Supplementary Material

Oxidation of alcohols to carbonyl compounds with molecular iodine in the presence of potassium *tert*-butoxide

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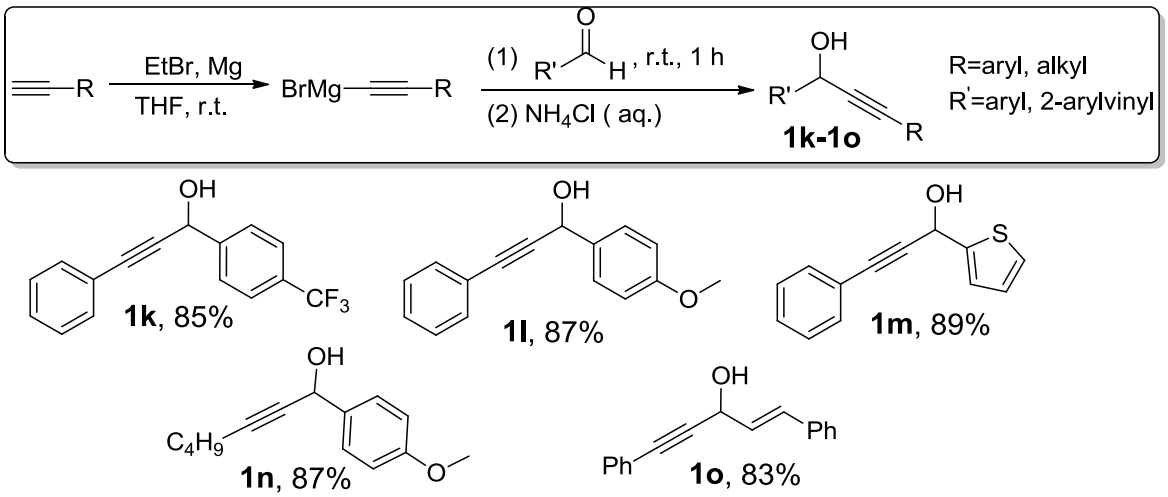
1. General procedure for the preparation of alcohols 1k–1o (Scheme S1)

In a typical run, under an argon atmosphere, a 50 mL Schlenk flask was charged with magnesium turnings (1.22 g, 50 mmol), dry tetrahydrofuran (THF, 20 mL) and bromoethane (4.5 mL, 60 mmol). The mixture was violently stirred at room temperature until magnesium turnings was fully dissolved, then kept on stirring for 15 min, followed by addition of alkyne (55 mmol). The mixture was stirred at room temperature for 1 h. After aldehyde (45 mmol) was added, the reaction system kept on stirring for 1 h at room temperature, then cooled with ice-water bath, quenched with saturated aqueous NH_4Cl, and extracted with ethyl acetate (three portions of 15 mL each). The combined organic phase was washed with deionized water and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and then filtered and concentrated. The crude product was purified by column chromatography (silica, hexane/EtOAc mixture as eluent).



Scheme S1. Synthesis of acohols **1k**–**1o.**

3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (1k).[S1] Yield 85%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.38–7.26 (m, 4H), 7.20 (d, *J* = 7.0 Hz, 2H), 5.70 (d, *J* = 6.6 Hz, 1H), 2.70 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.23 (q, *J* = 1.3 Hz), 131.67, 130.29 (q, *J* = 18.7 Hz), 128.83, 128.32, 126.86, 125.45 (q, *J* = 3.8 Hz), 123.98 (q, *J* = 270.4 Hz), 121.87, 87.91, 87.10, 64.16.

1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1l).[S2, S3] Yield 85%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.51–7.47 (m, 2H), 7.34–7.30 (m, 3H), 6.93 (d, *J* = 8.7 Hz, 2 H), 5.64 (d, *J* = 4.0 Hz, 1H), 3.81 (s, 3H), 2.79 (br.s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.52, 132.92, 131.64, 128.45, 128.21, 128.11, 122.40, 113.88, 88.93, 86.31, 64.52, 55.22.

3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-ol (1m).[S3] Yield 89%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.40 (m, 2H), 7.30–7.20 (m, 4H), 7.17 (d, *J* = 3.5 Hz, 1H), 6.91 (dd, *J* = 3.6, 5.0 Hz, 1H), 5.82 (d, *J* = 6.2 Hz, 1H), 3.51 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.45, 131.58, 128.51, 128.11, 126.59, 125.84, 125.46, 121.92, 88.09, 85.71, 60.30

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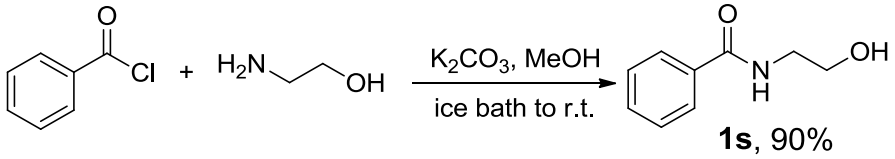
1-(4-methoxyphenyl)hept-2-yn-1-ol (1n).[S4] Yield 87%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.39 (s, 1H), 3.80 (s, 3H), 2.40 (br. s, 1H), 2.27 (dt, *J* = 2.8, 7.0 Hz, 2H), 1.58–1.35 (m, 4H), 0.92 (t, *J* = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.37, 133.59, 127.97, 113.74, 87.29, 80.03, 64.27, 55.21, 30.59, 21.91, 18.42, 13.53.
(*E*)-1,5-diphenylpent-1-en-4-yn-3-ol (1o).[S1, S3] Yield 83%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (dd, *J* = 2.3, 7.0 Hz, 2H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.39–7.18 (m, 6H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.36 (dd, *J* = 6.0, 15.8 Hz, 1H), 5.27 (br. s, 1H), 2.98 (br. s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.95, 131.81, 131.65, 128.47, 128.44, 128.21, 127.95, 126.72, 122.86, 87.96, 86.24, 63.23.

2. Syntheis of alcohol 1s (Scheme S2)



Scheme S2. Synthesis of alcohol **1s.**

A 50 mL reaction flask was charged with benzoyl chloride (1.55 g, 11 mmol) and methanol (20 mL). The mixture was stirred and cooled to –10 ^{o}C in an ice-salt bath, followed by addition of anhydrous K_2CO_3 (1.41 g, 10 mmol) and 2-aminoethanol (0.61 g, 10 mmol). The reaction mixture was stirred overnight with gradual warming to room temperature, then concentrated to near dryness on a rotary evaporator and extracted with ethyl acetate. The organic phase was washed with deionized water and saturated aqueous NaCl, dried over anhydrous Na_2SO_4. After filtration and concentration, the reaction residue was purified by chromatography to afford ***N*-(2-hydroxyethyl)benzamide** (**1s**) as a white solid (1.48 g, 90% yield).[S5] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H, with additional 0.65 H of active hydrogen), 4.13 (br. s, 1H), 3.75–3.67 (m, 2H), 3.53 (q, *J* = 5.1 Hz, 2H), 2.73 (br. s, 0.35 H of active hydrogen). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.73, 133.90, 131.53, 128.41, 126.92, 61.57, 42.69.

Reference

S1. Yao, X.; Li, C.-J. *Org. Lett.* **2005**, *7*, 4395–4398.
S2. Zhu, H.-T.; Ji, K.-G.; Yang, F.; Wang, L.-J.; Zhao, S.-C.; Ali, S.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2011**, *13*, 684–687.
S3. Downey, C. W.; Mahoney, B. D.; Lipari, V. R. *J. Org. Chem.* **2009**, *74*, 2904–2906.
S4. Lettan II, R. B.; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 3227–3230.
S5. Wu, W.; Zhang, Z.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2011**, *133*, 14256–14259.

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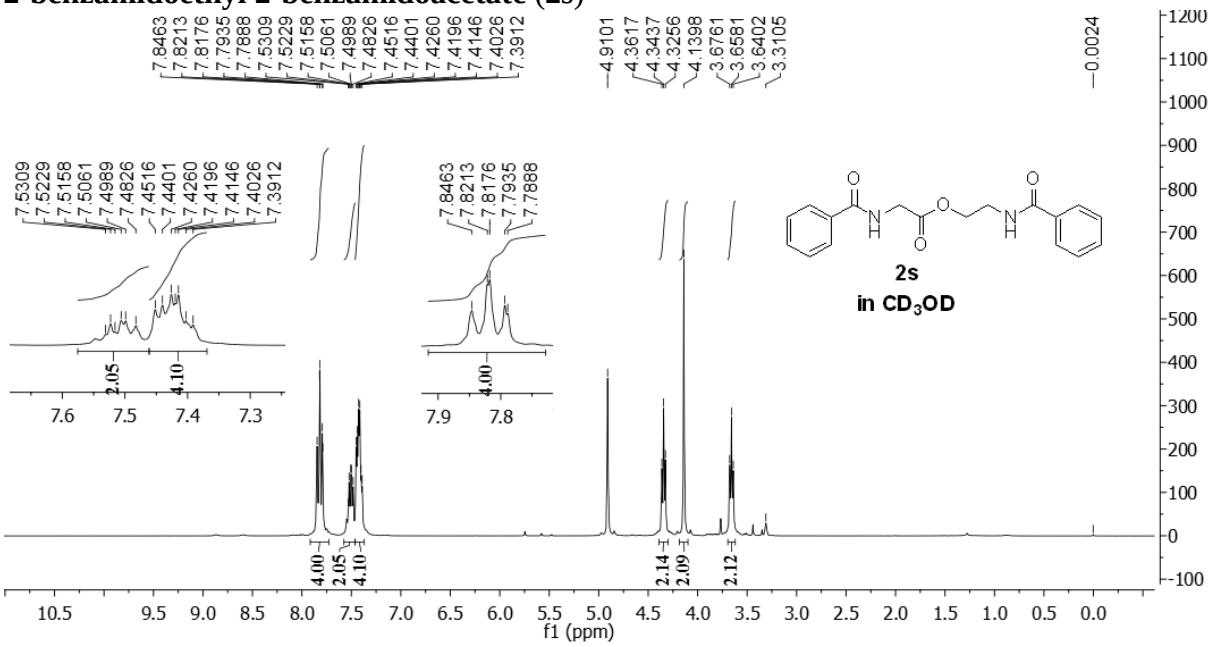
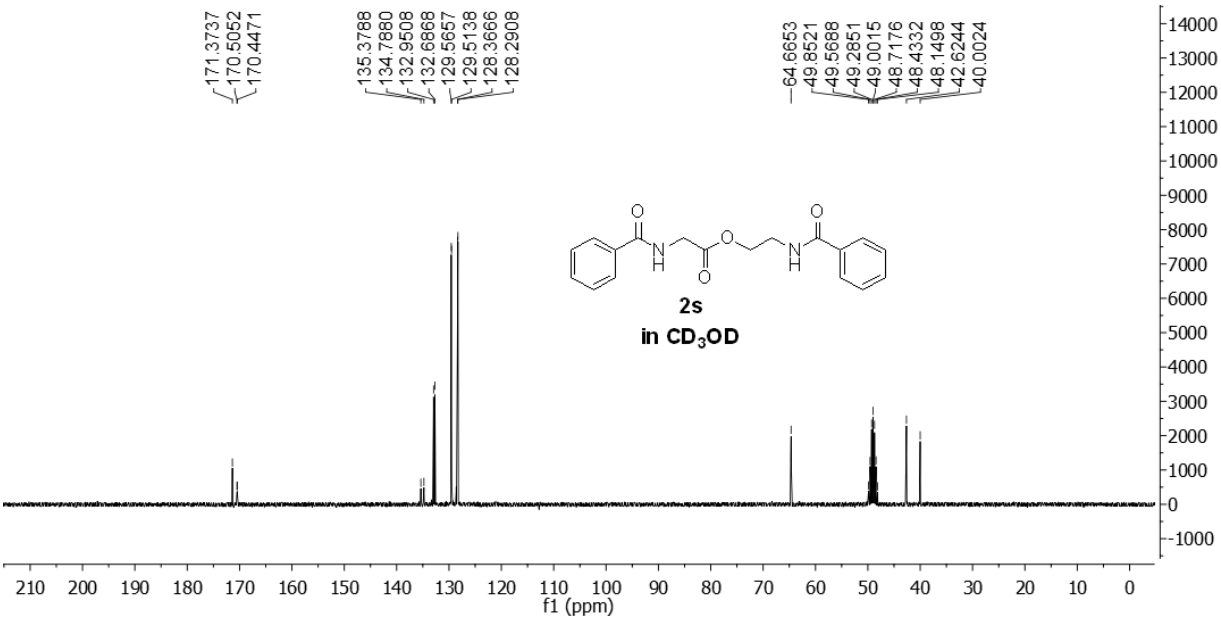
Appendix. NMR and MS spectra
A. Spectra of new compounds (2s and 2u)

2-benzamidoethyl 2-benzamidoacetate (2s)





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Mass Spectrum SmartFormula Report

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Comment			

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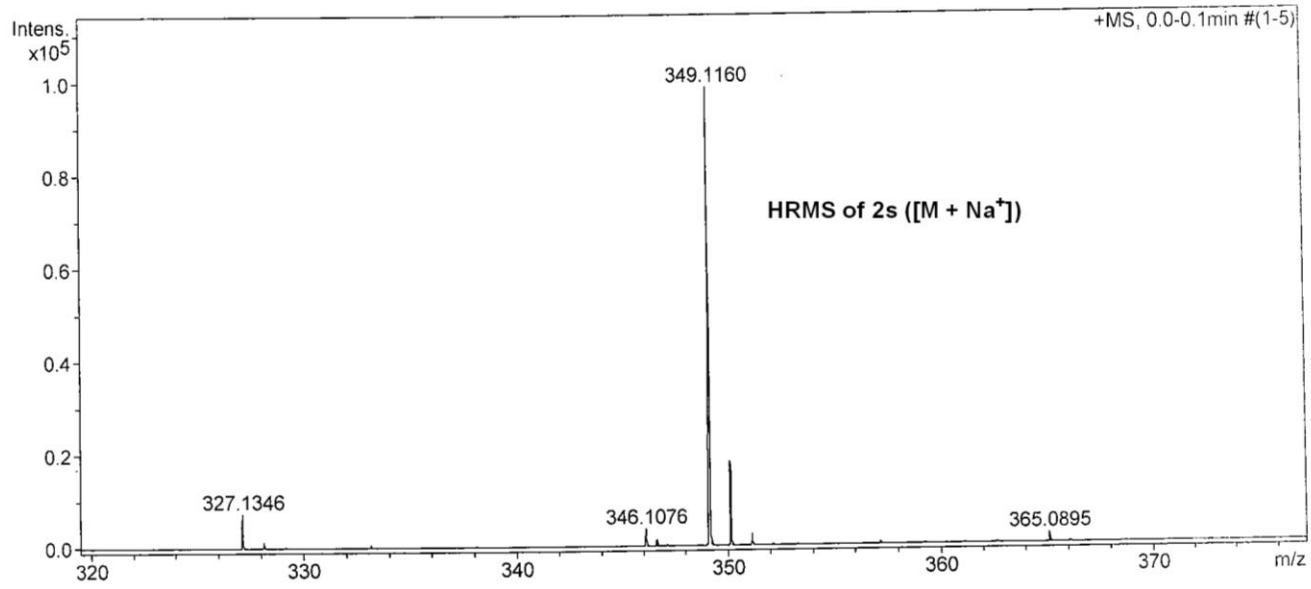

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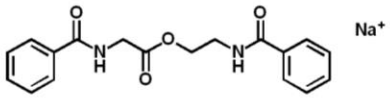

Chemical Formula: $C_{18}H_{18}N_2NaO_4^+$
Exact Mass: 349.1159

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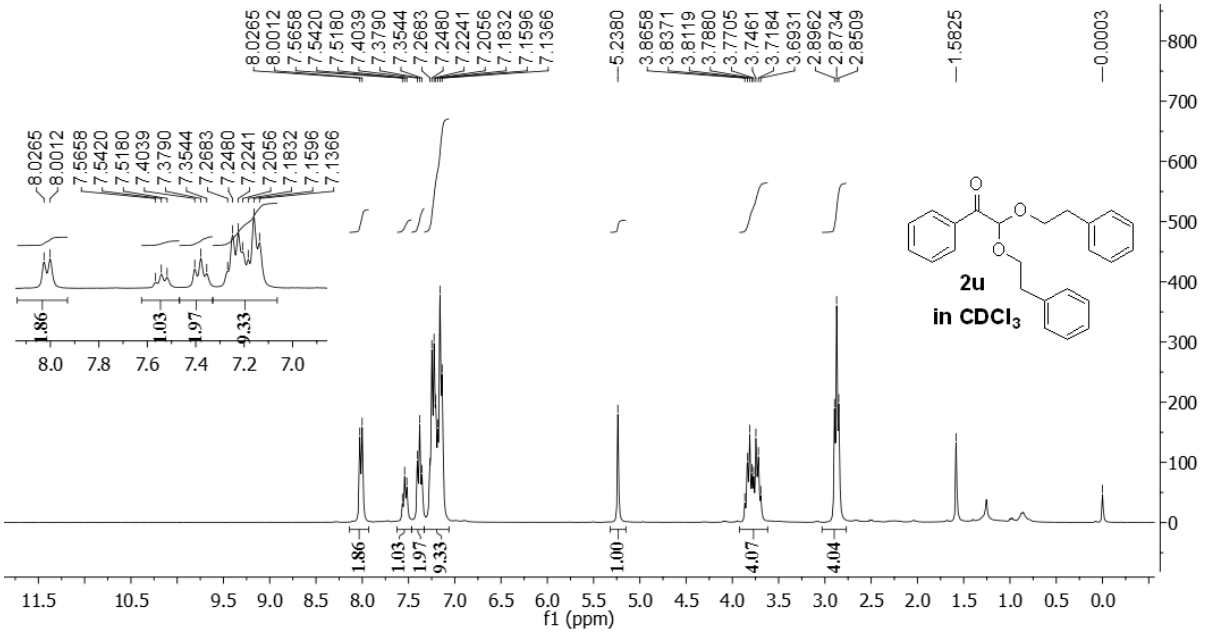
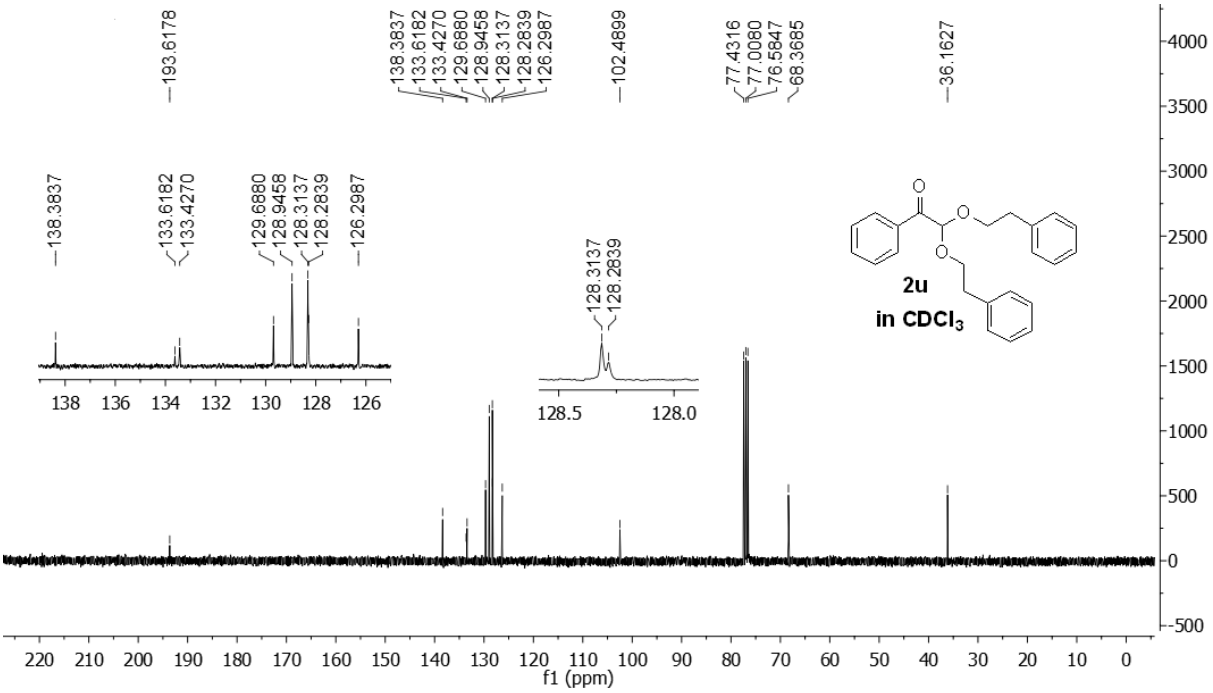
2,2-diphenethoxy-1-phenylethanone (2u)





