Direct C-S Bond Formation *via* C-O Bond Activation of Phenols in a Crossover Pd/Cu Dual-Metal Catalysis System

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General Information:

All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over silica gel 48-75 μm. All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm) and were obtained with ^{1}H-decoupling. Data for ^{1}H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; m, multiplet; app, apparent; br, broad signal), coupling constant (Hz), integration. Data for ^{13}C NMR spectra are described in terms of chemical shift (δ in ppm).

Preparation of Silica Nanoparticles

Silica nanoparticles were synthesized by sol-gel polymerization of tetraethyl ortho silicate (TEOS). To a round bottom flask (250 mL), ethanol (99%, 112 mL), ammonia solution (25%, 6 mL) and deionized water (7 mL) were added under stirring. After that, a mixture of TEOS (8 mL) in ethanol (99%, 75 mL) was added drop wise. The resultant mixture was stirred for 24 h at room temperature. Then, the sample was collected after centrifugation and calcined for 4 h (at 500 °C).

Preparation of SiO_2 @ Organic-linker

To a 100 mL of round-bottom flask were introduced 30 mL of anhydrous toluene and 1.0 g of SiO_2 NPs and 0.36 g (3.0 mmol) of 3-aminoropropyl trimethoxysilane (APTMS) were added. The solution was refluxed for 24 hrs under an inert atmosphere, filtered and washed subsequently with toluene, dichloromethane, and methanol, and dried under reduced pressure at 80 °C for 10 h. In another 100 ml round-bottom flask, to a solution of 1 g of aminopropyl functionalized SiO_2 NPs in 35 mL of THF, 0.5 ml of diisopropylethylamine was added. Then, 0.46 g (3 mmol) of cyanoric chloride was added in 0 °C. After 2h, the solution was decanted and washed with 2×25 of fresh THF and decanted. Then, 25 ml of acetonitrile and 1 ml of diisopropylethylamine was added to

residue. 7 mmol dipyridilamine was added to the mixture and stirred 2h in room temperature, refluxed for 12h. After completion of the reaction, the solid products were filtered, washed with deionized water and then acetone and dried at 100 °C for 12h. The clung dipyridilamine on triazine functionalized SiO_2 NPs (SiO_2 @ Organic-linker) was obtained through this simple procedure.

Immobilization of Pd(II) ions on the surface of SiO_2@organic-linker(OL)@$Pd^{(II)}$

The SiO_2 @ Organic-linker (1 g) was dispersed in CH_3CN (100 mL) in an ultrasonic bath for 30 min. Subsequently, a yellow solution of $PdCl_2$ (50 mg) in 30 mL acetonitrile was added to dispersion of SiO_2 NPs/CCPy and the mixture was stirred for 10 hours at 25 ºC. Then, the SiO_2@organic-linker(OL)@$Pd^{(II)}$ was separated by centrifuge and washed by CH_3CN, H_2O and acetone respectively to remove the unattached substrates.

X-Ray diffraction analysis of the catalyst

Anchor Scan Parameters

Start Position [°2Th.]:	5.0391
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Anode Material:	Cu
Generator Settings:	40 mA, 40 kV

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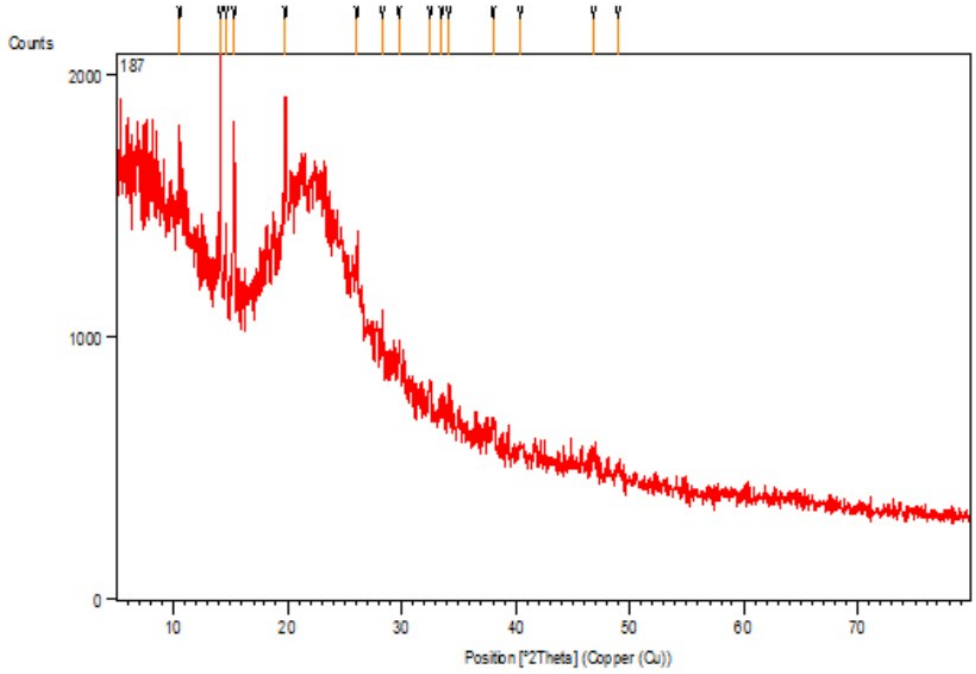
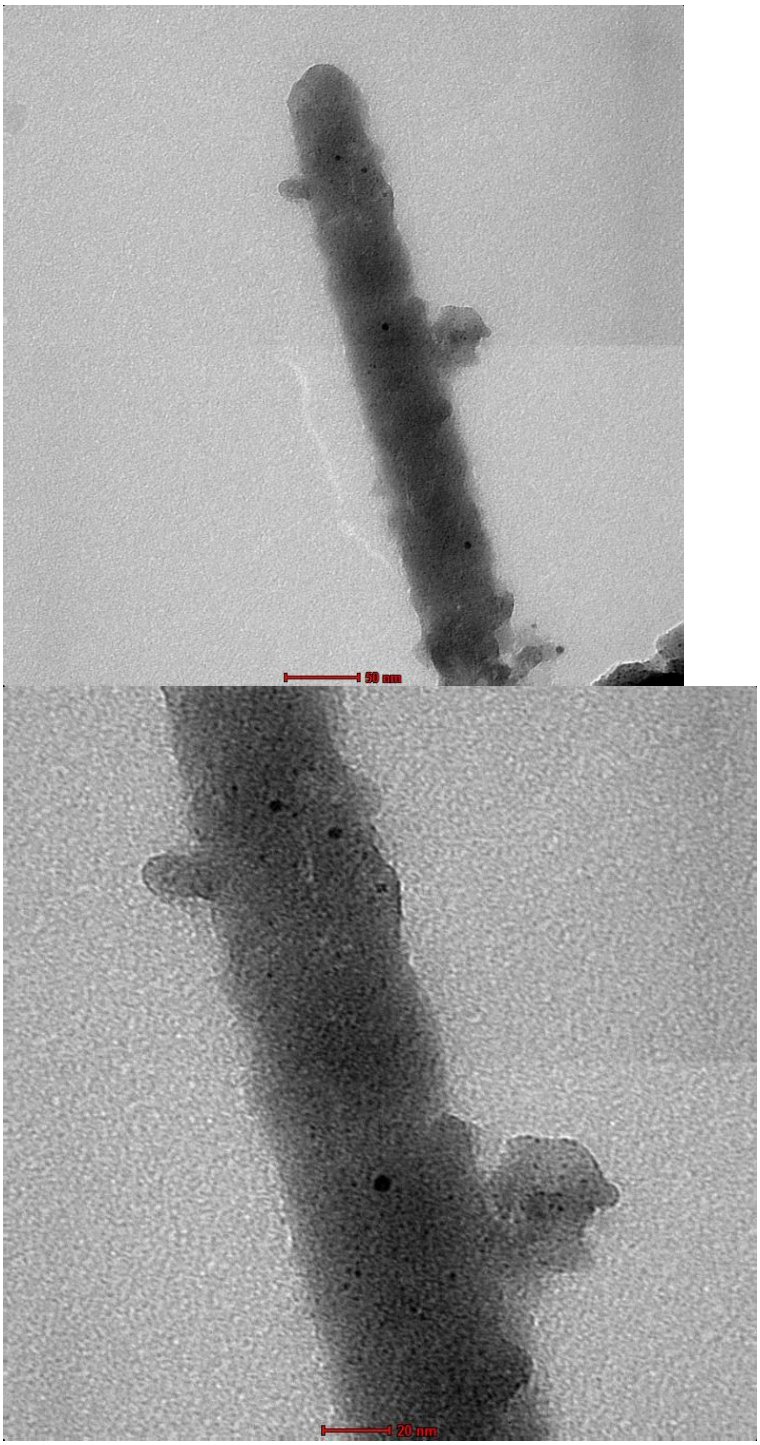


Peak List

Pos.[°2Th.]	Height [cts]	FWHMLeft[°2Th.]	d-spacing [Å]	Rel. Int. [%]
10.55(1)	240(57)	0.12(5)	8.38053	36.09
14.104(3)	666(55)	0.10(1)	6.27449	100.00
14.58(1)	192(37)	0.12(3)	6.06968	28.83
15.319(4)	506(89)	0.08(3)	5.77931	76.04
19.825(6)	326(41)	0.12(2)	4.47483	49.01
26.09(1)	142(31)	0.16(4)	3.41249	21.33
28.29(1)	121(39)	0.11(4)	3.15182	18.23
29.75(2)	96(19)	0.3(1)	3.00068	14.36
32.46(1)	101(26)	0.16(6)	2.75646	15.20
33.50(3)	53(13)	0.3(1)	2.67301	7.95
34.14(1)	107(30)	0.13(6)	2.62388	16.02
37.98(2)	68(12)	0.4(1)	2.36750	10.19
40.43(5)	34(10)	0.5(2)	2.22901	5.14
46.81(3)	50(10)	0.4(1)	1.93935	7.50
48.96(3)	33(10)	0.3(1)	1.85882	5.00

High-resolution TEM images of the catalyst



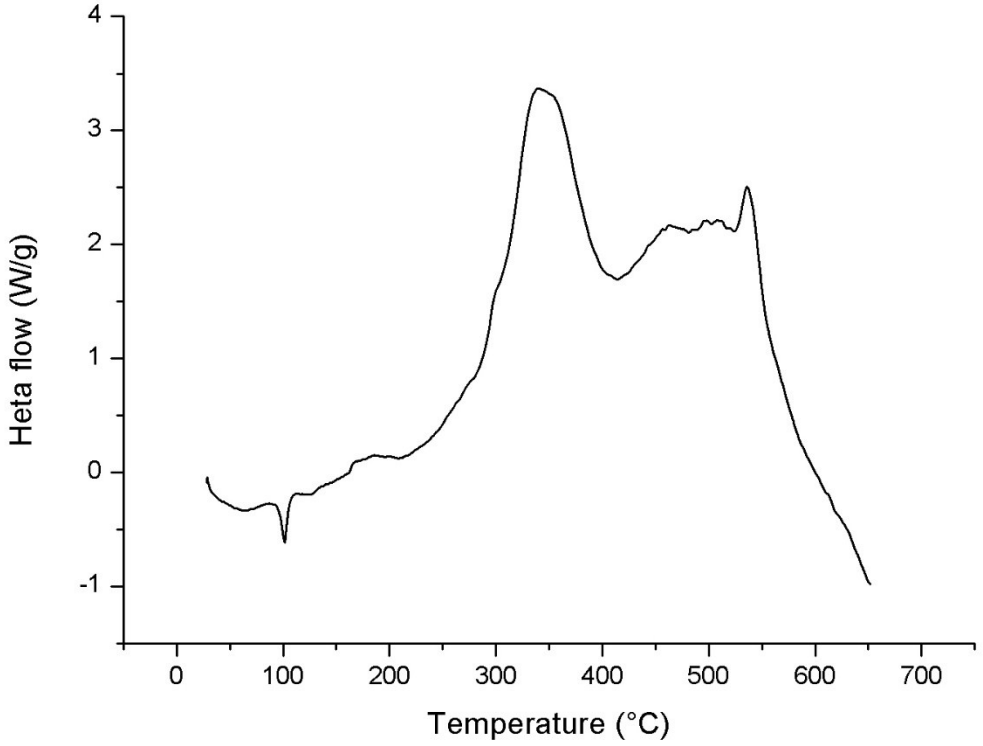
ICP Mass analysis of the catalyst

Row	Material	Pd (%)
1[a]	SiO_2 NPs / CCPy / Pd(II)	1.9

[a] total weight of the sample = 0.0265 g

Instrument = ICP MS ELAN DRC-e

DSC spectrum of the catalyst



Spectral Data

Diphenyl sulfide (2A) [3]

Colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 7.2-7.4 ppm (m, 10 H); ^{13}C NMR (100MHz, $CDCl_3$, 25 °C, TMS): δ= 127.1, 129.8, 131.6, 135.8 ppm.

Phenyl (*p*-tolyl) sulfide (2B) [3]

Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 2.3 ppm (s, 3H), 7.20 (d, J = 8.1 Hz, 2H) 7.40-7.42 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 21.2, 127.2, 127.5, 128.8, 129.1, 129.2, 131.0, 133.6, 137.0 ppm.

Phenyl 4-methoxy phenyl sulfide (2C) [2]

Colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): δ= 4.2(s, 3H), 7.1-7.2 ppm (m, 5H), 7.3-7.6 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS): δ= 55.3, 116.3, 126.8, 127.4, 128.5, 129.4, 137.4, 138.2, 158.2 ppm.

(4-methoxy phenyl) tolyl-p sulfide (2D) [7]

Yellow oil:^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 2.3 ppm (s, 3H), 3.8 (s, 3H), 6.92 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H) 7.21, (d, J = 8.4 Hz, 2H) 7.443, (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 21.0, 55.3, 114.9, 125.6, 129.4, 129.8, 132.2, 134.4, 136.1, 159.5 ppm.

Di-*p*-tolyl sulfide (2E) [4]

White solid: mp 55–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 2.25 ppm (s, 6H), 7.02 (d, J= 8, 4H), 7.34 (d, J= 8, 4H);^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 21.0, 128.5, 129.8, 131.1, 137.6 ppm.

Phenyl (*m*-Tolyl) Sulfide (2F) [2]

Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.36 (s, 3 H), 7.16–7.24 (m, 8H), 7.26–7.43 (1 H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.26, 126.3, 127.0, 127.9, 129.1, 129.6, 130.1, 133.0, 135.7, 137.0.

Phenyl (*o*-Tolyl) Sulfide (2G) [3]

Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (3 H, s), 7.30–7.37 (8 H, m), 7.39–7.54 (1 H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 127.5, 127.9, 129.1, 129.6, 130.6, 131.0, 133.0, 133.7, 136.1, 140.0.

(2,3-Dihydroinden-5-yl)phenyl Sulfide (2H) [5]

Yellow oil: yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54–7.56 (2 H, m), 7.47–7.50 (5 H, m), 7.29 (1 H, m), 2.84–2.87 (4 H, m), 2.06–2.14(2 H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.2, 146.0, 136.2, 133.3, 132.2, 131.6, 128.6, 128.5, 124.9, 33.0, 31.9, 25.8.

(2,3-Dihydroinden-5-yl) *p*-Tolyl Sulfide (2I) [5]

Yellow oil:^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50–7.51 (2 H, m), 7.48–7.49 (2 H, m), 7.29 (2 H, d, *J* = 7.5 Hz), 7.11 (2 H, d, *J* = 7.5 Hz), 2.86–2.91 (4 H, m), 2.46 (3 H, s), 2.08–2.12 (2 H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.2, 146.0, 141.2, 136.2, 134.9, 132.3, 132.2, 131.6, 128.5, 124.9, 33.0, 31.9, 25.8, 21.7.

