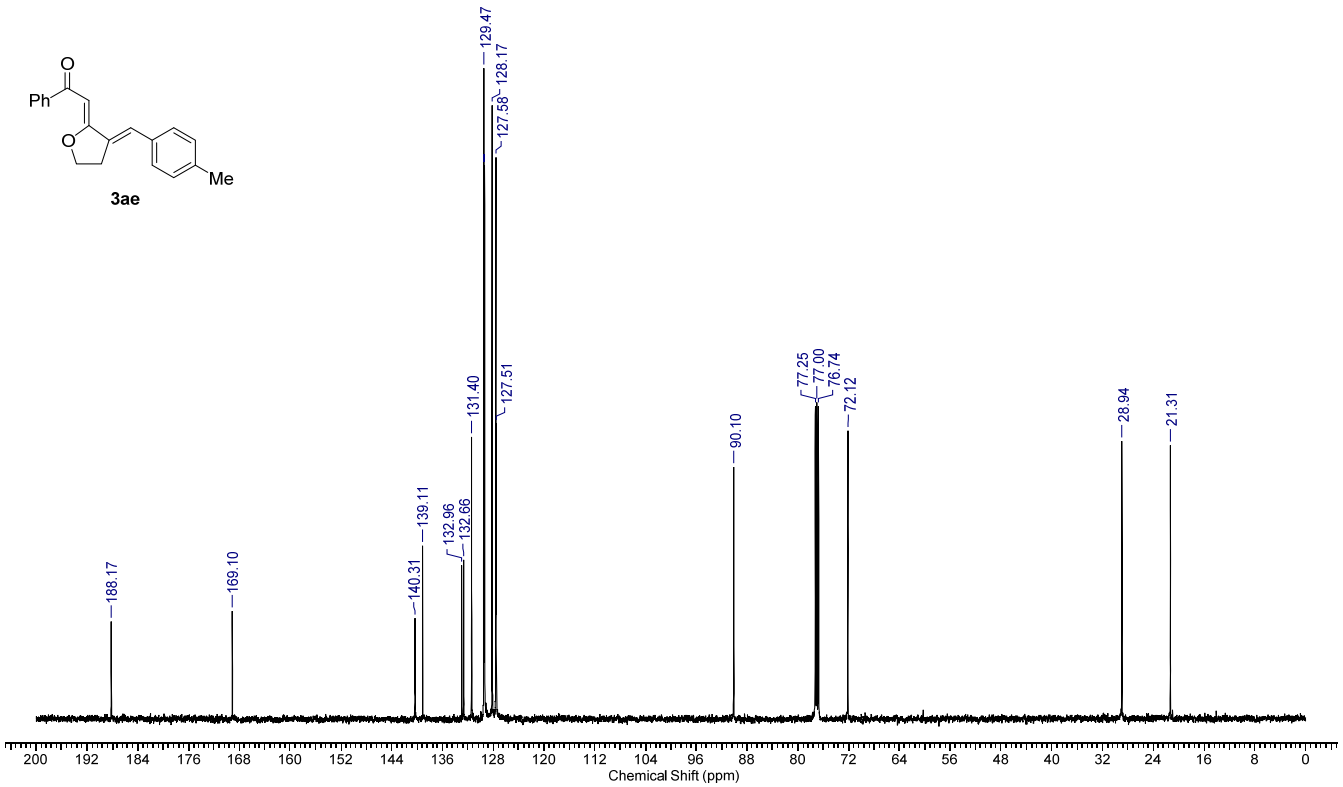

$^{13}$C NMR of **3ad**



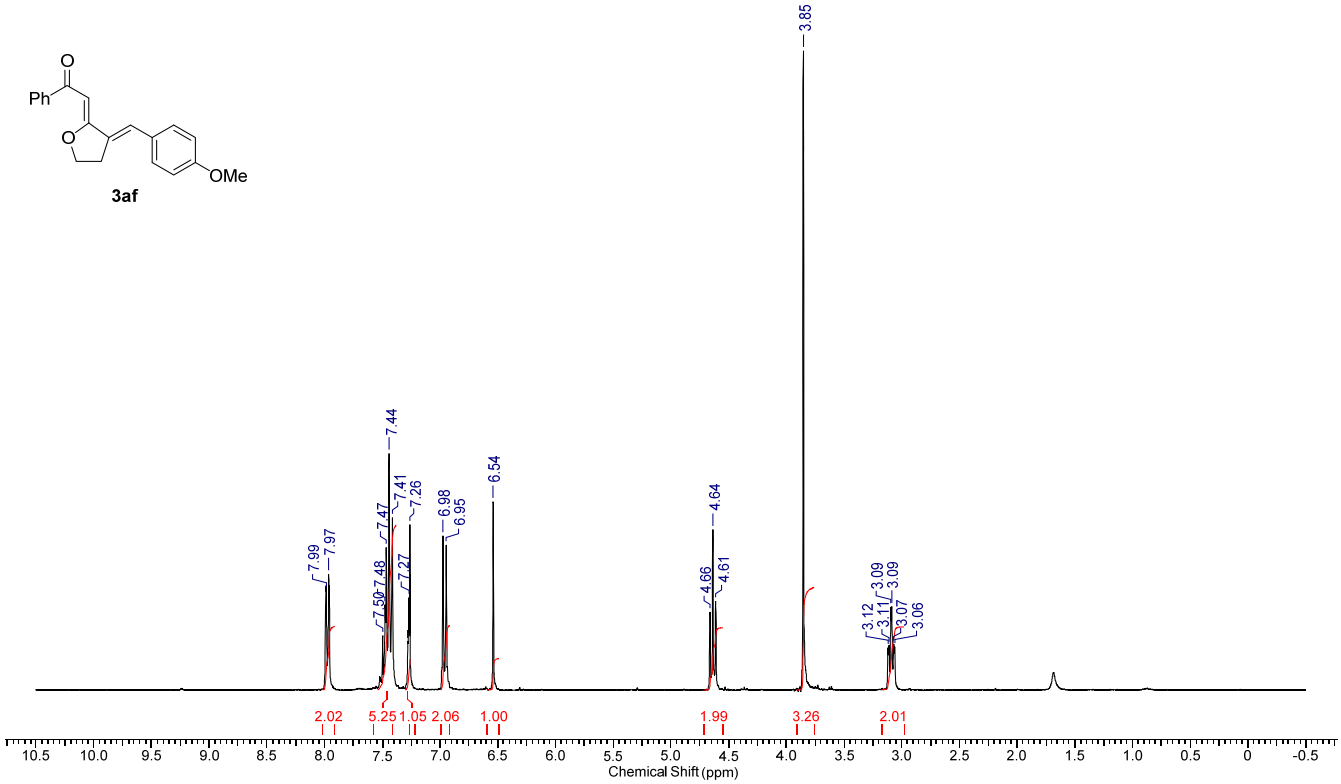
$^{1}$H NMR of **3ae**



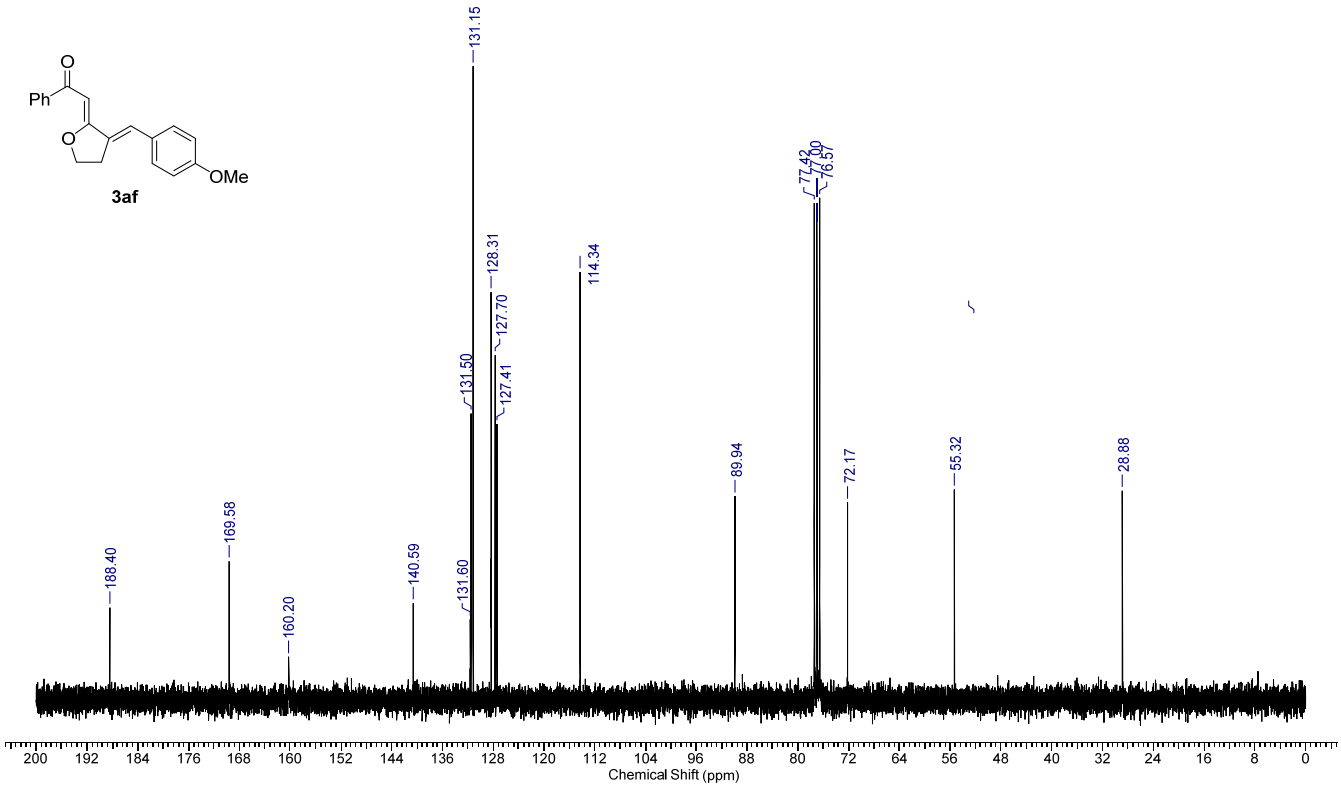

$^{13}$C NMR of **3ae**



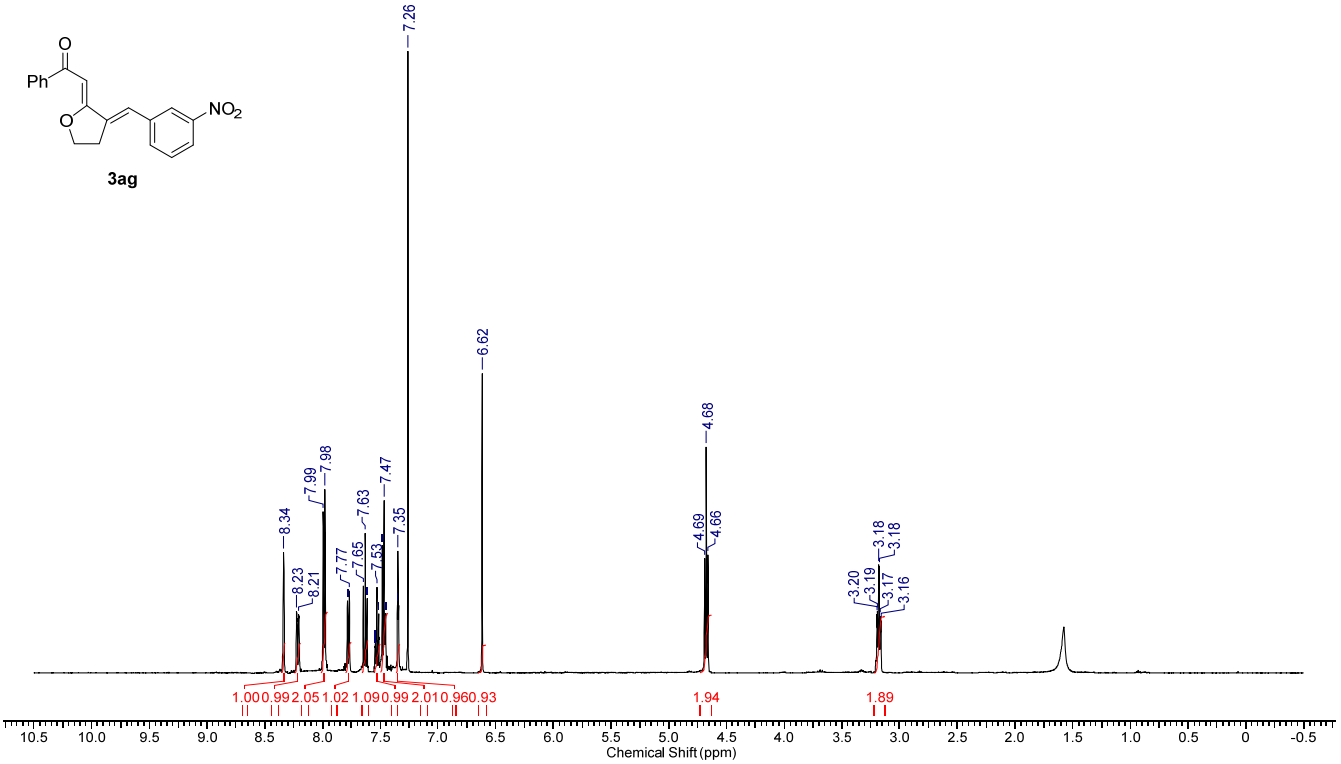
$^{1}$H NMR of **3af**




$^{13}$C NMR of **3af**



$^{1}$H NMR of **3ag**

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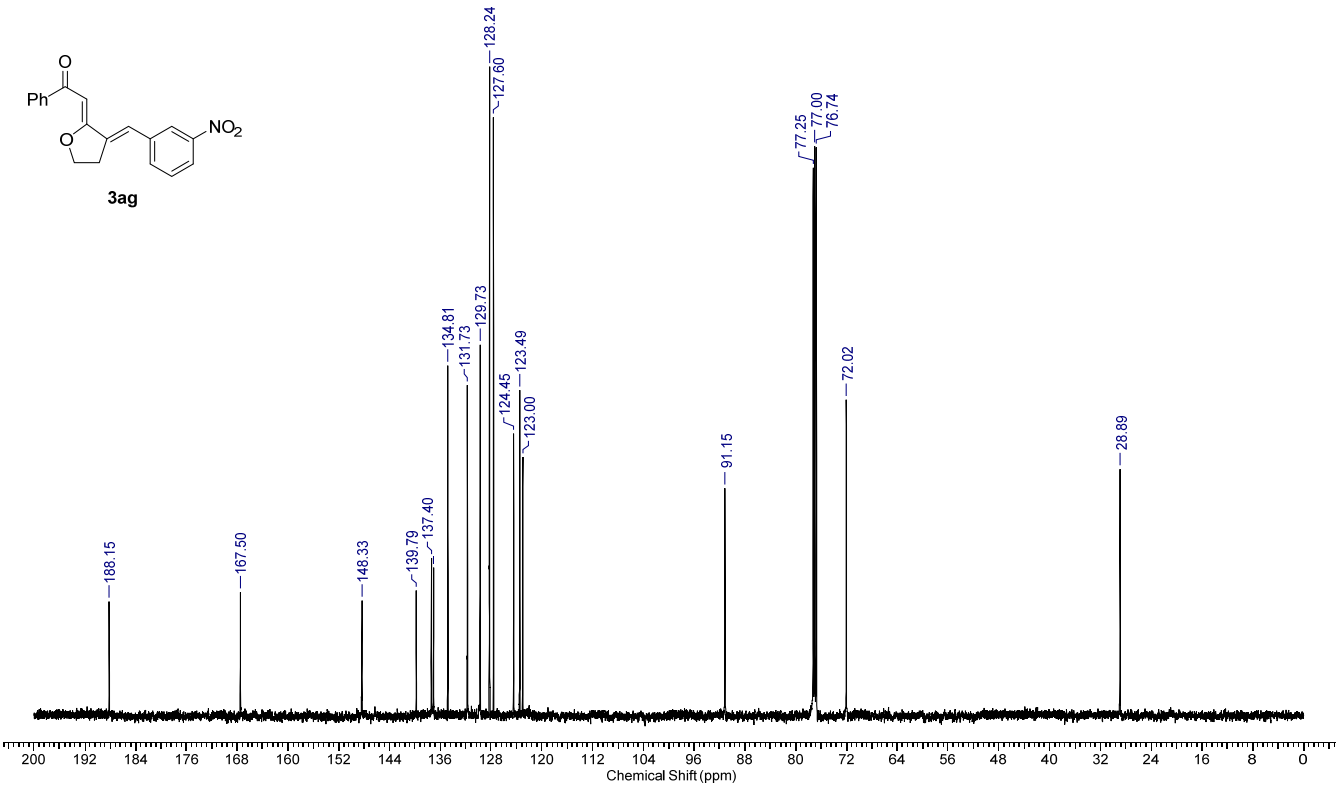
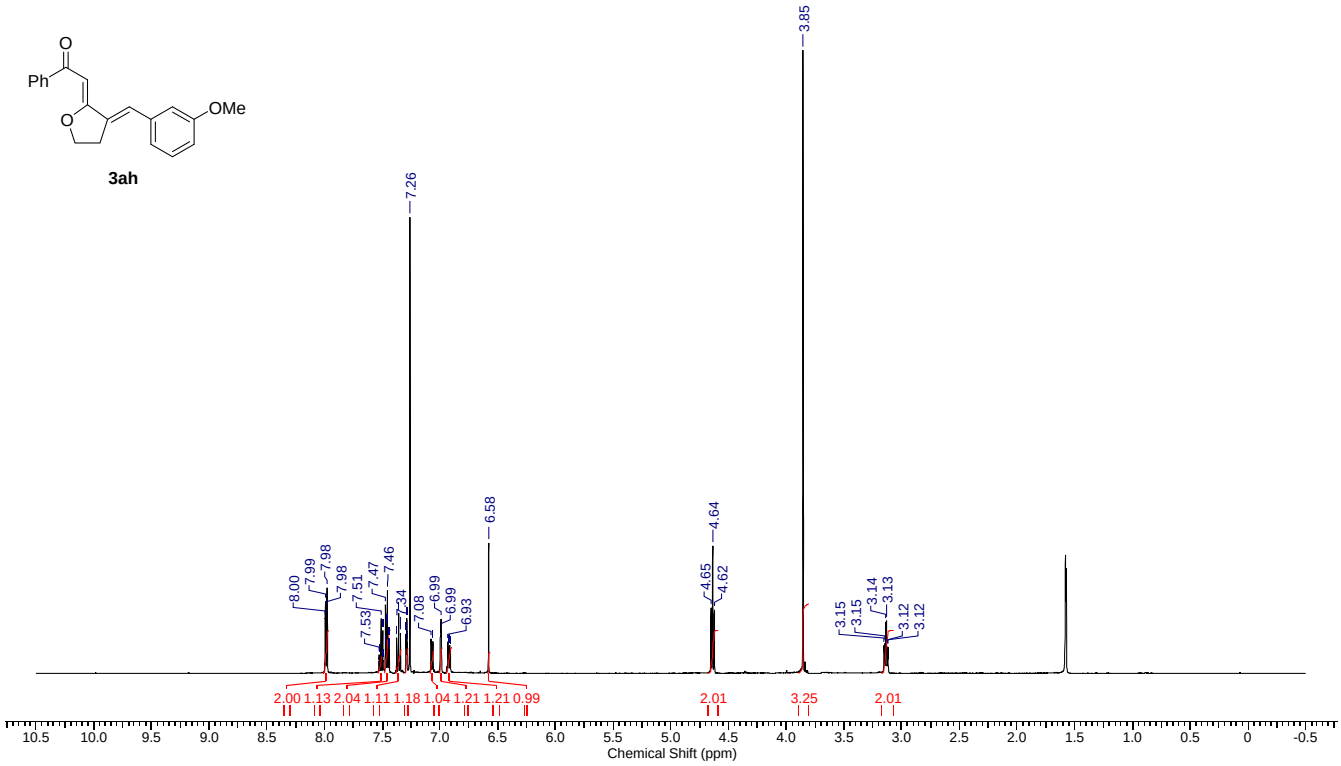
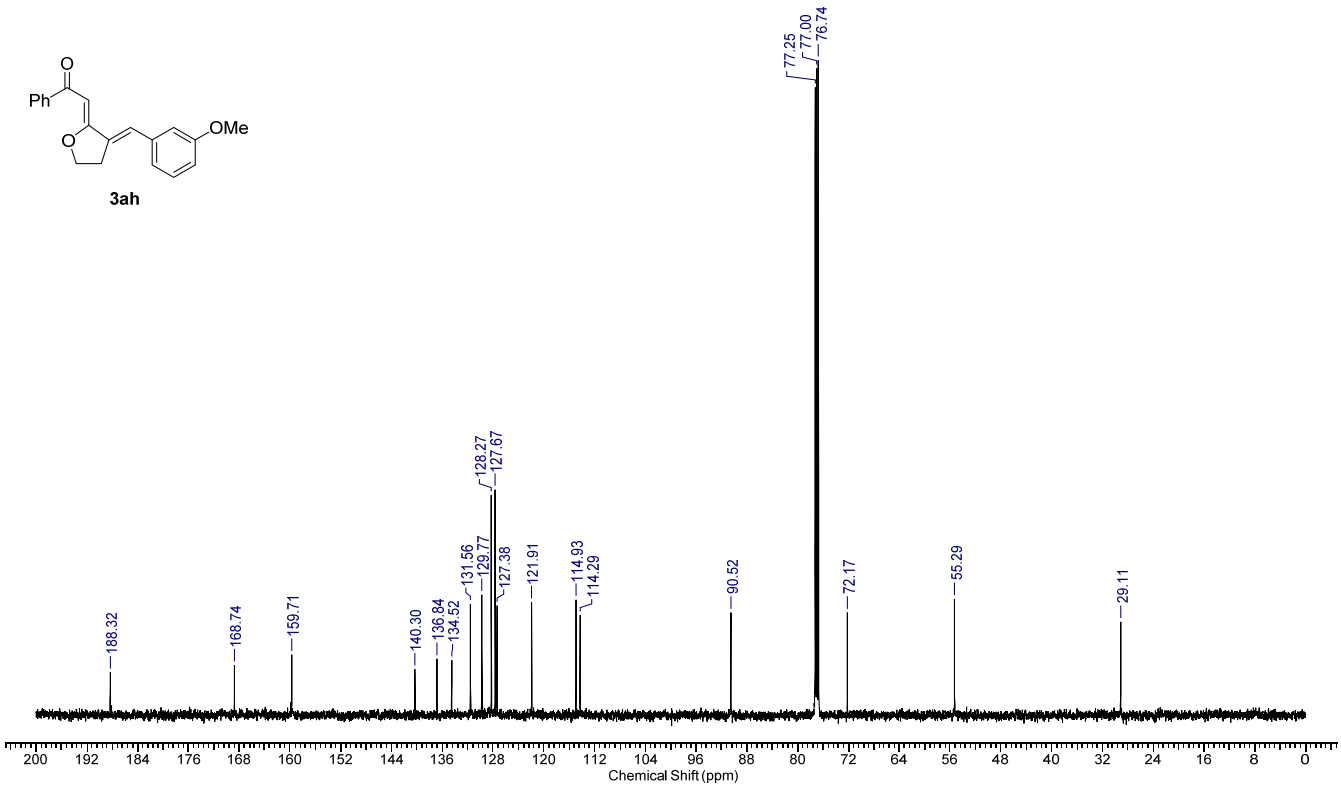


