Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

One-pot synthesis of 1,3-enynes with CF_3 group on the terminal sp^2 carbon by Sonogashira cross-coupling reaction

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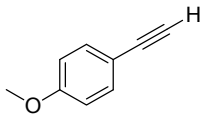
Supporting Information

Synthesis of starting arylacetylenes[1,2,3,4]:

To a mixture of aryl iodide (5.0 mmol), $PdCl_2(PPh_3)_2$ (175 mg, 5 mol%), CuI (48 mg, 5 mol%) and Et_3N (1.04 mL, 7.5 mmol) in dry THF (7.5 mL) was slowly added trimethylsilylacetylene (1.04 mL, 7.5 mmol). After the reaction mixture was stirred at room temperature for overnight, it was treated with standard aqueous wok-up and extraction by Et_2O. The organic layer was dried over anhydrous $MgSO_4$ and filtered the solid off. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the silylated arylacetylenes. The mixture of silylated arylacetylenes and K_2CO_3 (691 mg, 5.0 mmol) in dissolved in MeOH and H_2O was stirred at room temperature until staring silylated acetylenes were disappeared. Then, the mixture was extracted with CH_3Cl and dried over anhydrous $MgSO_4$. After filtration of the solid, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel chromatography to provide the arylacetylenes **2**.

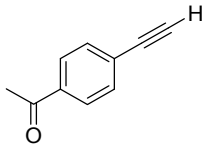
Spectroscopic Data of acetylenes:

1-ethynyl-4-methoxybenzene (**2d**);[5]



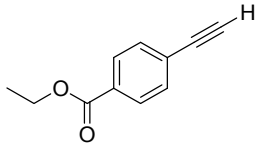
The title product (**2d**) was obtained as a light yellow oil (405 mg, 61% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). δ_H ($CDCl_3$, 400 MHz) 2.99 (1H, s), 3.81 (3H, s), 6.84 (2H, d, *J* 8.8Hz), 7.43 (2H, d, *J* 8.8Hz); δ_C ($CDCl_3$, 400 MHz) 55.3, 75.7, 83.7, 113.9, 114.2, 133.5, 159.9; *m/z* (EI) 132.0578 (M^+. C_9H_8O requires 132.0575).

1-(4-ethynylphenyl)ethanone (**2f**);[6]



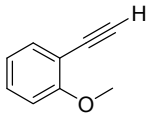
The title product (**2f**) was obtained as a light yellow solid (488 mg, 68% for 2 steps) after column chromatography (AcOEt : hexane = 10 : 90). mp 66-67 ^oC; δ_H ($CDCl_3$, 400 MHz) 2.61 (3H,s), 3.25 (1H, s), 7.58 (2H, d, *J* 8.3 Hz), 7.92 (2H, d, *J* 8.3 Hz); δ_C ($CDCl_3$, 400 MHz) 26.7, 80.3, 82.7, 126.8, 128.1, 132.2, 136.7, 197.1; *m/z* (EI) 144.0578 (M^+. $C_{10}H_8O$ requires 144.0575).

ethyl 4-ethynylbenzoate (**2g**);[7]



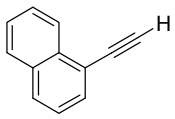
The title product (**2g**) was obtained as a light yellow oil (783 mg, 90% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). δ_H ($CDCl_3$, 400 MHz) 1.40 (3H, t, *J* 7.1 Hz), 3.23 (1H, s), 4.38 (2H, q, *J* 7.2 Hz), 7.55 (2H, d, *J* 8.3 Hz), 8.00 (2H, d, *J* 8.8 Hz); δ_C ($CDCl_3$, 400 MHz) 14.2, 61.2, 79.9, 82.6, 126.6, 129.4, 130.5, 132.0, 165.8; *m/z* (EI) 174.0680 (M^+. $C_{11}H_{10}O_2$ requires 174.0681).

1-ethynyl-2-methoxybenzene (**2h**);[5]



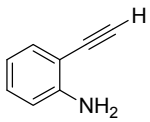
The title product (**2h**) was obtained as a light yellow oil (534 mg, 81% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). δ_H ($CDCl_3$, 400 MHz) 3.30 (1H, s), 3.90 (3H, s), 6.88-6.93 (2H, m), 7.30-7.35 (1H, m), 7.465 (1H, dd, *J* 1.8, 7.6 Hz); δ_C ($CDCl_3$, 400 MHz) 55.9, 80.1, 81.0, 110.7, 111.3, 120.4, 130.2, 134.1, 160.5; *m/z* (EI) 132.0568 (M^+. C_9H_8O requires 132.0575).

1-ethynylnaphthalene (**2i**);[5]



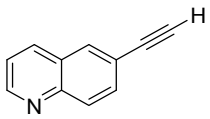
The title product (**2i**) was obtained as a light yellow oil (756 mg, 99% for 2 steps) after column chromatography (hexane 100%). δ_H ($CDCl_3$, 400 MHz) 3.46 (1H, s), 7.39-7.43 (1H, m), 7.49-7.54 (1H, m), 7.56-7.6 (1H, m), 7.74 (1H, d, *J* 6.8 Hz), 7.84 (2H, d, *J* 8.3 Hz), 8.36 (1H, d, *J* 8.3 Hz); δ_C ($CDCl_3$, 400 MHz) 81.7, 81.9, 119.7, 125.0, 126.0, 126.4, 126.9, 128.2, 129.2, 131.1, 133.0, 133.4; *m/z* (EI) 152.0620 (M^+. $C_{12}H_8$ requires 152.0626).

2-ethynylbenzenamine (**2j**);[5]



The title product (**2j**) was obtained as a yellow oil (245 mg, 42% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). δ_H ($CDCl_3$, 400 MHz) 3.37 (1H, s), 4.22 (2H, br s), 6.65-6.69 (2H, m), 7.13 (1H, td, *J* 1.3, 7.8Hz), 7.32 (1H, dd, 1.8, 8.1 Hz); δ_C ($CDCl_3$, 400 MHz) 80.6, 82.4, 106.5, 114.2, 117.7, 130.0, 132.5, 148.4; *m/z* (EI) 117.0577 (M^+. C_8H_7N requires 117.0578).

6-ethynylquinoline (**2k**);[8]



The title product (**2k**) was obtained as a light yellow solid (677 mg, 89% for 2 steps) after column chromatography (AcOEt : hexane = 10 : 90). mp 49-50 ^oC; δ_H ($CDCl_3$, 400 MHz) 3.19 (1H, s), 7.43 (1H, dd, *J* 3.9, 8.3 Hz), 7.77 (1H, dd, *J* 1.5, 8.8 Hz), 8.00 (1H, d, *J* 2.0 Hz), 8.06 (1H, d, *J* 8.8 Hz), 8.12 (1H, d, *J* 8.3 Hz), 8.9 (1H, dd, *J* 1.8, 4.2 Hz); δ_C ($CDCl_3$, 400 MHz) 78.4, 83.2, 120.4, 121.7, 127.8, 129.6, 132.0, 132.2, 135.7, 147.8, 151.2; *m/z* (EI) 153.0582 (M^+. $C_{11}H_7N$ requires 153.0578).

References:

[1] B. Zhou, H. Chen and C. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 1264.

[2] A. Pearson and J. B. Kim, *Tetrahedron Lett*., 2003, **44**, 8525; A. Molad, I. Goldberg and A. Vigalok, *J. Am. Chem. Soc.*, 2012, **134**, 7290; A. J. Lennox and G. C. Lloyd-Jones, *J. Am. Chem. Soc.*, 2012, **134**, 7431.

[3] S. Thorand and N. Krause, *J. Org. Chem.*, 1998, **63**, 8551; S. Goeb and R. Zissel, *Org. Lett.*, 2007, **9**, 737.

[4] U. Dutta, S. Maity, R. Lancherla and D. Maiti, *Org. Lett.*, 2014, **16**, 6302.

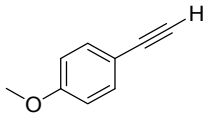
[5] H. Ueda, M. Yamaguchi, K. Sugimoto and H. Tokuyama, *Org. Lett.*, 2014, **16**, 4948.

[6] C. Xu, W. Du, Y. Zeng, B. Dai and H. Guo, *Org. Lett.,* 2014, **16**, 948.

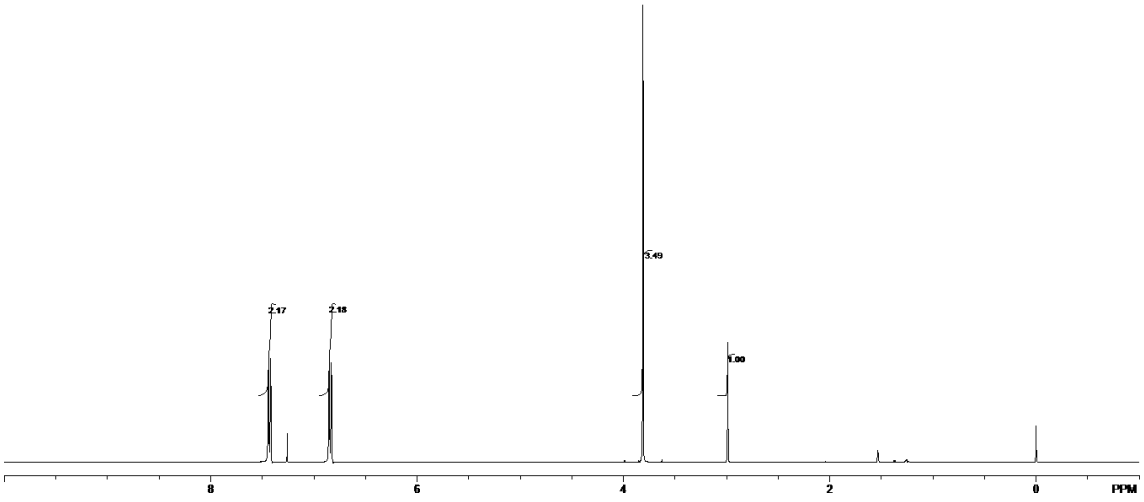
[7] M. Belema, V. N. Nguyen and C. Zusi, *Tetrahedron Lett.,* 2004, **45**, 1693.

