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Thieme

Supporting Information for

Expedient Synthesis of Terminal Vinylphosphonates via Palladium-Catalyzed C−C Cross-Coupling Reactions of (1-Halovinyl)phosphonates

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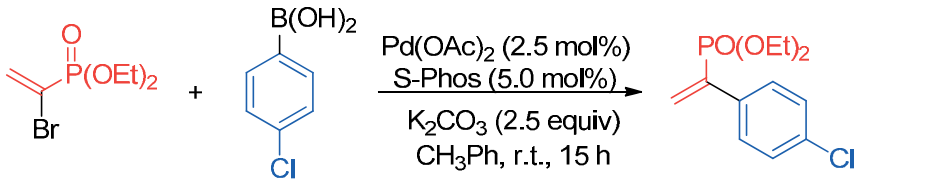

- mild reaction conditions
- good substrate tolerance
- gram-scale synthesis
- high efficiency

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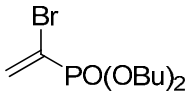
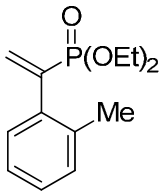
1. Characterizations of new compounds.

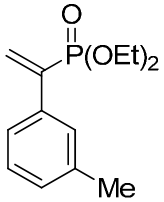


Dibutyl (1-bromovinyl)phosphonate (**2c**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.9-0.94 (m, 6H), 1.38-1.43 (m, 4H), 1.66-1.69 (m, 4H), 4.03-4.11(m, 4H), 6.43 (dd, *J* = 1.8, 37.2 Hz, 1H), 6.88 (dd, *J* = 1.8, 14.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 18.5, 32.2 (d, *J* = 6.5 Hz), 66.9 (d, *J* = 6.0 Hz), 119.1 (d, *J* = 199.4 Hz), 135.3 (d, *J* = 13.9 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 8.1; IR (KBr):

ν (cm^{-1}) 2988, 2942, 2908, 1623, 1362, 1261, 1195, 1185, 1170, 860, 780, 729; GC-MS: *m*/*z* (rel intensity) 299 (M+1, 0.24), 243 (8), 189 (100), 163 (37), 145 (4), 107 (11), 81 (9), 57 (29); HRMS (EI) calcd for $C_{10}H_{19}O_3BrP$ [M-H^+] 297.0255; found 297.0261.

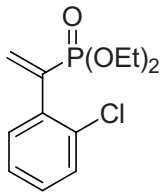


Diethyl (1-(*o*-tolyl)vinyl)phosphonate (**3b**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.0 Hz, 6H), 2.31 (s, 3H), 4.04-4.10 (m, 4H), 5.84 (dd, *J* = 2.0, 47.7 Hz, 1H), 6.42 (dd, *J* = 22.6, 2 Hz, 1H), 7.13-7.17 (m, 2H), 7.20 -7.21 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.3 (d, *J* = 6.4 Hz), 20.0, 62.2 (d, *J* = 6.1 Hz), 125.3 (d, *J* = 1.5 Hz), 127.8 (d, *J* = 1.8 Hz), 129.1 (d, *J* = 3.6 Hz), 130.2, 133.0 (d, *J* = 8.5 Hz), 136.0 (d, *J* = 5.4 Hz), 136.6 (d, *J* = 9.4 Hz), 140.0 (*J* = 175.8 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 16.0; IR (KBr): ν (cm^{-1}) 3450, 2983, 2928, 1489, 1392, 1256, 1234, 1022, 962; GC-MS: *m*/*z* (rel intensity) 254 (M, 27), 226 (11), 197 (48), 179 (5), 144 (4), 115 (100), 91 (12), 65 (8); HRMS (ESI) calcd for $C_{13}H_{19}O_3PNa$ [M+Na^+] 277.0970; found 277.1004.

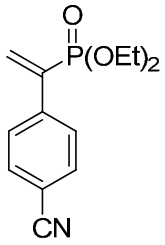


Diethyl (1-(*m*-tolyl)vinyl)phosphonate (**3c**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 6H), 2.36 (s, 3H), 4.05-4.16 (m, 4H), 6.14 (dd, *J* = 1.5, 45.8 Hz, 1H), 6.31 (dd, *J* = 1.5, 22.0 Hz, 1H), 7.14 (d, *J* = 7.6, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.32-7.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.2 (d, *J* = 6.3 Hz), 21.4, 62.1 (d, *J* = 5.6 Hz), 124.5 (d, *J* = 5.5 Hz), 128.0 (d, *J* = 5.9 Hz), 128.2, 129.0, 131.5 (d, *J* = 8.0 Hz), 136.6 (d, *J* = 11.7 Hz), 137.9, 139.8 (d, *J* = 173.2 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 17.2; IR (KBr): ν (cm^{-1}) 3452, 2985, 2924, 1488, 1392,

1243, 1054, 1030, 960; GC-MS: *m*/*z* (rel intensity) 254 (M, 38), 226 (34), 210 (22), 182 (21), 144 (77), 117 (100), 91 (35), 65 (25); HRMS (ESI) calcd for $C_{13}H_{19}O_3PNa$ [M+Na^+] 277.0970; found 277.0983.

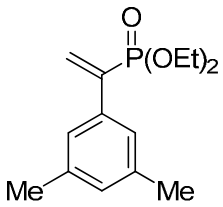


Diethyl (1-(2-chlorophenyl)vinyl)phosphonate (**3h**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.1, 6H), 4.07-4.13 (m, 4H), 6.02 (td, *J* = 0.8, 46.5 Hz, 1H), 6.55 (td, *J* =0.8, 22.4 Hz, 1H), 7.24 (t, *J* = 5.3 Hz, 2H), 7.35-7.36 (m, 1H), 7.40-7.42 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.2 (d, *J* = 6.5 Hz), 62.3 (d, *J* = 5.7 Hz), 126.3 (d, *J* = 1.2 Hz), 129.0 (d, *J* = 1.7 Hz), 129.7, 130.6 (d, *J* = 3.1 Hz), 132.6 (d, *J* = 6.4 Hz), 135.3 (d, *J* = 7.5 Hz), 135.6 (d, *J* = 10.7 Hz), 137.1 (d, *J* = 179.6 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 15.1; IR (KBr): ν (cm^{-1}) 3500, 2982, 2929, 1475, 1392, 1254, 1235, 1055, 1023, 960, 946; GC-MS: *m*/*z* (rel intensity) 275 (M+H^+, 1), 239 (6), 211 (28), 183 (100), 165 (16), 137 (18), 101 (30), 75 (15); HRMS (ESI) calcd for $C_{12}H_{16}ClO_3PNa$ [M+Na^+] 297.0423; found 297.0452.

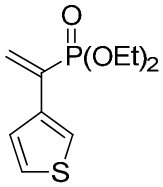


Diethyl (1-(4-cyanophenyl)vinyl)phosphonate (**3n**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 6H), 4.07-4.17 (m, 4H), 6.21 (dd, *J* =1.1, 44.8 Hz, 1H), 6.42 (dd, *J* = 1.1, 21.9 Hz, 1H), 7.64 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.1 (d, *J* = 6.2 Hz), 62.4 (d, *J* = 5.7 Hz), 111.8, 118.4, 128.0 (d, *J* = 5.5 Hz), 132.1, 133.4 (d, *J* = 7.2 Hz), 138.6 (d, *J* = 176.7 Hz), 141.2 (*J* = 11.8 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 15.4; IR (KBr): ν (cm^{-1}) 3510, 2984, 2931, 2228, 1444, 1394, 1237, 1028, 965; GC-MS: *m*/*z* (rel intensity) 265 (M, 25), 237 (73), 209 (15), 193 (24), 155 (65), 128 (100), 101 (41), 82 (23); HRMS (ESI) calcd for $C_{13}H_{16}NO_3PNa$ [M+Na^+]

288.0765; found 288.0815.



Diethyl (1-(3,5-dimethylphenyl)vinyl)phosphonate (**3p**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 6H), 2.32 (s, 6H), 4.10 (m, 4H), 6.12 (dd, *J* = 45.9, 1.6 Hz, 1H), 6.28 (dd, *J* = 22.0, 1.6 Hz, 1H), 6.97 (s, 1H), 7.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.3 (d, *J* = 6.3 Hz), 21.3, 62.2 (d, *J* = 5.8 Hz), 125.3 (d, *J* = 5.9 Hz), 130.0, 131.4 (d, *J* = 8.1 Hz), 136.6 (d, *J* = 11.5 Hz), 137.9, 139.8 (d, *J* = 172.8 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 17.4; IR (KBr): ν (cm^{-1}) 3446, 2982, 2921, 1600, 1394, 1252, 1025, 965, 788; GC-MS: *m*/*z* (rel intensity) 268 (M, 59), 240 (36), 196 (21), 158 (100), 143 (97), 131 (95), 115 (65), 91 (52); HRMS (ESI) calcd for $C_{14}H_{21}O_3PNa$ [M+Na^+] 291.1126; found 291.1168.

