Electronic Supplementary Material

Barluenga's Reagent with HBF_4 as An Efficient Catalyst for Alkyne-Carbonyl Metahesis of Unactivated Alkynes

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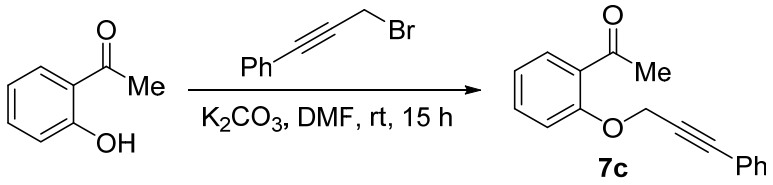
General information

Alkynes **1a-c**, 1g, aldehydes **2a-g**, bis(pyridine)iodonium(I) tetrafluoroborate (IPy_2BF_4), *N*-iodosuccinimide (NIS) and $HBF_4{\cdot}Et_2O$ are commercially available. Alkynes **1d**,[1] **1e**,[2] **1f**,[3] 1,6-ynal **4a**,[4] **4b**,[4] 1,7-ynal **4c**,[5] **6a**[5] and **6b**[5] were prepared by the method reported in the literatures. All solvents were purchased and dried over Molecular Sieves 4A prior to the use. All reactions were carried out under an argon atmosphere. For the TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Column chromatography was performed on silica gel 60N (63-200 μm, neutral, Kanto Kagaku Co., Ltd.). Medium-pressure liquid chromatography (MPLC) was carried out on YAMAZEN W-Prep 2XY. ^{1}H and ^{13}C NMR spectra were measured at 500 (or 400, 300) and 125 (or 100, 75) MHz in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). IR spectra were obtained on a JASCO FT/IR-6200. Mass spectra were recorded on a JEOL MStation MS700.

Preparation of 1,7-ynone 6c



7c

To a solution of 2-hydroxyacetophenone (2.17 mL, 18.0 mmol) and 1-bromo-3-phenylpropyne[6] (3.90 g, 20.0 mmol) in DMF (66 mL) was added K_2CO_3 (2.76 g, 20.0 mmol) at room temperature. After being stirred at the same temperature for 15 h, the reaction mixture was quenched with water and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. After concentration of the filtrate to dryness, the residue was purified by silica gel chromatography (hexane:AcOEt = 9:1) to give **6c** (1.89 g, 42%) as a pale yellow oil.

2-[(3-Phenyl-2-propyn-1-yl)oxy]-acetophenone (**6c**)
IR (neat) ν cm^{-1}; 3066, 3034, 3001, 2925, 2869, 2239, 1673, 1597, 1482, 1450, 1358, 1293, 1216, 1164, 1126, 1070, 1015, 962, 756, 691. ^{1}H NMR (500 MHz, $CDCl_3$): δ; 2.68 (s, 3H), 5.03 (s, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.29-7.36 (m, 3H), 7.43 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.47-7.51 (m, 1H), 7.76 (dd, *J* = 7.5, 1.9 Hz, 1H). ^{13}C NMR (75 MHz,

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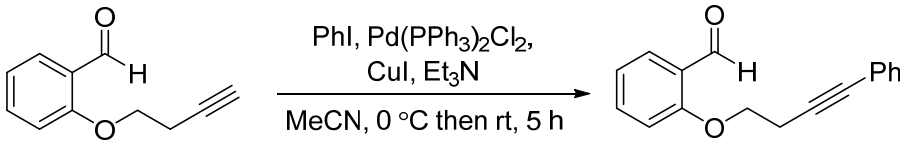
[5] J. U. Rhee, M. J. Krische, *Org. Lett.* **2005**, *7*, 2493.
[6] A. Saito, S. Oda, H. Fukaya, Y. Hanzawa, *J. Org. Chem.* **2009**, *74*, 1517.

$CDCl_3$): δ; 31.9, 57.0, 83.1, 87.7, 113.3, 121.4, 122.0, 128.4, 128.9, 128.9, 130.5, 131.8, 133.5, 157.1, 200.0. FAB-LM *m/z*: 251 $[M+H]^+$. HRMS (FAB) *m/z*: Calcd for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067; Found 251.1079.

Preparation of 1,8-ynal 6d



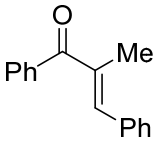
7d

To a mixture of $Pd(PPh_3)_2Cl_2$ (26.7 mg, 0.038 mmol), CuI (14.1 mg, 0.074 mmol), 2-(3-butyn-1-yloxy)benzaldehyde[7] (662 mg, 3.80 mmol) and iodobenzene (0.47 mL, 4.20 mmol) in MeCN was added Et_3N (0.79 mL, 5.70 mmol) at 0 °C. After being stirred at room temperature for 5 h, the reaction mixture was quenched with sat. NH_4Cl and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel column chromatography (hexane:AcOEt = 3:1) to give **7d** (803 mg, 84%) as a pale yellow oil.

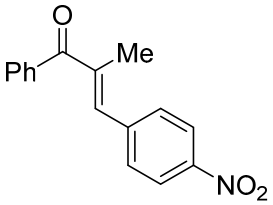
1-[2-[(4-Phenylbut-3-yn-1-yl)oxy]phenyl]ethan-1-one (6d)
IR (neat) ν cm^{-1}; 3077, 2943, 2865, 2760, 1682, 1599, 1456, 1384, 1286, 1240, 1162, 1104, 1027, 829, 756, 720, 651. ^1H NMR (300 MHz, $CDCl_3$): δ; 2.97 (t, J = 6.9 Hz, 2H), 4.30 (t, J = 6.9 Hz, 2H), 6.98-7.10 (m, 2H), 7.27-7.34 (m, 3H), 7.36-7.44 (m, 2H), 7.51-7.60 (m, 1H), 7.86 (dd, J = 7.7, 1.8 Hz, 1H), 10.58 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ; 20.3, 66.7, 82.4, 85.2, 112.8, 121.2, 123.2, 125.2, 128.1, 128.3, 128.4, 131.7, 135.9, 161.0, 189.9. FAB-LM *m/z*: 251 $[M+H]^+$. HRMS (FAB) *m/z*: Calcd for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067; Found: 251.1092.

General procedure for the catalytic alkyne-carbonyl metathesis of 1 and 2 (Table 2)

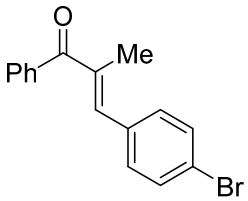
In a light-shielded test tube, to a solution of IPy_2BF_4 (59.5 mg, 0.16 mmol) pretreated with $HBF_4 \cdot Et_2O$ (43.5 μL, 0.32 mmol) in CH_2Cl_2 (4 mL) at 0 °C for 10 min was added aldehyde **2** (1.6 mmol) and alkyne **1** (0.80 mmol). After being stirring at room temperature (90 ºC in case of **2d**) until consumption of **1** (by TLC analysis), the reaction mixture was quenched with sat. $NaHCO_3$ (2 mL) and sat. $Na_2S_2O_3$ (2 mL), and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated to dryness. The residue was purified by MPLC (hexane:AcOEt = 98:2) to give **3**.