[8] A. Maji, A. Hazta and D. Maiti, *Org. Lett.*, 2014, **16**, 4524.

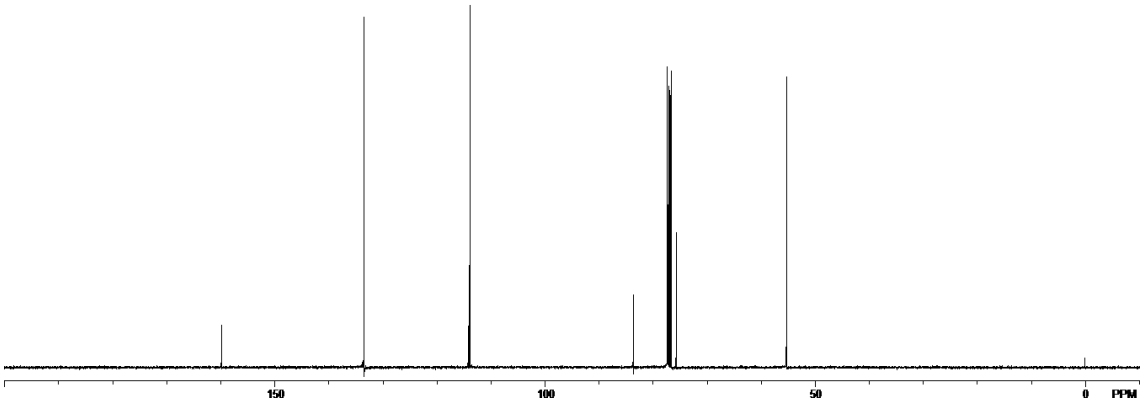
1-Ethynyl-4-methoxybenzene (**2d**);



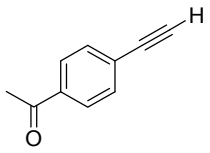
^{1}H NMR spectrum



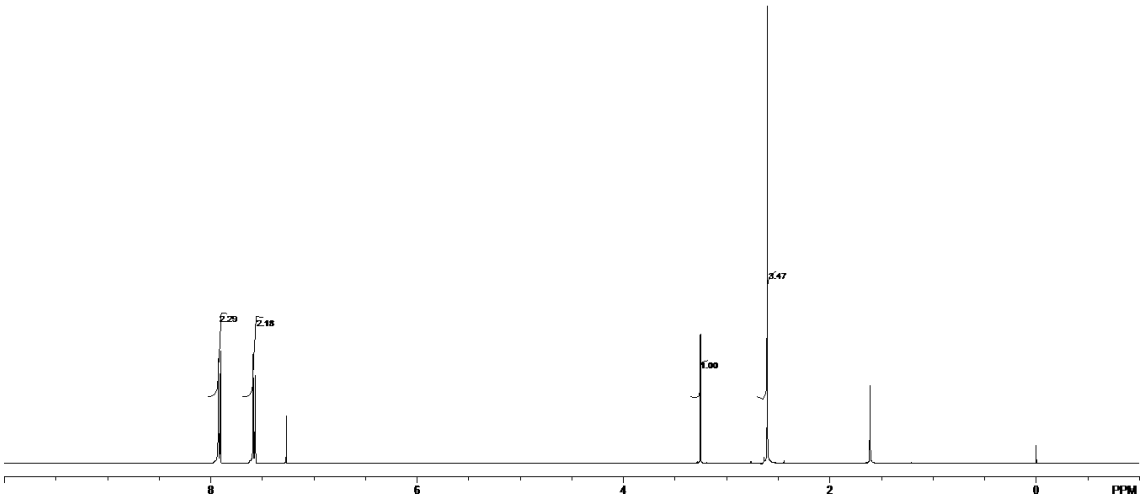
^{13}C NMR spectrum



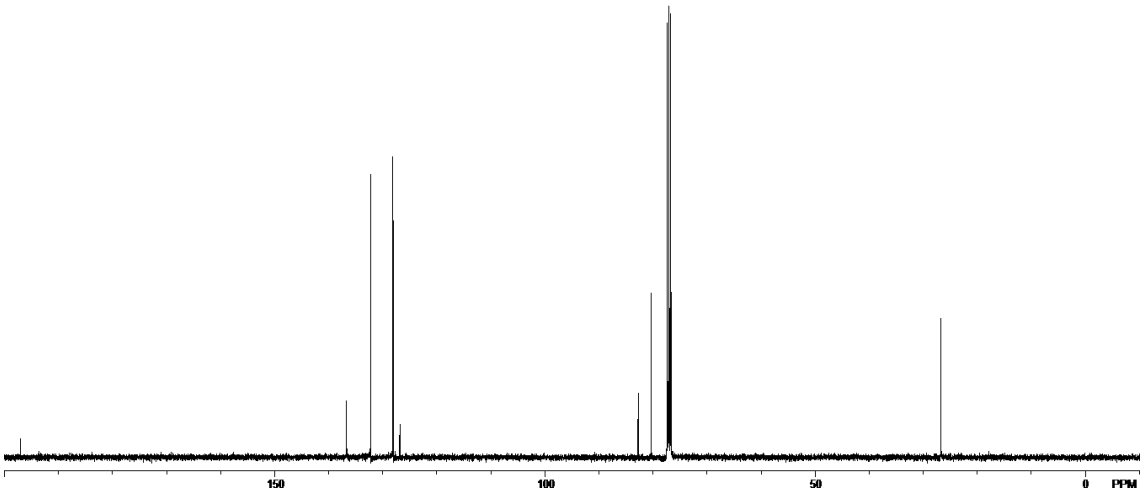
1-(4-Ethynylphenyl)ethanone (**2f**);