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Mass Spectrum SmartFormula Report

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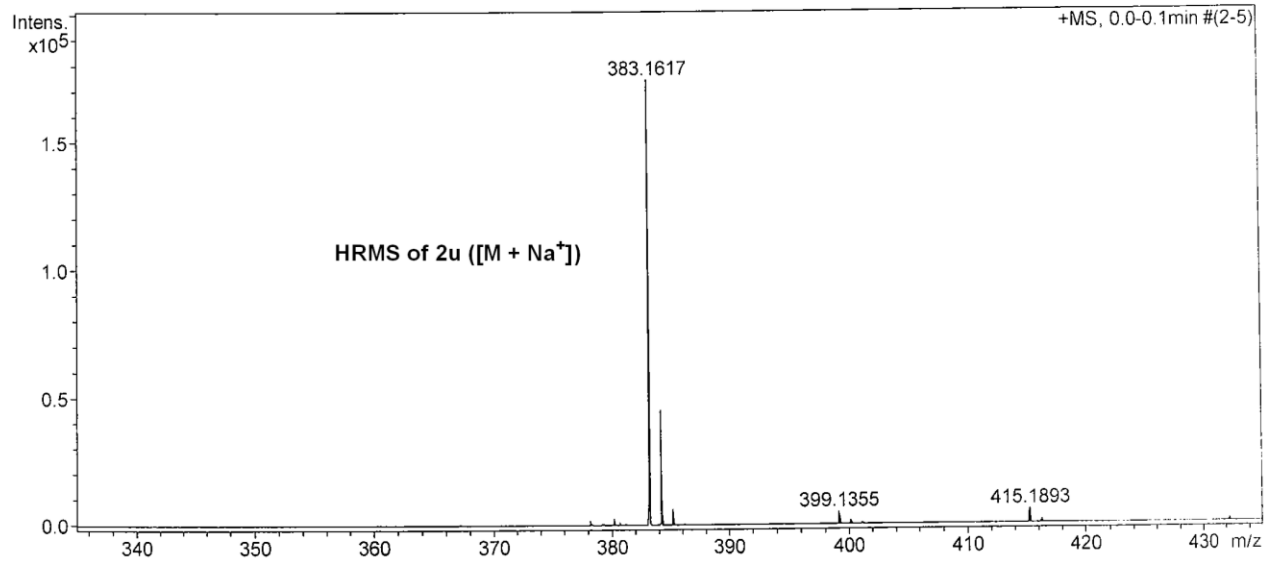

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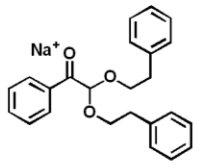

Chemical Formula: $C_{24}H_{24}NaO_3^+$
Exact Mass: 383.1618

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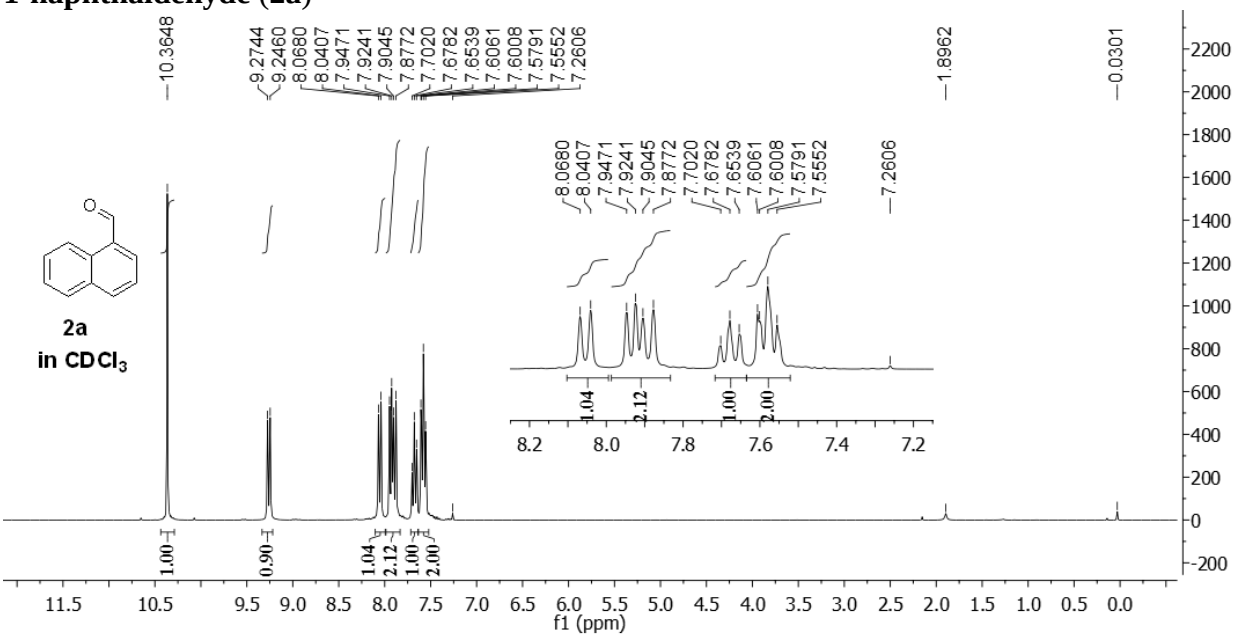
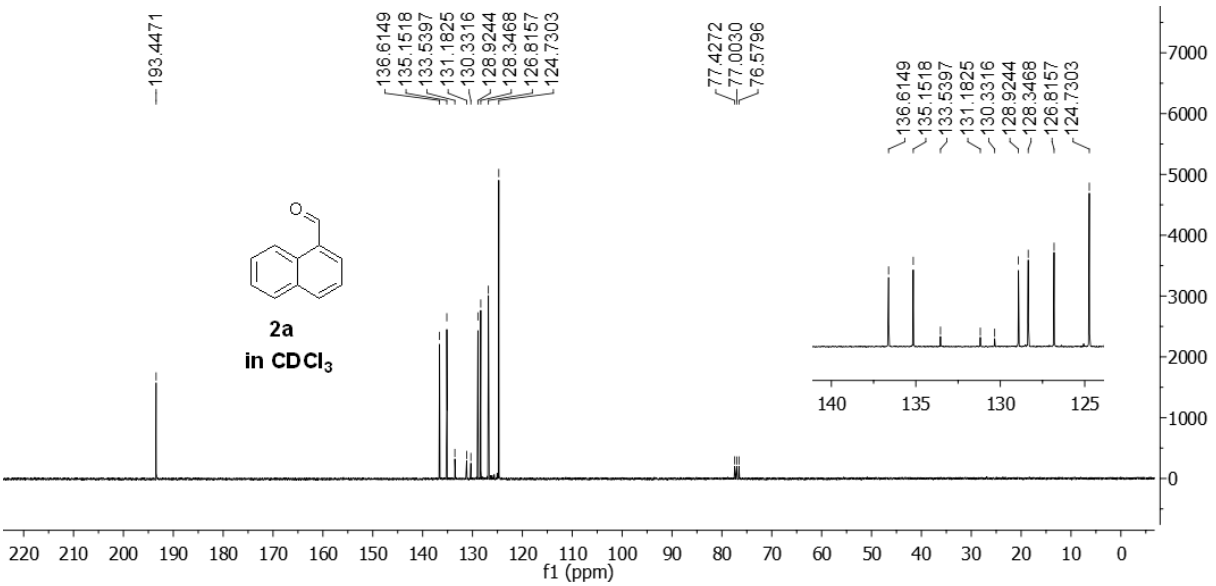
B. Spectra of 2a–2r, and 2t

1-naphthaldehyde (2a)





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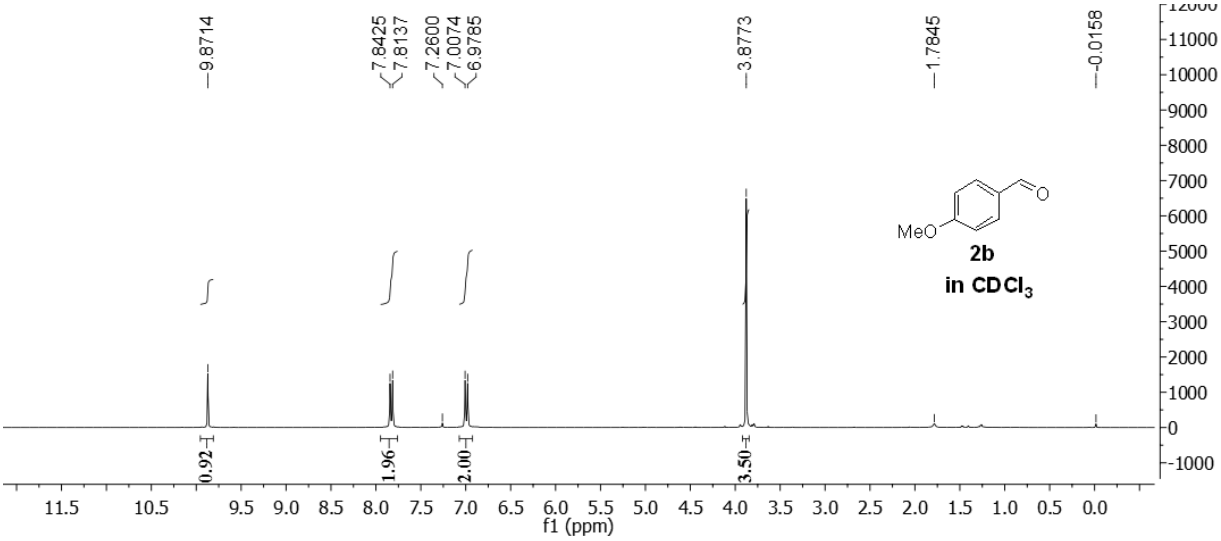
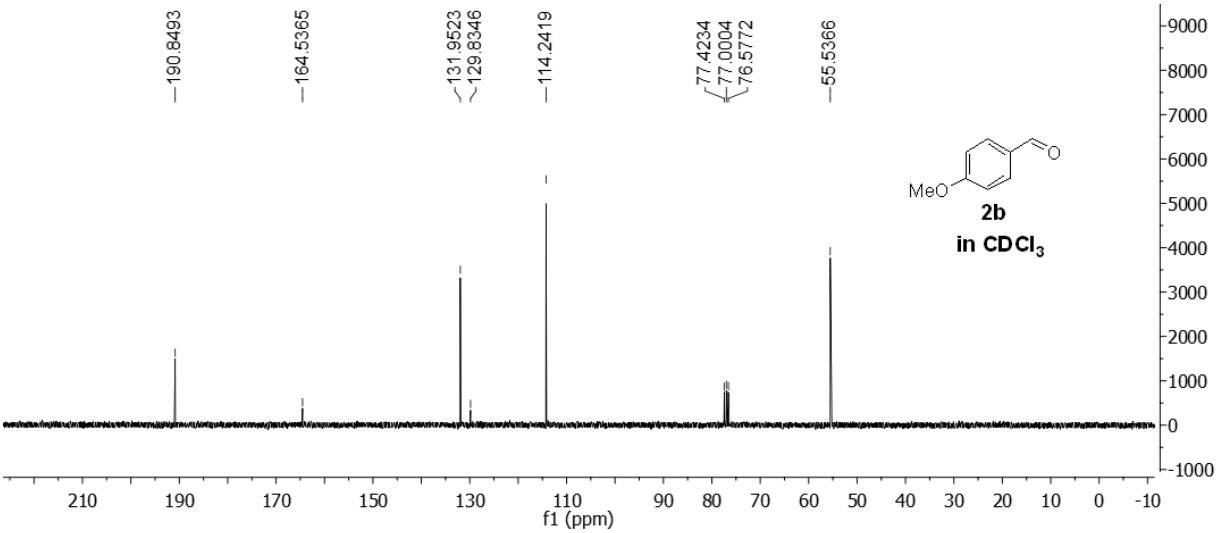
4-methoxybenzaldehyde (2b)





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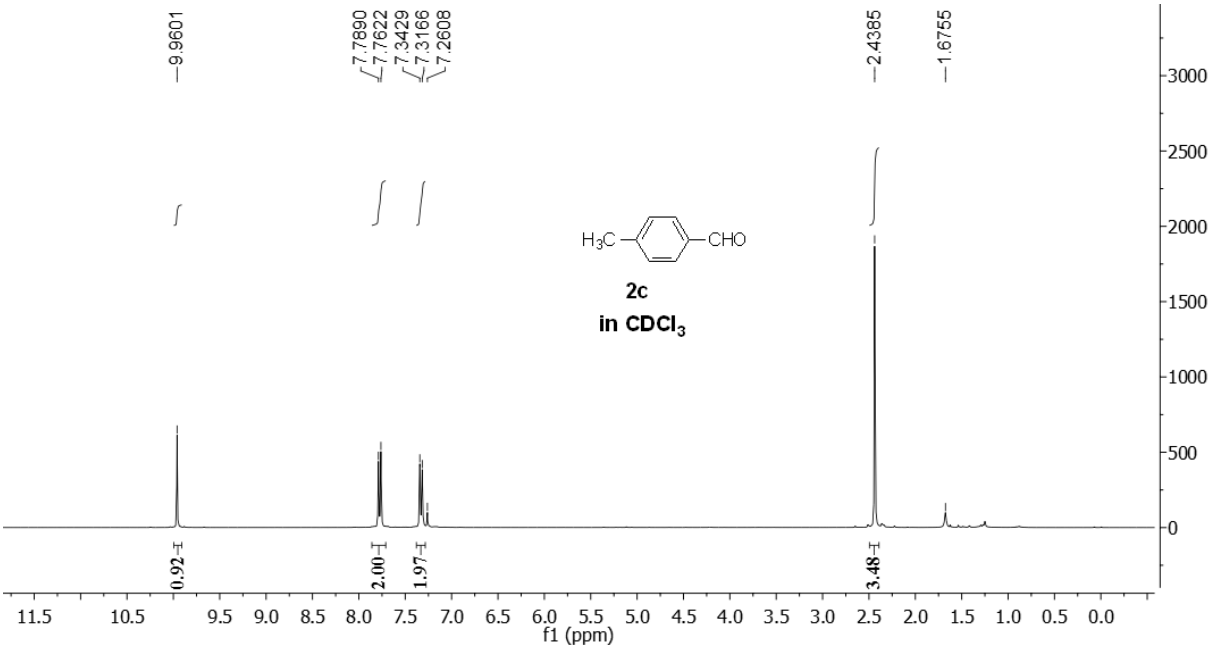
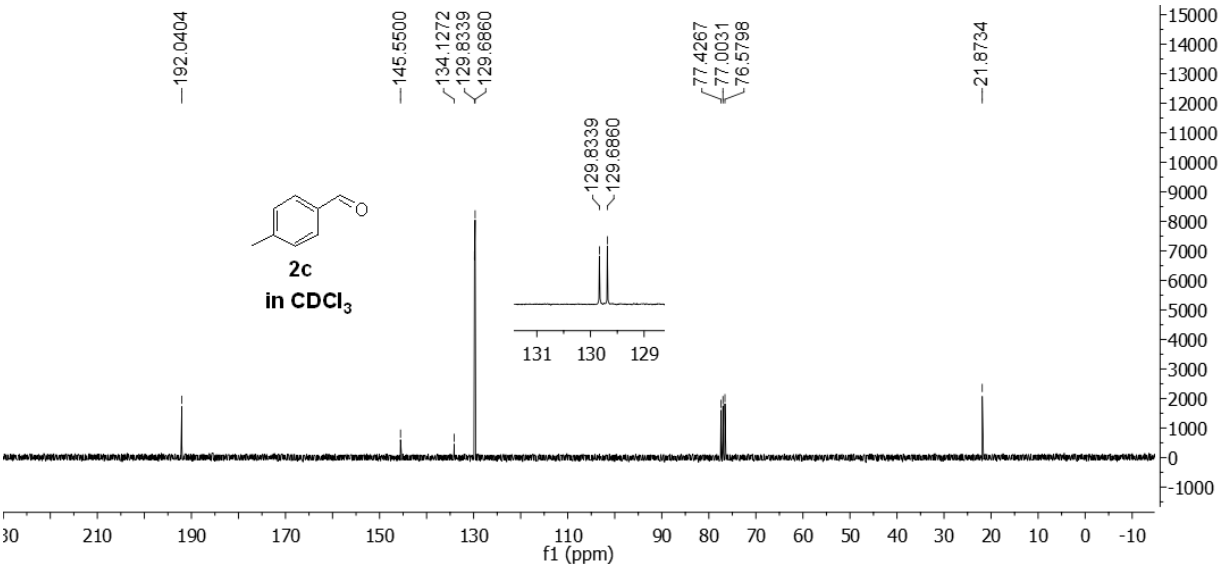
4-methylbenzaldehyde (2c)





