Supplementary Information

Supported Palladium Nanocatalyst for Copper free Acyl Sonogashira Reactions: One-Pot Multicomponent Synthesis of N-containing Heterocycles

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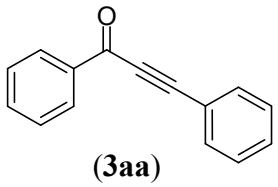
Contents

Characterization data

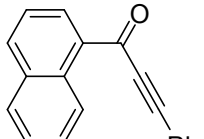
1,3-diphenylprop-2-yn-1-one:[1]



(**3aa**)

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.22-8.24 (dd, J = 7 Hz, 2H), 7.68-7.70 (dd, J = 6 Hz, 2H), 7.62-7.65 (m, 1H), 7.43-7.54 (m, 5H) ppm; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 178.0, 136.8, 134.1, 133.0, 130.8, 129.6, 128.7, 128.6, 120.1, 93.1, 86.8 ppm.

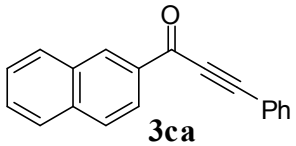
1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one:[2]



3ba

Eluent: Hexane:ethyl acetate (100:1.5); yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.30-9.32 (d, J = 8.7 Hz, 1H), 8.62-8.66 (dd, J = 6.9 Hz, 1H), 8.03-8.05 (d, J = 8.2 Hz, 1H), 7.83-7.86 (d, J = 14 Hz, 1H), 7.66-7.70 (m, 3H), 7.55-7.59 (m, 2H), 7.38-7.46 (m, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 179.5, 134.9, 134.4, 133.6, 132.7, 132.6, 130.5, 130.4, 128.7, 128.4, 128.4, 126.5, 125.7, 124.3, 120.0, 91.5, 88.3 ppm.

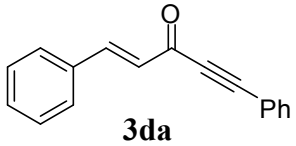
1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-one:



3ca

Eluent: Hexane:ethyl acetate (100:1.5); yellow solid; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.73 (s, 1H), 8.17-8.19 (dd, J = 6.8 Hz, 1H), 7.96-7.98 (d, J = 6.4 Hz, 1H), 7.83-7.87 (m, 2H), 7.69-7.72 (m, 2H), 7.51-7.59 (m, 2H), 7.39-7.48 (m, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 177.6, 135.9, 134.1, 132.8, 132.4, 132.1, 130.6, 129.6, 128.8, 128.5, 128.3, 127.7, 126.7, 123.6, 119.9, 92.8, 86.9 ppm; **MS** (EI): m/z (%) 256 ([M]$^+$, 100).

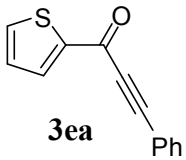
(*E*)-1,5-diphenylpent-1-en-4-yn-3-one[3]



3da

Eluent: Hexane:ethyl acetate (100:1.5); yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.86-7.90 (d, J = 16 Hz, 1H), 7.53-7.63 (m, 4H), 7.36-7.44 (m, 6H), 6.81-6.85 (d, J = 16 Hz, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 177.8, 148.0, 133.7, 132.7, 130.9, 130.4, 128.8, 128.4, 128.4, 128.1, 119.8, 91.3, 86.4 ppm.

3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-one[4]

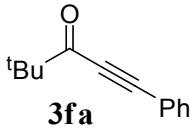


3ea

Eluent: Hexane:ethyl acetate (100:1); brown solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89-7.89 (dd, J = 3.7 Hz, 1H), 7.59-7.61 (dd, J = 4.6 Hz, 1H), 7.51-7.53 (m, 2H), 7.32-7.34 (m, 1H), 7.26-7.29 (m, 2H), 7.06-7.08 (m, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 169.3, 144.5, 135.1,

134.9, 132.7, 130.6, 128.4, 128.1, 119.5, 91.4, 86.2 ppm; **HRMS** (ESI) calcd for $C_{19}H_{13}O$ $[M+H]^+$: 256.0888; Found 257.0753.

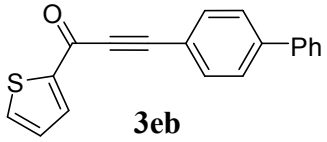
4,4-dimethyl-1-phenylpent-1-yn-3-one[3]



3fa

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.47-7.49 (d, J = 6.9 Hz, 2H), (t, J = 7.3 Hz, 1H), 7.26-7.30 (t, J = 8.3 Hz, 2H), 1.17 (s, 9H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 194.1, 132.8, 130.5, 128.5, 120.1, 92.1, 85.9, 44.7, 26.0 ppm.

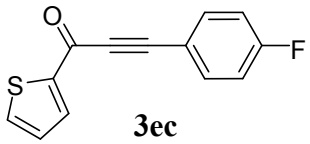
3-(biphenyl-4-yl)-1-(thiophen-2-yl)prop-2-yn-1-one:



3eb

Eluent: Hexane:ethyl acetate (100:1.5); white solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.03-8.04 (d, J = 3.6 Hz, 1H), 7.71-7.73 (d, J = 7.8 Hz, 3H), 7.59-7.64 (m, 4H), 7.45-7.49 (t, J = 7.4 Hz, 2H), 7.38-7.41 (t, J = 7.8 Hz, 1H), 7.18-7.21 (t, J = 4.1 Hz, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 169.5, 144.8, 143.4, 139.6, 135.4, 134.9, 133.4, 128.8, 128.2, 128.0, 126.9, 126.4, 118.4, 91.7, 87.0 ppm; **HRMS** (ESI) calcd for $C_{19}H_{13}OS$ $[M+H]^+$: 288.0609; Found 289.0468.

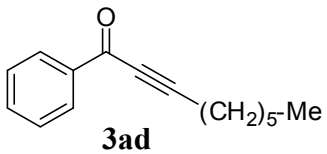
3-(4-fluorophenyl)-1-(thiophen-2-yl)prop-2-yn-1-one:



3ec

Eluent: Hexane:ethyl acetate (100:1.5); light yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.92 (dd, J = 3.7 Hz, 1H), 7.65-7.67 (dd, J = 5 Hz, 1H), 7.55-7.58 (m, 2H), 7.10-7.12 (m, 1H), 7.00-7.05 (m, 2H) ppm; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 169.3, 164.7, 162.7, 144.5, 135.2, 135.1, 135.0, 134.9, 128.2, 116.0, 115.9, 90.4, 86.1 ppm; **HRMS** (ESI) calcd for $C_{13}H_8FOS$ $[M+H]^+$: 230.0202; Found 231.0900.

1-phenylnon-2-yn-1-one:

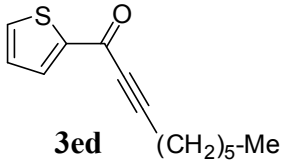


3ad

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.13-8.15 (d, J = 7.8 Hz, 2H), 7.57-7.61 (t, J = 7.3 Hz, 1H), 7.45-7.49 (t, J = 7.8 Hz, 2H), 2.48-2.51 (t, J = 6.9

Hz, 2H), 1.64-1.71 (m, 2H), 1.44-1.51 (m, 2H), 1.29-1.36 (m, 4H), 0.87-0.92 (t, J = 6.4 Hz, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 178.2, 136.9, 133.8, 129.5, 128.4, 96.9, 79.6, 31.2, 28.6, 27.7, 22.5, 19.2, 13.9 ppm; **HRMS** (ESI) calcd for $C_{15}H_{19}O$ $[M+H]^+$: 214.1358; Found 215.1706.

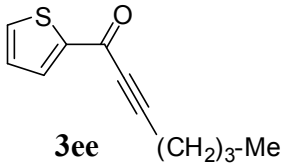
1-(thiophen-2-yl)non-2-yn-1-one[5]



3ed

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.82-7.83 (dd, J = 3.6 Hz, 1H), 7.61-7.62 (dd, J = 3.7 Hz, 1H), 7.06-7.08 (m, 1H), 2.38-2.41 (t, J = 7.3 Hz, 2H), 1.54-1.59 (m, 2H), 1.37-1.41 (m, 2H), 1.23-1.28 (m, 6H), 0.82-0.85 (m, 4H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 169.7, 144.7, 134.7, 134.6, 127.9, 95.2, 79.0, 30.9, 28.3, 27.5, 22.2, 18.8, 13.8 ppm.

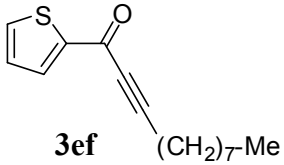
1-(thiophen-2-yl)hept-2-yn-1-one[6]



3ee

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.83-7.84 (dd, J = 4.2 Hz, 1H), 7.63-7.64 (dd, J = 5 Hz, 1H), 7.08-7.10 (m, 1H), 2.41-2.44 (t, J = 6.9 Hz, 2H), 1.57-1.61 (m, 2H), 1.42-1.47 (m, 2H), 0.89-0.92 (t, J = 7.3 Hz, 3H) ppm;**^{13}C NMR** ($CDCl_3$, 100 MHz): δ 169.8, 144.8, 134.7, 134.7, 128.1, 95.2, 79.0, 29.6, 21.8, 18.6, 13.3 ppm.

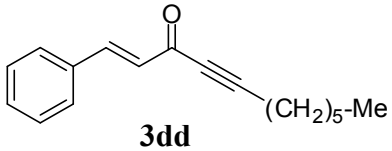
1-(thiophen-2-yl)undec-2-yn-1-one



3ef

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87-7.88 (dd, J = 3.6 Hz, 1H), 7.65-7.67 (dd, J = 3.7 Hz, 1H), 7.11-7.13 (m, 1H), 2.43-2.47 (t, J = 6.9 Hz, 2H), 1.59-1.67 (m, 2H), 1.41-1.46 (m, 2H), 1.25-1.29 (m, 8H), 0.85-0.88 (m, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 169.9, 144.9, 134.8, 134.7, 128.1, 95.4, 79.3, 31.7, 29.0, 28.9, 28.8, 27.7, 22.6, 19.0, 14.0 ppm; **HRMS** (ESI) calcd for $C_{15}H_{21}OS$ $[M+H]^+$: 248.1235; Found 249.1875.

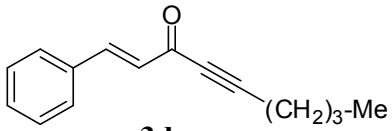
(*E*)-1-phenylundec-1-en-4-yn-3-one:



3dd

Eluent: Hexane:ethyl acetate (100:1.5); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.75-7.79 (d, J = 16 Hz, 1H), 7.51-7.53 (m, 2H), 7.36-7.38 (m, 3H), 6.71-6.75 (d, J = 16 Hz, 1H), 2.41-2.44 (t, J = 7.3 Hz, 2H), 1.59-1.64 (m, 2H), 1.40-1.48 (m, 2H), 1.26-1.31 (m, 4H), 0.86-0.89 (t, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 178.3, 147.9, 130.8, 128.8, 128.4, 128.3, 94.9, 79.1, 31.0, 28.4, 27.6, 22.3, 18.9, 13.8 ppm; **HRMS** (ESI) calcd for $C_{17}H_{21}O$ $[M+H]^+$: 240.1514; Found 241.3634.

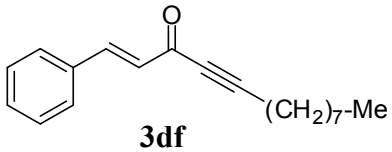
(*E*)-1-phenylnon-1-en-4-yn-3-one:



3de

Eluent: Hexane:ethyl acetate (100:1.5); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76-7.79 (d, J = 16 Hz, 1H), 7.52-7.54 (m, 2H), 7.35-7.39 (m, 3H), 6.71-6.75 (d, J = 16 Hz, 1H), 2.42-2.46 (t, J = 7.4 Hz, 2H), 1.58-1.65 (m, 2H), 1.45-1.50 (m, 2H), 0.91-0.94 (t, J = 5.5 Hz, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 178.4, 147.9, 133.9, 130.8, 128.8, 128.4, 94.9, 79.1, 29.7, 21.8, 18.6, 13.3 ppm; **HRMS** (ESI) calcd for $C_{15}H_{17}O$ $[M+H]^+$: 212.1201; Found 213.0852.

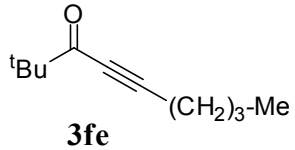
(*E*)-1-phenyltridec-1-en-4-yn-3-one:



3df

Eluent: Hexane:ethyl acetate (100:1.5); yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.77-7.81 (d, J = 16.5 Hz, 1H), 7.53-7.55 (m, 2H), 7.38-7.40 (m, 3H), 6.73-6.77 (d, J = 16 Hz, 1H), 2.42-2.44 (t, J = 6 Hz, 2H), 1.60-1.65 (m, 2H), 1.43-1.47 (m, 2H), 1.27-1.31 (m, 8H), 0.85-0.87 (m, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 178.5, 147.9, 133.9, 130.9, 128.9, 128.5, 128.4, 95.0, 79.5, 31.7, 29.0, 28.9, 28.8, 27.7, 22.5, 18.9, 13.9 ppm; **HRMS** (ESI) calcd for $C_{19}H_{25}O$ $[M+H]^+$: 268.1827; Found 269.0509.

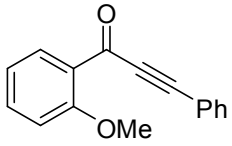
2,2-dimethylnon-4-yn-3-one:



3fe

Eluent: Hexane:ethyl acetate (100:1); yellow oil; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 2.34-2.37 (t, J = 7 Hz, 2H), 1.53-1.56 (m, 2H), 1.39-1.43 (m, 2H), 1.15 (s, 9H), 0.88-0.91 (t, J = 7 Hz, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 194.3, 99.6, 78.7, 44.5, 29.7, 25.9, 21.9, 18.6, 13.4 ppm; **HRMS** (ESI) calcd for $C_{11}H_{19}O$ $[M+H]^+$: 166.1358; Found 166.9756.

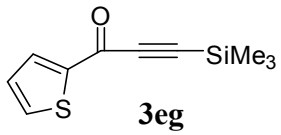
1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one:[3]



3ga

Eluent: Hexane:ethyl acetate (100:1.5); yellow oil; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.05-8.07 (dd, J = 7.5 Hz, 1H), 7.58-7.60 (m, 2H), 7.48-7.52 (m, 1H), 7.33-7.42 (m, 3H), 6.97-7.03 (m, 2H), 3.91 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 176.2, 159.4, 134.8, 132.5, 132.1, 130.2, 128.3, 126.2, 120.2, 119.9, 111.9, 91.2, 88.9, 55.5 ppm.

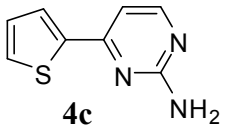
1-(thiophen-2-yl)-3-(trimethylsilyl)-prop-2-yn-1-one:[7]



3eg

Eluent: Hexane:ethyl acetate (100:0.5); colourless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89-7.90 (dd, J = 4.1 Hz, 1H), 7.68-7.69 (dd, J = 5 Hz, 1H), 7.12-7.14 (m, 1H), 0.27 (s, 9H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 169.3, 144.4, 135.5, 135.4, 128.2, 100.2, 99.0, -0.85 ppm.