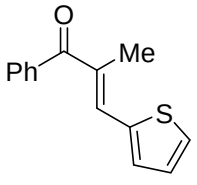
(*E*)-2-Methyl-1,3-diphenyl-2-propen-1-one (**3aa**): 124 mg (70%). Colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ; 2.28 (d, *J* = 1.7 Hz, 3 H), 7.19 (br.s, 1H), 7.32-7.37 (m, 1H), 7.39-7.43 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.52-7.57 (m, 1H), 7.75 (dd, *J* = 8.3, 1.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ; 14.4, 128.2, 128.4, 128.6, 129.5, 129.7, 131.6, 135.8, 136.8, 138.5, 142.2, 199.4. NMR data correspond to the reported values.[8]



(*E*)-2-Methyl-3-(4-nitrophenyl)-1-phenyl-2-propen-1-one (**3ab**): 136 mg (64%). Pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ; 2.27 (d, *J* = 1.7 Hz, 3H), 7.15 (br.s, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.76-7.80 (m, 2H), 8.27 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.8, 123.6, 128.4, 129.5, 130.1, 132.3, 137.5, 138.0, 140.1, 142.2, 147.2, 198.5. NMR data correspond to the reported values.[5]



(*E*)-3-(4-Bromophenyl)-2-methyl-1-phenyl-2-propen-1-one (**3ac**): 160 mg (66%). Pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ; 2.21 (d, *J* = 1.5 Hz, 3H), 7.05 (br.s, 1H), 7.23-7.26 (m, 2H), 7.40-7.55 (m, 5H), 7.69-7.73 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.5, 122.7, 128.2, 129.4, 131.1, 131.7, 131.8, 134.6, 137.5, 138.2, 140.5, 199.1. NMR data correspond to the reported values.[9]



(*E*)-2-Methyl-1-phenyl-3-(thienyl)-2-propen-1-one (**3ad**): 33 mg (18%). Pale yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ; 2.34 (d, *J* = 1.1 Hz, 3H), 7.13 (dd, *J* = 5.2, 4.0 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.40 (br.s, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.52-7.57 (m, 2H), 7.69 (dd, *J* = 8.3, 1.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.6, 127.5, 128.2, 129.3, 129.9, 131.4, 132.0, 133.4, 135.6, 138.7, 139.2, 198.8. NMR data correspond to the reported values.[10]

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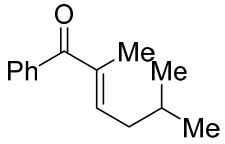
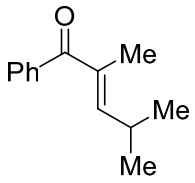
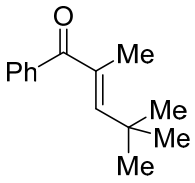
[8] A. Saito, M. Umakoshi, N. Yagyu, Y. Hanzawa, *Org. Lett.* **2008**, *10*, 1783.
[9] T. Xu, Q. Yang, D. Li, J. Dong, Z. Yu, Y. Li, *Chem. Eur. J.* **2010**, *16*. 9264.
[10] J. Hu, S. Chen, Y. Sun, J. Yang, Y. Rao, *Org. Lett*. **2012**, *14*, 5030.



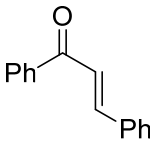
(*E*)-2,5-Dimethyl-1-phenyl-2-hexen-2-one (**3ae**): 118 mg (73%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.93 (d, *J* = 6.6 Hz, 6H), 1.74 (heptet, *J* = 6.6 Hz, 1H), 1.97 (br.d, *J* = 1.3Hz, 3H), 2.14-2.21 (m, 2H), 6.32 (tq, *J* = 7.3, 1.3 Hz, 1H), 7.38-7.45 (m, 2H), 7.46-7.54 (m, 1H), 7.60-7.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 12.6, 22.5, 28.4, 38.2, 128.0, 129.2, 131.3, 137.0, 138.8, 145.8, 199.1. NMR data correspond to the reported values.[5]



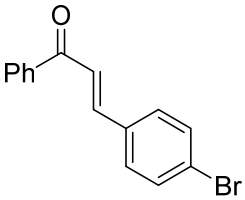
(*E*)-2,4-Dimethyl-1-phenyl-2-penten-1-one (**3af**): 108 mg (72%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.03 (d, *J* = 6.6 Hz, 6H), 1.98 (d, *J* = 1.3 Hz, 3H), 2.69-2.86 (m, 1H), 6.11 (dq, *J* = 9.5, 1.3 Hz, 1H), 7.37-7.45 (m, 2H), 7.47-7.54 (m, 1H), 7.60-7.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 12.3, 21.9, 28.4, 128.0, 129.4, 131.3, 134.0, 138.7, 153.2, 199.3. NMR data correspond to the reported values.[5]



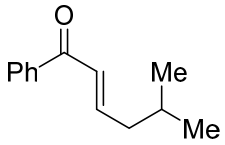
(*E*)-2,4,4-Trimethyl-1-phenyl-2-penten-1-one (**3ag**): 94 mg (58%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.19 (s, 9H), 2.08 (d, *J* = 1.4 Hz, 3H), 6.26 (q, *J* = 1.4 Hz, 1H), 7.38-7.44 (m, 2H), 7.46-7.53 (m, 1H), 7.61-7.66 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.4, 30.1, 33.7, 128.0, 129.5, 131.4, 134.9, 138.7, 155.0, 200.4. NMR data correspond to the reported values. [11]



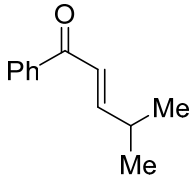
(*E*)-1,3-Diphenyl-2-propen-1-one (**3ba**): 105 mg (63%). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ; 7.40-7.45 (m, 3H), 7.48-7.55 (m, 2H), 7.53 (d, *J* = 17.4 Hz, 1H), 7.59 (tt, *J* = 7.3, 1.7 Hz, 1H), 7.63-7.69 (m, 2H), 7.82 (d, *J* = 17.4 Hz, 1H), 8.01-8.06 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ; 122.1, 128.4, 128.5, 128.6, 128.9, 130.5, 132.8, 134.9, 138.2, 144.8, 190.6. NMR data correspond to the reported values.[12]



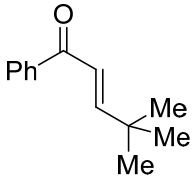
(*E*)-3-(4-Bromophenyl)-1-phenyl-2-propen-1-one (**3bc**): 126 mg (55%). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ; 7.49-7.63 (m, 8H), 7.75 (d, *J* = 15.5 Hz), 8.01-8.03 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 122.5, 124.8, 128.5, 128.7, 129.8, 132.2, 132.9, 133.8, 138.0, 143.4, 190.2. NMR data correspond to the reported values.[13]



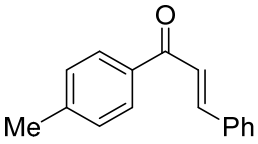
(*E*)-5-Methyl-1-phenyl-2-hexen-2-one (**3be**): 96 mg (63%). Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ; 0.97 (d, *J* = 7.5 Hz, 6H), 1.83 (nonet, *J* = 7.5 Hz, 1H), 2.19-2.24 (m, 2H), 6.87 (d, *J* = 15.4 Hz, 1H), 7.05 (dt, *J* = 15.4, 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.56 (tt, *J* = 7.7, 1.6 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 22.4, 27.9, 42.1, 126.9, 128.4, 128.5, 132.5, 138.0, 148.9, 190.8. NMR data correspond to the reported values.[12]



(*E*)-4-Methyl-1-phenyl-2-penten-1-one (**3bf**): 89 mg (64%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.14 (d, *J* = 6.8 Hz, 6H), 2.58 (octet·d, *J* = 6.8, 1.4 Hz, 1H), 6.82 (dd, *J* = 15.6, 1.4 Hz, 1H), 7.03 (dd, *J* = 15.6, 6.8 Hz, 1H), 7.45-7.49 (m, 2H), 7.56 (tt, *J* = 7.3, 1.7 Hz, 1H), 7.91-7.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 21.3, 31.4, 123.0, 128.4, 128.4, 132.5, 138.0, 156.0, 191.2. NMR data correspond to the reported values.[13]



(*E*)-4,4-Dimethyl-1-phenyl-2-penten-1-one (**3bg**): 78 mg (52%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.15 (s, 3H), 6.79 (d, *J* = 15.7 Hz, 1H), 7.07 (d, *J* = 15.7 Hz, 1H), 7.43-7.58 (m, 3H), 7.91-7.95(m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ; 28.7, 34.2, 121.0, 128.5, 128.5, 132.5, 138.2, 159.6, 191.6. NMR data correspond to the reported values.[14]



(*E*)-1-(4-Methylphenyl)-3-phenyl-2-propen-1-one (**3ca**): 97 mg (55%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ; 2.44 (s, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.40-7.44 (m, 3H), 7.56 (d, *J* = 15.6 Hz, 1H), 7.63-7.67 (m, 2H), 7.87 (d, *J* = 15.6 Hz, 1H), 7.96 (d, *J* = 8.1, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ; 21.6, 122.1, 128.4, 128.6, 128.9, 130.0, 130.4, 135.0, 135.6, 143.6, 144.4, 190.0. NMR data correspond to the reported values.[15]

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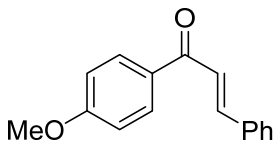
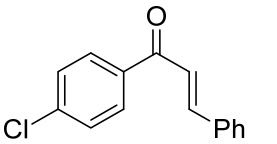
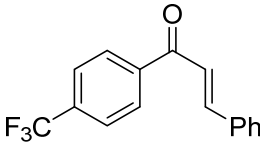