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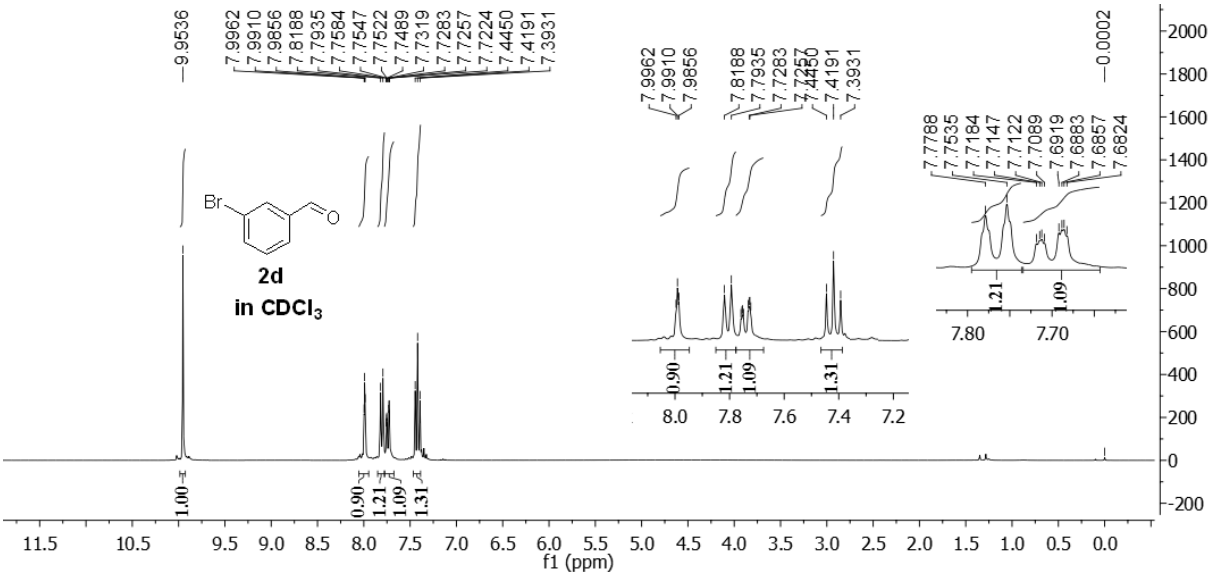
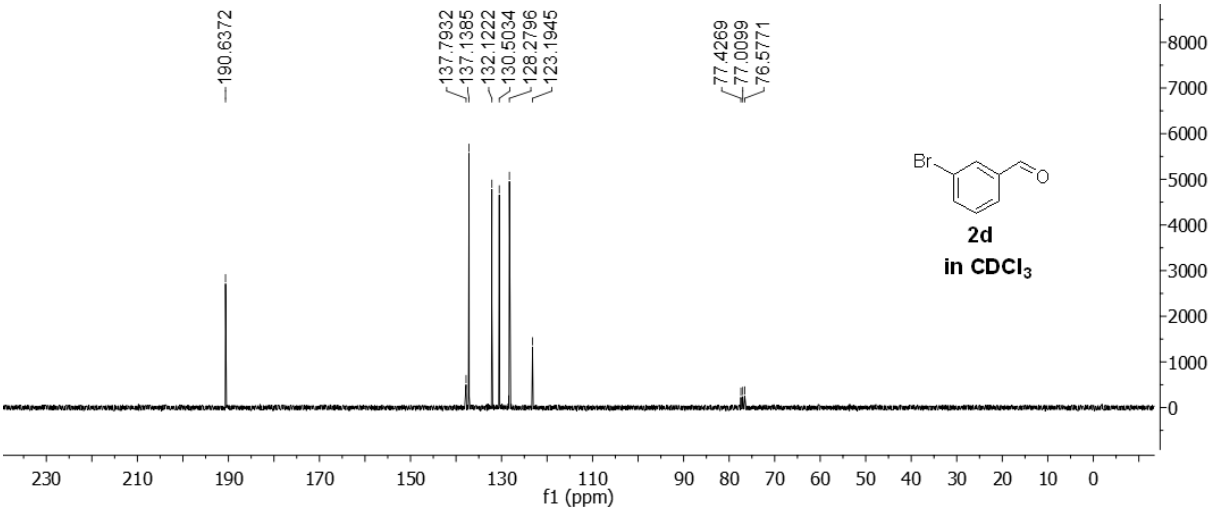
3-bromobenzaldehyde (2d)





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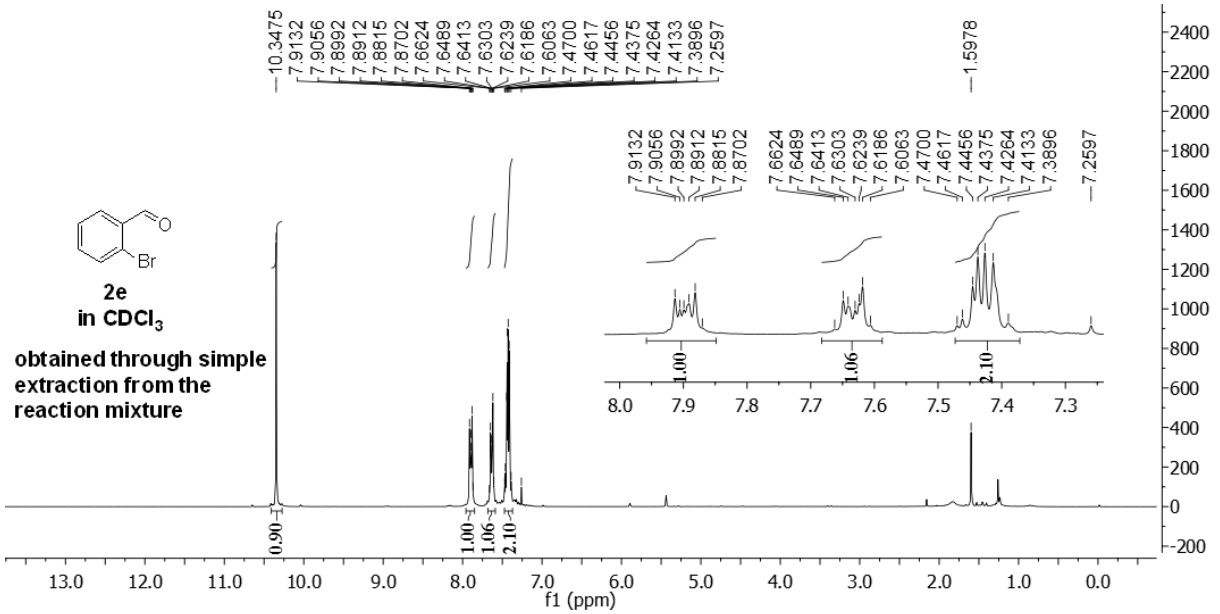
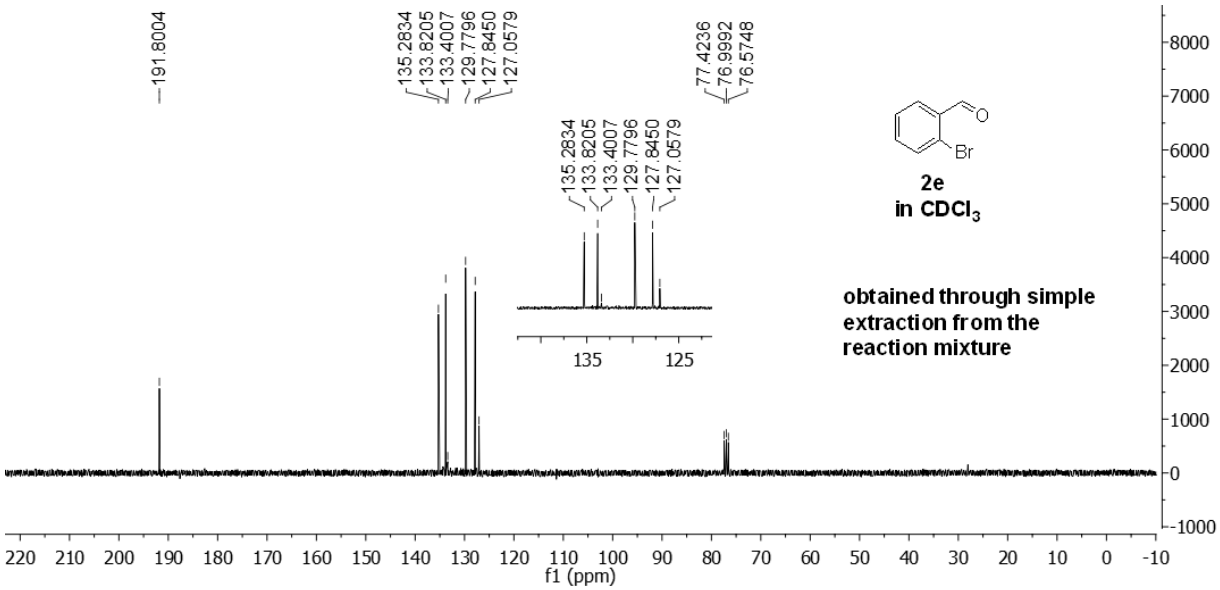
2-bromobenzaldehyde (2e)





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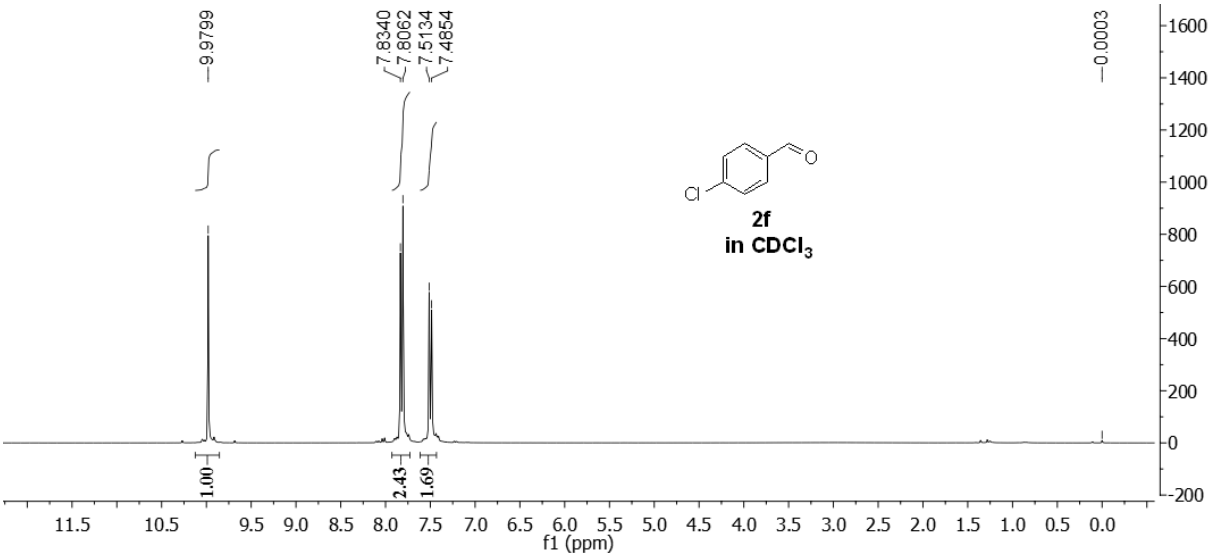
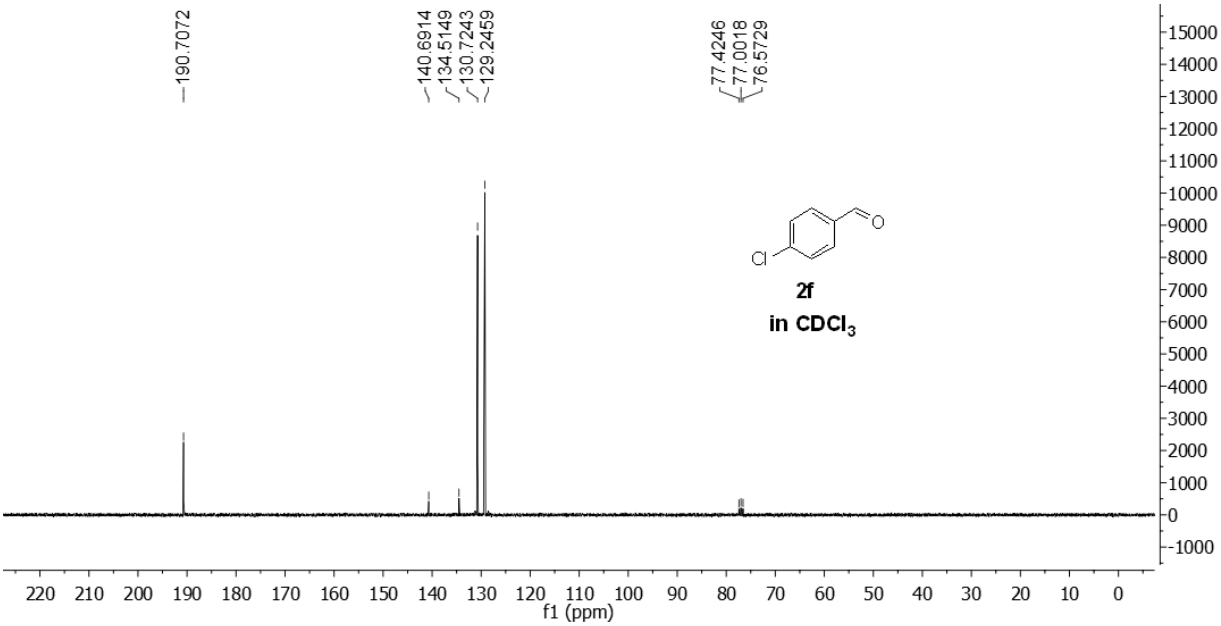
4-chlorobenzaldehyde (2f)





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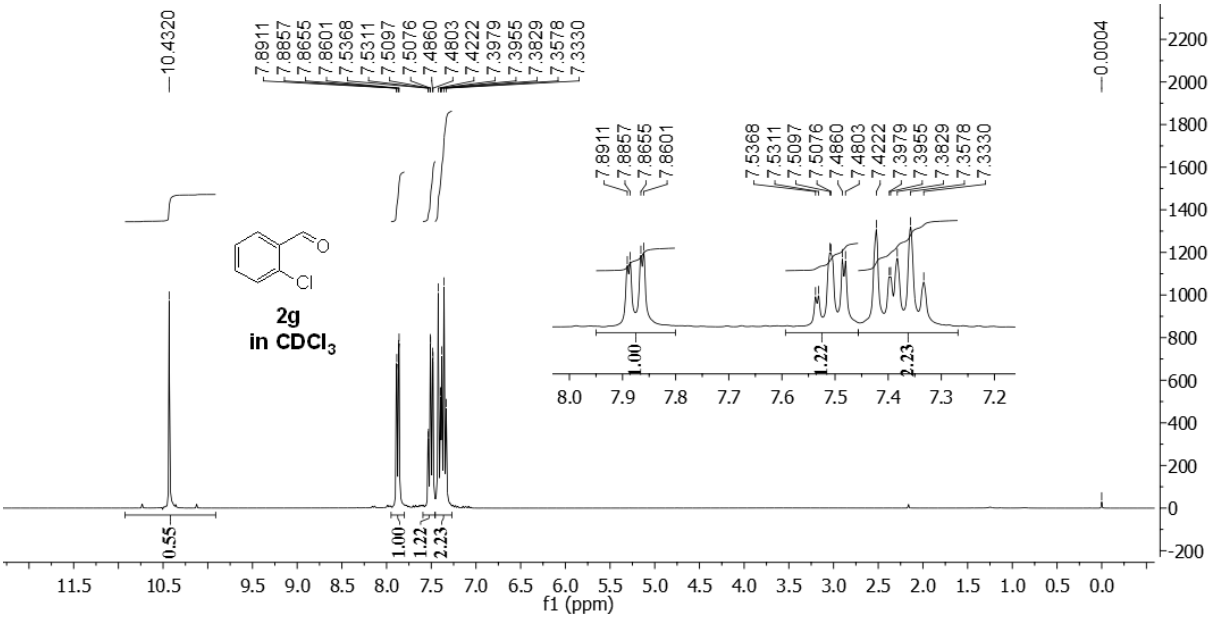
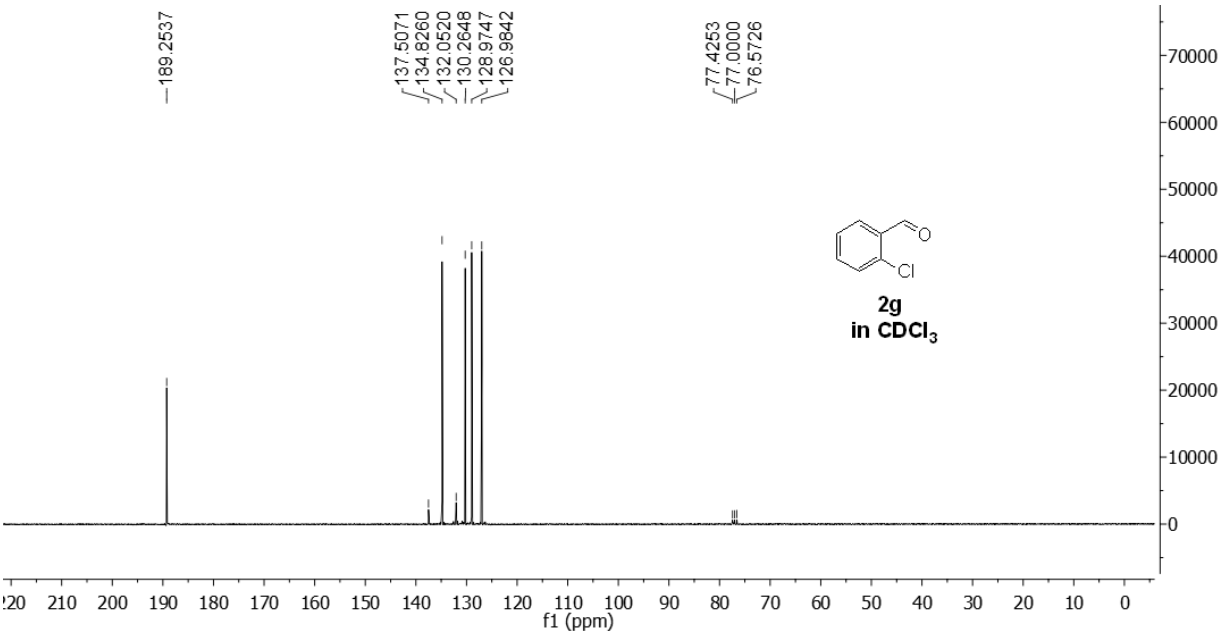
2-chlorobenzaldehyde (2g)





