

Sustainable H₂O/Ethyl Lactate System for Ligand-free Suzuki-Miyaura Reaction

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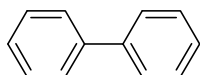
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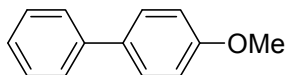
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General experimental information

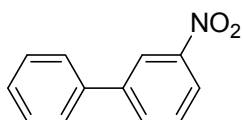
All chemicals were purchased from commercial resource in analytical purity and used without further purification. All reactions were performed in open air. ¹H NMR and ¹³C NMR were performed on 400 MHz and 100 MHz instrument using CDCl₃ as solvent, respectively. And the chemical shifts were recorded in ppm (δ) with TMS as internal standard.



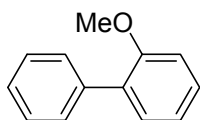
Biphenyl (3a).¹ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, 4 H, *J* = 8.0 Hz), 7.39 (t, 4H, *J* = 8.0Hz), 7.32 (t, 2 H, *J* = 8.0Hz); ¹³C NMR (100 MHz, CDCl₃): δ 141.3, 128.9, 127.4, 127.3.



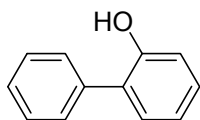
4-Methoxy biphenyl (3b).¹ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.53 (t, 4 H, *J* = 8.0 Hz), 7.40 (t, 2 H, *J* = 8.0 Hz), 7.30 (d, 1 H, *J* = 8.0 Hz), 6.97 (d, 2 H, *J* = 8.0 Hz), 3.83 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 140.9, 133.8, 128.8, 128.2, 126.8, 126.7, 114.2, 55.4.



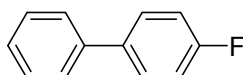
3-Nitrobiphenyl (3c).² Pale yellow solid; ¹H NMR (400 MHz, CDCl₃): δ 8.45 (s, 1 H), 8.20 (d, 1 H, *J* = 8.0 Hz), 7.91 (d, 1 H, *J* = 8.0 Hz), 7.64-7.59 (m, 3 H), 7.50 (t, 2 H, *J* = 8.0 Hz), 7.43 (t, 1 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 142.9, 138.7, 133.0, 129.7, 129.2, 128.5, 127.2, 122.0, 121.9.



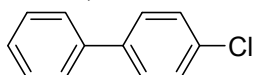
2-Methoxy biphenyl (3d).³ Colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, 2 H, *J* = 8.0 Hz), 7.40 (t, 2 H, *J* = 8.0 Hz), 7.33-7.29 (m, 3 H), 7.02-6.96 (m, 2 H), 3.79 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 156.5, 138.6, 130.9, 130.8, 129.6, 128.7, 128.0, 127.0, 120.9, 111.3, 55.6.



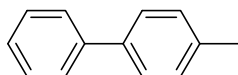
Biphenyl-2-ol (3e).⁴ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.45 (m, 4 H), 7.39 (t, 1 H, *J* = 8.0 Hz), 7.28-7.23 (m, 2 H), 6.99 (t, 2 H, *J* = 8.0 Hz), 5.22 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 152.4, 137.1, 130.2, 129.3, 129.2, 129.1, 128.1, 127.9, 120.8, 115.8.



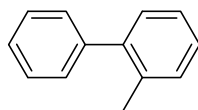
4-Fluorobiphenyl (3f).⁵ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.53-7.49 (m, 4 H), 7.40 (t, 2 H, *J* = 8.0 Hz), 7.31 (t, 1 H), 7.12-7.06 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 163.8, 161.4, 140.3, 137.4, 128.8 (t), 127.3, 127.1, 115.6 (d).



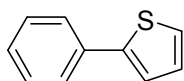
4-Chlorobiphenyl (3g).⁵ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.53-7.47 (m, 4 H), 7.43-7.31 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃): δ 140.0, 139.7, 133.4, 129.0, 128.9, 128.4, 127.6, 127.0.



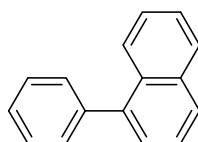
4-Methyl biphenyl (3h).¹ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, 2 H, *J* = 8.0 Hz), 7.48 (d, 2 H, *J* = 8.0 Hz), 7.42 (t, 2 H, *J* = 8.0 Hz), 7.32 (d, 1 H, *J* = 8.0 Hz), 7.24 (d, 2 H, *J* = 8.0 Hz), 2.38 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 141.2, 138.4, 137.1, 129.6, 129.5, 128.8, 127.1, 127.0, 21.2.



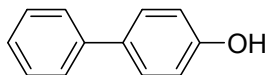
2-Methyl biphenyl (3i).² Pale yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, 2 H, *J* = 8.0 Hz), 7.35 (d, 3 H, *J* = 8.0 Hz), 7.29-7.27 (m, 4 H), 2.31 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 142.1, 142.0, 135.4, 130.4, 129.9, 129.3, 128.2, 127.4, 126.9, 125.9, 20.6.



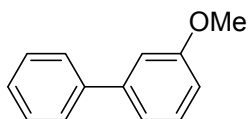
2-Phenylthiophene (3j).³ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, 2 H, *J* = 8.0 Hz), 7.35 (t, 2 H, *J* = 8.0 Hz), 7.31-7.24 (m, 3 H), 7.09-7.06 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 144.6, 134.4, 128.9, 128.0, 127.5, 126.0, 124.8, 123.1.



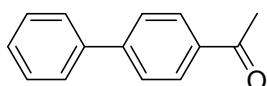
1-Phenylnaphthalene (3k).³ Pale yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.90-7.81 (m, 3 H), 7.50-7.37 (m, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ 140.9, 140.4, 133.9, 131.8, 130.2, 128.4, 127.8, 127.4, 127.1, 126.2, 125.9, 125.5.



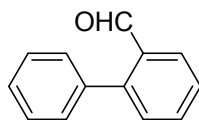
4-Hydroxybiphenyl (3l).² Yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, 2 H, *J* = 8.0 Hz), 7.47 (d, 2 H, *J* = 8.0 Hz), 7.40 (t, 2 H, *J* = 8.0 Hz), 7.31 (t, 1 H, *J* = 8.0 Hz), 6.90 (d, 2 H, *J* = 8.0 Hz), 5.20 (brs, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 155.2, 140.8, 134.0, 128.7, 128.4, 126.7, 126.6, 115.7.



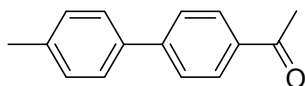
3-Methoxybiphenyl (3m).⁵ Pale yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, 2 H, *J* = 8.0 Hz), 7.42 (t, 2 H, *J* = 8.0 Hz), 7.36-7.32 (m, 2 H), 7.17 (d, 1 H, *J* = 8.0 Hz), 7.12 (s, 1 H), 6.89 (d, 1 H, *J* = 8.0 Hz), 3.85 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.0, 142.8, 141.1, 129.8, 128.8, 127.4, 127.2, 119.7, 113.0, 112.7, 55.3.



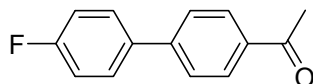
4-Acetylbiphenyl (3n).² White solid; ¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, 2 H, *J* = 8.0 Hz), 7.67 (d, 2 H, *J* = 8.0 Hz), 7.62 (d, 2 H, *J* = 8.0 Hz), 7.46 (t, 2 H, *J* = 8.0 Hz), 7.39 (t, 1 H, *J* = 8.0 Hz), 2.63 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.6.



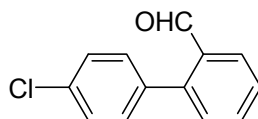
Biphenyl-2-carbaldehyde (3o).¹ Yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1 H), 8.02 (d, 1 H), 7.62 (t, 1 H), 7.50-7.42 (m, 4 H), 7.38-7.34 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 192.5, 146.0, 137.8, 133.7, 133.6, 130.8, 130.1, 128.4, 128.1, 127.8, 127.6.



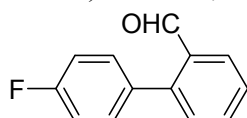
4-Methyl-4'-acetylbiphenyl (3p).⁶ White solid; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, 2 H, *J* = 8.0 Hz), 7.66 (d, 2 H, *J* = 8.0 Hz), 7.52 (d, 2 H, *J* = 8.0 Hz), 7.27 (d, 2 H, *J* = 8.0 Hz), 2.62 (s, 3 H), 2.40 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 197.7, 145.7, 138.2, 137.0, 135.6, 129.7, 128.9, 127.1, 126.9, 26.6, 21.2.



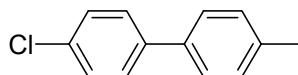
4-Fluoro-4'-acetylbiphenyl (3q).⁷ White solid; ¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, 2 H, *J* = 8.0 Hz), 7.64-7.57 (m, 4 H), 7.15 (t, 2 H, *J* = 8.0 Hz), 2.64 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 197.8, 164.4, 161.9, 144.7, 129.0, 128.9, 127.0, 116.0, 115.8, 26.6.



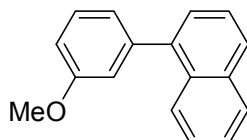
4'-Chlorobiphenyl-2-carbaldehyde (3r).⁸ Yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1 H), 8.01 (d, 1 H, *J* = 8.0 Hz), 7.63 (t, 1 H, *J* = 8.0 Hz), 7.50 (t, 1 H, *J* = 8.0 Hz), 7.45-7.38 (m, 3 H), 7.30 (d, 2 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 191.9, 144.5, 136.3, 134.5, 133.7, 131.3, 130.7, 128.7, 128.2, 127.9.



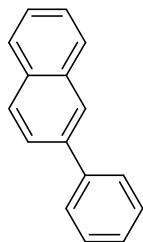
4'-Fluorobiphenyl-2-carbaldehyde (3s).⁹ Yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1 H), 8.01 (d, 1 H, *J* = 8.0 Hz), 7.63 (t, 1 H, *J* = 8.0 Hz), 7.50 (t, 1 H, *J* = 8.0 Hz), 7.41 (d, 1 H, *J* = 8.0 Hz), 7.37-7.33 (m, 2 H), 7.16 (t, 2 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 192.1, 164.0, 161.6, 144.8, 133.8 (q), 131.6 (d), 130.8, 128.0, 127.8, 115.6, 115.4.



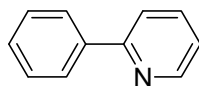
4-Methyl-4'-chloro-biphenyl (3t).¹⁰ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.43 (m, 4 H), 7.37 (d, 2 H, *J* = 8.0 Hz), 7.24 (d, 2 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 139.6, 137.4, 137.1, 133.0, 129.6, 128.8, 128.2, 126.8, 21.1.



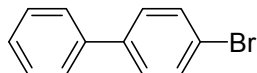
1-(3-Methoxyphenyl)naphthalene (3u).¹¹ Yellow solid; ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.73 (m, 3 H), 7.40-7.26 (m, 5 H), 6.99-6.94 (m, 2 H), 6.86 (d, 1 H, *J* = 8.0 Hz), 3.73 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 159.6, 142.3, 140.2, 133.9, 131.7, 129.3, 128.3, 127.8, 126.8, 126.1, 126.0, 125.8, 125.4, 122.7, 115.7, 113.0, 55.3.



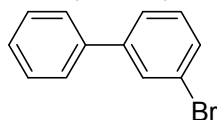
2-Phenylpyridine (3v).⁵ Pale yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, 2 H, *J* = 8.0 Hz), 7.85 (d, 1 H, *J* = 8.0 Hz), 7.53-7.46 (m, 6 H), 7.44-7.39 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 140.8, 140.3, 133.8, 131.7, 130.1, 128.3, 127.6, 127.3, 126.9, 126.0, 125.8, 125.4.



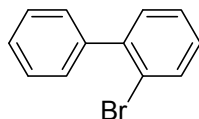
2-Phenylpyridine (3w).² Pale yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, 1 H, *J* = 4.8 Hz), 7.99 (d, 2 H, *J* = 8.0 Hz), 7.77-7.71 (m, 2 H), 7.47 (t, 2 H, *J* = 8.0 Hz), 7.41 (t, 1 H, *J* = 8.0 Hz), 7.24-7.21 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 157.5, 149.7, 139.4, 136.8, 129.0, 128.8, 126.9, 122.1, 120.6.



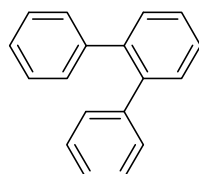
4-Bromobiphenyl (3x).⁴ White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.60-7.52 (m, 4 H), 7.48-7.36 (m, 4 H), 7.35 (t, 1 H, *J* = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 140.2, 140.0, 131.9, 128.9, 128.8, 127.6, 127.0, 121.6.



3-Bromobiphenyl (3y).¹² Colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 1 H), 7.53 (d, 2 H, *J* = 8.0 Hz), 7.50-7.40 (m, 4 H), 7.35 (t, 1 H, *J* = 8.0 Hz), 7.28 (t, 1 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 143.4, 139.8, 130.3, 130.25, 130.2, 128.9, 127.9, 127.2, 125.8, 122.9.



2-Bromobiphenyl (3z).¹² Colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, 1 H, *J* = 8.0 Hz), 7.40-7.38 (m, 5 H), 7.31 (d, 2 H, *J* = 8.0 Hz), 7.20-7.15 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 142.4, 140.8, 132.8, 131.0, 129.1, 128.4, 127.7, 127.3, 127.1, 126.9, 122.4.