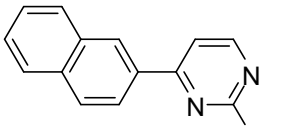
5-(thiophen-2-yl)pyrimidin-2-amine:[7]



4c

Eluent: Hexane:ethyl acetate (1:1); colorless crystal; **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 8.23-8.24 (d, J = 5 Hz, 1H), 7.86-7.87 (dd, J = 4 Hz, 1H), 7.71-7.72 (dd, J = 5 Hz, 1H), 7.17-7.18 (m, 1H), 7.05-7.06 (d, J = 5 Hz, 1H), 6.67 (s, 2H) ppm; **^{13}C NMR** (DMSO-d_6, 125 MHz): δ 163.5, 158.9, 158.7, 142.9, 129.8, 128.4, 127.6, 104.3 ppm.

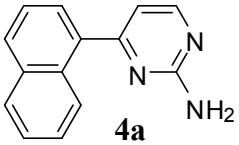
5-(naphthalen-2-yl)pyrimidin-2-amine:



4b

Eluent: Hexane:ethyl acetate (1:1); colorless crystal; **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 8.67 (s, 1H), 8.35-8.37 (d, J = 5.5 Hz, 1H), 8.19-8.21 (dd, J = 8.5 Hz, 1H), 7.95-8.05 (m, 3H), 7.56-7.61 (m, 2H), 7.28-7.29 (d, J = 5 Hz, 1H), 6.71 (s, 2H) ppm; **^{13}C NMR** (DMSO-d_6, 125 MHz): δ 163.8, 163.4, 159.0, 134.4, 133.9, 132.7, 128.7, 128.2, 127.6, 127.2, 126.6, 126.5, 123.9, 106.1 ppm; **HRMS** (ESI) calcd for $C_{14}H_{12}N_3$ $[M+H]^+$: 221.0953; Found 222.2204.

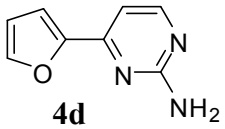
5-(naphthalen-1-yl)pyrimidin-2-amine:



4a

Eluent: Hexane:ethyl acetate (1:1); colorless crystal; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ 8.37-8.38 (d, J = 5 Hz, 1H), 8.18-8.20 (dd, J = 7.3 Hz, 1H), 7.98-8.02 (m, 2H), 7.53-7.61 (m, 4H), 6.79-6.81 (m, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz): δ 166.5, 163.6, 158.6, 136.6, 133.4, 130.0, 129.4, 128.3, 126.9, 126.6, 126.1, 125.3, 110.7 ppm; **HRMS** (ESI) calcd for $C_{14}H_{12}N_3$ $[M+H]^+$: 221.0953; Found 221.8721.

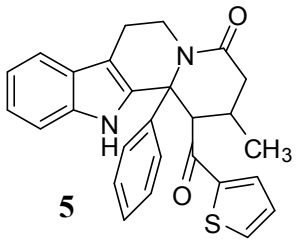
5-(furan-2-yl)pyrimidin-2-amine:[8]



4d

Eluent: Hexane:ethyl acetate (1:1); colorless crystal; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ 8.27-8.28 (d, J = 5.5 Hz, 1H), 7.85-7.86 (m, 1H), 7.16-7.17 (d, J = 3.2 Hz, 1H), 6.87-6.88 (d, J = 5 Hz, 1H), 6.71 (s, 2H), 6.64-6.65 (m, 1H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz): δ 163.6, 159.0, 155.4, 151.8, 145.3, 112.4, 111.4, 103.9 ppm.

2-methyl-12b-phenyl-1-(thiophene-2-carbonyl)-1,2,3,6,7,12b-hexahydroindolo[2,3-a]quinolizin-4(12H)-one 5. The NMR data was analyzed by comparing with related known analogue of tetrahydro-β-carboline derivative.[9]



5

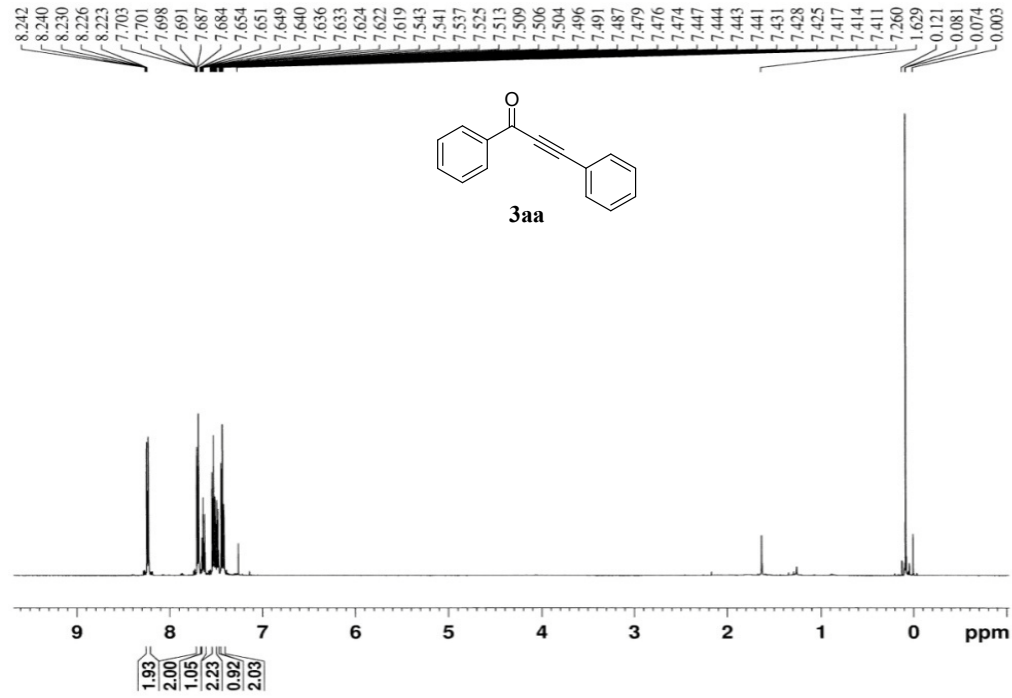
Eluent: Hexane:ethyl acetate (1:1); white solid; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ 11.78 (s, 1H), 8.09-8.11 (d, J = 4.3 Hz, 1H), 7.89-7.90 (d, J = 4.9 Hz, 1H), 7.51-7.53 (d, J = 8.6 Hz, 1H), 7.39-7.41 (d, J = 7.3 Hz, 1H), 7.27-7.29 (d, J = 7.3 Hz, 1H), 7.12-7.17 (m, 4H), 7.01-7.04 (m, 2H), 4.83 (s, 1H), 4.61-4.64 (dd, J = 12.8 Hz, 1H), 2.88-3.02 (m, 3H), 2.40-2.44 (dd, J = 15.3 Hz. 1H), 2.05-2.08 (m, 1H), 1.56-1.62 (m, 1H), 0.95-0.97 (d, J = 7.3 Hz, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 125 MHz): δ 192.1, 175.0, 144.7, 141.4, 136.2, 136.1, 135.8, 134.0, 128.3, 127.7, 126.9, 126.8, 126.6, 121.7, 118.9, 118.1, 111.4, 109.5, 67.0, 47.5, 32.0, 30.1, 19.7, 17.4 ppm; **HRMS** (ESI) calcd for $C_{27}H_{25}N_2O_2S$ $[M+H]^+$: 440.1558; Found 441.3213.

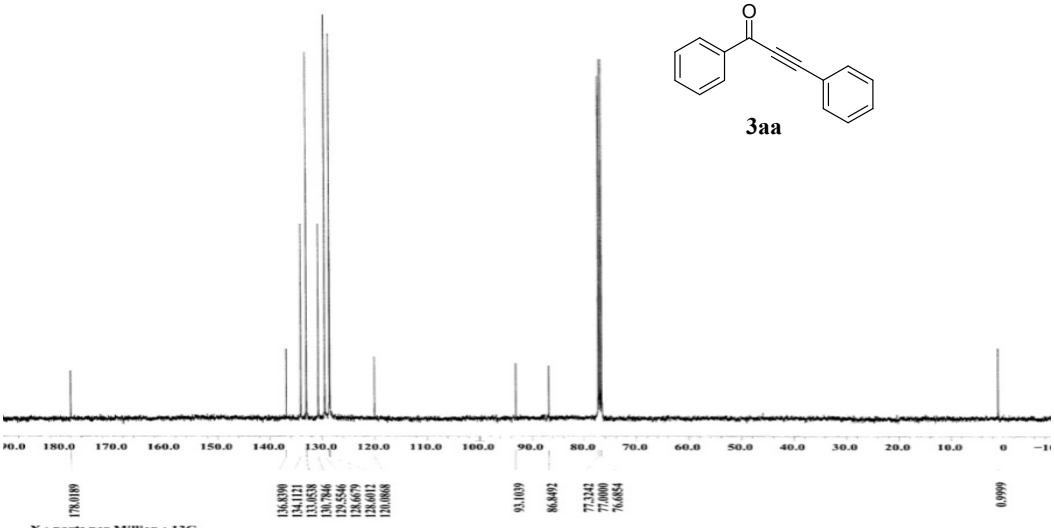
References:

1 X-F. Wu, H. Neumann and M. Beller, *Chem. Eur. J*., 2010, **16**, 12104.
2 J. Liu, X. Peng, Y. Zhao and C. Xia, *Org. Lett.,* 2008, **10**, 3933.
3 D. A. Alonso, C. A. Nájera, M[a]. C. Pacheco, *J. Org. Chem.,* 2004, **69**, 1615.
4 J-Y. Chen, T-C. Lin, S-C. Chen, A-J. Chen, C-Y. Mou and F-Y. Tsai, *Tetrahedron,* **2009**, *65*, 10134.
5 H-C. Shen, H-L. Su, Y-C. Hsueh and R-S. Liu, *Organometallics* **2004**, *23*, 4332.
6 B. Liang, M. Huang, Z. You, Z. Xiong, K. Lu, R. Fathi, J. Chen and Z. Yang, *J. Org. Chem*., 2005, **70**, 6097.
7 D. M. D'Souza, T. J. J. Müller, *Natr. Prot*., **2008**, *3*, 1660
8 A. Seggio, G. Priem, F. Chevallier and F. Mongin, *Synthesis,* 2009, **21**, 3617.
9 A. S. Karpov, F. Rominger and T. J. J. Müller, *Org. Biomol. Chem*., 2005, **3**, 4382.

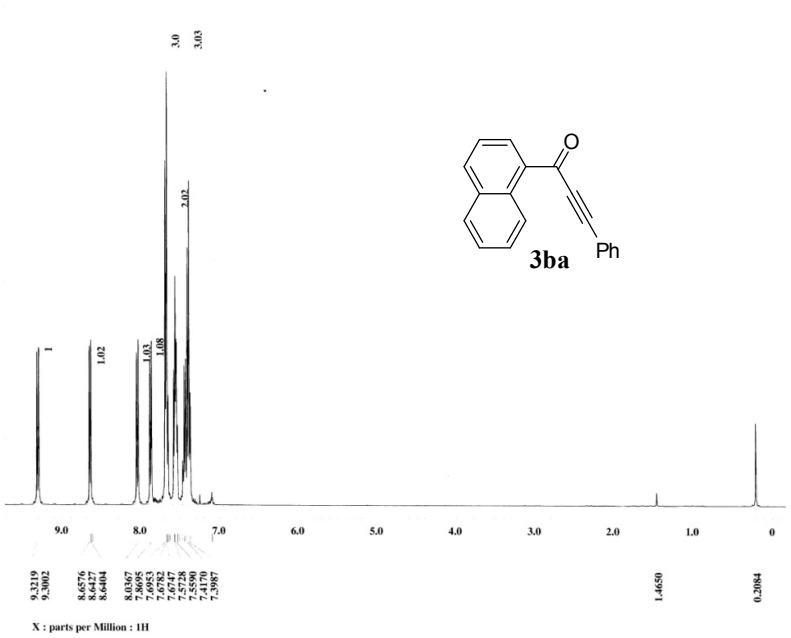
^{1}H and ^{13}C NMR spectra of the coupled products

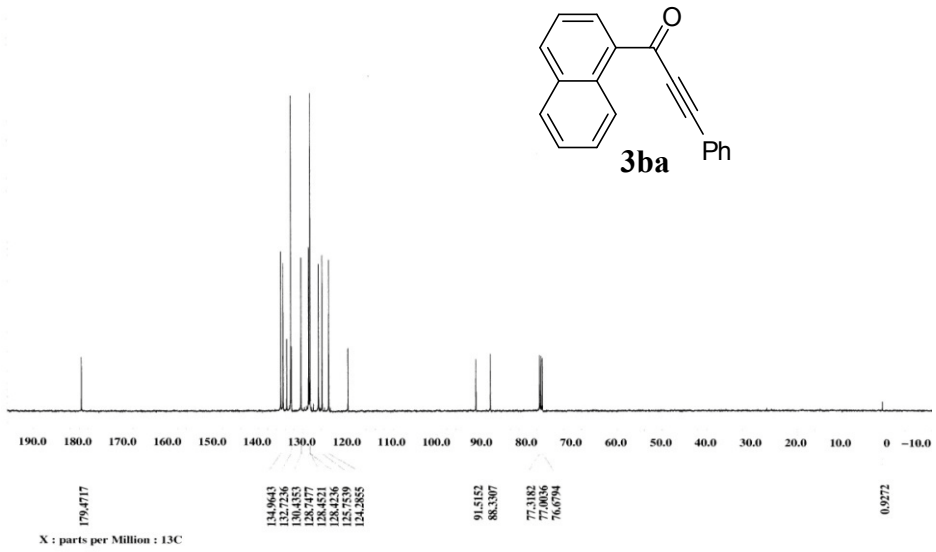
^{1}H and ^{13}C NMR spectra of **3aa:**



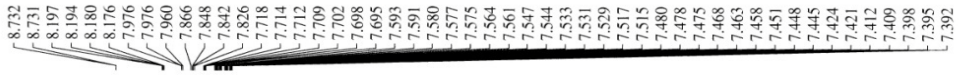


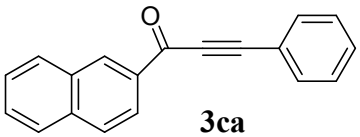
^{1}H and ^{13}C NMR spectra of **3ba**:



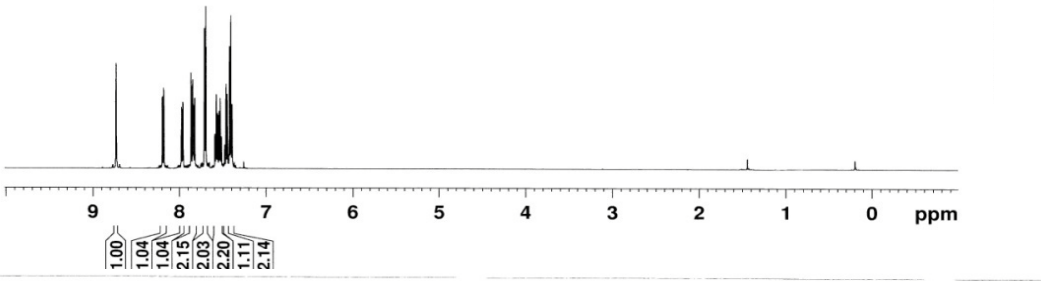


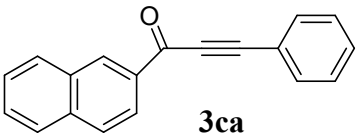
^{1}H and ^{13}C NMR spectra of **3ca:**