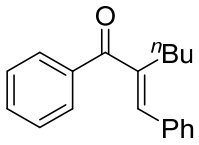
(*E*)-1-(4-Methoxyphenyl)-3-phenyl-2-propen-1-one (**3da**): 84 mg (44%). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ; 3.90 (s, 3H), 6.99 (d, *J* = 8.9, 2H), 7.40-7.44 (m, 3H), 7.56 (d, *J* = 15.5 Hz, 1H), 7.64-7.66 (m, 2H), 7.81 (d, *J* = 15.5 Hz, 1H), 8.05 (d, *J* = 8.9, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ; 55.5, 113.8, 121.9, 128.3, 128.9, 130.3, 130.8, 131.1, 135.1, 144.0, 163.4, 188.7. NMR data correspond to the reported values.[16]



(*E*)-1-(4-Chlorophenyl)-3-phenyl-2-propen-1-one (**3ea**): 123 mg (63%). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ; 7.40-7.46 (m, 3H), 7.46-7.52 (m, 3H), 7.62-7.68 (m, 2H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ; 121.5, 128.5, 128.9, 129.0, 129.9, 130.7, 134.7, 136.5, 139.2, 145.3, 189.2. NMR data correspond to the reported values.[17]



(*E*)-1-[4-(Trifluoromethyl)phenyl]-3-phenyl-2-propen-1-one (**3fa**): 172 mg (78%). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ; 7.42-7.47 (m, 3H), 7.49 (d, *J* = 15.8 Hz, 1H), 7.63-7.69 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 15.8 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ; 122.5, 123.6 (q, *J* = 272.8 Hz), 125.0 (q, *J* = 3.7 Hz), 128.6, 128.7, 129.0, 130.9, 133.9 (q, *J* = 32.6 Hz), 134.5, 141.0, 146.0, 189.6. NMR data correspond to the reported values.[18]

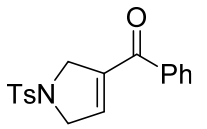


(*E*)-2-Benzylidene-1-phenylhexan-1-one (**3ga**): 85 mg (40%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ; 0.92 (t, J = 7.3 Hz, 3H), 1.36-1.48 (m, 2H), 1.52-1.58 (m, 2H), 2.75 (t,J = 7.8 Hz, 2H),7.05 (s, 1H), 7.30-7.48 (m, 7H), 7.53-7.57 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ; 13.9, 23.0, 27.5, 30.9, 128.2, 128.4, 128.5, 129.1, 129.6, 131.9, 135.7, 138.7, 140.6, 142.4, 199.4. NMR data correspond to the reported values.[19]

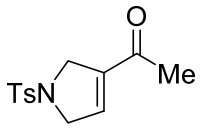
General procedure for the catalytic alkyne-carbonyl metathesis of yanls 4 or 6 (Scheme 2)

(a) **IPy_2BF_4/2 BF_4 catalytic systems**: in a light-shielded test tube, to a solution of IPy_2BF_4 (**6a**,**c**: 14.9 mg, 0.04 mmol; **6b**: 22.4 mg, 0.06 mmol; other substrates: 29.8 mg, 0.08 mmol) pretreated with $HBF_4{\cdot}Et_2O$ (**6a**,**c**: 10.9μL, 0.08 mmol; other substrates: 21.6 μL, 0.16 mmol) in CH_2Cl_2 (**6a**,**c**: 3 mL; other substrates: 1.5 mL) at 0 °C for 10 min was added a solution of **4** or **6** (**6a**,**c**: 0.8 mmol, other substrates: 0.4 mmol) in CH_2Cl_2 (**6a**,**c**: 1 mL; other substrates: 0.5 mL). After being stirring at room temperature until consumption of the starting material (by TLC analysis), the reaction mixture was quenched with sat. $NaHCO_3$ (**6a**,**c**: 2 mL; other substrates: 1 mL) and sat. $Na_2S_2O_3$ (**6a**,**c**: 2 mL; other substrates: 1 mL), and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated to dryness. The residue was purified by MPLC (hexane:AcOEt = 4:1 to 2:1) to give **5** or **7**.

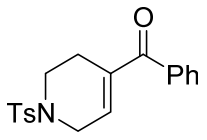
(b) **NIS/BF_4 catalytic systems**: in a light-shielded test tube, to a solution of NIS (18.0 mg, 0.08 mmol) pretreated with $HBF_4{\cdot}Et_2O$ (10.9μL, 0.08 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C for 10 min was added yanl a solution of **4a** (131 mg, 0.4 mmol) or **4b** (161 mg, 0.4 mmol) in CH_2Cl_2 (0.5 mL). After being stirring at room temperature for 20 h, the reaction mixture was quenched with sat. $NaHCO_3$ (1 mL) and sat. $Na_2S_2O_3$ (1 mL), and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated to dryness. The residue was purified by MPLC (hexane:AcOEt = 4:1 to 2:1) to give **5a** (107 mg, 82%) or **5b** (42 mg, 40%).



(2,5-Dihydro-1-tosyl-1*H*-pyrrol-3-yl)(phenyl)methanone (**5a**): 94 mg (72%). White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.44 (s, 3H), 4.39-4.48 (m, 4H), 6.35 (t, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.5, 54.3, 56.0, 127.5, 128.5, 128.7, 129.9, 132.8, 133.6, 137.2, 137.3, 138.9, 143.9, 190.6. NMR data correspond to the reported values.[5]



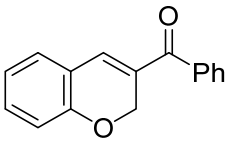
1-(2,5-Dihydro-1-tosyl-1*H*-pyrrol-3-yl)ethanone (**5b**): 33 mg (31%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ; 2.27 (s, 3H), 2.43 (s, 3H), 4.26 (td, *J* = 4.6, 2.1 Hz, 2H), 4.36 (td, *J* = 4.6, 2.1 H, 2H), 6.49 (quintet, *J* = 2.1 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 21.5, 26.3, 53.2, 55.7, 127.4, 129.9, 133.5, 135.6, 140.3, 143.8, 193.7. NMR data correspond to the reported values.[5]



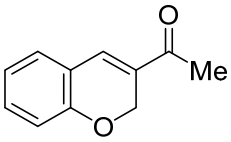
(1,2,3,6-Tetrahydro-1-tosylpyridin-4-yl)(phenyl)methanone (**5c**): 61 mg (45%). White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.44 (s, 3H), 2.60-2.69 (m, 2H), 3.29 (t, *J* = 5.8 Hz, 2H), 3.83 (dd, *J* = 5.8, 2.7 Hz, 2H), 6.39 (br.s, *1*H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.58-7.61 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.5, 24.3, 42.6, 44.8, 127.7, 128.3, 129.1, 129.8, 132.1, 133.0, 136.2, 136.5, 137.4, 143.9, 195.8. NMR data

[16] M. Markovič, P. Lopatka, P. Koóš, T. Gracza, *Org. Lett.* **2015**, *17*, 5618.
[17] J. R. Schmink, J. L. Holcomb, N. E. Leadbeater, *Org. Lett.* **2009**, *11*, 365.
[18] X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 14596.
[19] J. Y. Park, P. R. Ullapu, H. Choo, J. K. Lee, S.-J. Min, A. N. Pae, Y. Kim, D.-J. Baek, Y. S. Cho, *Eur. J. Org. Chem.* **2008**, 5461.