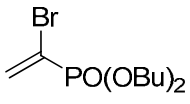


Diethyl (1-(thiophen-3-yl)vinyl)phosphonate (**3u**). Pale yellow oil; Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 6H), 4.06-4.17 (m, 4H), 6.21 (dd, *J* =1.3, 23.1 Hz, 1H), 6.28 (s, 1H), 7.29-7.30 (m, 2H), 7.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.1 (d, *J* = 6.2 Hz), 62.1 (d, *J* = 5.4 Hz), 123.7 (d, *J* = 5.1 Hz), 125.5, 126.0 (d, *J* = 8.1 Hz), 129.3 (d, *J* = 7.6 Hz), 133.4 (d, *J* = 175.2 Hz), 136.3 (*J* = 12.7 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 17.1; IR (KBr): ν (cm^{-1}) 3484, 2981, 2929, 1444, 1392, 1247, 1053, 962; GC-MS: *m*/*z* (rel intensity) 246 (M, 27), 217 (8), 202 (32), 174 (45), 136 (55), 109 (100), 82 (18), 65 (48); HRMS (ESI) calcd for $C_{10}H_{15}O_3PSNa$ [M+Na^+] 269.0377; found 269.0417.

2. References of known compounds.

Compounds	Reference
2a	Doğan, Ö.; Isci, M.; Aygun, M. *Tetrahedron Asymmetry* **2013**, *24*, 562.
2b	Berdnikov, E. A.; Mukhitova, F. K.; Tantasheva, F. R.; Kataev, E. G.; Khayarov, A. I. *Zh. Obshch. Khim.* **1979**, *49*, 296.
3a, 3d, 3e, 3f, 3g, 3j, 3m, 3s, 4a	Wang, D.-Y.; Hu, X.-P.; Deng, J.; Yu, S.-B.; Duan, Z.-C.; Zheng, Z. *J. Org. Chem.* **2009**, *74*, 4408.
3i, 3k, 3l, 3q, 3o	Li, S.-N.; Xu, L.-T.; Chen, Y.; Li, J.-L.; He, L. *Lett. Org. Chem.* **2011**, *8*, 416.
3r, 3t	Goulioukina, N. S.; Dolgina, T. M.; Bondarenko, G. N.; Belestkaya, I. P.; Ilyin, M. M.; Davankov, V. A.; Pfaltz, A. *Tetrahedron Asymmetry* **2003**, *14*, 1397.
4b	Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.*, **1996**, *118*, 1571.
4c	Vafina, N. M.; Zyablikova, T. A.; Il'yasov, A. V.; Shermergorn, I. M. *Zh. Obshch. Khim.* **1982**, *52*, 35.
4d	Karimov, K. R.; Shakhidoyatov, Kh. M.; Alovitdinov, A. B.; Kuchkarov, A. B. *Zh. Obshch. Khim.* **1984**, *54*, 2393.
5	Krawczyk, H.; Koszuk, J.; Bodalski, R. *Polish J. Chem.* **2000**, *74*, 1123.

3. ^{1}H, ^{13}C, and ^{31}P Spectra of New Compounds.