(*p*-nitro phenyl) *p*tolyl- sulfide (2J) [7]

Yellow solid, mp: 93-95 ^{o}C, ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.4 (s, 3H), 7.15 (d, *J* =7.6 Hz, 2H) 7.29, (d, *J* = 7.6 Hz, 2H) 7.48, (d, *J* = 8 Hz, 2H) 8.06, (d, *J* = 8 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)=21.3, 124.0 , 126.1, 126.4, 130.9, 135.1, 140.2, 145.1, 149.4.

(*p*-nitryl phenyl) *p*tolyl- sulfide (2K) [7]

White solid, mp: 81-83 °C, ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.44 (s, 3 H), 7.14 (d, *J*= 8.4 Hz, 2 H), 7.28 (d, *J*= 8.4 Hz, 2 H) 7.44-7.49, (m, 4 H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 21.36, 108.28, 118.96, 126.77, 130.79, 132.31, 133.44, 134.99, 140.00, 146.64.

1-Naphthyl phenyl sulfide (2L) [1]

Colorless oil; ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 7.03-7.38 (m, 3H), 7.57 (dd, *J* = 7.2, 1.2Hz, 4H), 7.58-7.66 (m, 2H), 8.36-8.39 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 123.7, 124.6, 126.1, 126.3, 127.0, 127.6, 128.7, 128.6, 129.7, 130.0, 131.8, 134.3, 135.4, 136.0. 136.5

Naphthalen-1-yl(p-tolyl)sulfane (2M) [7]

Colorless oil: ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.09 (s, 3H), 7.21-7.25 (m, 4H), 7.29-7.42 (m, 3H), 7.60-7.75 (m, 2H), 7.87-7.99 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 21.1, 123.8, 124.8, 126.7, 127.9, 128.6, 129.5, 130.0, 131.3, 134.3, 135.4, 135.9.

2-Naphthyl phenyl sulfide (2N) [1]

White solid, mp: 49-50 °C, ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 7.08-7.29 (m, 6H), 7.39-7.44 (m, 2H), 7.57-7.67 (m, 1H), 7.86-7.97 (m, 2H), 8.27-7.29 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 123.9, 124.7, 125.9, 126.4, 128.0, 128.6, 129.2, 129.5, 132.9, 134.4, 135.4, 137.3.

Naphthalen-2-yl(p-tolyl)sulfide (2O) [7]

White solid, mp: 68-70 °C, ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.30 (s, 3H), 7.00-7.10 (m, 4H), 7.39-7.44 (m, 3H), 7.53-7.7.58 (m, 2H), 7.60-7.87 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 20.9, 123.8, 124.8, 126.7, 127.9, 128.6, 129.6, 129.2, 123.0, 131.8, 132.7, 135.4,135.9.

2-Naphthyl *p*-Nitrophenyl Sulfide (2P) [5]

Yellow solid, mp: 156–157 °C, ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83–7.86 (2 H, d, *J* = 6.5 Hz), 7.63–7.77 (3 H, m), 7.56–7.60 (2 H, m), 7.52–7.55 (2 H, d, *J* = 6.5 Hz), 7.45–7.49 (2 H, m), ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.4, 151.2, 133.3, 132.4, 132.3, 132.2, 131.3, 131.2, 128.6, 128.4, 126.4, 124.4.

Phenyl(2-pyridyl)sulfide (2Q) [7]

Colorless oil: ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 6.86 (d, *J* = 4.8 Hz, 1 H), 6.94-6.97 (m, 1 H), 7.38-7.40 (m, 4 H), 7.54-7.58 (m, 2 H), 8.40 (d, *J* = 4.8 Hz, 1 H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 119.9, 121.3, 129.14, 129.6, 131.0, 134.9, 136.8, 149.5, 161.4.

2-Pyridyl(p-tolyl)sulfide (2R) [7]

Colorless oil: ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.37 (s, 3 H), 6.81 (d, *J* = 4.8 Hz, 1 H) 6.93-6-98 (m, 1 H), 7.21-7.30 (m, 2 H),7.38-7.40 (m, 1 H), 7.42-7.44 (m, 1 H), 7.50-7.54 (m, 1 H), 8.39 (d, *J* = 4.8 Hz, 1 H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 21.3, 119.6, 120.8, 127.6, 130.5, 135.2, 136.6, 139.4, 149.4, 162.1.

4-Acetylphenyl *p*-Nitrophenyl Sulfide (2S) [5]

Yellow solid, mp: 47–48 °C, ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (2 H, d, *J* = 6.8 Hz), 7.73 (2 H, d, *J* = 6.8 Hz), 7.48 (4 H, m), ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 197.0, 171.2, 135.8, 132.3, 131.9, 129.8, 129.1, 128.4, 123.5, 26.25.

Phenyl(o-formylphenyl)sulfide (2T) [1]

Colorless oil: 171 mg (80% yield);^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 7.12 -7.14 (m, 1 H), 7.29-7.48 (m, 7 H), 7.90-7.92 (m, 1 H), 10.42 (s, 1 H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 126.3, 128.4, 129.7, 130.3, 131.9, 133.2, 133.3, 133.7, 134.1, 141.6, 191.6.

o-Formylphenyl(*p*-tolyl)sulfide (2U) [8]

Colorless oil: ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.42 (s, 3 H), 7.04-7.06 (m, 1 H), 7.24-7.26 (m, 2 H), 7.30-7.33 (m, 2 H), 7.38-7.41 (m, 2 H), 7.87-7.89 (m, 1 H), 10.40 (s, 1 H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 21.2, 125.6, 128.9, 129.2, 130.6, 132.2, 133.1, 133.9, 134.0, 139.0, 142.8, 191.5.

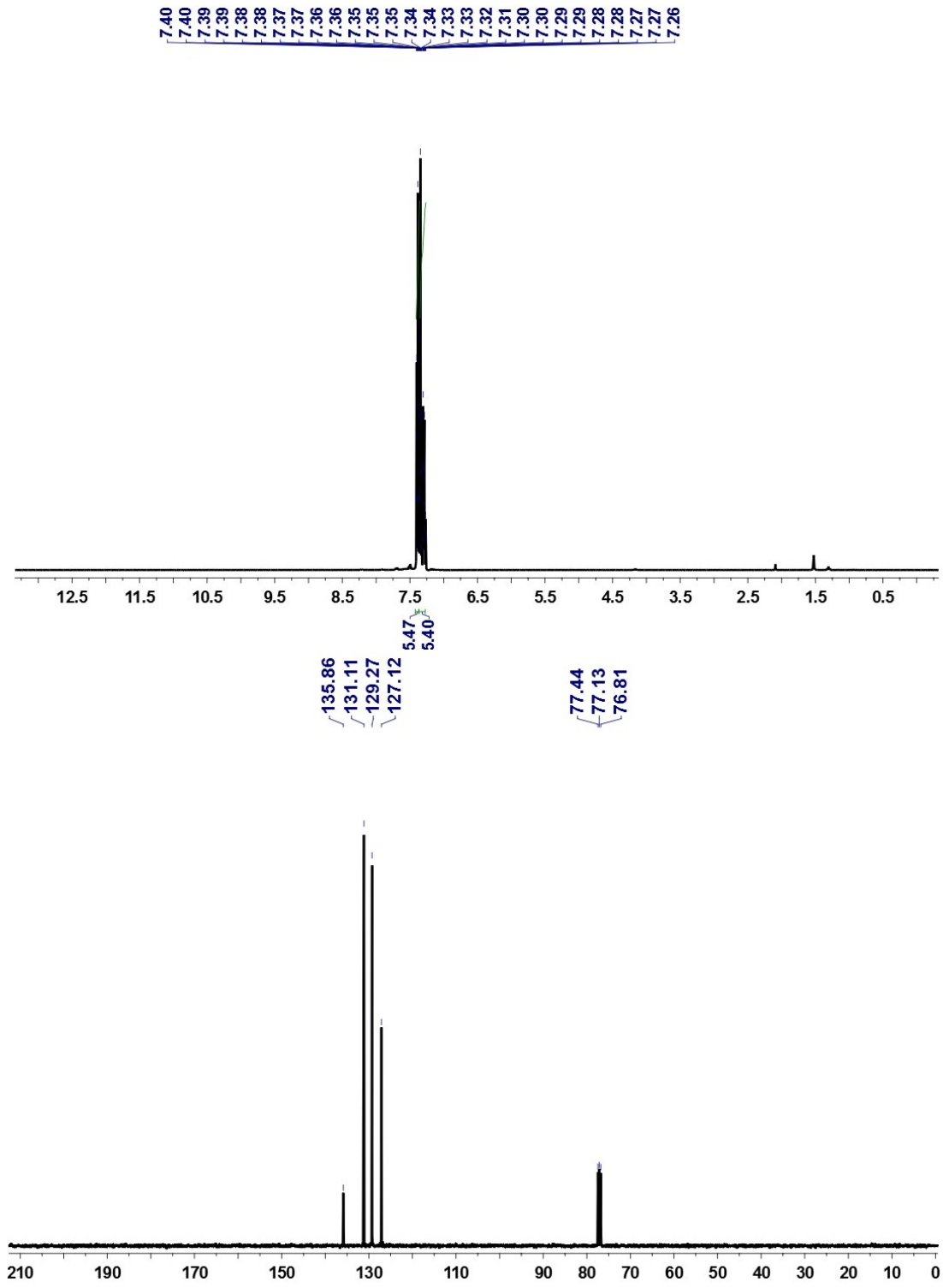
Phenyl(*m*-formylphenyl)sulfide (2V) [1]

Colorless oil: ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 7.43-7.63 (m, 6 H), 7.72-7.84 (m, 2 H), 8.04 (s, 1 H), 9.99 (s, 1 H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 128.4, 129.6, 129.7, 132.3, 132.5, 133.6, 135.3, 137.3, 138.0, 138.8, 191.6.

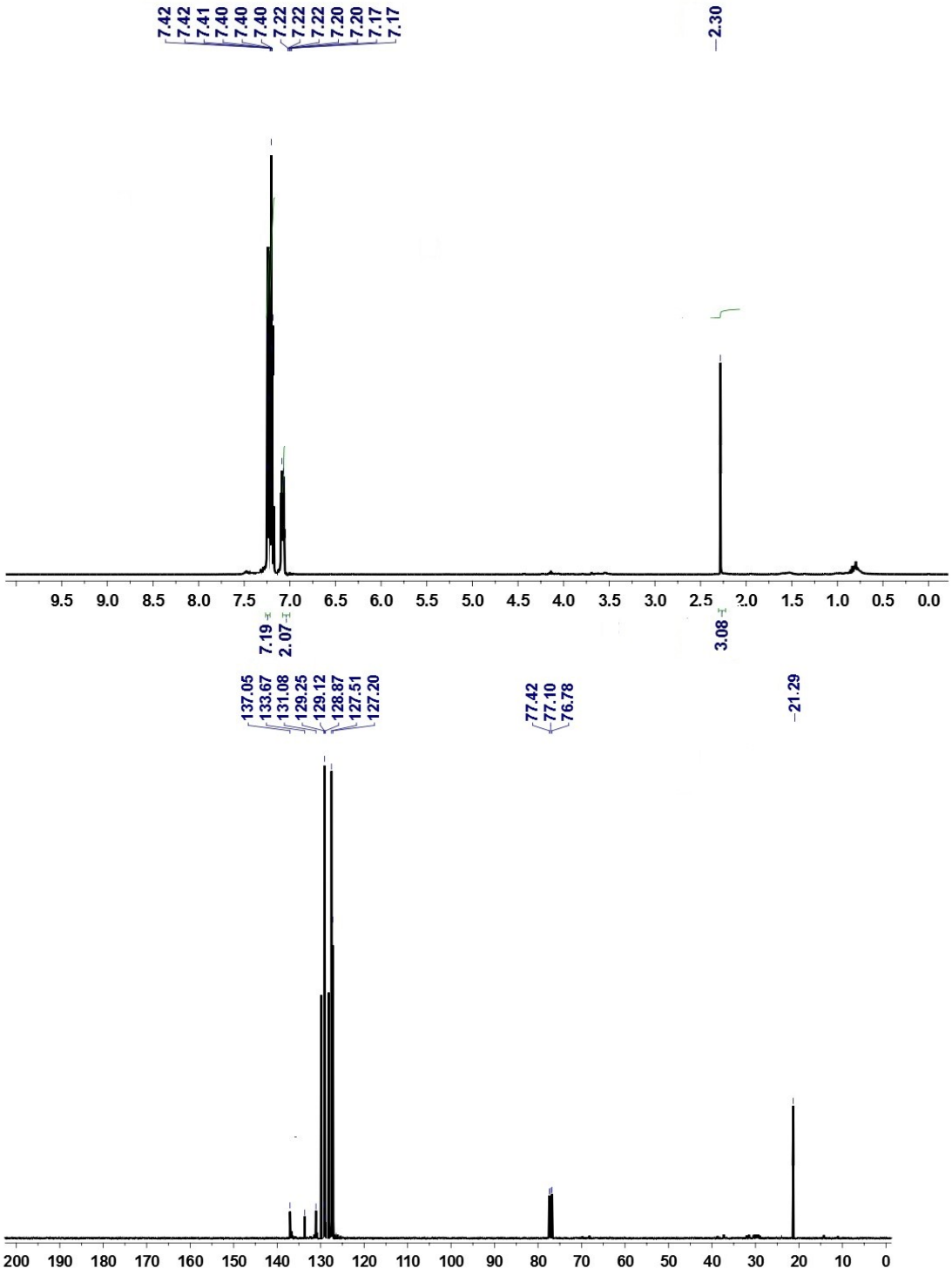
m-Formylphenyl(*p*-tolyl)sulfide (2V) [8]

Colorless oil: ^{1}HNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 2.41 (s, 3 H), 7.21-7.29 (m, 2 H), 7.38-7.49 (m, 2 H), 7.67-7.72 (m, 1 H), 7.77-7.85 (m, 3 H), 9.95 (s, 1 H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)= 21.2, 127.1, 128.4, 129.48, 130.4, 132.38, 133.5, 134.2, 137.0, 138.0, 139.9, 191.7.