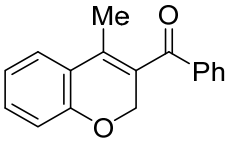
correspond to the reported values.[5]



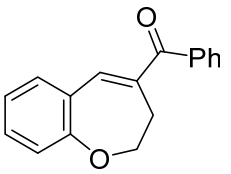
(2*H*-Chromen-3-yl)(phenyl)methanone (**7a**): 151 mg (80%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 5.18 (d, *J* = 1.1 Hz, 2H), 6.88-6.98 (m, 2H), 7.07-7.15 (m, 1H), 7.13 (br.s, 1H), 7.29 (td, *J* = 7.5, 2.0 Hz, 1H), 7.47-7.52 (m, 2H), 7.59 (tt, *J* = 7.3, 1.7 Hz, 1H), 7.71-7.75 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 65.2, 116.4, 121.0, 121.8, 128.4, 129.0, 129.3, 129.8, 132.0, 132.5, 137.1, 137.5, 155.5, 194.1. NMR data correspond to the reported values.[5]



1-(2*H*-Chromen-3-yl)ethanone (**7b**): 35 mg (50%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.40 (s, 3H), 5.00 (d, *J* = 1.1 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.94 (td, *J* = 7.4, 1.1 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.26 (td, *J* = 7.7, 1.6 Hz, 1H), 7.30 (br.s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 25.0, 64.2, 116.3, 120.7, 121.8, 129.1, 130.7, 132.4, 133.9, 155.5, 195.9. NMR data correspond to the reported values.[5]



(4-Methyl-2*H*-chromen-3-yl)(phenyl)methanone (**7c**): 120 mg (60%). Pale yellow oil. IR (neat) ν cm^{-1}; 3061, 3035, 3000, 2952, 2919, 2842, 1655, 1578, 1485, 1448, 1381, 1333, 1287, 1247, 1176, 1159, 1125, 1066, 1040, 1023, 1001, 930, 903. ^{1}H NMR (500 MHz, $CDCl_3$) δ; 2.02 (t, *J* = 1.4 Hz, 3H), 4.86 (q, *J* = 1.4 Hz, 2H), 6.95 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.02 (td, *J* = 7.7, 1.0 Hz, 1H), 7.27 (td, *J* = 7.7, 1.5 Hz, 2H), 7.37 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.58-7.62 (m, 1H), 7.93 (dd, *J* = 8.3, 1.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 15.8, 66.2, 116.3, 121.8, 124.2, 125.2, 127.7, 128.8, 129.2, 130.6, 133.3, 134.8, 137.6, 154.7, 196.5. FAB-LM *m/z*: 251 $[M+H]^+$. HRMS (FAB) *m/z*: Calcd for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067; Found: 251.1089.



(2,3-Dihydrobenzo[b]oxepin-4-yl)(phenyl)methanone (**7d**): 54 mg (54%). Pale yellow solid. IR (KBr) ν cm^{-1}; 3054, 3017, 2976, 2930, 2904, 2881, 1621, 1598, 1567, 1488, 1442, 1307, 1272, 1259, 1213, 1129, 1080, 765, 743, 712. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 3.14 (td, *J* = 4.4, 1.1 Hz, 2H), 4.36 (t, *J* = 4.4 Hz, 2H), 6.94-7.05 (m, 2H), 7.11 (br.s, 1H), 7.15 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.23-7.31 (m, 1H), 7.43-7.50 (m, 2H), 7.56 (tt, *J* = 7.3, 1.8 Hz, 1H), 7.70-7.74 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 33.0, 68.9, 120.4, 122.2, 123.3, 128.3, 129.4, 131.1, 131.7, 135.3, 138.5, 139.3, 142.1, 160.4, 198.1. FAB-LM *m/z*: 251 $[M+H]^+$. HRMS (FAB) *m/z*: Calcd for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067; Found: 251.1072.

^{13}C NMR experiments using alkyne 1a and aldehyde 2a (Table 3, Fig. S-1 and S-2)

To gain a qualitative understanding of the activation of alkynes and/or aldehydes by the present catalytic systems, we carried out NMR studies using 1:1 mixture of alkyne **1a** and benzaldehyde (**2a**) with various additives in CD_2Cl_2 at -78 ºC (Fig. S-1 and S-2). The ^{13}C NMR spectrum (125 MHz) in the presence of $PyHBF_4$ (1 equiv) showed slight upfield shifts of the sp-carbons (C^{α}: 78.06 ppm and C^{β}: 85.19 ppm) of **1a** and the carbonyl-carbon (C^{γ}: 192.07 ppm) of **2a** (Fig. S-2a) compared with that in the absence of any additives (Fig. S-1). On the other hand, the addition of $BF_3{\cdot}Et_2O$, HBF_4, NIS/HBF_4, or IPy_2BF_4/2 HBF_4 (0.5 equiv each) instead of $PyHBF_4$ led to the significant downfield shift of C^{γ} (Fig. S-2b,c,d,e), and the case of IPy_2BF_4/2 HBF_4 was particularly notable (C^{γ}: 193.99 ppm). These results suggest that an iodonium species such as IBF_4 and/or IF generated from IPy_2BF_4 and HBF_4 serve as a σ-acid for the activation of the aldehyde. Barluenga *et al*. proposed the involvement of the similar iodonium species in the oxidative arylation of aldehydes.[16] Furthermore, the present iodonium species was found out to have the stronger σ-acidity than HBF_4 and an iodine species **B** derived from NIS and HBF_4. Since the iodine species such as **B** was observed in a ^{13}C NMR spectrum of a mixture of NIS and an acid by Olah et al., **B** was considered to be involved in the present reaction.

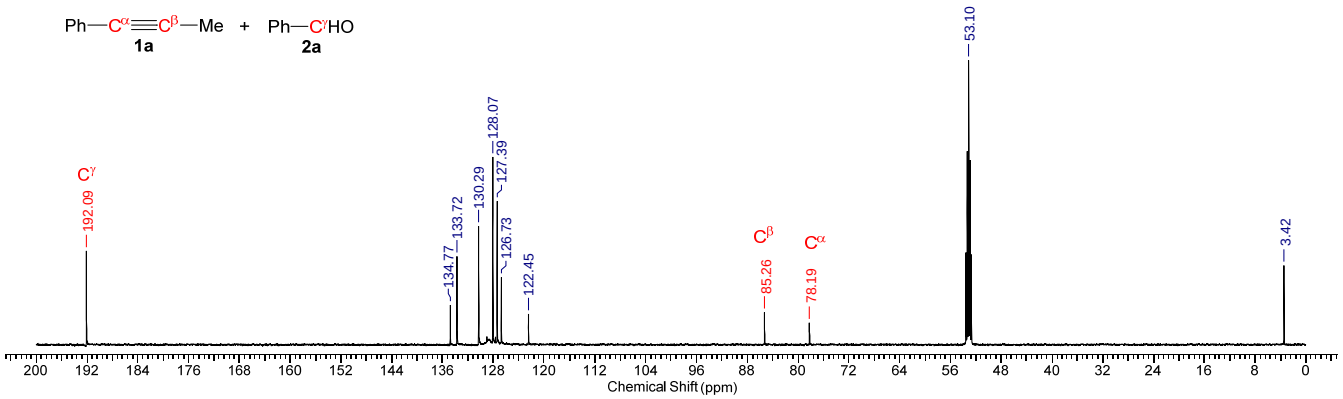
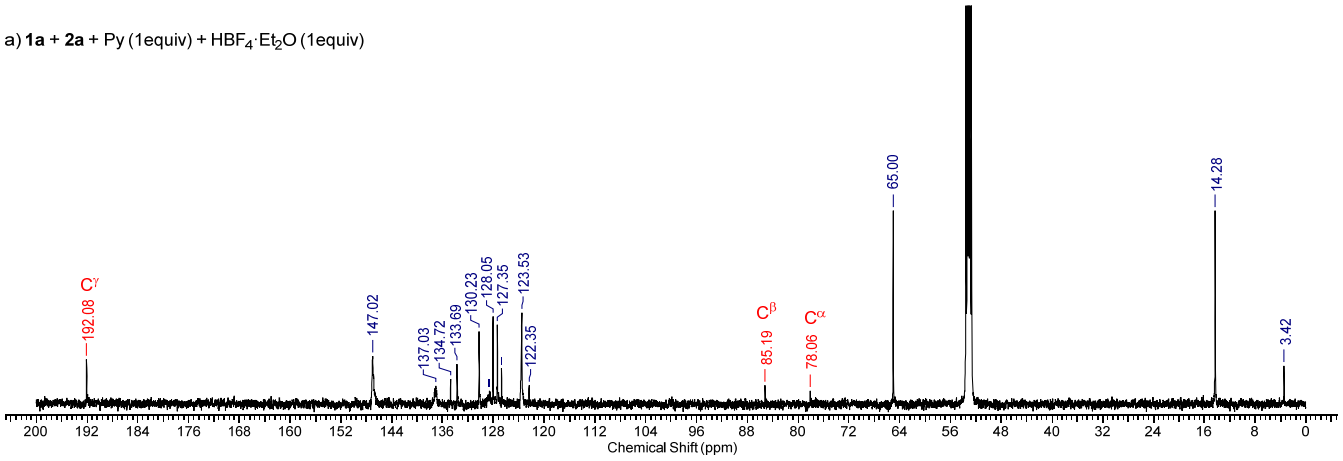
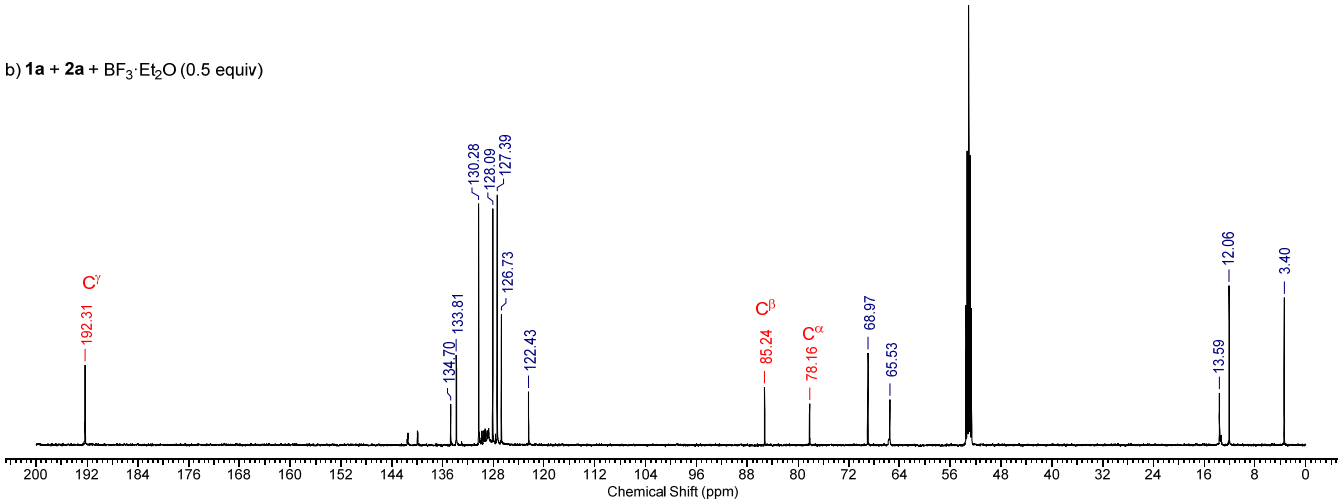