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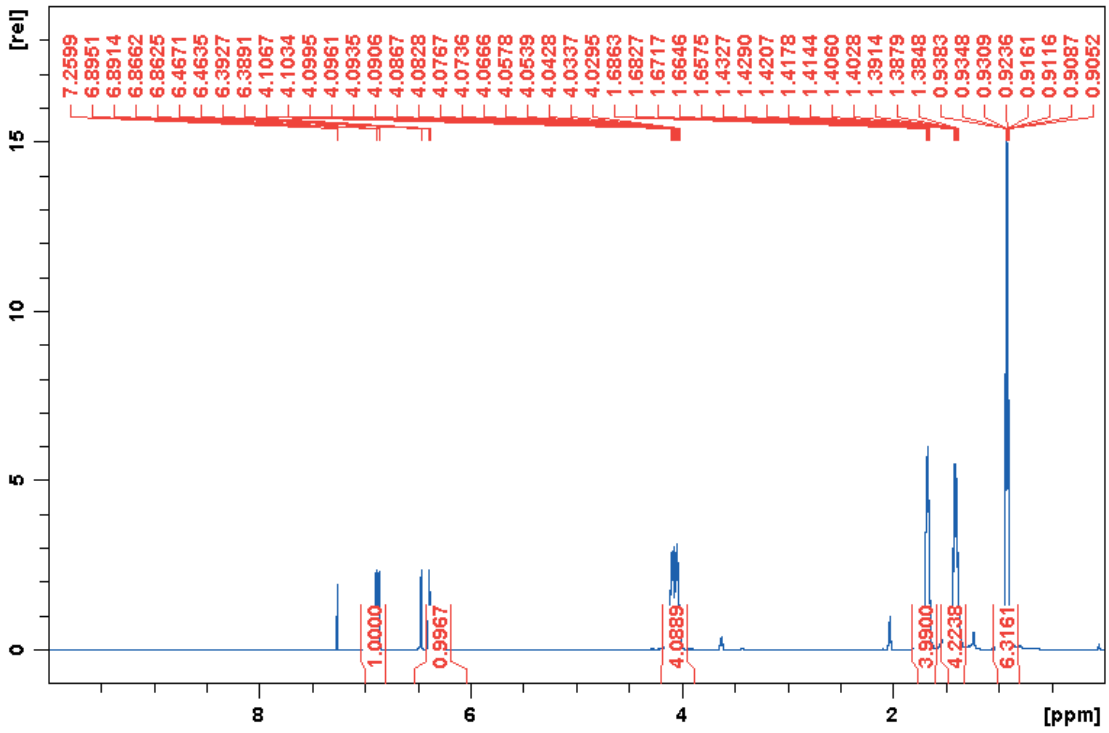
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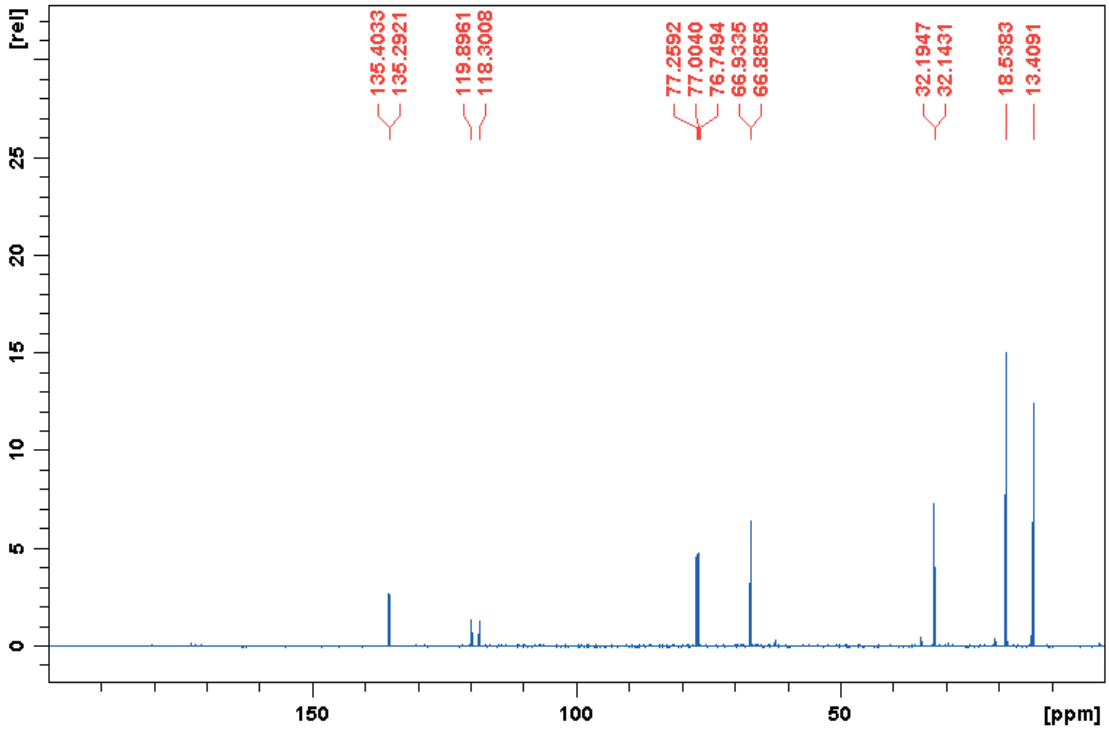
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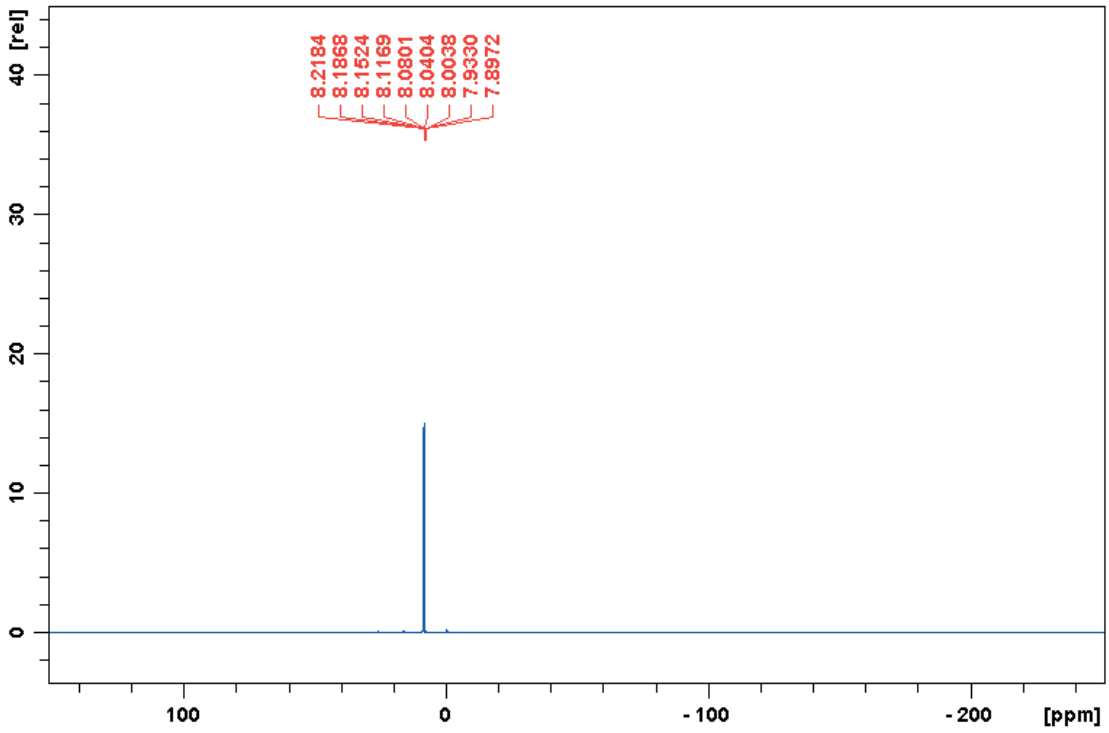
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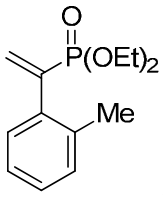
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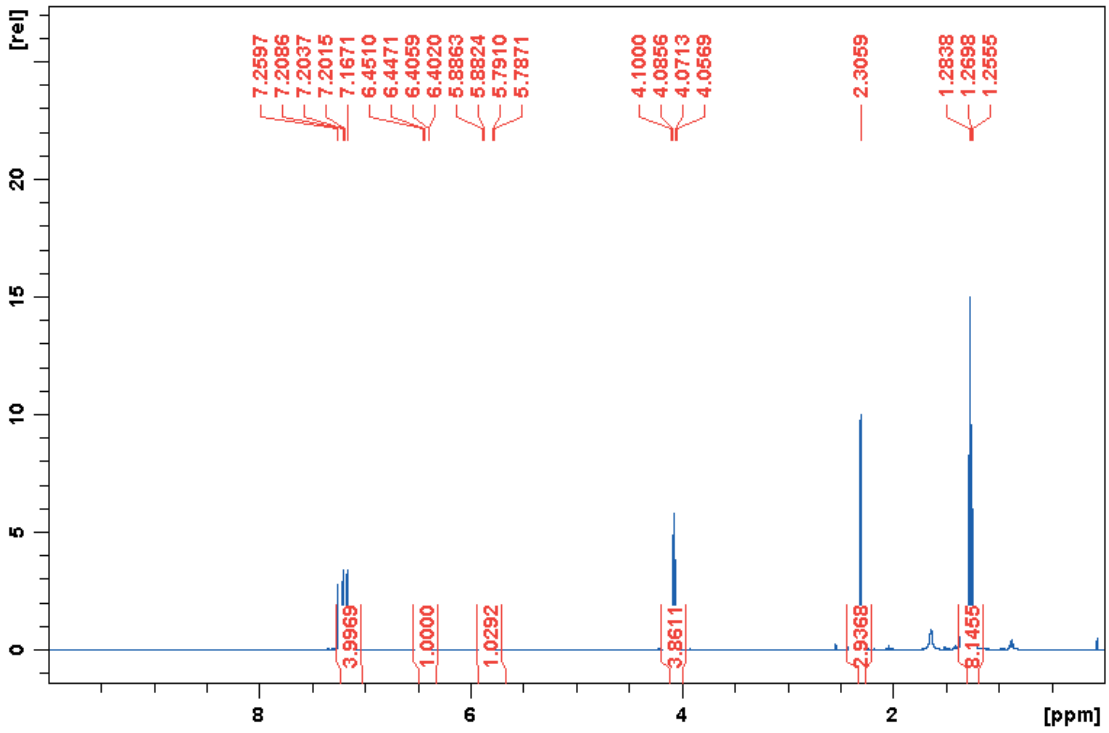
