Supporting Information

Synthesis of Pyrroles by Gold(I)-Catalyzed Amino-Claisen Rearrangement of N-Propargyl Enaminone Derivatives

Akio Saito,* Tomoyo Konishi, and Yuji Hanzawa*

Laboratory of Organic Reaction Chemistry, Showa Pharmaceutical University,
3-3165 Higashi-tamagawagakuen, Machida, Tokyo 194-8543 (Japan)
akio-sai@ac.shoyaku.ac.jp (A. Saito), hanzaway@ac.shoyaku.ac.jp (Y. Hanzawa)

Table of contents

General Information

(IPr)AuCl (IPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), $AgBF_4$, hexafluoroisopropanol (HFIP), and hexafluoroisopropan (ol-d) (HFIP-d_1) are commercially available. [(IPr)Au(MeCN)]BF_4 was prepared by the previously reported procedure.[1] 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, Kanto Kagaku Co., Ltd.). ^{1}H and ^{13}C NMR spectra were measured at 300.4 and 75.5 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).

A typical procedure for preparation of pyrrole 2 (Table 1 and 2)

[(IPr)Au(MeCN)]BF_4 (5 mol%, 14.3 mg) was added to a solution of **1** (0.4 mmol) in CH_2Cl_2 (2.0 mL), and the reaction mixture was stirred at room temperature until the consumption of **1** (by TLC analysis). The mixture was diluted with ether and filtered through a short alumina column. After concentration of the filtrate to dryness, the residue was dissolved in MeOH-THF (1:1, 2.0 mL), and then, 2.0M KOH (0.6 mL) was added. After being stirred at room temperature for 1 h, the reaction mixture was concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (hexane/AcOEt = 90/10) gave **2**.

[1] de Frémont, P.; Stevens, E. D.; Fructos, M. R.; Mar Díaz-Requejo, M.; Perez, P. J.; Nolan, S. P. *Chem. Commun*. **2006**, 2045–2047.

(5-Methyl-2-phenyl-1*H*-pyrrol-3-yl)(phenyl)methanone (2a): Colorless oil. IR (neat) ν cm^{-1}; 1651. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.50 (s, 3H), 6.71 (s, 1H), 7.12-7.21 (m, 1H), 7.25-7.32 (m, 2H), 7.35-7.43 (m, 2H), 7.44-7.51 (m, 1H), 7.53-7.58 (m, 2H), 7.71-7.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.4, 106.6, 122.4, 123.8, 127.8, 128.4, 128.8, 129.0, 130.0, 132.3, 139.2, 151.6, 159.0, 191.3. FAB-LM *m/z*: 262 (M^++1). FAB-HM Calcd for $C_{18}H_{16}NO$: 262.1232, Found: 262.1225. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.68; H, 5.42; N, 5.30.

(1,6-Dihydro-2-phenyl-1-tosylpyridin-3-yl)(phenyl)methanone (3a): White solid. Mp 143 ℃. IR (KBr) ν cm^{-1}; 1668. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.43 (s, 3H), 4.65 (dd, 2H, *J* = 4.4, 1.4 Hz), 5.53 (dt, 1H, *J* = 9.1, 4.4 Hz), 6.08 (dt, 1H, *J* = 9.1, 1.4 Hz), 7.04-7.19 (m, 5H), 7.20-7.36 (m, 5H), 7.46-7.56 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.6, 46.2, 119.2, 124.8, 127.5, 127.7, 128.0, 129.1, 129.3, 129.6, 130.4, 132.6, 135.5, 136.4, 136.9, 141.8, 144.1, 196.0. FAB-LM *m/z*: 416 (M^++1). FAB-HM Calcd for $C_{25}H_{22}NO_3S$: 416.1320, Found: 416.1320. Anal. Calcd for $C_{25}H_{21}NO_3S$: C, 71.86; H, 5.32; N, 3.37. Found: C, 72.09; H, 5.18; N, 3.18.

(Furan-2-yl)(5-methyl-2-phenyl-1*H*-pyrrol-3-yl)methanone (2b): White solid. Mp 58 ℃. IR (KBr) ν cm^{-1}; 1645. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.60 (s, 3H), 6.46 (dd, 1H, *J* = 3.3, 1.8 Hz), 6.58 (d, 1H, *J* = 3.3 Hz), 6.71 (s, 1H), 7.41 (d, 1H, *J* = 1.8 Hz), 7.44-7.52 (m, 2H), 7.54-7.61 (m, 1H), 7.81-7.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.2, 105.8, 106.5, 111.4, 121.9, 128.4, 129.0, 132.3, 138.9, 142.1, 144.2, 145.6, 158.8, 191.0. FAB-LM *m/z*: 252 (M^++1). FAB-HM Calcd for $C_{16}H_{14}NO_2$: 252.1025, Found: 252.0892.

(4-Methoxyphenyl)(5-methyl-2-phenyl-1*H*-pyrrol-3-yl)methanone (2c): Colorless oil. IR (neat) ν cm^{-1}; 1651. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.59 (s, 3H), 3.84 (s, 3H), 6.67 (s, 1H), 6.93 (d, 2H, *J* = 8.9 Hz), 7.45-7.52 (m, 2H), 7.53-7.62 (m, 3H), 7.81-7.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.3, 55.3, 104.9, 114.2, 122.3, 122.9, 125.2, 128.3, 128.9, 132.1, 139.2, 151.6, 158.2, 159.3, 191.3. FAB-LM *m/z*: 292 (M^++1). FAB-HM Calcd for $C_{19}H_{18}NO_2$: 292.1338, Found: 292.1337.

(5-Methyl-2-phenyl-1*H*-pyrrol-3-yl)(4-nitrophenyl)methanone (2d): White solid. Mp 159 ℃. IR (KBr) ν cm^{-1}; 1655, 1504, 1346. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.64 (s, 3H), 7.04 (s, 1H), 7.47-7.56 (m, 2H), 7.57-7.65 (m, 1H), 7.75-7.87 (m, 4H), 8.23-8.29 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.5, 110.4, 122.9, 123.9, 124.4, 128.6, 129.0, 132.6, 135.6, 138.7, 146.7, 149.3, 160.8, 190.7. FAB-LM *m/z*: 307 (M^++1). FAB-HM Calcd for $C_{18}H_{15}N_2O_3$: 307.1083, Found: 307.1079.

2,2-Dimethyl-1-(5-methyl-2-phenyl-1*H*-pyrrol-3-yl)propan-1-one (2e): Colorless oil. IR (neat) ν cm^{-1}; 1651. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.28 (s, 9H), 2.47 (s, 3H), 6.14 (s, 1H), 7.42-7.49 (m, 2H), 7.50-7.57 (m, 1H), 7.76-7.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.3, 28.9, 32.3, 103.8, 120.9, 128.2, 128.8, 131.9, 139.5, 157.8, 162.0, 191.7. FAB-LM *m/z*: 242 (M^++1). FAB-HM Calcd for $C_{16}H_{20}NO$: 242.1545, Found: 242.1550.