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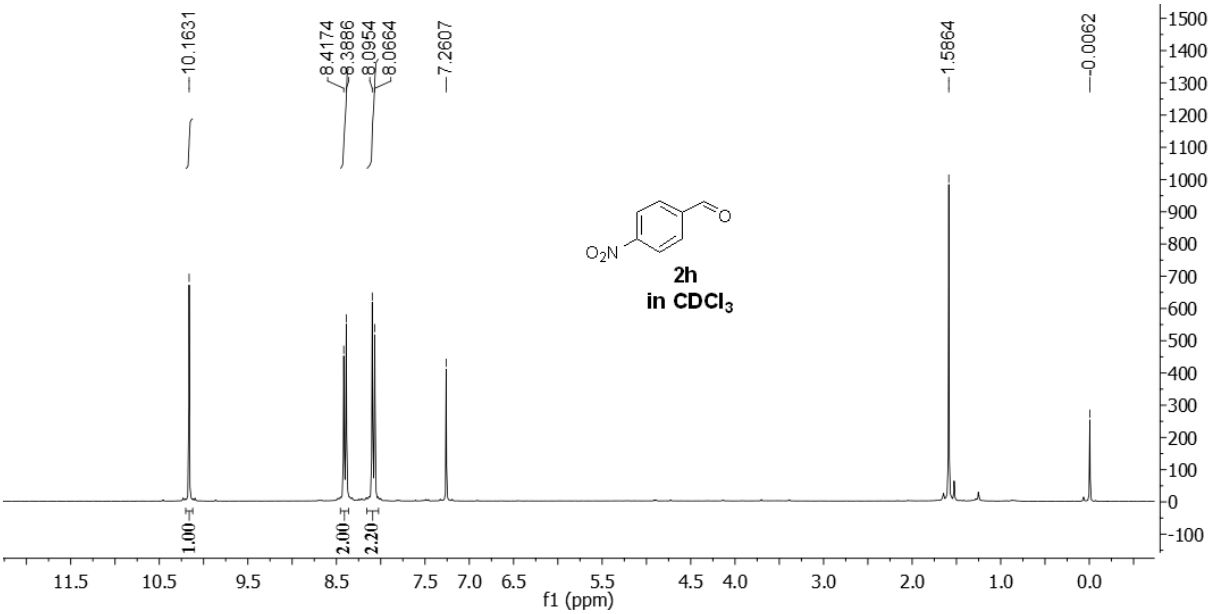
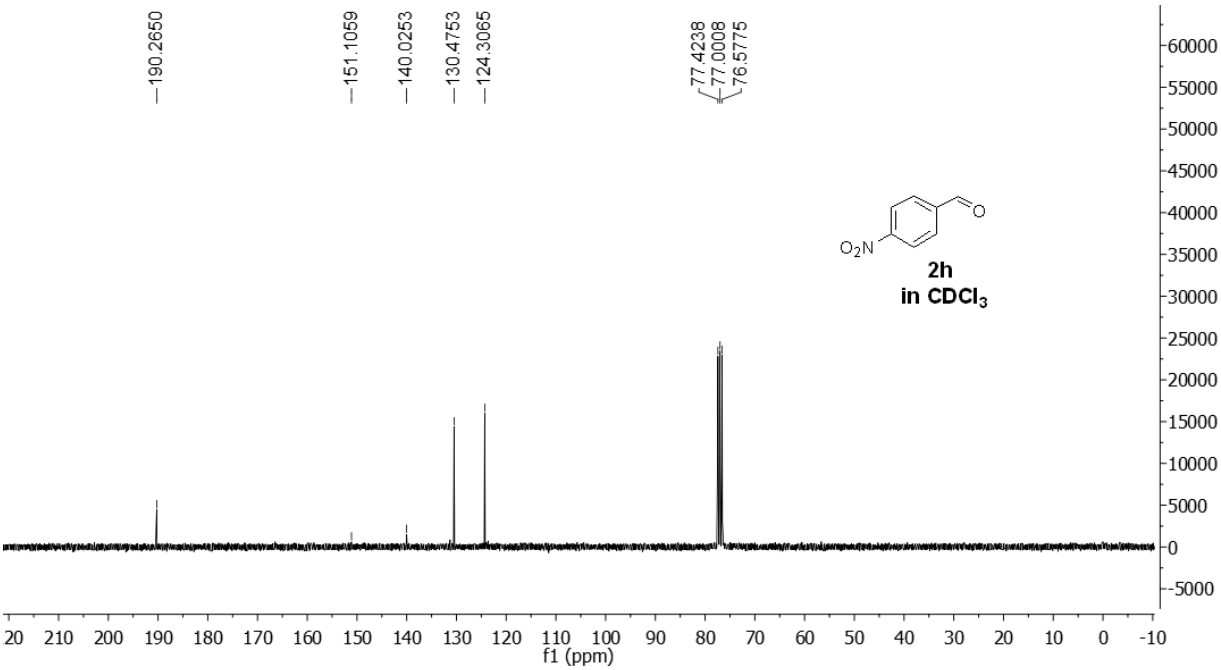
4-nitrobenzaldehyde (2h)





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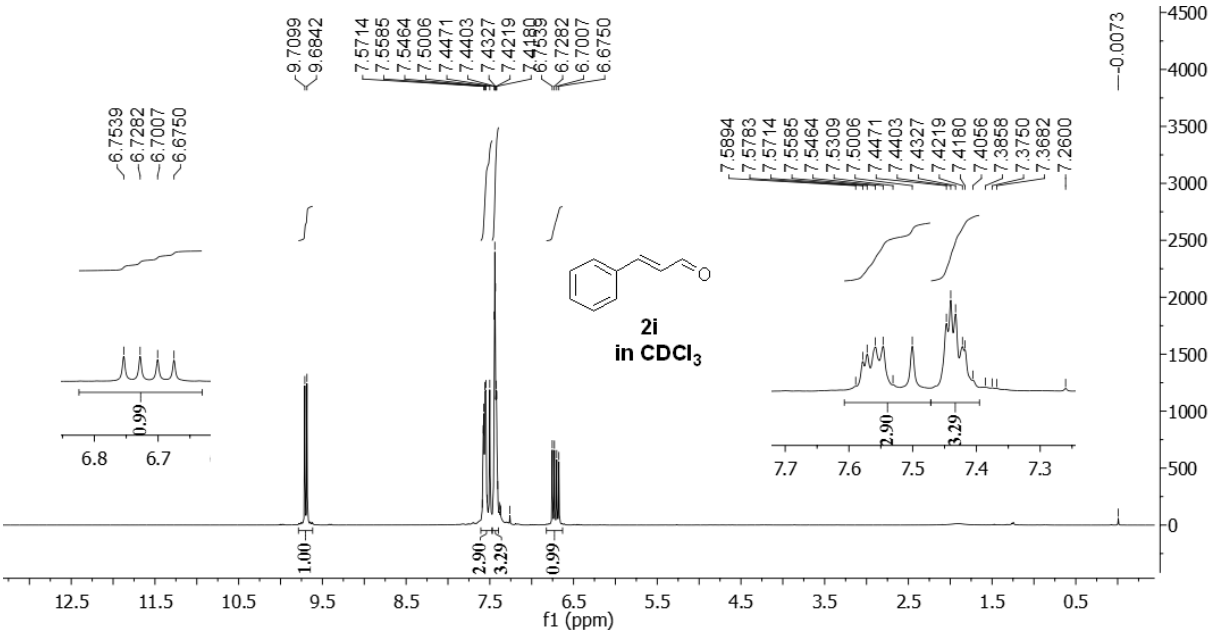
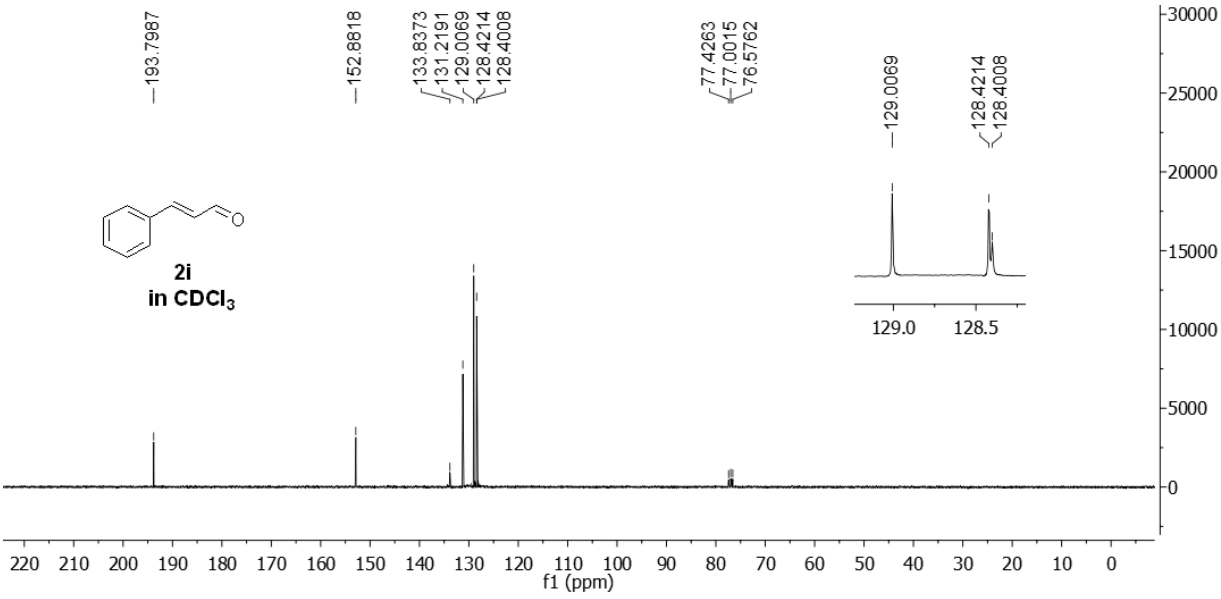
cinnamaldehyde (**2i**)





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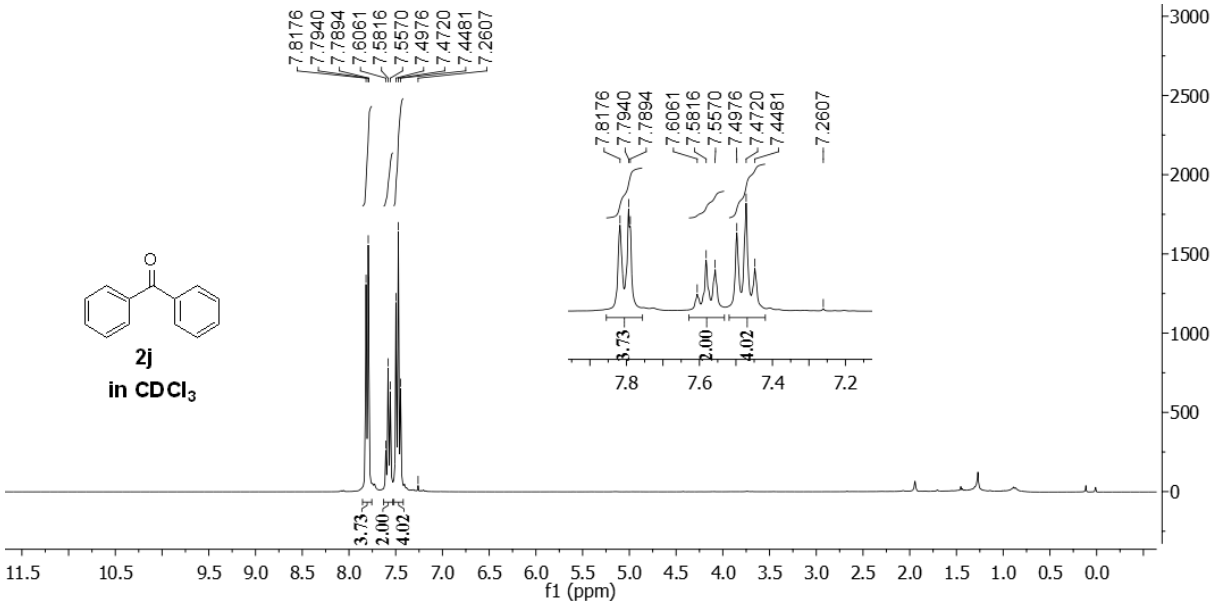
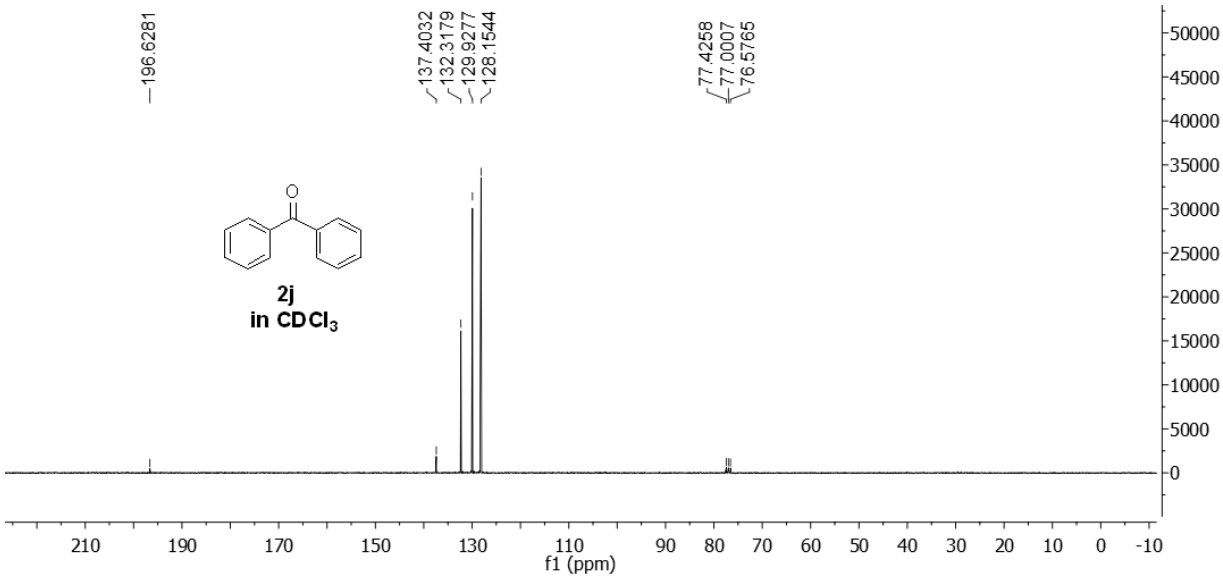
benzophenone (**2j**)





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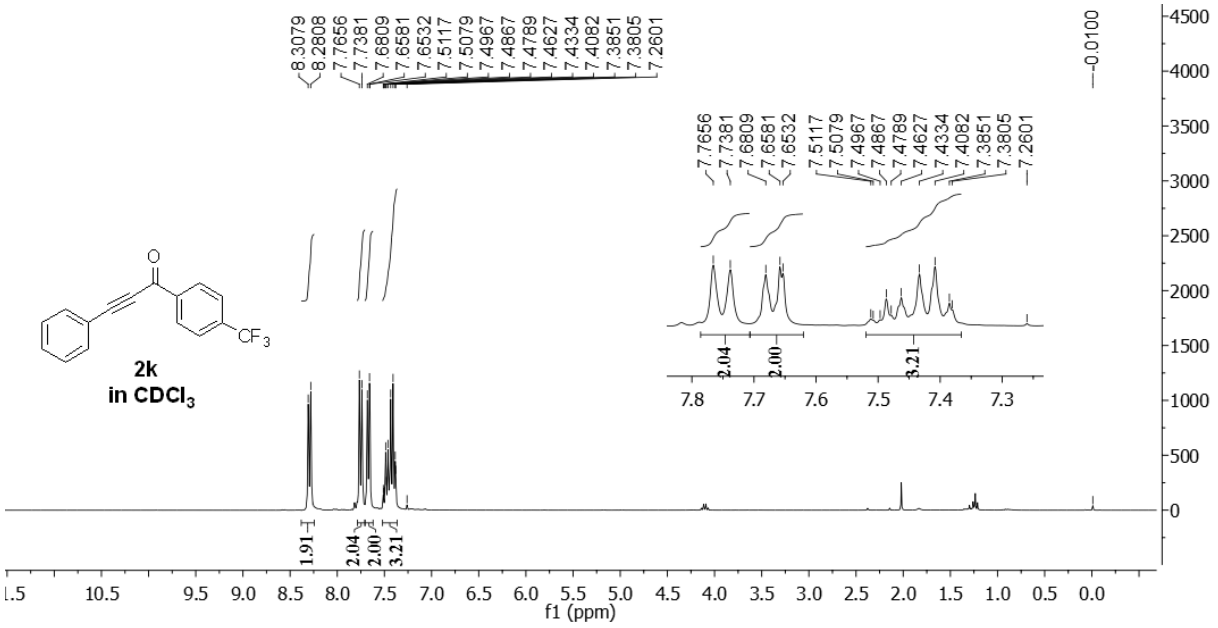
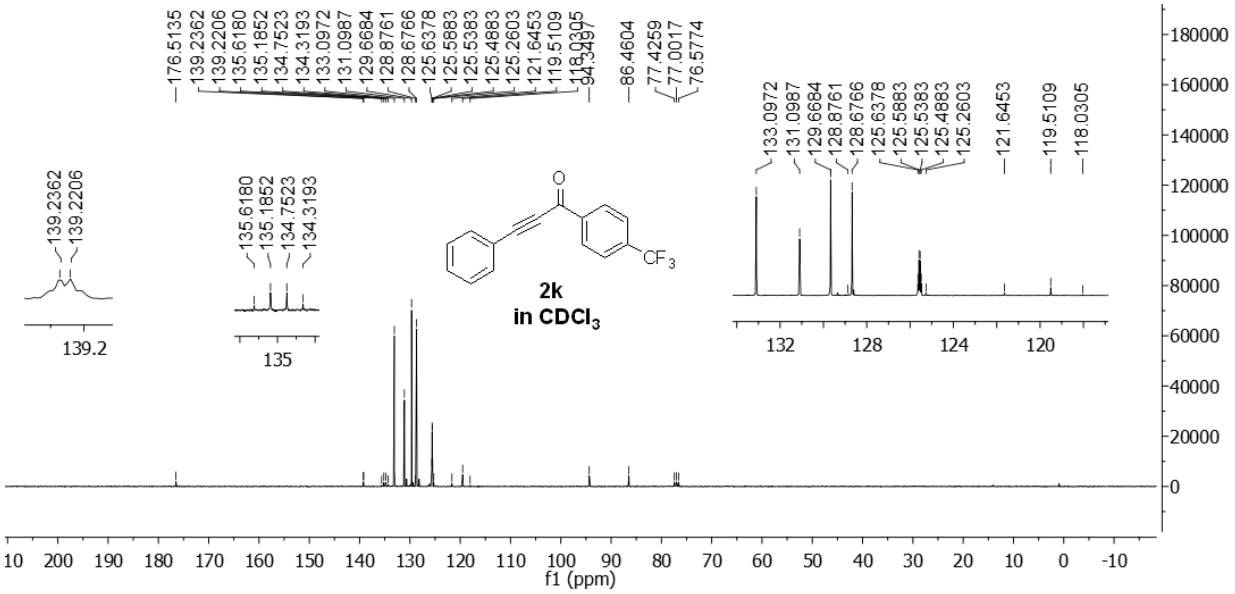
3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (2k)