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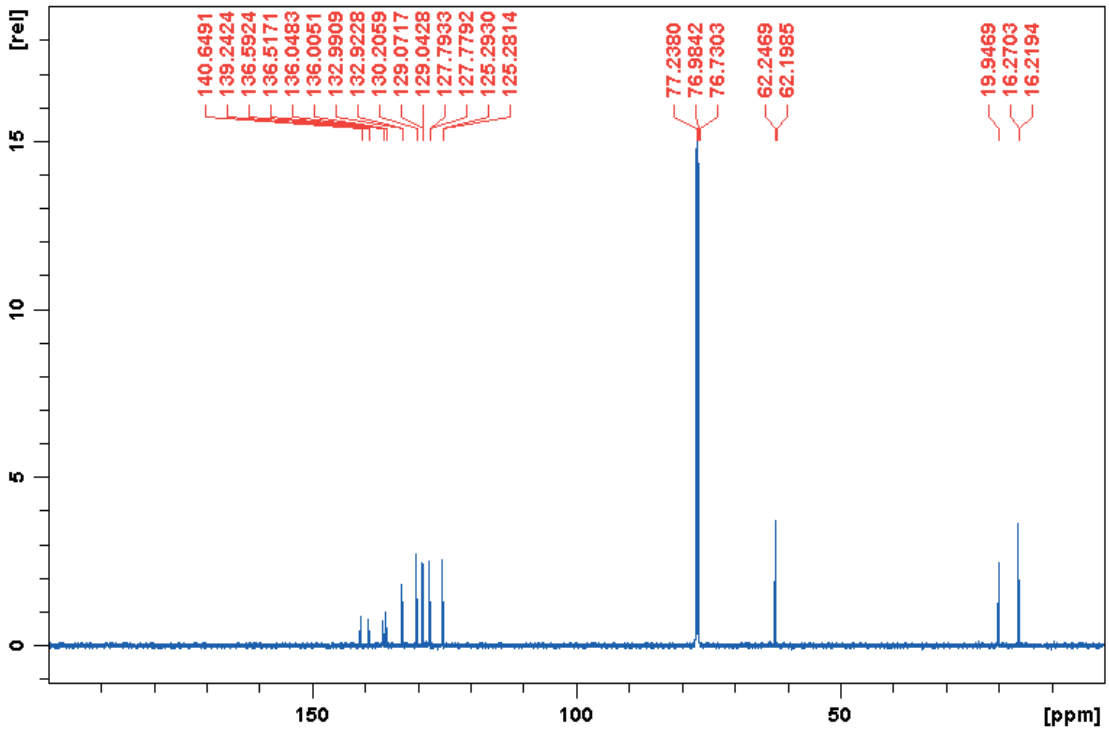
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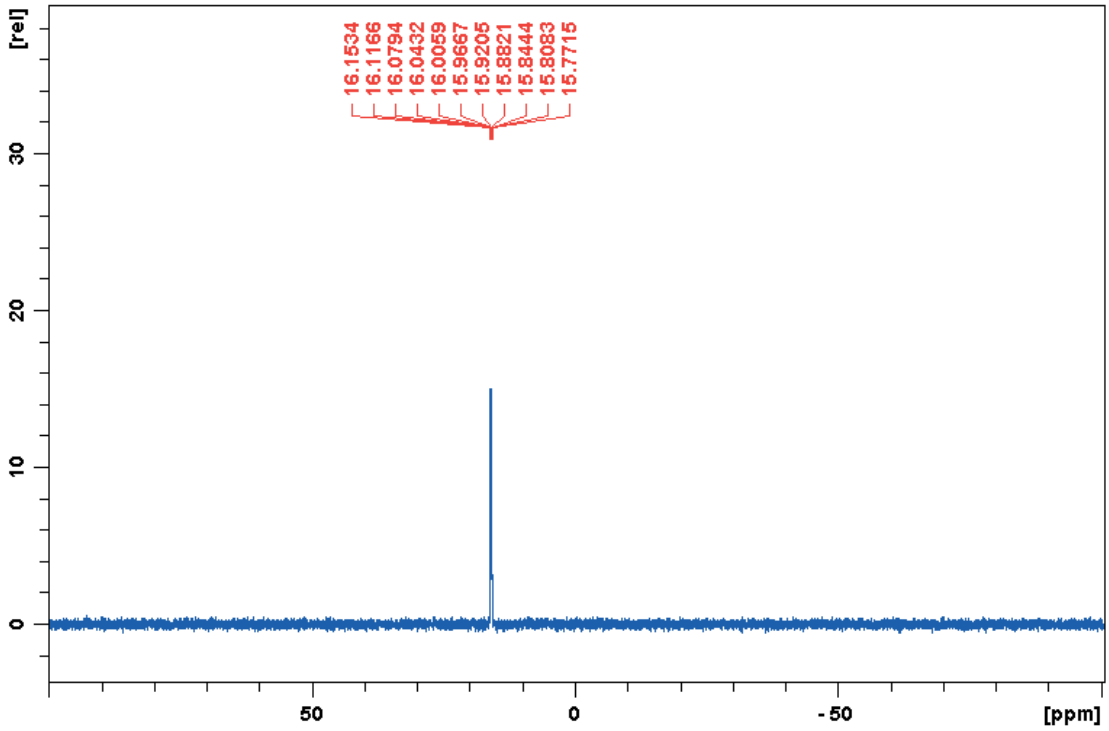
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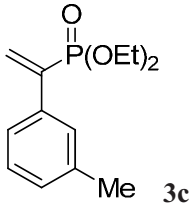
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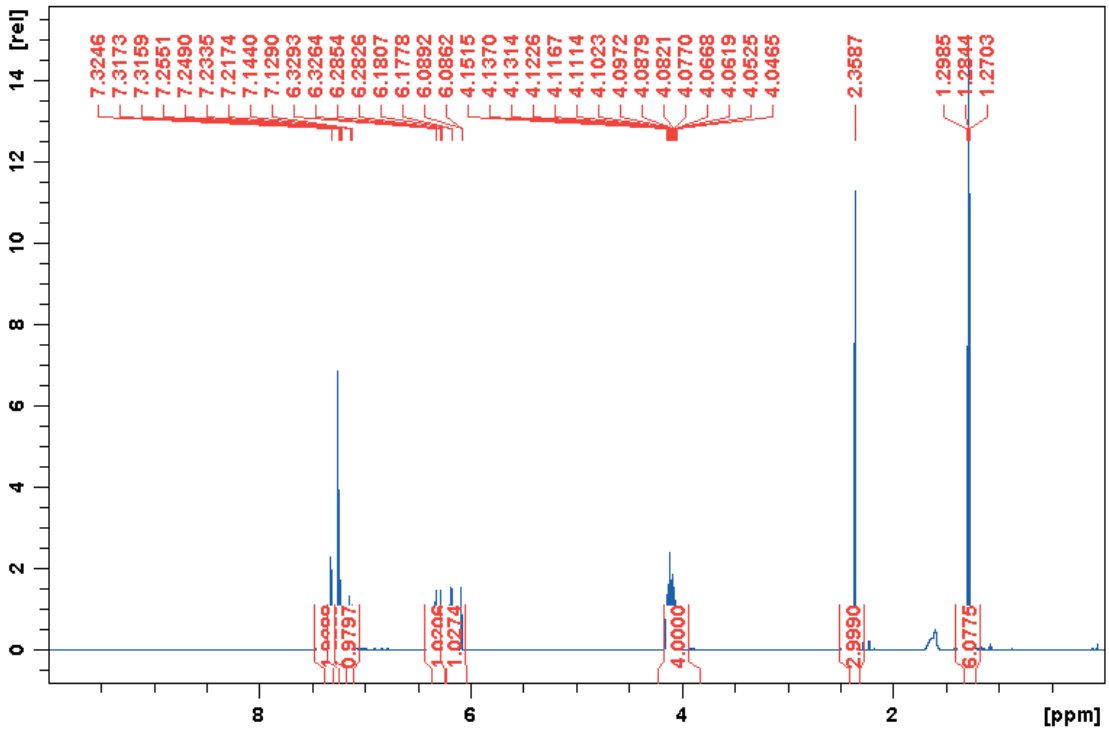
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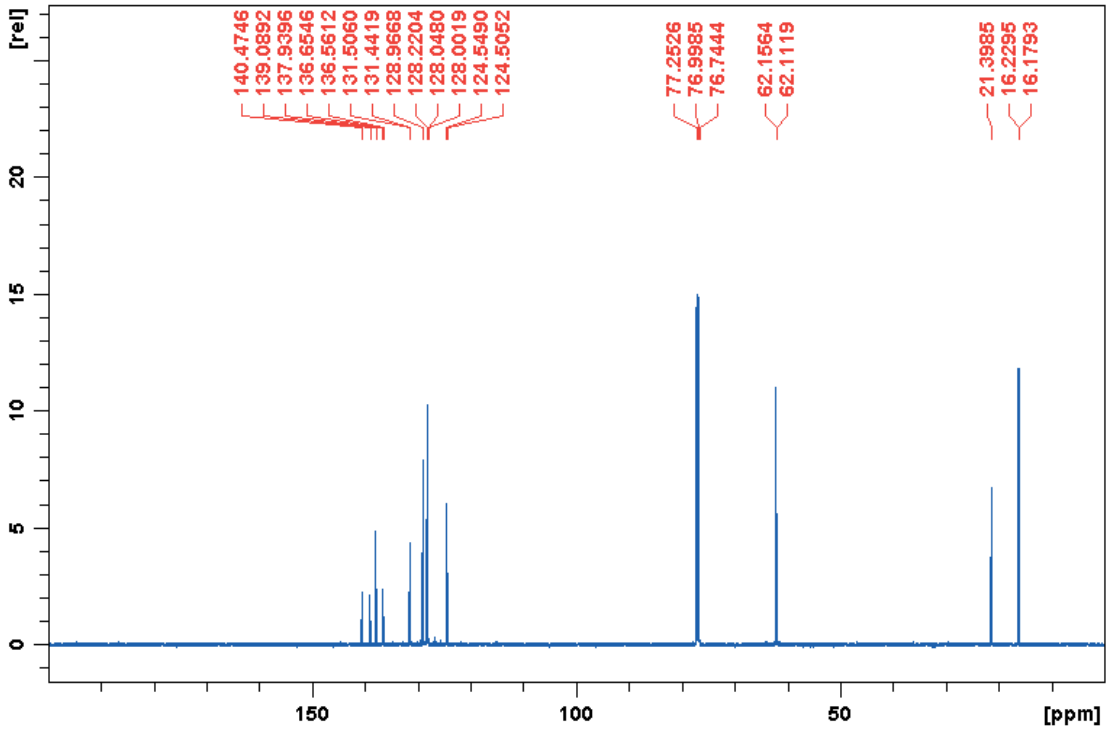
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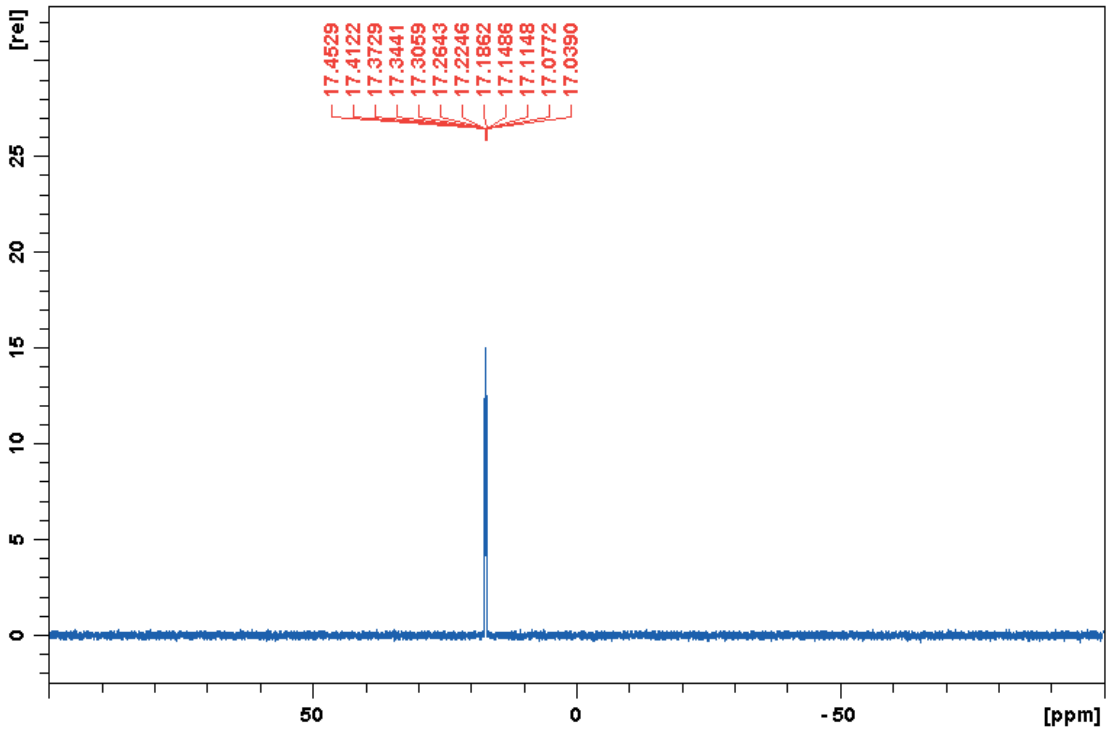