1-(1,6-Dihydro-1-tosylpyridin-3-yl)ethanone (3f): Colorless oil. IR (neat) ν cm^{-1}; 1705. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.26 (s, 3H), 2.45 (s, 3H), 4.19 (dd, 2H, *J* = 3.7, 2.1 Hz), 5.39 (dt, 1H, *J* = 10.1, 3.7 Hz), 6.40 (dt, 1H, *J* = 10.1, 2.1 Hz), 7.35-7.41 (m, 2H), 7.69-7.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.7, 24.6, 44.3, 116.1, 117.2, 119.8, 127.6, 130.3, 133.2, 136.5, 145.4, 193.4. FAB-LM *m/z*: 278 (M^++1). FAB-HM Calcd for $C_{14}H_{16}NO_3S$: 278.0851, Found: 278.0835.

A typical procedure for preparation of pyrrole 6 (Table 3)

[(IPr)Au(MeCN)]BF_4 (5 mol%, 14.3 mg) was added to a solution of **5** (0.4 mmol) in CH_2Cl_2-HFIP (3:1, 2.0 mL) or HFIP (2.0 mL), and the reaction mixture was stirred at room temperature until the consumption of **5** (by TLC analysis). The mixture was diluted with ether and filtered through a short alumina column. After concentration of the filtrate to dryness, purification of the residue by silica gel column chromatography (hexane/AcOEt =95/5) gave pyrrole **6**.

Diethyl 5-methyl-1-tosyl-1*H*-pyrrole-2,3-dicarboxylate (6a): Colorless oil. IR (neat) ν cm^{-1}; 1732, 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.30 (t, 3H, *J* = 7.1 Hz), 1.43 (t, 3H, *J* = 7.2 Hz), 2.29 (s, 3H), 2.43 (s, 3H), 4.25 (q, 2H, *J* = 7.1 Hz), 4.65 (q, 2H, *J* = 7.2 Hz), 6.27 (s, 1H), 7.34 (d, 2H, *J* = 8.3 Hz), 7.93 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.8, 14.1, 21.7, 60.6, 62.6, 111.8, 117.0, 127.7, 130.1, 130.8, 131.5, 135.0, 145.9, 162.5, 162.7. FAB-LM *m/z*: 380 (M^++1). FAB-HM Calcd for $C_{18}H_{22}NO_6S$: 380.1168, Found: 380.1168. Anal. Calcd for $C_{18}H_{21}NO_6S$: C, 56.98; H, 5.58; N, 3.69. Found: C, 56.90; H, 5.75; N, 3.58.

Diethyl 1,6-dihydro-1-tosylpyridine-2,3-dicarboxylate (7a): Colorless oil. IR (neat) ν cm^{-1}; 1747, 1713. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.27 (t, 3H, *J* = 7.2 Hz), 1.38 (t, 3H, *J* = 7.2 Hz), 2.41 (s, 3H), 4.20 (q, 2H, *J* = 7.2 Hz), 4.27 (dd, 2H, *J* = 4.4, 1.6 Hz), 4.35 (q, 2H, *J* = 7.2 Hz), 5.39 (dt, 1H, *J* = 9.1, 4.4 Hz), 6.13 (dt, 1H, *J* = 9.1, 1.6 Hz), 7.27 (d, 2H, *J* = 8.2 Hz), 7.74 (d, 2H, *J* = 8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.8, 13.9, 21.6, 44.7, 61.4, 62.3, 120.2, 121.8, 122.1, 127.2, 129.7, 135.9, 136.1, 144.6, 163.6, 164.8. FAB-LM *m/z*: 380 (M^++1). FAB-HM Calcd for $C_{18}H_{22}NO_6S$: 380.1168, Found: 380.1149.

Ethyl 5-methyl-2-phenyl-1-tosyl-1*H*-pyrrole-3-carboxylate (6b): Colorless oil. IR (neat) ν cm^{-1}; 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.94 (t, 3H, *J* = 7.1 Hz), 2.35 (s, 3H), 2.53 (s, 3H), 3.95 (q, 2H, *J* = 7.1 Hz), 6.41 (s, 1H), 7.03-7.08 (m, 2H), 7.11-7.16 (m, 2H), 7.20-7.27 (m, 4H), 7.30-7.37 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.7, 15.8, 21.5, 59.8, 112.5, 117.8, 126.8, 126.9, 128.4, 129.5, 131.1, 131.5, 132.8, 136.4, 139.4, 144.9, 163.5. FAB-LM *m/z*: 384 (M^++1). FAB-HM Calcd for $C_{21}H_{22}NO_4S$: 384.1270, Found: 384.1267. Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 65.78; H, 5.52; N, 3.65. Found: C, 65.71; H, 5.53; N, 3.52.

Ethyl 2,5-dimethyl-1-tosyl-1*H*-pyrrole-3-carboxylate (6c): White solid. Mp 77 ℃. IR (KBr) ν cm^{-1}; 1709. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.31 (t, 3H, *J* = 7.1 Hz), 2.41 (s, 6H), 2.72 (s, 3H), 4.24 (q, 2H, *J* = 7.1 Hz), 6.29 (s, 1H), 7.30 (d, 2H, *J* = 8.5 Hz), 7.60 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.3, 14.3, 15.6, 21.6, 60.0, 112.3, 115.7, 126.5, 130.1, 131.6, 136.7, 138.6, 145.1, 164.5. FAB-LM *m/z*: 322 (M^++1). FAB-HM Calcd for $C_{16}H_{20}NO_4S$: 322.1113, Found: 322.1125.

Ethyl 2,4,5-trimethyl-1-tosyl-1*H*-pyrrole-3-carboxylate (6d): White solid. Mp 98 ℃. IR (KBr) ν cm^{-1}; 1713. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.33 (t, 3H, *J* = 7.1 Hz), 2.08 (s, 3H), 2.32 (s, 3H), 2.41 (s, 3H), 2.69 (s, 3H), 4.26 (q, 2H, *J* = 7.1 Hz), 7.29 (d, 2H, *J* = 8.3 Hz), 7.58 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 11.1, 12.3, 13.5, 14.2, 21.5, 59.9, 116.8, 119.2, 126.3, 127.5, 130.0, 136.9, 137.4, 144.8, 165.4. FAB-LM *m/z*: 336 (M^++1). FAB-HM Calcd for $C_{17}H_{22}NO_4S$: 336.1270, Found: 336.1263. Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31; N, 4.18. Found: C, 60.96; H, 6.24; N, 4.03.

Ethyl 2,5-dimethyl-4-phenyl-1-tosyl-1*H*-pyrrole-3-carboxylate (6e): White solid. Mp 121 ℃. IR (KBr) ν cm^{-1}; 1697. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.88 (t, 3H, *J* = 7.1 Hz), 2.28 (s, 3H), 2.44 (s, 3H), 2.74 (s, 3H), 3.98 (q, 2H, *J* = 7.1 Hz), 7.11-7.15 (m, 2H), 7.26-7.38 (m, 5H), 7.68 (d, 2H, *J* = 7.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.2, 13.4, 13.5, 21.6, 59.9, 116.9, 125.7, 126.6, 126.7, 127.6, 128.7, 130.1, 130.2, 134.9, 136.8, 137.0, 145.2, 165.0. FAB-LM *m/z*: 398 (M^++1). FAB-HM Calcd for $C_{22}H_{24}NO_4S$: 398.1426, Found: 398.1425. Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52. Found: C, 66.53; H, 5.86; N, 3.38.

