

Supporting Information

Palladium incorporated MIL-101(Cr): a heterogeneous and reusable catalyst for the C-H functionalization of unactivated arenes

Phillip Kumar Sarkar,^a Sushmita Gajurel,^a Lenida Kyndiah,^a Rajib Sarkar,^a Rupesh S. Devan,^b
Amarta Kumar Pal^{a,*}

^a*Department of Chemistry, Centre for Advanced Studies, North-Eastern Hill University, Shillong-793022, Meghalaya, India.*

E-mail: amartya_pal22@yahoo.com, akpal@nehu.ac.in Tel: +91 364 2722606

^b*Department of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore 453552, India*

Table of content	Page No.
1. TON and TOF Calculation	S2
2. Single crystal X-ray data of compounds 3i and 3o	S2 - S4
3. Spectral data of the compounds (3a-o and 5a-5m)	S4 - S13
4. References	S13
5. ¹ H and ¹³ C NMR spectra of compounds (3a-o and 5a-5m)	S14 - S41

1. TON and TOF Calculation.

1. 15 mg (catalyst used) x 0.0246 [Pd weight ratio (2.46 % by ICP) in the catalyst]/106.42

= 0.00347 mmol Pd (Pd mmol for the catalytic reaction)

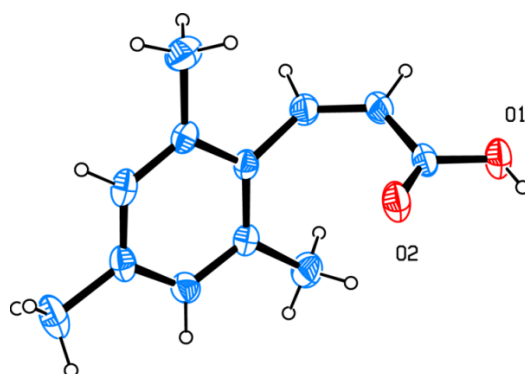
2. TON = 0.87 (mmol of product)/ 0.00347 (mmol of Pd) = 250.7

3. TOF = 250.7/6 = 41.8 h⁻¹

2. Single crystal X-ray data of compounds **3i** and **3o**:

Single crystal of **3i** and **3o** were obtained from dichloromethane and ethyl acetate respectively. The X-ray diffraction data were collected at 293 K (296 K for **3i**) using BRUKER D8 VENTURE SC-XRD system, equipped with dual X-ray sources (Mo and Cu), Photon II detector. The software used for data collection was APEX3. The structure were solved by using the program SHELXT and refined by full-matrix least-squares calculations (F^2) by using the SHELXL-2018/3 software¹ in WinGX-Version 2021.3.²

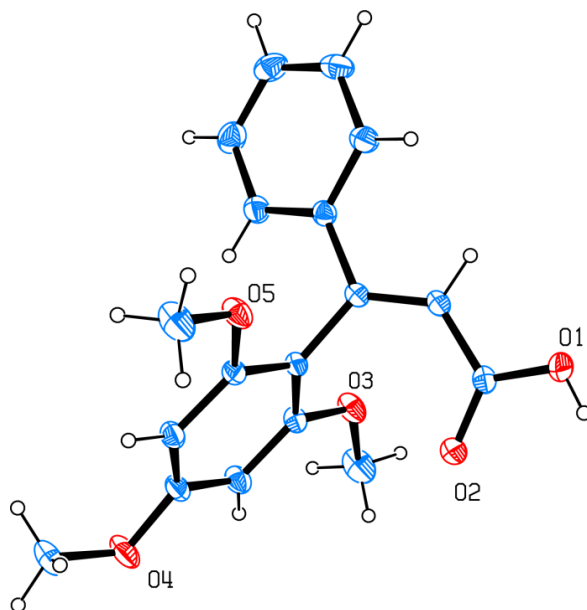
Table S1. X-ray Crystallography data of compound **3i** (CCDC 2217412).



Empirical formula	C ₁₂ H ₁₄ O ₂
Formula weight	190.23
Crystal system	Triclinic
T(K)	296 (2)
Space group	<i>P</i> -1
a(Å)	7.8281 (3)
b(Å)	8.1444 (4)
c(Å)	8.5668 (4)
α(°)	81.284 (2)

$\beta(^{\circ})$	88.323 (10)
$\gamma(^{\circ})$	85.455 (10)
Volume (\AA^3)	538.09 (4)
ρ (calculated) (mg mm^{-3})	1.174
Absorption coefficient (μ/mm^{-1})	0.079
Total reflection collected	16179
Independent reflection	2046
θ range ($^{\circ}$)	2.465 to 28.272
Final R Indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0521$, $wR_2 = 0.1551$
Final R indexes [all data]	$R_1 = 0.0666$, $wR_2 = 0.1667$
Goodness-of-fit on F^2	1.066

Table S2. X-ray Crystallography data of compound **3o** (CCDC 2217413).

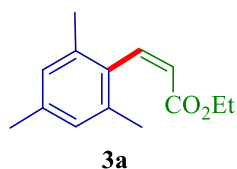


Empirical formula	$\text{C}_{18}\text{H}_{18}\text{O}_5$
Formula weight	314.34
Crystal system	monoclinic
T(K)	293 (2)
Space group	$P2_1/c$
a(\AA)	11.4985 (10)
b(\AA)	8.0962 (7)

$c(\text{\AA})$	17.0148 (16)
$\alpha(^{\circ})$	90
$\beta(^{\circ})$	101.743 (3)
$\gamma(^{\circ})$	90
Volume (\AA^3)	1550.8 (2)
ρ (calculated) (mg mm^{-3})	1.346
Absorption coefficient (μ/mm^{-1})	0.098
Total reflection collected	36263
Independent reflection	3019
θ range ($^{\circ}$)	2.445 to 28.304
Final R Indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0425$, $wR_2 = 0.1130$
Final R indexes [all data]	$R_1 = 0.0565$, $wR_2 = 0.1189$
Goodness-of-fit on F^2	1.050

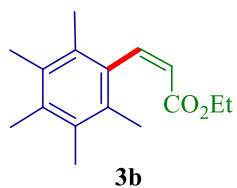
3. Spectral data of the compounds (3a-o and 5a-5m).

1. (Z)-ethyl 3-mesitylacrylate (3a).³



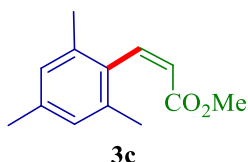
Colourless liquid. ¹H NMR (CDCl₃, 400 MHz): δ = 6.94 (d, J = 11.6 Hz, 1H), 6.75 (s, 2H), 6.03 (d, J = 11.6 Hz, 1H), 3.96 (q, J = 7.2 Hz, 2H), 2.17 (s, 3H), 2.06 (s, 6H), 1.02 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 165.4, 144.2, 136.7, 134.5, 132.9, 127.9, 122.8, 59.9, 21.1, 20.2, 14.0. HRMS (ESI, m/z) calcd. for C₁₄H₁₈O₂ [M+Na]⁺: 241.1204; found: 241.1215.

2. (Z)-ethyl 3-(2,3,4,5,6-pentamethylphenyl)acrylate (3b).³



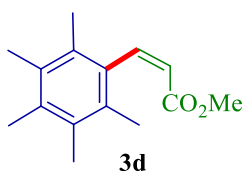
White Solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.06$ (d, $J = 12$ Hz, 1H), 6.06 (d, $J = 12$ Hz, 1H), 3.96 (q, $J = 7$ Hz, 2H), 2.14 (s, 3H), 2.11 (s, 6H), 2.05 (s, 6H), 1.04 (t, $J = 7$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 165.4, 146.6, 134.0, 133.2, 131.9, 129.7, 122.1, 59.8, 17.6, 16.7, 16.4, 14.0$. **HRMS** (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 269.1517; found: 269.1510.

3. (Z)-methyl 3-mesitylacrylate (3c).³



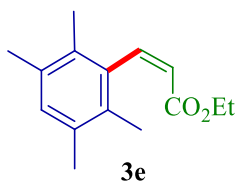
Colourless liquid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.06$ (d, $J = 11.6$ Hz, 1H), 6.85 (s, 2H), 6.15 (d, $J = 11.6$ Hz, 1H), 3.59 (s, 3H), 2.27 (s, 3H), 2.15 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 165.8, 144.7, 136.8, 134.5, 132.5, 127.9, 122.1, 51.2, 21.1, 20.1$. **HRMS** (ESI, m/z) calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 227.1048; found: 227.1060.

4. (Z)-methyl 3-(2,3,4,5,6-pentamethylphenyl)acrylate (3d).³



White Solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.09$ (d, $J = 12$ Hz, 1H), 6.10 (d, $J = 12$ Hz, 1H), 3.52 (s, 3H), 2.15 (s, 3H), 2.13 (s, 6H), 2.07 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 165.7, 147.0, 134.1, 133.0, 132.0, 129.8, 121.5, 51.1, 17.6, 16.8, 16.4$. **HRMS** (ESI, m/z) calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 255.1361; found: 255.1366.

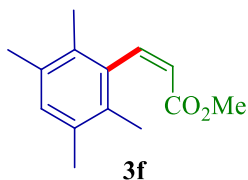
5. (Z)-ethyl 3-(2,3,5,6-tetramethylphenyl)acrylate (3e).³



White Solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.10$ (d, $J = 12$ Hz, 1H), 6.90 (s, 1H), 6.15 (d, $J = 12$ Hz, 1H), 4.03 (q, $J = 7.2$ Hz, 2H), 2.21 (s, 6H), 2.08 (s, 6H), 1.08 (t, $J = 7.2$ Hz, 3H).

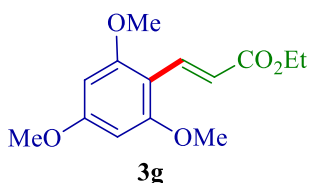
^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 165.5, 145.6, 135.7, 133.1, 130.5, 130.2, 122.5, 59.8, 19.9, 16.5, 13.9$. HRMS (ESI, m/z) calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 255.1361; found: 255.1358.

6. (Z)-methyl 3-(2,3,5,6-tetramethylphenyl)acrylate (3f).³



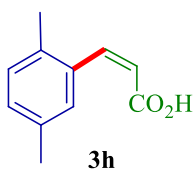
White Solid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.14$ (d, $J = 12$ Hz, 1H), 6.93 (s, 1H), 6.20 (d, $J = 12$ Hz, 1H), 3.60 (s, 3H), 2.24 (s, 6H), 2.10 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 165.7, 146.2, 135.4, 133.1, 130.7, 130.0, 121.8, 51.2, 20.0, 16.5$. HRMS (ESI, m/z) calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 241.1204; found: 241.1205.

7. (E)-ethyl 3-(2,4,6-trimethoxyphenyl)acrylate (3g).⁴



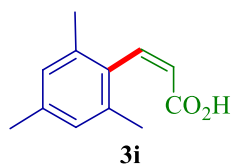
White Solid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.10$ (d, $J = 16.4$ Hz, 1H), 6.77 (d, $J = 16.4$ Hz, 1H), 6.10 (s, 2H), 4.26 (q, $J = 7$ Hz, 2H), 3.86 (s, 6H), 3.84 (s, 3H), 1.34 (t, $J = 7$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 169.0, 162.7, 161.2, 135.4, 117.5, 105.8, 90.3, 59.9, 55.6, 55.3, 14.4$. HRMS (ESI, m/z) calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_5$ $[\text{M}+\text{Na}]^+$: 289.1052; found: 289.1068.

8. (Z)-3-(2,5-dimethylphenyl)acrylic acid (3h).⁵



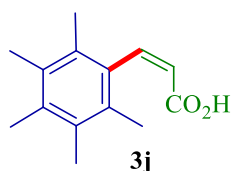
White Solid. ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.21$ (d, $J = 12$ Hz, 1H), 7.13 (s, 1H), 7.07-7.01 (m, 2H), 6.01 (d, $J = 12$ Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 169.9, 145.6, 134.7, 134.2, 132.7, 129.7, 129.5, 129.3, 119.7, 20.8, 19.3$. HRMS (ESI, m/z) calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 199.0735; found: 199.0747.

9. (Z)-3-mesitylacrylic acid (**3i**).⁶



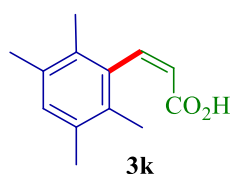
White Solid. ¹H NMR (CDCl₃, 300 MHz): δ = 7.11 (d, *J* = 12 Hz, 1H), 6.83 (s, 2H), 6.11 (d, *J* = 12 Hz, 1H), 2.26 (s, 3H), 2.14 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 170.4, 146.2, 137.1, 134.6, 132.0, 128.0, 122.1, 21.0, 20.1. HRMS (ESI, *m/z*) calcd. for C₁₂H₁₄O₂ [M+Na]⁺: 213.0891; found: 213.0919.

10. (Z)-3-(2,3,4,5,6-pentamethylphenyl)acrylic acid (**3j**).³



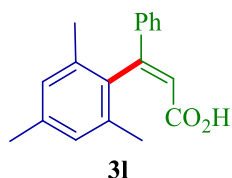
White Solid. ¹H NMR (CDCl₃, 300 MHz): δ = 7.22 (d, *J* = 12 Hz, 1H), 6.14 (d, *J* = 12 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 6H), 2.12 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 169.1, 148.1, 134.7, 132.4, 132.1, 130.0, 121.7, 17.6, 16.8, 16.4. HRMS (ESI, *m/z*) calcd. for C₁₄H₁₈O₂ [M+Na]⁺: 241.1204; found: 241.1228.

11. (Z)-3-(2,3,5,6-tetramethylphenyl)acrylic acid (**3k**).



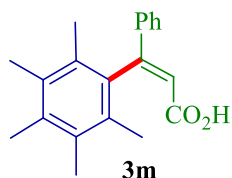
White Solid. ¹H NMR (CDCl₃, 300 MHz): δ = 7.19 (d, *J* = 12 Hz, 1H), 6.91 (s, 1H), 6.16 (d, *J* = 12 Hz, 1H), 2.20 (s, 6H), 2.07 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 169.5, 147.5, 134.8, 133.4, 131.0, 130.4, 121.9, 19.9, 16.5. HRMS (ESI, *m/z*) calcd. for C₁₃H₁₆O₂ [M+Na]⁺: 227.1048; found: 227.1049.

12. (Z)-3-mesityl-3-phenylacrylic acid (**3l**).⁷



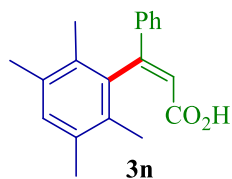
White Solid. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.38\text{-}7.33$ (m, 5H), 6.92 (s, 2H), 6.62 (s, 1H), 2.34 (s, 3H), 2.04 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 169.4$, 157.1, 138.1, 137.1, 134.7, 134.3, 129.9, 128.7, 128.2, 127.1, 116.9, 21.1, 19.7. **HRMS** (ESI, m/z) calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 289.1204; found: 289.1205.

13. **(Z)-3-(2,3,4,5,6-pentamethylphenyl)-3-phenylacrylic acid (3m).**³



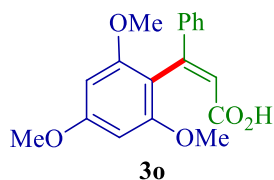
White Solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.38\text{-}7.33$ (m, 5H), 6.69 (s, 1H), 2.30 (s, 3H), 2.24 (s, 6H), 2.05 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 167.2$, 157.7, 138.3, 135.5, 133.4, 133.1, 130.5, 129.8, 128.7, 127.2, 117.1, 17.5, 16.9, 16.5. **HRMS** (ESI, m/z) calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 317.1517; found: 317.1542.

14. **(Z)-3-(2,3,5,6-tetramethylphenyl)-3-phenylacrylic acid (3n).**⁸



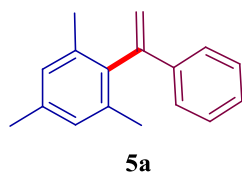
White Solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.38\text{-}7.32$ (m, 5H), 7.03 (s, 1H), 6.68 (s, 1H), 2.26 (s, 6H), 1.99 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 167.7$, 157.5, 138.2, 133.9, 131.4, 130.8, 129.9, 128.7, 127.2, 116.8, 20.0, 16.3. **HRMS** (ESI, m/z) calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1361; found: 303.1353.

15. **(Z)-3-(2,4,6-trimethoxyphenyl)-3-phenylacrylic acid (3o).**



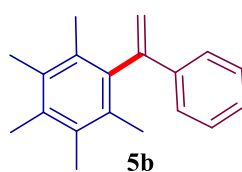
White Solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.37\text{-}7.30$ (m, 5H), 6.51 (s, 1H), 6.20 (s, 2H), 3.88 (s, 3H), 3.67 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 168.1, 161.7, 158.0, 150.6, 129.1, 128.3, 126.9, 118.6, 90.9, 55.9, 55.32$. **HRMS** (ESI, m/z) calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_5$ $[\text{M}+\text{Na}]^+$: 337.1052; found: 337.1056.

16. **1,3,5-trimethyl-2-(1-phenylvinyl)benzene (5a)**.³



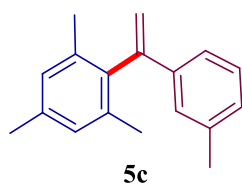
Colourless liquid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.35\text{-}7.32$ (m, 5H), 6.99 (s, 2H), 6.03 (s, 1H), 5.17 (s, 1H), 2.40 (s, 3H), 2.20 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 147.1, 139.7, 138.3, 136.6, 136.3, 128.6, 128.3, 127.7, 126.0, 114.6, 21.2, 20.3$.

17. **1,2,3,4,5-pentamethyl-6-(1-phenylvinyl)benzene (5b)**.³



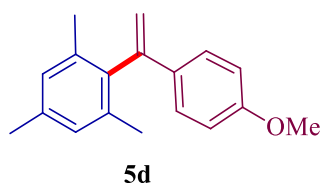
White solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.23\text{-}7.15$ (m, 5H), 5.89 (d, $J = 0.8$ Hz, 1H), 4.99 (d, $J = 0.8$ Hz, 1H), 2.21 (s, 3H), 2.16 (s, 6H), 2.02 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 148.6, 140.0, 138.7, 133.7, 132.3, 131.6, 128.3, 127.4, 126.0, 114.3, 17.9, 16.8, 16.6$.

18. **1,3,5-trimethyl-2-(1-(*m*-tolyl)vinyl)benzene (5c)**.³



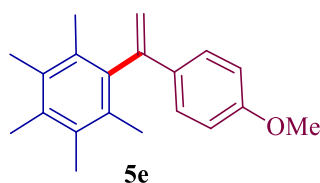
Colourless liquid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.16\text{--}7.13$ (m, 2H), 7.06–7.02 (m, 2H), 6.90 (s, 2H), 5.93 (d, $J = 1.2$ Hz, 1H), 5.06 (d, $J = 1.2$ Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.11 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 147.0$, 139.6, 138.3, 137.9, 136.4, 136.1, 128.4, 128.3, 128.1, 126.4, 123.1, 114.5, 21.6, 21.1, 20.2.

19. **2-(1-(4-methoxyphenyl)vinyl)-1,3,5-trimethylbenzene (5e).**⁹



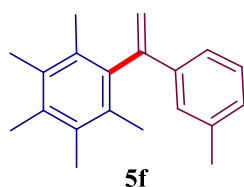
Colourless liquid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.21\text{--}7.18$ (m, 2H), 6.90 (s, 2H), 6.81–6.77 (m, 2H), 5.83 (d, $J = 1.2$ Hz, 1H), 4.97 (d, $J = 1.2$ Hz, 1H), 3.77 (s, 3H), 2.31 (s, 3H), 2.10 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 159.2$, 146.2, 138.4, 136.3, 136.1, 132.2, 128.1, 127.1, 113.8, 112.5, 55.2, 21.1, 20.1.

