

Supplementary Information

Recyclable Imidazolium Ion tagged Nickel Catalyst for Microwave Assisted C-S Cross-Coupling in Water using Sulfonyl hydrazide as a Sulfur Source

Vaishali Saini, Bharti Khungar*

Department of Chemistry

Birla Institute of Technology and Science Pilani

Pilani Campus, Vidya Vihar, Pilani, 333 031, India

E-mail: bkhungar@pilani.bits-pilani.ac.in

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1. IR spectra of 2 and 3

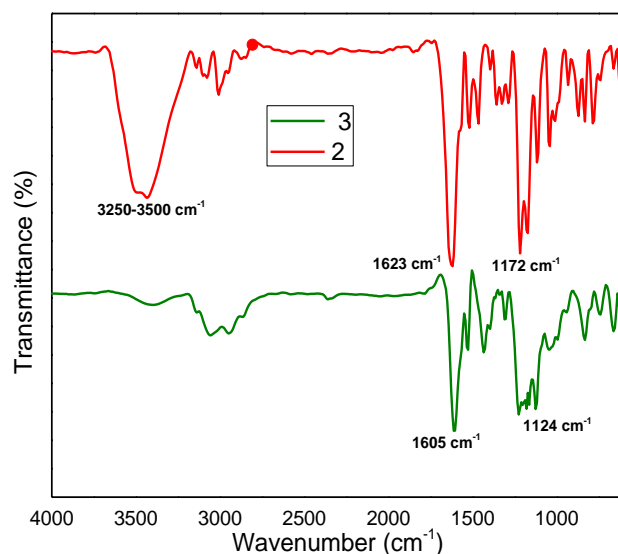


Fig. S1 IR Spectra of 2 and 3

2. UV spectra of 2 and 3

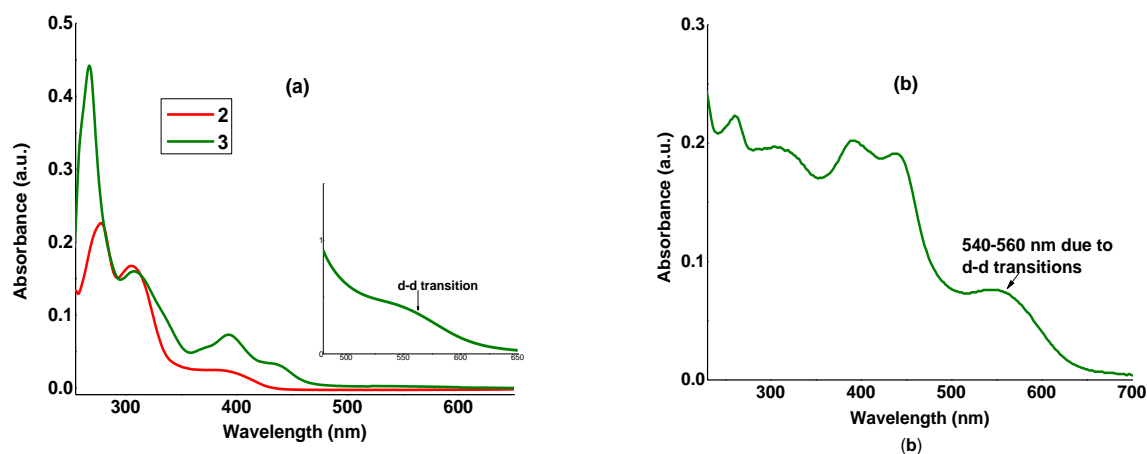


Fig. S2 UV-visible spectra (a) 2 and 3 in solvent (b) 3 in solid state

3. ¹H and ¹³C NMR analysis of 2 and 3

Compound 2 Bright yellow solid; Yield: 92%; mp 130-135 °C;

¹H NMR (400 MHz, DMSO) δ 13.79 (s, 2H), 9.22 (s, 2H), 8.45 (s, 2H), 7.83 (s, 2H), 7.74 (s, 2H), 7.27 (d, $J = 8.6$ Hz, 2H), 6.35 (d, $J = 2.3$ Hz, 2H), 6.33 (d, $J = 2.3$ Hz, 2H), 6.29 (d, $J = 2.2$ Hz, 2H), 4.35 (t, $J = 6.8$ Hz, 4H), 4.03 (t, $J = 5.9$ Hz, 4H), 3.85 (s, 6H), 3.83 (s, 4H), 2.33 – 2.20 (m, 4H). ¹³C NMR (100 MHz, DMSO-d₆) δ 166.1, 163.2, 161.8, 137.2, 134.3, 124.0, 122.9, 115.3, 105.5, 102.4, 64.9, 58.3, 46.9, 36.3, 29.4.

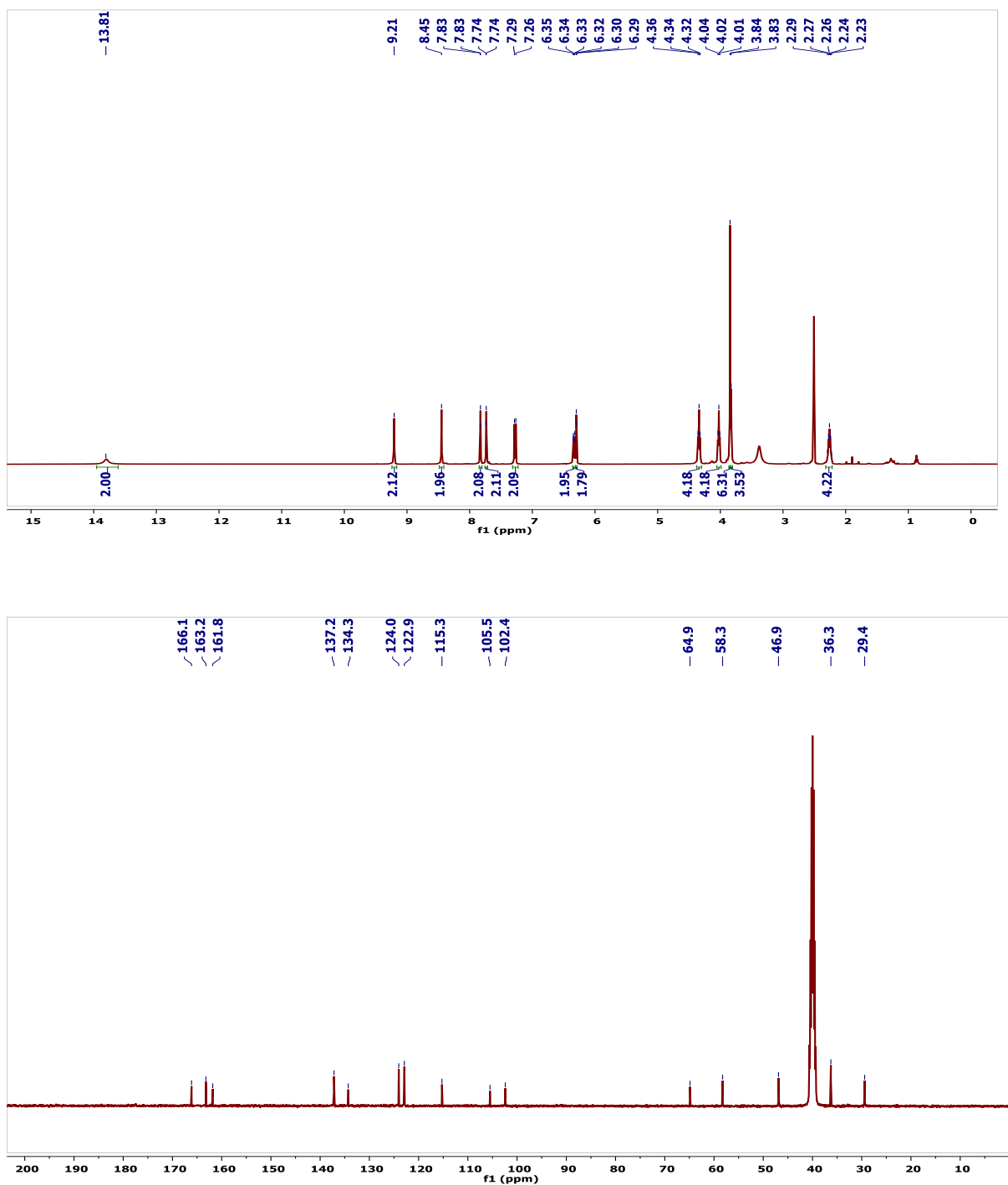


Fig. S3 ¹H and ¹³C NMR Spectra of **2**

Compound 3 Brown solid; Yield: 95%; mp 210-215 °C;

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.19 (s, 2H), 7.81 (s, 2H), 7.73 (d, *J* = 7.9 Hz, 4H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.16 (s, 2H), 6.10 (d, *J* = 8.6 Hz, 2H), 4.34 (t, *J* = 6.9 Hz, 4H), 3.97 (t, *J* = 6.0 Hz, 4H), 3.85 (s, 6H), 3.33 (s, 4H), 2.41 – 2.16 (m, 4H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.3, 165.8, 162.6, 137.2, 133.7, 124.0, 122.9, 112.6, 106.5, 102.0, 65.1, 57.6, 46.8, 36.2, 29.4.

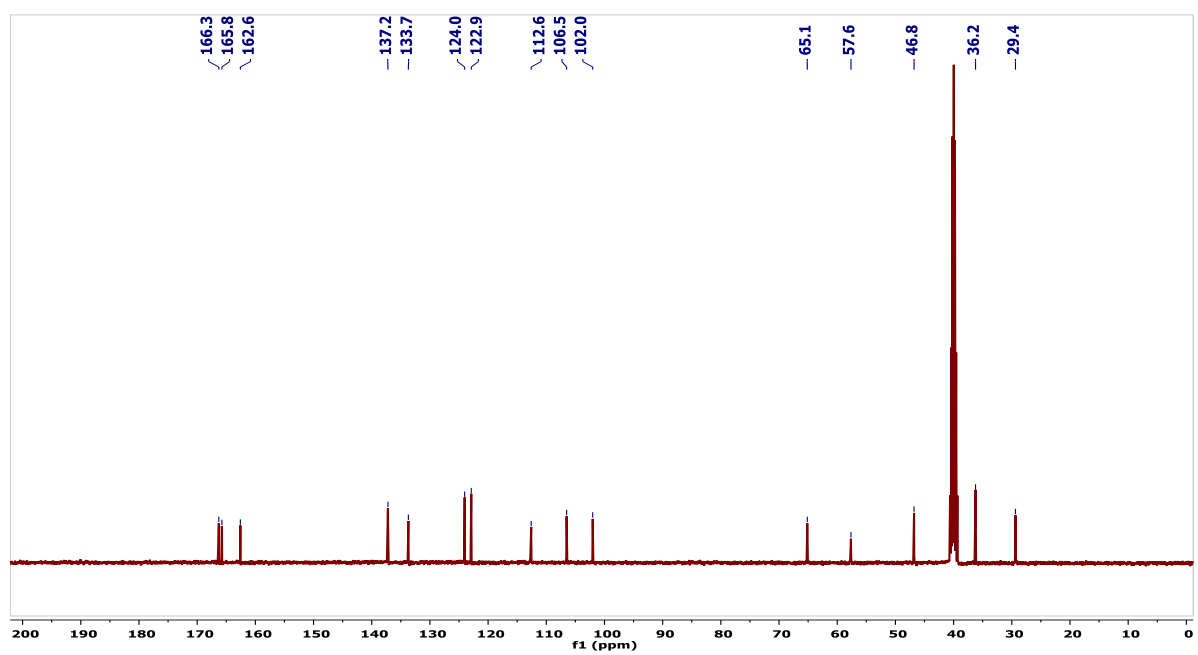
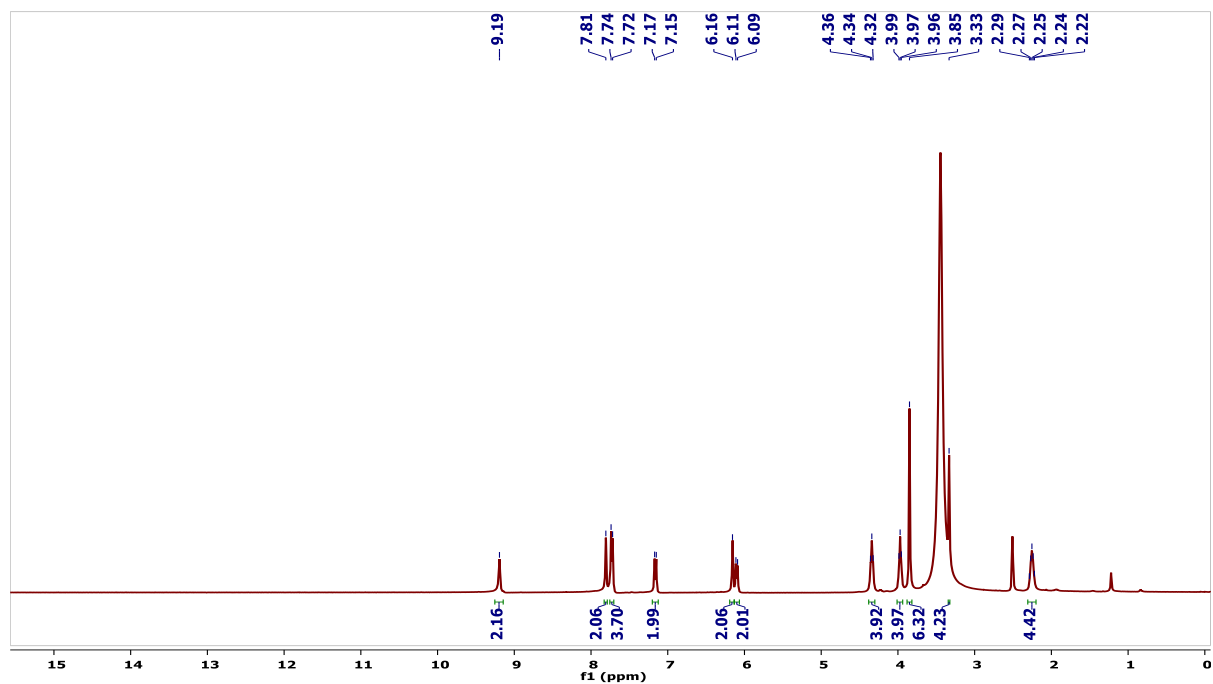


Fig. S4 ^1H and ^{13}C NMR Spectra of **3**

4. HRMS of 2 and 3

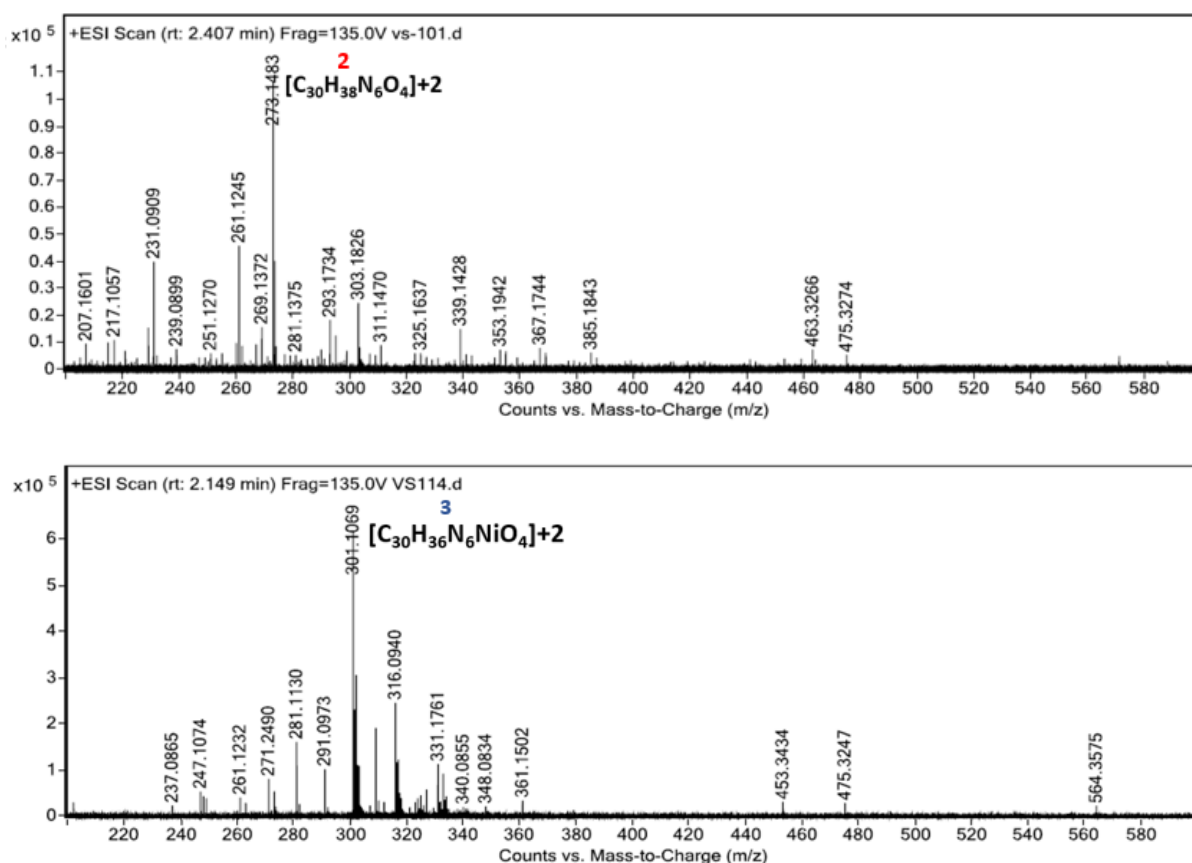
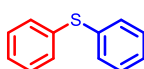


Fig. S5 HRMS of 2 and 3

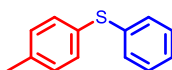
5. 1H NMR and ^{13}C NMR Spectral data

1. Diphenylsulfane (6a)¹



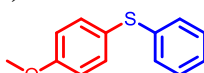
Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 131.1, 129.2, 127.0.

