Electronic Supplementary Information

Metal-Catalyzed Formation of 1,3-Cyclohexadienes: A Catalyst-Dependent Reaction

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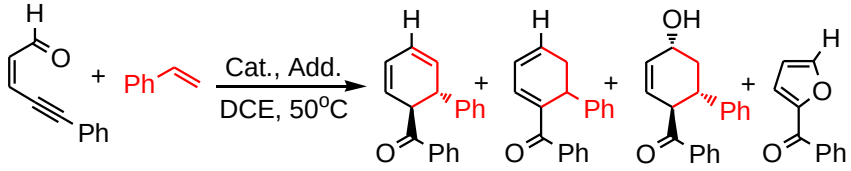
Table of Contents

Table S1. Optimization of Reaction Conditions.[a]

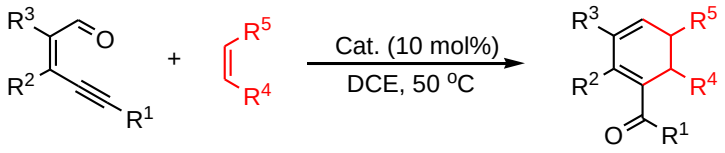


1a **2a** **3a** **4a** **5a** **6a**

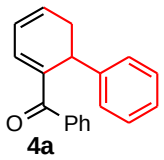
Entry	Cat.	Add.	**3a**	**4a**	**5a**	**6a**	Conv.
1[b]	$Cu(OTf)_2$	-	45%	-	-	-	> 99%
2[c,d]	IMes-AuCl	Selectfluor	-	80%	-	-	> 99%
3	$InCl_3$	-	-	79%	-	-	> 99%
4	ZnI_2	-	-	-	64%	-	> 99%
5	$AgSbF_6$	-	-	-	74%	-	> 99%
6	AgF	-	-	-	58%	-	> 99%
7	$CuCl_2 \cdot 2H_2O$	-	-	-	-	61%	> 99%
8	$AgNO_3$	-	-	-	-	67%	> 99%

[a] Unless otherwise noted, the reactions were performed in DCE at 50 °C for 24h using 10 mol% catalyst under N_2, **1**/**2** = 1:3. [**1**] = 0.25 M; The yield refers to isolated yield. IMes: 1,3-dimesityl-imidazol-2-ylidene; The stereochemistry of products **3a** and **5a** were determined by noe spectrum; [b] trans-**1a** could be detected (32 %) after reaction; [c] 80 °C; [d] 5 mol% IMes-AuCl, 15 mol% Selectfluor.

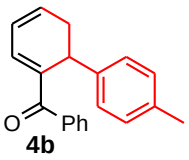
Scheme S1. Some representative examples with gold and indium salts as catalysts.



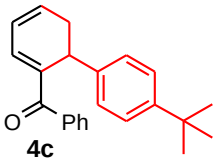
1 **2** **4**



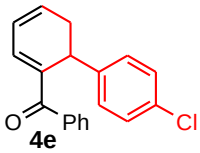
4a
80% **[Au]**
79% **[In]**



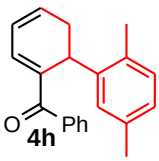
4b
27% **[Au]**
71% **[In]**



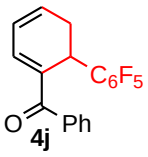
4c
28% **[Au]**
83% **[In]**



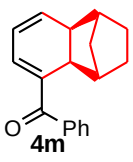
4e
63% **[Au]**
68% **[In]**



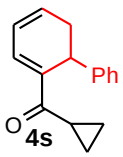
4h
43% **[Au]**
65% **[In]**



4j
28 % **[Au]**
trace **[In]**



4m
20% **[Au]**
92% **[In]**



4s
40% **[Au]**
80% **[In]**

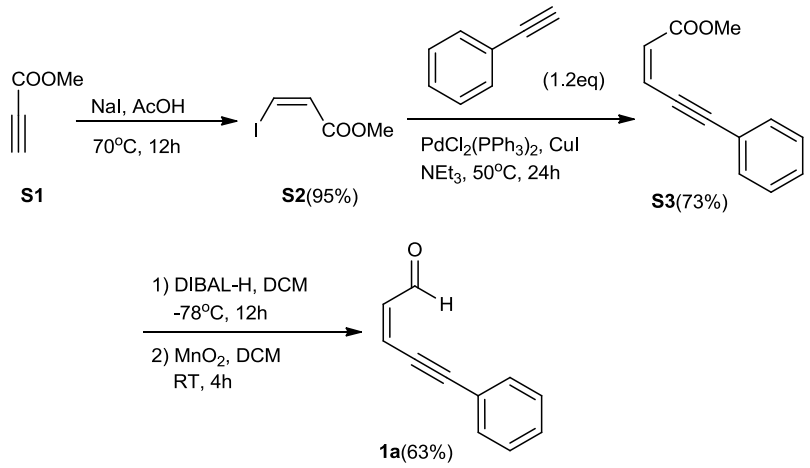
[Au] 5 mol% IMes-AuCl and15 mol% Selectfluor; **[In]** $InCl_3$ (10 mol%)

1. General Information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube, solvents were purified by standard method. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer.
All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

2.Experimental Procedures and Characterization

2.1 Preparation of 1a



step 1:

Procedure for the synthesis of **S2** was identical to the literature.[1]

step 2:

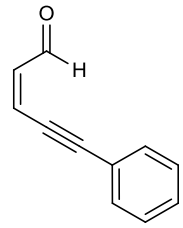
To a solution of the corresponding (*Z*)-methyl 3-iodoacrylate (1.0 eq.), $Pd(PPh_3)_2Cl_2$ (1.0 mol%), and CuI (0.5 mol%) in NEt_3 (0.25 M) was added the appropriate acetylene (1.2 eq.). The resulting mixture was stirred under nitrogen atmosphere at 50 ℃ overnight. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product **S3**.

step 3:

A solution of diisobutylaluminium hydride (1.0 M) in toluene (25.2 mL, 25.2 mmol, 2.1 eq.) was added dropwise to a solution of the ester **S3** (2.24 g, 12 mmol, 1 eq.) in dichloromethane (60 mL, 0.2 M) at -78 ℃ and stirred for 12 h. The reaction mixture was quenched with a 1 M aqueous solution of hydrochloric acid. The solution was diluted with 20 ml of ether and

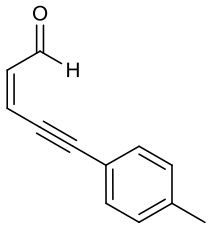
allowed to warm up to room temperature. The separated aqueous phase was extracted with ether (3*10 mL), and the combined organic layers were washed successively with 1M HCl , water and saturated sodium chloride solution then dried over $MgSO_4$. The mixture was filtered and the mother liquor was concentrated to yield a white oil (1.7 g, 90%). The crude material was used without any further purification. MnO_2 (8.6 g, 100 mmol, 10 eq)were added to a solution of the crude alcohol (1.58 g, 10 mmol, 1eq) in DCM (20 ml). Then the reaction mixture was stirred at room temperature for 4 hours. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduce pressure and the residue was purified by flash chromatography gel (Hex/EtOAc = 10/1) to afford the desired product **1a** (1.04 g, 63%) as a yellow oil.

(*Z*)-5-Phenylpent-2-en-4-ynal (1a)[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (d, J = 8.2 Hz, 1H), 7.43 (dd, J = 7.8, 1.6 Hz, 2H), 7.34 – 7.28 (m, 3H), 6.79 (d, J = 10.8 Hz, 1H), 6.25 (dd, J = 10.8, 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.93, 137.30, 131.99, 129.79, 128.79, 128.62, 121.70, 101.42, 84.03.

(*Z*)-5-(p-Tolyl)pent-2-en-4-ynal (1b)

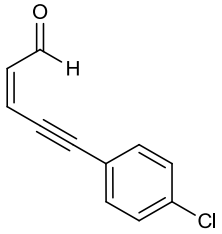


The synthesis of **1b** was similar with **1a**.

Brown yellow oil, dr (*Z*:*E*) = 89:11; R_f = 0.40 (Hex/EtOAc = 20/1).

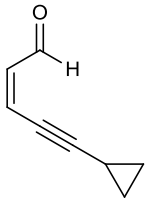
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.77 (d, J = 10.8 Hz, 1H), 6.22 (dd, J = 10.7, 8.4 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.99, 140.29, 136.90, 131.94, 129.40, 129.01, 118.65, 101.91, 83.71, 21.65; IR (KBr) ν_{max} 3030.91, 2923.06, 2854.12, 2190.35, 1682.14, 1594.79, 1507.62, 1122.65, 817.04, 766.55; HRMS (EI) calcd for $C_{12}H_{10}O$ [M]: 170.0732, Found: 170.0730.

(*Z*)-5-(4-Chlorophenyl)pent-2-en-4-ynal (1c)



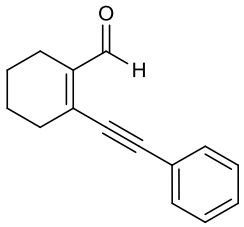
The synthesis of **1c** was similar with that of **1a**.
Yellow oil, dr (*Z*:*E*) = 91:9; R_f = 0.35 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 2H), 6.86 (dd, *J* = 10.8, 0.9 Hz, 1H), 6.41 – 6.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.65, 137.58, 136.01, 133.16, 129.03, 128.27, 120.17, 100.00, 84.87; IR (KBr) ν_{max} 3032.98, 2968.27, 2834.88, 2192.93, 1681.23, 1576.42, 1488.18, 1092.91, 828.69, 769.40; HRMS (EI) calcd for $C_{11}H_7OCl$ [M]: 190.0185, Found: 190.0182.

(*Z*)-5-Cyclopropylpent-2-en-4-ynal (1d)



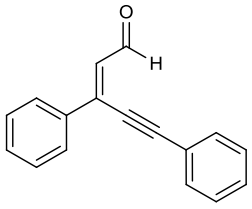
The synthesis of **1d** was similar with **1a**
Pale yellow oil, R_f = 0.35 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (d, *J* = 8.3 Hz, 1H), 6.52 (dd, *J* = 10.7, 1.9 Hz, 1H), 6.13 (dd, *J*=10.5, 8.5Hz, 1H),1.45–1.35(m, 1H),0.92–0.85(m, 2H),0.81–0.73(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.45, 136.28, 129.33, 107.12, 70.74, 8.77, 0.00; IR (KBr) ν_{max} 3027.16, 2925.30, 2857.41, 2225.59, 1632.19, 1528.04, 1384.42, 1097.46, 639.19, 618.44; HRMS (EI) calcd for C_8H_8O [M]: 120.0575, Found: 120.0571.

2-(Phenylethynyl)cyclohex-1-enecarbaldehyde (1e)[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.50 – 7.44 (m, 2H), 7.38 – 7.33 (m, 3H), 2.51 (d, *J* = 5.8 Hz, 2H), 2.32 (d, *J* = 5.9 Hz, 2H), 1.75 – 1.64 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.89, 142.61, 139.94, 131.66, 129.11, 128.51, 122.33, 98.54, 86.29, 32.36, 22.12, 21.91, 21.08.

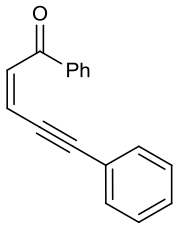
(*Z*)-3,5-Diphenylpent-2-en-4-ynal (1f)[4]



Enynal **1f** was prepared according to the method of Yukie Isogai and coworkers.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 5.7 Hz, 3H), 7.46 (t, *J* = 6.6 Hz, 3H), 6.84 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR

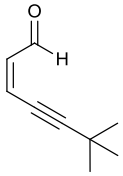
(100 MHz, $CDCl_3$) δ 193.16, 142.47, 135.64, 132.00, 131.12, 131.07, 129.87, 128.93, 128.69, 127.21, 121.68, 102.20, 84.25.

(*Z*)-1,5-diphenylpent-2-en-4-yn-1-one (1t) [5]



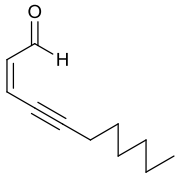
Ene-yne-ketone **1g** was prepared according to the method of Xiangwei Du and coworkers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.60 (ddd, *J* = 6.6, 3.8, 1.2 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.34 (ddd, *J* = 7.6, 4.2, 1.3 Hz, 3H), 7.11 (d, *J* = 11.6 Hz, 1H), 6.48 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.01, 137.84, 132.99, 132.84, 132.22, 129.19, 128.69, 128.62, 128.31, 122.59, 121.41, 100.81, 87.62.

(Z)-6,6-dimethylhept-2-en-4-ynal (1h)



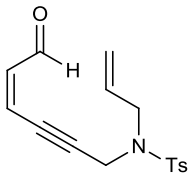
Pale yellow oil; R_f = 0.35; IR (KBr) ν_{max} 2961.73, 2925.34, 2857.62, 2363.83, 1648.40, 1564.36, 1459.66, 1261.05, 1022.02, 799.84; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (d, J = 8.2 Hz, 1H), 6.56 (d, J = 10.7 Hz, 1H), 6.18 – 6.00 (m, 1H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.27, 135.90, 128.98, 110.79, 76.32, 76.00, 75.68, 73.30, 29.46, 27.54, -0.00; HRMS (EI) calcd for $C_9H_{13}O$ [M+H]: 137.0966, Found: 137.0961.

(Z)-undec-2-en-4-ynal (1i)



Pale yellow oi; R_f = 0.38; IR (KBr) ν_{max} 2961.73, 2925.34, 2857.62, 2363.83, 1648.40, 1564.36, 1459.66, 1261.05, 1022.02, 799.84; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (d, *J* = 8.2 Hz, 1H), 6.56 (d, *J* = 10.7 Hz, 1H), 6.14 (t, *J* = 9.4 Hz, 1H), 2.35 (t, *J* = 6.8 Hz, 2H), 1.56 – 1.47 (m, 2H), 1.38 – 1.31 (m, 2H), 1.24 (s, 4H), 0.83 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.16, 137.16, 129.92, 104.20, 77.36, 77.04, 76.72, 75.77, 31.24, 28.58, 28.19, 22.48, 19.81, 13.98; HRMS (EI) calcd for $C_{11}H_{16}ONa$ [M+Na]: 187.1099, Found: 187.1093.

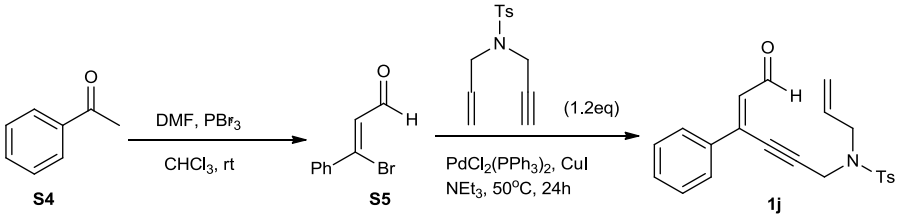
(*Z*)-N-allyl-4-methyl-N-(6-oxohex-4-en-2-yn-1-yl)benzenesulfonamide (8a)



To a solution of the corresponding (*Z*)-methyl 3-iodoacrylate (1.0 eq.), $Pd(PPh_3)_2Cl_2$ (1.0 mol%), and CuI (0.5 mol%) in NEt_3 (0.25 M) was added the appropriate N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide[6] (1.2 eq.). The resulting mixture was stirred under nitrogen atmosphere at 50 ℃ overnight. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product. A solution of diisobutylaluminium hydride (1.0 M) in toluene (10.5 mL, 10.5 mmol, 2.1 eq.) was added dropwise to a solution of the ester (1.66 g, 5 mmol, 1 eq.) in dichloromethane (30 mL, 0.2 M) at -78 ℃ and stirred for 12 h. The reaction mixture was quenched with a 1 M aqueous solution of hydrochloric acid. The solution was diluted with 20 ml of ether and allowed to warm up to room temperature. The separated aqueous phase was extracted with ether (3*10 mL), and the combined organic layers were washed successively with 1M HCl , water and saturated sodium chloride solution then dried over $MgSO_4$. The mixture was filtered and the mother liquor was concentrated to yield a pale yellow oil (1.36 g, 90%). The crude material was used without any further purification. MnO_2 (8.6 g, 100 mmol, 10 eq)were added to a solution of the crude alcohol in DCM (20 ml). Then the reaction mixture was stirred at room temperature for 4 hours. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduce pressure and the residue was purified by flash chromatography gel (Hex/EtOAc = 5/1) to afford the desired product **1i** (1.04 g, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 10.9 Hz, 1H), 6.13 – 6.03 (m, 1H), 5.70 (ddt, *J* = 16.7, 10.4, 6.5 Hz, 1H), 5.26 – 5.16 (m, 2H), 4.25 (s, 2H), 3.76 (d, *J* = 6.4 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.95, 144.08, 138.11, 135.70, 131.78, 129.66, 127.68, 127.47, 120.24, 94.65, 80.14, 49.61, 36.66, 21.47; IR (KBr) ν_{max} 2956.89, 2924.84, 2849.52, 2225.59, 1679.56, 1492.20, 1377.94, 1161.35, 1089.91, 744.11; HRMS (EI) calcd for $C_{16}H_{17}NaO_3S$ $[M+Na]^+$: 326.0827, Found: 326.0821.

(*Z*)-N-allyl-4-methyl-N-(6-oxo-4-phenylhex-4-en-2-yn-1-yl)benzenesulfonamide(8b)

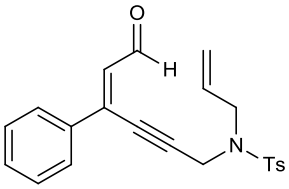


step 1:

Procedure for the synthesis of **S5** was identical to the literature.[7]

step 2:

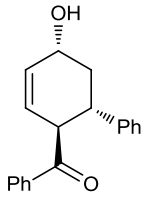
The synthesis of **1i** was similar with **1a**



Brown yellow oil; R_f = 0.35 (Hex/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.55 (d, *J* = 7.9 Hz, 1H), 5.72 (ddd, *J* = 13.5, 12.9, 6.4 Hz, 1H), 5.28 – 5.18 (m, 2H), 4.38 (s, 2H), 3.82 (d, *J* = 6.3 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.19, 144.13, 141.31, 135.64, 135.06, 131.86, 131.68, 131.20, 129.75, 128.87, 127.57, 126.94, 120.30, 95.38, 80.50, 49.77, 36.70, 21.43; IR (KBr) ν_{max} 2966.20, 2925.07, 2859.12, 2229.58, 1669.36, 1491.37, 1348.75, 1161.35, 911.42, 750.73; HRMS (EI) calcd for $C_{22}H_{21}NO_3S$ [M]: 379.1242, Found: 379.1241.

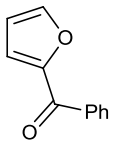
(5-Hydroxy-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (5a)



Pale yellow oil; yield: 73% (61 mg); R_f = 0.23 (Hex/EtOAc = 5/1).

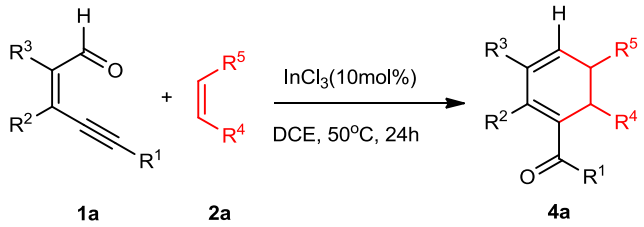
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 9.2 Hz, 4H), 7.05 (t, *J* = 6.8 Hz, 1H), 6.03 (dd, *J* = 6.3, 3.5 Hz, 1H), 5.78 (d, *J* = 9.9 Hz, 1H), 4.27 (d, *J* = 8.9 Hz, 1H), 4.21 (d, *J* = 3.0 Hz, 1H), 3.55 (dd, *J* = 16.3, 8.1 Hz, 1H), 2.06 (dd, *J* = 7.7, 3.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.50, 143.88, 136.31, 133.18, 130.68, 128.61, 128.50, 128.15, 127.55, 126.60, 63.73, 51.14, 37.68, 37.18; IR (KBr) ν_{max} 3604.83, 3027.12, 2921.47, 2848.98, 1685.77, 1597.62, 1493.23, 1284.34, 959.84, 698.81; HRMS (EI) calcd for $C_{19}H_{18}NaO_2$ $[M+Na]^+$: 301.1204, Found: 301.1199.

Furan-2-yl(phenyl)methanone (6a)[5]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.64 (s, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 3.4 Hz, 1H), 6.53 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.59, 152.34, 147.10, 137.29, 132.58, 129.30, 128.43, 120.55, 112.21.

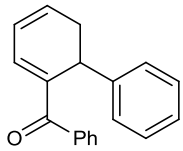
2.2 General procedure for Indium-catalyzed tandem reaction of enynals with olefins



1a **2a** **4a**

To a dichloroethane (DCE, 2 ml) suspension of $InCl_3$ (10% mmol) in schlenk tube with a magnetic bar under a nitrogen atmosphere was added olefin (**2a**, 0.9 mmol) and enynals (**1a**, 0.3 mmol), the reaction was stirred at 50 ℃ unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography (Hex/EtOAc = 20/1), **4a** was obtained.

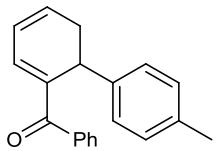
(1,6-Dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4a)[2]



Pale yellow oil; yield: 79% (61 mg); R_f = 0.33 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 6.9 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.11 (d, J = 7.3 Hz, 1H), 6.73 (d, J = 5.0 Hz, 1H), 6.14 – 6.01 (m, 2H), 4.30 – 4.20 (m, 1H), 2.86 (dd, J = 18.6, 10.4 Hz, 1H), 2.65 – 2.55 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.86, 143.17, 138.71, 137.48, 137.07, 133.01, 132.07, 131.41, 129.05, 128.43, 128.11, 127.23, 126.59, 123.84, 35.34, 32.03.

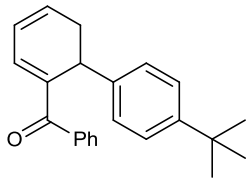
(4'-Methyl-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4b)



Pale yellow oil; yield: 71% (58 mg); R_f = 0.30 (Hex/EtOAc = 20/1).

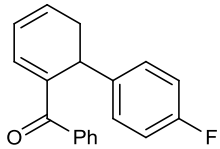
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 6.85 (d, J = 5.1 Hz, 1H), 6.25 – 6.12 (m, 2H), 4.35 (d, J = 8.7 Hz, 1H), 2.97 (dd, J = 18.5, 10.3 Hz, 1H), 2.71 (ddd, J = 18.5, 4.9, 2.7 Hz, 1H),2.34(s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.88, 140.16, 138.79, 137.69, 136.93, 136.10, 133.02, 131.40, 129.17, 129.09, 128.12, 127.15, 123.87, 35.01, 32.17, 21.06; IR (KBr) ν_{max} 3035.60, 2922.95, 2860.17, 1639.78, 1564.76, 1508.48, 1271.00, 812.09, 742.08, 702.71; HRMS (EI) calcd for $C_{20}H_{18}O$ [M]: 274.1358, Found: 274.1360.

(4'-(Tert-butyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4c)



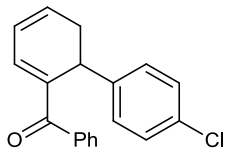
Yellow oil; yield: 81% (76 mg); R_f = 0.32 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.22 – 7.14 (m, 4H), 6.73 (d, J = 5.2 Hz, 1H), 6.13 – 6.00 (m, 2H), 4.23 (dd, J = 10.2, 2.5 Hz, 1H), 2.89 – 2.77 (m, 1H), 2.61 (ddd, J = 18.5, 5.2, 2.7 Hz, 1H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.92, 149.20, 139.94, 138.81, 137.62, 137.04, 133.14, 131.34, 129.09, 128.08, 126.84, 125.30, 123.82, 34.66, 34.35, 32.01, 31.38 IR (KBr) ν_{max} 3058.13, 2959.27, 2856.56, 1723.10, 1567.19, 1455.90, 1404.68, 1269.77, 1018.41, 705.42; HRMS (EI) calcd for $C_{23}H_{22}O$ $[M\text{-}H_2]^+$: 314.1671, Found: 314.1668.

(4'-Fluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4d)



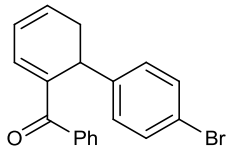
Pale yellow oil; yield: 73% (60 mg); R_f = 0.35 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.1 Hz, 2H), 7.41 (t, J = 6.9 Hz, 1H), 7.33 (t, J = 7.1 Hz, 2H), 7.20 (s, 2H), 6.85 (t, J = 8.2 Hz, 2H), 6.74 (d, J = 4.1 Hz, 1H), 6.08 (d, J = 11.2 Hz, 2H), 4.21 (d, J = 10.1 Hz, 1H), 2.84 (dd, J = 18.2, 10.4 Hz, 1H), 2.55 (d, J = 18.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.79, 161.70 (d, $J_{C\text{-}F}$ = 242.6Hz), 138.89, 138.59, 137.35, 137.19, 132.97, 131.52, 129.02, 128.68 (d, $J_{C\text{-}F}$ = 7.8Hz), 128.18, 123.93, 115.20 (d, $J_{C\text{-}F}$ = 21.3Hz), 34.67, 32.09; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.67; IR (KBr) ν_{max} 3054.37, 2923.59, 2857.00, 1634.52, 1505.76, 1269.07, 1229.19, 1163.58, 830.49, 705.44; HRMS (EI) calcd for $C_{19}H_{15}FO$ [M]: 278.1107, Found: 278.1106 .

(4'-Chloro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4e)



Pale yellow oil; yield: 68% (59 mg); R_f = 0.35 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.16 (q, J = 8.5 Hz, 4H), 6.75 (d, J = 5.3 Hz, 1H), 6.14 – 6.02 (m, 2H), 4.20 (dd, J = 10.3, 2.5 Hz, 1H), 2.85 (dd, J = 18.6, 10.3 Hz, 1H), 2.55 (ddd, J = 18.6, 5.4, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.69, 141.68, 138.52, 137.27, 137.07, 132.91, 132.29, 131.52, 128.99, 128.61, 128.55, 128.17, 123.94, 34.91, 31.91; IR (KBr) $\nu_{max.}$ 3075.12, 2924.85, 2850.42, 1731.58, 1560.59, 1487.96, 1274.70, 1034.23, 928.91, 702.59; HRMS (EI) calcd for $C_{19}H_{15}ClO$ [M]: 294.0811, Found: 294.0810.

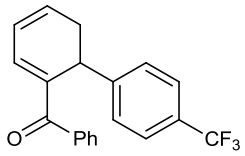
(4'-Bromo-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4f)



Yellow oil; yield: 85% (86 mg); R_f = 0.36 (Hex/EtOAc = 20/1).

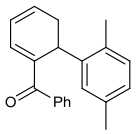
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.31 (dd, J = 19.7, 7.7 Hz, 4H), 7.12 (d, J = 7.9 Hz, 2H), 6.75 (d, J = 5.1 Hz, 1H), 6.08 (d, J = 11.5 Hz, 2H), 4.18 (d, J = 9.7 Hz, 1H), 2.85 (dd, J = 18.3, 10.3 Hz, 1H), 2.54 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.64, 142.23, 138.51, 137.29, 136.99, 132.89, 131.52, 131.51, 129.02, 128.99, 128.18, 123.96, 120.39, 35.00, 31.85; IR (KBr) ν_{max} 3056.78, 2924.64, 2858.43, 1719.93, 1656.25, 1589.77, 1483.95, 1271.98, 1070.10, 704.30; HRMS (EI) calcd for $C_{19}H_{15}BrO$ [M]: 338.0306, Found: 338.0301.

Phenyl(4'-(trifluoromethyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4g)



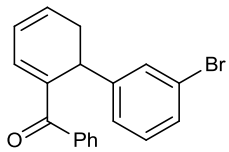
Pale yellow oil; yield: 55% (54 mg); R_f = 0.31 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.8 Hz, 3H), 7.35 (d, J = 7.1 Hz, 4H), 6.81 (d, J = 5.2 Hz, 1H), 6.25 – 5.98 (m, 2H), 4.28 (d, J = 9.9 Hz, 1H), 2.88 (dd, J = 18.5, 10.4 Hz, 1H), 2.57 (d, J = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.56, 147.23, 138.39, 137.75, 136.62, 132.92, 131.61, 129.00, 128.22, 127.56, 125.42 (m, J_{C-F} = 3.8Hz), 124.06, 35.51, 31.83, 22.13; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.37; IR (KBr) ν_{max} 3061.76, 2924.22, 2848.49, 1726.27, 1565.95, 1452.10, 1324.47, 1274.43, 1121.20, 702.98; HRMS (EI) calcd for $C_{20}H_{15}F_3O$ [M]: 328.1075, Found: 328.1079.

(2',5'-Dimethyl-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4h)



Brown yellow oil; yield: 69% (59 mg); R_f = 0.32 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d,J = 7.4 Hz, 2H), 7.43 – 7.37 (m, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.02 – 6.92 (m, 2H), 6.81 (d, J = 6.0 Hz, 2H), 6.10 (s, 1H), 5.97 (d, J = 4.2 Hz, 1H), 4.43 (dd, J = 11.1, 2.9 Hz, 1H), 2.82 (dd, J = 18.3, 11.4 Hz, 1H), 2.40 (d, J = 19.0 Hz, 1H), 2.35 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.71, 140.84, 138.71, 137.93, 137.24, 135.03, 132.63, 132.00, 131.36, 130.67, 129.02, 128.09, 127.19, 127.15, 123.60, 31.44, 31.14, 21.25, 19.26; IR (KBr) ν_{max} 3051.19, 2921.71, 2856.98, 1725.05, 1566.51, 1451.59, 1272.30, 929.16, 733.08, 701.74; HRMS (EI) calcd for $C_{20}H_{18}O$ [M]: 288.1514, Found: 288.1516.

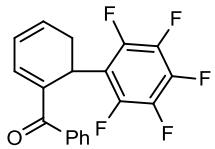
(3'-Bromo-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4i)



Pale yellow oil; yield: 59% (60 mg); R_f = 0.32 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.43 (dd, J = 13.0, 5.5 Hz, 1H), 7.35 (dd, J = 14.6, 7.0 Hz, 3H), 7.24 (d, J = 7.9 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.04 (t, J = 7.8 Hz, 1H), 6.78

(d, *J* = 5.4 Hz, 1H), 6.21 – 5.97 (m, 2H), 4.20 (dd, *J* = 10.3, 2.5 Hz, 1H), 2.85 (ddt, *J* = 18.3, 10.3, 2.6 Hz, 1H), 2.56 (ddd, *J* = 18.6, 5.6, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.55, 145.51, 138.51, 137.60, 136.69, 132.92, 131.52, 130.26, 130.02, 129.74, 129.00, 128.19, 126.00, 124.01, 122.50, 35.19, 31.90; IR (KBr) $\nu_{max.}$ 3055.73, 2922.94, 2854.50, 1631.83, 1560.93, 1460.08, 1271.60, 1068.59, 735.47, 695.80; HRMS (EI) calcd for $C_{19}H_{15}BrO$ [M]: 338.0306; Found: 338.0309.

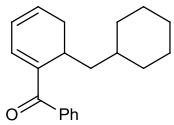
(2',3',4',5',6'-Pentafluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4j)



Brown yellow oil; yield: 28% (29 mg); R_f = 0.29 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 3.8 Hz, 1H), 6.25 – 6.16 (m, 1H), 6.16 – 6.07 (m, 1H), 4.50 (dd, *J* = 14.3, 10.4 Hz, 1H), 2.69 – 2.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.78, 137.37, 136.86, 135.83, 132.76, 132.20, 129.42, 128.29, 123.78, 30.25, 30.05; ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.16, -141.18, -141.21, -141.23, -157.59, -157.65, -157.70, -162.51, -162.53, -162.57, -162.58, -162.62, -162.64; IR (KBr) ν_{max} 3056.28, 2924.44, 2864.21, 1642.90, 1501.48, 1401.21, 1274.77, 1126.44, 705.11, 619.38; HRMS (EI) calcd for $C_{19}H_{11}F_5O$ [M]: 350.0730, Found: 350.0735.

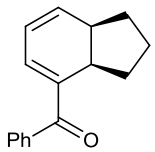
(6-(Cyclohexylmethyl)cyclohexa-1,3-dien-1-yl)(phenyl)methanone (4k)



Pale yellow oil; yield: 70% (59 mg); R_f = 0.32 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 6.46 (d, *J* = 4.4 Hz, 1H), 6.01 (s, 2H), 3.06 (s, 1H), 2.44 – 2.28 (m, 2H), 1.76 (d, *J* = 12.8 Hz, 1H), 1.68 – 1.49 (m, 5H), 1.37 – 1.25 (m, 2H), 1.18 – 1.00 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.29, 140.50, 139.02, 136.07, 132.91, 131.22, 129.01, 128.04, 123.57, 38.43, 34.81, 34.20, 32.64, 27.78, 26.66, 26.61, 26.42, 26.29; IR (KBr) $\nu_{max.}$ 3057.48, 2922.03, 2851.58, 1663.01, 1588.05, 1449.13, 1266.32, 1072.80, 928.32, 705.01; HRMS (EI) calcd for C20H24O [M]: 280.1827, Found: 280.1825.

Phenyl(2,3,3a,7a-tetrahydro-1H-inden-4-yl)methanone (4l)

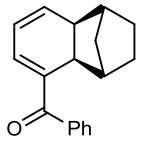


Pale yellow oil; yield: 75% (50 mg); R_f = 0.38 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 6.44 – 6.38 (m, 1H), 5.85 (dd, *J* = 3.3, 1.8 Hz, 2H), 3.08 (dt, *J* = 11.3, 8.9 Hz, 1H), 2.99 –

2.89 (m, 1H), 2.18 (ddd, *J* = 12.1, 7.2, 3.5 Hz, 1H), 2.09 (dt, *J* = 14.0, 7.8 Hz, 1H), 1.61 (ddd, *J* = 12.4, 9.9, 6.2 Hz, 1H), 1.49 – 1.41 (m, 2H), 1.39 – 1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 197.94, 139.20, 139.12, 139.03, 134.53, 131.19, 128.96, 128.04, 120.72, 38.74, 36.12, 34.42, 34.37, 22.98; IR (KBr) ν_{max} 2957.05, 2925.60, 2852.12, 1640.62, 1561.97, 1447.15, 1383.94, 1104.89, 701.34, 619.20; HRMS (EI) calcd for $C_{16}H_{16}O$ [M]: 224.1201, Found: 224.1202.

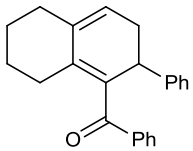
(1,2,3,4,4a,8a-Hexahydro-1,4-methanonaphthalen-5-yl)(phenyl)methanone (4m)



Pale yellow oil; yield: 92% (69 mg); R_f = 0.30 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.57 – 7.51 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 6.24 (d, *J* = 5.9 Hz, 1H), 5.78 (dd, *J* = 9.5, 4.2 Hz, 1H), 5.68 (ddd, *J* = 9.5, 5.9, 1.7 Hz, 1H), 3.11 (d, *J* = 12.3 Hz, 1H), 2.66 (dd, *J* = 12.2, 3.2 Hz, 1H), 2.11 (d, *J* = 8.0 Hz, 2H), 1.70 (d, *J* = 9.7 Hz, 1H), 1.55 – 1.47 (m, 3H), 1.43 – 1.38 (m, 1H), 1.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 198.27, 139.27, 136.61, 136.39, 135.50, 131.28, 128.91, 128.05, 120.85, 45.60, 45.55, 44.88, 41.21, 34.81, 30.67, 30.36; IR (KBr) ν_{max} 3054.12, 2952.00, 2873.57, 1641.71, 1569.84, 1451.32, 1265.82, 928.55, 729.37, 702.49; HRMS (EI) calcd for $C_{18}H_{18}O$ [M]: 250.1358, Found: 250.1359.

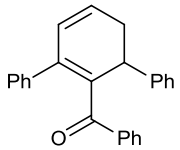
Phenyl(2-phenyl-2,3,5,6,7,8-hexahydronaphthalen-1-yl)methanone (4n)



Yellow oil; yield: 52% (49 mg); R_f = 0.36 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.67 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.14 – 7.08 (m, 4H), 7.03 (d, *J* = 6.5 Hz, 1H), 5.75 (s, 1H), 3.89 (s, 1H), 2.43 – 2.27 (m, 2H), 2.20 (d, *J* = 15.1 Hz, 1H), 2.15 – 2.02 (m, 4H), 1.80 (dt, *J* = 11.3, 5.3 Hz, 1H), 1.67 – 1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 199.86, 142.96, 137.86, 136.55, 133.63, 133.07, 132.68, 129.01, 128.62, 128.44, 128.10, 126.29, 44.32, 31.66, 28.68, 27.49, 25.87, 23.02; IR (KBr) ν_{max} 3026.36, 2926.19, 2857.48, 1668.87, 1597.36, 1384.34, 1242.73, 1096.58, 700.51, 618.42; HRMS (EI) calcd for $C_{23}H_{23}O$ $[M+H]^+$: 315.1743, Found: 315.1734.

(1',6'-dihydro-[1,1':3',1''-terphenyl]-2'-yl)(phenyl)methanone (4o)

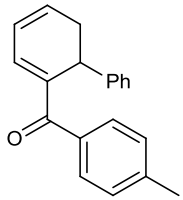


Yellow oil; yield: 52% (52 mg); R_f = 0.33 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.18 – 7.06 (m, 7H), 6.98 (t, *J* = 7.3 Hz, 4H), 6.25 (d, *J* = 9.7 Hz, 1H), 6.09 – 5.98 (m, 1H), 4.11 (dd, *J* =

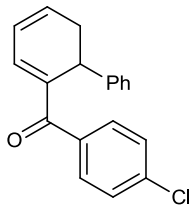
9.6, 5.2 Hz, 1H), 2.98 – 2.85 (m, 1H), 2.63 (dt, *J* = 18.1, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.84, 142.83, 139.68, 139.35, 137.84, 134.31, 131.89, 129.11, 129.07, 128.42, 128.33, 128.03, 127.75, 127.68, 127.67, 126.72, 41.17, 31.64; IR (KBr) ν_{max} 3058.80, 2924.45, 2851.59, 1642.72, 1578.39, 1492.40, 1238.46, 1073.31, 736.70, 698.22; HRMS (MALDI/DHB) calcd for $C_{25}H_{21}O$ $[M+H]^+$: 337.1586 ±0.002, Found: 337.15869.

(1,6-Dihydro-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone (4p)



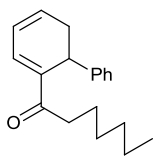
Pale yellow oil; yield: 95% (78 mg); R_f = 0.33(Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 1H), 7.13 (dt, *J* = 16.8, 7.9 Hz, 6H), 6.71 (d, *J* = 5.3 Hz, 1H), 6.11 – 5.98 (m, 2H), 4.23 (dd, *J* = 10.3, 2.9 Hz, 1H), 2.85 (ddd, *J* = 15.7, 9.0, 5.2 Hz, 1H), 2.58 (ddd, *J* = 18.5, 5.3, 3.1 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.63, 143.29, 142.07, 137.65, 136.30, 135.92, 132.61, 129.30, 128.80, 128.41, 127.25, 126.54, 123.83, 35.58, 32.03, 21.53; IR (KBr) ν_{max} 3050.66, 2924.10, 2858.77, 1639.84, 1565.86, 1449.24, 1270.24, 1178.22, 742.54, 704.81; HRMS (EI) calcd for $C_{20}H_{18}O$ [M]: 274.1358, Found: 274.1362.

(4-Chlorophenyl)(1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4q)



White solid; yield: 71% (62 mg); R_f = 0.35 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.69 (d, *J* = 4.3 Hz, 1H), 6.07 (s, 2H), 4.21 (d, *J* = 8.5 Hz, 1H), 2.84 (dd, *J* = 18.6, 10.4 Hz, 1H), 2.59 (d, *J* = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.52, 143.10, 137.76, 137.36, 136.98, 136.94, 133.35, 130.49, 128.50, 128.45, 127.19, 126.69, 123.73, 35.47, 32.01; IR (KBr) ν_{max} 3056.43, 2920.63, 2856.42, 1682.32, 1583.12, 1481.11, 1396.18, 1099.04, 751.11, 615.01; HRMS (EI) calcd for $C_{19}H_{15}ClO$ [M]: 294.0811, Found: 294.0813.

