reactions

MDPI

Supplementary Material

C-N, C-O and C-S Ullmann-Type Coupling Reactions of Arenediazonium *o*-Benzenedisulfonimides

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Physical and NMR data of anilines 3

N-(*n*-hexyl)-4-nitroaniline (3a): 384 mg (87% yield). Yellow solid (MeOH; mp 64–65°C; Lit[1] mp 64–67°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.05 (d, 2H, *J* = 7.8 Hz), 6.80 (d, 2H, *J* = 7.8 Hz), 4.50 (br s, 1H), 3.11–3.08 (m, 2H), 1.53–1.48 (m, 2H), 1.39–1.28 (m, 6H), 0.99 (t, 3H, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 157.1, 138.2, 125.3, 112.8, 44.4, 31.7, 29.3, 27.8, 22.8, 14.1. MS: *m*/*z* 222 (M^+). IR (neat): ν_{NH} 3386.

N-(*n*-hexyl)-4-methoxyaniline (3b): 330 mg (79% yield). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 6.75 (d, 2H, *J* = 7.2 Hz), 6.51 (d, 2H, *J* = 7.2 Hz), 3.81 (s, 3H), 3.45 (br s 1H), 3.12 (t, 2H, *J* = 7.8 Hz), 1.56–1.52 (m, 2H), 1.40–1.31 (m, 6H), 0.99 (t, 3H, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 150.9, 141.3, 115.1, 113.4, 56.0, 44.5, 31.6, 29.4, 27.7, 22.9, 14.0. MS: *m*/*z* 207 (M^+). IR (neat): ν_{NH} 3394.

N-(*n*-benzyl)-4-methoxyaniline (3c): 310 mg (73% yield). Grey solid (MeOH; mp 51–52°C; Lit[2] mp 48–50°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.30–7.20 (m, 5H), 6.76 (d, 2H, *J* = 7.2 Hz), 6.53 (d, 2H, *J* = 7.2 Hz), 4.48 (s, 2H), 3.81 (s, 3H), 3.61 (br s 1H). ^{13}C NMR ($CDCl_3$, 150 MHz): 151.6, 140.6, 139.8, 128.4, 127.6, 126.9, 115.5, 113.5, 56.0. MS: *m*/*z* 213 (M^+). IR (neat): ν_{NH} 3399.

N-(*n*-benzyl)-4-nitroaniline (3d): 388 mg (85% yield). Yellow solid (MeOH; mp 143–144°C; Lit[3] mp 146–147°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.89 (d, 2H, *J* = 7.8 Hz), 7.29–7.21 (m, 5H), 6.80 (d, 2H, *J* = 7.8 Hz), 4.48 (s, 2H), 4.19 (br s 1H). ^{13}C NMR ($CDCl_3$, 150 MHz): 156.4, 139.8, 138.1, 128.4, 127.6, 126.9, 125.4, 114.3, 46.9. MS: *m*/*z* 228 (M^+). IR (neat): ν_{NH} 3412.

N-(*n*-hexyl)-2-nitroaniline (3e): 228 mg (51% yield). Viscous yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.06–8.05 (m, 1H), 7.51–7.49 (m, 1H), 6.93–6.91 (m, 1H), 6.80–6.79 (m, 1H), 3.12 (t, 2H, *J* = 5.4 Hz), 1.53–1.49 (m, 2H), 1.38–1.27 (m, 6H), 0.98 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 143.2, 134.1, 133.4, 127.7, 117.3, 116.2, 44.5, 31.7, 29.4, 27.6, 22.9, 14.0. MS: *m*/*z* 222 (M^+). IR (neat): ν_{NH} 3365.

N-(*n*-hexyl)-3-nitroaniline (3f): 382 mg (86% yield). Waxy solid. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.58–7.57 (m, 1H), 7.52–7.51 (m, 1H), 7.39–7.38 (m, 1H), 6.89–6.78 (m, 1H), 5.55 (br s, 1H), 3.09 (t, 2H, *J* = 7.8 Hz), 2.17 (s, 3H), 1.53–1.48 (m, 2H), 1.37–1.28 (m, 6H), 0.98 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 151.0, 149.0, 130.1, 117.4, 112.7, 109.2, 44.5, 31.6, 29.4, 27.7, 22.9, 14.0. MS: *m*/*z* 222 (M^+). IR (neat): ν_{NH} 3388.

N-(*n*-hexyl)-2-toluidine (3g): 175 mg (46% yield). Viscous brown oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.01–6.98 (m, 2H), 6.61–6.58 (m, 1H), 6.48–6.47 (m, 1H), 6.17 (s, 1H), 3.12–3.09 (m, 2H), 1.54–1.49 (m, 2H), 1.36–1.29 (m, 6H), 0.98 (t, 3H, *J* =

6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 148.1, 129.3, 127.4, 126.7, 118.9, 114.8, 44.5, 31.6, 29.4, 27.7, 22.9, 17.3, 14.0. MS*:* *m*/*z* 191 (M^+). IR (neat): ν_{NH} 3374.

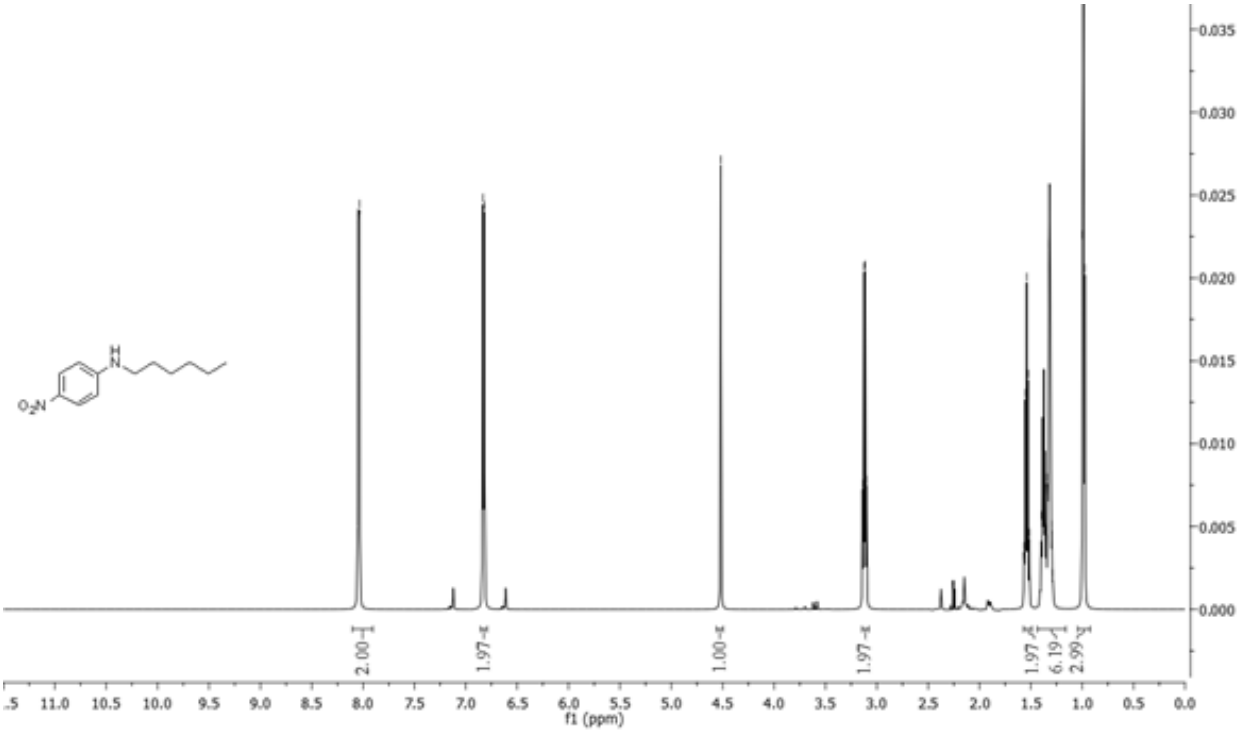
N-(*n*-hexyl)-3-toluidine (3h): 195 mg (51% yield). Viscous brown oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.09–7.05 (m, 2H), 6.53–6.51 (m, 1H), 6.42–6.41 (m, 1H), 5.53 (br s, 1H), 3.14–3.07 (m, 2H), 2.32 (s, 3H), 1.54–1.49 (m, 2H), 1.37–1.29 (m, 6H), 0.98 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 147.9, 138.9, 128.9, 120.1, 115.6, 112.6, 44.5, 31.7, 29.4, 27.6, 22.9, 21.2, 14.0. MS*:* *m*/*z* 191 (M^+). IR (neat): ν_{NH} 3324.

N-(*n*-hexyl)-4-iodoaniline (3i): 520 mg (86% yield). Waxy solid. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.46 (d, 2H, *J* = 7.8 Hz), 6.28 (d, 2H, *J* = 7.8 Hz), 3.11– 3.08 (m, 2H), 1.54–1.49 (m, 2H), 1.37–1.29 (m, 6H), 0.98 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 148.4, 136.9, 114.9, 93.2, 44.5, 31.7, 29.4, 27.6, 22.9, 14.0. MS*:* *m*/*z* 303 (M^+). IR (neat): ν_{NH} 3414.

2-[(4-Nitrophenyl)amino]ethan-1-ol (3j): 289 mg (79% yield). Pale yellow solid (MeOH; mp 109–110°C; Lit[4] mp 108 °C). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.05 (d, 2H, *J* = 7.8 Hz), 6.80 (d, 2H, *J* = 7.8 Hz), 3.60 (t, 2H, *J* = 7.2 Hz), 3.31 (t, 2H, *J* = 7.2 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz): 157.1, 138.3, 125.3, 112.7, 60.7, 44.8. MS*:* *m*/*z* 182 (M^+). IR (neat): ν_{NH} 3434, ν_{OH} 3278.

References

1. P. Gaur, K. D. B. Yamajala, S. Banerjee, Efficient synthetic route to aromatic secondary amines via Pd/RuPhos/TBAB-catalyzed cross coupling, *New J. Chem*., **2017**, *41*, 6523–6529. https://doi.org/10.1039/C7NJ01095H.
2. E. Petricci, N. Santillo, D. Castagnolo, E. Cini, M. Taddei, Iron-Catalyzed Reductive Amination of Aldehydes in Isopropyl Alcohol/Water Media as Hydrogen Sources, *Adv. Synth. Catal.* **2018**, *360*, 2560–2565. https://doi.org/10.1002/adsc.201701619.
3. C. Yang, F. Zhang, G.-J. Deng, H. Gong, Amination of Aromatic Halides and Exploration of the Reactivity Sequence of Aromatic Halides, *J. Org. Chem.* **2019**, *84*, 181–190. https://doi.org/10.1021/acs.joc.8b02588.
4. P. Lo Meo, F. D'Anna, M. Gruttadauria, S. Riela, R. Noto, Thermodynamics of binding between α- and β-cyclodextrins and some p-nitroaniline derivatives: reconsidering the enthalpy–entropy compensation effect, *Tetrahedron*, **2004**, *60*, 9099–9111. http://dx.doi.org/10.1016/j.tet.2004.07.079.