2. Phenyl(*p*-tolyl)sulfane (6b and 6b')²



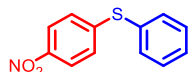
Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, $J = 1.9$ Hz, 1H), 7.32 (d, $J = 1.8$ Hz, 2H), 7.30 (s, 2H), 7.24 – 7.21 (m, 1H), 7.19 – 7.15 (m, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.1, 132.3, 131.3, 130.1, 129.8, 129.0, 126.4, 21.2.

3. (4-Methoxyphenyl)(phenyl)sulfane (6c)¹



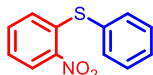
Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J = 8.8$ Hz, 2H), 7.27 – 7.15 (m, 5H), 6.93 (d, $J = 8.8$ Hz, 2H), (3.85 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 138.6, 135.4, 128.9, 128.2, 125.8, 124.3, 115.0, 55.4.

4. (4-Nitrophenyl)(phenyl)sulfane (6d and 6d')¹



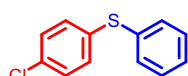
Yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 9.1 Hz, 2H), 7.58-7.58 (m, 2.6 Hz, 2H), 7.50-7.47 (m, 2H), 7.20 (d, *J* = 9.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 145.5, 134.8, 130.5, 130.1, 129.7, 126.7, 124.1.

5. 2-Nitrophenyl phenyl sulfane (6e)³



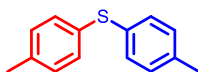
Yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.53 – 7.50 (m, 3H), 7.36 (d, *J* = 2.5 Hz, 1H), 7.28 – 7.19 (m, 1H), 6.88 (dd, *J* = 8.2, 1.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.0, 139.5, 135.9, 133.4, 131.0, 130.1, 130.0, 128.3, 125.8, 124.9.

6. (4-Chlorophenyl)(phenyl)sulfane (6f)²



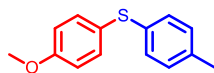
White solid; ¹H NMR (400 MHz, CDCl₃) 7.38–7.25 (m, 9H); ¹³C NMR (100 MHz, CDCl₃); δ 135.1, 134.7, 133.0, 132.0, 131.3, 129.3, 127.4.

7. Di-(*p*-tolyl)sulfane (6g)¹



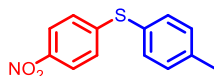
White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 7.9 Hz, 4H), 7.12 (d, *J* = 7.9 Hz, 4H), 2.35 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 132.7, 131.1, 129.9, 21.1.

8. (4-Methoxyphenyl)(*p*-tolyl)sulfane (6h)¹



Colorless oil; ¹H NMR (400 MHz, DMSO) δ 7.35 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.07 (m, 4H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.26 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 159.8, 136.4, 134.7, 134.1, 130.4, 129.4, 124.8, 115.7, 55.7, 21.0.

9. (4-Nitrophenyl)(*p*-tolyl)sulfane (6i and 6i')¹



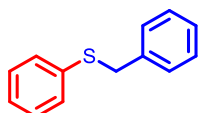
Light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 9.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.4, 145.1, 140.3, 135.1, 130.9, 126.5, 126.1, 124.0, 21.4.

10. (4-Chlorophenyl)(*p*-tolyl)sulfane (6j)⁴



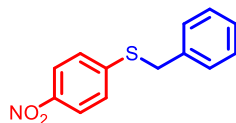
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.29 (m, 4H), 7.21 – 7.16 (m, 4H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.1, 136.0, 132.5, 132.3, 130.8, 130.2, 129.5, 129.1, 21.2.

11. Benzyl(phenyl)sulfane (6k)¹



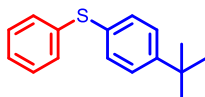
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.19 (m, 10H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 136.4, 129.8, 128.9, 128.5, 127.2, 126.4, 39.1.

12. Benzyl(4-nitrophenyl)sulfane (6l)⁴



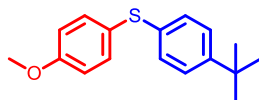
Yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 9.0 Hz, 2H), 7.44 – 7.30 (m, 7H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.2, 145.2, 135.4, 128.9, 128.7, 127.8, 126.6, 123.9, 37.0.

13. (4-(tert-butyl)phenyl)(phenyl)sulfane (6m)²



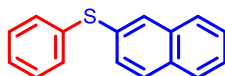
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.25 (m, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 136.7, 131.5, 131.1, 130.3, 129.1, 126.6, 126.3, 34.6, 31.3.

14. (4-(tert-Butyl)phenyl)(4-methoxyphenyl)sulfane (6n)¹



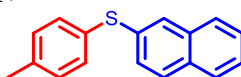
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 149.2, 134.8, 134.7, 128.6, 126.0, 125.1, 114.9, 55.4, 34.4, 31.3.

15. Naphthalen-2-yl(phenyl)sulfane (6o)²



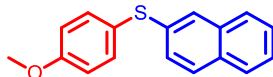
White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 1.4 Hz, 1H), 7.85 – 7.74 (m, 3H), 7.53 – 7.29 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.8, 133.8, 133.0, 132.3, 131.0, 129.9, 129.2, 128.9, 128.8, 127.7, 127.4, 127.1, 126.6, 126.2.

16. Naphthalen-2-yl(p-tolyl)sulfane (6p)⁴



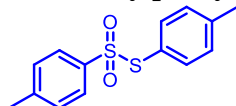
White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.67 (m, 3H), 7.62 (s, 1H), 7.50 – 7.42 (m, 4H), 7.32 (dd, J = 8.6, 1.9 Hz, 1H), 6.94 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 135.9, 135.2, 133.8, 131.7, 128.5, 127.7, 127.1, 126.7, 126.5, 126.5, 125.6, 124.4, 115.0, 55.4.

17. (4-methoxyphenyl)(naphthalen-2-yl)sulfane (6q)²



White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.71 (m, 4H), 7.47 – 7.35 (m, 5H), 7.19 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.6, 134.3, 133.8, 132.1, 130.1, 128.7, 128.4, 127.9, 127.7, 127.3, 126.5, 125.9, 21.2.

18. 4-methylbenzenesulfonylthioic acid S-(4-methylphenyl) ester (8)⁵



White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.3$ Hz, 2H), 7.28 – 7.21 (t, 4H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 142.1, 140.4, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5.

6. Mass spectra of *in situ* generated species for C-S cross coupling reaction

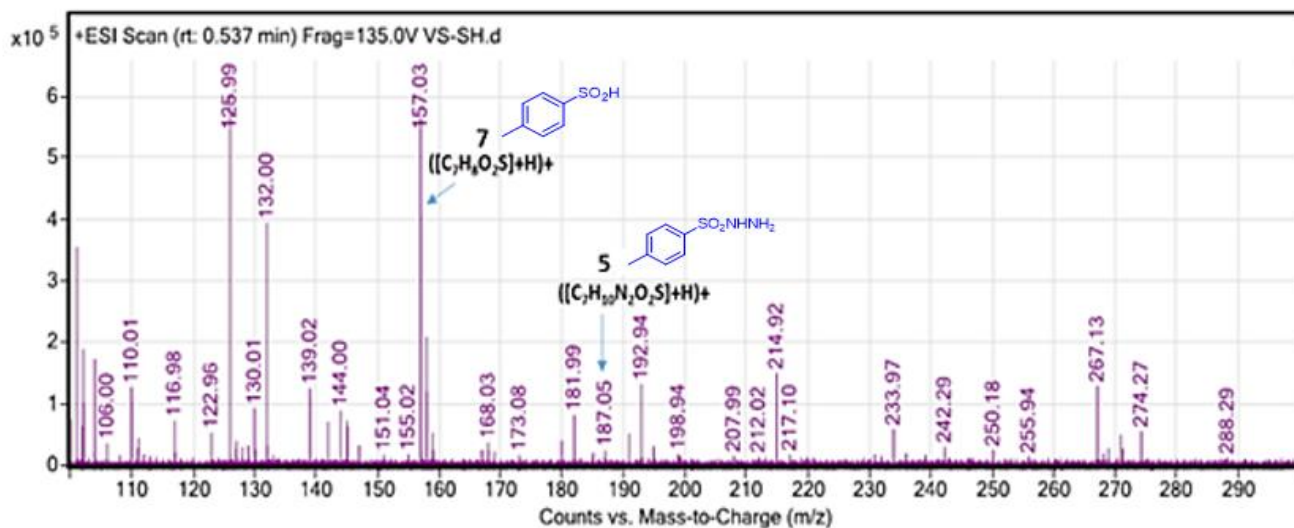


Fig. S6 Mass spectra of reaction mixture (step 1)

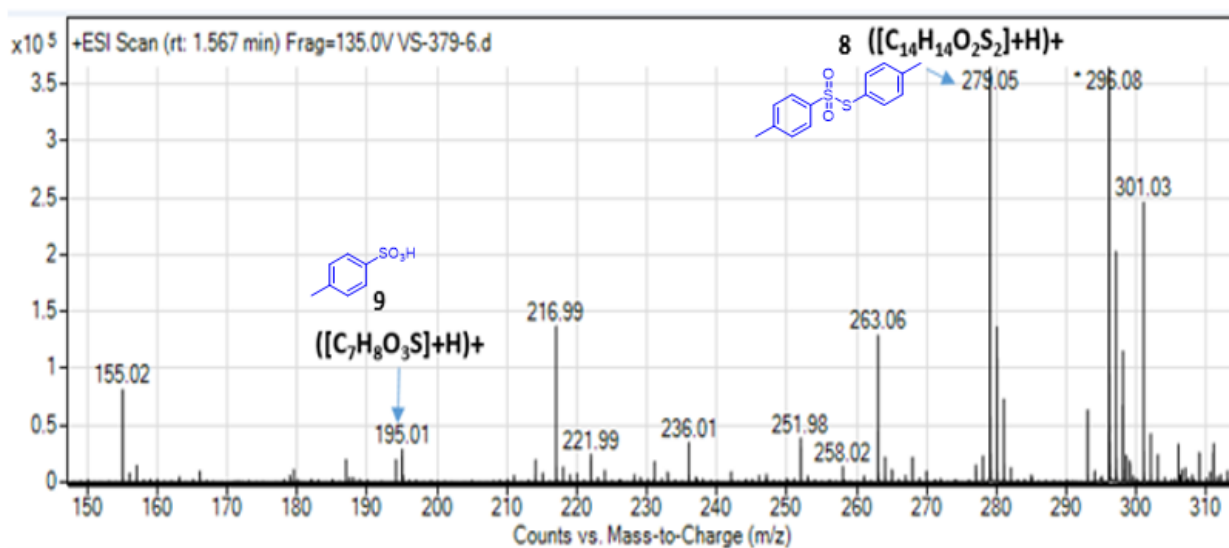


Fig. S7 Mass spectra of reaction mixture (step 2)