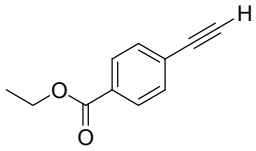
^{1}H NMR spectrum



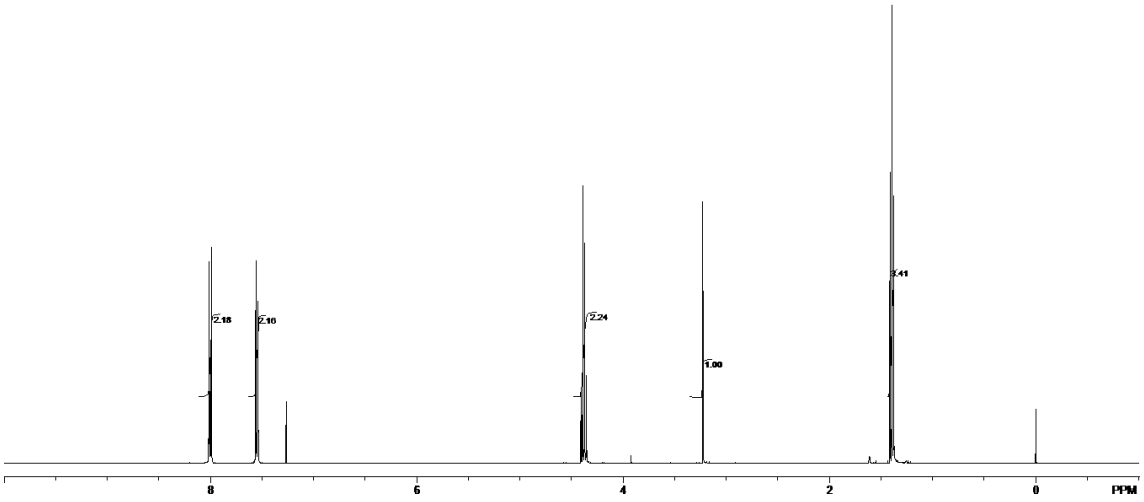
^{13}C NMR spectrum



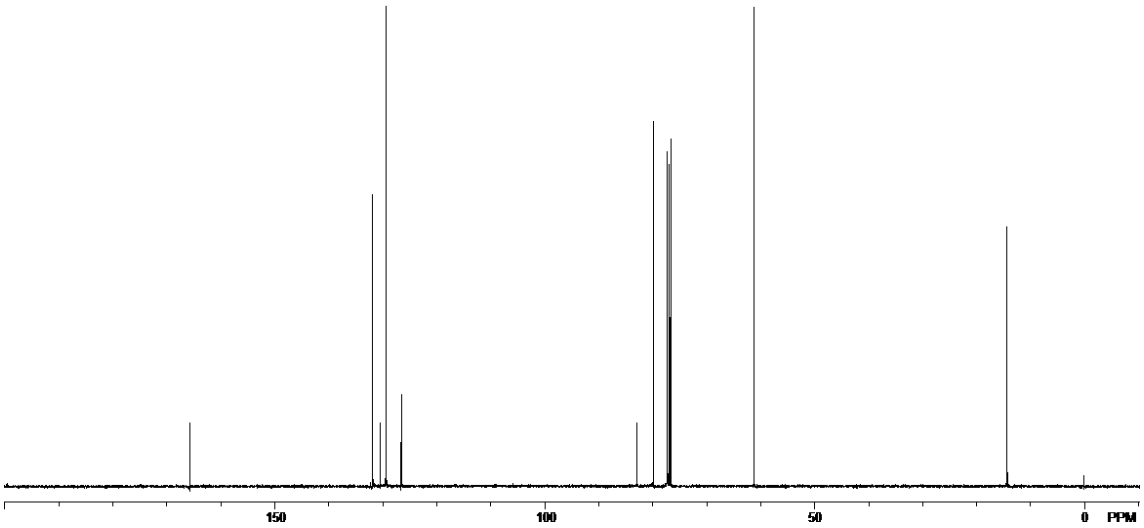
Ethyl 4-ethynylbenzoate (**2g**);



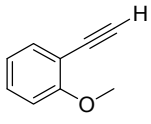
^{1}H NMR spectrum



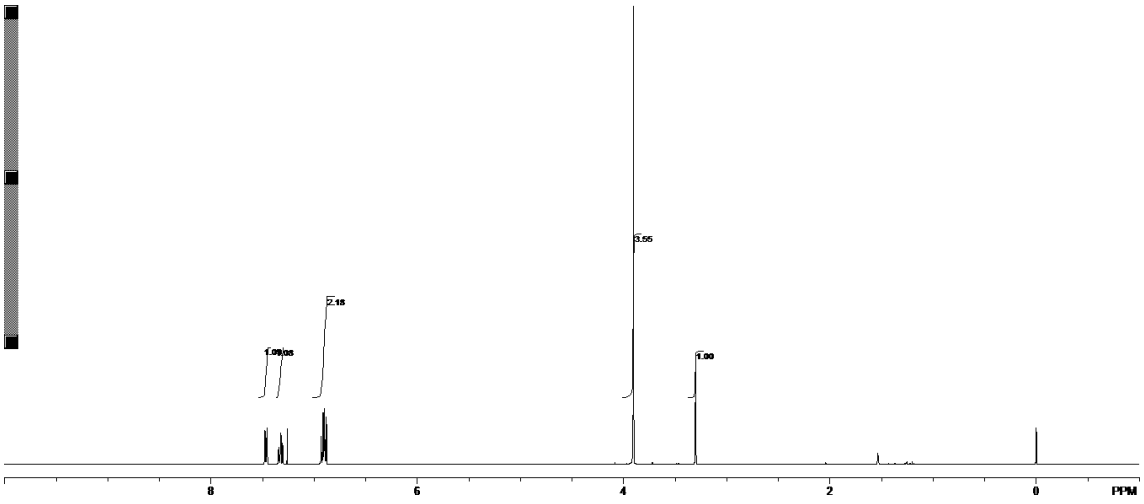
^{13}C NMR spectrum



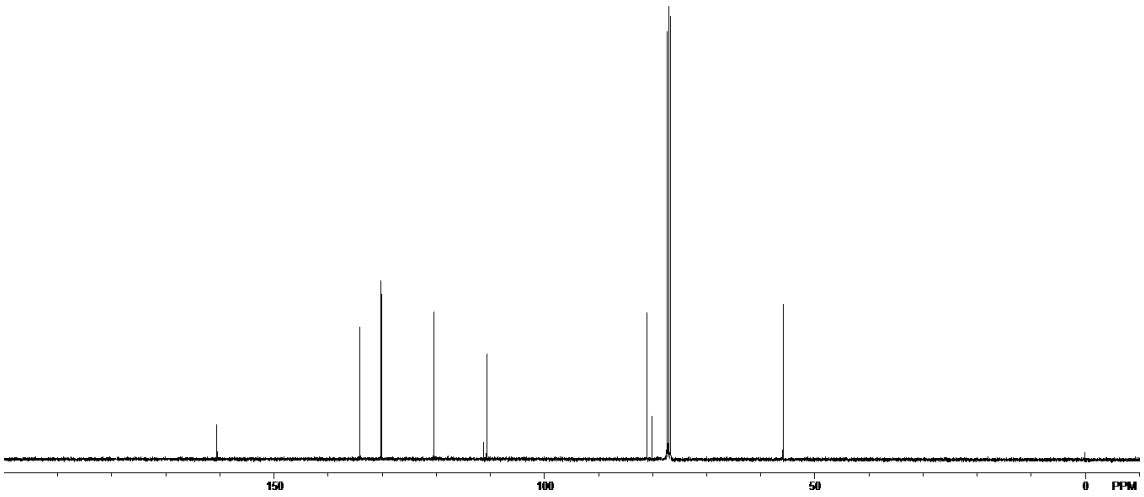
1-Ethynyl-2-methoxybenzene (**2h**);



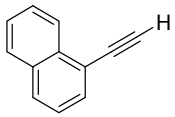
^{1}H NMR spectrum



^{13}C NMR spectrum



1-Ethynylnaphthalene (**2i**);



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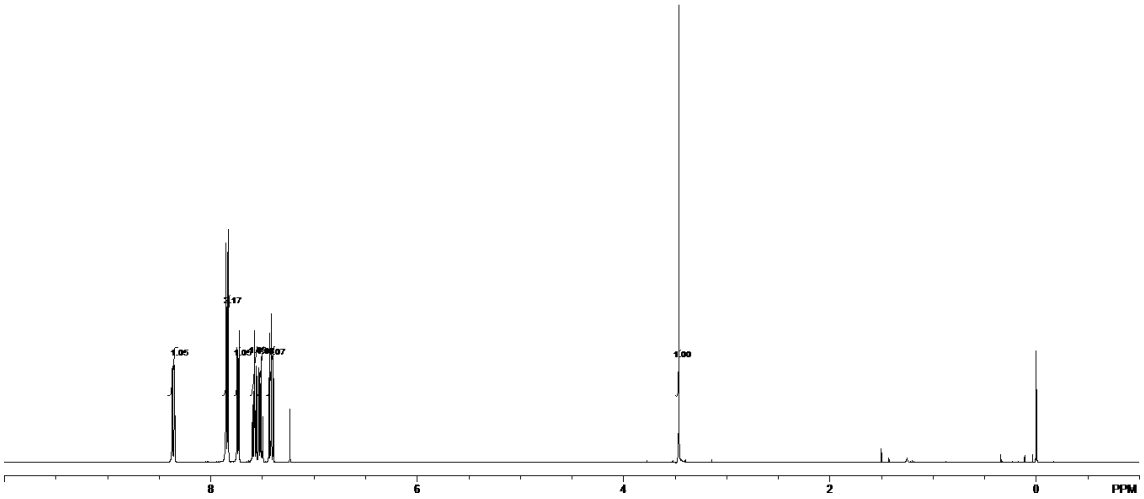

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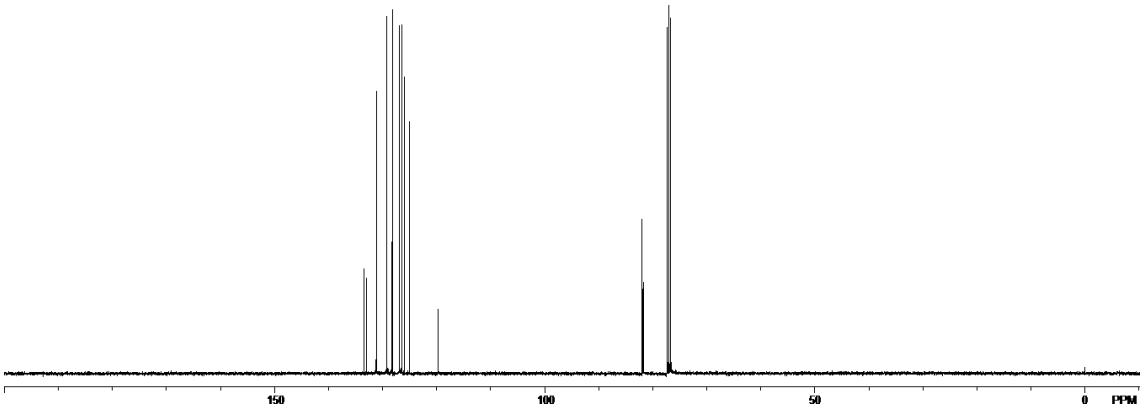
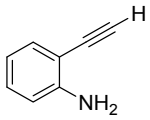


2-Ethynylbenzenamine (**2j**);