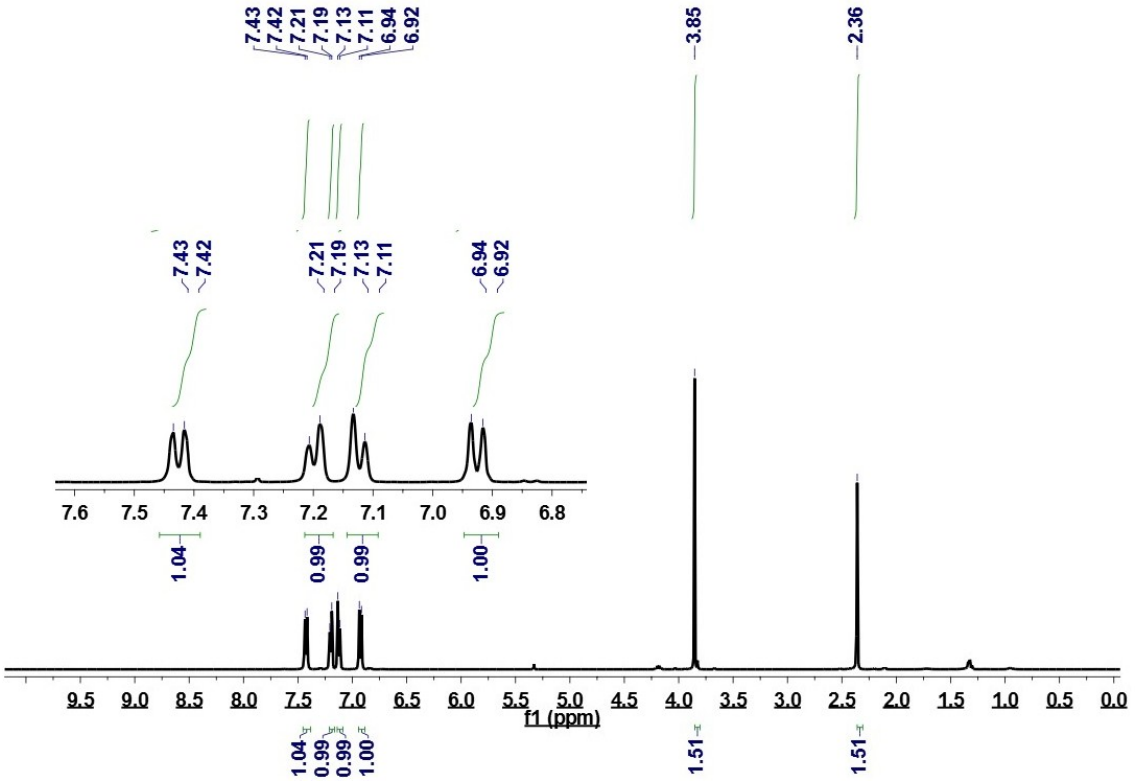
Diphenyl sulfide (2A)

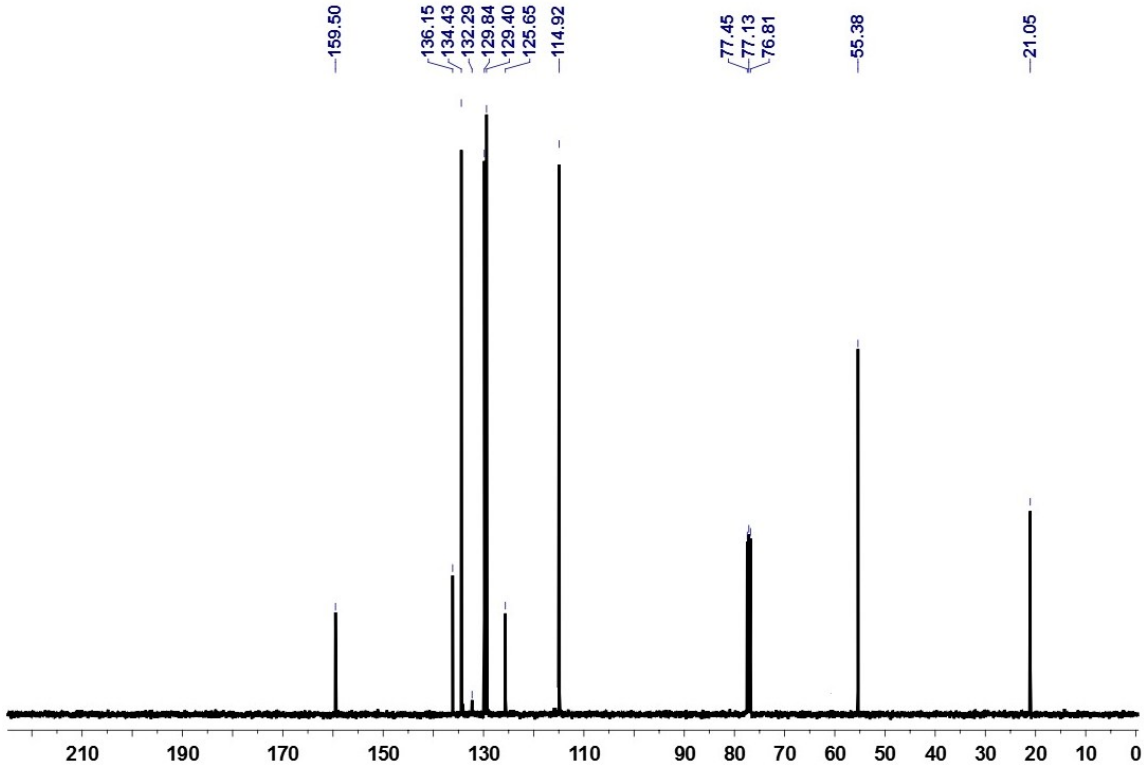


Phenyl (*p*-tolyl) sulfide (2B)

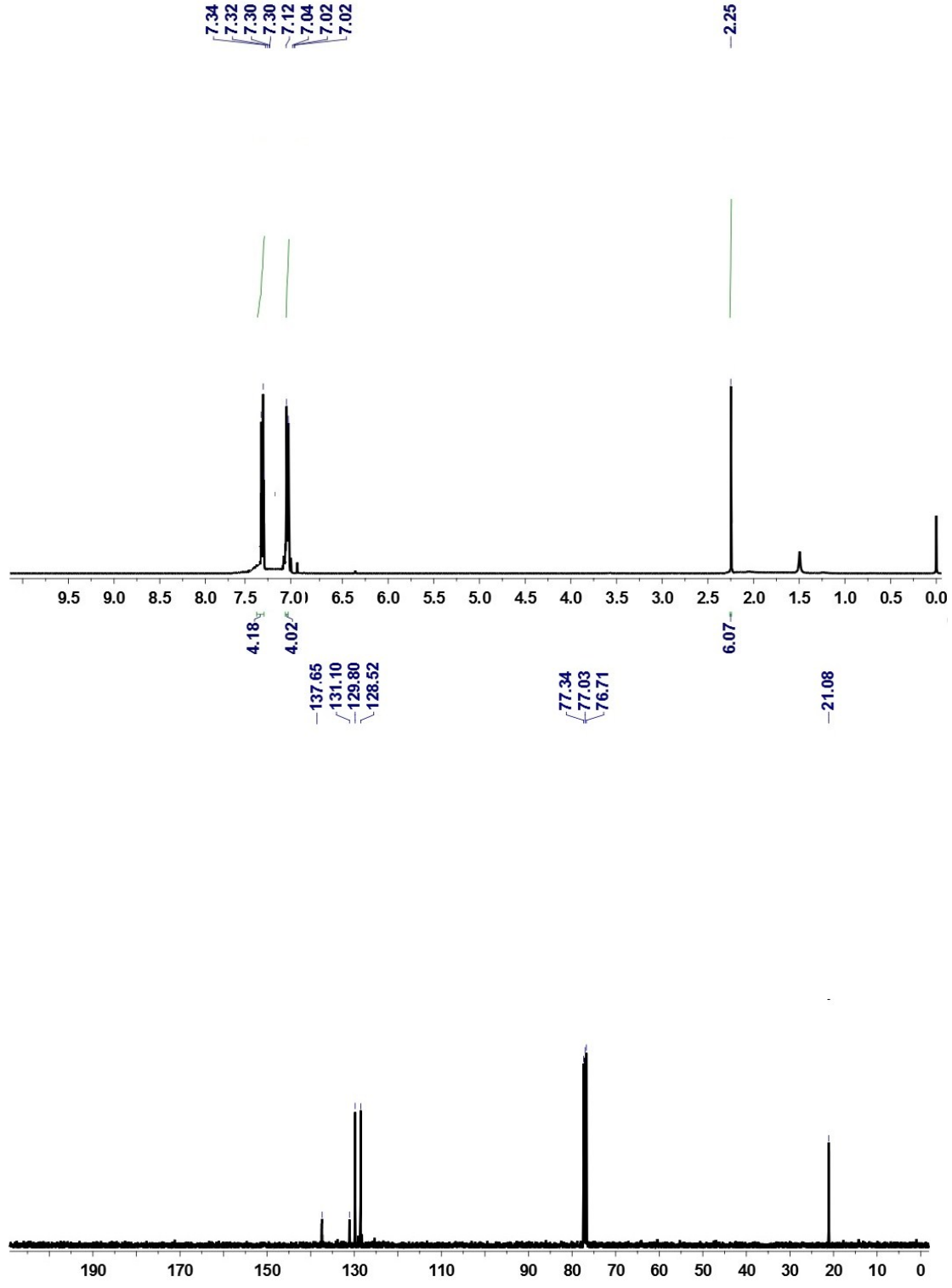


(4-methoxy phenyl) *p*tolyl- sulfide (2D)

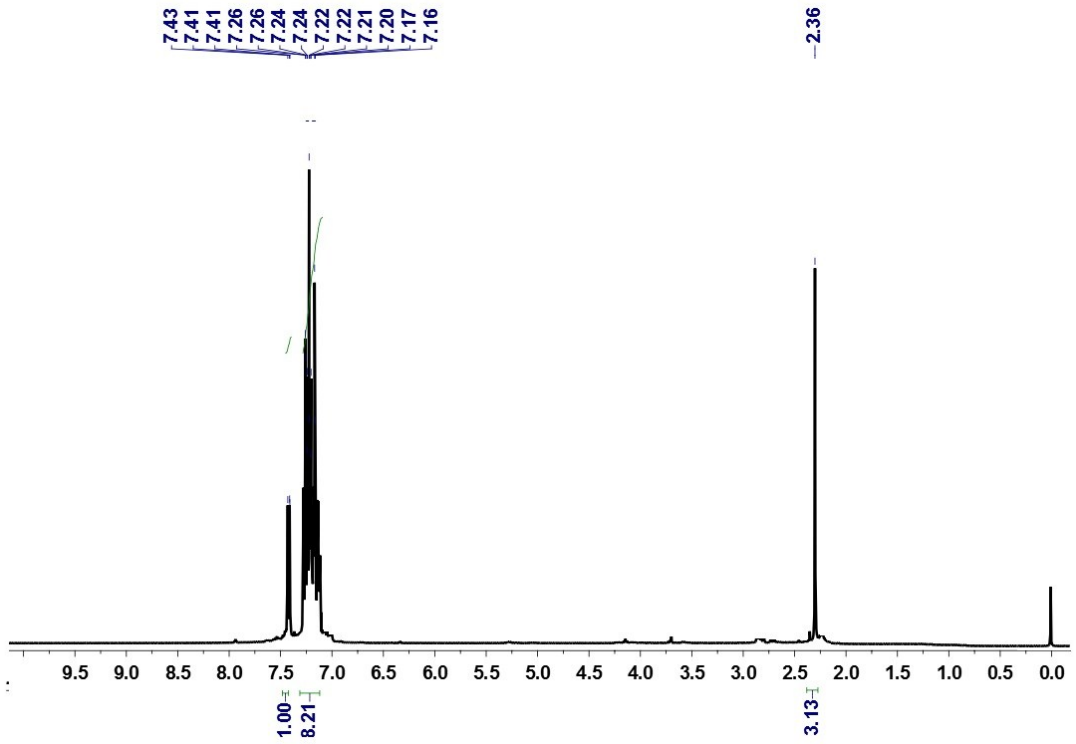


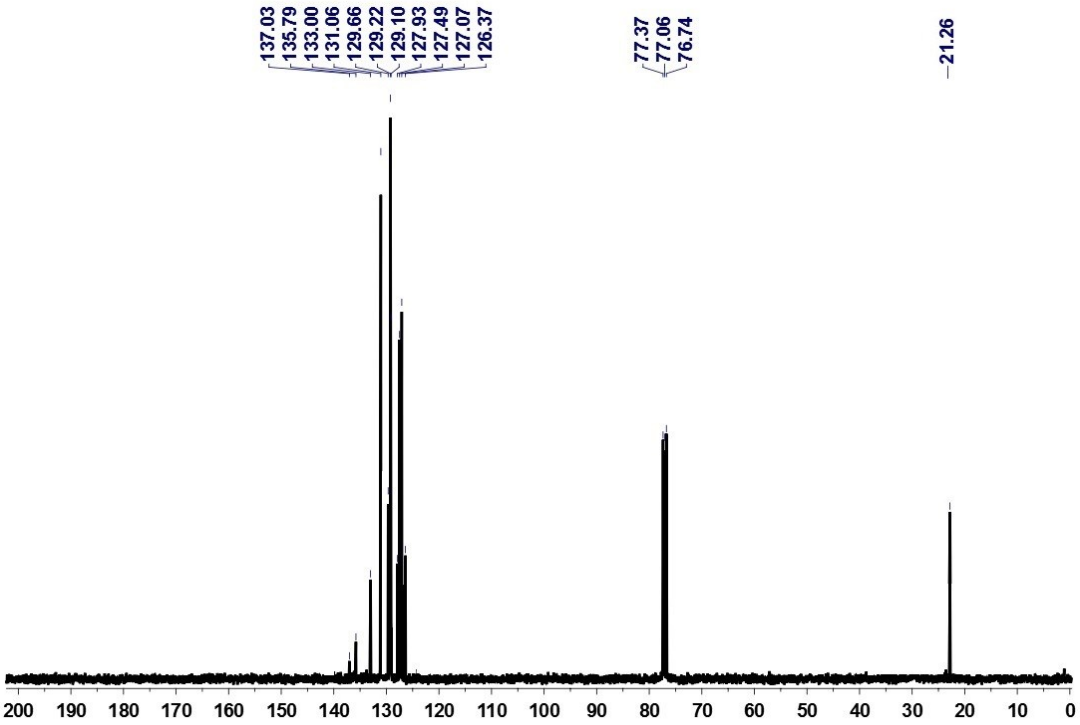


Di-*p*-tolyl sulfide (2E)

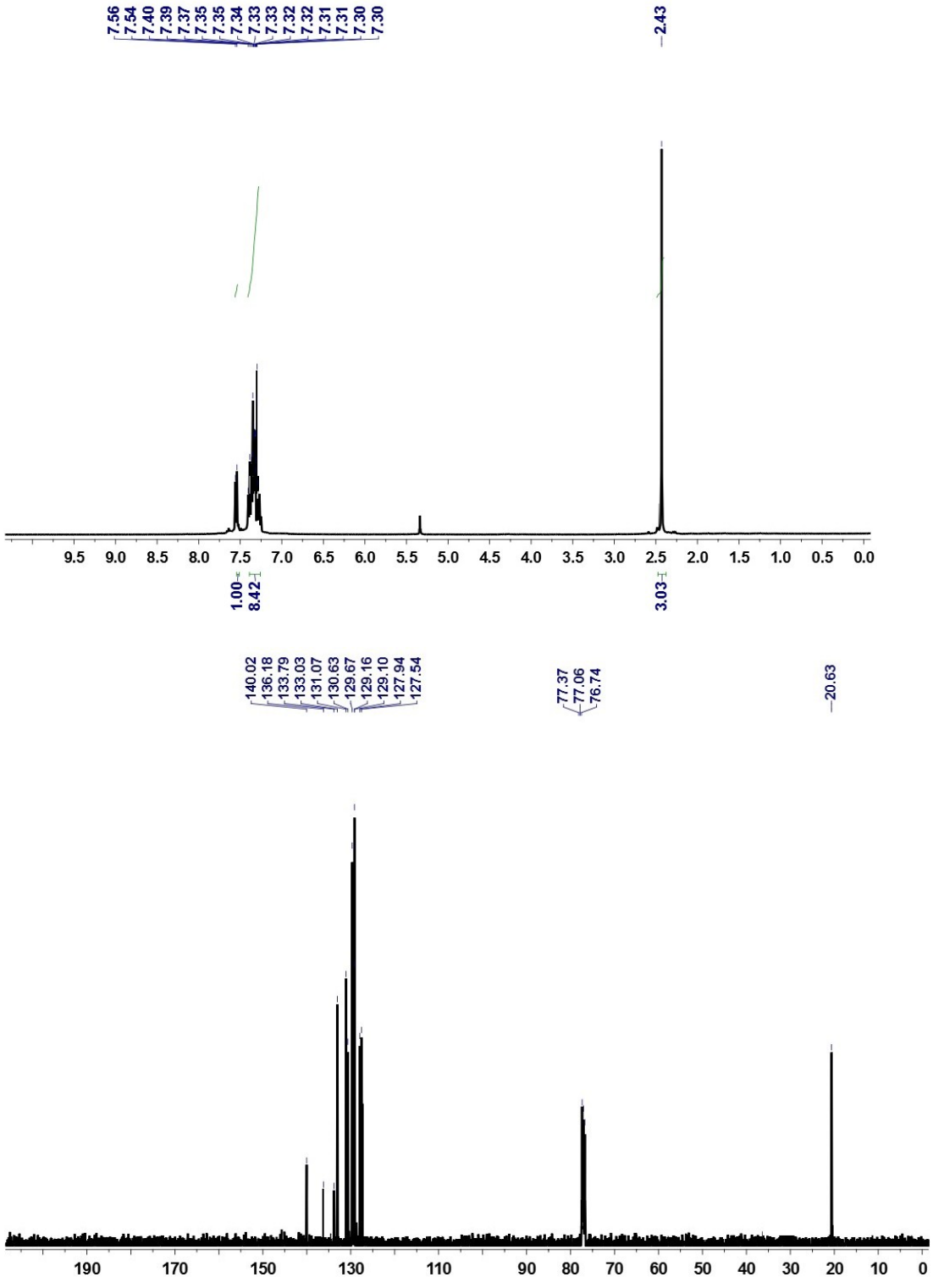


Phenyl *(m*-Tolyl) Sulfide (2F)