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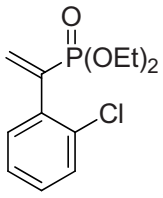
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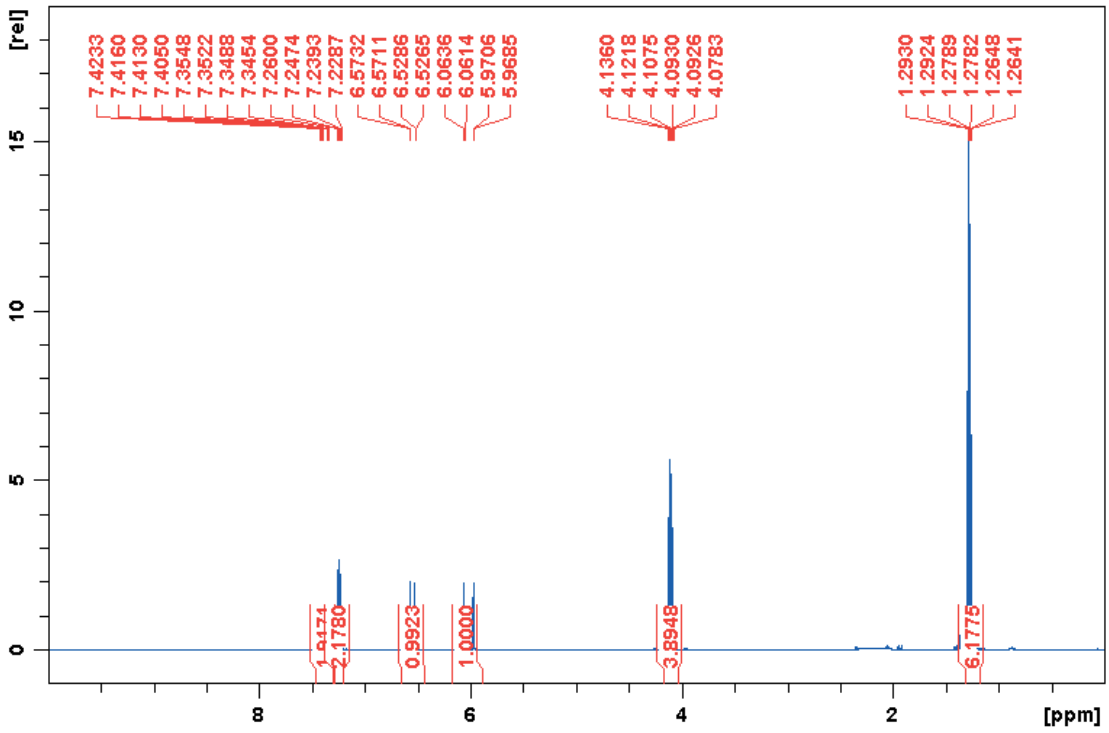
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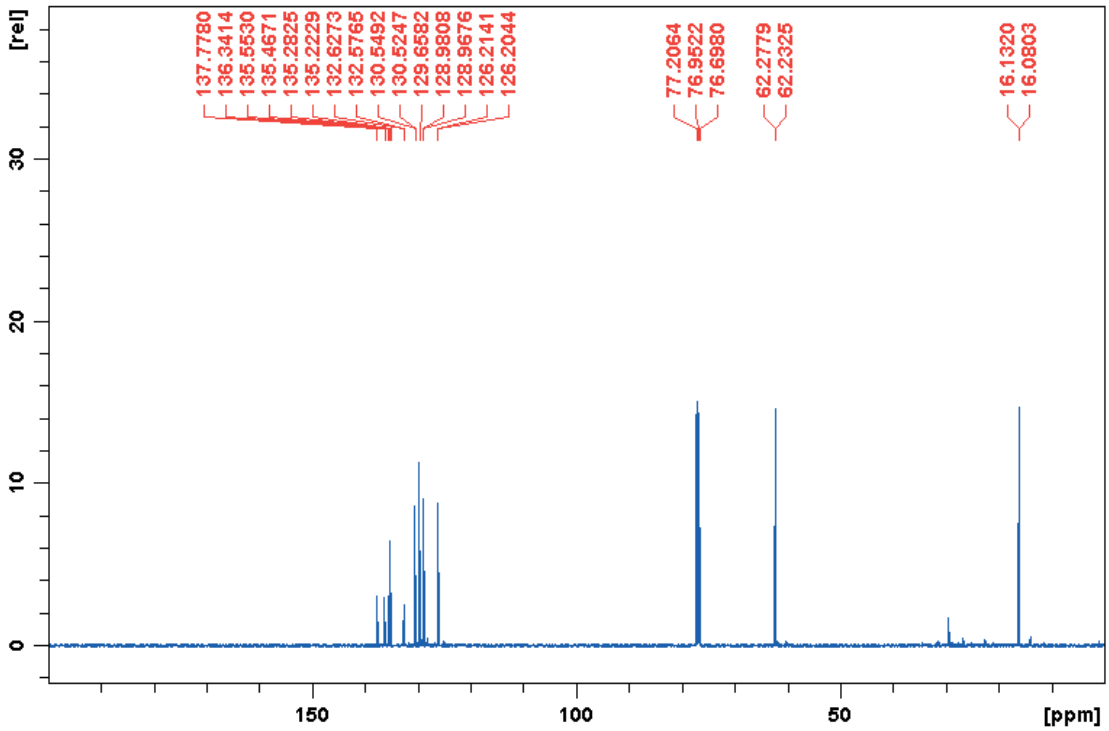
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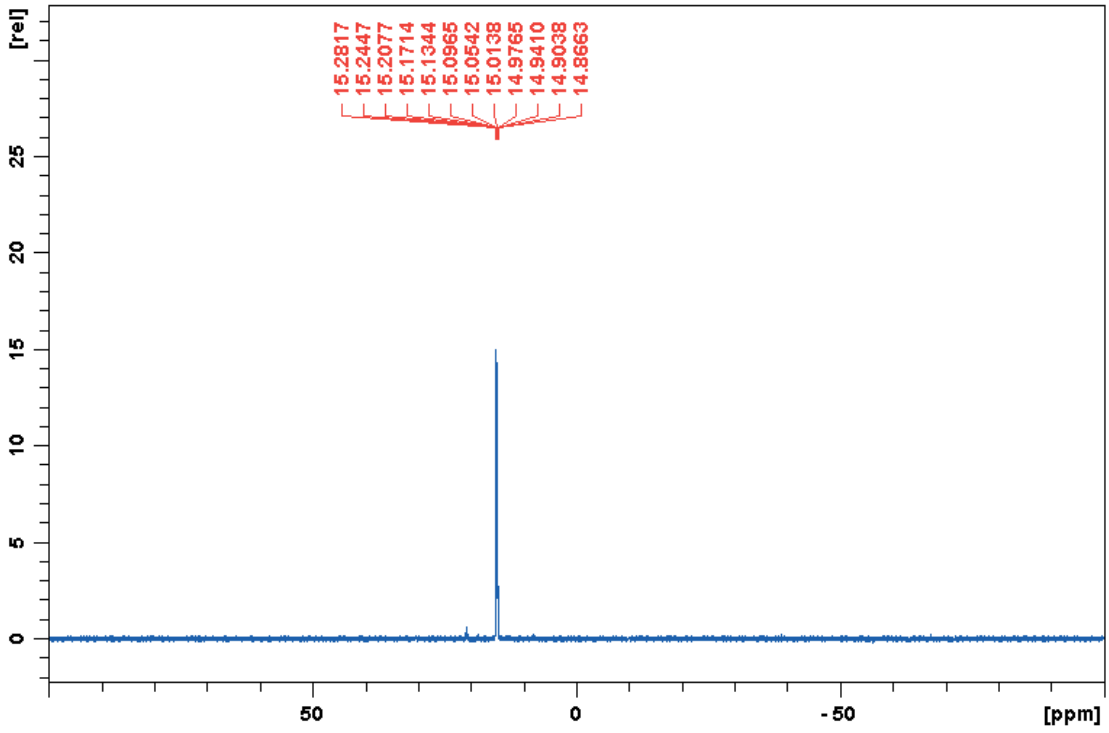
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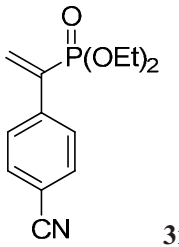
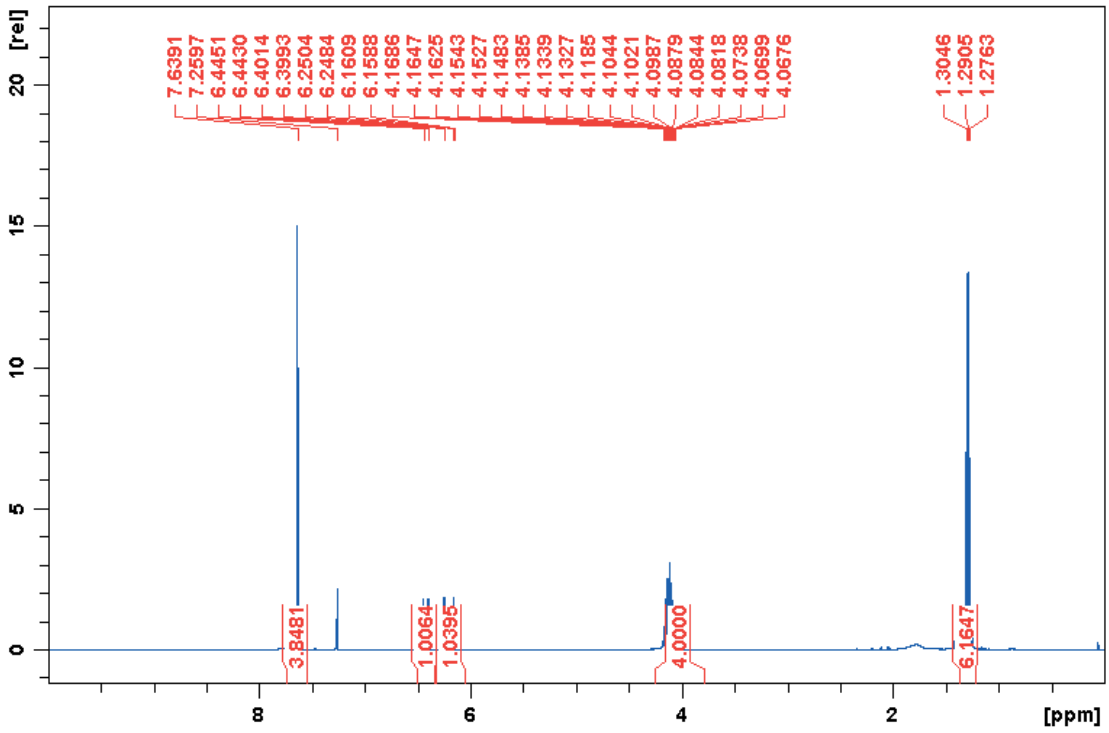