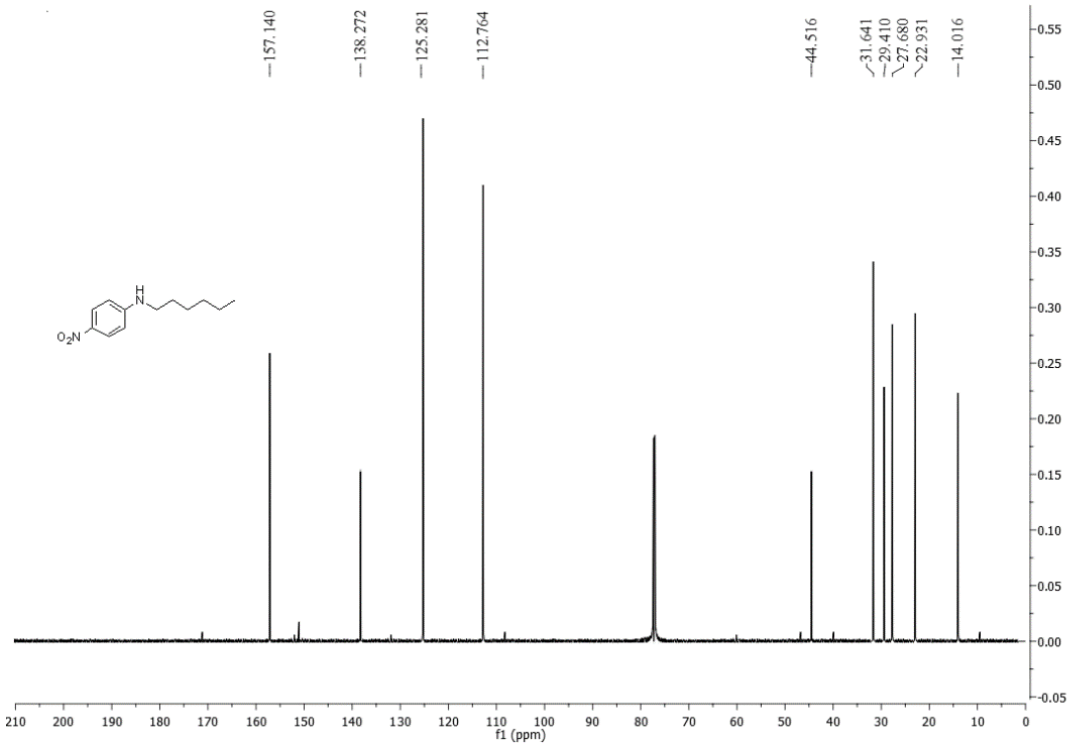
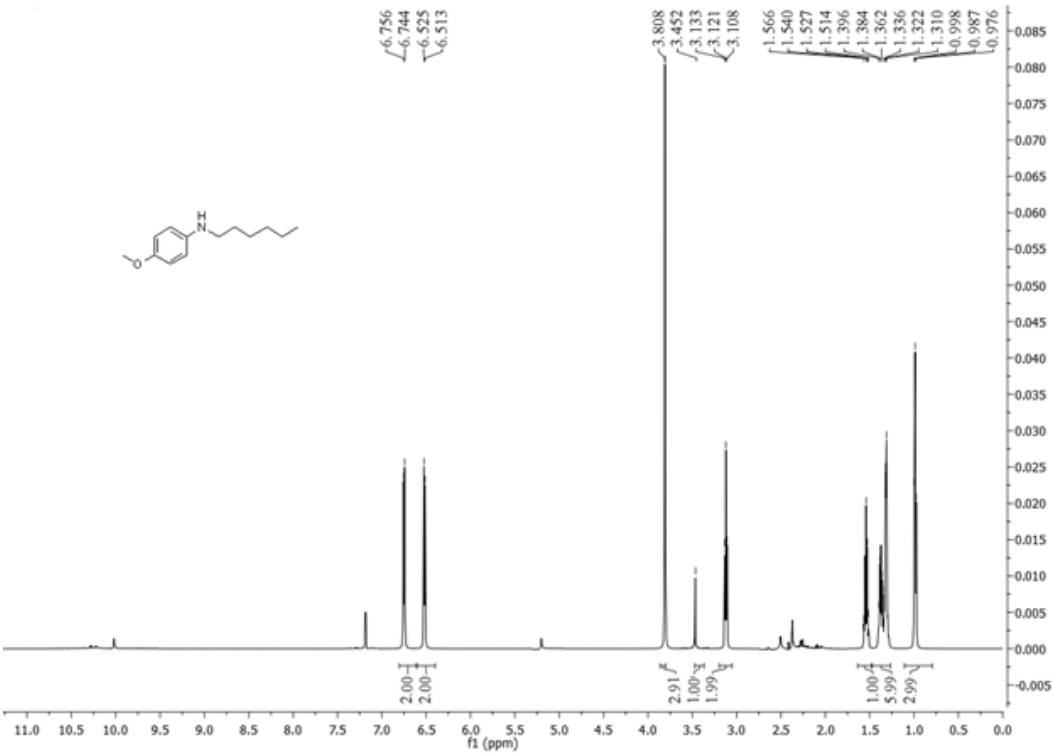


Figure S1. NMR spectra of N-(*n*-hexyl)-4-nitroaniline (**3a**).



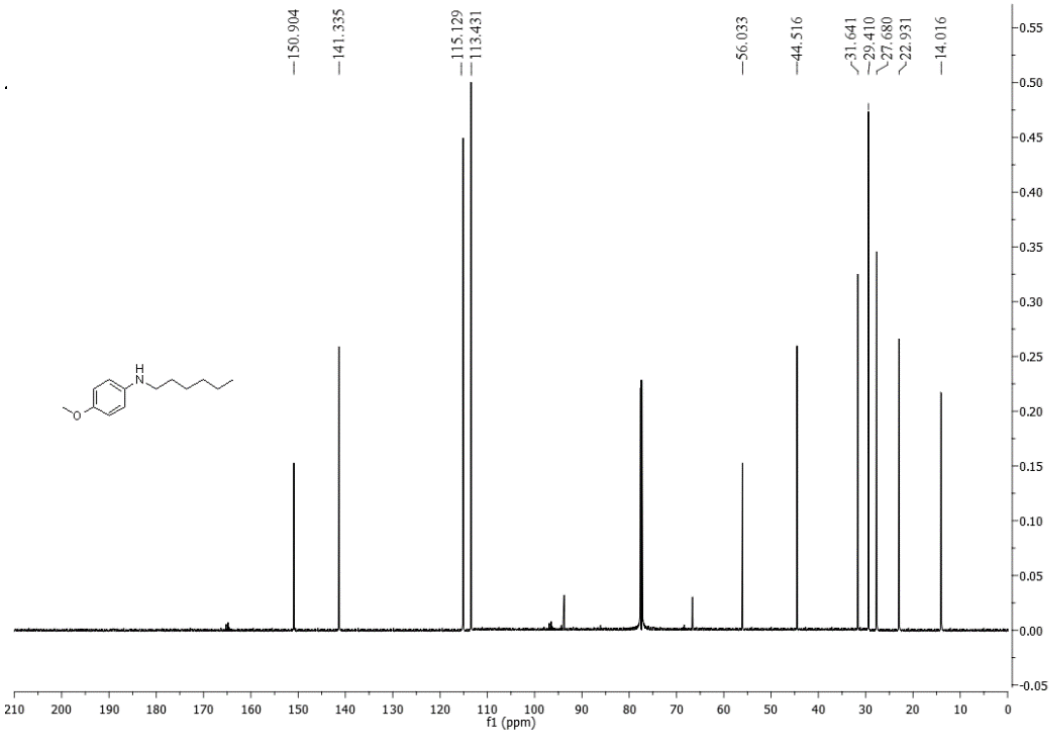
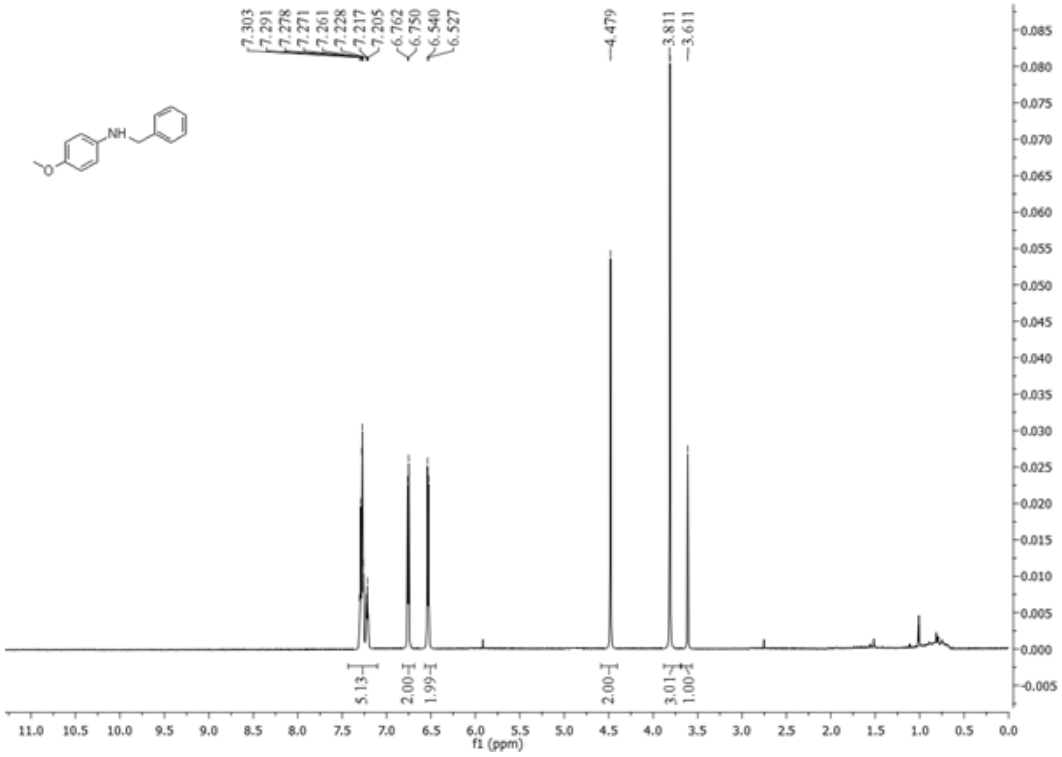


Figure S2. NMR spectra of N-(*n*-hexyl)-4-methoxyaniline (**3b**).



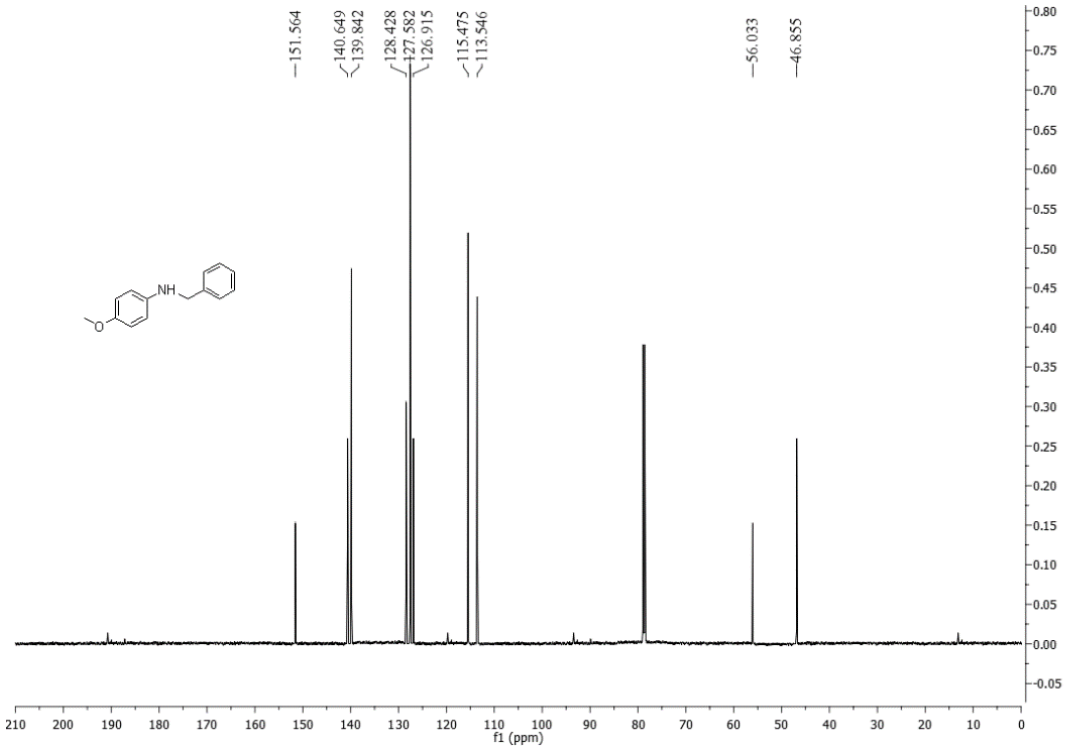
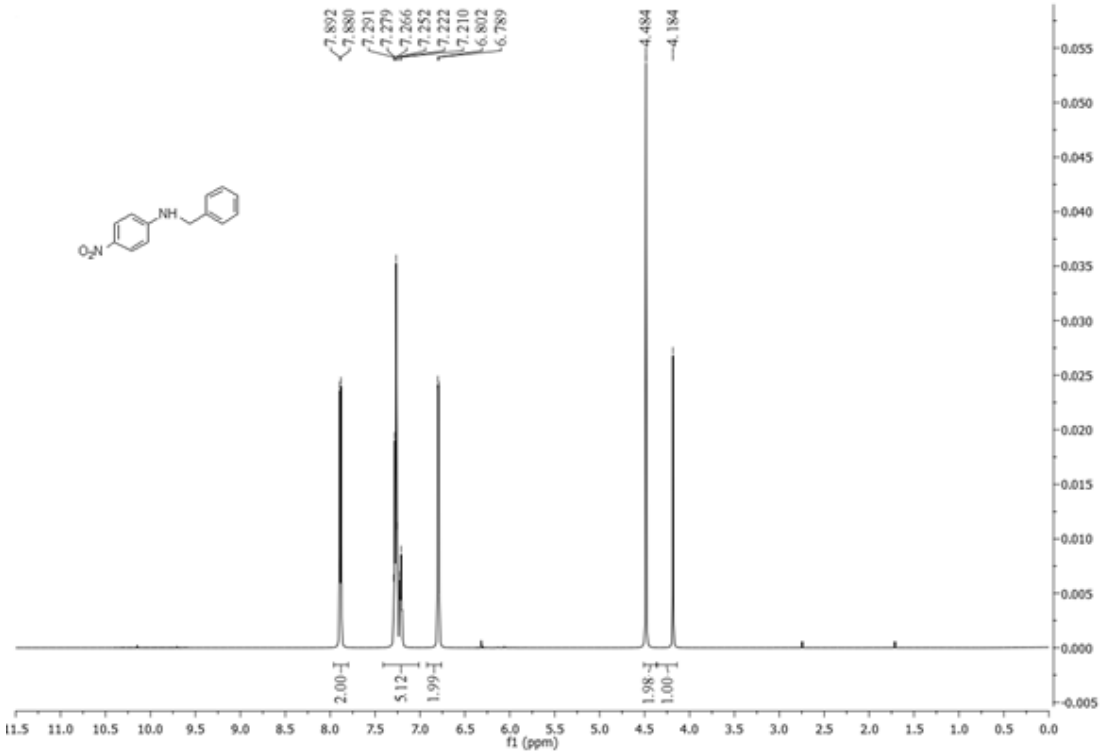