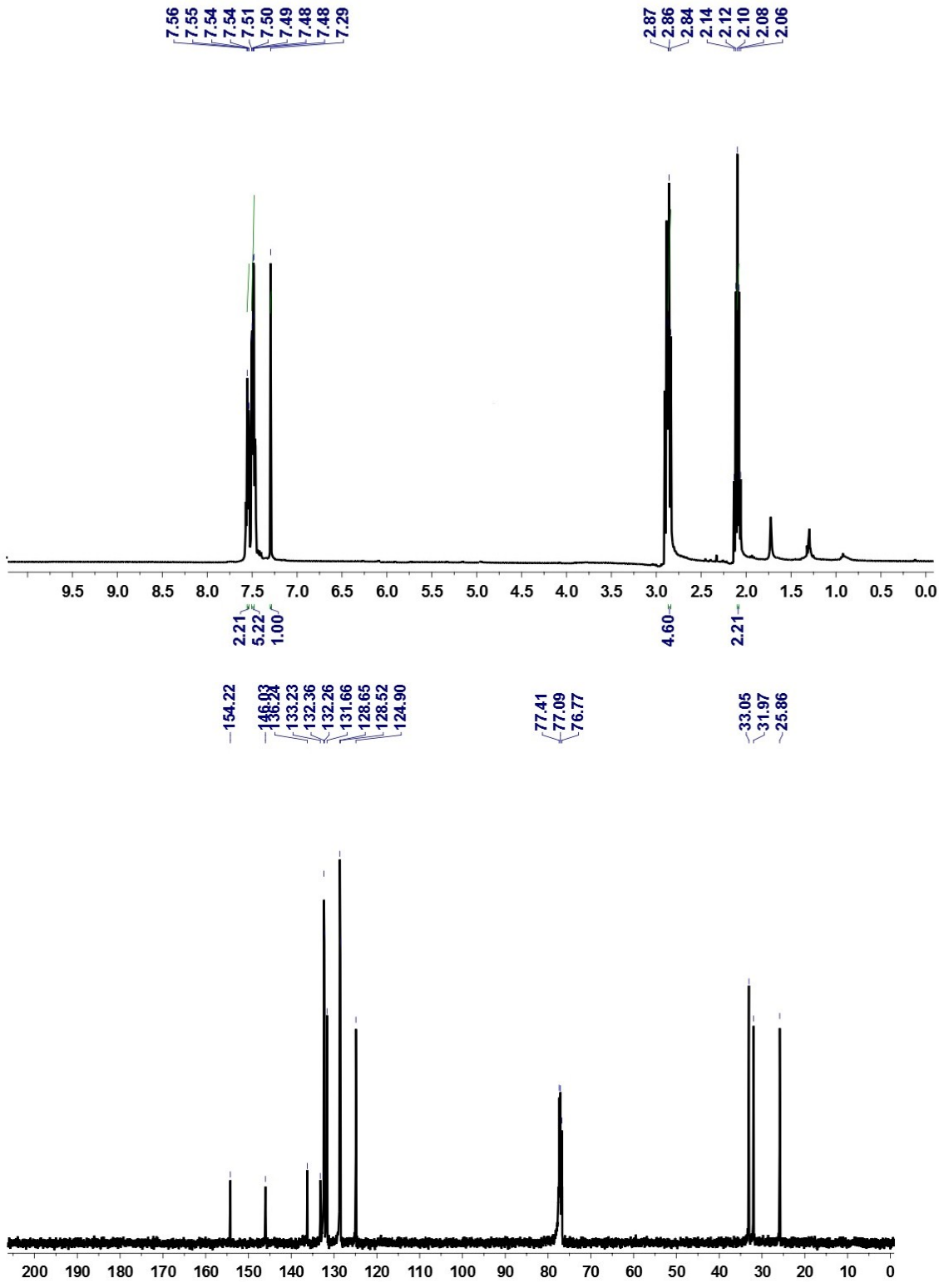




Phenyl *(o*-Tolyl) Sulfide (2G)



(2,3-Dihydroinden-5-yl)phenyl Sulfide (2H)



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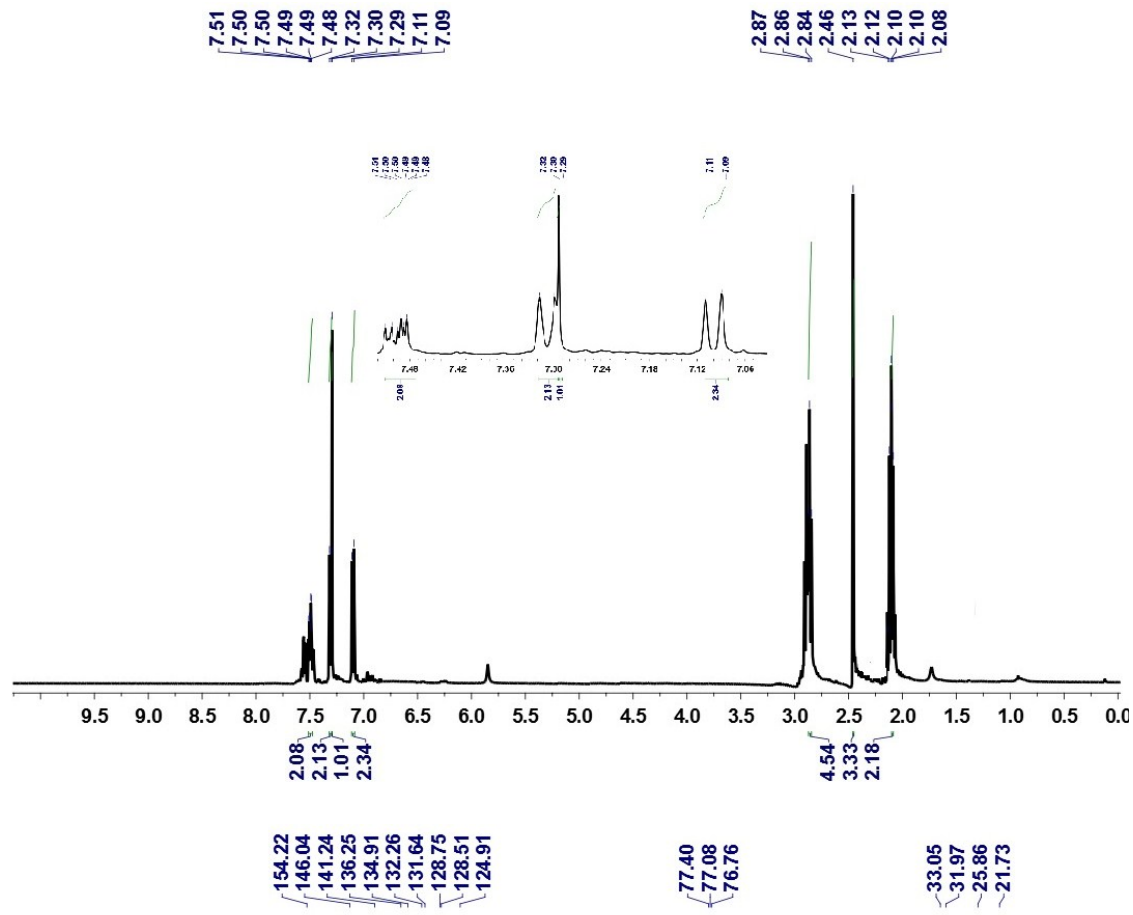
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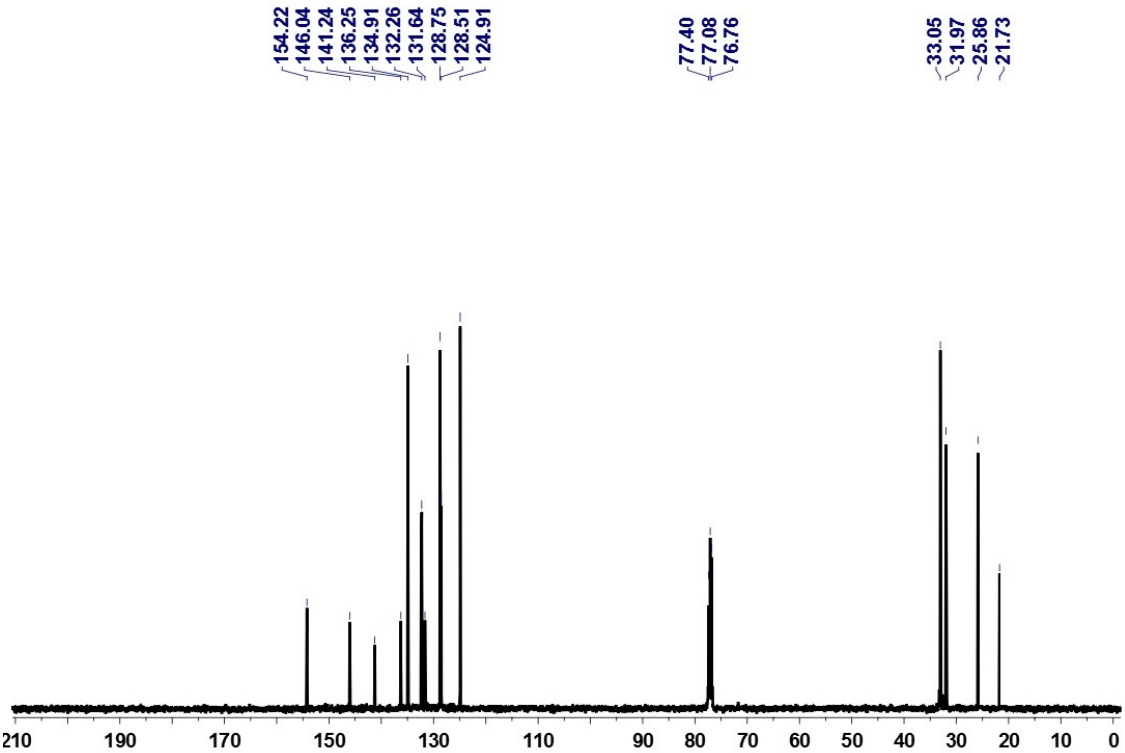
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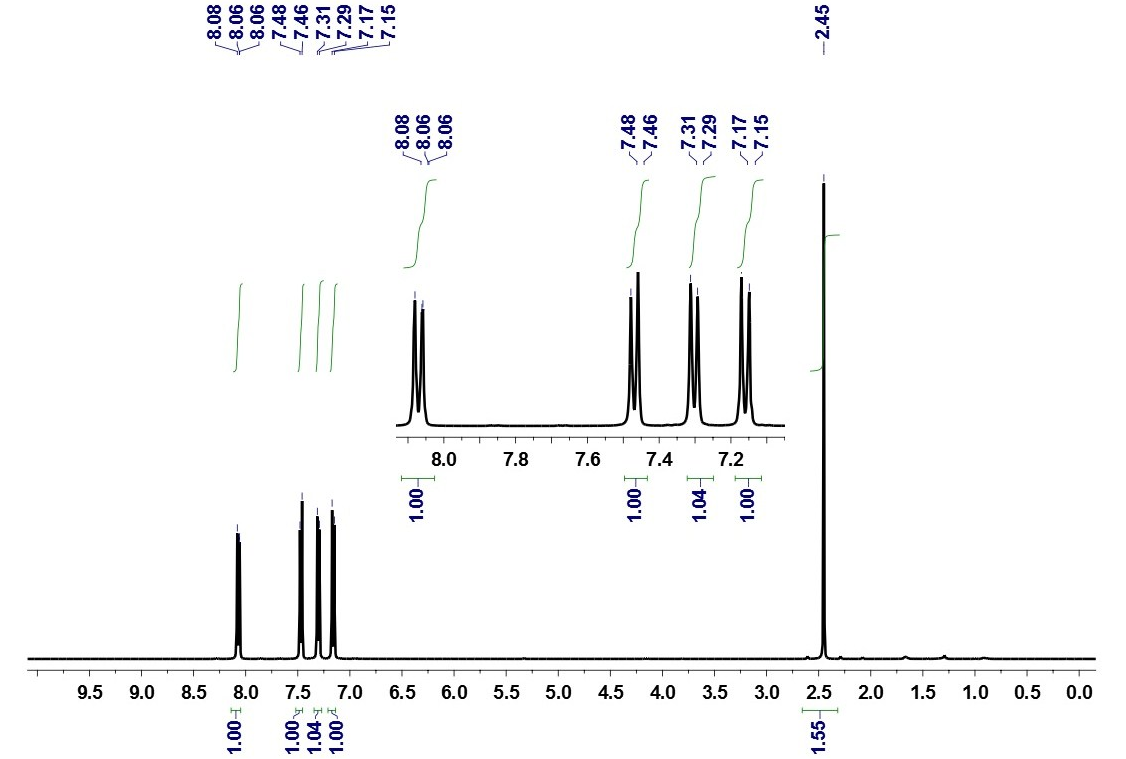
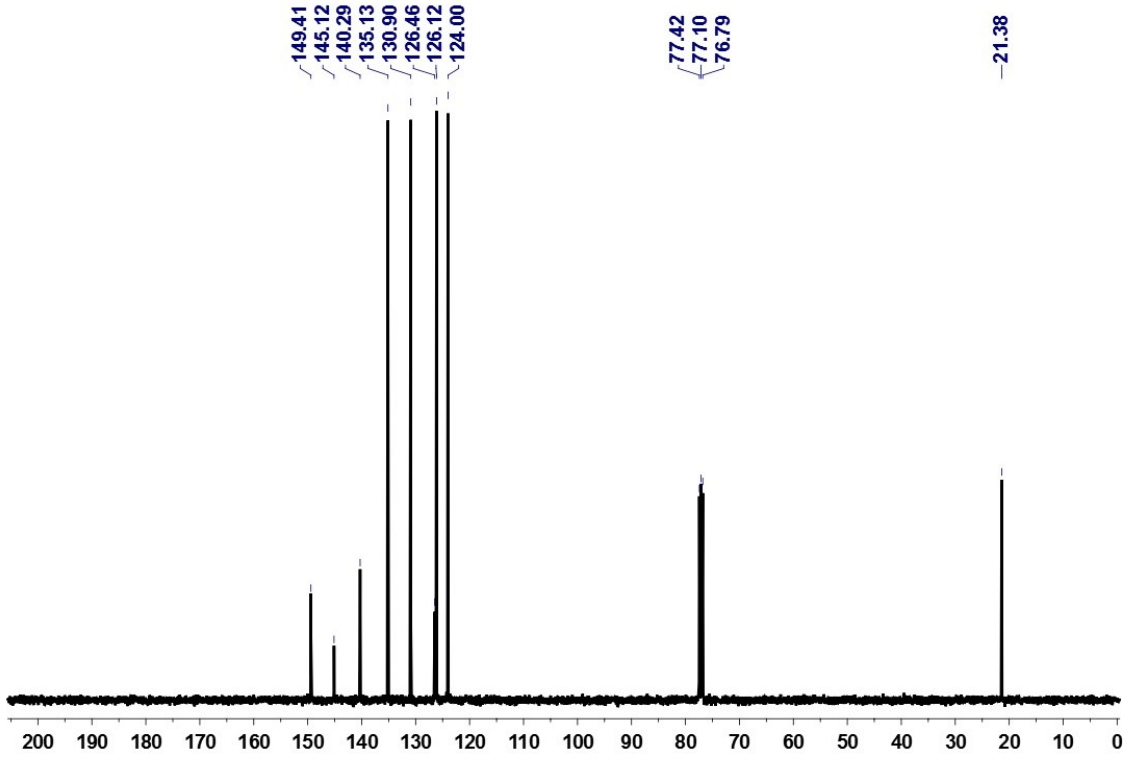
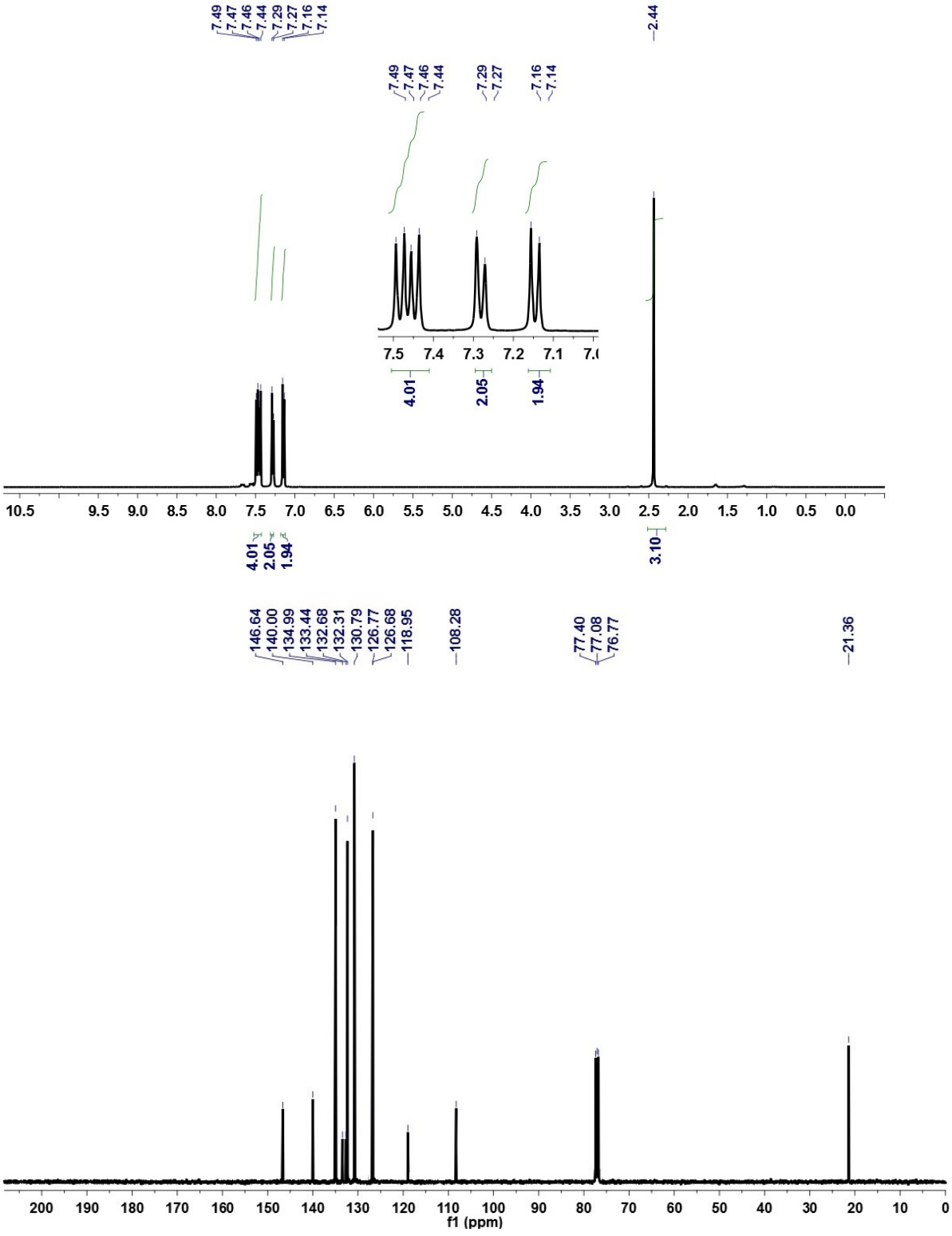
128.75
128.51
124.91
77.40
77.08
76.76
33.05
31.97
25.86
21.73
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