O
P(OEt)2
CN

3n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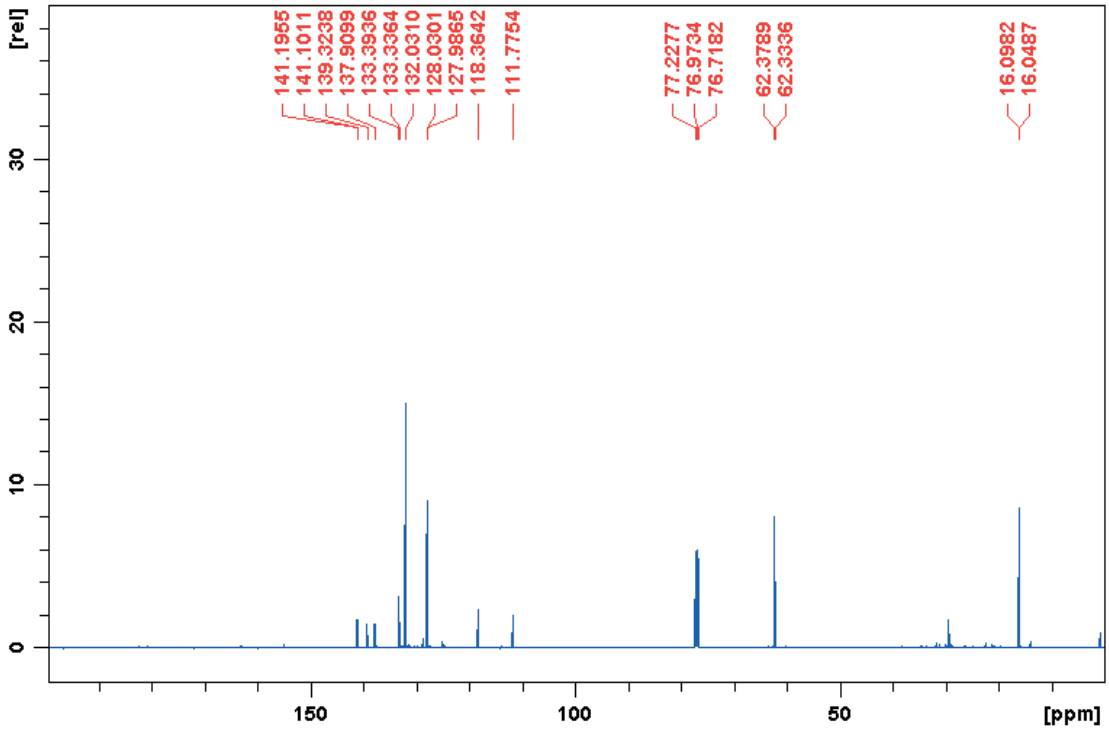
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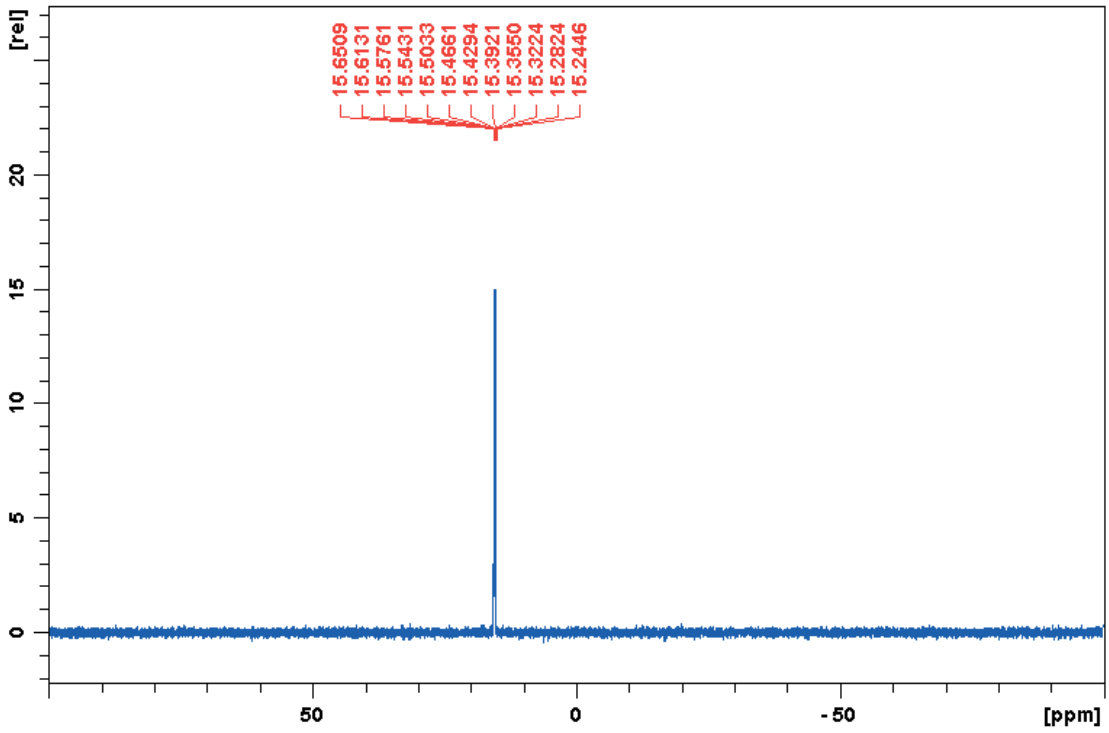
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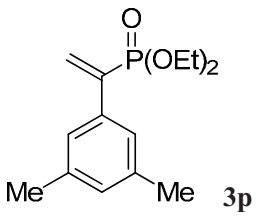
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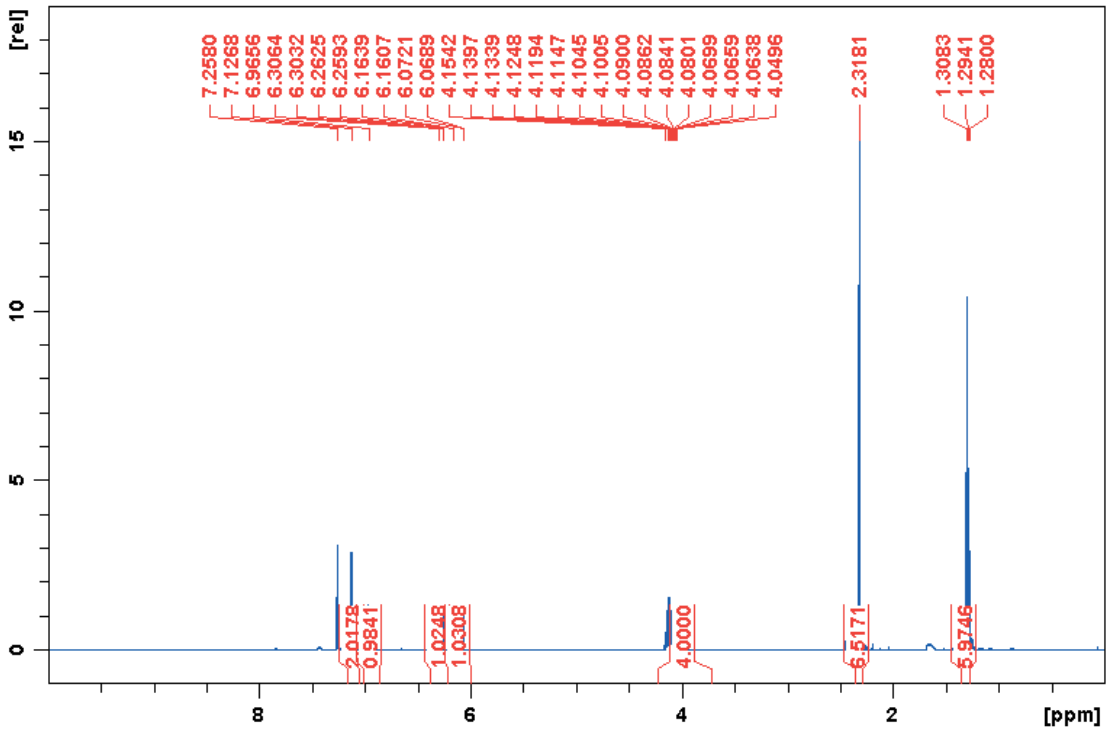
Me
Me