Figure S3. NMR spectra of N-(*n*-benzyl)-4-methoxyaniline (**3c**).



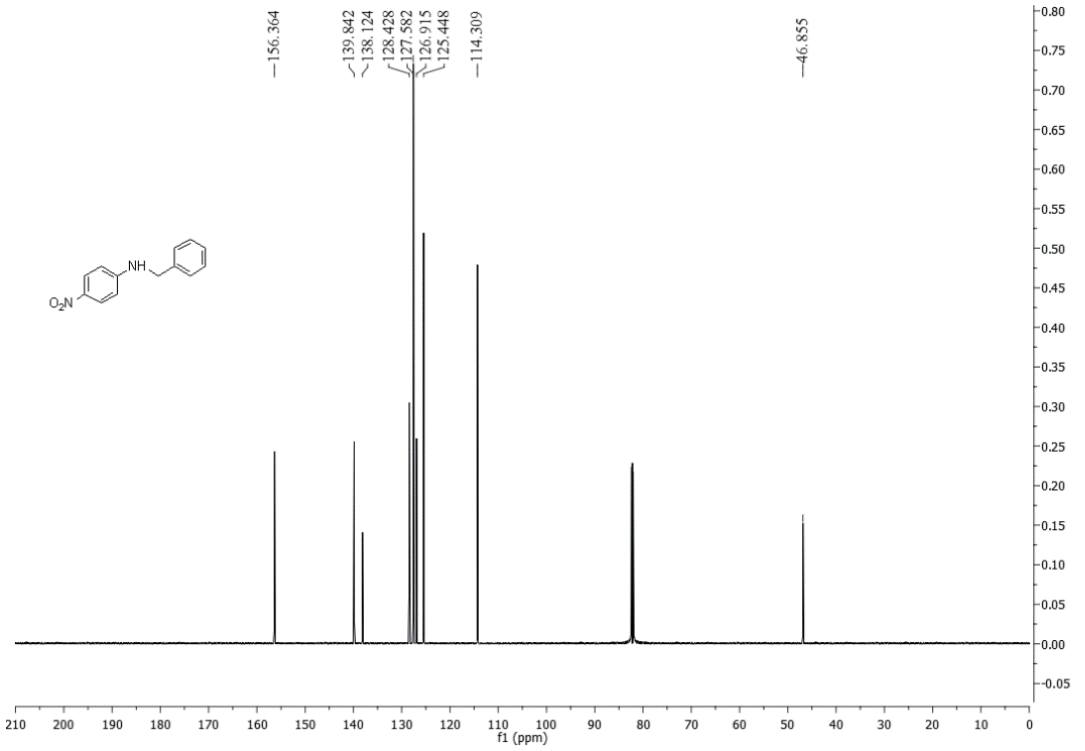
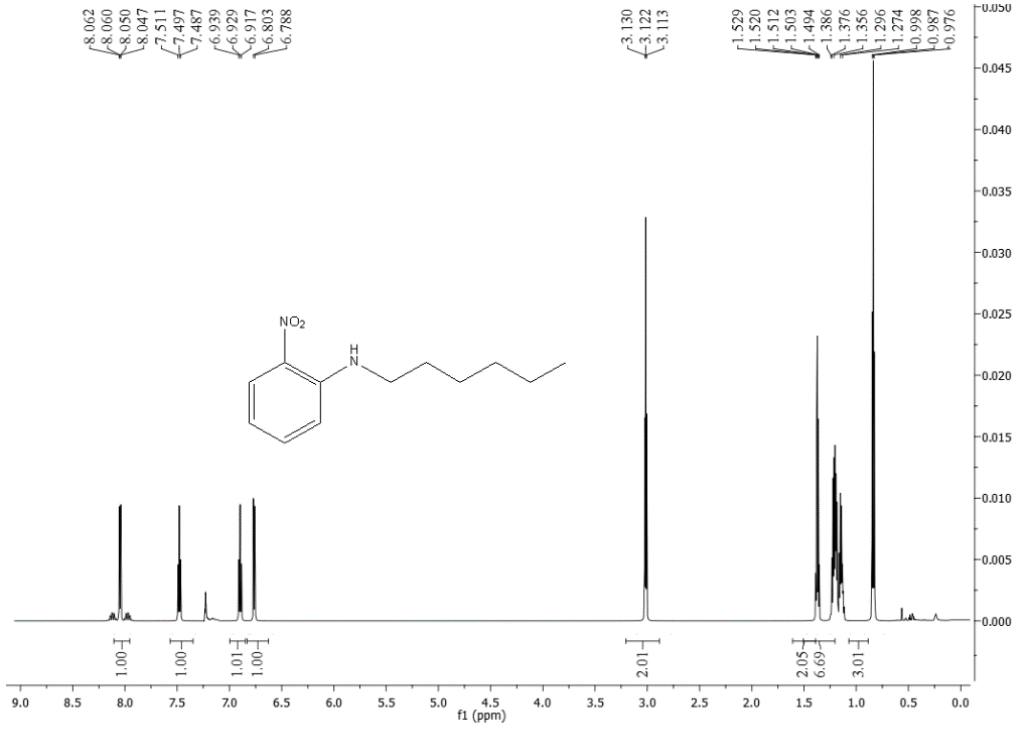


Figure S4. NMR spectra of N-(*n*-benzyl)-4-nitroaniline (**3d**).



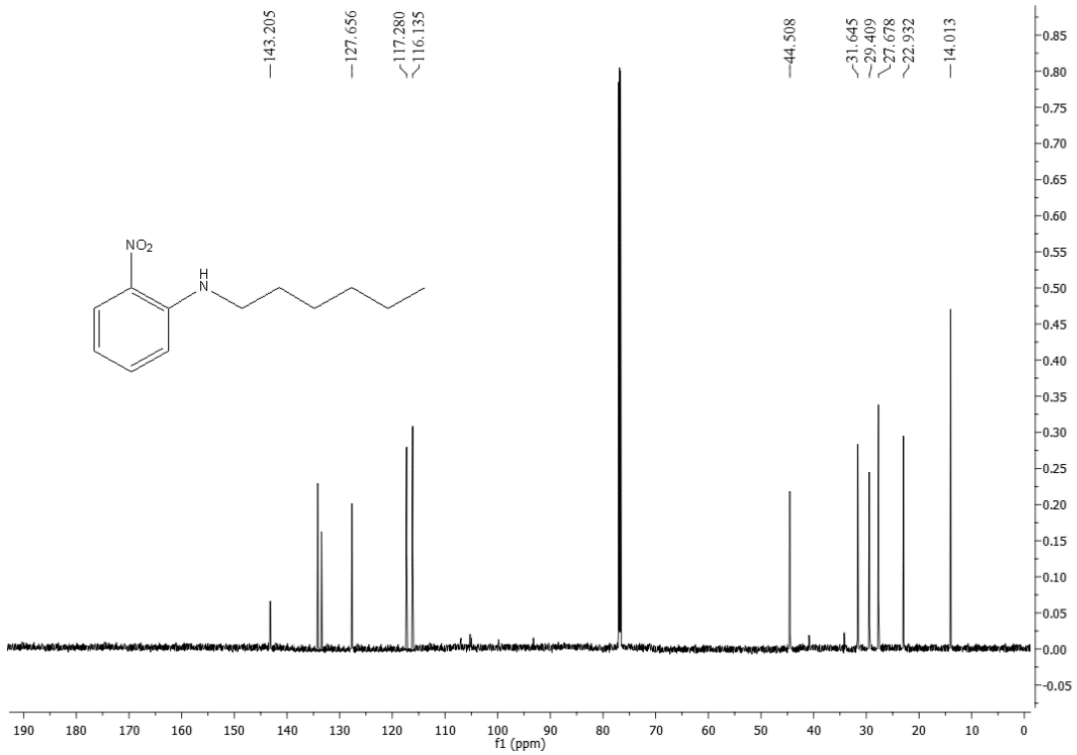
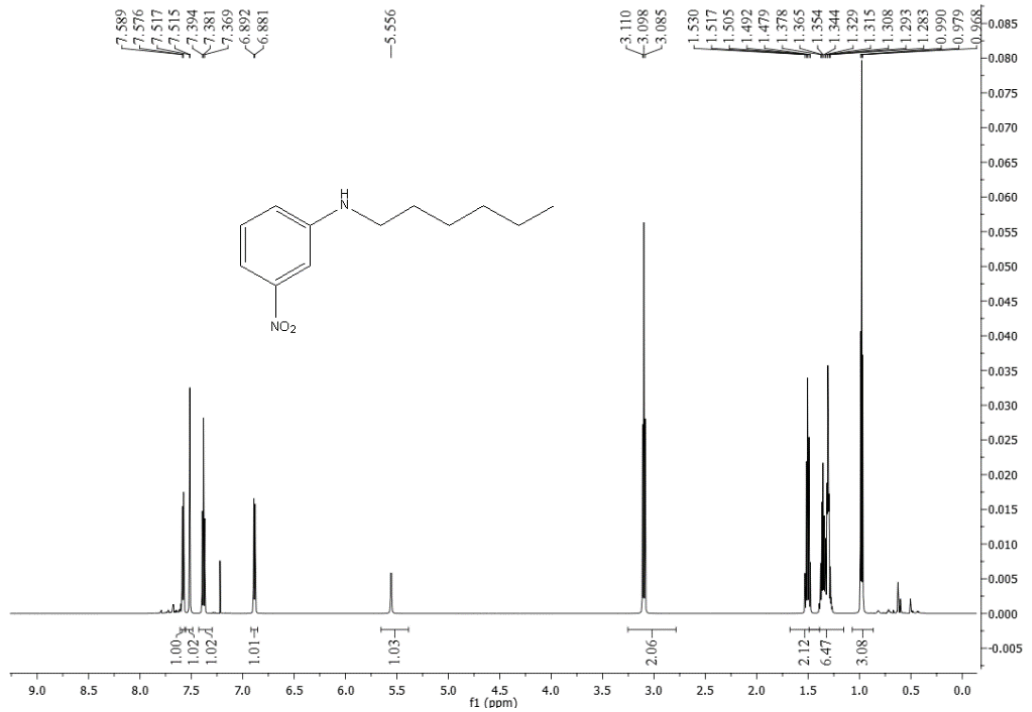


Figure S5. NMR spectra of N-(*n*-hexyl)-2-nitroaniline (**3e**).



