Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Sustainable Carbonaceous Nanomaterial Supported Palladium as an Efficient Ligand-Free Heterogeneous Catalyst for Suzuki-Miyaura Coupling

Apoorva Shetty et al

The analytical data of biphenyl derivatives

1. **[1,1'-biphenyl]-4-ol (1f):** ^{1}H NMR (400 MHz, DMSO) δ 9.55 (s, 1H), 7.60 – 7.53 (m, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H); MS, *m/z* (%): 170 [M^{+}].

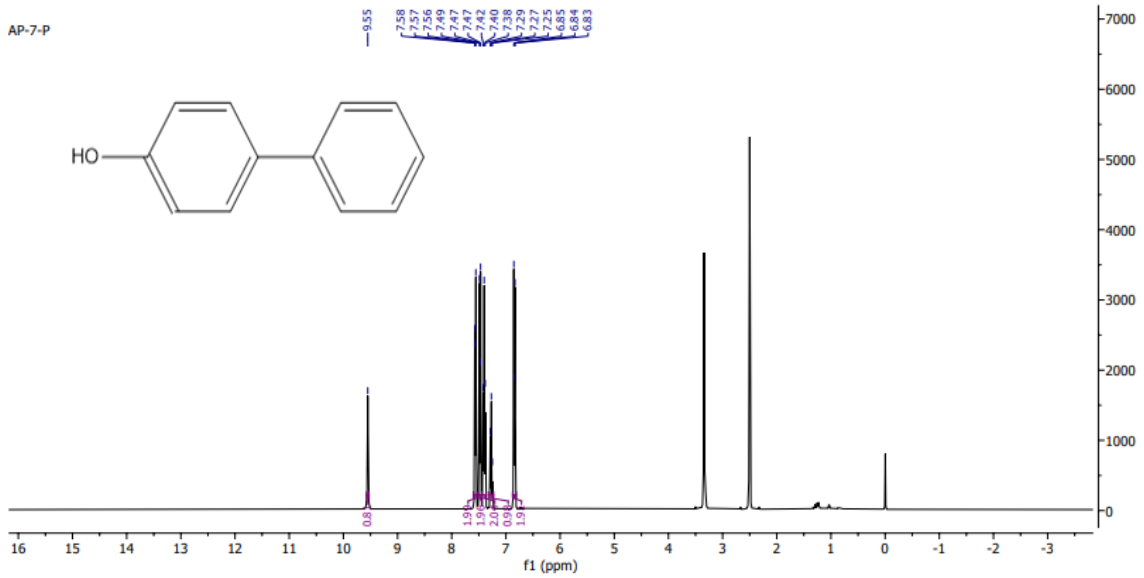


Figure 1A: ^{1}H NMR (400 MHz, DMSO) of [1,1'-biphenyl]-4-ol (1f)

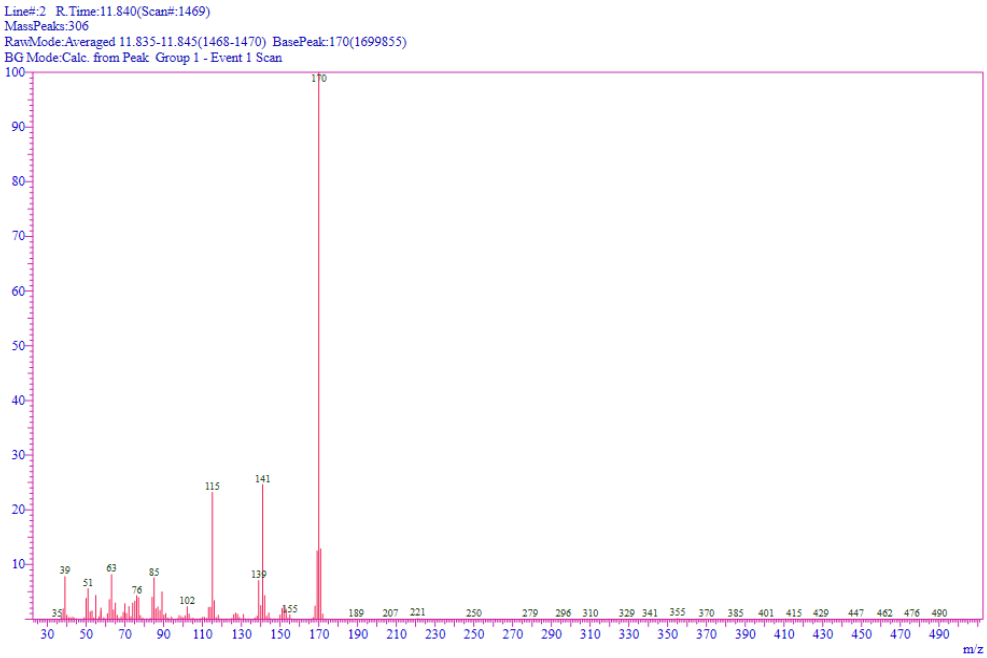


Figure 1B: GC-MS spectrum of [1,1'-biphenyl]-4-ol (1f)

2. 4-(naphthalen-1-yl)phenol (2f): MS, *m/z* (%): 220 [M^+].

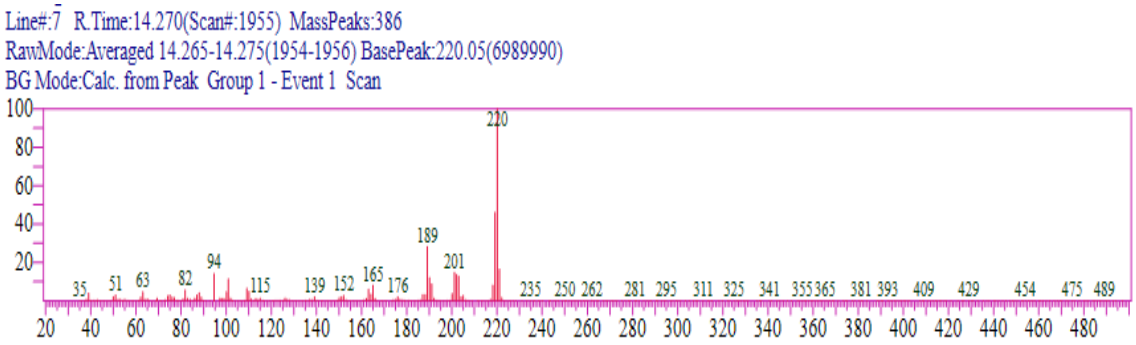


Figure 2A: GC-MS spectrum of 4-(naphthalen-1-yl)phenol (2f)

3. **4'-methoxy-[1,1'-biphenyl]-4-ol (3f):** ^{1}H NMR (400 MHz, DMSO) δ 9.45 (s, 1H), 7.49 (dd, J = 8.5, 1.5 Hz, 2H), 7.41 (dd, J = 8.4, 1.5 Hz, 2H), 6.97 (dd, J = 8.5, 1.5 Hz, 2H), 6.81 (dd, J = 8.5, 1.5 Hz, 2H), 3.77 (s, 3H); 13C NMR (101 MHz, DMSO) δ 158.11, 156.51, 132.76, 130.75, 127.24, 127.02, 115.64, 114.23, 55.12; MS, *m/z* (%): 200 [M^{+}].

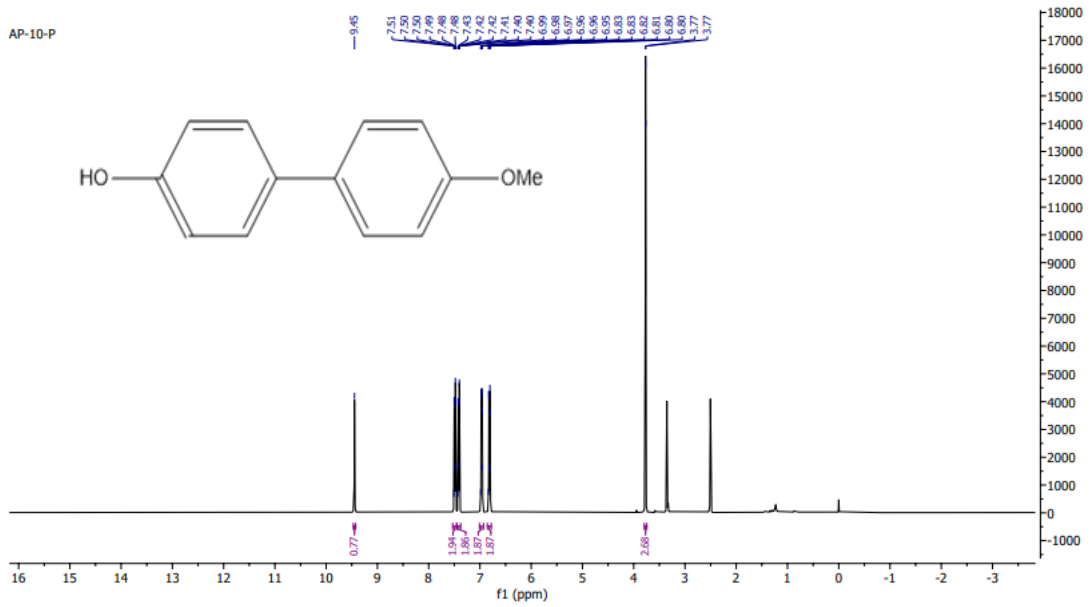


Figure 3A: ^{1}H NMR (400 MHz, DMSO) of 4'-methoxy-[1,1'-biphenyl]-4-ol (3f)

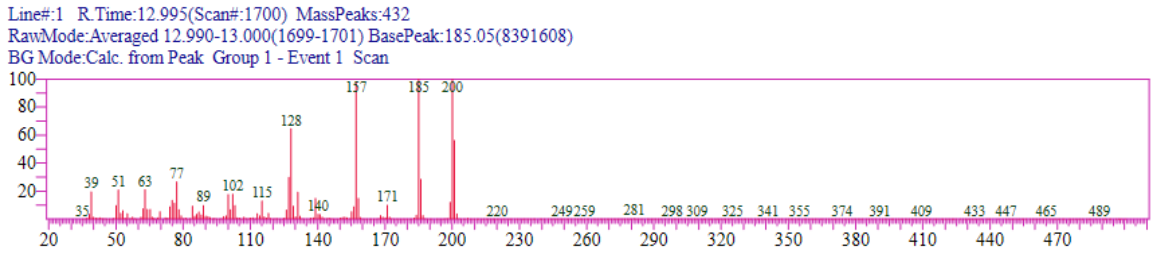


Figure 3B: GC-MS spectrum of 4'-methoxy-[1,1'-biphenyl]-4-ol (3f)

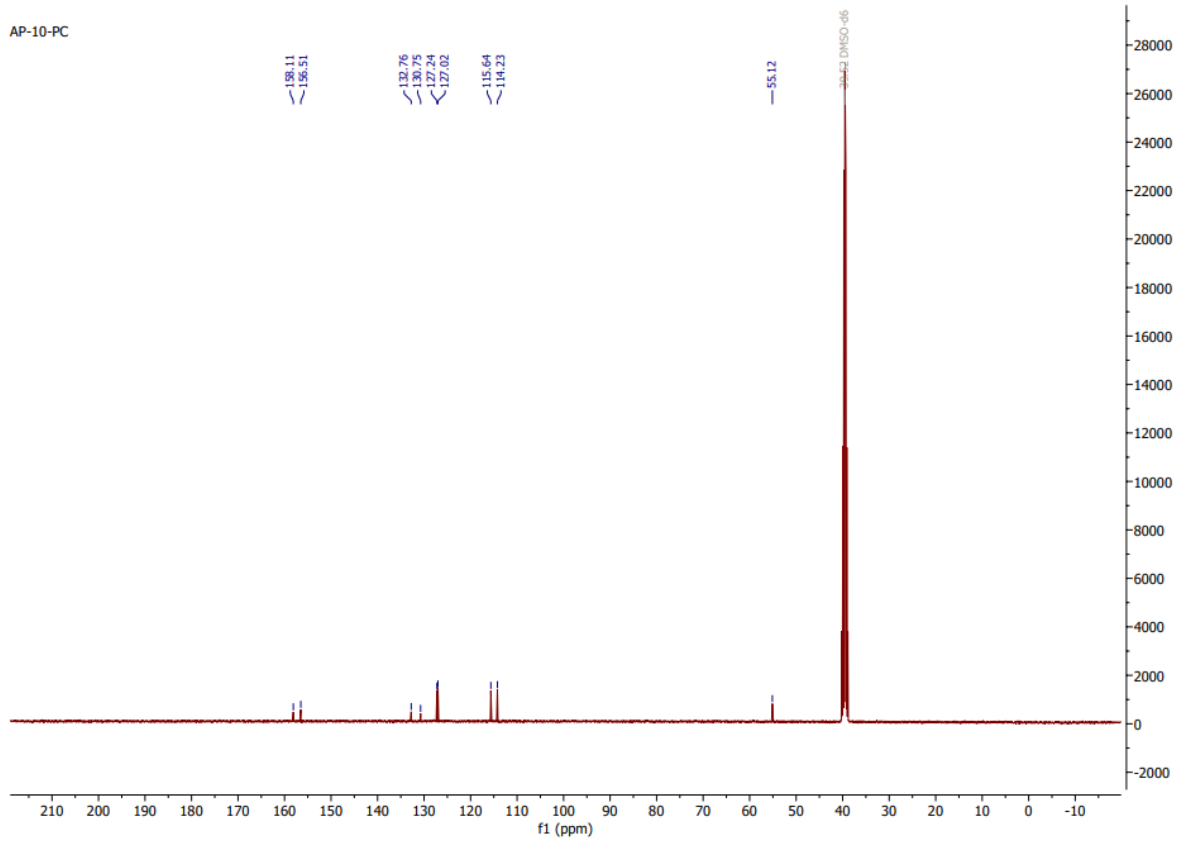


Figure 3C: 13C NMR (101 MHz, DMSO) of 4'-methoxy-[1,1'-biphenyl]-4-ol (3f)

4. **4-methoxy-1,1'-biphenyl (4f) :** ^{1}H NMR (400 MHz, DMSO) δ 7.61 (dd, J = 8.4, 3.1 Hz, 4H), 7.43 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 3.80 (s, 3H.MS, *m/z* (%): 184 [M^{+}].