20. **1-(1-(4-methoxyphenyl)vinyl)-2,3,4,5,6-pentamethylbenzene (5f).**³



White solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.17$ (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 8.8$ Hz, 2H), 5.79 (d, $J = 1.2$ Hz, 1H), 4.89 (d, $J = 0.8$ Hz, 1H), 3.72 (s, 3H), 2.22 (s, 3H), 2.17 (s, 6H), 2.04 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 159.1$, 147.9, 138.9, 133.6, 132.7, 132.3, 131.5, 127.2, 113.7, 112.3, 55.2, 17.8, 16.8, 16.6.

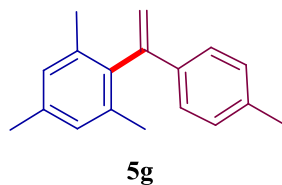
21. **1,2,3,4,5-pentamethyl-6-(1-(*m*-tolyl)vinyl)benzene (5d).**



White solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.17\text{--}7.13$ (m, 2H), 7.06–7.02 (m, 2H), 5.94 (d, $J = 0.8$ Hz, 1H), 5.03 (d, $J = 0.8$ Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.23 (s, 6H), 2.10 (s,

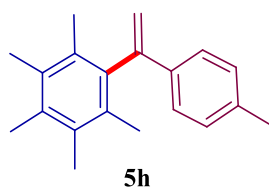
6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 163.5, 161.1, 147.5, 138.4, 136.16, 136.13, 133.9, 132.4, 131.4, 127.7, 127.6, 115.3, 115.1, 114.04, 114.02, 29.7, 17.8, 16.8, 16.6$.

22. **1,3,5-trimethyl-2-(1-(*p*-tolyl)vinyl)benzene (5g).**³



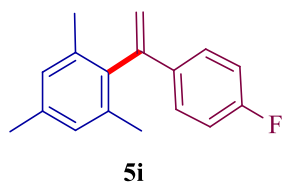
Colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.17$ (d, $J = 8$ Hz, 2H), 7.07 (d, $J = 8$ Hz, 2H), 6.90 (s, 2H), 5.91 (d, $J = 1.2$ Hz, 1H), 5.03 (d, $J = 1.2$ Hz, 1H), 2.31 (s, 6H), 2.10 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 146.8, 138.5, 137.4, 136.8, 136.4, 136.2, 129.3, 128.2, 125.8, 113.6, 21.29, 21.23, 20.2$.

23. **1,2,3,4,5-pentamethyl-6-(1-(*p*-tolyl)vinyl)benzene (5h).**¹⁰



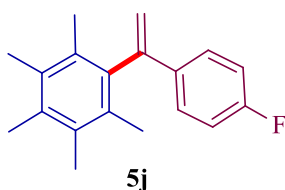
White solid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.14$ (d, $J = 8$ Hz, 2H), 7.03 (d, $J = 8$ Hz, 2H), 5.87 (d, $J = 0.8$ Hz, 1H), 4.95 (d, $J = 1.2$ Hz, 1H), 2.26 (s, 3H), 2.23 (s, 3H), 2.18 (s, 6H), 2.04 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 148.4, 138.9, 137.3, 137.2, 133.6, 132.3, 131.6, 129.1, 125.9, 113.4, 21.1, 17.9, 16.8, 16.3$.

24. **2-(1-(4-fluorophenyl)vinyl)-1,3,5-trimethylbenzene (5i).**³



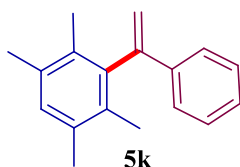
Colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.25$ - 7.21 (m, 2H), 6.97 - 6.91 (m, 4H), 5.88 (s, 1H), 5.06 (s, 1H), 2.31 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 163.6, 161.2, 145.8, 137.9, 136.6, 136.0, 135.7, 135.6, 128.2, 127.5, 127.4, 115.3, 115.1, 114.28, 114.27, 21.07, 21.06$.

25. 1-(1-(4-fluorophenyl)vinyl)-2,3,4,5,6-pentamethylbenzene (**5j**).¹¹



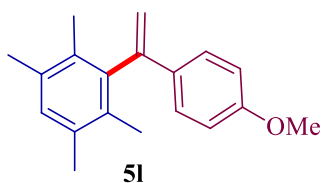
White solid. ¹H NMR (CDCl₃, 400 MHz): δ = 7.20-7.17 (m, 2H), 6.91-6.85 (m, 2H), 5.83 (s, 1H), 4.97 (s, 1H), 2.22 (s, 3H), 2.17 (s, 6H), 2.02 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 162.5, 160.0, 146.5, 137.4, 135.08, 135.05, 132.8, 131.4, 130.4, 126.6, 126.5, 114.2, 114.0, 112.9, 16.7, 15.7, 15.5.

26. 1,2,4,5-tetramethyl-3-(1-phenylvinyl)benzene (**5k**).¹⁰



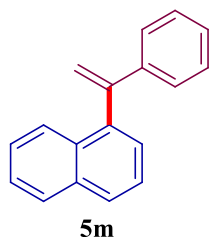
White solid. ¹H NMR (CDCl₃, 400 MHz): δ = 7.31-7.27 (m, 5H), 7.00 (s, 1H), 6.01 (s, 1H), 5.10 (s, 1H), 2.28 (s, 6H), 2.07 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 148.0, 141.0, 139.7, 133.5, 132.0, 130.3, 128.4, 127.5, 125.9, 114.2, 20.2, 16.7.

27. 3-(1-(4-methoxyphenyl)vinyl)-1,2,4,5-tetramethylbenzene (**5l**).¹¹



White solid. ¹H NMR (CDCl₃, 400 MHz): δ = 7.25 (d, *J* = 8.8 Hz, 2H), 6.99 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.89 (s, 1H), 4.97 (s, 1H), 3.81 (s, 3H), 2.27 (s, 6H), 2.07 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ = 159.4, 147.6, 141.5, 133.7, 132.7, 132.1, 130.4, 127.3, 113.9, 112.3, 55.4, 20.3, 16.7.

28. 1-(1-phenylvinyl)naphthalene (**5m**).⁹



White solid. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 7.90 (dd, J = 3.2, 8 Hz, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.47-7.44 (m, 2H), 7.37-7.34 (m, 3H), 7.31-7.25 (m, 3H), 6.01 (s, 1H), 5.42 (s, 1H). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ = 148.5, 141.3, 140.0, 133.9, 132.1, 128.5, 128.3, 128.1, 127.9, 127.4, 126.8, 126.6, 126.0, 125.8, 125.6, 116.4.

4. Reference

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5. ^1H and ^{13}C NMR spectra of compounds (3a-o and 5a-5m).

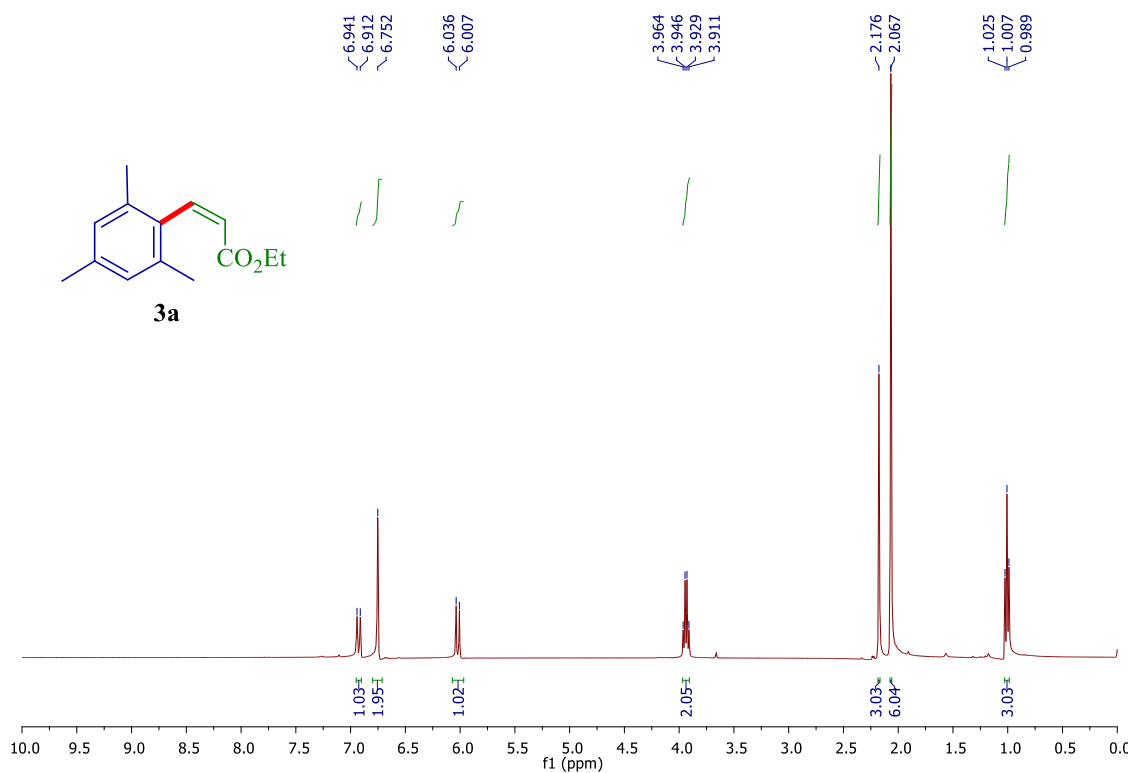


Figure S1. ^1H NMR Spectrum of **3a** in CDCl_3 .

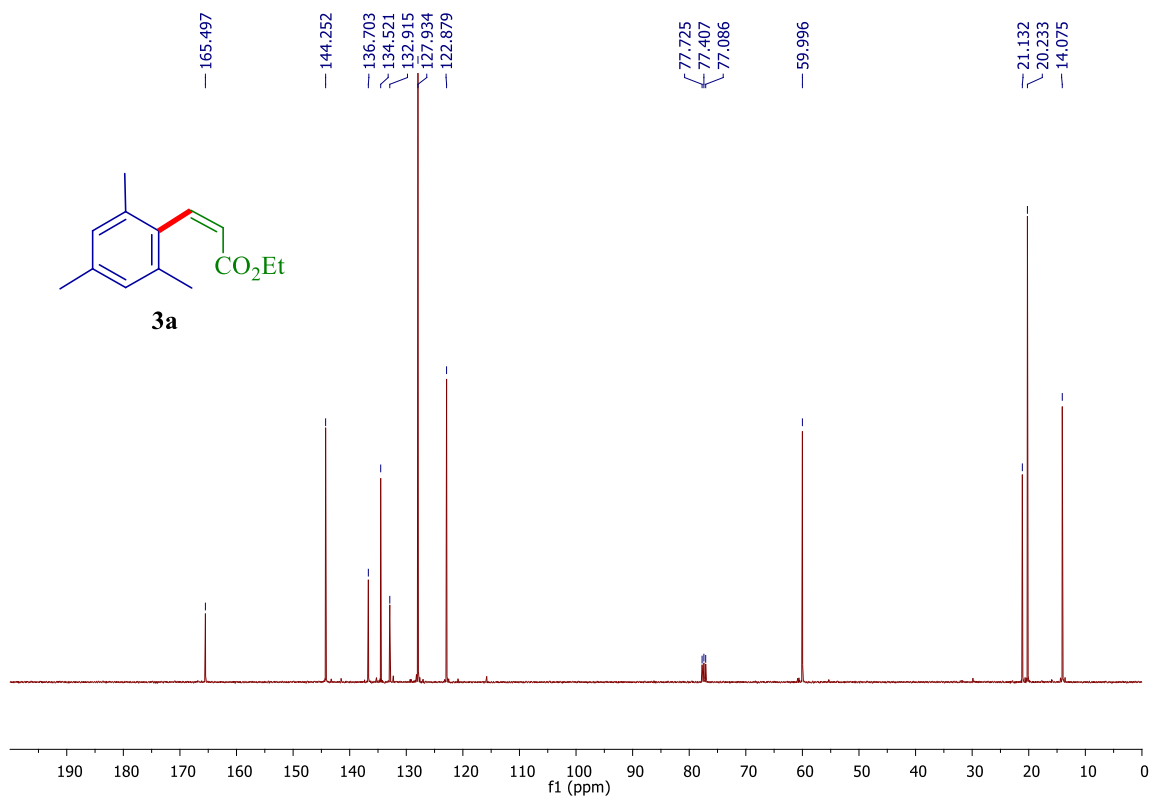


Figure S2. ^{13}C NMR Spectrum of **3a** in CDCl_3 .

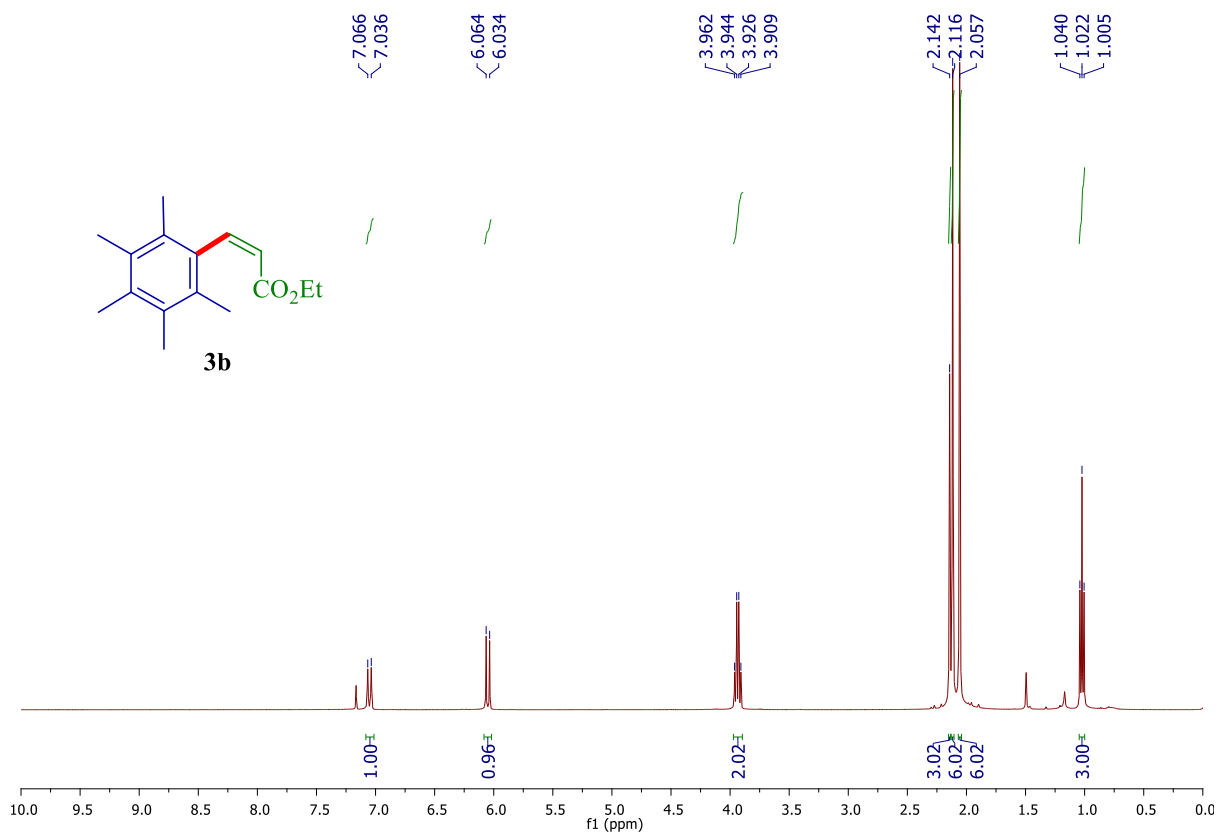


Figure S3. ^1H NMR Spectrum of **3b** in CDCl_3 .