Fig. S-1. ^{13}C NMR spectra of a 1:1 mixture of **1a** and **1b** without any additives

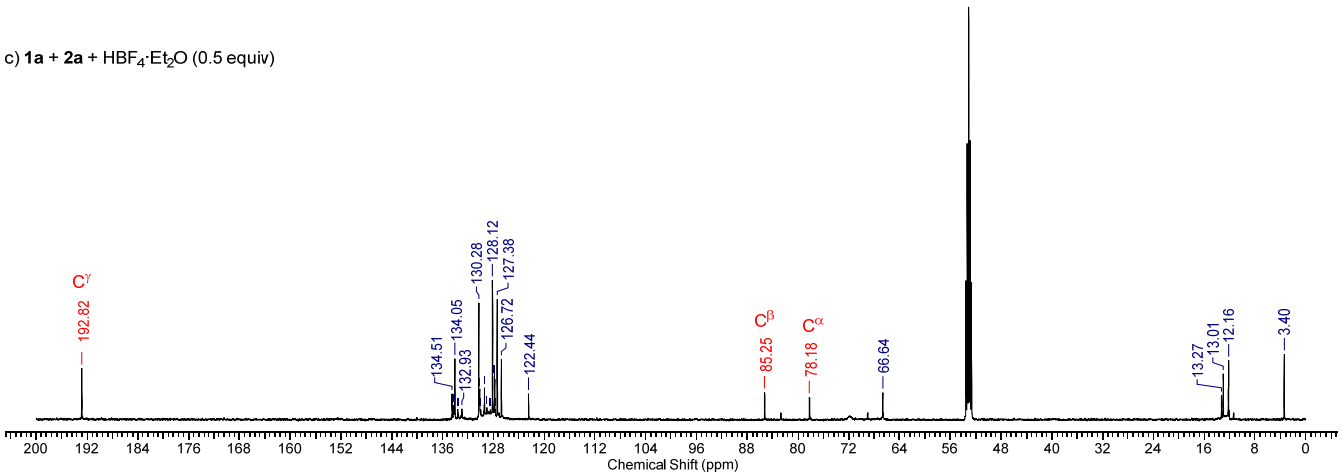
a) **1a** + **2a** + Py (1equiv) + $HBF_4 \cdot Et_2O$ (1equiv)



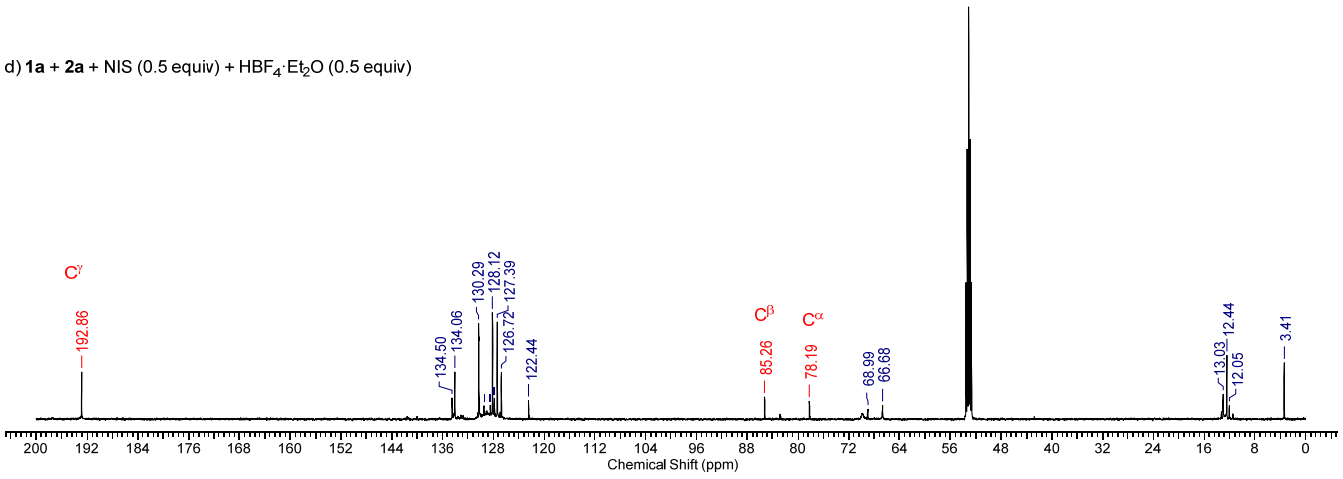
b) **1a** + **2a** + $BF_3 \cdot Et_2O$ (0.5 equiv)



c) **1a** + **2a** + $HBF_4 \cdot Et_2O$ (0.5 equiv)



d) **1a** + **2a** + NIS (0.5 equiv) + $HBF_4 \cdot Et_2O$ (0.5 equiv)