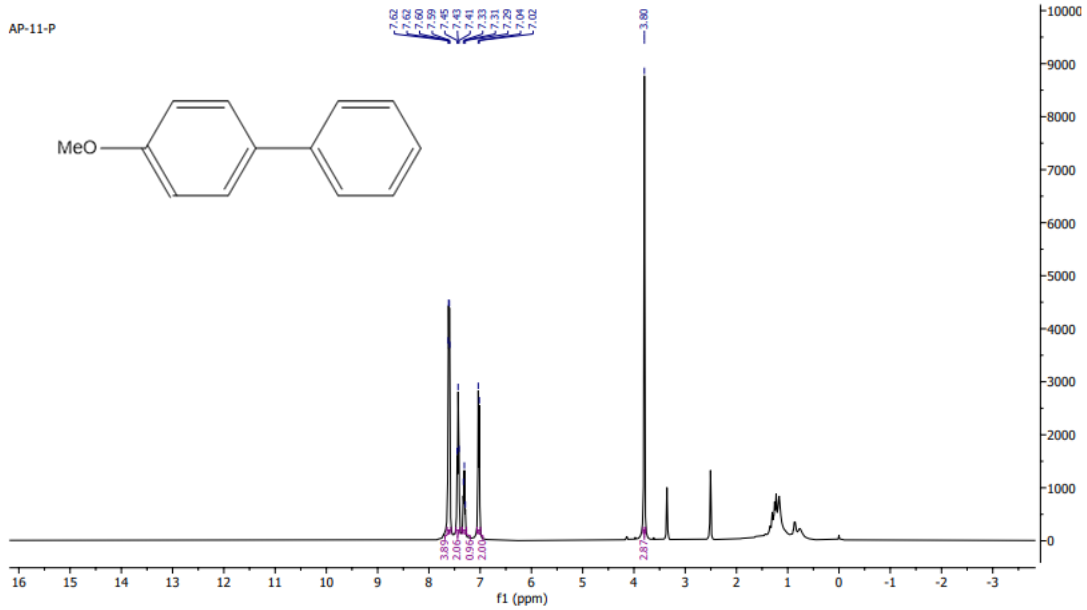


Figure 4A: ^{1}H NMR (400 MHz, DMSO) of 4-methoxy-1,1'-biphenyl (4f)

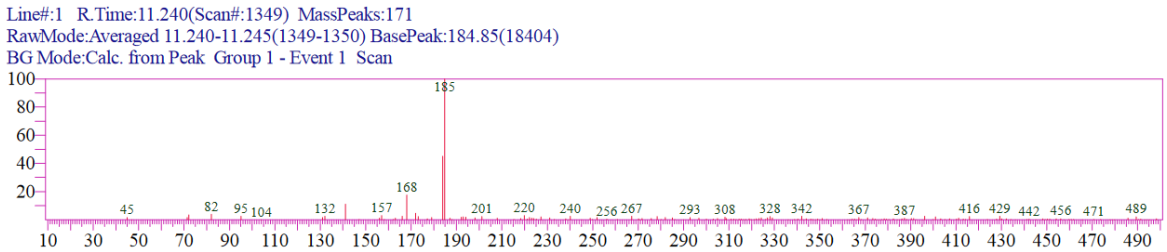


Figure 4B: GC-MS spectrum of 4-methoxy-1,1'-biphenyl (4f)

5. **1-(4-methoxyphenyl)naphthalene (5f):** ^{1}H NMR (400 MHz, DMSO) δ 8.03 – 7.96 (m, 1H), 7.92 (dd, J = 8.3, 1.2 Hz, 1H), 7.83 (dd, J = 8.3, 1.4 Hz, 1H), 7.60 – 7.37 (m, 6H), 7.14 – 7.06 (m, 2H), 3.84 (s, 3H).MS, *m/z* (%): 234 [M^{+}].

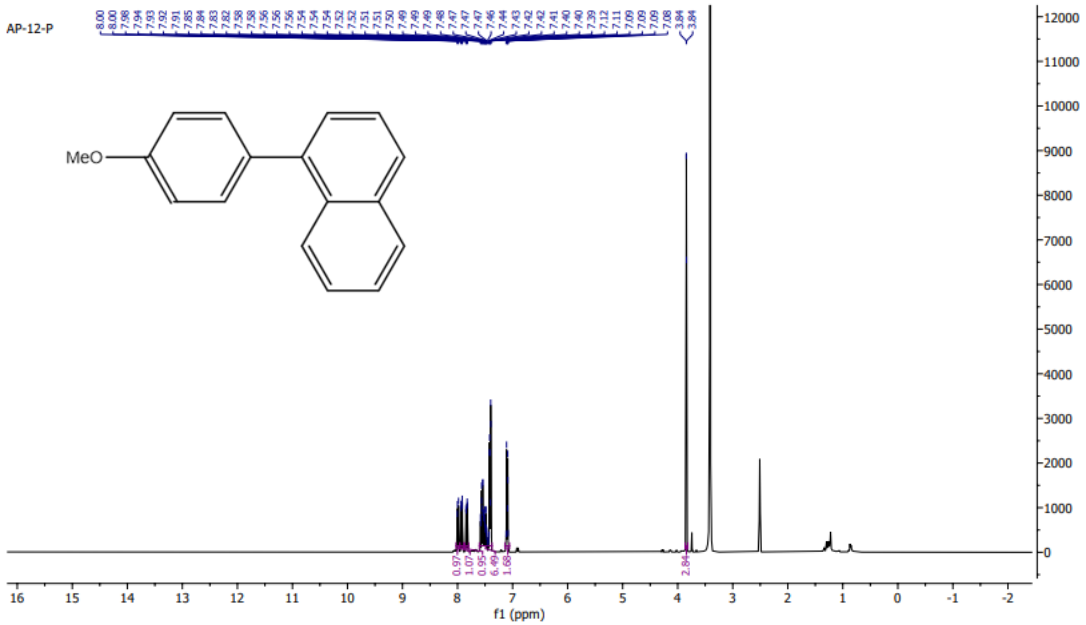


Figure 5A: ^{1}H NMR (400 MHz, DMSO) of 1-(4-methoxyphenyl)naphthalene (5f)

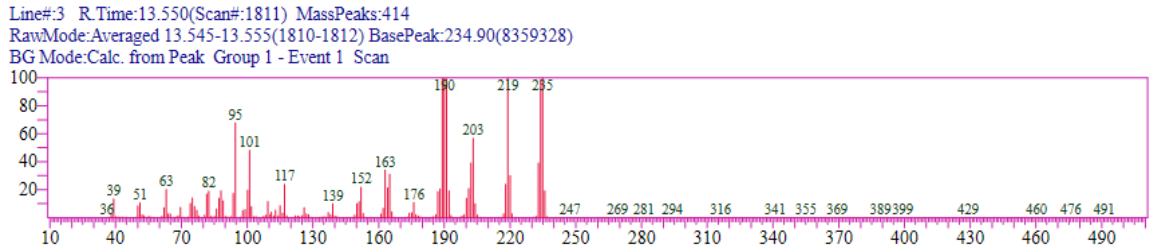


Figure 5B: GC-MS spectrum of 1-(4-methoxyphenyl)naphthalene (5f)

6. **4,4'-dimethoxy-1,1'-biphenyl (6f):** ^{1}H NMR (400 MHz, DMSO) δ 7.83 – 7.16 (m, 4H), 7.09 – 6.77 (m, 4H), 3.78 (s, 6H).MS, *m/z* (%): 214 [M^{+}].

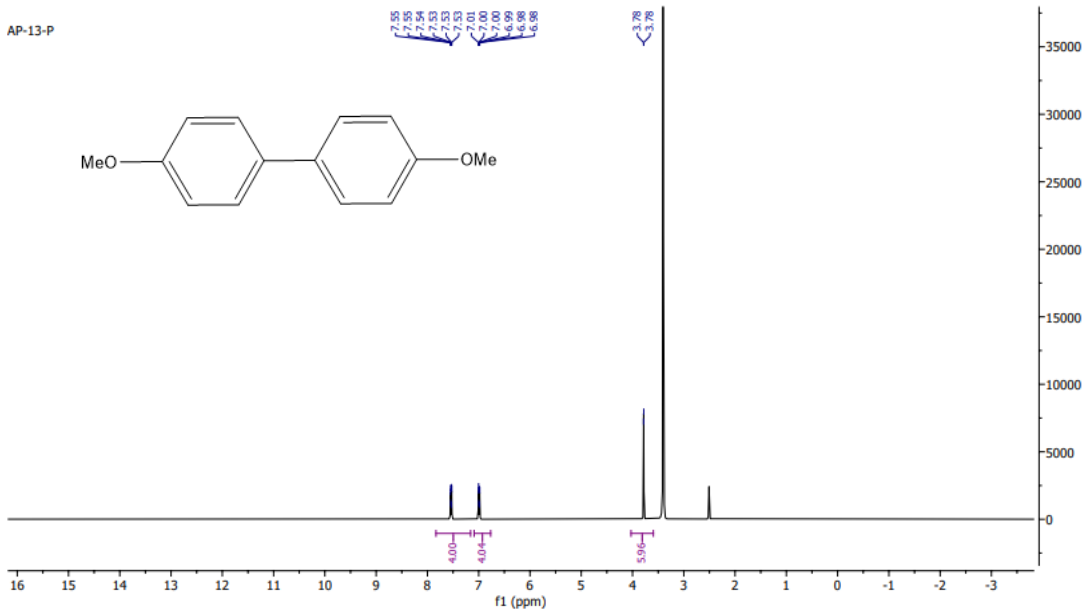


Figure 6A: ^{1}H NMR (400 MHz, DMSO) of 4,4'-dimethoxy-1,1'-biphenyl (6f)

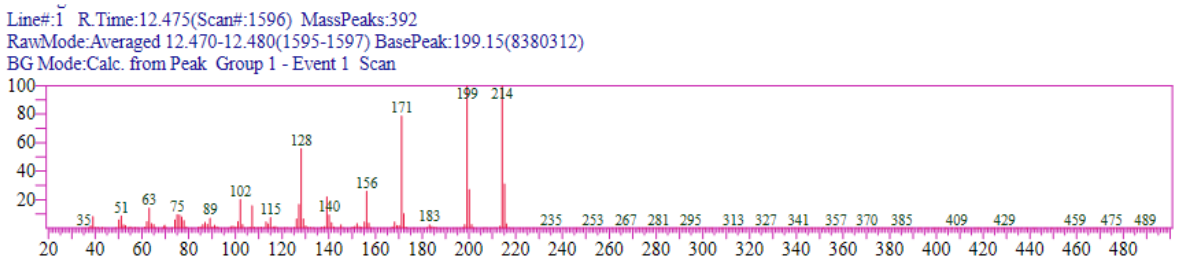


Figure 6B: GC-MS spectrum of 4,4'-dimethoxy-1,1'-biphenyl (6f)

7. **1,1'-biphenyl (7f):** ^{1}H NMR (400 MHz, DMSO) δ 8.06 (d, J = 0.9 Hz, 1H), 7.79 (dt, J = 7.8, 1.3 Hz, 1H), 7.66 (dd, J = 8.2, 1.4 Hz, 2H), 7.47 (dd, J = 8.3, 7.1 Hz, 3H), 7.44 – 7.36 (m, 1H), 7.39 – 7.29 (m, 2H). MS, *m/z* (%): 154 [M^{+}].

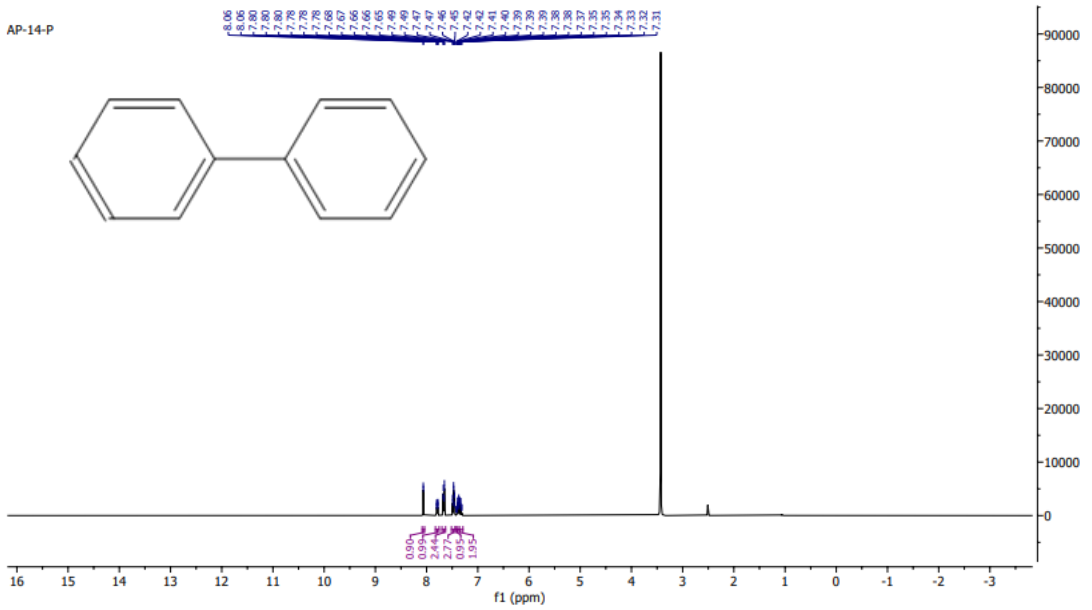


Figure 7A: ^{1}H NMR (400 MHz, DMSO) of 1,1'-biphenyl (7f)

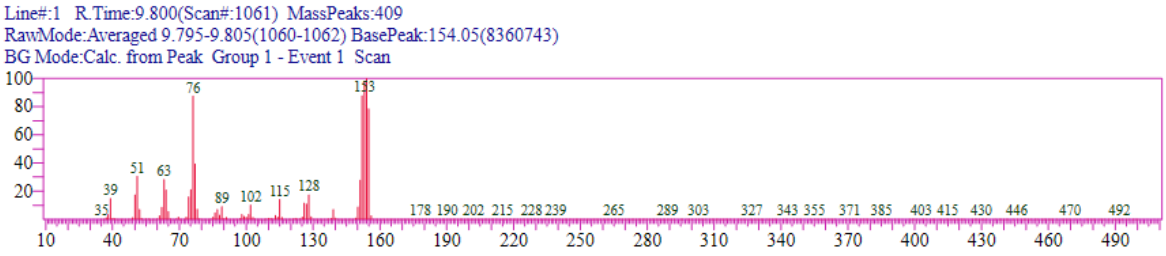


Figure 7B: GC-MS spectrum of 1,1'-biphenyl (7f)

8. **1-phenylnaphthalene (8f):** ^{1}H NMR (400 MHz, DMSO) δ 7.99 (dd, J = 18.8, 8.2 Hz, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.63 – 7.40 (m, 9H). MS, *m/z* (%): 204 [M^{+}].