Ethyl 5-hexyl-2-methyl-1-tosyl-1*H*-pyrrole-3-carboxylate (6f): White solid. Mp 67 ℃. IR (KBr) ν cm^{-1}; 1711. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.88 (t, 3H, *J* = 6.7 Hz), 1.21-1.42 (m, 9H), 1.56-1.73 (m, 2H), 2.41 (s, 3H), 2.71 (s, 3H), 2.79 (t, 2H, *J* = 7.7 Hz), 4.24 (q, 2H, *J* = 7.1 Hz), 6.33 (s, 1H), 7.29 (d, 2H, *J* = 8.3 Hz), 7.56 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.2, 13.9, 14.2, 21.4, 22.4, 28.7, 28.8, 28.9, 31.5, 59.9, 110.9, 115.8, 126.2, 130.0, 136.8, 136.9, 138.6, 144.9, 164.4. FAB-LM *m/z*: 392 (M^++1). FAB-HM Calcd for $C_{21}H_{30}NO_4S$: 392.1896, Found: 392.1909. Anal. Calcd for $C_{21}H_{29}NO_4S$: C, 64.42; H, 7.47; N, 3.58. Found: C, 64.21; H, 7.50; N, 3.31.

A typical procedure for preparation of furan 10 (Table 4)

[(IPr)Au(MeCN)]BF_4 (5 mol%, 14.3 mg) was added to a solution of **8** (0.4 mmol) in CH_2Cl_2 (2.0 mL), and the reaction mixture was stirred at room temperature until the consumption of **8** by TLC analysis. The mixture was diluted with ether and filtered through a short alumina column. After concentration of the filtrate to dryness, purification of the residue by silica gel column chromatography (hexane/AcOEt = 95/5) gave pyrrole **10**.

(4,5-Dimethyl-2-phenylfuran-3-yl)(phenyl)methanone (10a): The ^{1}H NMR spectra of **10a** was identical to those reported in literature.[2]

Ethyl 2,5-dimethylfuran-3-carboxylate (10b): The ^{1}H NMR spectra of **10b** was identical to those reported in literature.[2]

Ethyl 2,4,5-trimethylfuran-3-carboxylate (10c): The ^{1}H NMR spectra of **10c** was identical to those reported in literature.[2]

Ethyl 2,5-dimethyl-4-phenylfuran-3-carboxylate (10d): The ^{1}H NMR spectra of **10d** was identical to those reported in literature.[2]

Preparation of deuterated pyrrole 6d-D (Scheme 2)

[(IPr)Au(MeCN)]BF_4 (5 mol%, 14.3 mg) was added to a solution of **5d** (134 mg, 0.4 mmol) in CH_2Cl_2-HFIP-d_1 (3:1, 2.0 mL), and the reaction mixture was stirred at room temperature for 1 h. The mixture was diluted with ether and filtered through a short alumina column. After concentration of the filtrate to dryness, purification of the residue by silica gel column chromatography (hexane/AcOEt = 95/5) gave pyrrole **6d-D** (132.1 mg, 98%, 50%-D).

Ethyl 2,4,5-trimethyl-1-tosyl-1H-pyrrole-3-carboxylate-d_1 (6d-D): White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.33 (t, 3H, *J* = 7.1 Hz), 2.08 (s, 3H), 2.31 (br.s, 1H), 2.32 (s, 1.5H), 2.41 (s, 3H), 2.69 (s, 3H), 4.26 (q, 2H, *J* = 7.1 Hz), 7.29 (d, 2H, *J* = 8.3 Hz), 7.58 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 11.1, 12.1 (t, *J* = 19.8 Hz)12.3, 13.5, 14.2, 21.5, 59.9, 116.8, 119.2, 126.3, 127.5, 130.0, 136.9, 137.4, 144.8, 165.4. FAB-LM *m/z*: 336, 337 (M^++1). FAB-HM Calcd for $C_{17}H_{22}NO_4S$: 336.1270, Found: 336.1271. FAB-HM Calcd for $C_{17}H_{21}DNO_4S$: 337.1332, Found: 337.1322.

A typical procedure for preparation of enaminoketone 1

To a solution of *N*-2-propynyl *p*-toluenesulfonamide (418 mg, 2 mmol) and α,β-ynone (4 mmol) in THF (10 mL) was added tri-*n*-butylphosphine (0.1～0.2 mL, 0.4～0.8 mmol), and mixture was stirred at room temperature until the consumption of starting material (by TLC analysis). After concentration of the reaction mixture to dryness, purification by silica gel column

[2] Suhre, M. H.; Reif, M.; Kirsch, S. F. *Org. Lett.* **2005**, *7*, 3925.–3927.

chromatography (hexane/AcOEt =95/5) gave **1a** or **1d-f**.

***N*-[(1*E*)-3-oxo-1,3-diphenylprop-1-en-1-yl]-*N*-prop-2-yn-1-yl-*p*-toluenesulfonamide (1a,** *E:Z*=67:33**):** White solid. Mp 126 ℃. IR (KBr) ν cm^{-1}; 1639. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.40 (t, 1H, *J* = 2.3 Hz), 2.53 (s, 3H), 4.39 (d, 2H, *J* = 2.3 Hz), 6.68 (s, 1H), 7.21-7.99 (m, 14H). *The following signals were assigned to Z-isomer*: 2.35 (t, 1H, *J* = 2.5 Hz), 2.42 (s, 3H), 4.70 (d, 2H, *J* = 2.5 Hz), 7.18 (s, 1H), 7.21-7.99 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.6, 38.8, 73.9, 77.6, 123.1, 127.9, 128.2 (NA = the signals could not be assigned to either isomer), 128.3 (NA), 128.3 (NA), 128.4 (NA), 128.5 (NA), 128.7 (NA), 128.9 (NA), 129.3 (NA), 129.5 (NA), 129.6 (NA), 129.8 (NA), 130.4 (NA), 132.7, 134.2, 136.5, 137.4, 144.5, 148.3, 192.8. *The following signals were assigned to Z-isomer*: 21.5, 41.1, 73.8, 78.3, 120.1, 127.8, 132.8, 136.3, 138.3, 138.5, 143.7, 149.9, 187.7. FAB-LM *m/z*: 416 (M^++1). FAB-HM Calcd for $C_{25}H_{22}NO_3S$: 416.1320, Found: 416.1318. Anal. Calcd for $C_{25}H_{21}NO_3S$: C, 72.27; H, 5.09; N, 3.37. Found: C, 72.22; H, 5.18; N, 3.19.

***N*-[(1*E*)-3-(4-nitrophenyl)-3-oxo-1-phenylprop-1-en-1-yl]-*N*-prop-2-yn-1-yl-*p*-toluenesulfonamide (1d,** *E:Z*=74:26**):** White solid. Mp 111 ℃. IR (KBr) ν cm^{-1}; 1662. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.33 (t, 1H, *J* = 2.5 Hz), 2.47 (s, 3H), 4.32 (d, 2H, *J* = 2.5 Hz), 6.55 (s, 1H), 7.01-8.32 (m, 13H). *The following signals were assigned to Z-isomer*: 2.27 (t, 1H, *J* = 2.5 Hz), 2.38 (s, 3H), 4.54 (d, 2H, *J* = 2.5 Hz), 7.00 (s, 1H), 7.01-8.32 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.6, 38.8, 74.1, 77.3, 121.4, 123.2, 127.8, 128.5, 129.6, 129.7, 130.0, 130.7, 133.9, 136.2, 142.4, 144.8, 149.6, 150.6, 191.7. *The following signals were assigned to Z-isomer*: 21.5, 40.4, 74.3, 77.6, 119.1, 123.7, 128.8, 129.3, 129.4, 130.9, 136.1, 137.7, 143.1, 144.1, 149.9, 151.4, 186.3. FAB-LM *m/z*: 461 (M^++1). FAB-HM Calcd for $C_{25}H_{21}N_2O_5S$: 461.1171, Found: 461.1175.