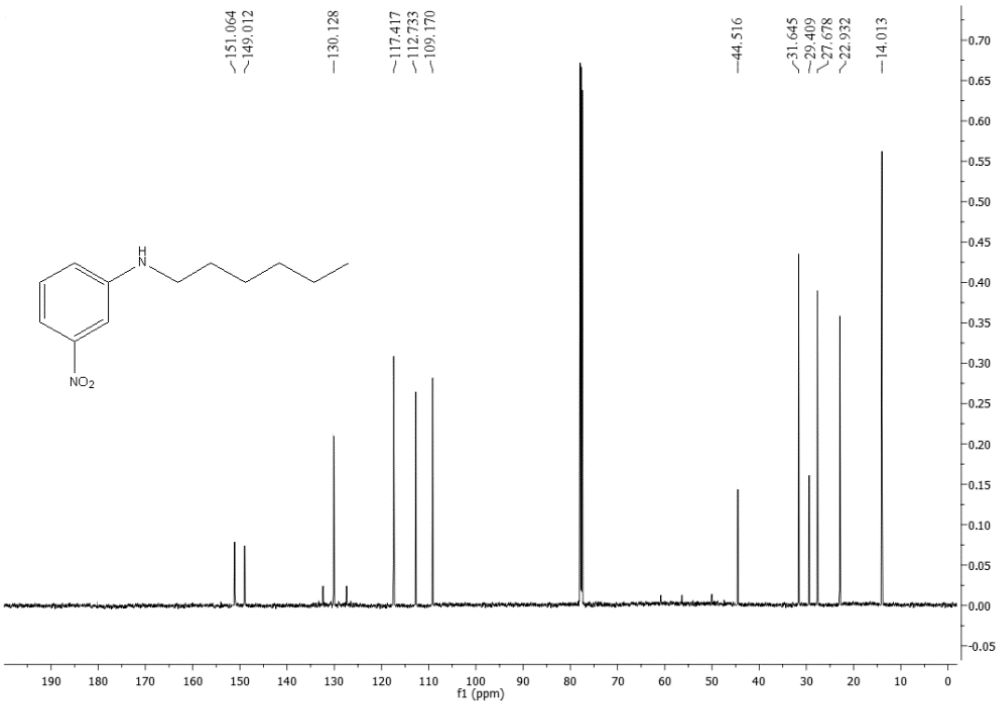
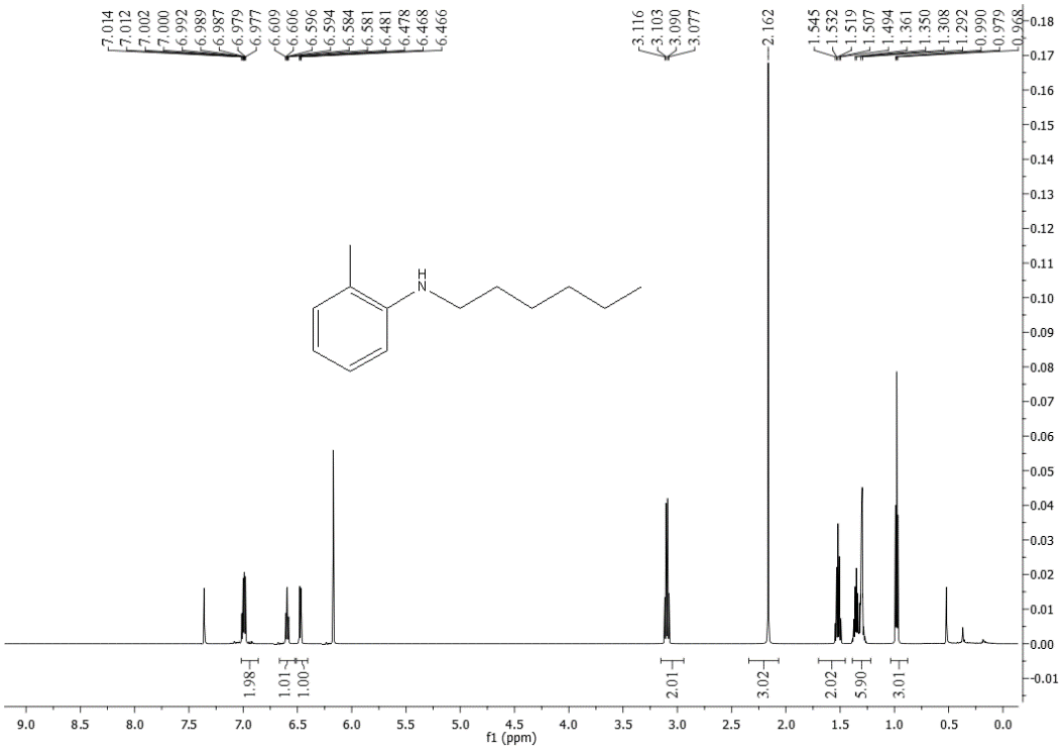


Figure S6. NMR spectra of N-(*n*-hexyl)-3-nitroaniline (**3f**).



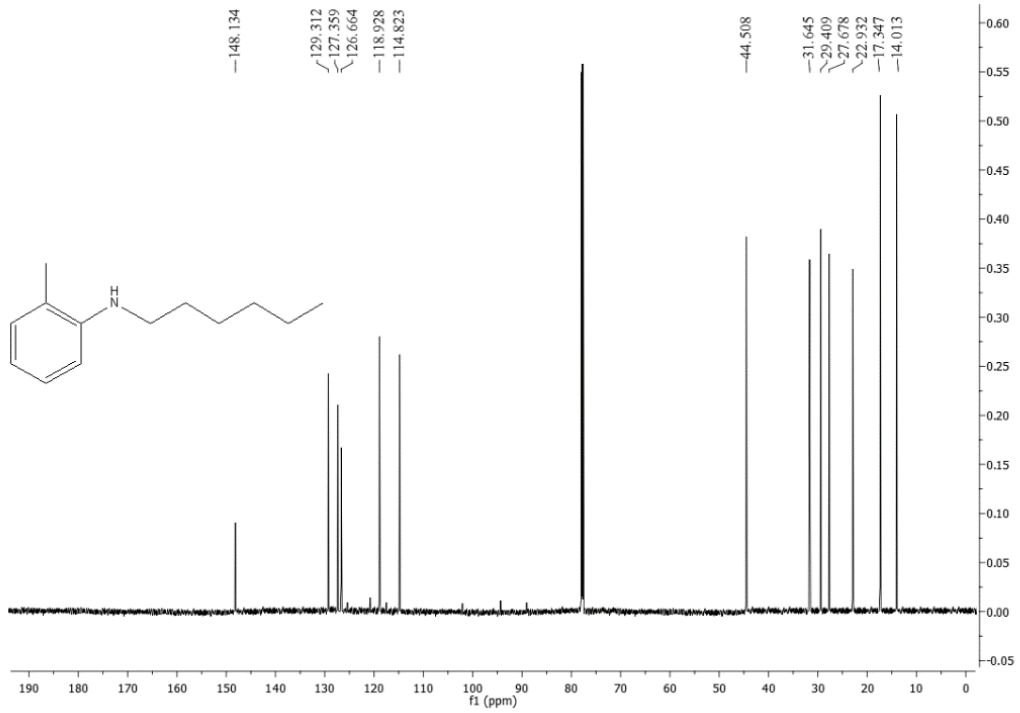
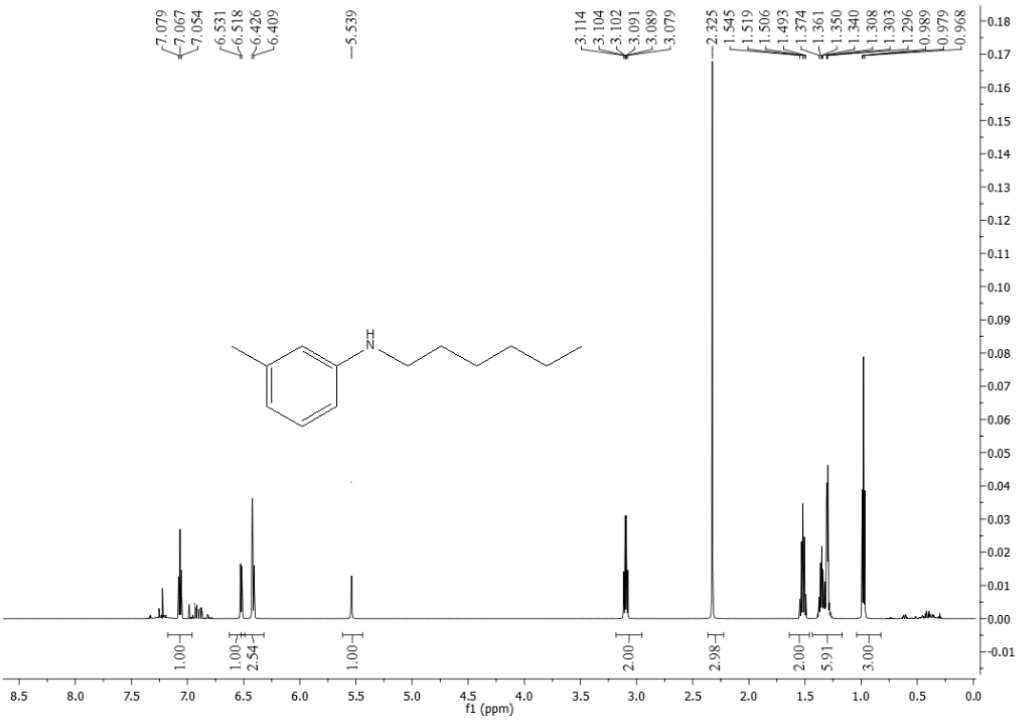


Figure S7. NMR spectra of N-(*n*-hexyl)-2-toluidine (**3g**).