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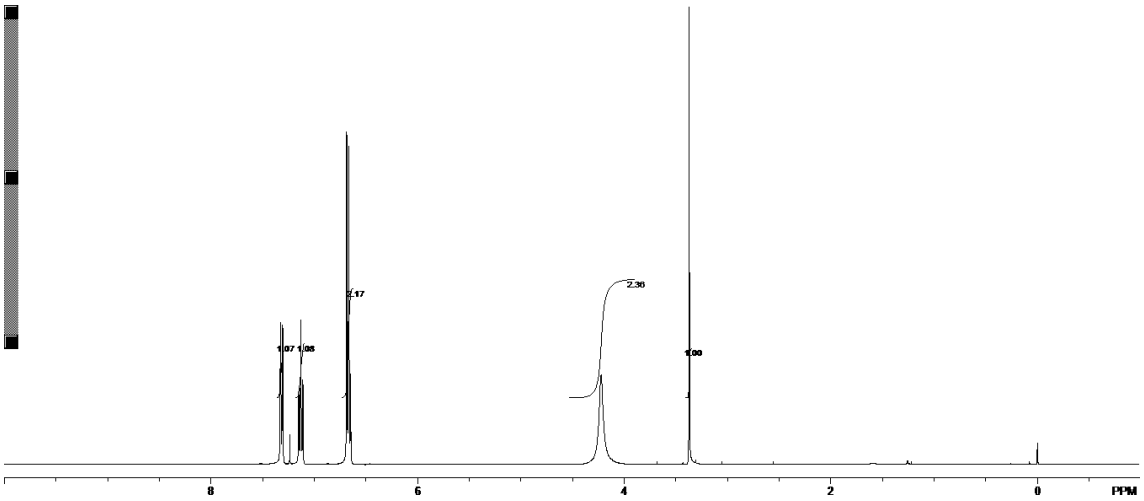

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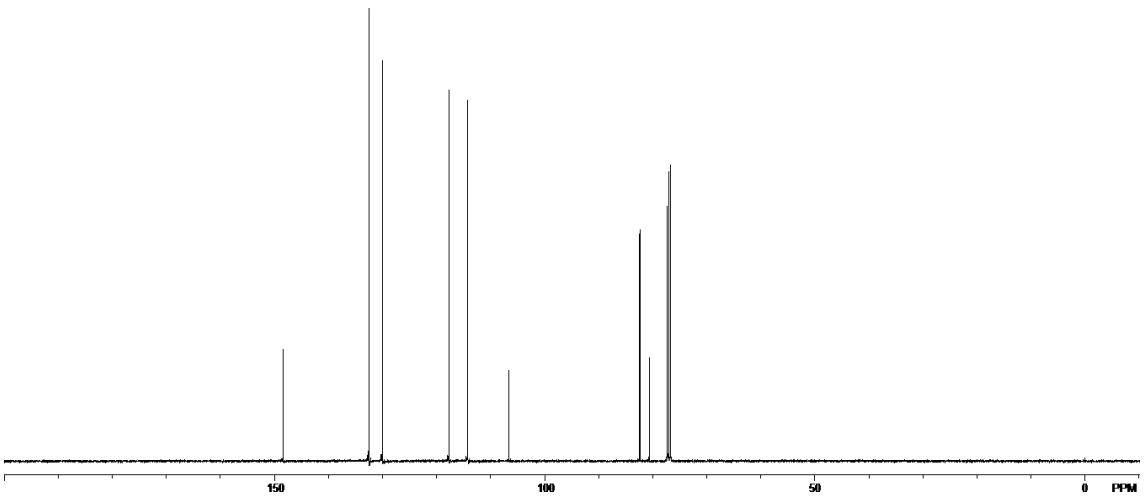
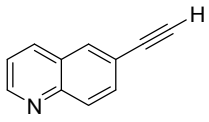
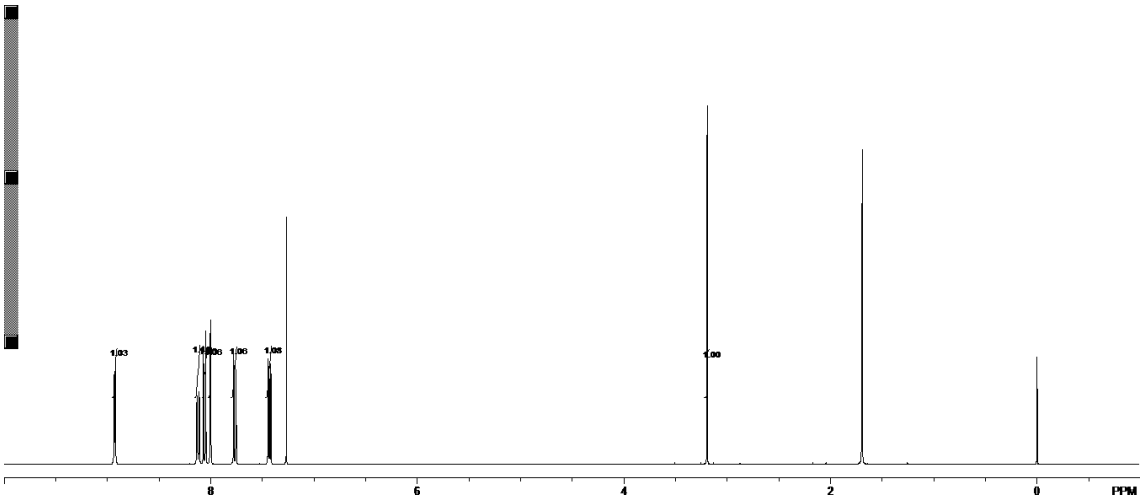


6-Ethynylquinoline (**2k**);



^{1}H NMR spectrum



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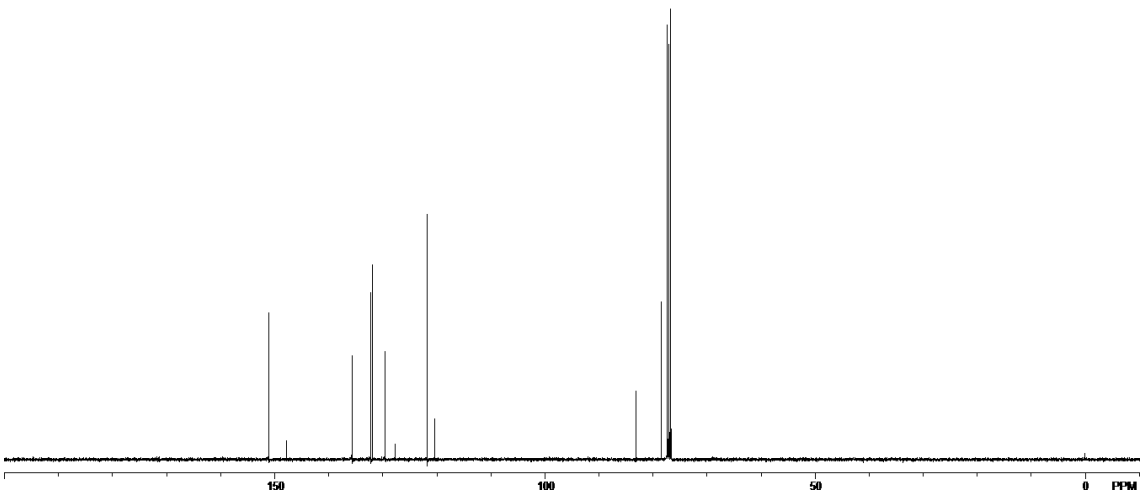
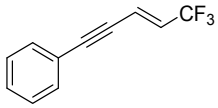
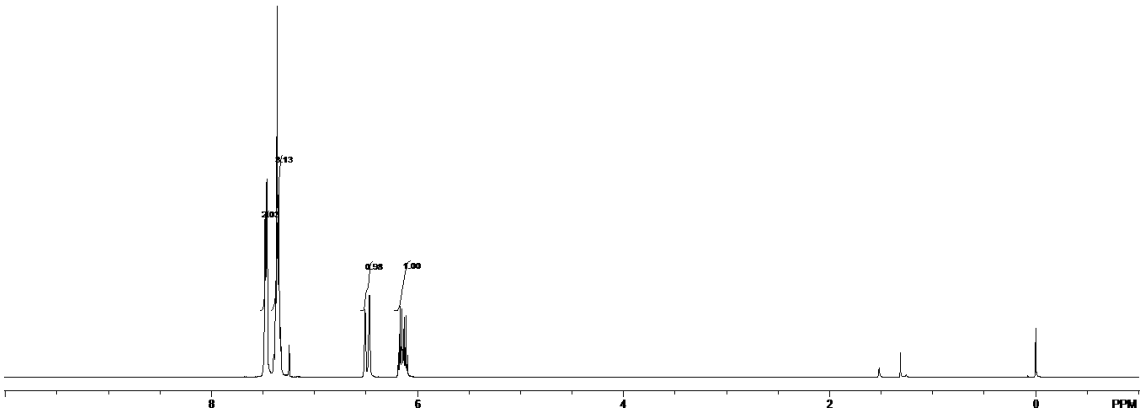