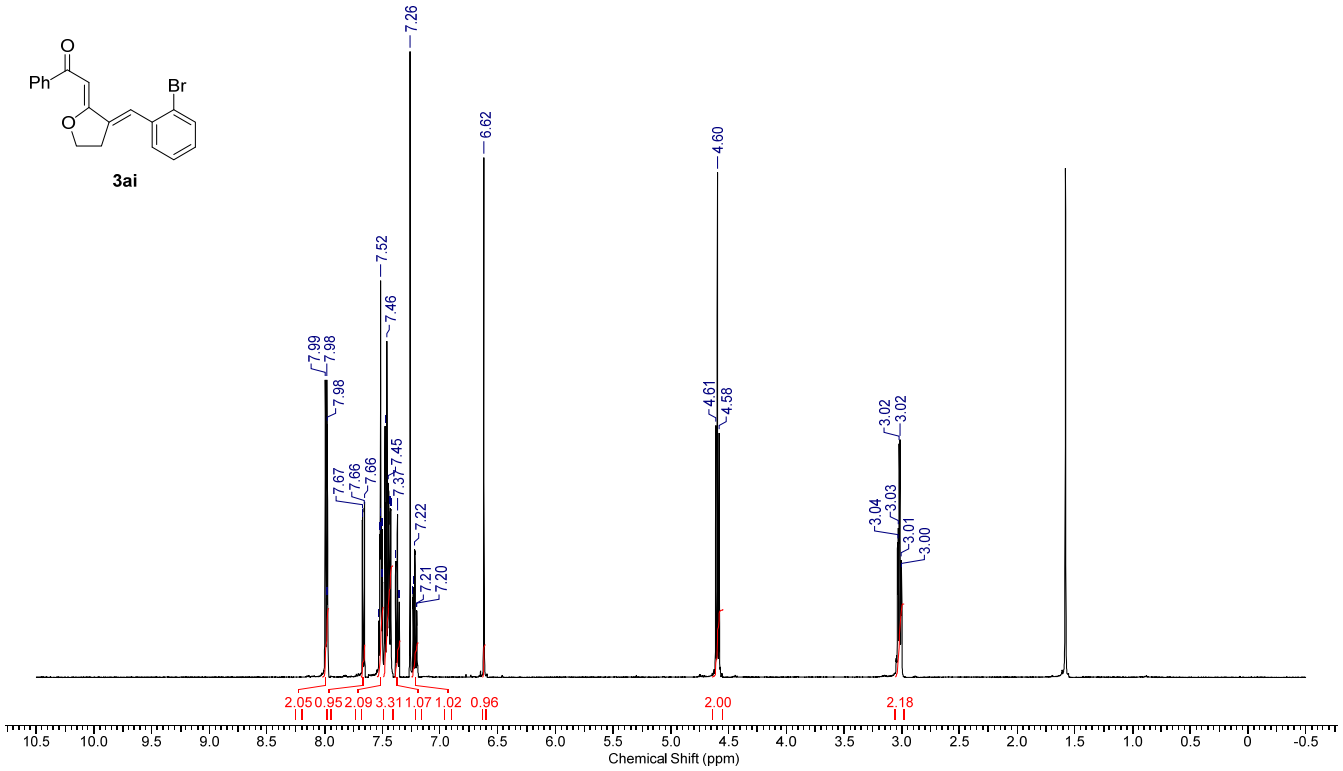
$^{1}$H NMR of **3ah**



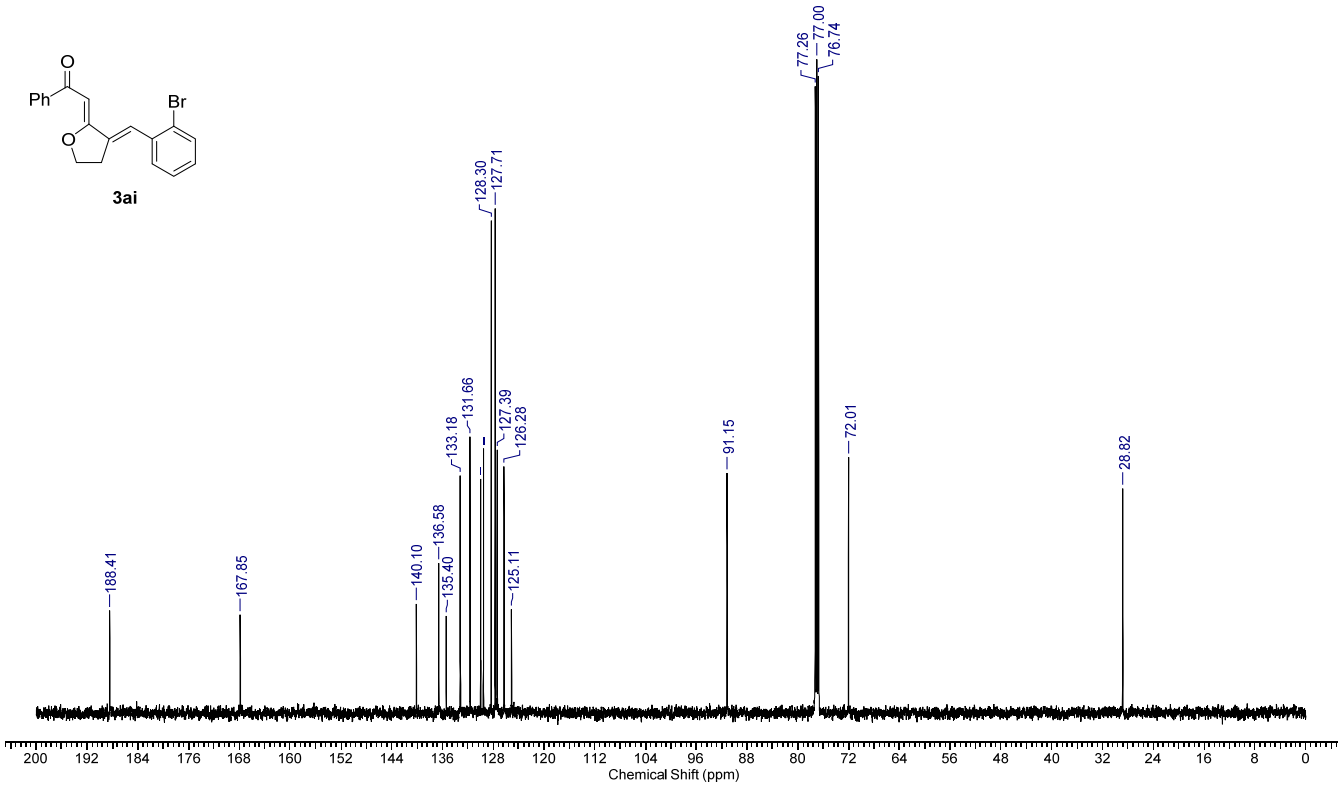

$^{13}$C NMR of **3ah**



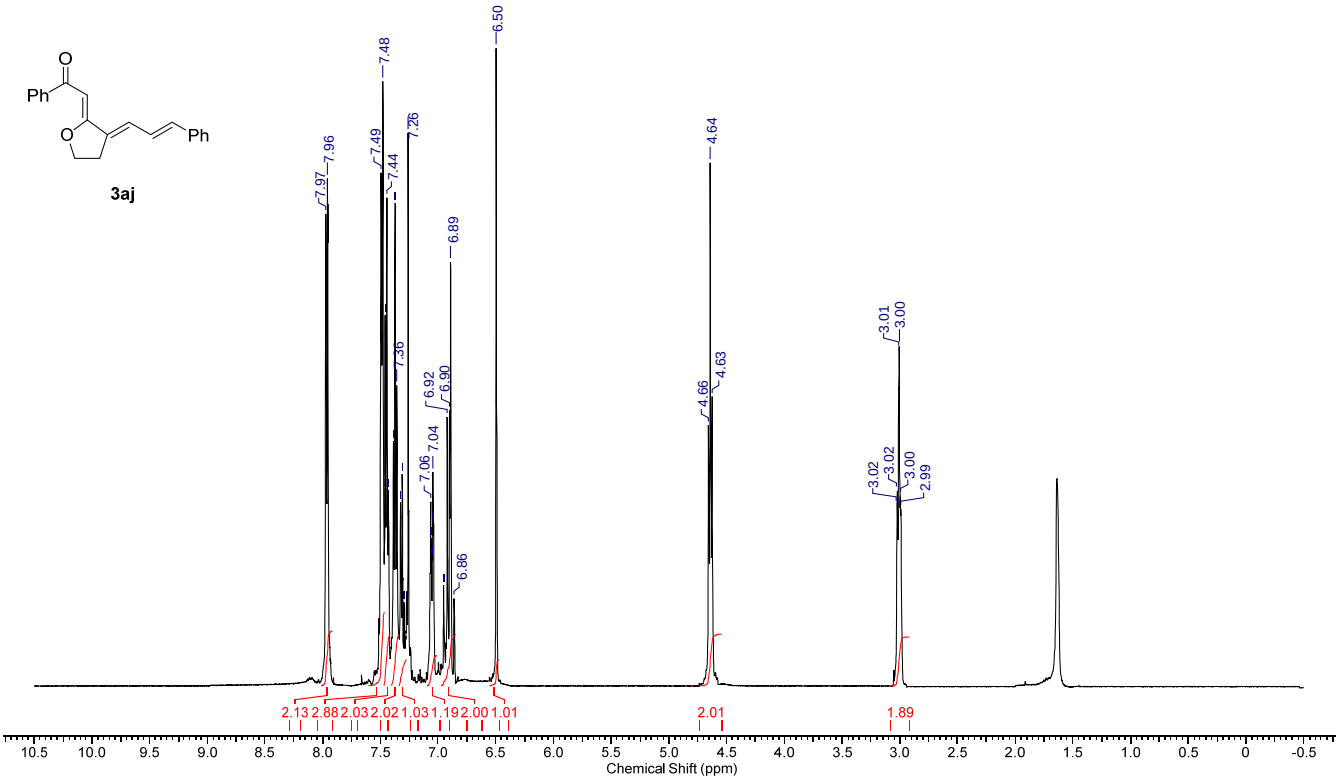
$^{1}$H NMR of **3ai**



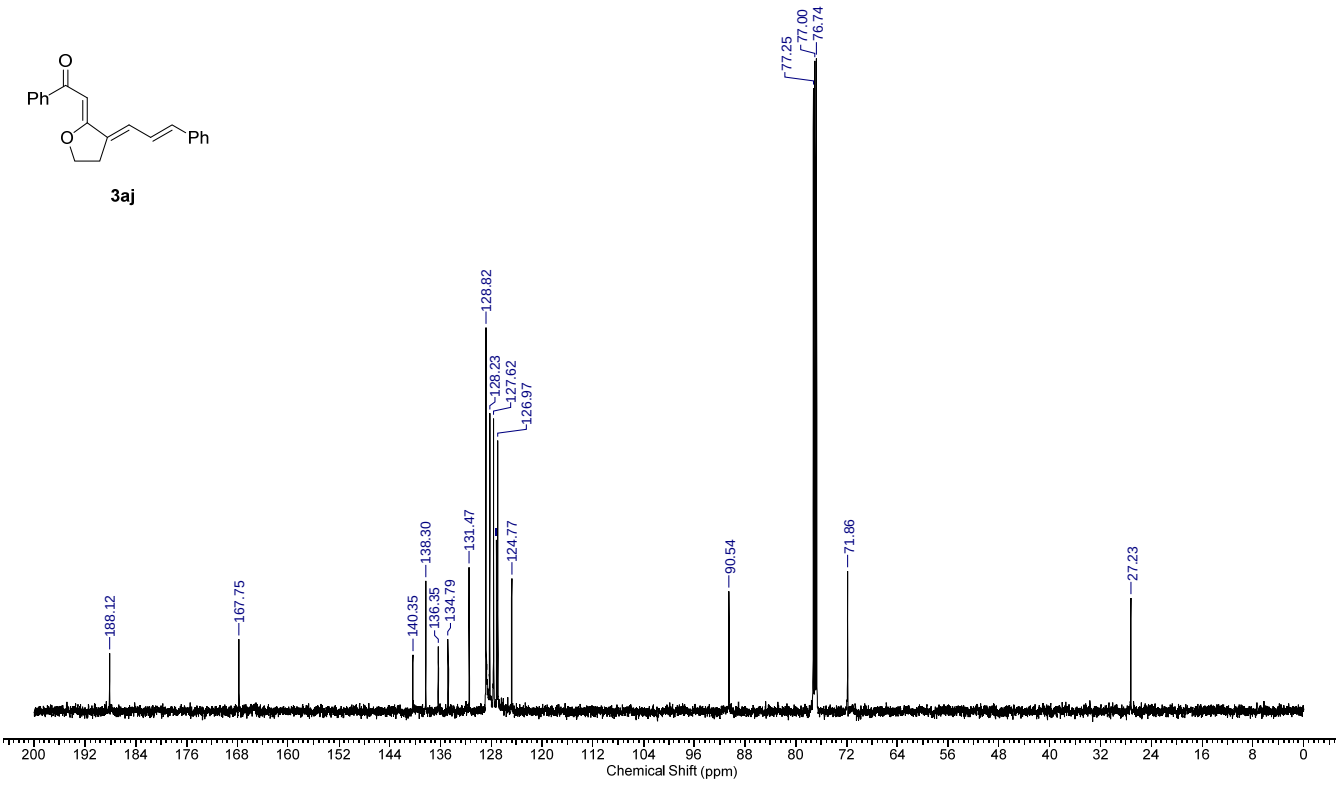

$^{13}$C NMR of **3ai**



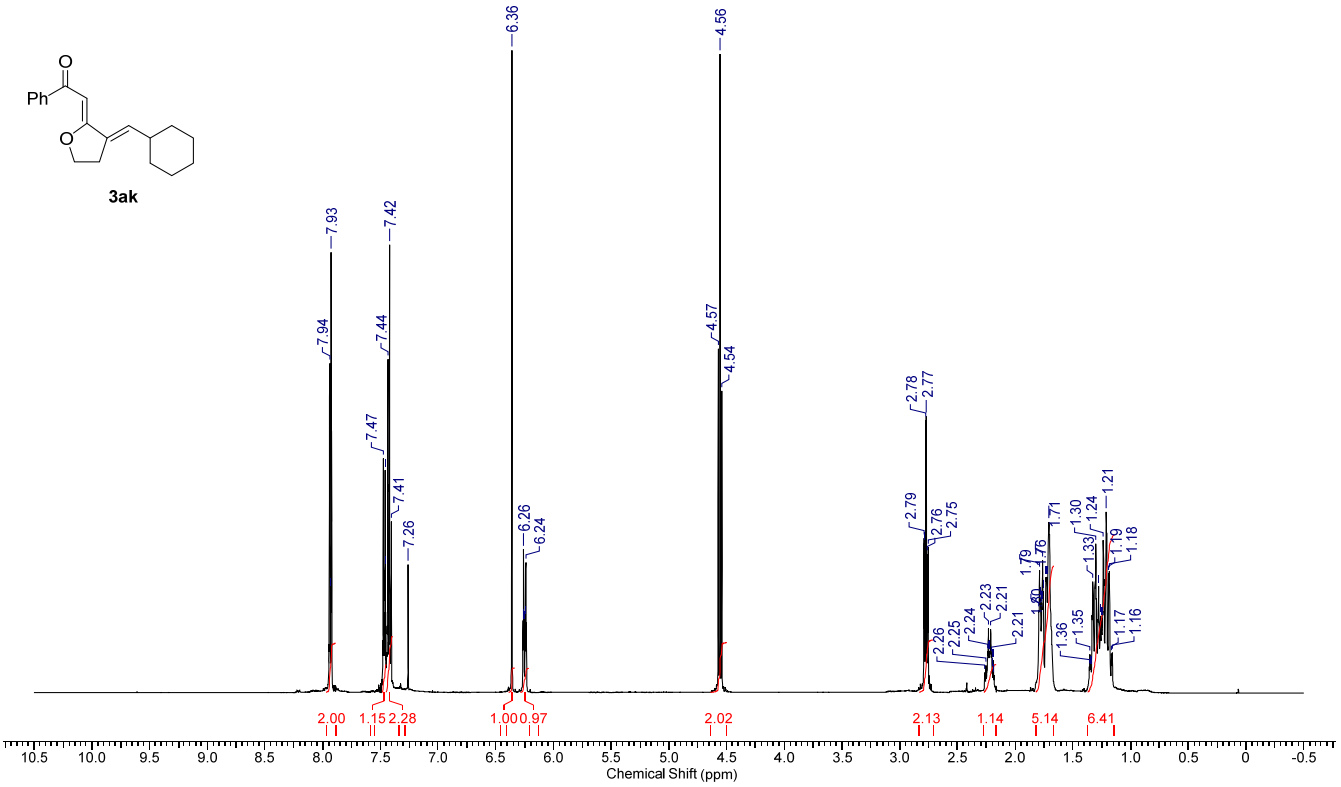