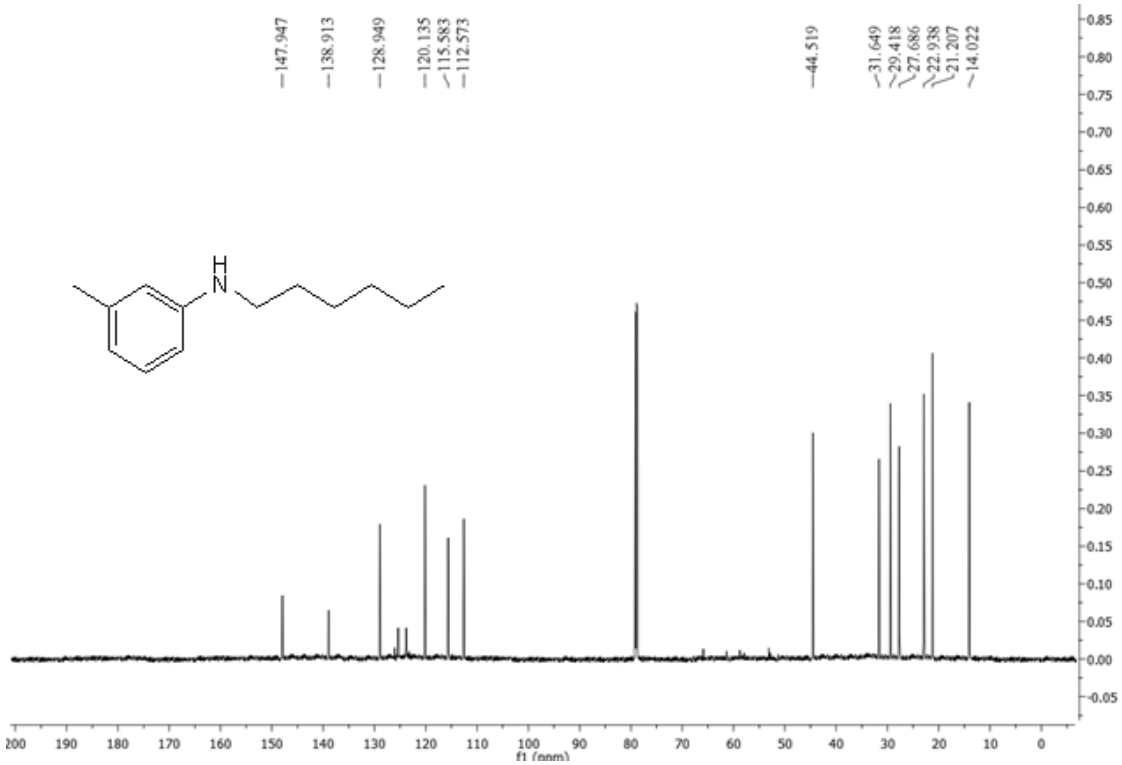
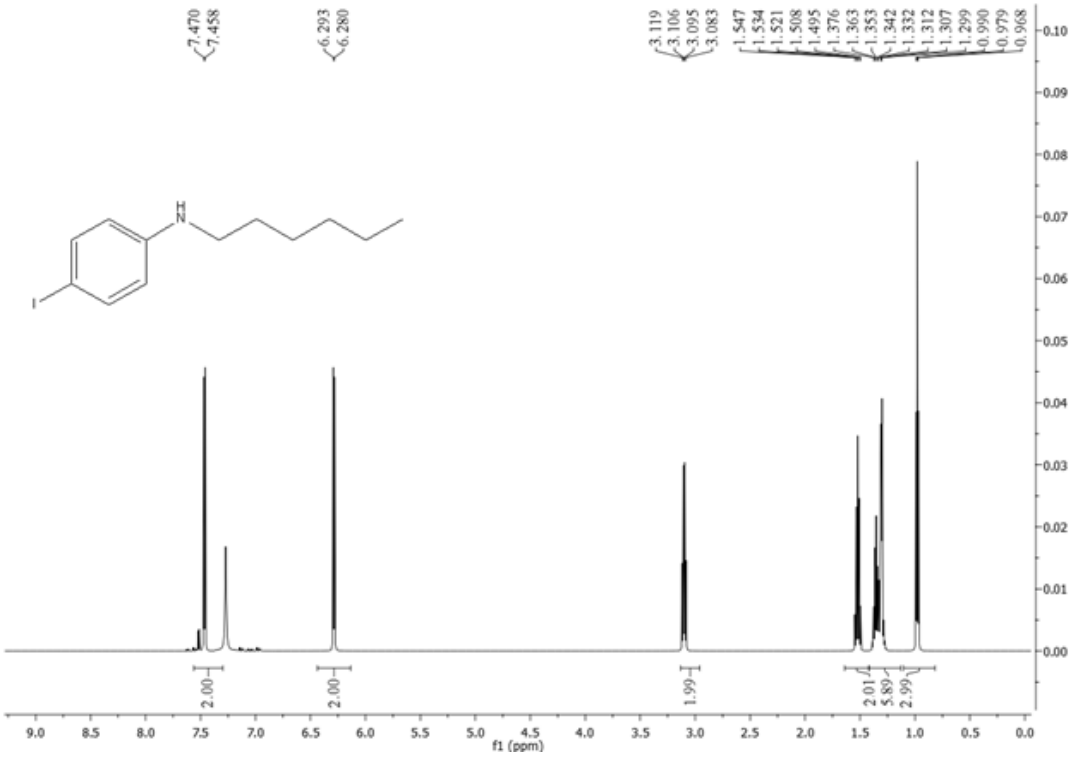


Figure S8. NMR spectra of N-(*n*-hexyl)-3-toluidine (**3h**).



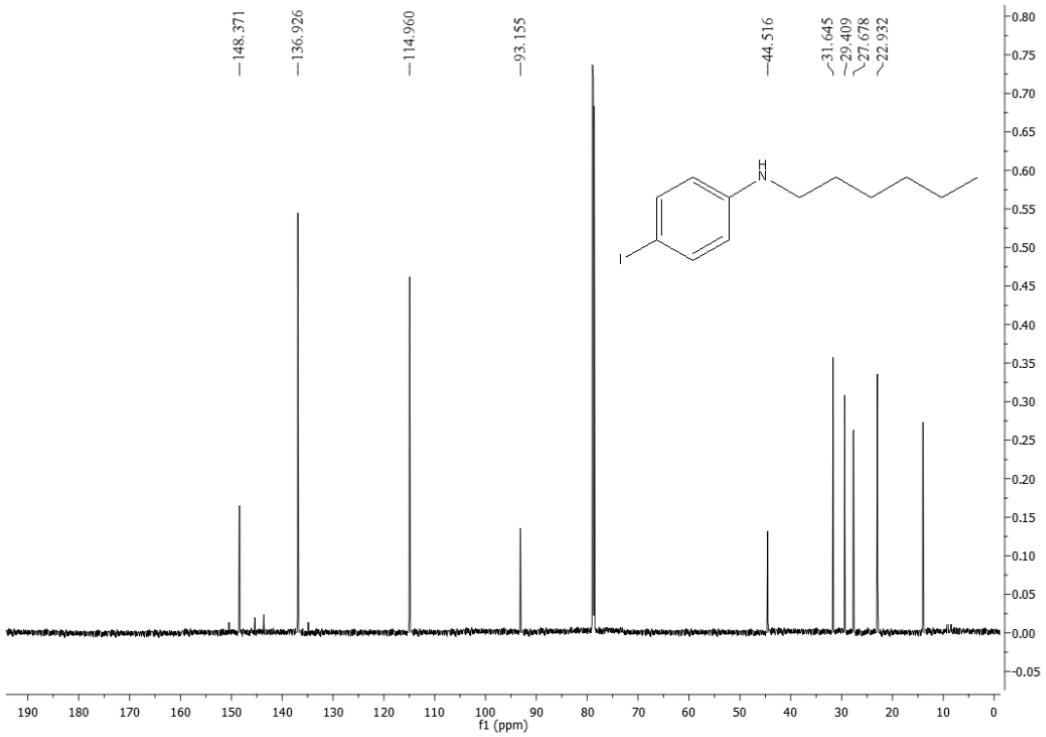
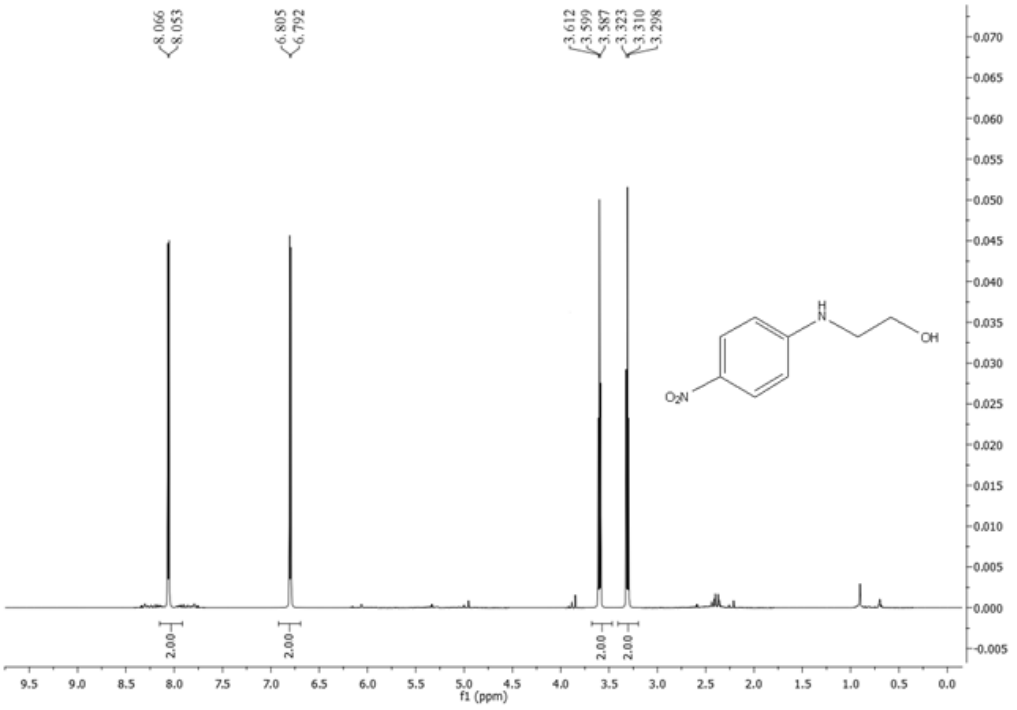


Figure S9. NMR spectra of N-(*n*-hexyl)-4-iodoaniline (**3i**).



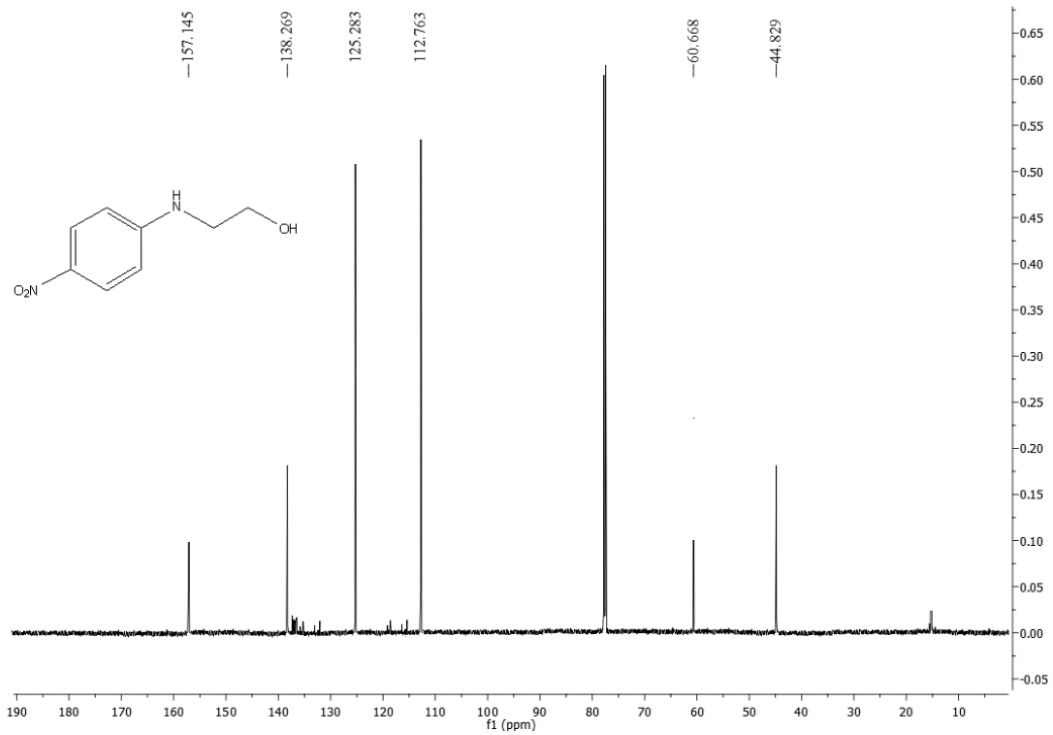


Figure S10. NMR spectra of 2-[(4-Nitrophenyl)amino]ethan-1-ol (**3j**).

Physical and NMR data of ethers 7

1-(*n*-Hexyloxy)-4-nitrobenzene (7a): 300 mg (67% yield). Pale red waxy solid. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.13 (d, 2H, *J* = 7.8 Hz), 7.15 (d, 2H, *J* = 7.8 Hz), 3.96 (t, 2H, *J* = 7.8 Hz), 1.76–1.71 (m, 2H), 1.36–1.29 (m, 6H), 0.99 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 164.0, 142.5, 127.7, 114.6, 69.6, 31.7, 28.7, 26.8, 22.9, 14.0. MS*: m*/*z* 223 (M^+).

1-(*n*-Hexyloxy)-4-methoxybenzene (7b): 205 mg (49% yield). Pale yellow viscous oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 6.86 (s, 4H), 3.95 (t, 2H, *J* = 7.2 Hz), 3.81 (s, 3H), 1.76–1.71 (m, 2H), 1.39–1.29 (m, 6H), 0.99 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 153.9, 153.8, 116.4, 115.1, 69.6, 56.0, 31.6, 28.7, 26.8, 22.9, 14.1. MS*: m*/*z* 208 (M^+).

2-Ethoxynaphthalene (7c): 231 mg (67% yield). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.73–7.68 (m, 2H), 7.58–7.57 (m, 1H), 7.39 –7.36 (m, 1H), 7.35 –7.33 (m, 2H), 7.00–6.99 (m, 1H), 4.11 (q, 2H, *J* = 6.0 Hz), 1.40 (t, 3H, *J* = 6.0 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz): 157.0, 135.1, 131.1, 130.2, 128.7, 127.3, 127.2, 123.9, 115.8, 108.6, 63.8, 13.8. MS*: m*/*z* 172 (M^+).