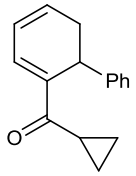
1-(1,6-Dihydro-[1,1'-biphenyl]-2-yl)heptan-1-one (4r)



Pale yellow oil; yield: 56% (45 mg); R_f = 0.35; IR (KBr) ν_{max} 2958.92, 2926.43, 2856.19, 1659.59, 1565.79, 1493.39, 1275.19, 1182.05, 751.25, 697.83; ^{1}H NMR (400 MHz, $CDCl_3$) δ

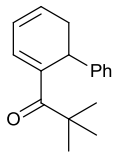
7.14 (d, J = 3.7 Hz, 4H), 7.06 (d, J = 5.5 Hz, 2H), 6.15 – 6.06 (m, 1H), 6.04 – 5.95 (m, 1H), 4.07 (d, J = 10.2 Hz, 1H), 2.75 (dd, J = 18.3, 10.4 Hz, 1H), 2.53 (dt, J = 18.5, 6.6 Hz, 3H), 1.51 – 1.43 (m, 2H), 1.16 (s, 6H), 0.78 (t, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.57, 143.02, 137.63, 133.06, 132.90, 128.29, 127.24, 126.48, 123.93, 77.38, 77.06, 76.74, 37.37, 34.35, 32.05, 31.66, 29.02, 24.86, 22.52, 14.05; HRMS (EI) calcd for $C_{16}H_{16}O$ [M]: 269.1905, Found: 269.1900.

Cyclopropyl(1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4s)



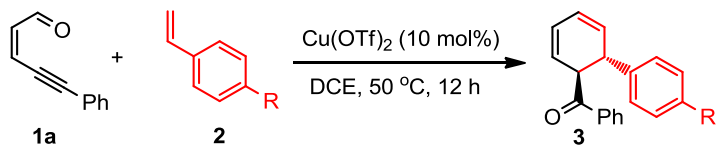
Pale yellow oil; yield: 80% (54 mg); R_f = 0.32 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.22 (d, *J* = 5.5 Hz, 1H), 7.17 – 7.14 (m, 3H), 7.11 – 7.06 (m, 1H), 6.14 (ddd, *J* = 8.9, 5.5, 3.1 Hz, 1H), 6.07 – 5.93 (m, 1H), 4.08 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.51 (ddd, *J* = 18.4, 6.0, 1.4 Hz, 1H), 2.34 – 2.25 (m, 1H), 0.96 – 0.87 (m, 2H), 0.78 – 0.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 199.78, 142.94, 138.26, 133.04, 132.75, 128.32, 127.24, 126.46, 124.08, 34.83, 32.14, 16.01, 10.81, 10.54; IR (KBr) ν_{max} 3068.52, 2920.54, 2854.64, 1733.21, 1555.45, 1457.14, 1263.94, 1207.13, 1023.88, 741.92; HRMS (EI) calcd for $C_{16}H_{16}O$ [M]: 224.1201, Found: 224.1197.

1-(1,6-Dihydro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpro-pan-1-one. (4t).



Pale yellow oil; yield: 41% (30 mg); R_f = 0.35; IR (KBr) ν_{max} 2958.58, 2924.85, 2851.36, 1647.09, 1564.74, 1453.18, 1268.55, 1147.64, 749.96, 701.09; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 3.7 Hz, 4H), 7.19 (d, J = 4.2 Hz, 1H), 7.09 (d, J = 5.4 Hz, 1H), 6.18 (s, 1H), 6.01 (s, 1H), 4.14 (d, J = 9.9 Hz, 1H), 2.85 (dd, J = 17.8, 10.0 Hz, 1H), 2.58 (d, J = 18.2 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.85, 142.17, 134.98, 130.31, 130.03, 127.23, 126.24, 125.35, 122.60, 76.31, 76.00, 75.68, 42.80, 35.30, 31.11, 27.63; HRMS (EI) calcd for $C_{17}H_{20}NaO$ [M]: 263.1412, Found: 263.1406.

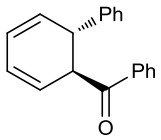
2.3 General procedure for copper -catalyzed tandem reaction of enynals with olefins



To a dichloroethane (DCE, 2 ml) suspension of $Cu(OTf)_2$ (10% mmol) in schlenk tube with

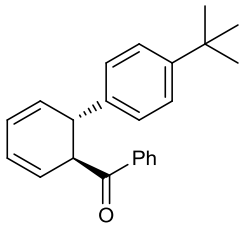
a magnetic bar under a nitrogen atmosphere was added olefin (**2**, 0.6 mmol) and enynals (**1a**, 0.3 mmol), the reaction was stirred at 50 ℃ unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography (Hex/EtOAc = 20/1). **3** was obtained.

(1,2-Dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3a)



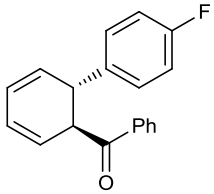
Pale yellow oil; yield: 45% (35 mg); R_f = 0.38 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 6.8 Hz, 1H), 7.34 (t, J = 7.3 Hz, 2H), 7.25 (d, J = 6.9 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.13 (d, J = 6.6 Hz, 1H), 5.98 (s, 2H), 5.82 (d, J = 8.2 Hz, 1H), 5.54 (d, J = 7.6 Hz, 1H), 4.35 (d, J = 8.6 Hz, 1H), 4.27 (d, J = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.82, 144.12, 135.91, 133.07, 130.61, 128.69, 128.64, 128.24, 126.81, 125.14, 122.30, 121.86, 50.47, 40.88; IR (KBr) ν_{max} 3056.49, 2957.19, 2858.46, 1686.72, 1596.71, 1537.84, 1386.63, 1210.16, 947.53, 702.17; HRMS (EI) calcd for $C_{19}H_{14}O$ $[M\text{-}H_2]^+$: 258.1045, Found: 258.1043.

(4'-(Tert-butyl)-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3b)



Brown yellow oil; yield: 48% (45 mg); R_f = 0.36 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.4 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.17 (t, J = 6.1 Hz, 2H), 5.97 (dd, J = 14.5, 6.6 Hz, 2H), 5.83 (dd, J = 8.7, 3.8 Hz, 1H), 5.54 (dd, J = 8.6, 4.1 Hz, 1H), 4.38 – 4.29 (m, 1H), 4.26 – 4.18 (m, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.90, 149.58, 140.93, 136.06, 132.92, 130.74, 128.63, 128.61, 127.77, 125.49, 125.14, 122.06, 121.89, 50.47, 40.37, 34.40, 29.70; IR (KBr) ν_{max} 3057.07, 2958.49, 2855.18, 1692.35, 1596.86, 1517.61, 1223.71, 932.67, 815.21, 708.78; HRMS (EI) calcd for $C_{23}H_{24}O$ [M]: 316.1827, Found: 316.1831.

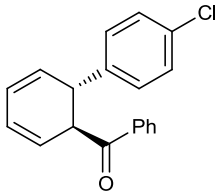
(4'-Fluoro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3c)



Pale yellow oil; yield: 62% (51 mg); R_f = 0.33 (Hex/EtOAc = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.21 (dd, J = 7.9, 6.3 Hz, 2H), 6.88 (t, J = 8.5 Hz, 2H), 6.07 – 5.91 (m, 2H), 5.85 – 5.74

(m, 1H), 5.61 – 5.48 (m, 1H), 4.36 – 4.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.73, 161.75 (d, $J_{C\text{-}F}$= 243.0Hz), 139.88, 135.90, 133.12, 130.55, 129.72 (d, $J_{C\text{-}F}$= 7.9Hz), 128.64 (d, $J_{C\text{-}F}$= 12.1Hz), 125.07, 122.50, 121.89, 115.44, 115.23, 50.70, 40.24; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.27; IR (KBr) ν_{max} 3049.15, 2928.07, 2854.30, 1661.55, 1596.03, 1443.43, 1250.46, 953.71, 724.50, 697.93; HRMS (EI) calcd for $C_{19}H_{13}FO$ $[M\text{-}H_2]^+$: 276.0950, Found: 276.0954.

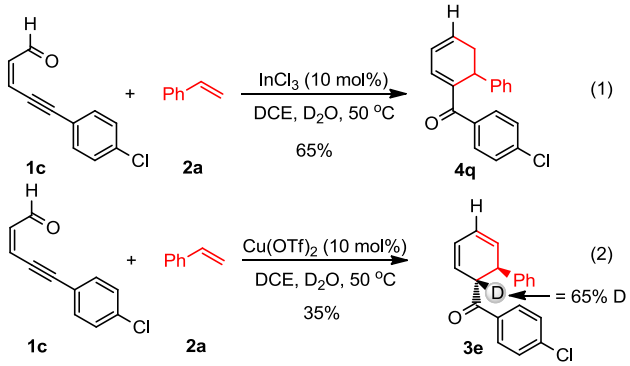
(4'-Chloro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3d)



Brown yellow oil; yield: 45% (39 mg); R_f = 0.35 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.3 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.20 – 7.14 (m, 4H), 6.06 – 5.95 (m, 2H), 5.77 (dd, J = 10.1, 2.7 Hz, 1H), 5.59 – 5.49 (m, 1H), 4.33 – 4.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.48, 142.67, 135.82, 133.14, 132.53, 130.21, 129.63, 128.71, 128.68, 128.58, 125.06, 122.66, 121.86, 50.51, 40.31; IR (KBr) ν_{max} 3042.12, 2921.44, 2854.81, 1660.30, 1528.62, 1401.66, 1384.31, 1105.97, 699.84, 619.39; HRMS(EI)calcd for $C_{19}H_{13}ClO$ $[M\text{-}H_2]^+$: 292.0655, Found: 292.0657.

2.4 Deuterium-labeling experiments.



To gain more information about the reaction mechanism, additional D_2O (12 mg, 0.6mmol) was added in the reaction of enynals (**1c**, 0.3 mmol) and olefin (**2a**, 0.6 mmol) at 50 ℃. The olefinic carbon atom in product **4q** (1) does not have the deuterium label. Instead, 65 % incorporation of deuterium was found at the position of the alkyl group **3e** (2). a result that is consistent with the proposed mechanism involving β-H (path a) or δ-M elimination (Scheme 2).

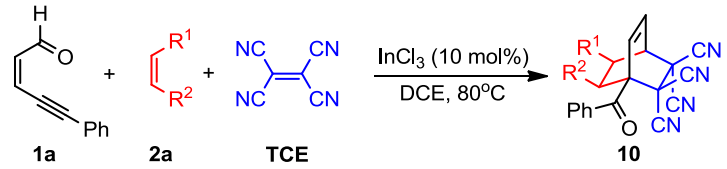
(4-Chlorophenyl)(2-deuterio-1,2-dihydro-[1,1'-biphenyl]-2-yl)methanone (3e)

Pale yellow oil; ield: 35%(23 mg); R_f = 0.33 (Hex/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 3H), 7.22 (s, 6H), 7.14 (d, J = 7.5 Hz, 2H), 6.00 (t, J = 9.2 Hz, 2H), 5.83 (s, 1H), 5.50 (d, J = 9.0 Hz, 1H), 4.28 (s, 0.3H), 4.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.82, 143.88, 139.50, 134.31, 131.04, 130.61, 129.99, 128.96, 128.64, 128.16, 126.88, 126.06, 125.38, 122.31, 121.49, 50.54,

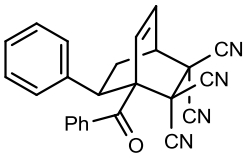
41.10.IR (KBr) ν_{max} 3054.27, 2918.95, 2850.03, 1679.28, 1588.17, 1489.53, 1384.00, 1109.57, 701.39, 618.86; HRMS (EI)calcd for $C_{19}H_{14}DClO$ $[M]^+$: 295.0874, Found: 295.0877.

2.5 General procedure for Indium-catalyzed tandem reaction of enynals with olefins and tetracyanoethylene



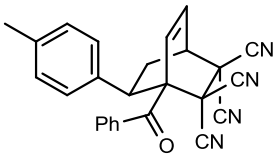
To a dichloroethane (DCE, 2 ml) suspension of $InCl_3$ (10% mmol) in schlenk tube with a magnetic bar under a nitrogen atmosphere, was added olefin (**2a**, 0.9 mmol) and enynals (**1a**, 0.3 mmol) and tetracyanoethylene (0.6 mmol), the reaction was stirred at 80 ℃ unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography (Hex/EtOAc = 5/1). **10** was obtained.

1-Benzoyl-7-phenylbicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10a)



Brown yellow solid (m.p.159 ℃); yield: 70% (81 mg); R_f = 0.30 (Hex/EtOAc = 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 4.6 Hz, 3H), 7.10 (t, J = 7.8 Hz, 2H), 7.06 – 6.99 (m, 2H), 6.98 – 6.91 (m, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 4.05 (dd, J = 9.7, 5.0 Hz, 1H), 3.86 – 3.72 (m, 1H), 2.84 (dd, J = 14.3, 10.7 Hz, 1H), 2.19 – 2.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.21, 138.25, 135.92, 134.54, 132.54, 132.07, 129.60, 129.28, 128.97, 128.28, 127.94, 111.64, 111.31, 111.27, 111.18, 61.30, 47.22, 45.95, 43.17, 40.80, 28.61; IR (KBr) ν_{max} 3057.09, 2925.18, 2856.70, 2232.62, 1715.02, 1620.45, 1380.52, 1096.28, 701.68, 620.75; HRMS (DART POS) calcd for $C_{25}H_{17}ON_4$ $[M+H]^+$: 389.1397, Found: 389.1386.

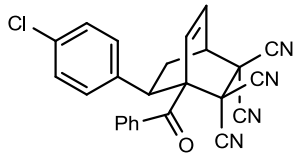
1-Benzoyl-7-(p-tolyl)bicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile（10b）



Brown solid (m.p.162 ℃); yield: 72% (87 mg); R_f = 0.28 (Hex/EtOAc =5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.3 Hz, 1H), 7.11 (t, J = 7.6 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.92 (dd, J = 13.2, 7.9 Hz, 3H), 6.78 (d, J = 8.6 Hz, 1H), 6.69 (d, J = 7.9 Hz, 2H), 4.02 (dd, J = 9.6, 5.0 Hz, 1H), 3.78 (s, 1H), 2.82 (dd, J = 15.1, 9.9 Hz, 1H), 2.20 (s, 3H), 2.13 – 2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.30, 139.03, 135.94, 135.16, 134.43, 132.50, 132.12, 129.87, 129.43, 128.21, 128.08, 111.67, 111.33, 111.29, 111.23, 61.37, 47.16, 45.95, 42.83, 40.82, 28.60, 20.93; IR (KBr) ν_{max} 3037.09, 2919.97, 2858.13, 2225.52, 1745.70,

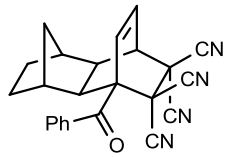
1630.45, 1384.52, 1096.80, 700.68, 618.31; HRMS (DART Postive) calcd for $C_{26}H_{19}ON_4$ $[M+H]^+$: 403.1546, Found: 403.1553.

1-Benzoyl-7-(4-chlorophenyl)bicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10c)



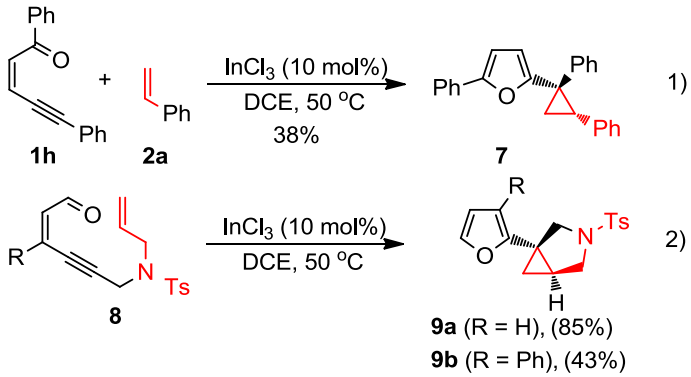
Brown solid (m.p.167 ℃); yield: 46% (58 mg); R_f = 0.25 (Hex/EtOAc = 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, J = 7.4 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.06 (d, J = 8.1 Hz, 3H), 6.94 (d, J = 8.6 Hz, 1H), 6.87 (d, J = 7.8 Hz, 2H), 4.12 (dd, J = 9.8, 5.1 Hz, 1H), 3.90 (s, 1H), 2.95 (dd, J = 14.5, 10.0 Hz, 1H), 2.21 – 2.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.62, 136.74, 135.69, 135.18, 134.77, 132.88, 131.91, 130.84, 129.38, 128.46, 128.02, 111.51, 111.18, 111.14, 110.99, 61.09, 47.20, 45.83, 42.53, 40.67, 28.79; IR (KBr) ν_{max} 3040.58, 2935.20, 2859.07, 2228.41, 1760.13, 1642.45, 1388.52, 1099.57, 702.26, 619.82; HRMS (DART POS) calcd for $C_{25}H_{16}ON_4Cl$ $[M+H]^+$: 423.1007, Found: 423.0995.

1-Benzoyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-ethano-5,8-methanonaphthalene-10,10,11,11-tetracarbonitrile (10d)



Brown yellow solid (m.p.150 ℃); yield: 45% (51 mg); R_f = 0.30 (Hex/EtOAc = 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 6.92 (d, J = 8.5 Hz, 1H), 6.75 – 6.65 (m, 1H), 3.72 (d, J = 6.2 Hz, 1H), 2.55 (d, J = 8.4 Hz, 1H), 2.43 (d, J = 8.3 Hz, 1H), 2.28 (d, J = 11.6 Hz, 2H), 2.07 (d, J = 10.7 Hz, 1H), 1.57 – 1.50 (m, 1H), 1.48 – 1.41 (m, 1H), 1.29 (dd, J = 16.8, 9.9 Hz, 1H), 1.03 (d, J = 10.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.92, 134.42, 134.40, 133.67, 131.88, 130.22, 129.02, 111.69, 111.52, 111.41, 111.37, 61.33, 47.41, 47.02, 46.58, 43.82, 41.70, 41.04, 40.92, 34.59, 30.82, 30.60; IR (KBr) ν_{max} 3031.51, 2964.92, 2878.06, 2225.50, 1668.95, 1596.01, 1383.62, 1094.63, 785.28, 618.12; HRMS (DART POS) calcd for $C_{24}H_{19}ON_4$ $[M+H]^+$: 379.1553, Found: 379.1543.

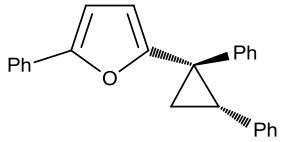
2.6 Procedure for intramolecular reaction of tethered alkenyl enynals



1)To a dichloroethane (DCE, 2 ml) suspension of $InCl_3$ (10% mmol) in schlenk tube with a magnetic bar under a nitrogen atmosphere was added olefin (**2a**, 0.9 mmol) and enynals (**1h**, 0.3 mmol), the reaction was stirred at 50 ℃ unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography (Hex/EtOAc = 20/1), **7** was obtained.

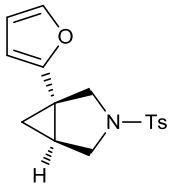
2)To a dichloroethane (DCE, 2 ml) suspension of $InCl_3$ (10% mmol) in schlenk tube with a magnetic bar under a nitrogen atmosphere was added olefin (**8**, 0.3 mmol). the reaction was stirred at 50 ℃ unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography (Hex/EtOAc = 5/1), **9** was obtained.

1,2-diphenylcyclopropyl)-5-phenylfuran (7)



Pale yellow oli; yield: 38% (38 mg); dr (*Z*:*E*) = 84:16; R_f = 0.4 (Hex/EtOAc = 50/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.18 – 7.14 (m, 1H), 7.10 (s, 5H), 6.98 (t, *J* = 8.1 Hz, 3H), 6.76 (d, *J* = 7.4 Hz, 2H), 6.45 – 6.40 (m, 1H), 5.69 – 5.64 (m, 1H), 3.00 (t, *J* = 7.7 Hz, 1H), 2.06 (dd, *J* = 8.7, 5.6 Hz, 1H), 1.91 (t, *J* = 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.50, 152.46, 143.82, 138.04, 131.61, 131.03, 128.48, 128.42, 128.20, 127.83, 126.75, 126.60, 126.23, 123.49, 110.78, 105.50, 77.37, 77.05, 76.73, 32.89, 32.67, 19.53; IR (KBr) ν_{max} 2957.38, 2923.42, 2850.31, 1461.67, 1385.26, 1277.84, 913.14, 746.40, 697.89, 632.96; HRMS (EI) calcd for $C_{25}H_{20}NaO_2$[M+Na]$^+$: 359.1412, Found: 359.1406.

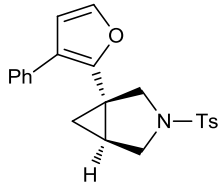
1-(Furan-2-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (9a)



Brown yellow solid (m.p.89℃); yield: 85% (80 mg); R_f = 0.34 (Hex/EtOAc = 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.15 (s, 1H), 6.19 (s, 1H), 5.90 (d, *J* = 2.8 Hz, 1H), 3.69 (d, *J* = 9.0 Hz, 1H), 3.54 (d, *J* = 9.3 Hz, 1H), 3.25 (d, *J* = 9.0 Hz, 1H), 3.12 (dd, *J* = 9.2, 3.6 Hz, 1H), 2.37 (s, 3H), 1.69 (dt, *J* = 8.1, 4.2 Hz, 1H),

1.14 – 1.08 (m, 1H), 0.97 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.45, 143.66, 141.11, 133.42, 129.73, 127.59, 110.40, 104.91, 51.23, 49.80, 25.70, 24.19, 21.55, 14.75; IR (KBr) ν_{max} 3056.45, 2922.68, 2851.24, 1734.39, 1598.32, 1462.51, 1349.00, 1165.19, 1101.18, 740.74; HRMS (EI) calcd for $C_{16}H_{17}NO_3S$ [M]: 303.0929, Found: 303.0925.

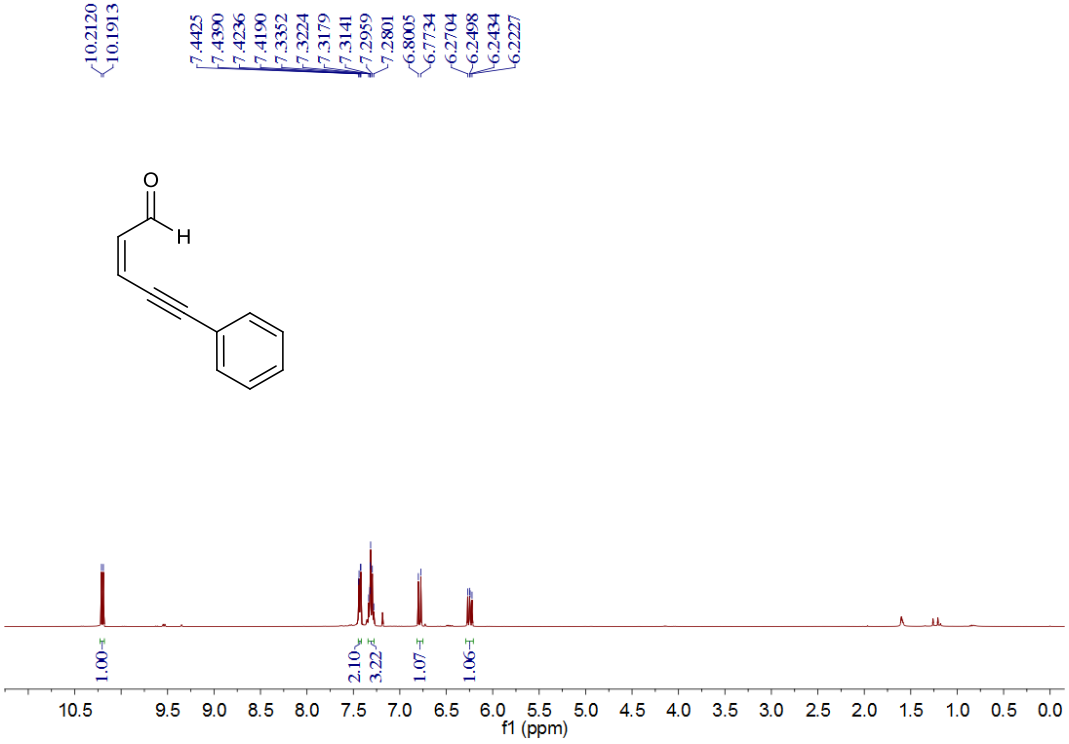
1-(3-Phenylfuran-2-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (9b)



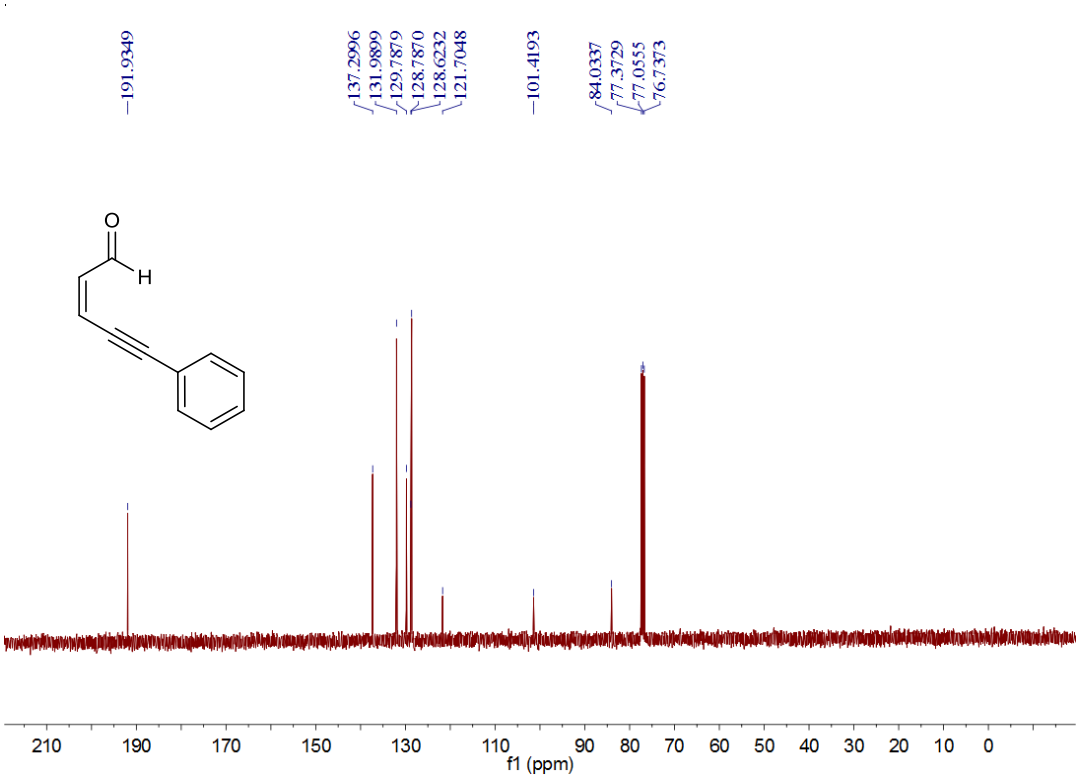
Brown yellow solid (m.p.124℃); yield: 43% (49 mg); R_f = 0.30 (Hex/EtOAc = 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.20 (s, 6H), 6.39 (s, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 3.54 (d, *J* = 9.3 Hz, 1H), 3.15 (dd, *J* = 9.3, 3.7 Hz, 1H), 3.10 (d, *J* = 9.2 Hz, 1H), 2.39 (s, 3H), 1.63 (dt, *J* = 8.1, 4.0 Hz, 1H), 1.02 (t, *J* = 4.8 Hz, 1H), 0.92 – 0.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.61, 143.63, 141.15, 133.02, 132.91, 129.71, 128.38, 127.90, 127.64, 126.95, 123.73, 111.65, 52.62, 49.89, 24.48, 24.31, 21.58, 15.09; IR (KBr) ν_{max} 2955.99, 2919.67, 2848.53, 1737.17, 1564.40, 1446.96, 1346.64, 1162.84, 745.48, 700.54; HRMS (EI) calcd for $C_{22}H_{21}NO_3S$ [M]: 379.1242, Found: 379.1246.

3. ^{1}H, ^{19}F and ^{13}C NMR Spectra

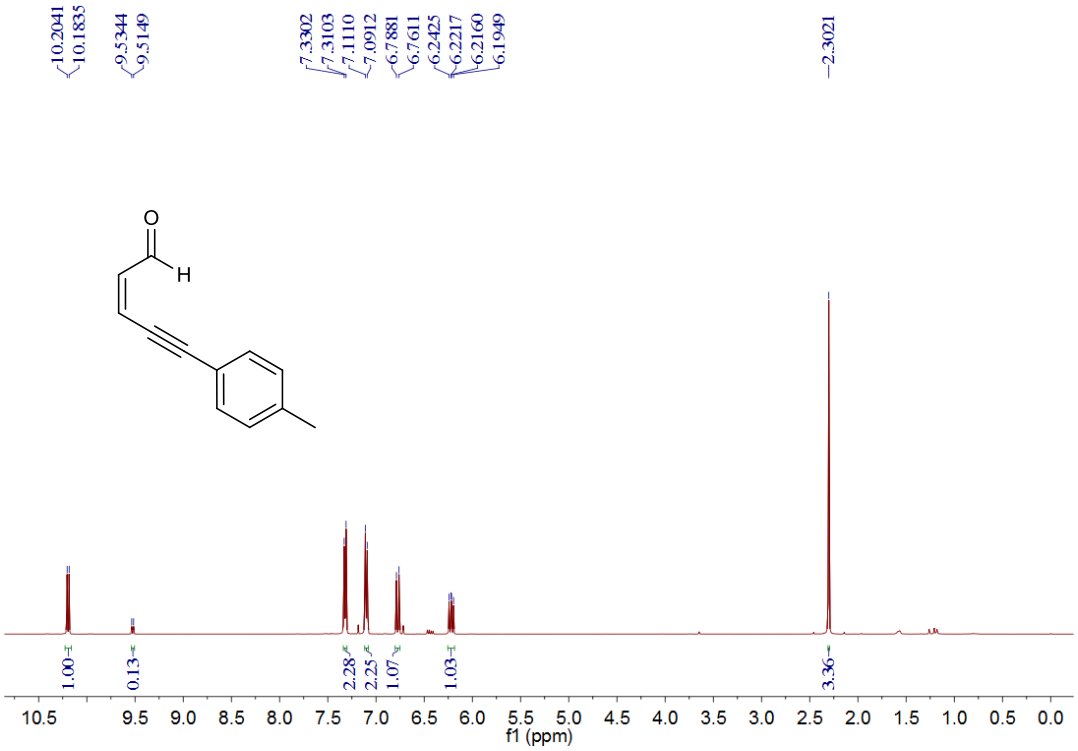
(*Z*)-5-Phenylpent-2-en-4-ynal (1a) $^{1}HNMR$ (400 MHz, $CDCl_3$)



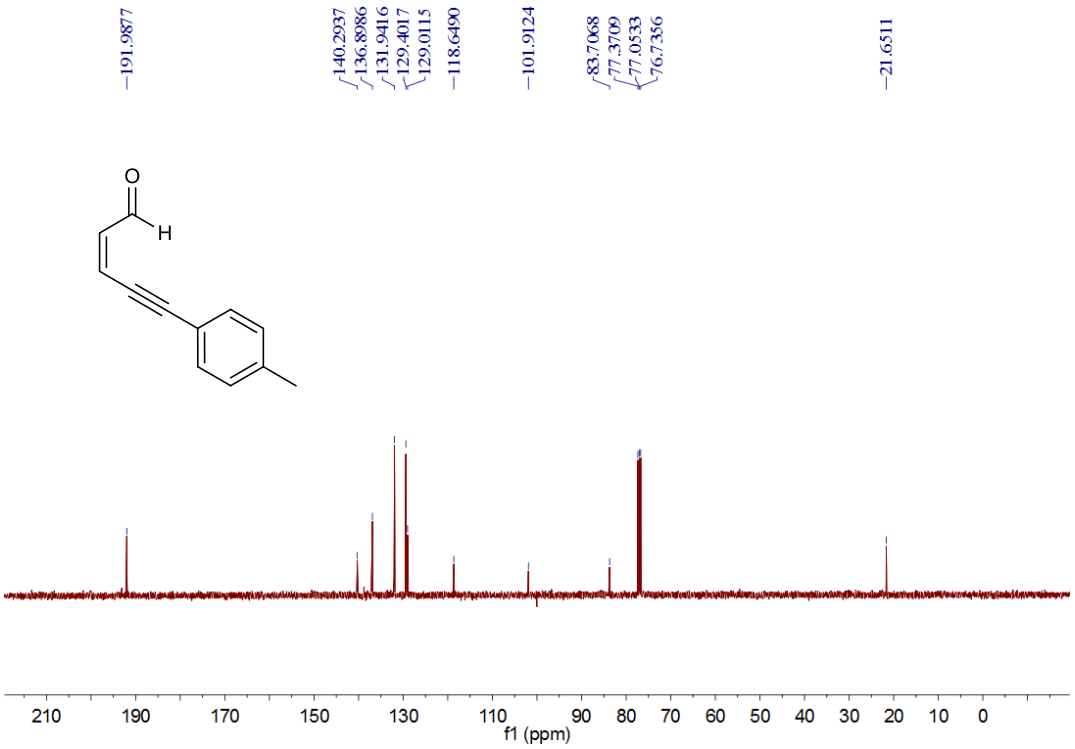
(*Z*)-5-Phenylpent-2-en-4-ynal (1a) ^{13}C NMR (100 MHz, $CDCl_3$)



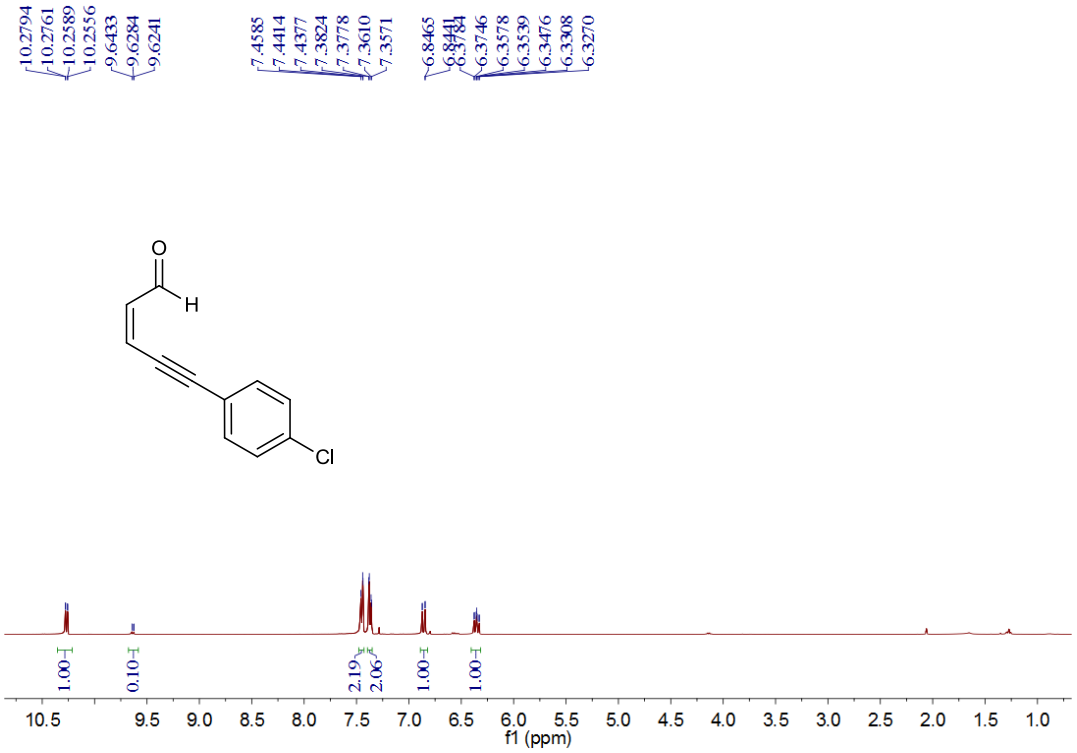
(*Z*)-5-(p-Tolyl)pent-2-en-4-ynal (1b) ^{1}H NMR (400 MHz, $CDCl_3$)



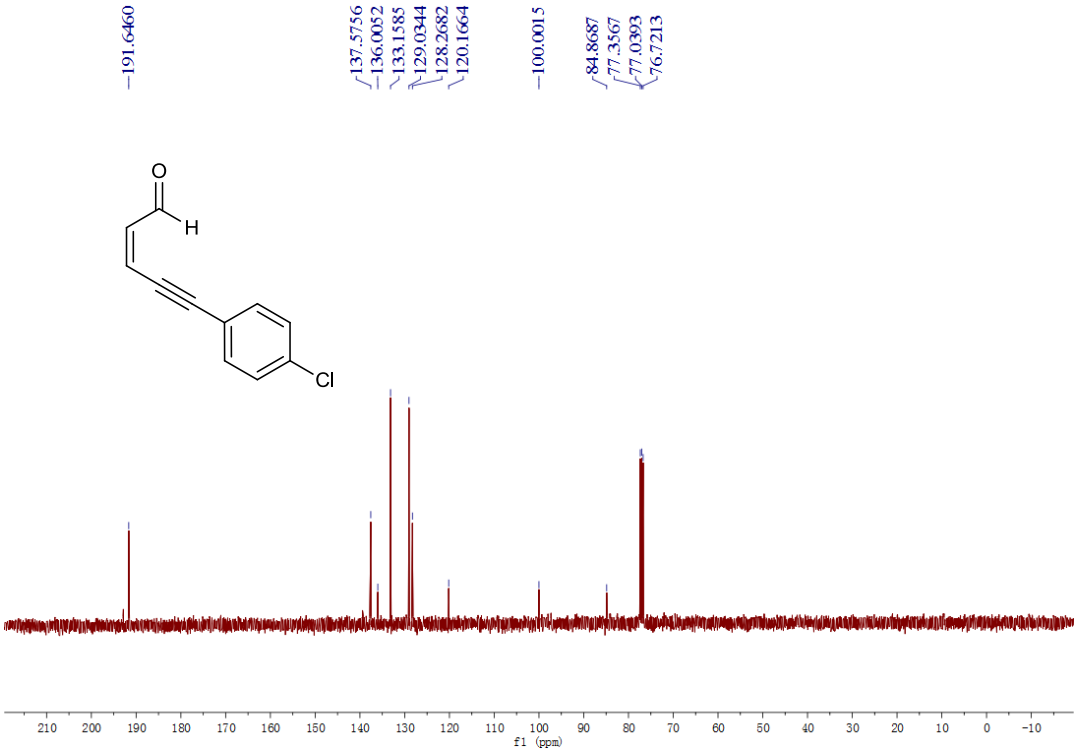
(*Z*)-5-(p-Tolyl)pent-2-en-4-ynal (1b) ^{13}C NMR (100 MHz, $CDCl_3$)



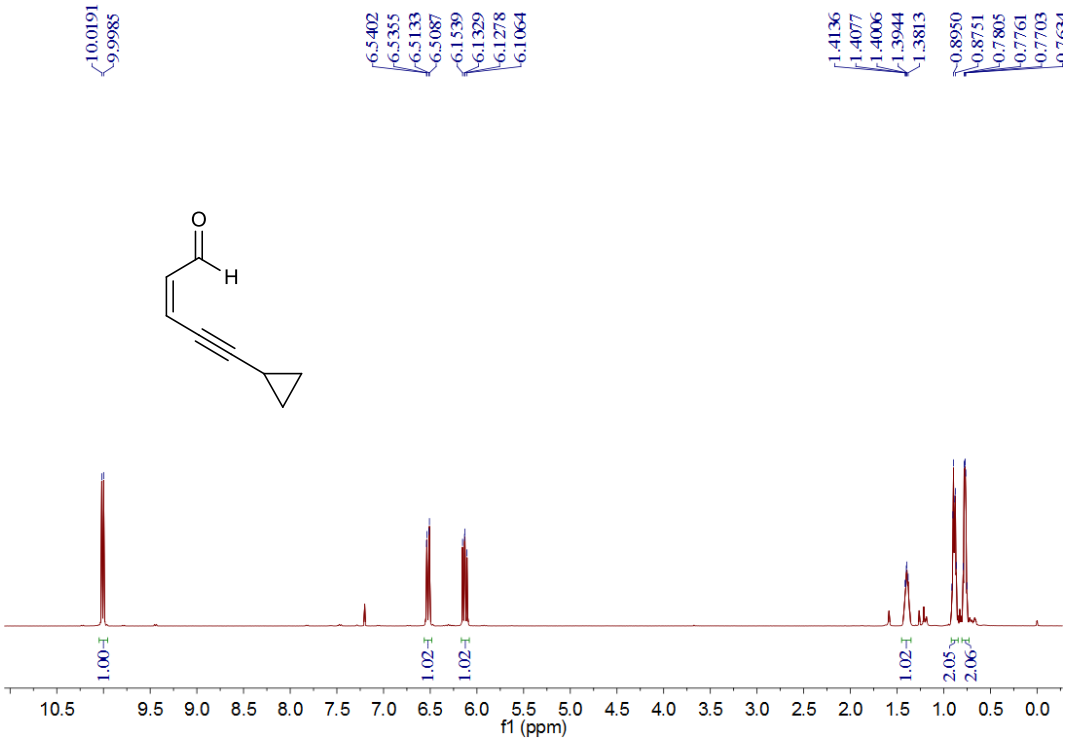
(*Z*)-5-(4-Chlorophenyl)pent-2-en-4-ynal (1c) ^{1}H NMR (400 MHz, $CDCl_3$)