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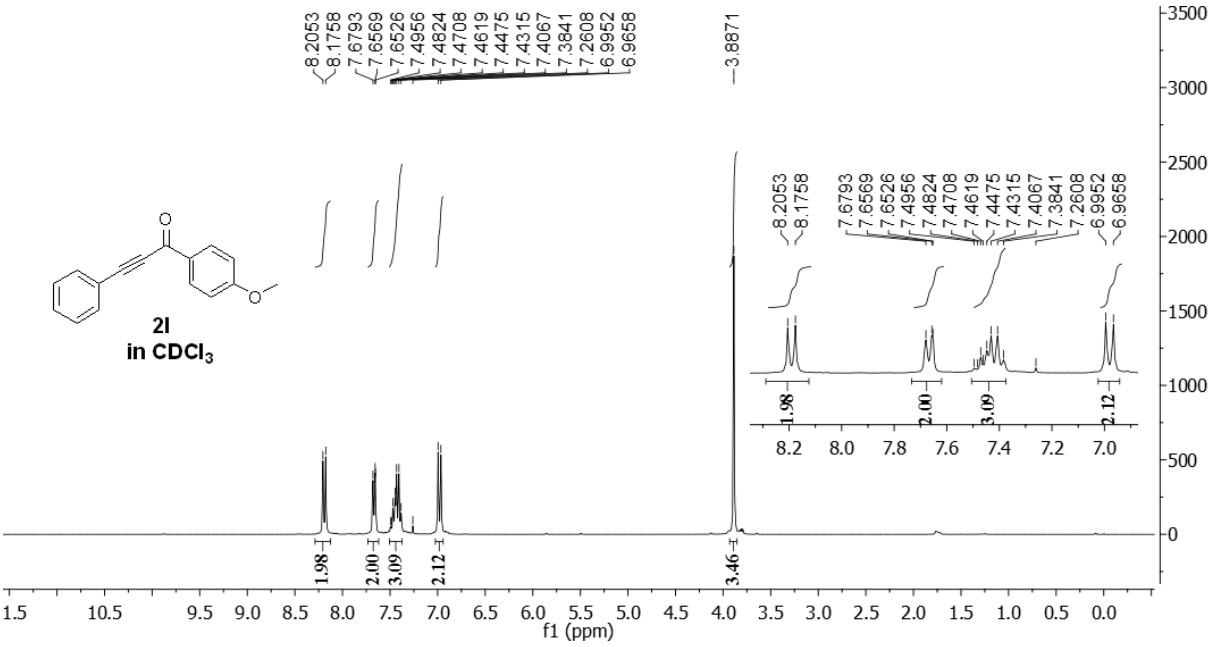
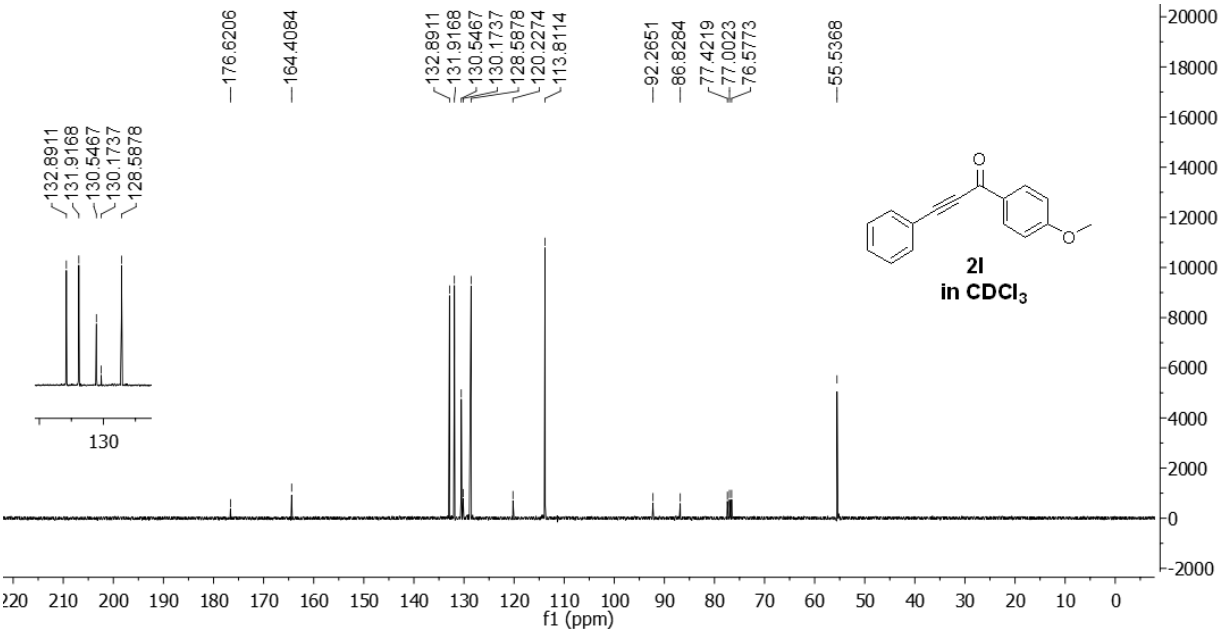
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (2l)





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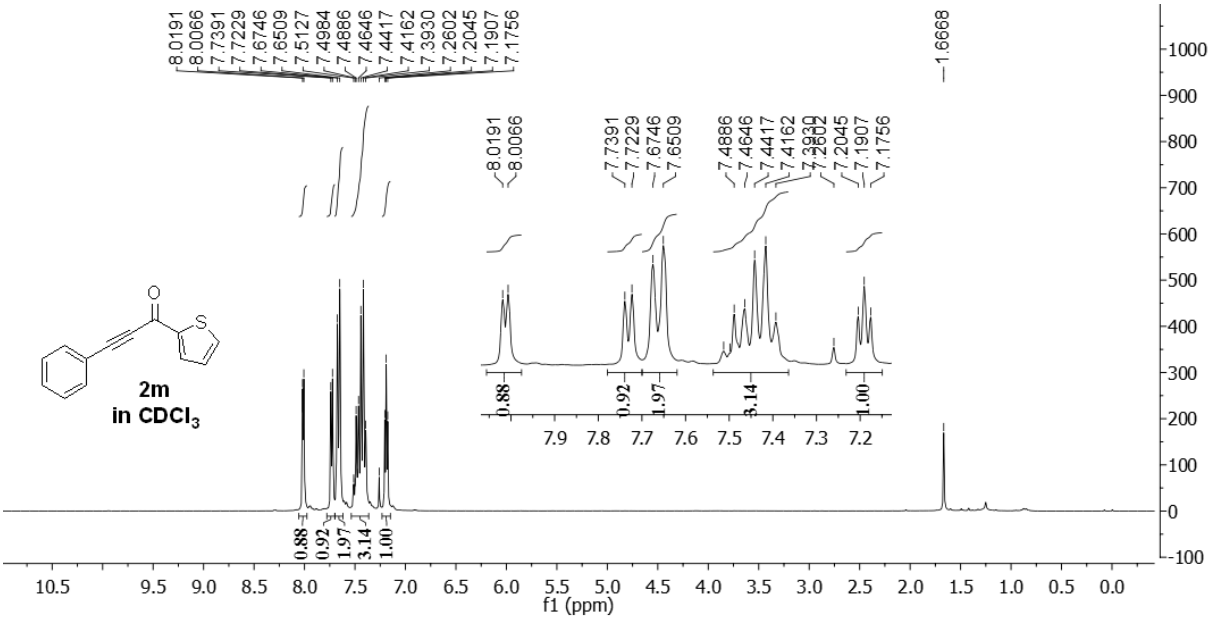
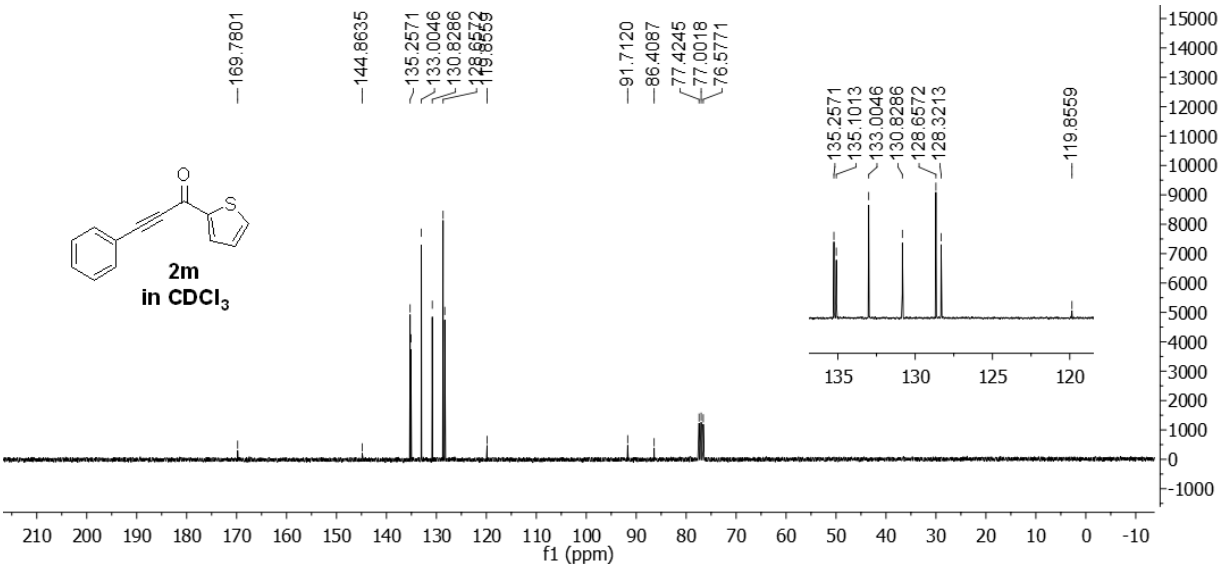
3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (2m)





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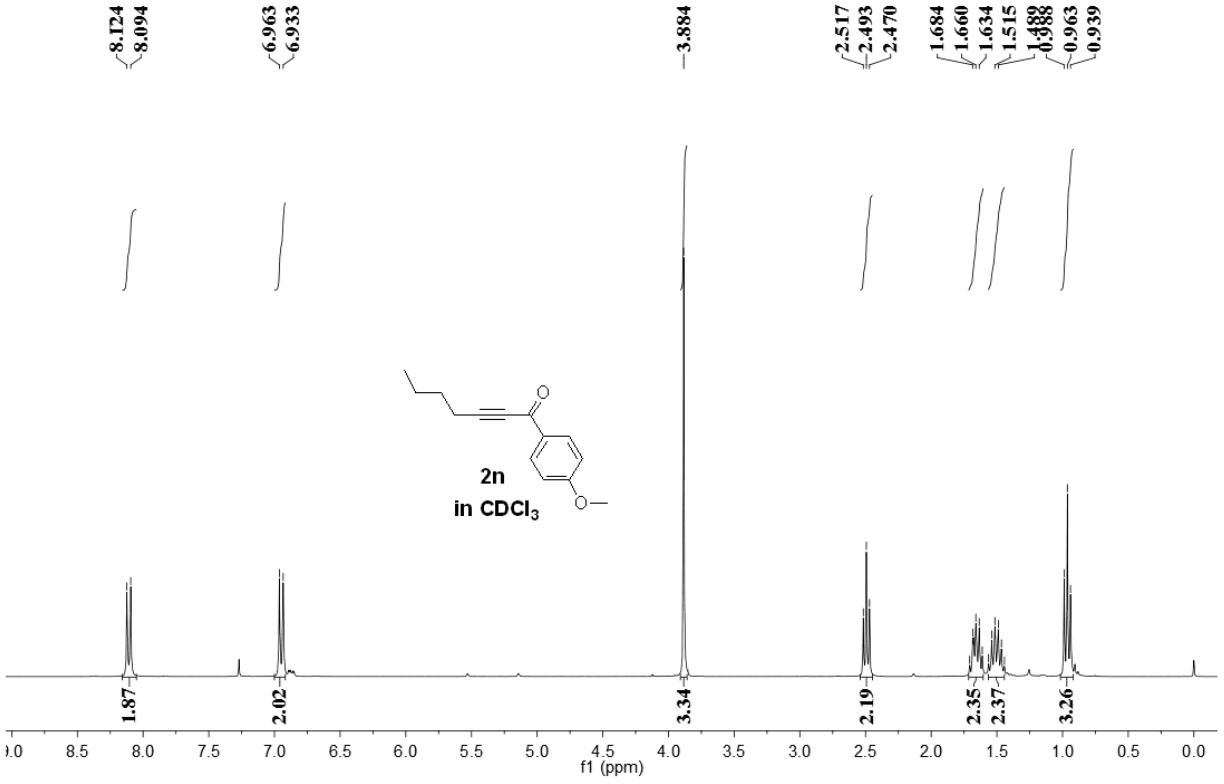
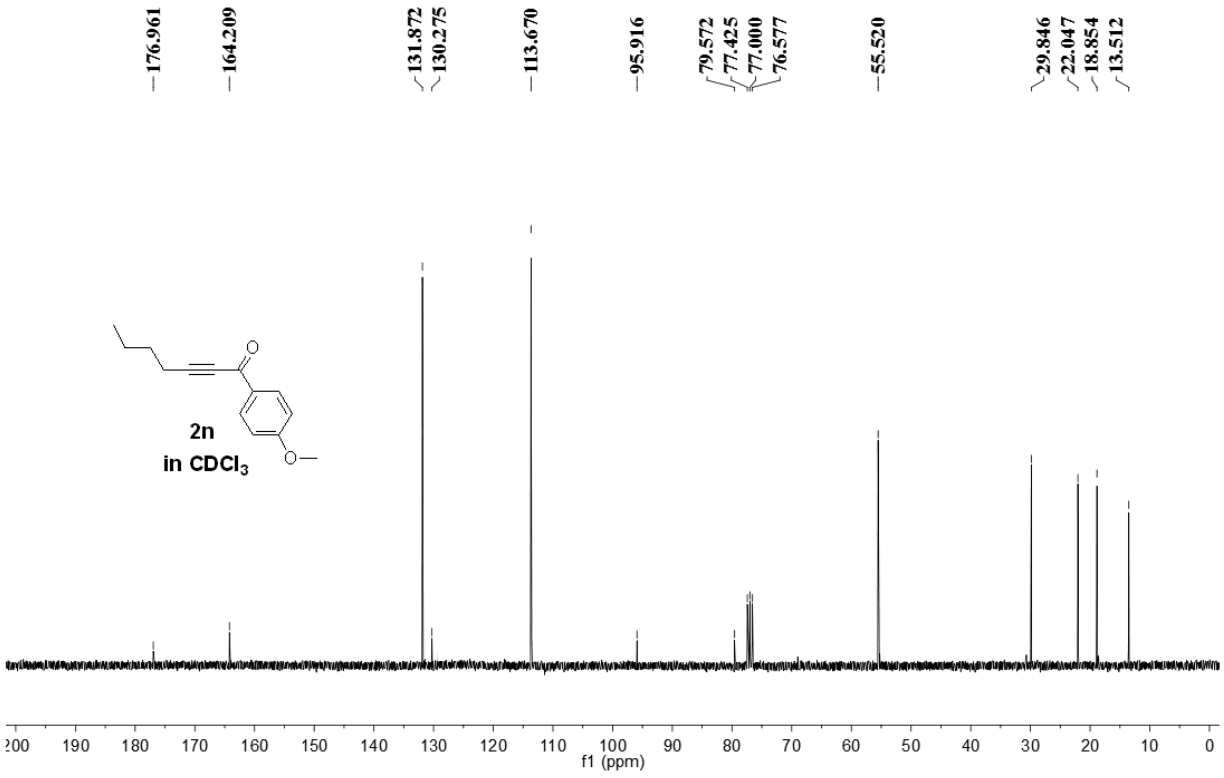
1-(4-methoxyphenyl)hept-2-yn-1-one (2n)