$^{1}$H NMR of **3aj**



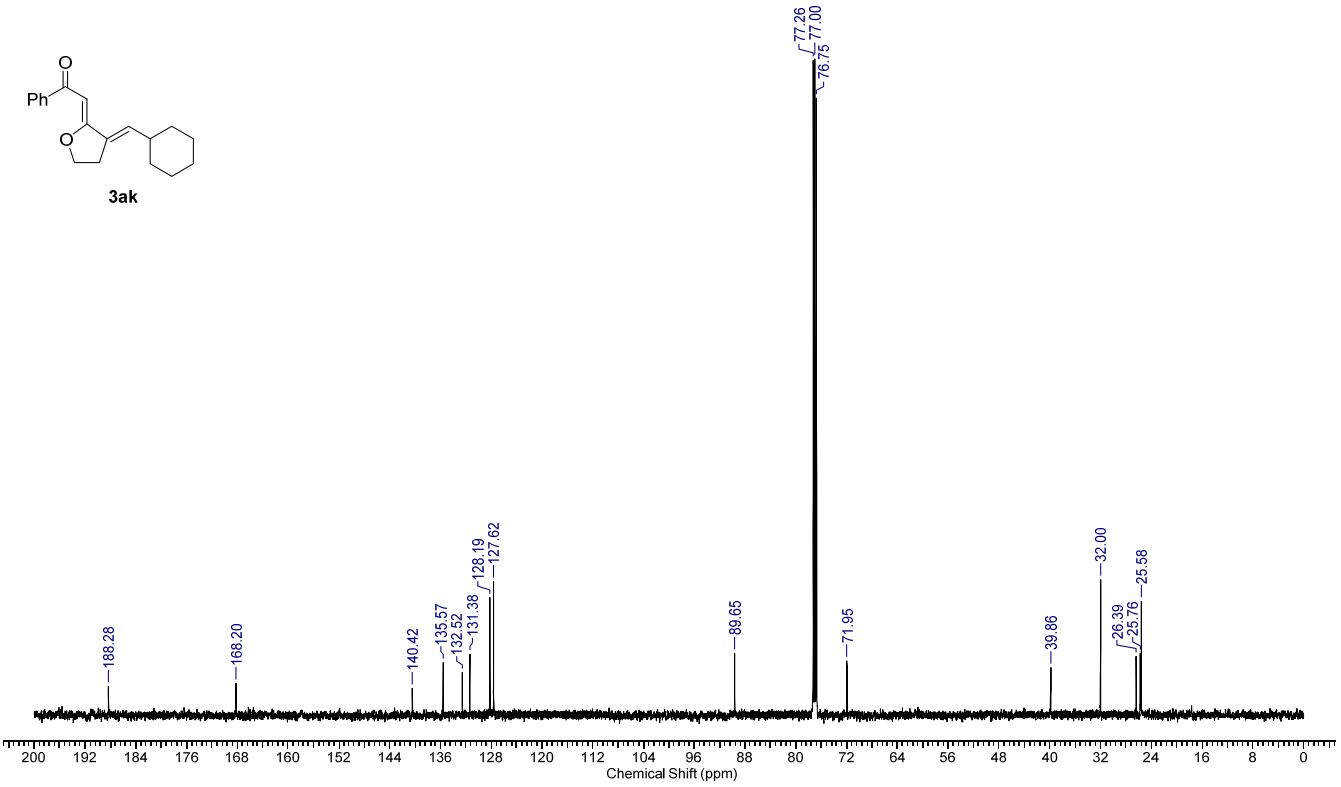

$^{13}$C NMR of **3aj**



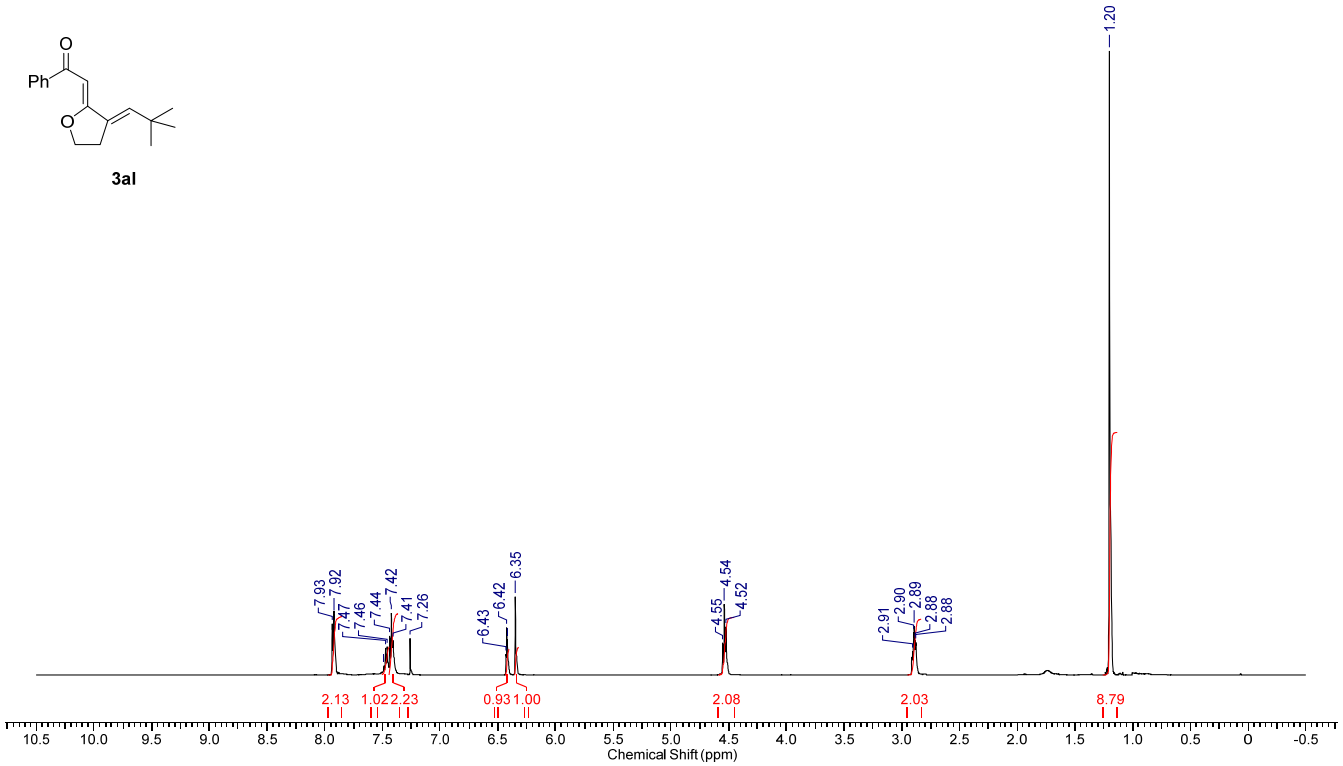
$^{1}$H NMR of **3ak**



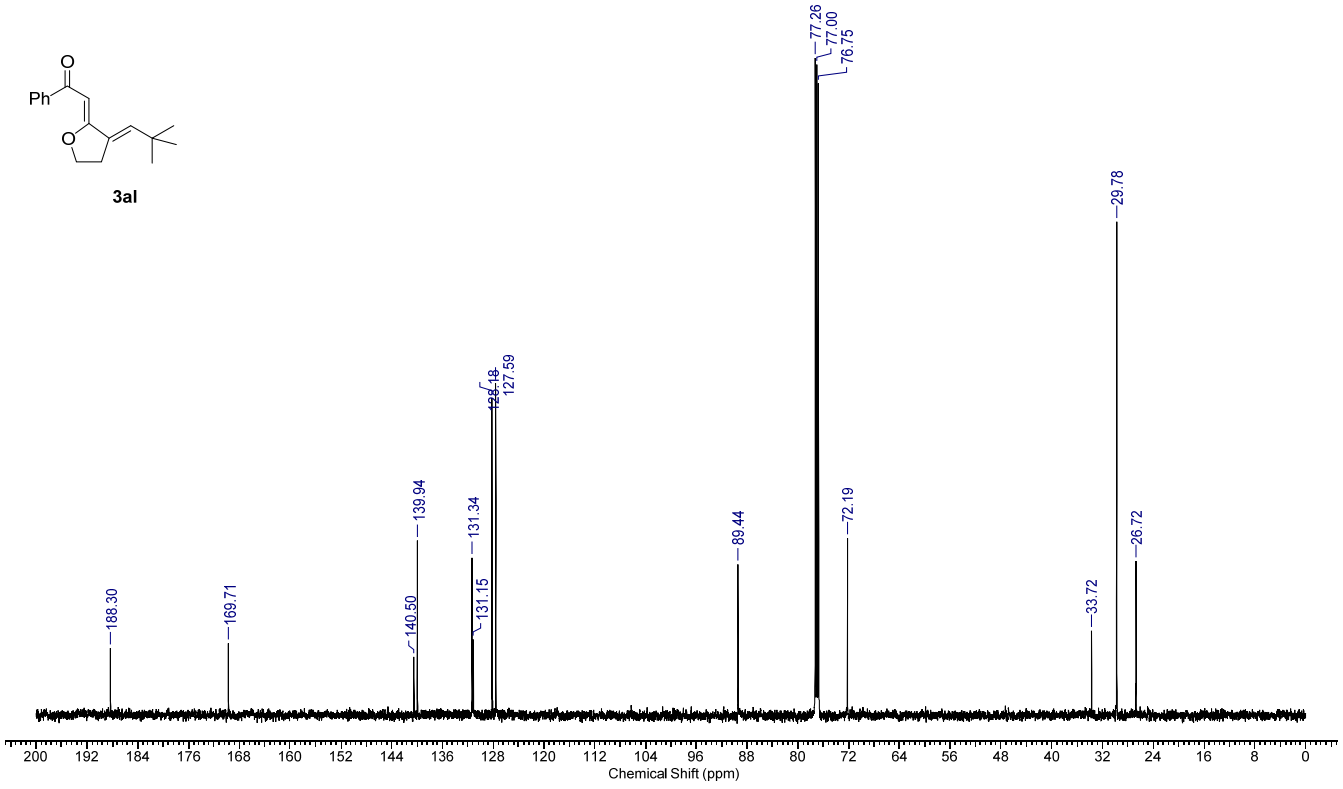

$^{13}$C NMR of **3ak**



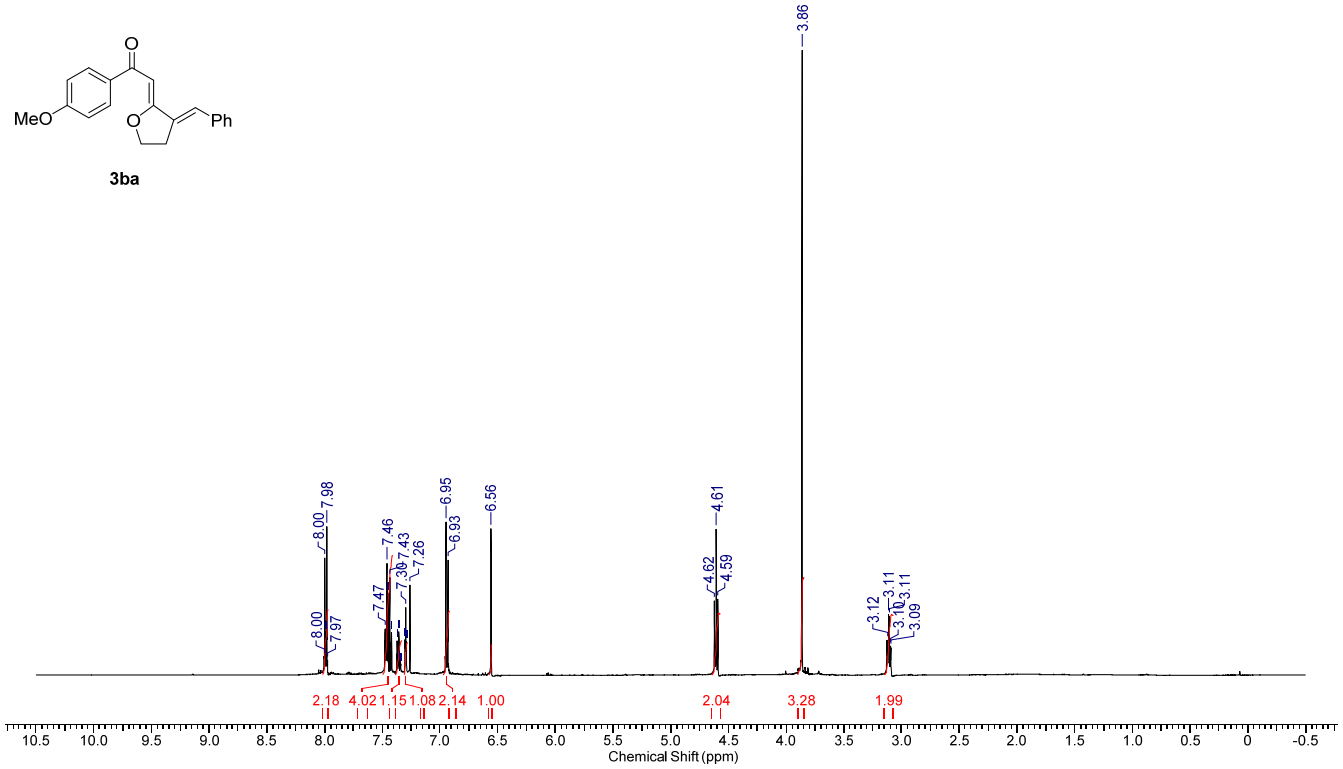
$^{1}$H NMR of **3al**