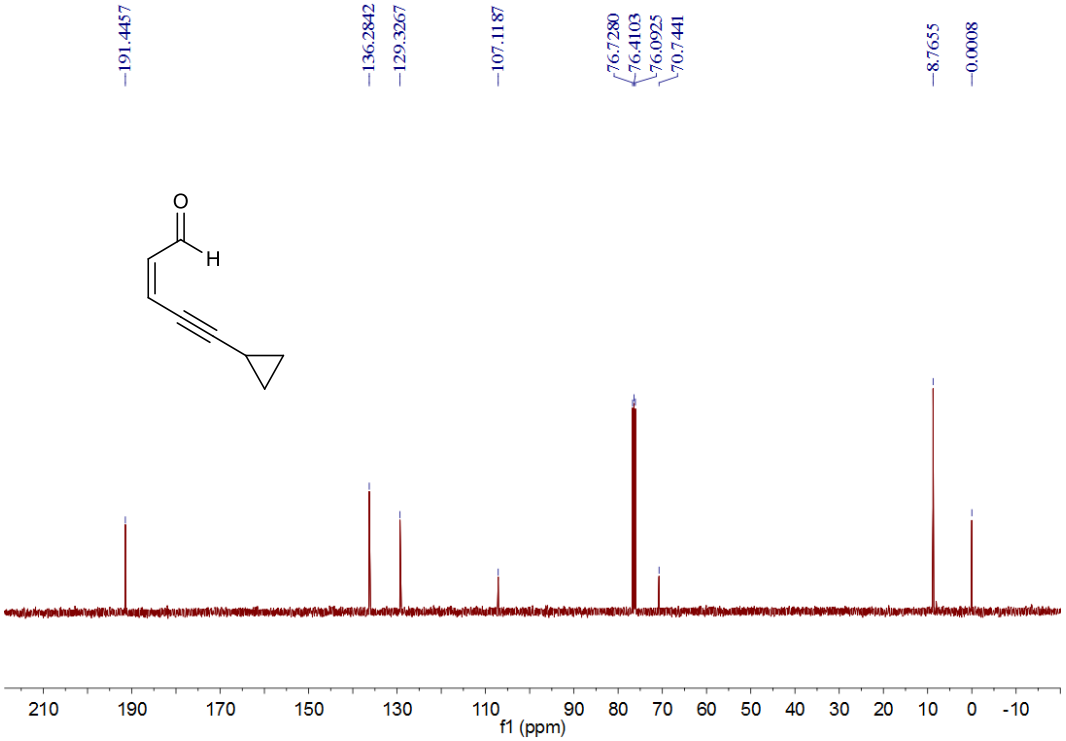
(*Z*)-5-(4-Chlorophenyl)pent-2-en-4-ynal (1c) ^{13}C NMR (100 MHz, $CDCl_3$)



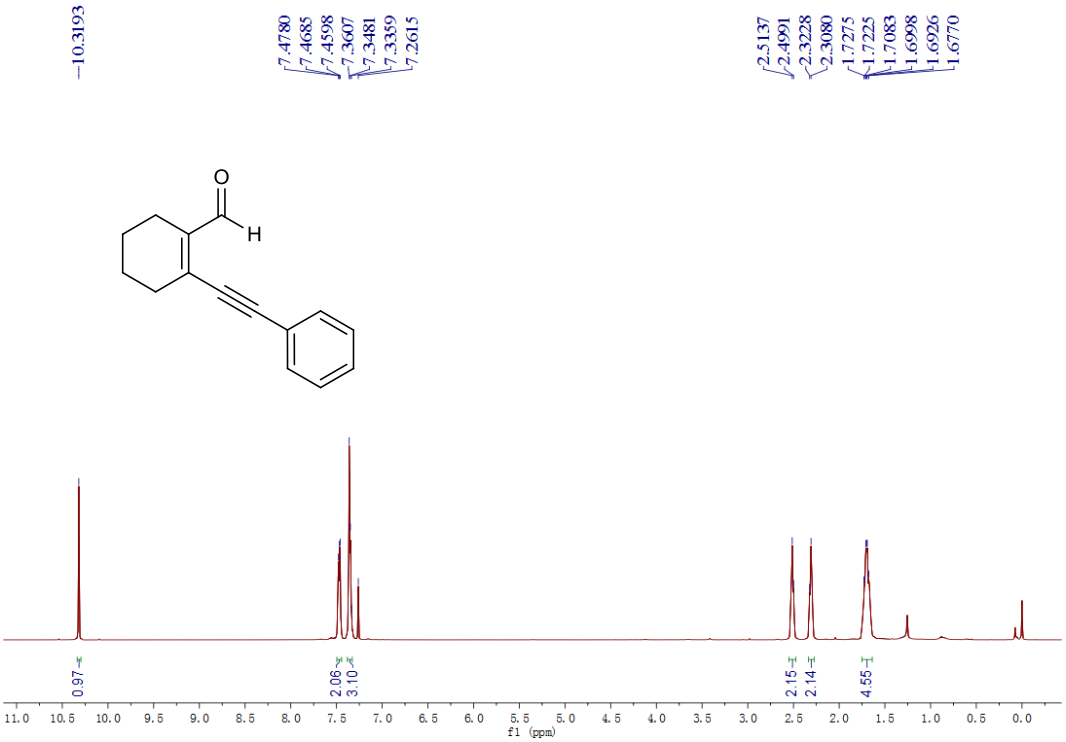
(*Z*)-5-Cyclopropylpent-2-en-4-ynal (1d) ^{1}H NMR (400 MHz, $CDCl_3$)



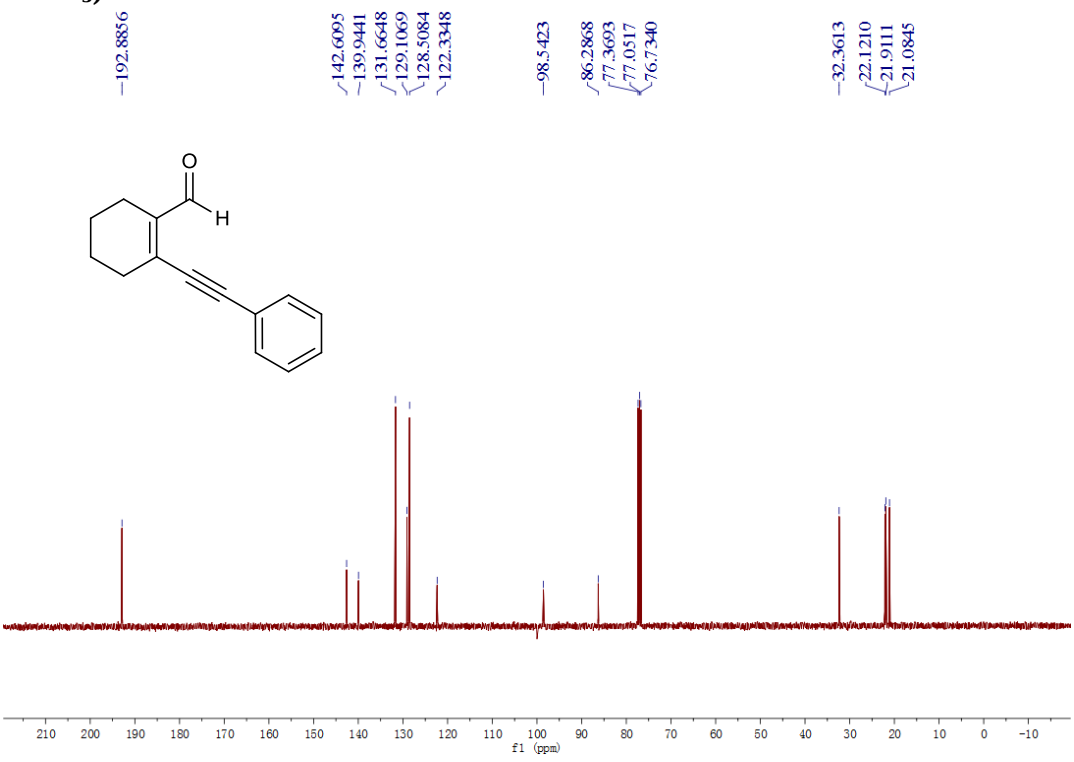
(*Z*)-5-Cyclopropylpent-2-en-4-ynal (1d) ^{13}C NMR (100 MHz, $CDCl_3$)



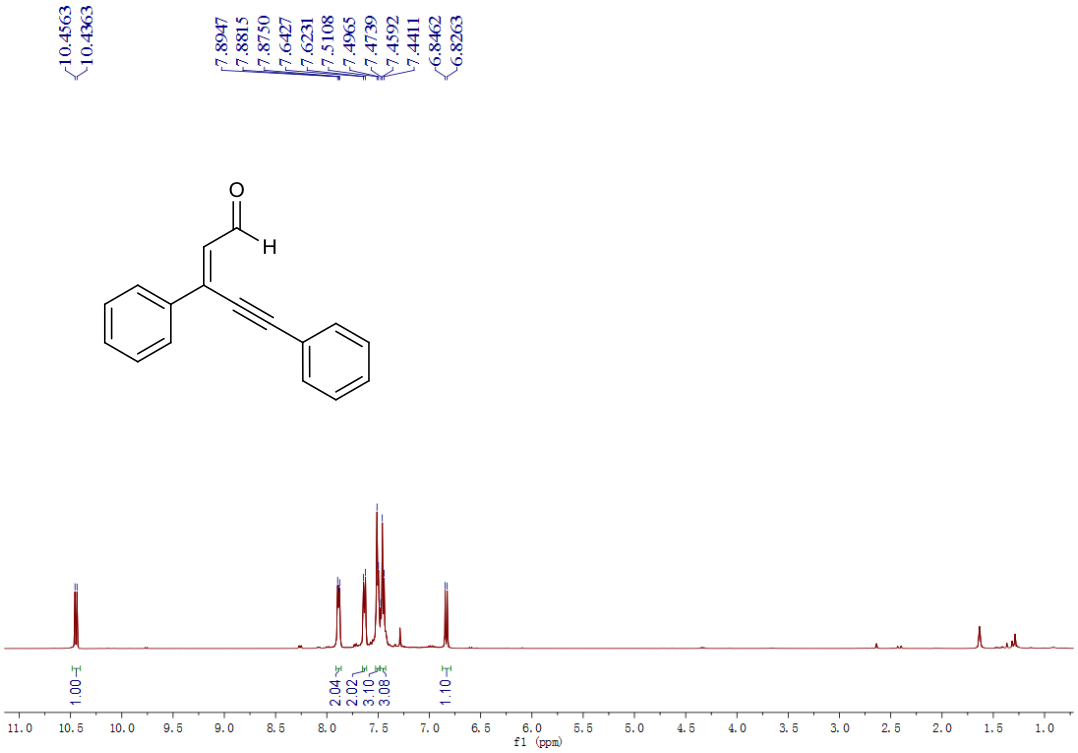
2-(Phenylethynyl)cyclohex-1-enecarbaldehyde (1e) ^{1}H NMR (400 MHz, $CDCl_3$)



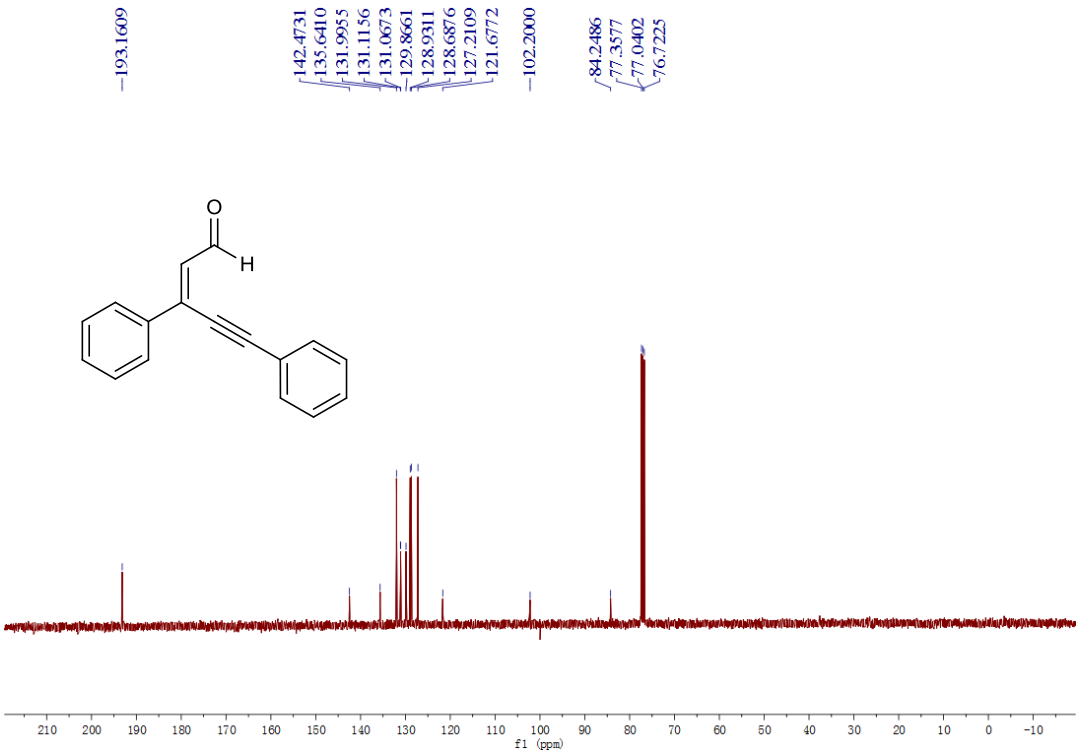
2-(Phenylethynyl)cyclohex-1-enecarbaldehyde (1e) ^{13}C NMR (100 MHz, $CDCl_3$)



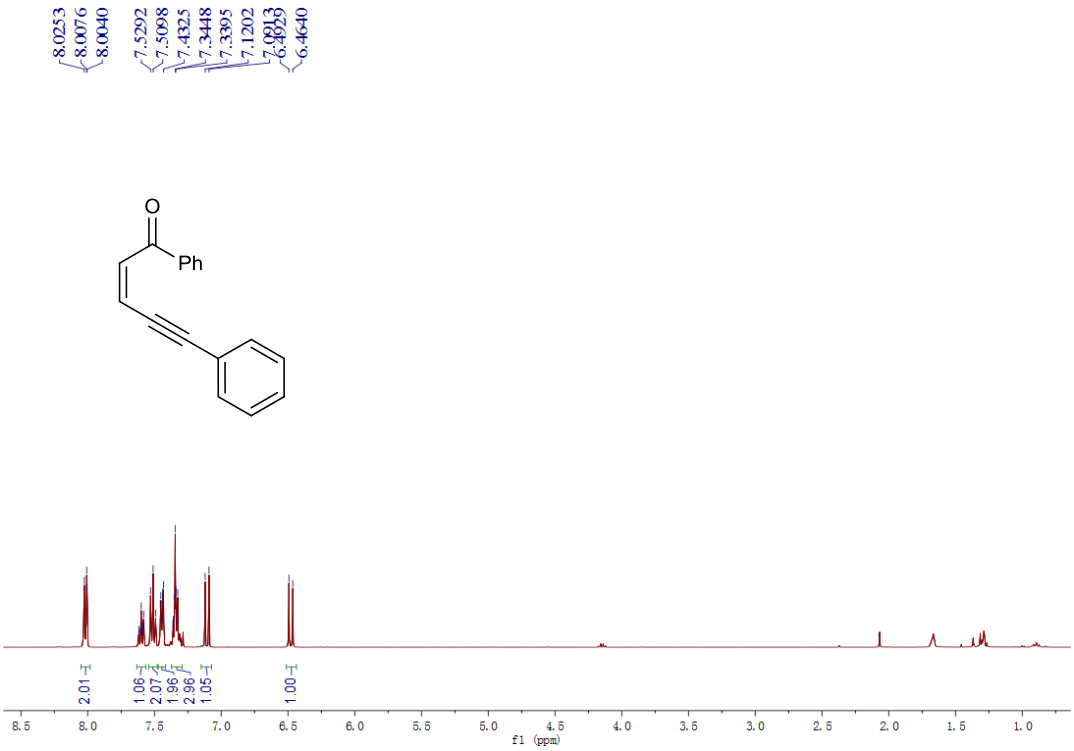
(*Z*)-3,5-Diphenylpent-2-en-4-ynal (1f) ^{1}H NMR (400 MHz, $CDCl_3$)



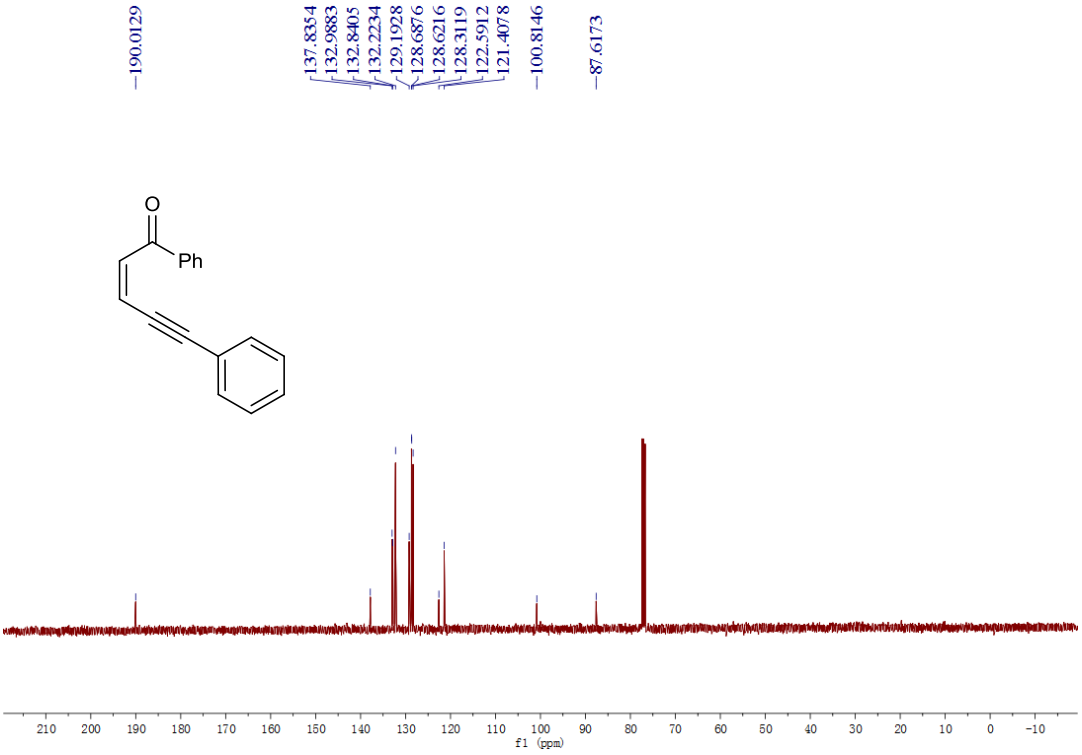
(*Z*)-3,5-Diphenylpent-2-en-4-ynal (1f) ^{13}C NMR (100 MHz, $CDCl_3$)



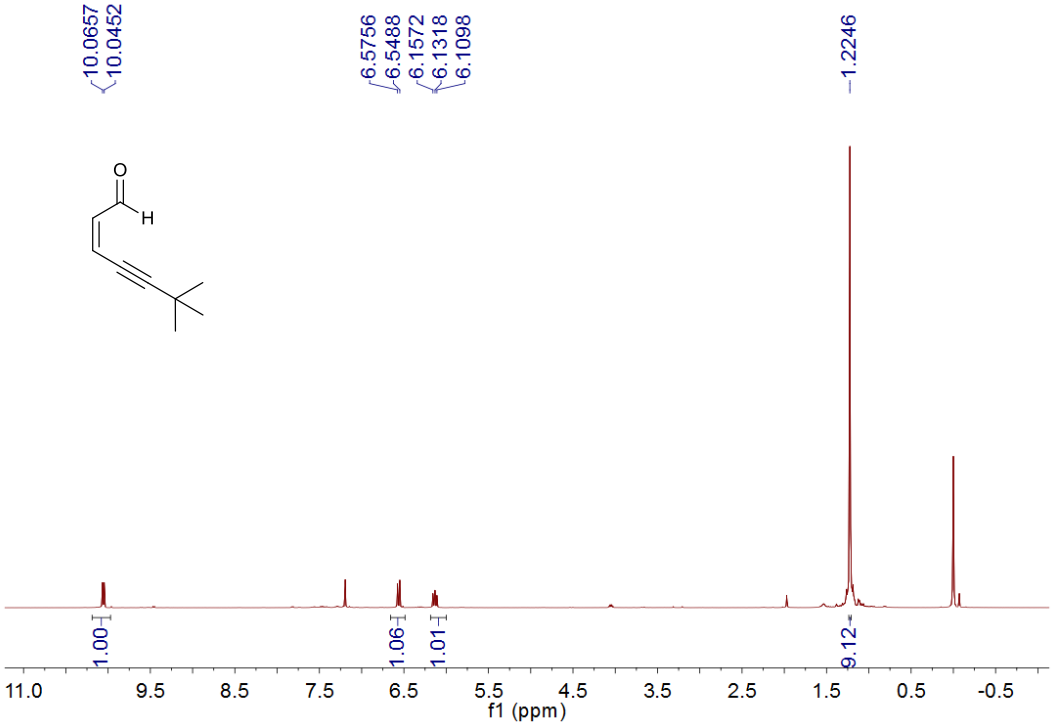
(*Z*)-1,5-Diphenylpent-2-en-4-yn-1-one (1t) ^{1}H NMR (400 MHz, $CDCl_3$)



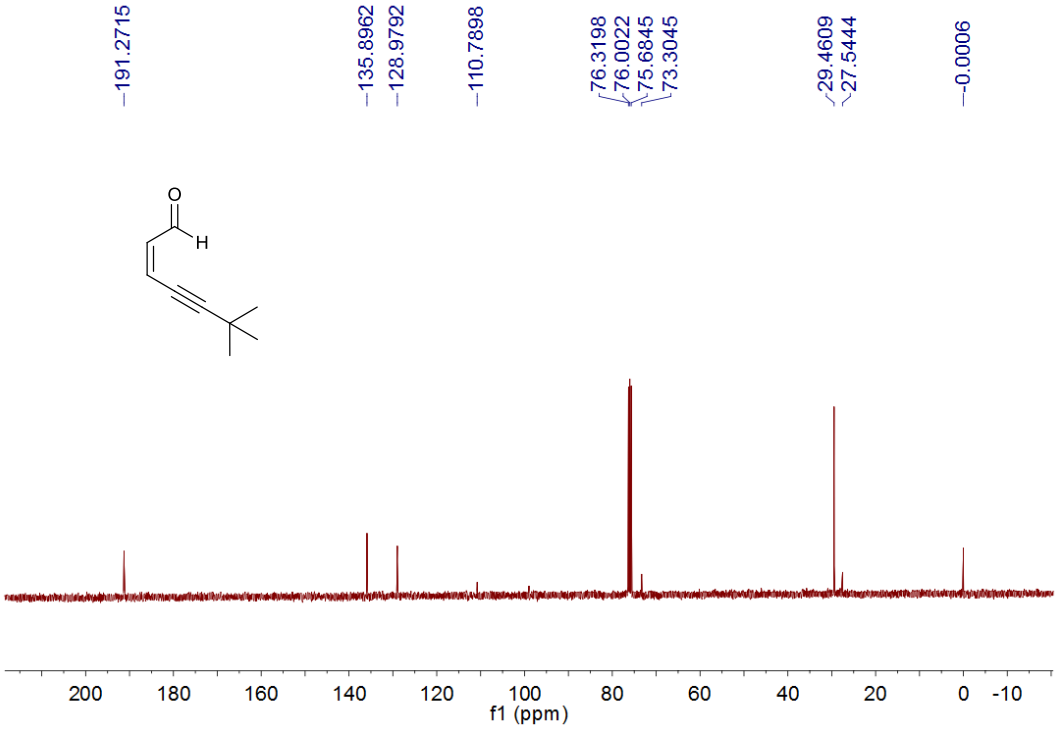
(*Z*)-1,5-diphenylpent-2-en-4-yn-1-one (1t) ^{13}C NMR (100 MHz, $CDCl_3$)



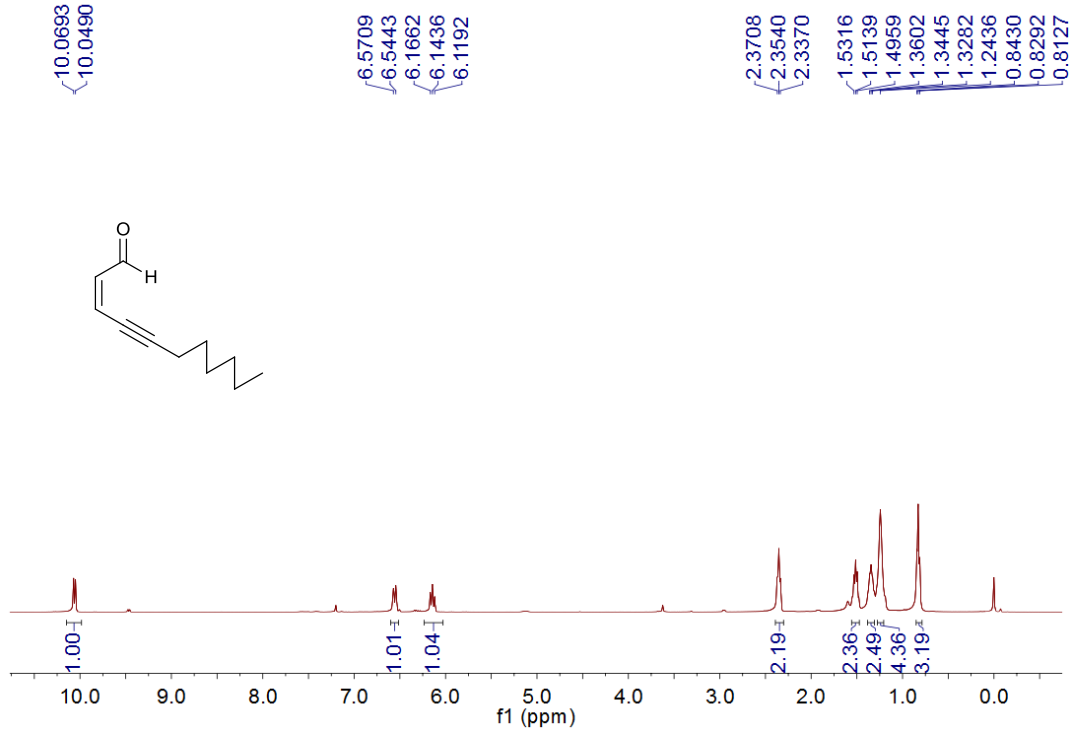
(Z)-6,6-dimethylhept-2-en-4-ynal (1h) ^{1}H NMR (400 MHz, $CDCl_3$)



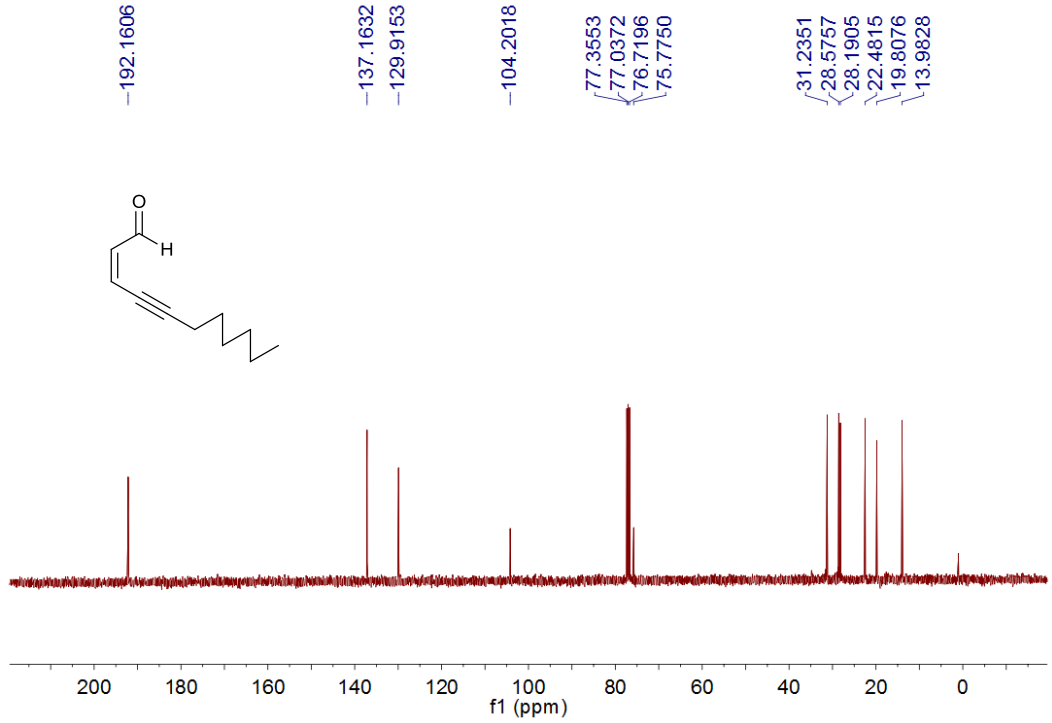
(Z)-6,6-dimethylhept-2-en-4-ynal (1h) ^{13}C NMR (100 MHz, $CDCl_3$)



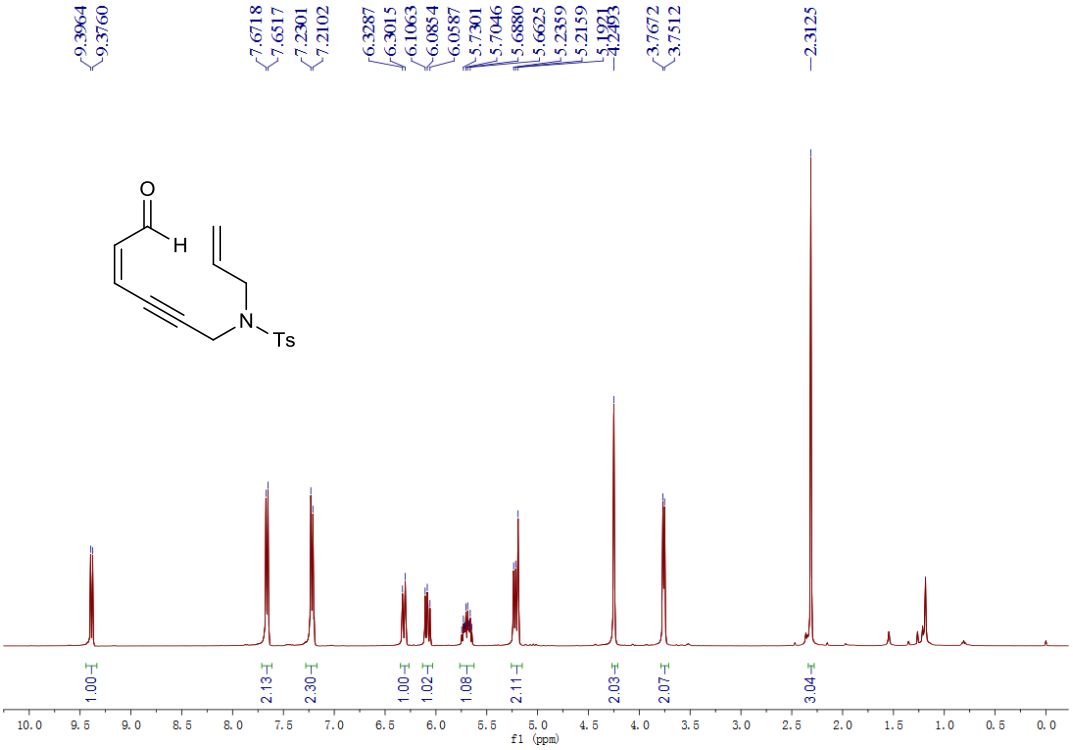
(Z)-undec-2-en-4-ynal (1i) ^{1}H NMR (400 MHz, $CDCl_3$)



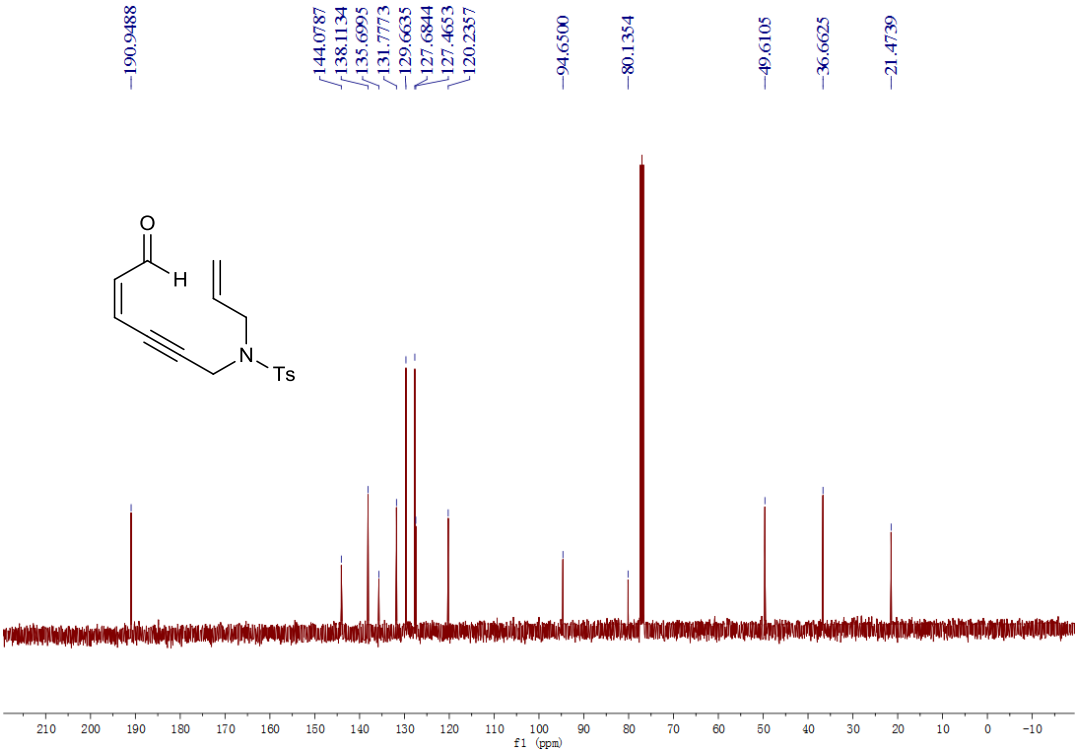
(Z)-undec-2-en-4-ynal (1i) ^{13}C NMR (100 MHz, $CDCl_3$)



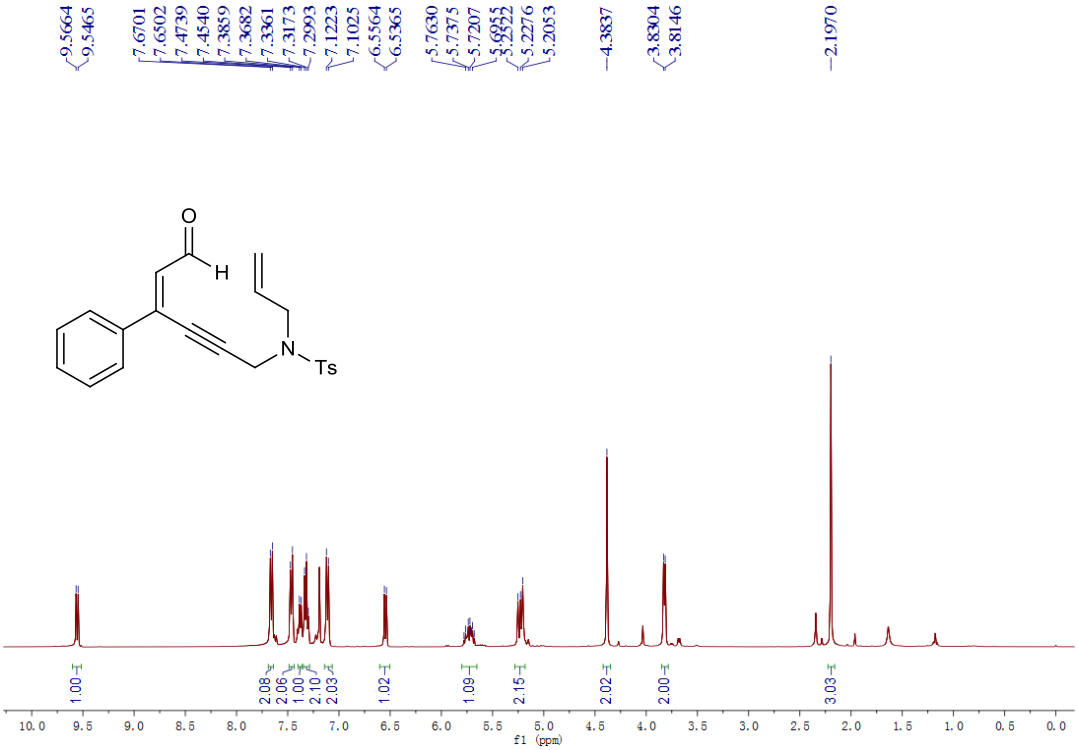
(*Z*)-N-allyl-4-methyl-N-(6-oxohex-4-en-2-yn-1-yl)benzenesulfonamide (8a) ^{1}H NMR (400 MHz, $CDCl_3$))



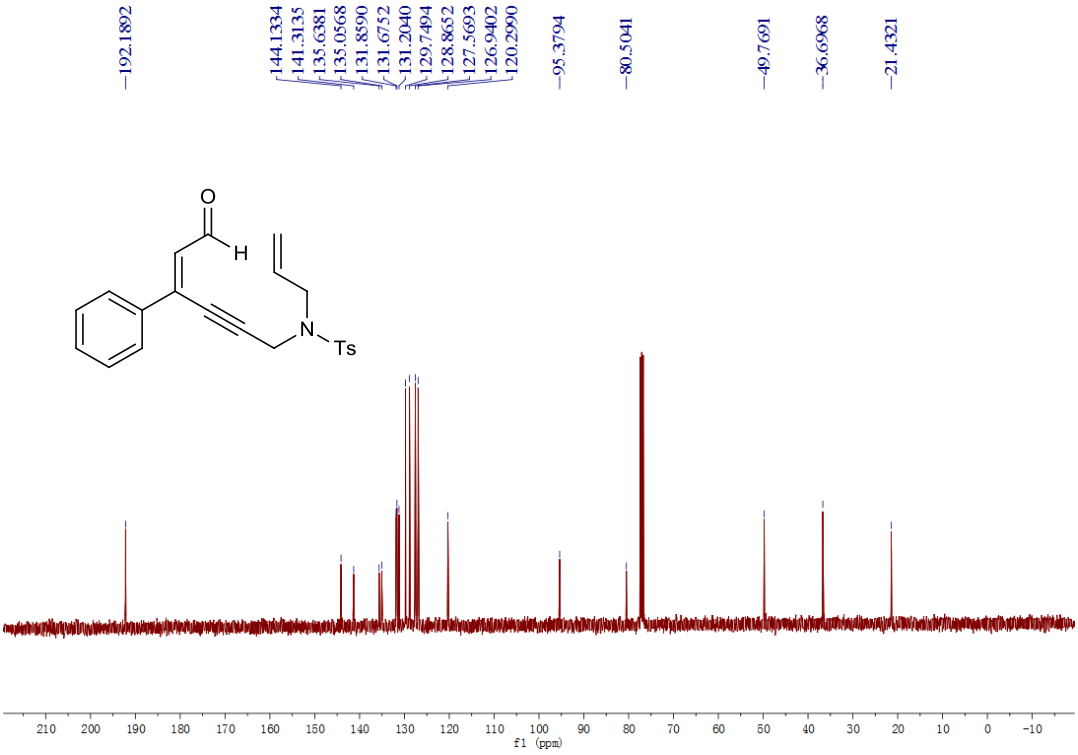
(*Z*)-N-allyl-4-methyl-N-(6-oxohex-4-en-2-yn-1-yl)benzenesulfonamide (8a) ^{13}C NMR (100 MHz, $CDCl_3$)