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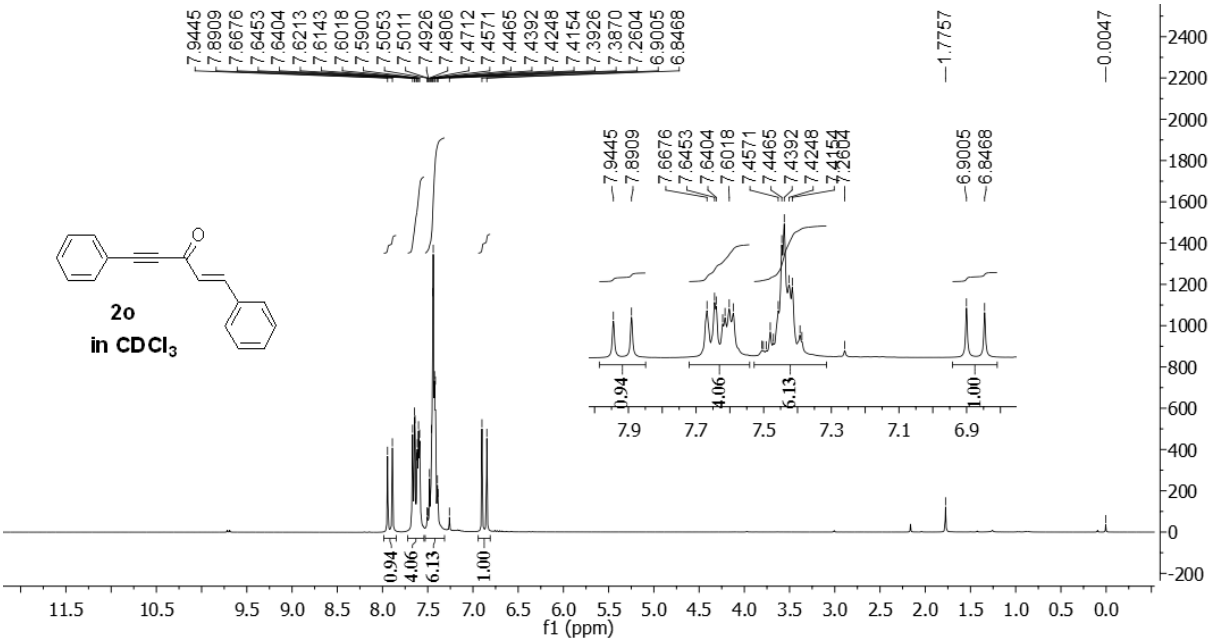
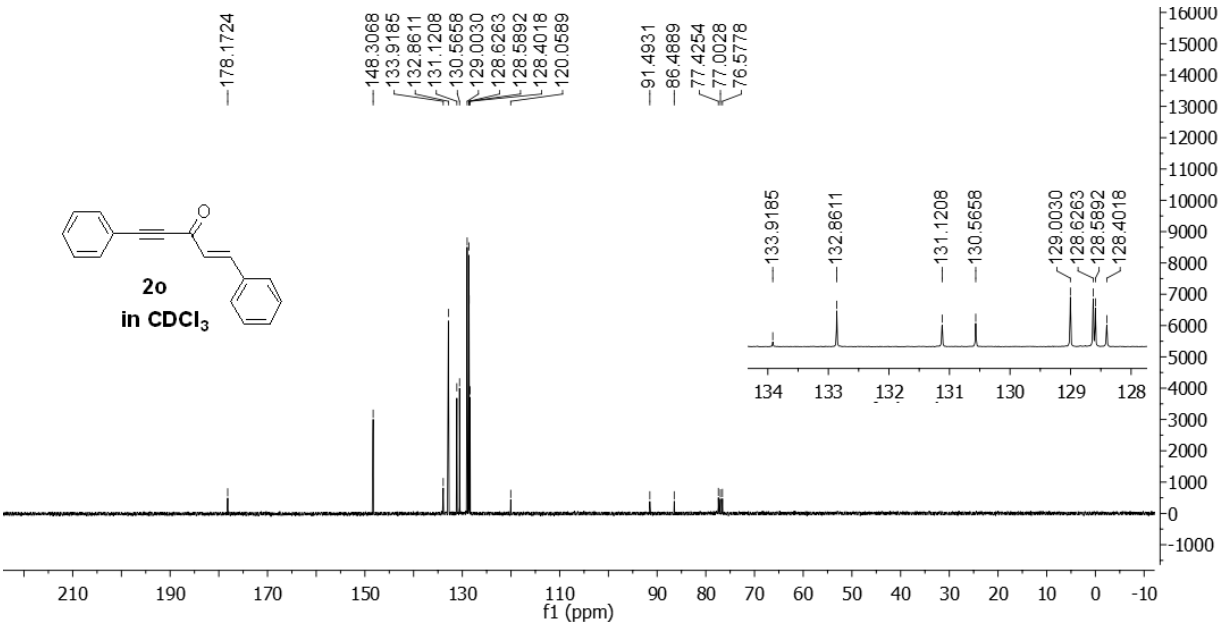
(*E*)-1,5-diphenylpent-1-en-4-yn-3-one (2o)





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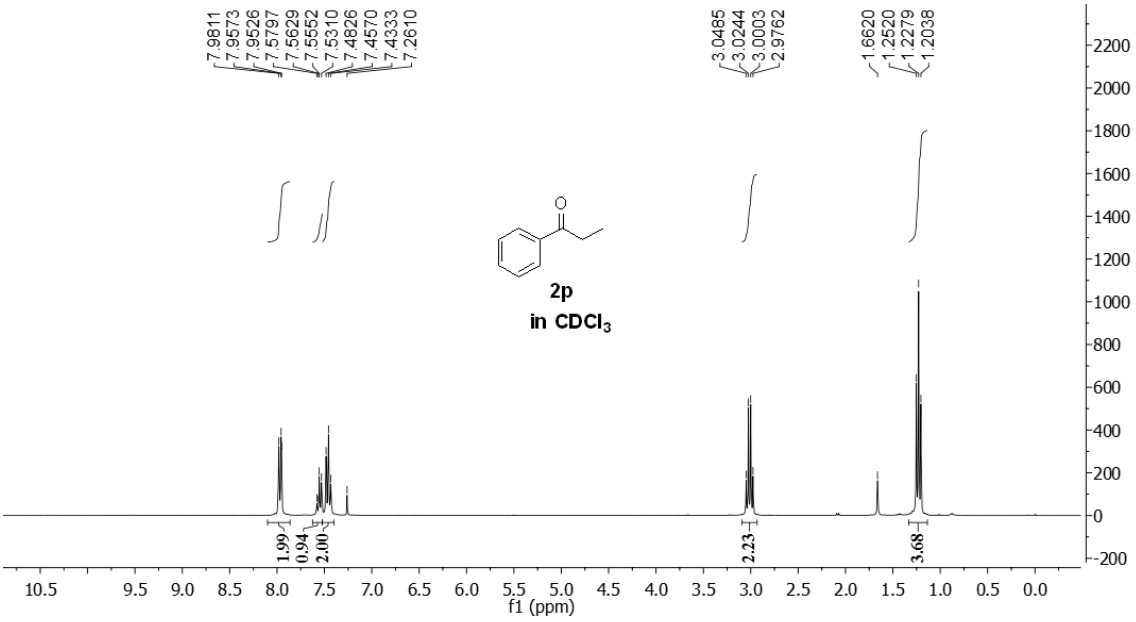
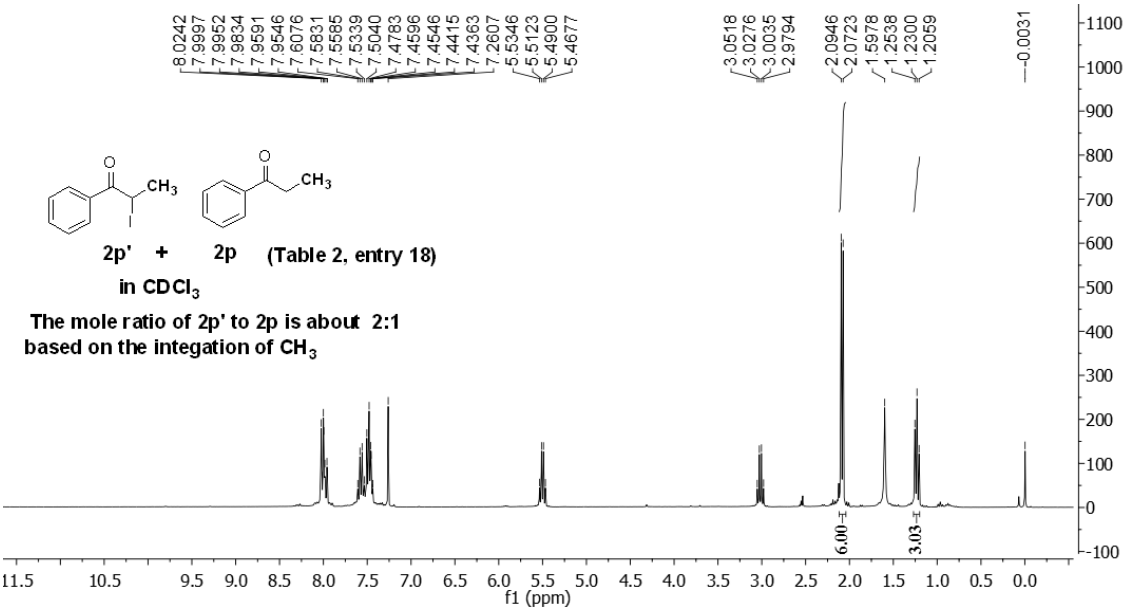
propiophenone (2p)





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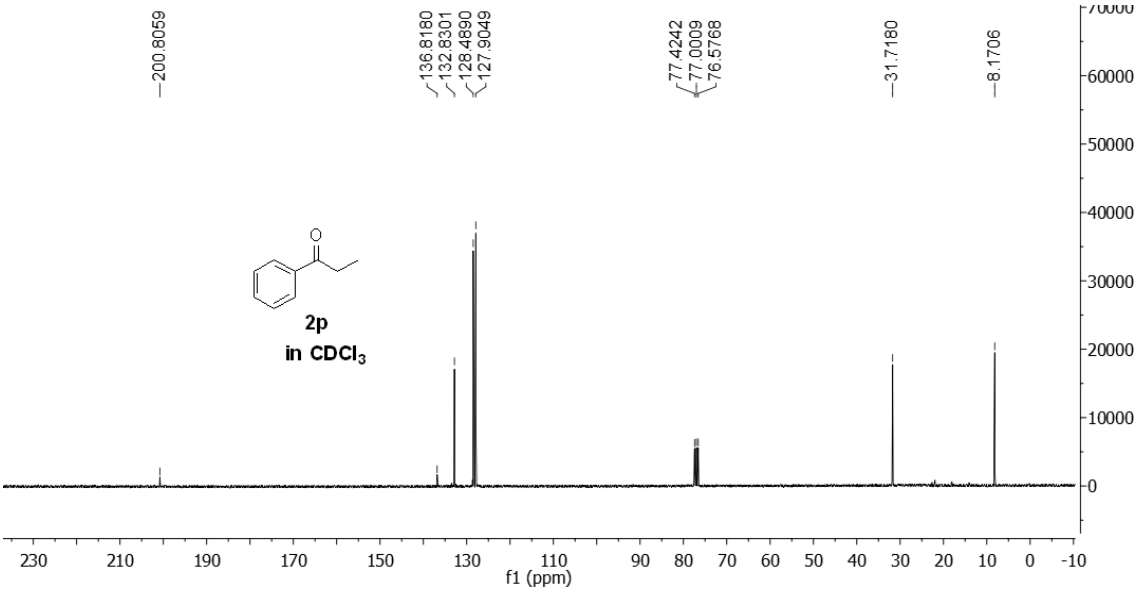
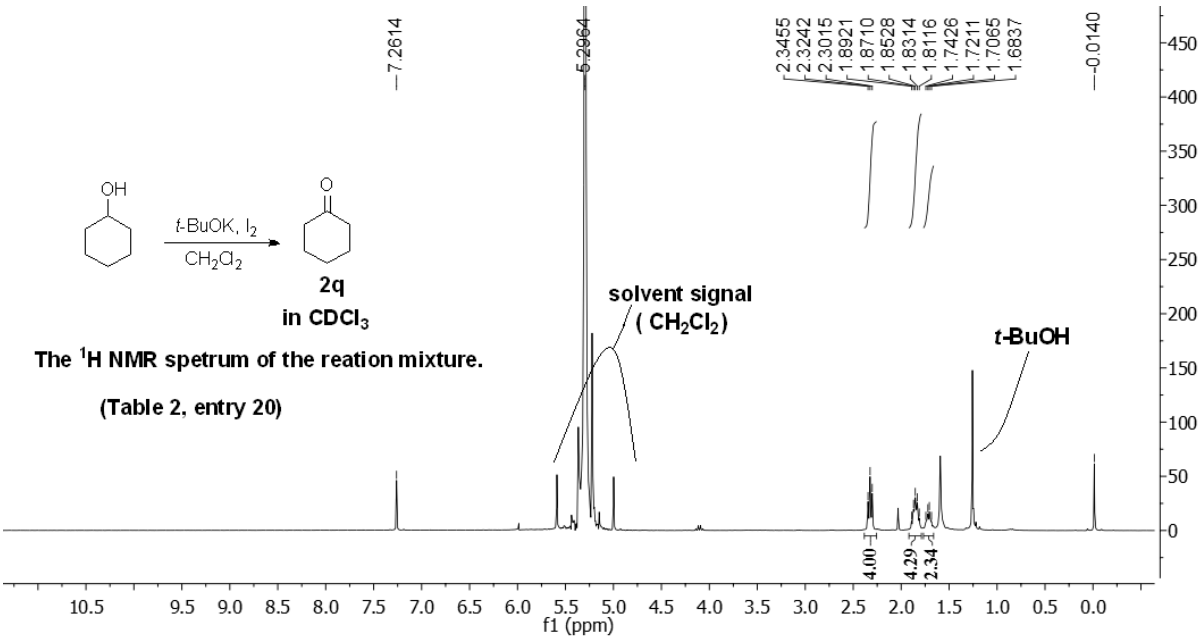


cyclohexanone (2q)



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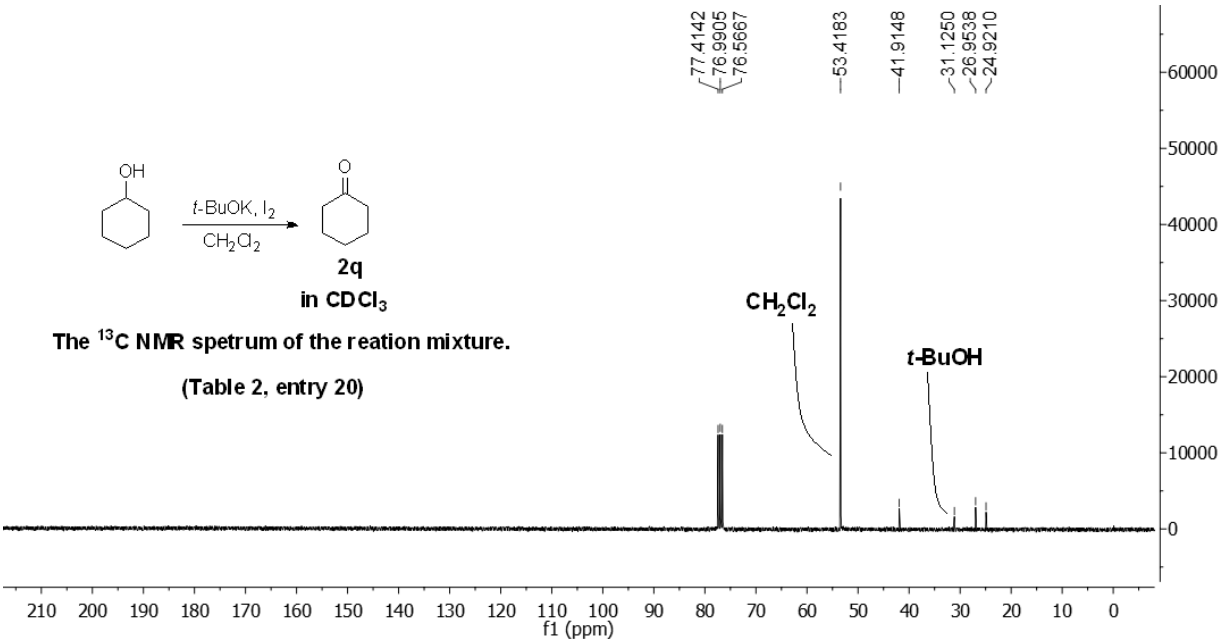
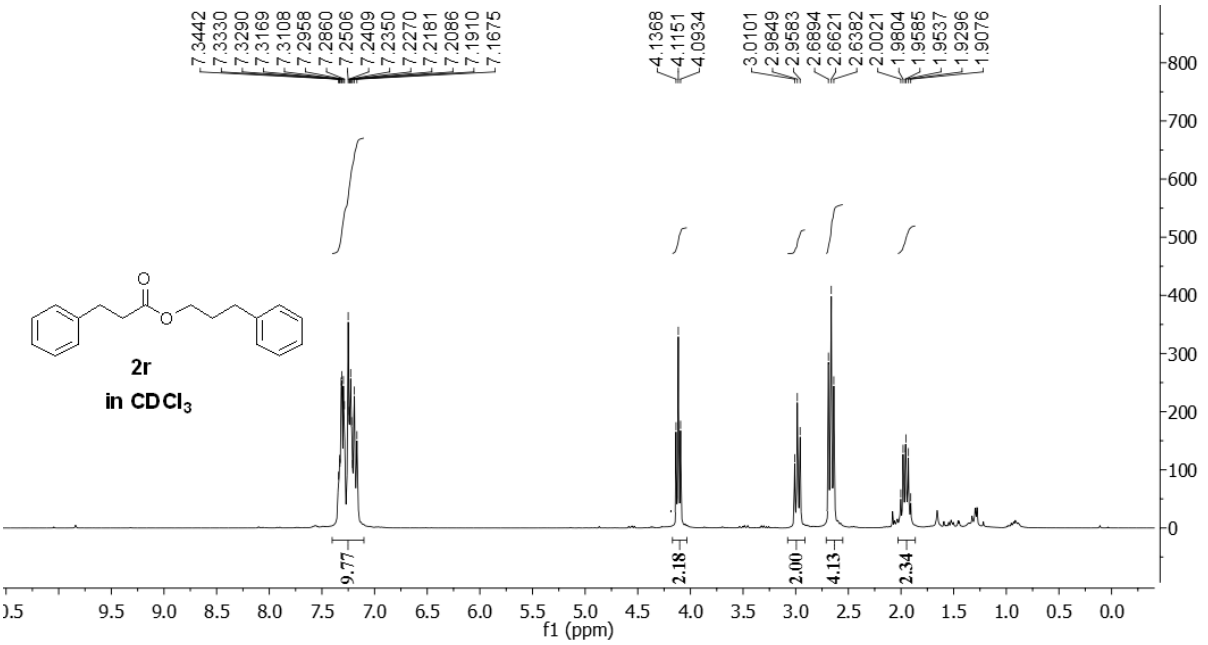


3-phenylpropyl 3-phenylpropanoate (2r)