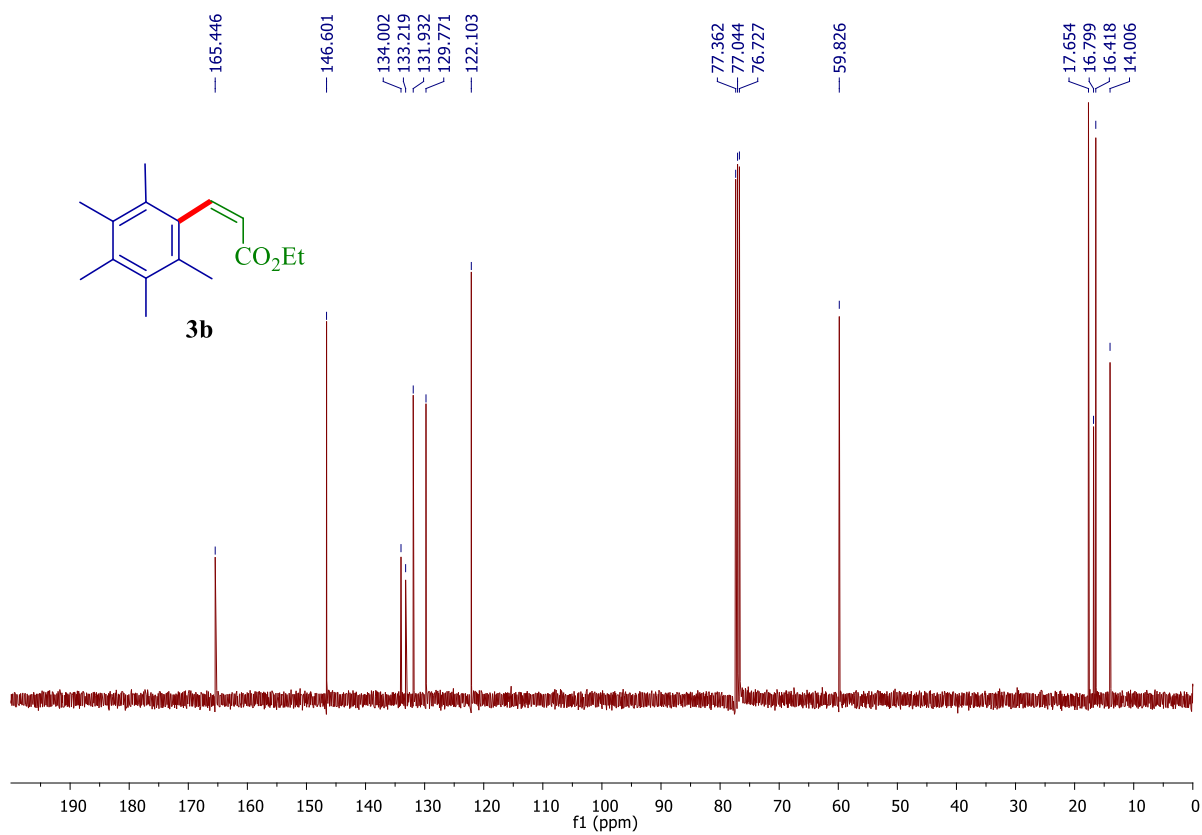
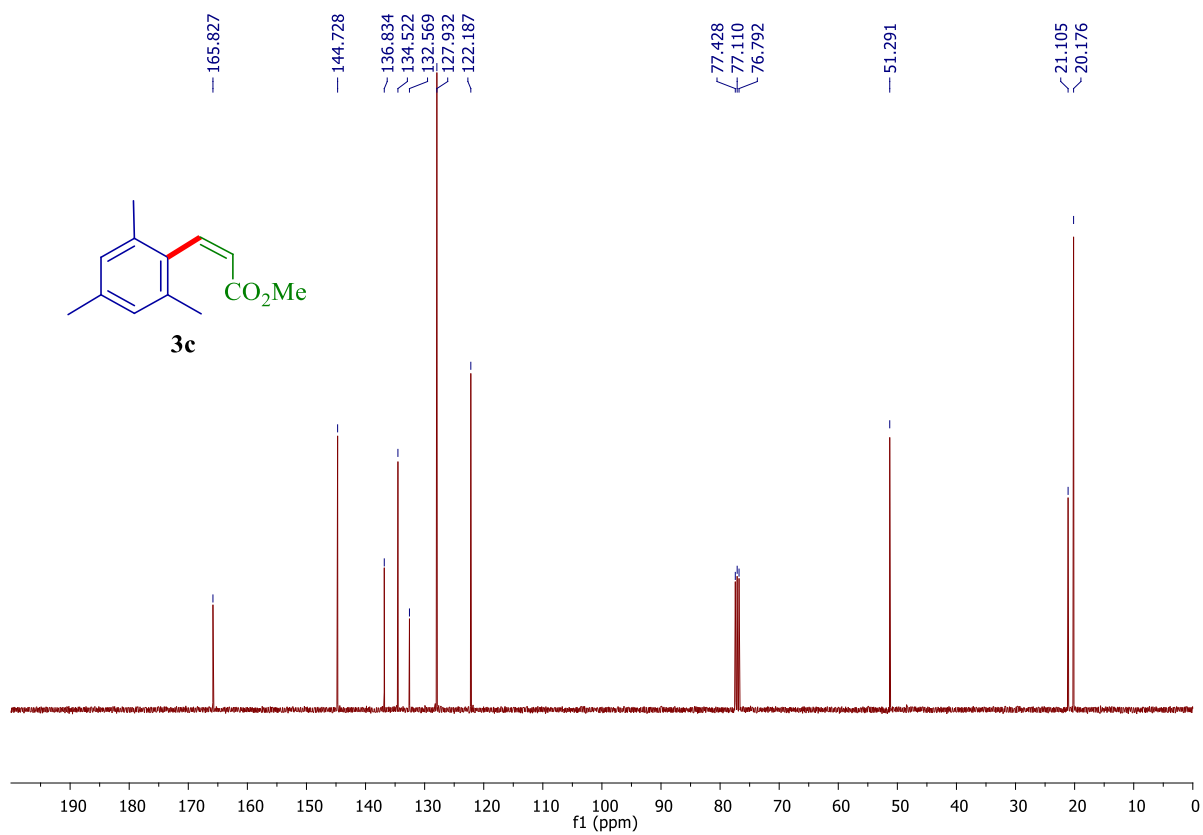
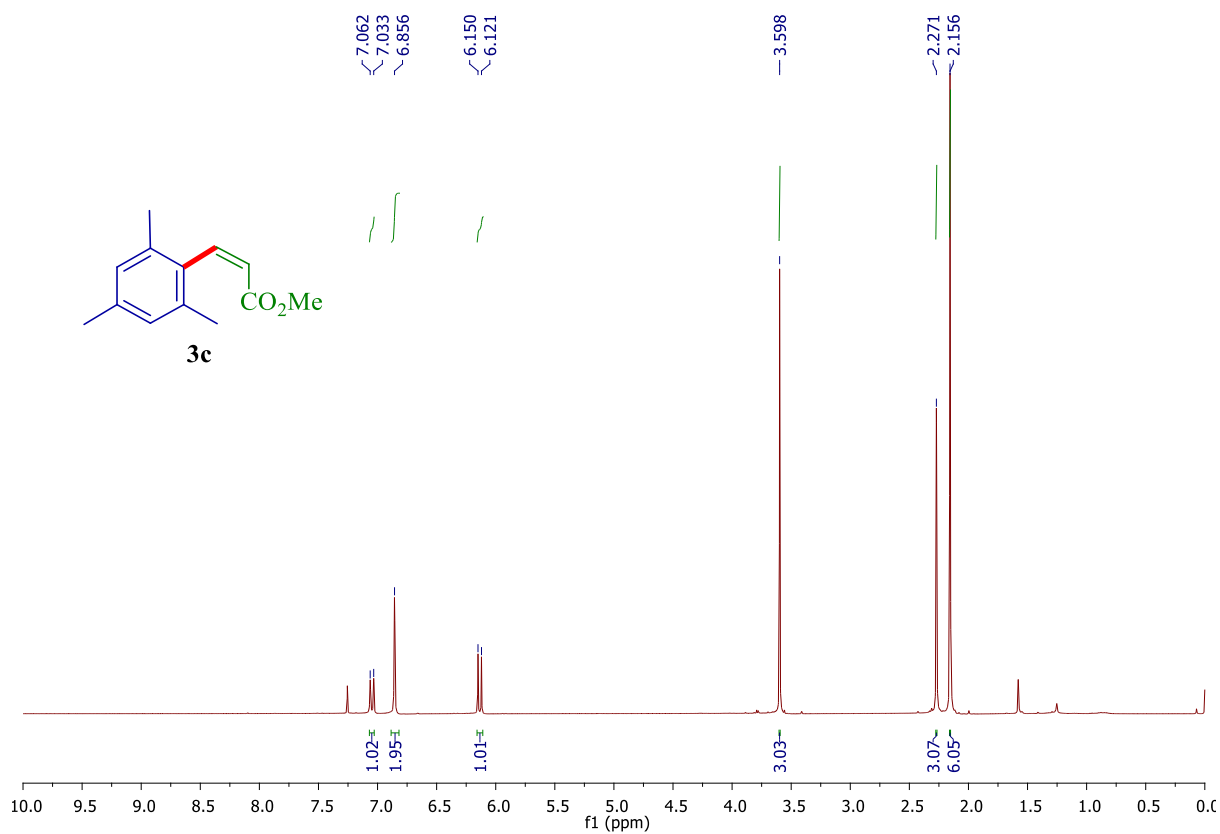
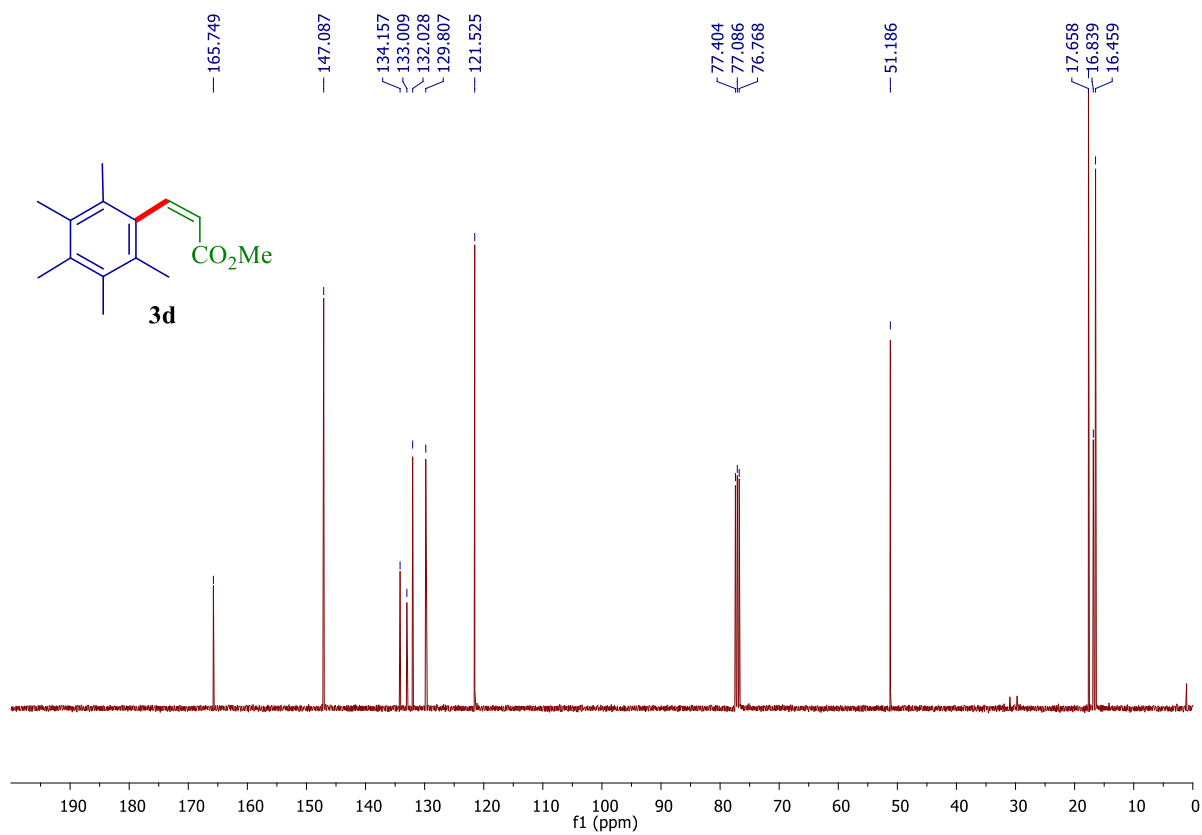
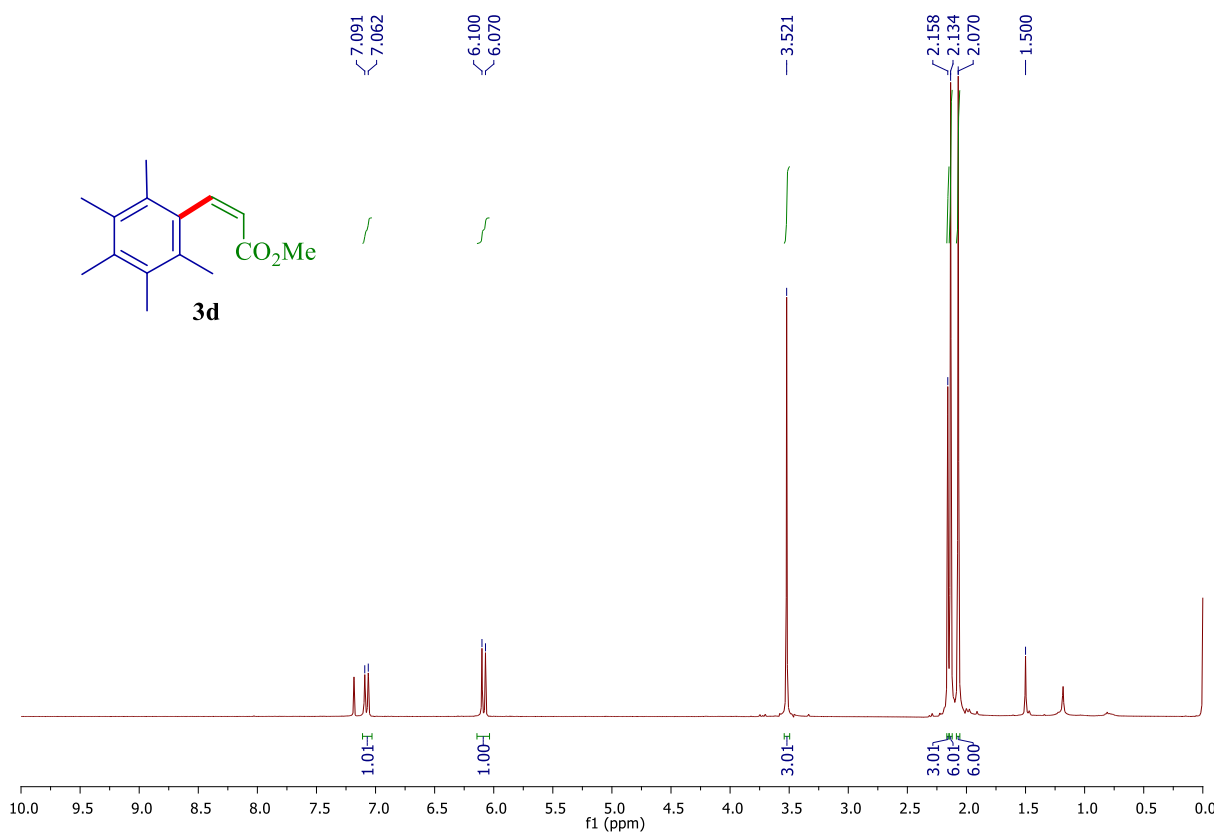
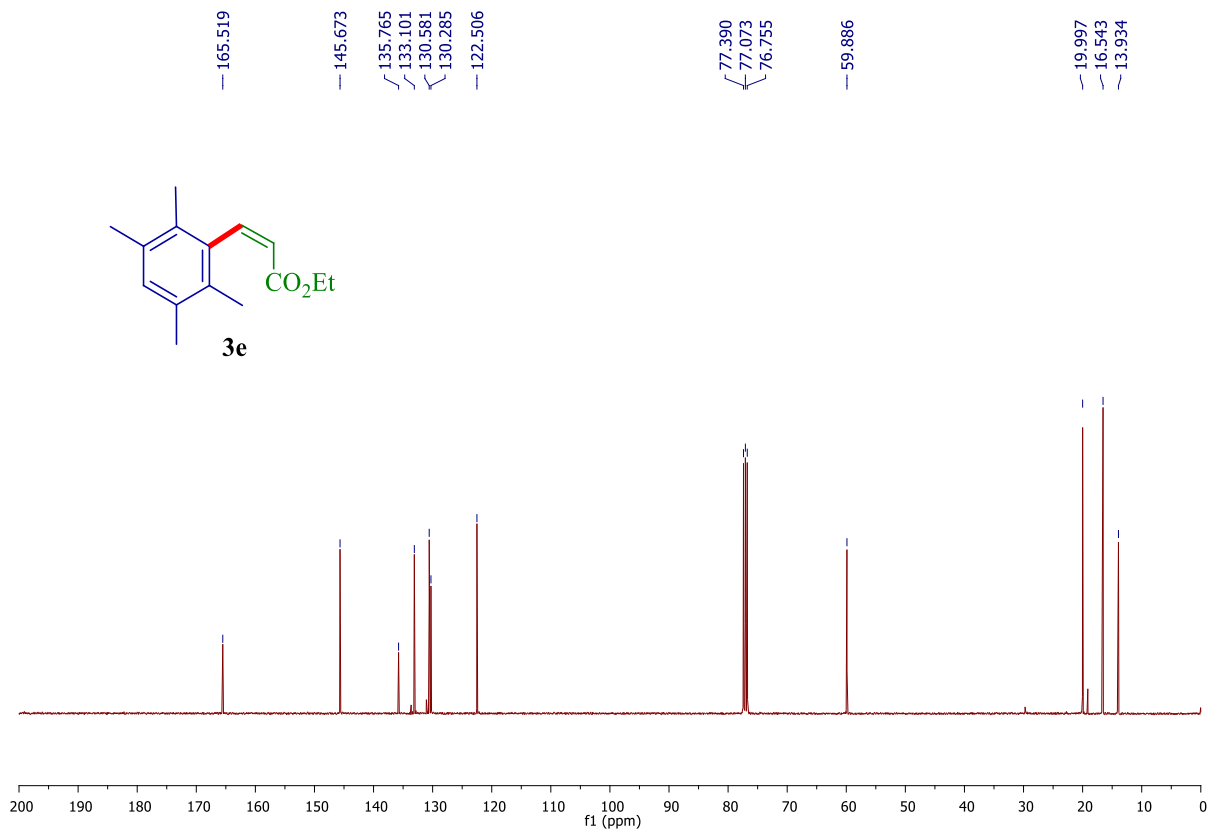
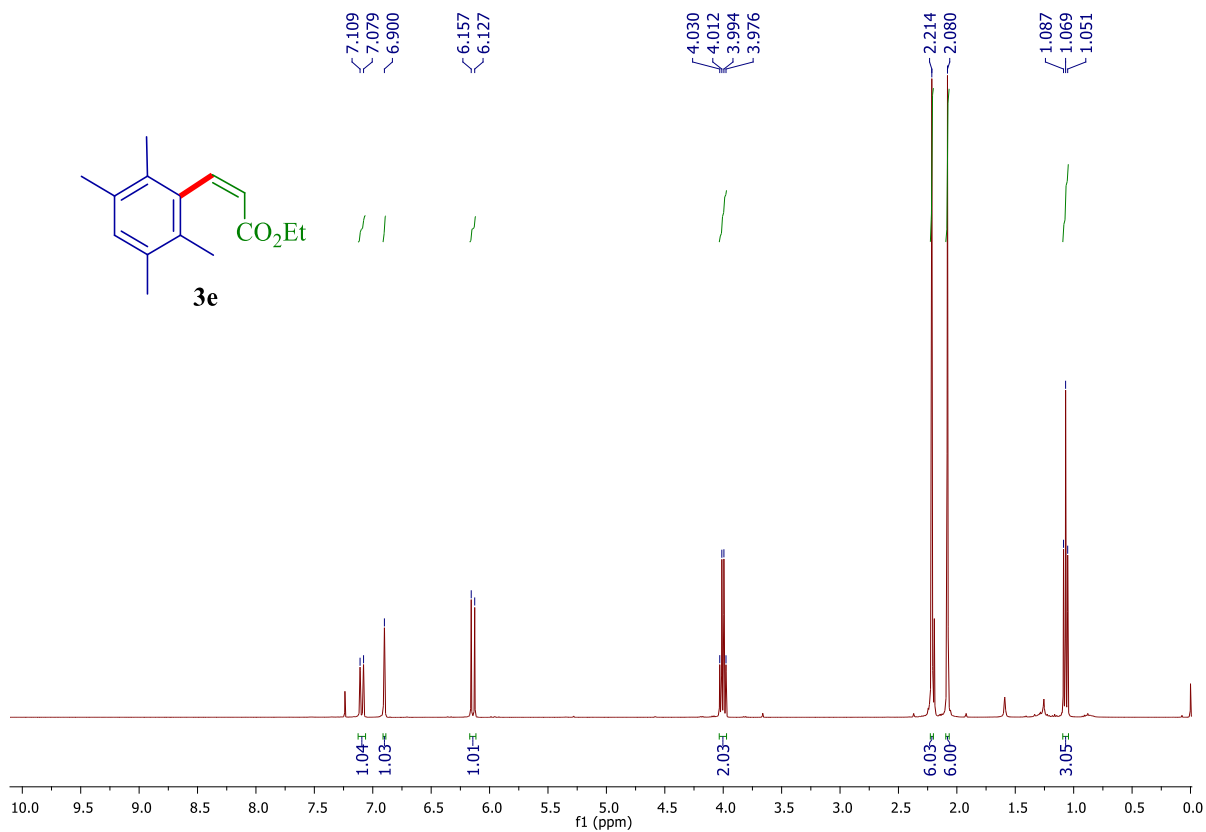
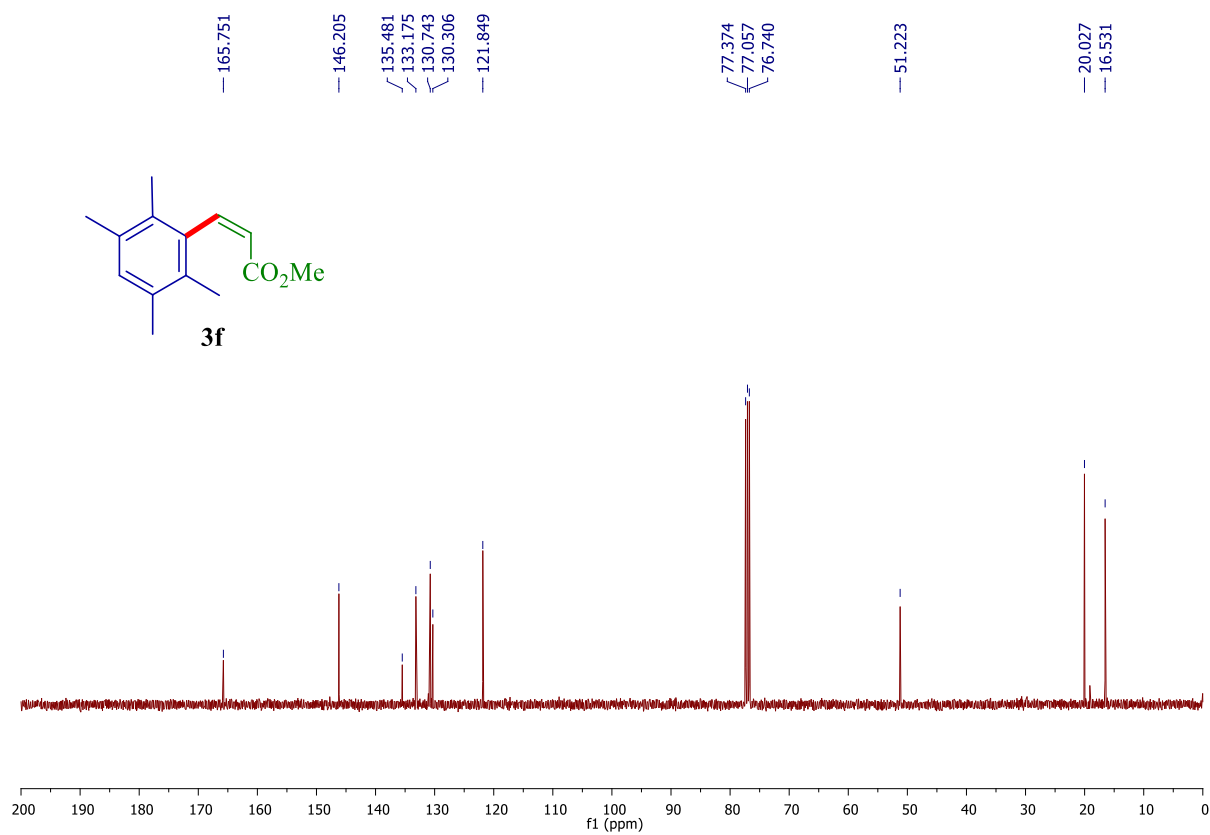
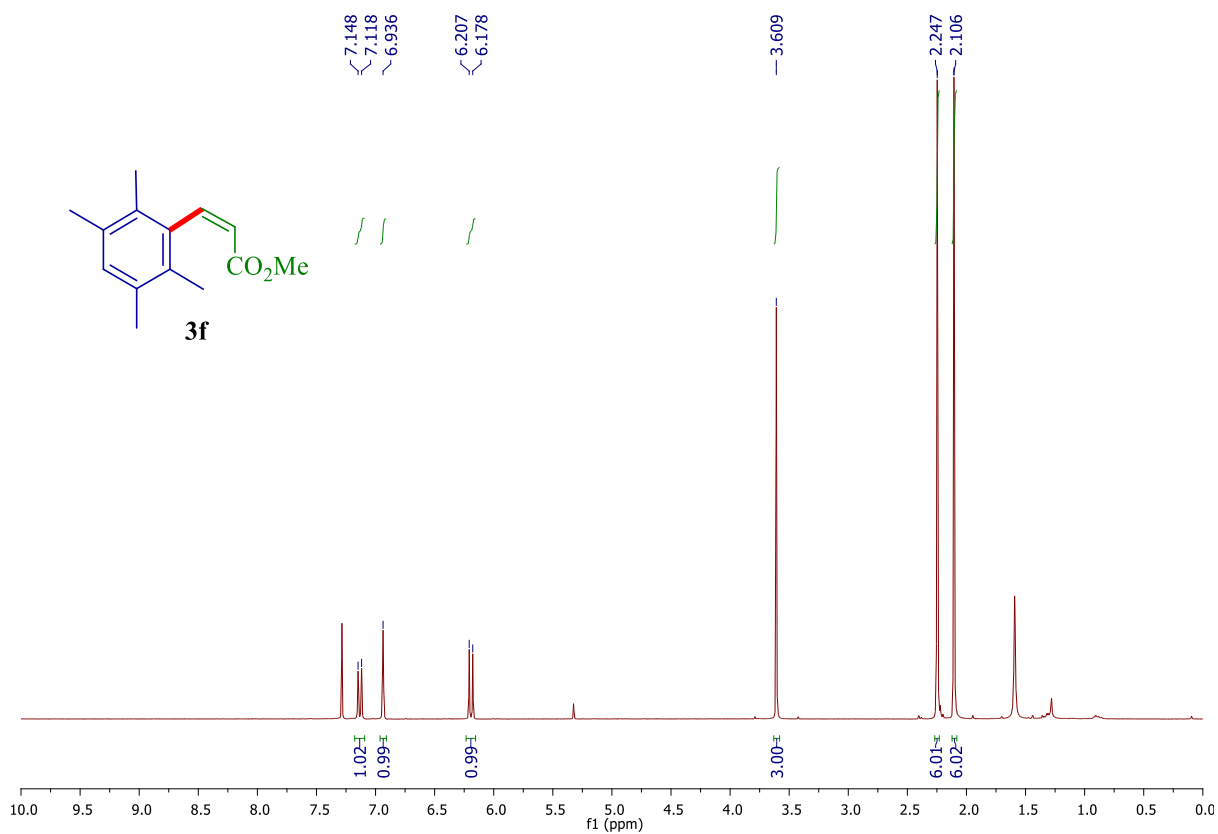