(*Z*)-N-allyl-4-methyl-N-(6-oxo-4-phenylhex-4-en-2-yn-1-yl)benzenesulfonamide (8b) ^{1}H NMR (400 MHz, $CDCl_3$)

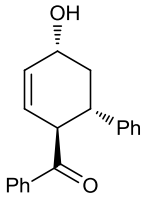


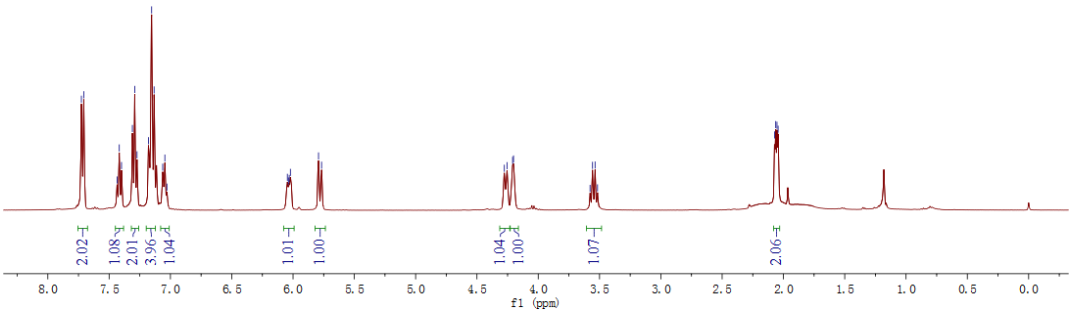
(*Z*)-N-allyl-4-methyl-N-(6-oxo-4-phenylhex-4-en-2-yn-1-yl)benzenesulfonamide (8b) ^{13}C NMR (100 MHz, $CDCl_3$)



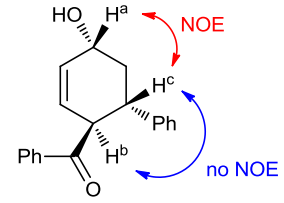
(5-Hydroxy-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (5a)

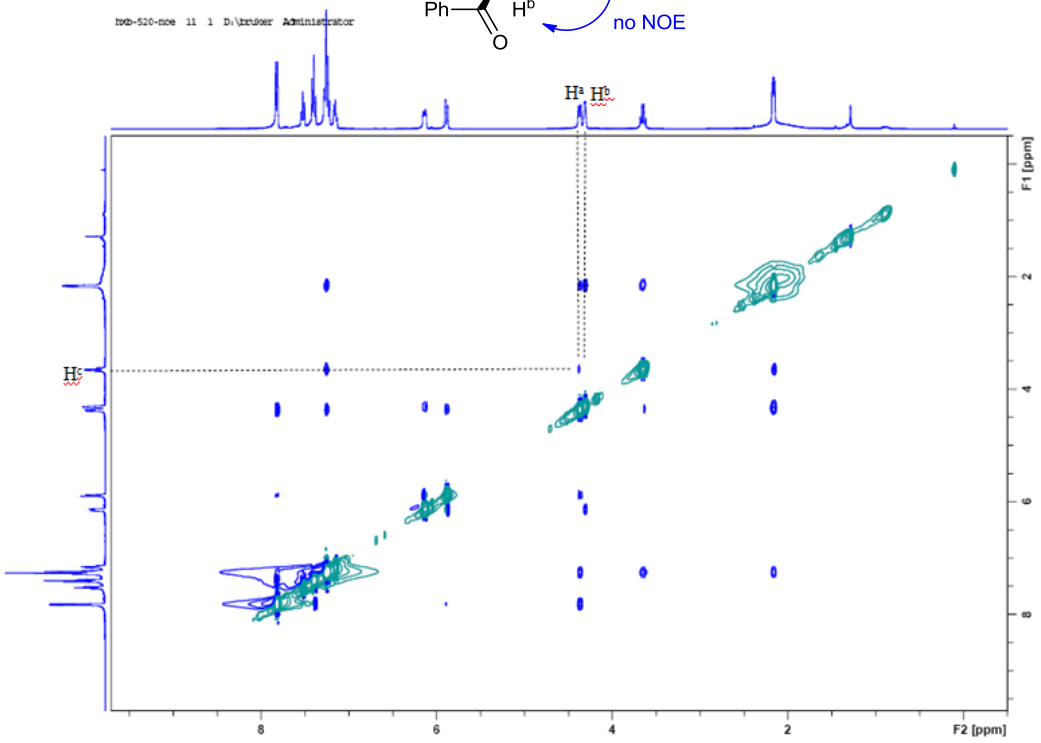
^{1}H NMR (400 MHz, $CDCl_3$)



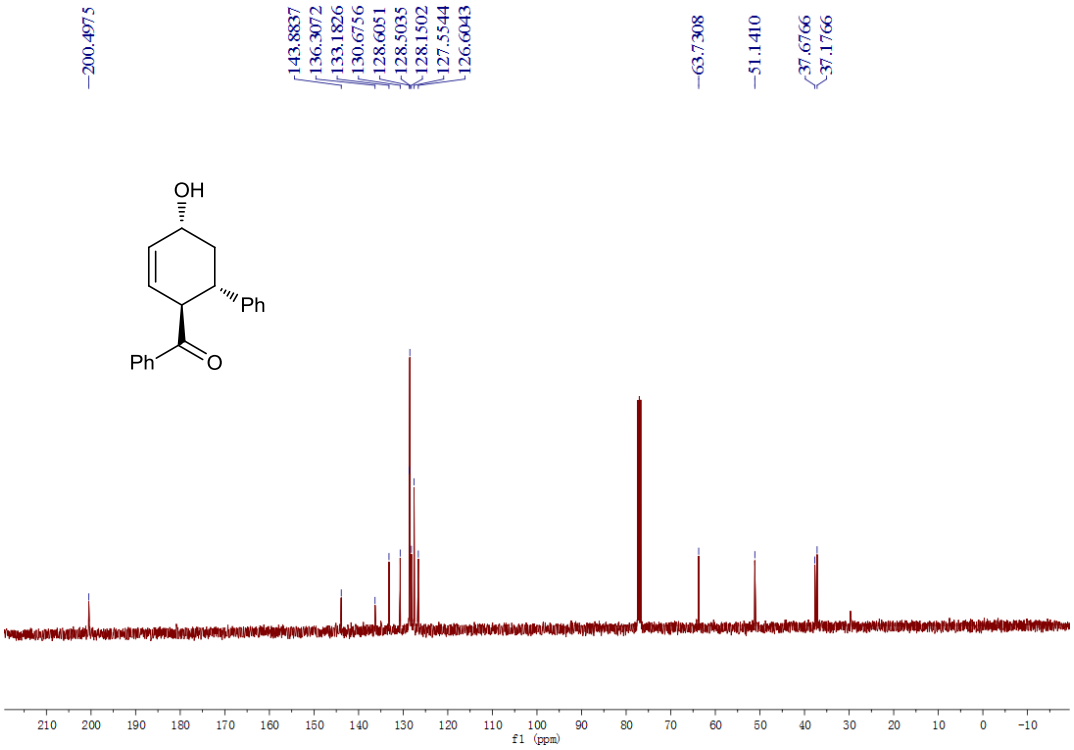


NOE spectrum of **5a**

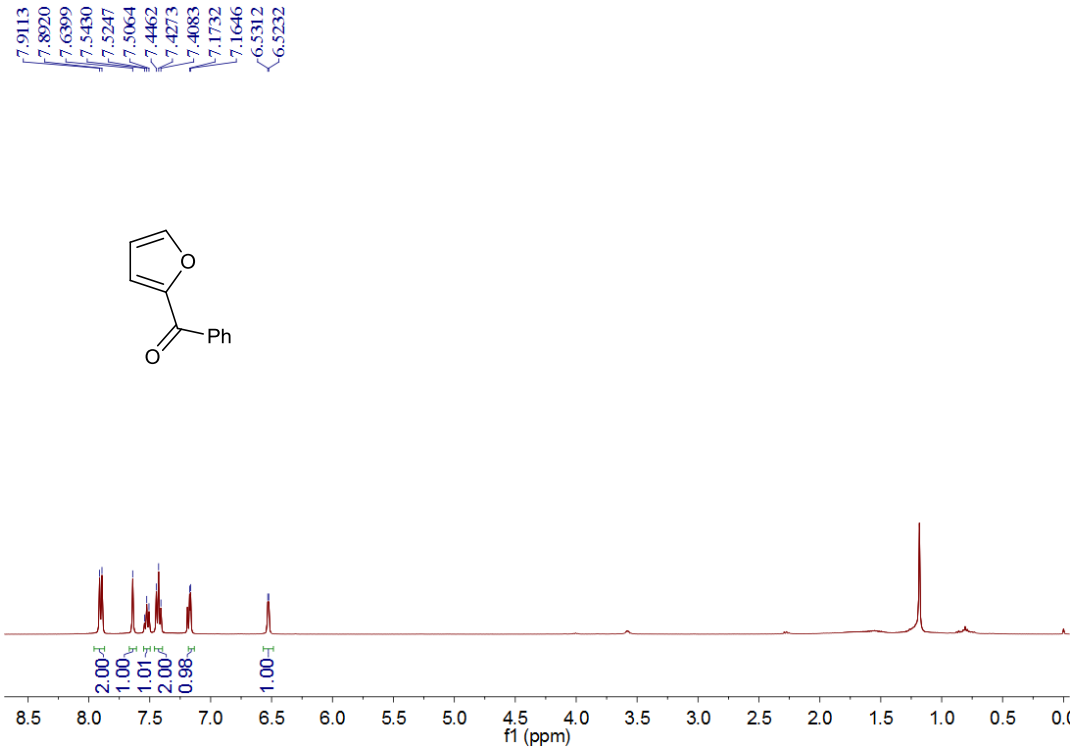




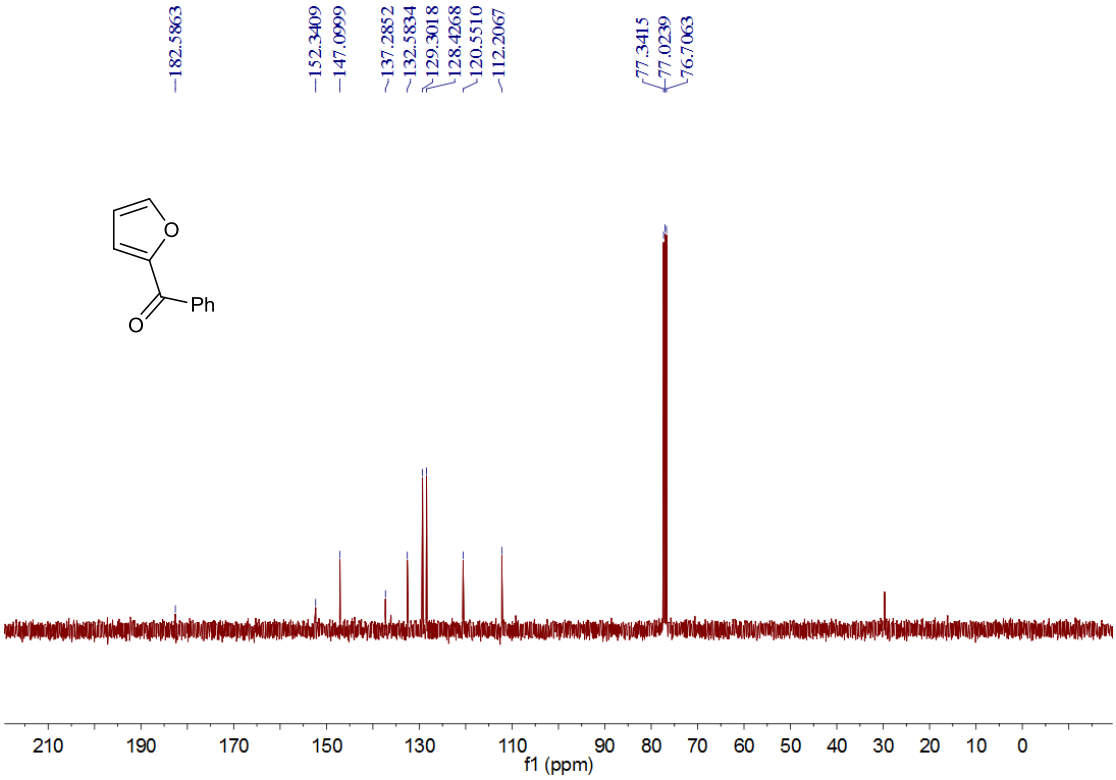
(5-Hydroxy-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (5a)
^{13}C NMR (100 MHz, $CDCl_3$)



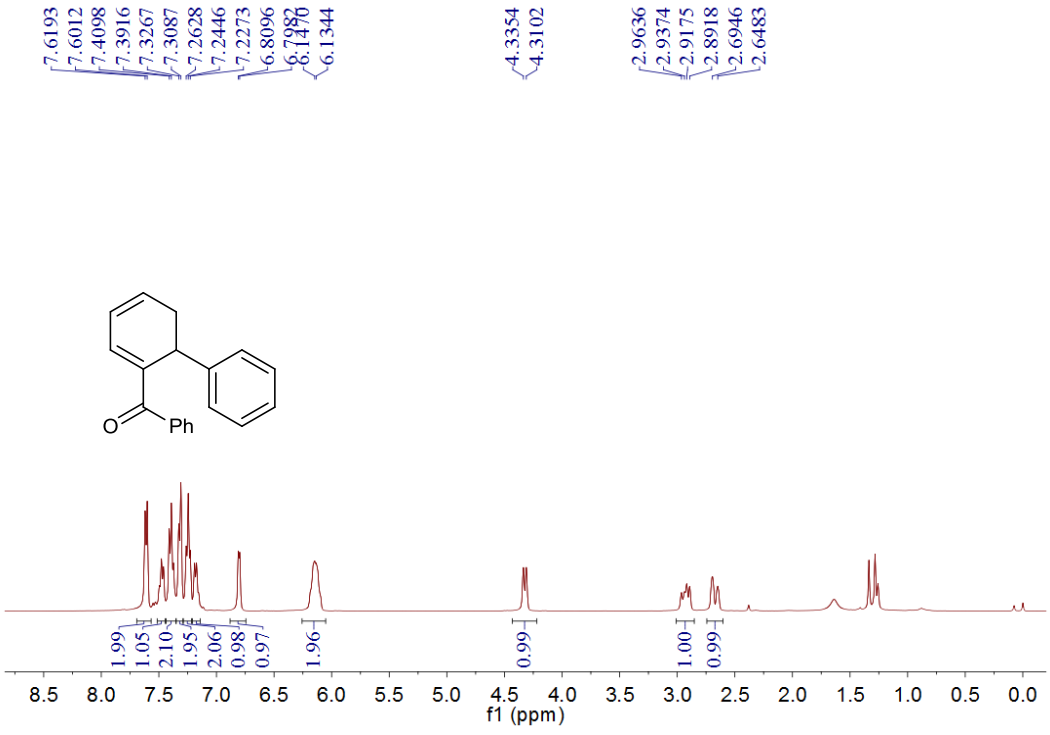
Furan-2-yl(phenyl)methanone (6a) ^{1}H NMR (400 MHz, $CDCl_3$)



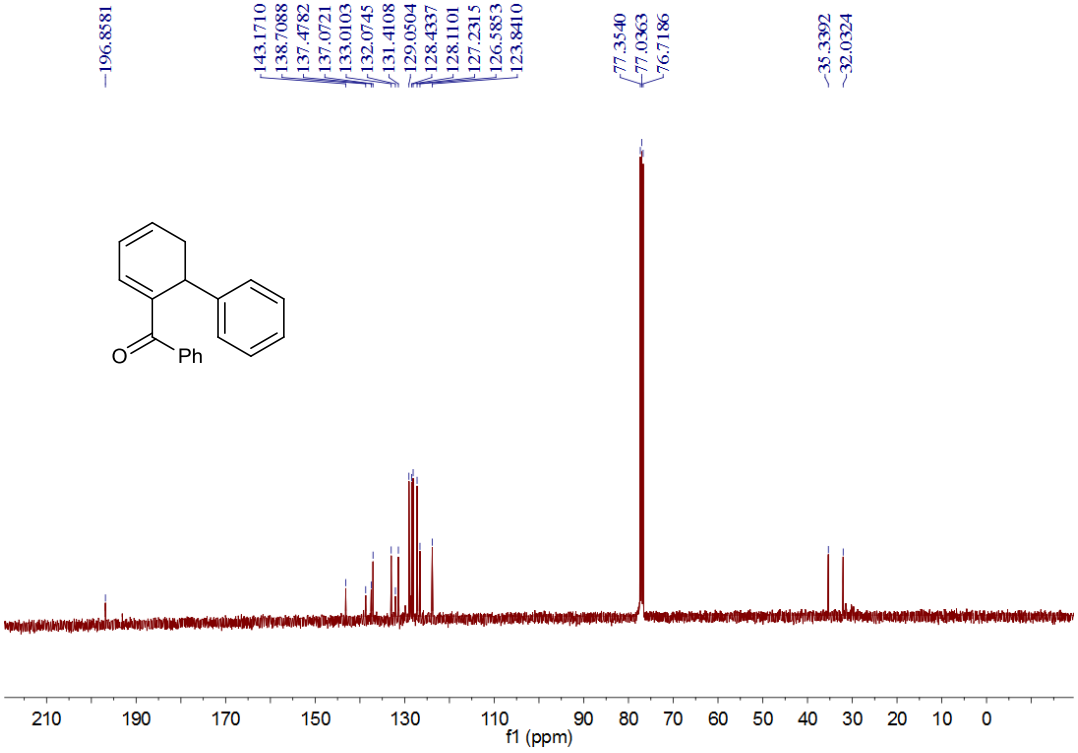
Furan-2-yl(phenyl)methanone (6a) ^{13}C NMR (100 MHz, $CDCl_3$)



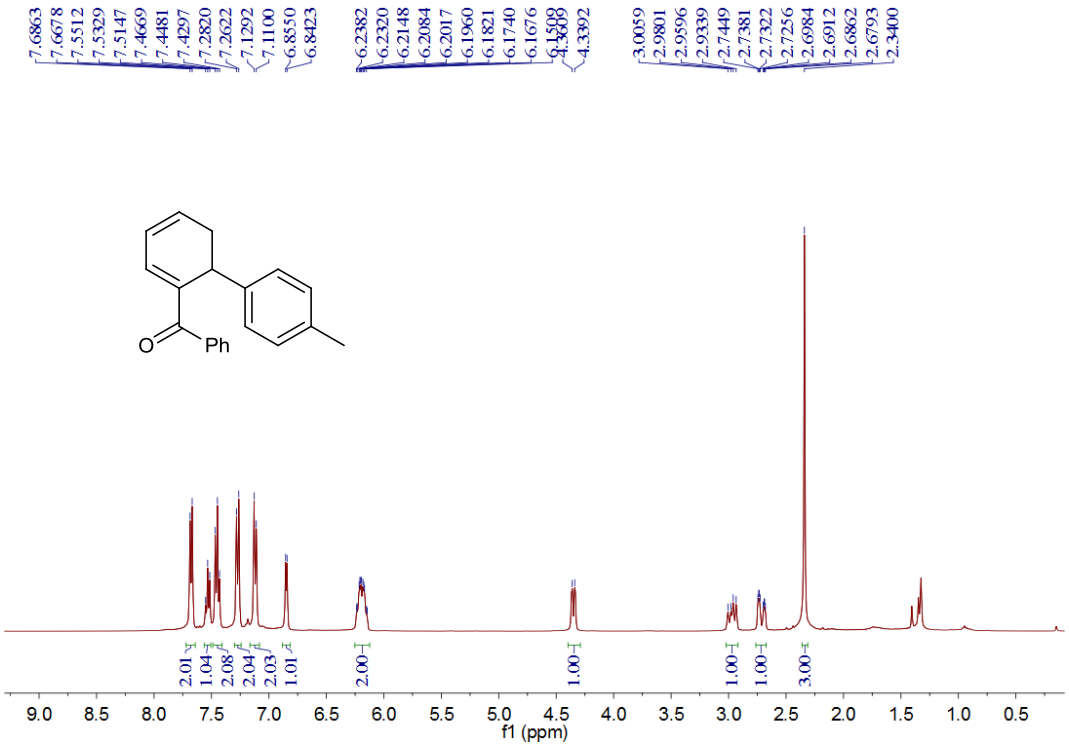
(1,6-Dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4a) ^{1}H NMR (400 MHz, $CDCl_3$)



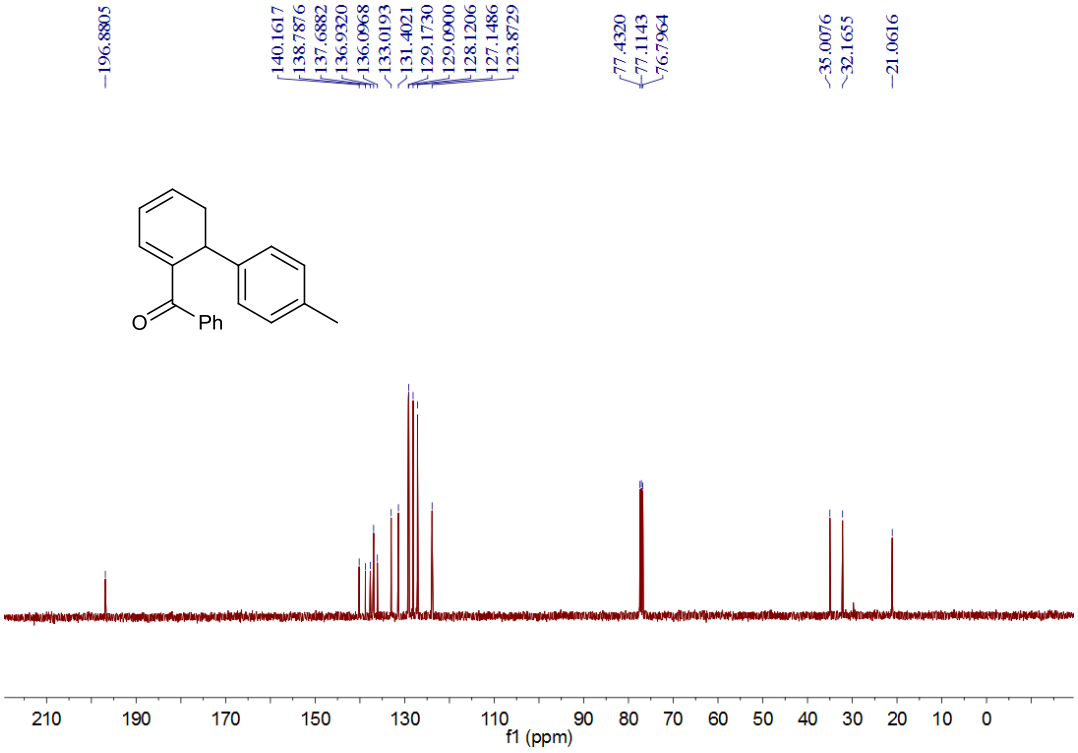
(1,6-Dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4a) ^{13}C NMR (100 MHz, $CDCl_3$)



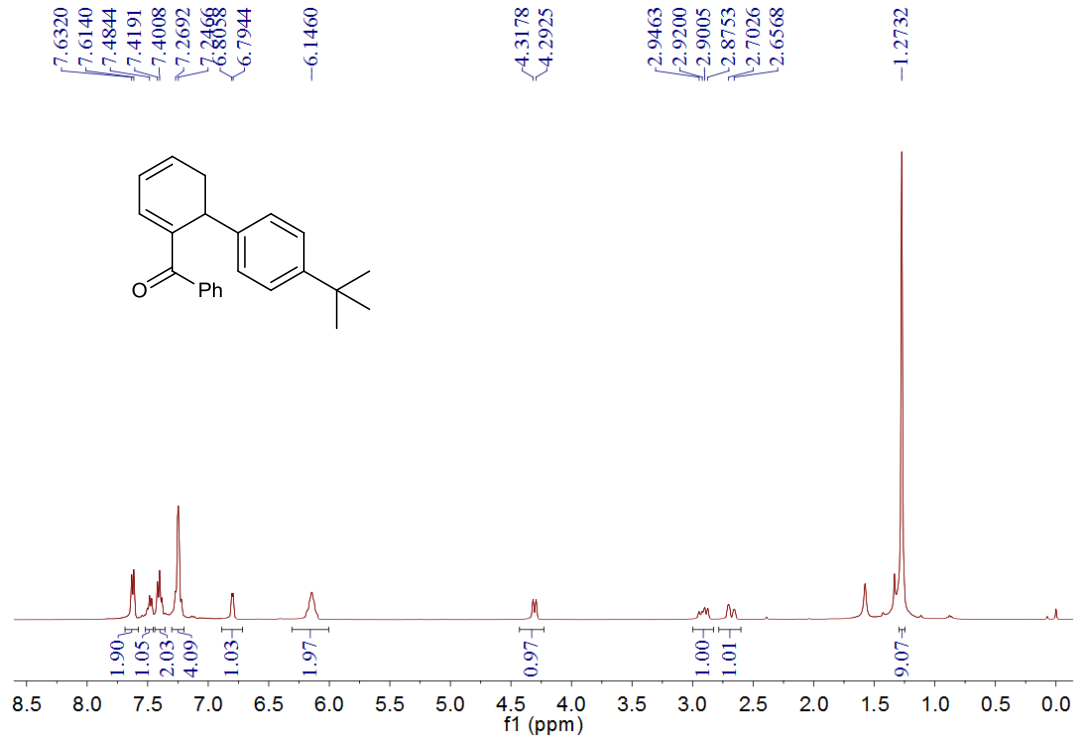
(4'-Methyl-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4b) ^{1}H NMR (400 MHz, $CDCl_3$)



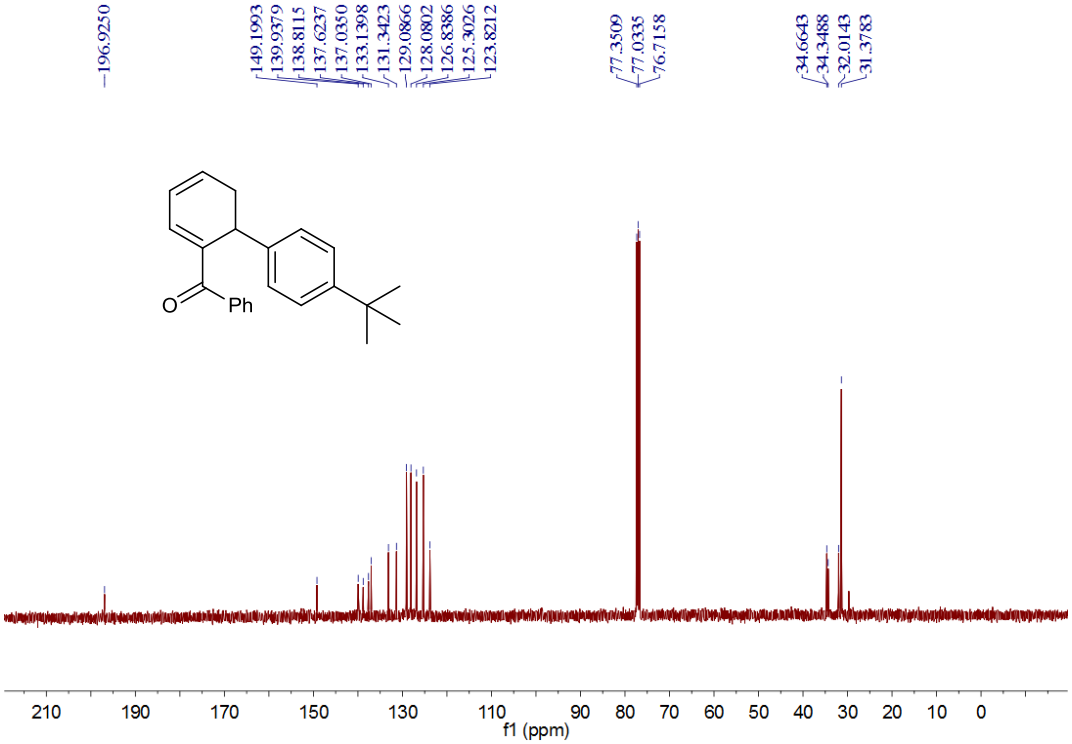
(4'-Methyl-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4b) ^{13}C NMR (100 MHz, $CDCl_3$)



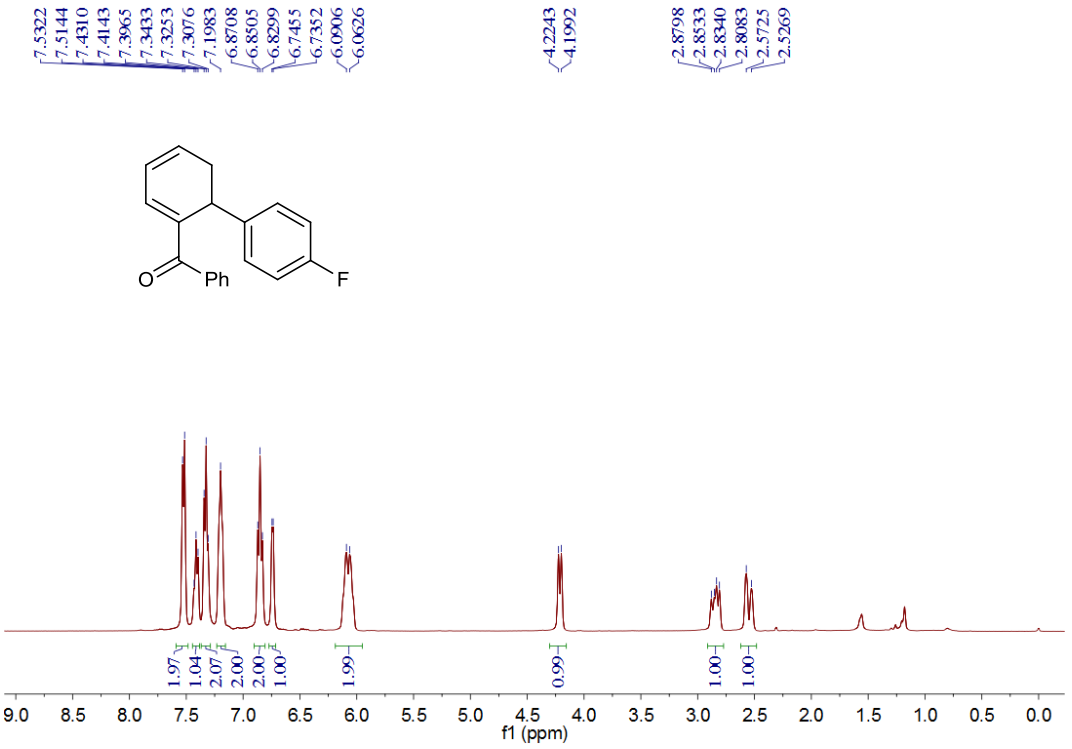
(4'-(Tert-butyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4c) ^{1}H NMR (400 MHz, $CDCl_3$)



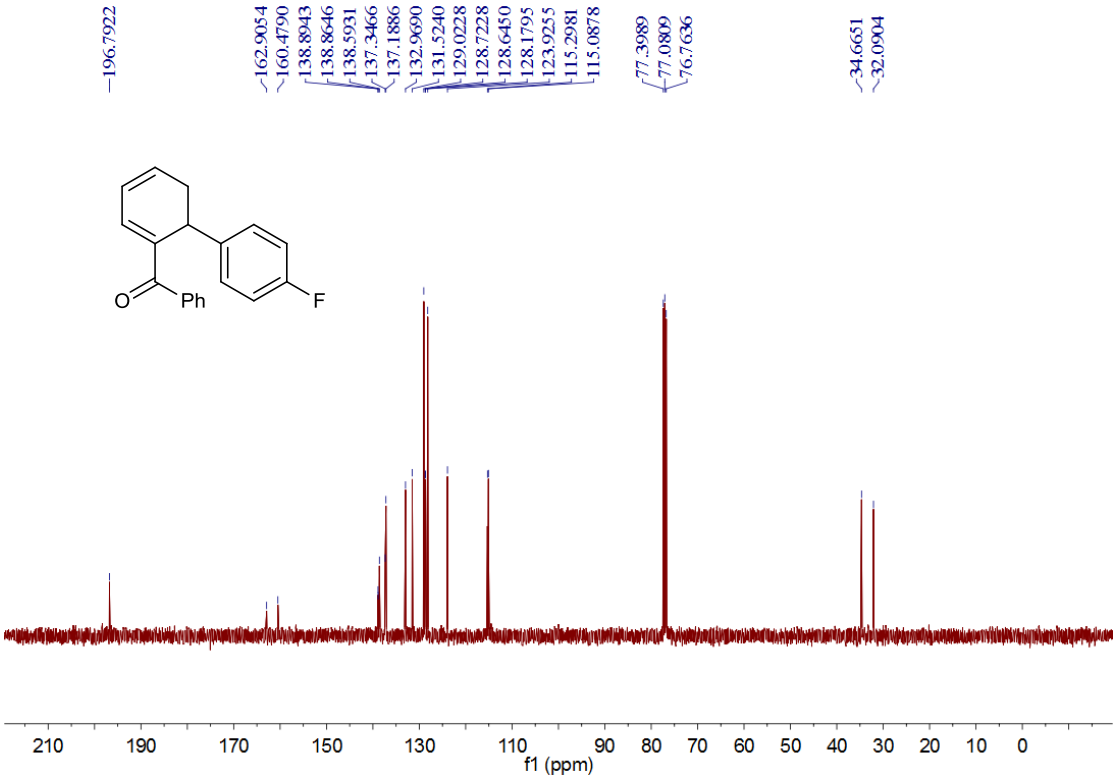
(4'-(Tert-butyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4c) ^{13}C NMR (100 MHz, $CDCl_3$)



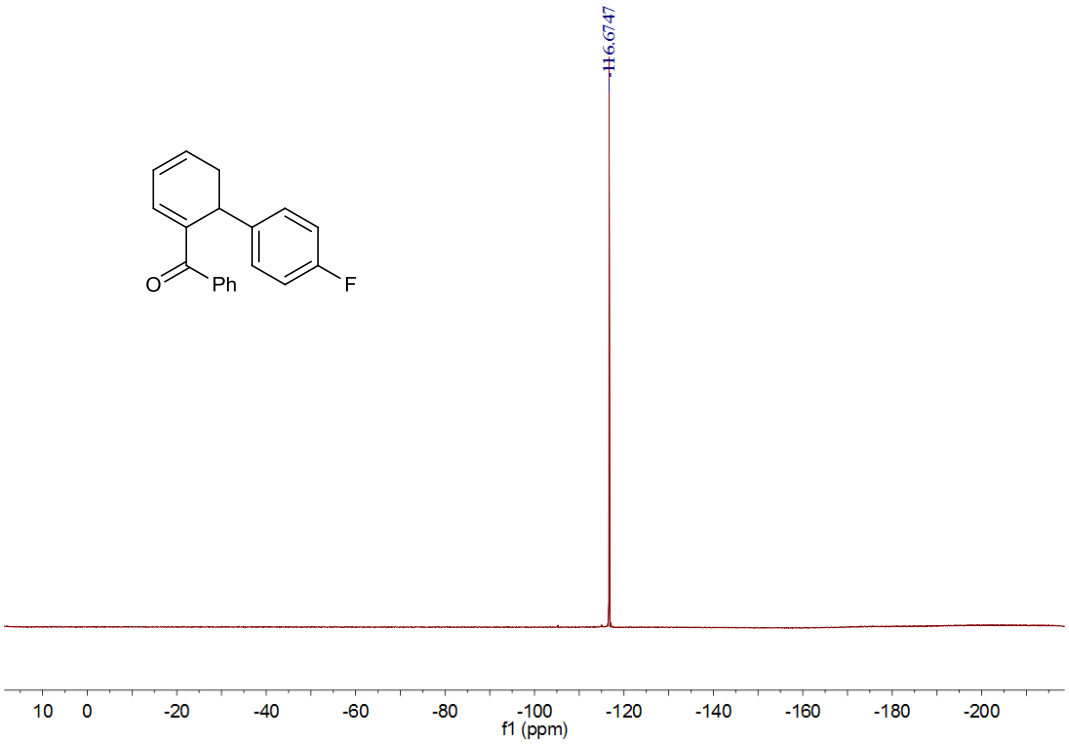
(4'-Fluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4d) ^{1}H NMR (400 MHz, $CDCl_3$)



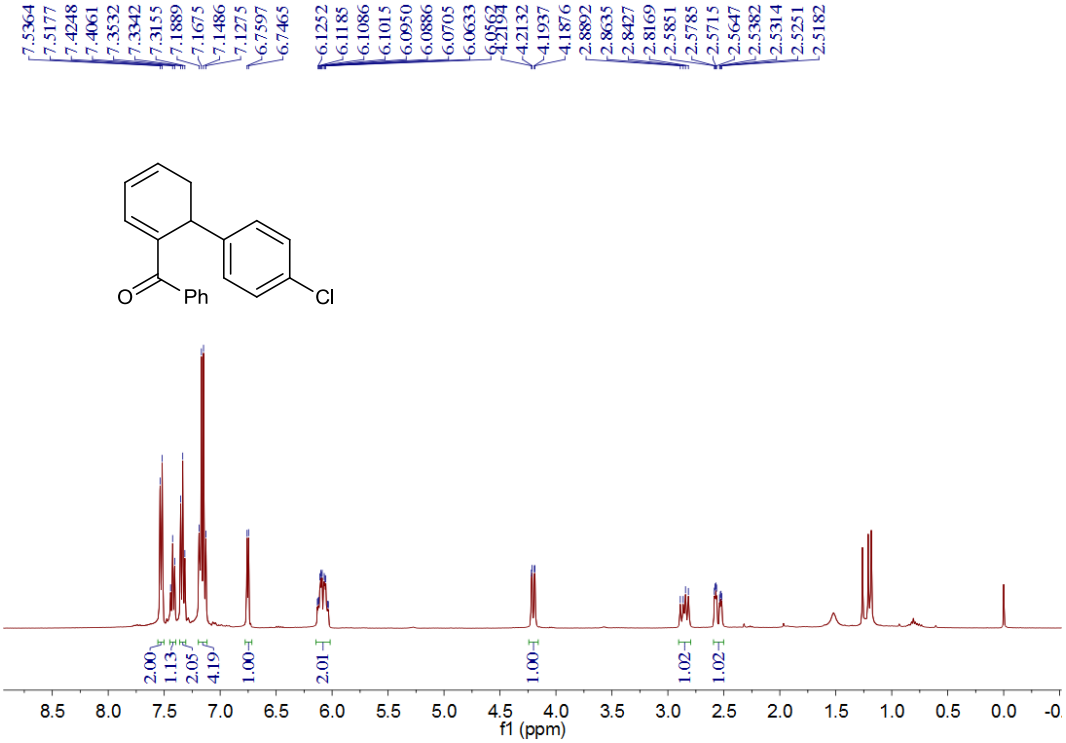
(4'-Fluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4d) ^{13}C NMR (100 MHz, $CDCl_3$)