(*p*-nitro phenyl) *p*tolyl- sulfide (2J)

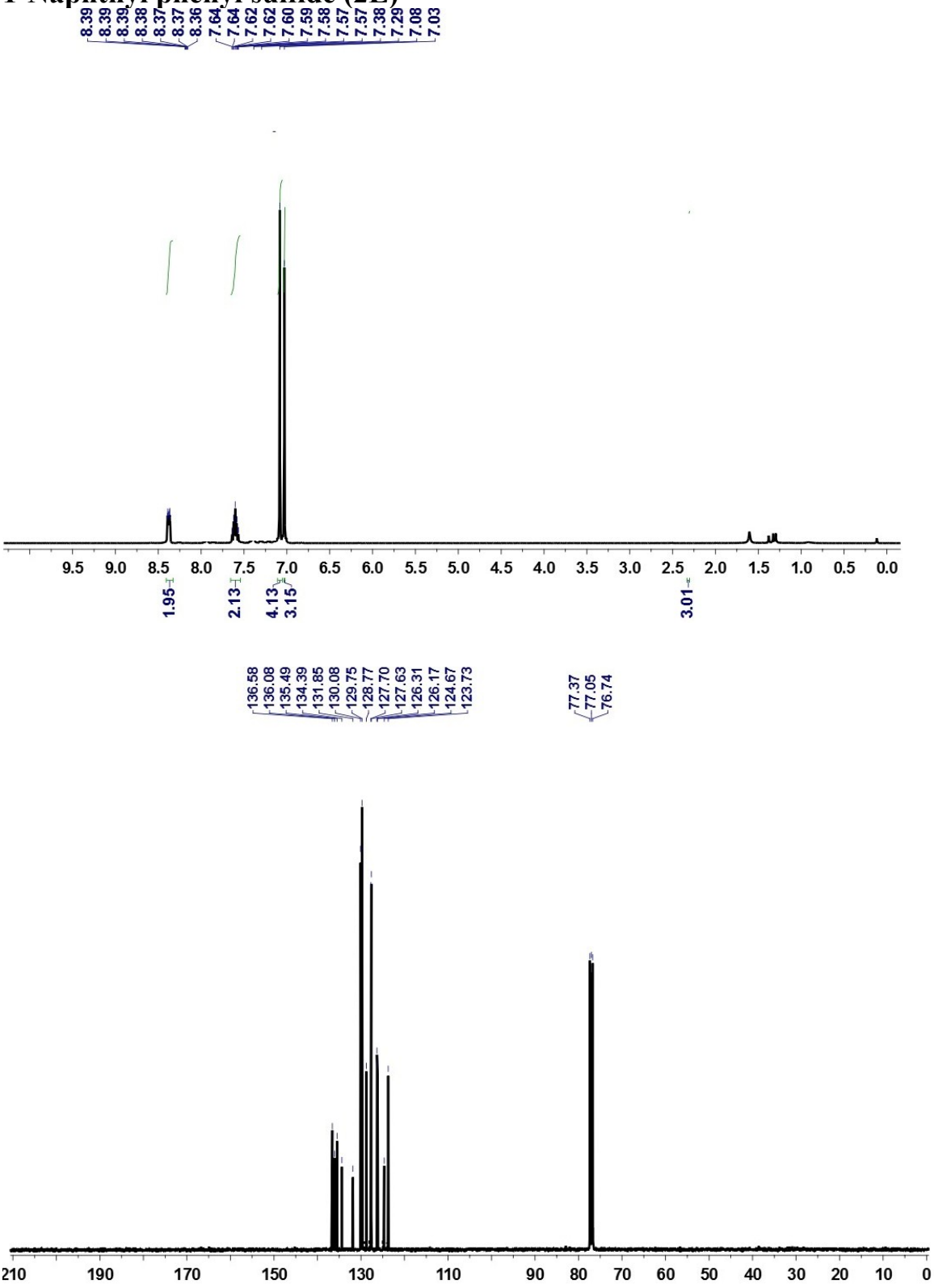




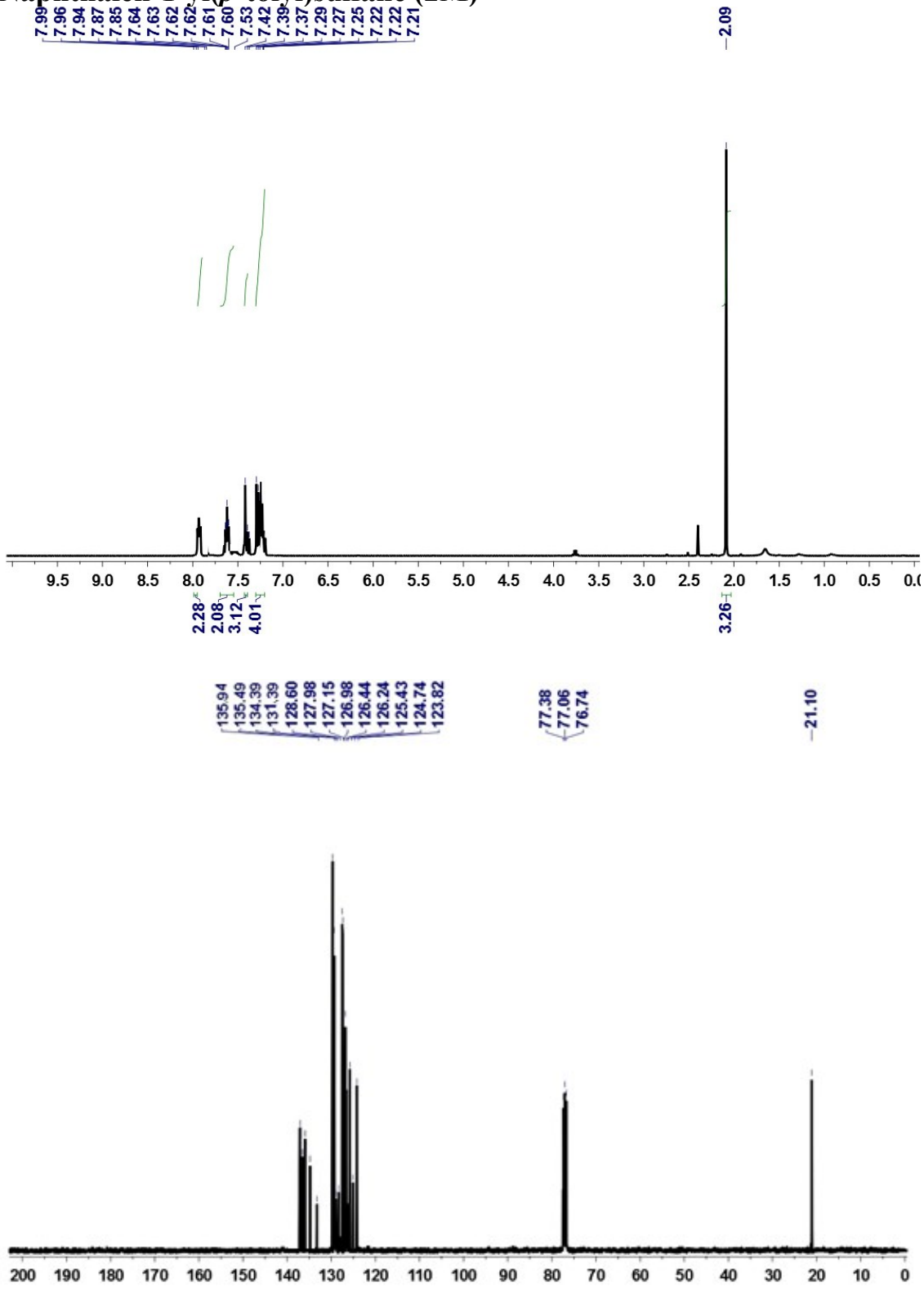
(*p*-nitryl phenyl) *p*tolyl- sulfide (2K)



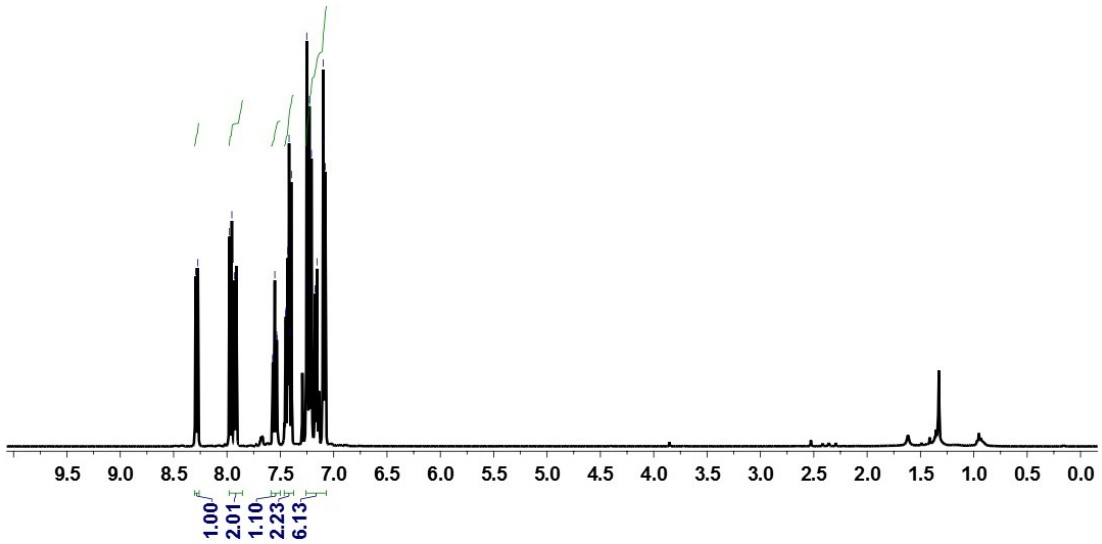
1-Naphthyl phenyl sulfide (2L)