Figure S4. ^{13}C NMR Spectrum of **3b** in CDCl_3 .









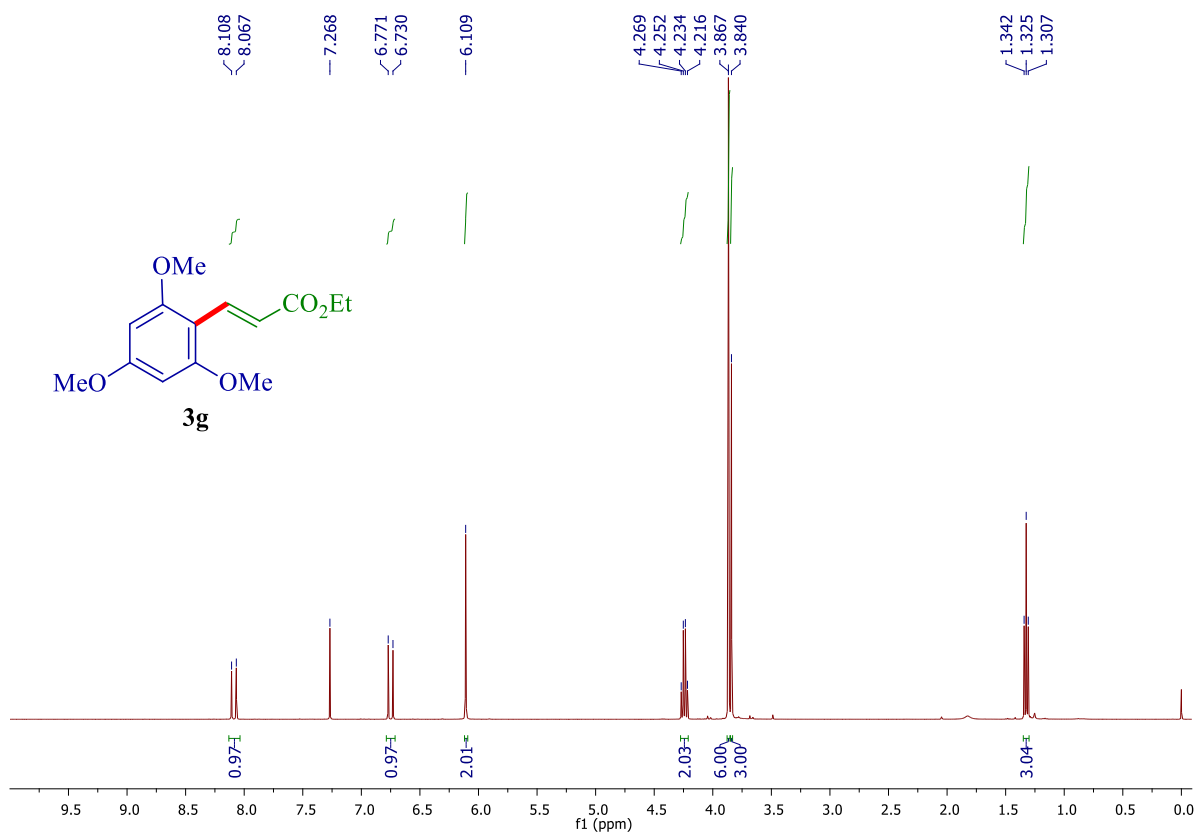


Figure S13. ^1H NMR Spectrum of **3g** in CDCl_3 .

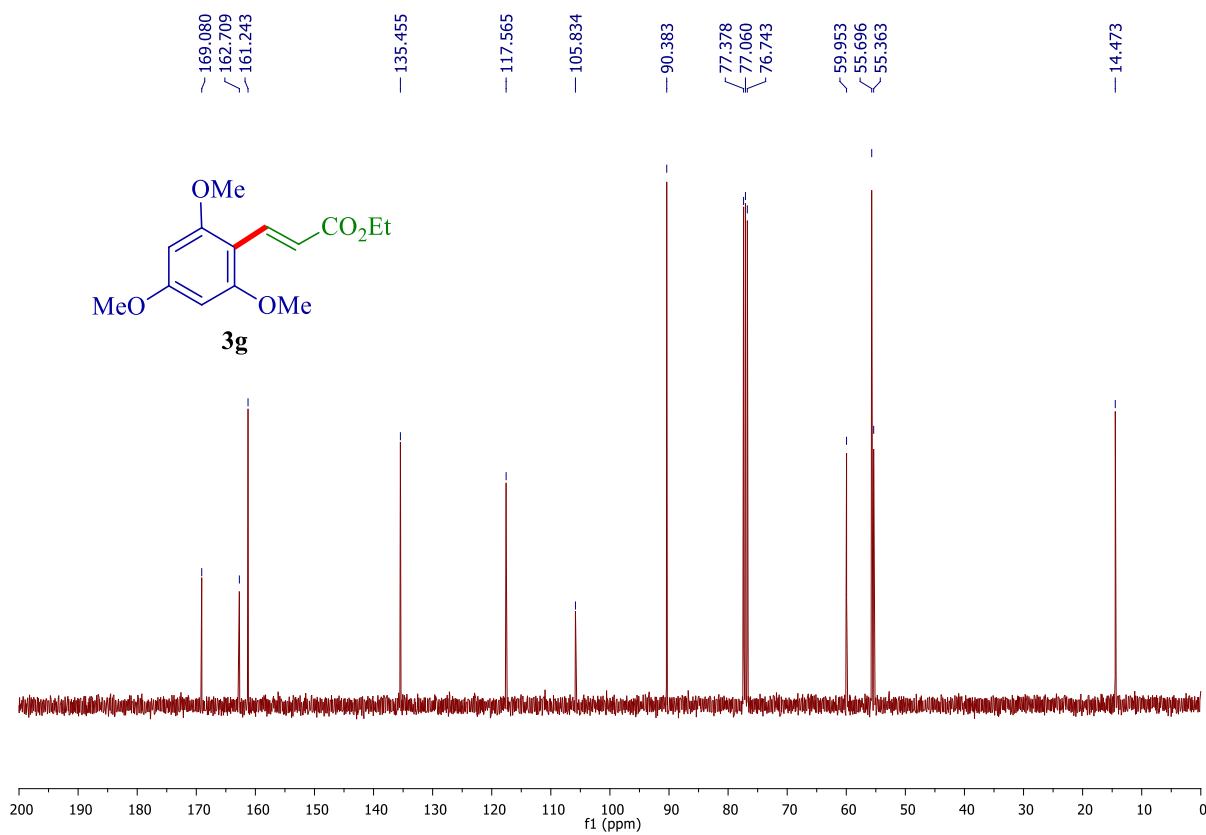


Figure S14. ^{13}C NMR Spectrum of **3g** in CDCl_3 .

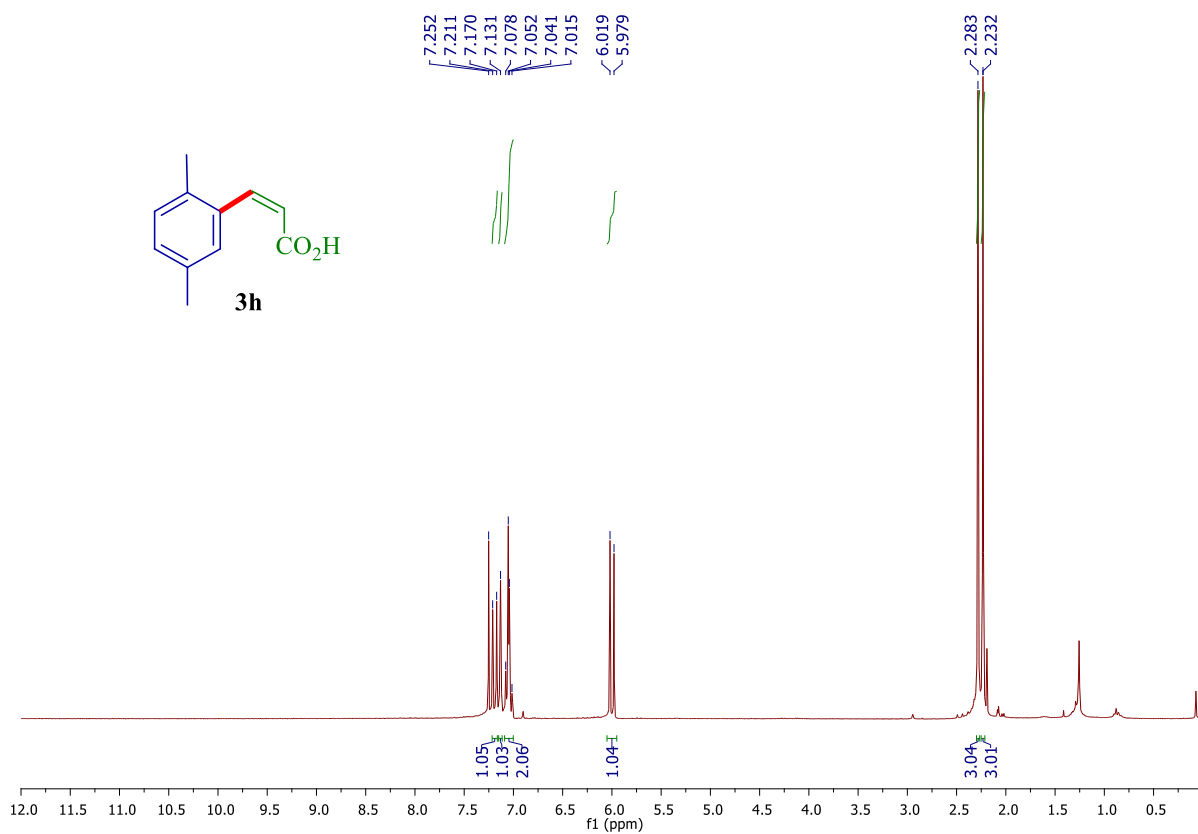


Figure S15. ^1H NMR Spectrum of **3h** in CDCl_3 .

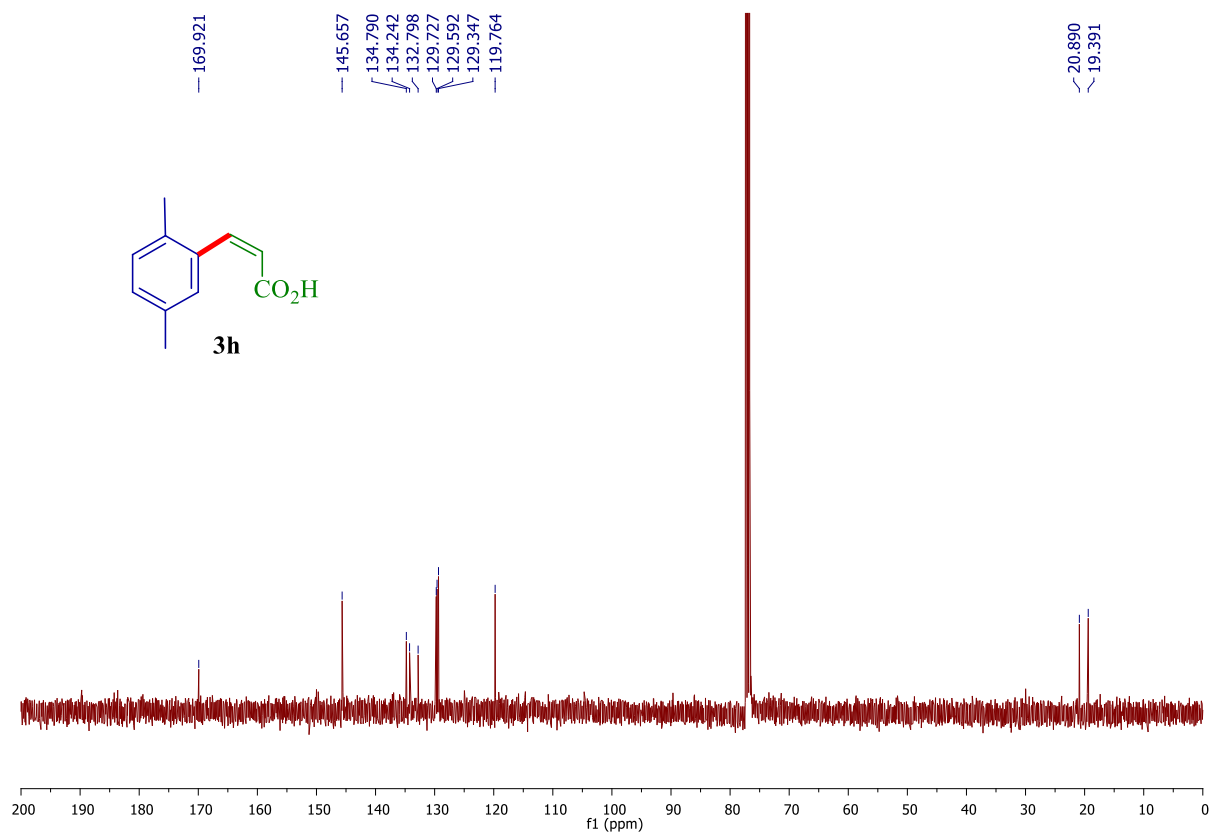


Figure S16. ^{13}C NMR Spectrum of **3h** in CDCl_3 .

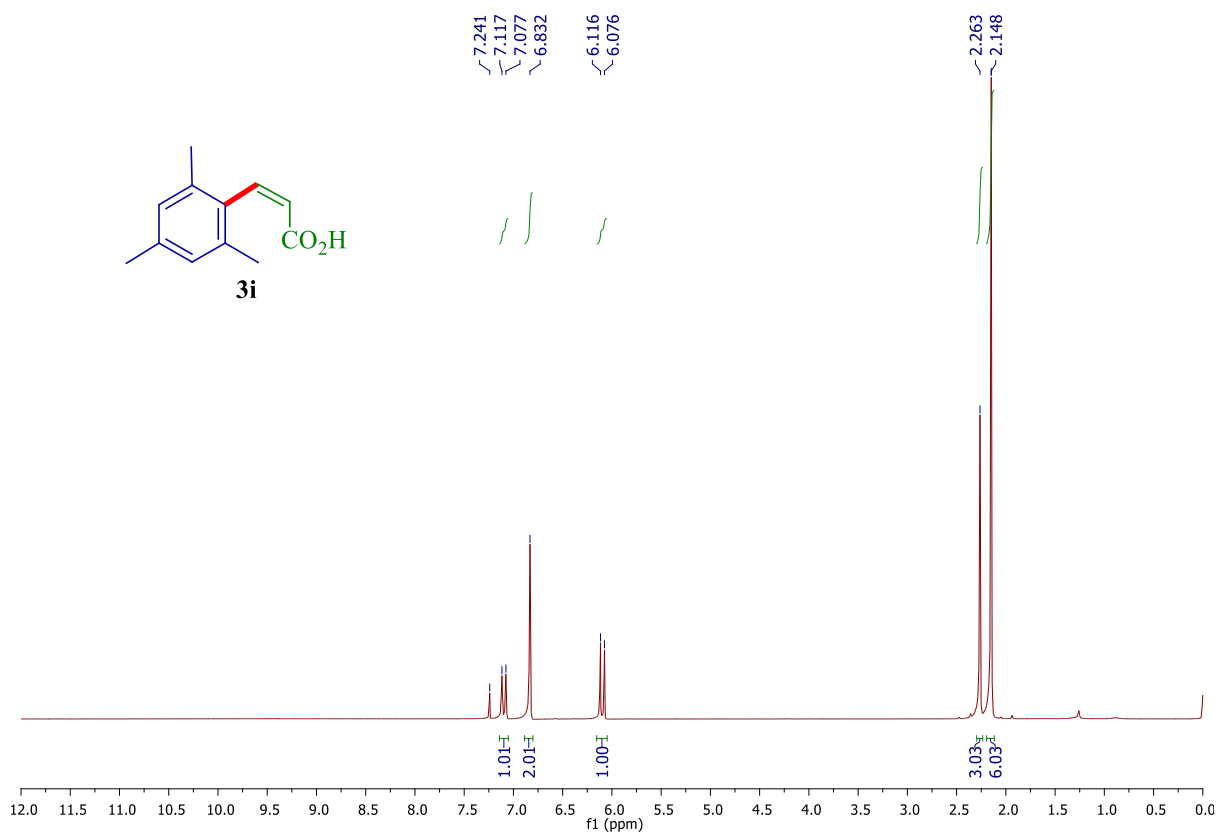


Figure S17. ¹H NMR Spectrum of **3i** in CDCl₃.