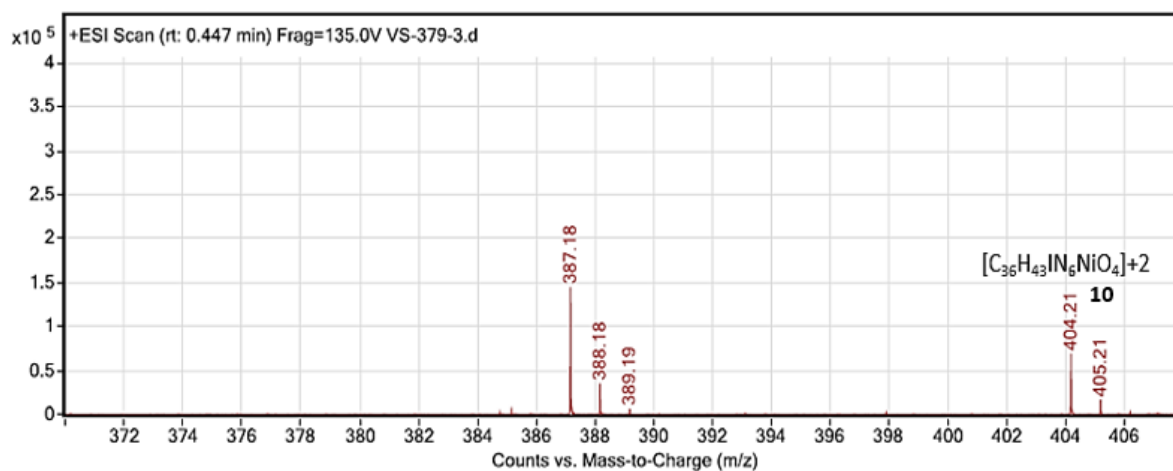


Fig. S8 Mass spectra of species 10

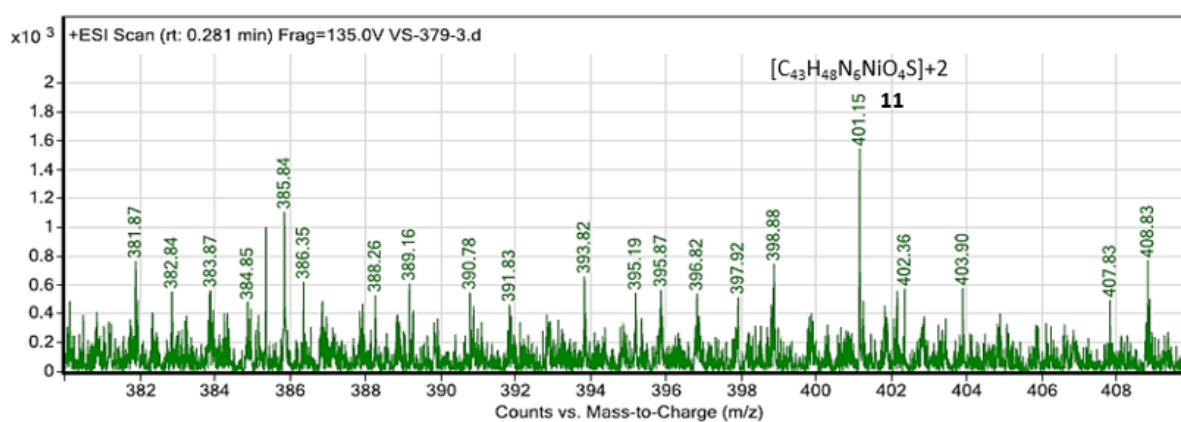


Fig. S9 Mass spectra of species 11

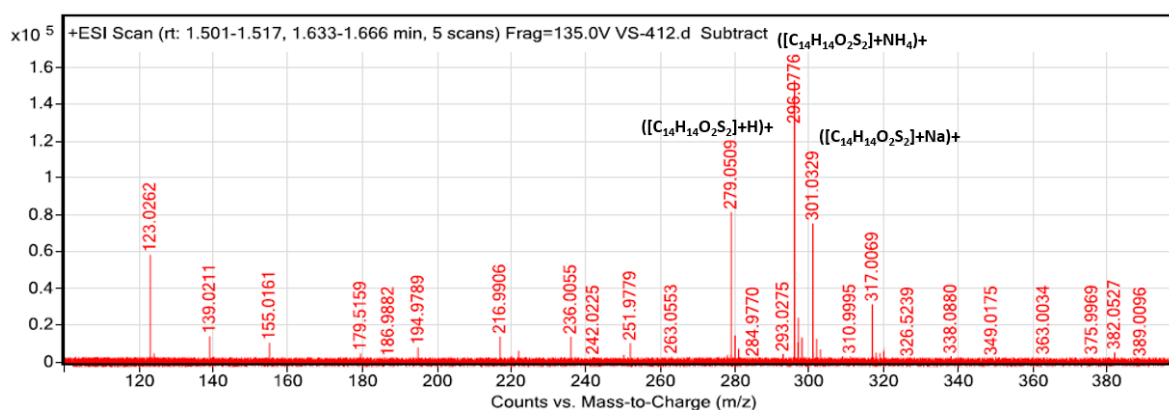


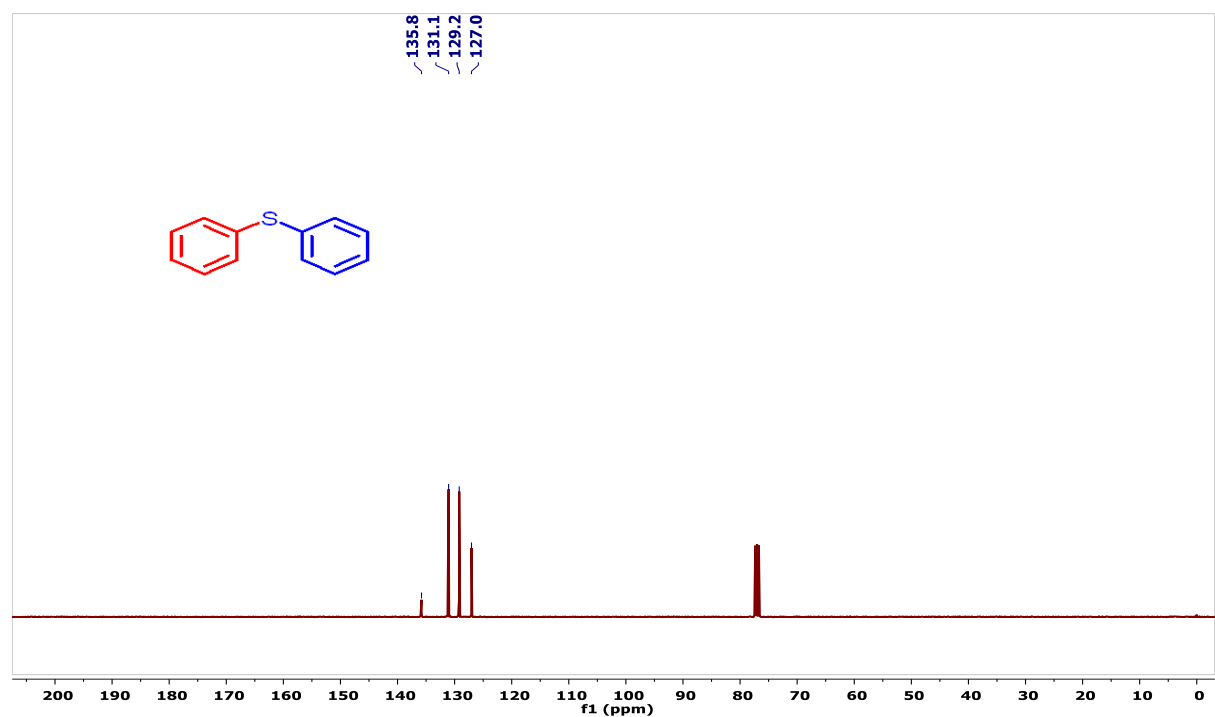
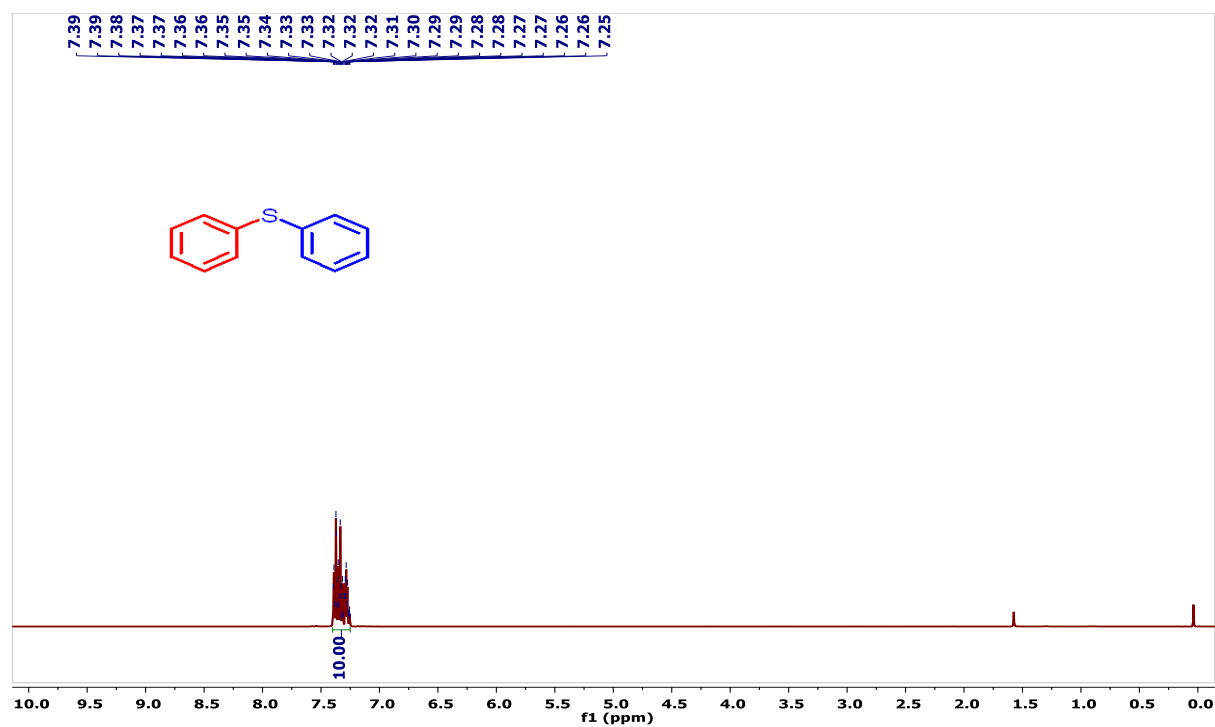
Fig. S10 HRMS of 8

7. References

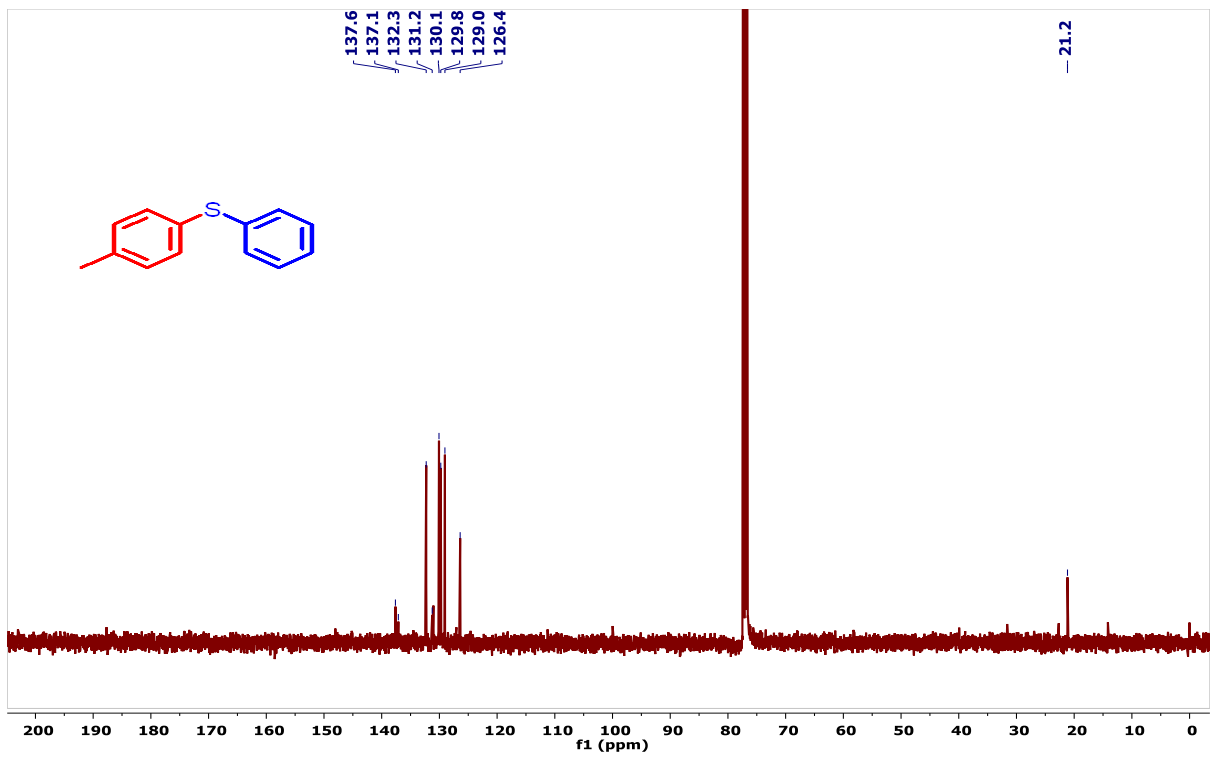
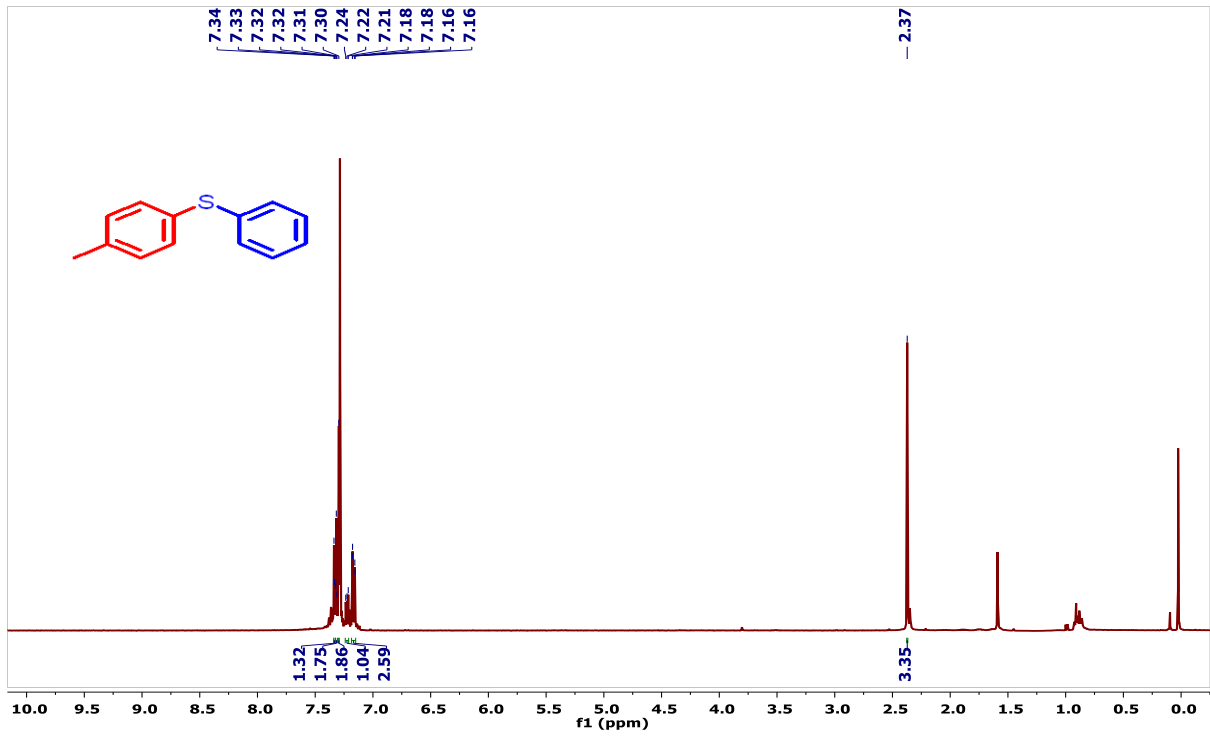
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2. T.-T. Wang, F.-L. Yang and S.-K. Tian, *Adv. Synth. Catal.*, 2015, **357**, 928-932.
3. V. P. Reddy, K. Swapna, A. V. Kumar and K. R. Rao, *J. Org. Chem.*, 2009, **74**, 3189-3191.
4. W.-Y. Wu, J.-C. Wang and F.-Y. Tsai, *Green chem.*, 2009, **11**, 326-329.
5. Y. Yang, S. Zhang, L. Tang, Y. Hu, Z. Zha and Z. Wang, *Green chem.*, 2016, **18**, 2609-2613.