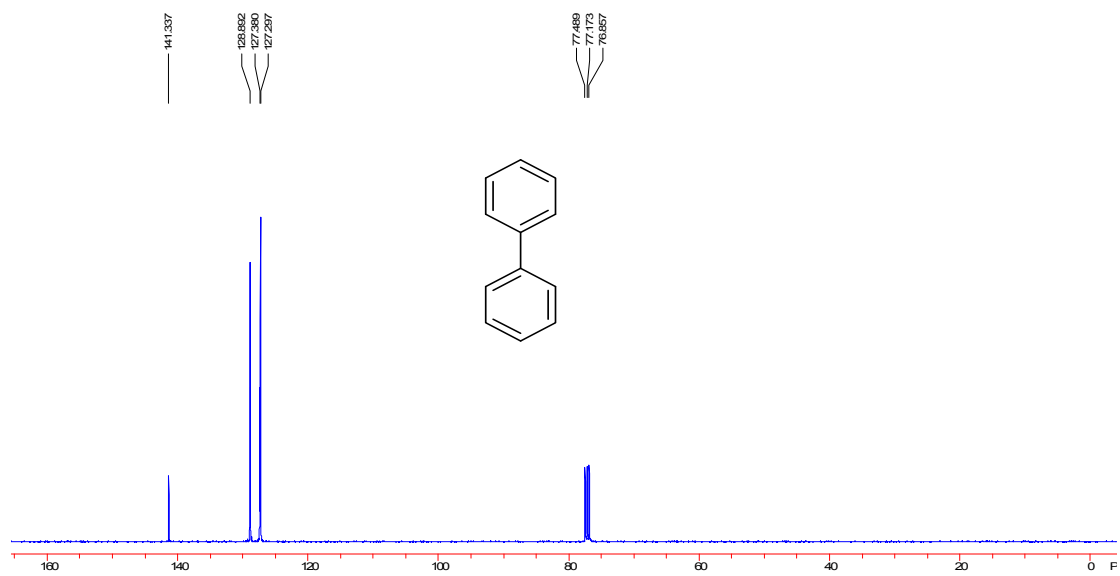
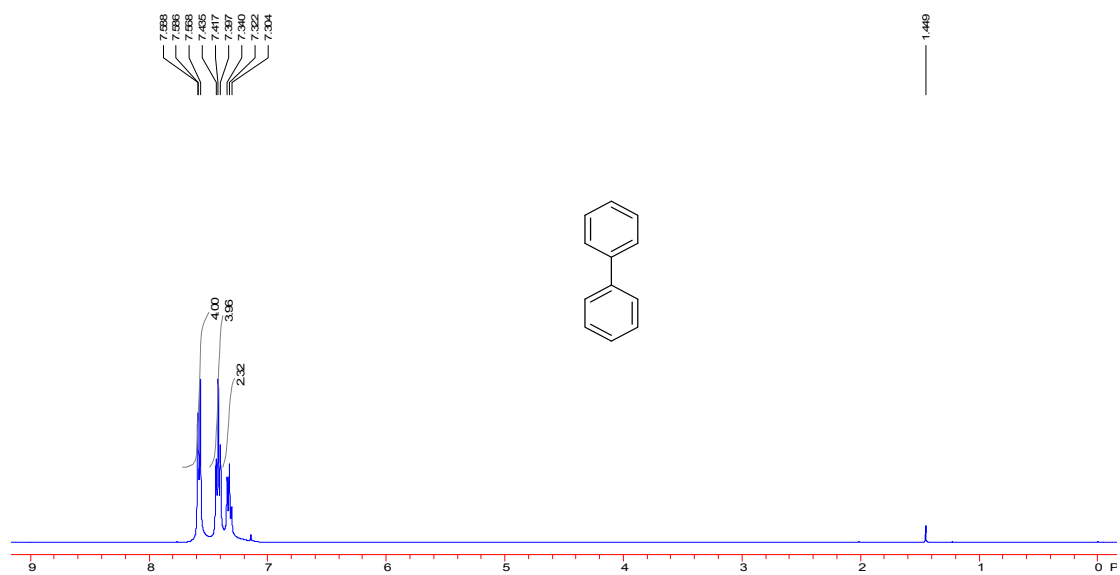


2-Phenylbiphenyl (4z).¹³ Colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.39 (m, 4 H), 7.22-7.17 (m, 6 H), 7.14-7.12 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 141.6, 140.6, 130.6, 129.9, 127.9, 127.5, 126.5.

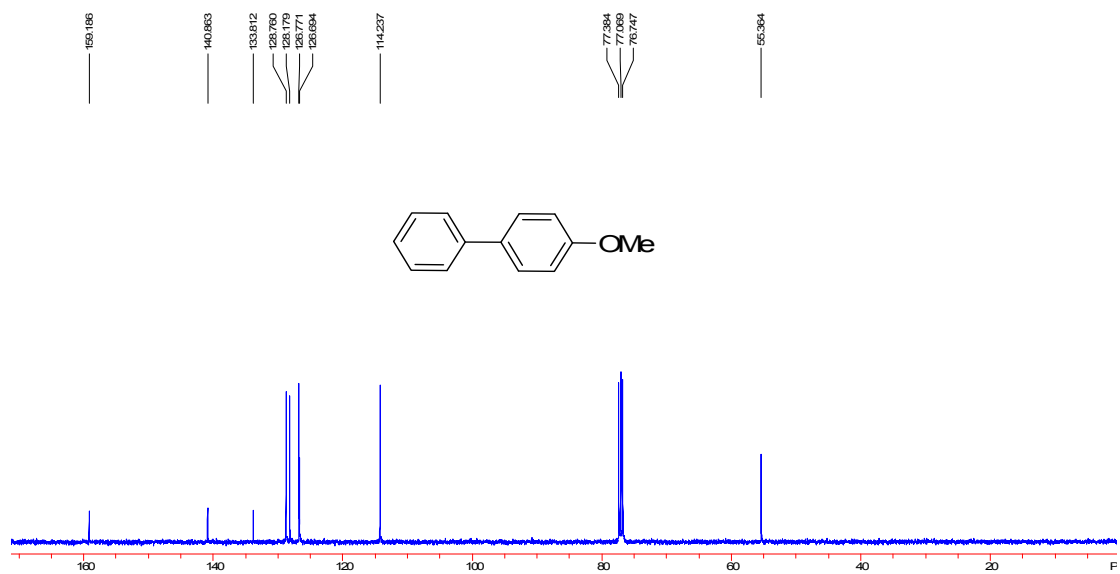
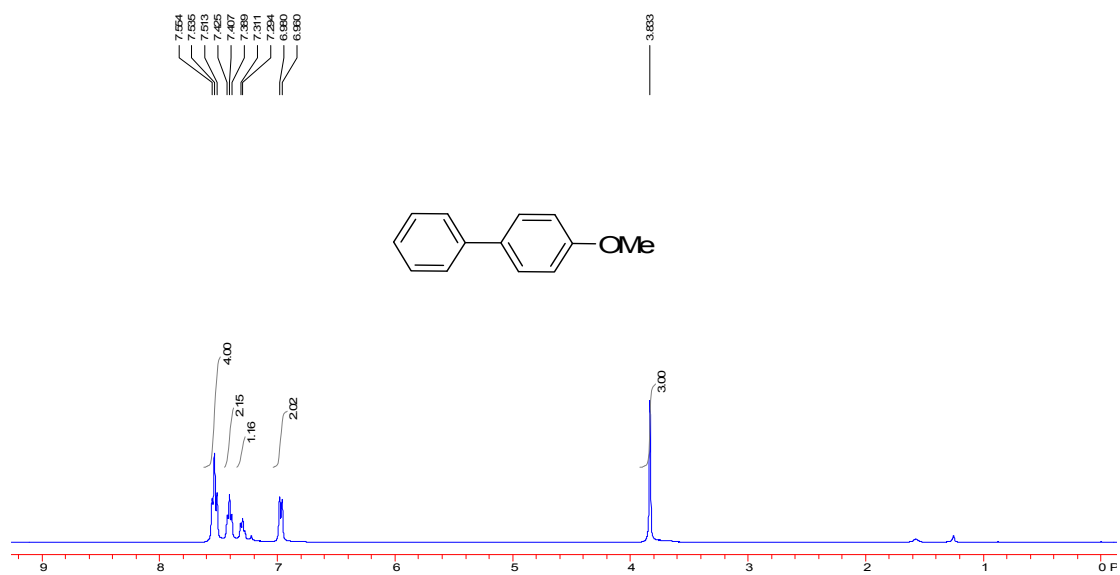
References

- (1) B. Karimi, D. Elhamifar, J. H. Clark and J. Hunt, *Chem. Eur. J.* **2010**, *16*, 8047-8053.
- (2) L. Wu, B.-L. Li, Y.-Y. Huang, H.-F. Zhou, Y.-M. He, Q.-H. Fan, *Org. Lett.* **2006**, *8*, 3605-3608.
- (3) D.-H. Lee, M. Choi, B.-W. Yu, R. Ryoo, A. Taher, S. Hossain, M. J. Jin, *Adv. Synth. Catal.* **2009**, *351*, 2912-2920.
- (4) J.-F. Wei, J. Jiao, J.-J. Feng, J. Lv, X.-R. Zhang, X.-Y. Shi and Z.-G. Chen, *J. Org. Chem.* **2009**, *74*, 6283-6286.
- (5) W. Liu, H. Cao, J. Xin, L. Jin and A. Lei, *Chem. Eur. J.* **2011**, *13*, 3588-3592.
- (6) N. E. Leadbeater, M. Marco, *Angew. Chem. Int. Ed.* **2003**, *42*, 1407-1409.
- (7) P. Liu, W. Zhang, R. He, *Appl. Organometal. Chem.* **2009**, *23*, 135-139.
- (8) F. Ye, Y. Shi, L. Zhou, Q. Xiao, Y. Zhang, J. Wang, *Org. Lett.* **2011**, *13*, 5020-5023.
- (9) S. Darses, J.-P. Genêt, *Tetrahedron Lett.* **1997**, *38*, 4393-4396.
- (10) J. M. A. Miguez, L. A. Adrio, A. Sousa-Pedrares,† J. M. Vila, K. K. Hii, *J. Am. Chem Soc.* **2007**, *72*, 7771-7774.
- (11) Y. Hatanaka, K. Goda, Y. Okahara, T. Hiyama, *Tetrahedron* **1994**, *50*, 8301-8316.
- (12) A. S. Demir, H. Findik, N. Saygili, N. T. Subasi, *Tetrahedron* **2010**, *66*, 1308-1312.
- (13) J. Bolliger, C.nM. Frech, *Adv. Synth. Catal.* **2010**, *352*, 1075-1080.

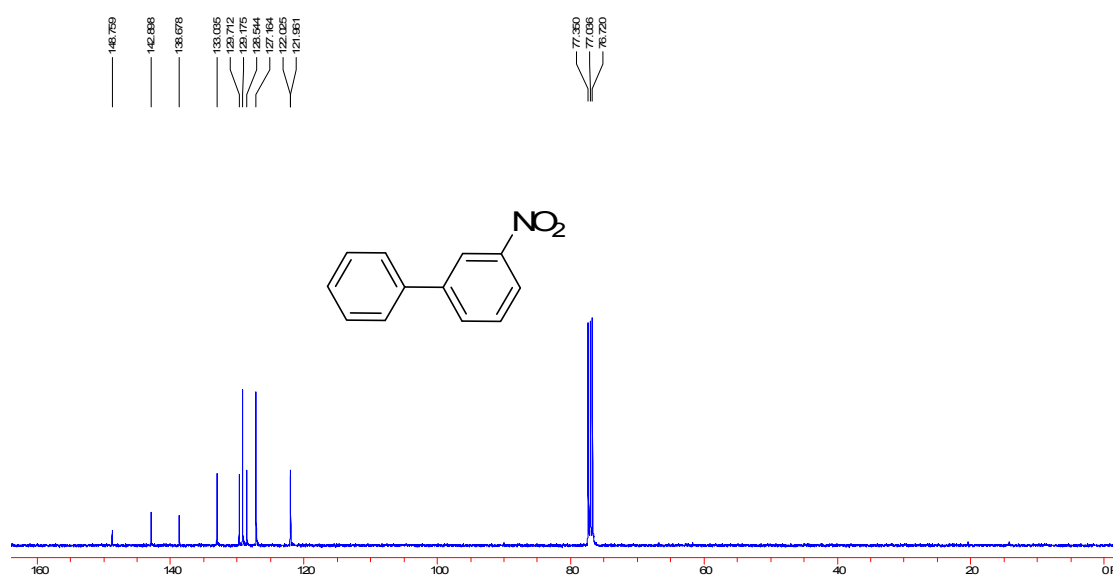
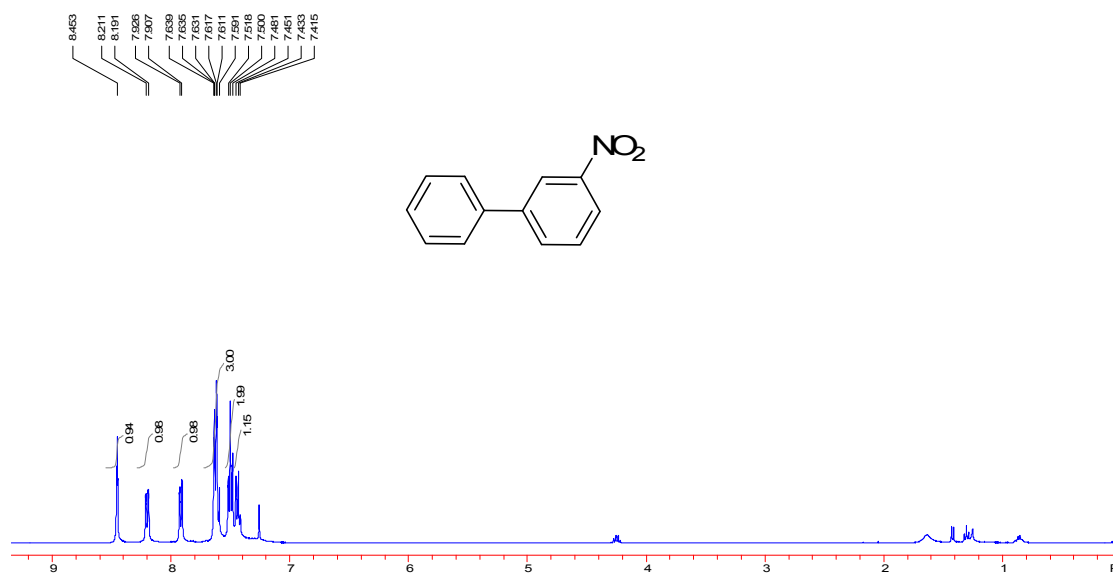
3a



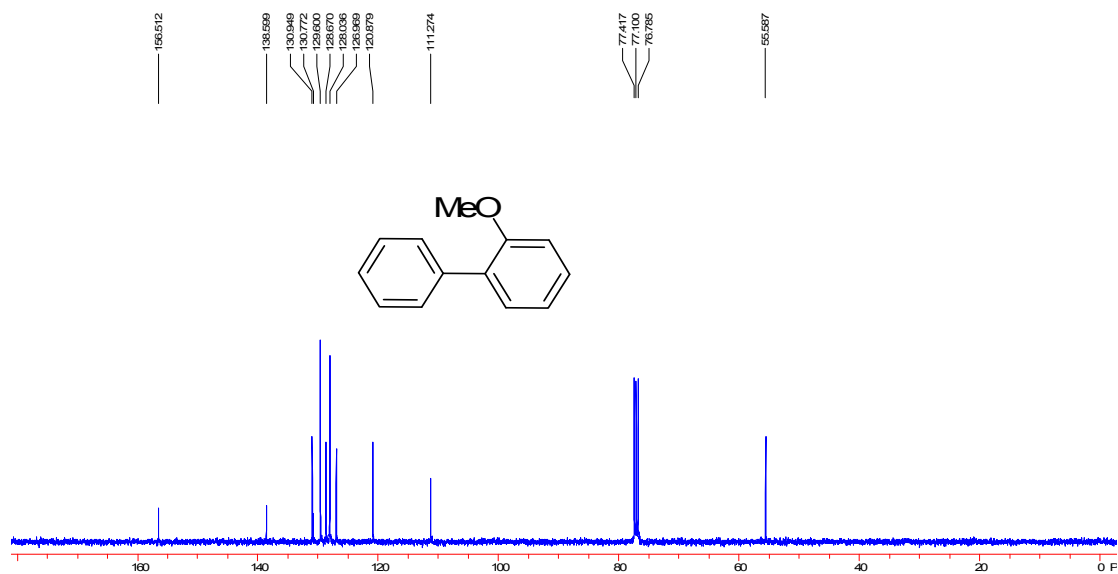
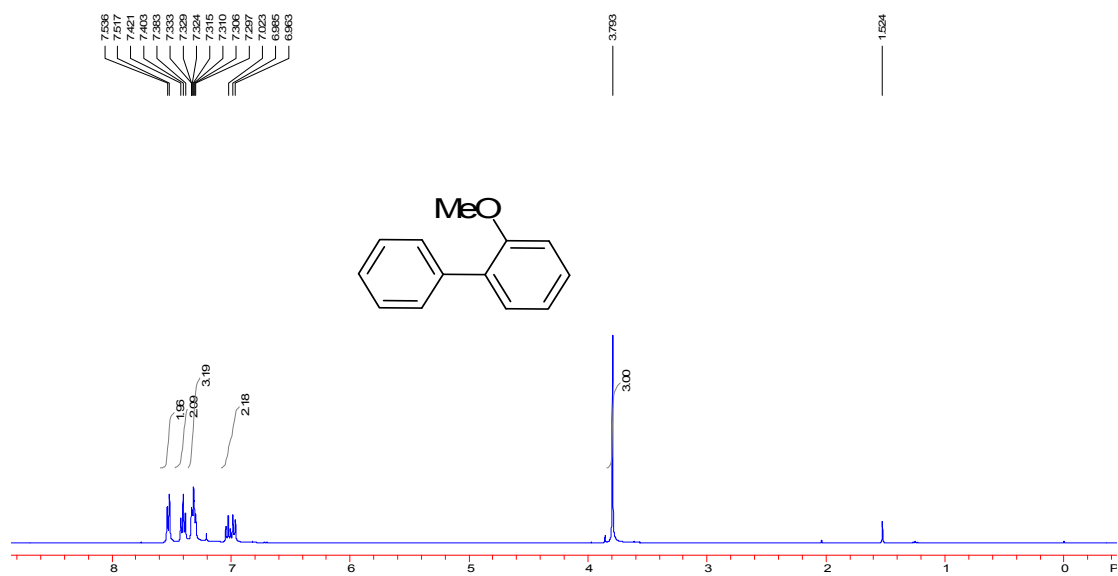
3b