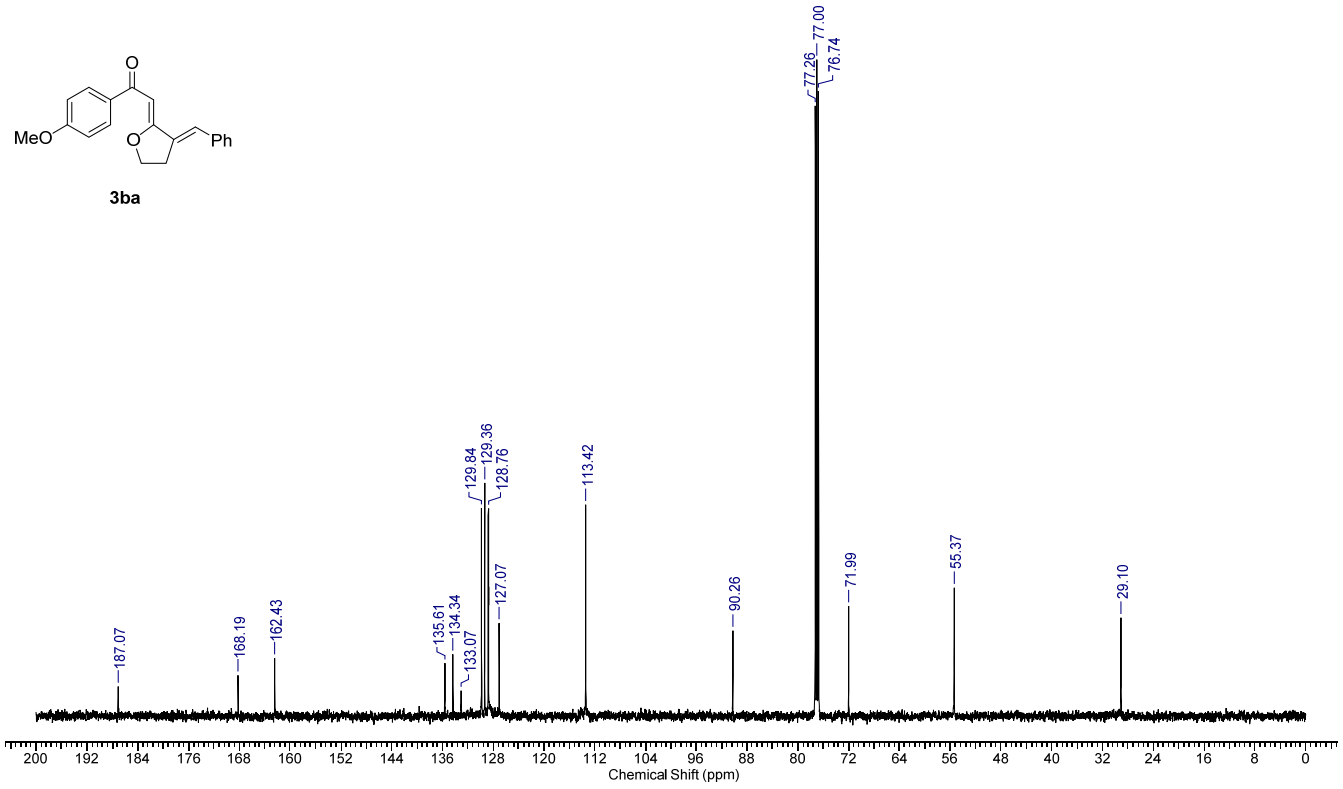

$^{13}$C NMR of **3al**



$^{1}$H NMR of **3ba**




$^{13}$C NMR of **3ba**



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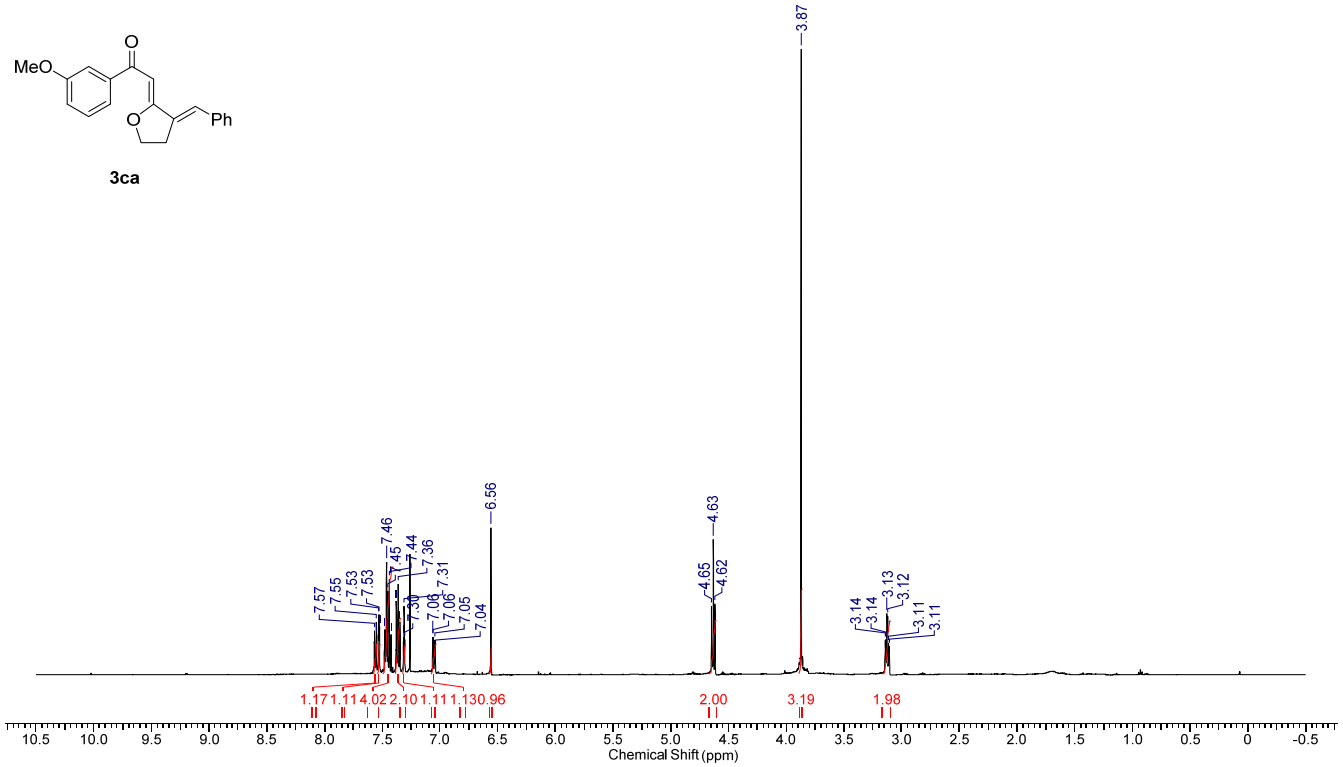
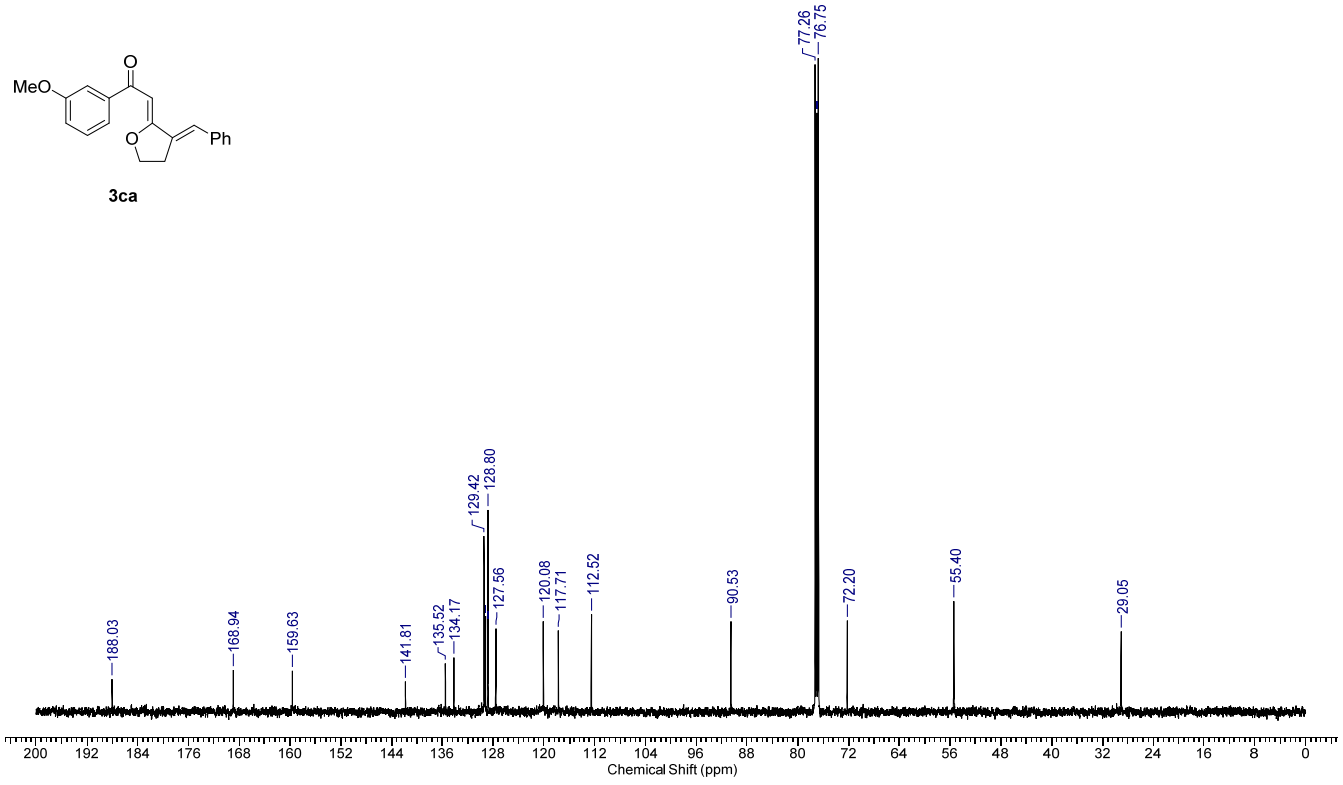
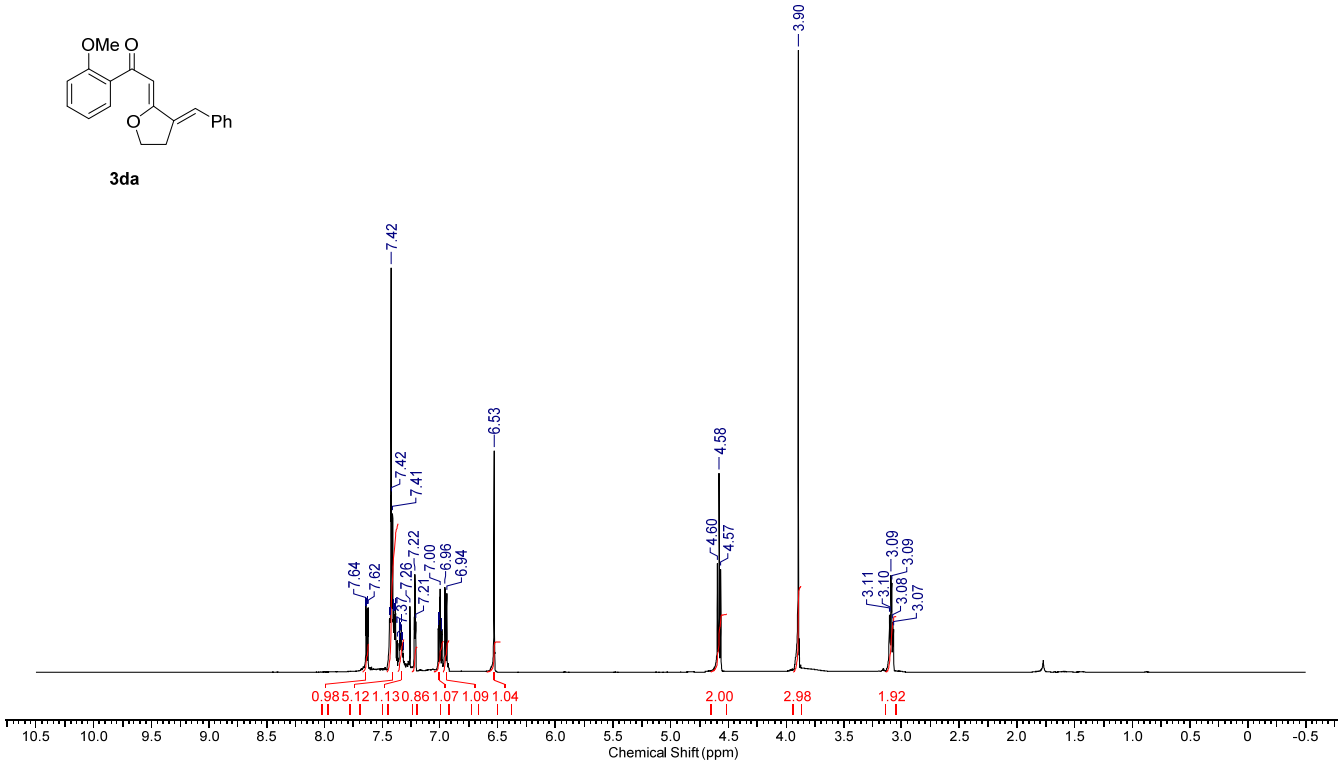