8. ^1H NMR and ^{13}C NMR spectra of C-S cross coupling products

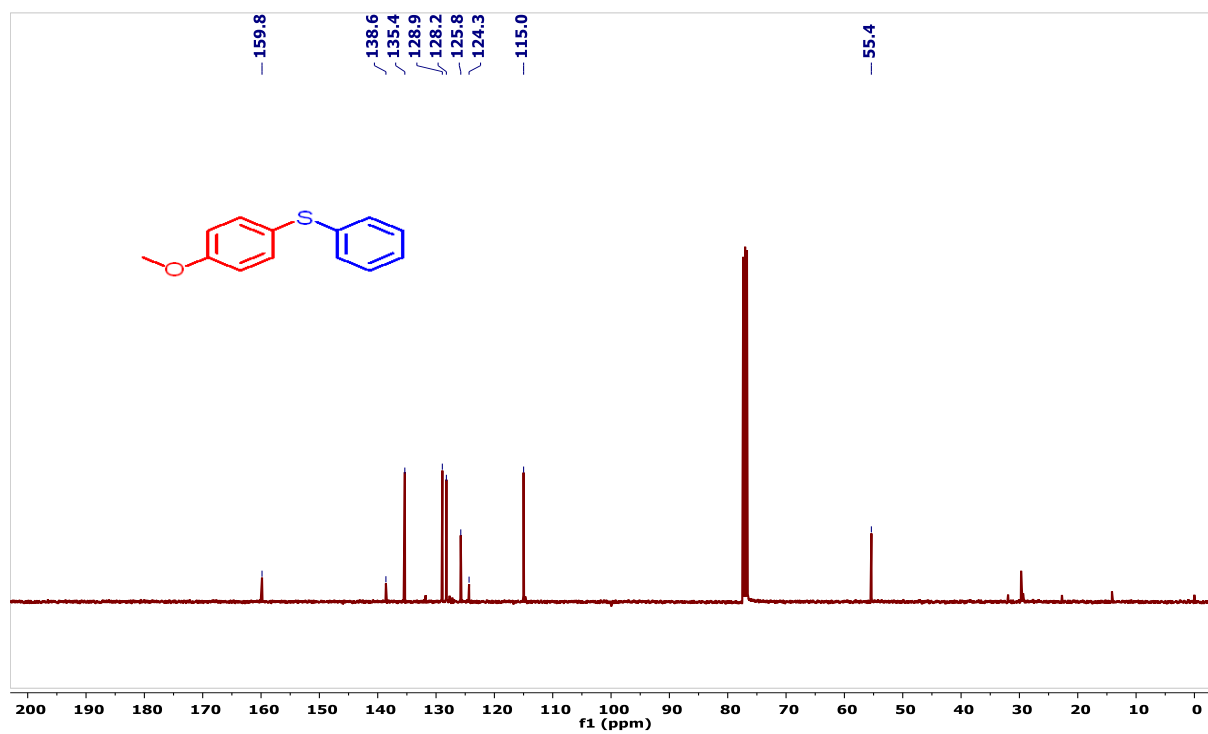
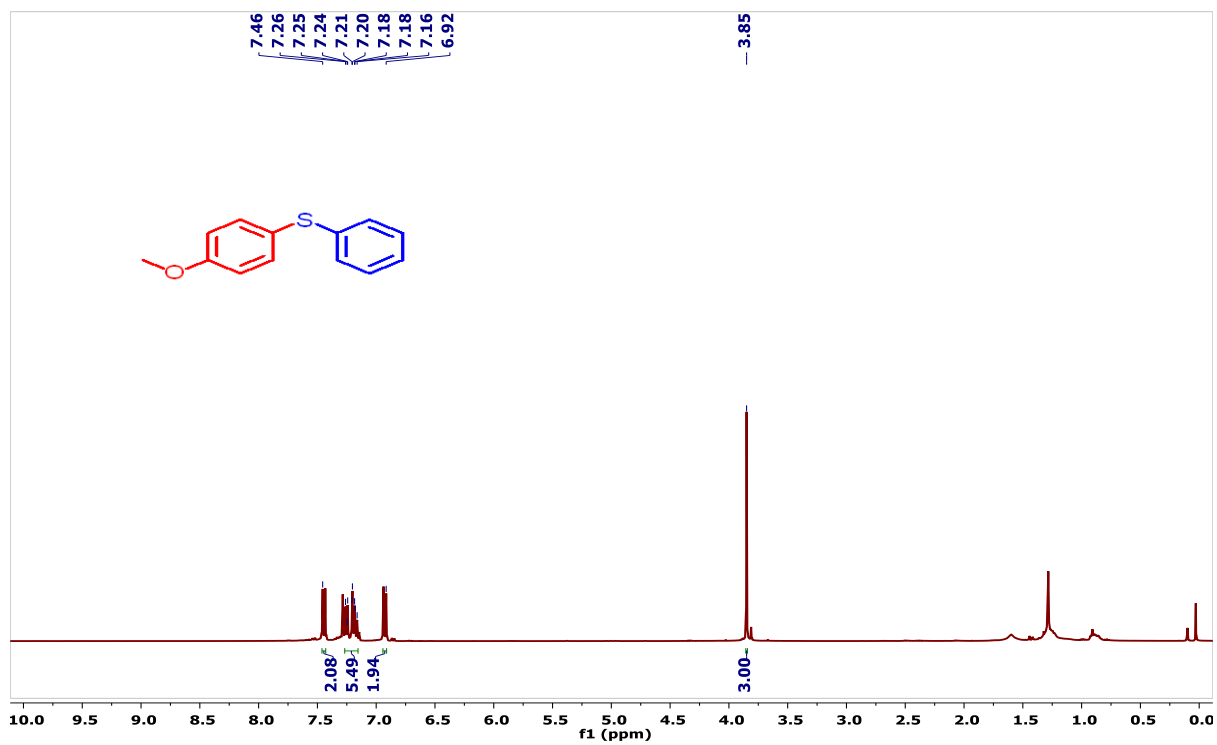
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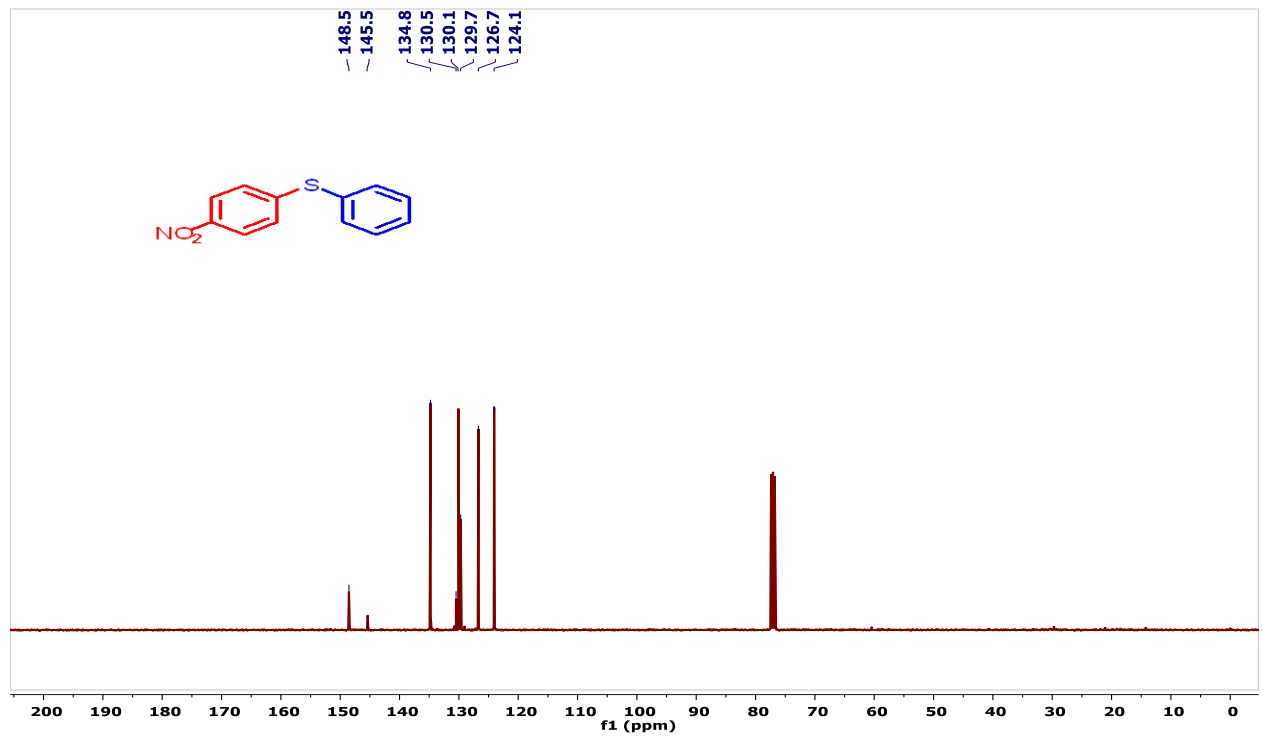
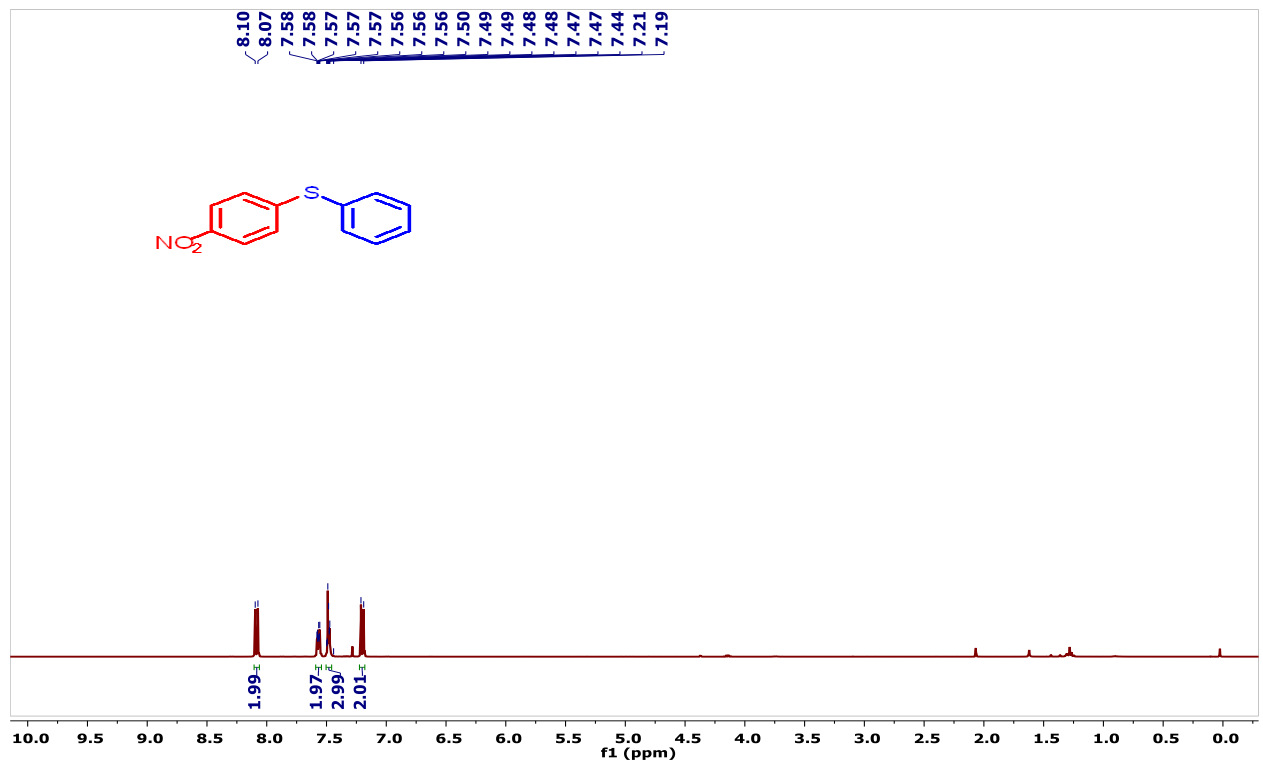
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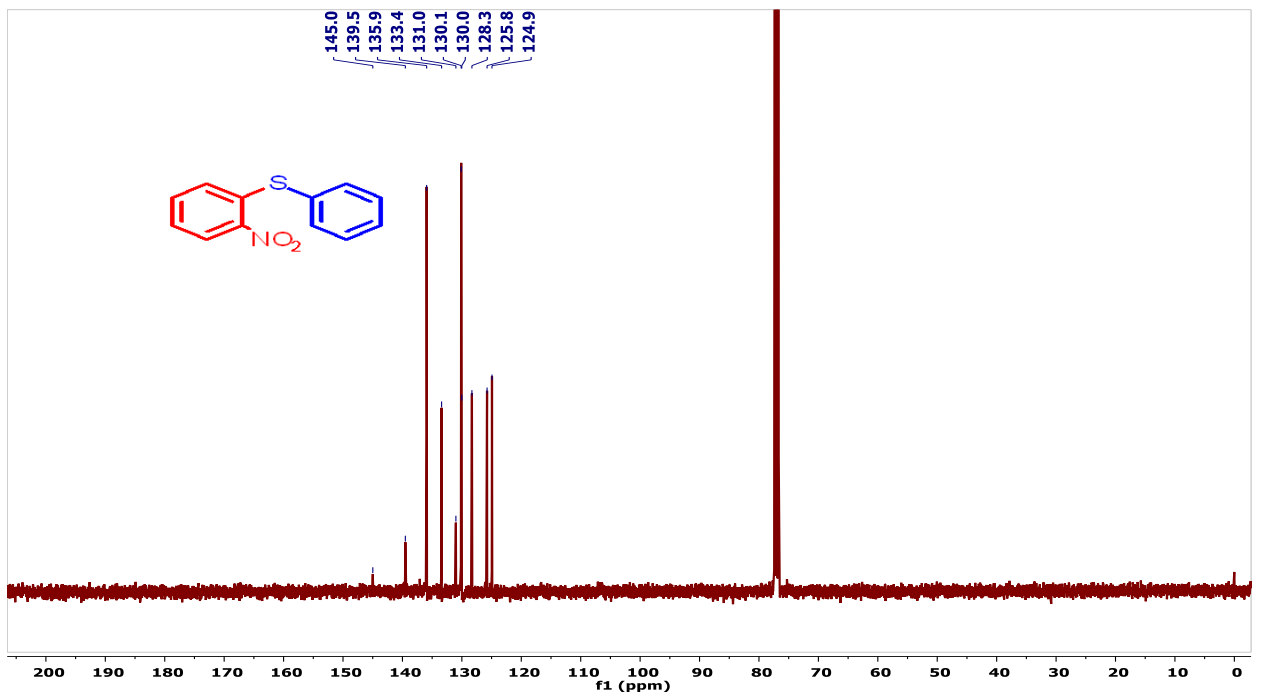
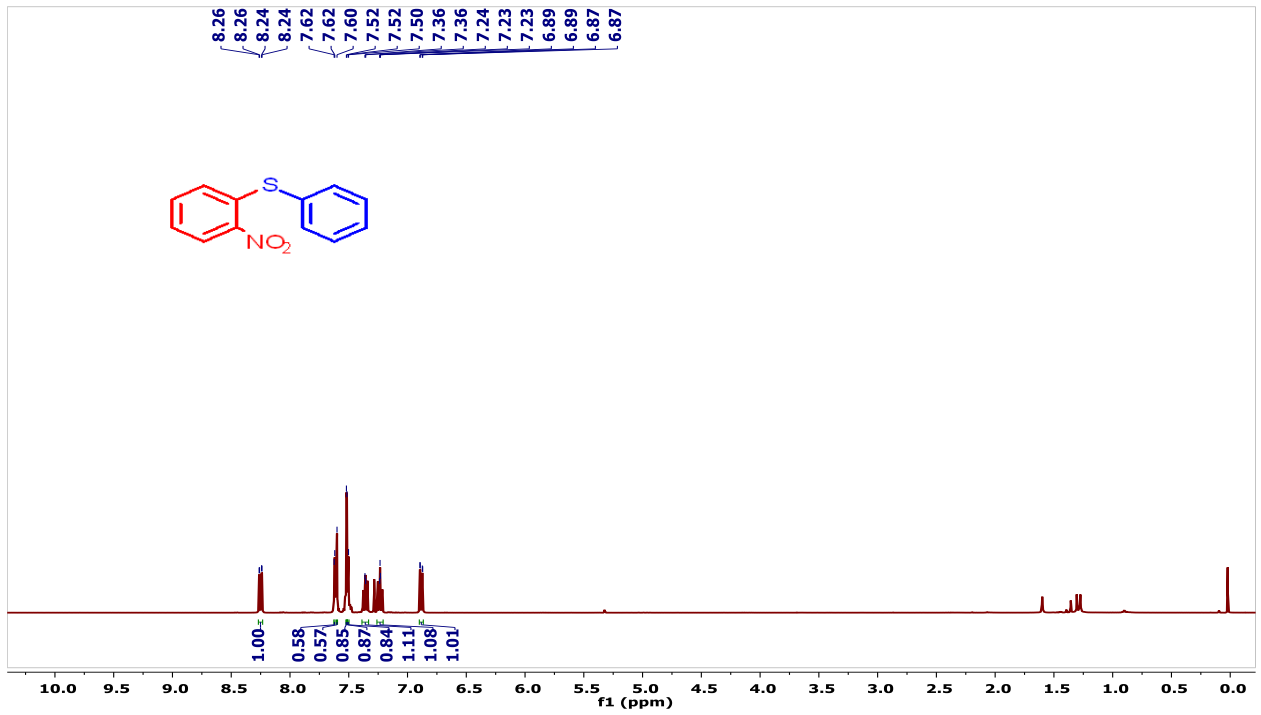