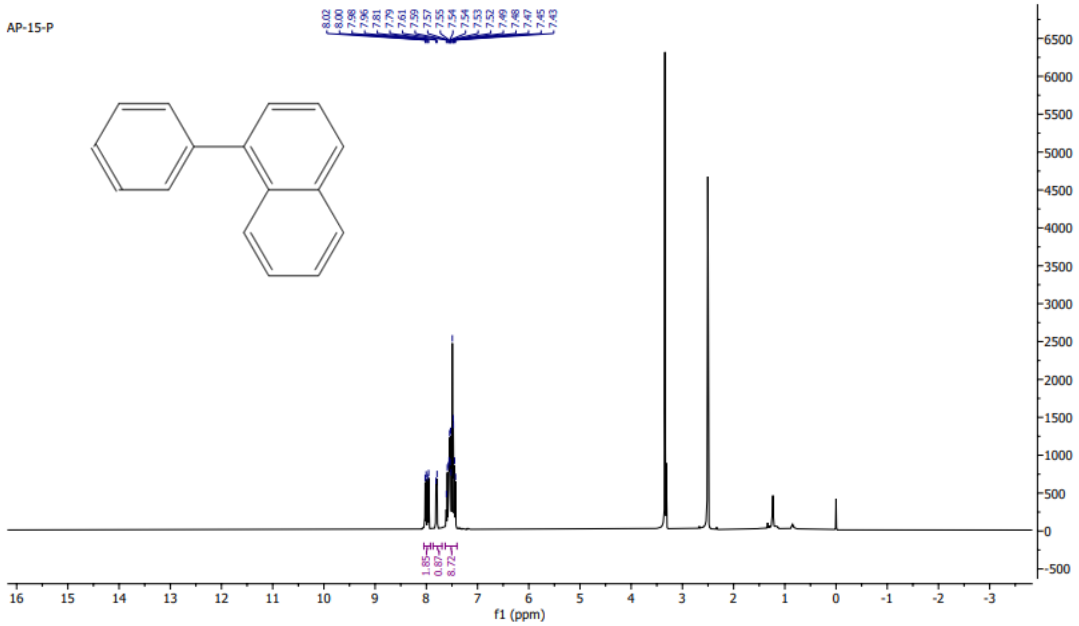


Figure 8A: ^{1}H NMR (400 MHz, DMSO) of 1-phenylnaphthalene (8f)

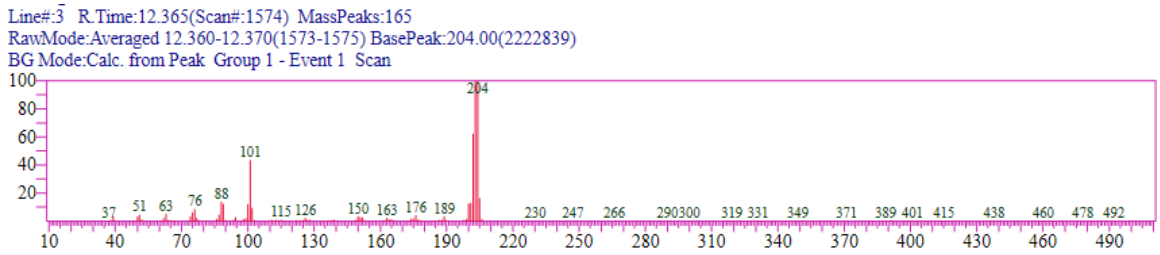


Figure 8B: GC-MS spectrum of 1-phenylnaphthalene (8f)

9. **4-methoxy-1,1'-biphenyl (9f):** ^{1}H NMR (400 MHz, DMSO) δ 7.65 – 7.57 (m, 4H), 7.43 (dd, J = 8.3, 7.1 Hz, 2H), 7.31 (td, J = 7.2, 1.3 Hz, 1H), 7.07 – 7.00 (m, 2H), 3.80 (s, 3H); 13C NMR (101 MHz, DMSO) δ 158.89, 139.84, 132.53, 128.86, 127.76, 126.70, 126.18, 114.36, 55.17; MS, *m/z* (%): 184 [M^{+}].

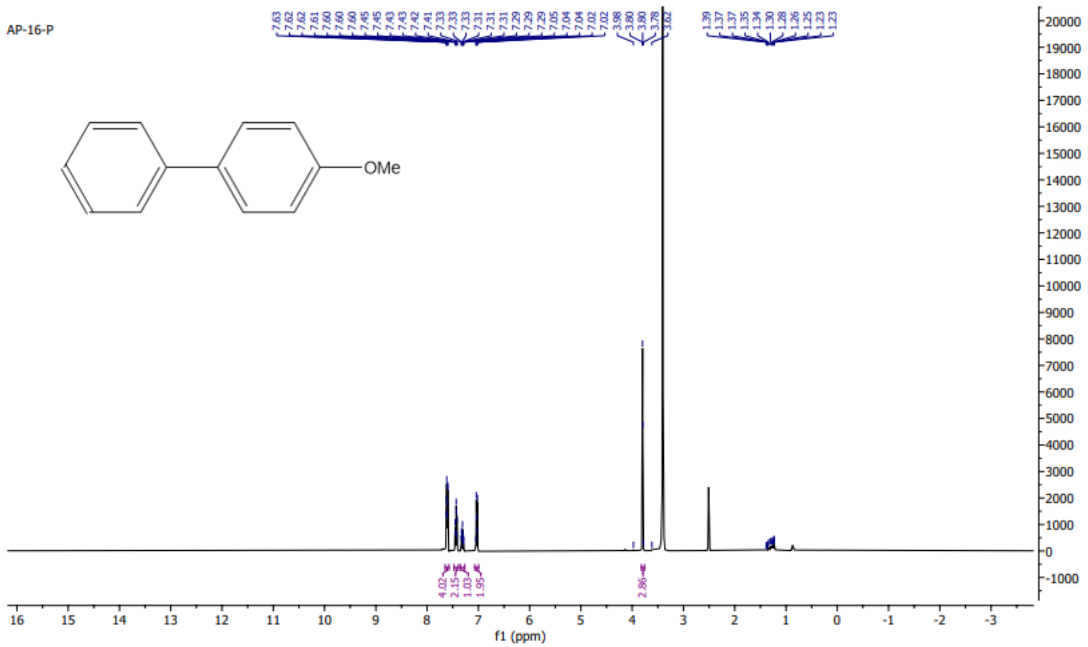


Figure 9A: ^{1}H NMR (400 MHz, DMSO) of 4-methoxy-1,1'-biphenyl (9f)

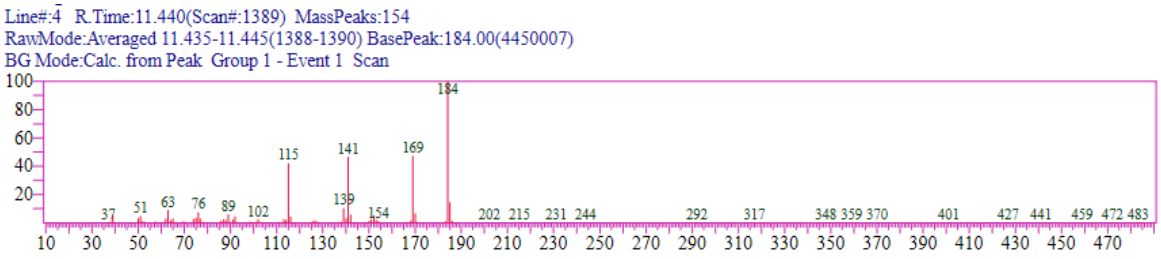


Figure 9B: GC-MS spectrum of 4-methoxy-1,1'-biphenyl (9f)

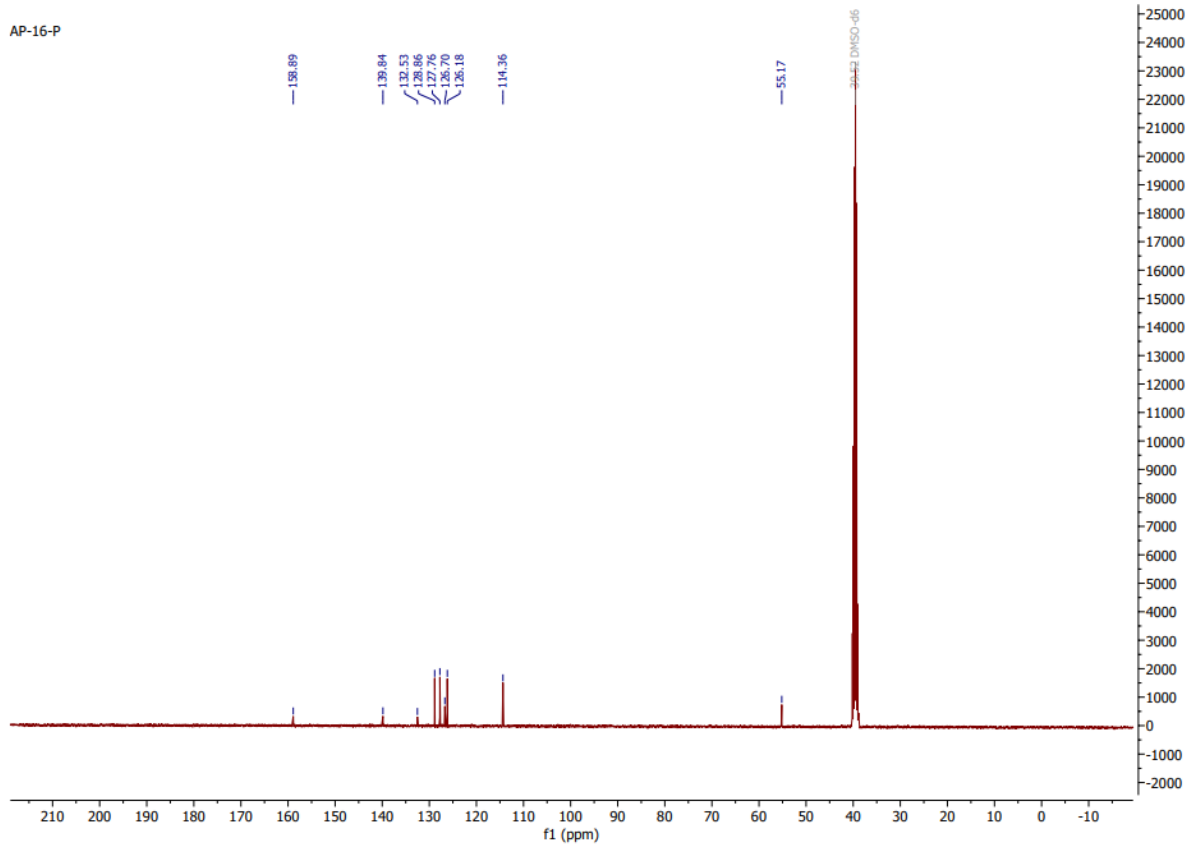


Figure 9C: 13C NMR (101 MHz, DMSO) of 4-methoxy-1,1'-biphenyl (9f)

10. **4-nitro-1,1'-biphenyl (10f):** ^{1}H NMR (400 MHz, DMSO) δ 8.35 – 8.27 (m, 2H), 8.01 – 7.93 (m, 2H), 7.83 – 7.76 (m, 2H), 7.59 – 7.44 (m, 3H); 13C NMR (101 MHz, DMSO) δ 146.46, 146.41, 137.61, 129.03, 128.85, 127.65, 127.06, 123.88; MS, *m/z* (%): 199 [M^{+}].

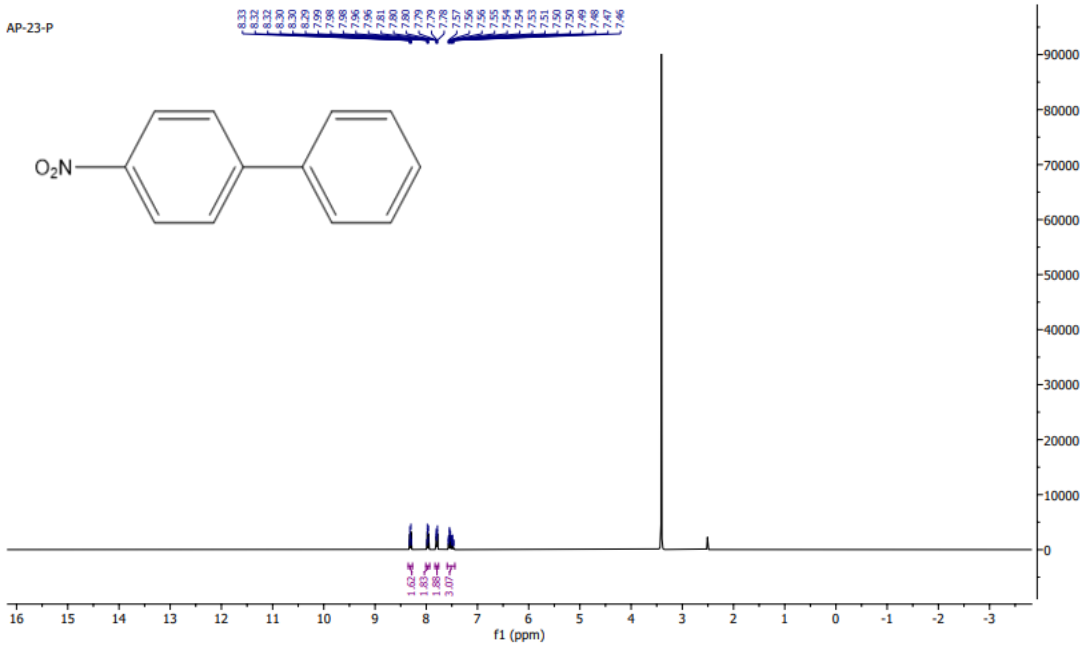


Figure 10A: ^{1}H NMR (400 MHz, DMSO) of 4-nitro-1,1'-biphenyl (10f)

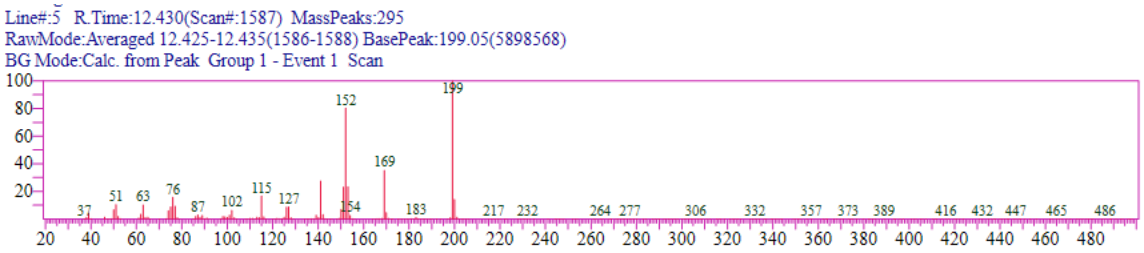


Figure 10B: GC-MS spectrum of 4-nitro-1,1'-biphenyl (10f)