***N*-[(1*E*)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-1-yl]-*N*-prop-2-yn-1-yl-*p*-toluenesulfonamide (1e,** *E:Z*=55:45**):** Colorless oil. IR (neat) ν cm^{-1}; 1684. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.07 (s, 9H), 2.27-2.32 (m, 1H), 2.45 (s, 3H), 4.24 (d, 2H, *J* = 2.5 Hz), 6.62 (s, 1H), 7.10-7.55 (m, 7H) 7.59-7.65 (m, 2H). *The following signals were assigned to Z-isomer*: 1.13 (s, 9H), 2.27-2.32 (m, 1H), 2.39 (s, 3H), 4.60 (d, 2H, *J* = 2.5 Hz), 6.67 (s, 1H), 7.10-7.55 (m, 7H) 7.75-7.81 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, all signals could not be assigned to either isomer) δ; 21.2, 21.3, 26.0, 26.1, 38.3, 41.0, 43.7, 44.0, 73.6, 77.7, 78.4, 118.3, 119.3, 127.7, 127.8, 128.1, 128.3, 128.6, 129.1, 129.2, 129.6, 129.8, 130.3, 133.9, 136.3, 136.6, 138.5, 143.3, 144.2, 148.4, 149.2, 201.5, 204.1. FAB-LM *m/z*: 396 (M^++1). FAB-HM Calcd for $C_{23}H_{26}NO_3S$: 396.1633, Found: 396.1620.

***N*-[(1*E*)-3-oxobut-1-en-1-yl]-*N*-prop-2-yn-1-yl-*p*-toluenesulfonamide (1f,** *E* only**):** White solid. Mp 92 ℃. IR (KBr) ν cm^{-1}; 1682. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.07 (t, 2H, *J* = 2.5 Hz), 2.19 (s, 3H), 2.38 (s, 3H), 4.27 (d, 2H, *J* = 2.5 Hz), 5.63 (d, 1H, *J* = 14.1 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 7.68 (d, 2H, *J* = 8.2 Hz) 7.88 (d, 1H, *J* = 14.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.5, 27.9, 35.2, 74.2, 74.8, 109.5, 127.3, 130.0, 134.7, 139.6, 145.1, 196.1. FAB-LM *m/z*: 278 (M^++1). FAB-HM Calcd for $C_{14}H_{16}NO_3S$: 278.0851, Found: 278.0846. Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.65; H, 5.45; N, 4.95.

(2*E*)-3-(But-2-yn-1-yloxy)-1,3-diphenyl-2-propenone (8a, *E:Z*=67:33**):** As well as the typical procedure for **1**, the treatment of a solution of 1,3-diphenyl-2-propynone (412 mg, 2 mmol) and 2-butyn-1-ol (0.18 mL, 2.4 mmol) in THF (4 mL) with tri-*n*-butylphosphine (0.2 mL, 0.8 mmol) at room temperature for 18 h gave **8a** (373 mg, 68%) as a colorless oil. IR (neat) ν cm^{-1}; 1662. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.94 (t, 1H, *J* = 2.3 Hz), 4.76 (d, 2H, *J* = 2.3 Hz), 6.38 (s, 1H), 7.29-7.52 (m, 8H), 7.92-7.95 (m, 2H). *The following signals were assigned to Z-isomer*: 1.76 (t, 1H, *J* = 2.3 Hz), 4.88 (d, 2H, *J* = 2.3 Hz), 6.63 (s, 1H), 7.29-7.52 (m, 6H), 7.72-7.81 (m, 2H), 7.98-8.05 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 3.6, 57.4, 72.7, 84.9, 127.7, 128.2, 128.9, 129.8, 132.0,

134.8, 139.4, 168.8, 190.4. *The following signals were assigned to Z-isomer*: 3.5, 61.7, 73.6, 84.8, 128.2, 128.3, 128.4, 130.6, 132.2, 135.9, 139.1, 165.7, 189.3. FAB-LM *m/z*: 277 (M^++1). FAB-HM Calcd for $C_{19}H_{17}O_2$: 277.1229, Found: 277.1222.

***N*-[(1*E*)-3-furan-2-yl-3-oxo-1-phenylprop-1-en-1-yl]-*N*-prop-2-yn-1-yl-p-toluenesulfonamide (1b,** *E:Z*=52:48**):** To a solution of *N*-2-propynyl *p*-toluenesulfonamide (418 mg, 2 mmol) and 1-(2-furyl)-3-phenyl-2-propynone (784 mg, 4 mmol) in benzene (4 mL) was added 1,4-diaza-bicyclo[2.2.2]octane (DABCO, 44.8 mg, 0.4 mmol), and mixture was refluxed for 48 h. After concentration of the reaction mixture to dryness, purification by silica gel column chromatography (hexane/AcOEt = 25 : 1) gave **1b** (381 mg, 47%) as a white solid. Mp 98 ℃. IR (KBr) ν cm^{-1}; 1655. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.28 (t, 1H, *J* = 2.5 Hz), 2.45 (s, 3H), 4.30 (d, 2H, *J* = 2.5 Hz), 6.39 (dd, 1H, *J* = 3.6, 1.7 Hz), 6.71 (s, 1H), 7.02 (dd, 1H, *J* = 3.6, 0.7 Hz), 7.16-7.61 (m, 8H), 7.80-7.86 (m, 2H). *The following signals were assigned to Z-isomer*: 2.30 (t, 1H, *J* = 2.5 Hz), 2.38 (s, 3H), 4.65 (d, 2H, *J* = 2.5 Hz), 6.54 (dd, 1H, *J* = 3.6, 1.7 Hz), 7.05 (s, 1H), 7.14 (dd, 1H, *J* = 3.6, 0.7 Hz), 7.16-7.61 (m, 8H), 7.71-7.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.3, 38.4, 73.8, 77.5, 112.1, 118.4, 119.4, 127.7, 128.0, 129.1, 129.6, 129.8, 133.7, 136.1, 144.4, 146.4, 149.6, 152.8, 178.3. *The following signals were assigned to Z-isomer*: 40.9, 78.1, 112.4, 117.0, 117.7, 127.6, 128.5, 129.0, 130.4, 136.0, 138.5, 143.6, 146.2, 150.6, 153.6, 174.7. FAB-LM *m/z*: 406 (M^++1). FAB-HM Calcd for $C_{23}H_{20}NO_4S$: 406.1113, Found: 406.1116. Anal. Calcd for $C_{23}H_{19}NO_4S$: C, 68.13; H, 4.72; N, 3.45. Found: C, 68.01; H, 4.74; N, 3.27.