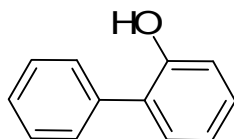
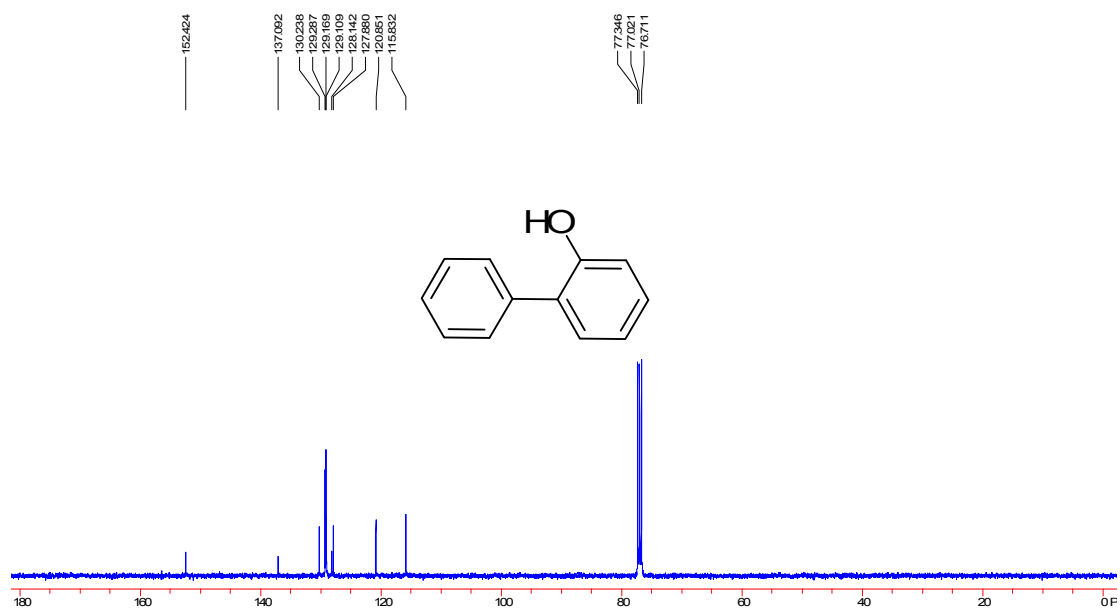
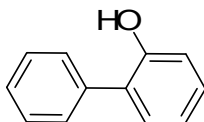
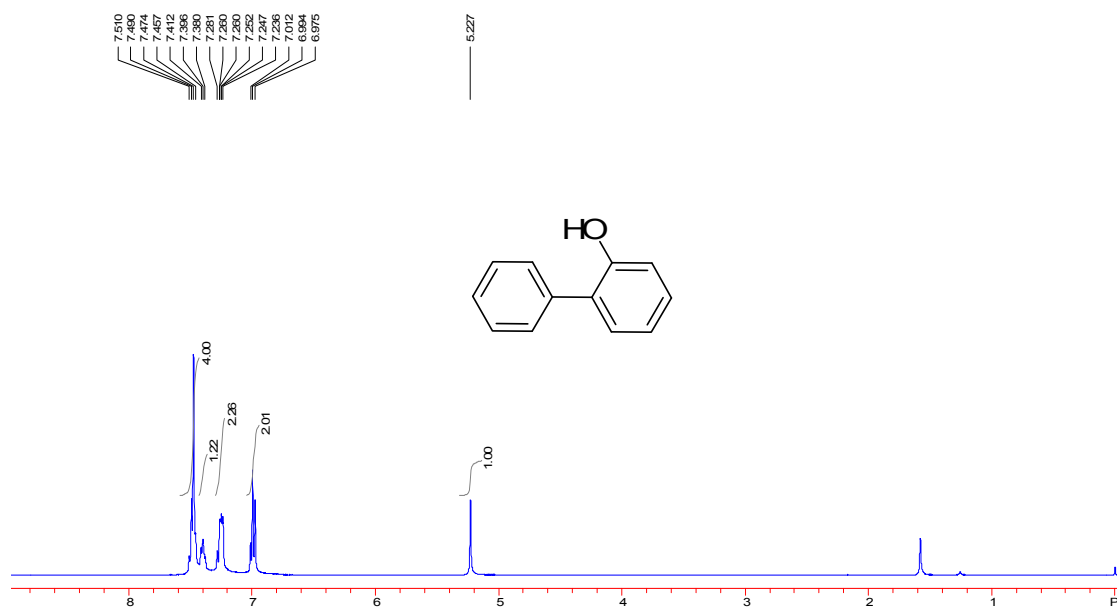
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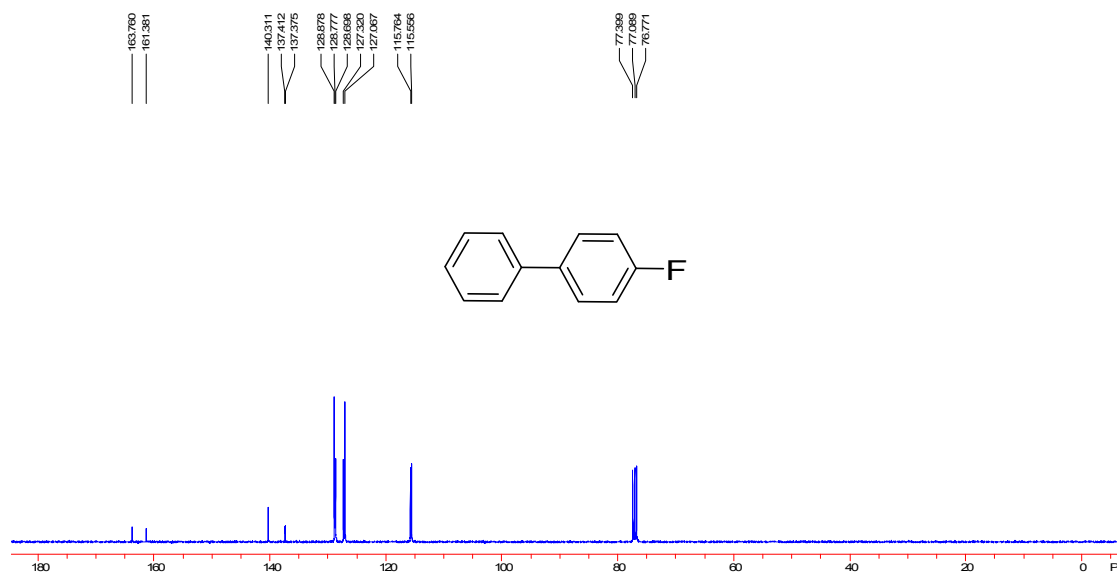
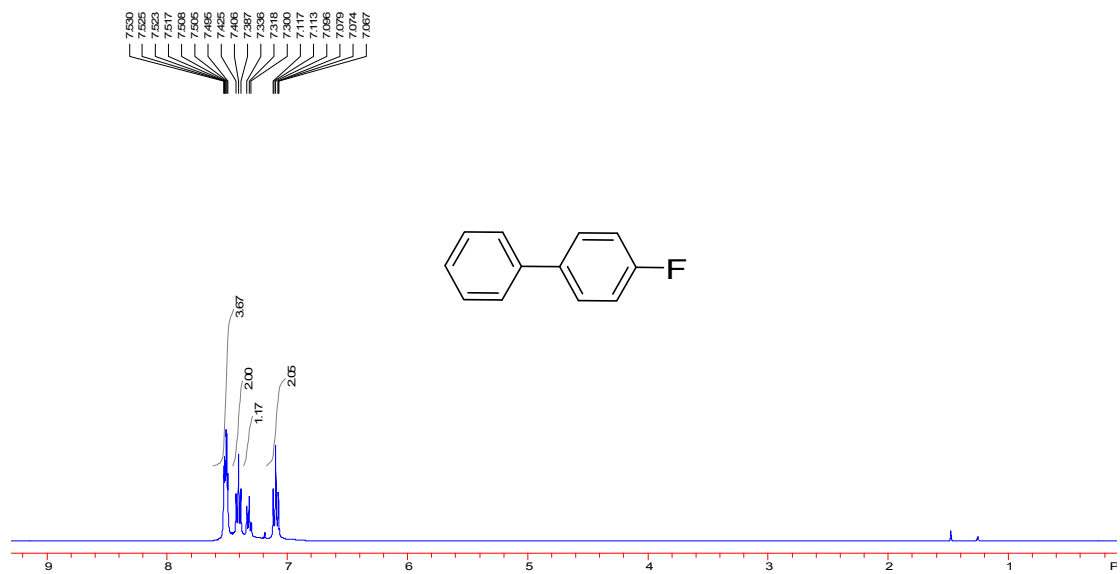
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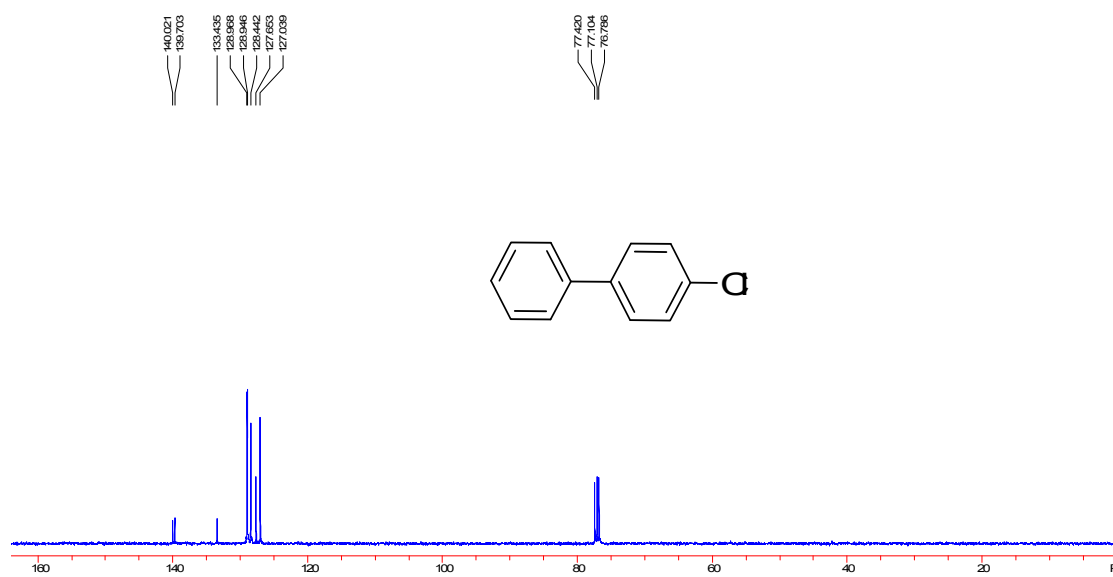
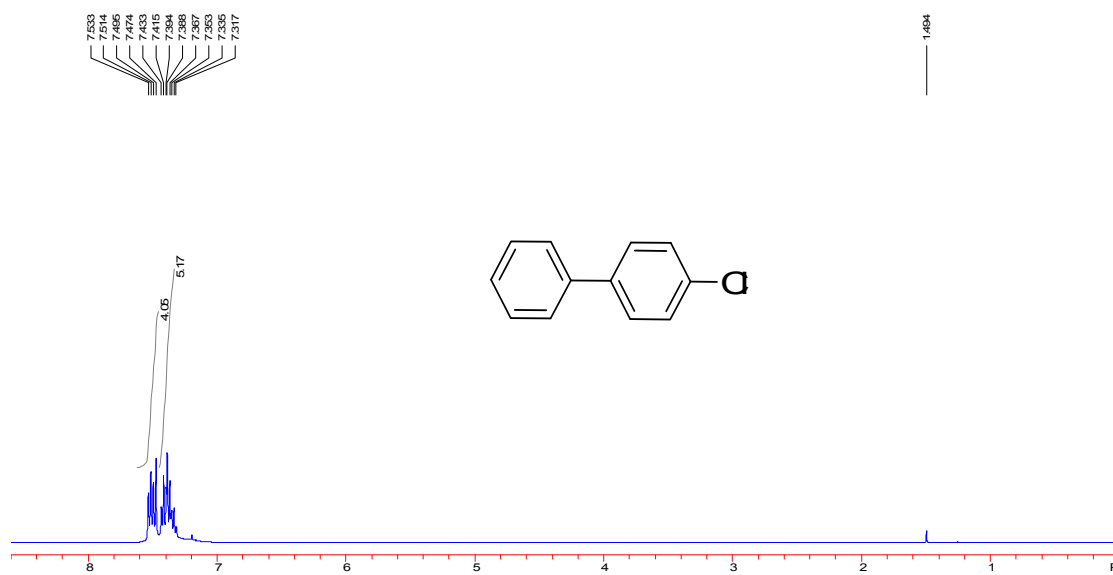
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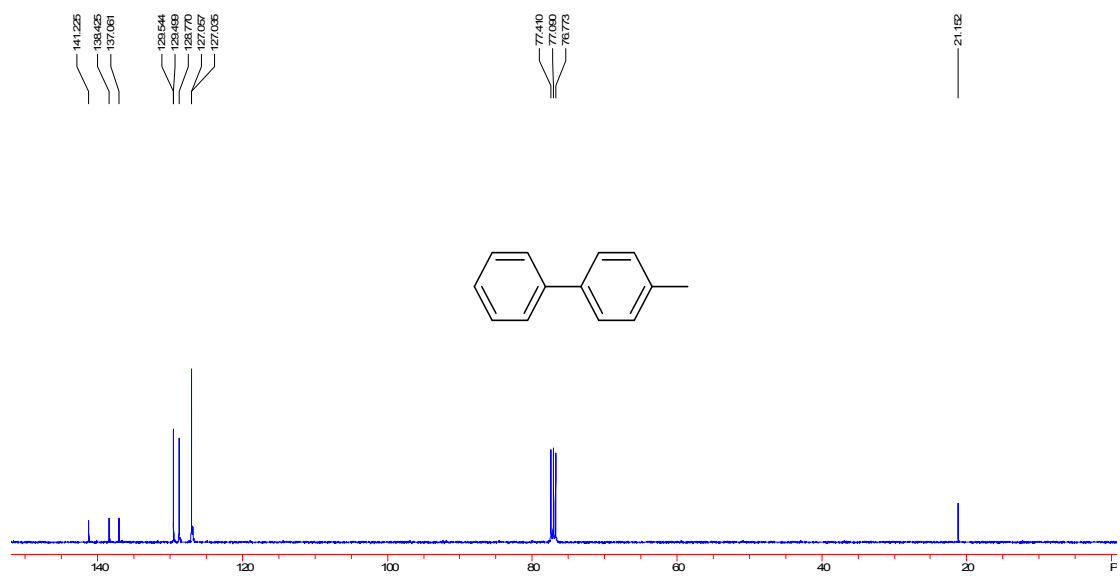