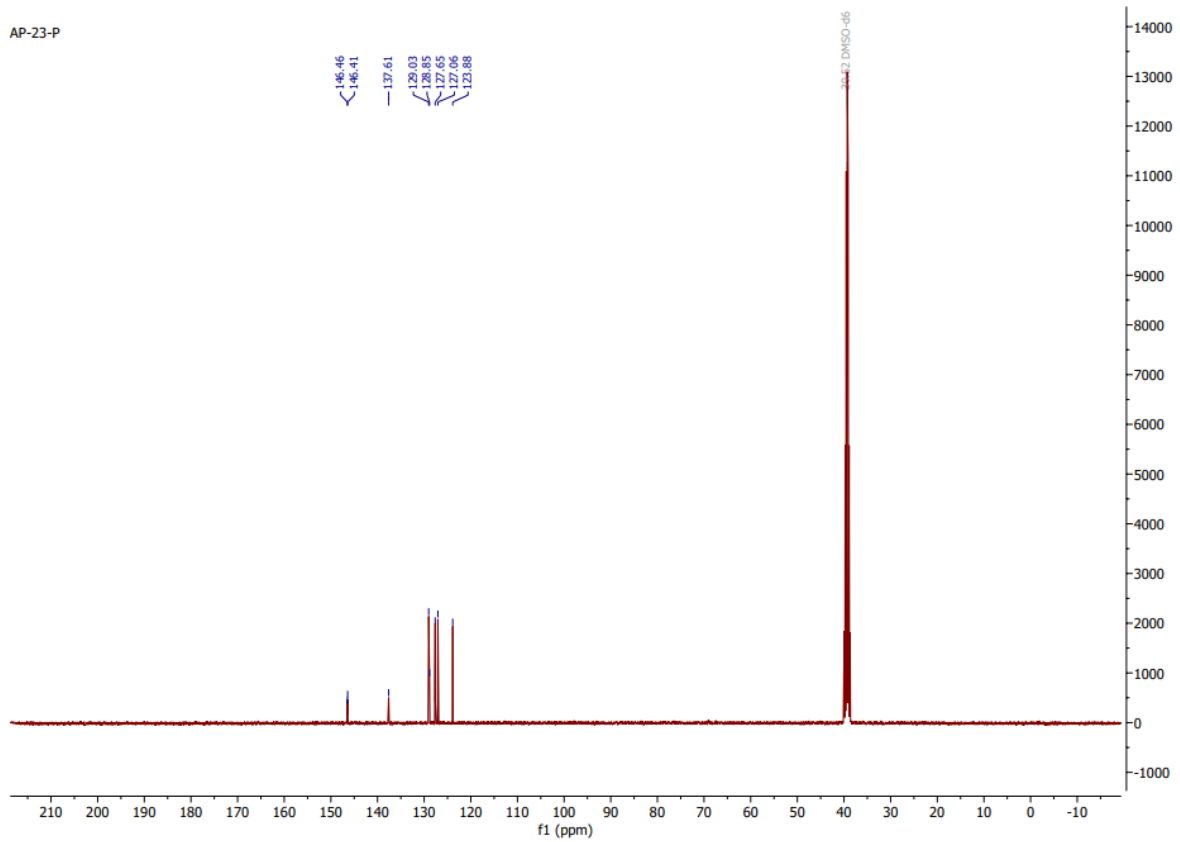


Figure 10C: 13C NMR (101 MHz, DMSO) of 4-nitro-1,1'-biphenyl (10f)

11. **1-(4-nitrophenyl)naphthalene (11f):** ^{1}H NMR (400 MHz, DMSO) δ 8.38 (dt, J = 8.4, 1.9 Hz, 2H), 8.09 – 8.02 (m, 2H), 7.82 – 7.73 (m, 3H), 7.68 – 7.48 (m, 4H). MS, *m/z* (%): 249 [M^{+}].

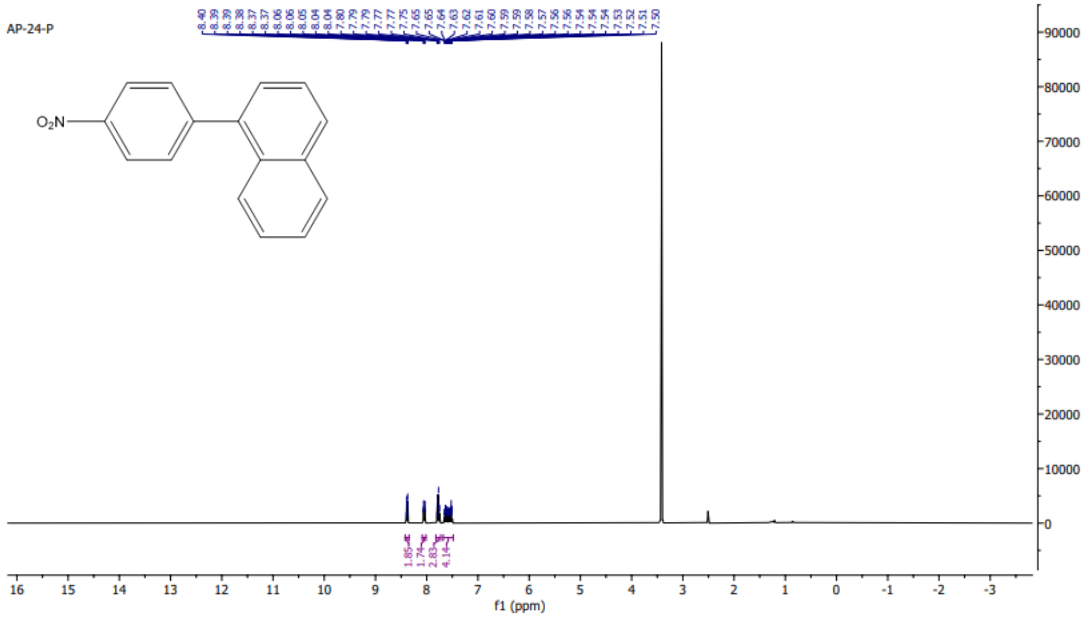


Figure 11A: ^{1}H NMR (400 MHz, DMSO) of 1-(4-nitrophenyl)naphthalene (11f)

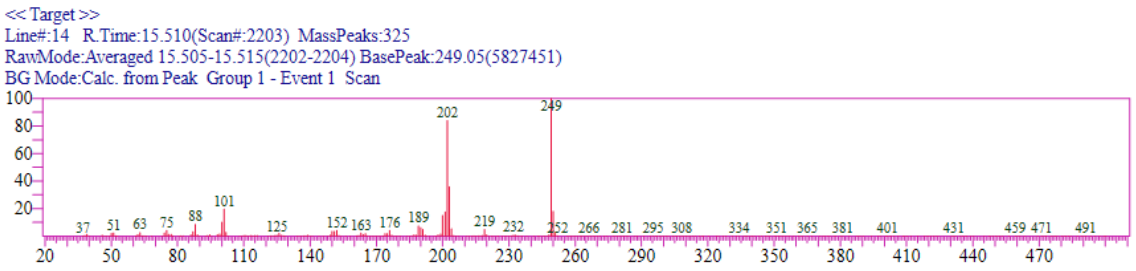


Figure 11B: GC-MS spectrum of 1-(4-nitrophenyl)naphthalene (11f)

12. **4-methoxy-4'-nitro-1,1'-biphenyl (12f):** ^{1}H NMR (400 MHz, DMSO) δ 8.26 (d, J = 8.6 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 3.82 (s, 3H); 13C NMR (101 MHz, DMSO) δ 160.20, 146.30, 146.02, 129.94, 128.60, 127.03, 124.12, 114.71, 55.34; MS, *m/z* (%): 229 [M^{+}].

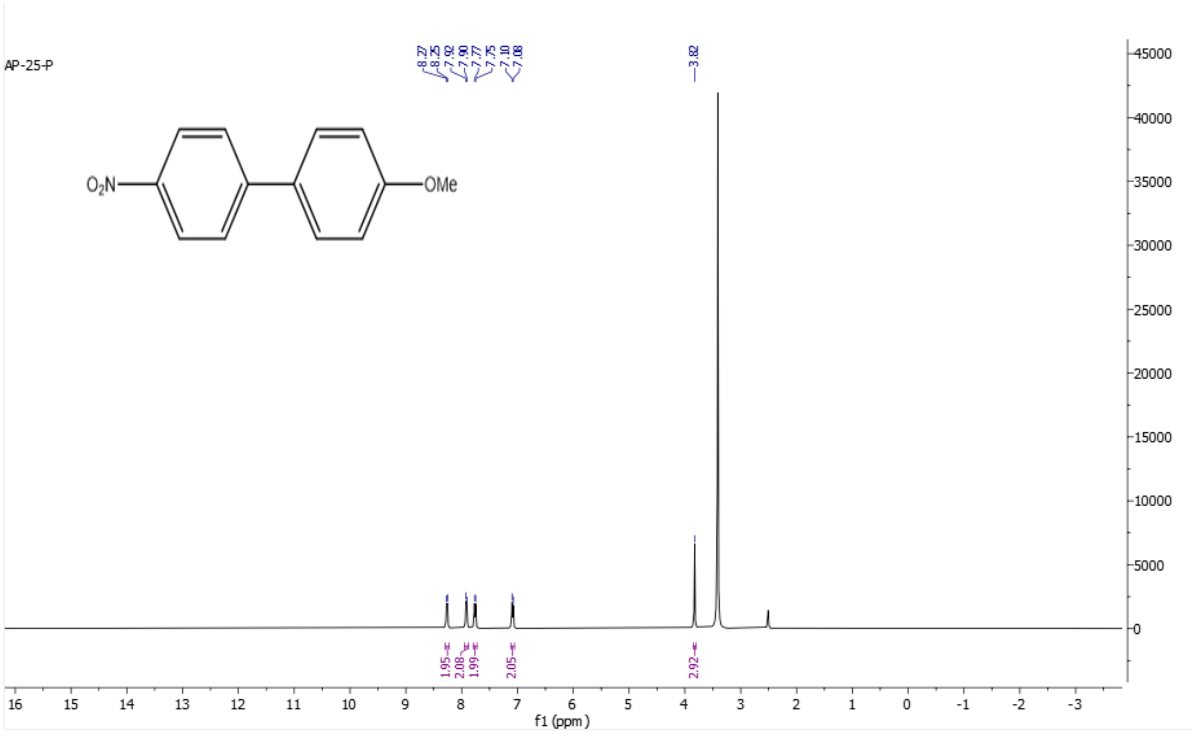


Figure 12A: ^{1}H NMR (400 MHz, DMSO) of 4-methoxy-4'-nitro-1,1'-biphenyl (12f)

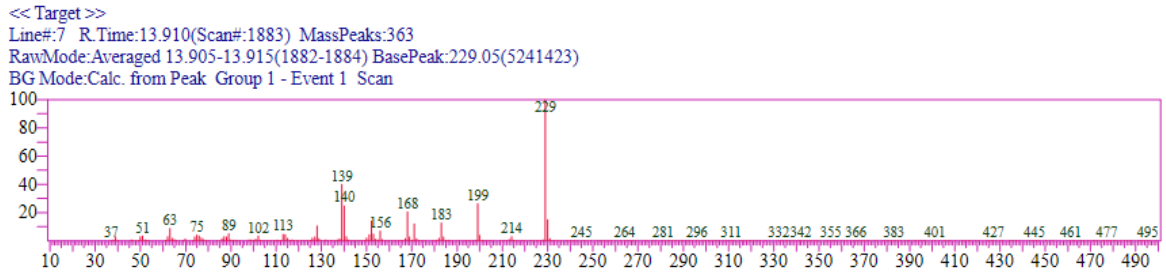


Figure 12B: GC-MS spectrum of 4-methoxy-4'-nitro-1,1'-biphenyl (12f)

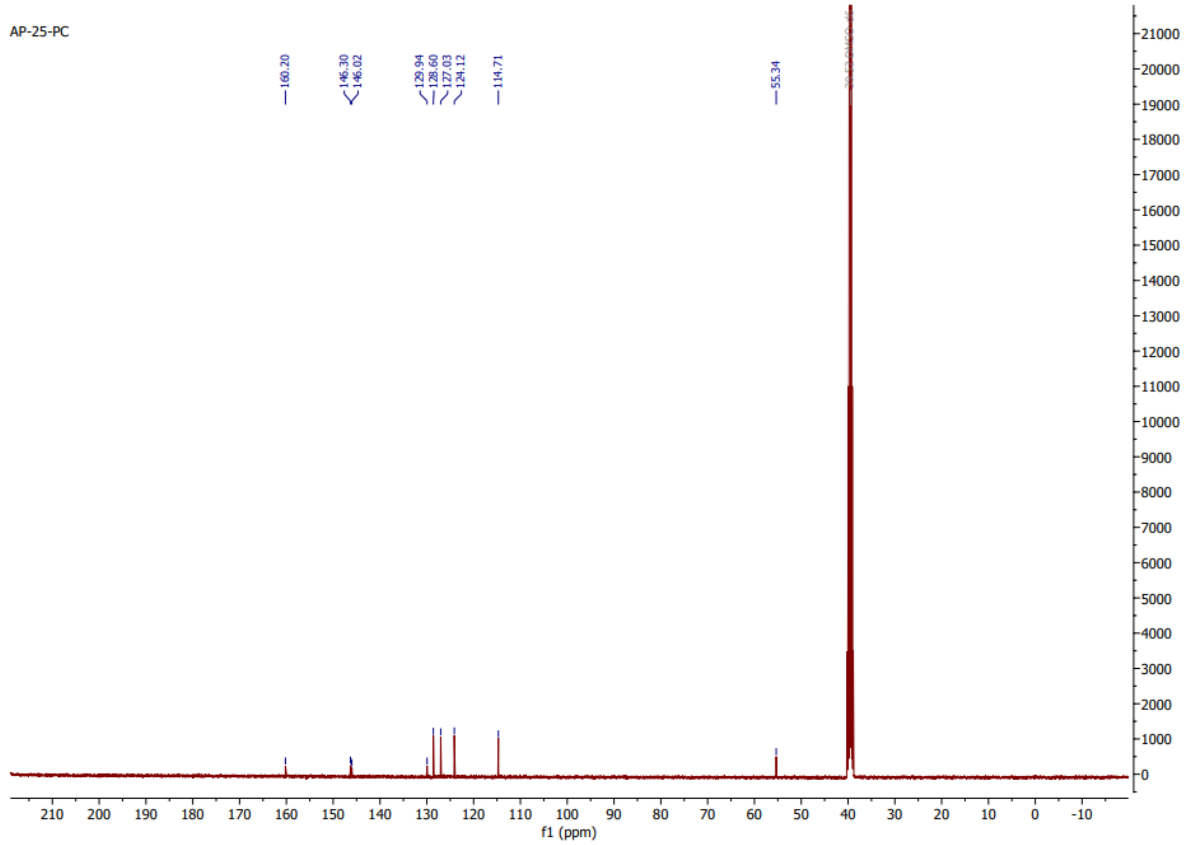


Figure 12C: 13C NMR (101 MHz, DMSO) of 4-methoxy-4'-nitro-1,1'-biphenyl (12f)

13. **[1,1'-biphenyl]-4-carbonitrile (13f):** ^{1}H NMR (400 MHz, DMSO) δ 7.96 – 7.84 (m, 4H), 7.78 – 7.71 (m, 2H), 7.56 – 7.49 (m, 2H), 7.49 – 7.41 (m, 1H).