3p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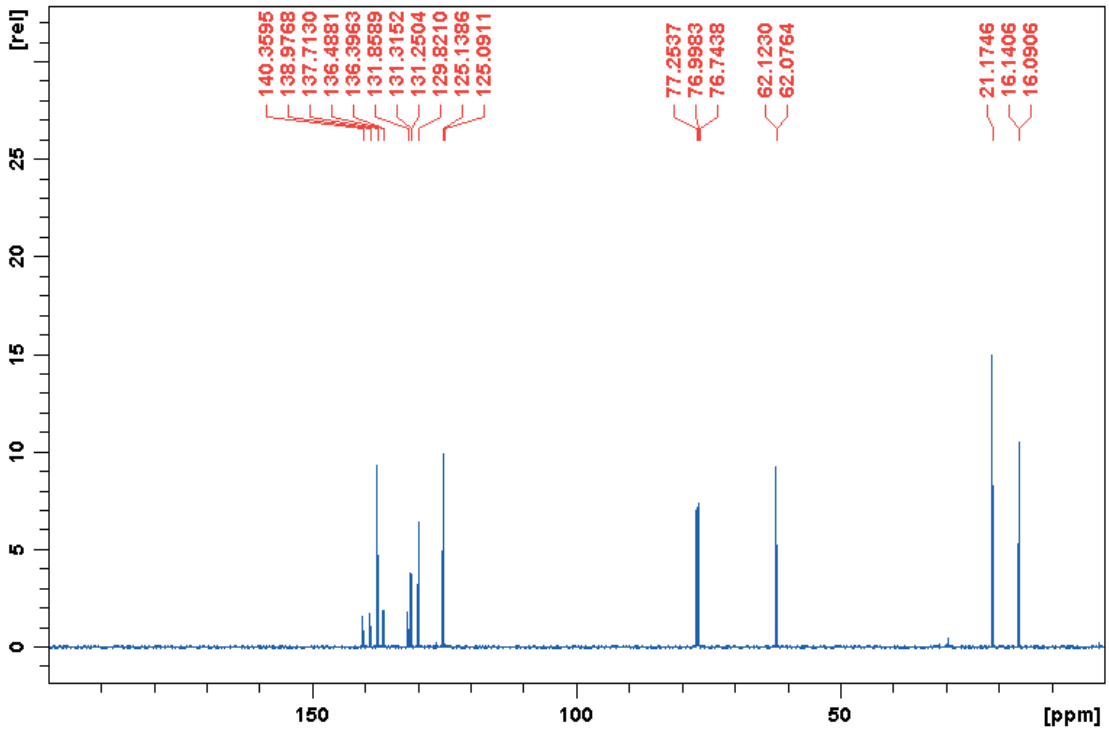
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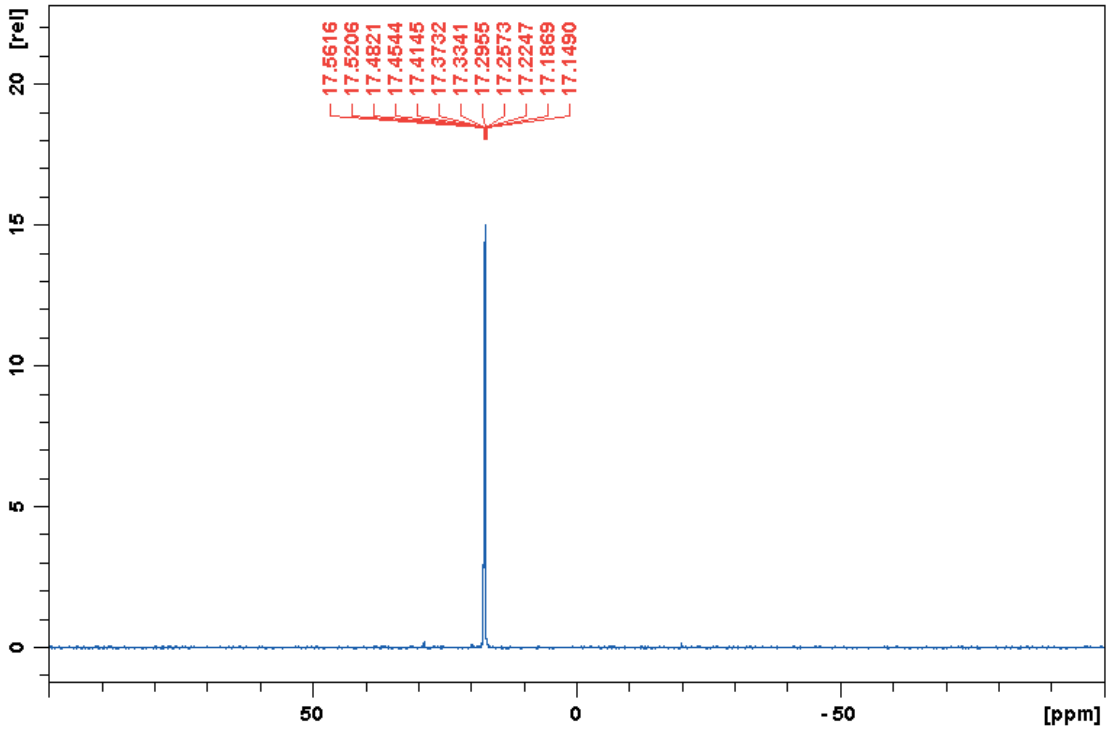
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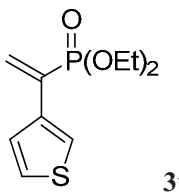
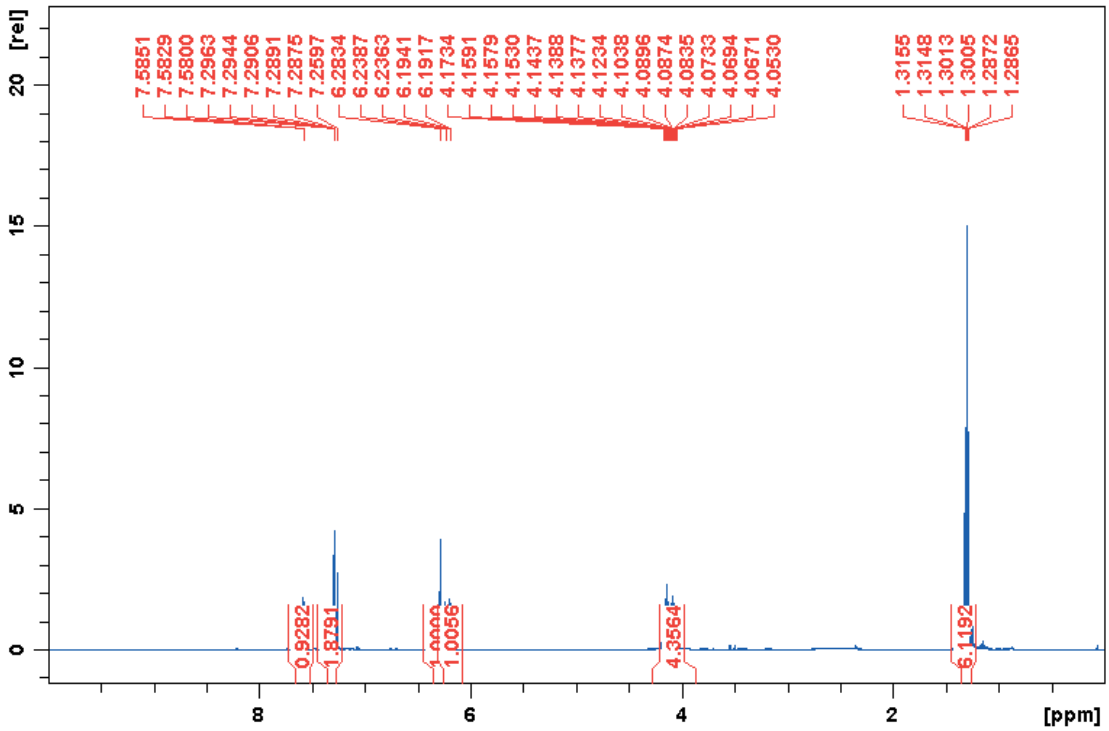