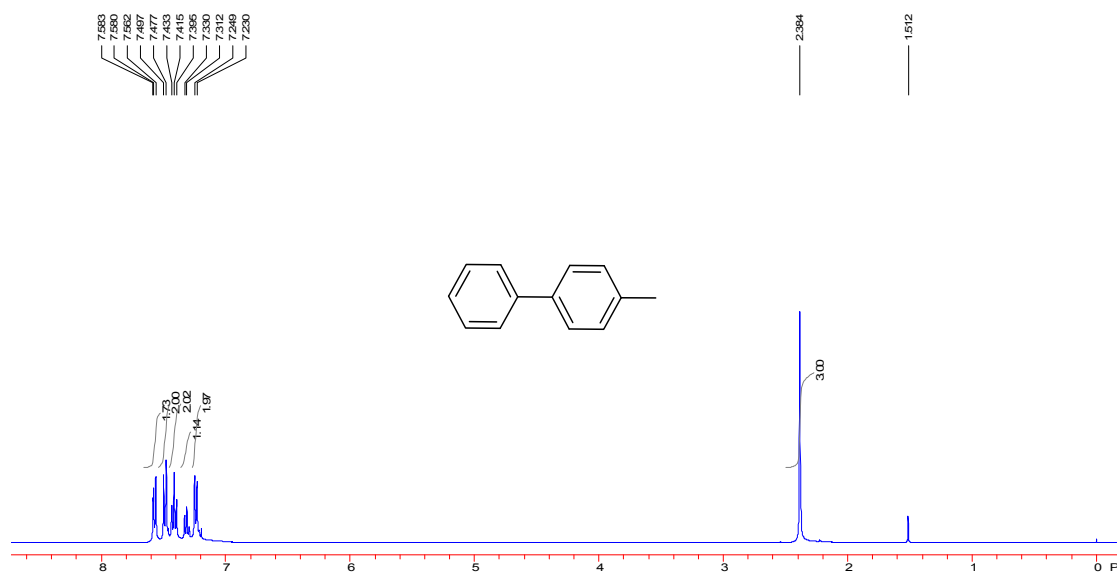
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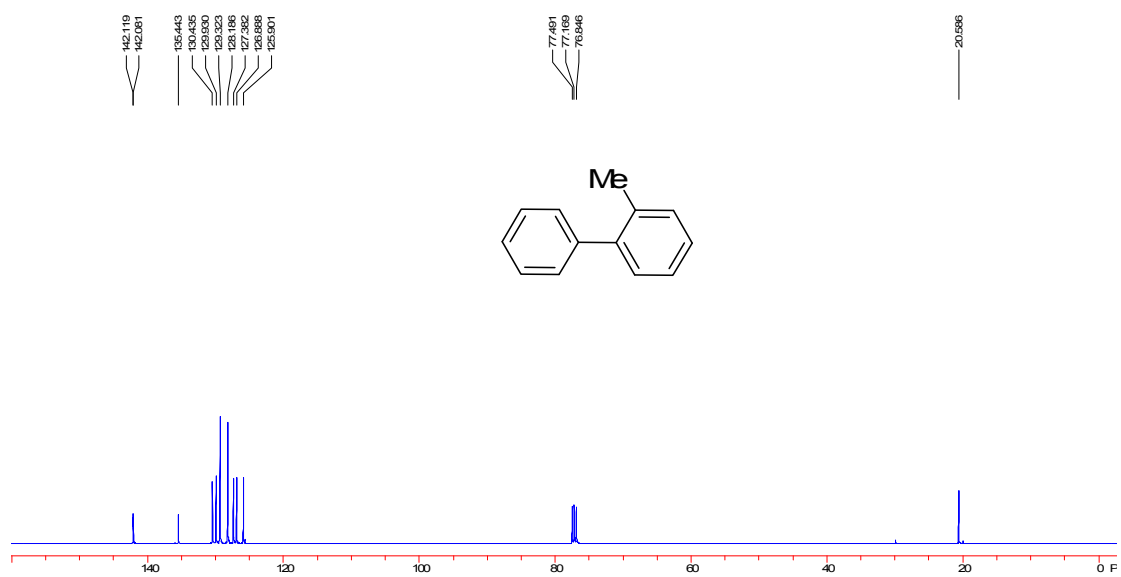
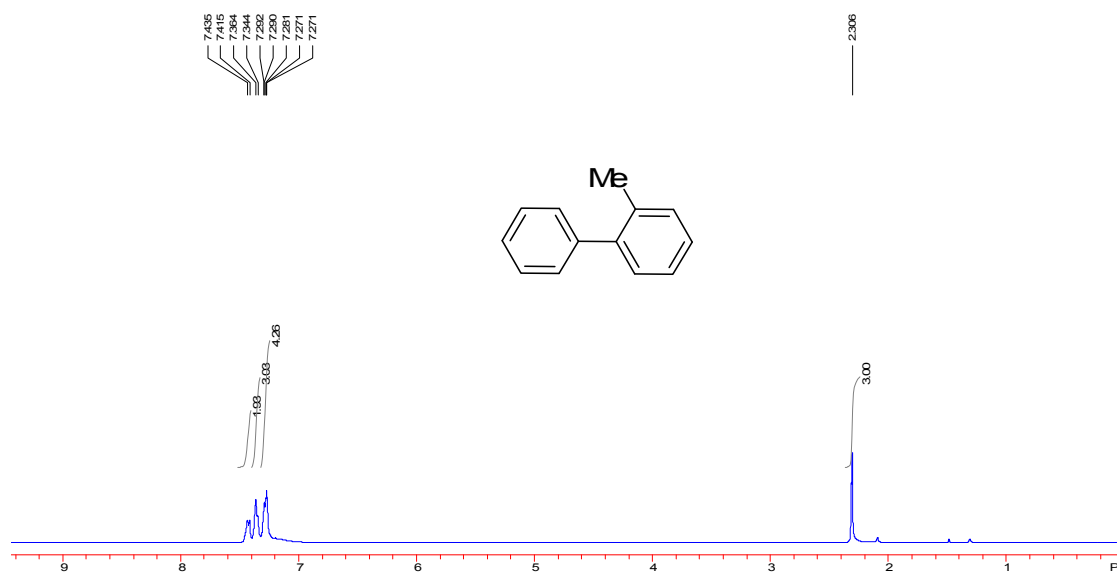
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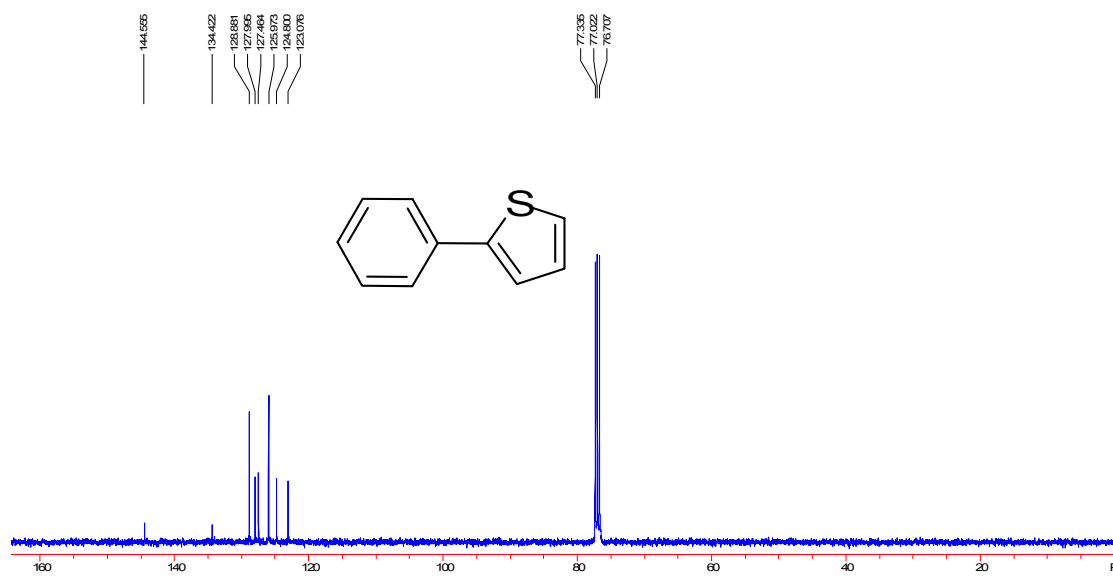
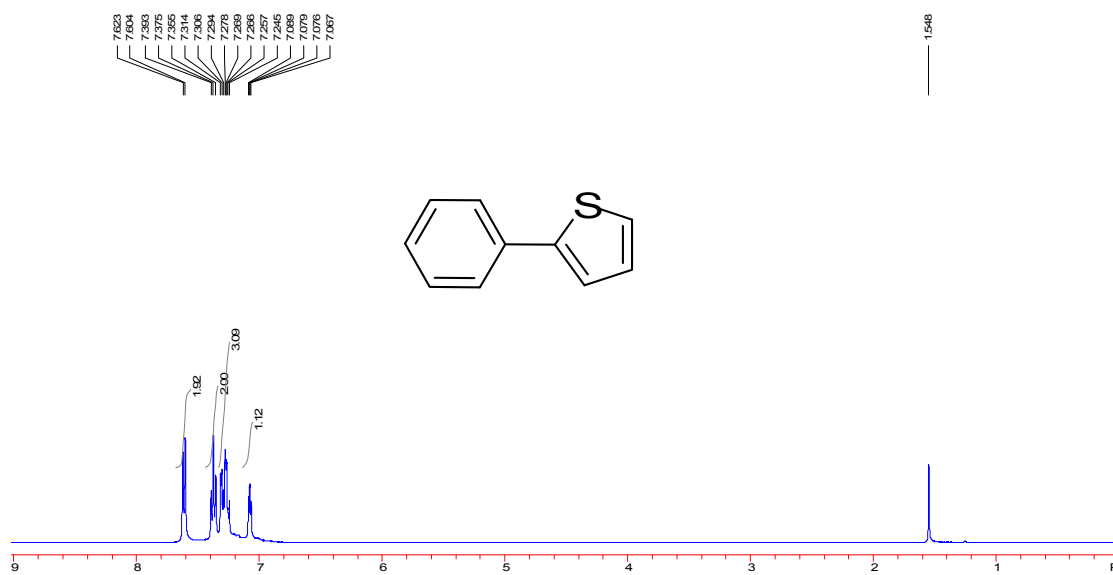
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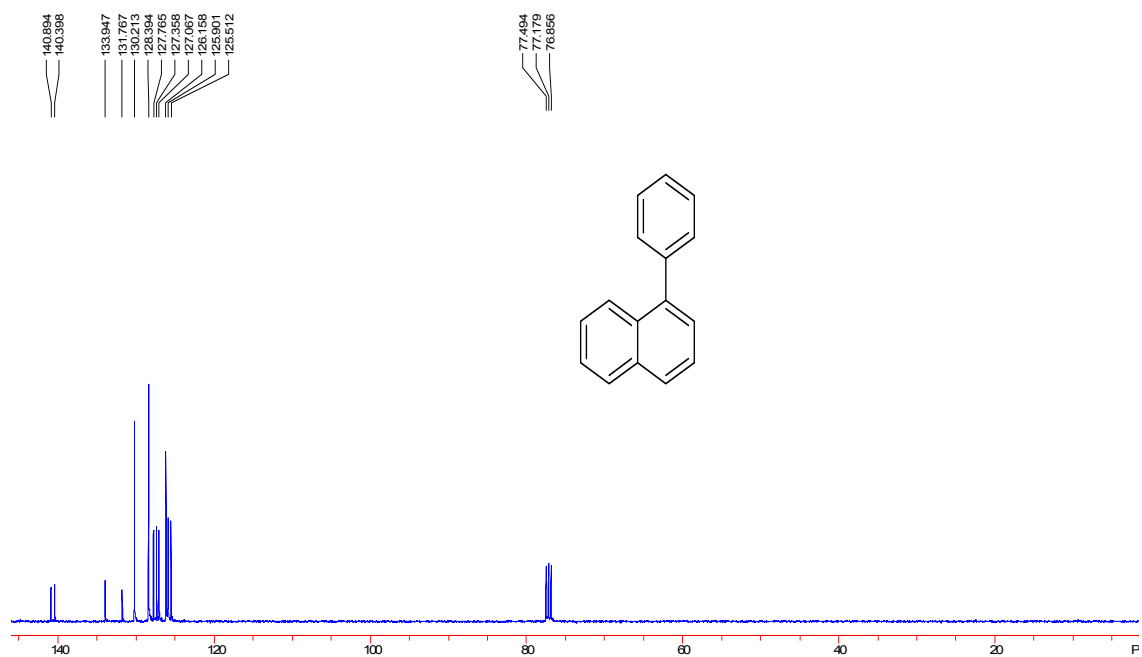
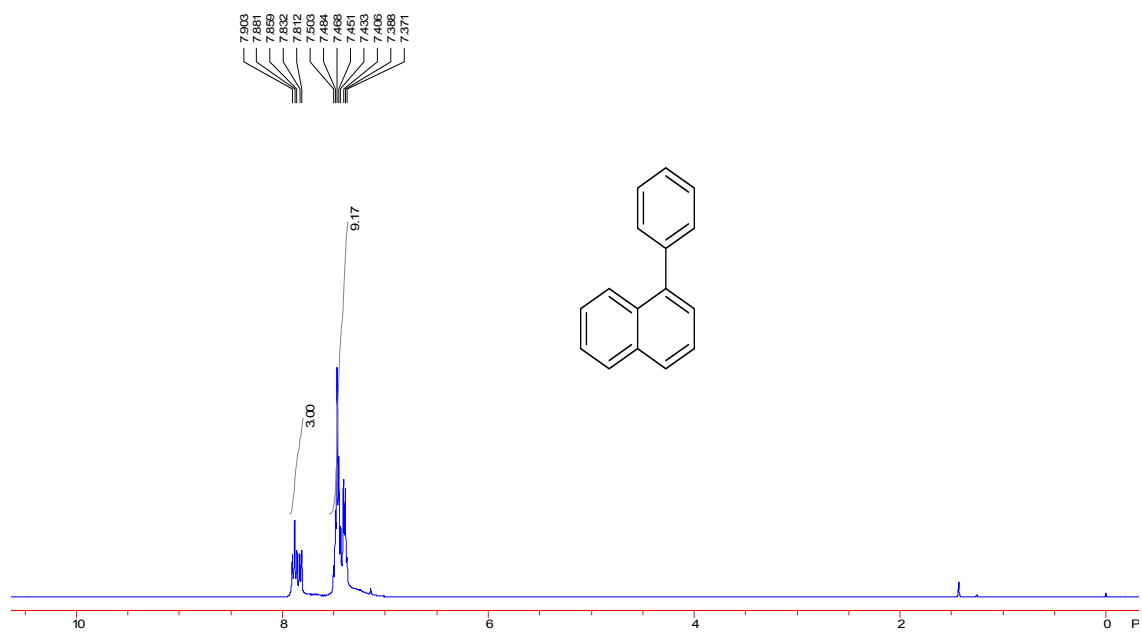