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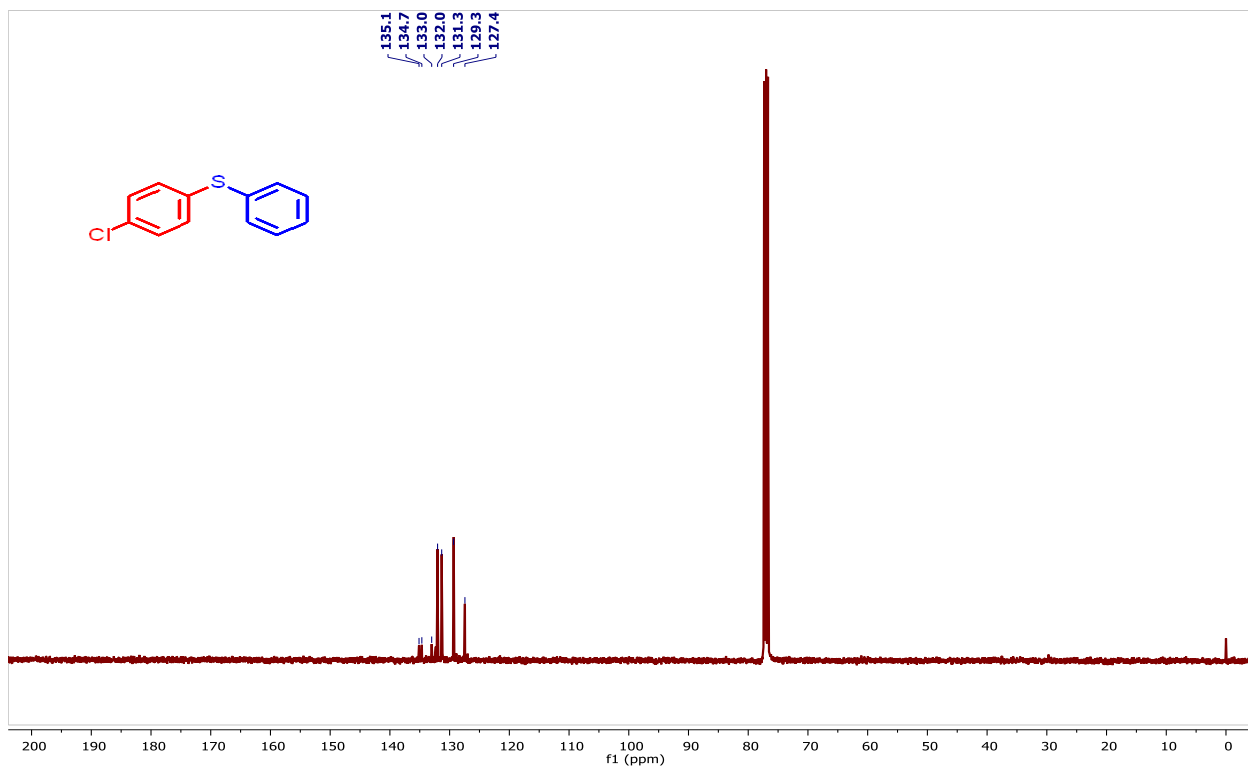
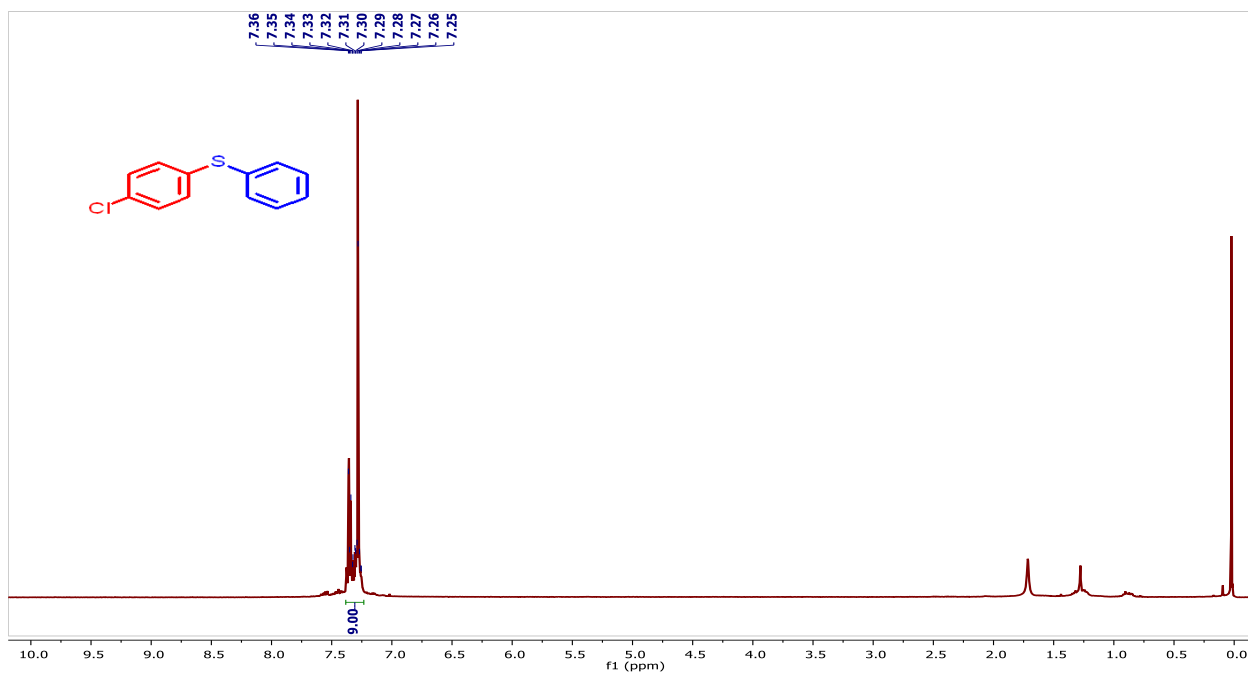
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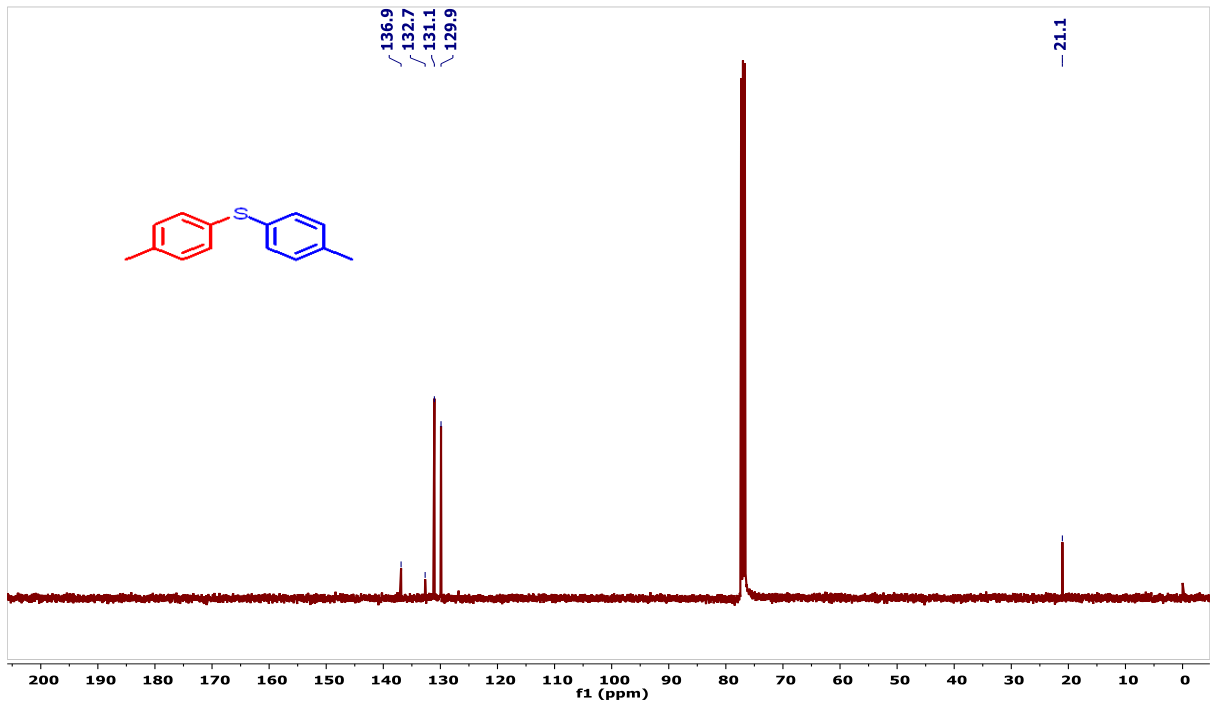
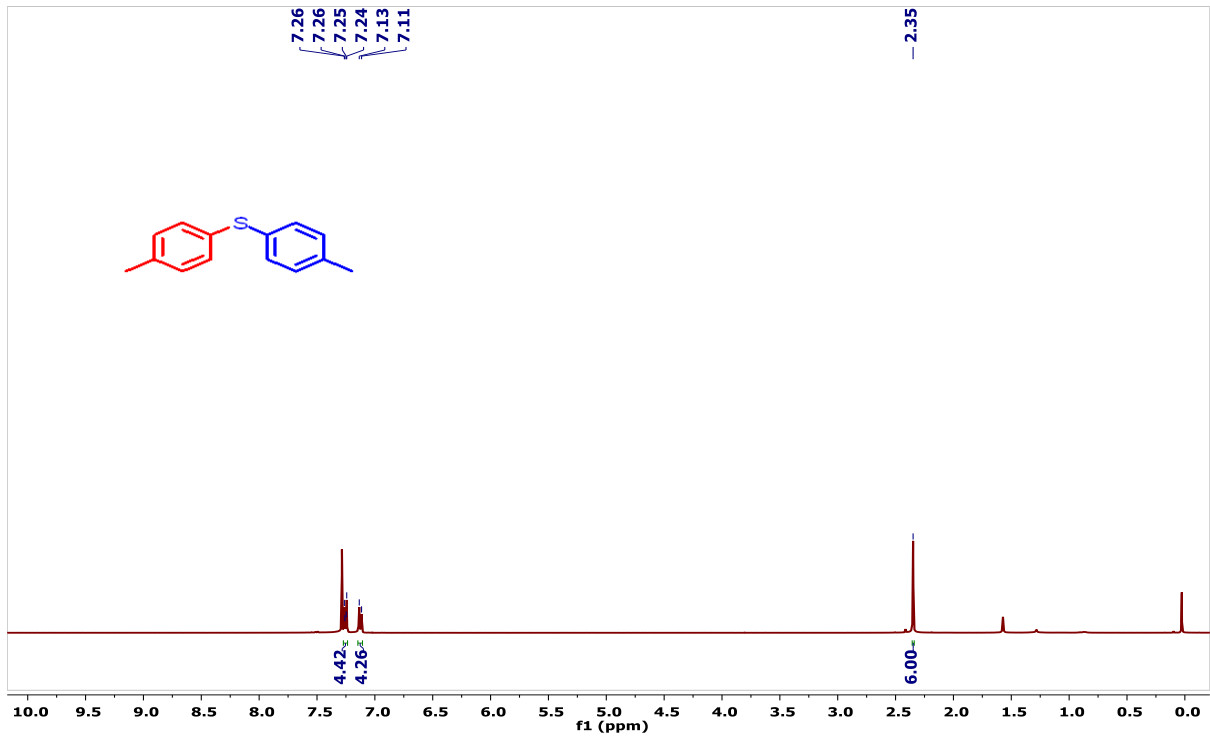
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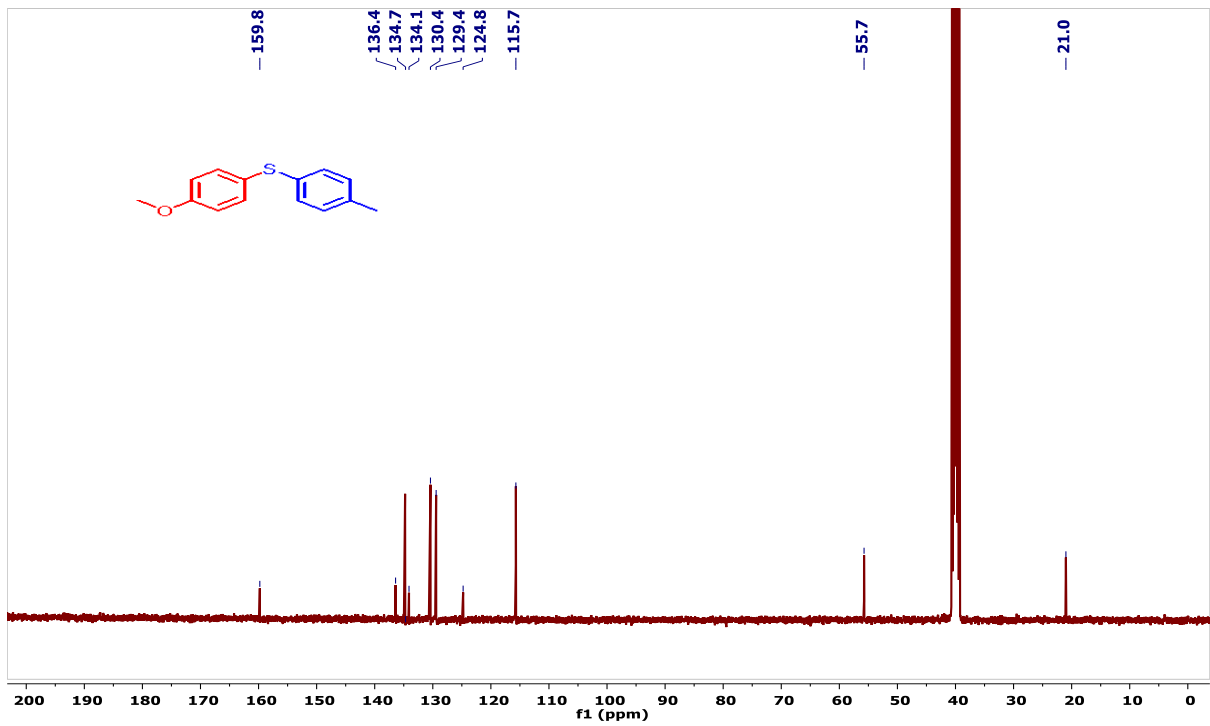
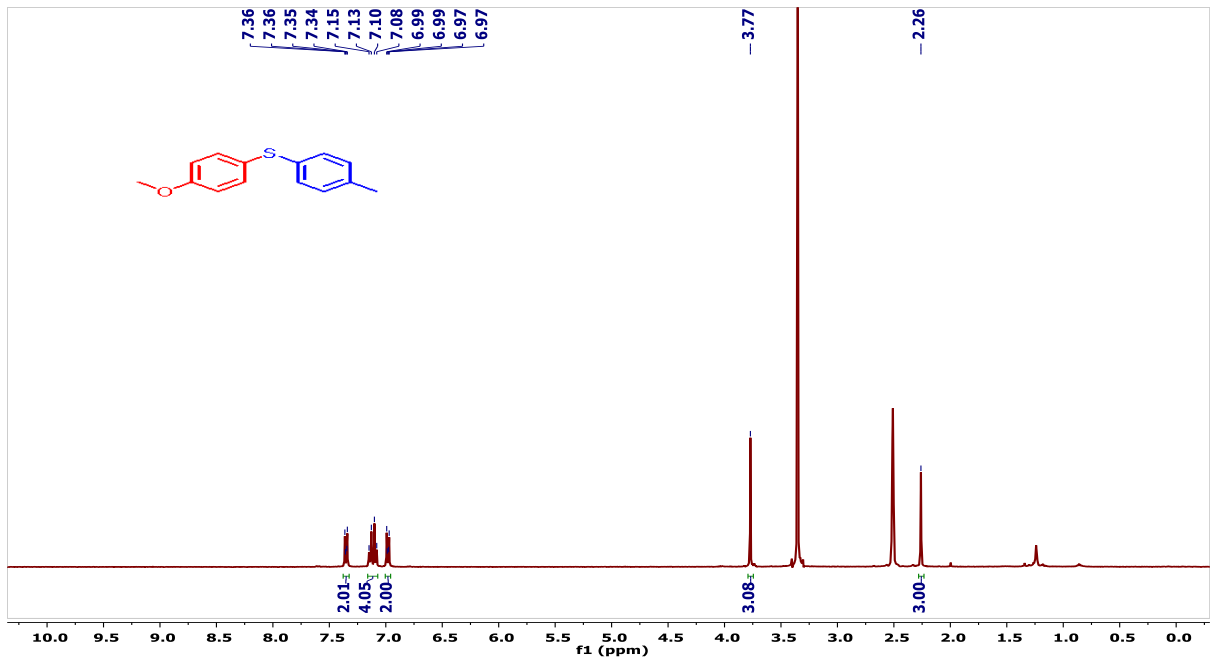