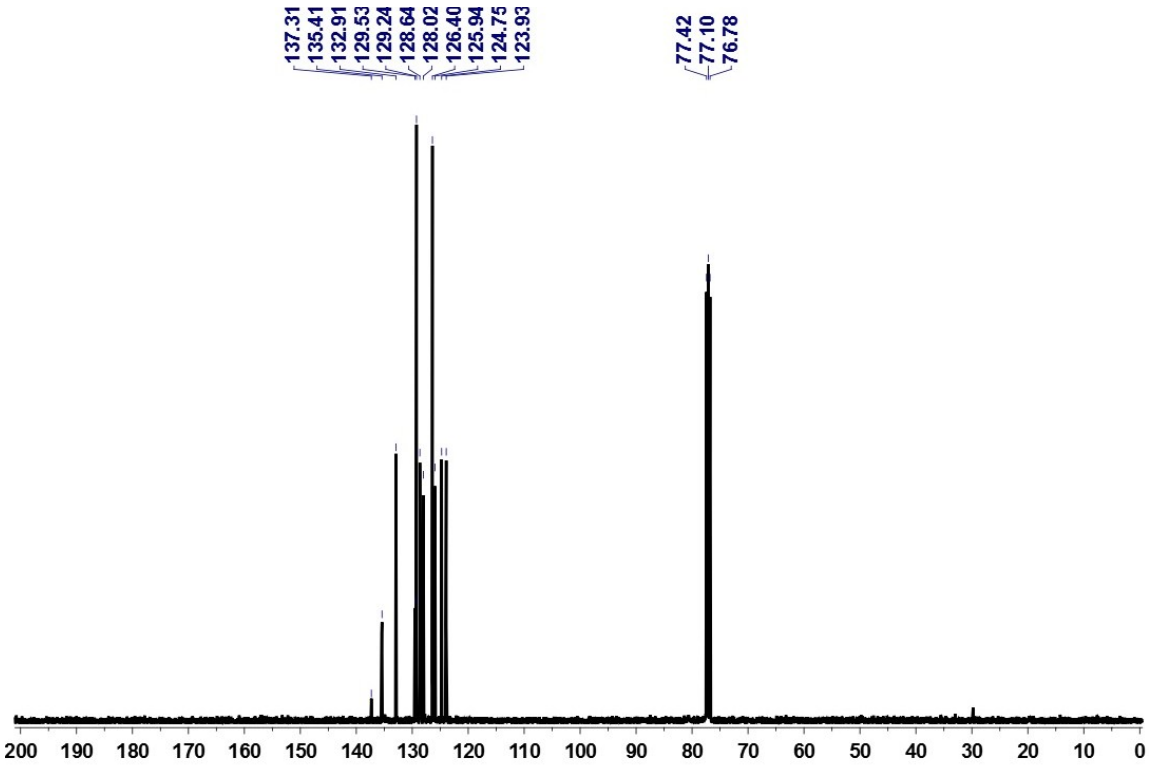


Naphthalen-1-yl(*p*-tolyl)sulfane (2M)

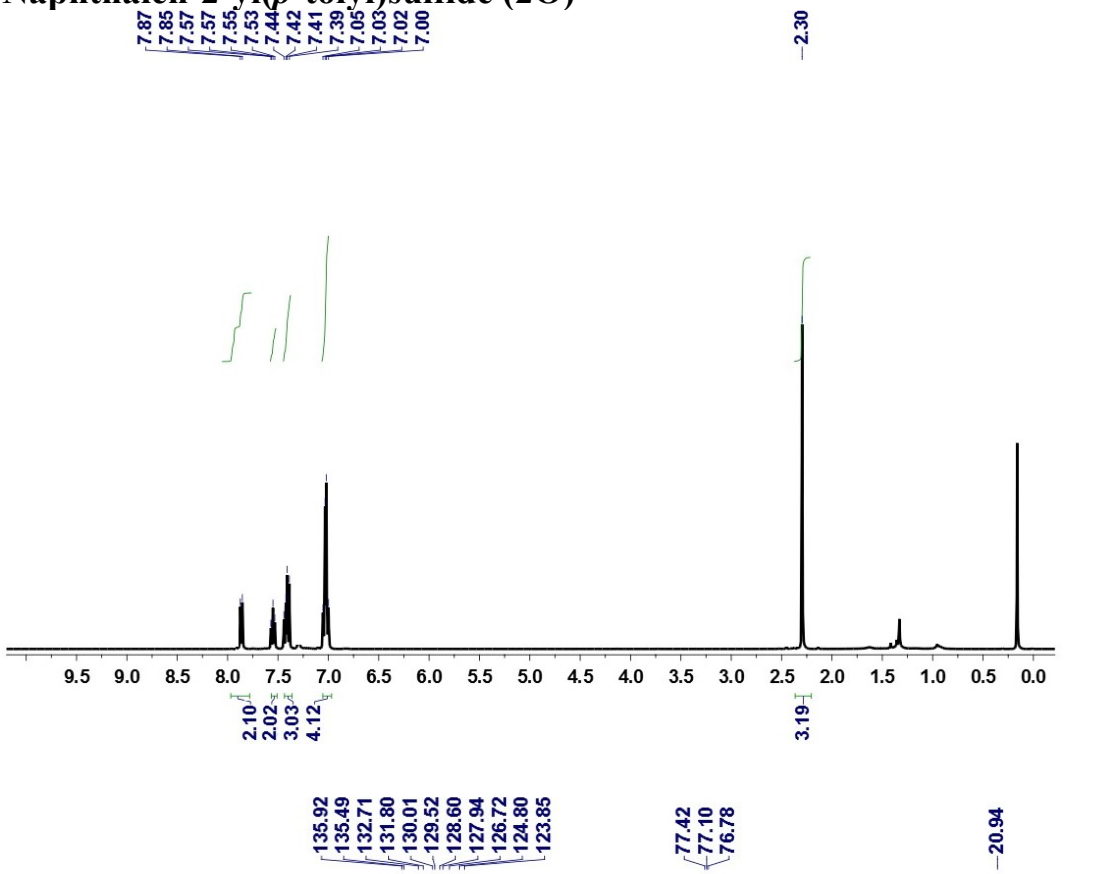


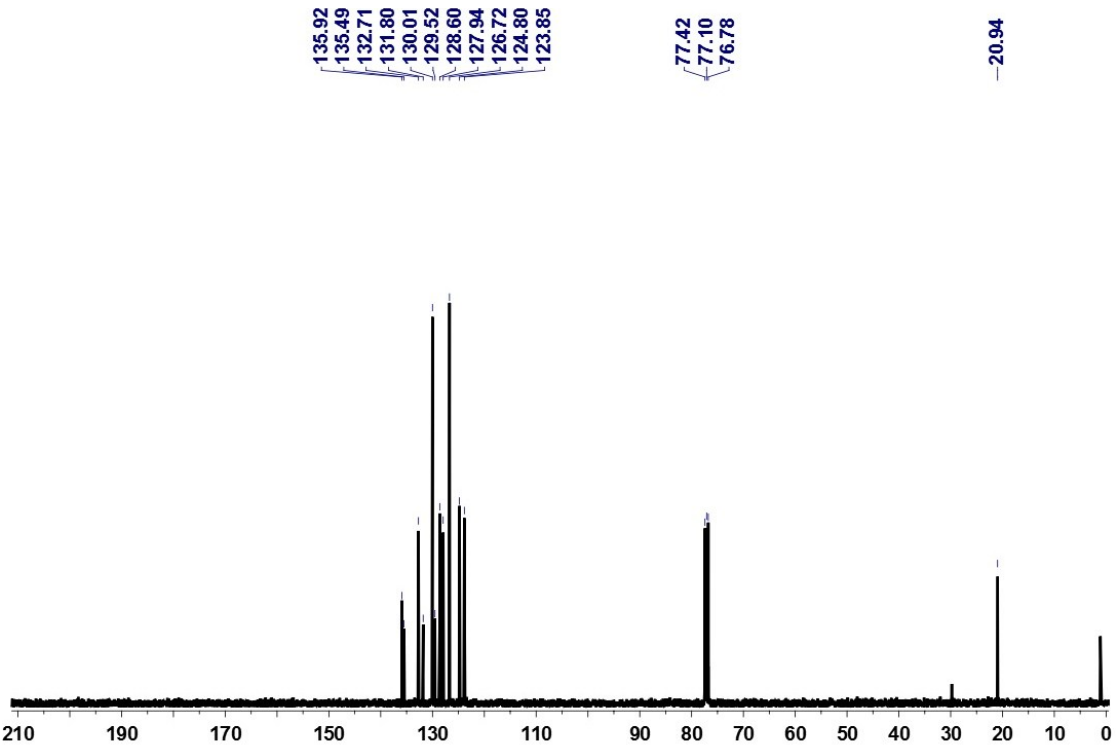
2-Naphthyl phenyl sulfide (2N)



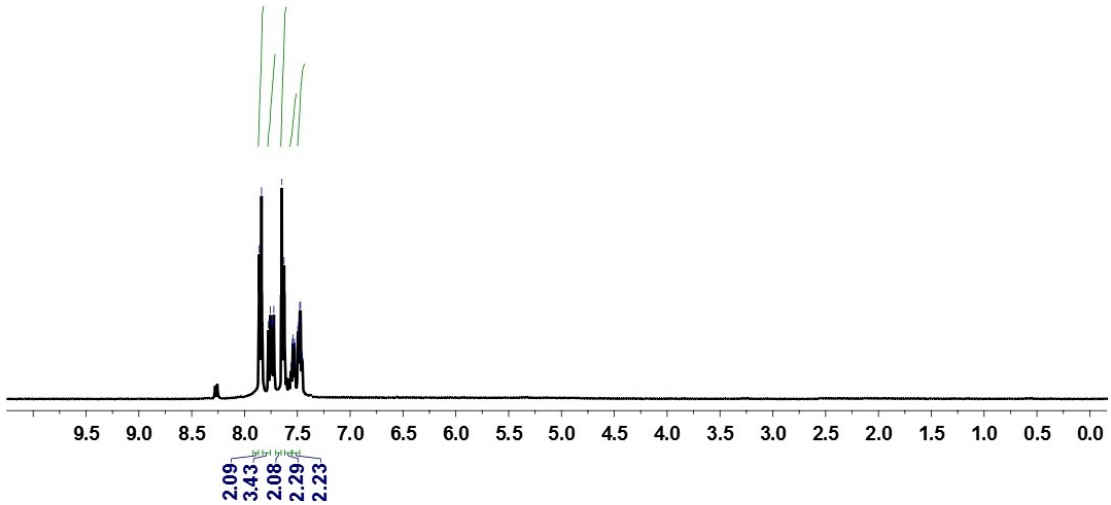


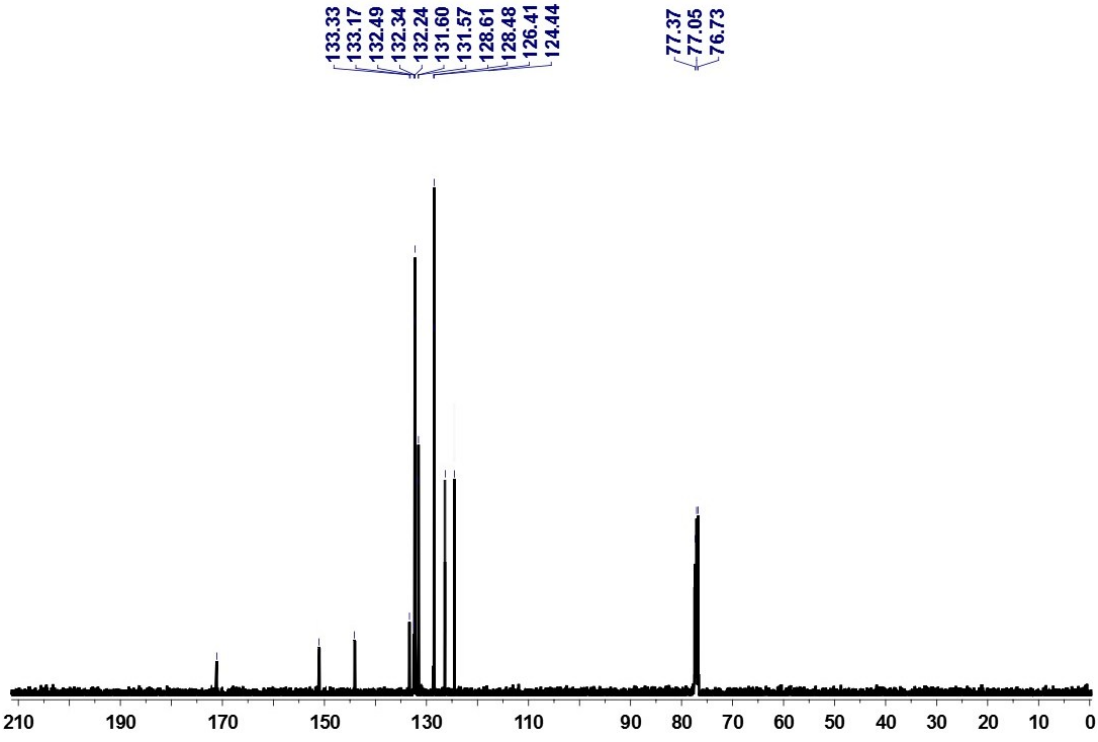
Naphthalen-2-yl(*p*-tolyl)sulfide (2O)