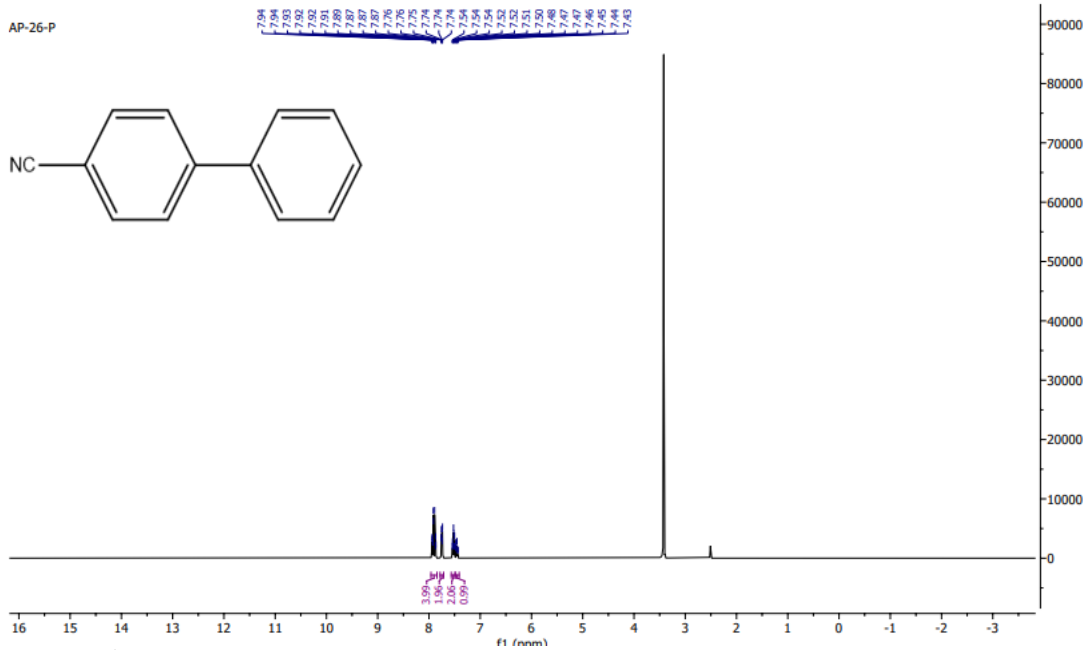


Figure 13A: ^{1}H NMR (400 MHz, DMSO) of [1,1'-biphenyl]-4-carbonitrile (13f)

14. **4-(naphthalen-1-yl)benzonitrile (14f):** ^{1}H NMR (400 MHz, DMSO) δ 8.06 – 7.95 (m, 4H), 7.76 – 7.64 (m, 3H), 7.65 – 7.50 (m, 3H), 7.47 (dd, J = 7.1, 1.3 Hz, 1H). MS, *m/z* (%): 229 [M^{+}].

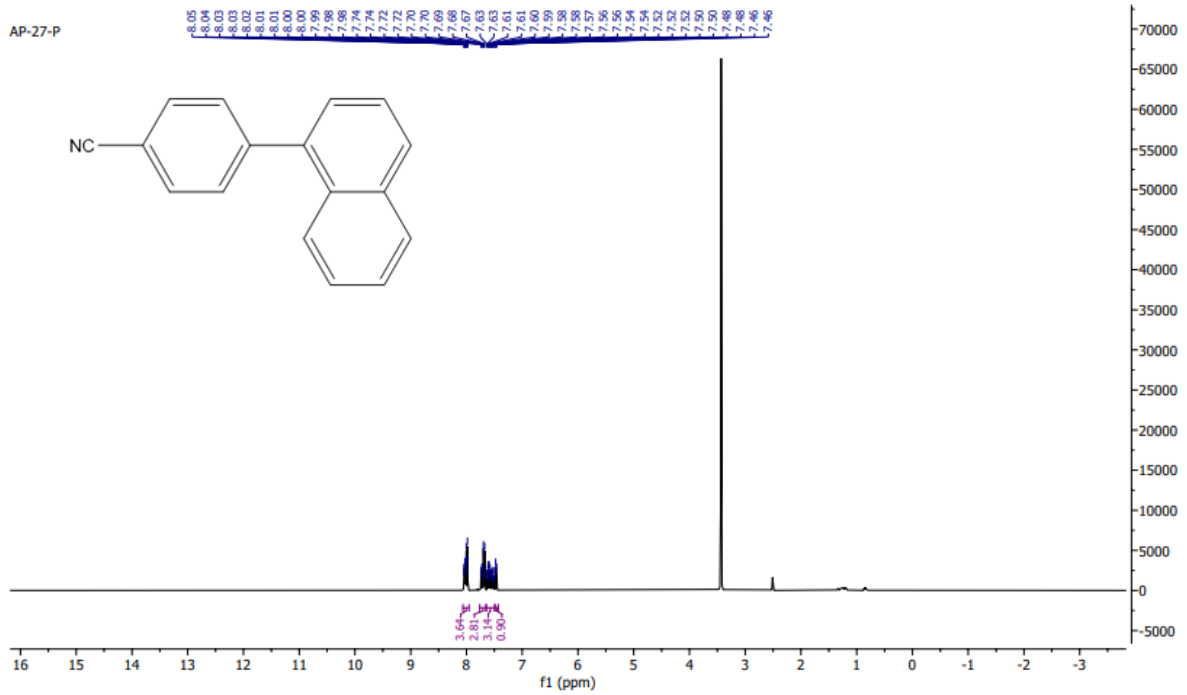


Figure 14A: ^{1}H NMR (400 MHz, DMSO) of 4-(naphthalen-1-yl)benzonitrile (14f)

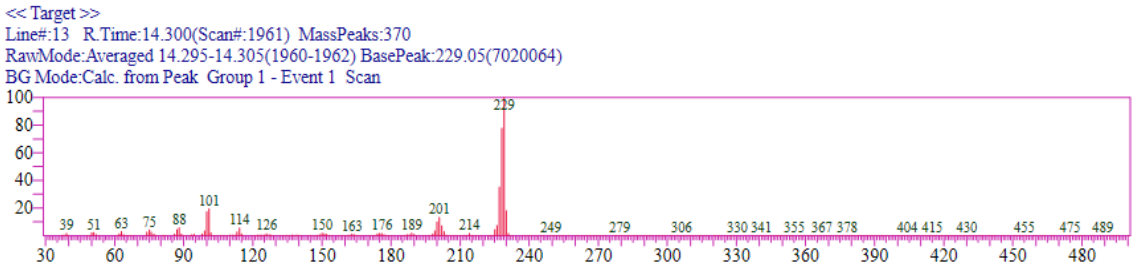


Figure 14B: GC-MS spectrum of 4-(naphthalen-1-yl)benzonitrile (14f)

15. **4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (15f):** ^{1}H NMR (400 MHz, DMSO) δ 7.91 – 7.80 (m, 4H), 7.76 – 7.67 (m, 2H), 7.07 (dd, J = 8.7, 1.3 Hz, 2H), 3.81 (d, J = 1.1 Hz, 3H). MS, *m/z* (%): 209 [M^{+}].

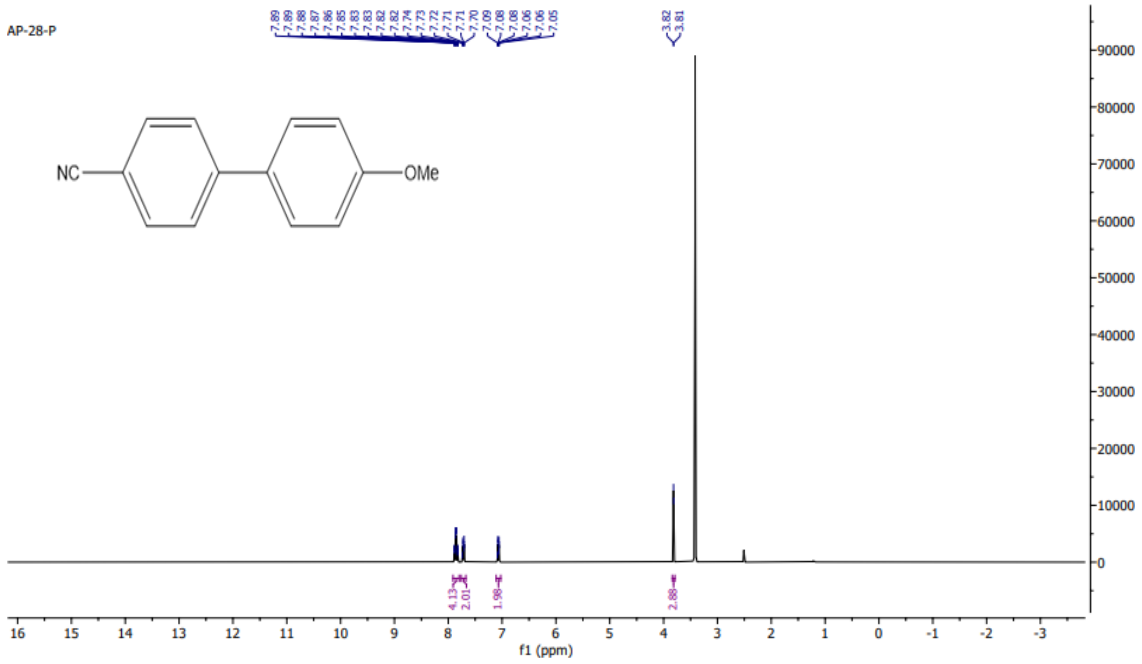


Figure 15A: ^{1}H NMR (400 MHz, DMSO) of 4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (15f)

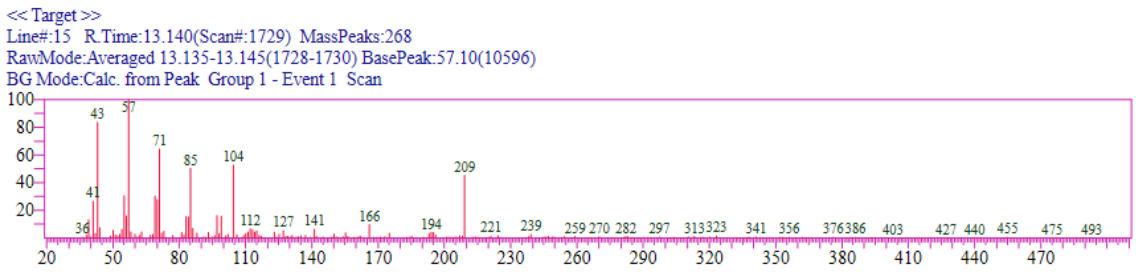


Figure 15B: GC-MS spectrum of 4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (15f)

16. **4-methyl-1,1'-biphenyl (16f):** ^{1}H NMR (400 MHz, DMSO) δ 8.07 (s, 1H), 7.84 – 7.78 (m, 1H), 7.62 (s, 1H), 7.54 (s, 1H), 7.48 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 (s, 1H), 2.34 (s, 3H). MS, *m/z* (%): 168 [M^{+}].

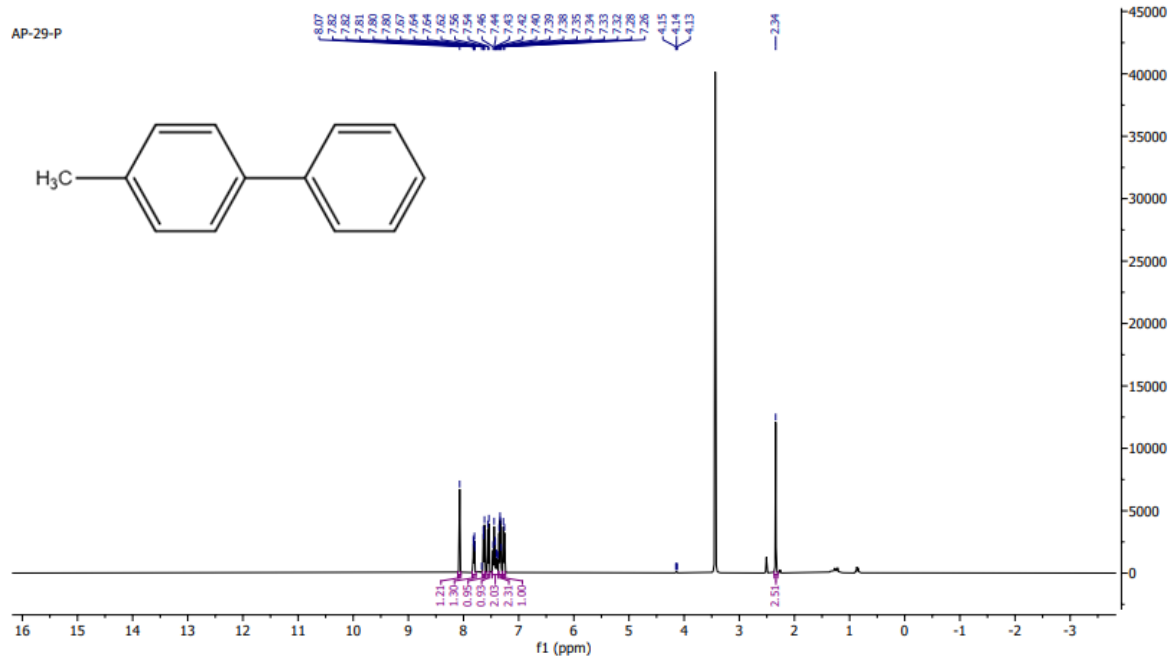


Figure 16A: ^{1}H NMR (400 MHz, DMSO) of 4-methyl-1,1'-biphenyl (16f)

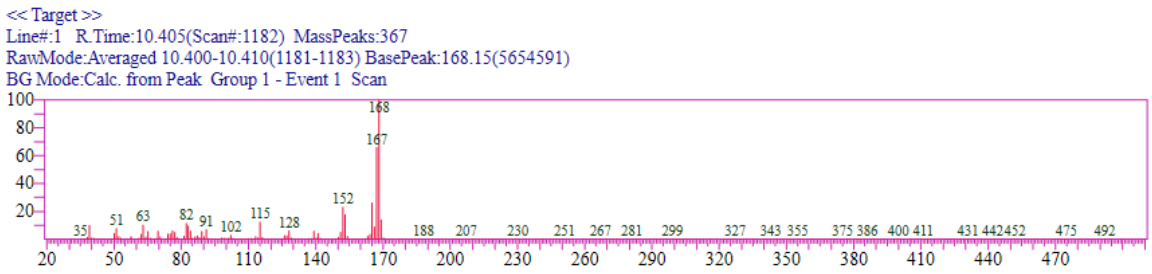


Figure 16B: GC-MS spectrum of 4-methyl-1,1'-biphenyl (16f)

17. **1-(p-tolyl)naphthalene (17f):** ^{1}H NMR (400 MHz, DMSO) δ 8.10 – 7.97 (m, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.62 – 7.45 (m, 3H), 7.44 – 7.31 (m, 5H), 2.41 (s, 3H). MS, *m/z* (%): 218 [M^{+}].