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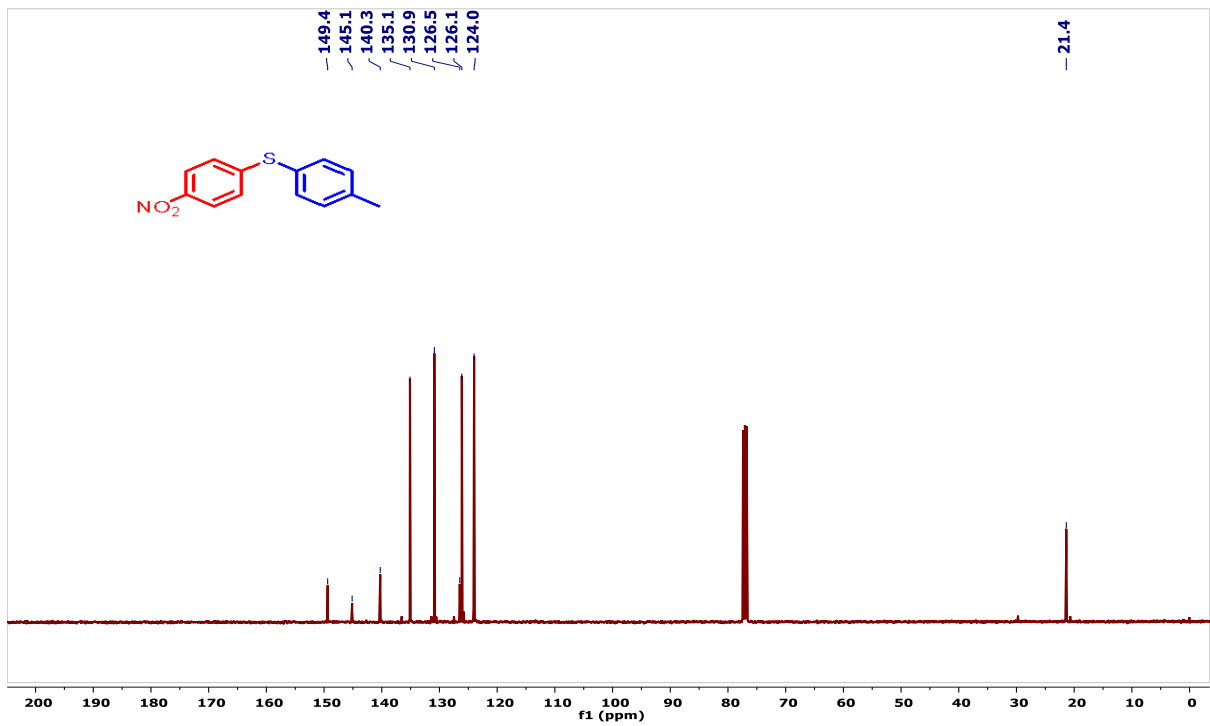
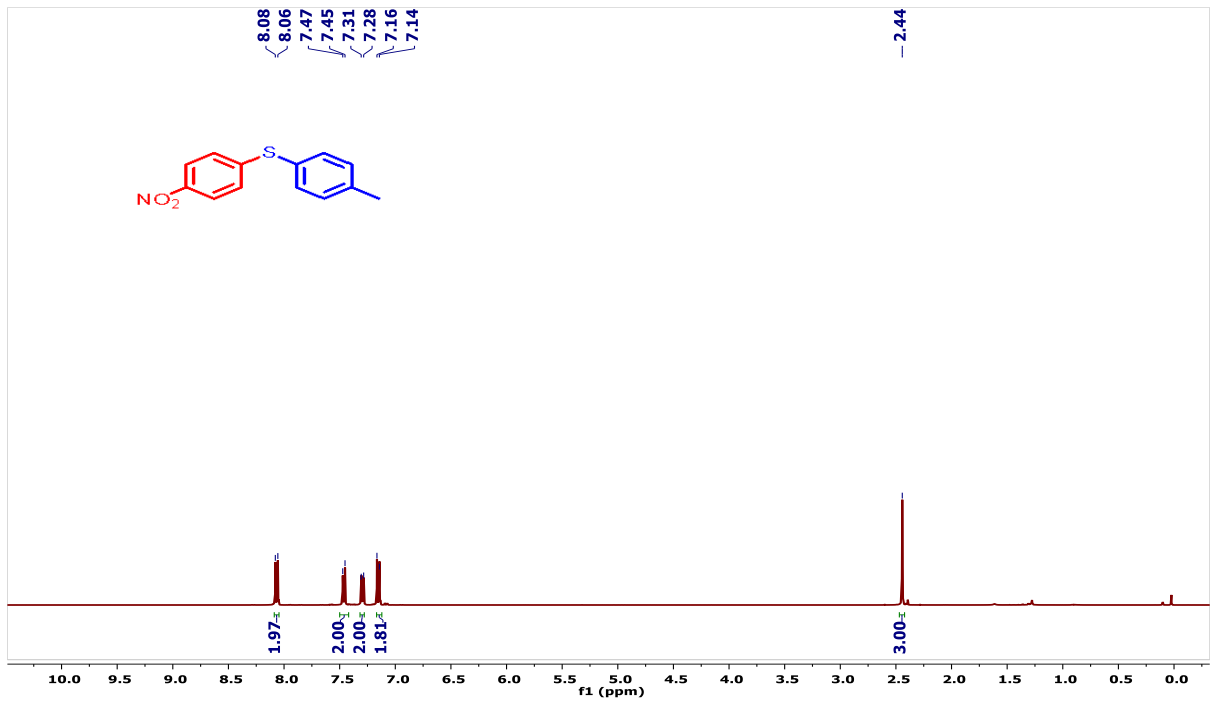
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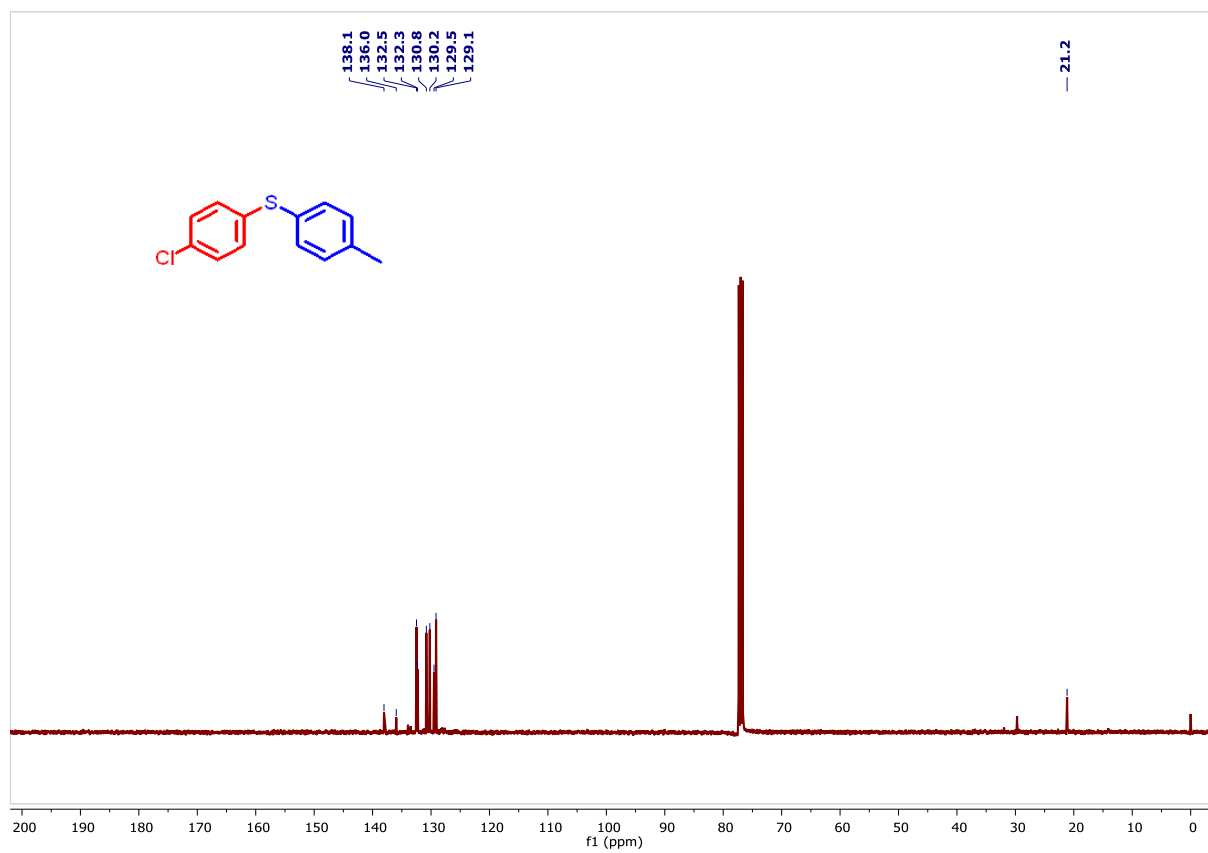
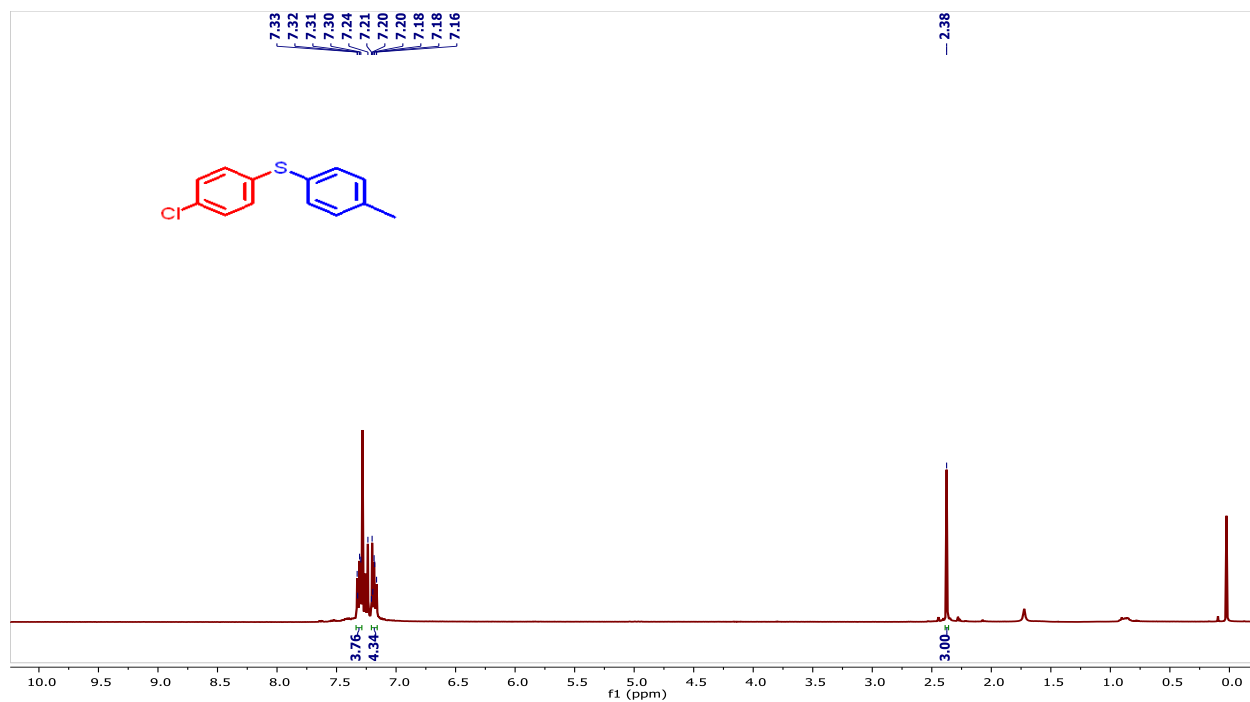
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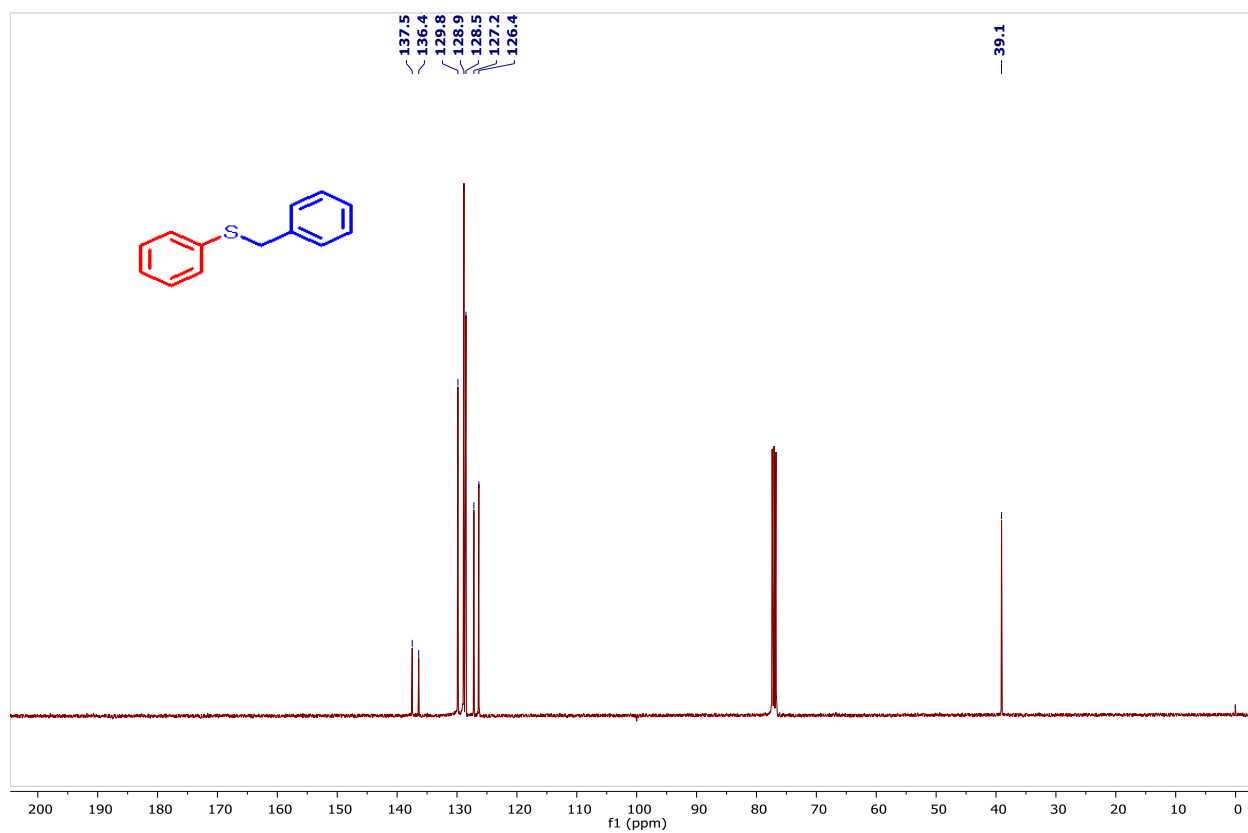
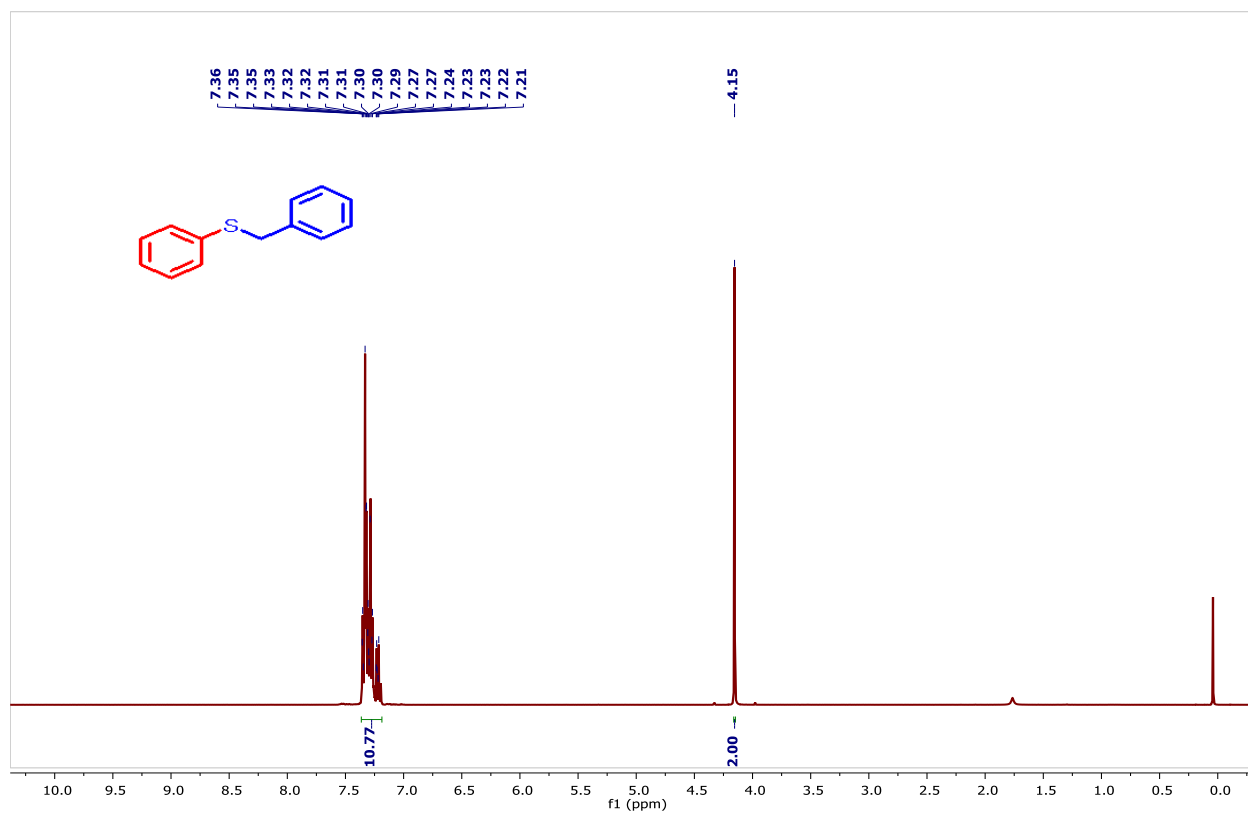