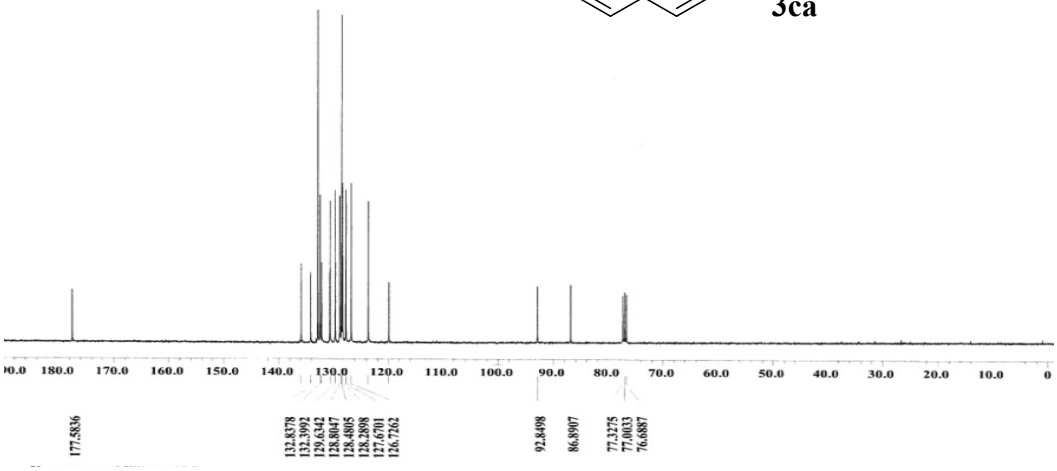


3ca

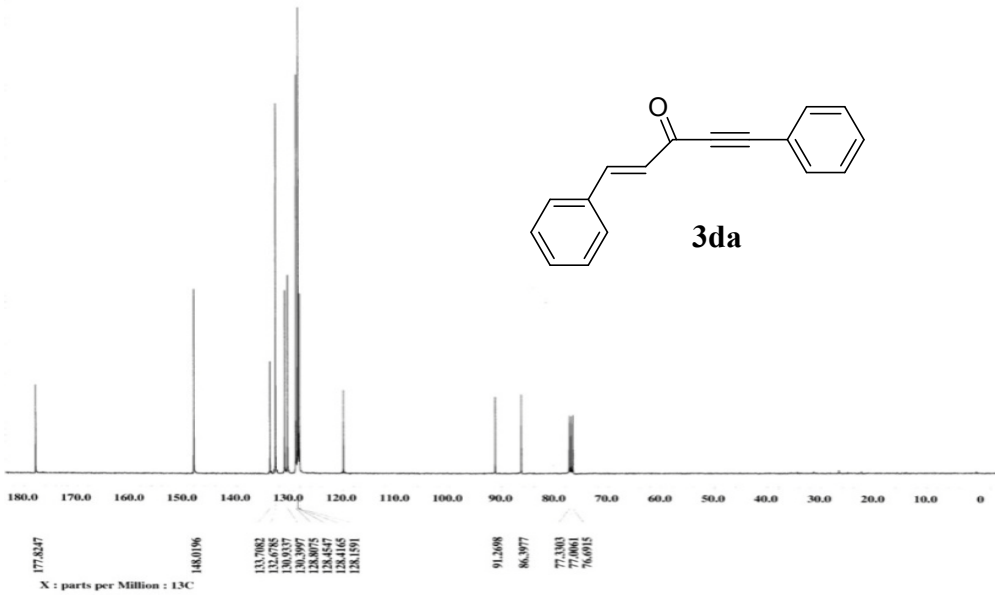




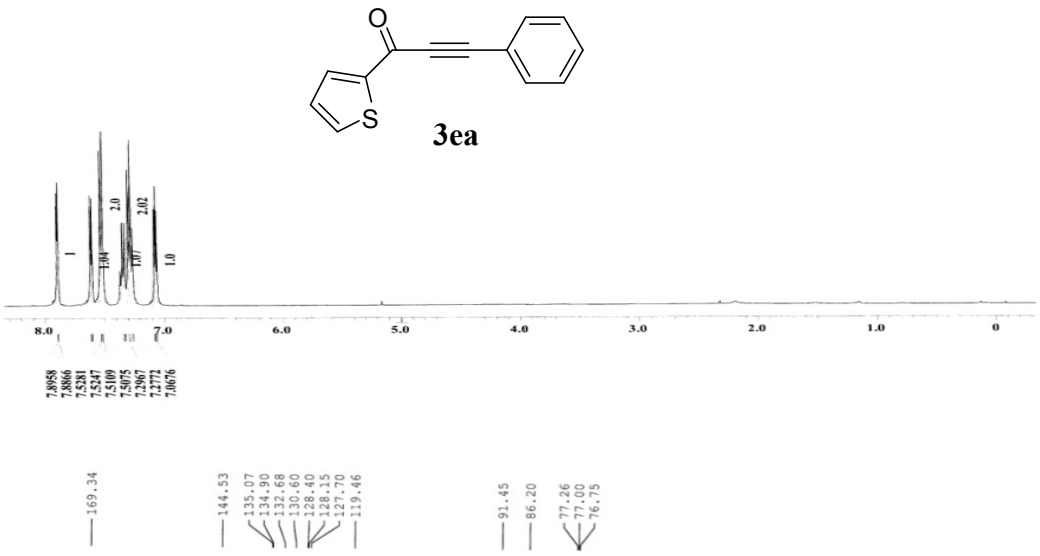
3ca

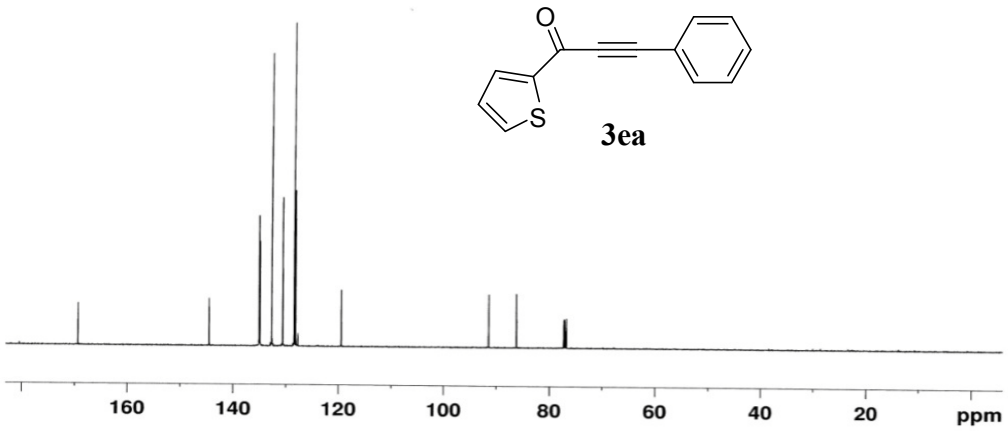


^{1}H and ^{13}C NMR spectra of **3da**:

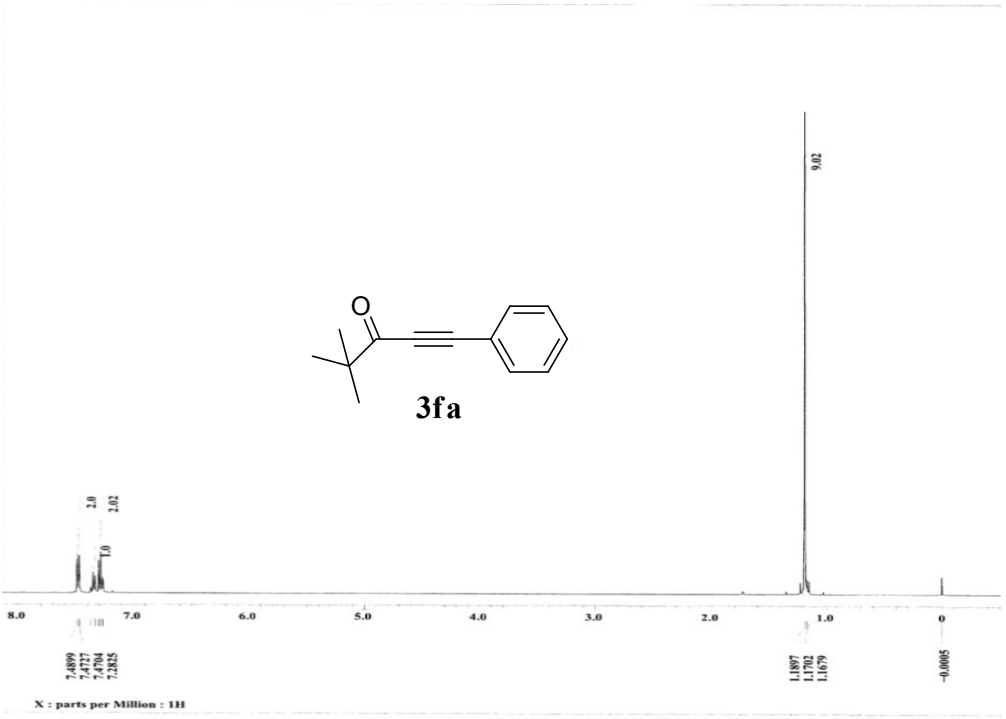


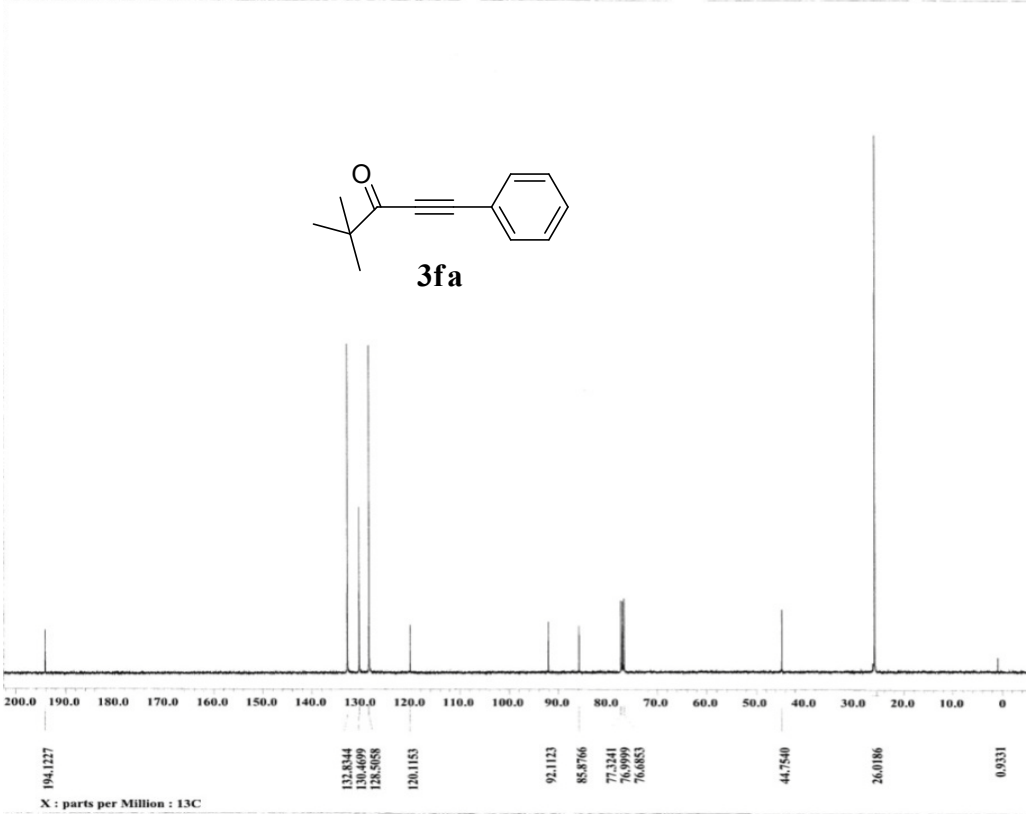
^{1}H and ^{13}C NMR spectra of **3ea:**



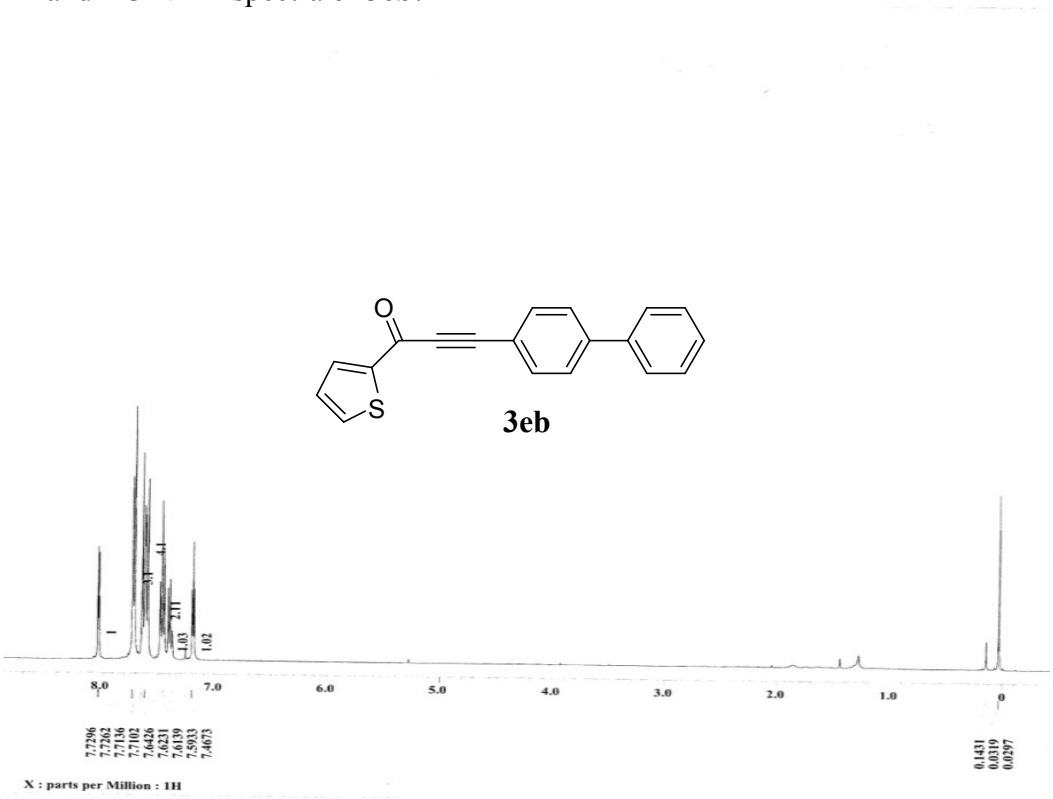


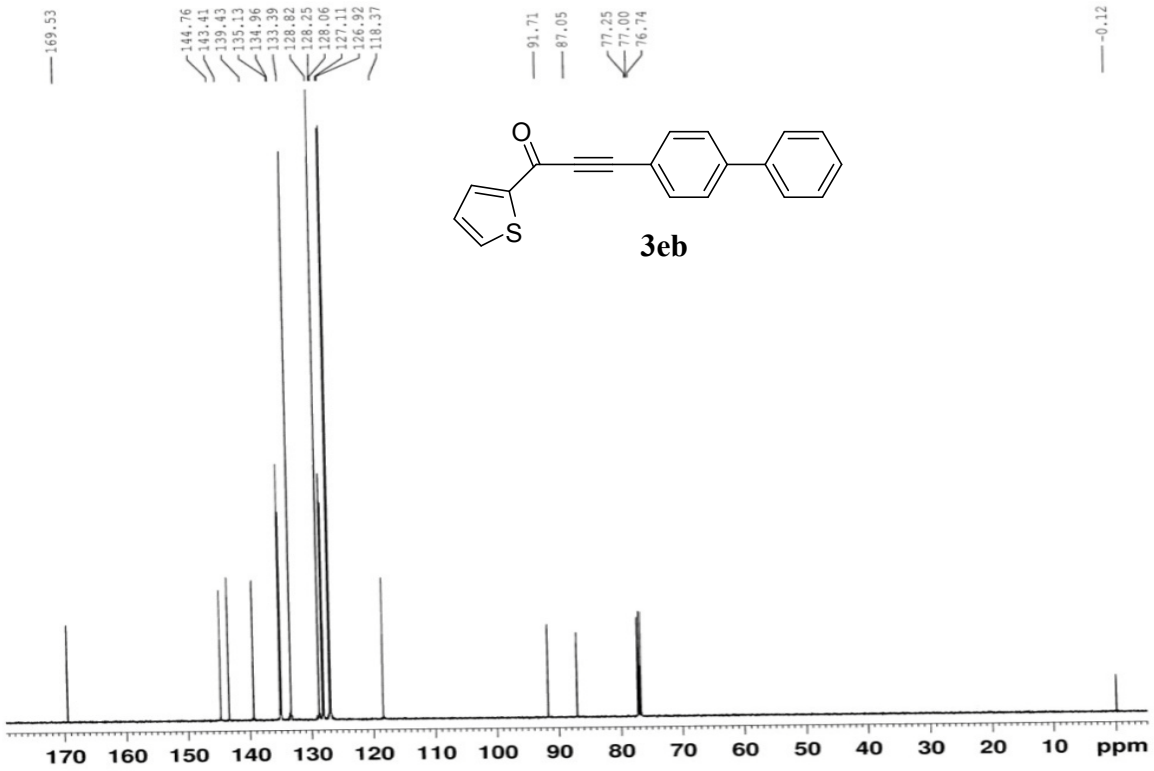
^{1}H and ^{13}C NMR spectra of **3fa**:



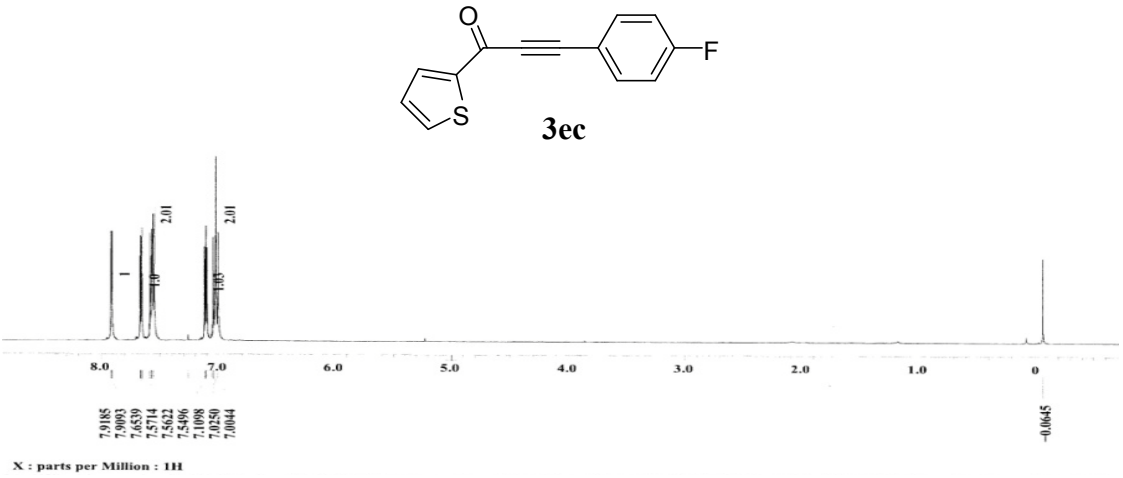


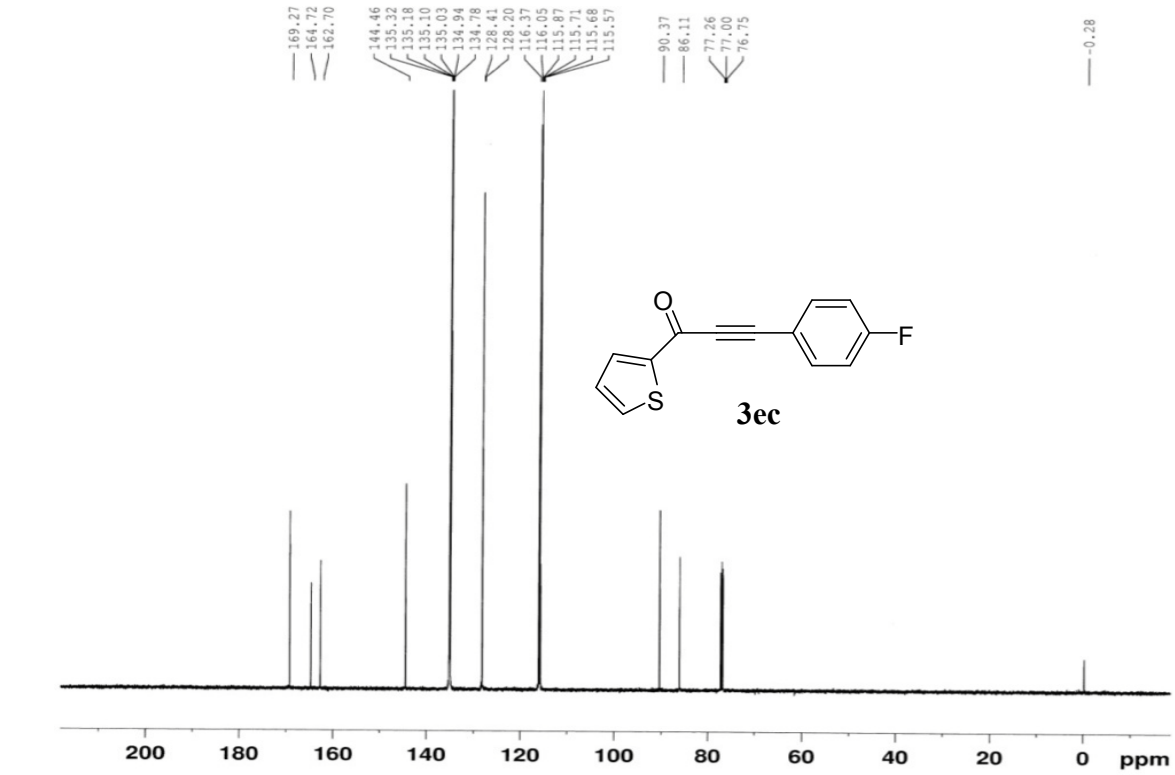
^{1}H and ^{13}C NMR spectra of **3eb:**



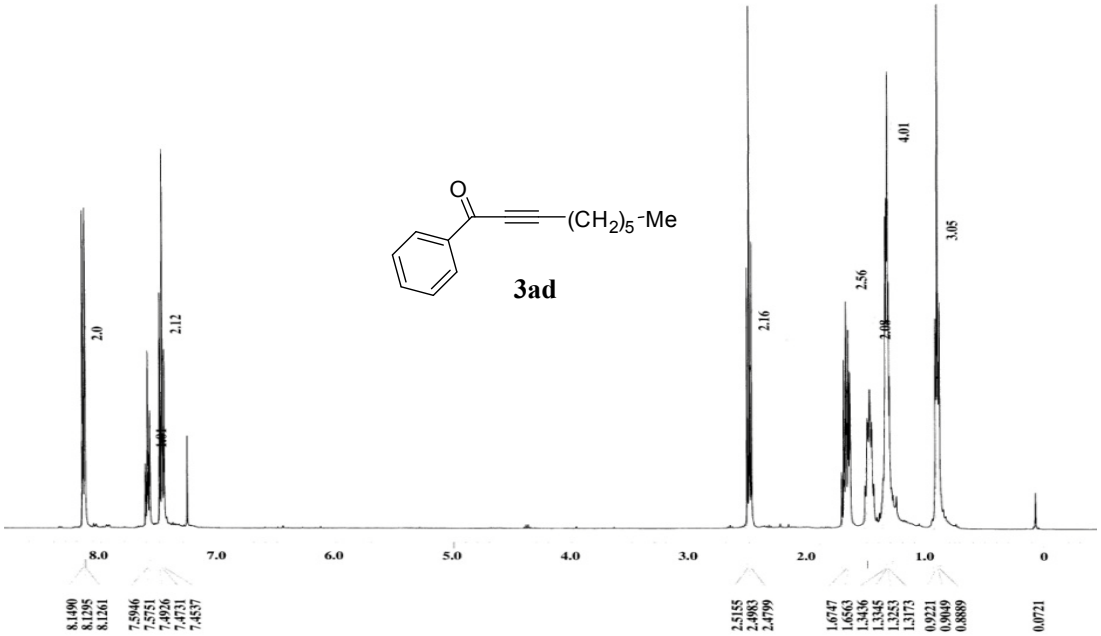


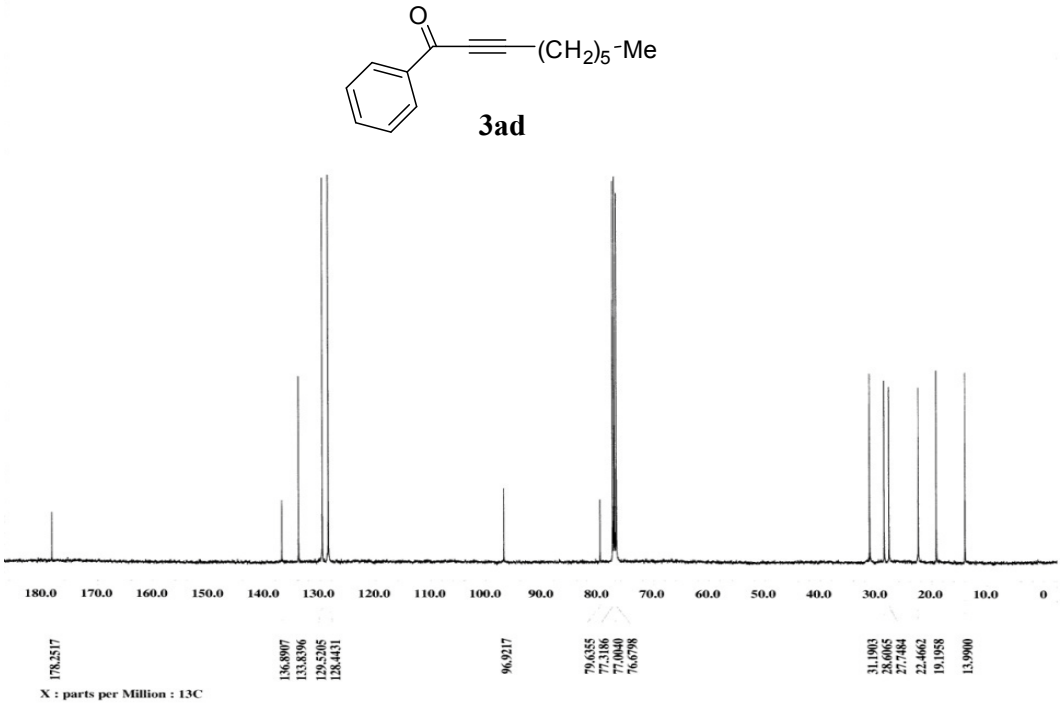
^{1}H and ^{13}C NMR spectra of **3ec**:





^{1}H and ^{13}C NMR spectra of **3ad**:





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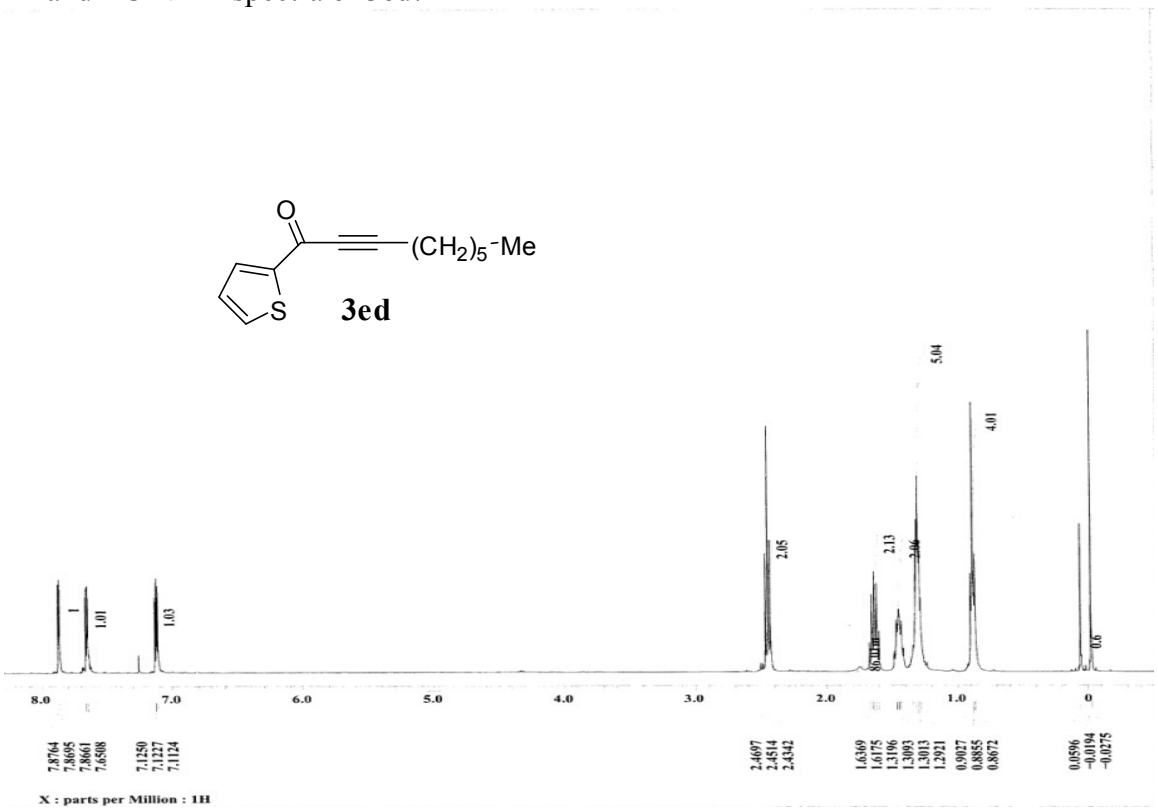