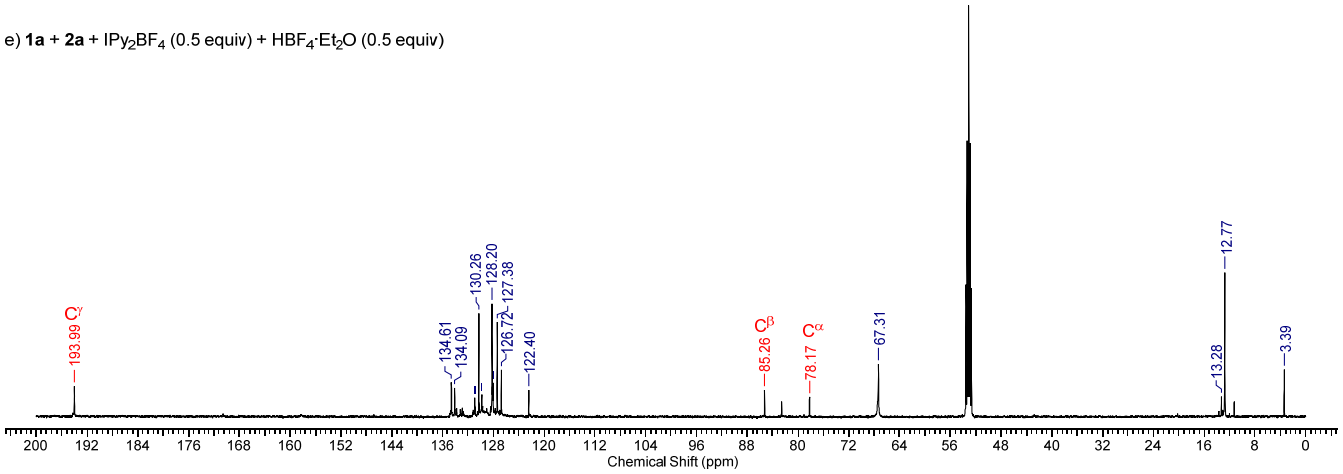
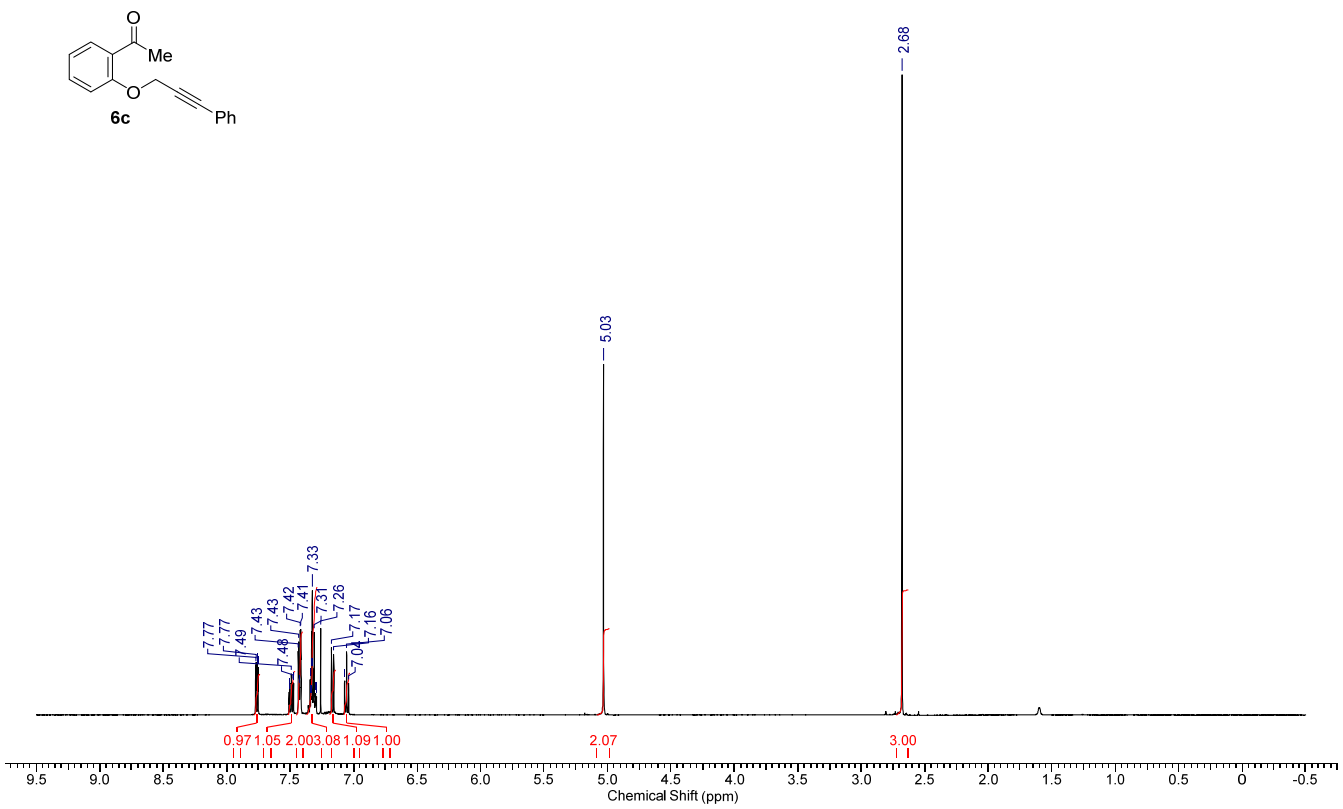
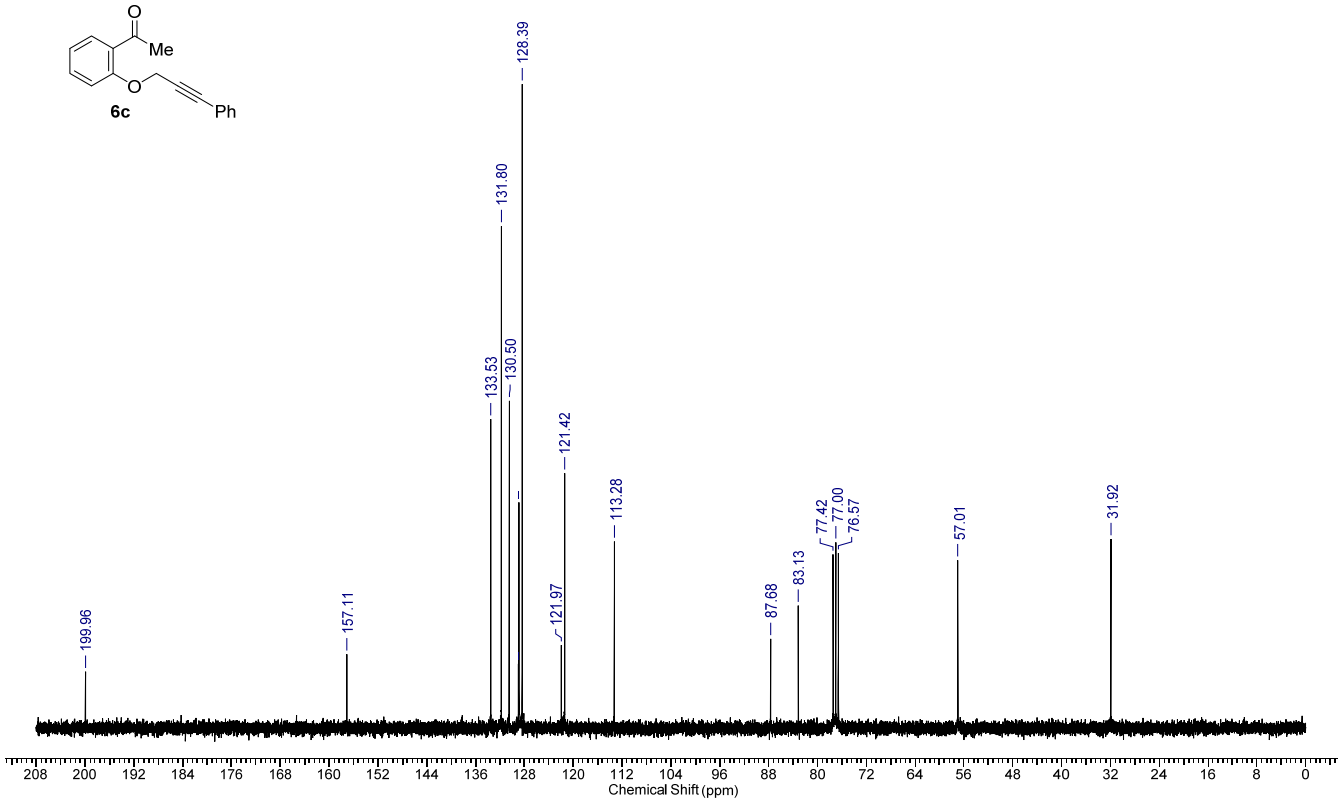


Fig. S-2. ^{13}C NMR spectra of a 1:1 mixture of **1a** and **2a** with additives