***N*-{(1*E*)-3-[4-(methyloxy)phenyl]-3-oxo-1-phenylprop-1-en-1-yl}-*N*-prop-2-yn-1-yl-*p*-toluenesulfonamide (1c,** *E:Z*=84:16**):** In the similar procedure to **1b**, in the presence of DABCO (89.6 mg, 0.4 mmol), the reaction of *N*-2-propynyl *p*-toluenesulfonamide (418 mg, 2 mmol) and 1-[4-(methyloxy)phenyl]-3-phenyl-2-propynone (784 mg, 4 mmol) in refluxed benzene (4 mL) for 48 h gave **1c** (439 mg, 99%) as a colorless oil. IR (neat) ν cm^{-1}; 1655. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.30 (t, 1H, *J* = 2.5 Hz), 2.46 (s, 3H), 3.80 (s, 3H), 4.31 (d, 2H, *J* = 2.5 Hz), 6.50 (s, 1H), 6.76 (d, 2H, *J* = 9.0 Hz), 7.09-7.89 (m, 13H). *The following signals were assigned to Z-isomer*: 2.26 (t, 1H, *J* = 2.5 Hz), 2.35 (s, 3H), 3.88 (s, 3H), 4.60 (d, 2H, *J* = 2.5 Hz), 6.92 (d, 2H, *J* = 9.0 Hz), 7.09 (s, 1H), 7.09-7.89 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 21.6, 38.7, 55.3, 73.9, 77.6, 113.5, 124.0, 127.9, 128.2, 129.4, 129.8, 131.4, 134.3, 136.6, 144.4, 146.8, 163.3, 191.5. *The following signals were assigned to Z-isomer*: 21.5, 41.1, 55.5, 73.8, 78.4, 113.6, 120.6, 127.8, 128.4, 128.5, 129.2, 130.2, 130.7, 136.4, 138.5, 143.6, 149.1, 163.4, 186.5. FAB-LM *m/z*: 446 (M^++1). FAB-HM Calcd for $C_{26}H_{24}NO_4S$: 446.1437, Found: 446.1426.

A typical procedure for preparation of enaminoketone 5

To a solution of *N*-propargyl *p*-toluenesulfonamide derivative (2 mmol) and α,β-ynoate (4 mmol) in benzene (4 mL) was added 1,4-diaza-bicyclo[2.2.2]octane (DABCO, 22.4～44.8 mg, 0.2～0.4 mmol), and mixture was refluxed until the consumption of starting material (by TLC analysis). After concentration of the reaction mixture to dryness, purification by silica gel column chromatography (hexane/AcOEt =95/5) gave **5a-f**.

Diethyl (2*E*)-2-{[(4-methylphenyl)sulfonyl](prop-2-yn-1-yl)amino}but-2-enedioate (5a, *E:Z*=69:31**):** Colorless oil. IR (neat) ν cm^{-1}; 1738, 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.27 (t, 3H, *J* = 7.1 Hz), 1.35 (t, 3H, *J* = 7.1 Hz), 2.18 (t, 1H, *J* = 2.6 Hz), 2.43 (s, 3H), 4.17 (q, 2H, *J* = 7.1 Hz), 4.33 (d, 2H, *J* = 2.6 Hz), 4.35 (q, 2H, *J* = 7.1 Hz), 5.87 (s, 1H), 7.32 (d, 2H, *J* = 8.4 Hz), 7.85 (d, 2H, *J* = 8.4 Hz). *The following signals were assigned to Z-isomer*: 1.22 (t, 3H, *J* = 7.1 Hz), 1.29 (t, 3H, *J* = 7.1 Hz), 2.25 (t, 1H, *J* = 2.6 Hz), 2.42 (s, 3H), 4.18 (q, 4H, *J* = 7.1 Hz), 4.33 (d, 2H, *J* = 2.6 Hz), 7.00 (s, 1H), 7.28 (d, 2H, *J* = 8.4 Hz), 7.71 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.5, 13.9, 21.5, 38.9, 60.7, 62.3, 75.0, 75.6, 109.9, 128.0, 129.5, 134.6, 143.6, 144.9, 163.1, 164.6.

The following signals were assigned to Z-isomer: 13.7, 13.8, 21.4, 39.3, 61.2, 62.2, 74.2, 127.6, 129.3, 129.9, 135.9, 136.5, 143.9, 163.4. FAB-LM *m/z*: 380 (M^++1). FAB-HM Calcd for $C_{18}H_{22}NO_6S$: 380.1168, Found: 380.1173. Anal. Calcd for $C_{18}H_{21}NO_6S$: C, 56.98; H, 5.58; N, 3.69. Found: C, 57.20; H, 5.63; N, 3.59.

Eethyl (2*E*)-3-{[(4-methylphenyl)sulfonyl](prop-2-yn-1-yl)amino}-3-phenylprop-2-enoate (5b, *E*:*Z*=76:24**):** Colorless oil. IR (neat) ν cm^{-1}; 1722. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.05 (t, 3H, *J* = 7.1 Hz), 2.27 (t, 1H, *J* = 2.5 Hz), 2.45 (s, 3H), 3.97 (q, 2H, *J* = 7.1 Hz), 4.25 (d, 2H, *J* = 2.5 Hz), 6.05 (s, 1H), 7.07-7.39 (m, 7H), 7.72-7.80 (m, 2H). *The following signals were assigned to Z-isomer*: 1.25 (t, 3H, *J* = 7.1 Hz), 2.30 (t, 1H, *J* = 2.5 Hz), 2.40 (s, 3H), 4.07 (q, 2H, *J* = 7.1 Hz), 4.61 (d, 2H, *J* = 2.5 Hz), 6.19 (s, 1H), 7.07-7.39 (m, 7H), 7.54-7.61 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.8, 21.5, 38.6, 60.1, 73.7, 77.6, 114.9, 127.8, 127.9, 129.1, 129.2, 129.6, 133.9, 136.3, 144.3, 151.1, 165.4. *The following signals were assigned to Z-isomer*: 14.0, 21.4, 41.2, 60.4, 73.9, 78.3, 117.0, 127.7, 128.2, 128.3, 129.5, 130.2, 136.8, 137.4, 143.6, 150.9, 163.5. FAB-LM *m/z*: 384 (M^++1). FAB-HM Calcd for $C_{21}H_{22}NO_4S$: 384.1270, Found: 384.1281. Anal. Calcd for $C_{21}H_{21}NO_4S$: C, 65.78; H, 5.52; N, 3.65. Found: C, 66.03; H, 5.66; N, 3.41.

Ethyl (2*E*)-3-{[(4-methylphenyl)sulfonyl](prop-2-yn-1-yl)amino}but-2-enoate (5c, *E* only**):** Colorless oil. IR (neat) ν cm^{-1}; 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.26 (t, 3H, *J* = 7.1 Hz), 2.30 (t, 1H, *J* = 2.5 Hz), 2.32 (d, 3H, *J* = 0.9 Hz), 2.43 (s, 3H), 4.14 (q, 2H, *J* = 7.1 Hz), 4.37 (q, 2H, *J* = 2.5 Hz), 5.81 (d, 1H, *J* = 0.9 Hz), 7.31 (d, 2H, *J* = 8.6 Hz), 7.74 (d, 2H, *J* = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.0, 17.7, 21.3, 38.4, 59.9, 73.9, 77.4, 114.0, 127.4, 129.5, 135.7, 144.2, 152.4, 165.9. FAB-LM *m/z*: 322 (M^++1). FAB-HM Calcd for $C_{16}H_{20}NO_4S$: 322.1113, Found: 322.1119. Anal. Calcd for $C_{16}H_{19}NO_4S$: C, 59.79; H, 5.96; N, 4.36. Found: C, 59.54; H, 6.03; N, 4.26.