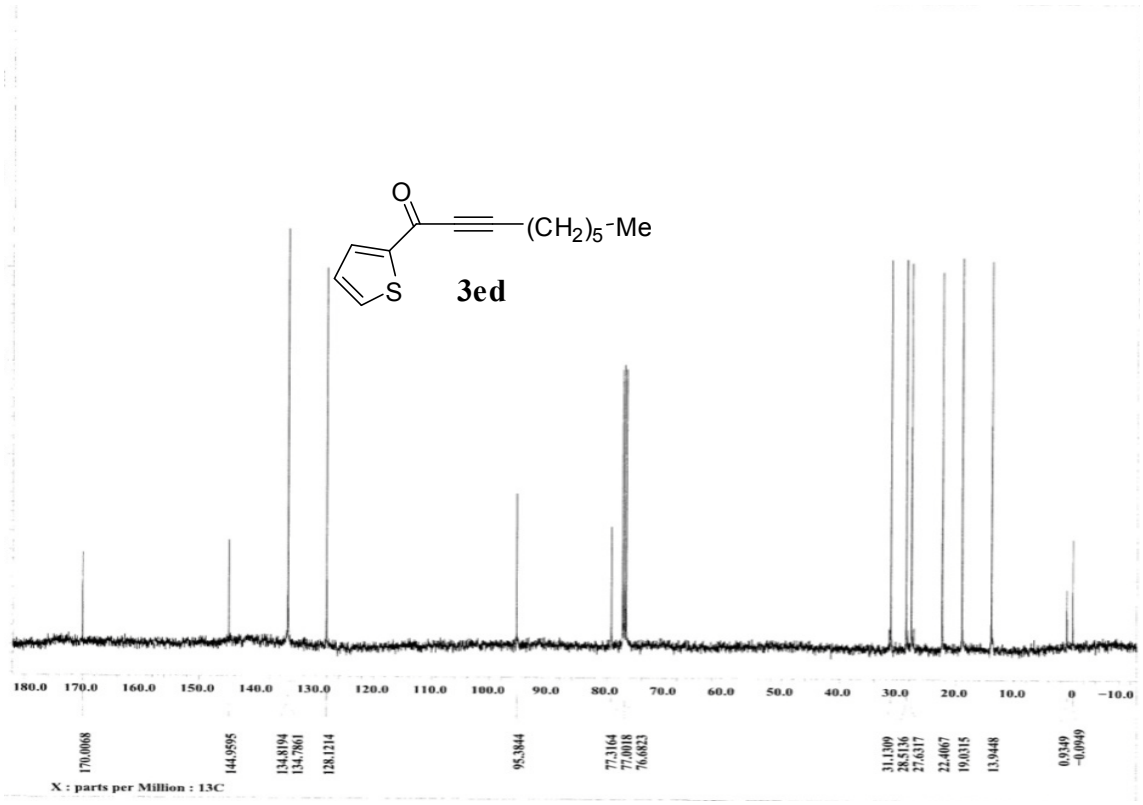

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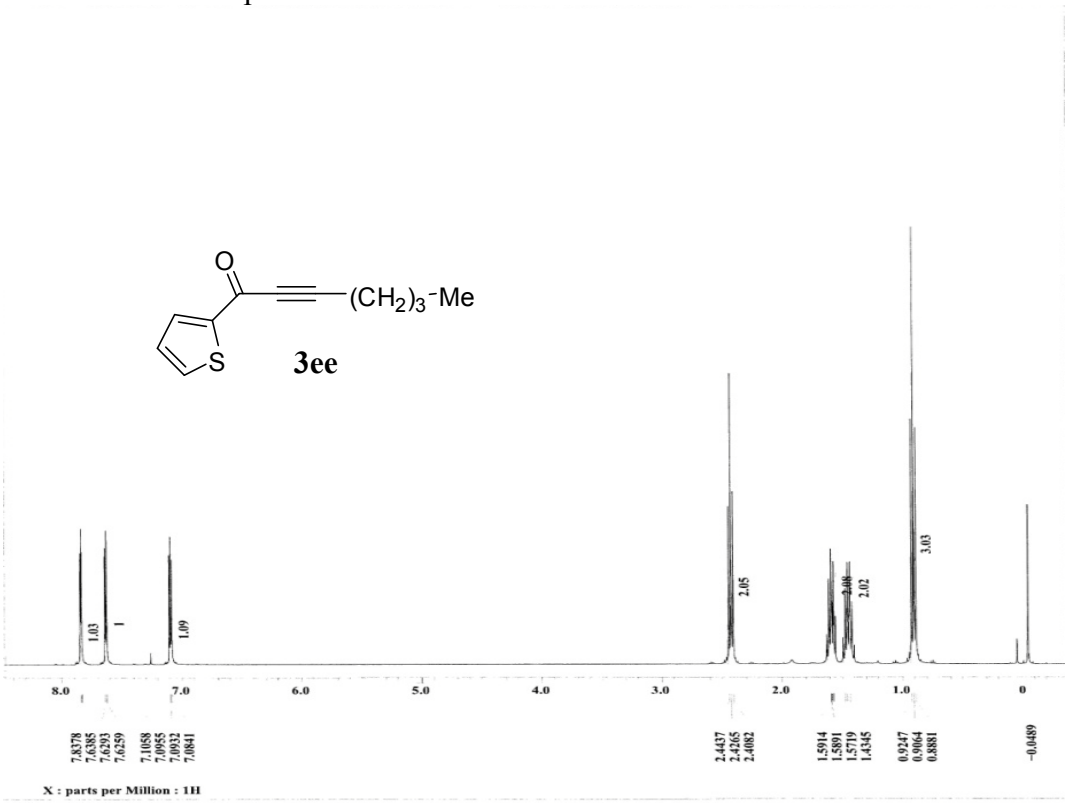

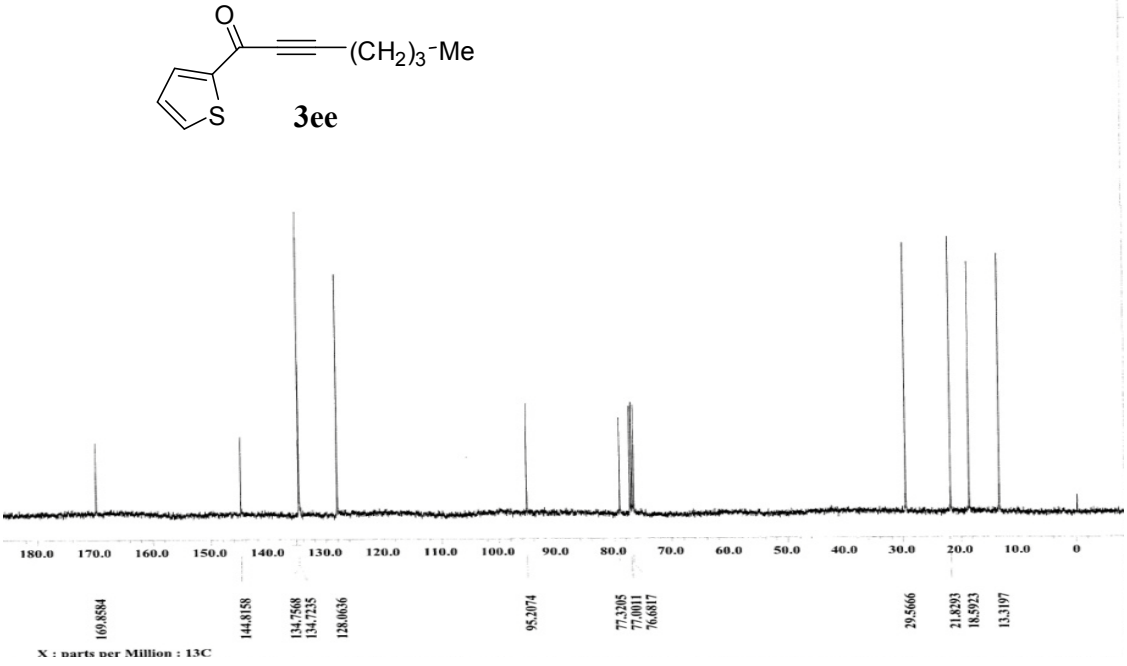

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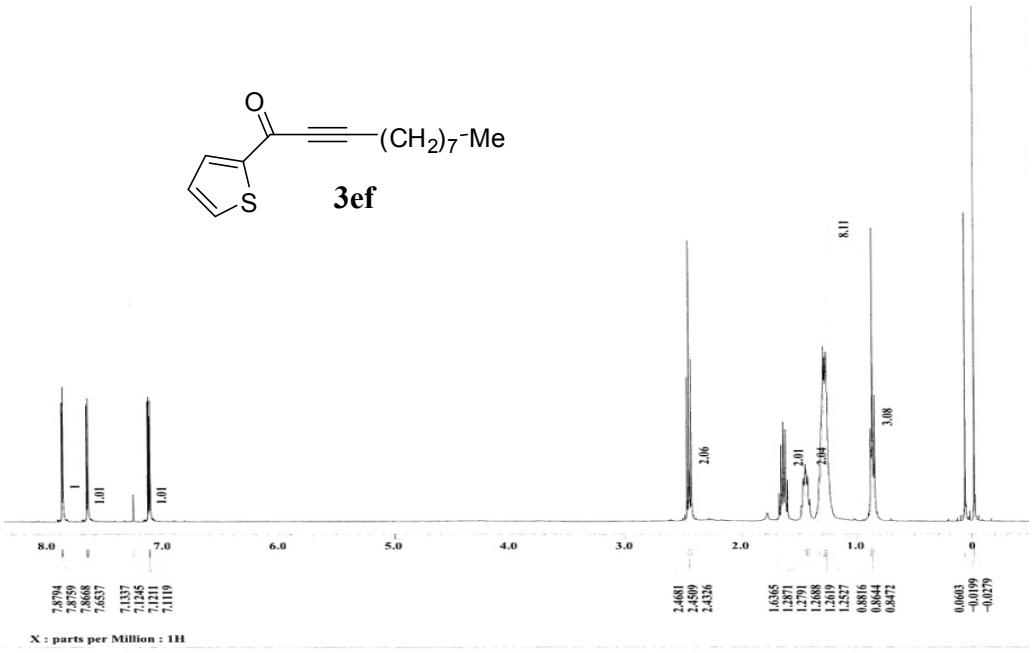
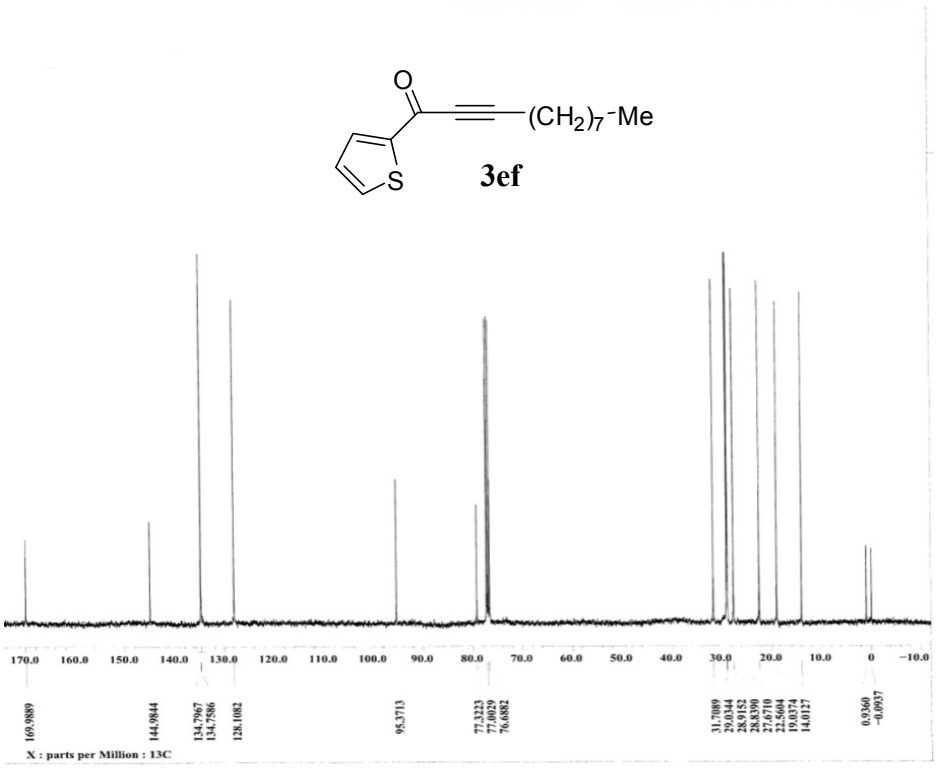
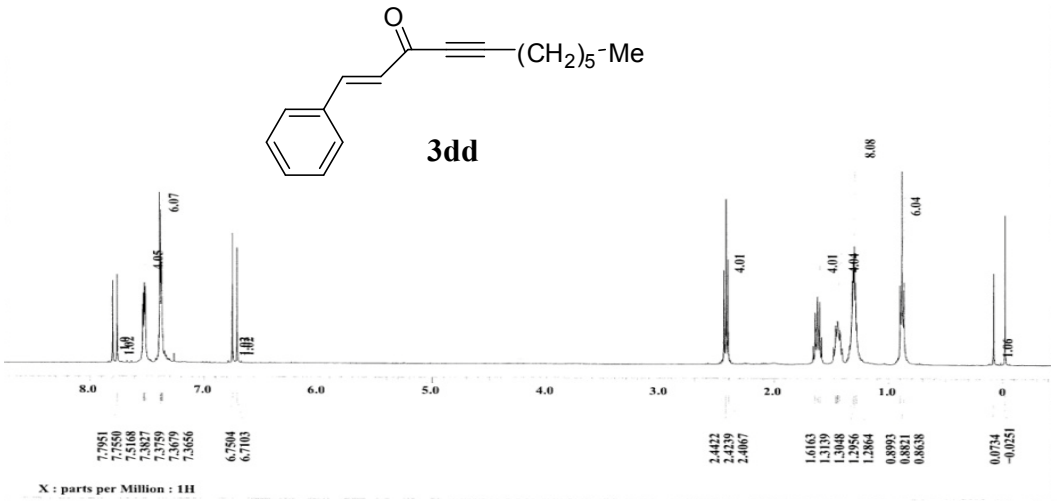
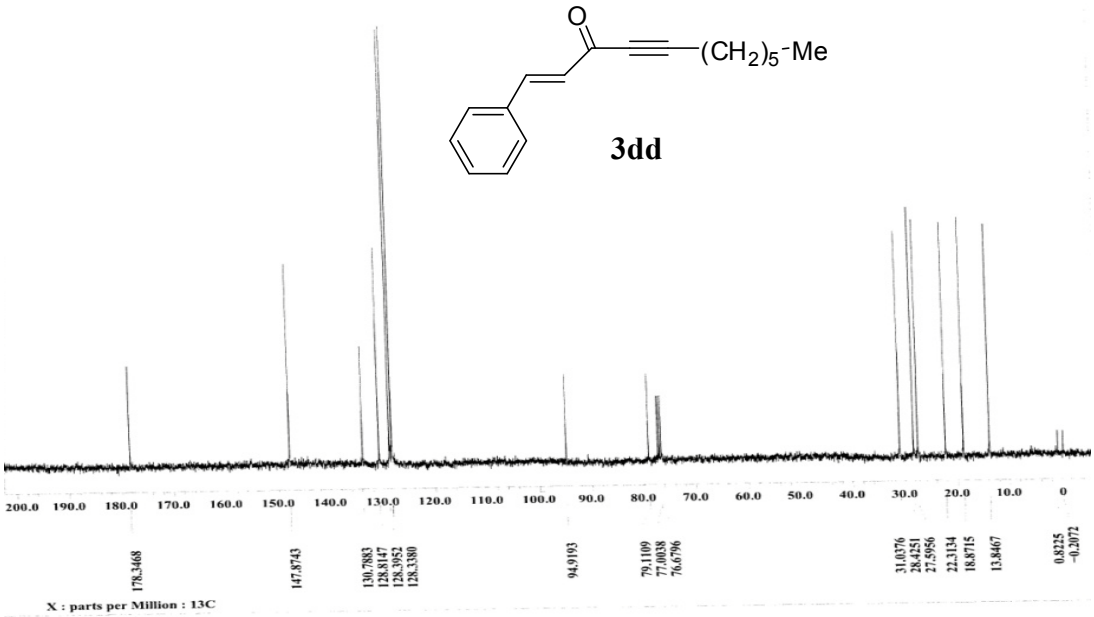