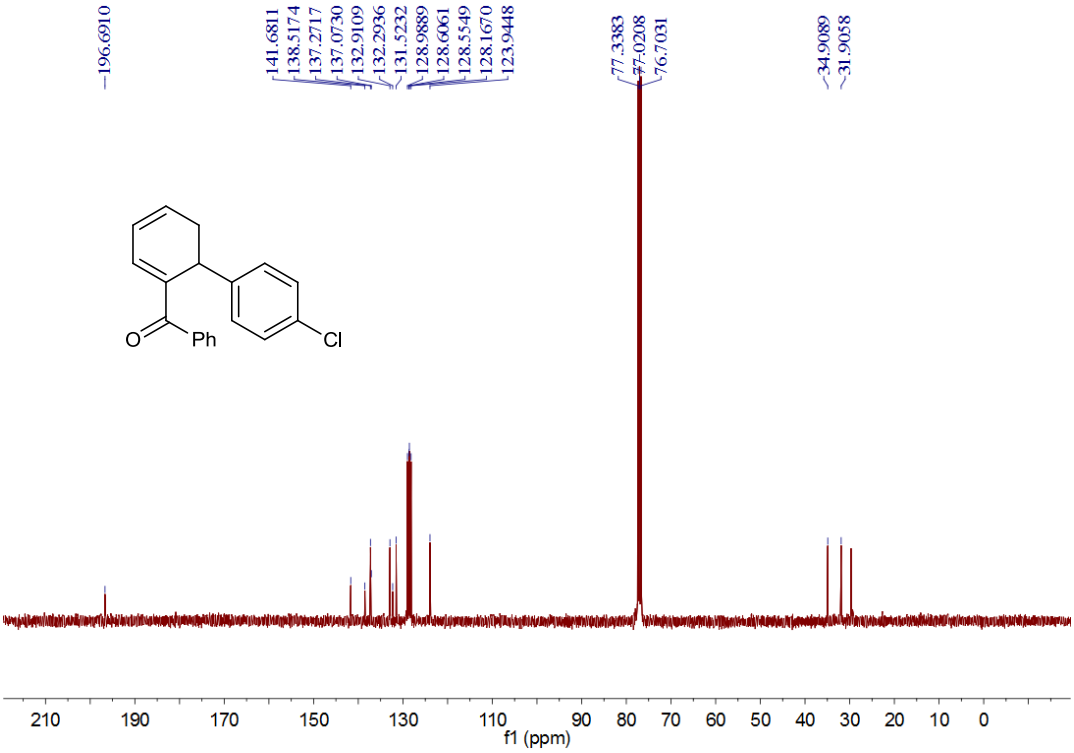
(4'-Fluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4d) ^{19}F NMR (376 MHz, CDCl3)



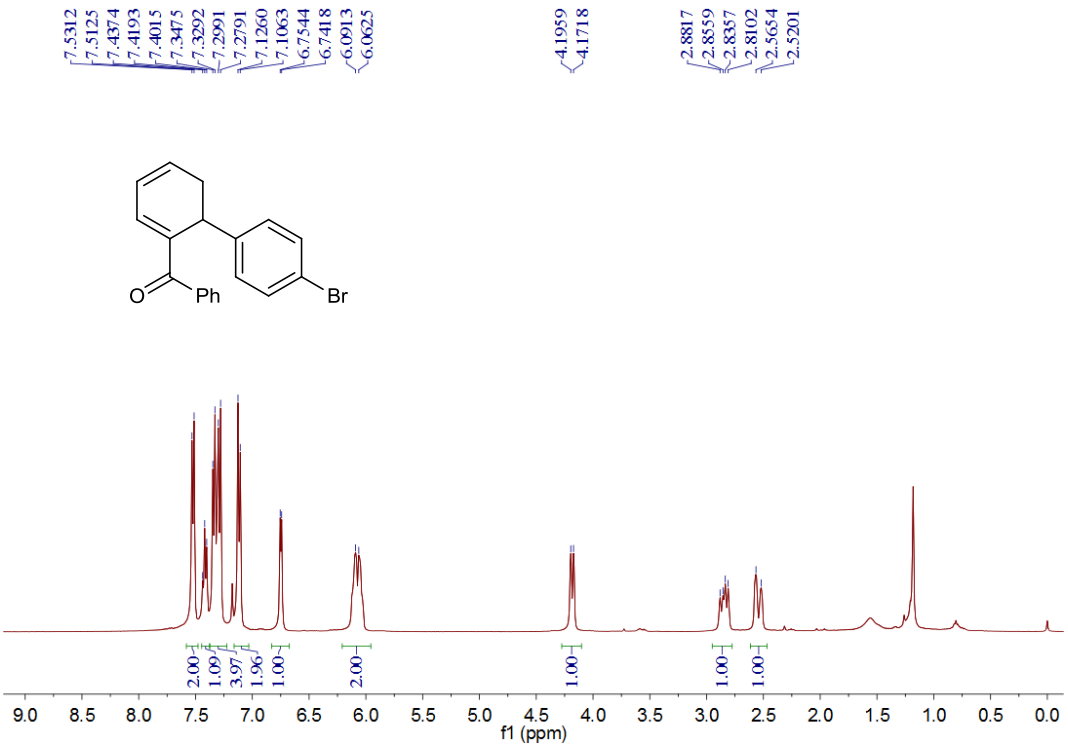
(4'-Chloro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4e) ^{1}H NMR (400 MHz, $CDCl_3$)



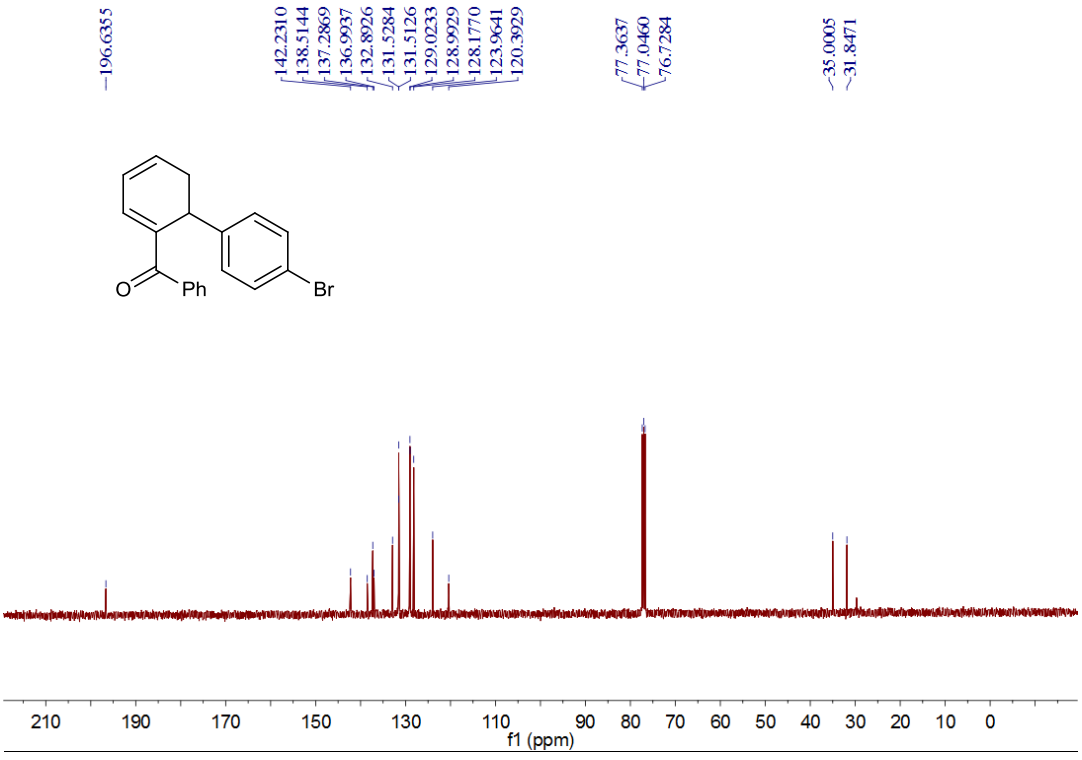
(4'-Chloro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4e) ^{13}C NMR (100 MHz, $CDCl_3$)



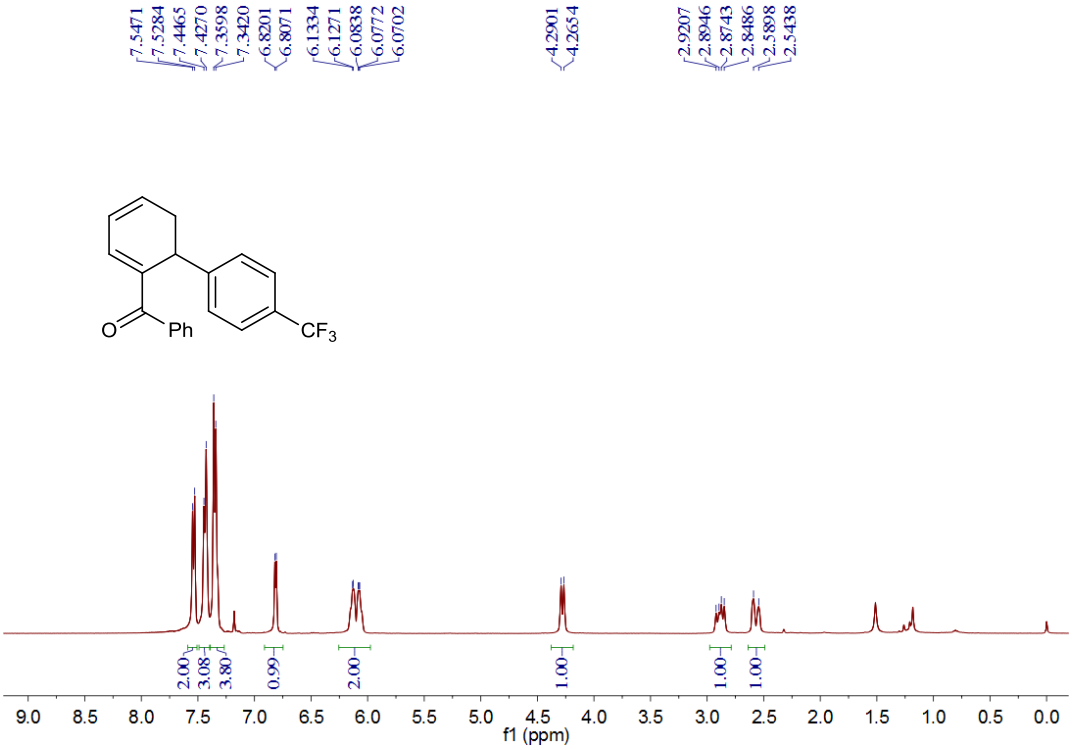
(4'-Bromo-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4f) ^{1}H NMR (400 MHz, $CDCl_3$)



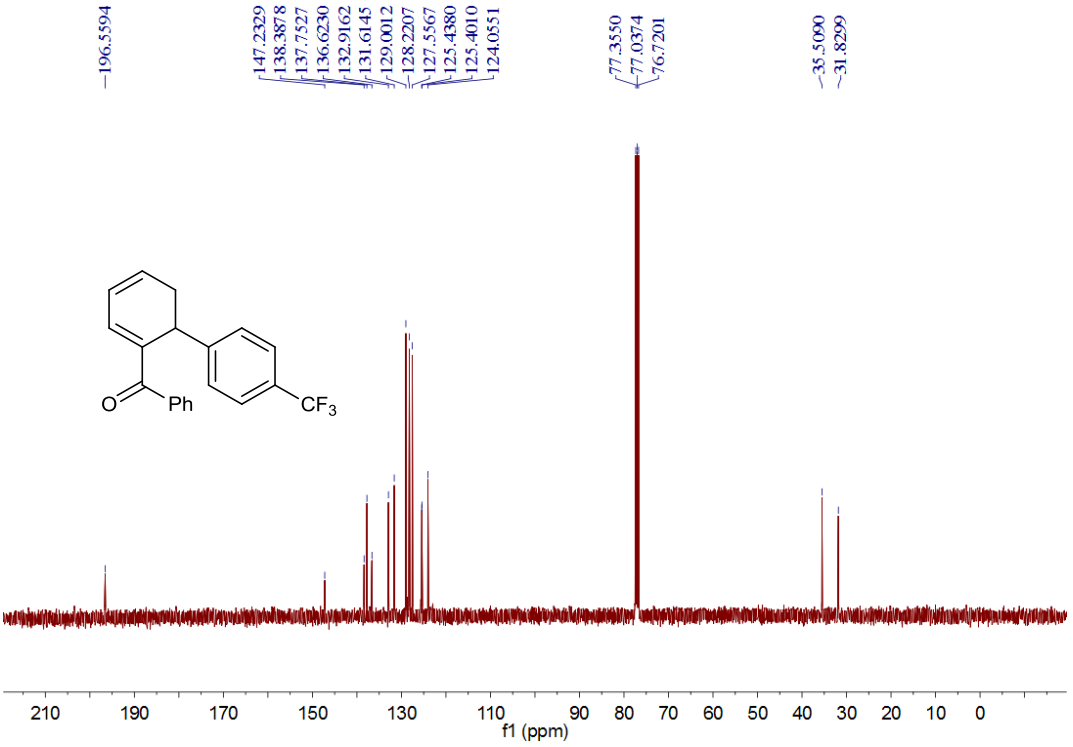
(4'-Bromo-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4f) ^{13}C NMR (100 MHz, $CDCl_3$)



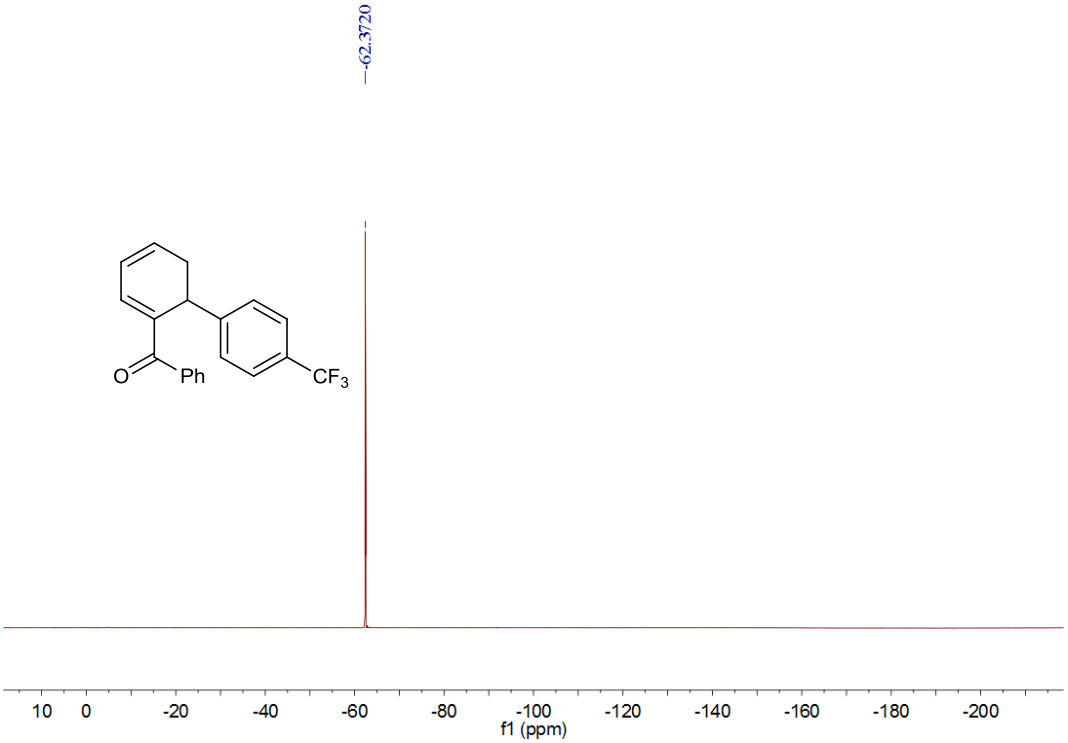
Phenyl(4'-(trifluoromethyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4g)
^{1}H NMR (400 MHz, $CDCl_3$)



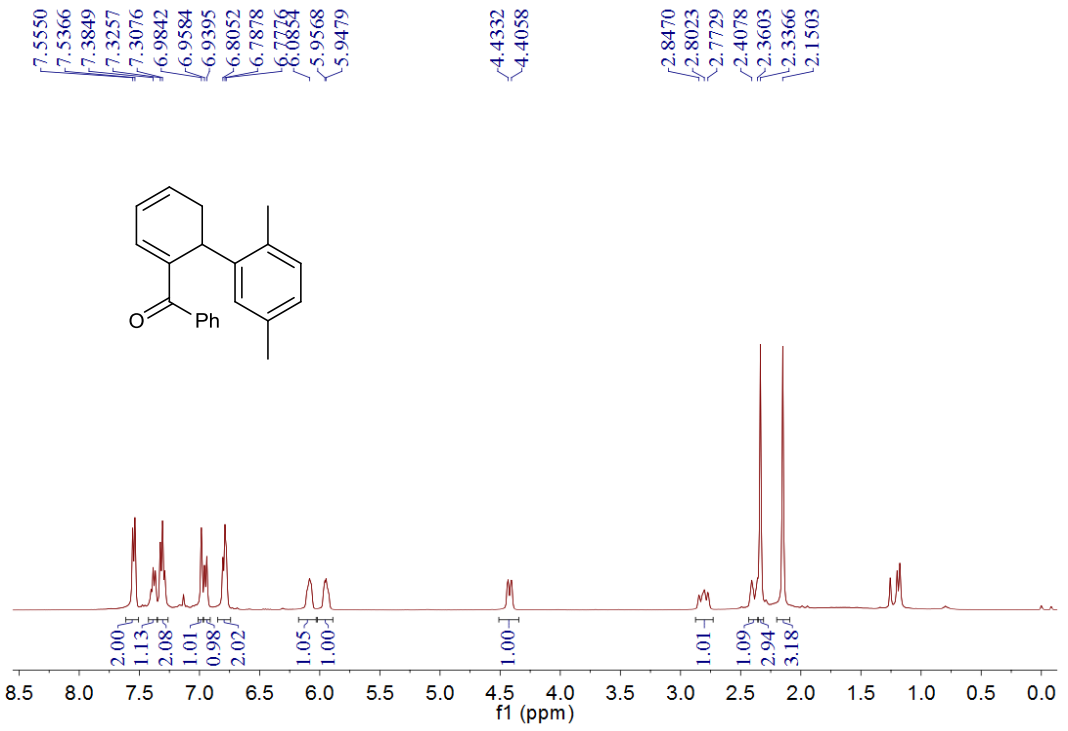
Phenyl(4'-(trifluoromethyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4g)
^{13}C NMR (100 MHz, $CDCl_3$)



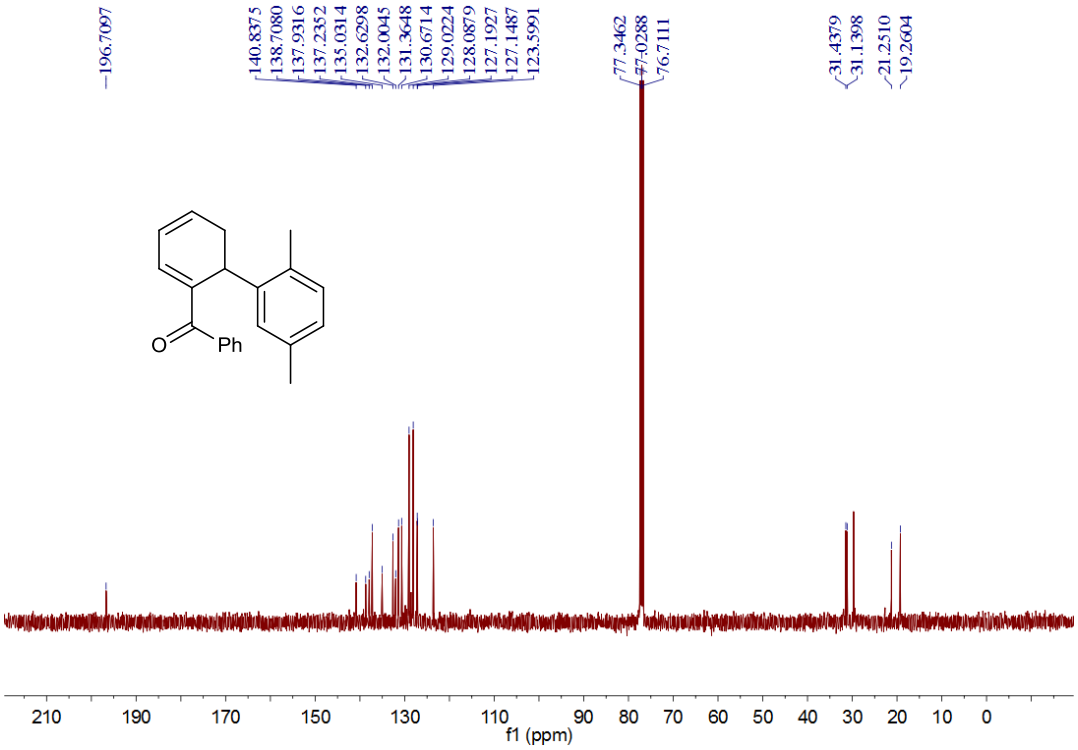
Phenyl(4'-(trifluoromethyl)-1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4g) ^{19}F NMR (376 MHz, CDCl3)



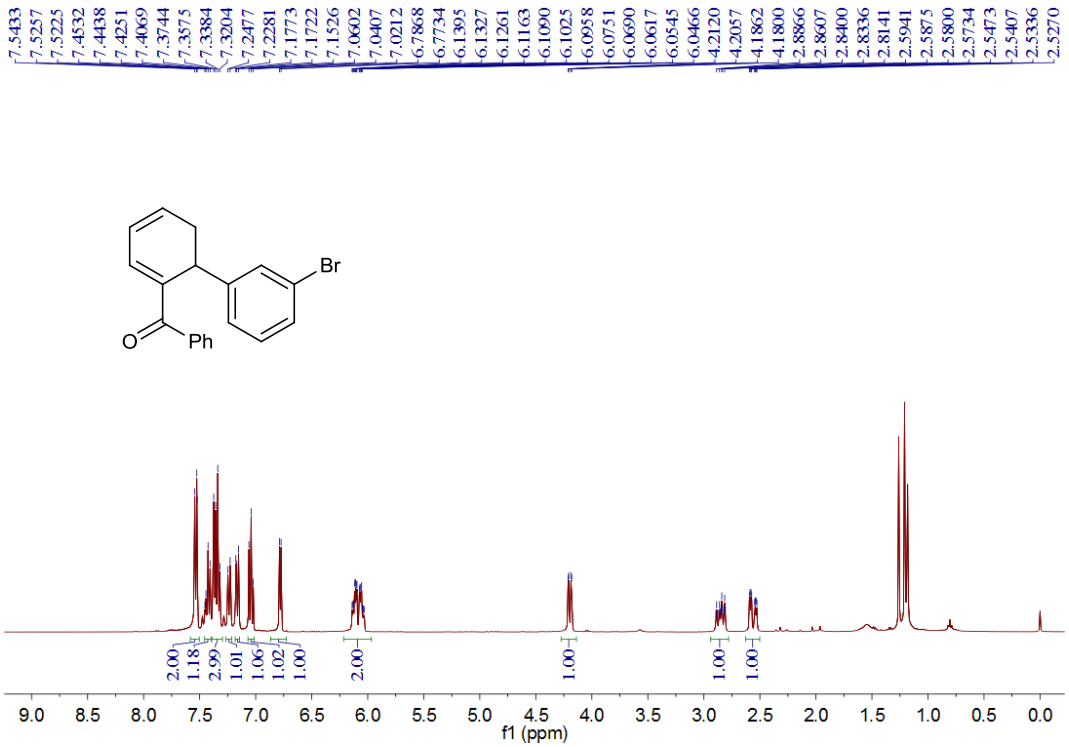
(2',5'-Dimethyl-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4h) ^{1}H NMR (400 MHz, $CDCl_3$)



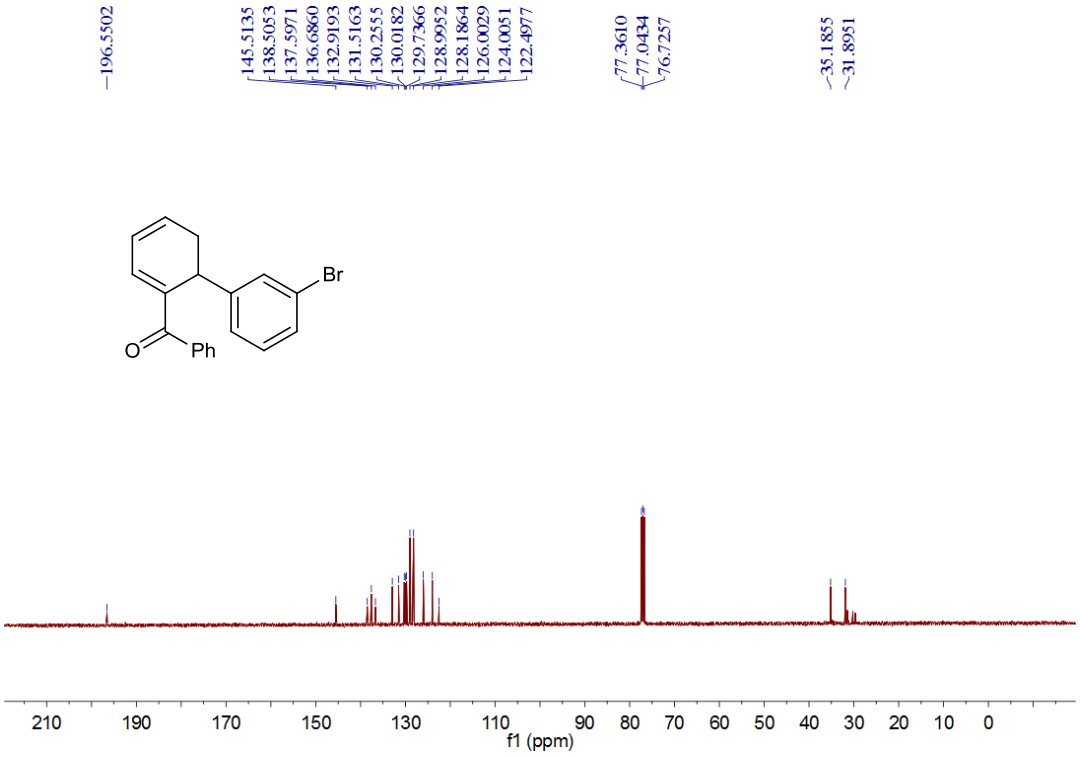
(2',5'-Dimethyl-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4h) ^{13}C NMR (100 MHz, $CDCl_3$)



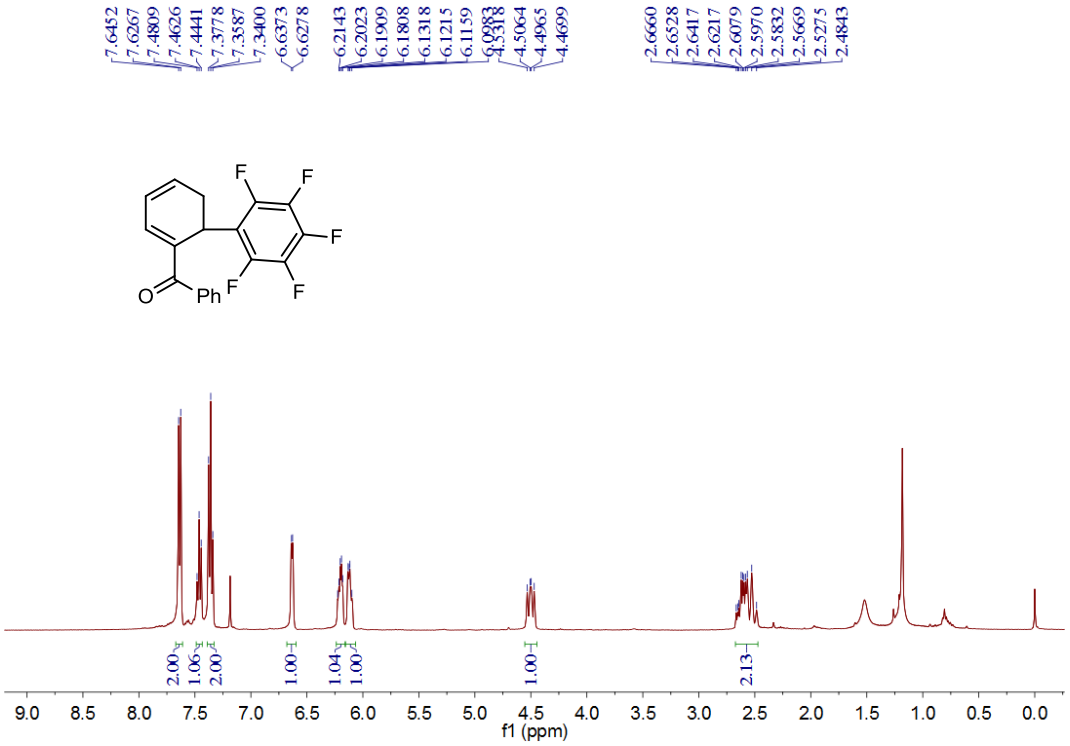
(3'-Bromo-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4i) ^{1}H NMR (400 MHz, $CDCl_3$)



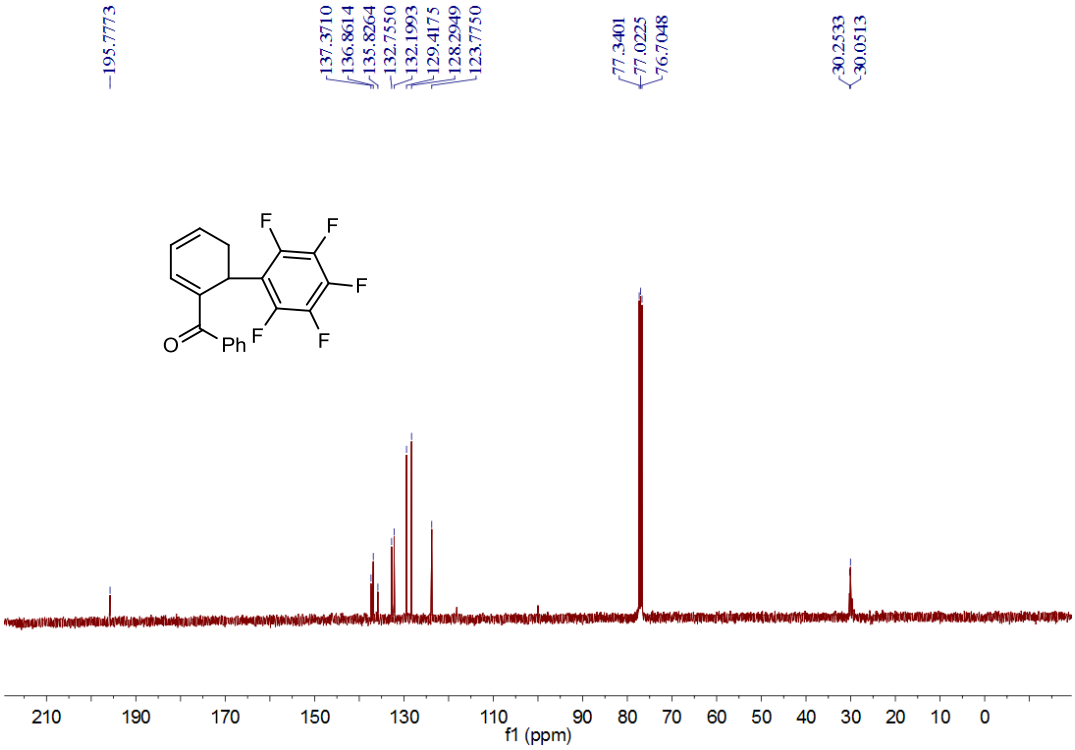
(3'-Bromo-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4i) ^{13}C NMR (100 MHz, $CDCl_3$)



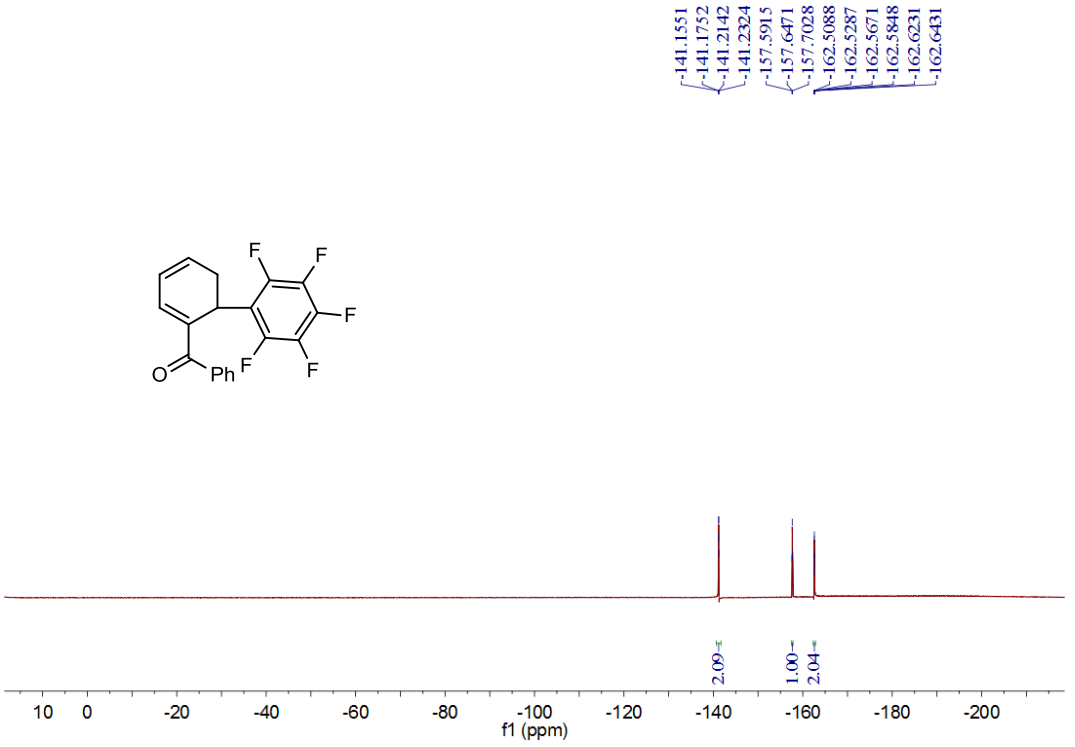
(2',3',4',5',6'-Pentafluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4j) ^{1}H NMR (400 MHz, $CDCl_3$)



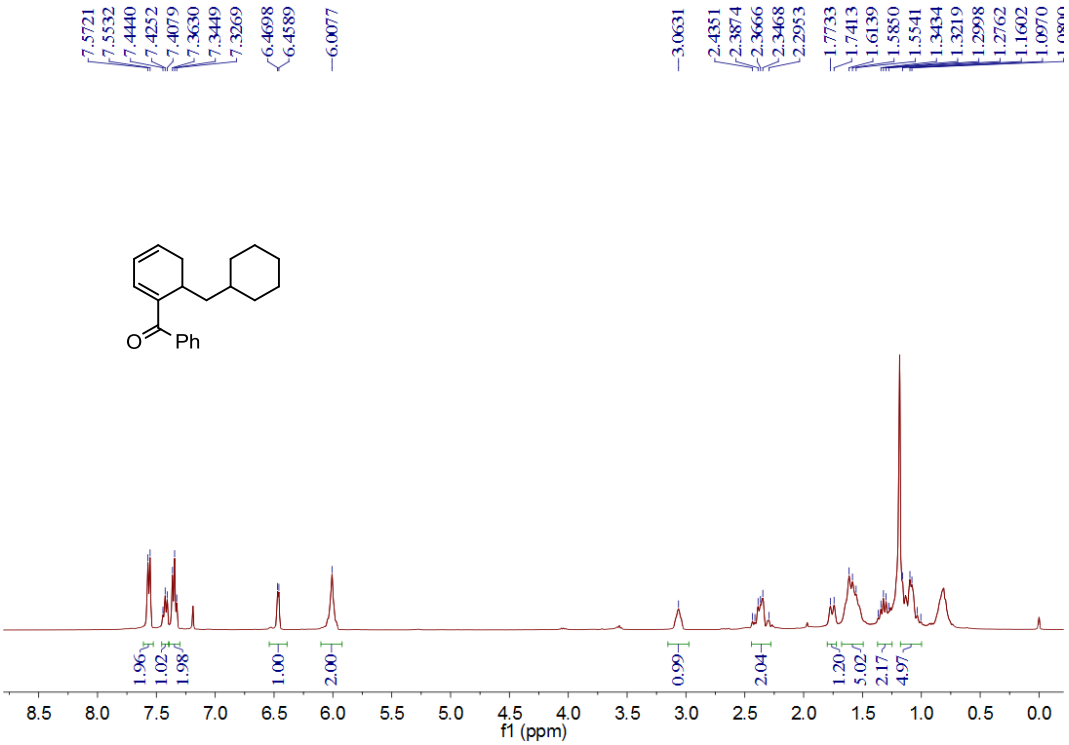
(2',3',4',5',6'-Pentafluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4j) ^{13}C NMR (100 MHz, $CDCl_3$)



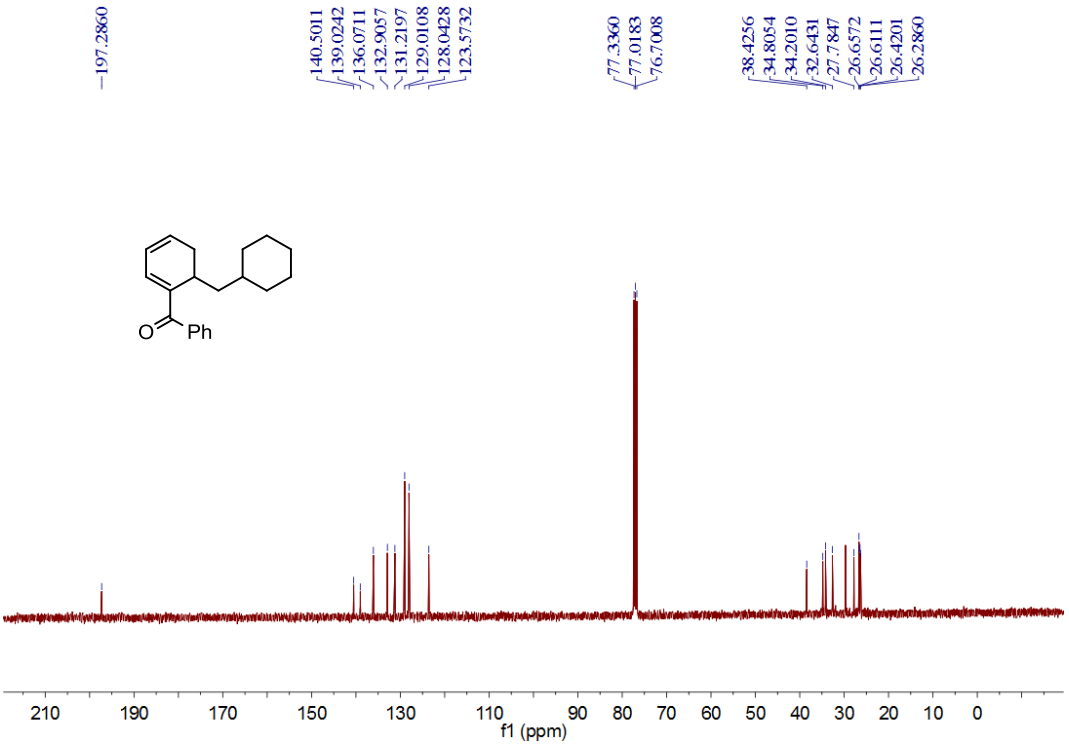
(2',3',4',5',6'-Pentafluoro-1,6-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (4j) ^{19}F NMR (376 MHz, $CDCl_3$)