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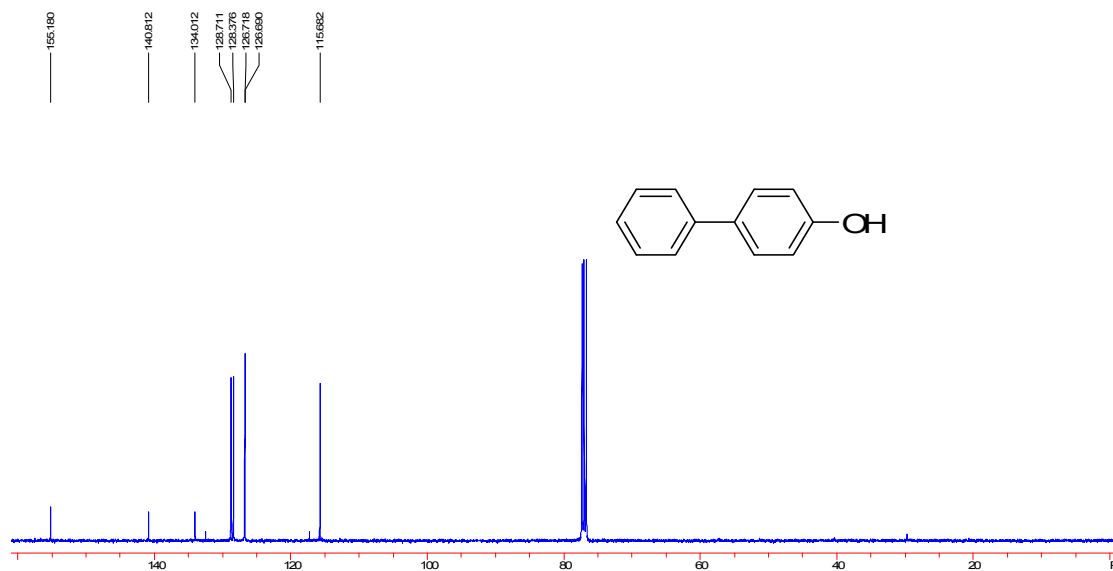
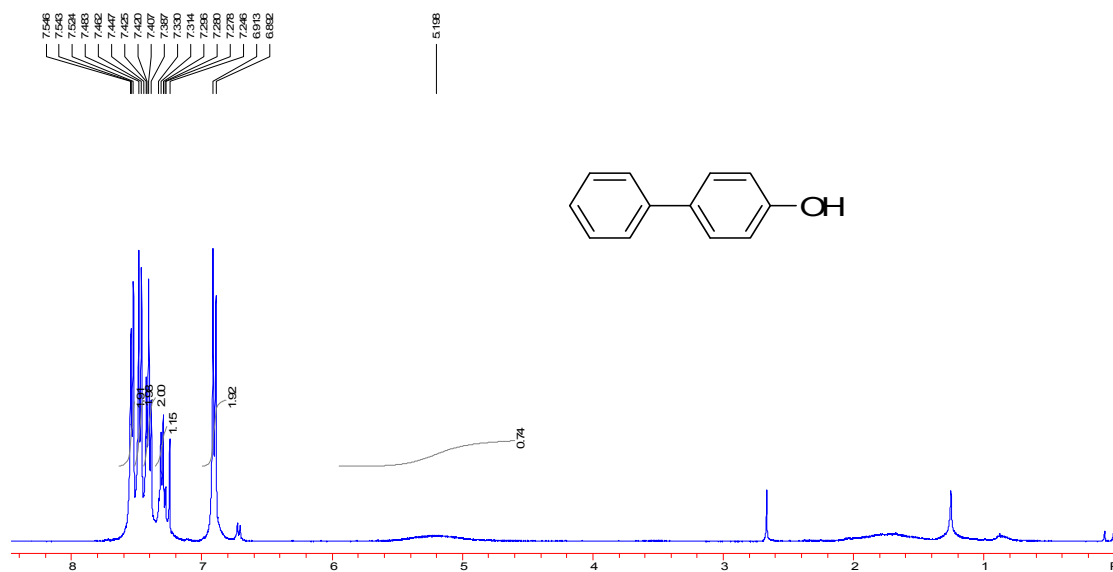
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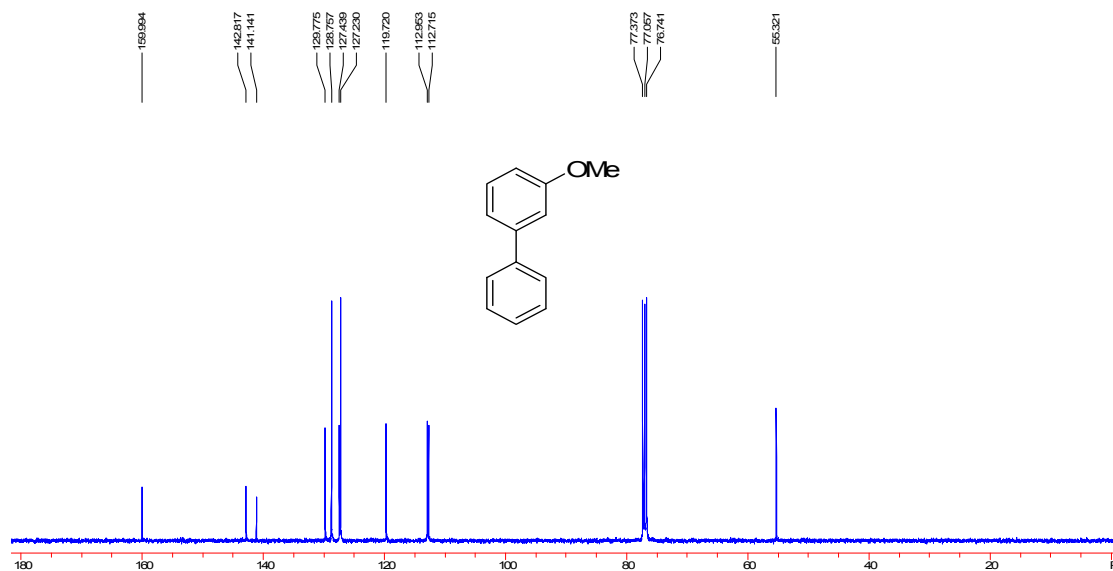
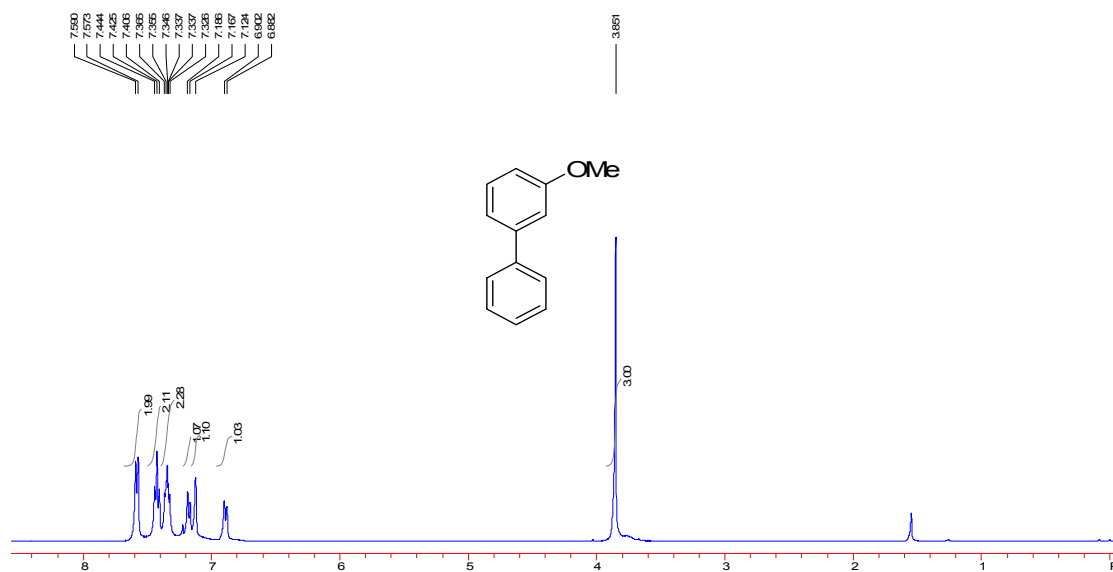
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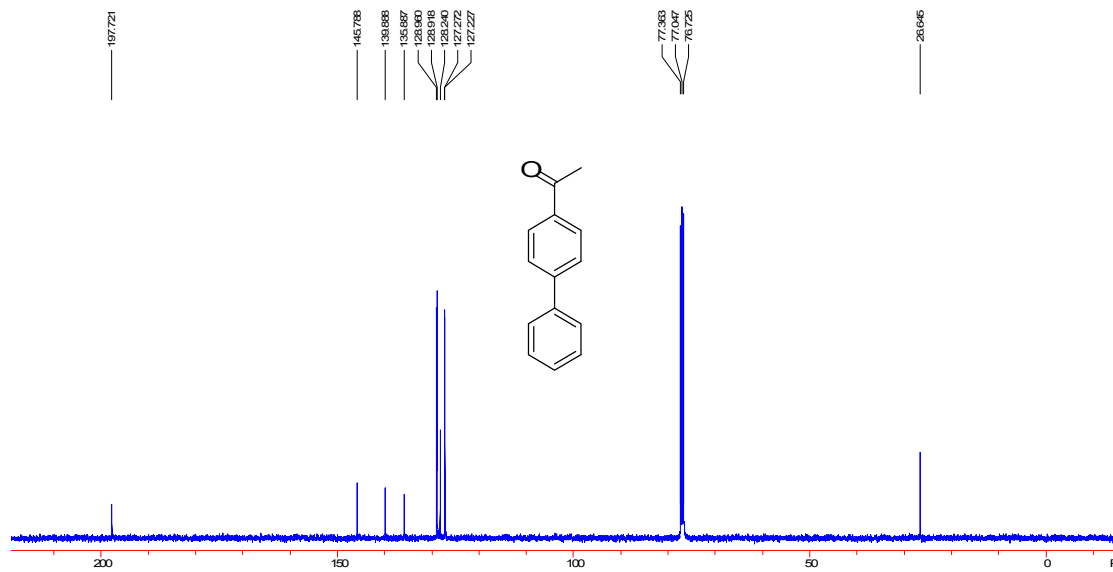
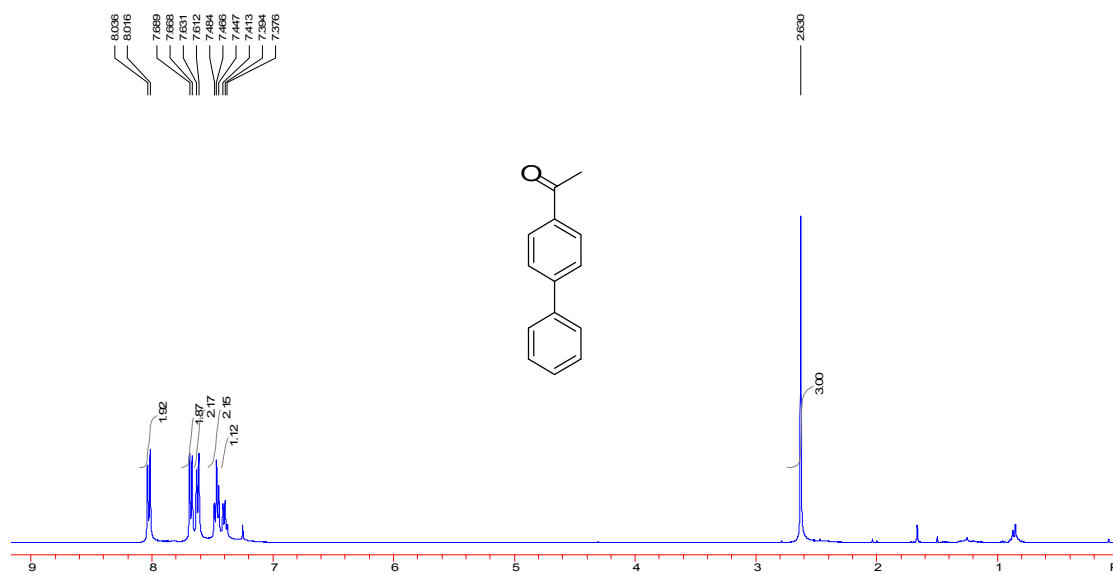
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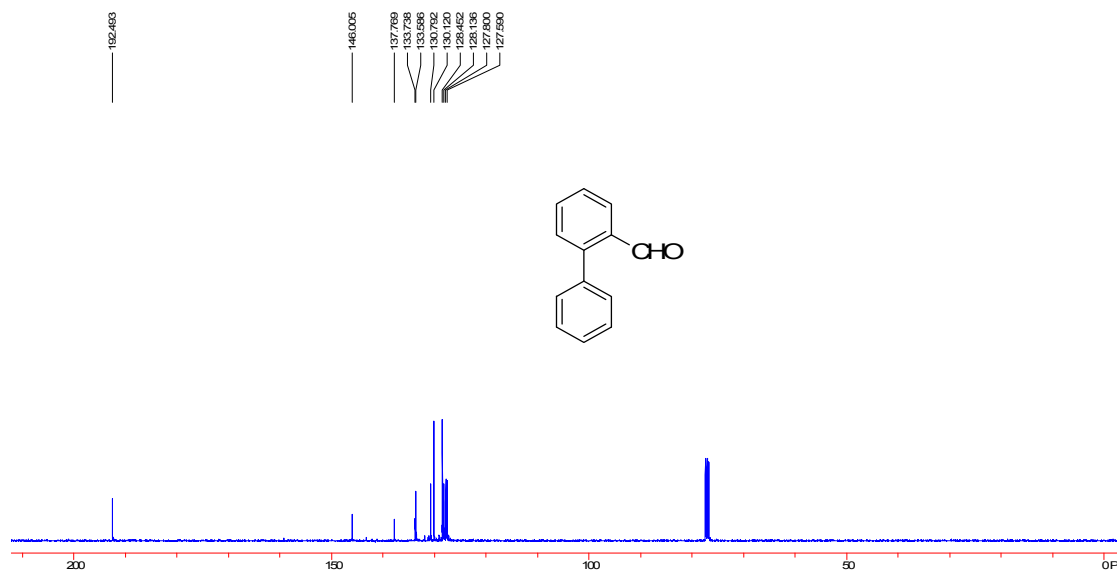
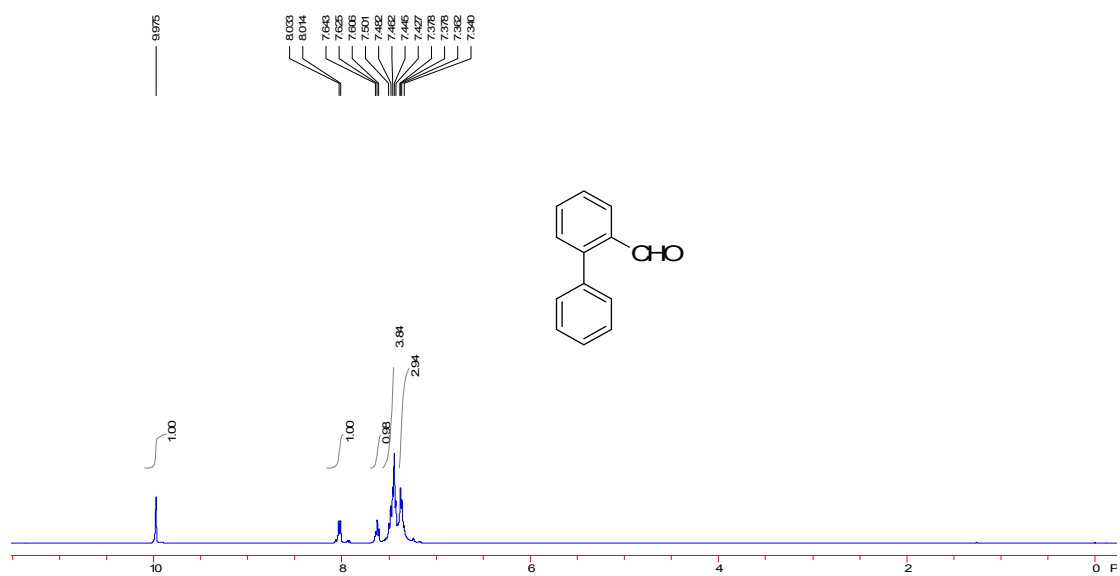