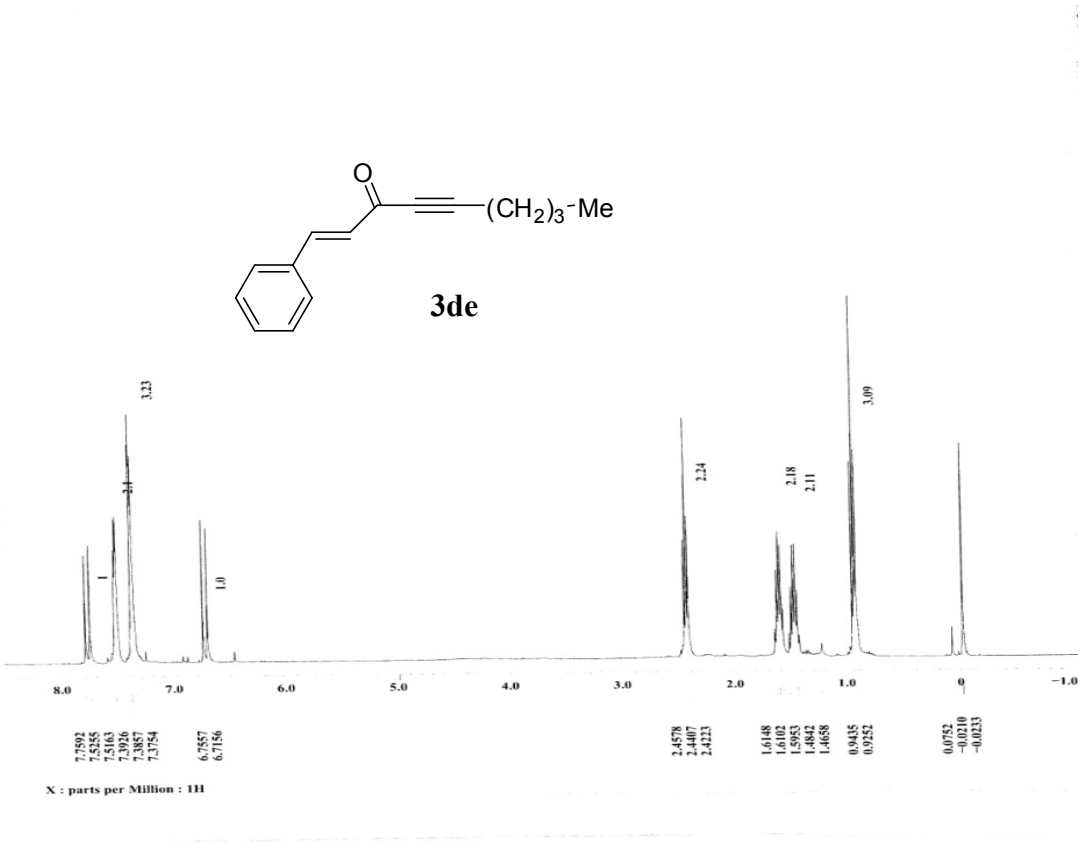


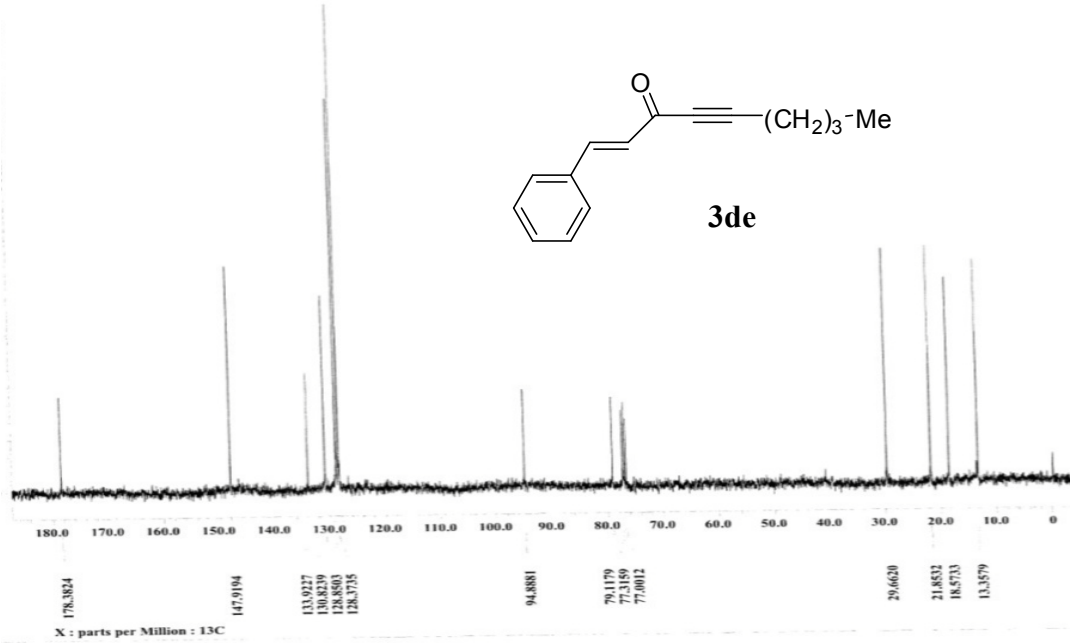
^{1}H and ^{13}C NMR spectra of **3dd:**



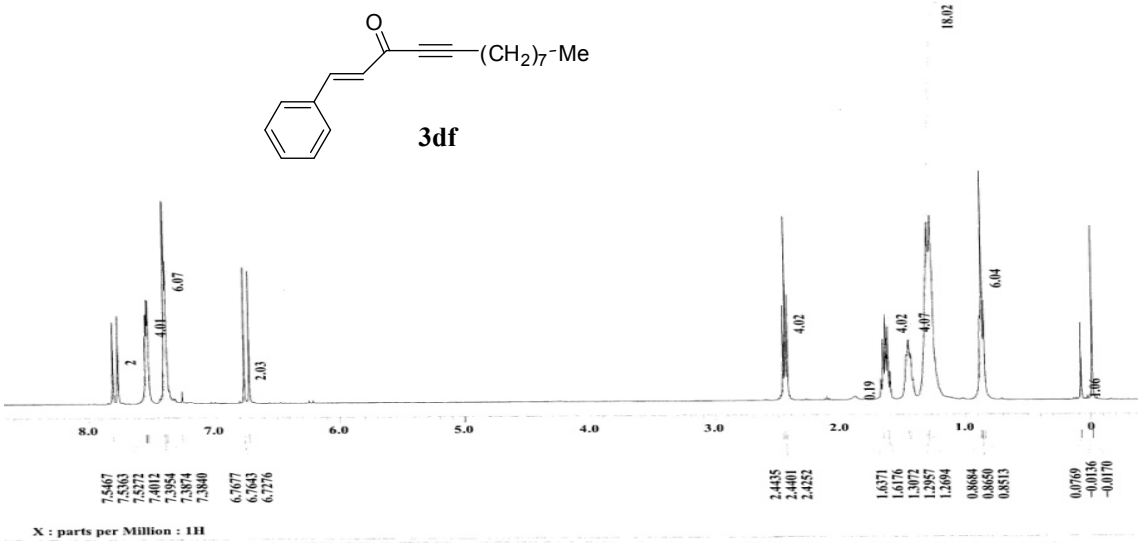


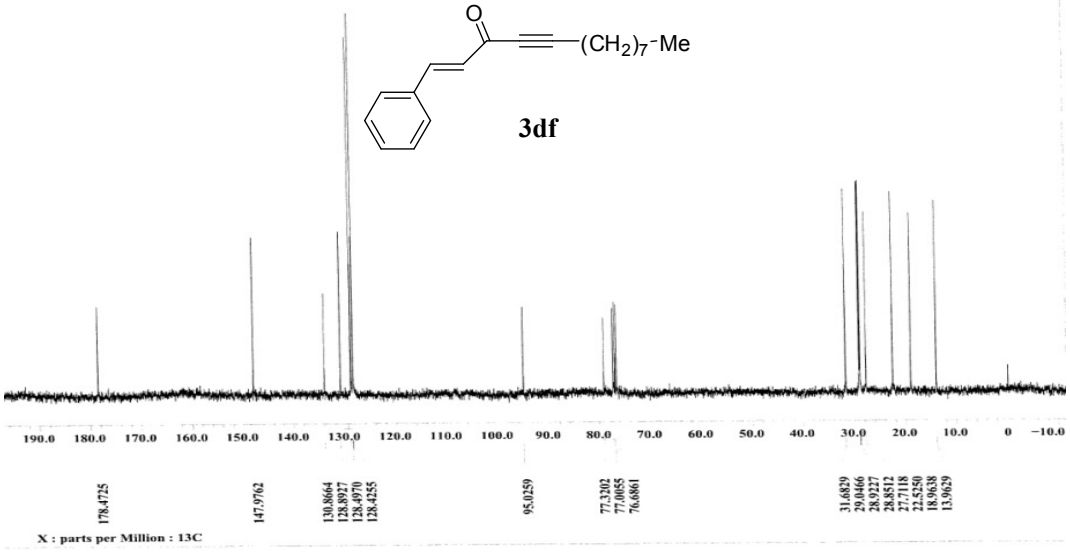
^{1}H and ^{13}C NMR spectra of **3de:**





^{1}H and ^{13}C NMR spectra of **3df**:





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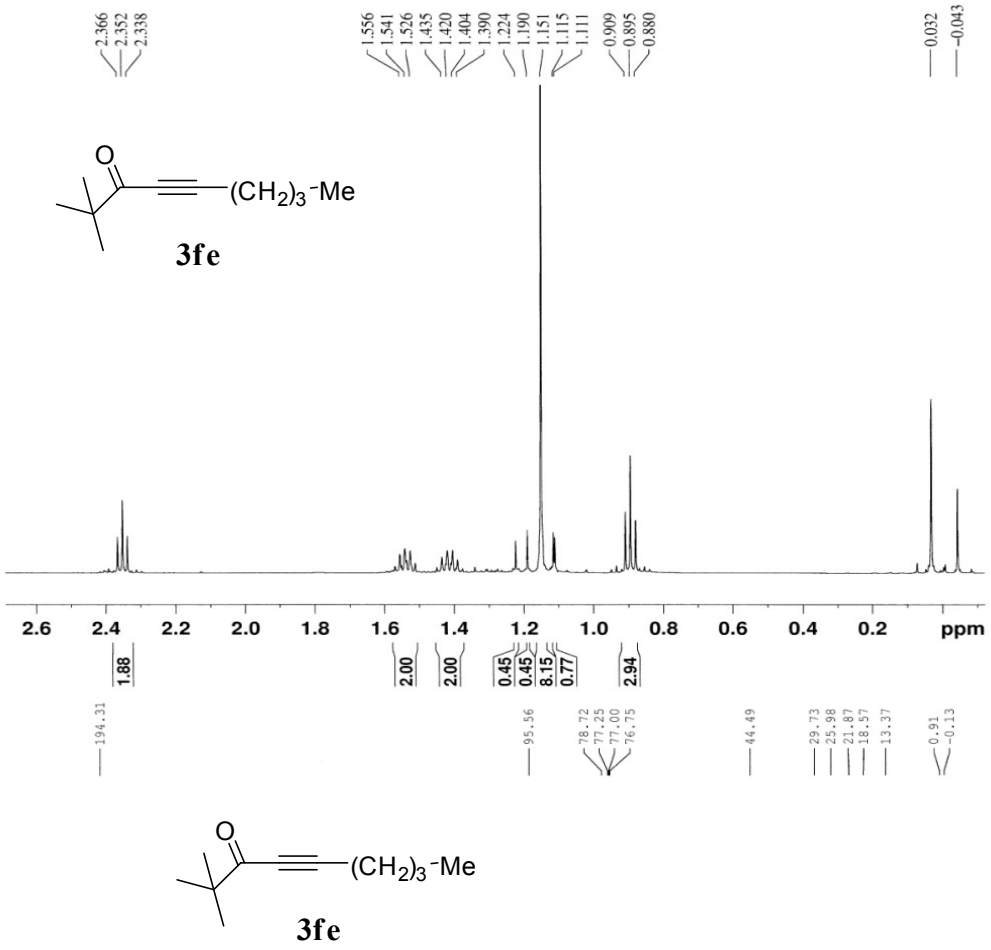
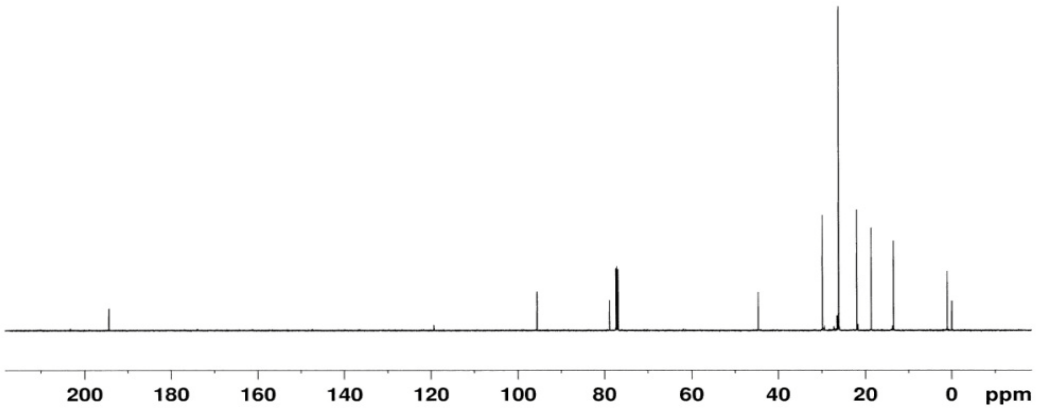
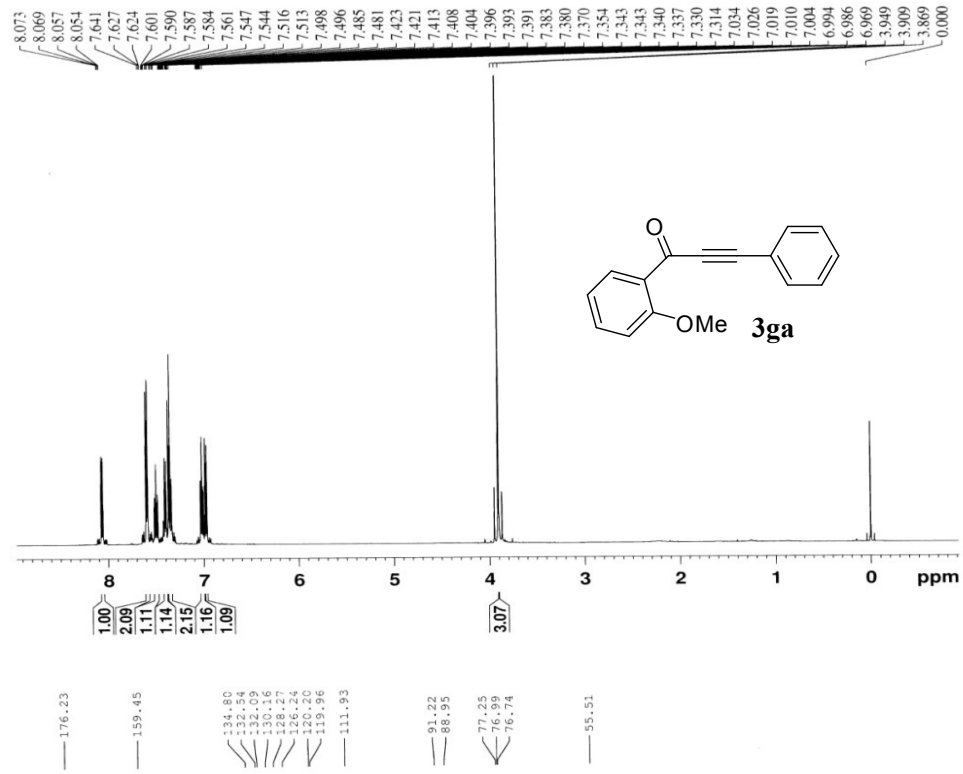
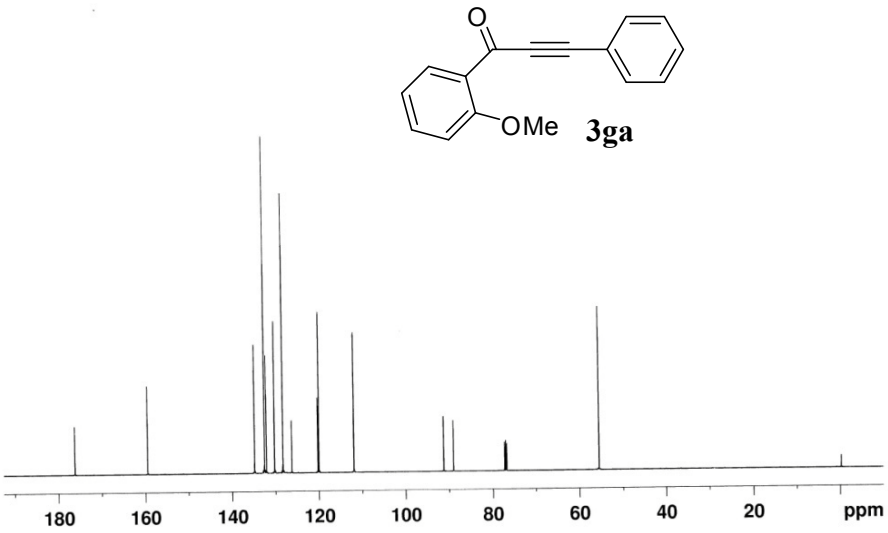
^{1}H and ^{13}C NMR spectra of **3fe:**