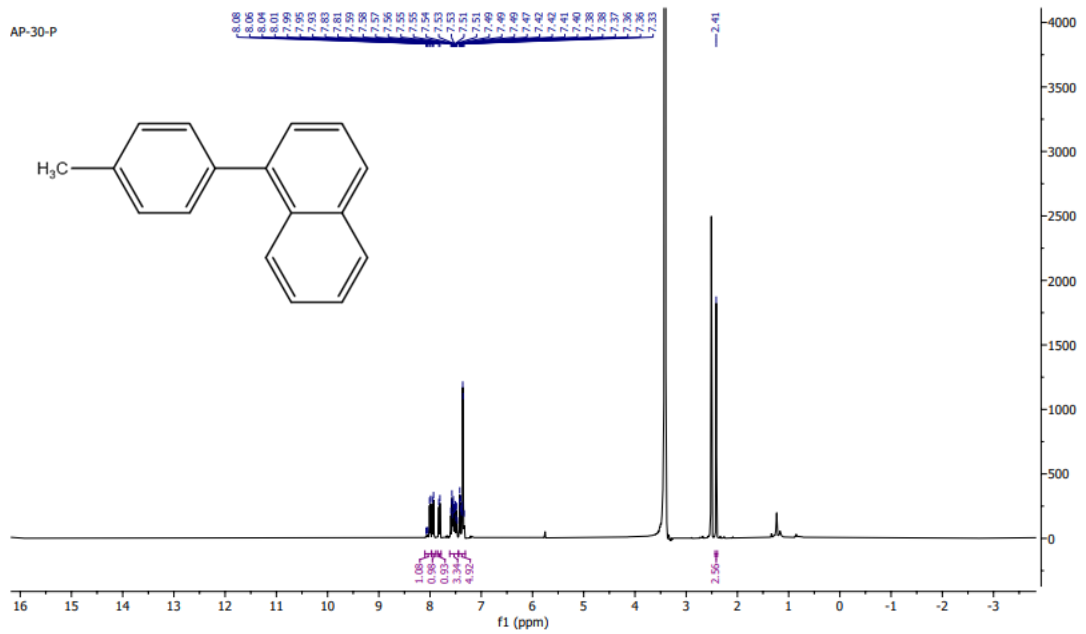


Figure 17A: ^{1}H NMR (400 MHz, DMSO) of 1-(p-tolyl)naphthalene (17f)

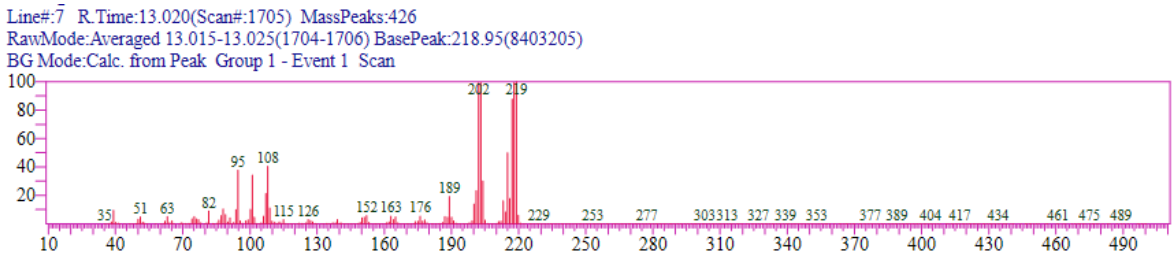


Figure 17B: GC-MS spectrum of 1-(p-tolyl)naphthalene (17f)

18. **4-methoxy-4'-methyl-1,1'-biphenyl (18f):** ^{1}H NMR (400 MHz, DMSO) δ 7.61 – 7.54 (m, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.05 – 6.97 (m, 2H), 3.79 (s, 3H), 2.32 (s, 3H); 13C NMR (101 MHz, DMSO) δ 159.08, 137.39, 136.29, 132.90, 129.87, 127.89, 126.42, 114.73, 55.57, 21.04; MS, *m/z* (%): 183 [M^{+}].

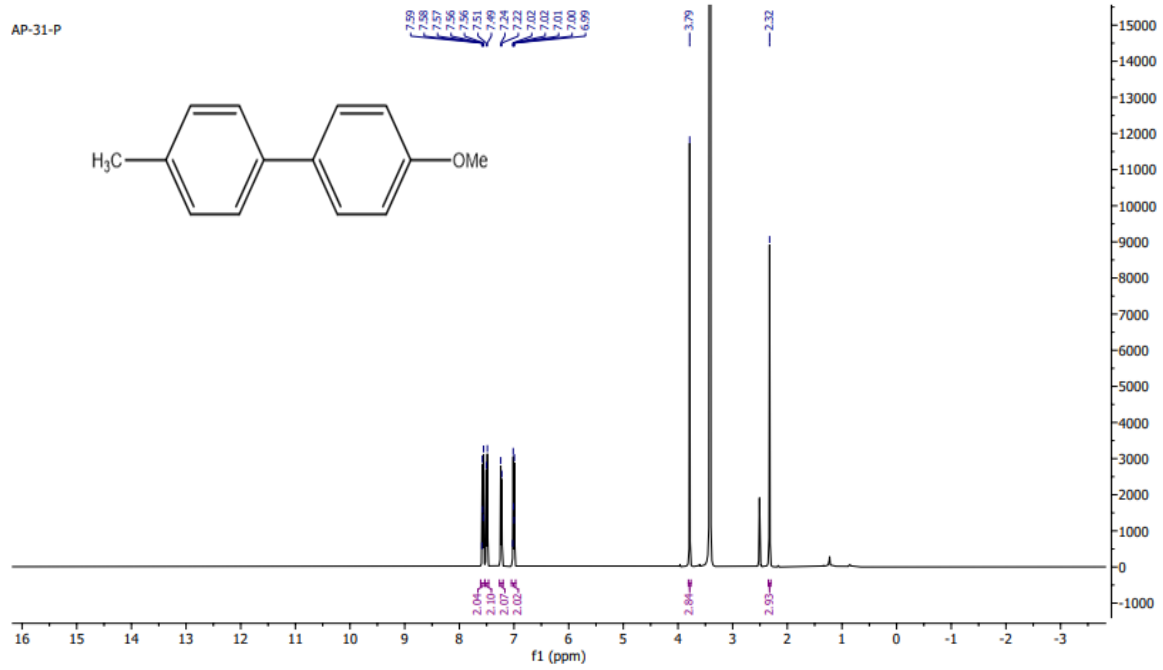


Figure 18A: ^{1}H NMR (400 MHz, DMSO) of 4-methoxy-4'-methyl-1,1'-biphenyl (18f)

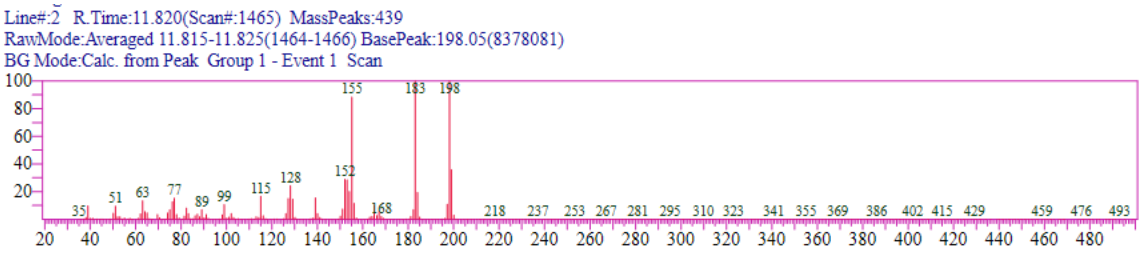


Figure 18B: GC-MS spectrum of 4-methoxy-4'-methyl-1,1'-biphenyl (18f)

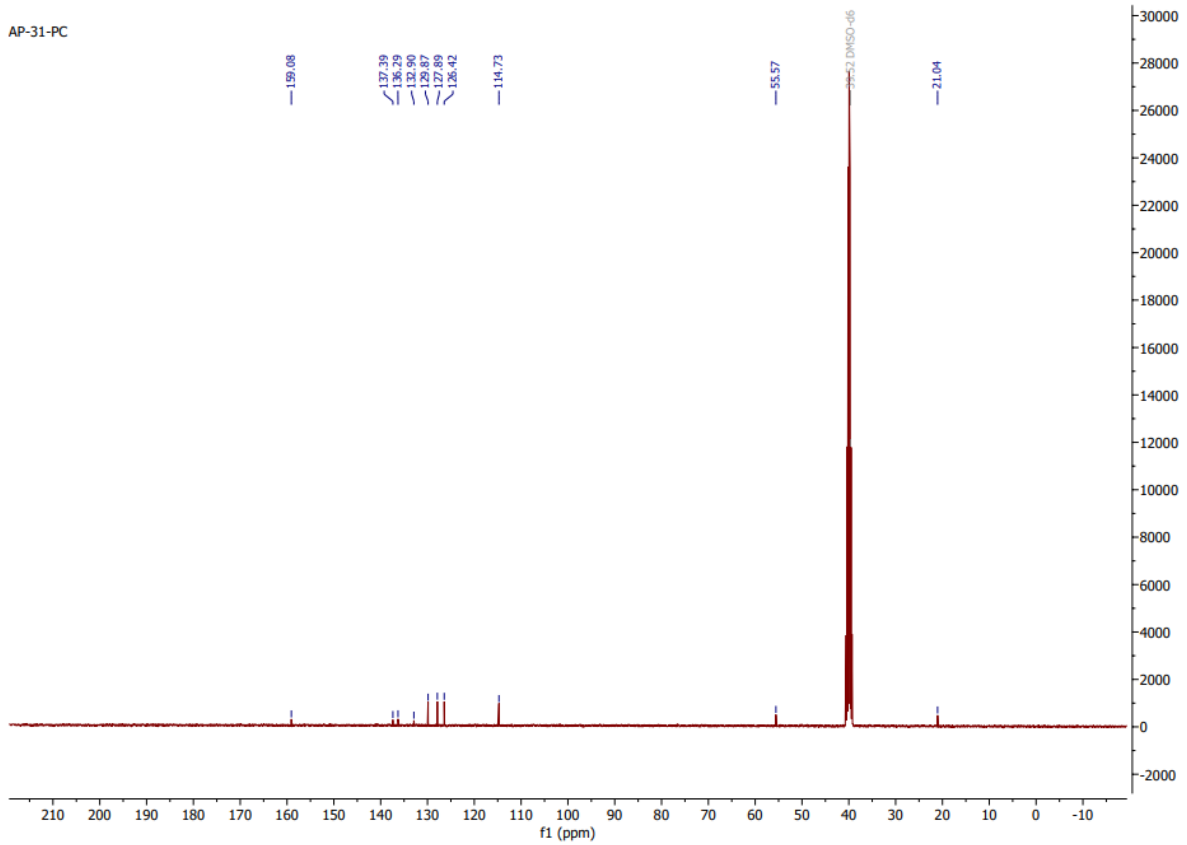


Figure 18C: 13C NMR (101 MHz, DMSO) of 4-methoxy-4'-methyl-1,1'-biphenyl (18f)

19. **[1,1'-biphenyl]-4-carbaldehyde (19f):** ^{1}H NMR (400 MHz, DMSO) δ 10.06 (s, 1H), 8.04 – 7.97 (m, 2H), 7.95 – 7.88 (m, 2H), 7.81 – 7.69 (m, 2H), 7.52 (dd, J = 8.3, 6.7 Hz, 2H), 7.49 – 7.41 (m, 1H).

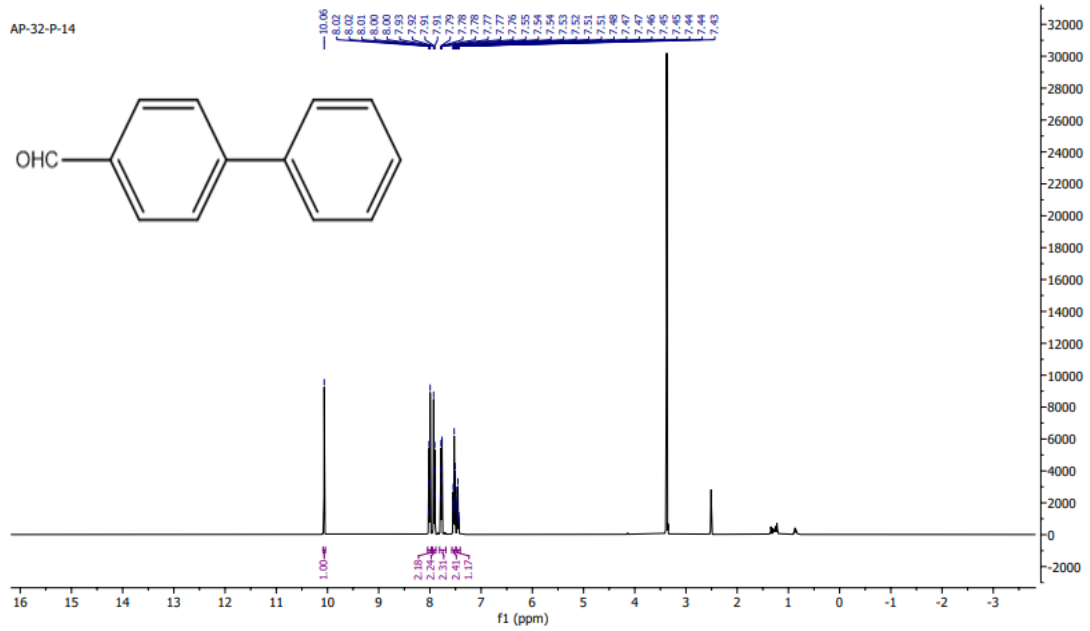


Figure 19A: [1]H NMR (400 MHz, DMSO) of [1,1'-biphenyl]-4-carbaldehyde (19f)

20. **4-(naphthalen-1-yl)benzaldehyde (20f):** [1]H NMR (400 MHz, DMSO) δ 10.13 (s, 1H), 8.11 – 7.99 (m, 4H), 7.78 (dd, J = 8.5, 1.2 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.68 – 7.54 (m, 2H), 7.57 – 7.47 (m, 2H); 13C NMR (101 MHz, DMSO) δ 193.09, 146.35, 138.47, 135.41, 133.63, 130.82, 130.60, 129.89, 128.72, 128.67, 127.31, 126.98, 126.38, 125.79, 125.10.