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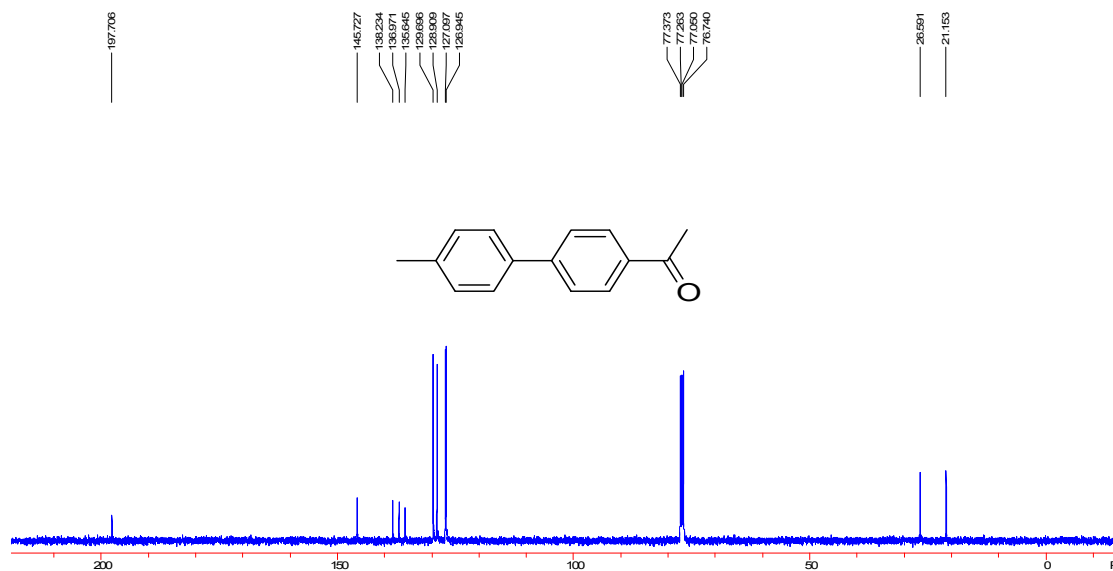
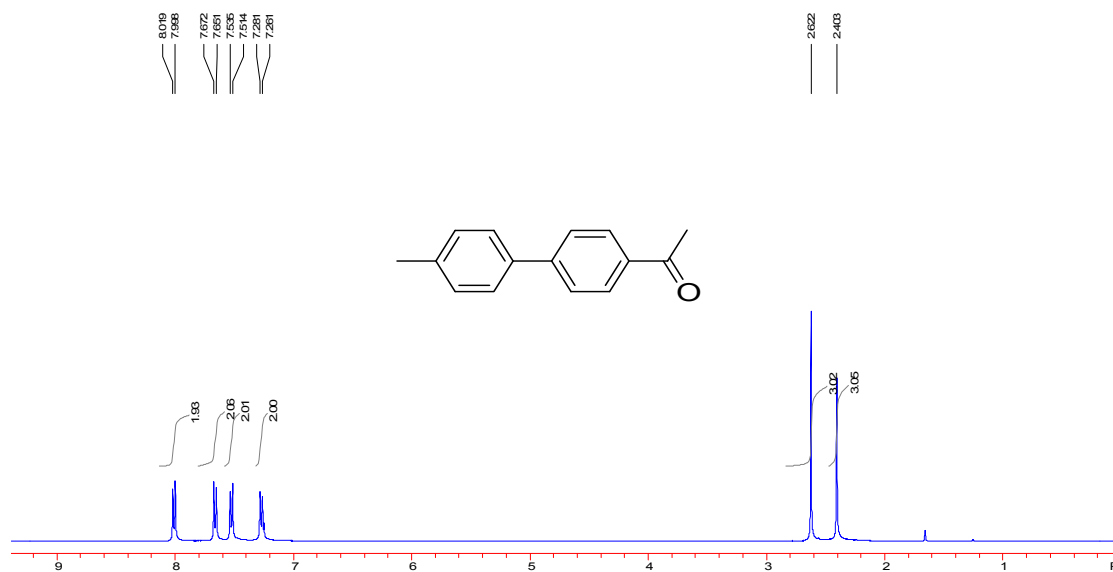
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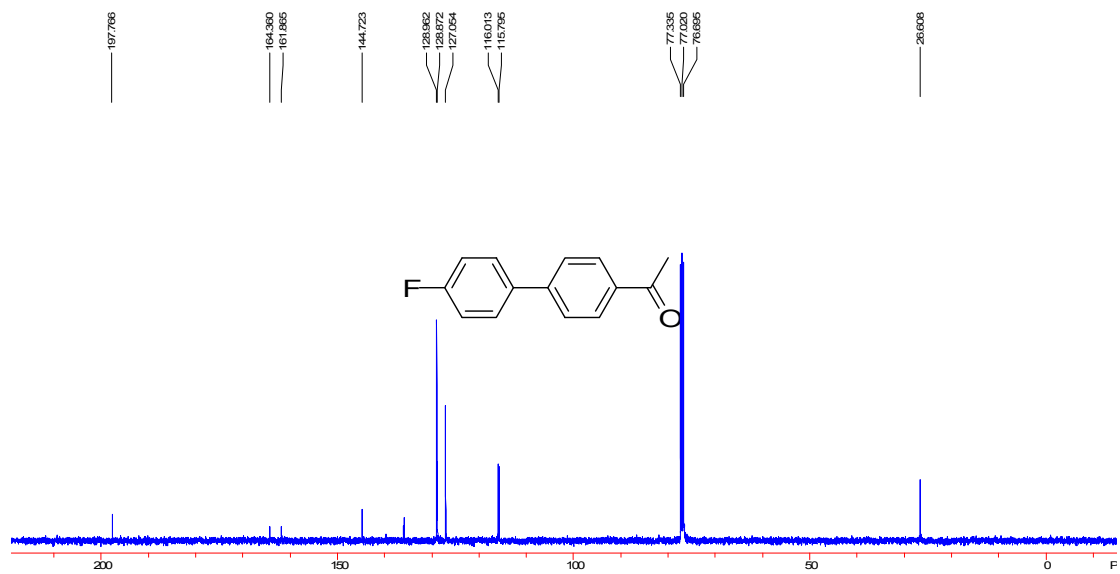
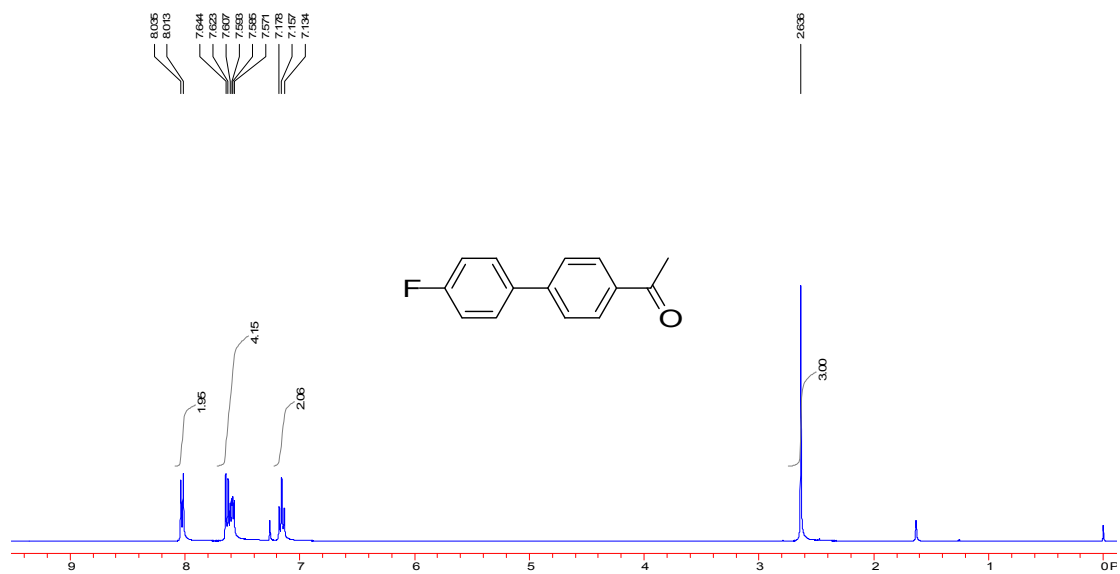
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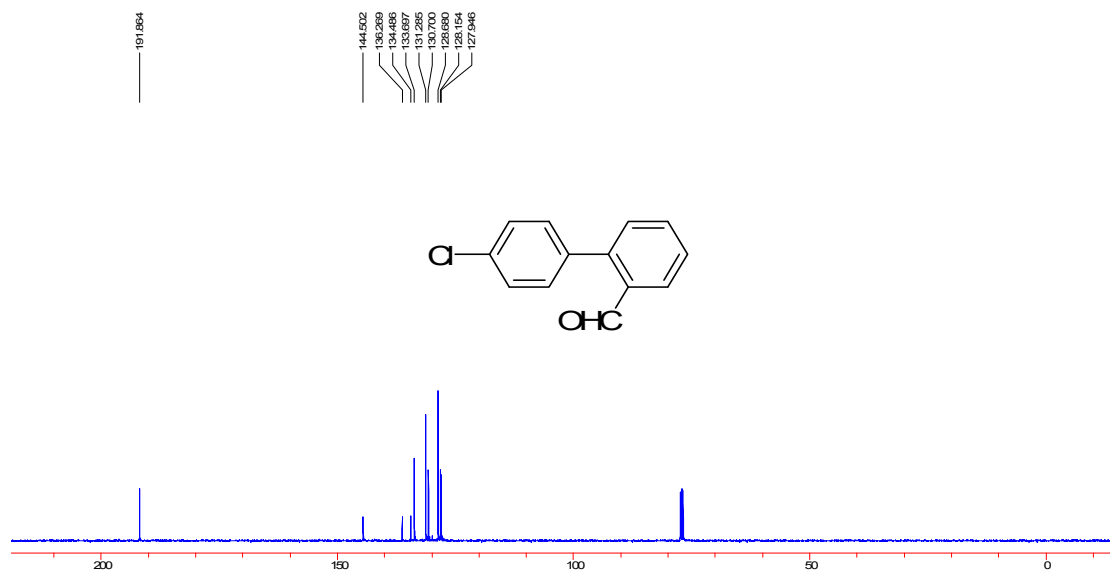
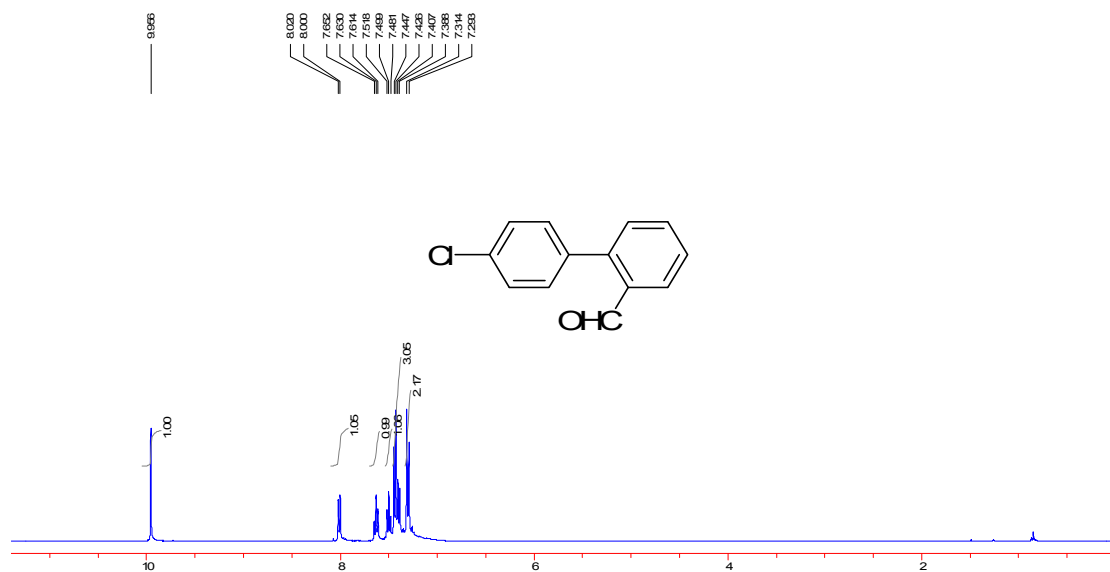
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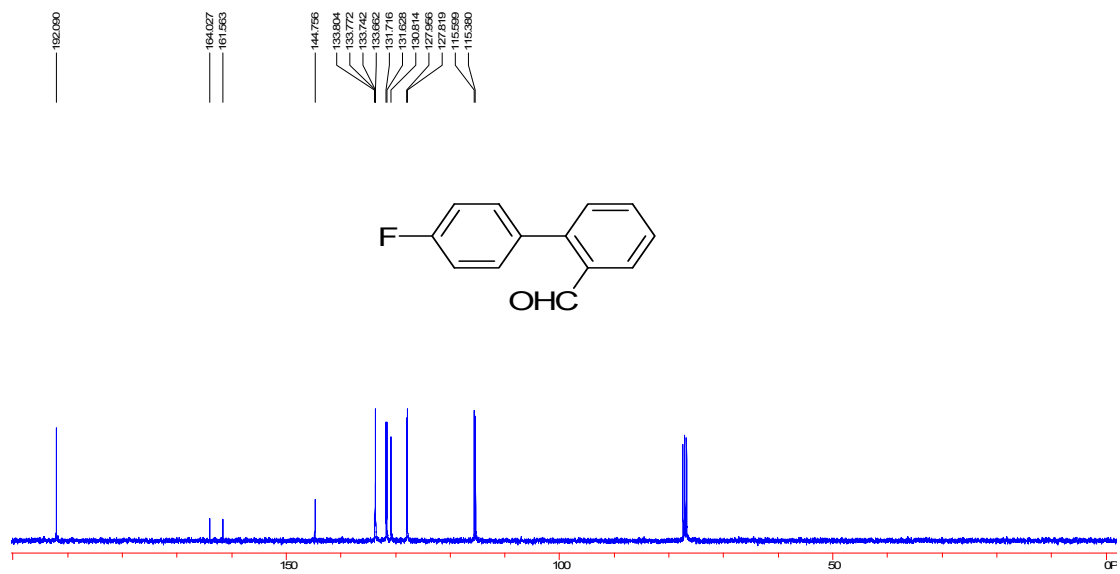