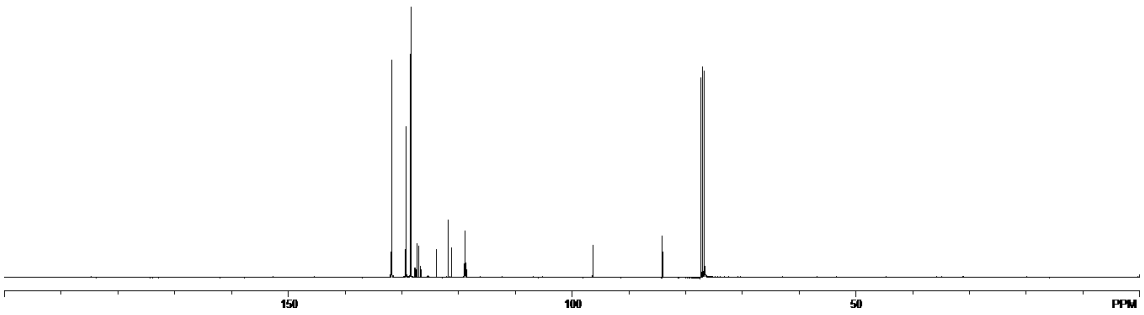
(*E*)-(5,5,5-Trifluoropent-3-en-1-ynyl)benzene (**3a**);



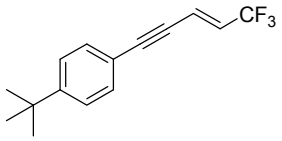
^{1}H NMR spectrum



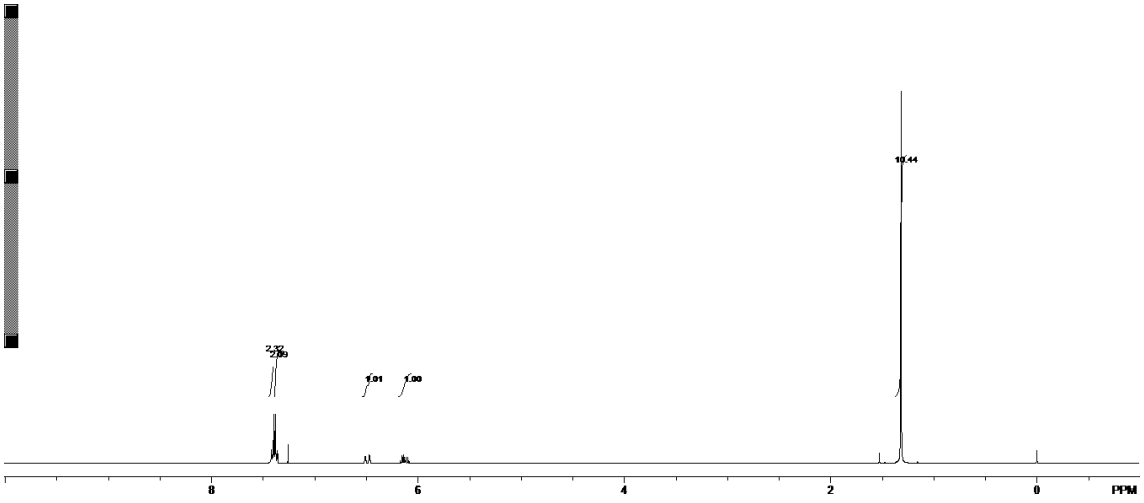
^{13}C NMR spectrum



(*E*)-1-*tert*-Butyl-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene (**3b**);



^{1}H NMR spectrum



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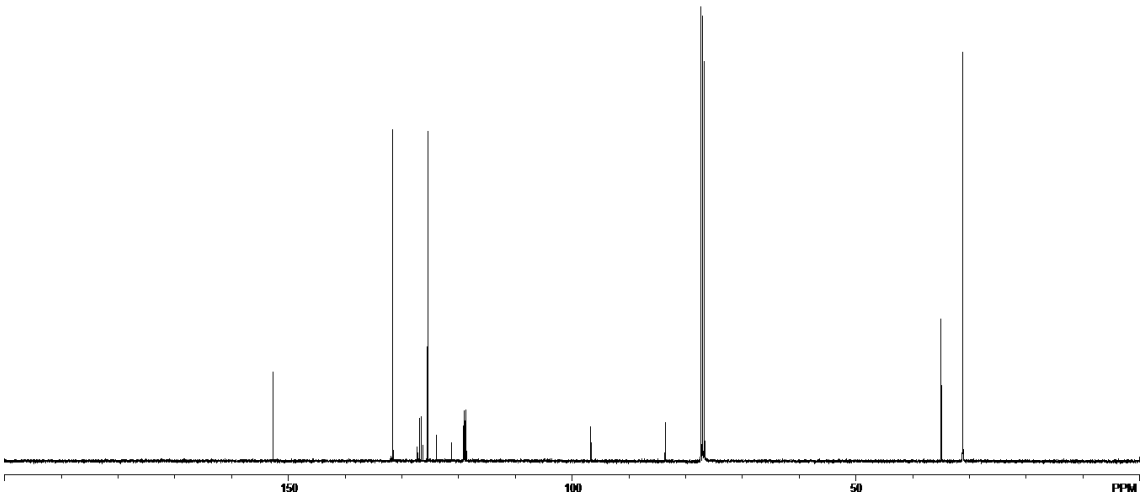
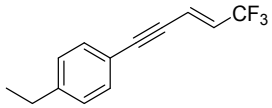
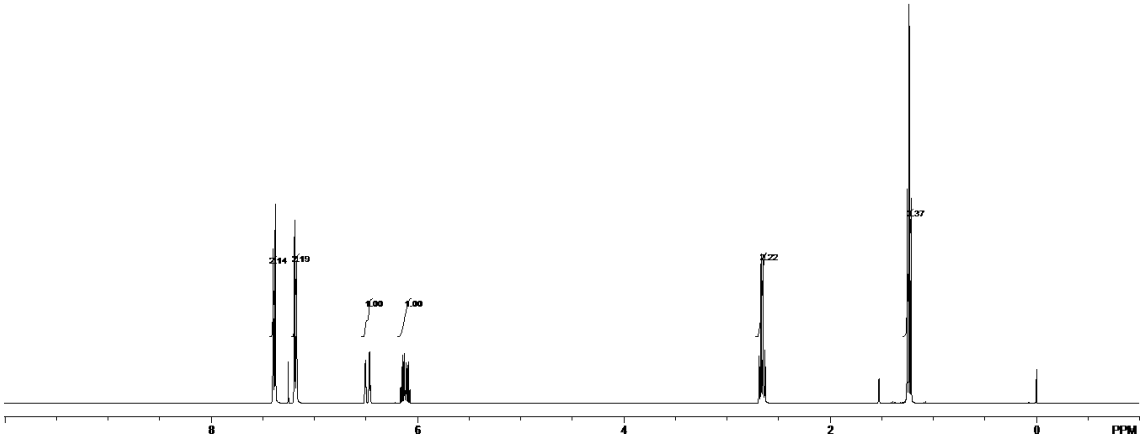


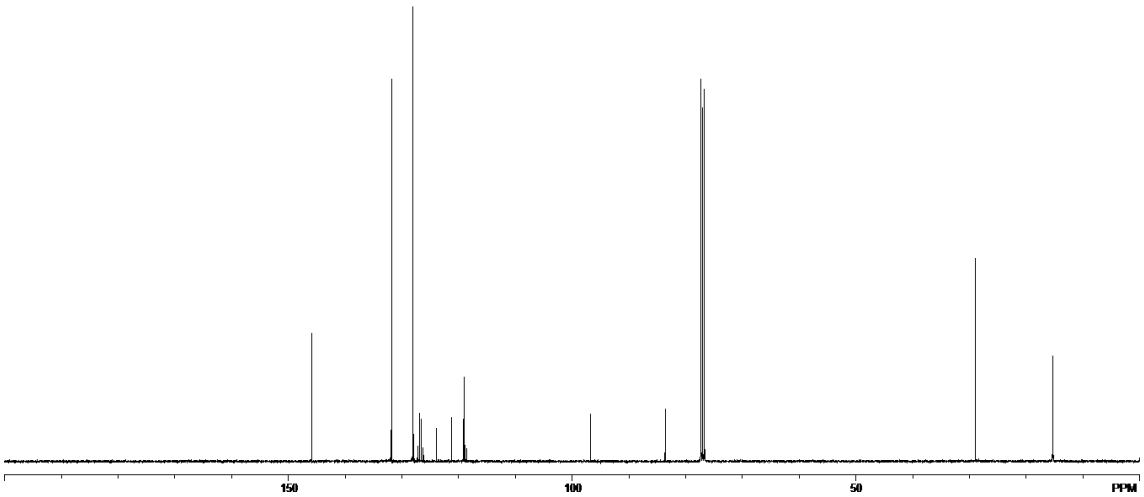
(*E*)-1-Ethyl-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene (**3c**);