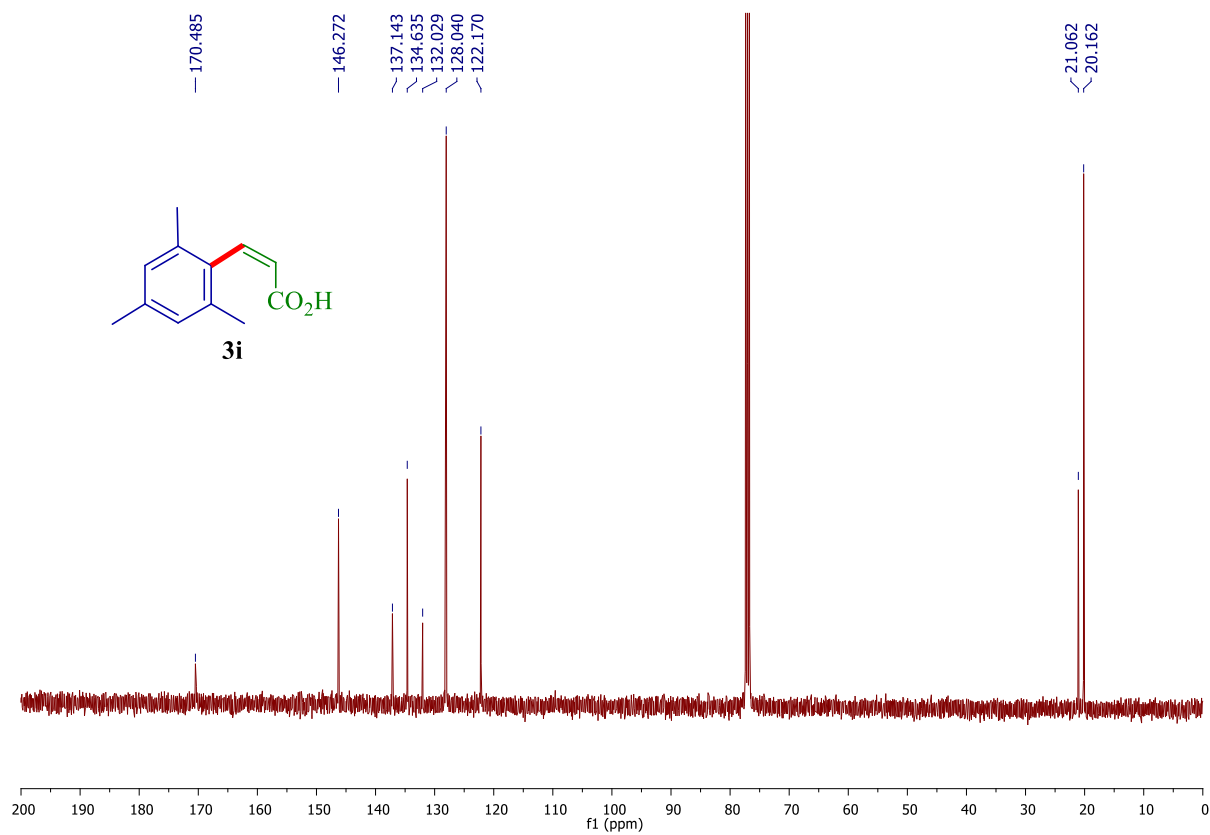
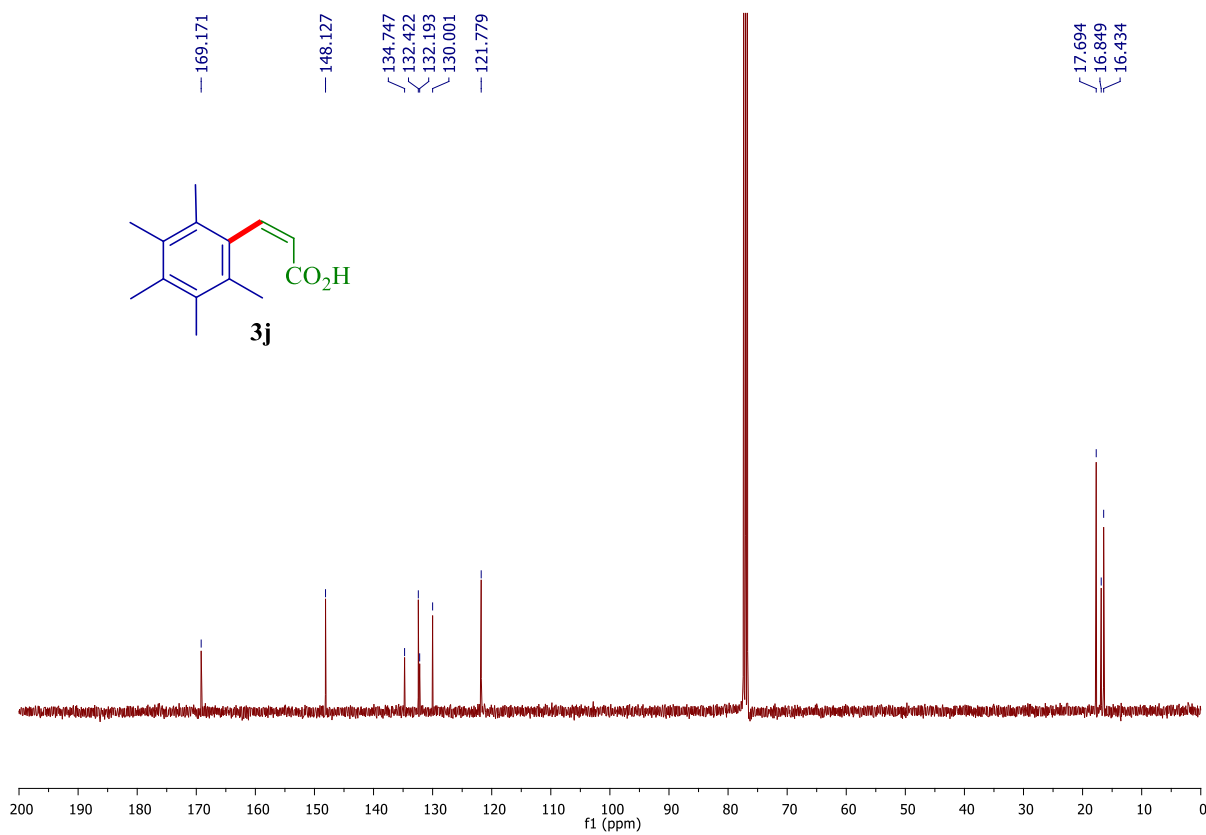
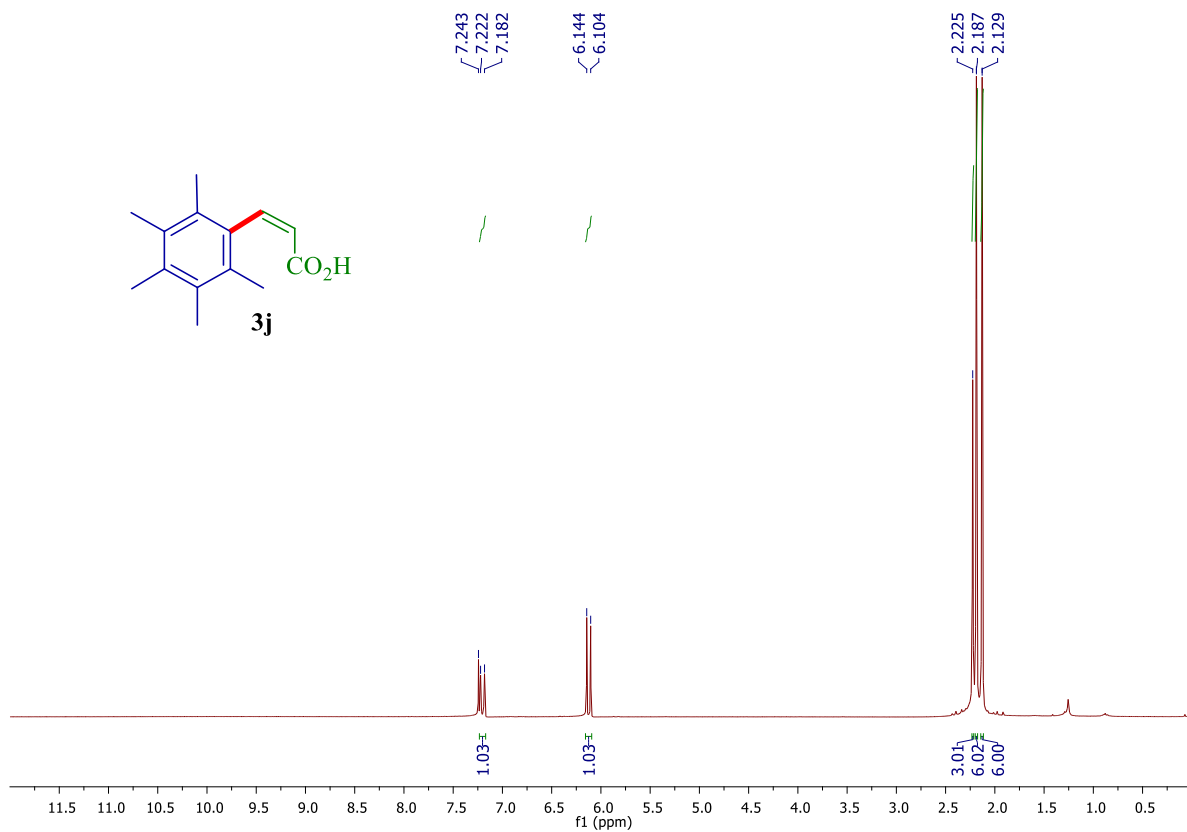


Figure S18. ¹³C NMR Spectrum of **3i** in CDCl₃.



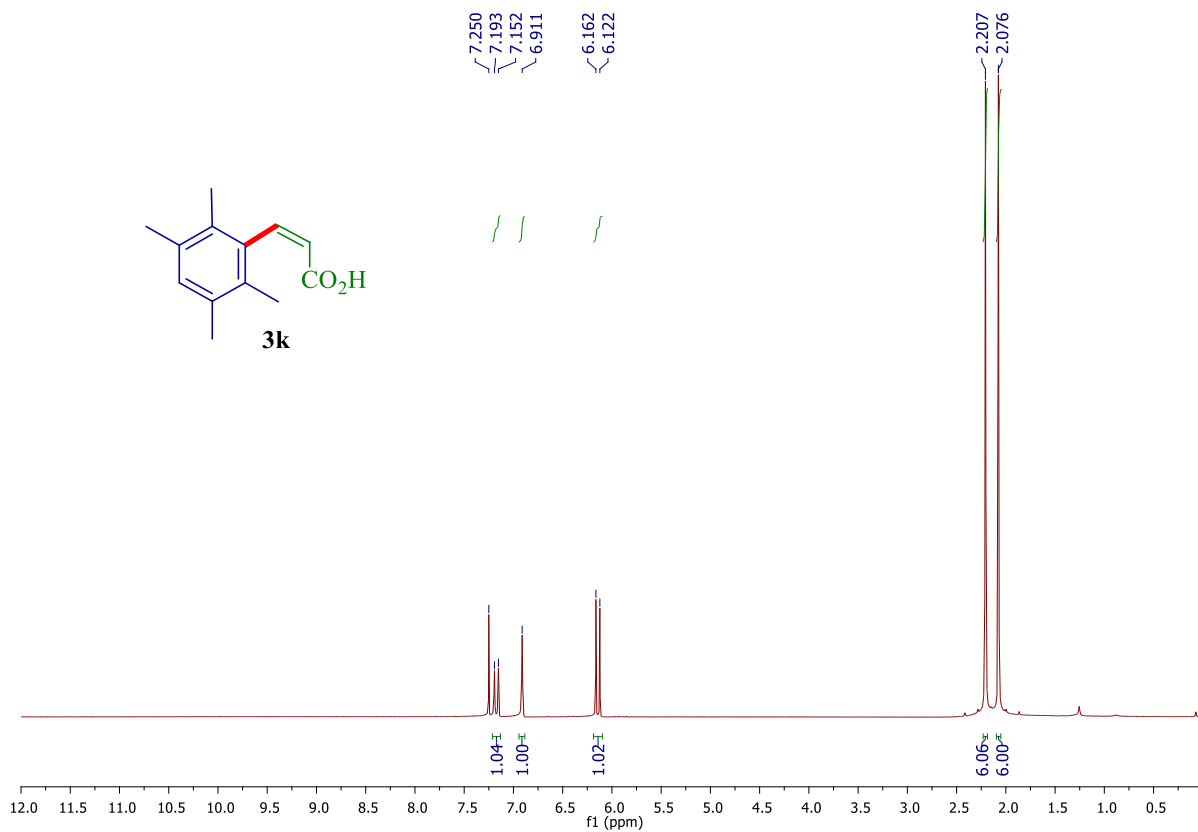


Figure S21. ^1H NMR Spectrum of **3k** in CDCl_3 .

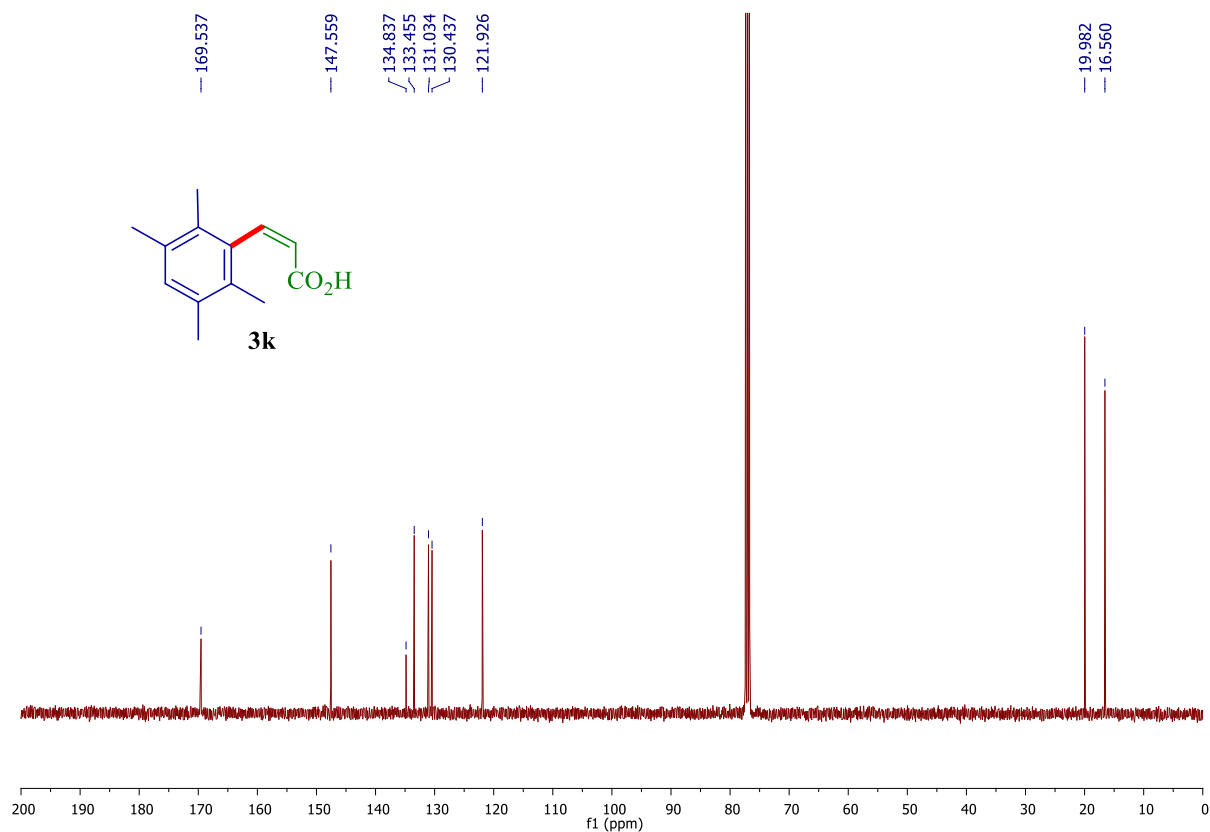


Figure S22. ^{13}C NMR Spectrum of **3k** in CDCl_3 .

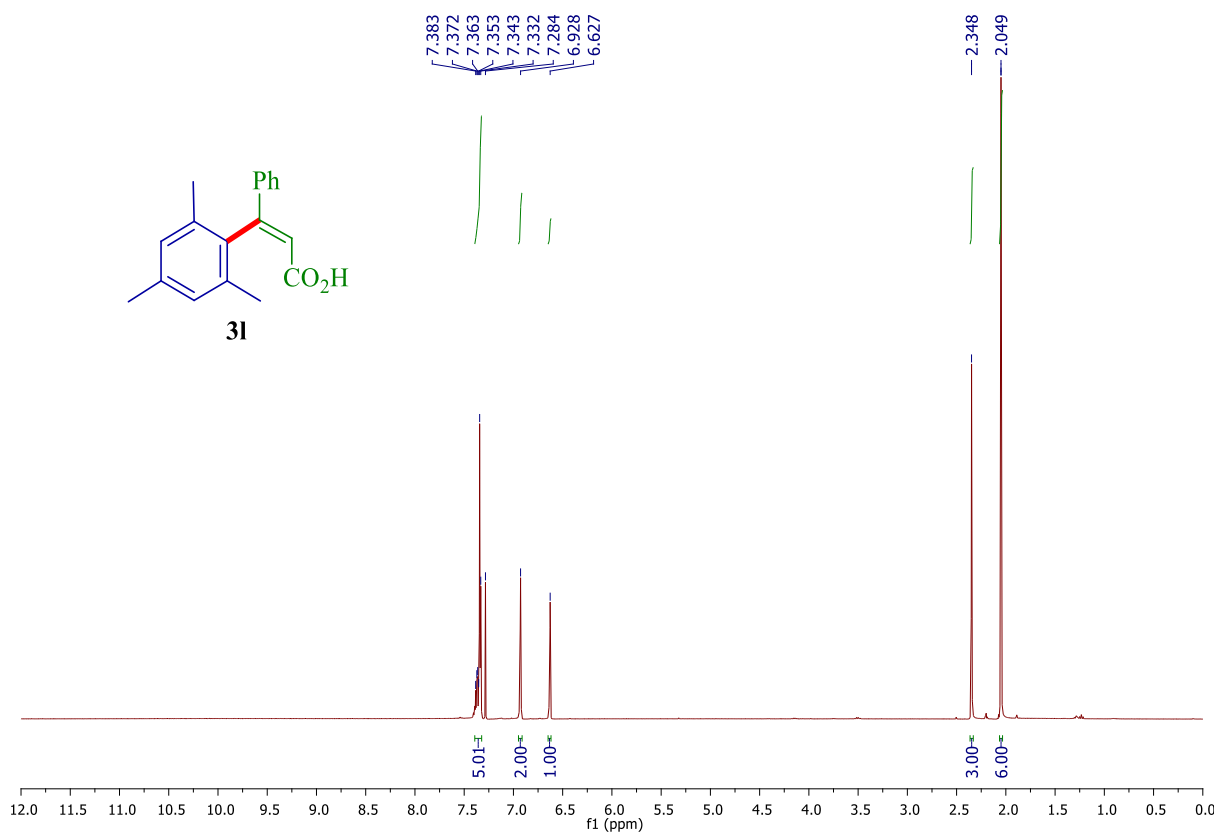


Figure S23. ¹H NMR Spectrum of **31** in CDCl₃.