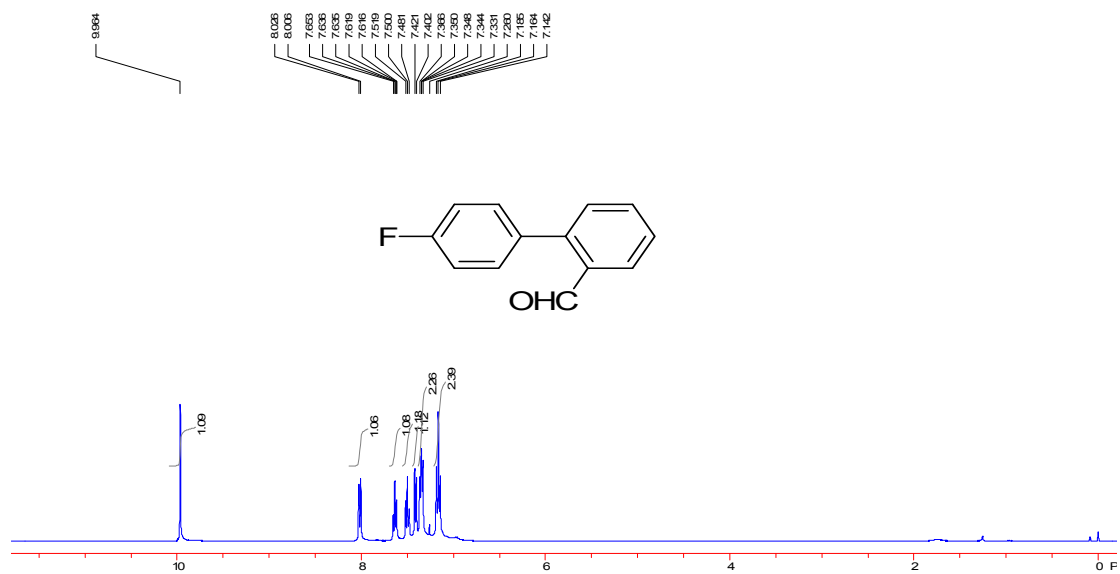
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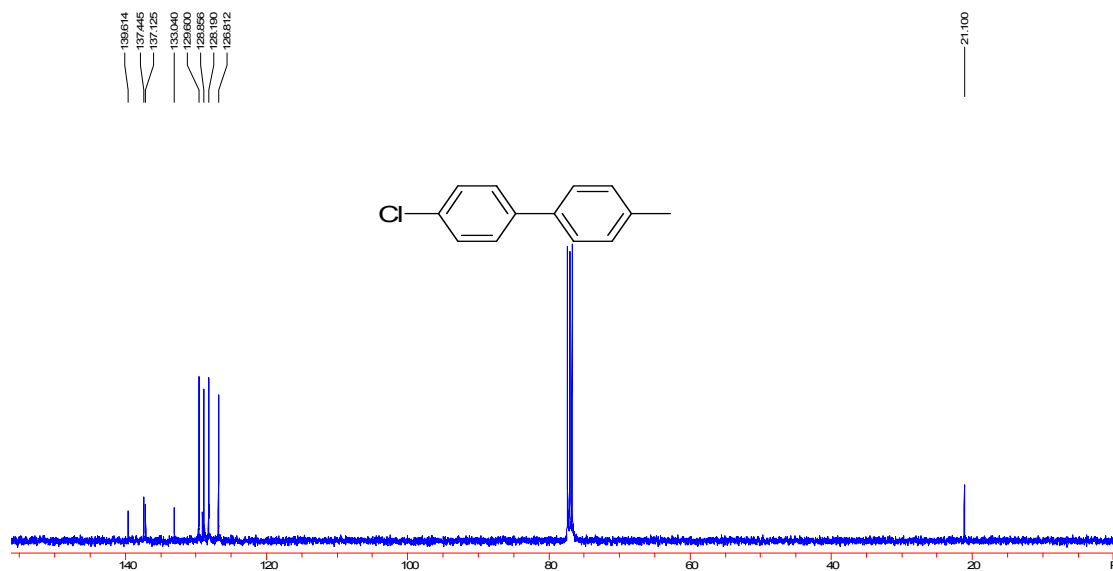
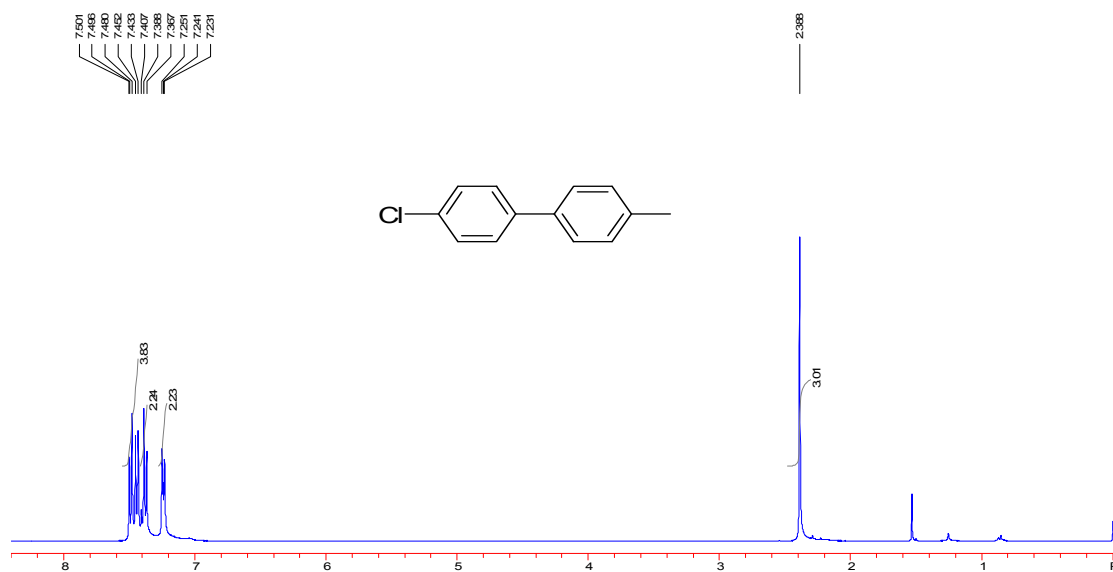
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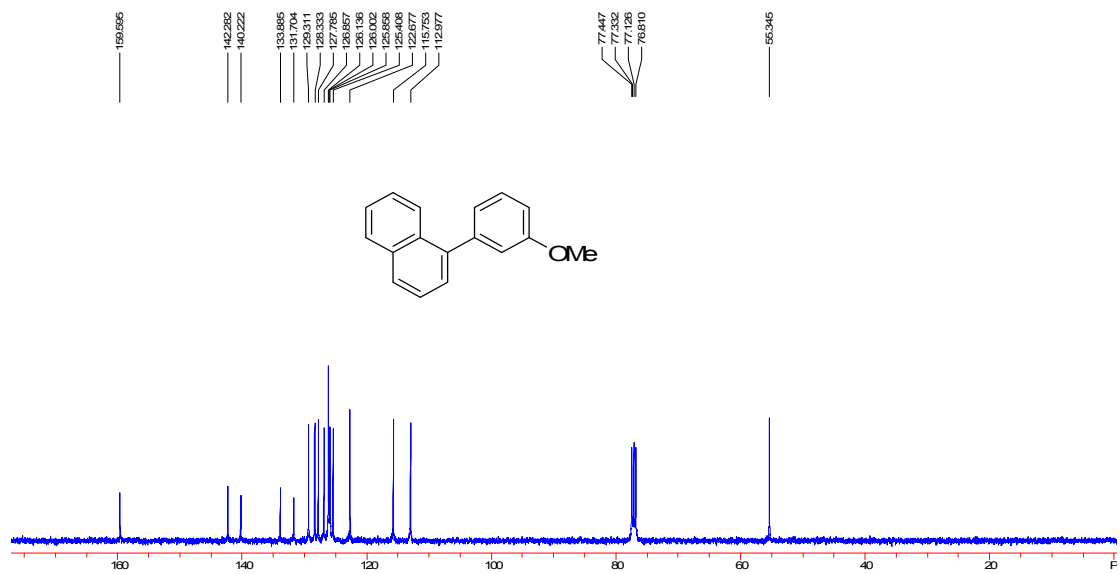
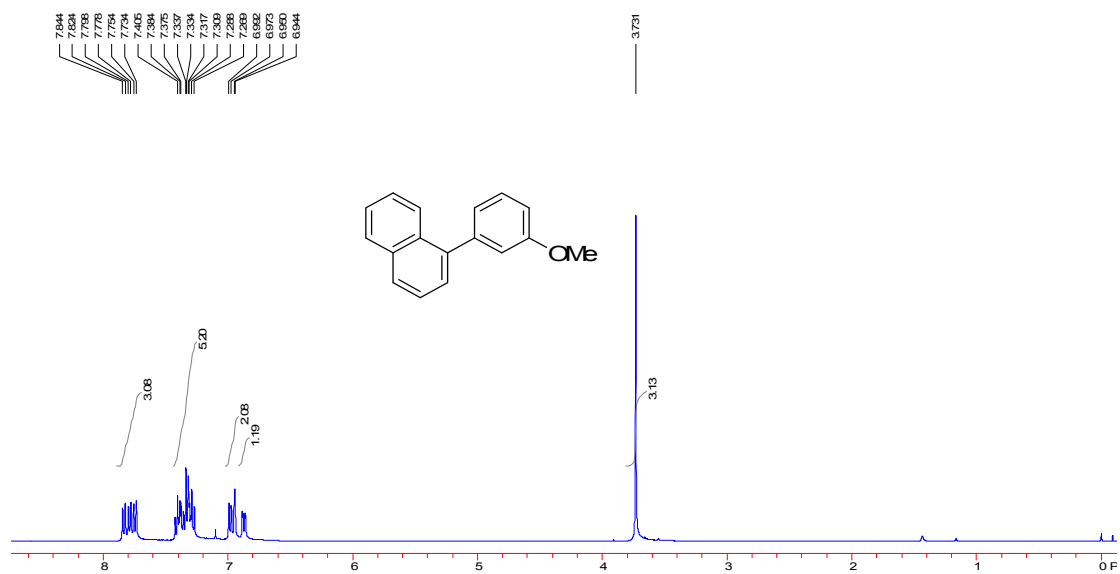
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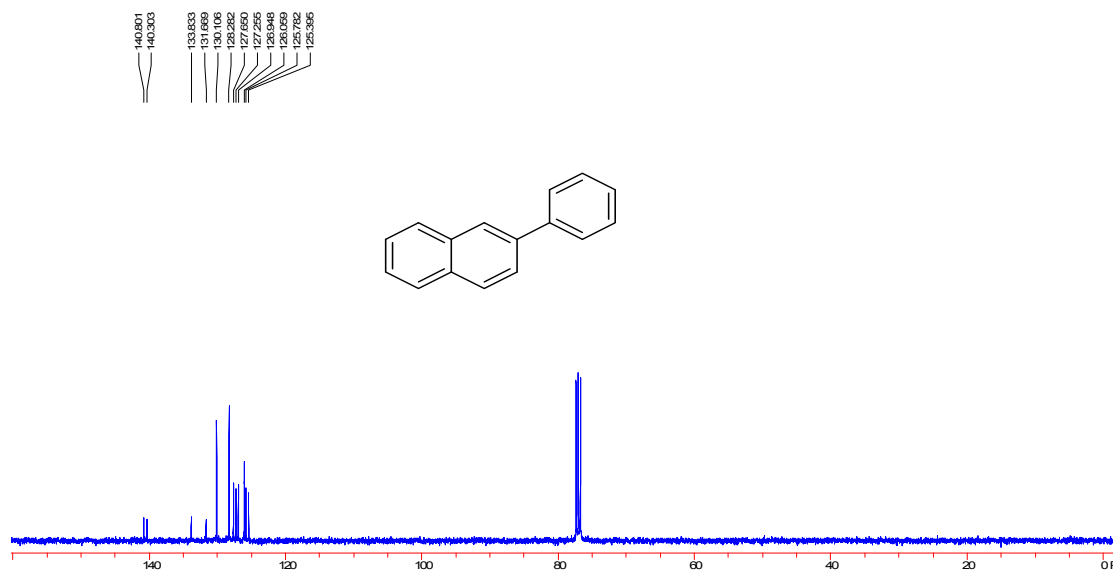
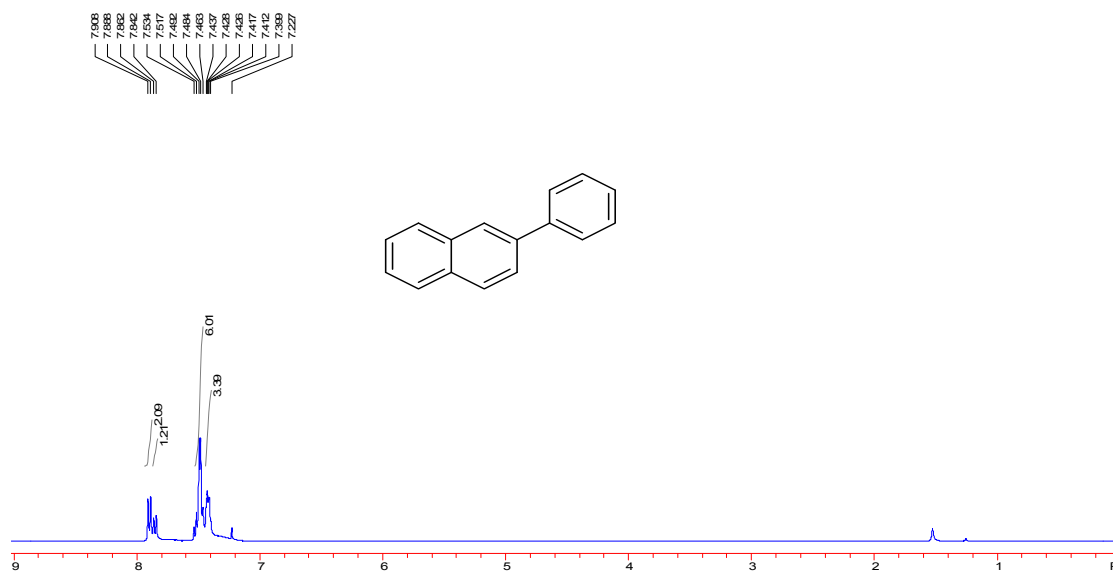
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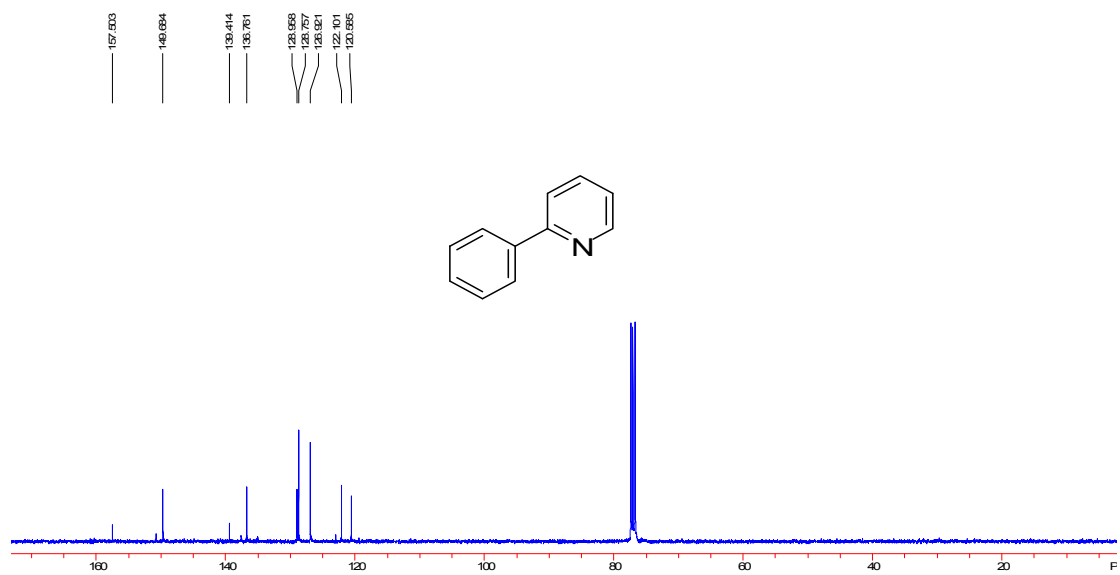