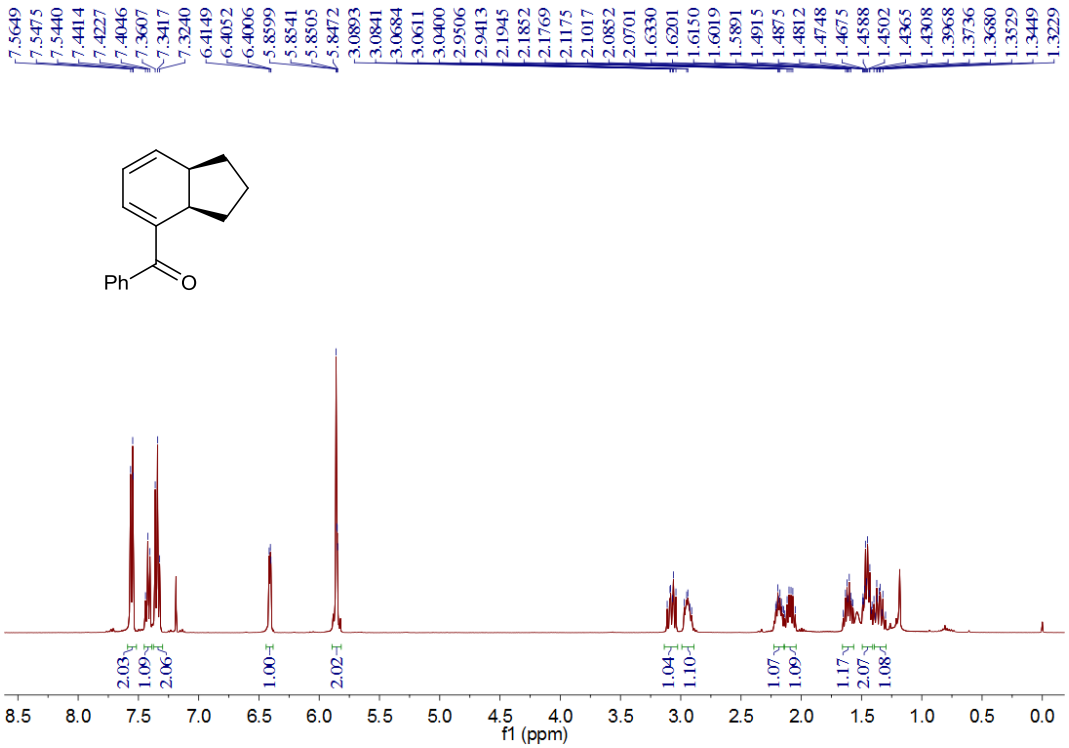
(6-(Cyclohexylmethyl)cyclohexa-1,3-dien-1-yl)(phenyl)methanone (4k) ^{1}H NMR (400 MHz, $CDCl_3$)



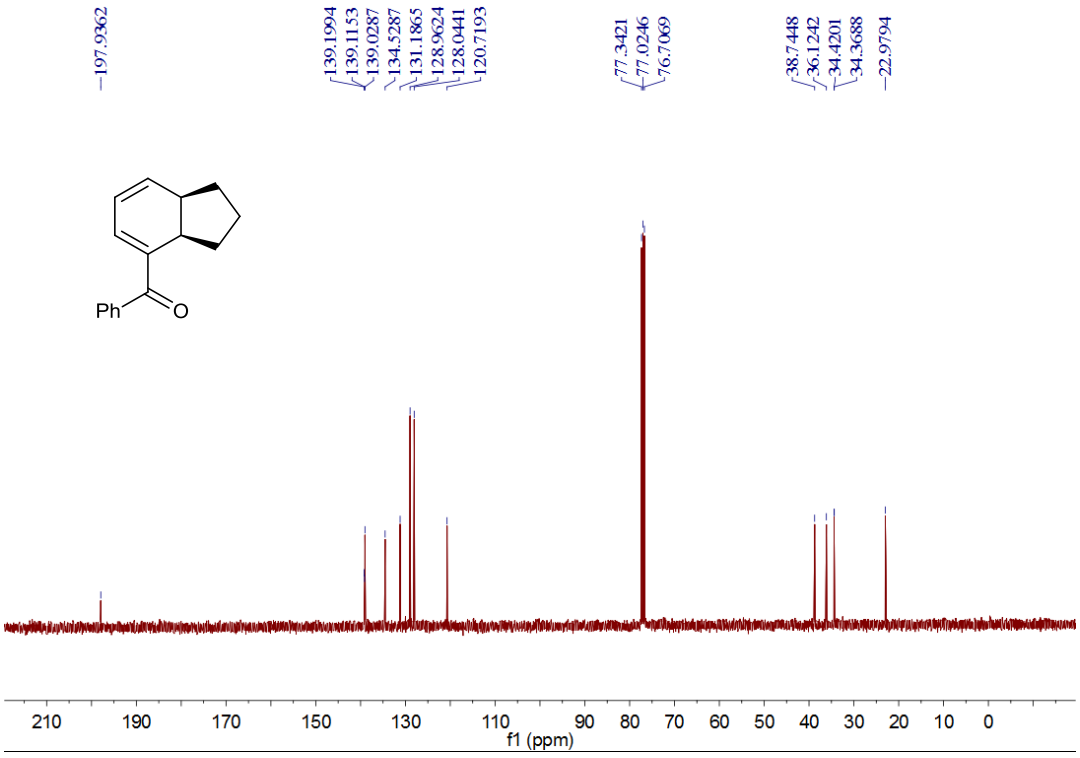
(6-(Cyclohexylmethyl)cyclohexa-1,3-dien-1-yl)(phenyl)methanone (4k) ^{13}C NMR (100 MHz, $CDCl_3$)



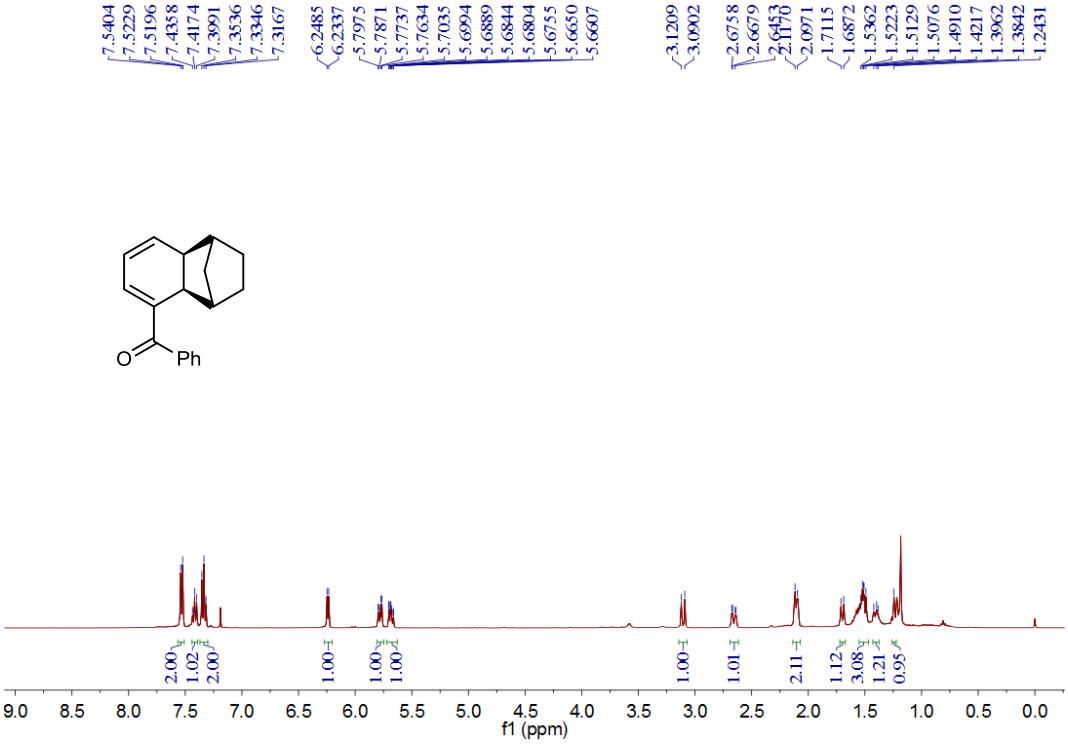
Phenyl(2,3,3a,7a-tetrahydro-1H-inden-4-yl)methanone (4l) ^{1}H NMR (400 MHz, $CDCl_3$)



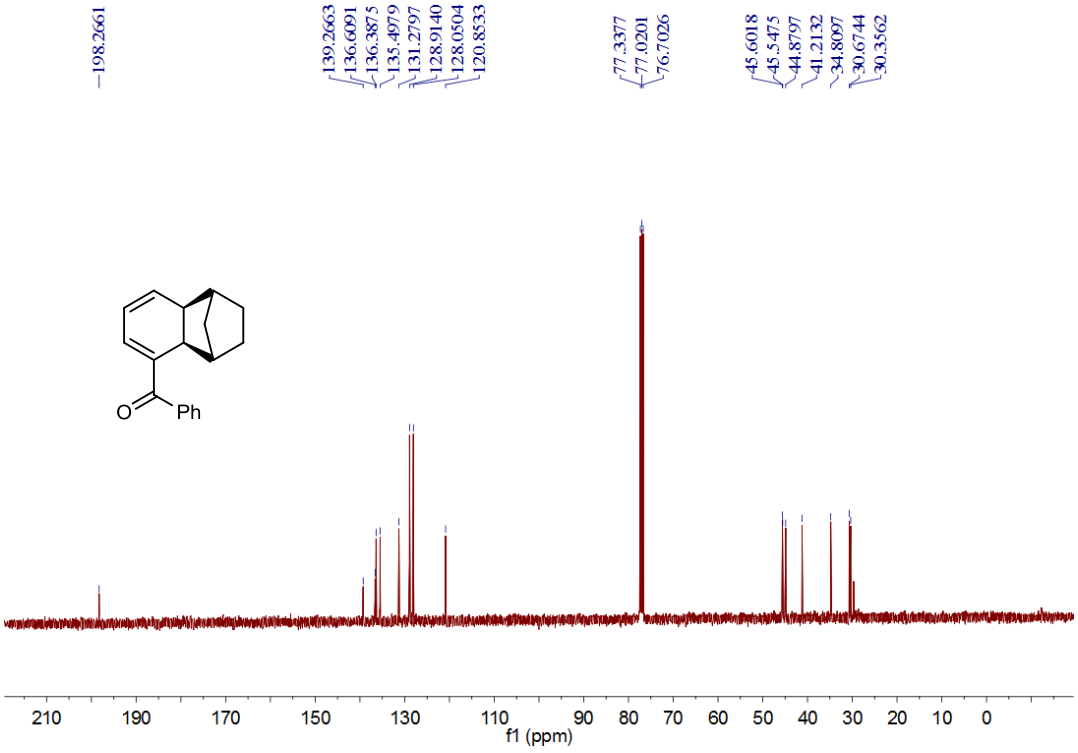
Phenyl(2,3,3a,7a-tetrahydro-1H-inden-4-yl)methanone (4l) ^{13}C NMR (100 MHz, $CDCl_3$)



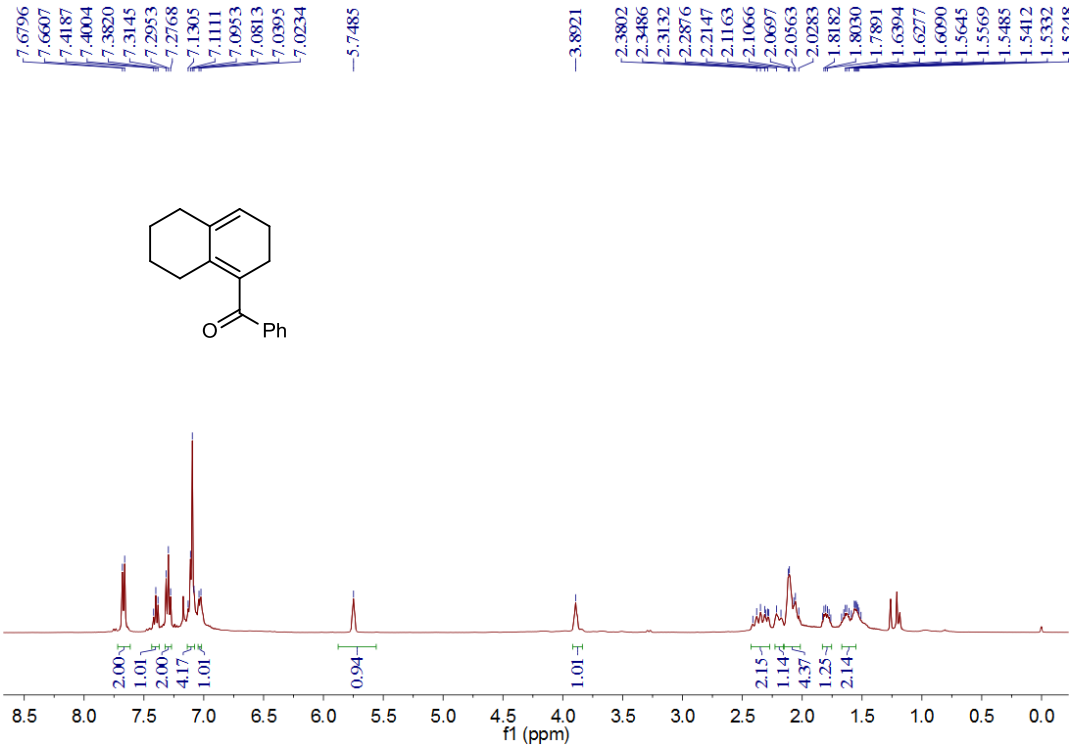
(1,2,3,4,4a,8a-Hexahydro-1,4-methanonaphthalen-5-yl)(phenyl)methanone (4m) ^{1}H NMR (400 MHz, $CDCl_3$)



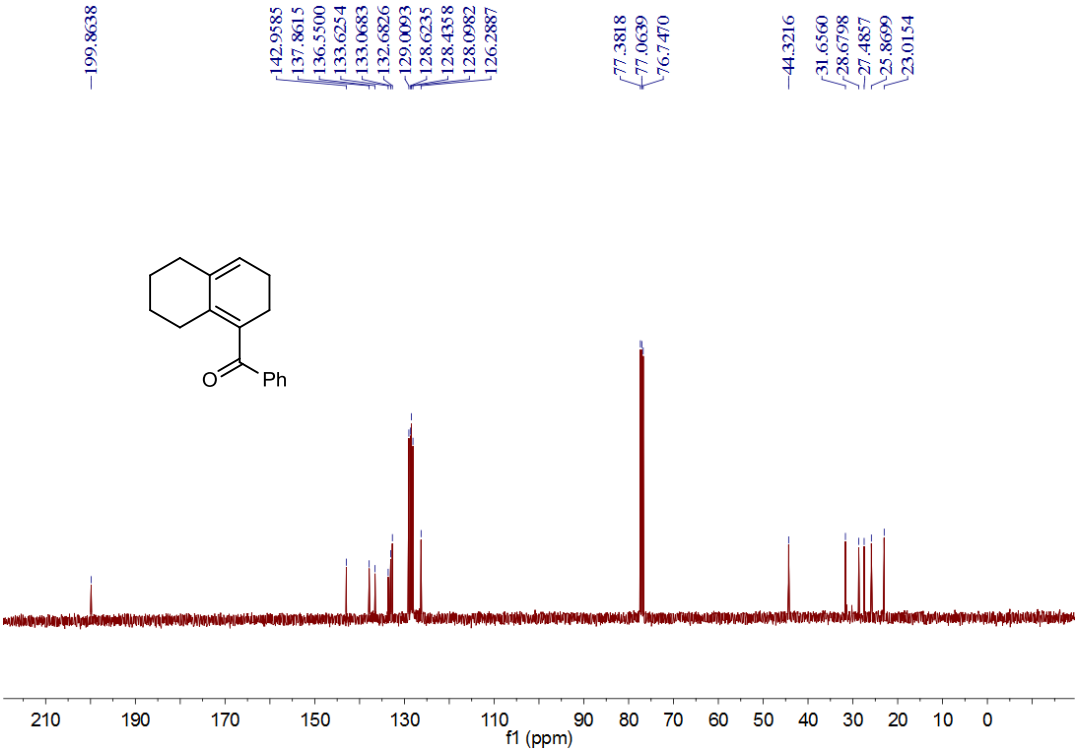
(1,2,3,4,4a,8a-Hexahydro-1,4-methanonaphthalen-5-yl)(phenyl)methanone (4m) ^{13}C NMR (100 MHz, $CDCl_3$)



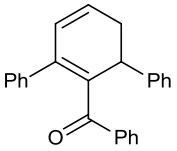
Phenyl(2-phenyl-2,3,5,6,7,8-hexahydronaphthalen-1-yl)methanone (4n) ^{1}H NMR (400 MHz, $CDCl_3$)

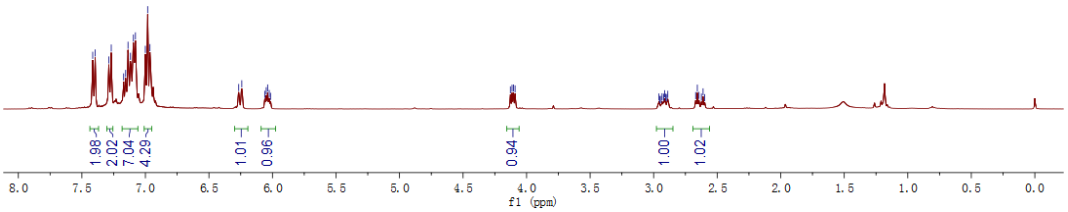


Phenyl(2-phenyl-2,3,5,6,7,8-hexahydronaphthalen-1-yl)methanone (4n) ^{13}C NMR (100 MHz, $CDCl_3$)

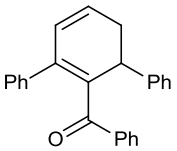


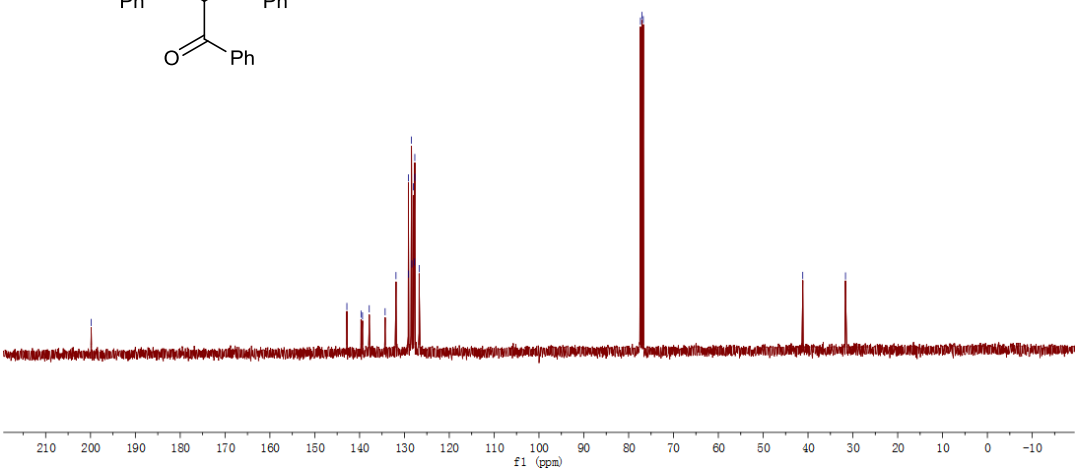
(1',6'-Dihydro-[1,1':3',1''-terphenyl]-2'-yl)(phenyl)methanone (4o) ^{1}H NMR (400 MHz, $CDCl_3$)



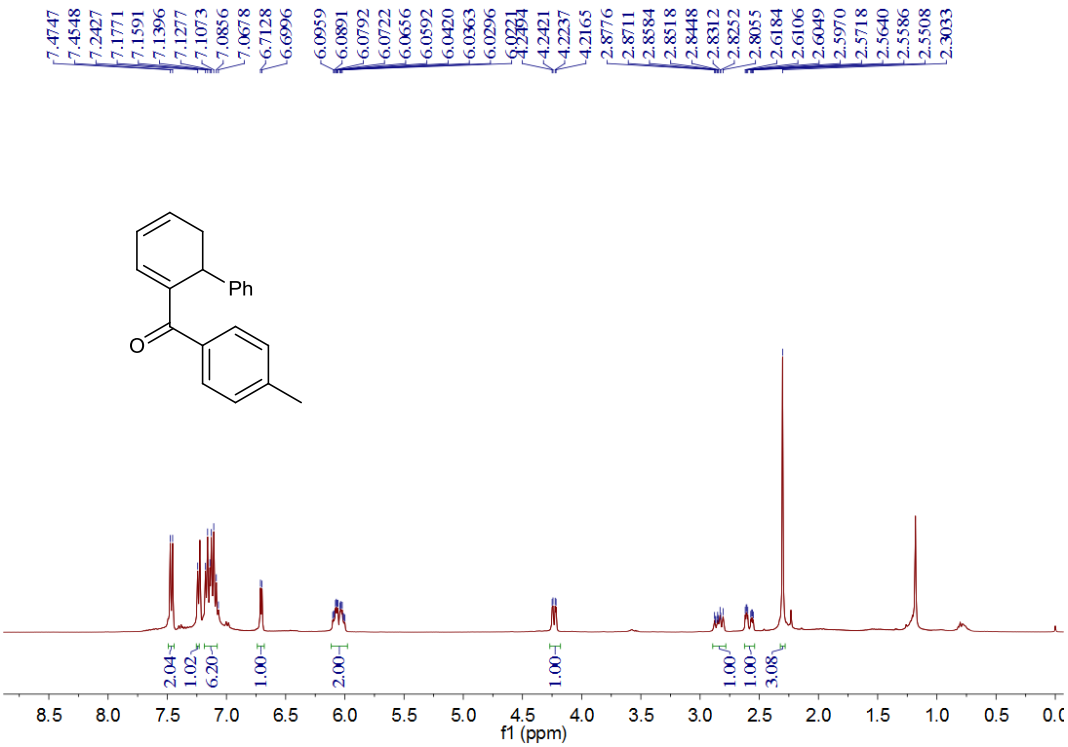


(1',6'-Dihydro-[1,1':3',1''-terphenyl]-2'-yl)(phenyl)methanone (4o) ^{13}C NMR (100 MHz, $CDCl_3$)

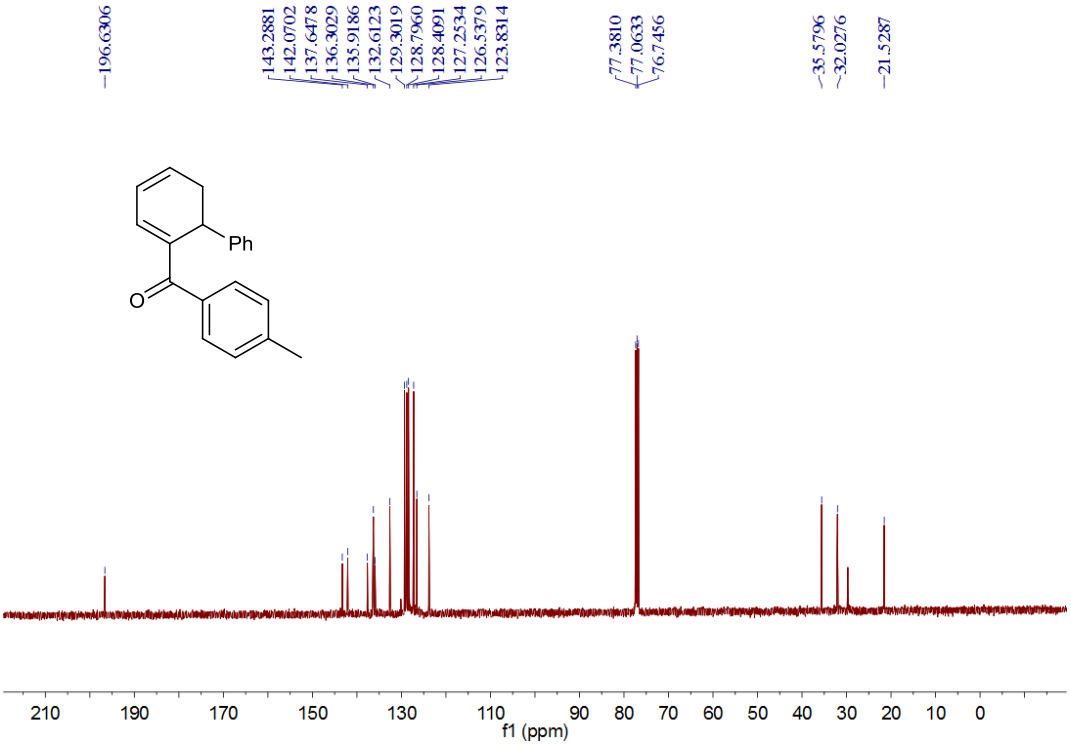




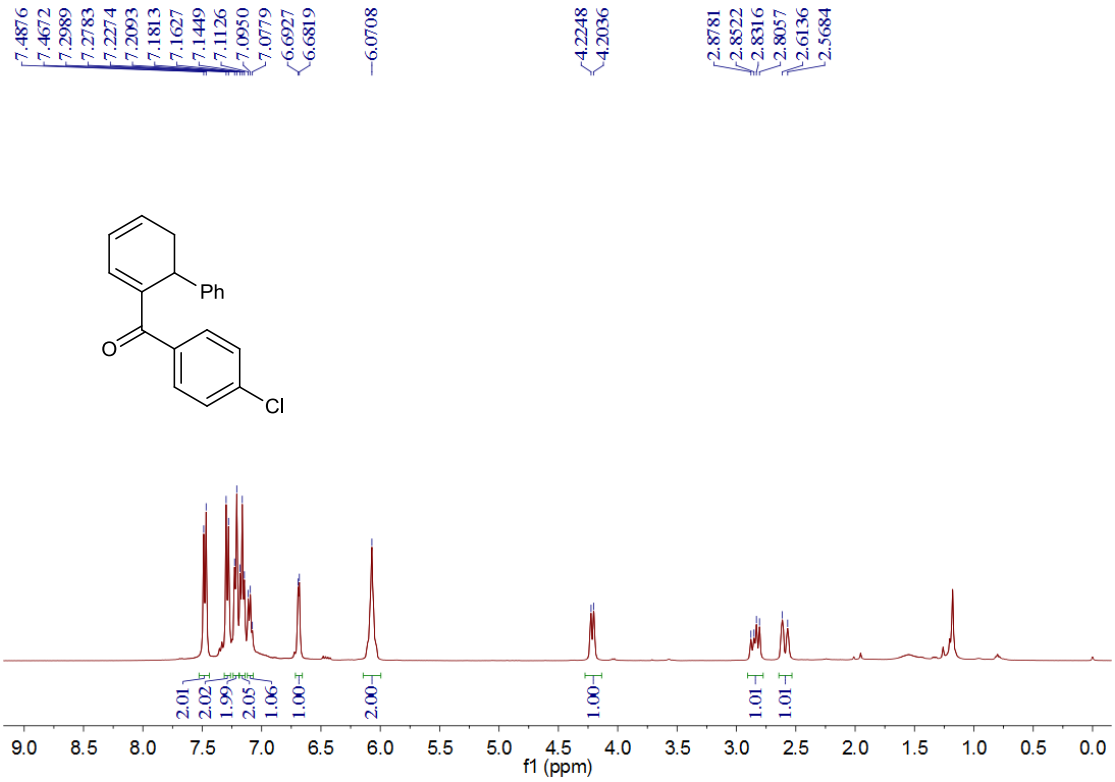
(1,6-Dihydro-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone (4p) ^{1}H NMR (400 MHz, $CDCl_3$)



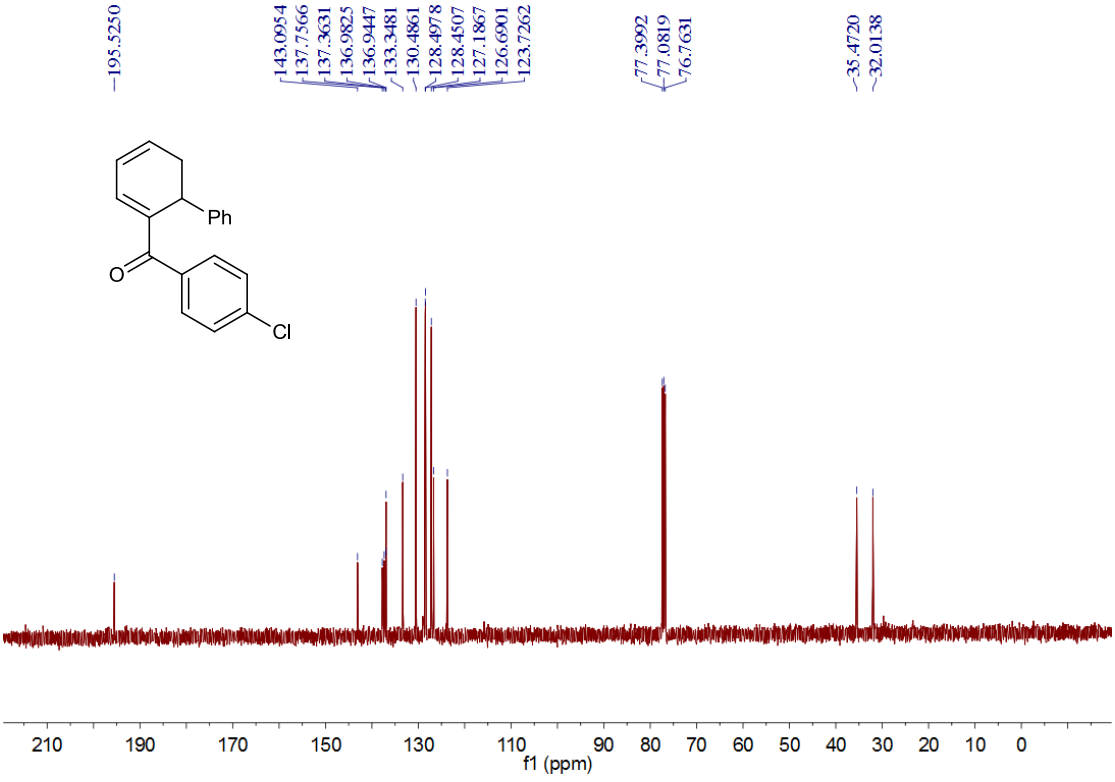
(1,6-Dihydro-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone (4p) ^{13}C NMR (100 MHz, $CDCl_3$)



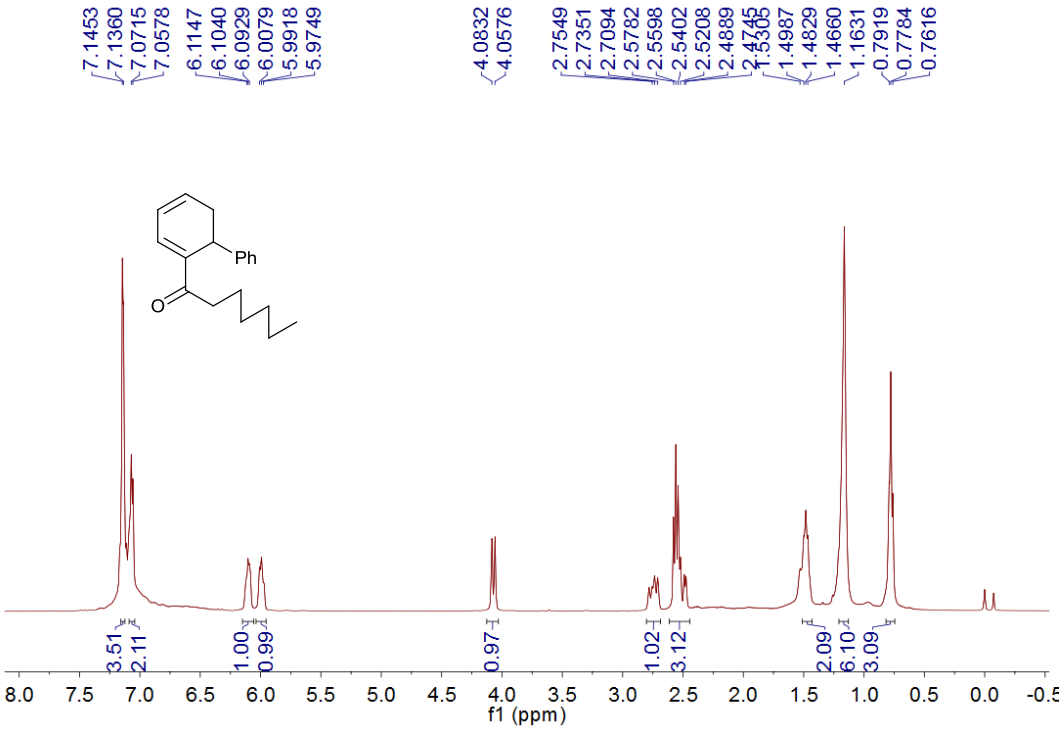
(4-Chlorophenyl)(1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4q) ^{1}H NMR (400 MHz, $CDCl_3$)



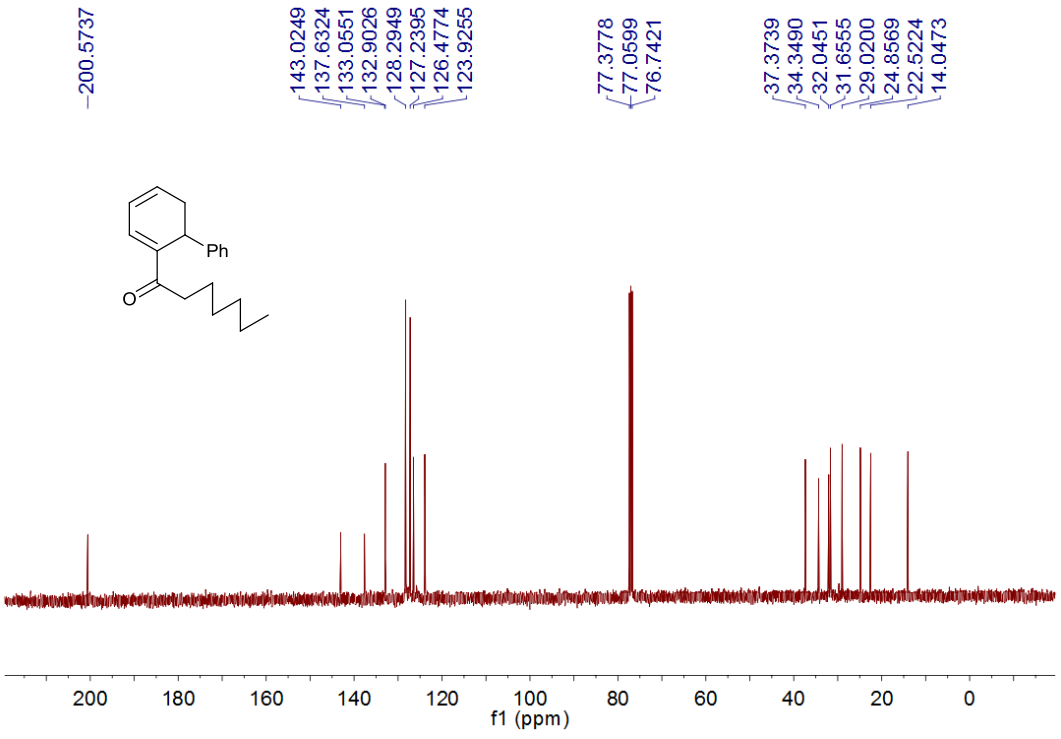
(4-Chlorophenyl)(1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4q) ^{13}C NMR (100 MHz, $CDCl_3$)



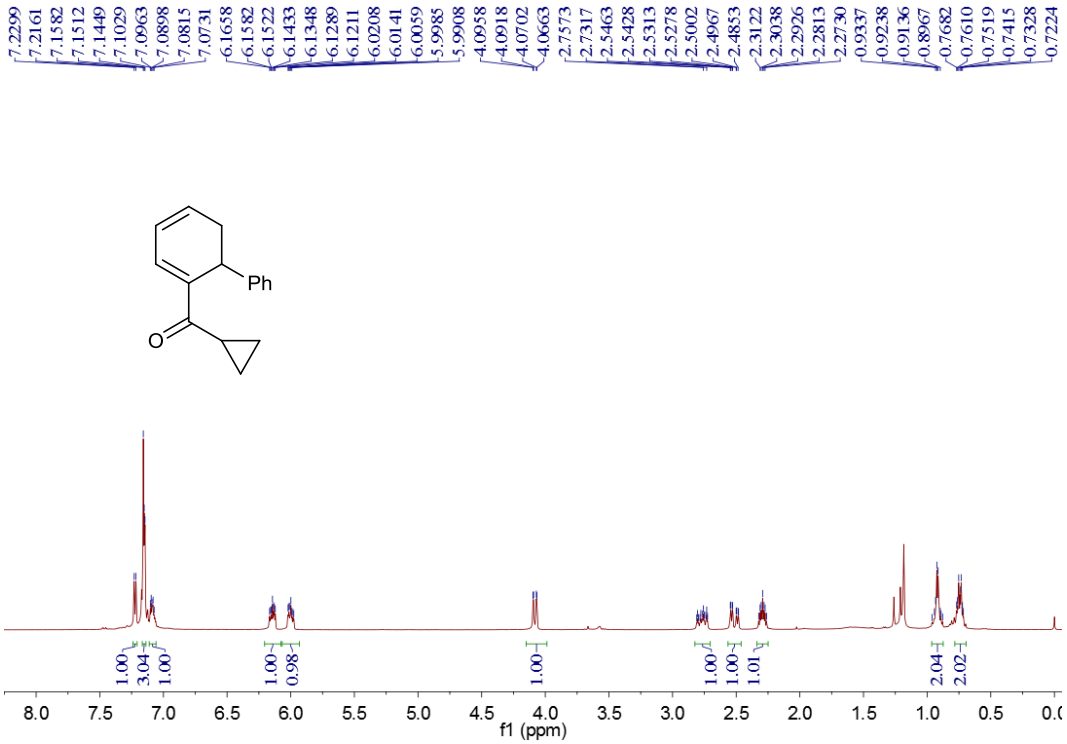
1-(1,6-Dihydro-[1,1'-biphenyl]-2-yl)heptan-1-one (4r) ^{1}H NMR (400 MHz, $CDCl_3$)



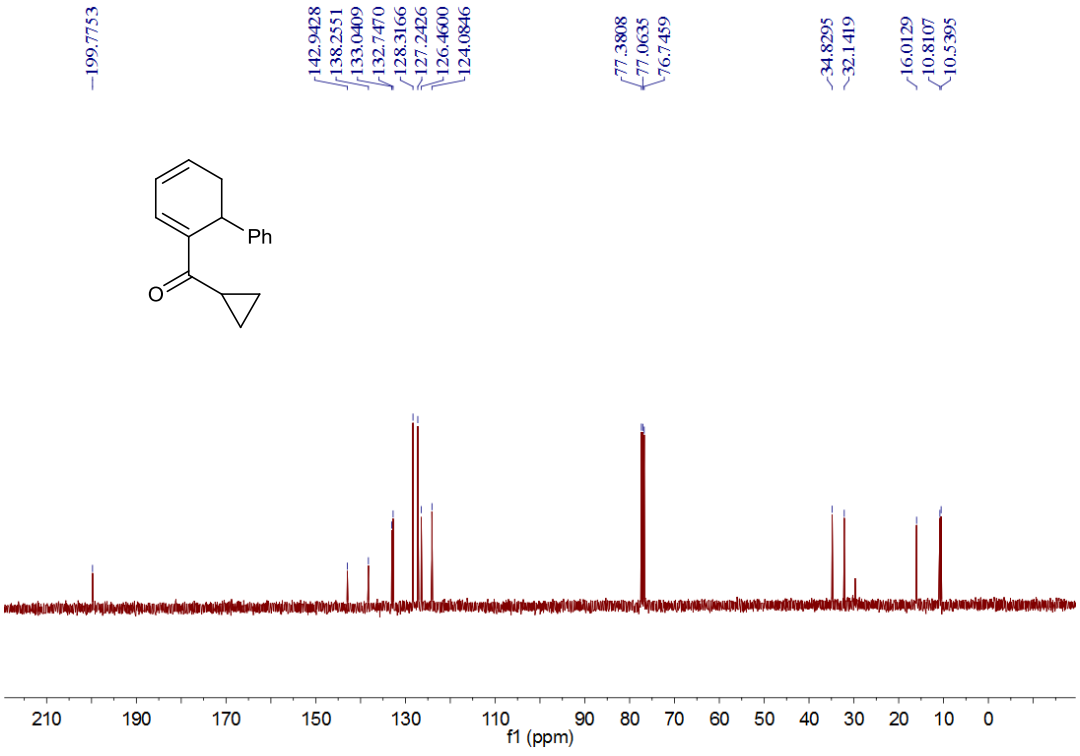
1-(1,6-Dihydro-[1,1'-biphenyl]-2-yl)heptan-1-one (4r) ^{13}C NMR (100 MHz, $CDCl_3$)