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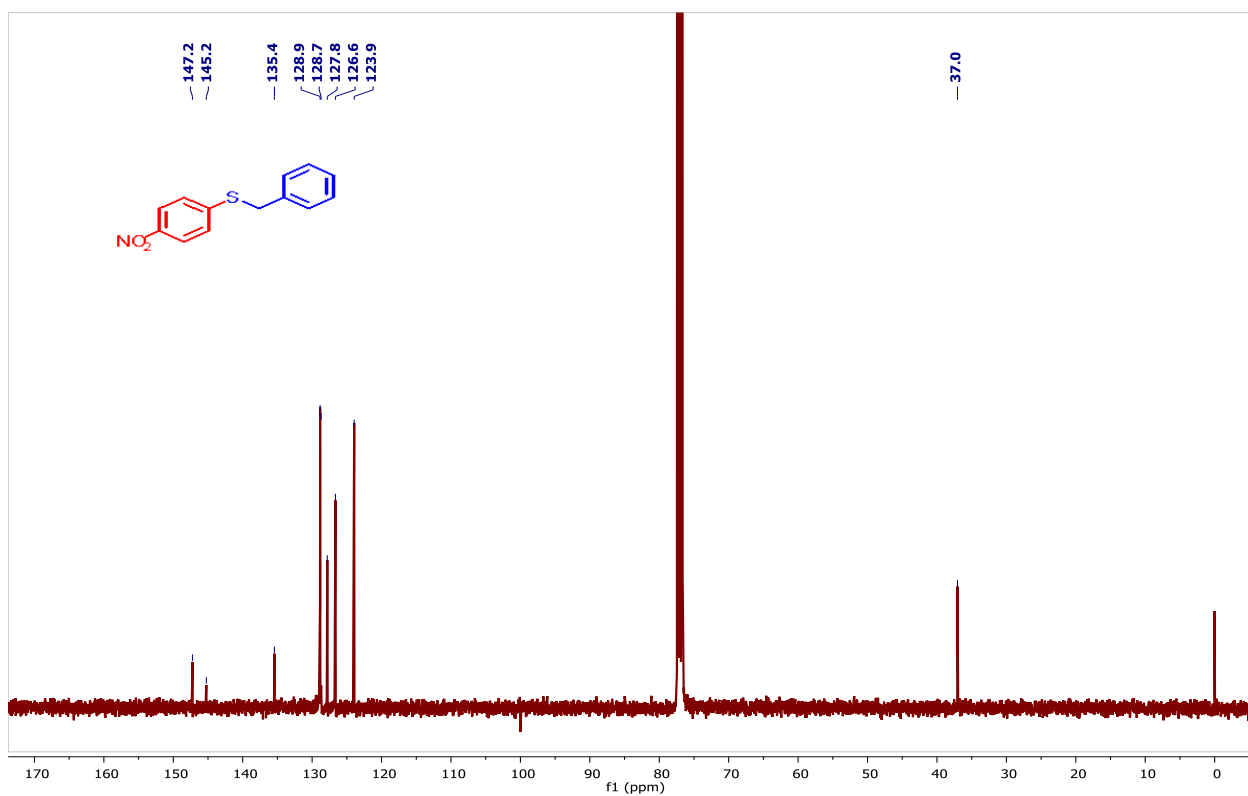
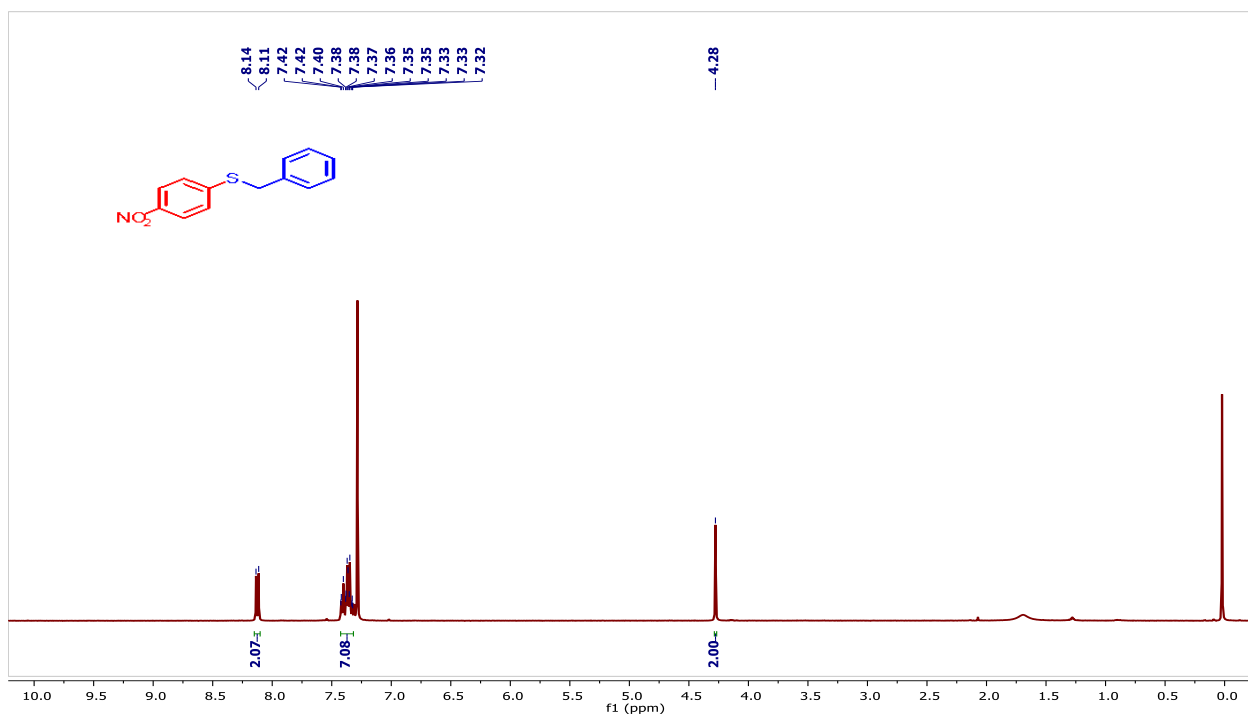
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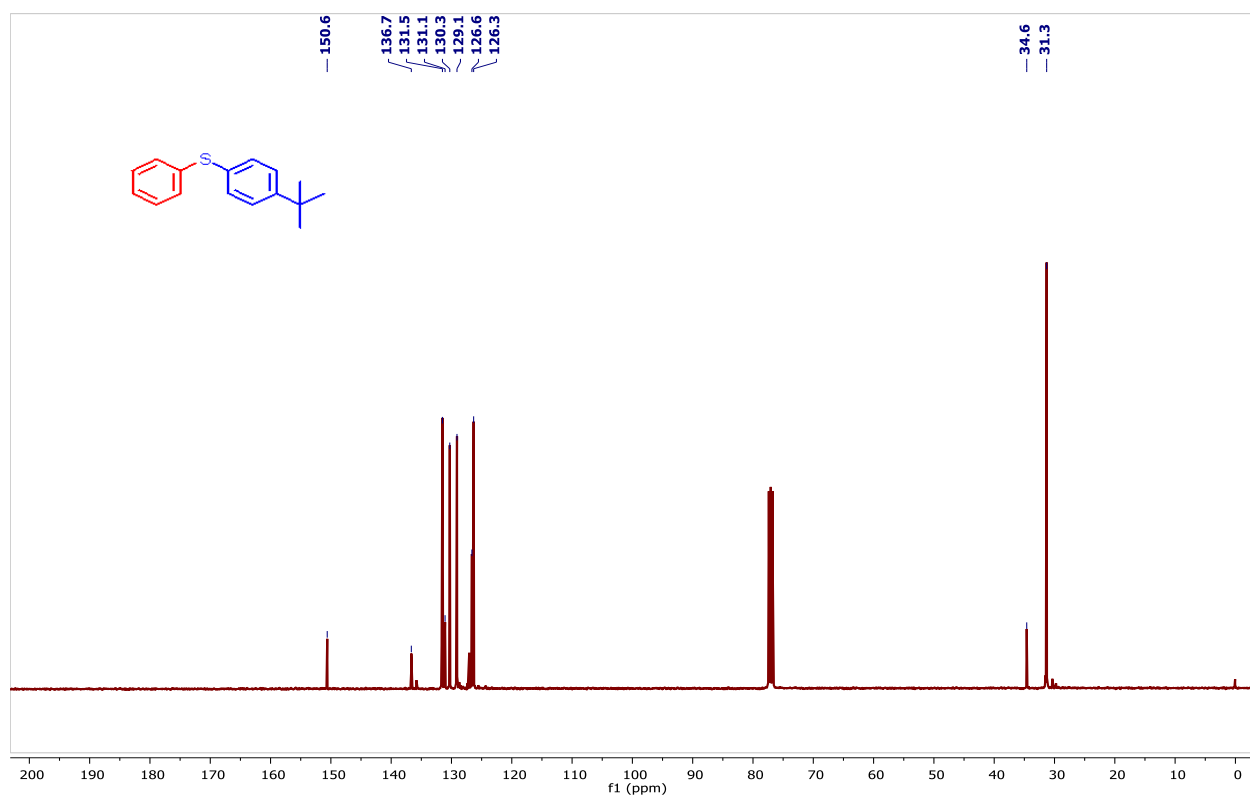
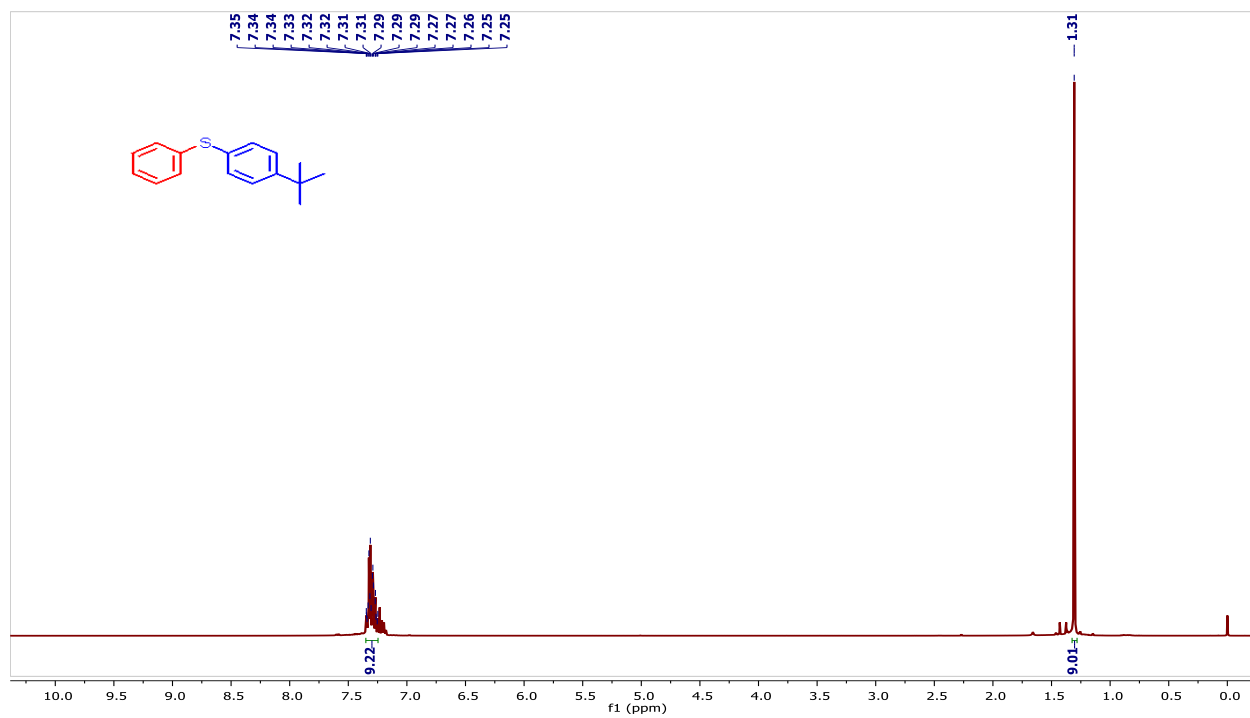
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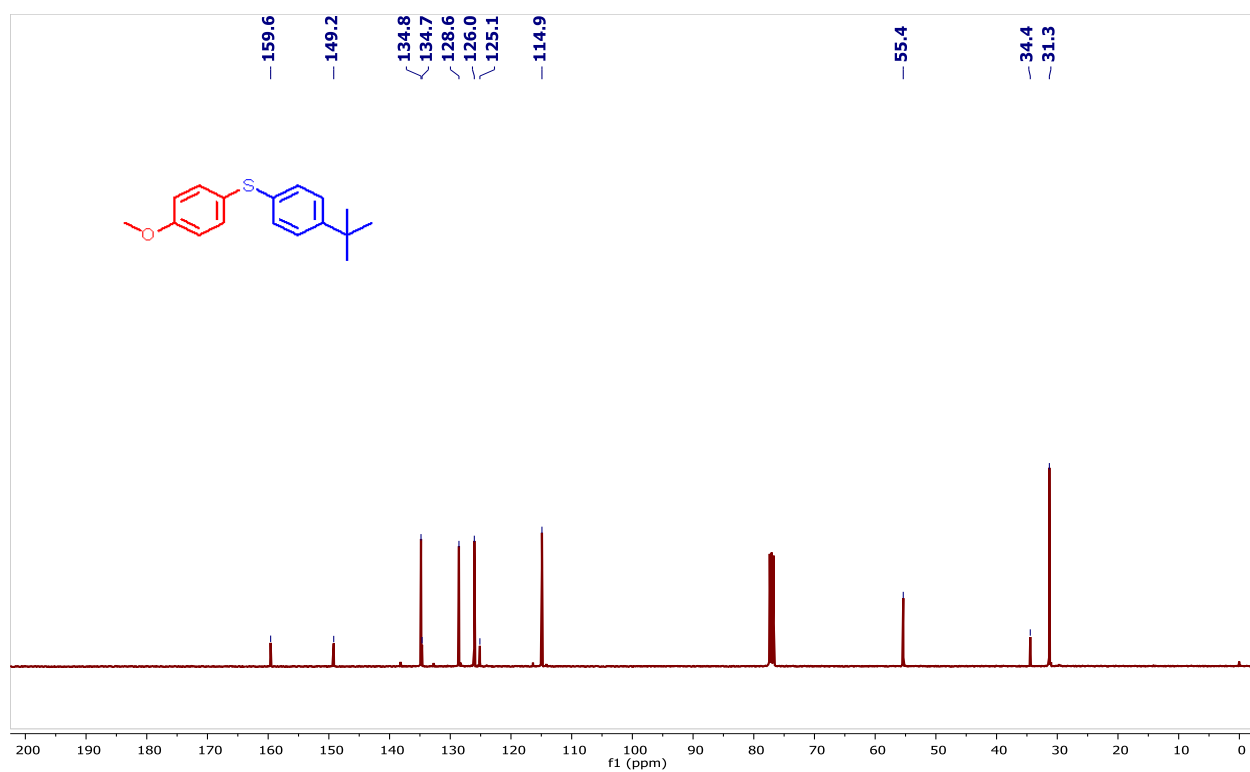
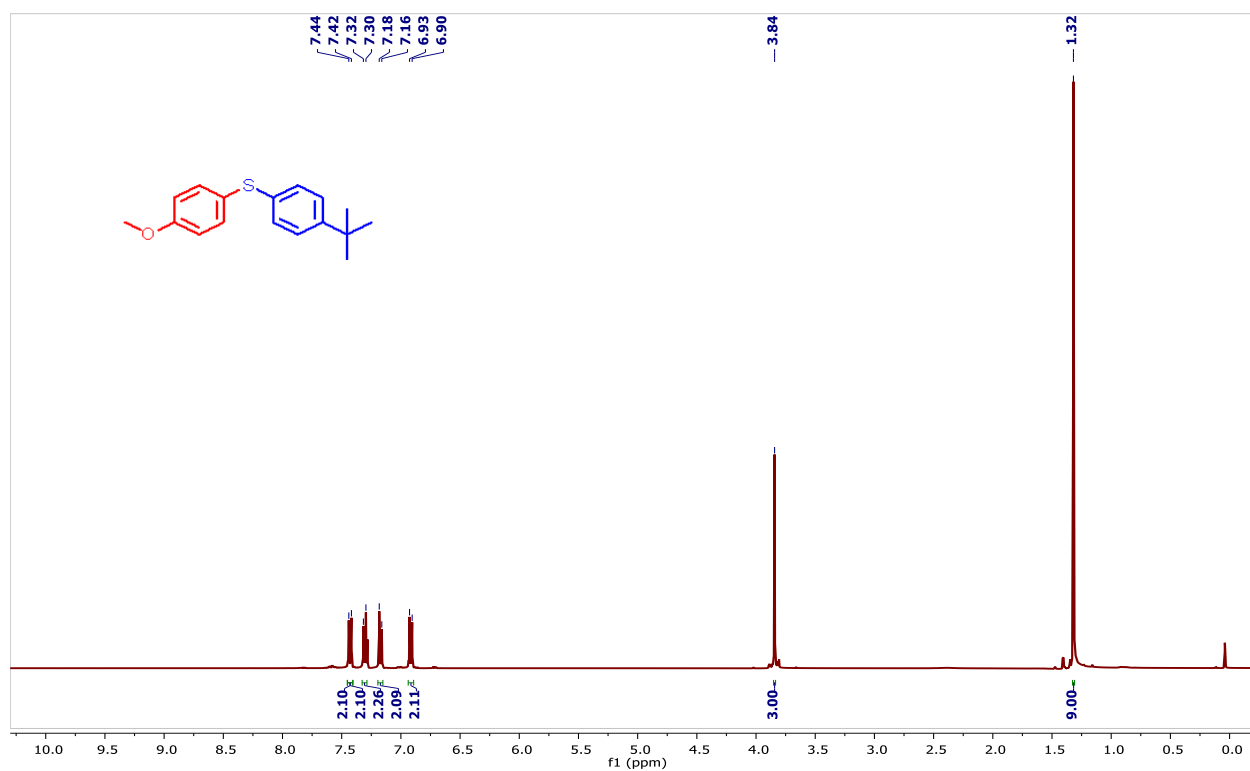