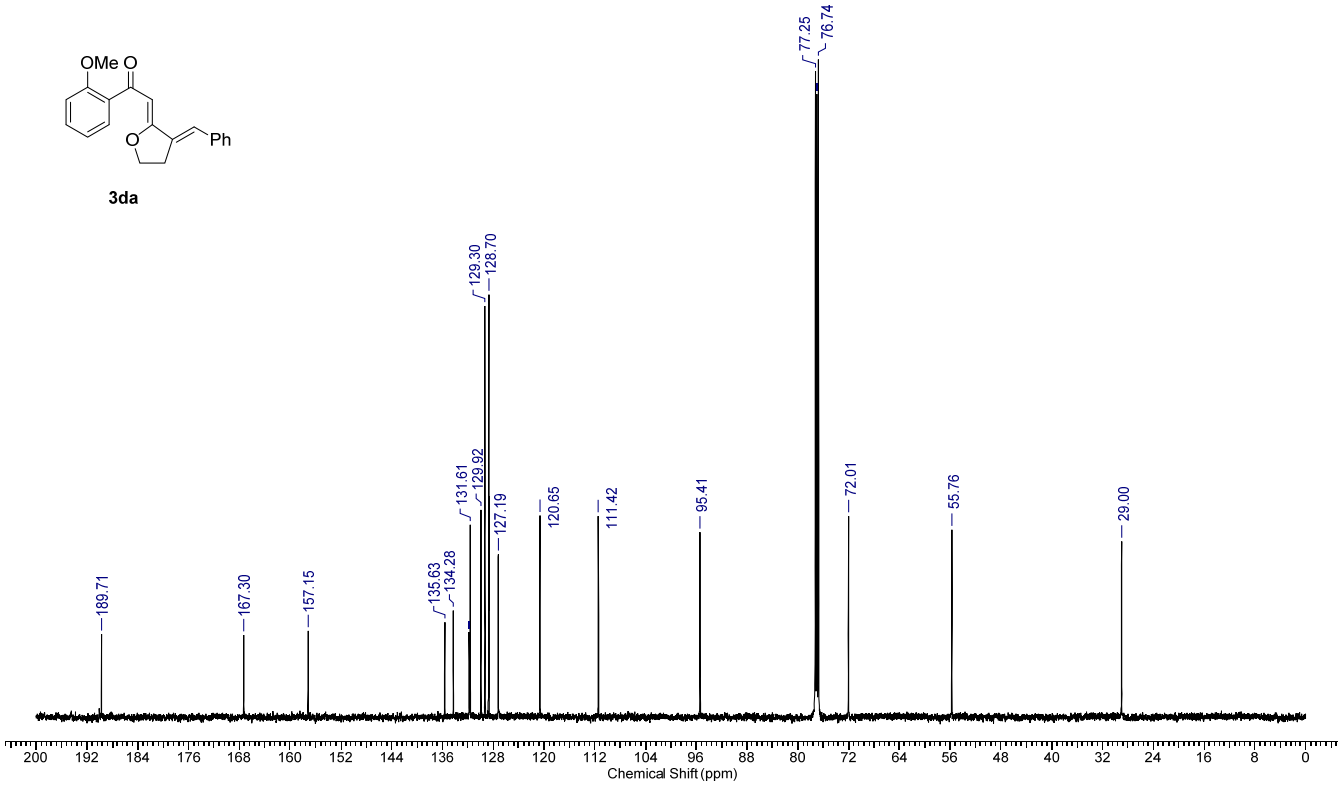

$^{13}$C NMR of **3ca**



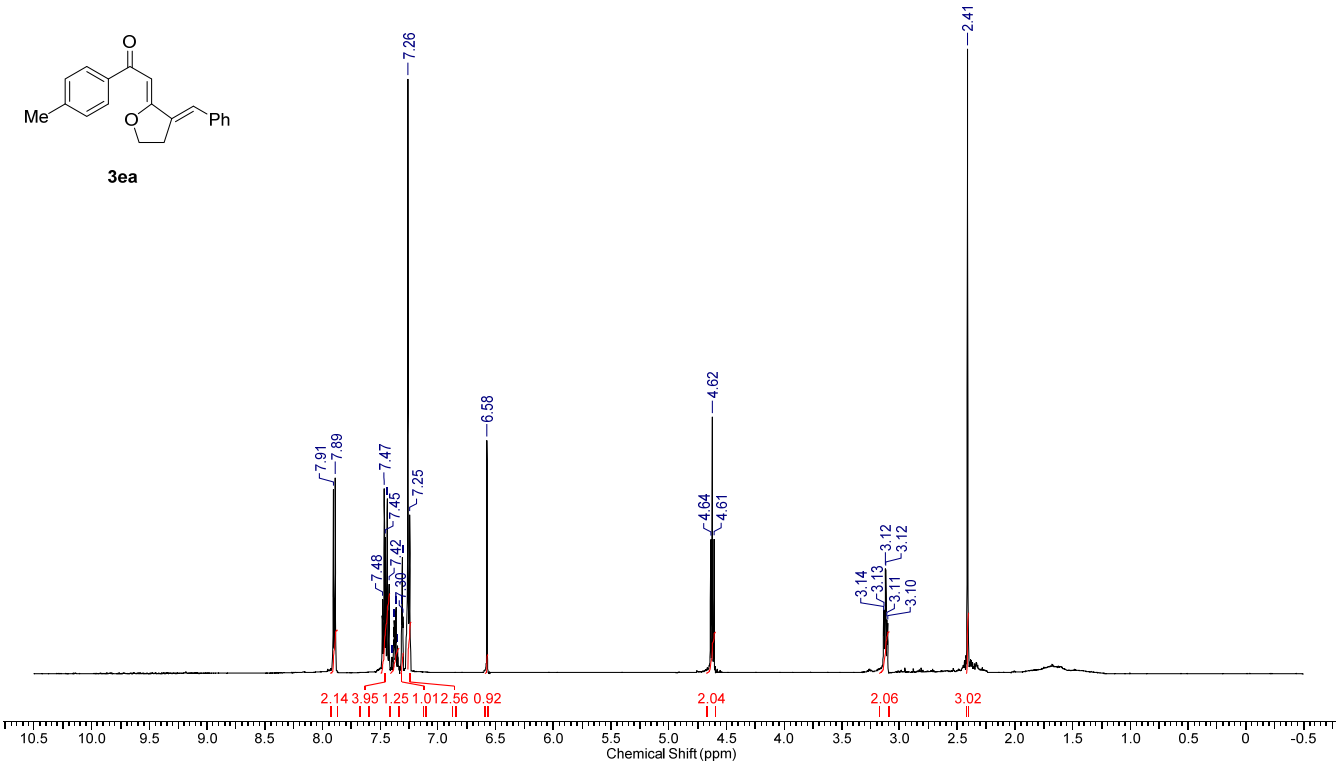
$^{1}$H NMR of **3da**



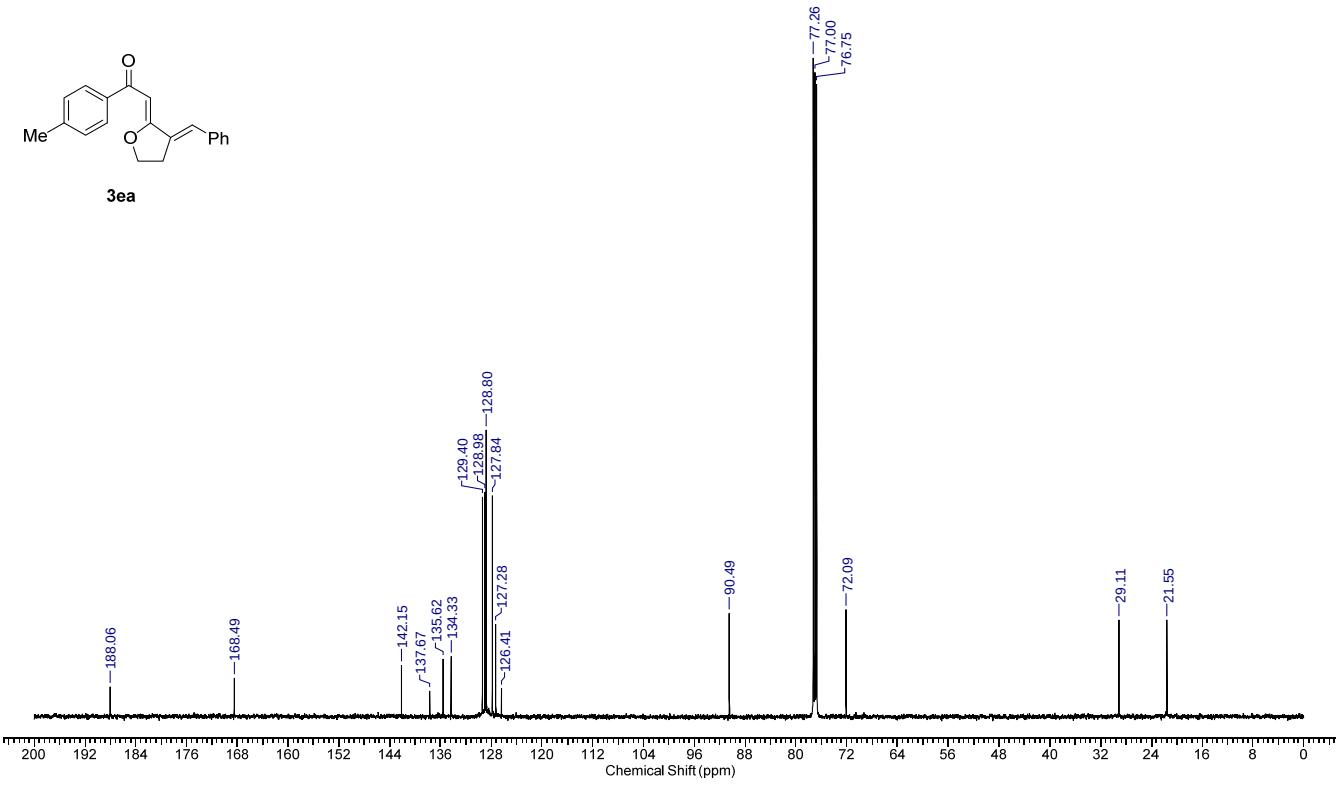

$^{13}$C NMR of **3da**



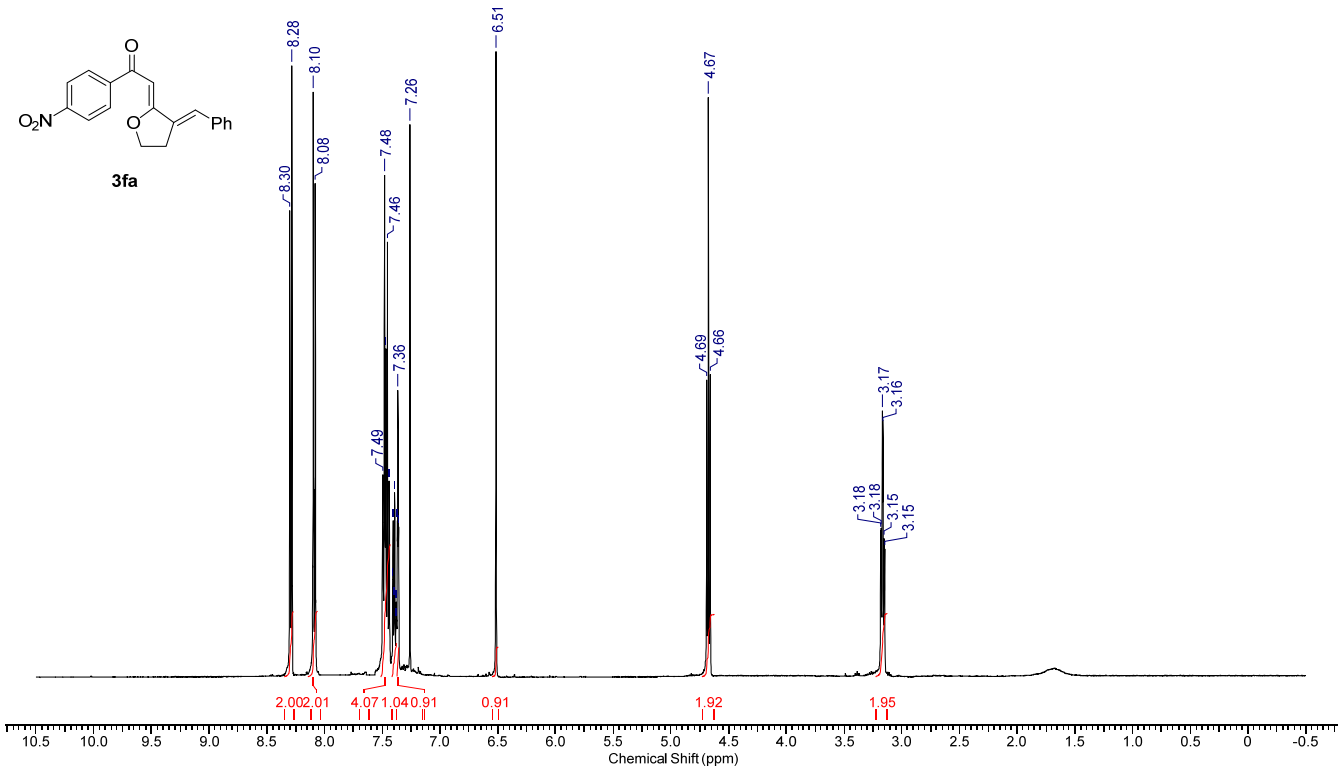
$^{1}$H NMR of **3ea**



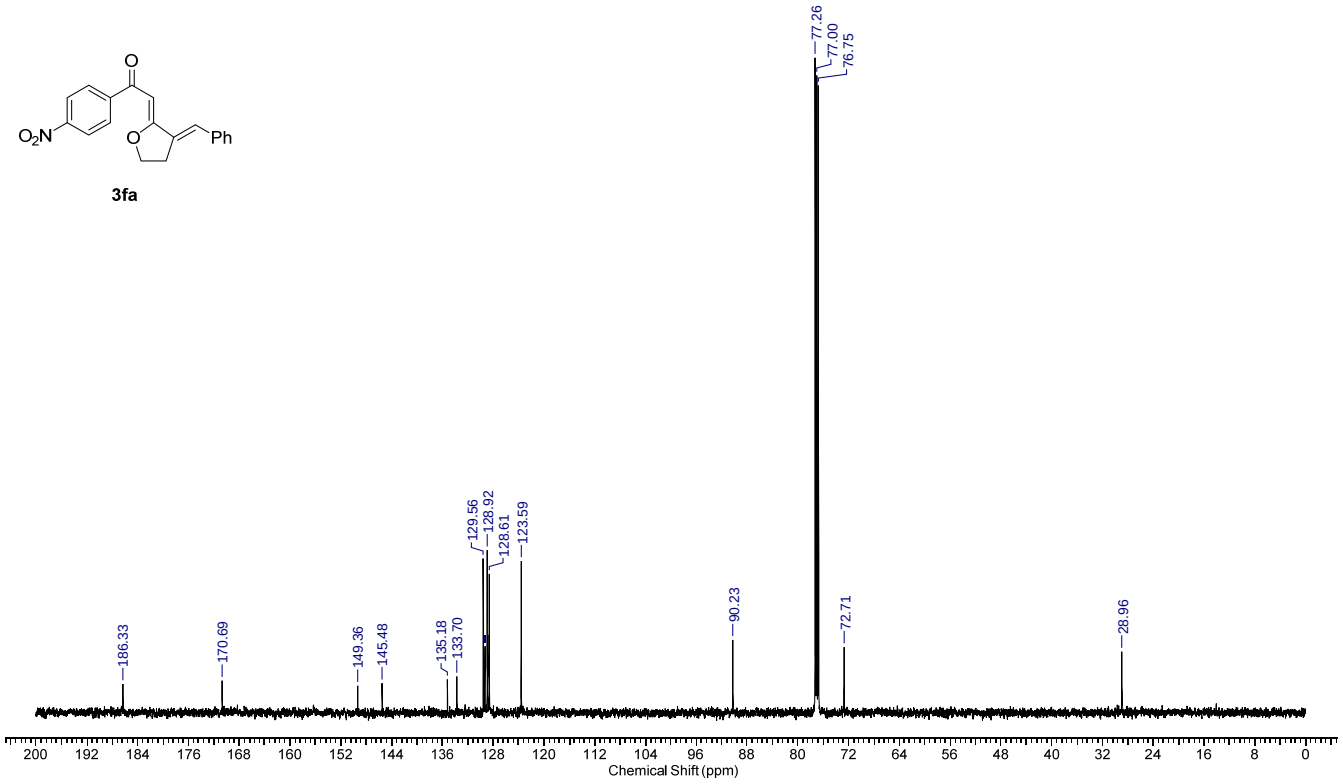