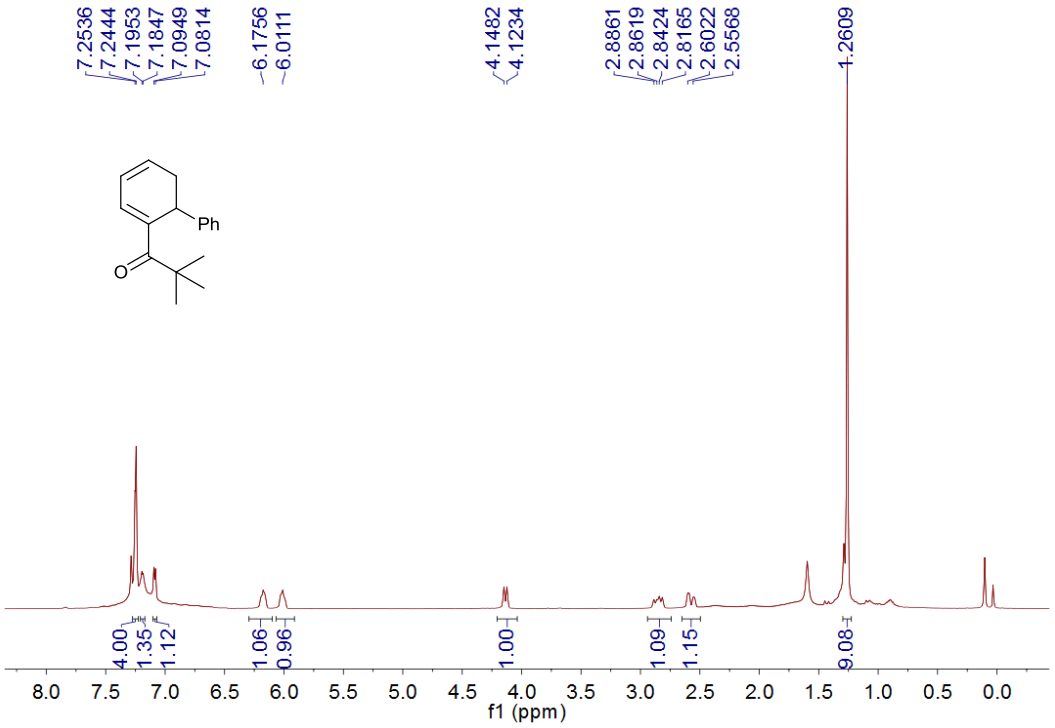
Cyclopropyl(1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4s) ^{1}H NMR (400 MHz, $CDCl_3$)



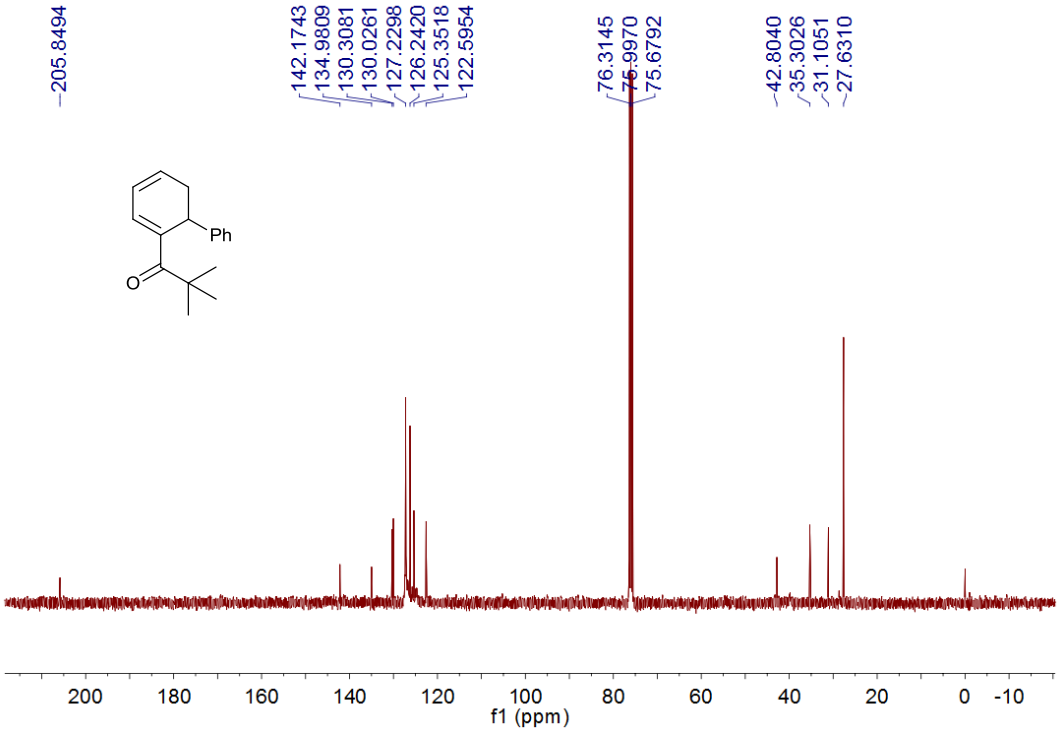
Cyclopropyl(1,6-dihydro-[1,1'-biphenyl]-2-yl)methanone (4s) ^{13}C NMR (100 MHz, $CDCl_3$)



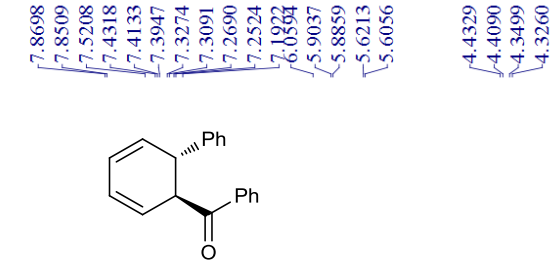
1-(1,6-Dihydro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpro-pan-1-one. (4t) ^{1}H NMR (400 MHz, $CDCl_3$)

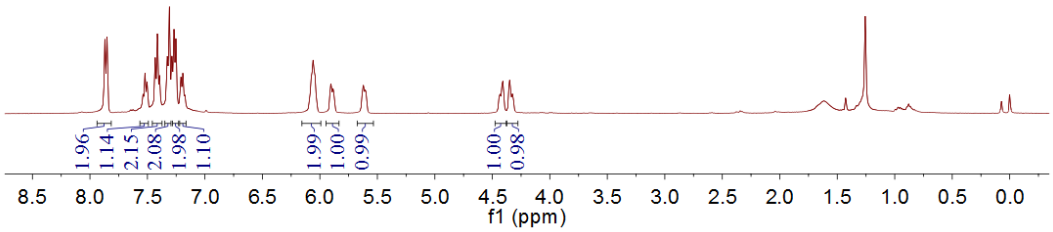


1-(1,6-Dihydro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpro-pan-1-one. (4t) ^{13}C NMR (100 MHz, $CDCl_3$)

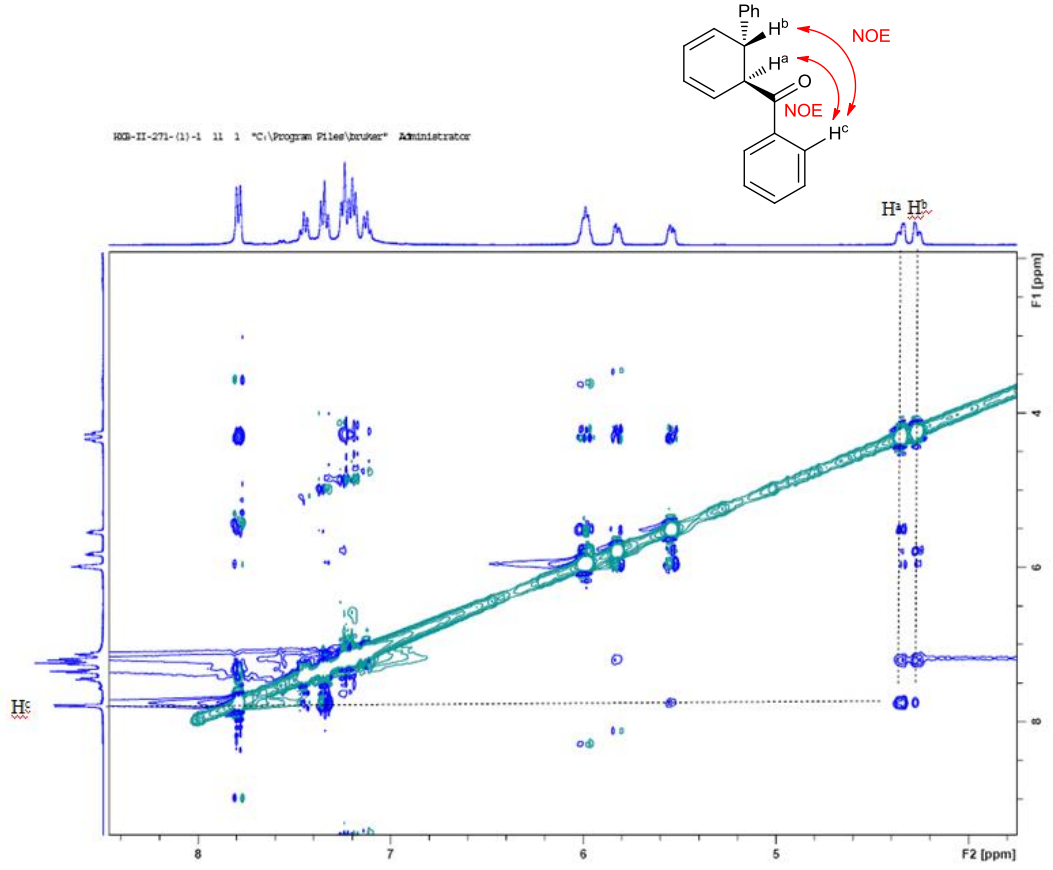


(1,2-Dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3a) ^{1}H NMR (400 MHz, $CDCl_3$)

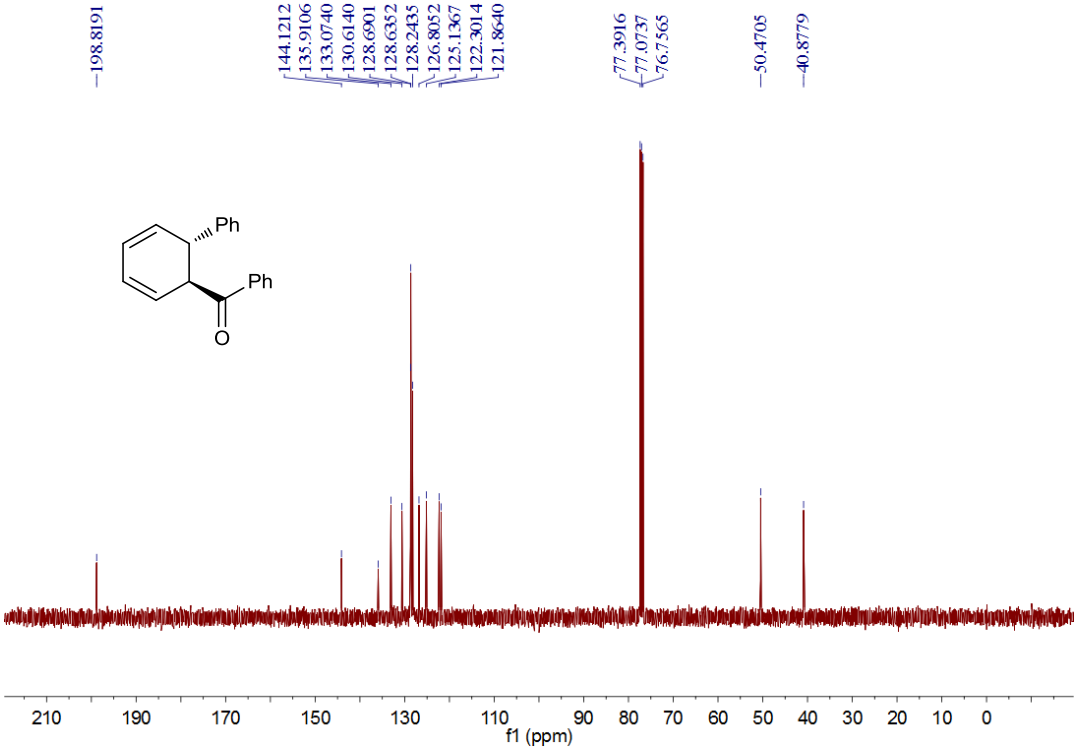




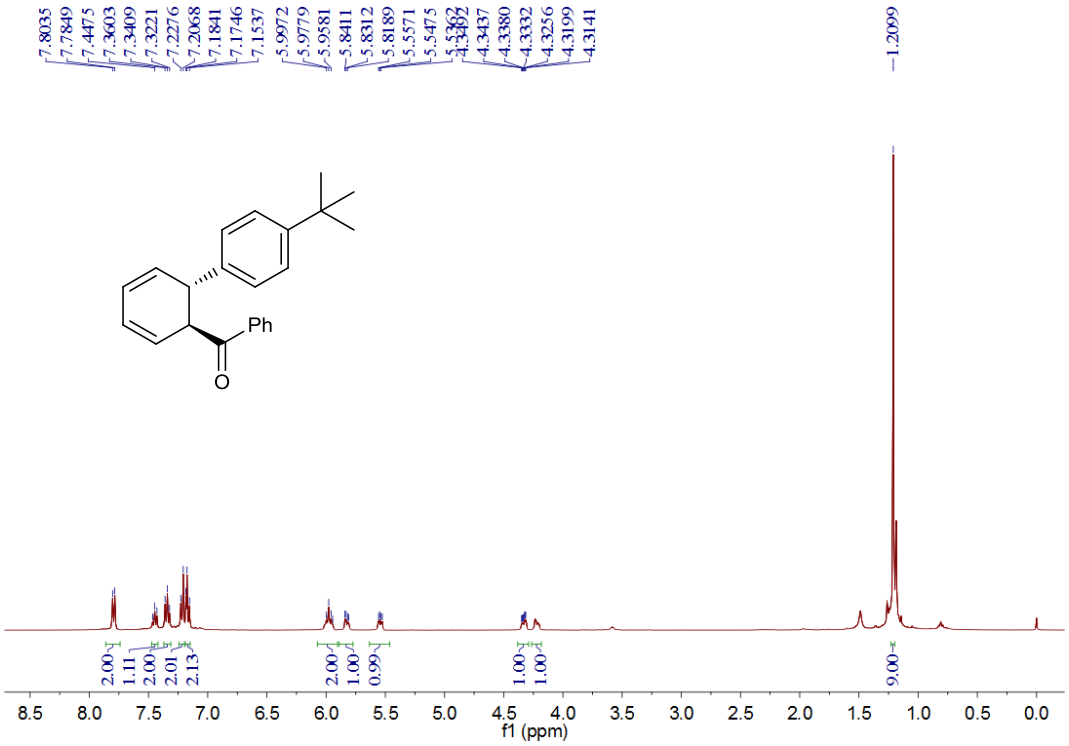
NOE spectrum of **3a**



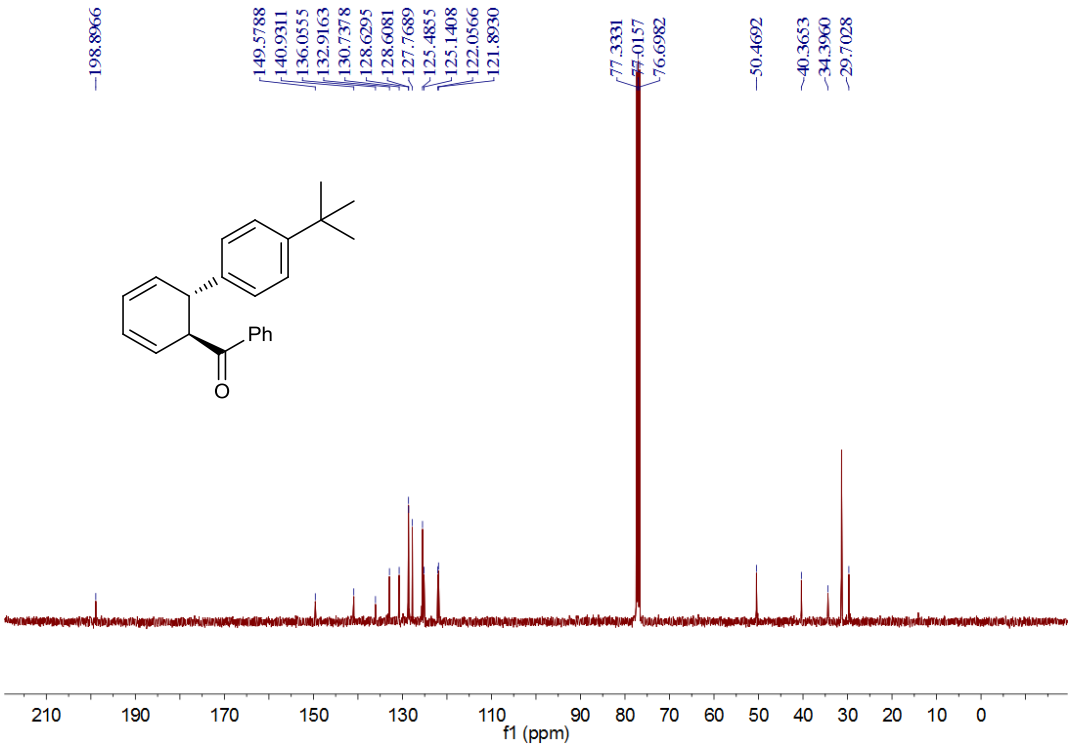
(1,2-Dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3a) ^{13}C NMR (100 MHz, $CDCl_3$)



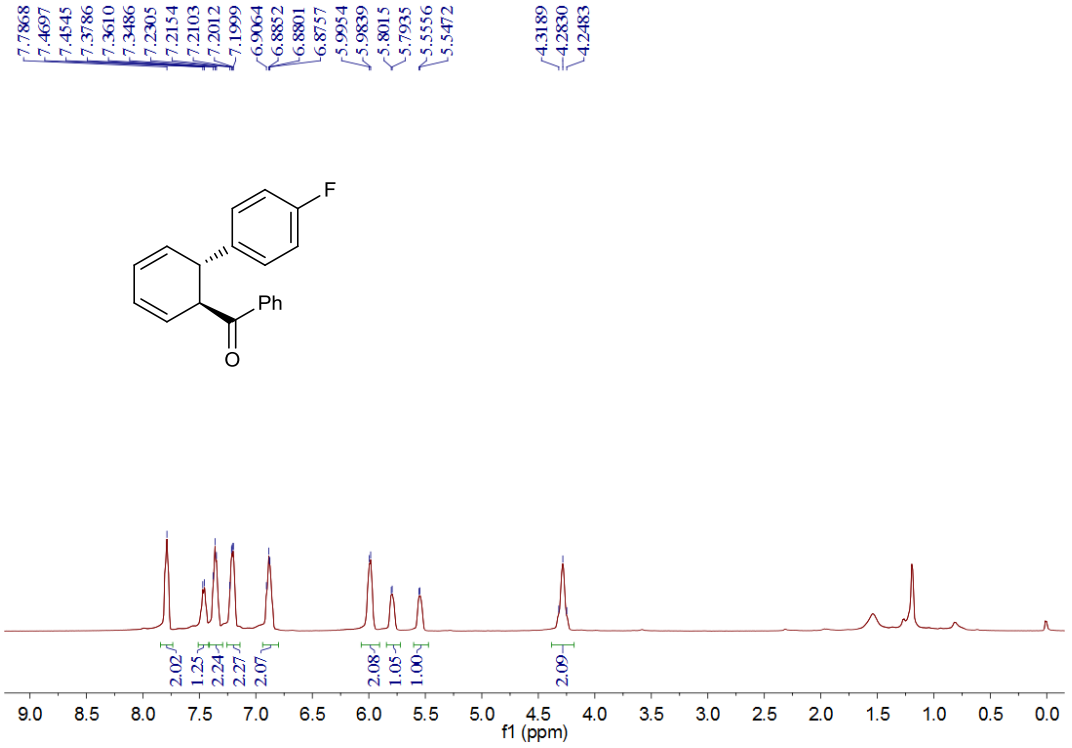
(4'-(Tert-butyl)-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3b) ^{1}H NMR (400 MHz, $CDCl_3$)



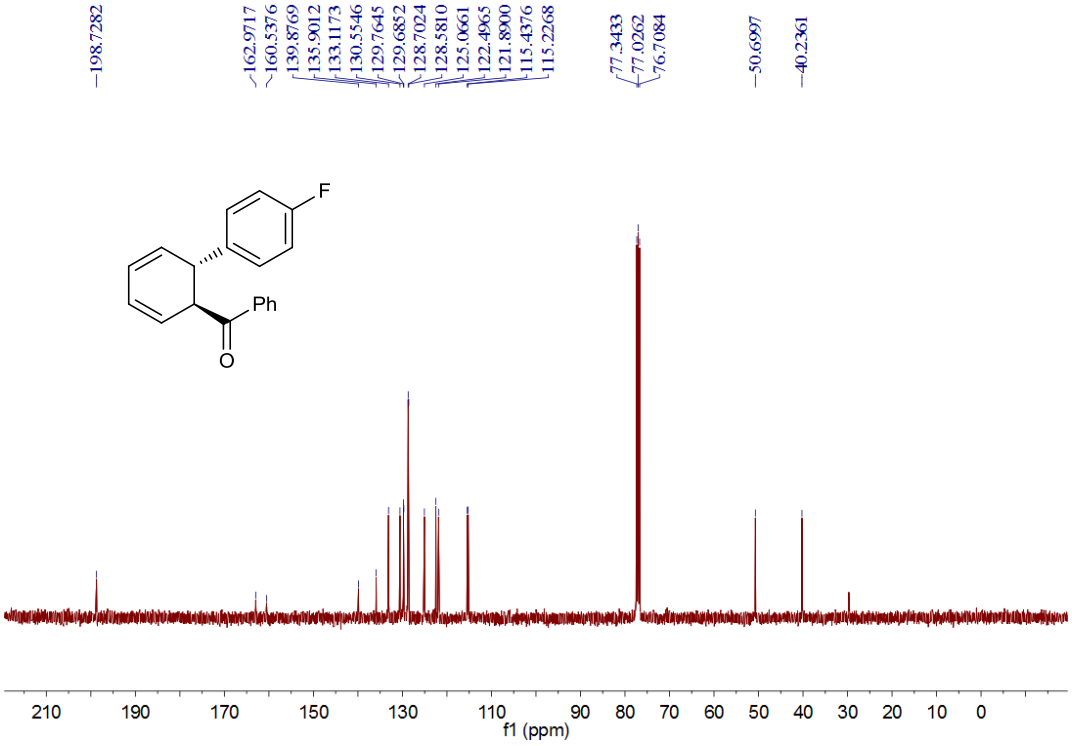
(4'-(Tert-butyl)-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3b) ^{13}C NMR (100 MHz, $CDCl_3$)



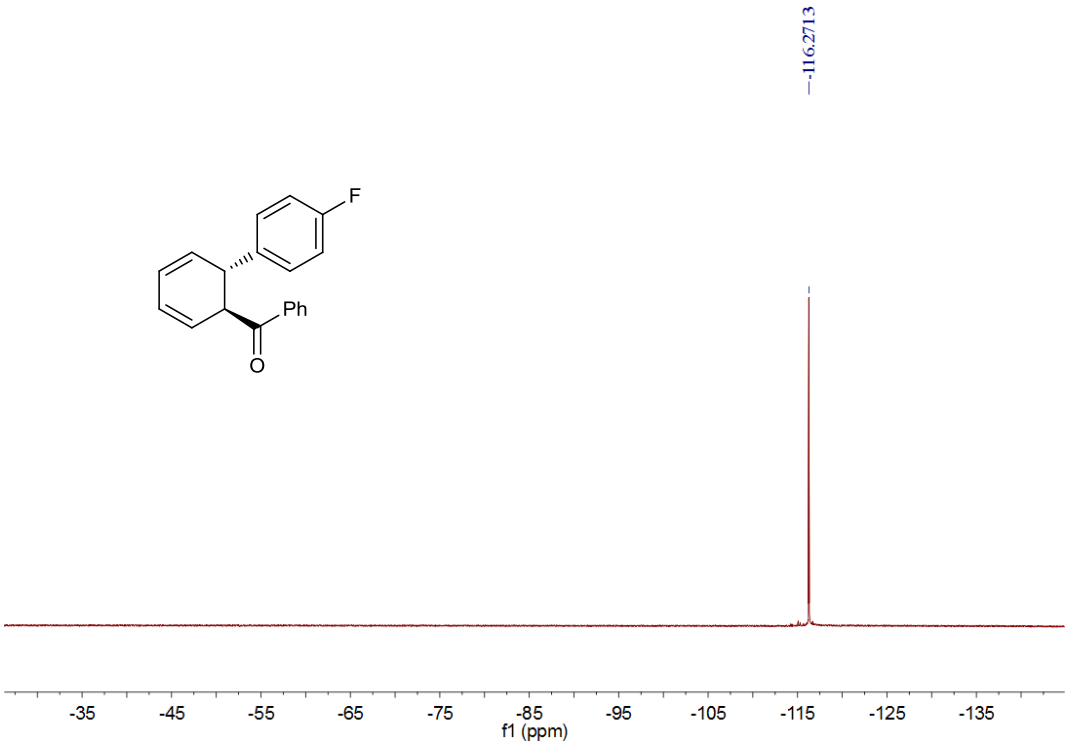
(4'-Fluoro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3c) ^{1}H NMR (400 MHz, $CDCl_3$)



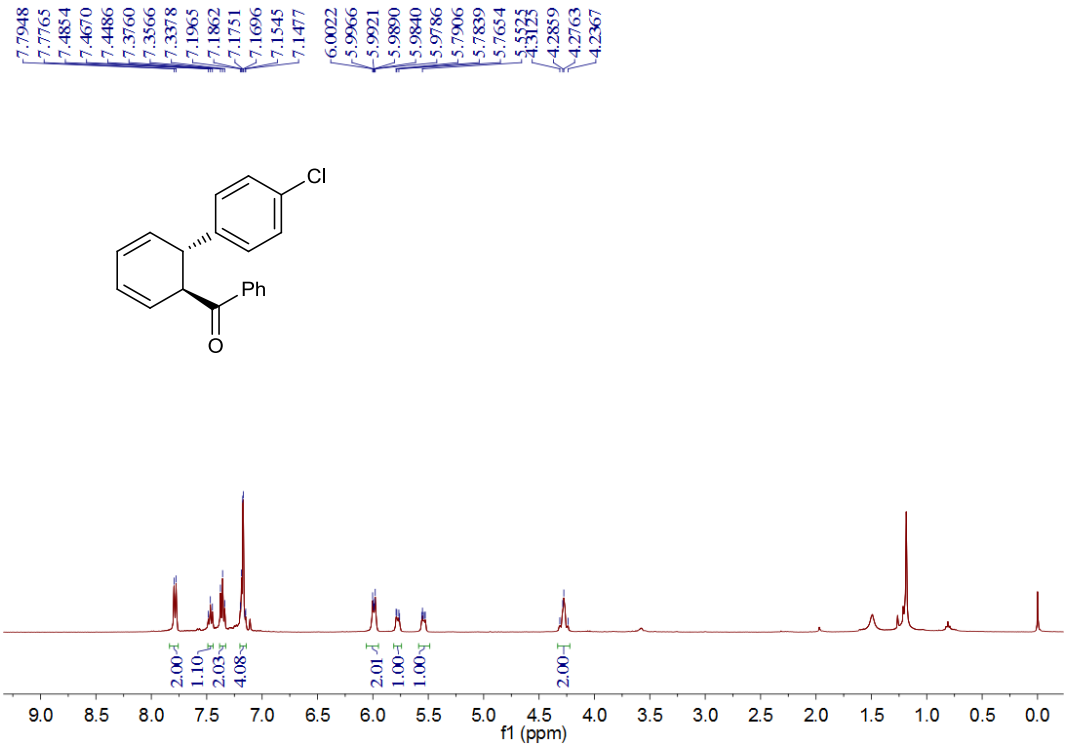
(4'-Fluoro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3c) ^{13}C NMR (100 MHz, $CDCl_3$)



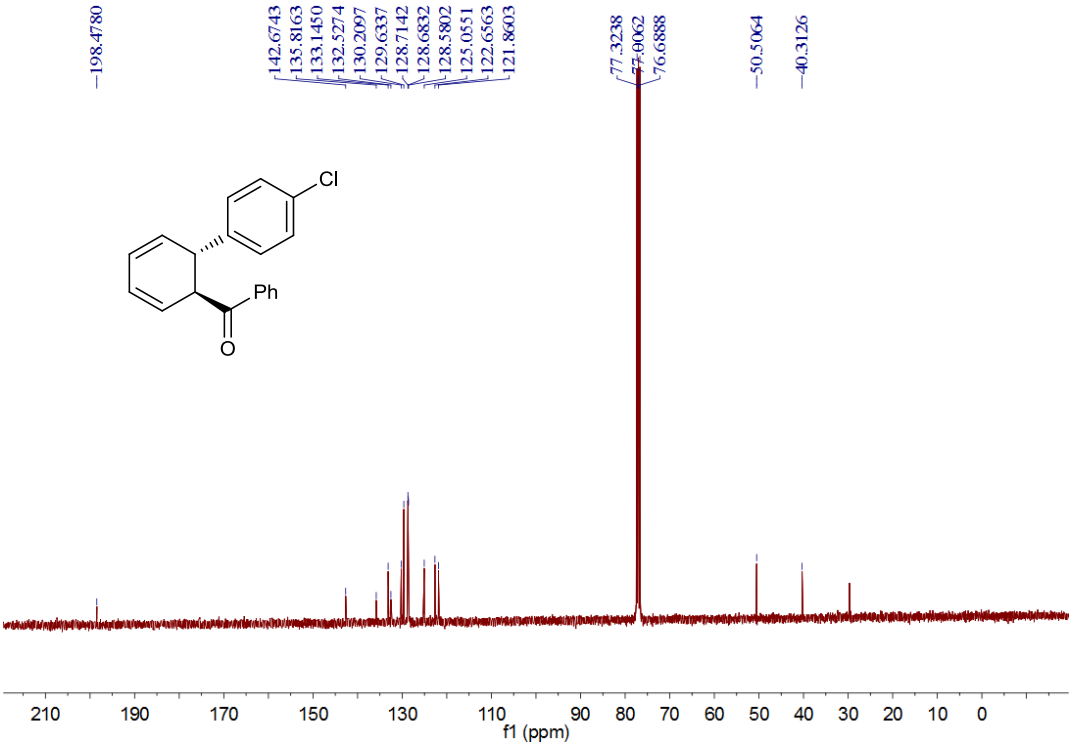
(4'-Fluoro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3c) ^{19}F NMR (376 MHz, $CDCl_3$)



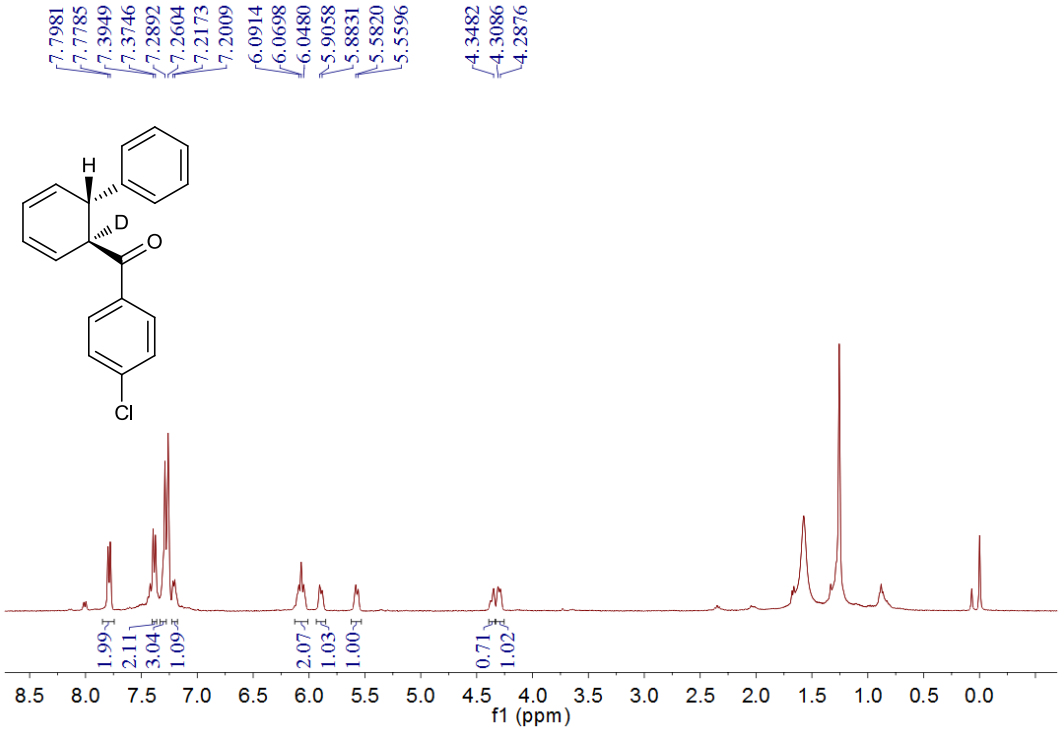
(4'-Chloro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3d) ^{1}H NMR (400 MHz, $CDCl_3$)



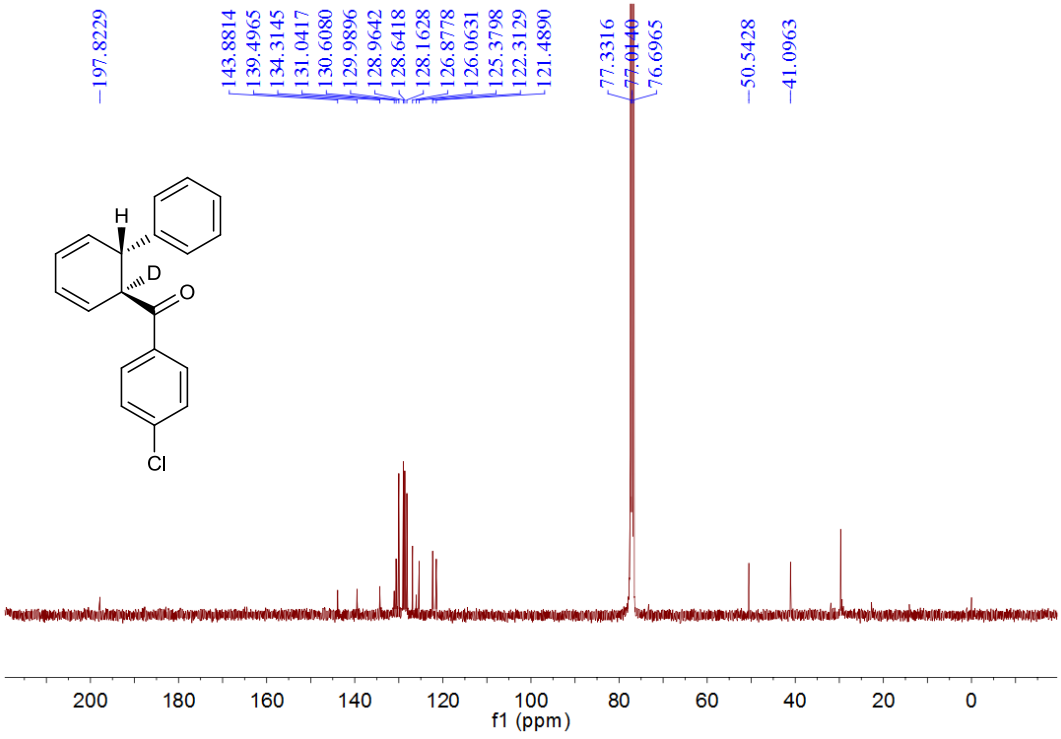
(4'-Chloro-1,2-dihydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (3d) ^{13}C NMR(100 MHz, $CDCl_3$)



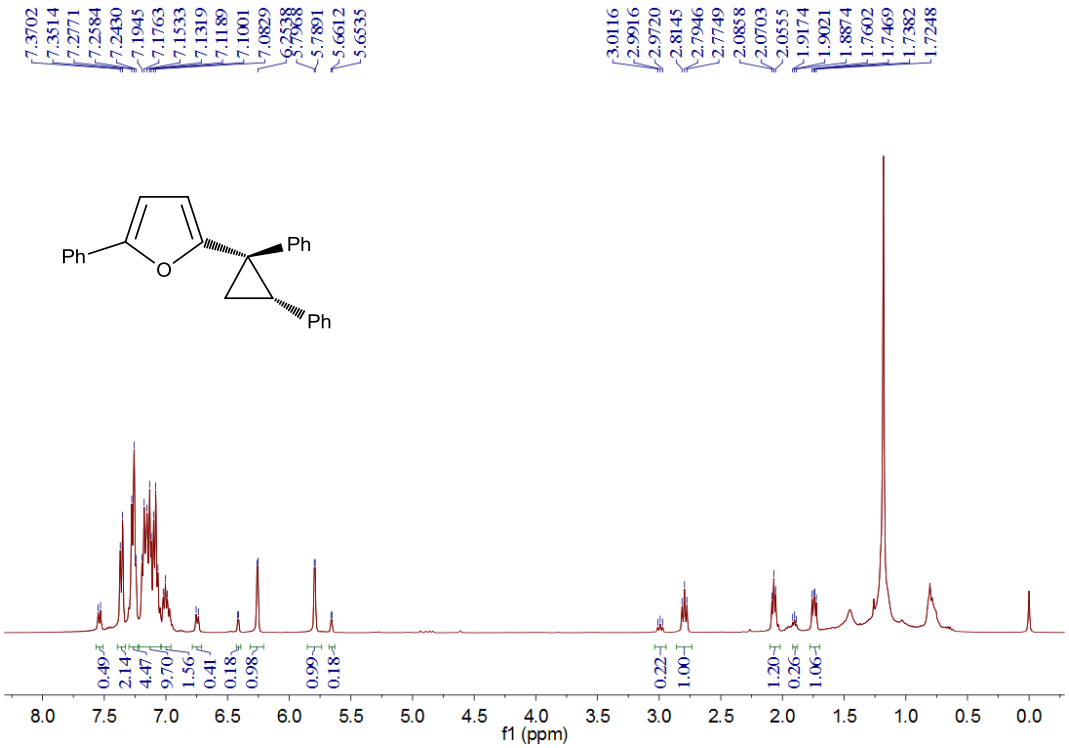
(4-Chlorophenyl)(2-deuterio-1,2-dihydro-[1,1'-biphenyl]-2-yl)methanone (3e) ^{1}H NMR (400 MHz, $CDCl_3$)



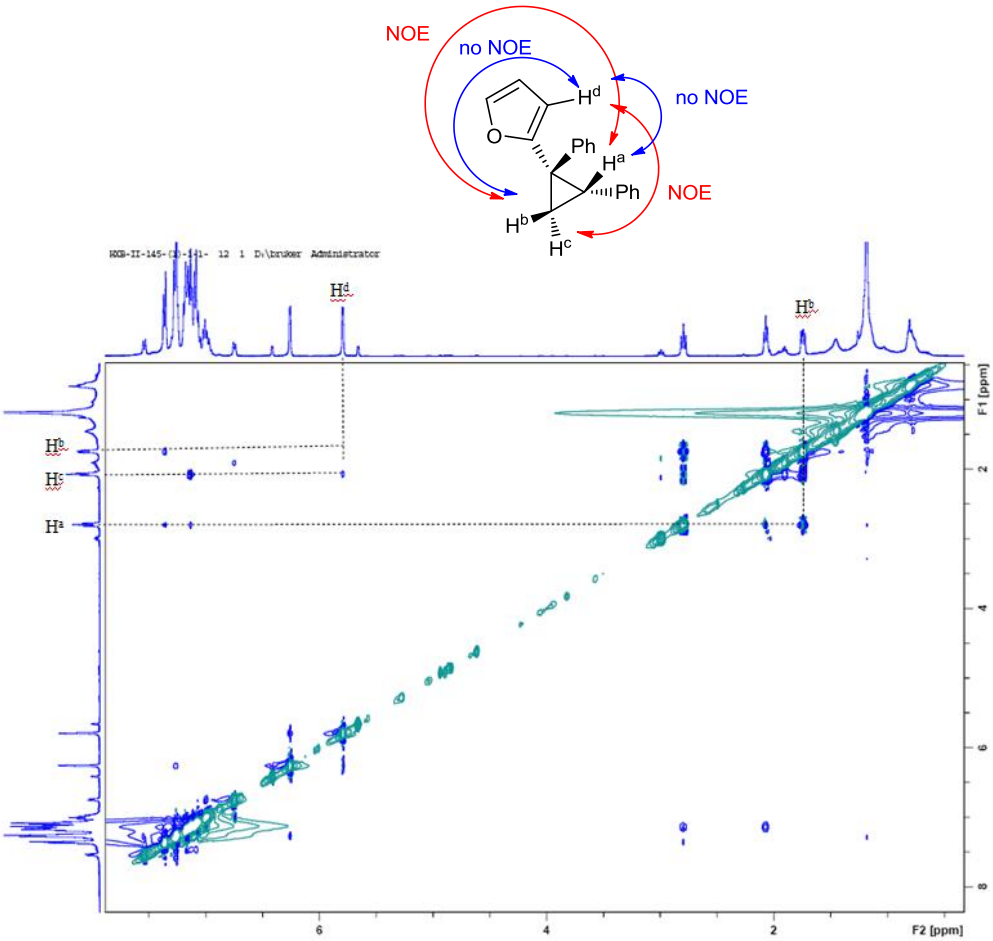
(4-Chlorophenyl)(2-deuterio-1,2-dihydro-[1,1'-biphenyl]-2-yl)methanone (3e) ^{13}C NMR (100 MHz, $CDCl_3$)