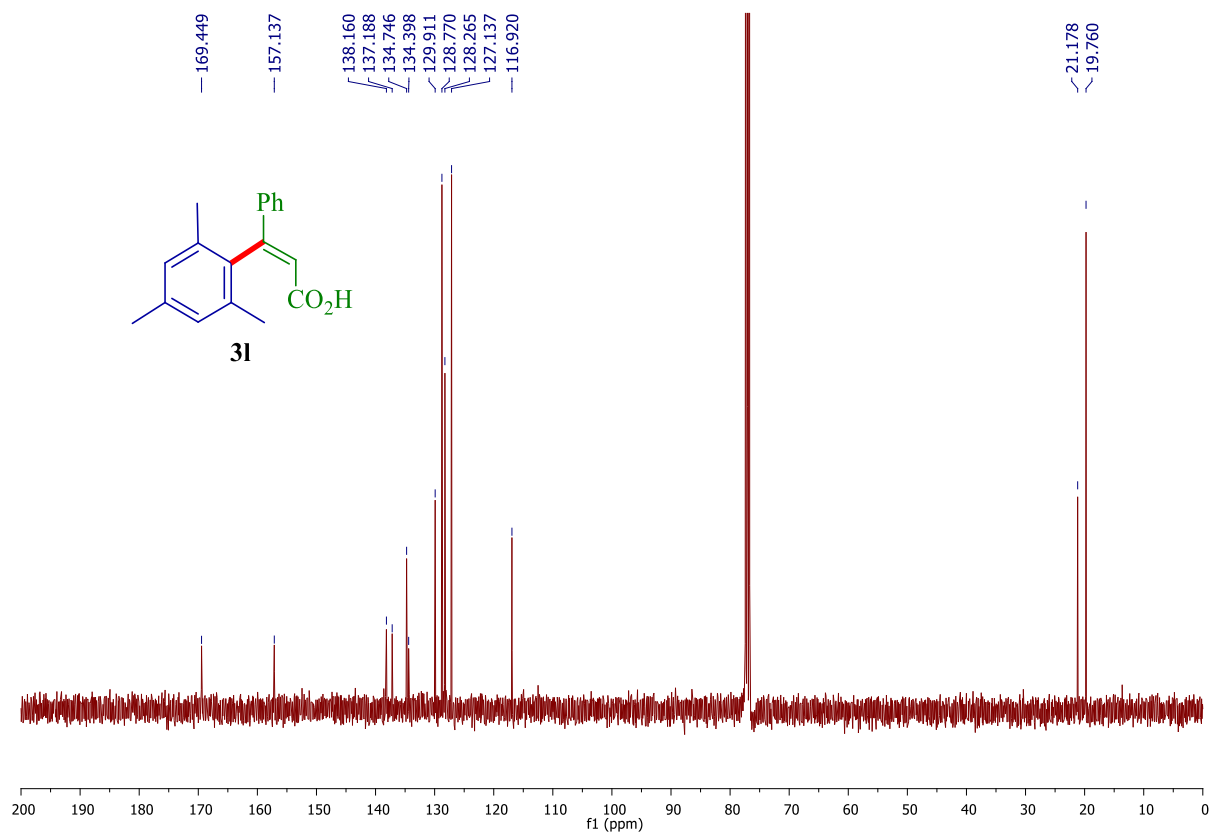


Figure S24. ¹³C NMR Spectrum of **31** in CDCl₃.

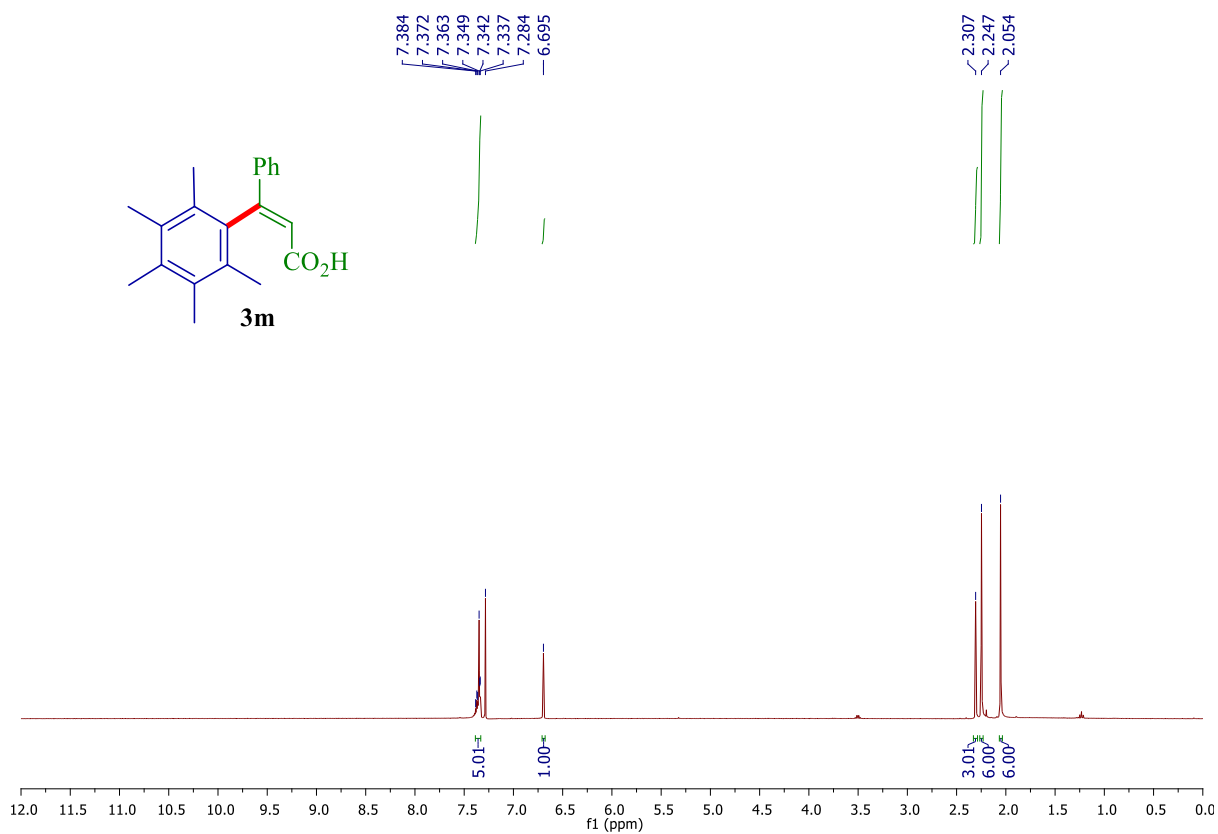


Figure S25. ¹H NMR Spectrum of **3m** in CDCl₃.

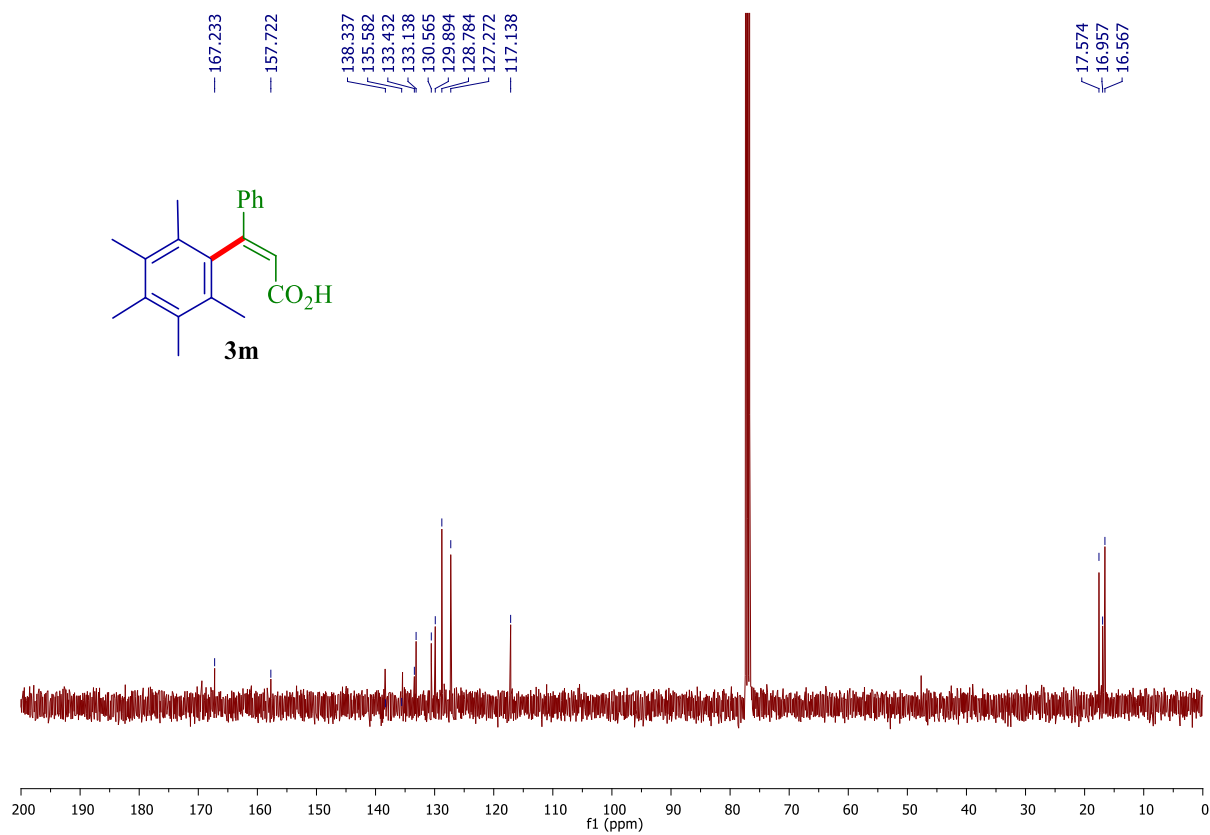


Figure S26. ¹³C NMR Spectrum of **3m** in CDCl₃.

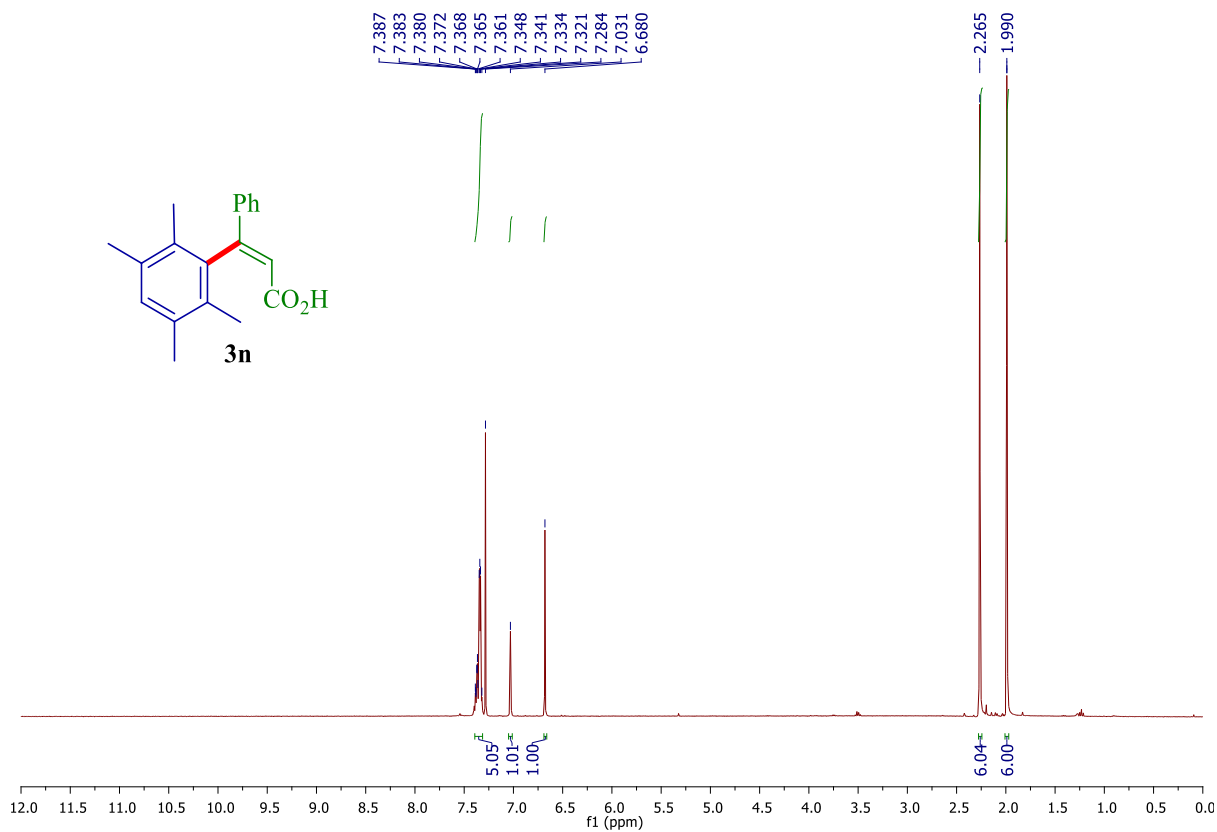


Figure S27. ¹H NMR Spectrum of **3n** in CDCl₃.

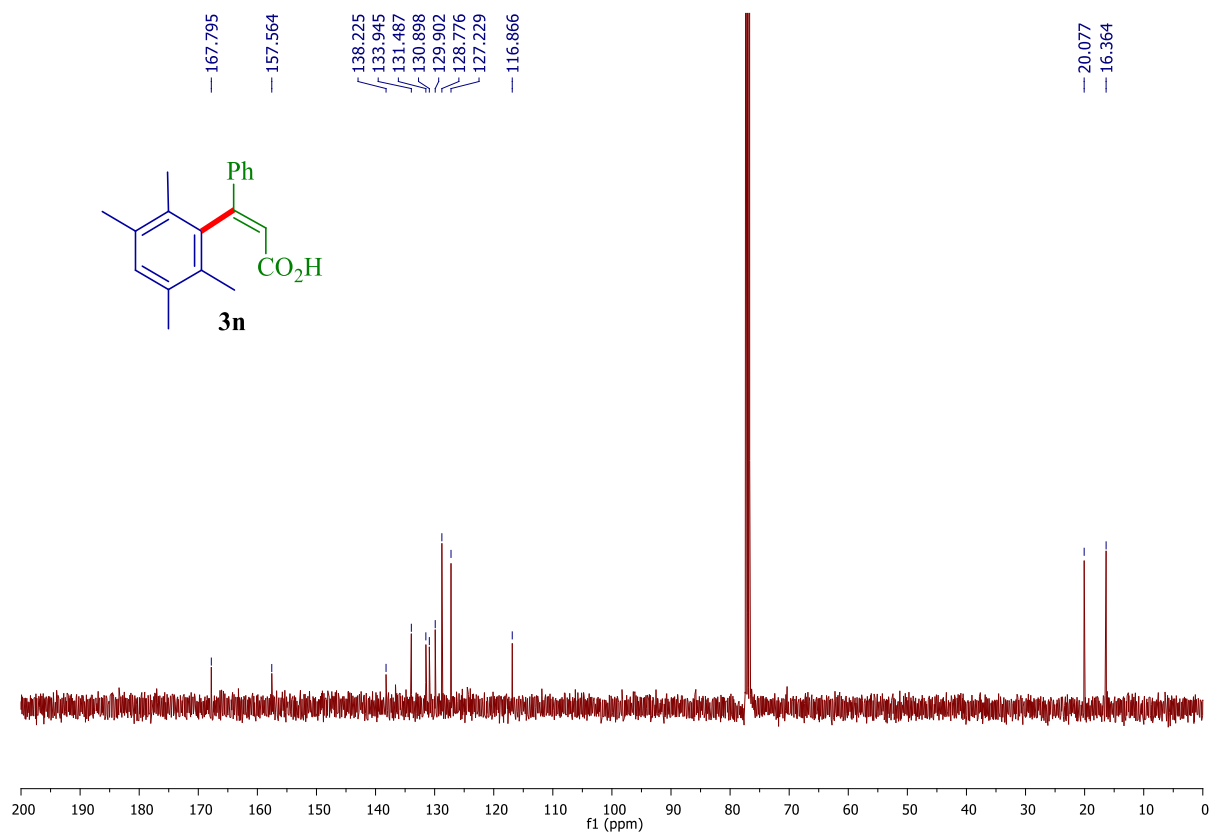


Figure S28. ¹³C NMR Spectrum of **3n** in CDCl₃.

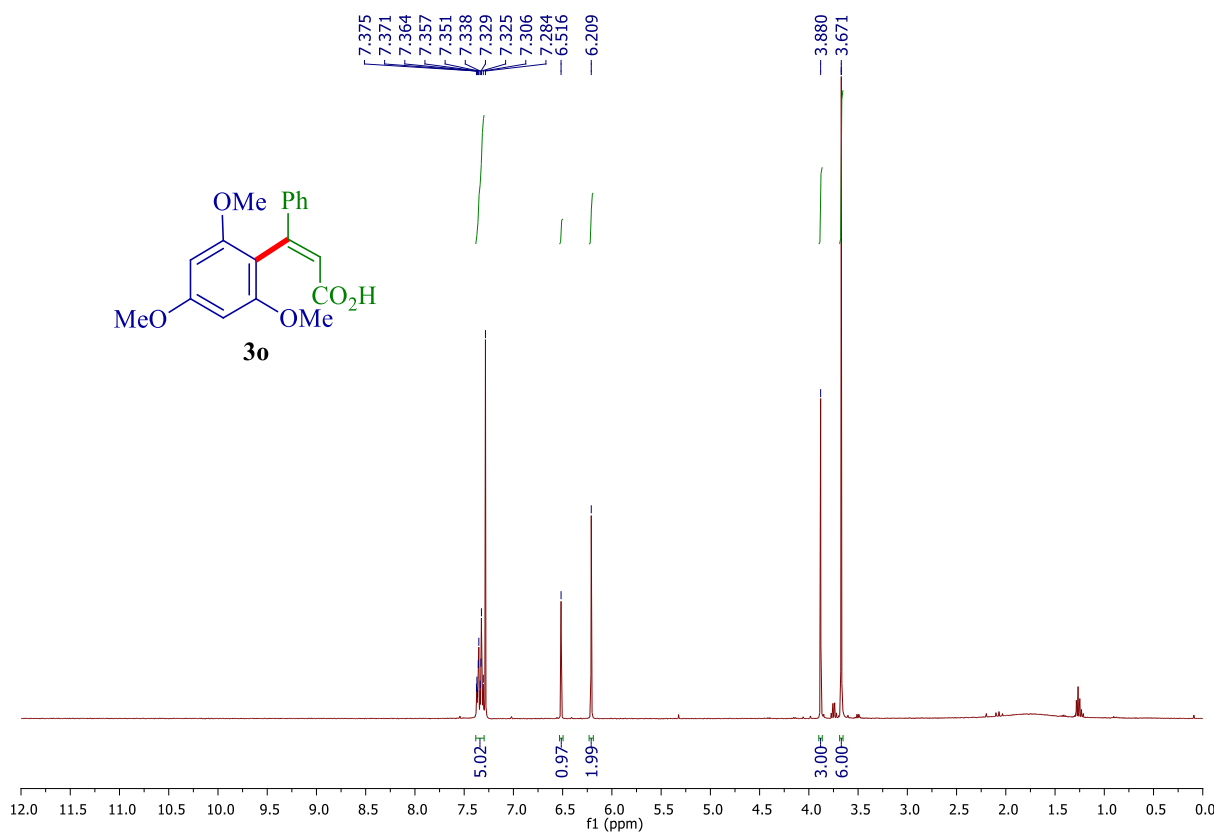


Figure S29. ¹H NMR Spectrum of **3o** in CDCl₃.