Ethyl (2*E*)-3-{but-2-yn-1-yl[(4-methylphenyl)sulfonyl]amino}but-2-enoate (5d, *E* only**):** Colorless oil. IR (neat) ν cm^{-1}; 1714. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.27 (t, 3H, *J* = 7.1 Hz), 1.75 (t, 3H, *J* = 2.4 Hz), 2.17 (s, 3H), 2.33 (d, 3H, *J* = 0.9 Hz), 2.43 (s, 3H), 4.14 (q, 2H, *J* = 7.1 Hz), 4.32 (q, 2H, *J* = 2.4 Hz), 5.81 (d, 1H, *J* = 0.9 Hz), 7.30 (d, 2H, *J* = 8.6 Hz), 7.74 (d, 2H, *J* = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 3.5, 14.2, 18.0, 21.5, 39.3, 60.0, 72.9, 81.8, 113.6, 127.7, 129.5, 136.2, 144.1, 153.1, 166.4. FAB-LM *m/z*: 336 (M^++1). FAB-HM Calcd for $C_{17}H_{22}NO_4S$: 336.1270, Found: 336.1272. Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31; N, 4.18. Found: C, 60.55; H, 6.29; N, 4.35.

Ethyl (2*E*)-3-{[(4-methylphenyl)sulfonyl](3-phenylprop-2-yn-1-yl)amino}but-2-enoate (5e, *E* only**):** Colorless oil. IR (neat) ν cm^{-1}; 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.26 (t, 3H, *J* = 7.1 Hz), 2.39 (s, 3H), 2.44 (s, 3H), 2.40 (d, 3H, *J* = 0.9 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 4.60 (s, 2H), 5.90 (d, 1H, *J* = 0.9 Hz), 7.25-7.32 (m, 8H), 7.79 (d, 2H, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.1, 18.1, 21.3, 39.6, 59.9, 82.9, 85.6, 114.1, 121.9, 127.5, 128.1, 128.5, 129.5, 131.4, 135.9, 144.1, 152.8, 166.1. FAB-LM *m/z*: 398 (M^++1). FAB-HM Calcd for $C_{22}H_{24}NO_4S$: 398.1426, Found: 398.1423.

Ethyl (2*E*)-3-{(1-ethynylhexyl)[(4-methylphenyl)sulfonyl]amino}but-2-enoate (5f, *E* only**):** Colorless oil. IR (neat) ν cm^{-1}; 1720. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.89 (t, 3H, *J* = 6.9 Hz), 1.28 (t, 3H, *J* = 7.1 Hz), 1.23-1.55 (m, 6H), 1.64-1.76 (m, 2H), 2.24 (t, 1H, *J* = 2.4 Hz), 2.31 (d, 3H, *J* = 1.1 Hz), 2.43 (s, 3H), 4.16 (q, 2H, *J* = 7.1 Hz), 4.86 (td, 2H, *J* = 7.8, 2.4 Hz), 5.91 (q, 2H, *J* = 1.1 Hz), 7.28 (d, 2H, *J* = 8.3 Hz), 7.75 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 13.8, 14.0, 21.3, 21.4, 22.3, 25.7, 30.9, 34.5, 50.8, 60.2, 74.3, 81.4, 122.8, 127.9, 129.2, 136.2, 143.7, 150.9, 165.5. FAB-LM *m/z*: 392 (M^++1). FAB-HM Calcd for $C_{21}H_{30}NO_4S$:

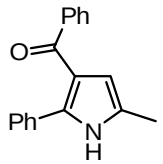
392.1896, Found: 392.1909. Anal. Calcd for $C_{21}H_{29}NO_4S$: C, 64.42; H, 7.47; N, 3.58. Found: C, 64.44; H, 7.42; N, 3.48.

Ethyl (2*E*)-3-(prop-2-yn-1-yloxy)but-2-enoate (8b, *E* only): As well as the typical procedure for **5**, the treatment of a solution of ethyl but-2-ynoate (0.47 mL, 4 mmol) and 2-propyn-1-ol (0.7 mL, 12 mmol) in refluxed benzene (4 mL) with DABCO (90 mg, 0.8 mmol) for 18 h gave **8b** (612 mg, 91%) as a colorless oil. IR (neat) ν cm^{-1}; 1711. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.27 (t, 3H, *J* = 7.1 Hz), 2.31 (s, 3H), 2.56 (t, 1H, *J* = 2.4 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 4.48 (q, 2H, *J* = 2.4 Hz), 5.09 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.0, 18.4, 55.4, 59.1, 76.0, 76.8, 92.3, 167.0, 170.3. FAB-LM *m/z*: 169 (M^++1). FAB-HM Calcd for $C_9H_{13}O_3$: 169.0865, Found: 169.0859.

Ethyl (2*E*)-3-(but-2-yn-1-yloxy)but-2-enoate (8c, *E* only): As well as the typical procedure for **5**, the treatment of a solution of ethyl but-2-ynoate (0.47 mL, 4 mmol) and 2-butyn-1-ol (0.9 mL, 12 mmol) in refluxed benzene (4 mL) with DABCO (90 mg, 0.8 mmol) for 18 h gave **8b** (694 mg, 95%) as a white solid. Mp 42 ℃. IR (KBr) ν cm^{-1}; 1706. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.22 (t, 3H, *J* = 7.1 Hz), 1.82 (t, 3H, *J* = 2.3 Hz), 4.08 (q, 2H, *J* = 2.4 Hz), 4.39 (q, 2H, *J* = 7.1 Hz), 5.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 3.5, 14.3, 18.8, 56.4, 59.3, 72.5, 84.3, 92.2, 167.5, 170.9. FAB-LM *m/z*: 183 (M^++1). FAB-HM Calcd for $C_{10}H_{15}O_3$: 183.1021, Found: 183.1011.

Ethyl (2*E*)-3-[(3-phenylprop-2-yn-1-yl)oxy]but-2-enoate (8d, *E* only): As well as the typical procedure for **5**, the treatment of a solution of 3-phenyl2-propyn-1-ol (0.25 mL, 2 mmol) and ethyl but-2-ynoate (0.47 mL, 4 mmol) in refluxed benzene (4 mL) with DABCO (45 mg, 0.4 mmol) for 18 h gave **8b** (217 mg, 89%) as a colorless oil. IR (neat) ν cm^{-1}; 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.28 (t, 3H, *J* = 7.1 Hz), 2.35 (s, 3H), 4.15 (q, 2H, *J* = 7.1 Hz), 4.71 (s, 2H), 5.17 (s, 1H), 7.28-7.37 (m, 3H), 7.43-7.49 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.1, 18.6, 56.3, 59.2, 82.2, 87.4, 92.3, 121.8, 128.1, 128.6, 131.6, 167.2, 170.6. FAB-LM *m/z*: 245 (M^++1). FAB-HM Calcd for $C_{15}H_{17}O_3$: 245.1178, Found: 245.1174.