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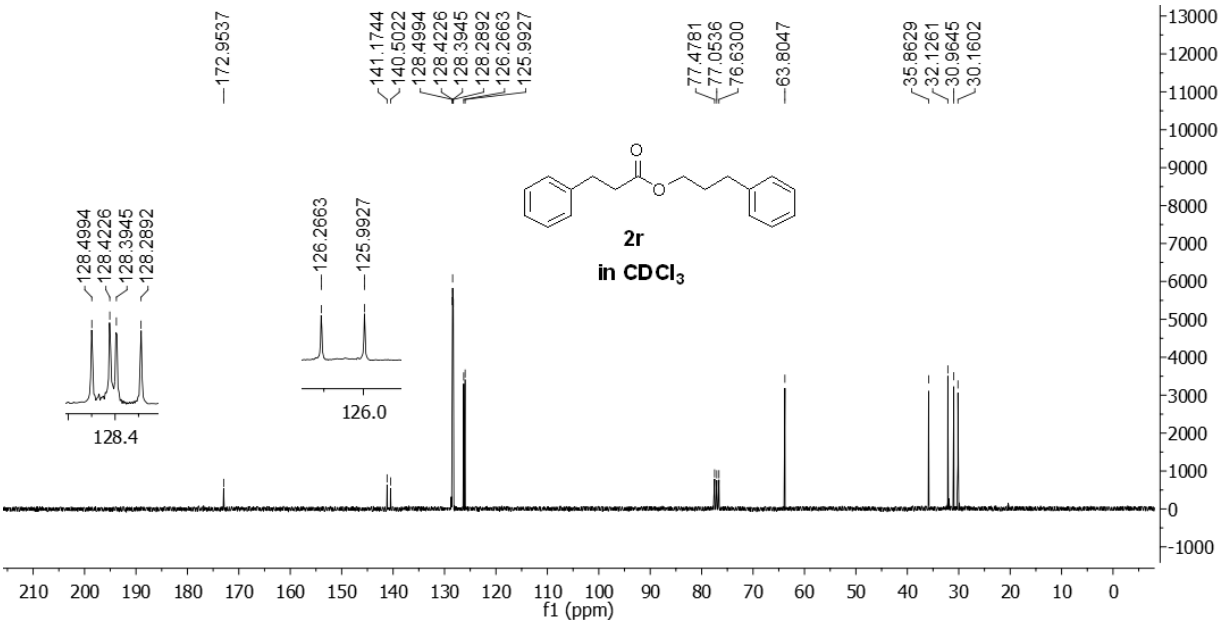
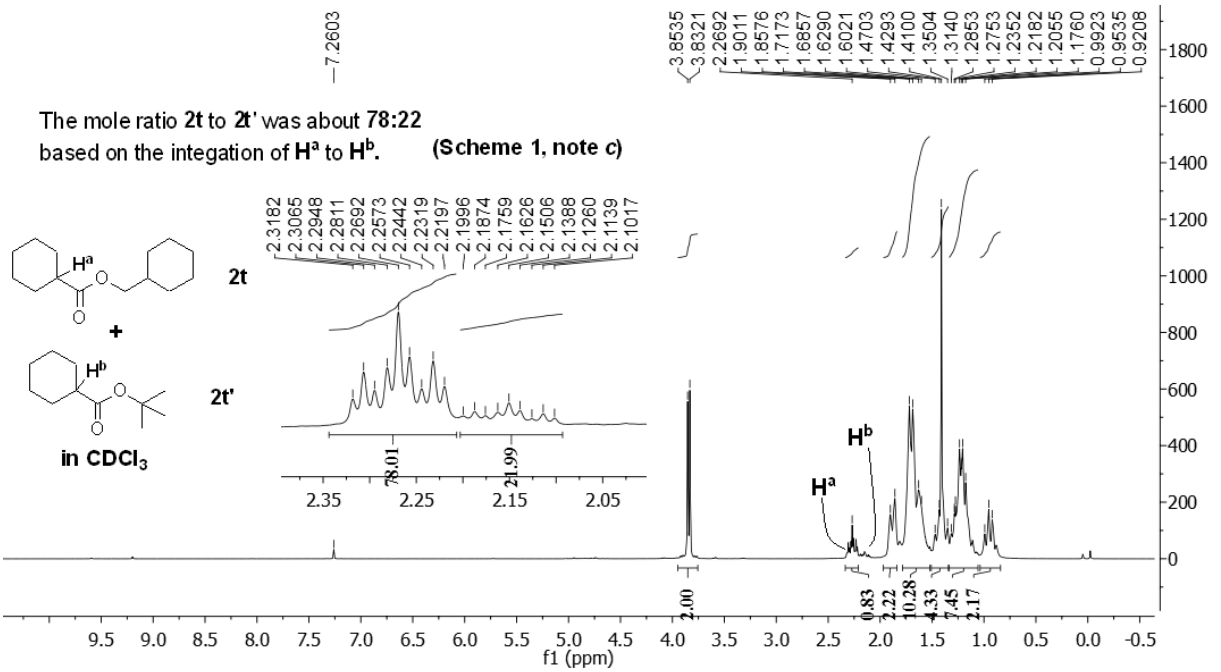


cyclohexylmethyl cyclohexanecarboxylate (2t)



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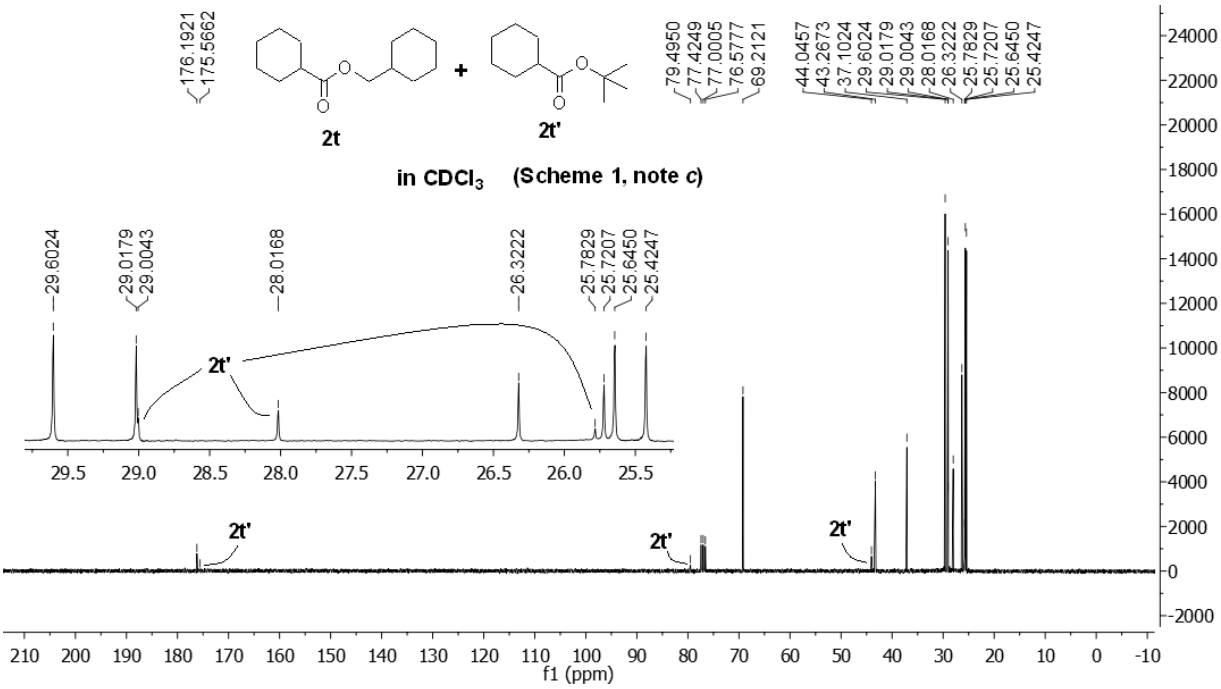

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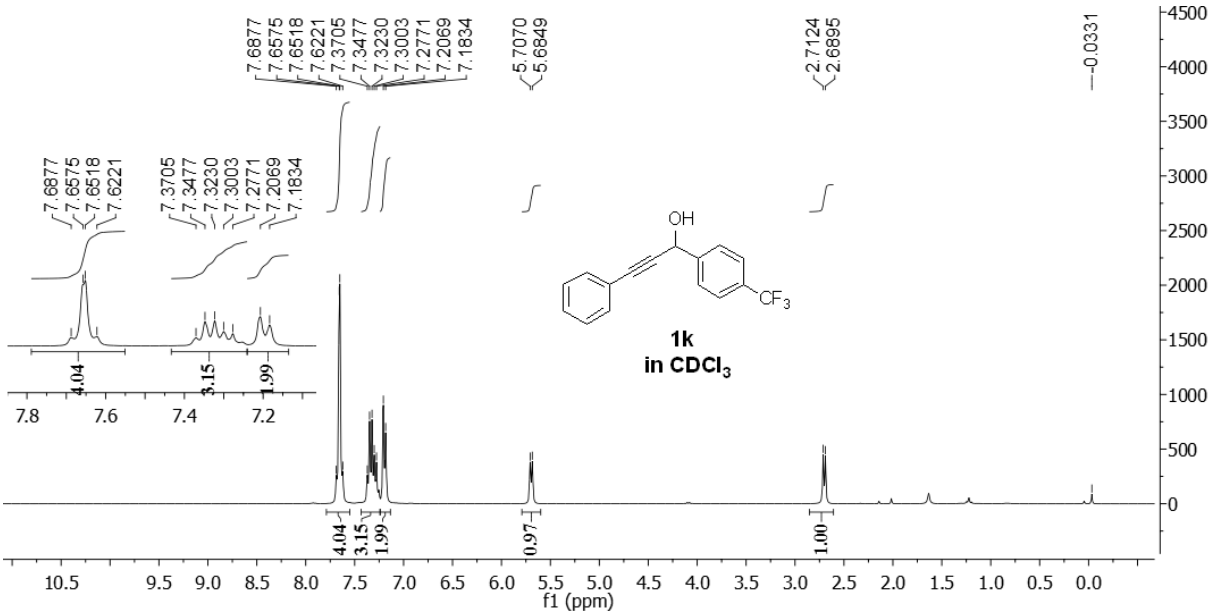
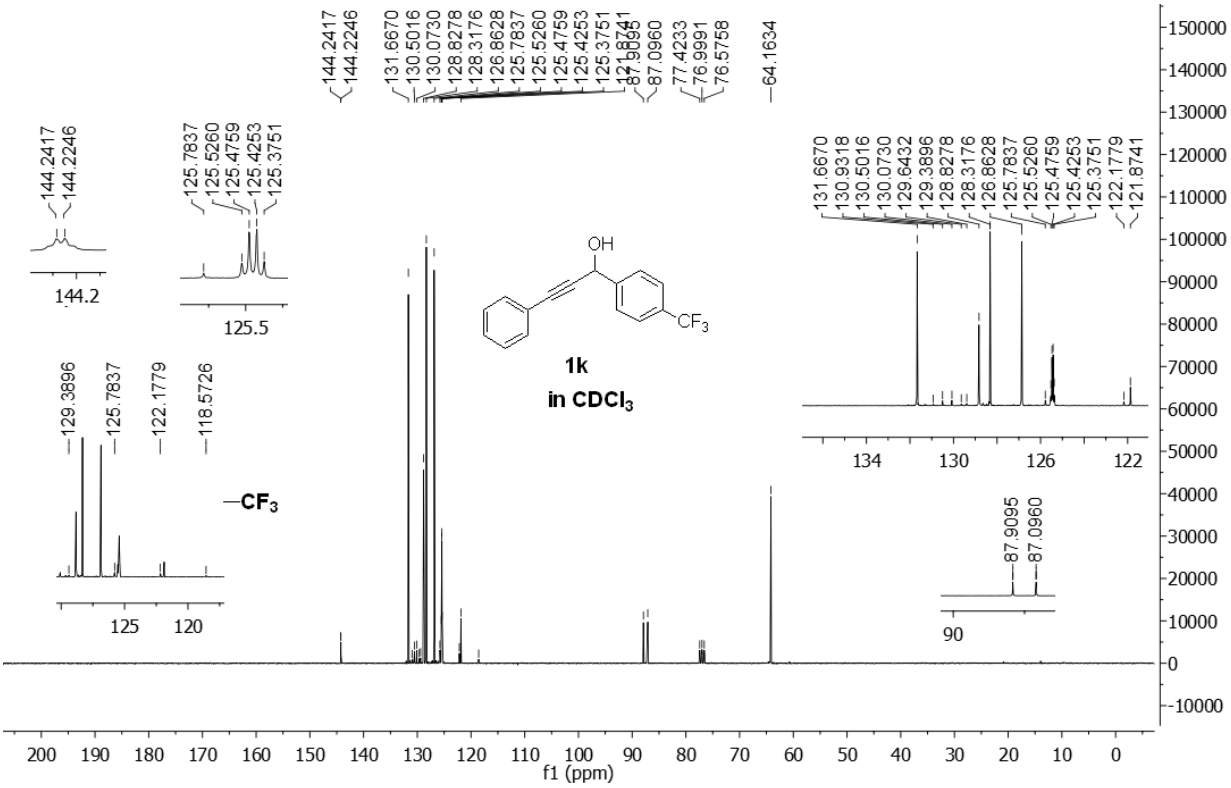
C. Spectra of 1k–1o, and 1s

3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (1k)





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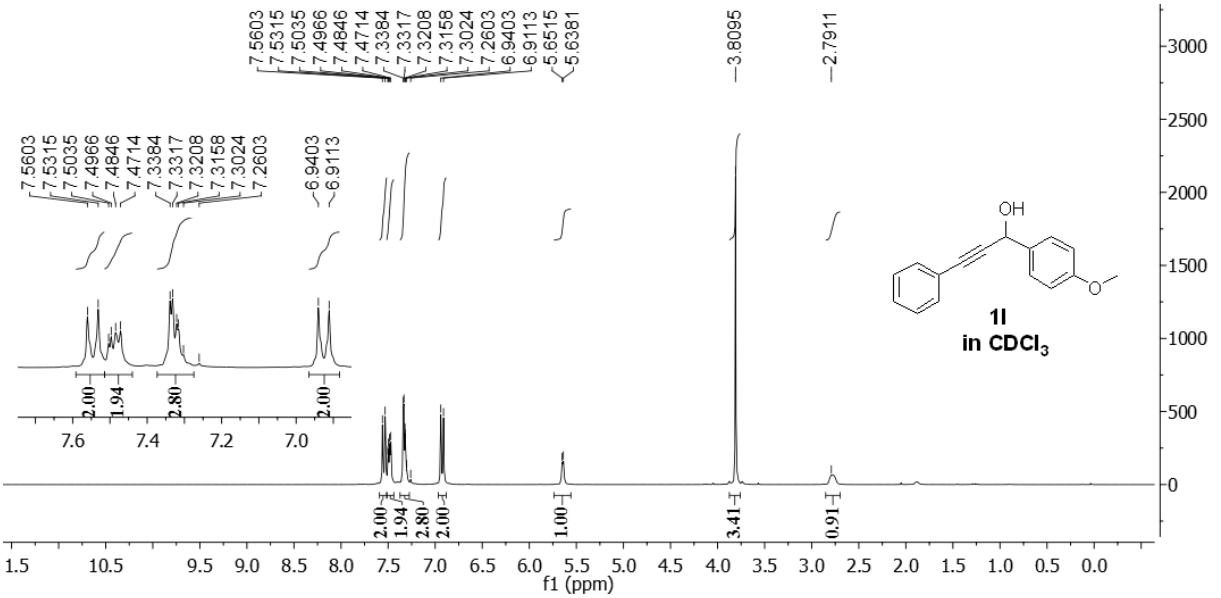
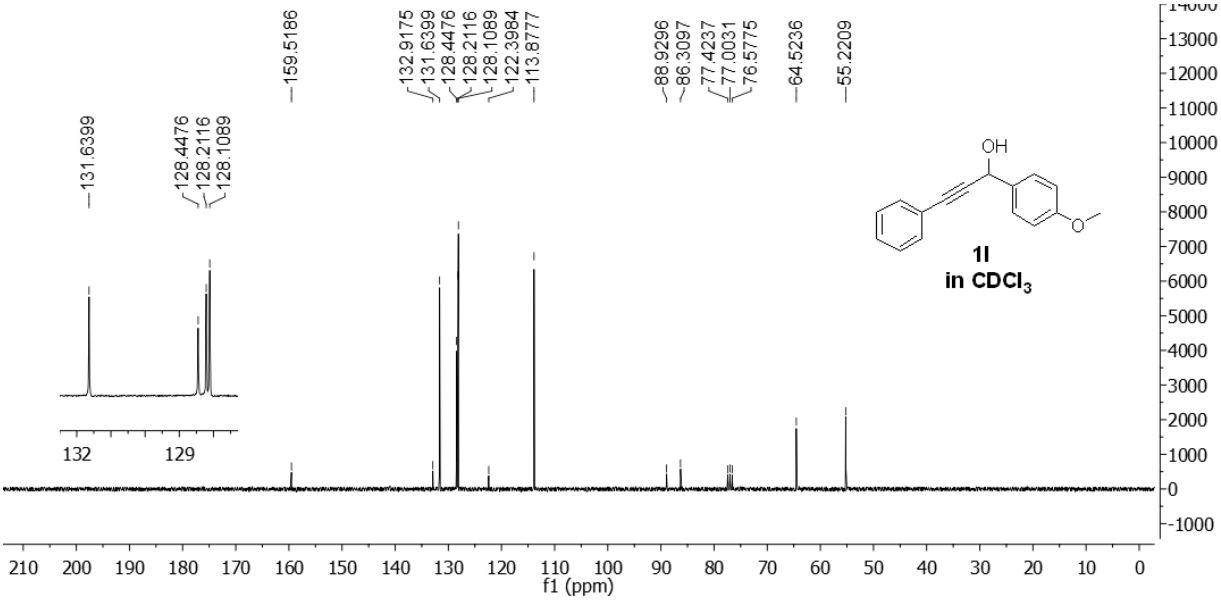
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1l)