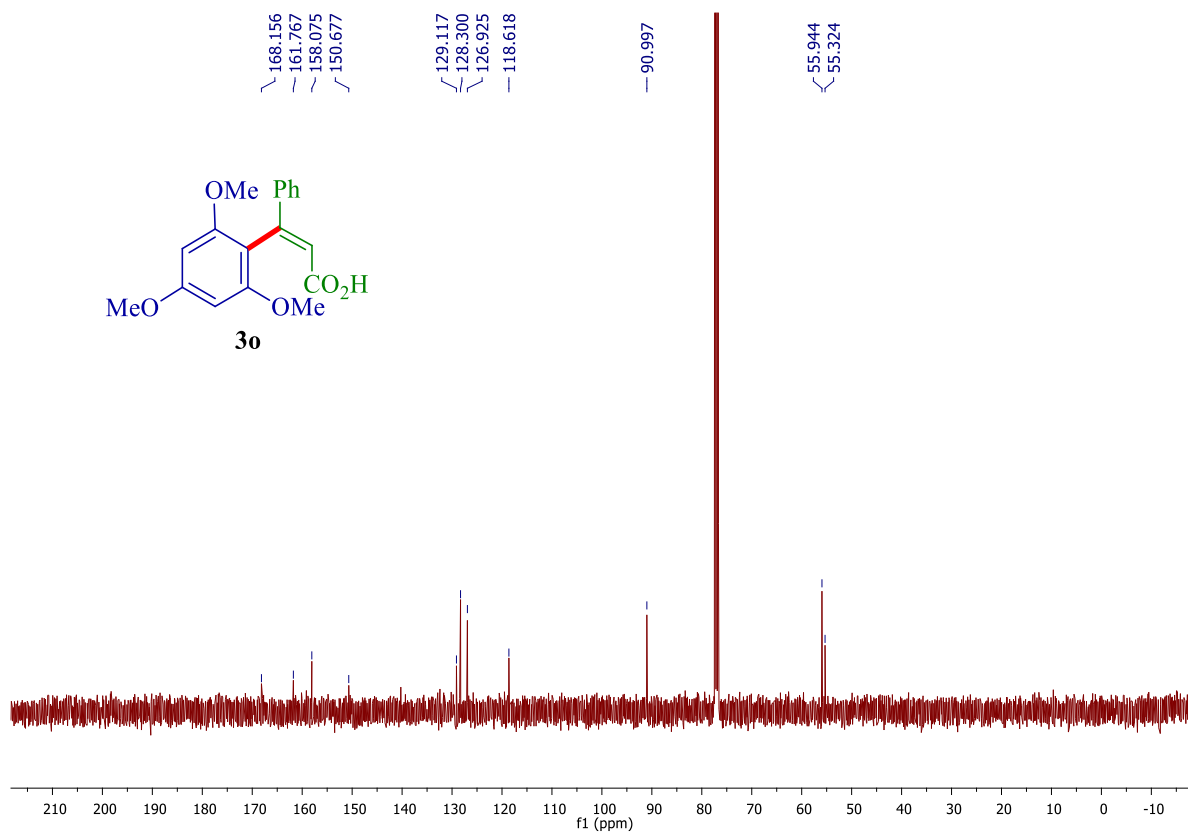


Figure S30. ¹³C NMR Spectrum of **3o** in CDCl₃.

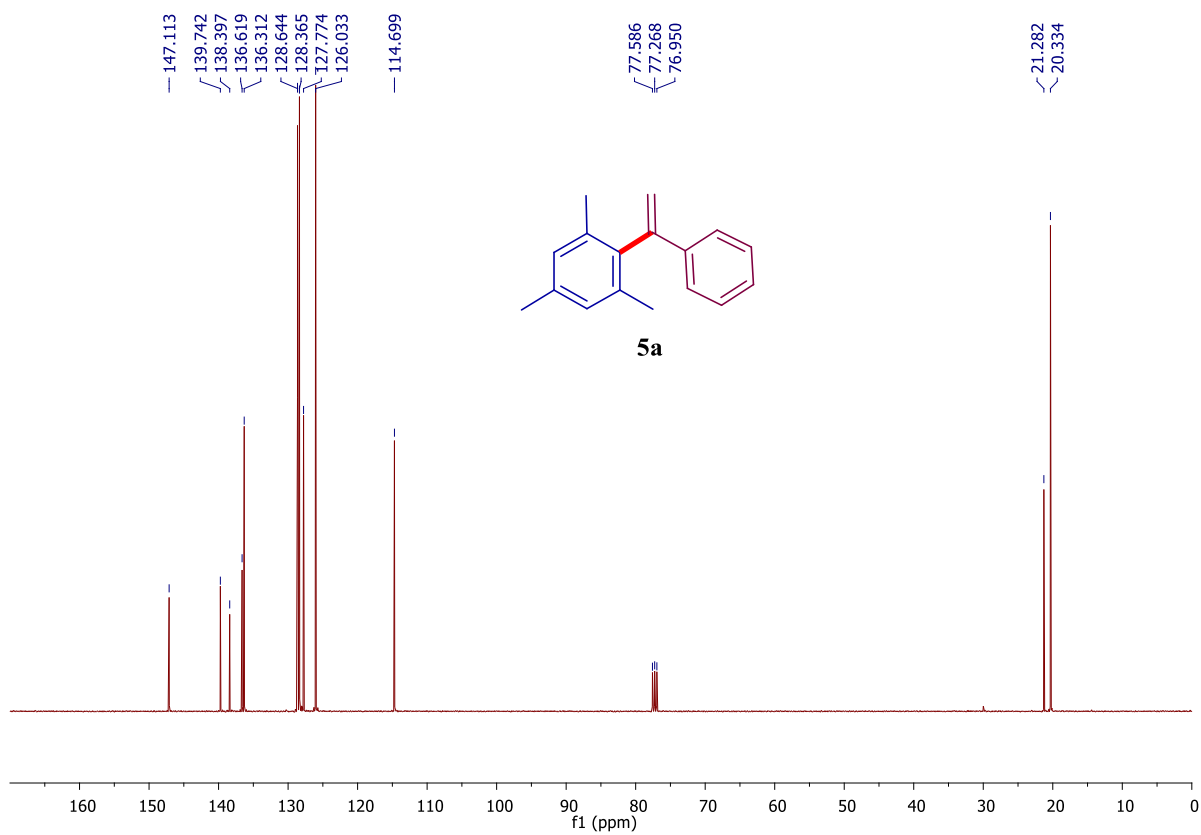
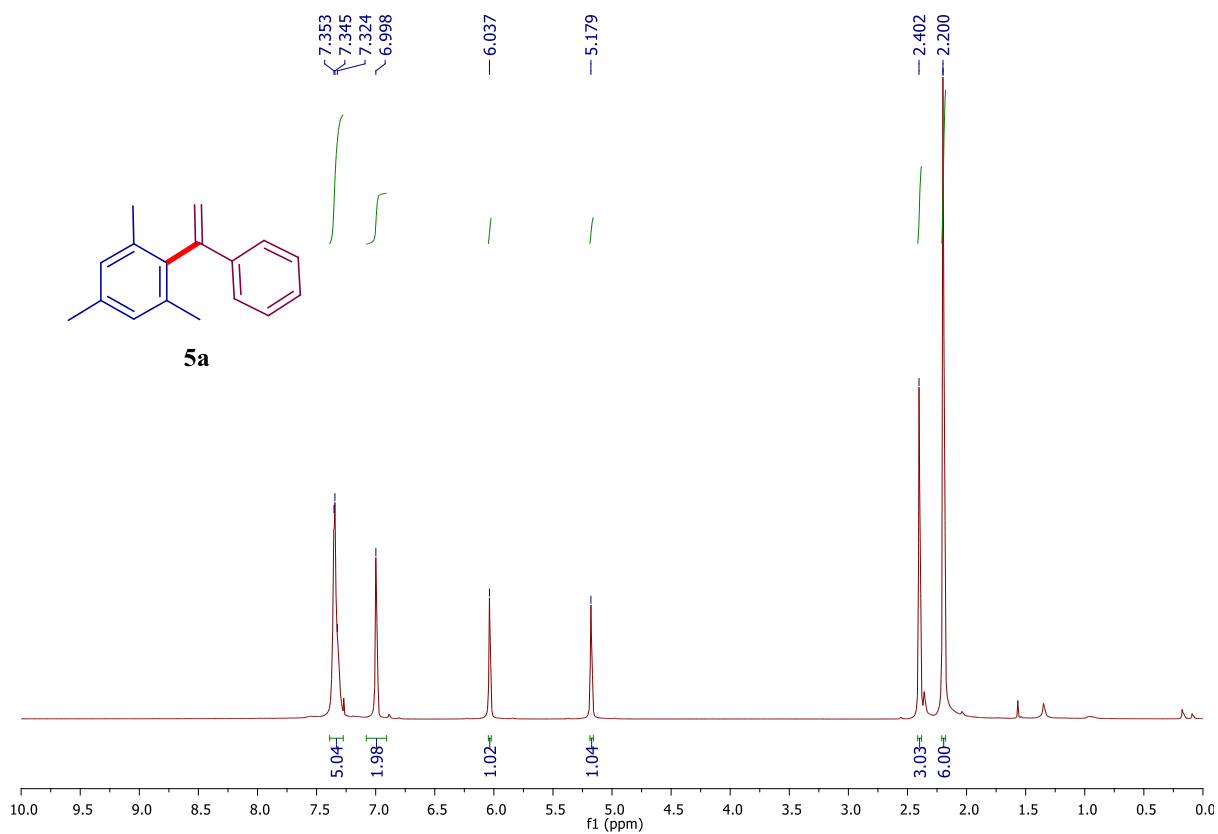


Figure S32. ^{13}C NMR Spectrum of **5a in CDCl_3 .**

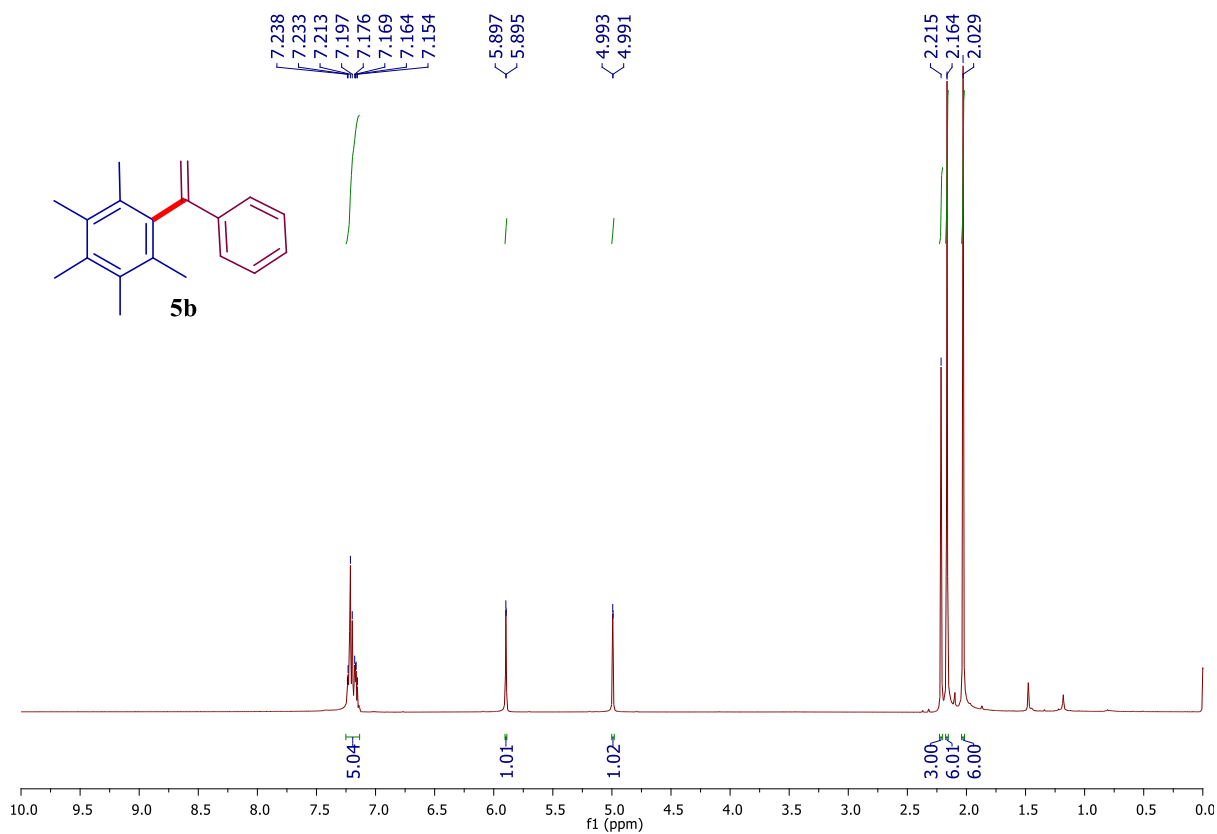


Figure S33. ¹H NMR Spectrum of **5b** in CDCl₃.

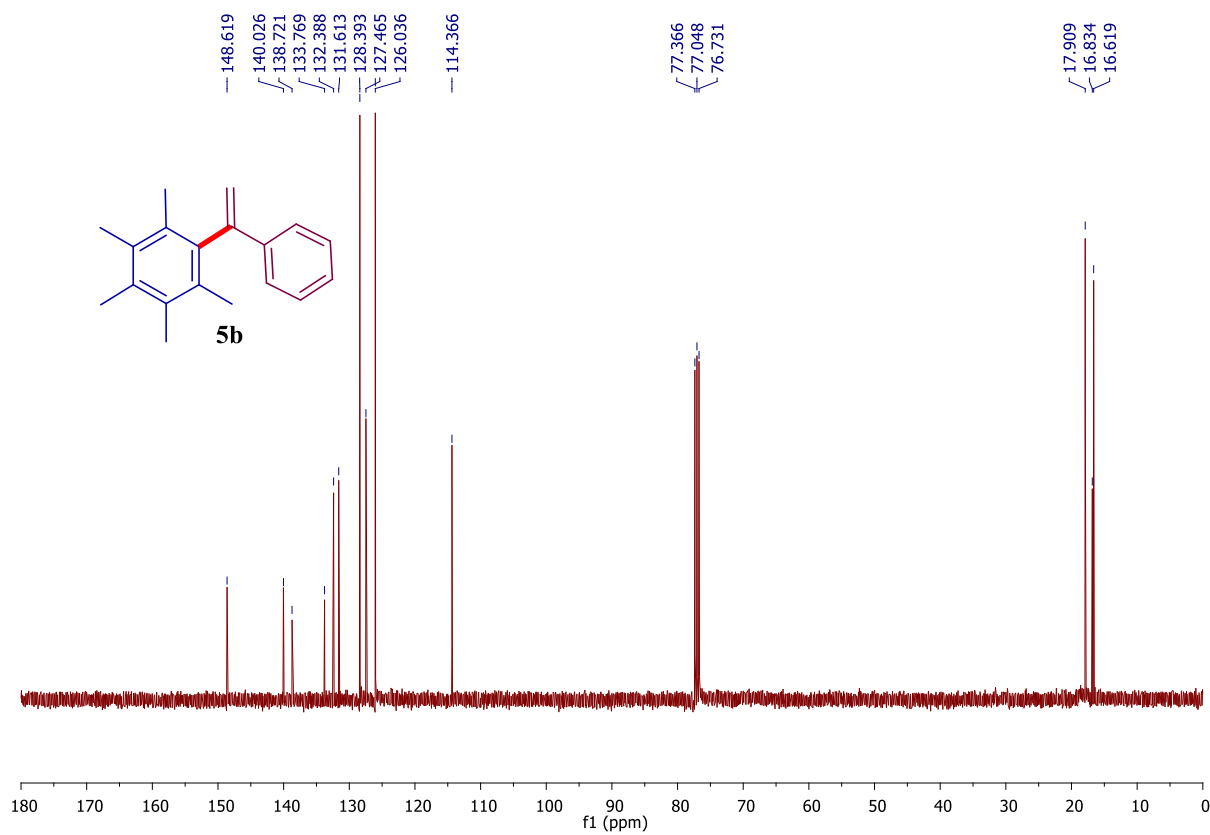


Figure S34. ¹³C NMR Spectrum of **5b** in CDCl₃.