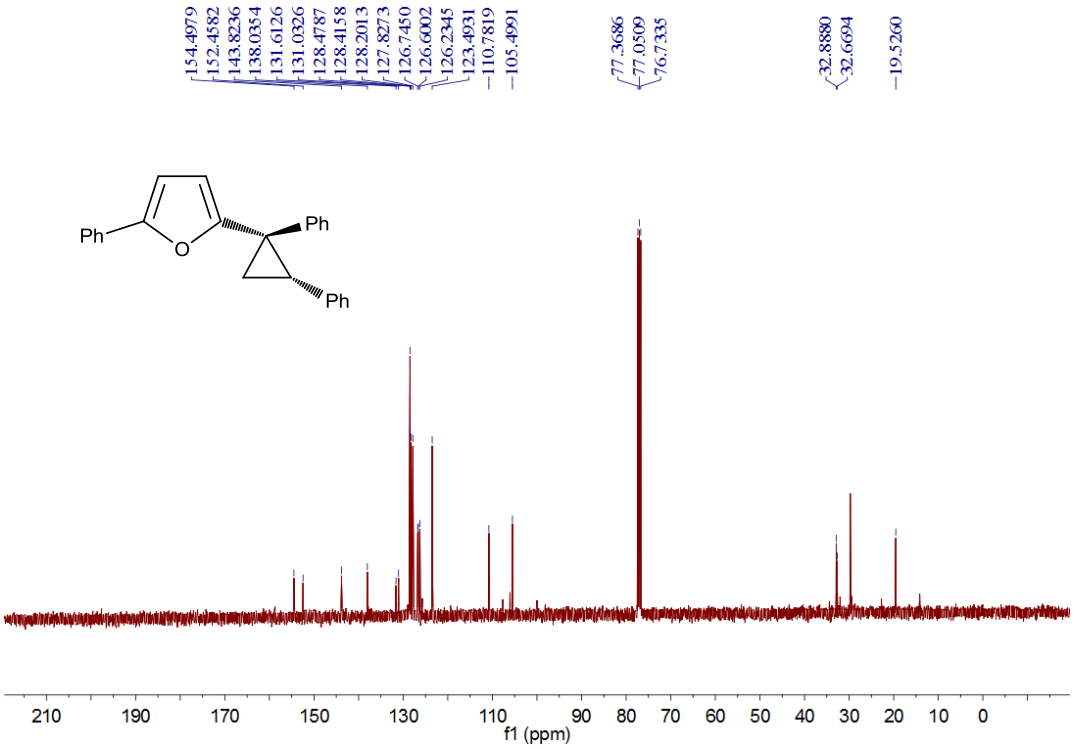
1,2-Diphenylcyclopropyl)-5-phenylfuran (7) ^{1}H NMR (400 MHz, $CDCl_3$)



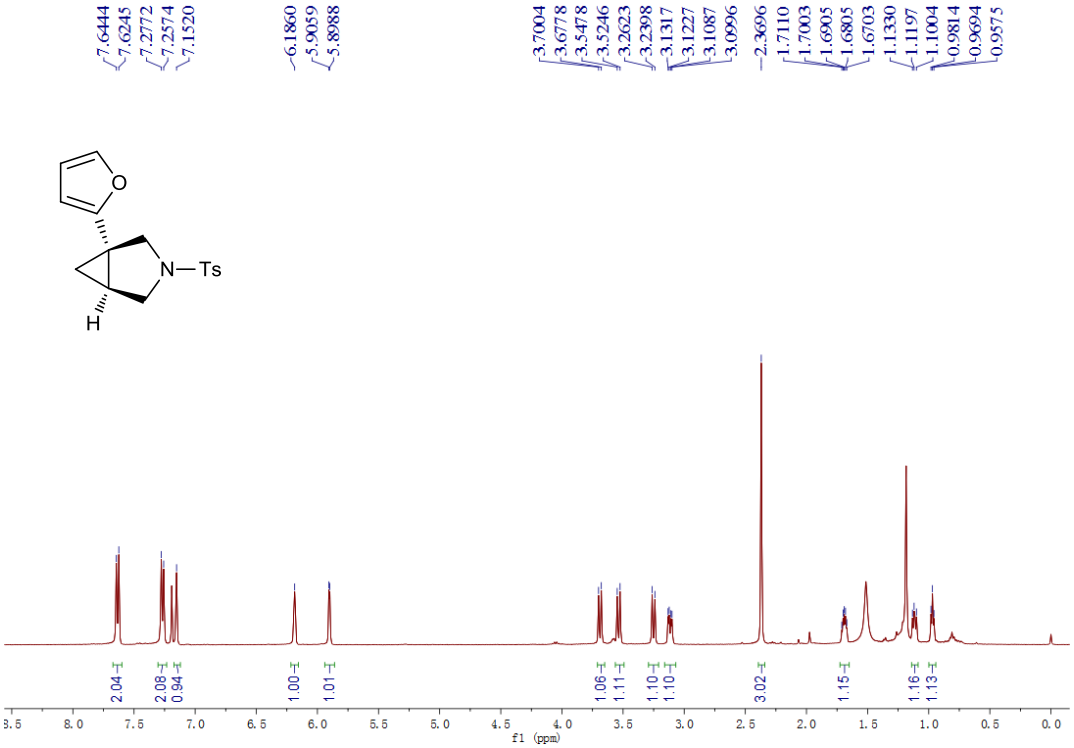
NOE spectrum of **7**



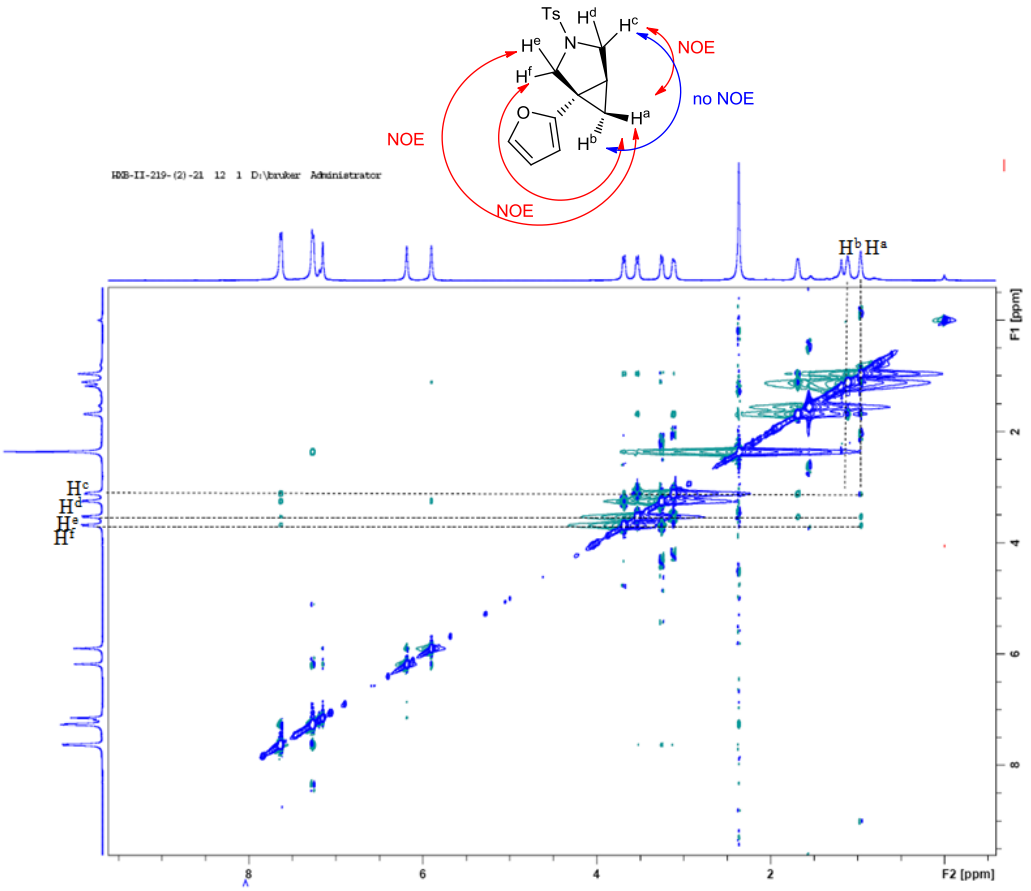
1,2-Diphenylcyclopropyl)-5-phenylfuran (7) ^{13}C NMR (100 MHz, $CDCl_3$)



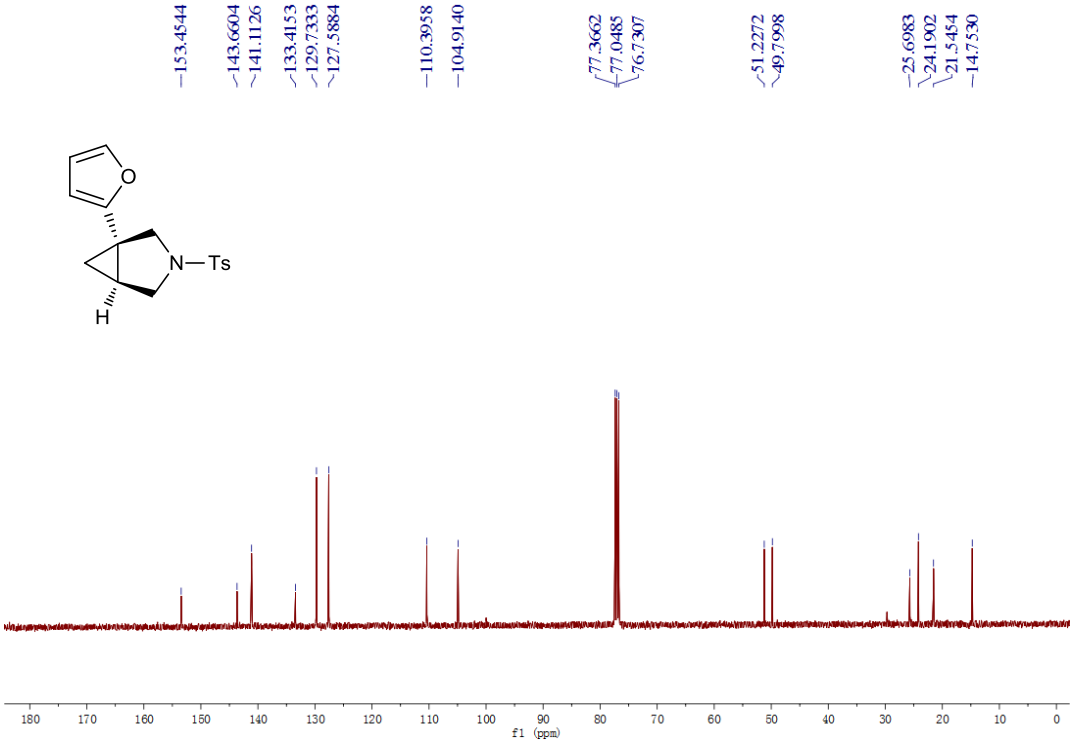
1-(Furan-2-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (9a) ^{1}H NMR (400 MHz, $CDCl_3$)



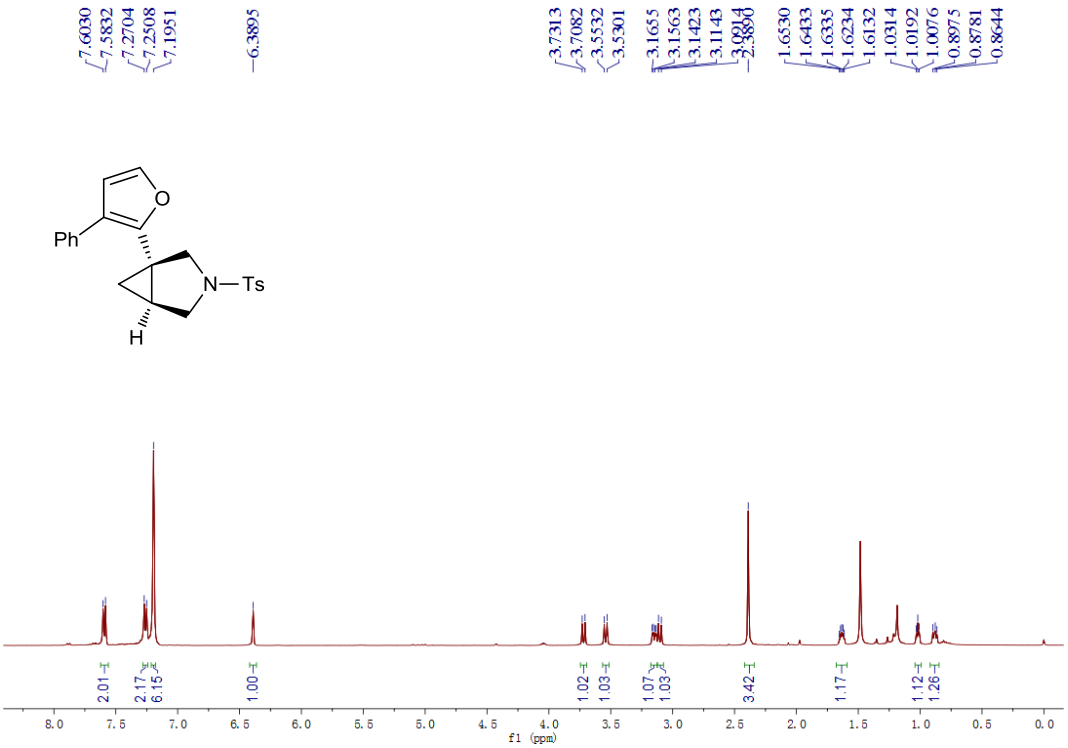
NOE spectrum of **9a**



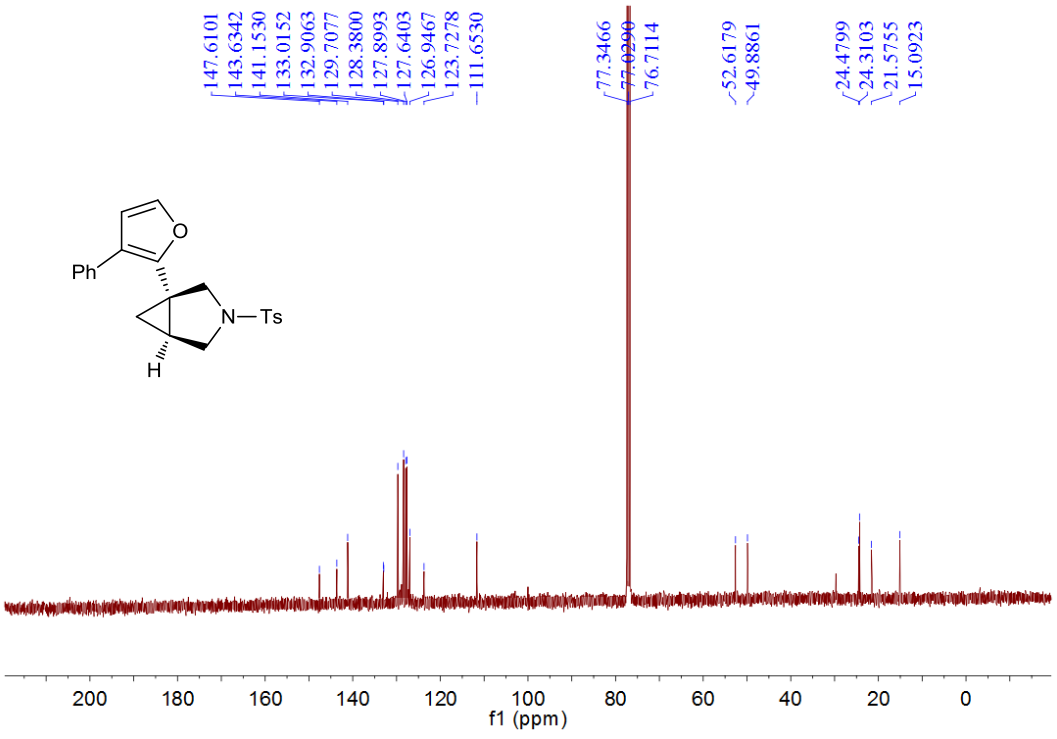
1-(Furan-2-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (9a) ^{13}C NMR (100 MHz, $CDCl_3$)



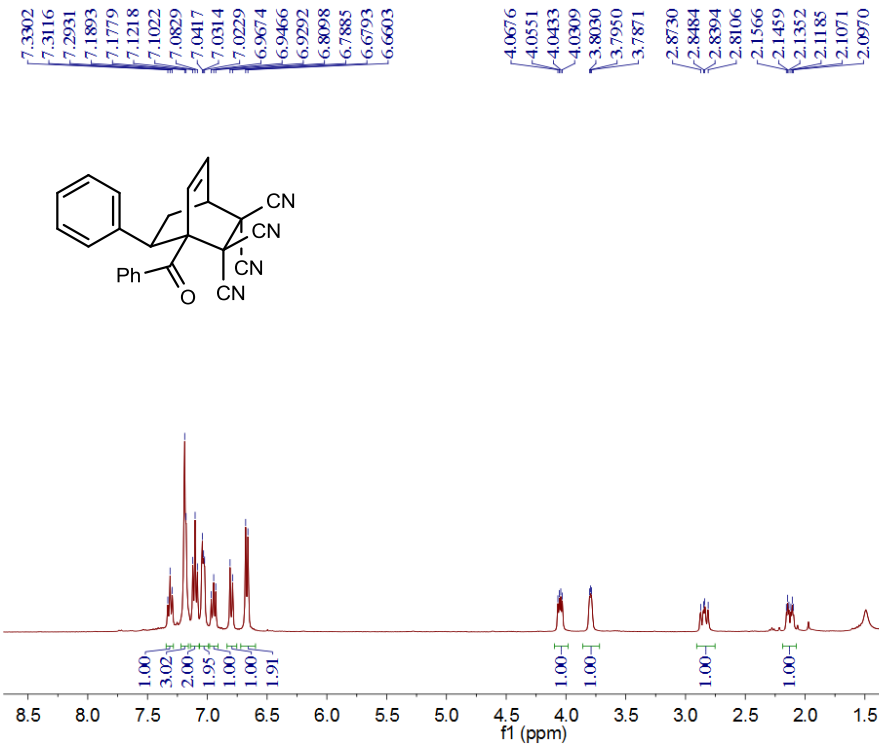
1-(3-Phenylfuran-2-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (9b) ^{1}H NMR (400 MHz, $CDCl_3$)



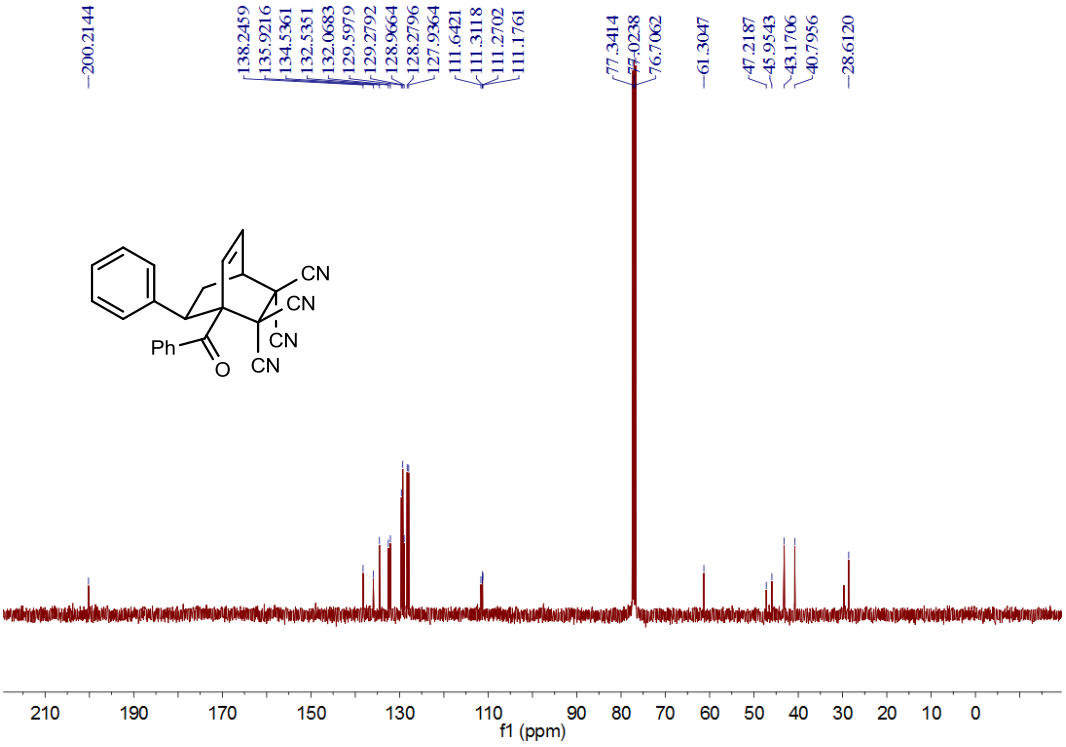
1-(3-Phenylfuran-2-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (9b) ^{13}C NMR (100 MHz, $CDCl_3$)



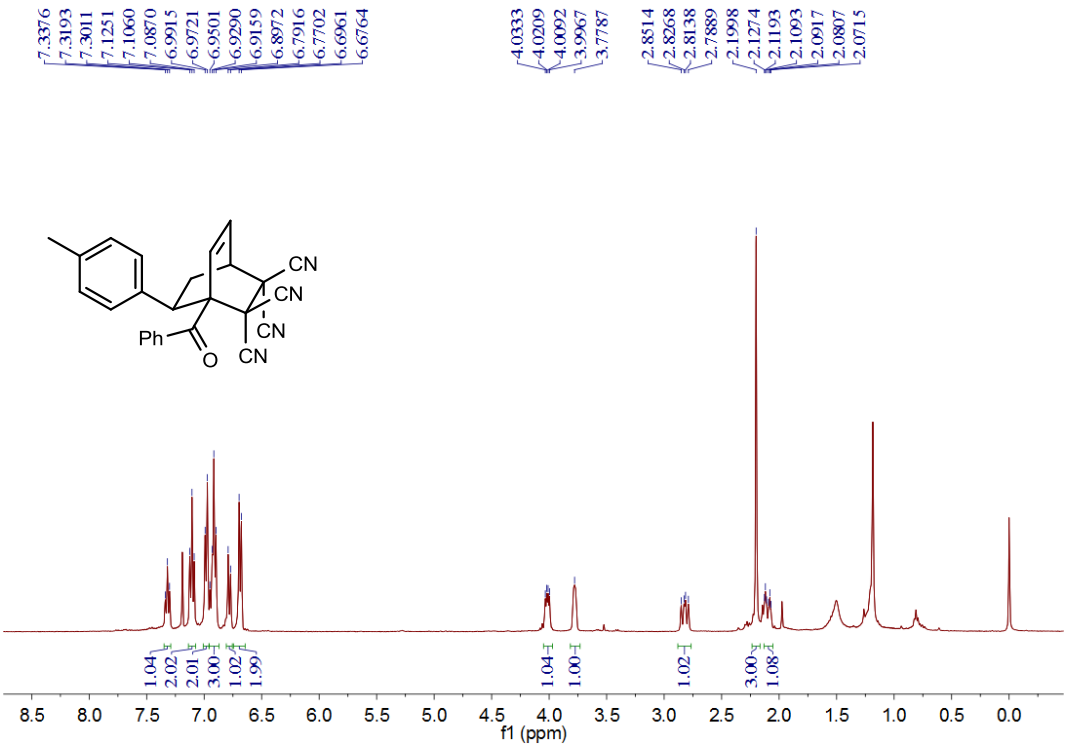
1-Benzoyl-7-phenylbicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10a)
^{1}HNMR (400 MHz, $CDCl_3$)



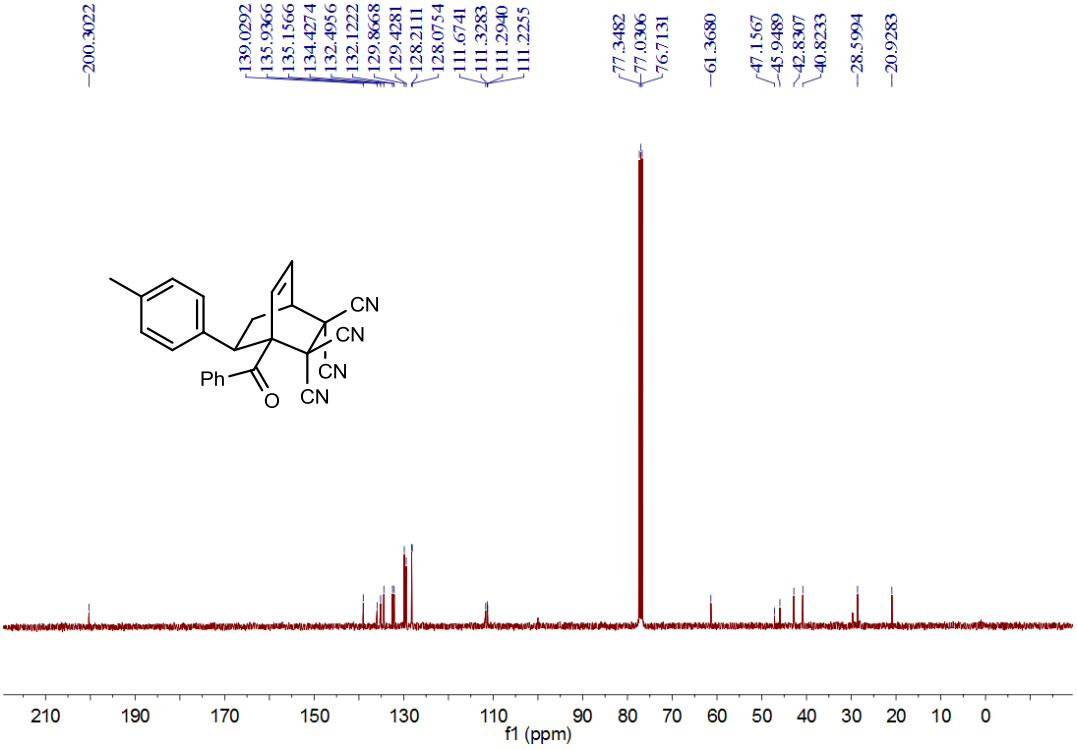
1-Benzoyl-7-phenylbicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10a) ^{13}C NMR (100 MHz, $CDCl_3$)



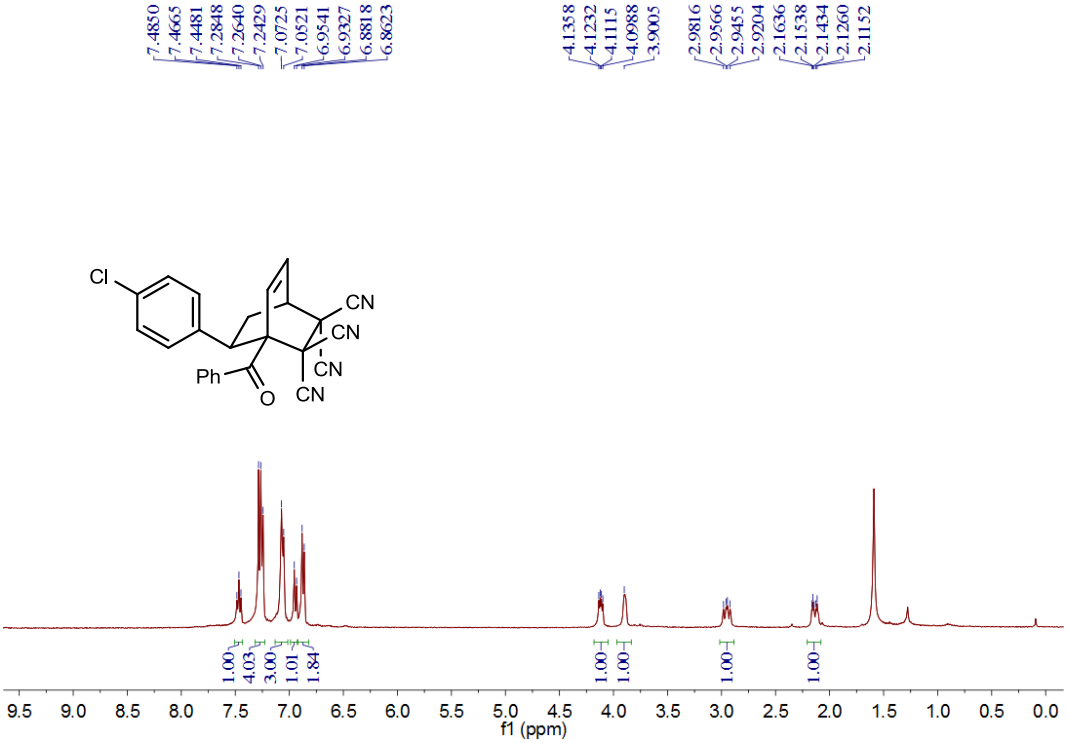
1-Benzoyl-7-(p-tolyl)bicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10b)
^{1}HNMR (400 MHz, $CDCl_3$)



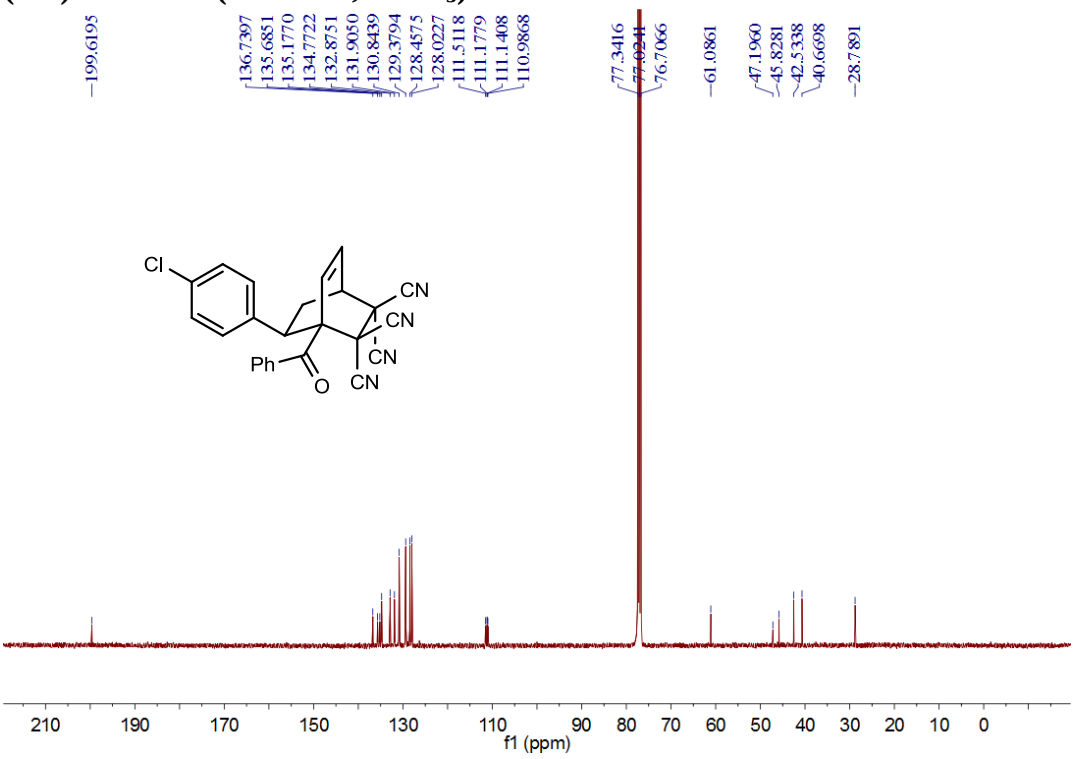
1-Benzoyl-7-(p-tolyl)bicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10b) ^{13}C NMR (100 MHz, $CDCl_3$)



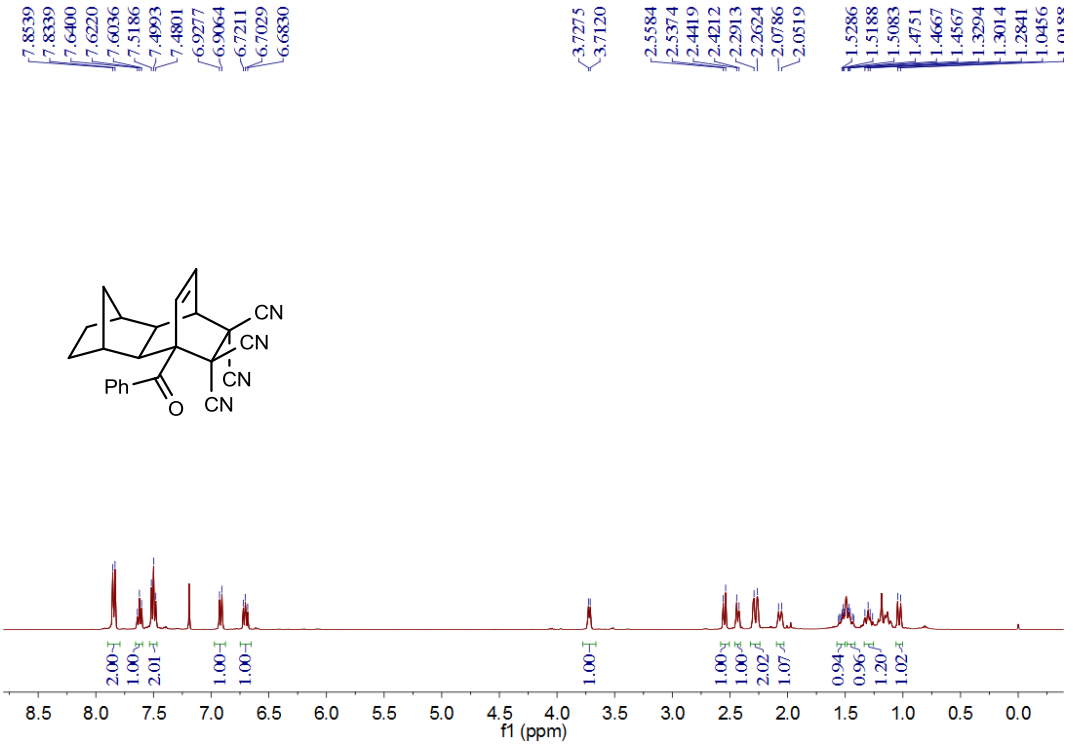
1-Benzoyl-7-(4-chlorophenyl)bicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10c) ^{1}H NMR (400 MHz, $CDCl_3$)



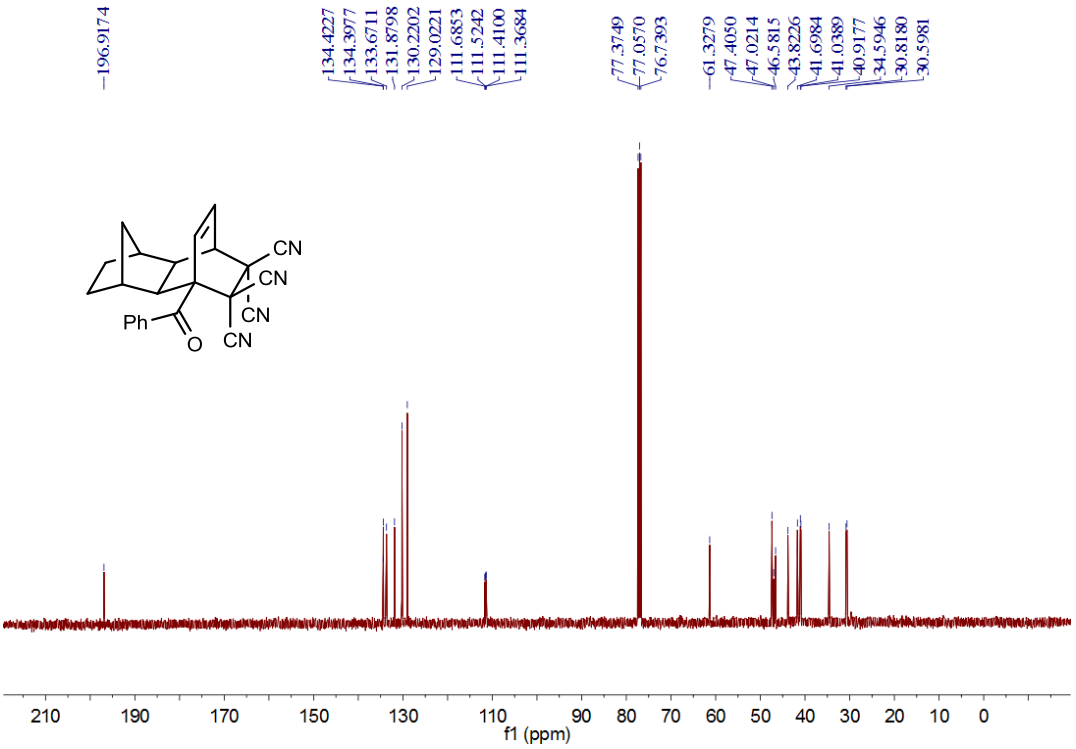
1-Benzoyl-7-(4-chlorophenyl)bicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile (10c) ^{13}C NMR (100 MHz, $CDCl_3$)



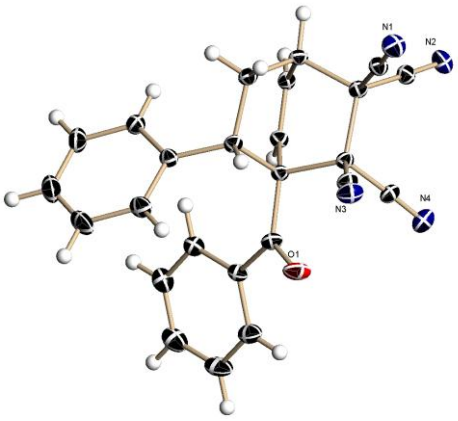
1-Benzoyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-ethano-5,8-methanonaphthalene-10,10,11,11-tetracarbonitrile (10d) ^{1}H NMR (400 MHz, $CDCl_3$)



1-Benzoyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-ethano-5,8-methanonaphthalene-10,10,11,11-tetracarbonitrile (10d) ^{13}C NMR (100 MHz, $CDCl_3$)



4.X-ray Crystallography data for compound 10a



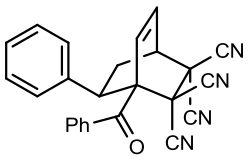


Table 1. Crystal data and structure refinement for shelxl.

Identification code	**shelxl**
Empirical formula	**C25 H16 N4 O**
Formula weight	**388.42**
Temperature	**293(2) K**
Wavelength	**0.71073 Å**
Crystal system, space group	**Triclinic, P -1**
Unit cell dimensions	**a = 7.3662(15) Å alpha = 72.49(3) deg.**
	b = 12.232(2) Å beta = 75.10(3) deg.
	c = 12.351(3) Å gamma = 88.58(3) deg.
Volume	**1024.0(4) $Å^3$**
Z, Calculated density	**2, 1.260 Mg/m^3**
Absorption coefficient	**0.080 mm^{-1}**
F(000)	**404**
Crystal size	**0.20 x 0.20 x 0.10 mm**
Theta range for data collection	**3.23 to 25.00 deg.**
Limiting indices	**-8<=h<=8, -14<=k<=14, -14<=l<=14**
Reflections collected / unique	**8015 / 3603 [R(int) = 0.0402]**
Completeness to theta = 25.00	**99.6 %**
Max. and min. transmission	**0.9921 and 0.9842**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**3603 / 7 / 271**
Goodness-of-fit on F^2	**0.994**
Final R indices [I>2sigma(I)]	**R1 = 0.0419, wR2 = 0.1120**
R indices (all data)	**R1 = 0.1181, wR2 = 0.1693**
Largest diff. peak and hole	**0.208 and -0.213 e. $Å^{-3}$**

5.References

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