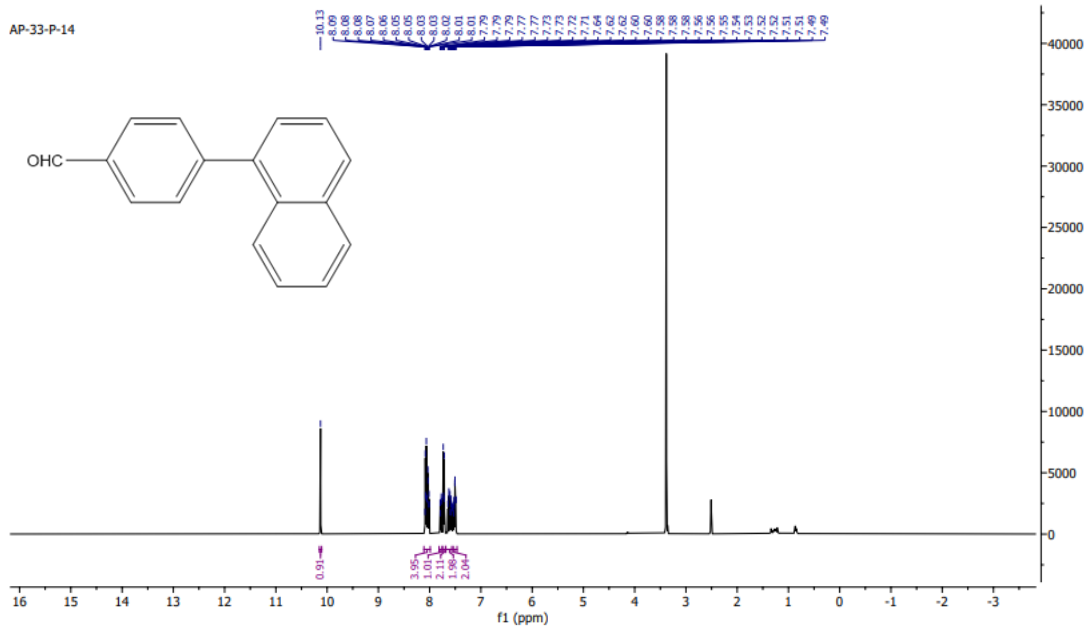


Figure 20A: [1]H NMR (400 MHz, DMSO) of 4-(naphthalen-1-yl)benzaldehyde (20f)

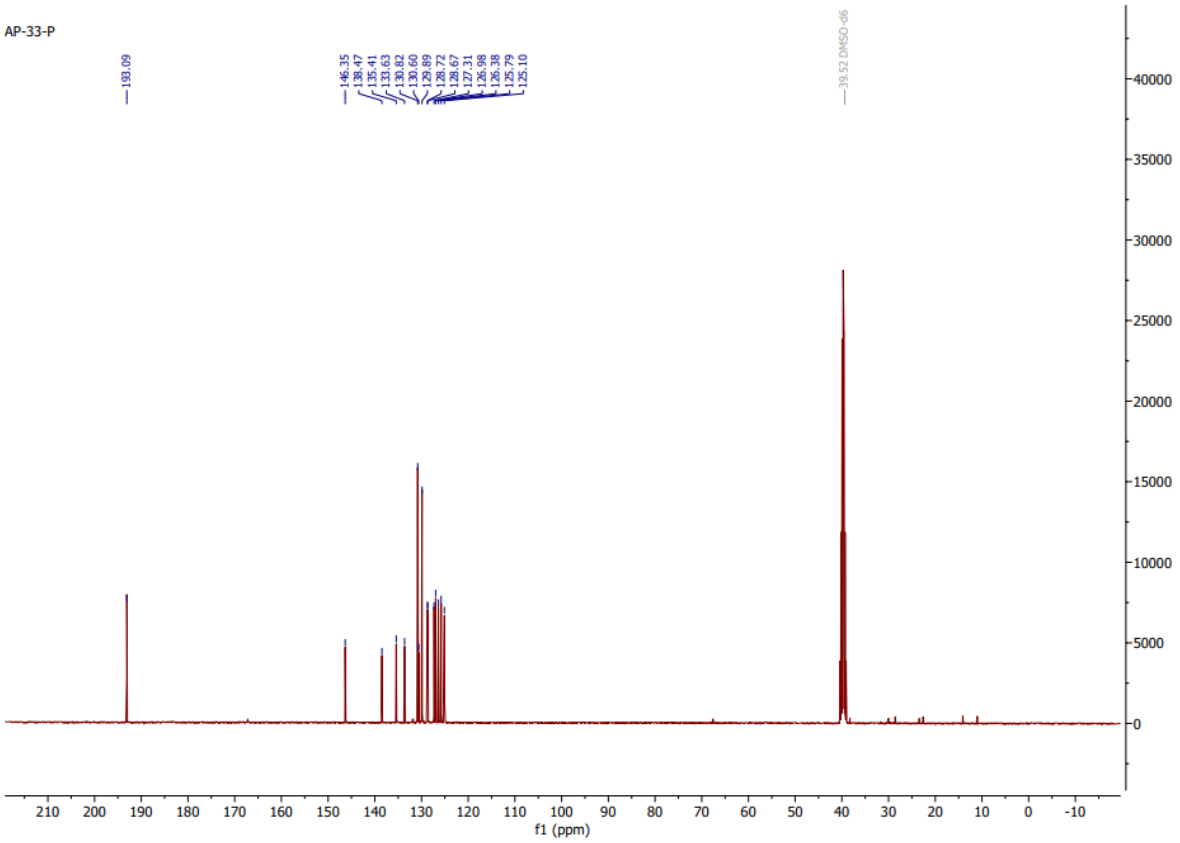


Figure 20B: 13C NMR (101 MHz, DMSO) of 4-(naphthalen-1-yl)benzaldehyde (20f)

21. **4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (21f):** ^{1}H NMR (400 MHz, DMSO) δ 10.03 (s, 1H), 8.00 – 7.93 (m, 2H), 7.92 – 7.85 (m, 2H), 7.79 – 7.71 (m, 2H), 7.12 – 7.04 (m, 2H), 3.82 (s, 3H). MS, *m/z* (%): 212 [M^{+}].

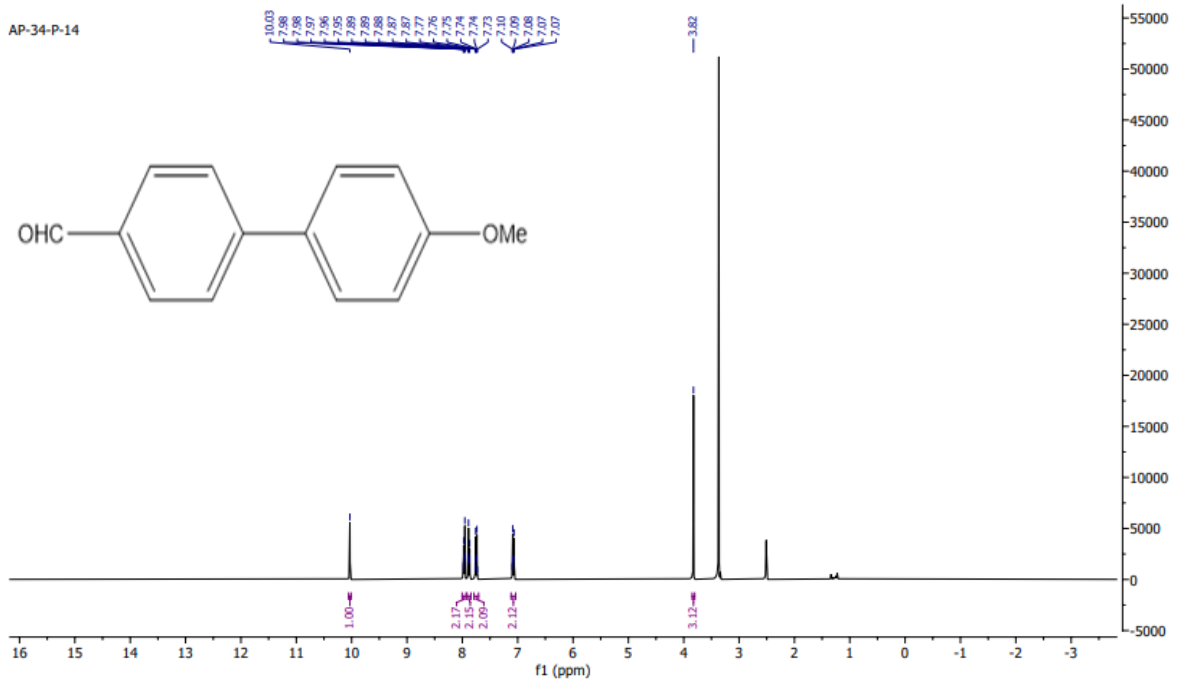


Figure 21A: ^{1}H NMR (400 MHz, DMSO) of 4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (21f)

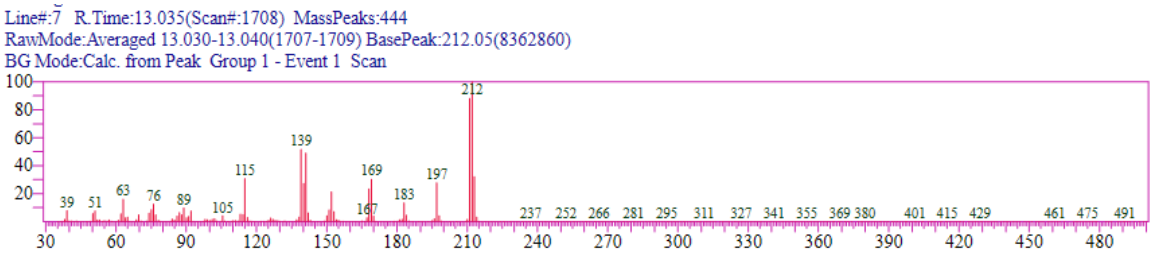


Figure 21B: GC-MS spectrum of 4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (21f)

22. **1,1'-biphenyl (22f):** ^{1}H NMR (400 MHz, DMSO) δ 8.05 (s, 1H), 7.82 – 7.76 (m, 1H), 7.66 (dd, 2H), 7.57 – 7.42 (m, 4H), 7.41 – 7.30 (m, 2H). MS, *m/z* (%): 154 [M^{+}].

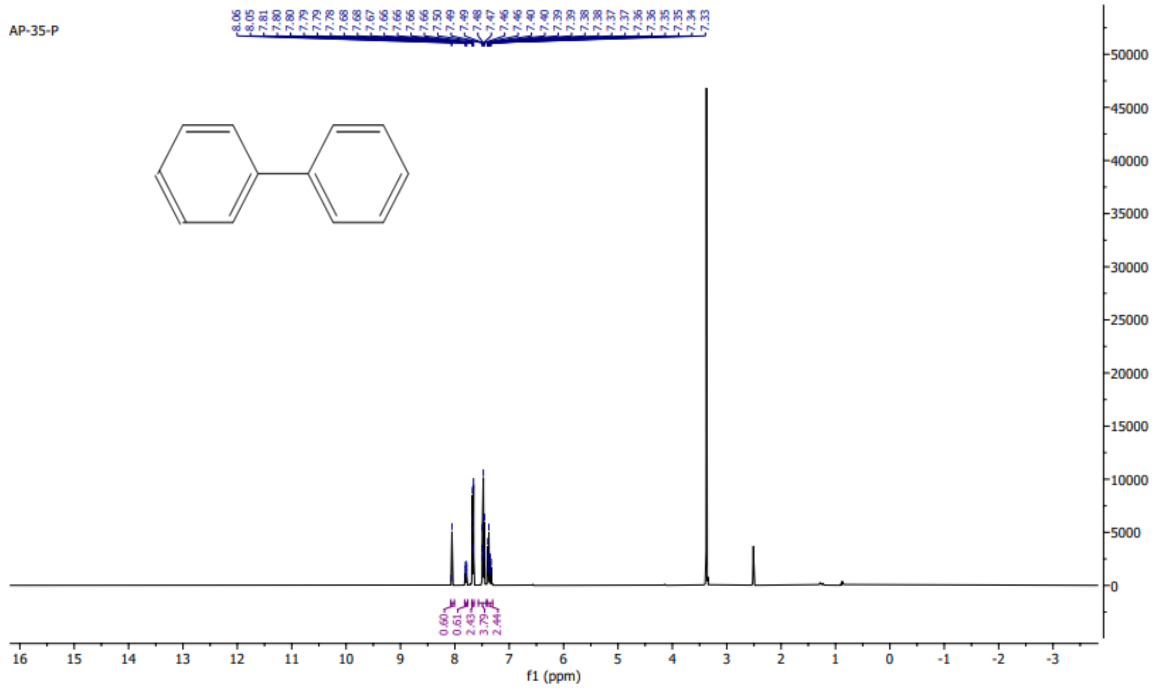


Figure 22A: ^{1}H NMR (400 MHz, DMSO) of 1,1'-biphenyl (22f)

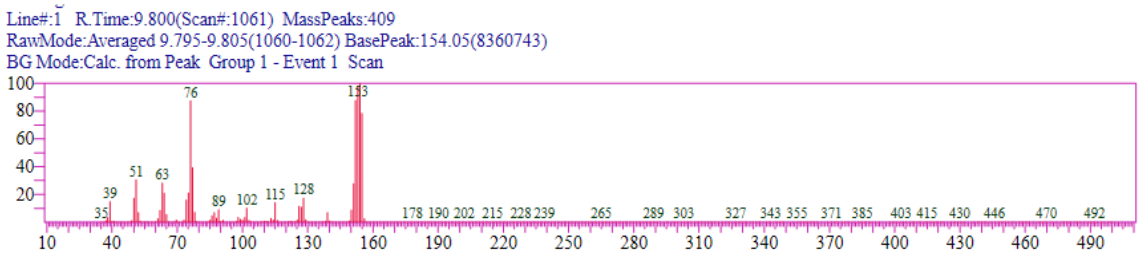


Figure 22B: GC-MS spectrum of 1,1'-biphenyl (22f)

23. 1-phenylnaphthalene (23f): ^{1}H NMR (400 MHz, DMSO) δ 8.10 – 7.93 (m, 2H), 7.84 – 7.77 (m, 1H), 7.68 – 7.36 (m, 9H). MS, *m/z* (%): 204 [M^{+}].