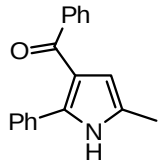
^{1}H-NMR


Ph
O
Ph
N
H

2a

2.50
6.71
7.54
7.28
7.73
7.38
7.75
7.56
7.41
7.25
7.47
7.17
7.14
2.02
2.07
2.14
1.18
1.00
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

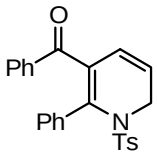
^{13}C-NMR


Ph
O
Ph
N
H

2a

123.75
128.78
128.43
129.01
77.52
77.10
76.68
127.78
106.55
132.27
14.39
129.97
139.15
158.97
122.38
151.61
191.27
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

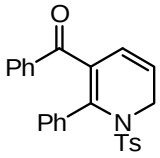
^{1}H-NMR


O
Ph
Ph
N
Ts

3a

2.43
7.49
7.47
7.50
7.24
7.24
7.09
7.16
7.52
7.25
7.07
7.26
7.30
7.33
7.05
7.04
6.09
6.06
5.53
5.55
5.52
5.56
5.50
4.65
4.66
4.64
4.64
4.91
11.99
1.00
1.07
2.07
3.63
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

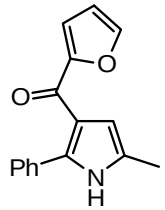
^{13}C-NMR


O
Ph
Ph
N
Ts

3a

127.96
127.45
129.26
130.41
77.01
77.43
76.59
124.76
119.18
132.61
21.59
46.24
144.08
135.48
136.92
196.00
141.81
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

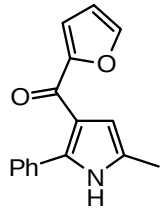
^{1}H-NMR


O
O
Ph
N
H

2b

2.60
6.71
7.82
7.48
7.85
7.82
7.5
7.41
7.42
6.58
6.59
6.47
7.57
6.47
6.46
6.46
7.26
2.02
4.09
0.93
0.96
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

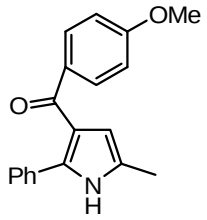
^{13}C-NMR


O
O
Ph
N
H

2b

128.98
128.39
77.01
77.43
76.59
105.79
111.42
106.48
142.12
132.30
14.22
138.90
144.17
158.80
145.55
121.86
190.99
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

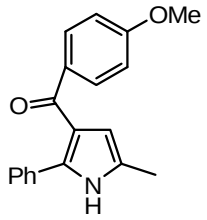
^{1}H-NMR


OMe
O
Ph
N
H

2c

3.84
2.59
7.57
7.60
7.83
7.85
7.82
7.49
7.26
7.46
6.94
6.91
6.67
2.01
1.99
2.04
0.95
3.06
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

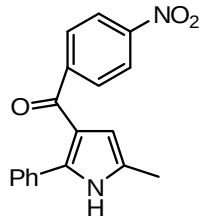
^{13}C-NMR


OMe
O
Ph
N
H

2c

128.32
114.16
125.16
128.92
55.26
132.11
104.84
14.28
77.01
77.43
76.59
159.30
151.62
158.27
139.16
122.90
122.26
191.32
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

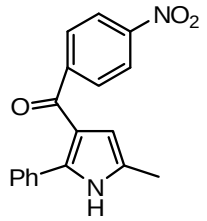
^{1}H-NMR


NO2
O
Ph
N
H

2d

2.64
8.24
8.27
7.80
7.77
7.82
7.51
7.26
7.04
7.84
7.85
7.54
7.61
7.49
2.02
4.10
2.07
1.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

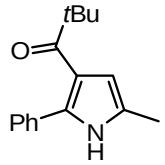
^{13}C-NMR


NO2
O
Ph
N
H

2d

77.44
77.01
76.58
123.92
124.39
128.96
128.56
132.59
110.41
14.45
138.67
135.58
122.94
160.80
149.31
146.67
190.72
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

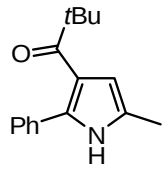
^{1}H-NMR


tBu
O
Ph
N
H

2e

1.28
2.47
6.14
7.77
7.52
7.78
7.51
7.80
7.48
7.45
7.43
7.80
7.54
7.44
7.43
7.26
2.03
3.15
1.00
3.05
9.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

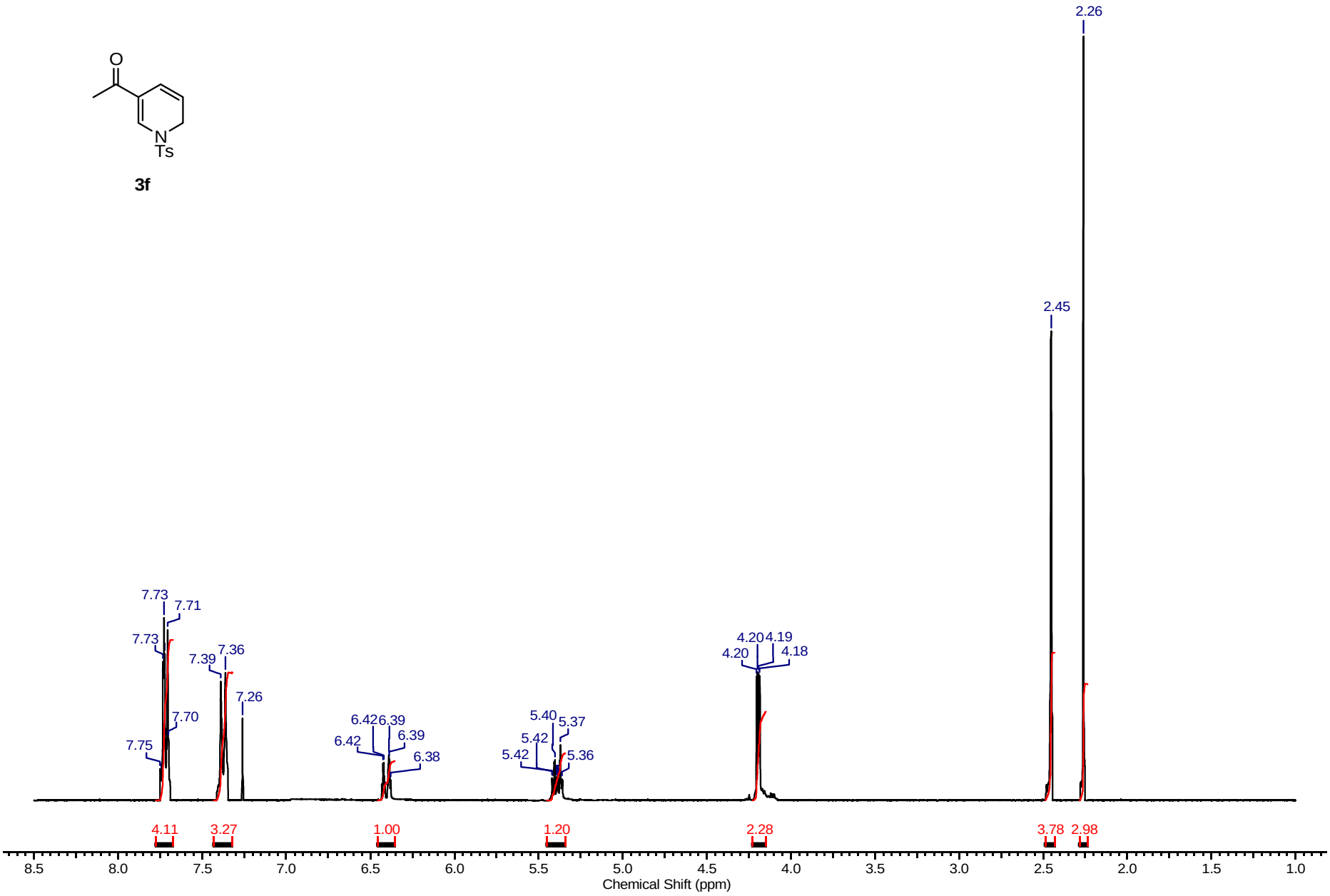
^{13}C-NMR


tBu
O
Ph
N
H

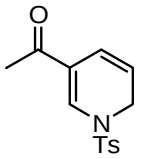
2e

28.85
128.23
128.83
103.81
131.85
14.28
77.01
77.44
76.58
32.34
161.98
139.45
157.76
120.88
191.66
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