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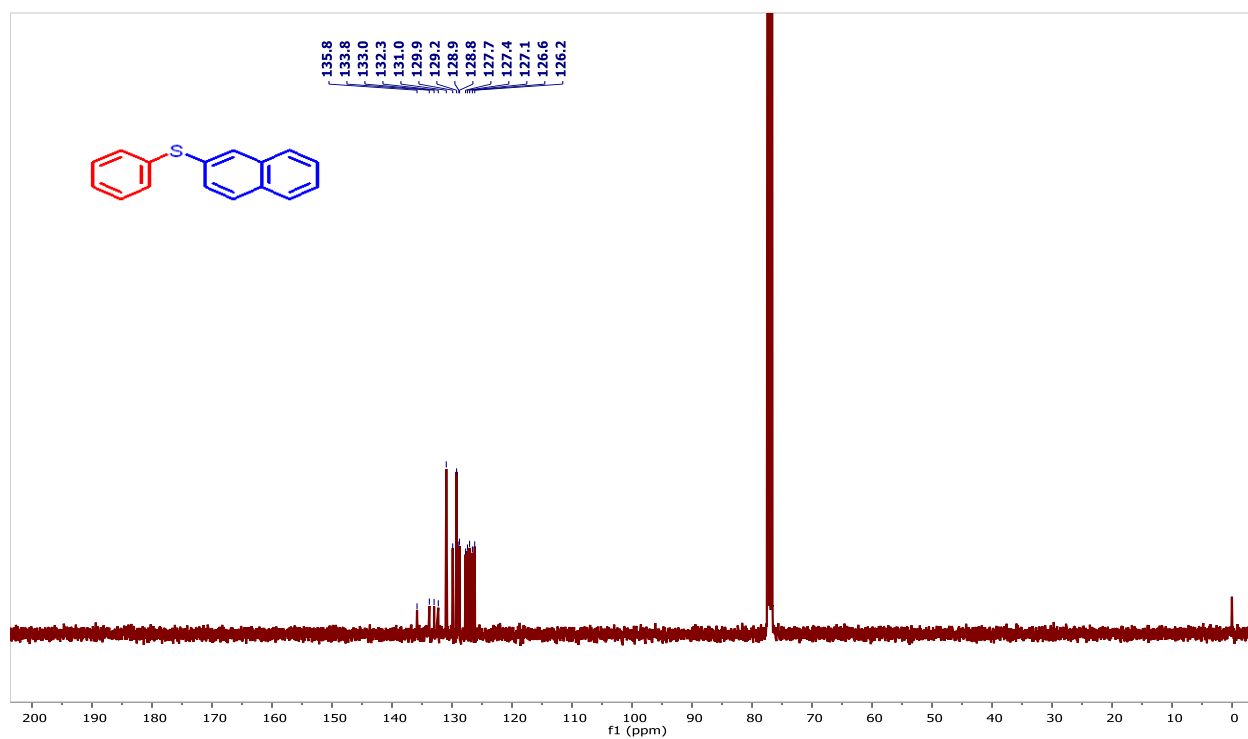
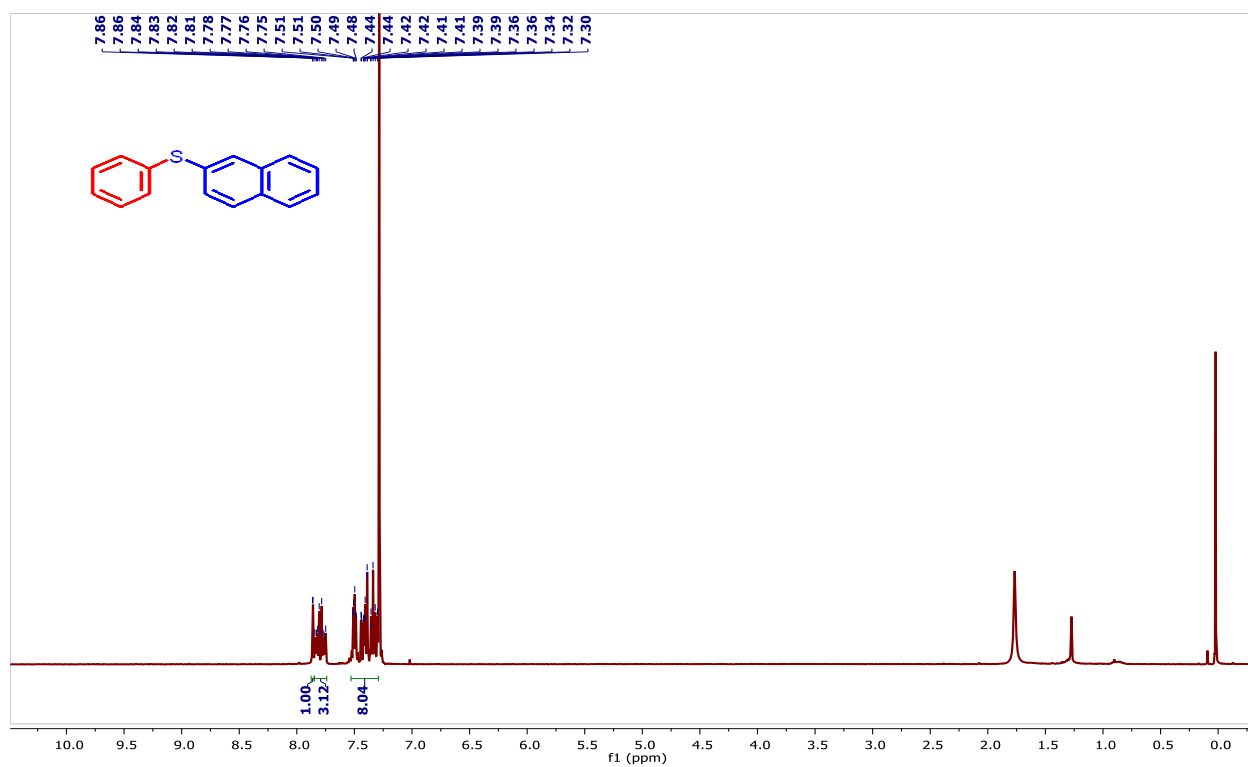
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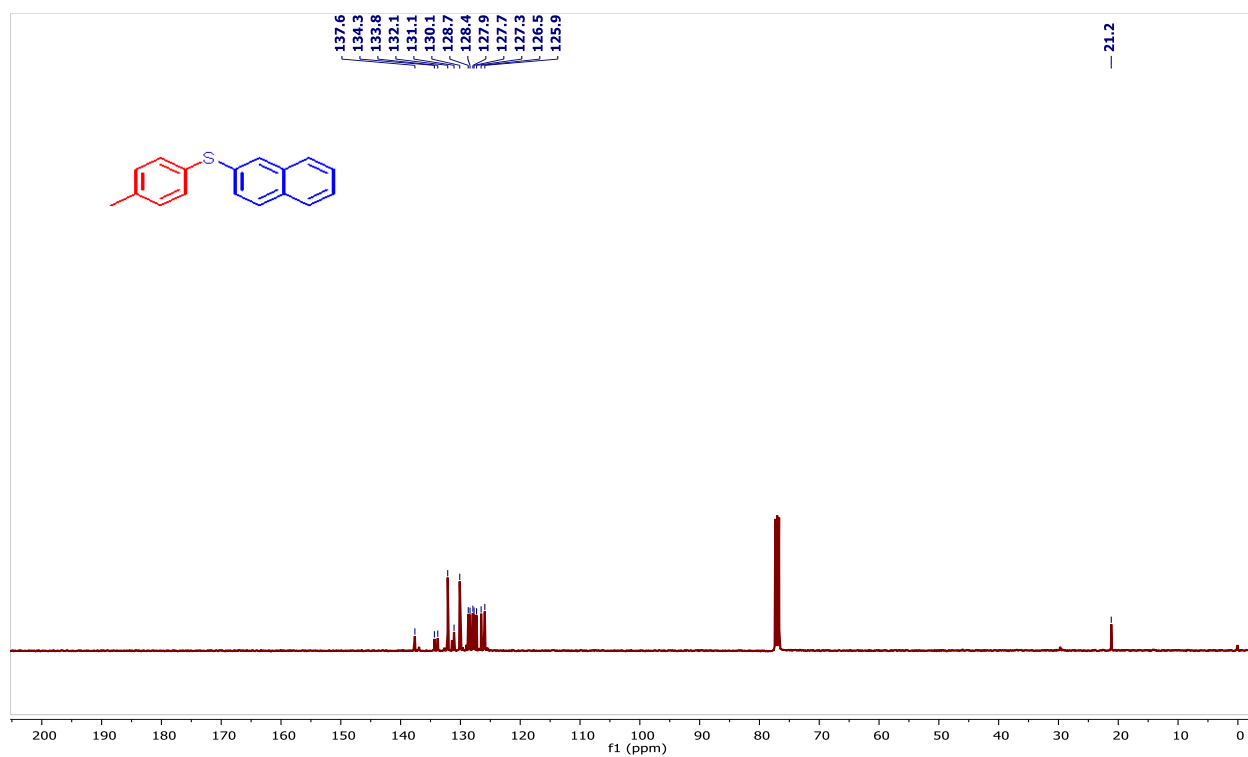
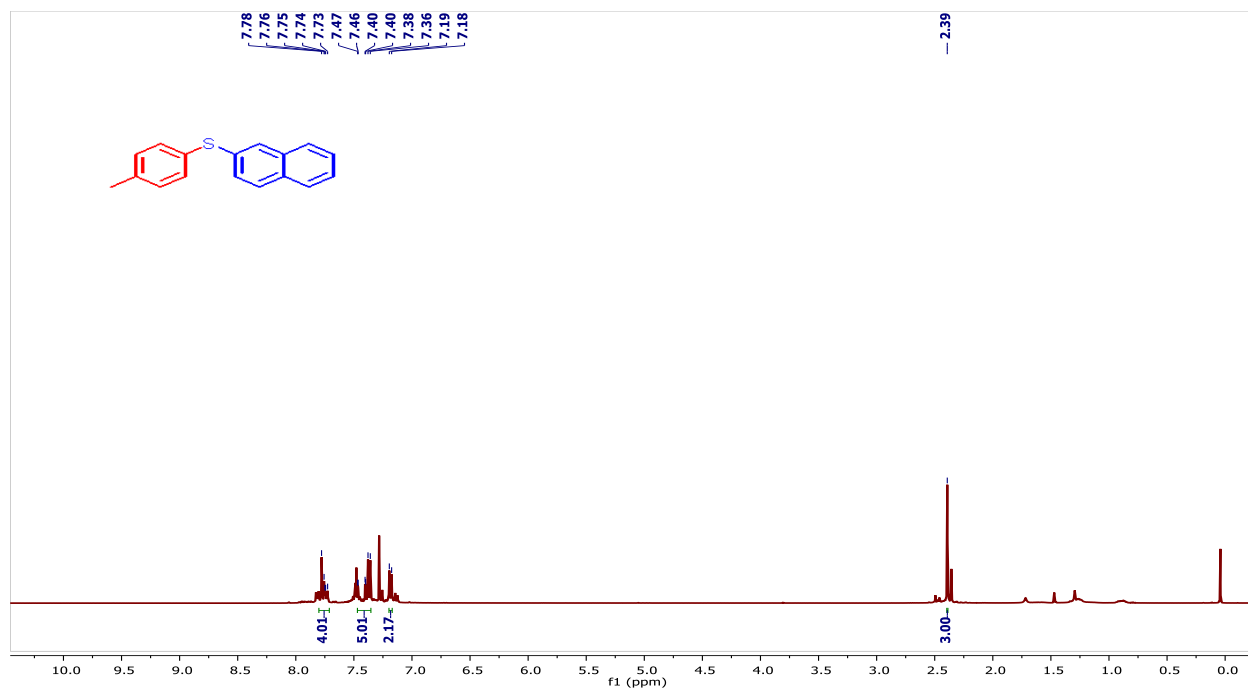
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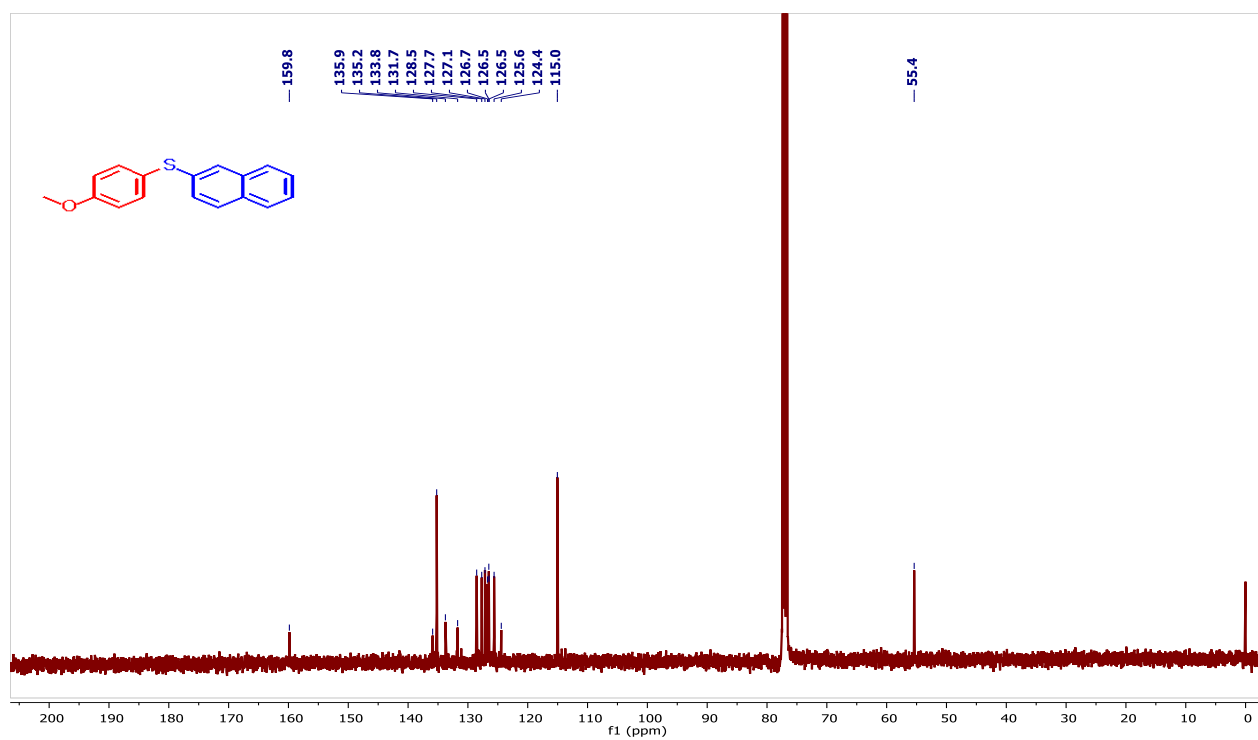
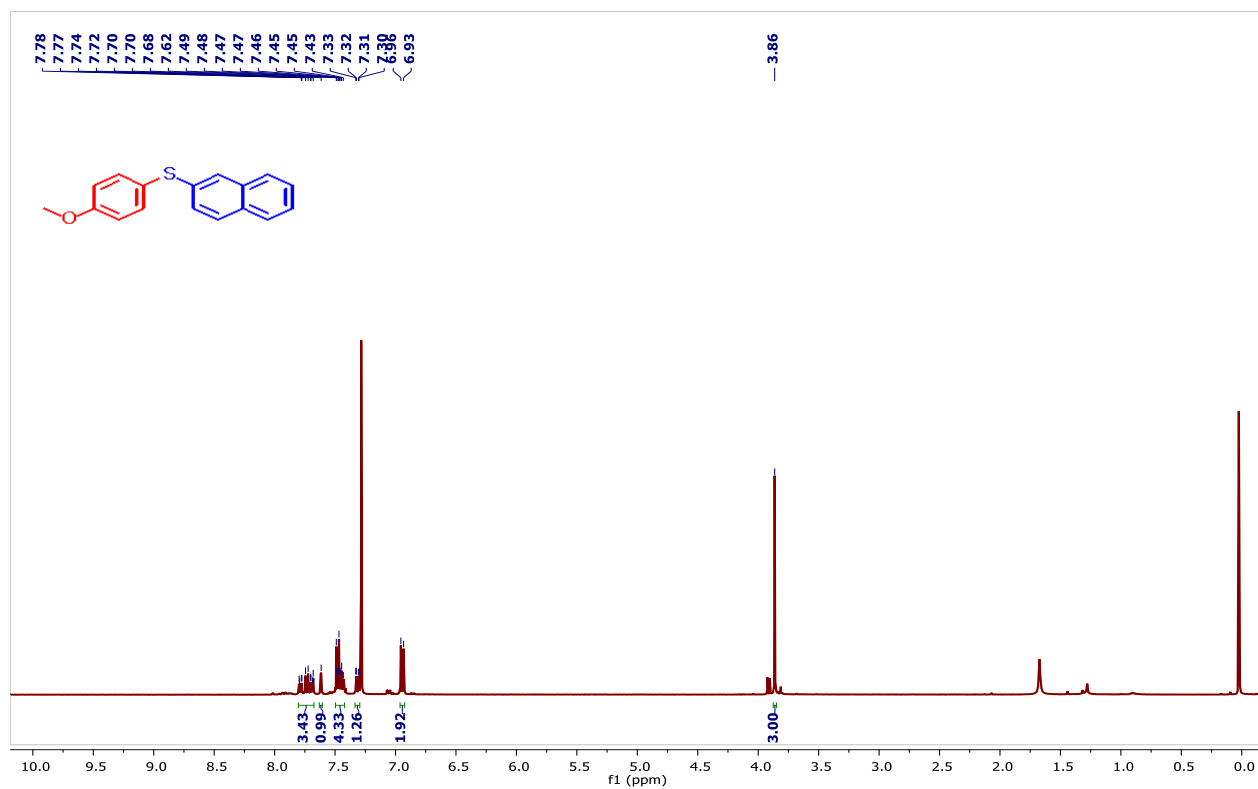
15.



16.



17.



18.