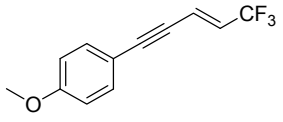
^{1}H NMR spectrum



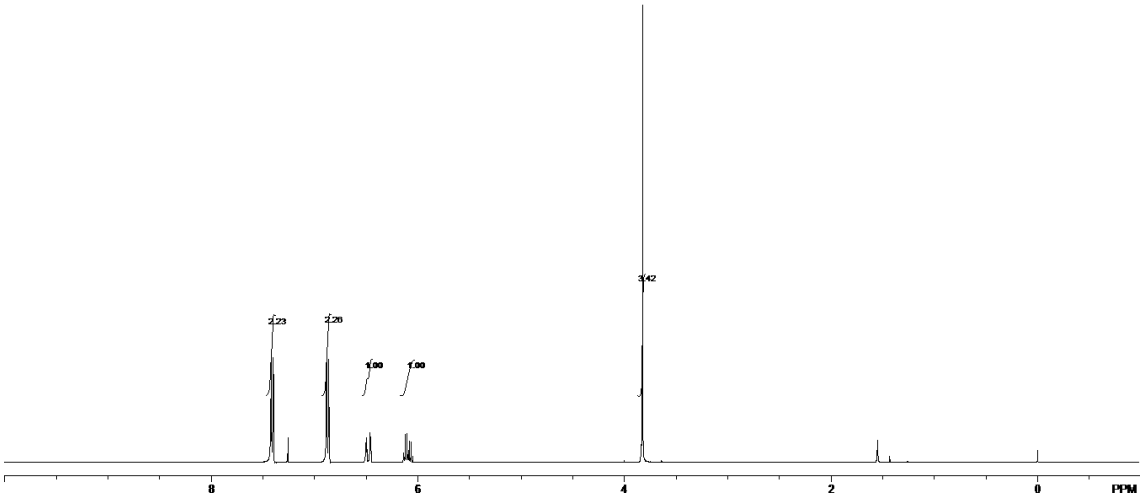
^{13}C NMR spectrum



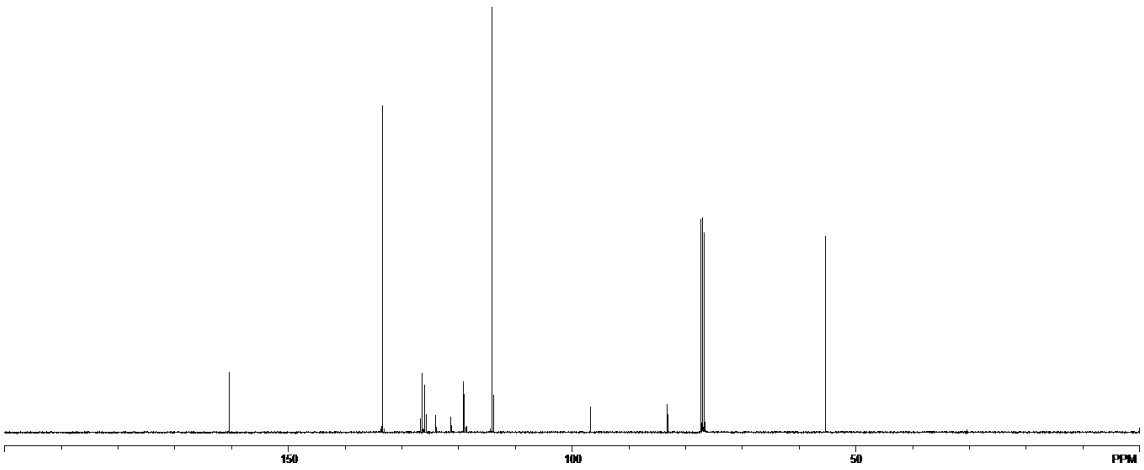
(*E*)-1-Methoxy-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene (**3d**);



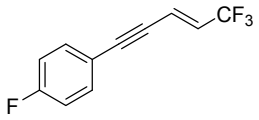
^{1}H NMR spectrum



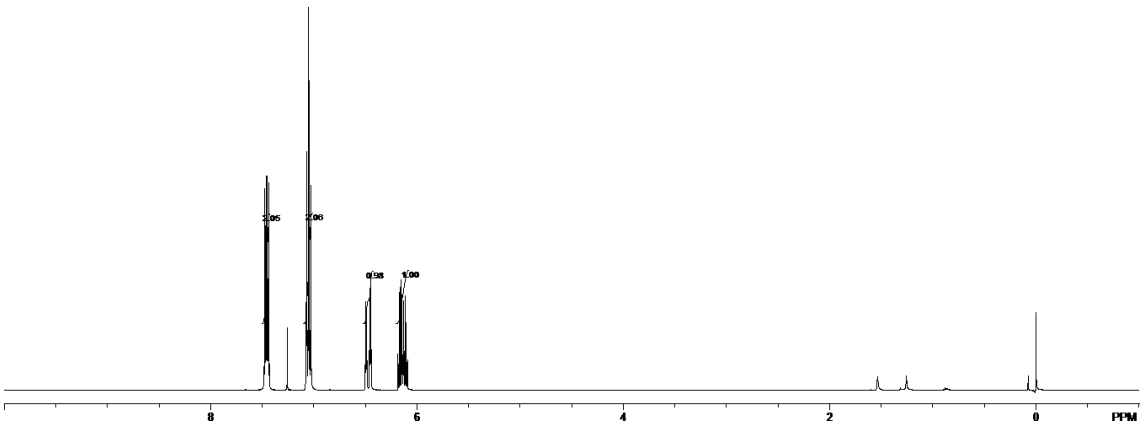
^{13}C NMR spectrum



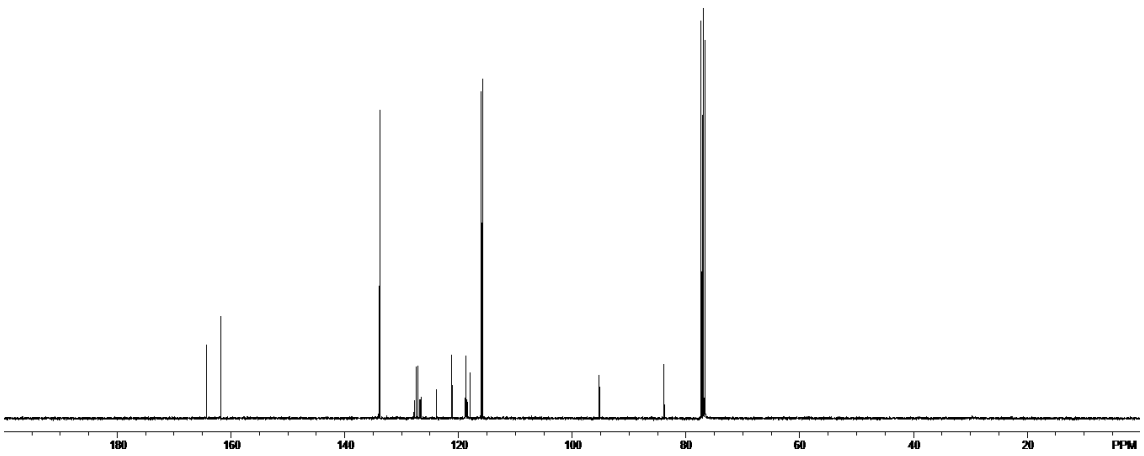
(*E*)-1-Fluoro-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene (**3e**);