2-Ethoxybenzo[*d*]thiazole (7d): 238 mg (66% yield). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.05–8.03 (m, 1H), 7.96–7.95 (m, 1H), 7.44 –7.40 (m, 1H), 4.05 (q, 2H, *J* = 6.0 Hz), 1.39 (t, 3H, *J* = 6.0 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz): 164.4, 141.9, 133.8, 128.1, 125.1, 123.7, 120.4, 66.2, 14.7. MS*: m*/*z* 179 (M^+).

Methyl 3-ethoxythiophene-2-carboxylate (7e): 189 mg (51% yield). White oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.36 (d, 1H, *J* = 7.2 Hz), 6.85 (d, 1H, *J* = 7.2 Hz), 4.05 (q, 2H, *J* = 6.0 Hz), 3.92 (s, 3H), 1.40 (t, 3H, *J* = 6.0 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz): 167.3, 164.9, 131.4, 119.0, 110.2, 123.7, 67.4, 52.0, 14.7. MS*: m*/*z* 186 (M^+).

3-Ethoxypyridine (7f): 150 mg (60% yield). White oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.24 –8.22 (m, 2H), 7.46 (t, 1H, *J* = 7.8Hz), 7.36–7.35 (m, 1H), 4.02 (q, 2H, *J* = 6.0 Hz), 1.38 (t, 3H, *J* = 6.0 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz): 156.7, 143.7, 137.6, 125.7, 123.8, 63.9, 13.8. MS*: m*/*z* 124 (M^+).

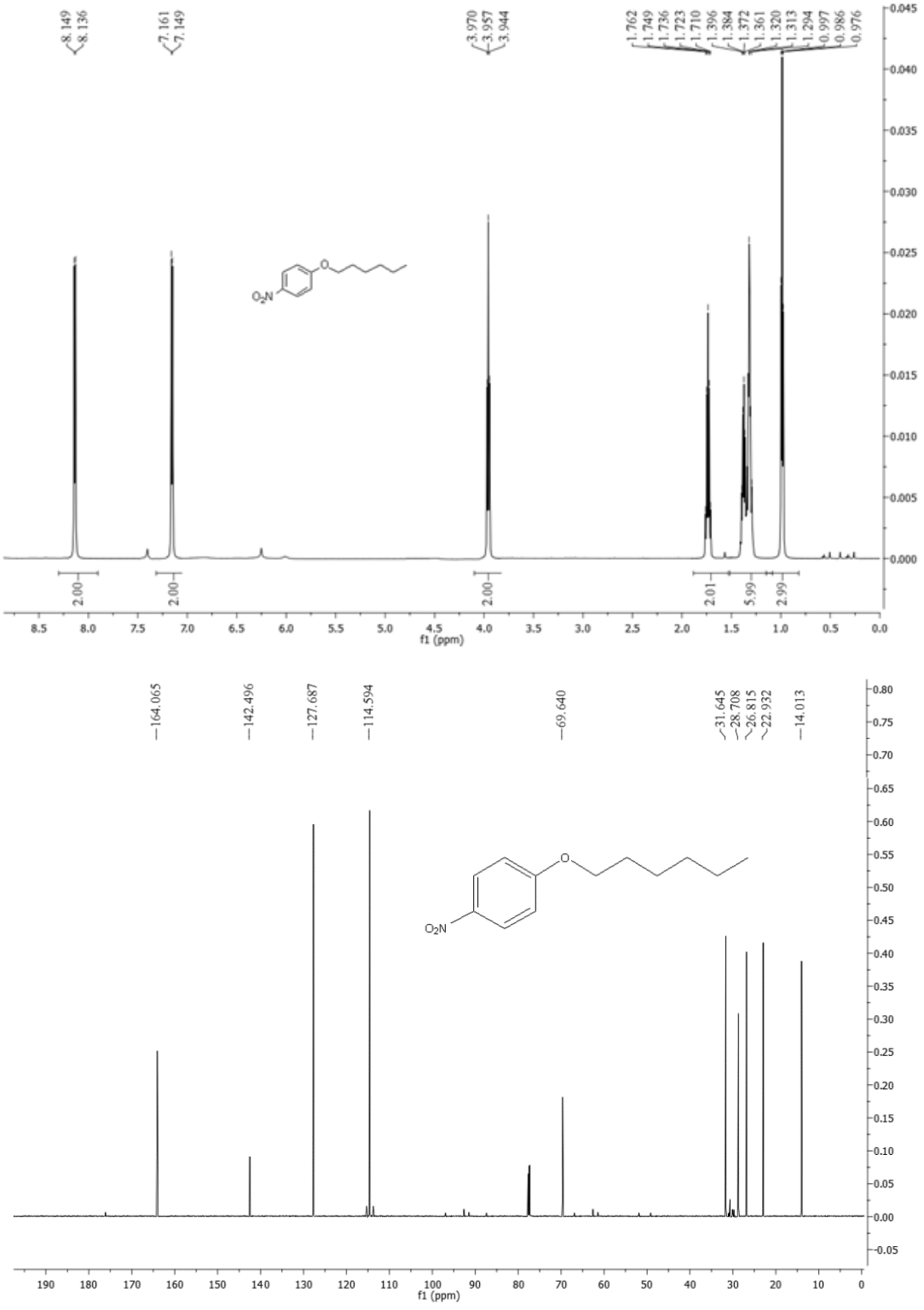


Figure S11. NMR spectra of 1-(*n*-Hexyloxy)-4-nitrobenzene (**7a**).

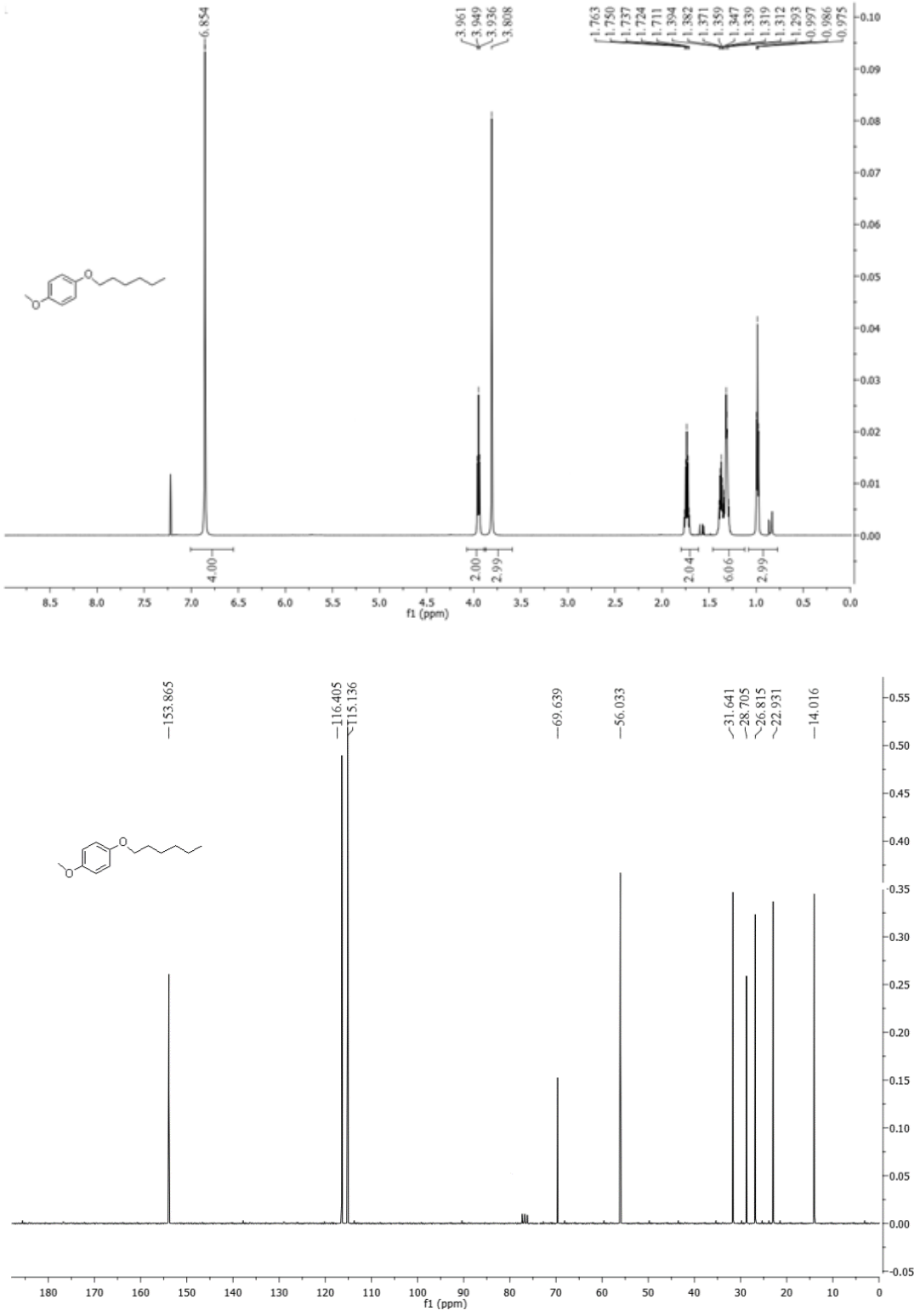


Figure S12. NMR spectra of 1-(*n*-Hexyloxy)-4-methoxybenzene (**7b**).

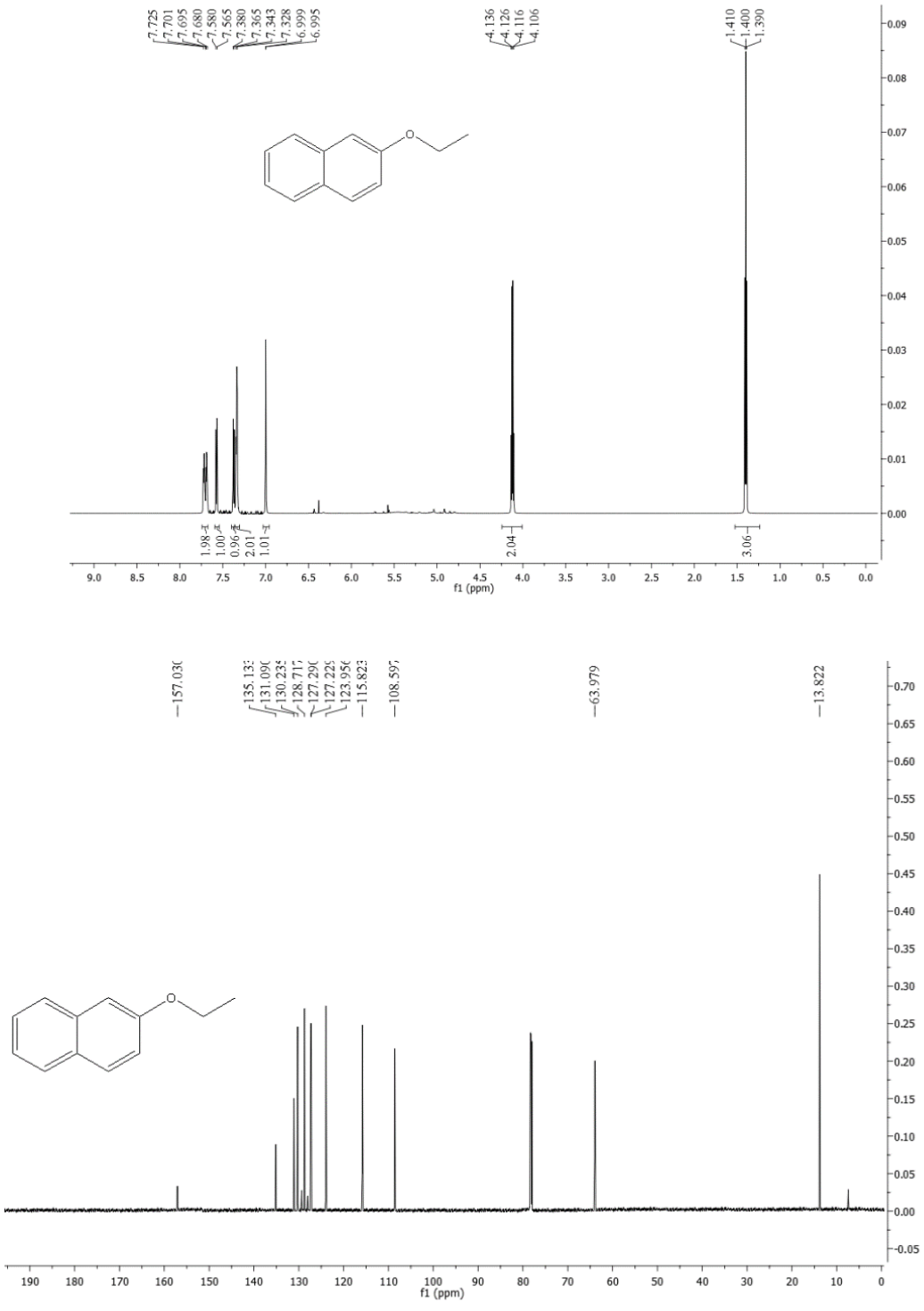


Figure S13. NMR spectra of 2-Ethoxynaphthalene (**7c**).