^{1}H-NMR


O
N
Ts
3f
2.26
2.45
7.73
7.71
7.73
7.39
7.36
7.26
7.70
7.75
6.42
6.39
6.42
6.39
6.38
5.40
5.37
5.42
5.42
5.36
4.20
4.19
4.20
4.18
4.11
3.27
1.00
1.20
2.28
3.78
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

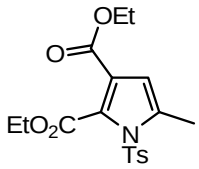
^{13}C-NMR


O
N
Ts

3f

77.01
77.44
76.59
127.57
130.27
136.53
119.79
116.10
145.35
193.36
133.15
117.19
44.27
24.62
21.65
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

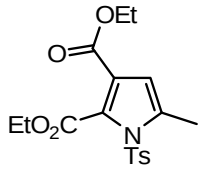
^{1}H-NMR


OEt
O
EtO2C
N
Ts

6a

2.41
2.27
1.42
1.29
1.44
1.31
1.26
4.47
4.44
4.25
4.23
4.49
4.42
4.20
7.91
7.94
7.34
7.31
7.26
6.27
6.26
2.06
2.14
1.00
2.10
2.12
3.12
3.14
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

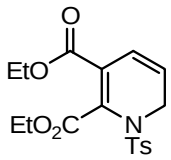
^{13}C-NMR


OEt
O
EtO2C
N
Ts

6a

13.80
130.11
127.72
77.01
77.43
76.59
111.84
64.64
62.63
14.10
21.65
131.51
145.89
134.95
116.96
162.46
162.67
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

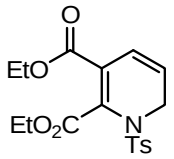
^{1}H-NMR


O
EtO
EtO2C
N
Ts

7a

2.41
1.38
1.27
1.41
1.30
1.25
7.73
7.75
7.29
7.26
4.37
4.34
4.21
4.19
4.27
6.15
6.11
5.41
5.38
5.39
4.39
4.17
2.18
2.23
1.00
1.08
2.30
2.48
4.17
3.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

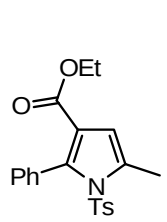
^{13}C-NMR


O
EtO
EtO2C
N
Ts

7a

129.69
127.24
77.01
77.43
76.59
122.11
120.18
61.41
62.28
44.68
13.86
13.76
21.56
144.59
135.87
164.79
163.62
136.05
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

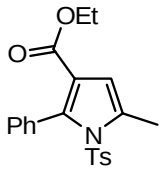
^{1}H-NMR


OEt
O
Ph
N
Ts

6b

2.35
2.53
0.94
7.23
7.26
7.14
7.07
7.04
7.04
7.33
6.41
3.96
3.93
3.98
3.91
0.97
0.92
4.13
1.99
1.00
2.08
3.10
3.13
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

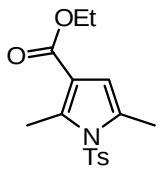
^{13}C-NMR


OEt
O
Ph
N
Ts

6b

129.54
126.93
131.52
126.75
112.48
77.01
76.58
77.44
15.81
13.72
21.52
59.77
132.77
144.93
136.40
139.41
163.50
117.84
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

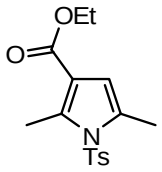
^{1}H-NMR


OEt
O
N
Ts

6c

2.41
2.72
1.30
1.33
1.28
4.24
4.22
7.59
7.61
7.31
7.29
7.26
6.29
4.27
4.19
2.04
2.09
1.00
2.14
3.11
6.34
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

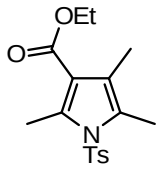
^{13}C-NMR


OEt
O
N
Ts

6c

77.01
76.59
77.43
130.08
126.48
13.26
14.32
15.56
112.26
59.98
21.59
131.58
145.11
138.61
136.74
115.65
164.54
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

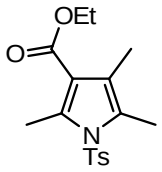
^{1}H-NMR


OEt
O
N
Ts

6d

2.69
2.41
2.07
2.32
1.33
7.26
7.56
7.59
7.30
4.28
4.25
4.30
4.23
1.35
1.31
2.01
2.10
2.26
3.00
3.02
3.03
3.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

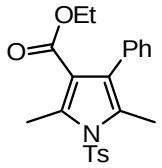
^{13}C-NMR


OEt
O
N
Ts

6d

129.96
126.30
13.48
12.24
14.21
11.05
59.90
21.47
77.01
77.44
76.58
144.81
137.38
127.48
119.18
165.37
136.90
116.76
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

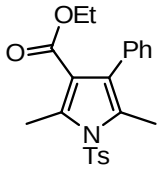
^{1}H-NMR


OEt
O
Ph
N
Ts

6e

2.74
2.28
2.44
0.88
7.33
7.67
7.35
7.30
7.69
7.14
7.12
7.29
7.27
3.99
3.97
4.01
3.95
0.91
0.86
1.96
5.34
2.01
2.00
2.98
3.04
3.06
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

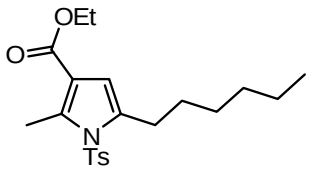
^{13}C-NMR


OEt
O
Ph
N
Ts

6e

77.01
77.44
76.59
130.14
126.63
127.62
59.92
13.53
13.20
21.63
145.16
136.97
134.91
125.68
165.02
116.86
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

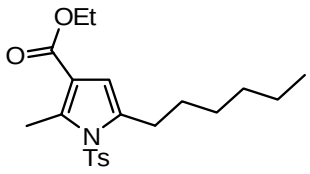
^{1}H-NMR


OEt
O
N
Ts

6f

2.11
2.07
1.00
2.17
2.99
3.28
2.77
10.48
3.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

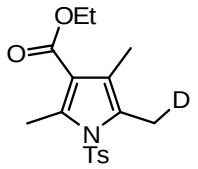
^{13}C-NMR


OEt
O
N
Ts

6f

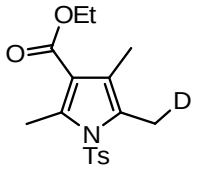
129.95
126.21
31.49
22.44
13.93
14.22
13.22
28.90
28.80
21.43
28.66
59.87
110.90
136.83
138.57
144.91
136.80
115.75
164.44
77.01
76.59
77.43
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

^{1}H-NMR



6d-D (50%D)

^{13}C-NMR



6d-D (50%D)