$^{13}$C NMR of **3ea**



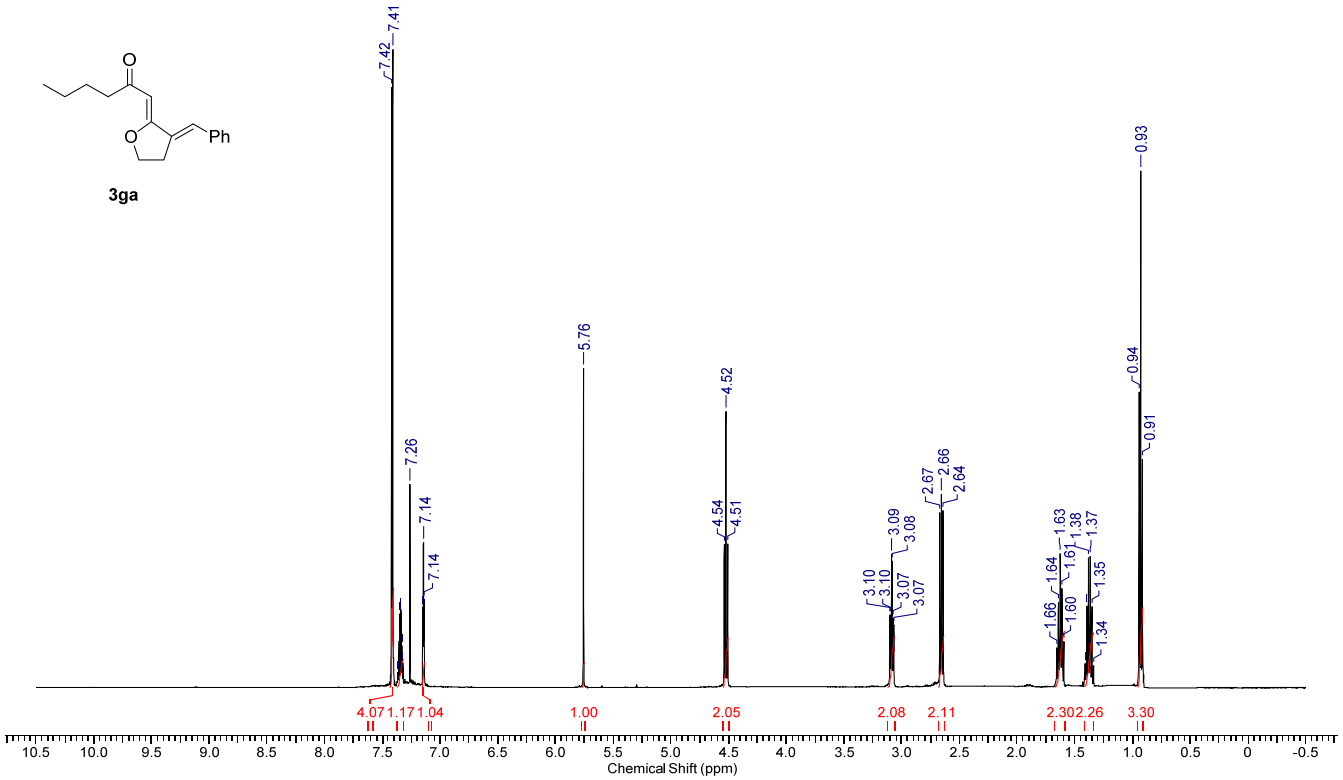
$^{1}$H NMR of **3fa**



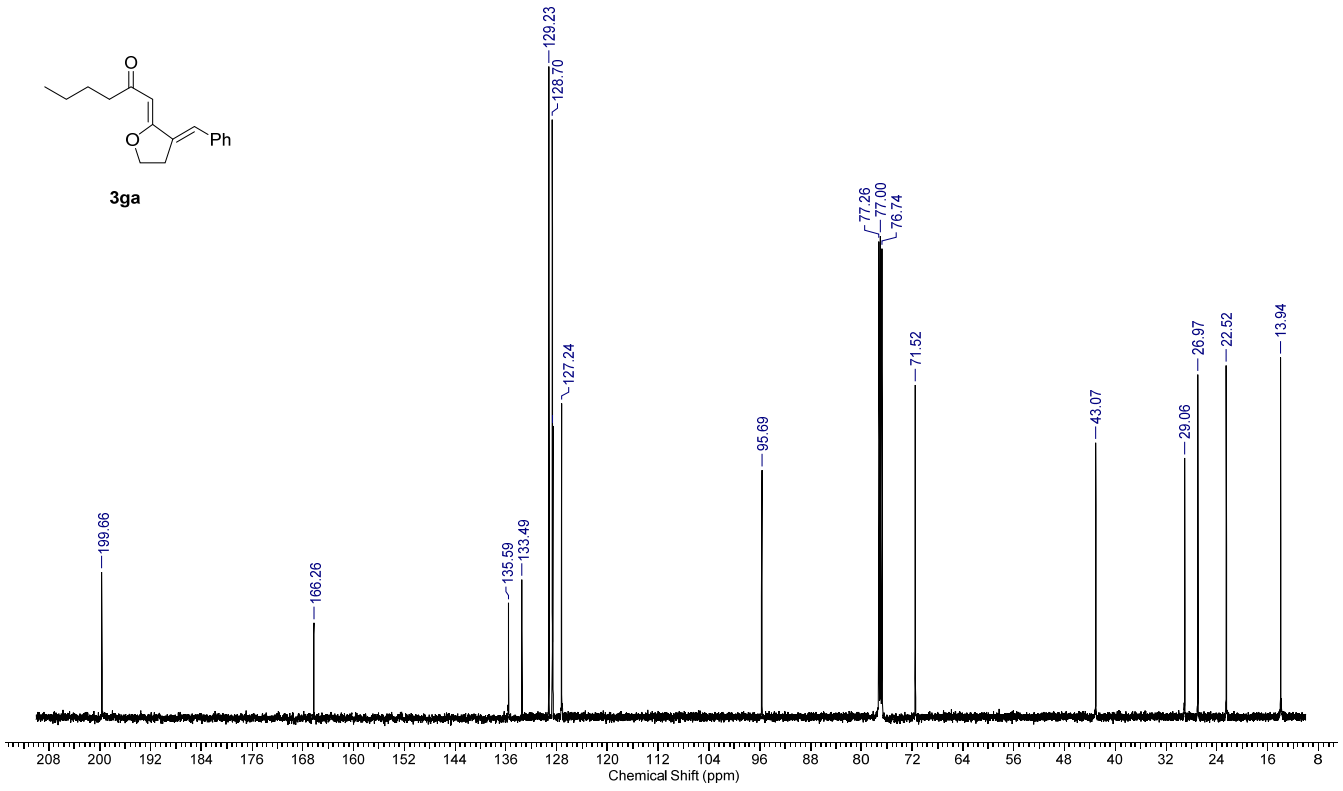

$^{13}$C NMR of **3fa**



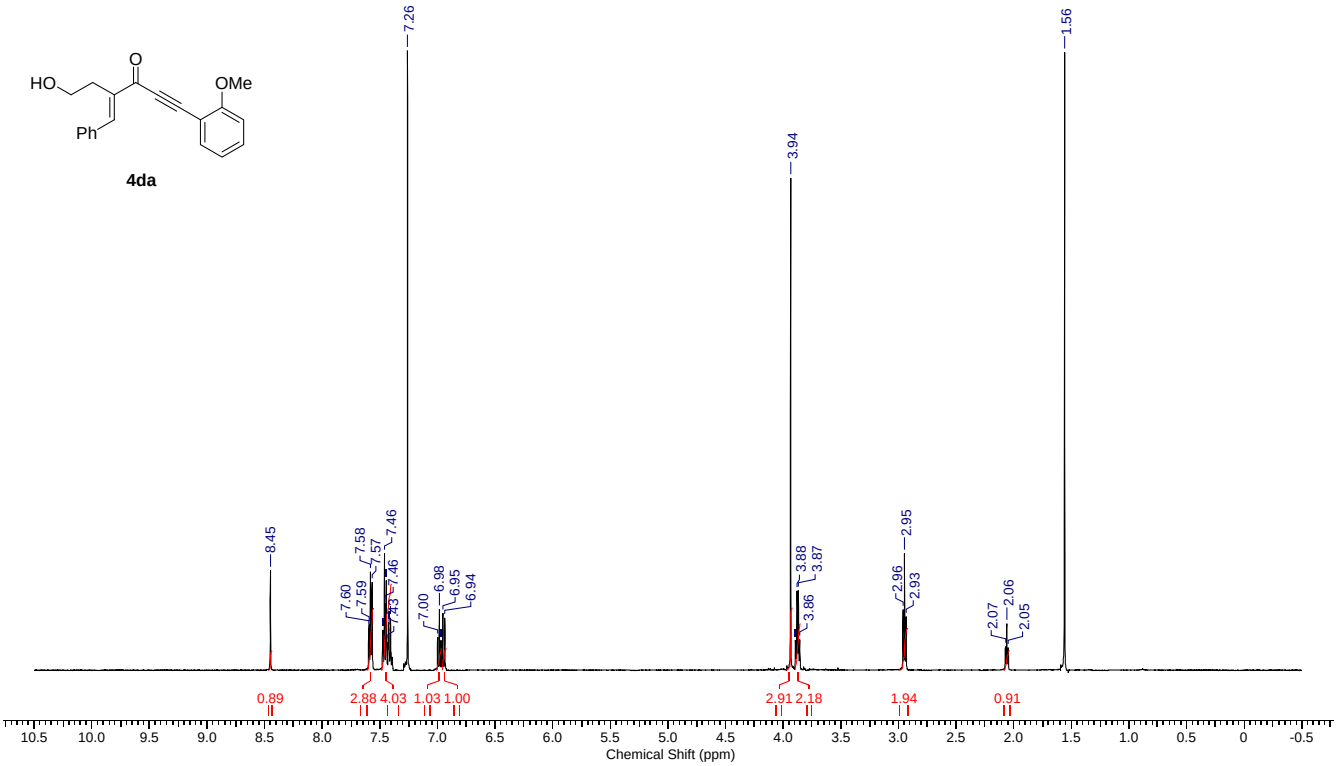
$^{1}$H NMR of **3ga**



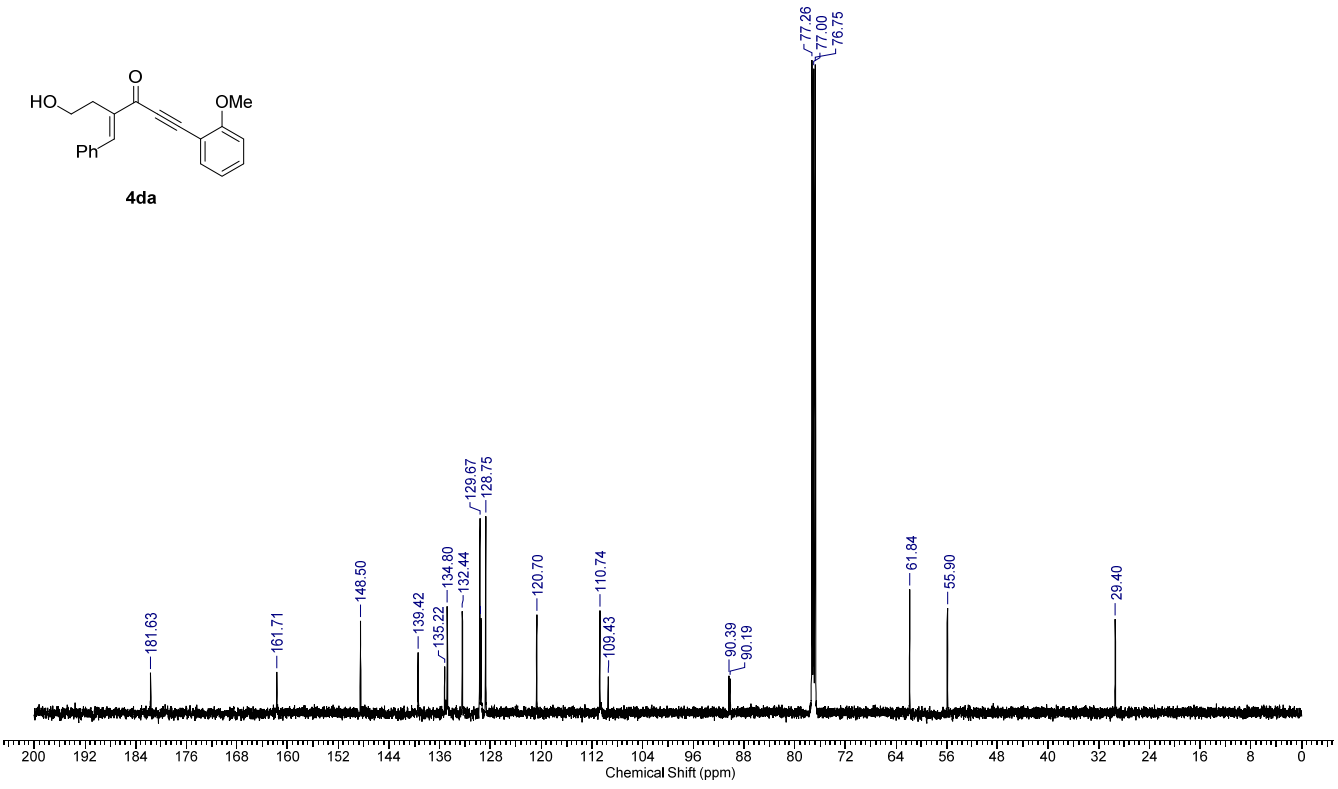

$^{13}$C NMR of **3ga**



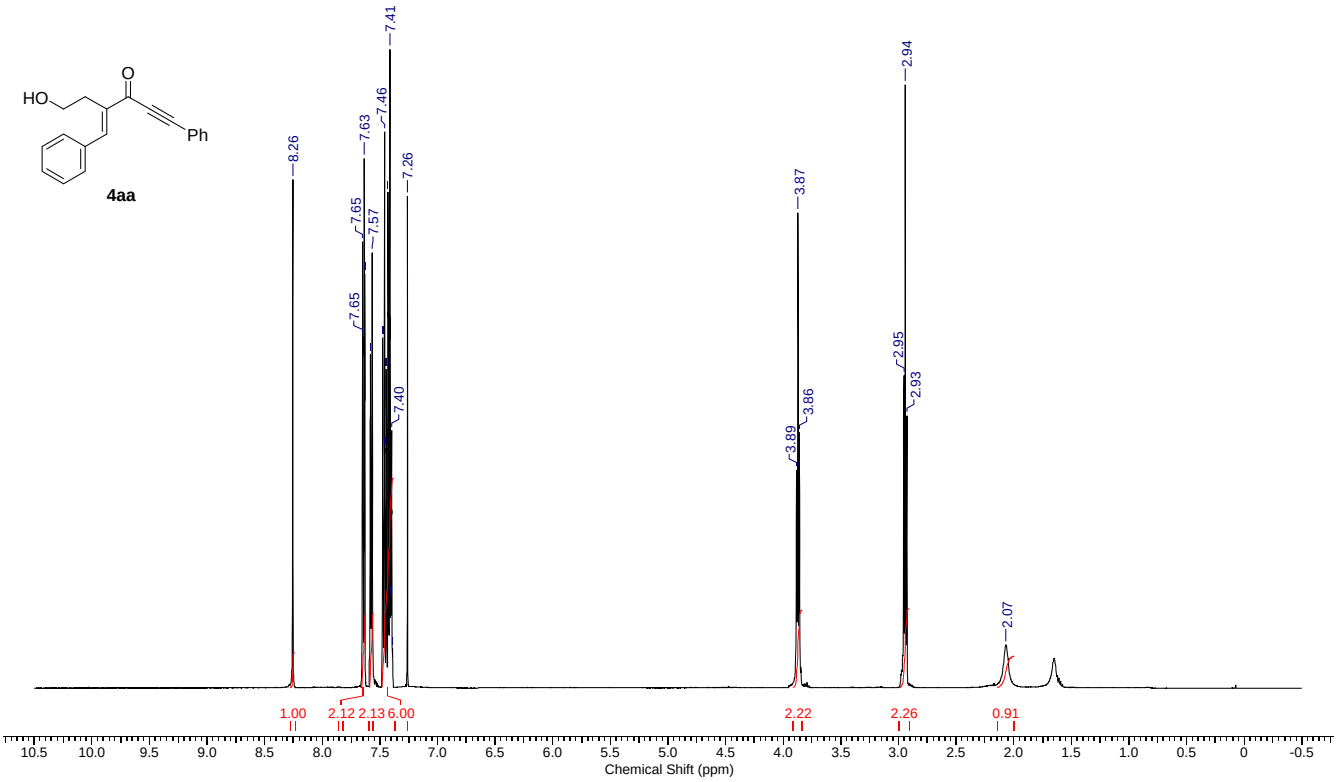