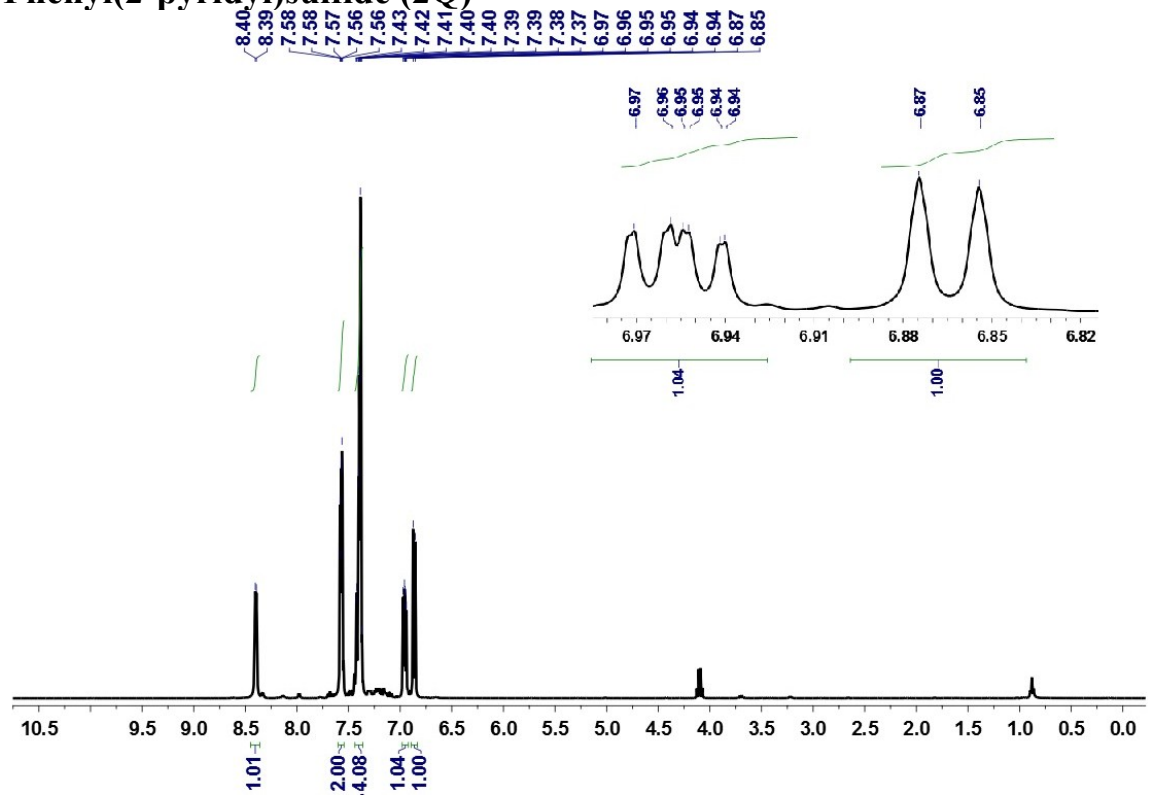


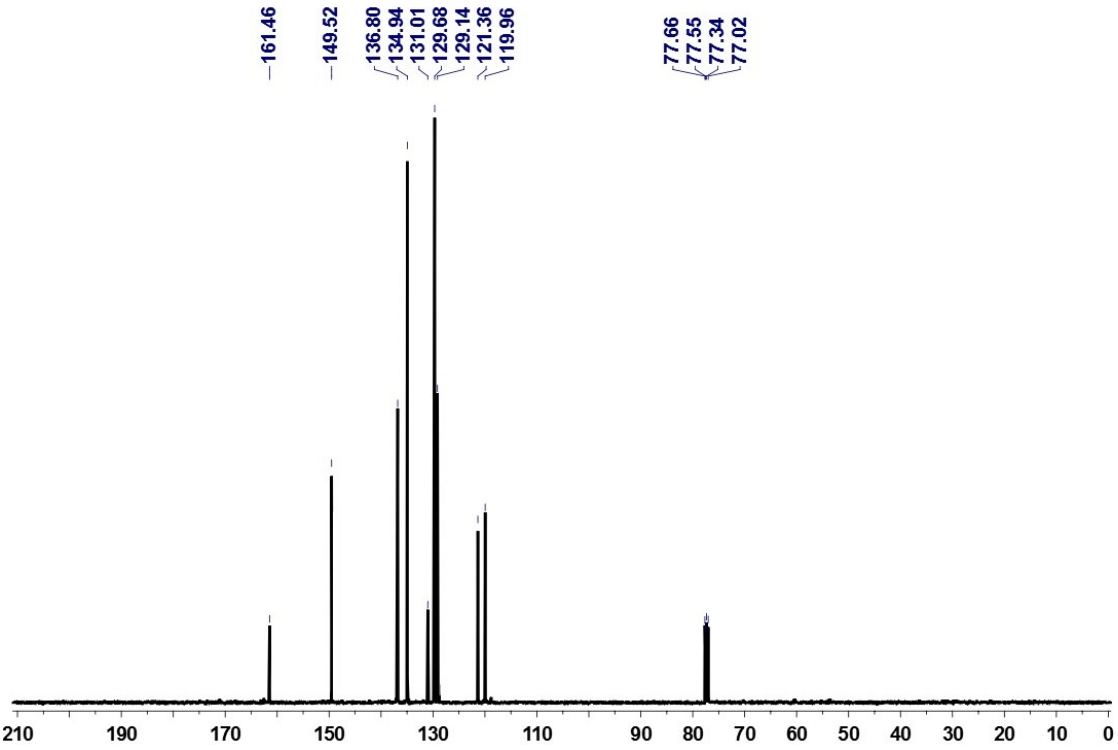
2-Naphthyl *p*-Nitrophenyl Sulfide (2P)



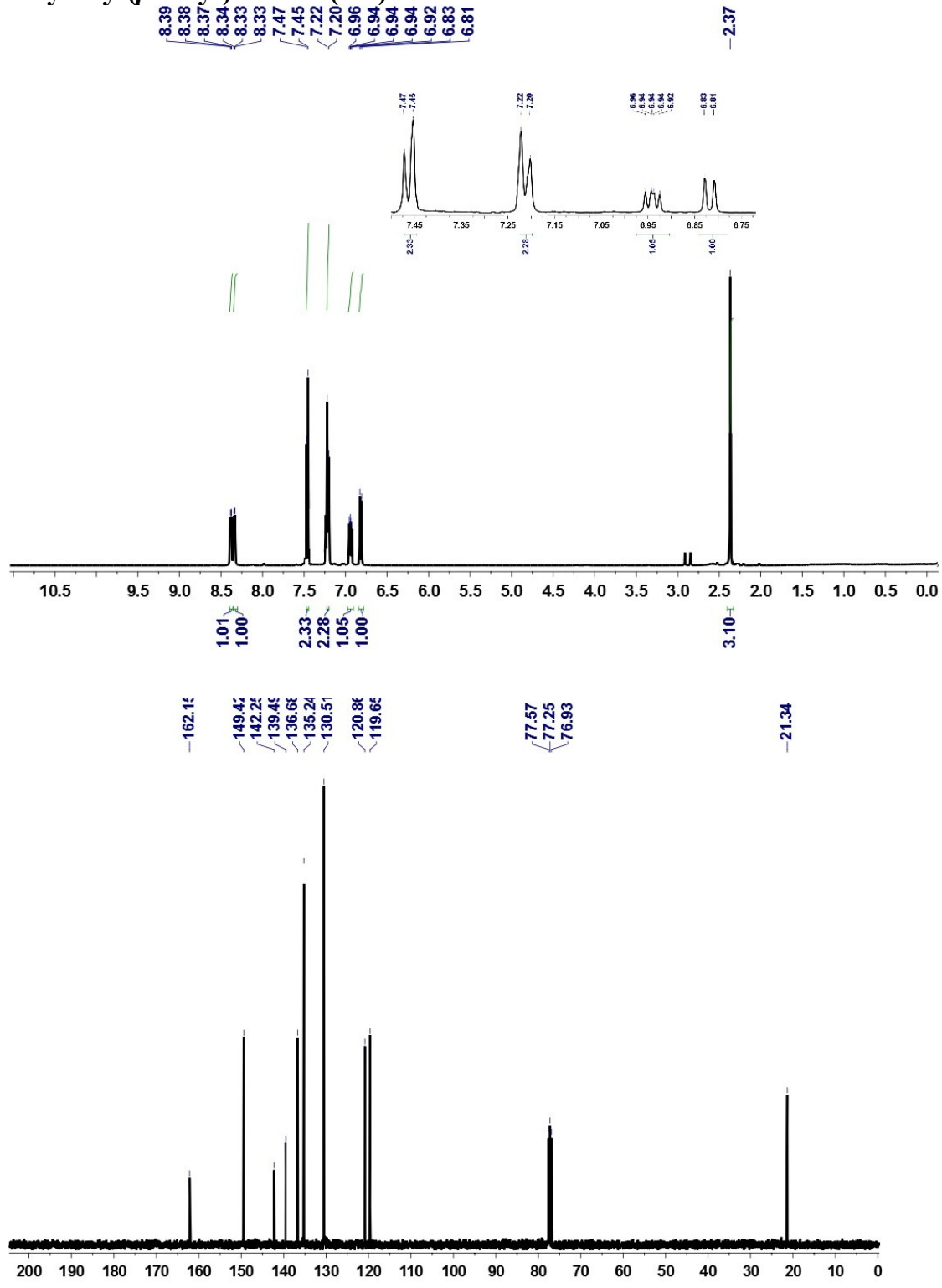


Phenyl(2-pyridyl)sulfide (2Q)

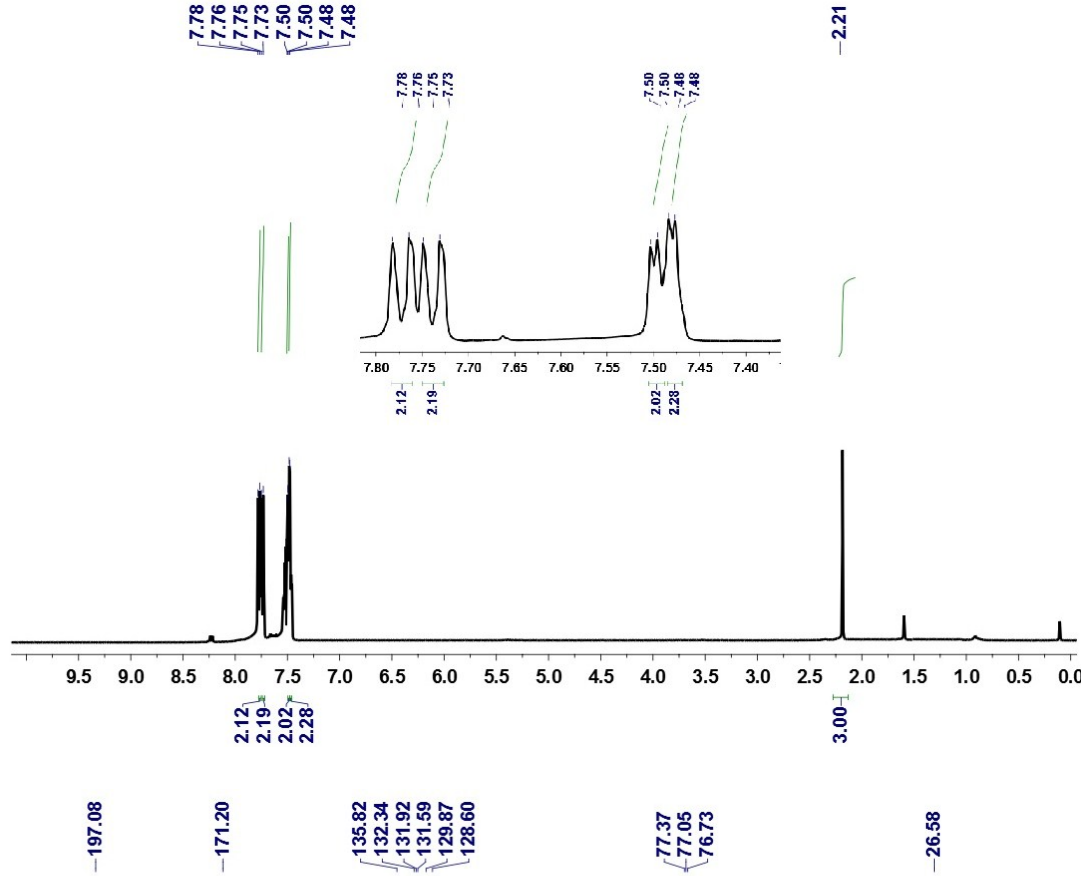


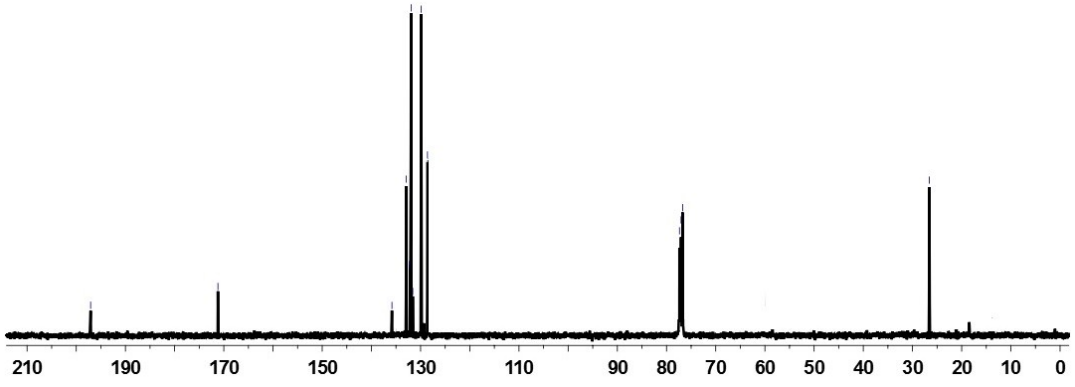


2-Pyridyl(*p*-tolyl)sulfide (2R)

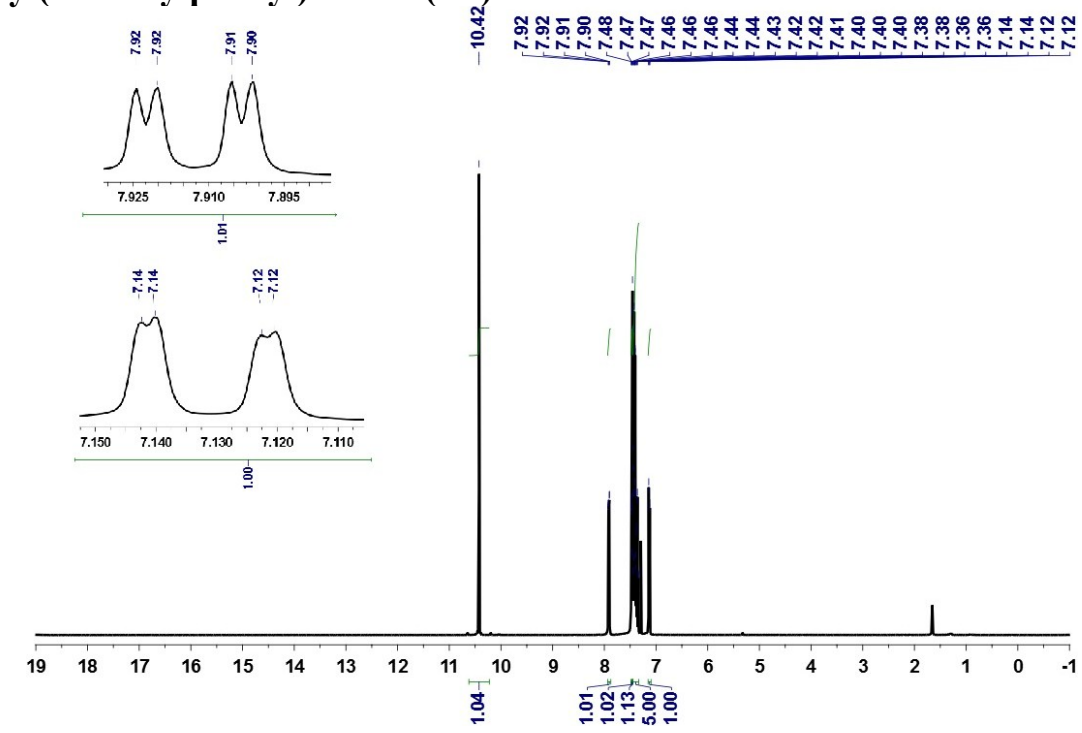


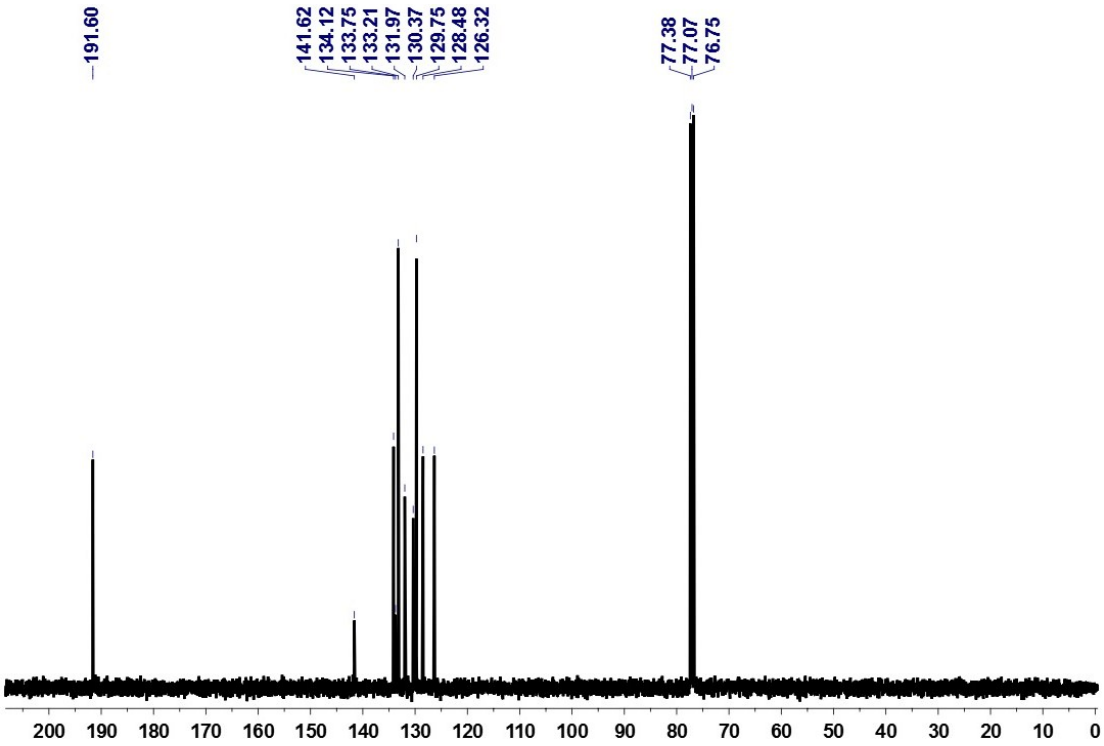
4-Acetylphenyl *p*-Nitrophenyl Sulfide (2S)