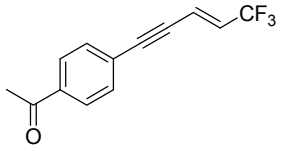
^{1}H NMR spectrum



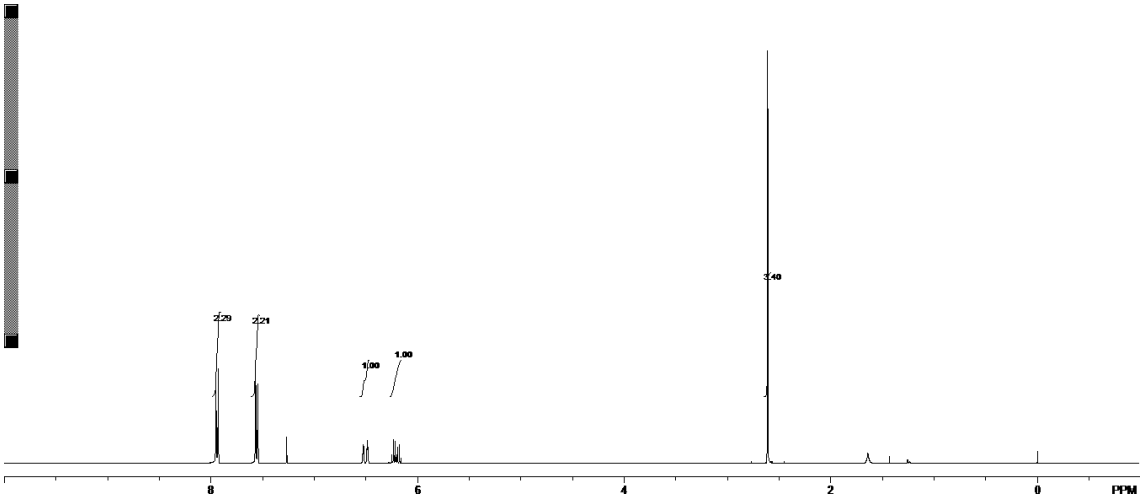
^{13}C NMR spectrum



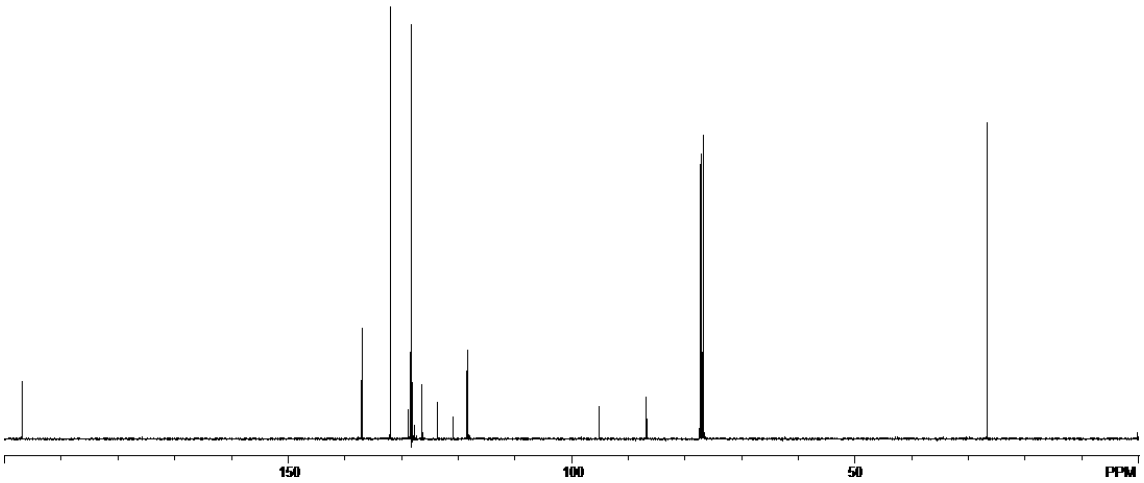
(*E*)-1-(4-(5,5,5-Trifluoropent-3-en-1-ynyl)phenyl)ethanone (**3f**);



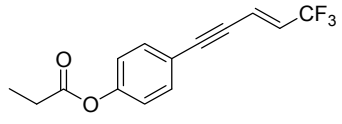
^{1}H NMR spectrum



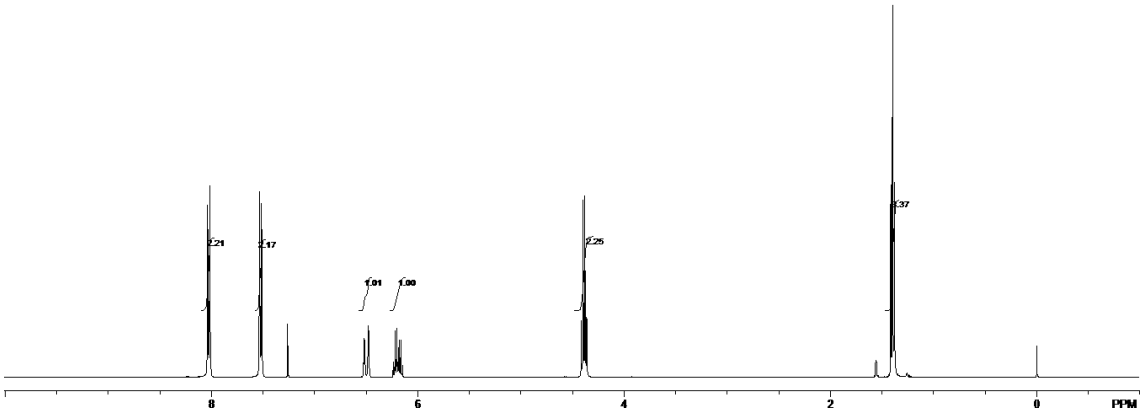
^{13}C NMR spectrum



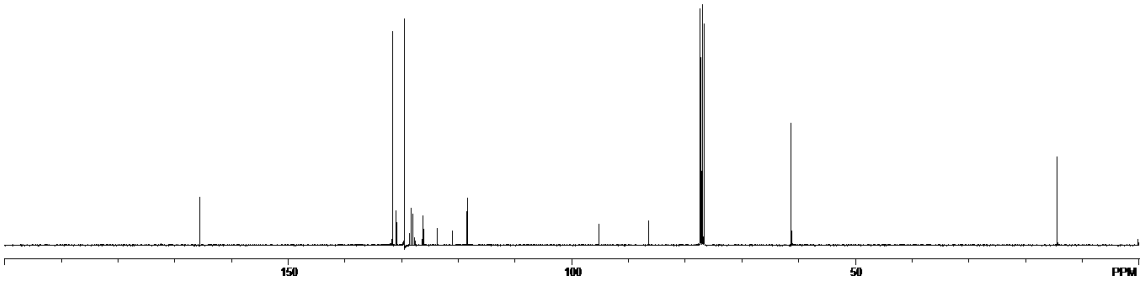
(*E*)-Ethyl 4-(5,5,5trifluoropent-3-en-1-ynyl)benzoate (**3g**);



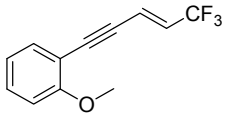
^{1}H NMR spectrum



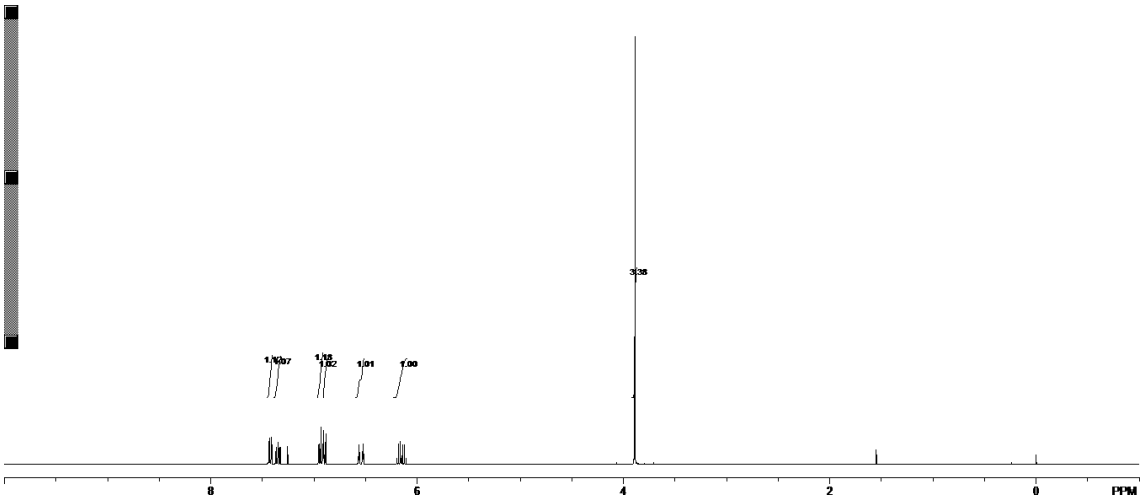
^{13}C NMR spectrum



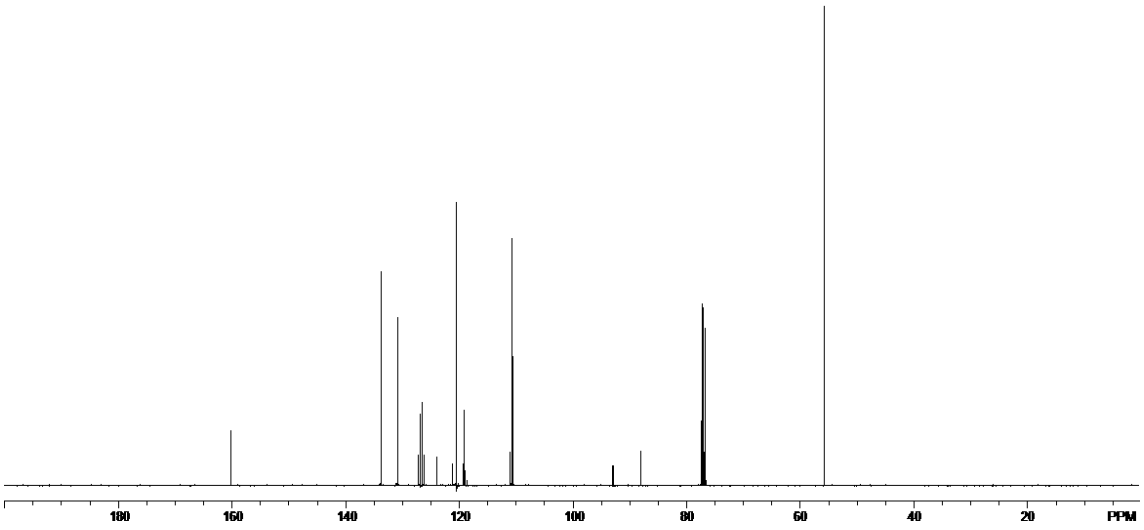
(*E*)-1-Fluoro-4-(5,5,5-Trifluoropent-3-en-1-ynyl)benzene (**3h**);