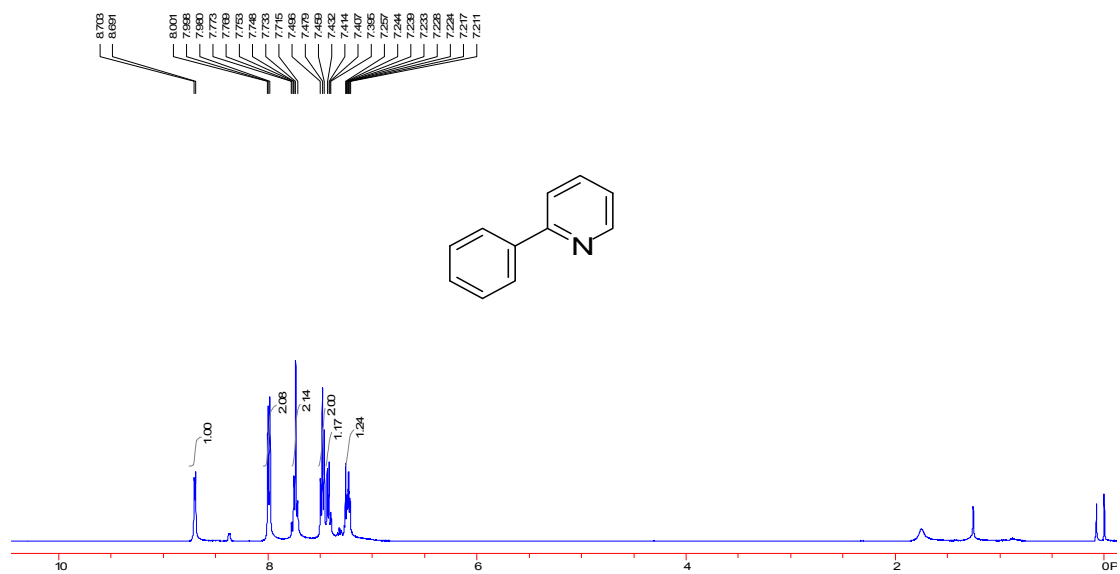
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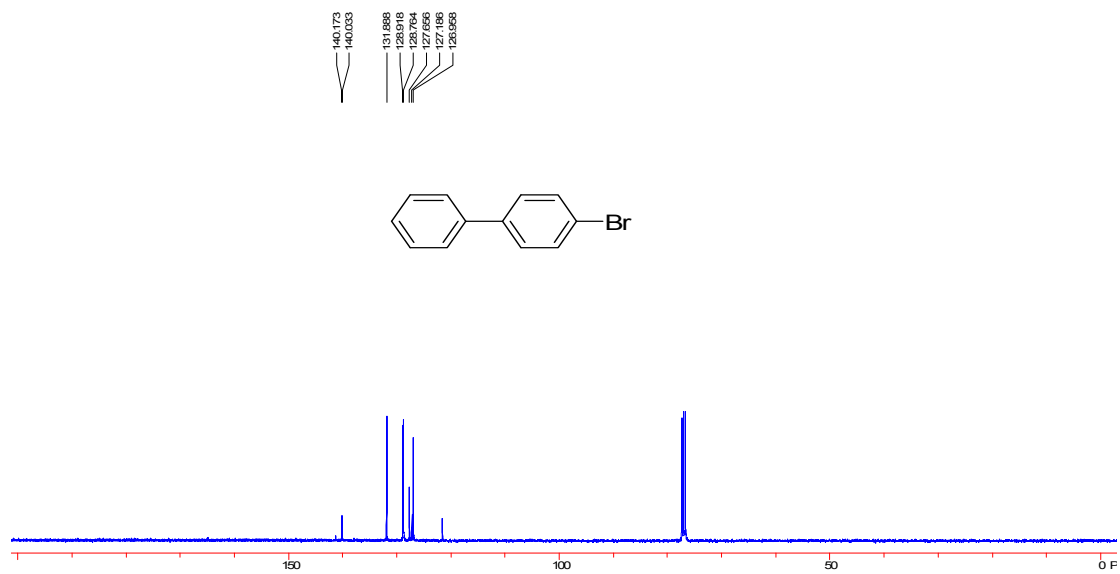
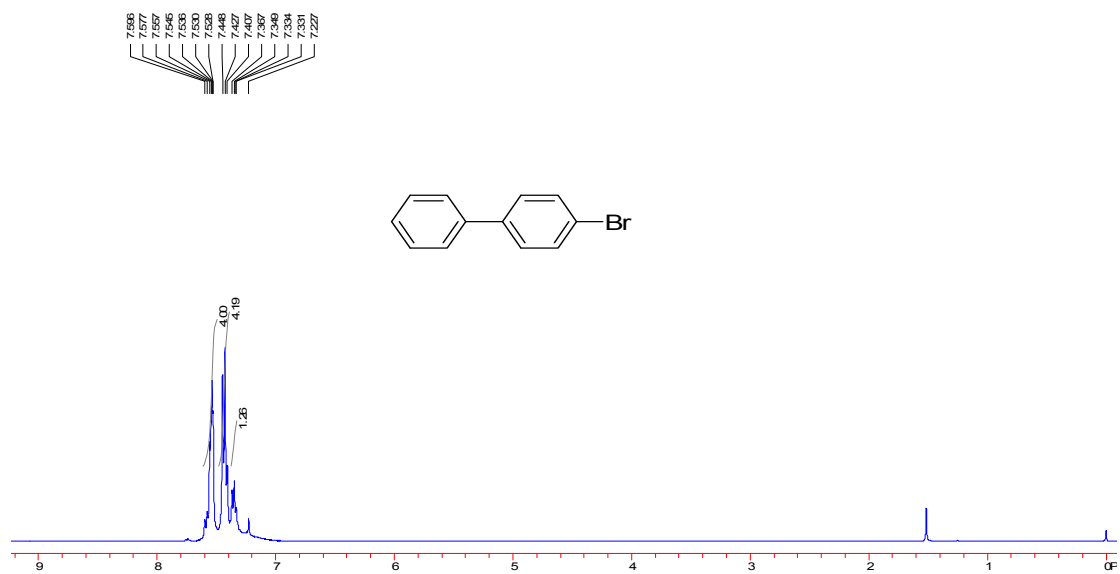
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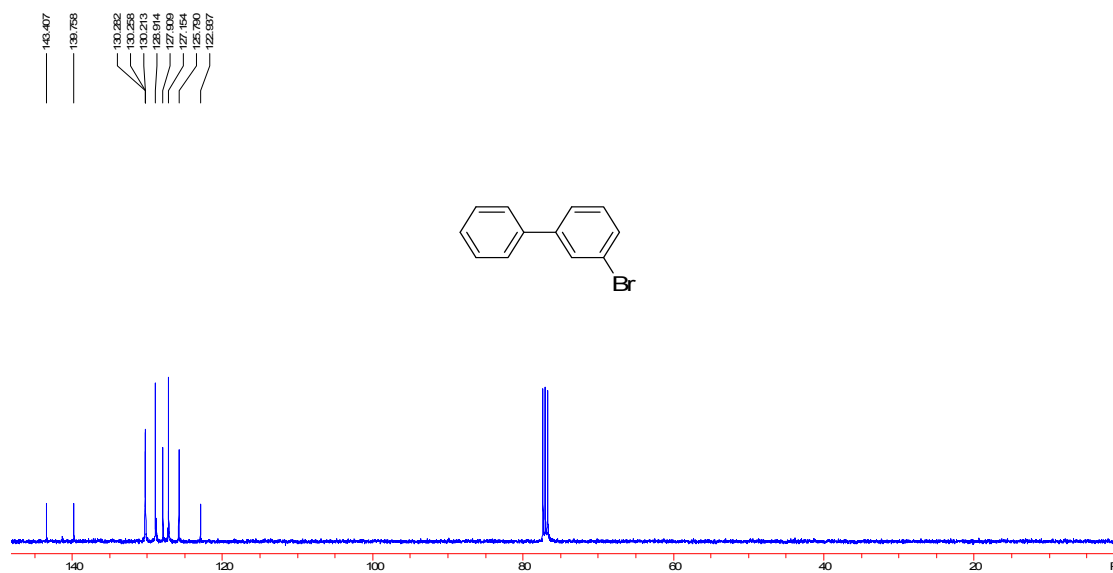
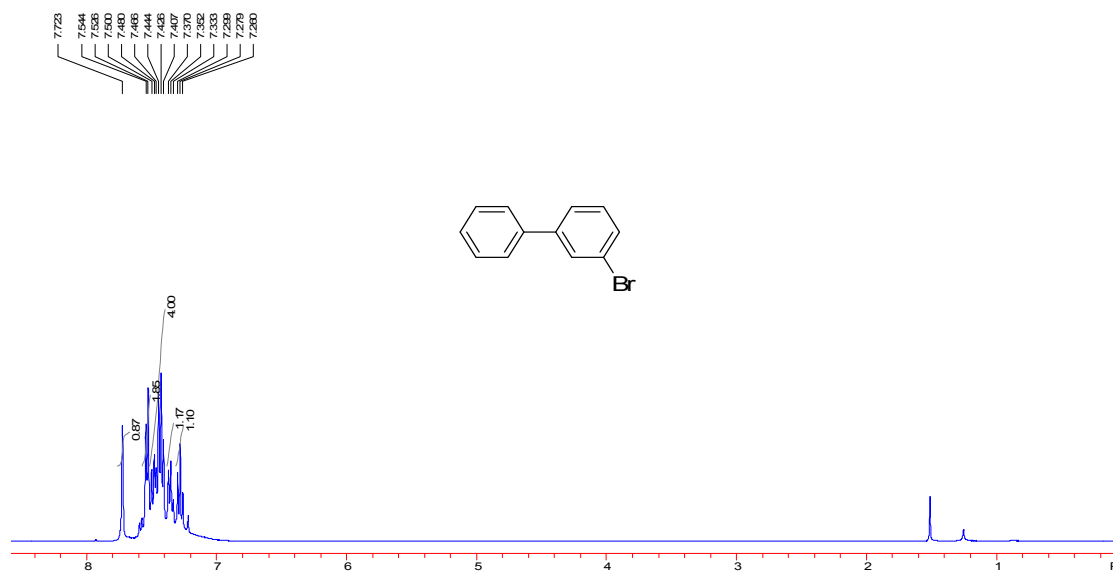
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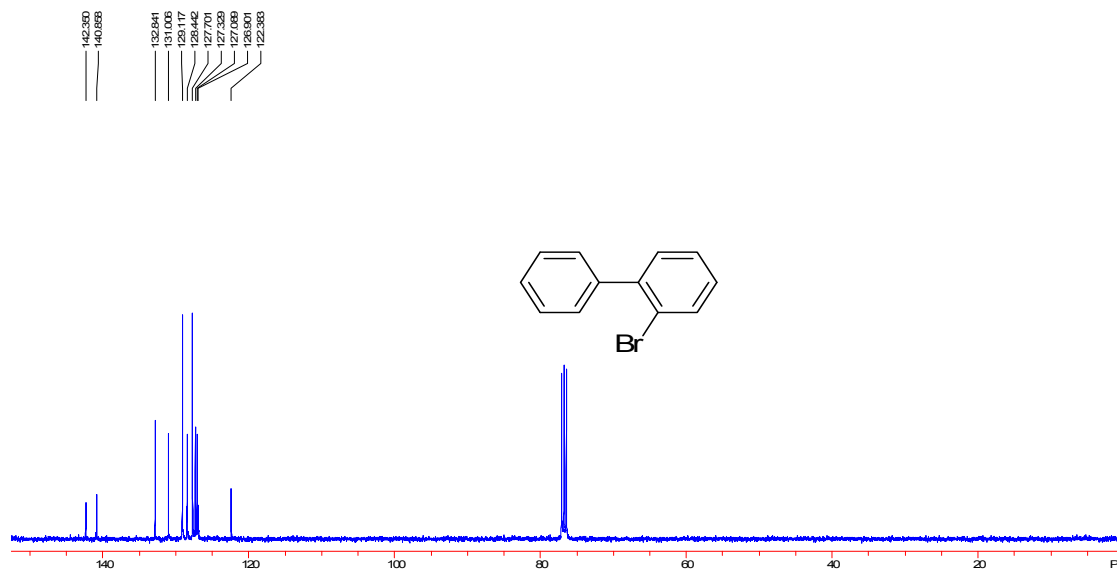
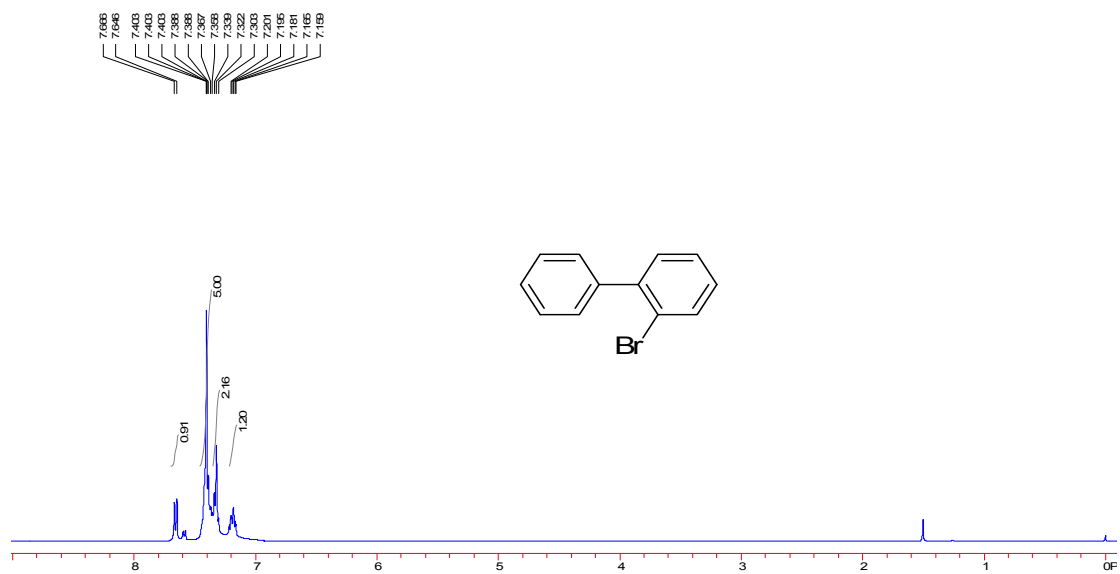
3x



3y



3z



4z