O
P(OEt)2
S

3u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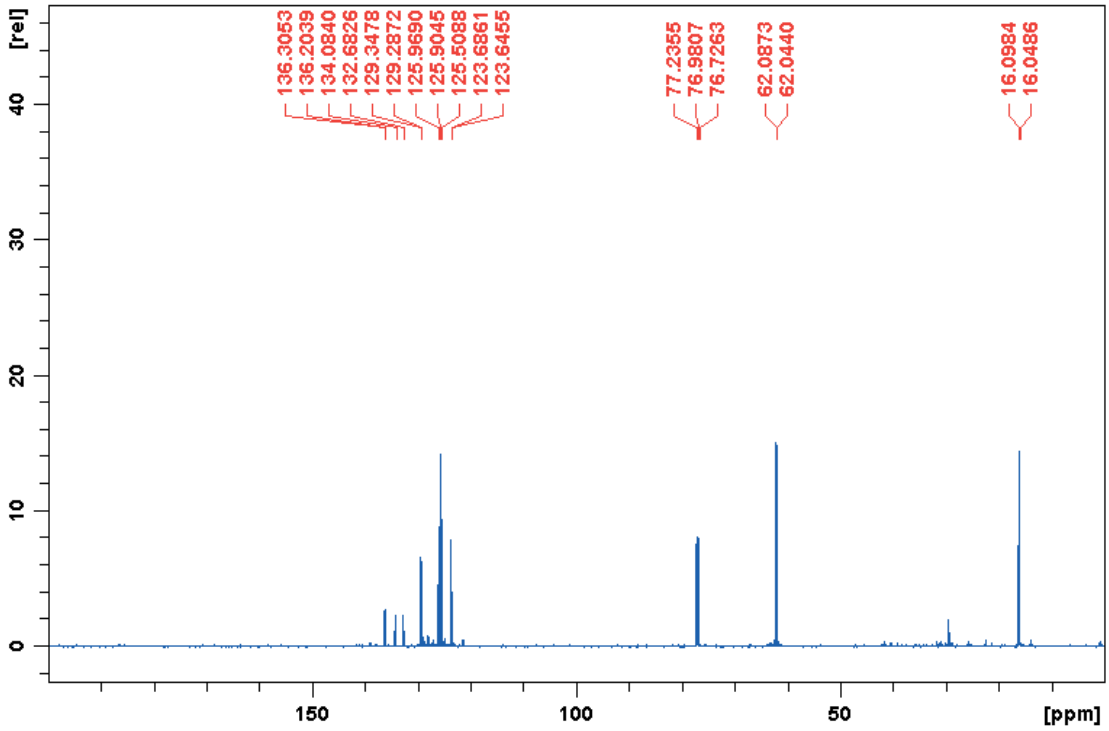
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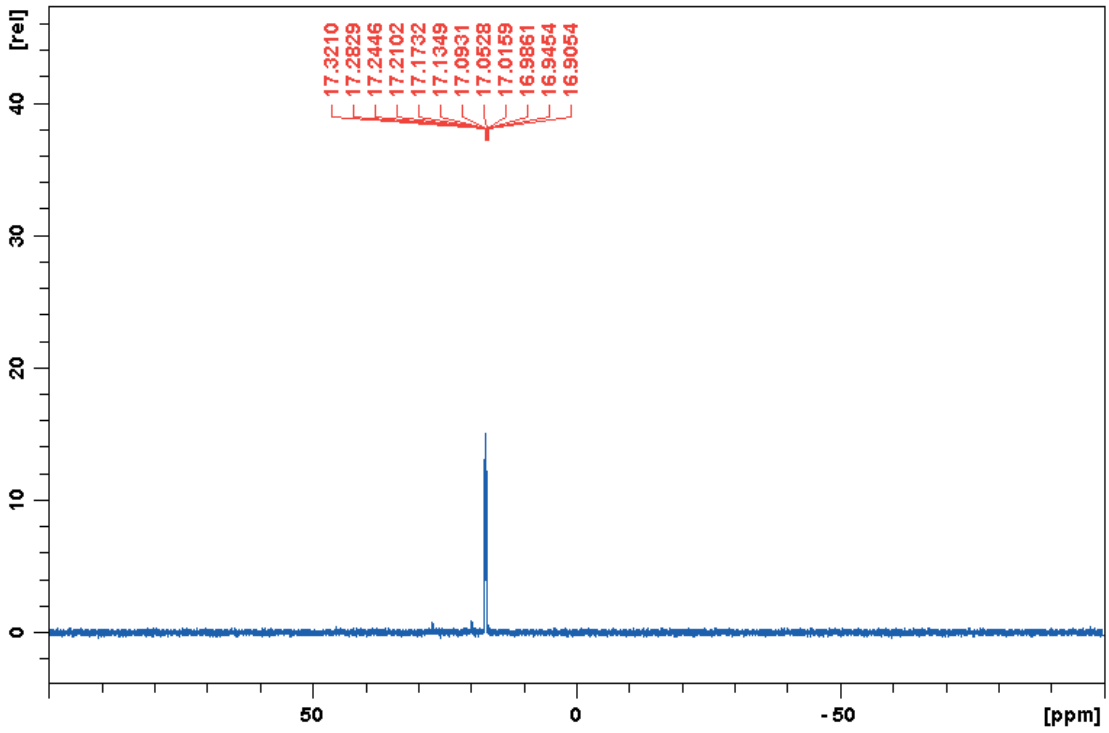
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