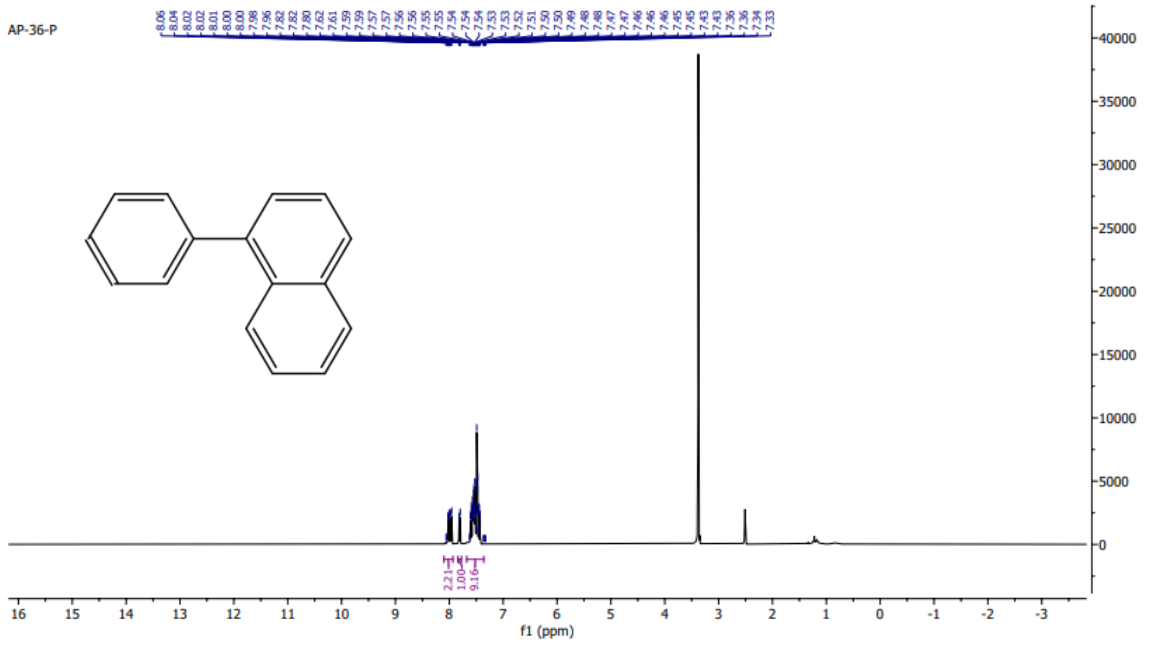


Figure 23A: ^{1}H NMR (400 MHz, DMSO) of 1-phenylnaphthalene (23f)

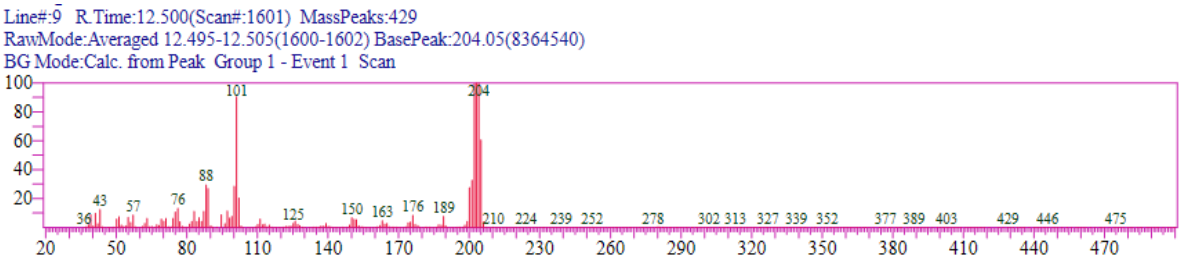


Figure 23B: GC-MS spectrum of 1-phenylnaphthalene (23f)

24. **4-methoxy-1,1'-biphenyl (24f):** ^{1}H NMR (400 MHz, DMSO) δ 7.64 – 7.56 (m, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.35 – 7.26 (m, 1H), 7.06 – 6.98 (m, 2H), 3.79 (s, 3H).

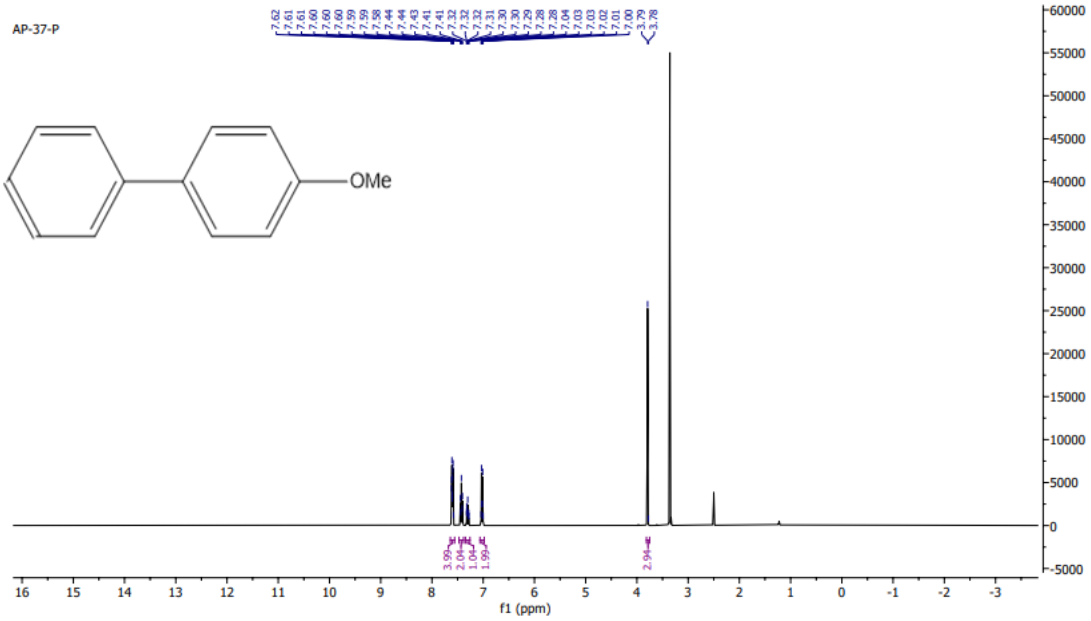


Figure 24A: ^{1}H NMR (400 MHz, DMSO) of 4-methoxy-1,1'-biphenyl (24f)

25. **4-methoxy-1,1'-biphenyl (25f):** MS, *m/z* (%): 184 [M^{+}].

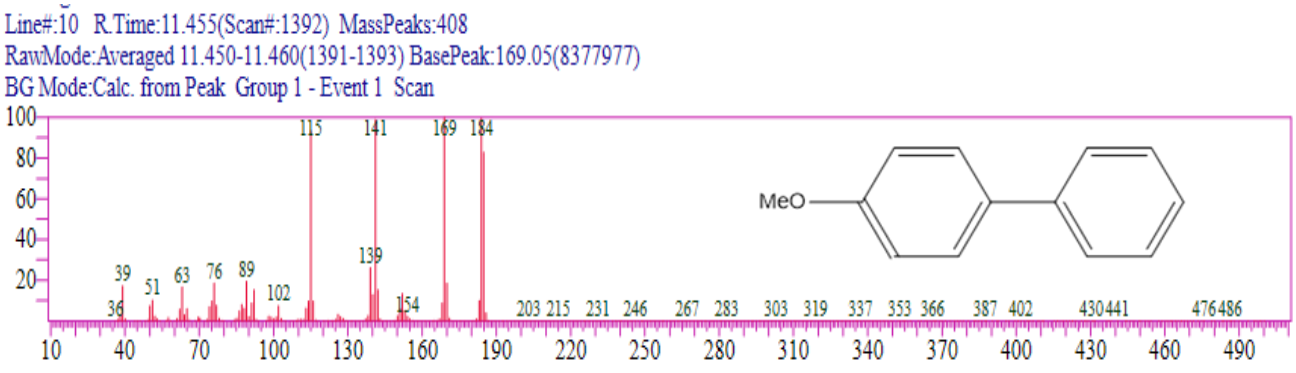


Figure 25A: GC-MS spectrum of 4-methoxy-1,1'-biphenyl (25f)

26. 1-(4-methoxyphenyl)naphthalene (26f): MS, *m/z* (%): 234 [M^+].

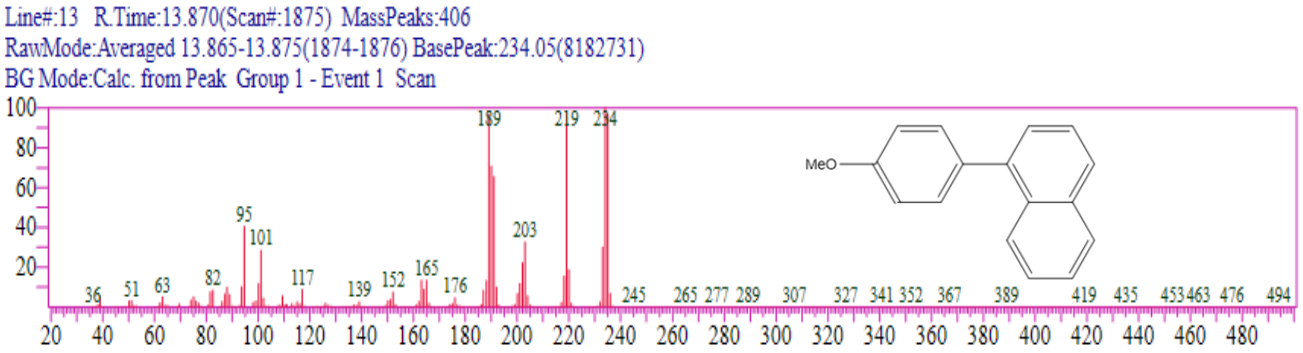


Figure 26A: GC-MS spectrum of 1-(4-methoxyphenyl)naphthalene (26f)

27. 4,4'-dimethoxy-1,1'-biphenyl (27f): MS, *m/z* (%): 214 [M^+].

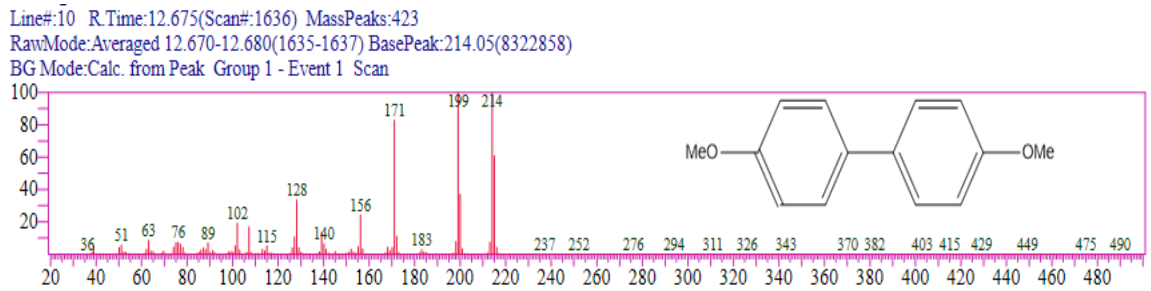


Figure 27A: GC-MS spectrum of 4,4'-dimethoxy-1,1'-biphenyl (27f)

28. 1,1'-biphenyl (28f): MS, *m/z* (%): 154 [M^+].

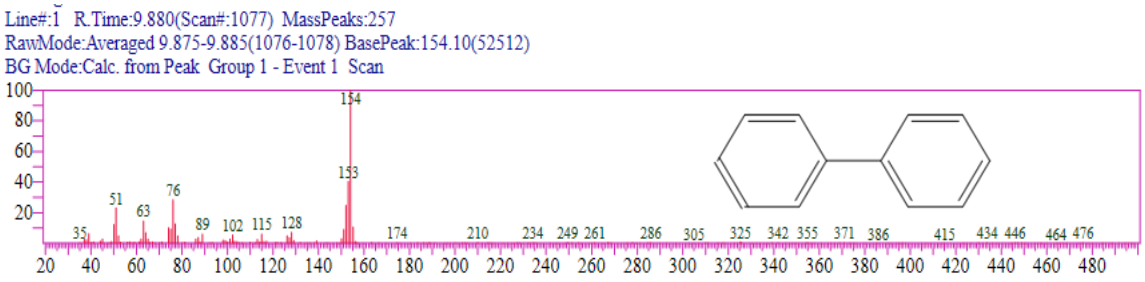
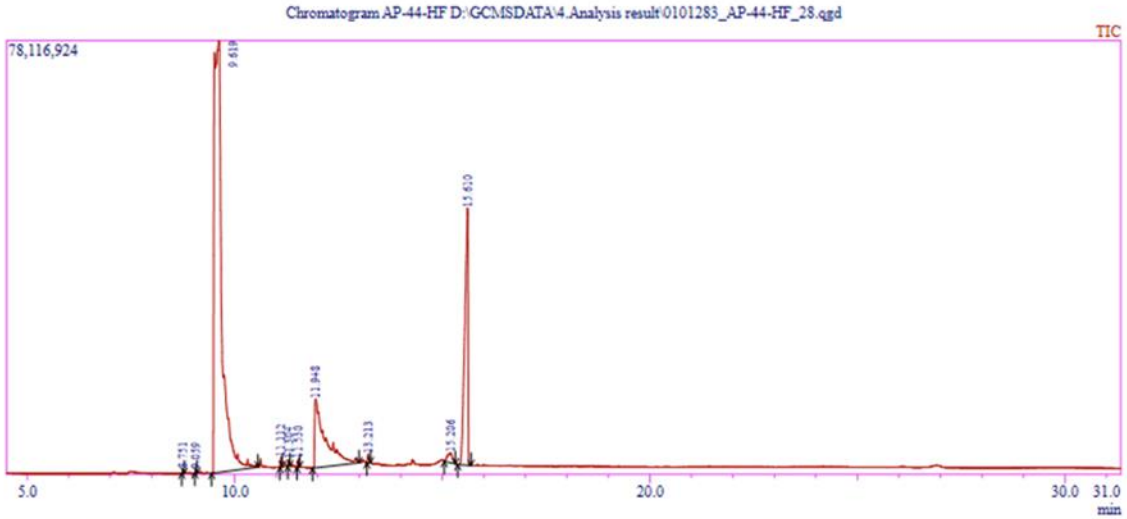


Figure 28A: GC-MS spectrum of 1,1'-biphenyl (28f)

29. GC-MS spectrum of Hot filtration analysis.

D:\GCMSDATA\2.Method files\M-1 (product confirmation met



Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	8.751	1007292	0.07	761594	0.52	1.32	Decane, 3,7-dimethyl-
2	9.059	833305	0.06	619721	0.43	1.34	Dodecane, 2,6,11-trimethyl-
3	9.619	1019378365	67.52	77761112	53.41	13.11	Phenol, 3-bromo-
4	11.112	2145295	0.14	1655715	1.14	1.30	Nonadecane
5	11.304	1407708	0.09	1148306	0.79	1.23	Hexadecane
6	11.530	2119052	0.14	1488817	1.02	1.42	Cetene
7	11.948	218307859	14.46	12418531	8.53	17.58	3-Hydroxybiphenyl
8	13.213	4130104	0.27	1548581	1.06	2.67	Hexadecanoic acid, 1,1-dimethylethyl ester
9	15.206	14711980	0.97	1791267	1.23	8.21	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphit
10	15.610	245651422	16.27	46385995	31.86	5.30	Bis(2-ethylhexyl) phthalate
		1509692382	100.00	145579639	100.00		

[1,1'-biphenyl]-4-ol: MS, *m/z* (%): 170 [M^+].