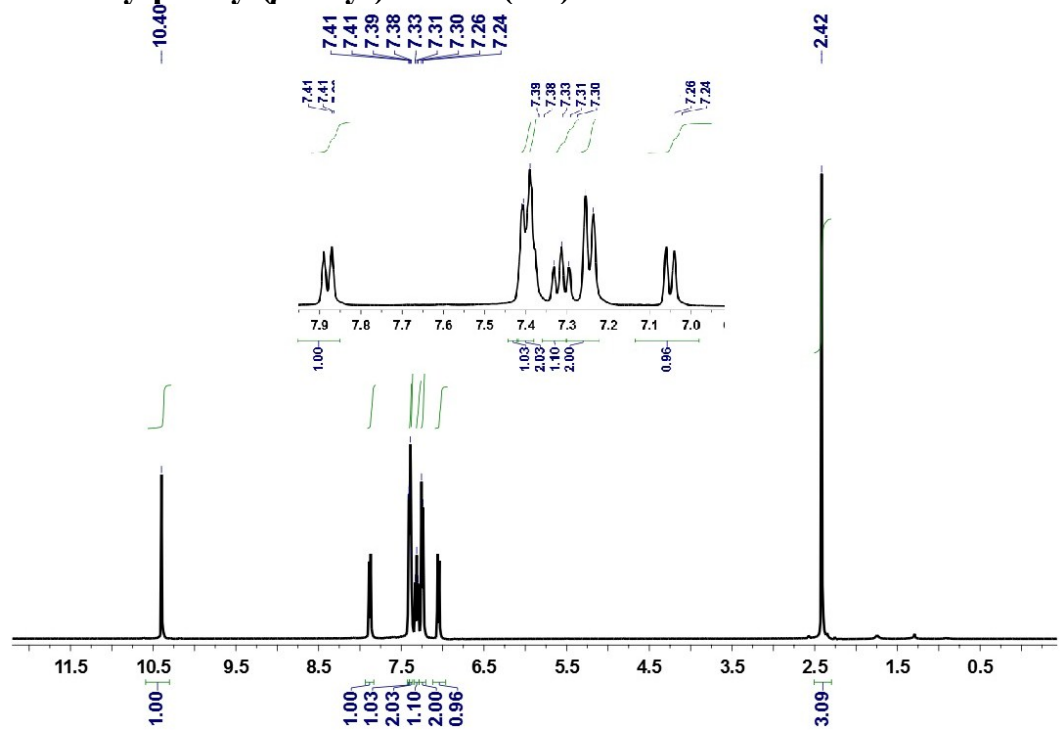


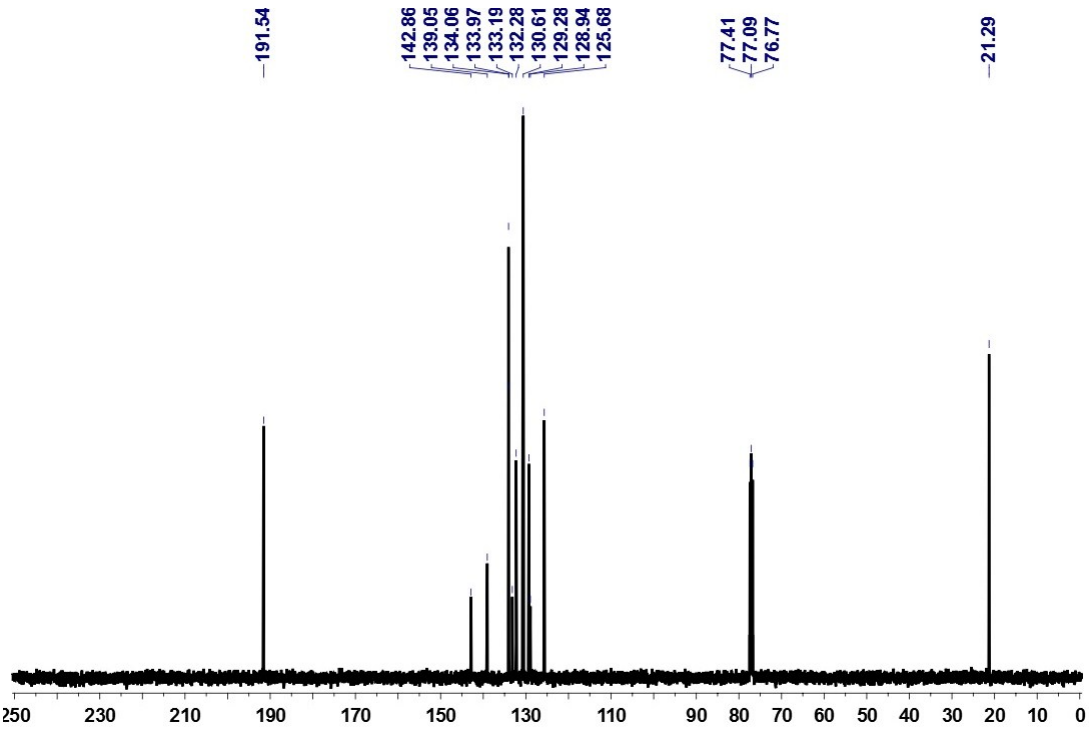
Phenyl(*o*-formylphenyl)sulfide (2T)



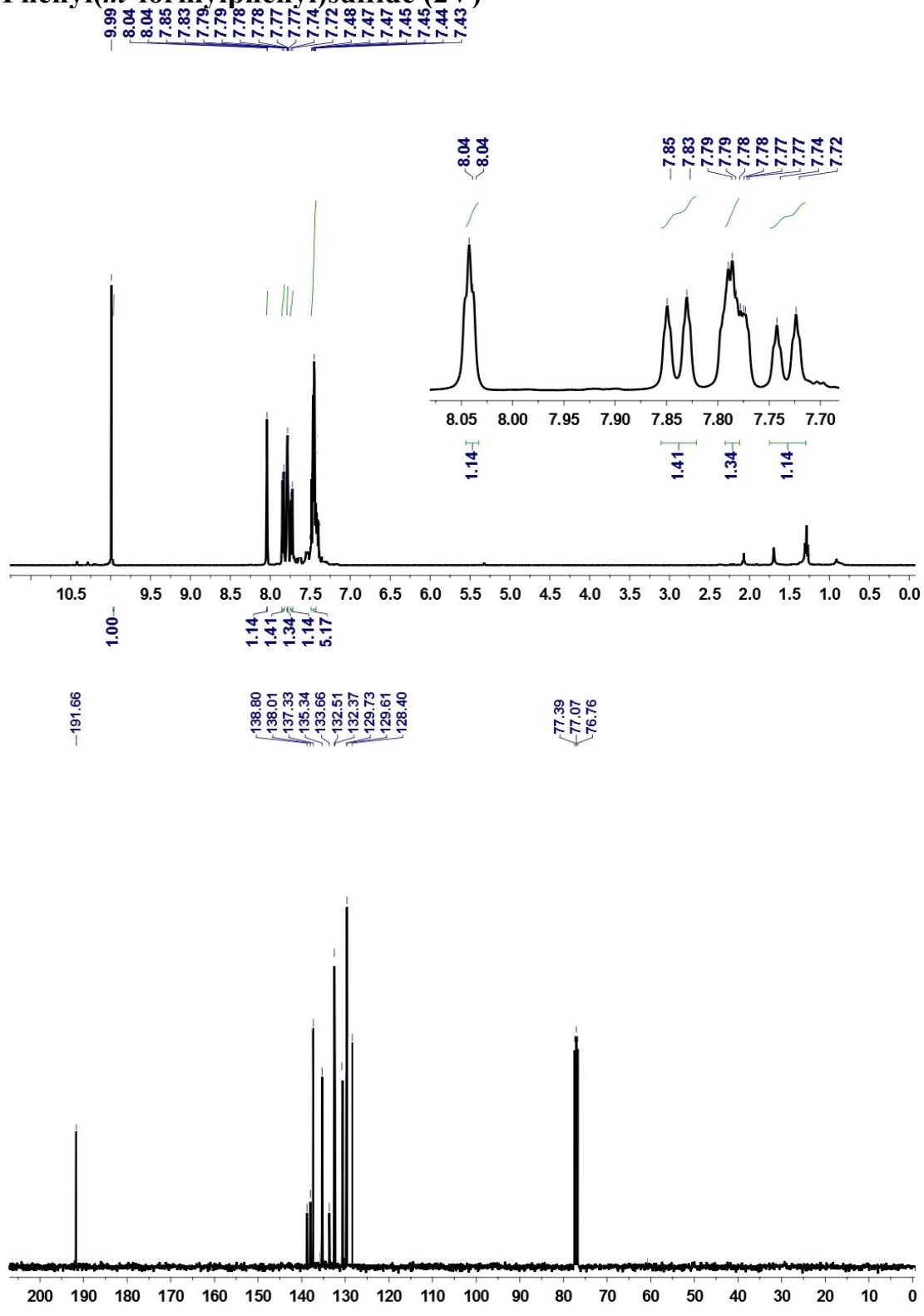


o-Formylphenyl(*p*-tolyl)sulfide (2U)

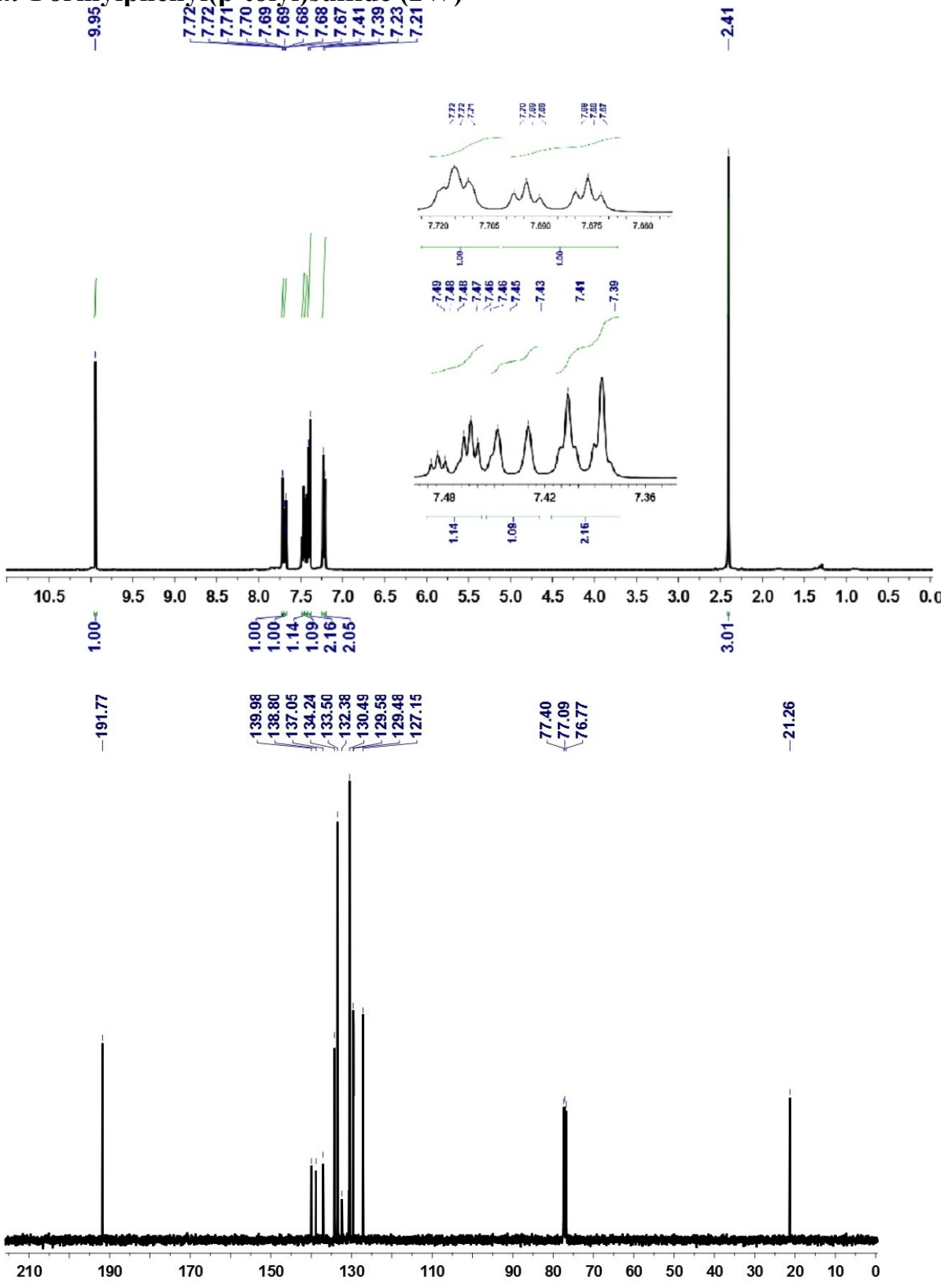




Phenyl(*m*-formylphenyl)sulfide (2V)



m-Formylphenyl(p-tolyl)sulfide (2W)



References

[1] Lee, J. Y.; Lee, P. H. *J. Org. Chem.* **2008**, *73*, 7413

[2] Fernandez-Rodreguez, M. A.; Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 2180.

[3] Park, N.; Park, K.; Jang, M.; Lee, S. *J. Org. Chem.* **2011**, *76*, 4371.

[4] Kuhn, M.; Falk, F. C.; Paradies, J. *Org. Lett.* **2011**, *13*, 4100.

[5] Rostami, A. Rostami, A. Ghaderi, A. Gholinejad, M. and Gheisarzadeh,S. *Synthesis.* **2017**, *49*, 5028

[6] Prasad, D. J. C.; Sekar, G. *Org. Lett.* **2011**, *13*, 1008.

[7] Singh, N.; Singh, R.; Raghuvanshi, D. S.; Singh, K. N. *Org. Lett.* **2013**, *15*, 5874.

[8] Sheng-Rong, G.; Yan-Gain, Y.; Li-Jin, W. *J. Sulfur Chem*. **2009**, *30*, 10.