$^{1}$H NMR of **4da**



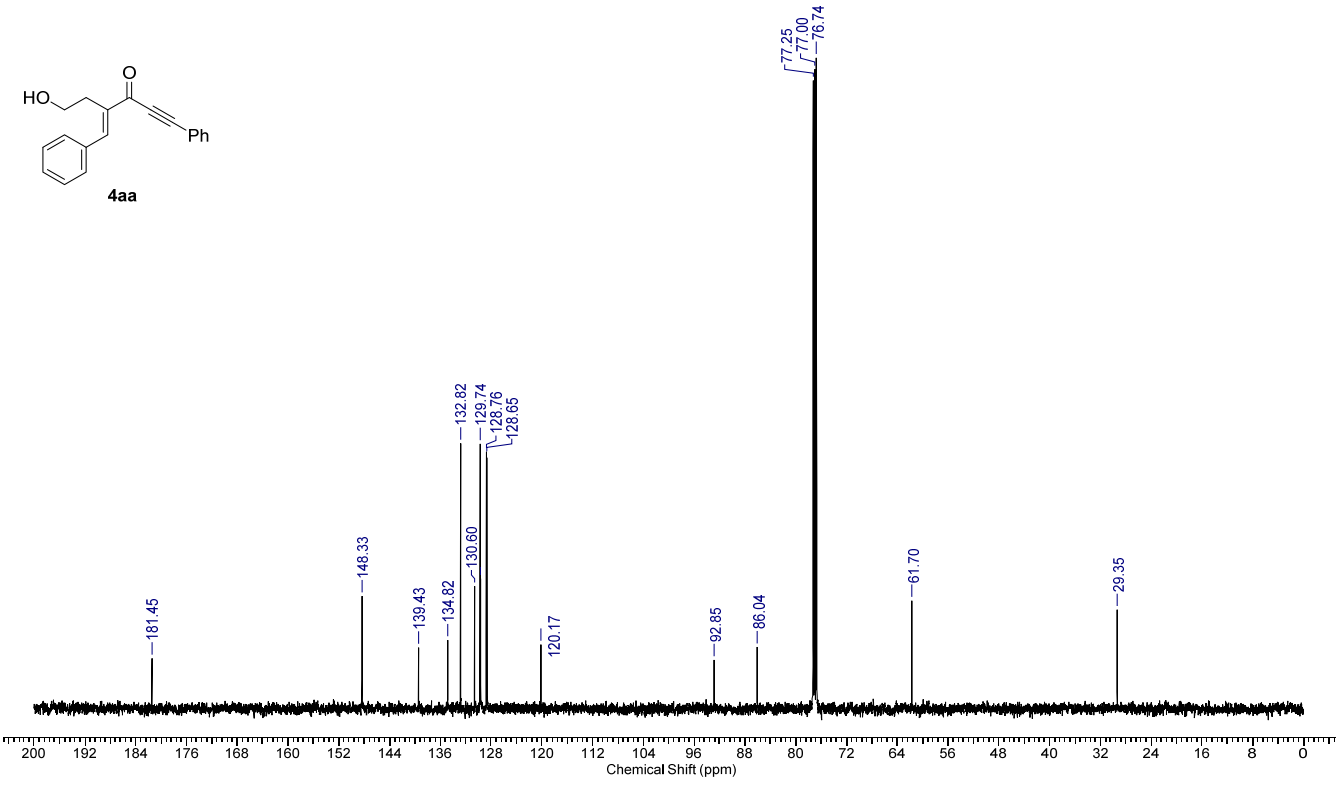

$^{13}$C NMR of **4da**



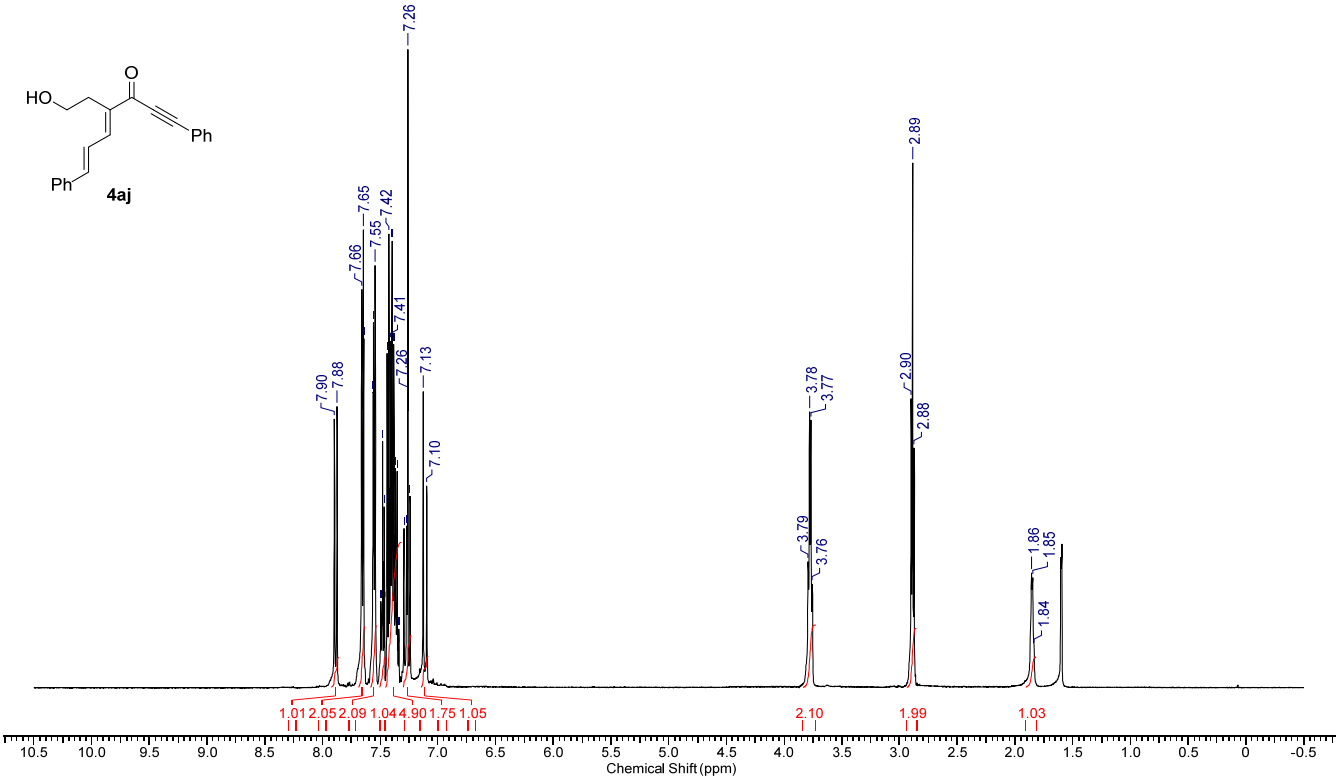
$^{1}$H NMR of **4aa**



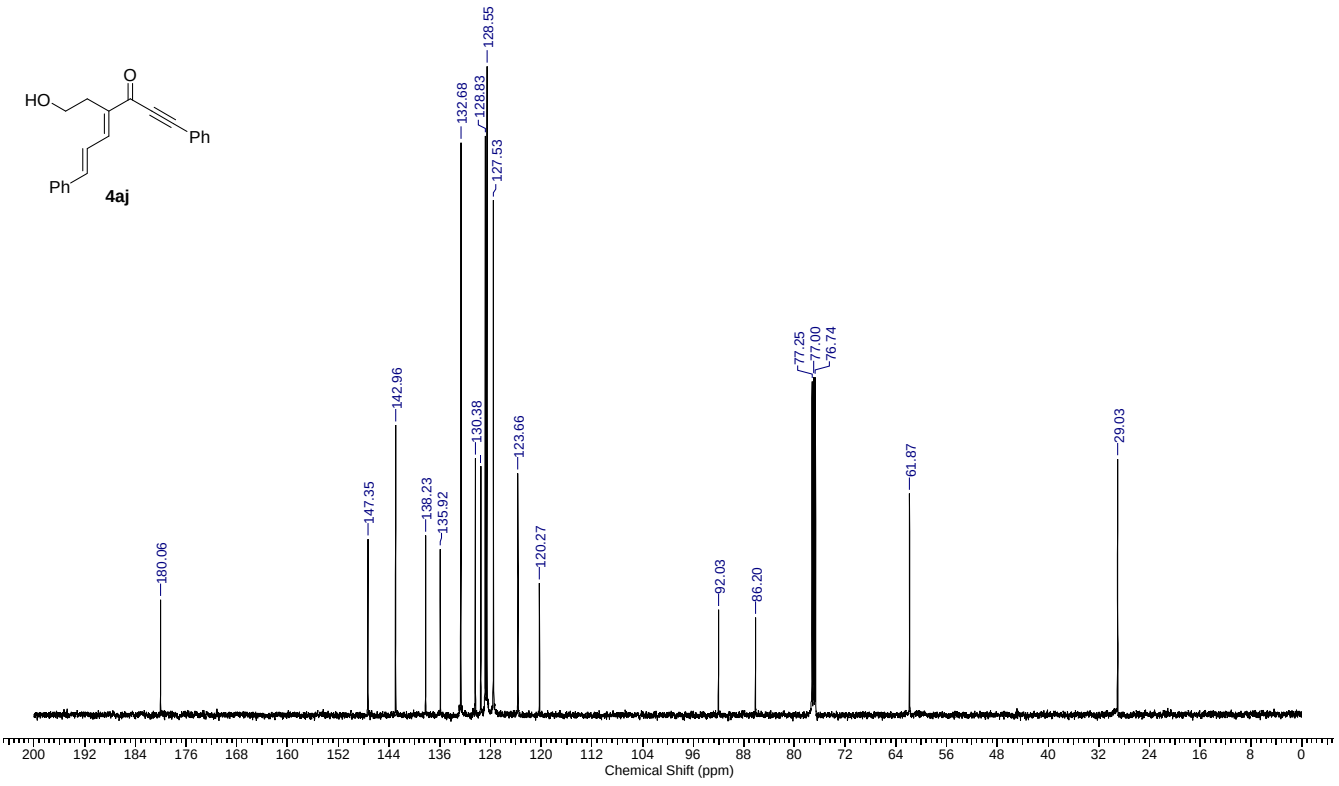

$^{13}$C NMR of **4aa**



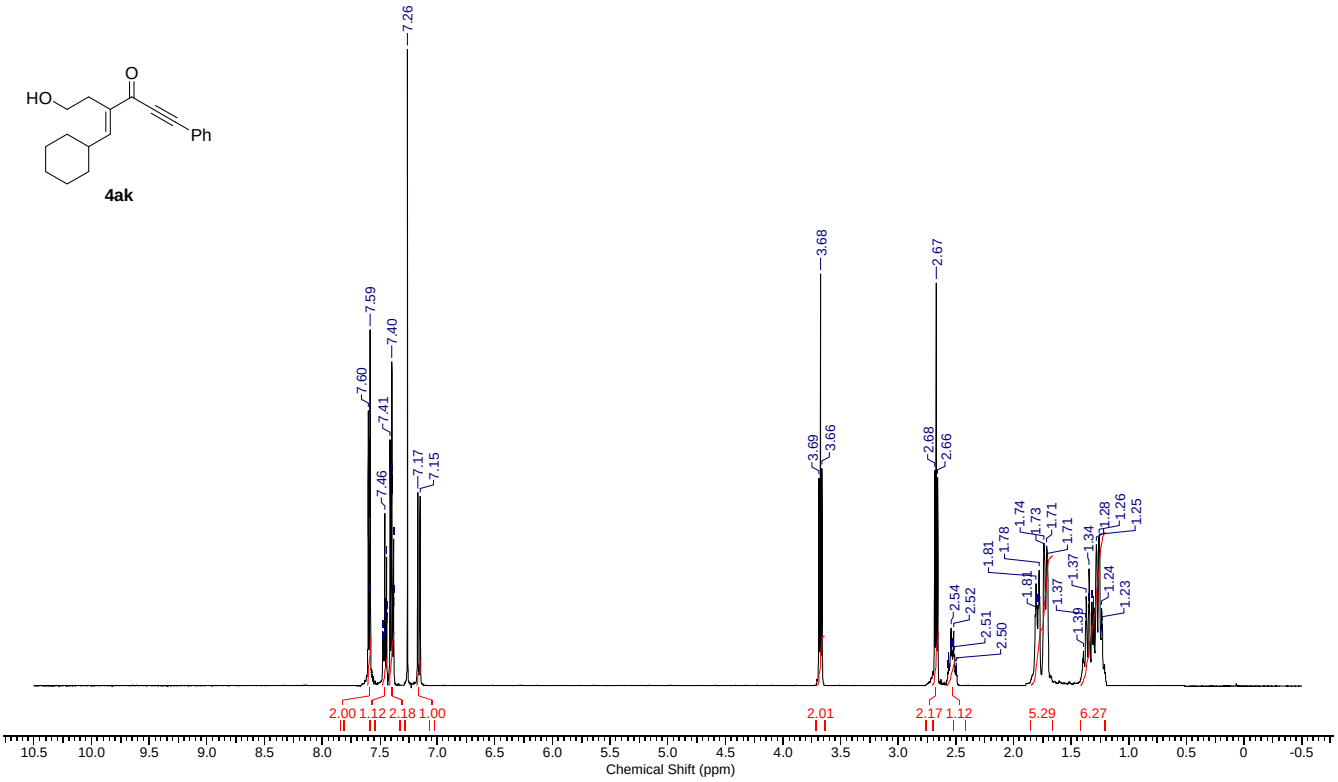
$^{1}$H NMR of **4aj**