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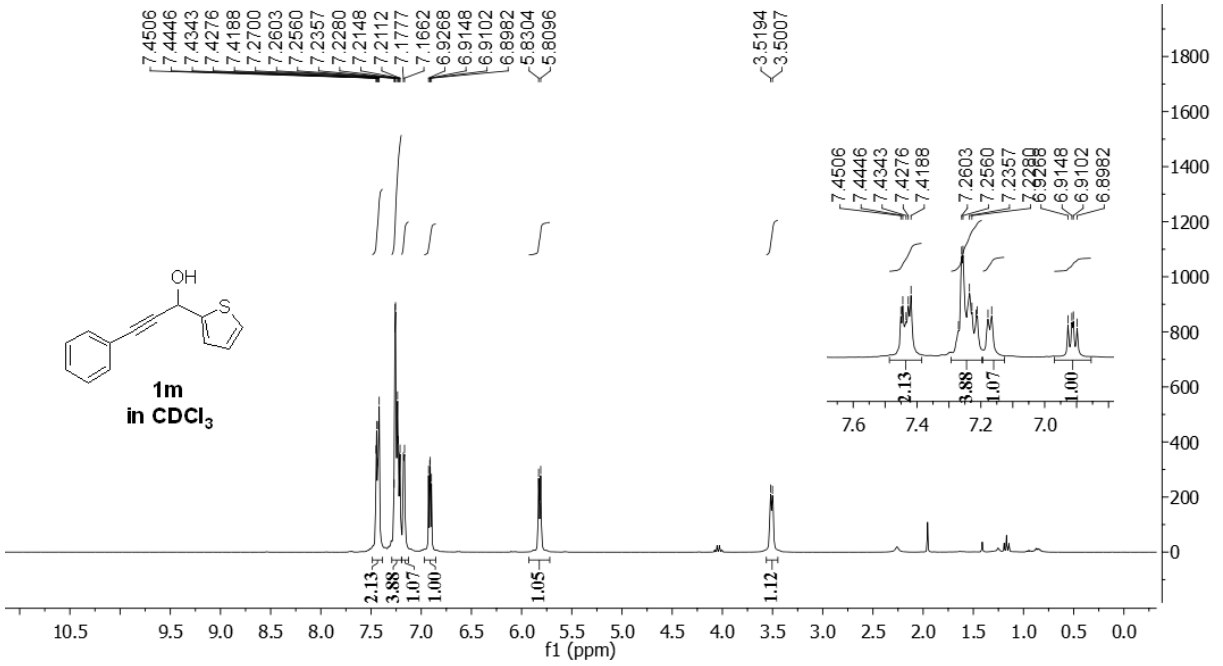
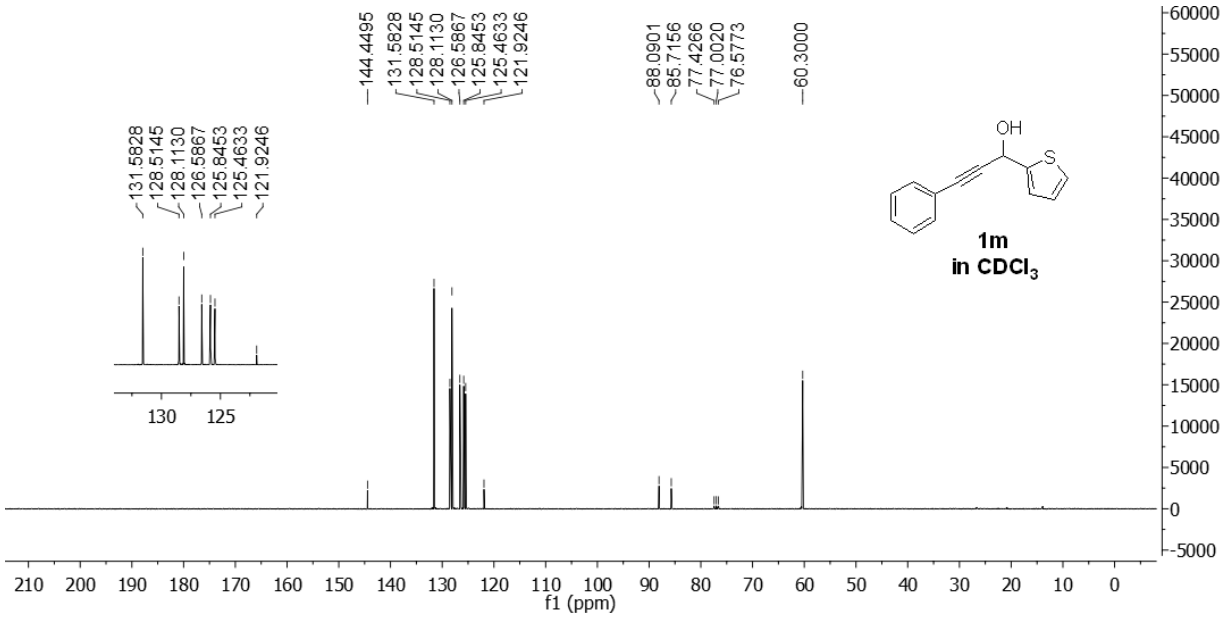
3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-ol (1m)





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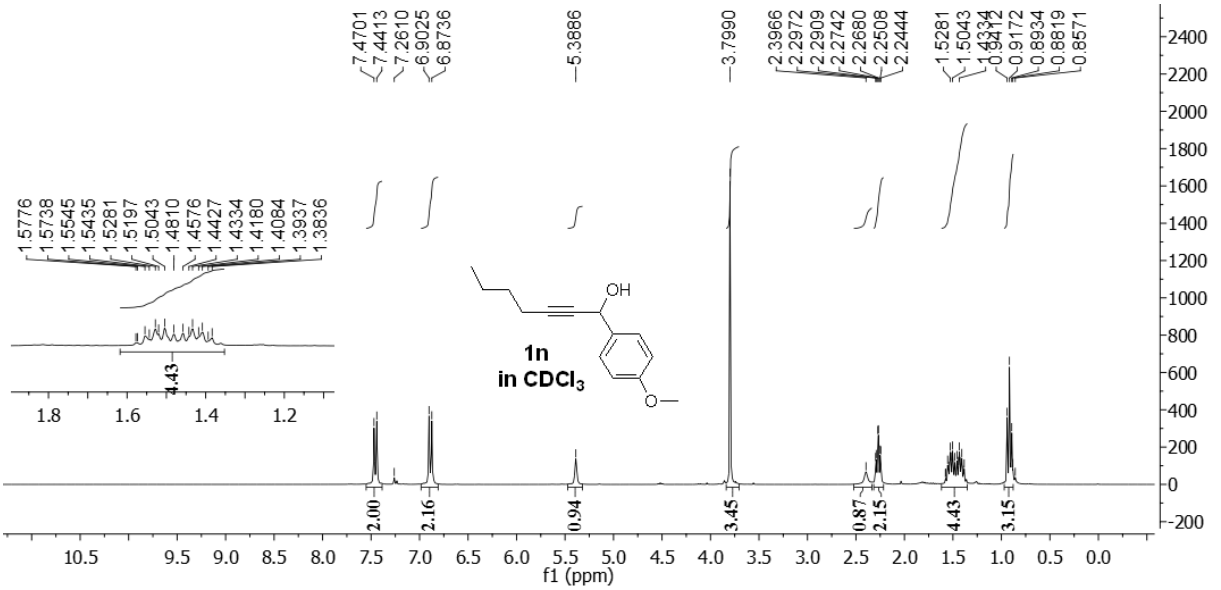
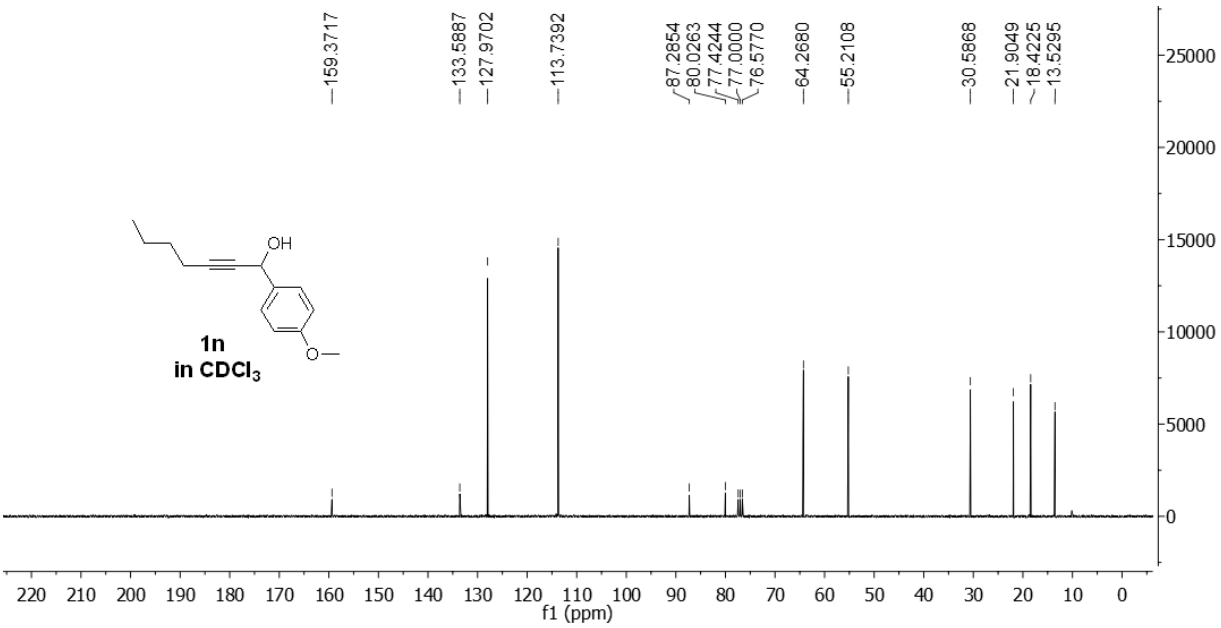
1-(4-methoxyphenyl)hept-2-yn-1-ol (1n)





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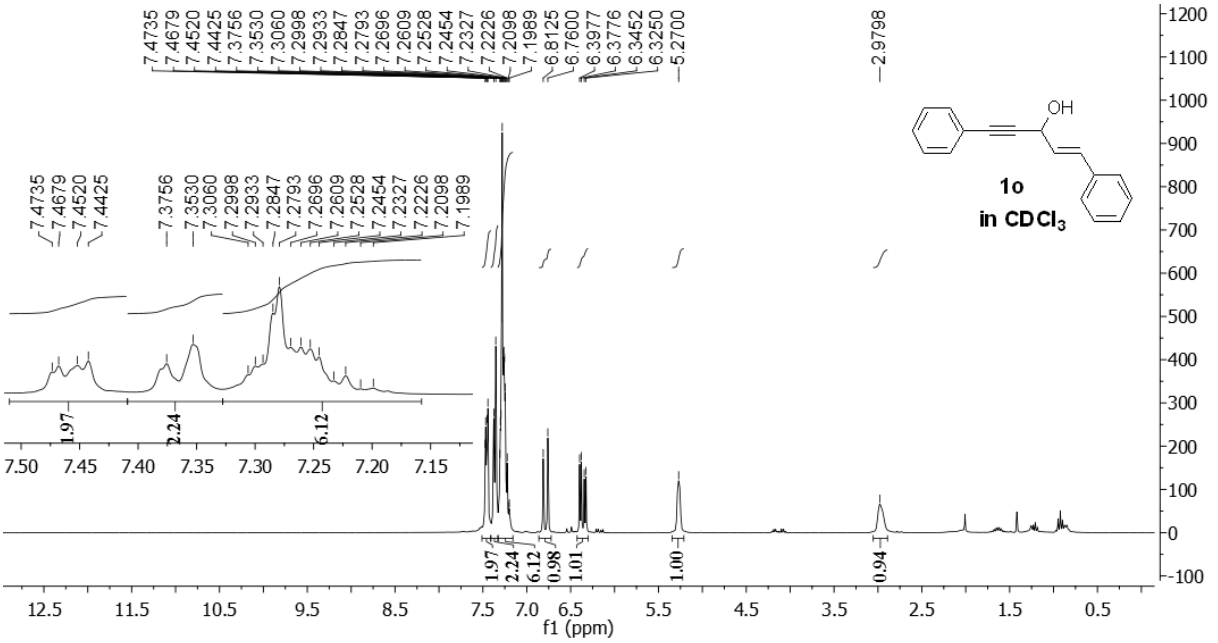
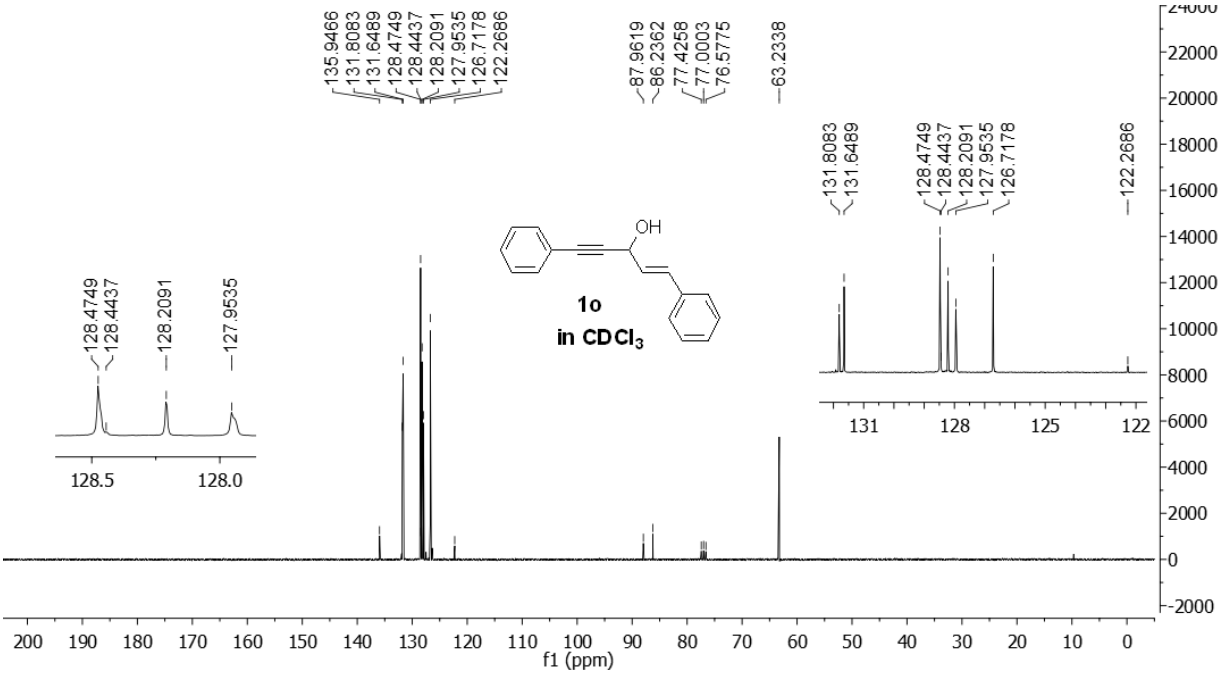
(*E*)-1,5-diphenylpent-1-en-4-yn-3-ol (1o)





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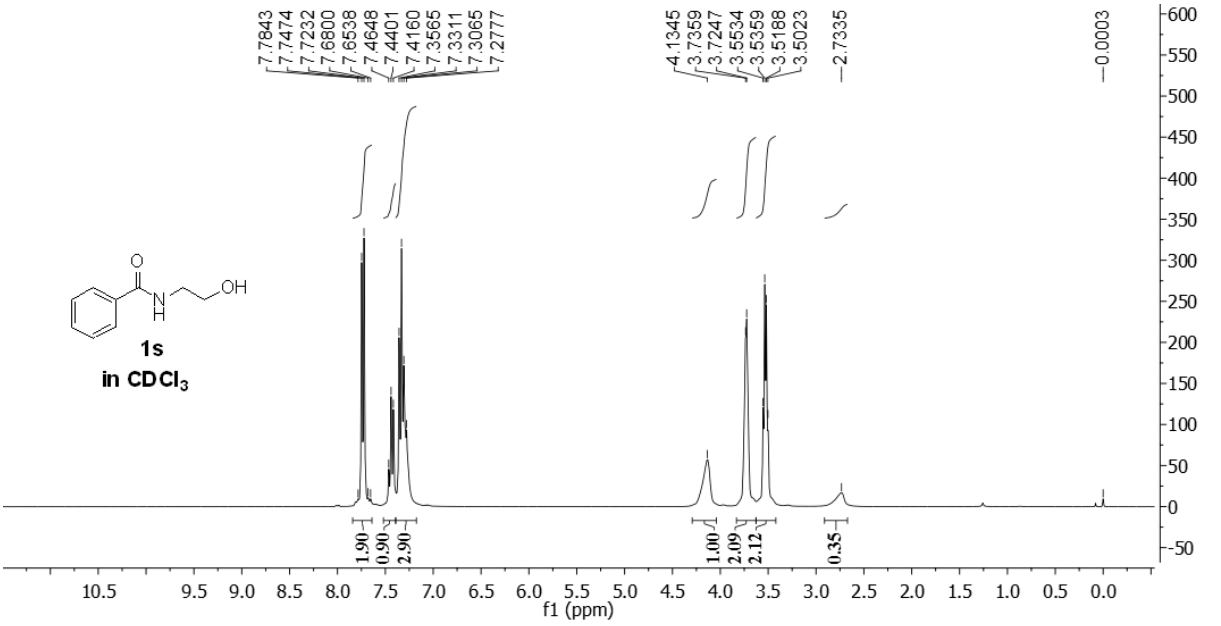
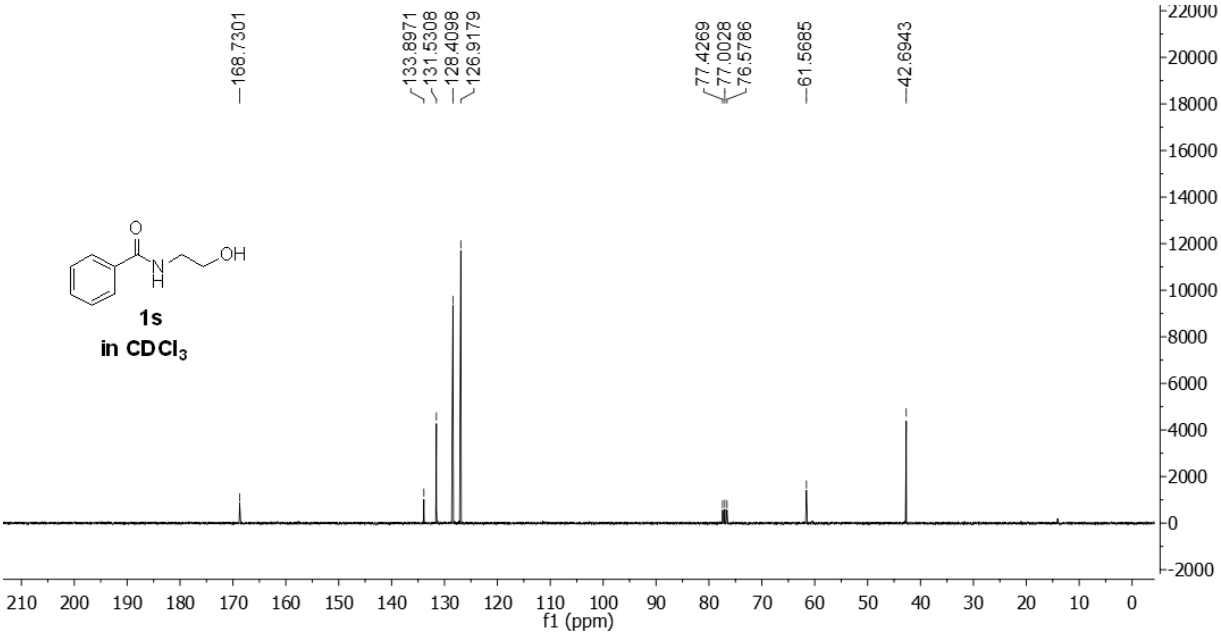
N-(2-hydroxyethyl)benzamide (1s)





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