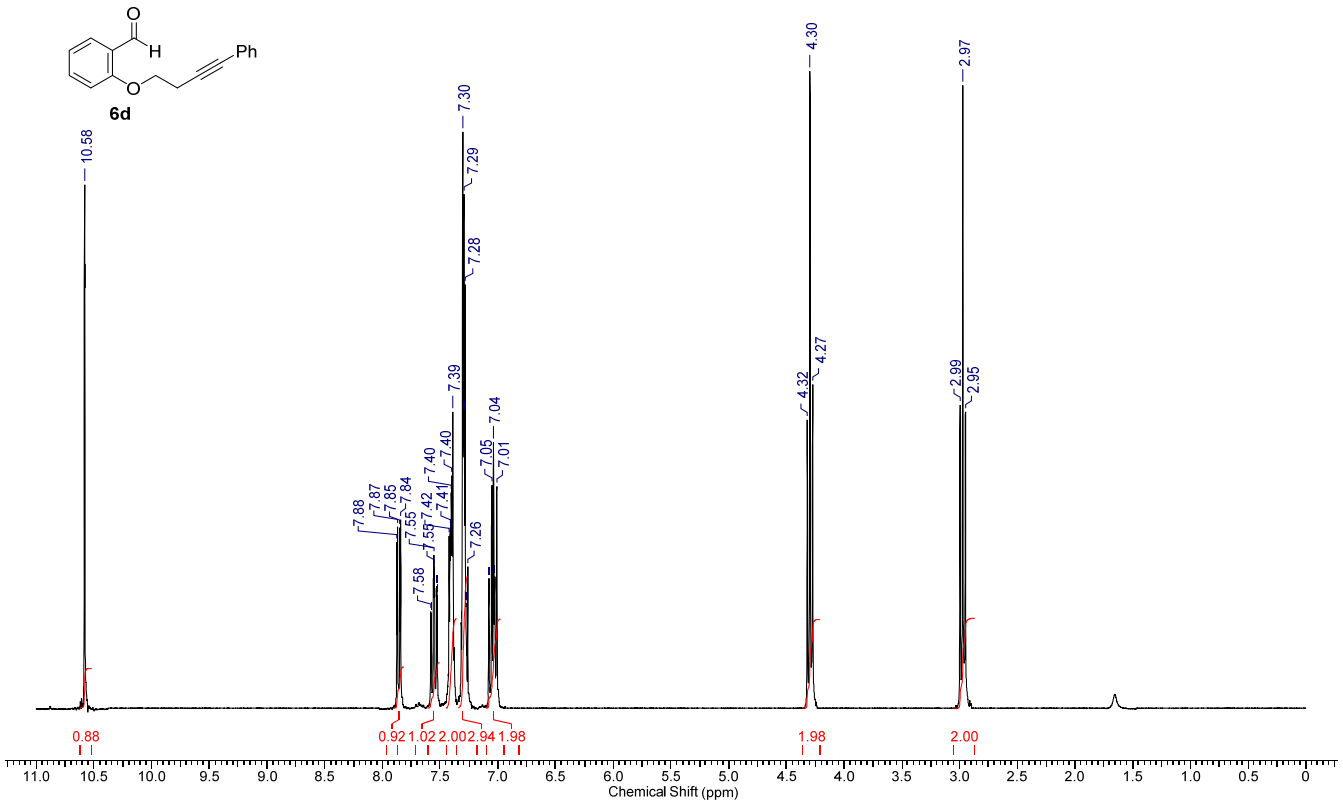
^{1}H-NMR of **6c**



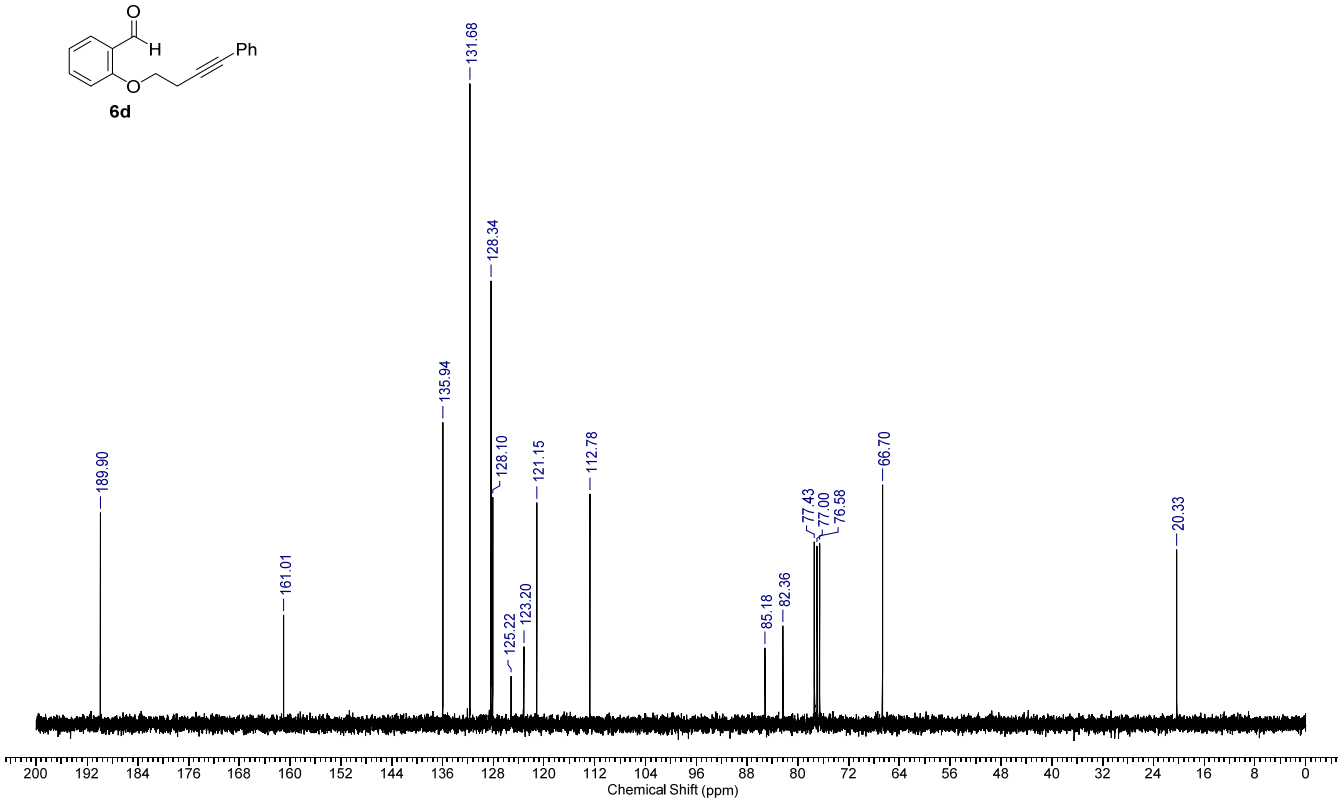
^{13}C-NMR of **6c**



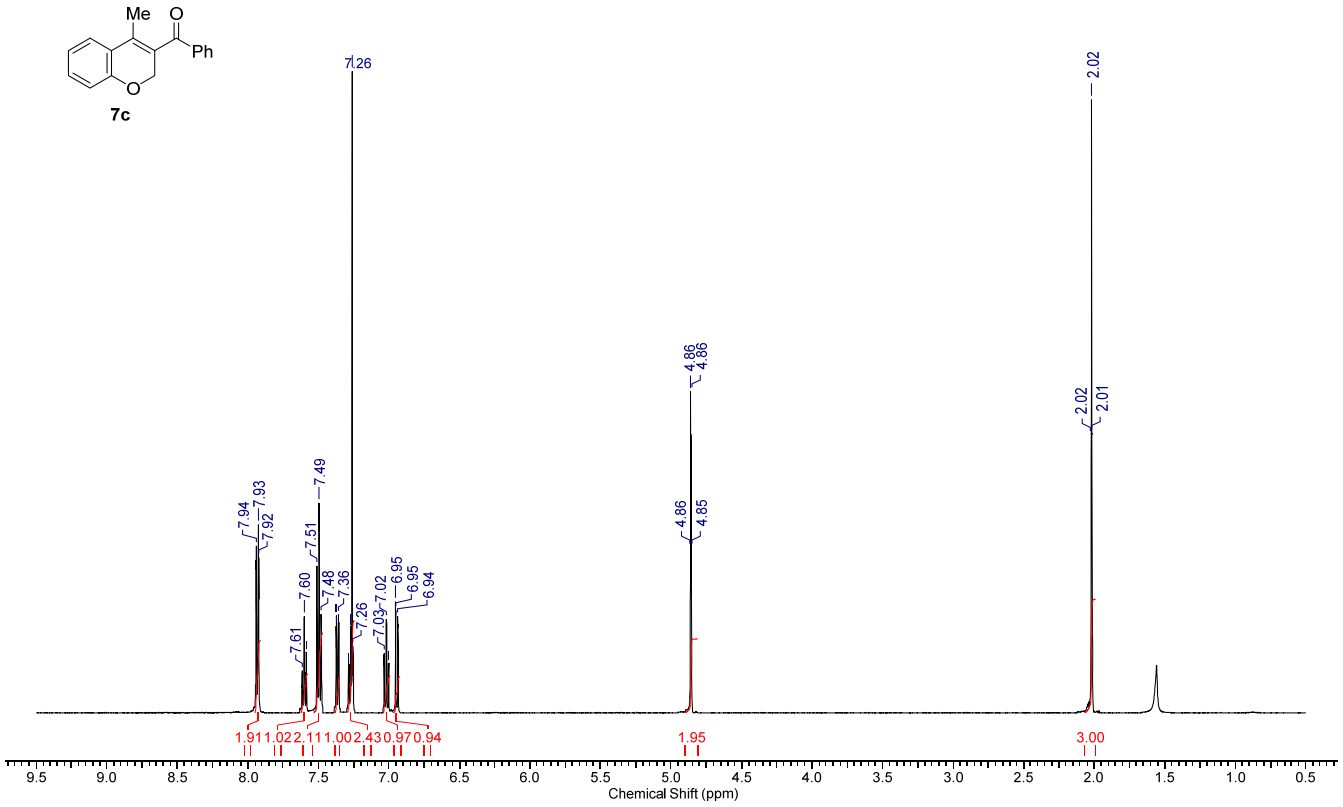
^{1}H-NMR of **6d**