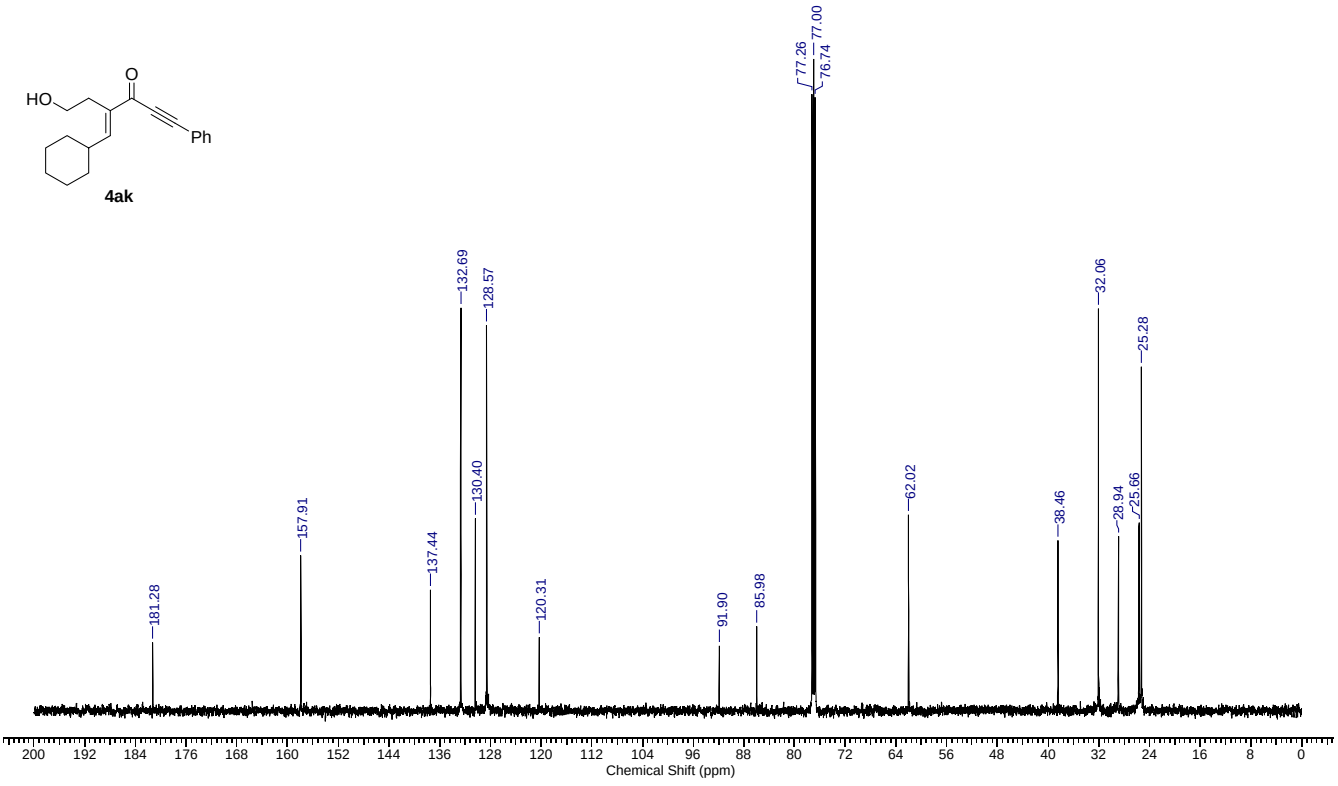

$^{13}$C NMR of **4aj**



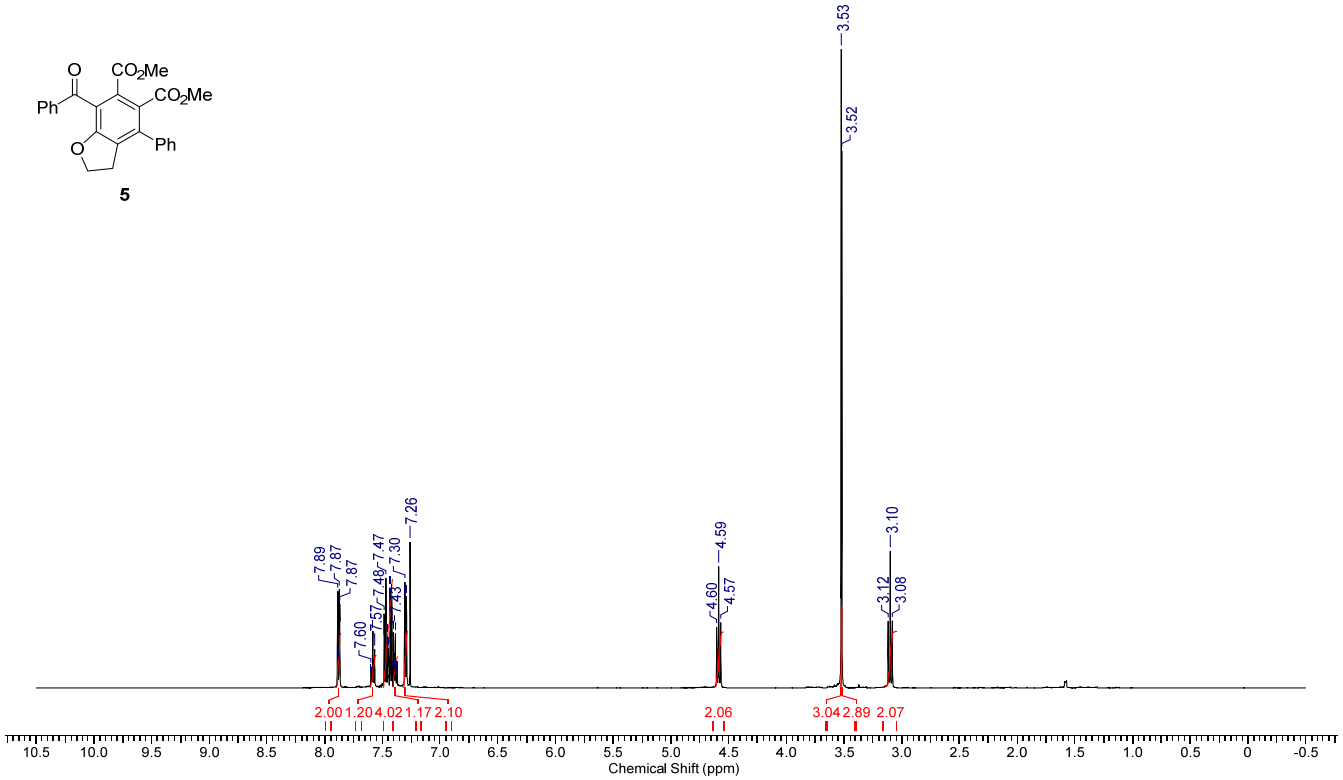
$^{1}$H NMR of **4ak**



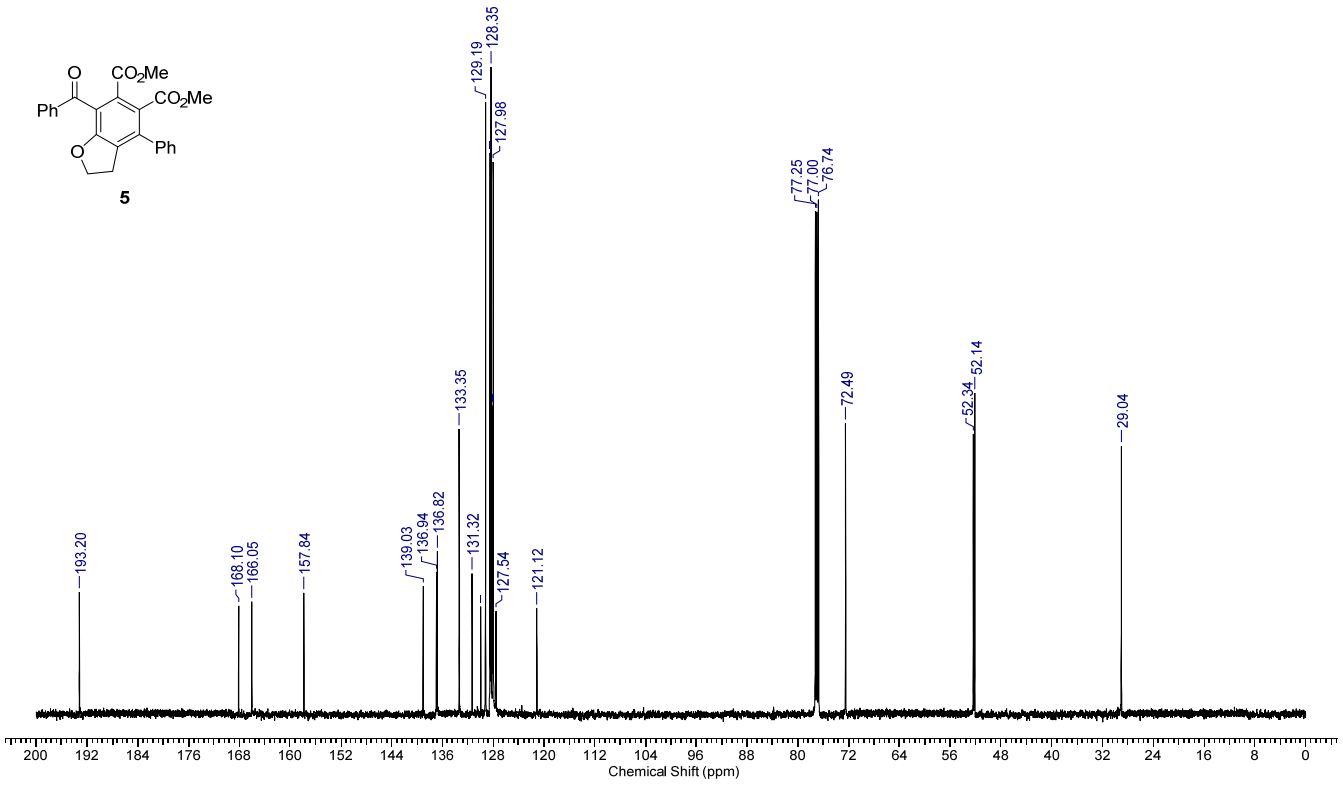

$^{13}$C NMR of **4ak**



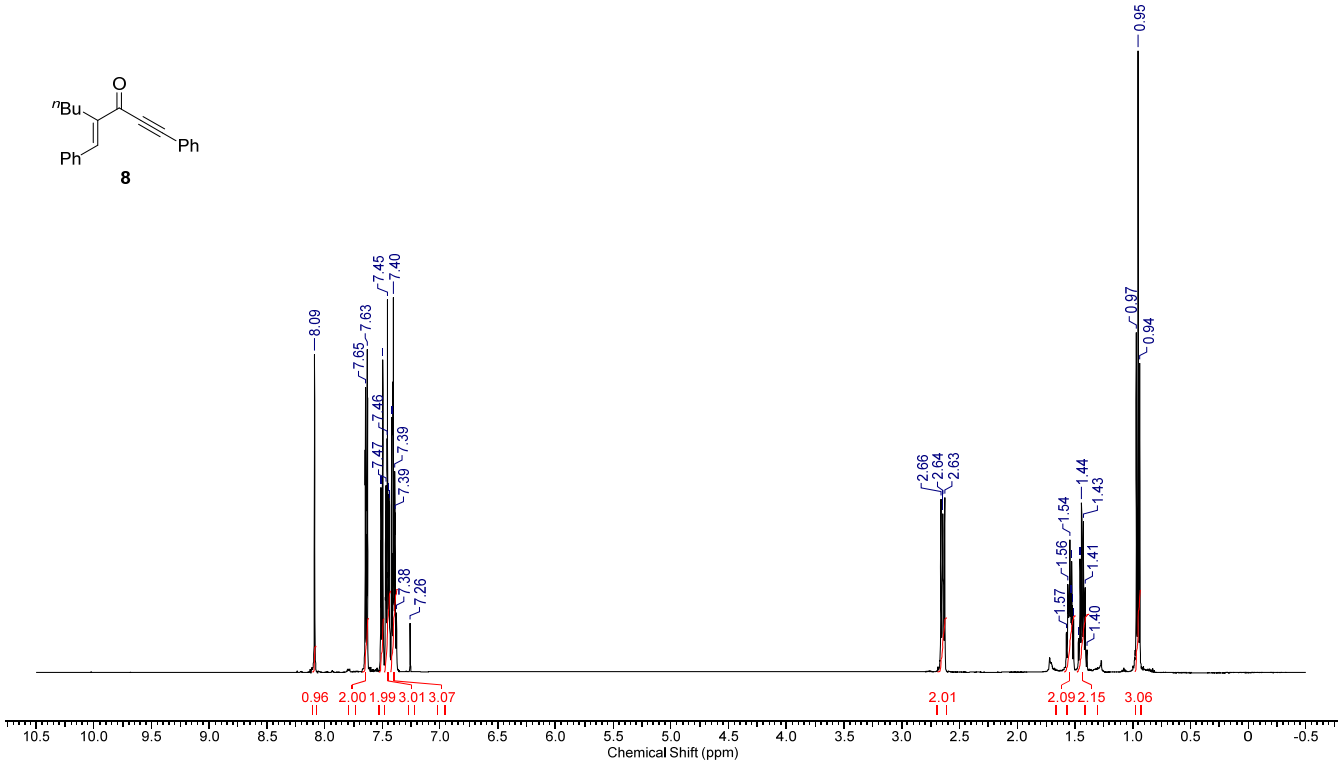
$^{1}$H NMR of **5**




$^{13}$C NMR of **5**



$^{1}$H NMR of **8**




$^{13}$C NMR of **8**