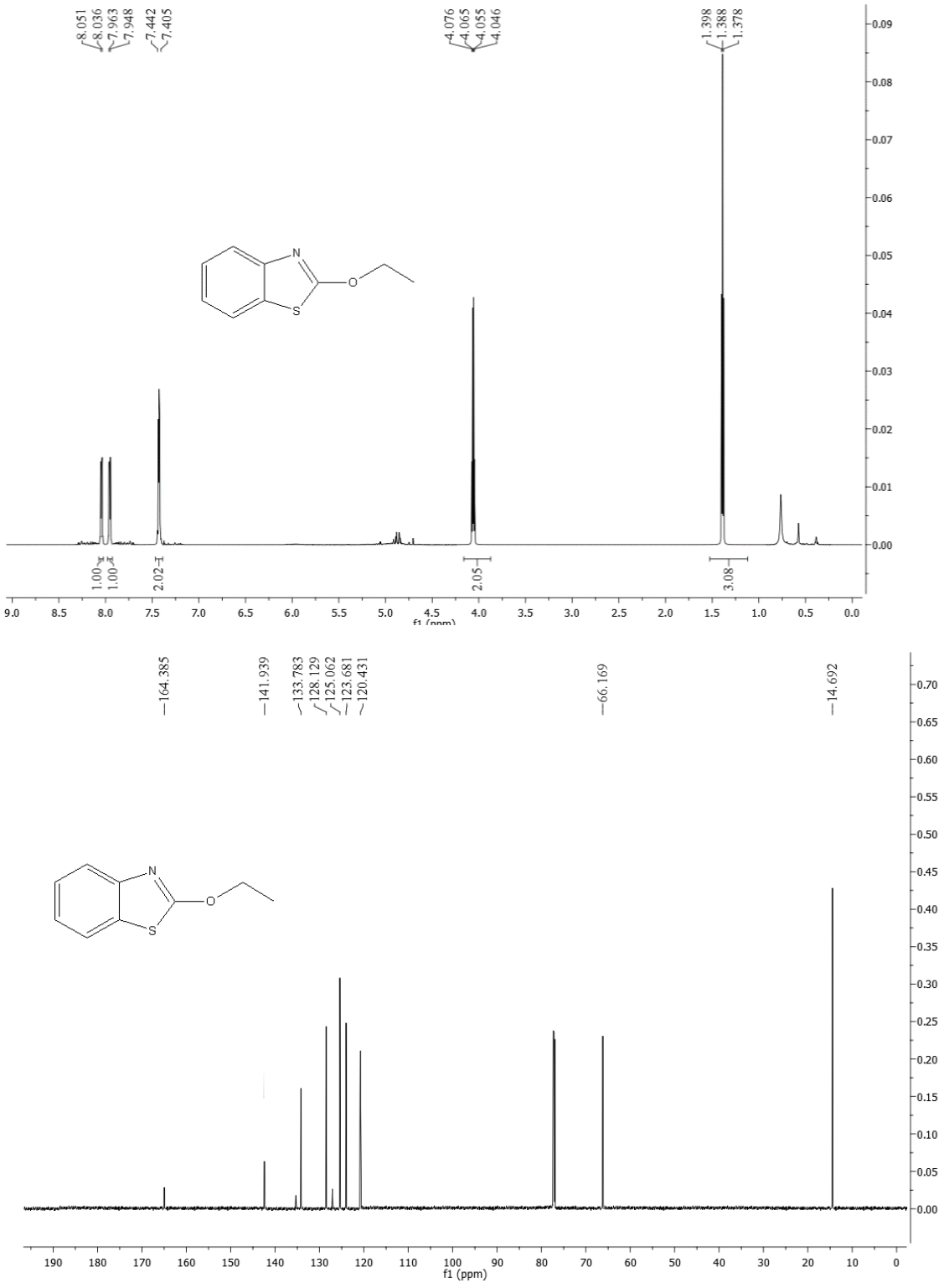


Figure S14. NMR spectra of 2-Ethoxybenzo[d]thiazole (**7d**).

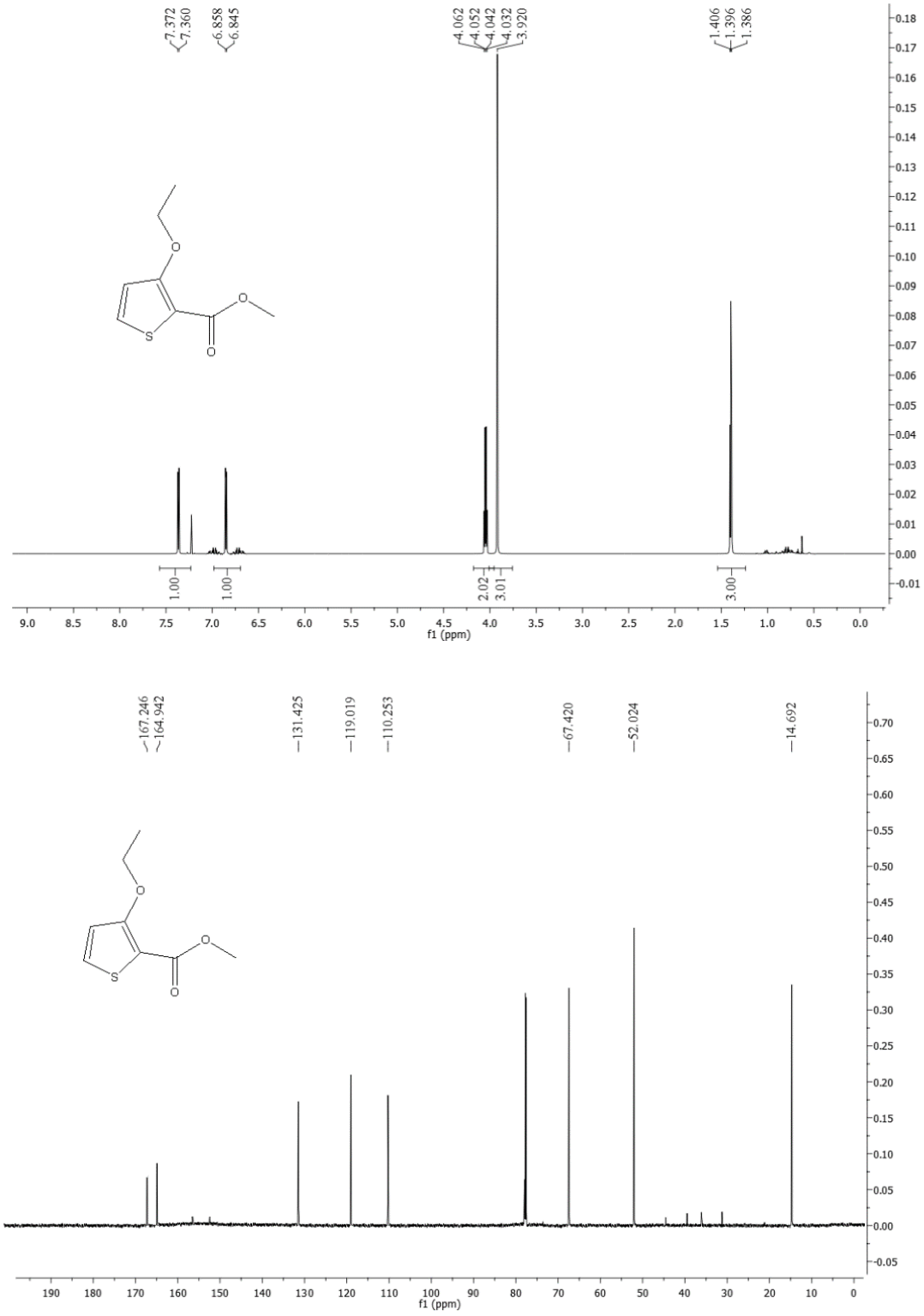


Figure S15. NMR spectra of Methyl 3-ethoxythiophene-2-carboxylate (**7e**).

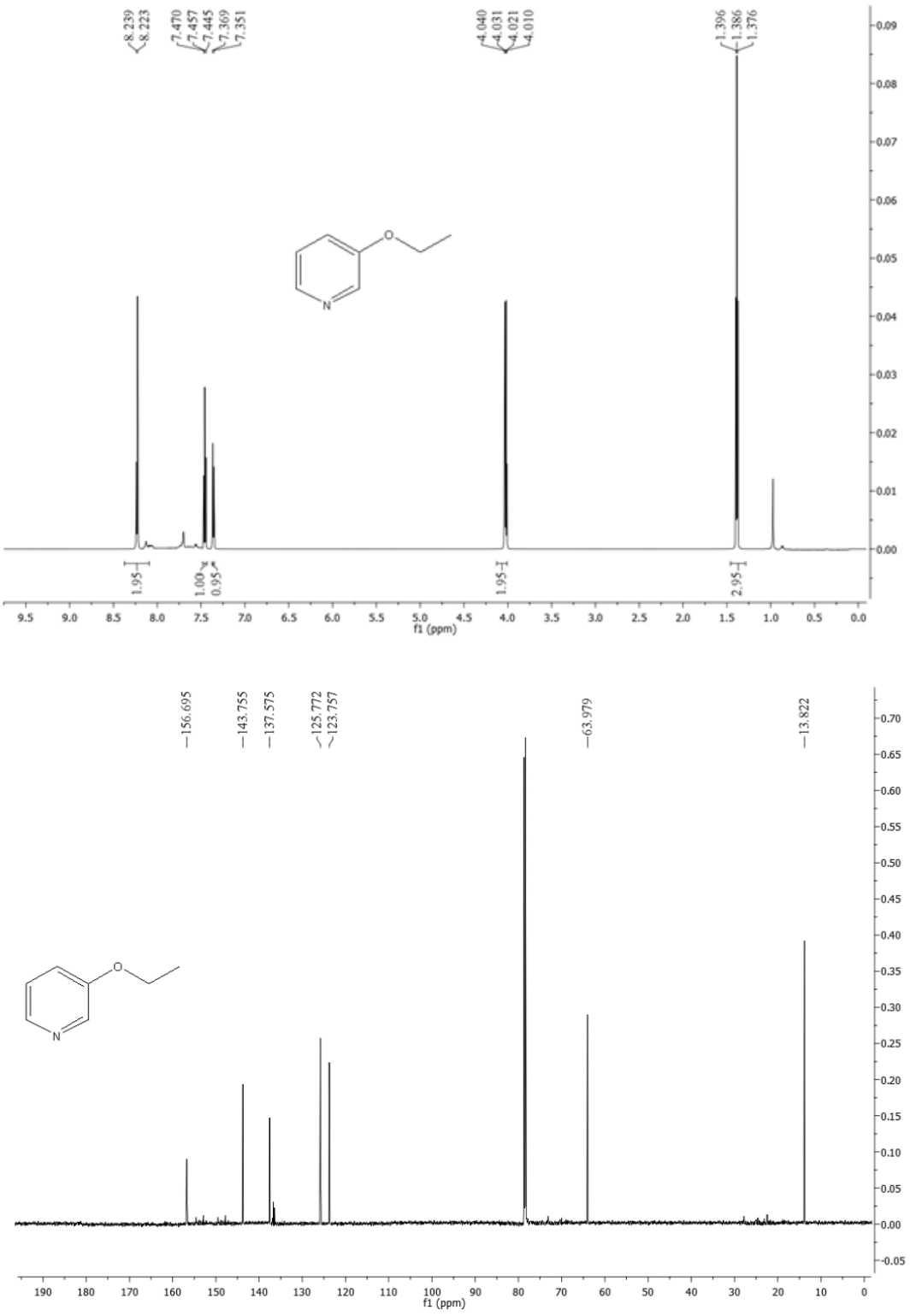
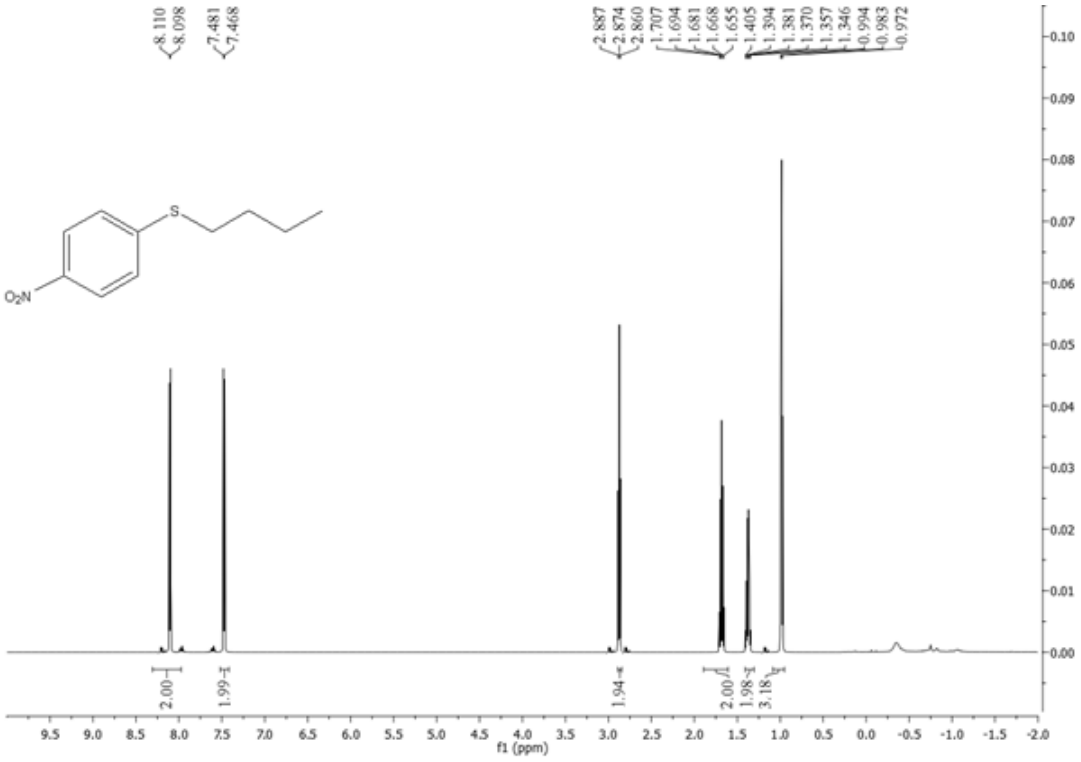