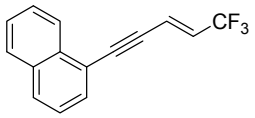
^{1}H NMR spectrum



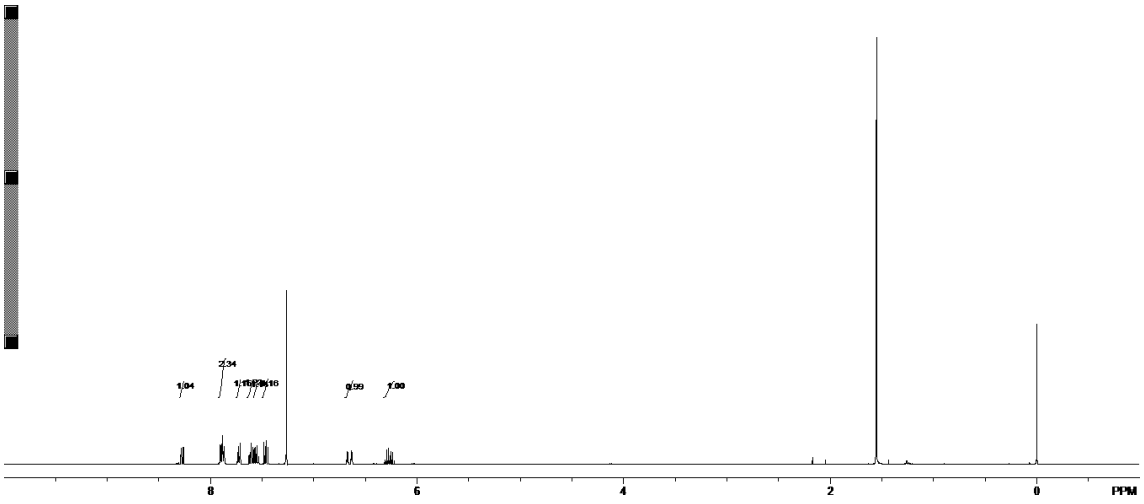
^{13}C NMR spectrum



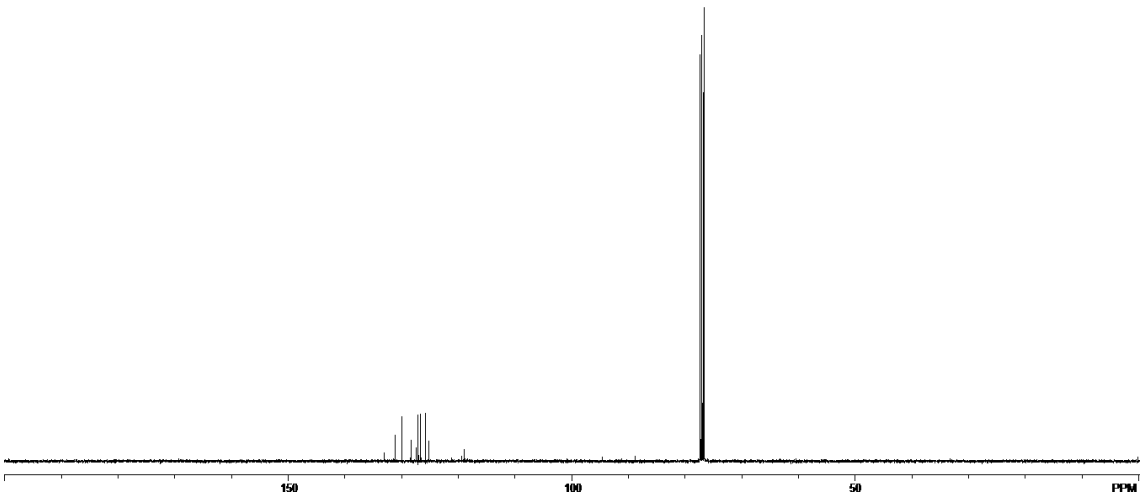
(*E*)-1-(5,5,5-Trifluoropent-3-en-1-ynyl)naphthalene (**3i**);



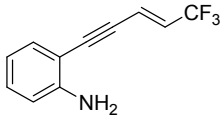
^{1}H NMR spectrum



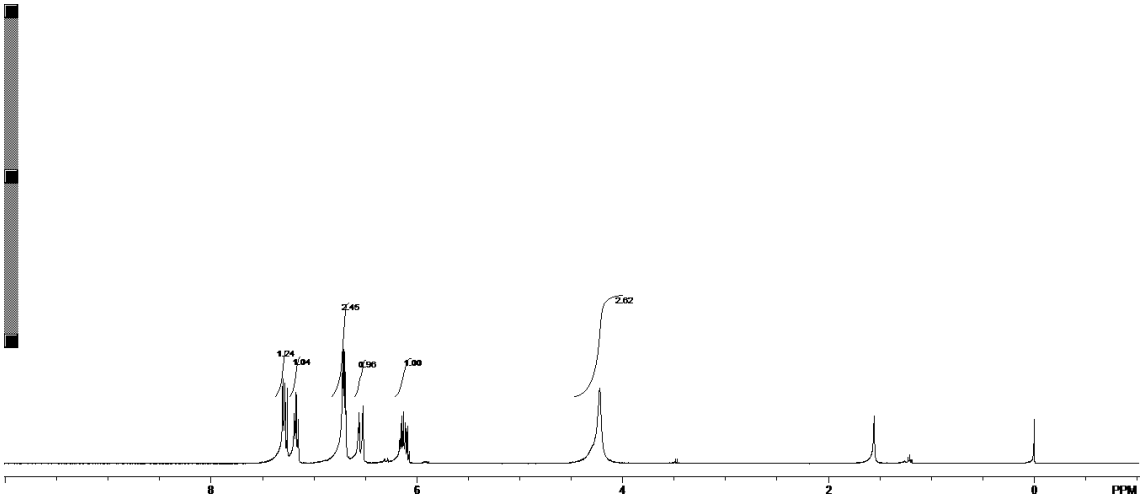
^{13}C NMR spectrum



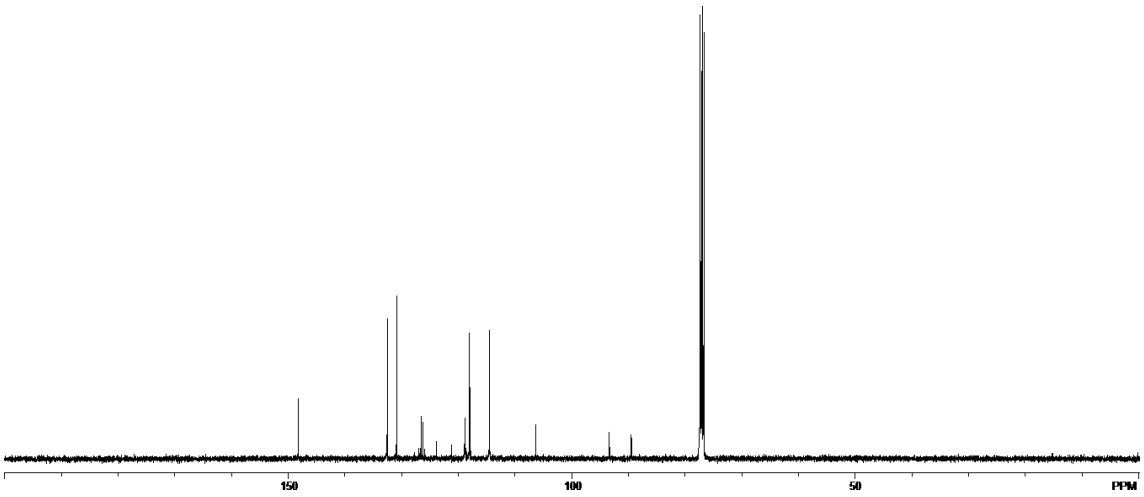
(*E*)-2-(5,5,5-Trifluoropent-3-en-1-ynyl)benzenamine (**3j**);



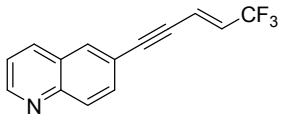
^{1}H NMR spectrum



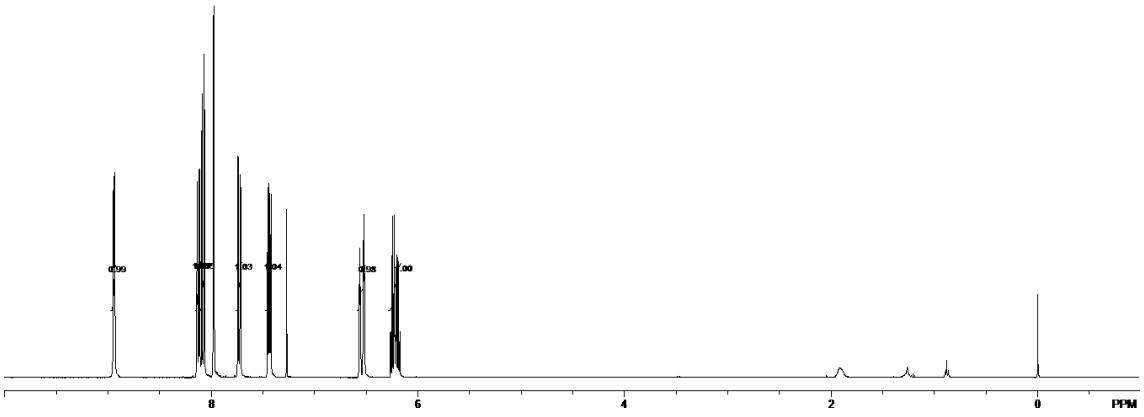
^{13}C NMR spectrum



(*E*)-6-(5,5,5-Trifluoropent-3-en-1-ynyl)quinolone (**3k**);



^{1}H NMR spectrum



^{13}C NMR spectrum