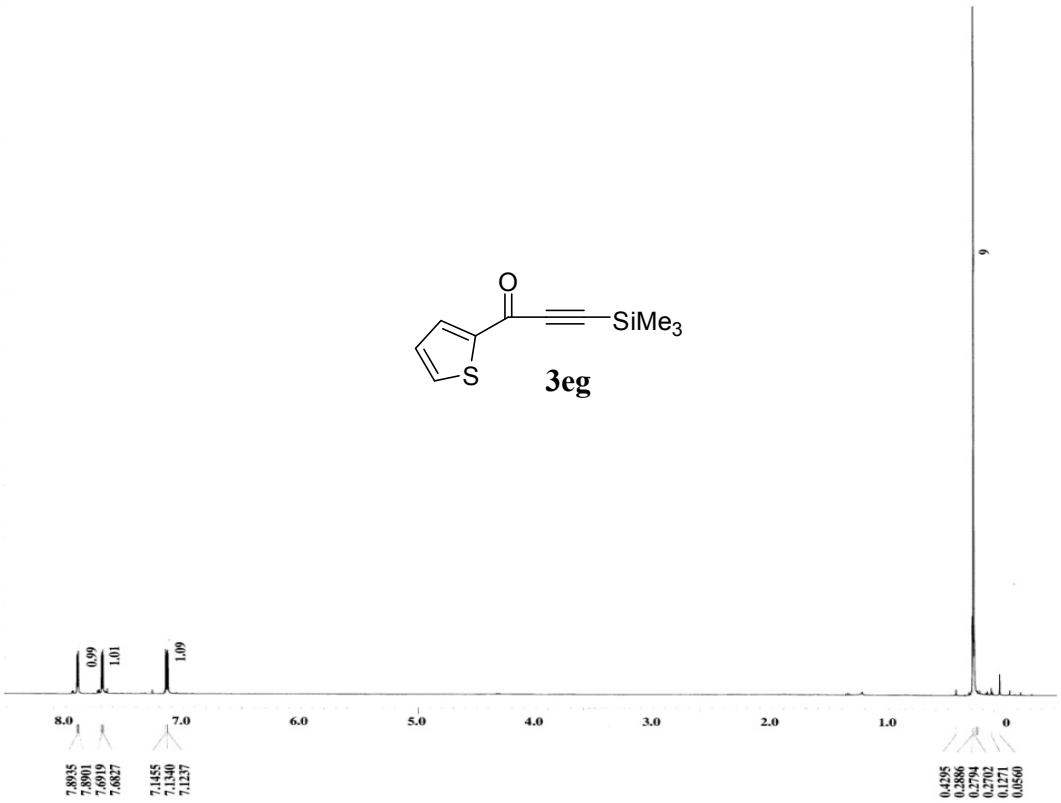


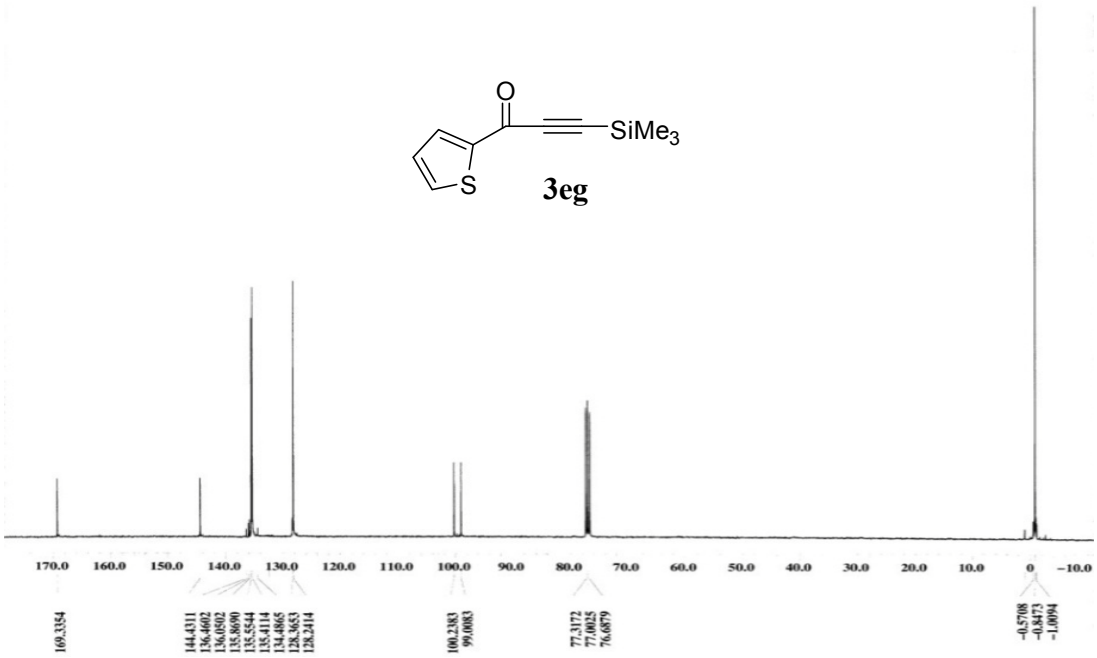
^{1}H and ^{13}C NMR spectra of **3ga:**