Figure S16. NMR spectra of 3-Ethoxypyridine (**7f**).

Physical and NMR data of thioethers 8

***n*-Butyl 4-nitrophenyl sulfide (8a):** 273 mg (65% yield). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.10 (d, 2H, *J* = 7.8 Hz), 7.47 (d, 2H, *J* = 7.8 Hz), 2.87 (t, 2H, *J* = 7.8 Hz), 1.71–1.65 (m, 2H), 1.41–1.35 (m, 2H), 0.98 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 146.7, 145.5, 127.0, 125.5, 33.6, 30.7, 21.0, 14.0. MS*: m*/*z* 211 (M^+).

***n*-Butyl 4-tolyl sulfide (8b):** 174 mg (48% yield). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.15 (d, 2H, *J* = 7.8 Hz), 7.04 (d, 2H, *J* = 7.8 Hz), 2.89 (t, 2H, *J* = 7.8 Hz), 2.31 (s, 3H), 1.71–1.68 (m, 2H), 1.39–1.37 (m, 2H), 0.99 (t, 3H, *J* = 6.6Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 150.9, 141.3, 115.1, 113.4, 56.0, 44.5, 31.6, 29.4, 27.7, 22.9, 14.0. MS*: m*/*z* 180 (M^+).



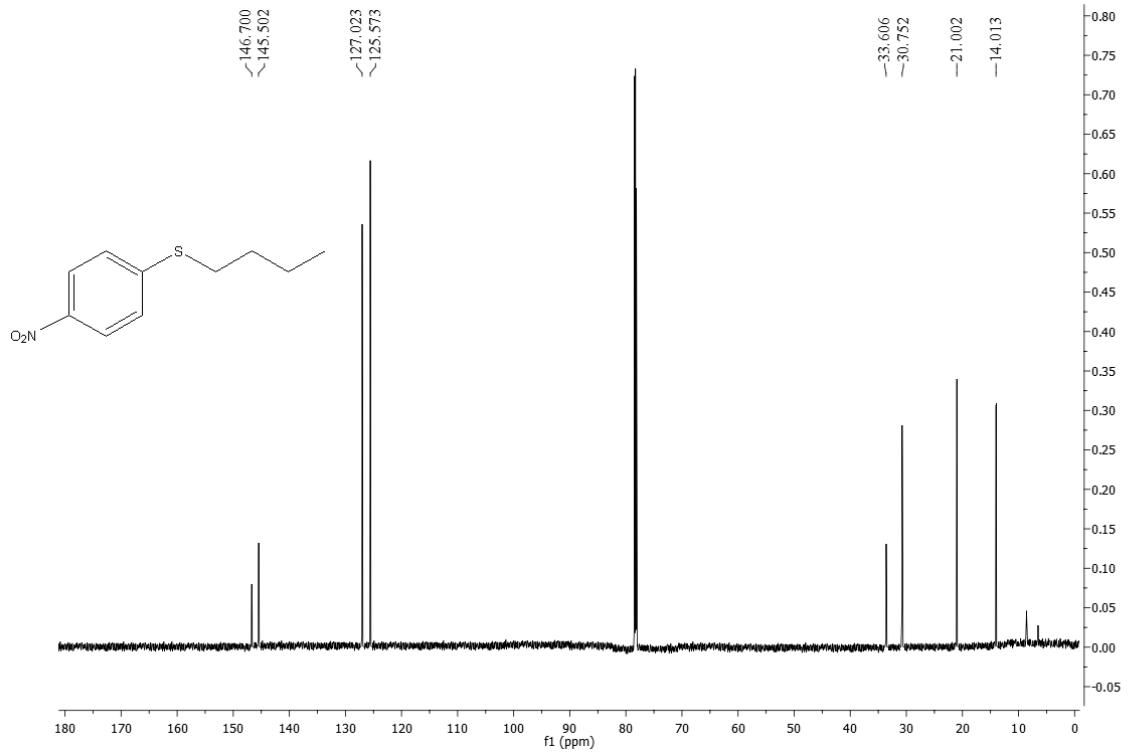
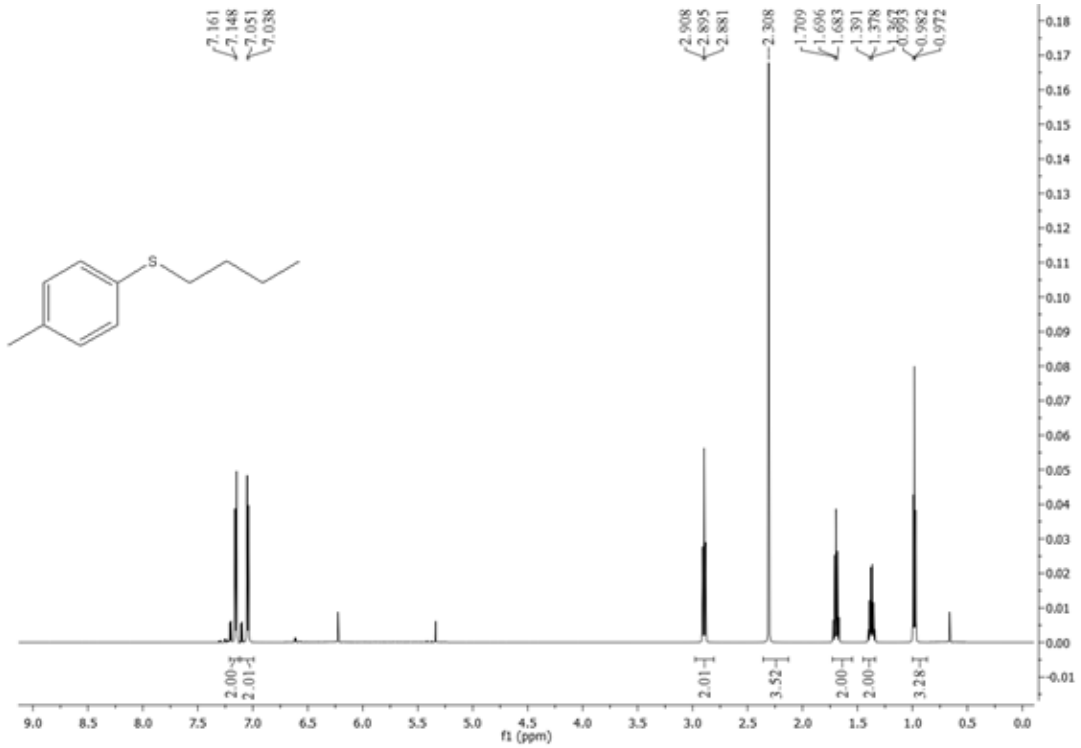


Figure S17. *n*-Butyl 4-nitrophenyl sulfide (**8a**).



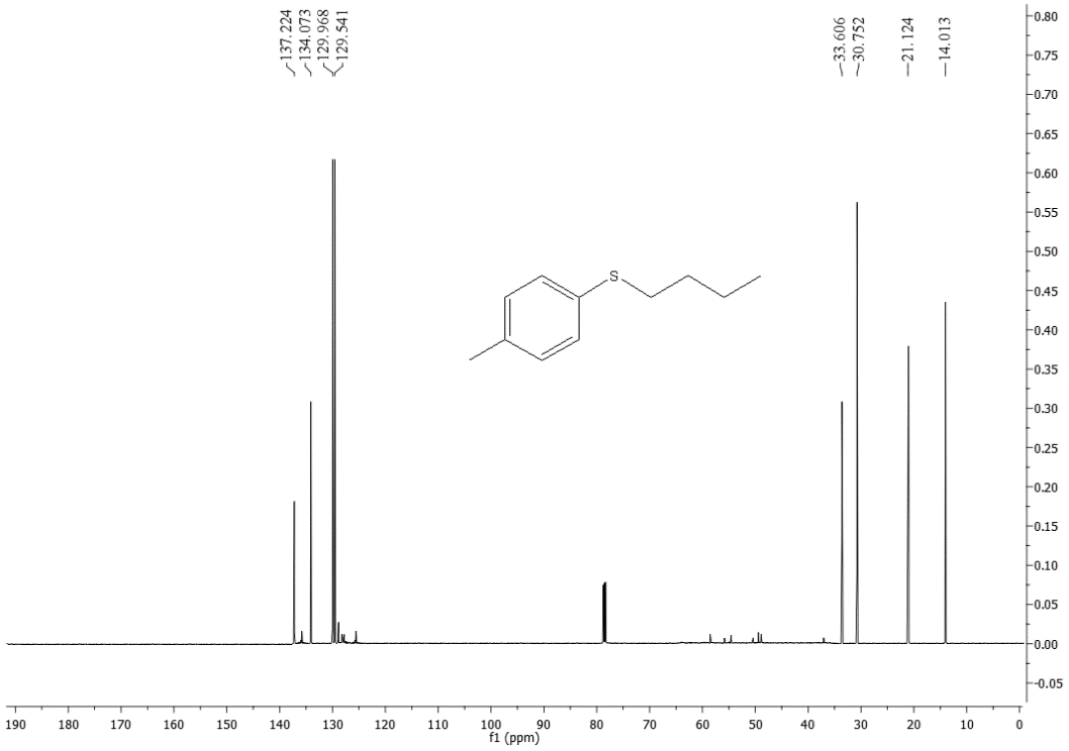


Figure S18. *n*-Butyl 4-tolyl sulfide (**8b**).