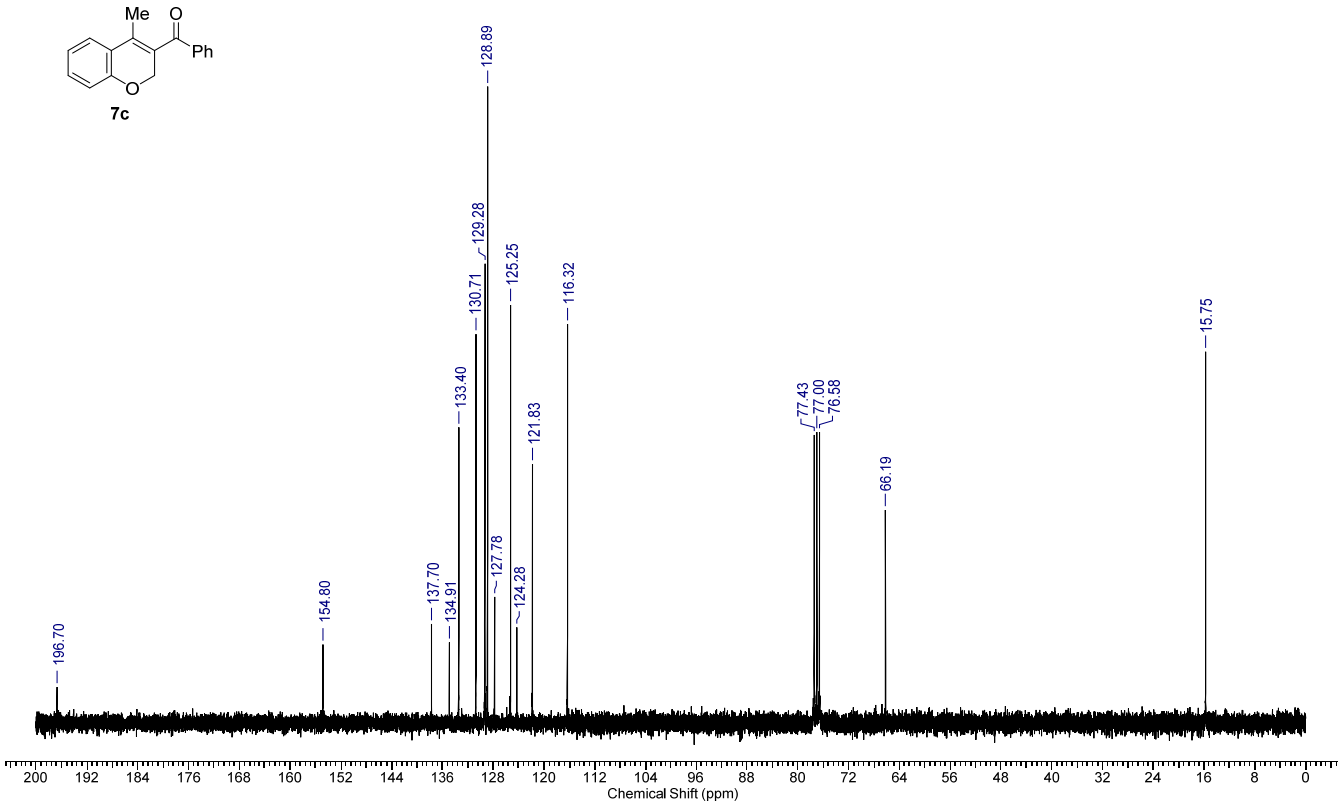
^{13}C-NMR of **6d**



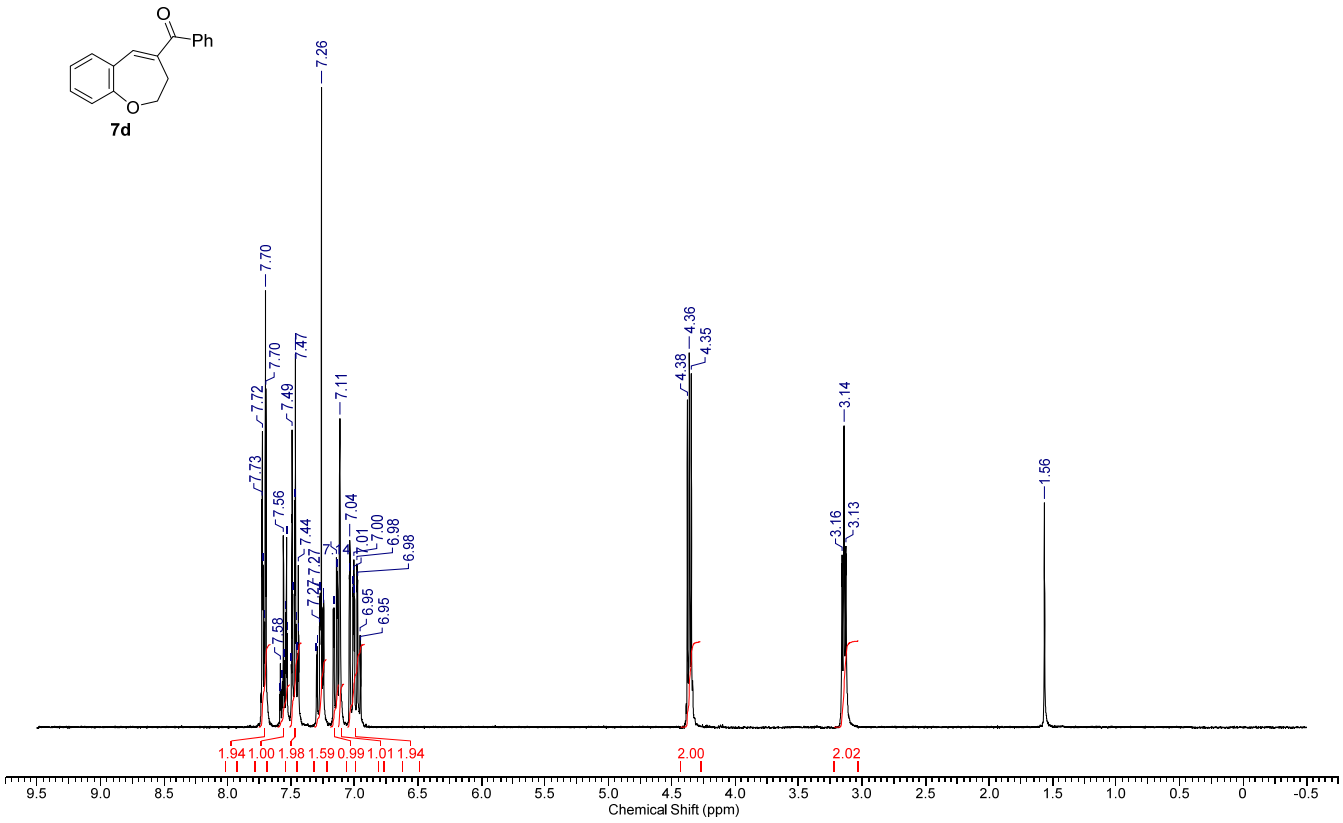
^{1}H-NMR of **7c**



^{13}C-NMR of **7c**



^{1}H-NMR of **7d**



^{13}C-NMR of **7d**