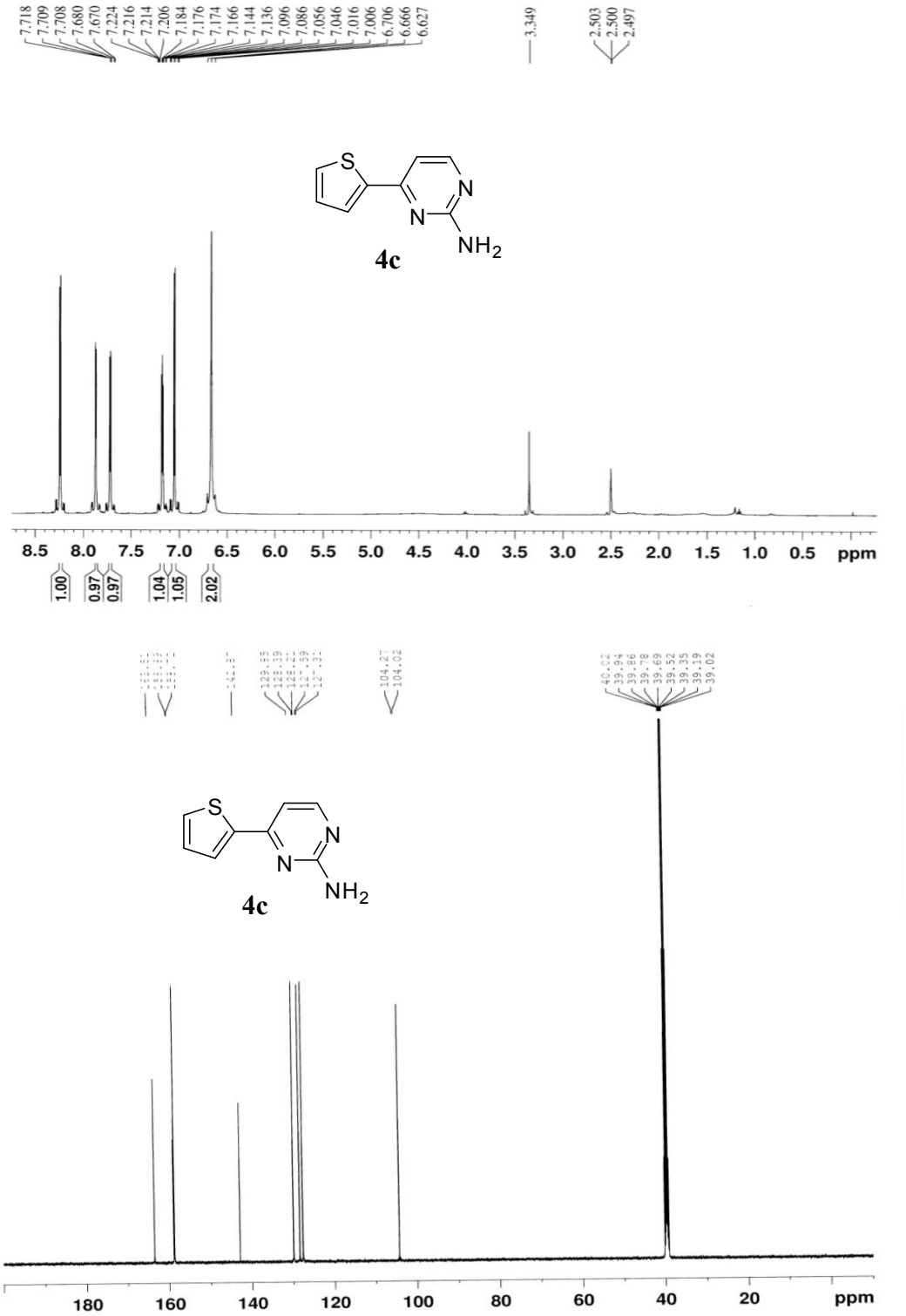


^{1}H and ^{13}C NMR spectra of **3eg:**

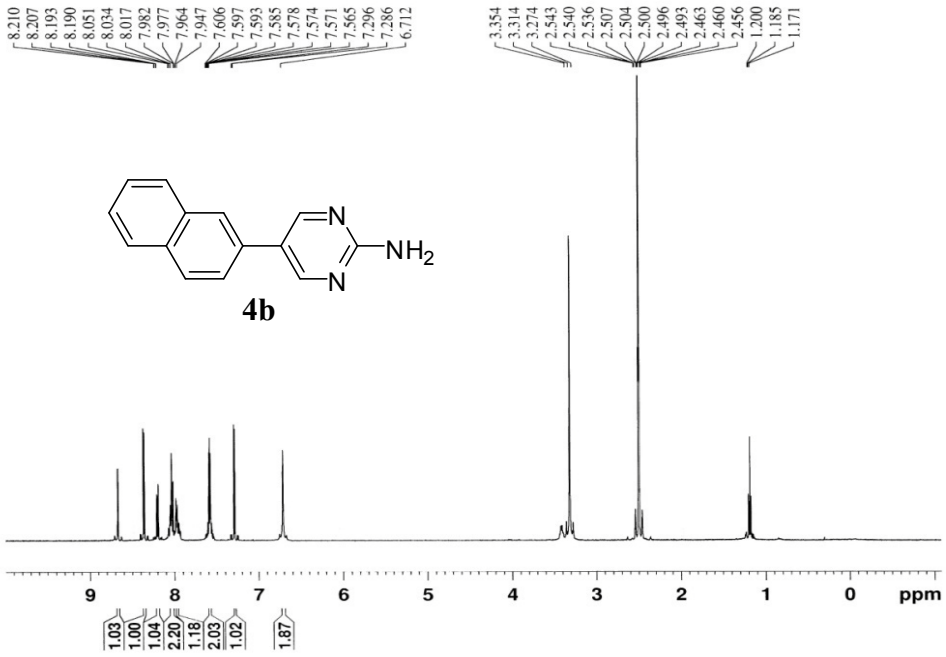


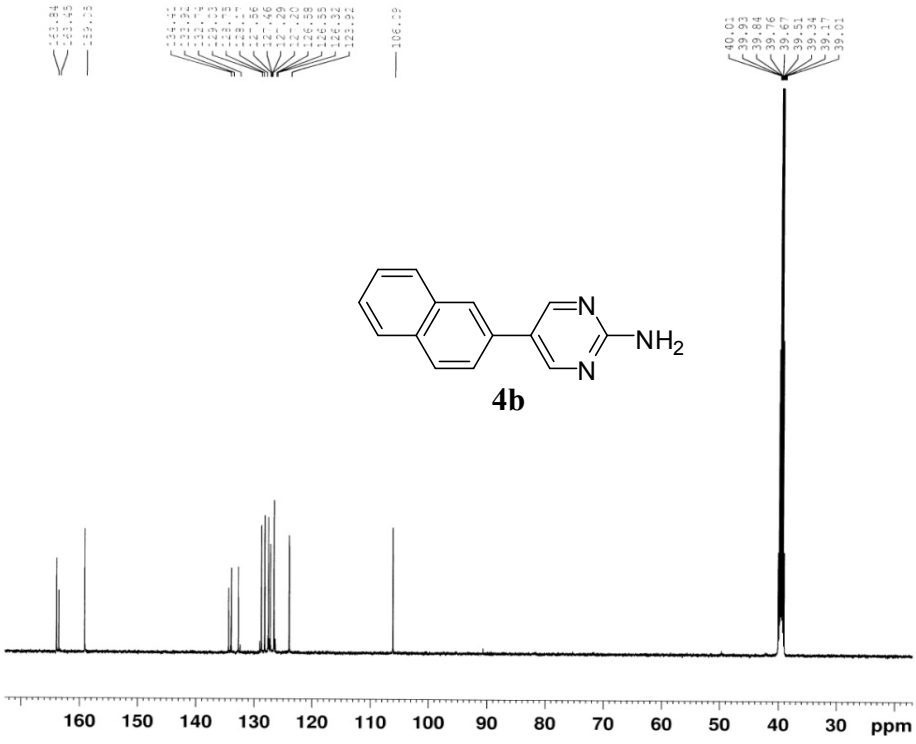


^{1}H and ^{13}C NMR spectra of **4c:**

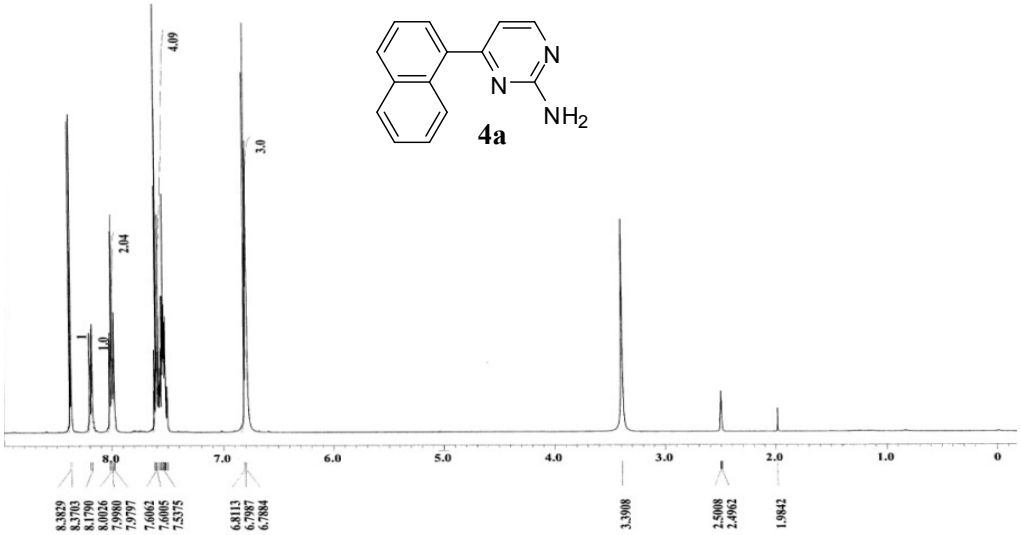


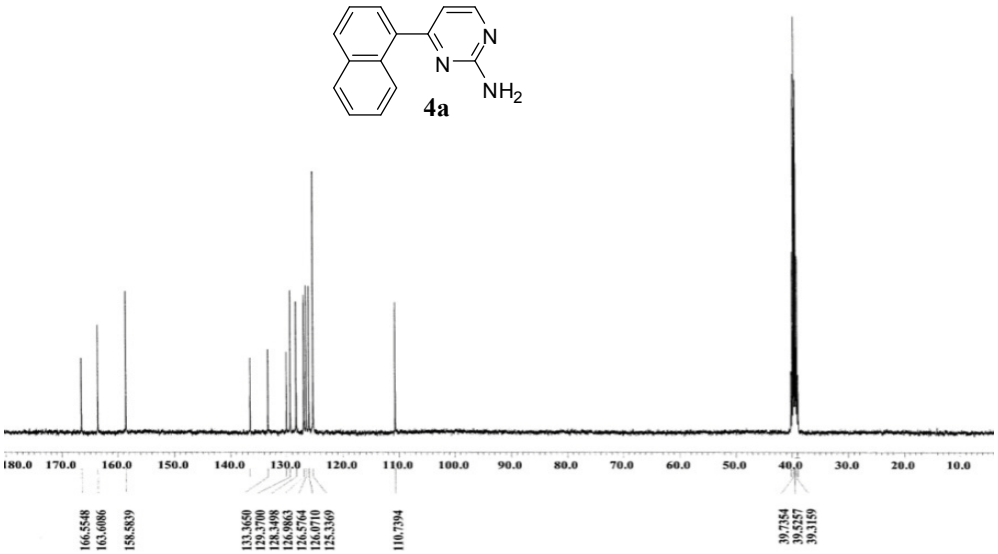
^{1}H and ^{13}C NMR spectra of **4b**:



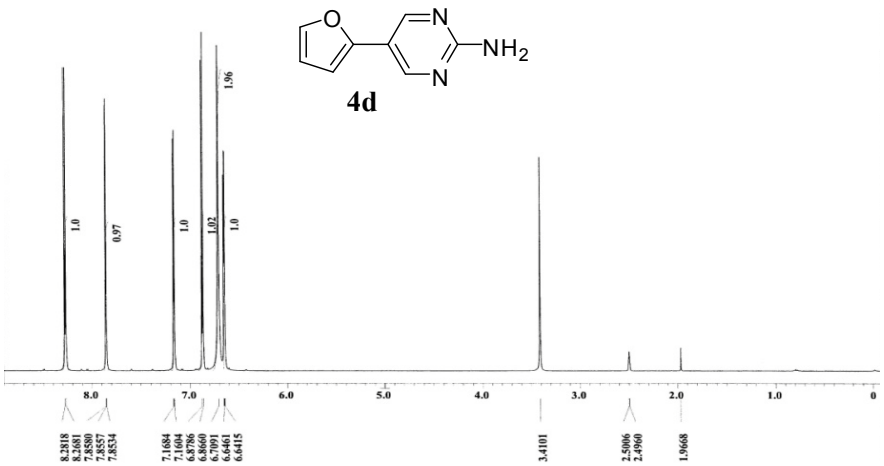


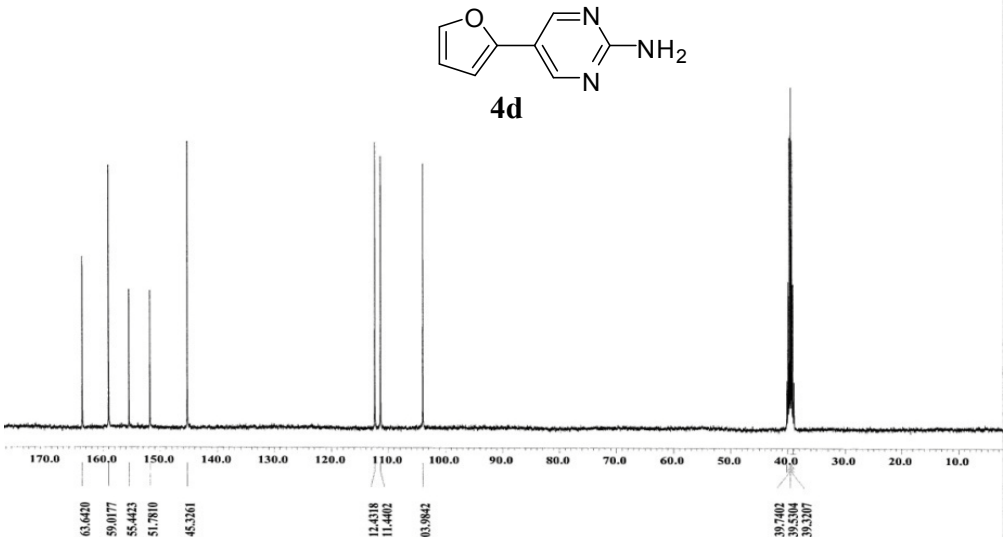
^{1}H and ^{13}C NMR spectra of **4a:**



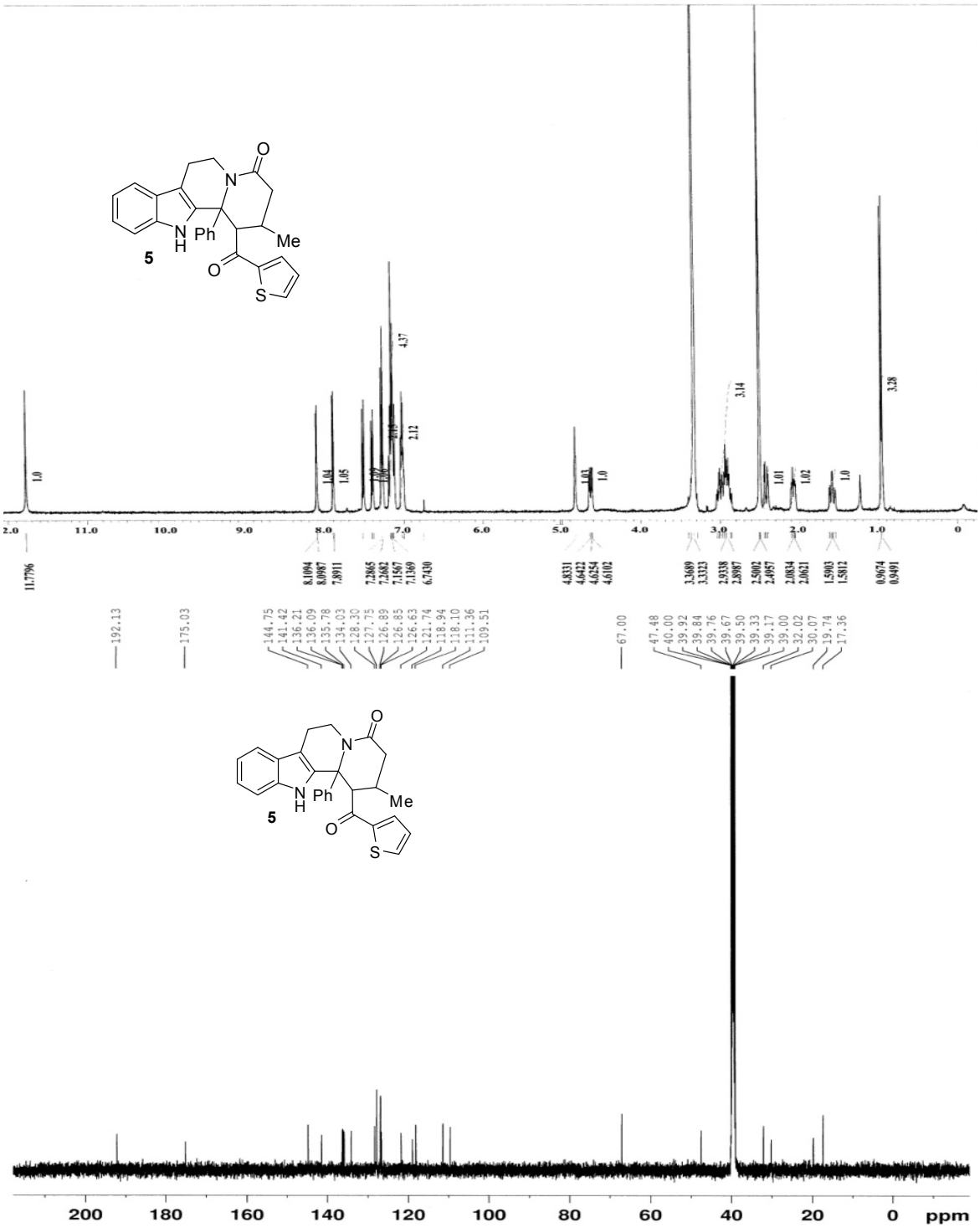


^{1}H and ^{13}C NMR spectra of **4d:**





^{1}H and ^{13}C NMR spectra of **5:**



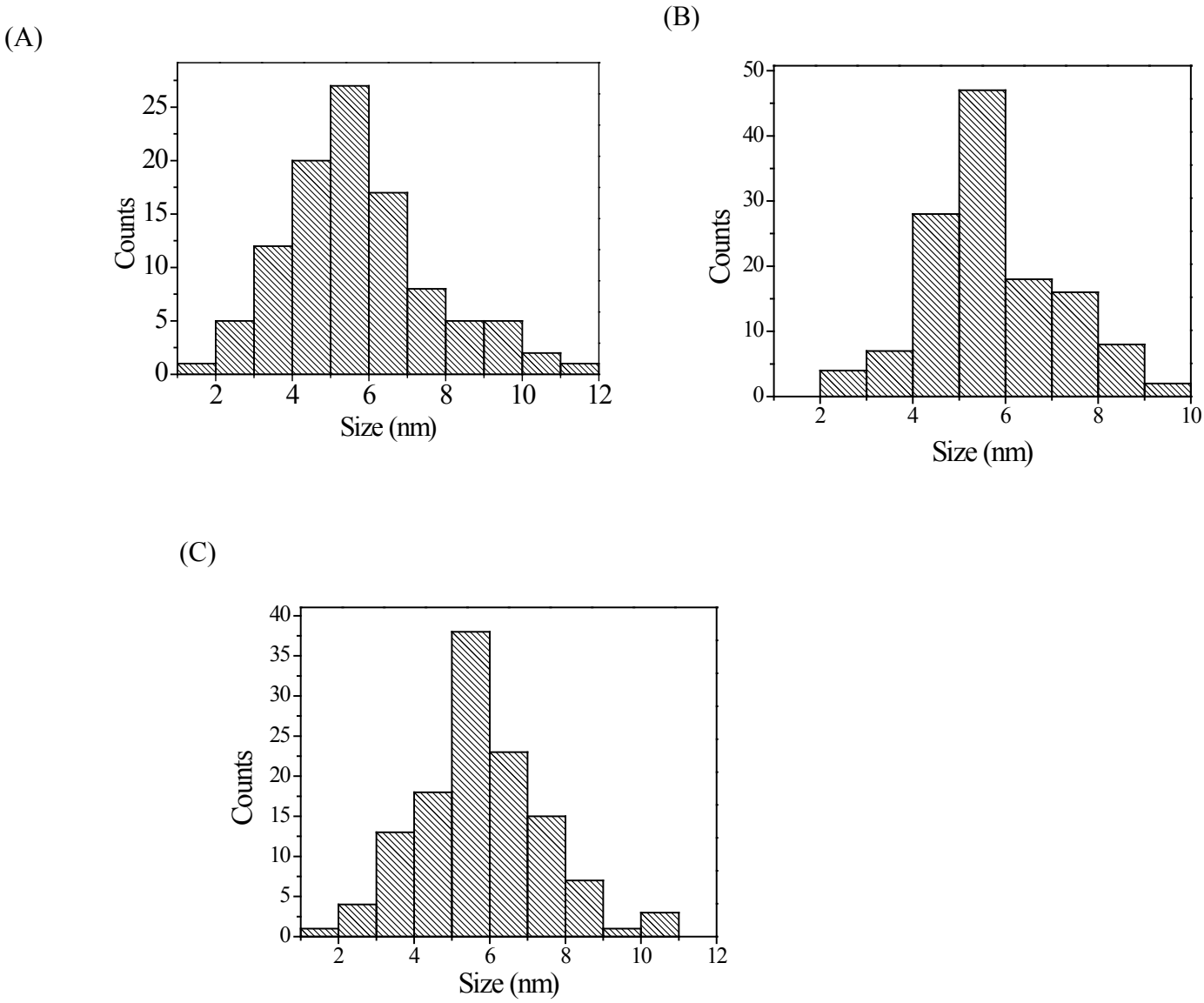


Fig. S1 Size distribution histogram of palladium nanoparticles from TEM images: (A) before catalysis; (B) after first catalytic cycle, (C) after fourth catalytic cycle revealing no changes in particle size.