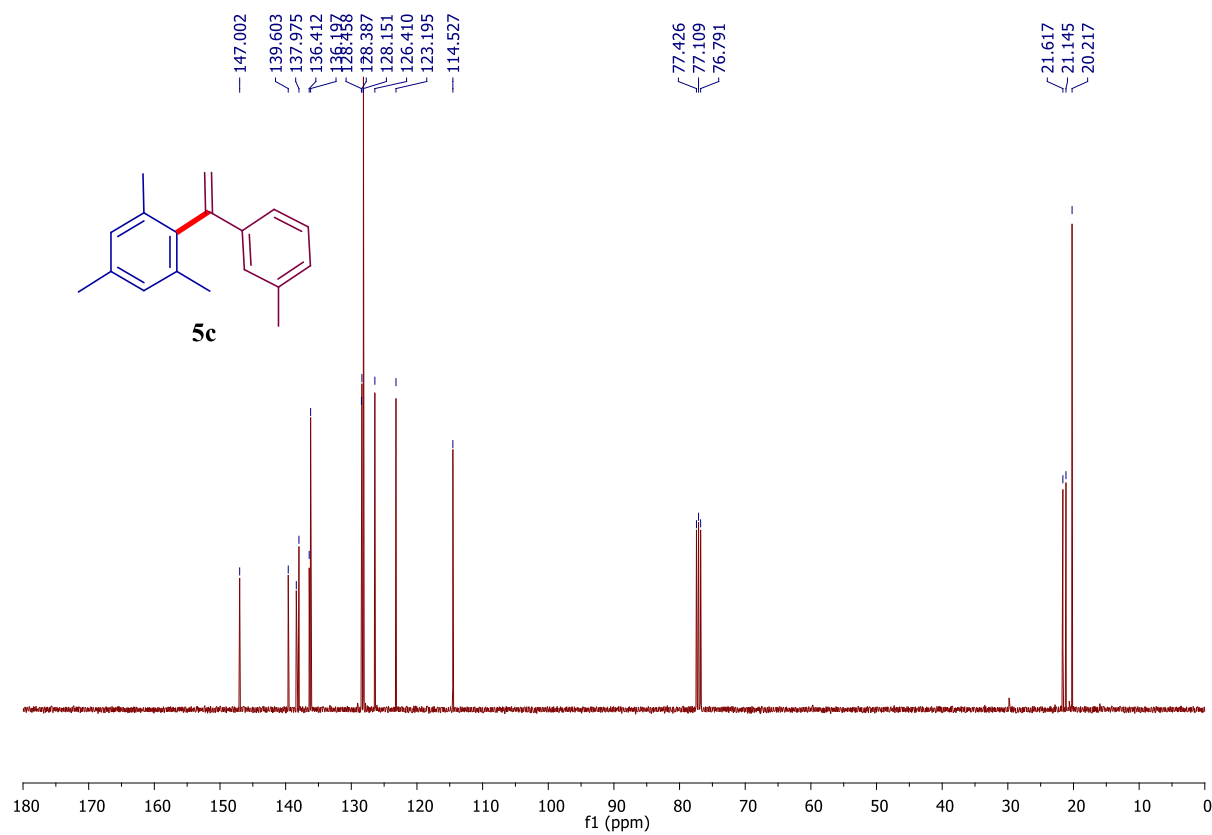
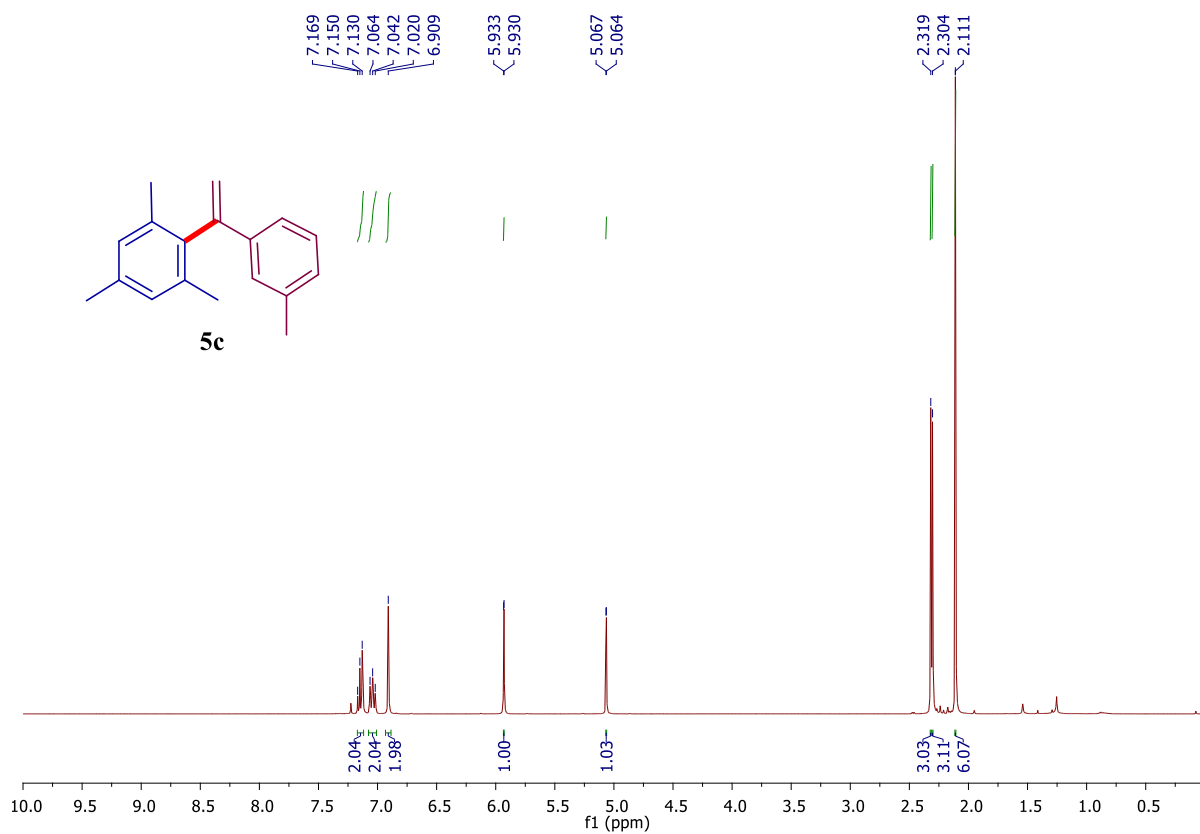


Figure S36. ^{13}C NMR Spectrum of **5c in CDCl_3 .**

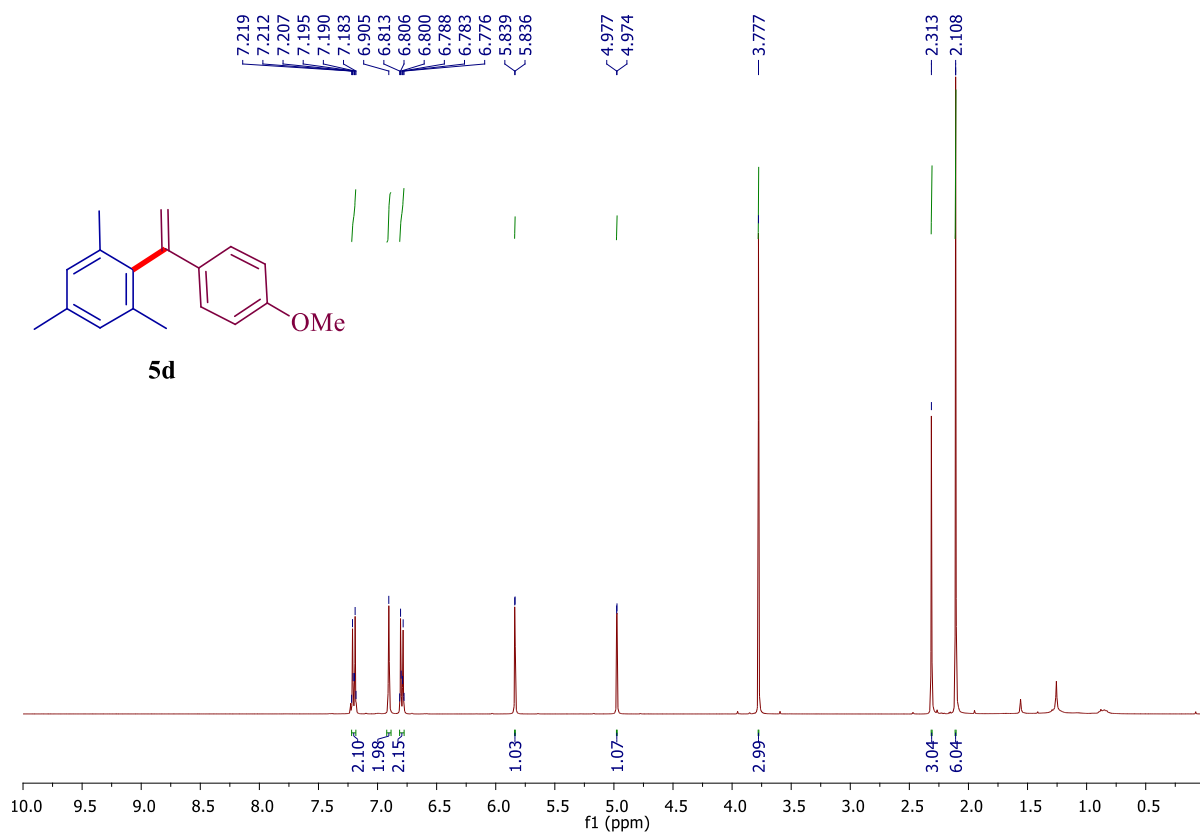


Figure S37. ¹H NMR Spectrum of **5d** in CDCl₃.

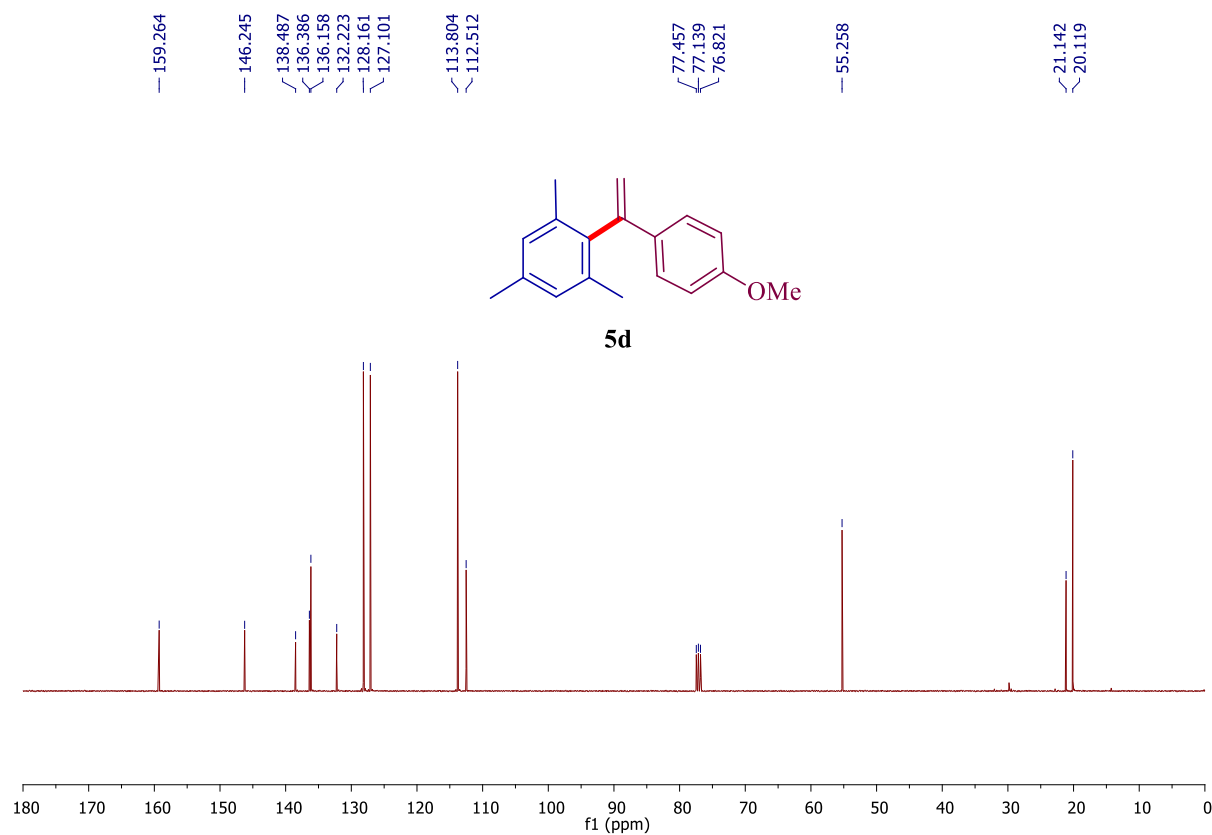
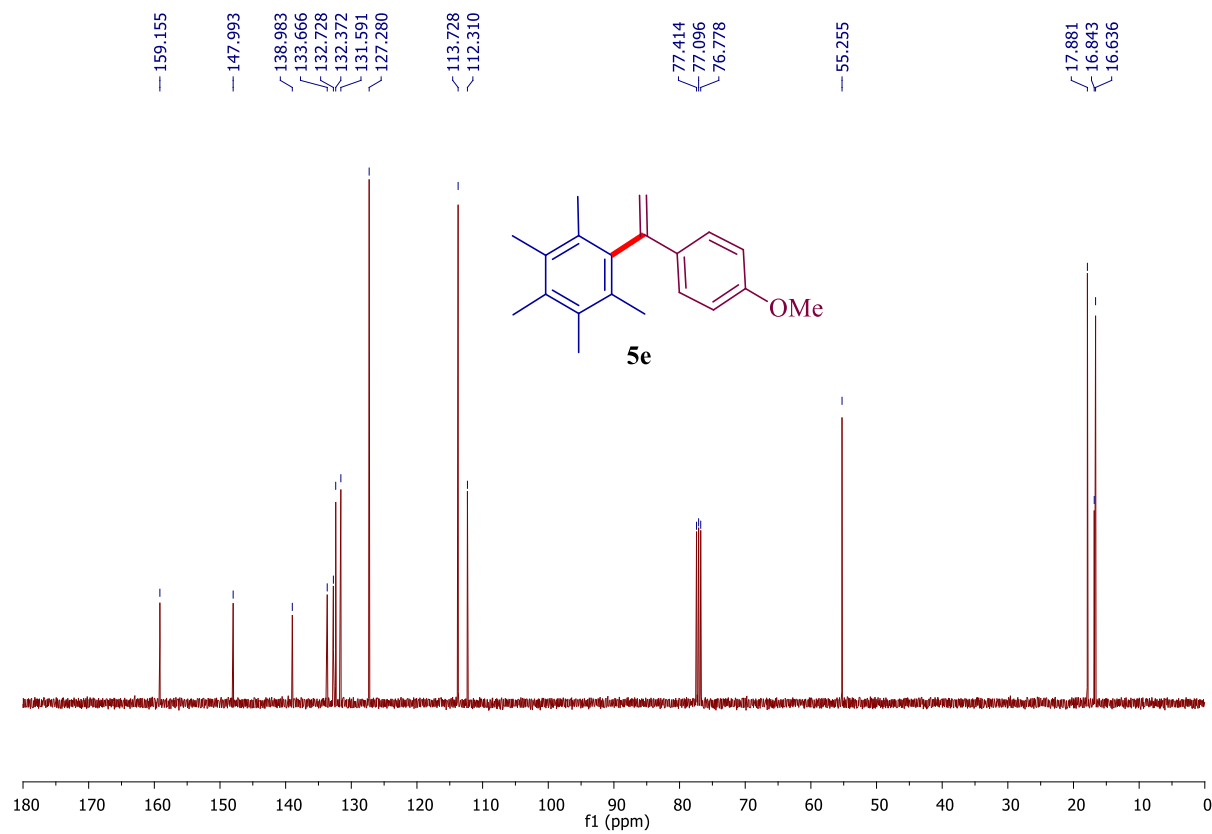
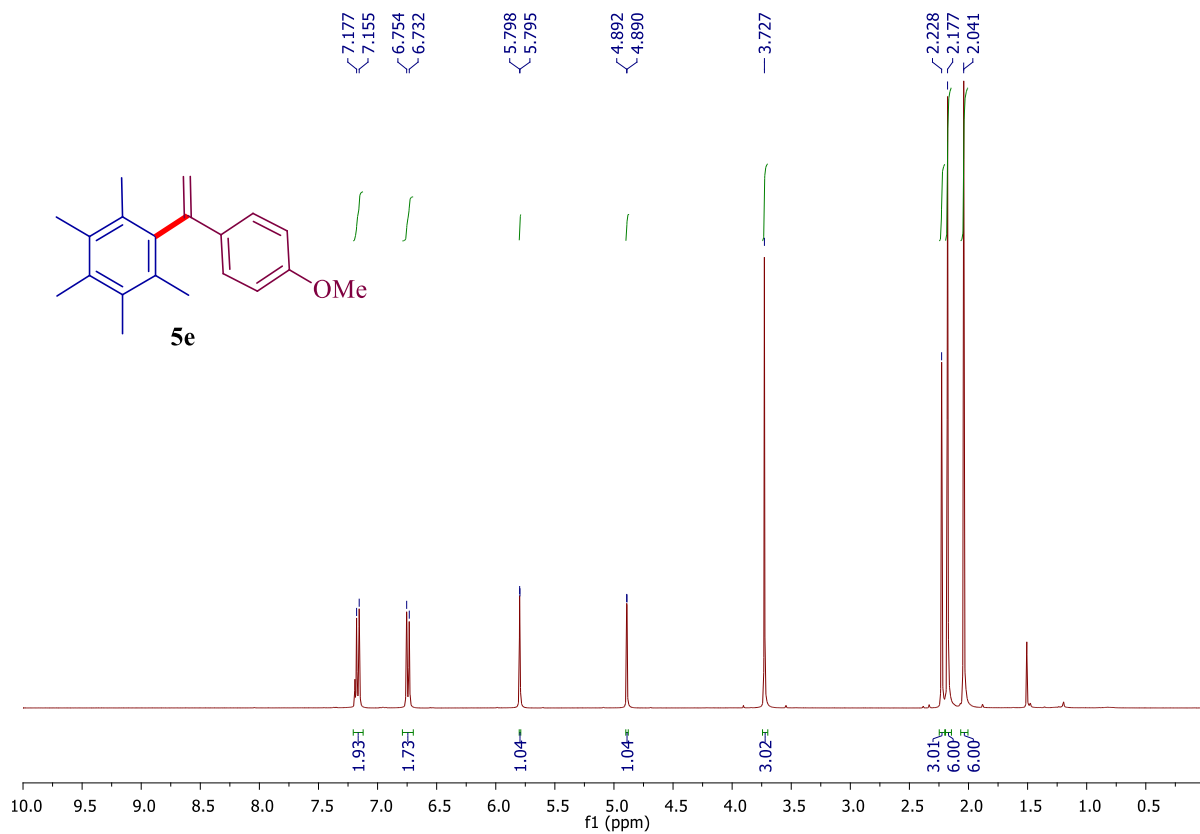
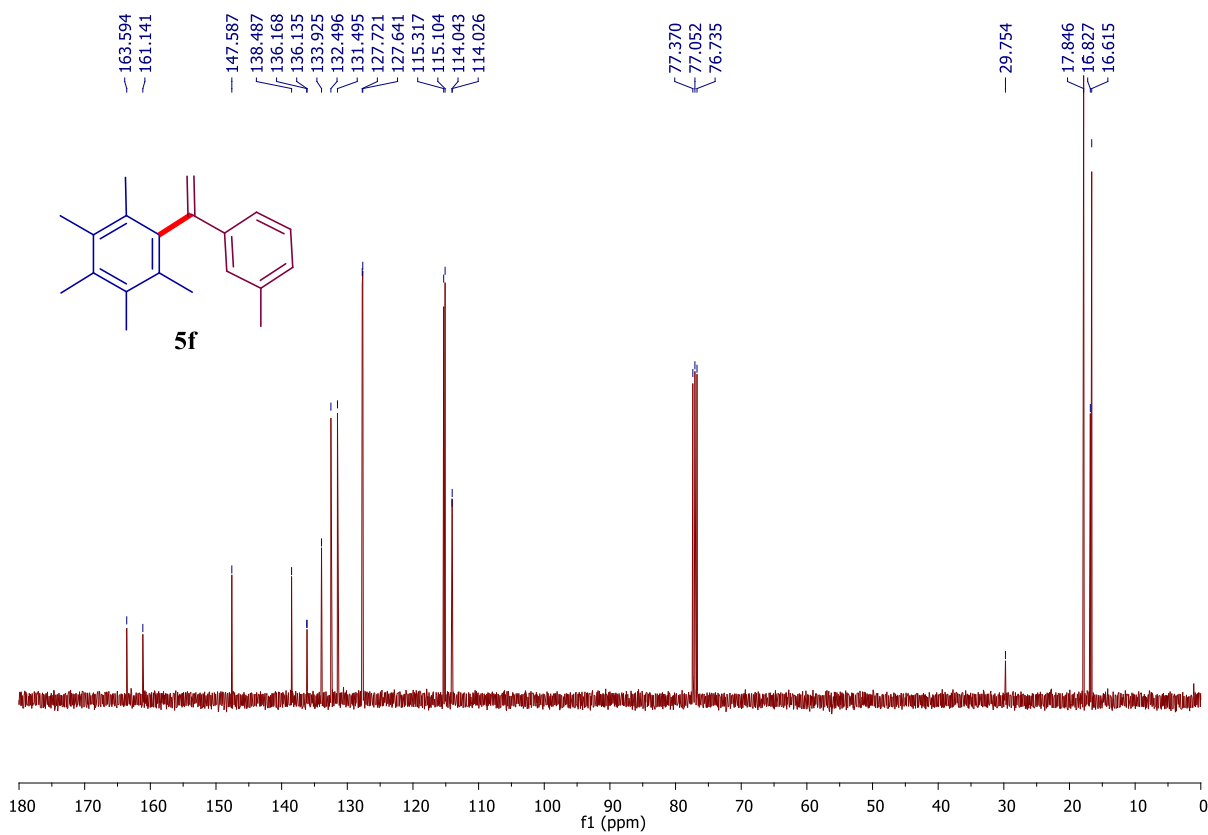
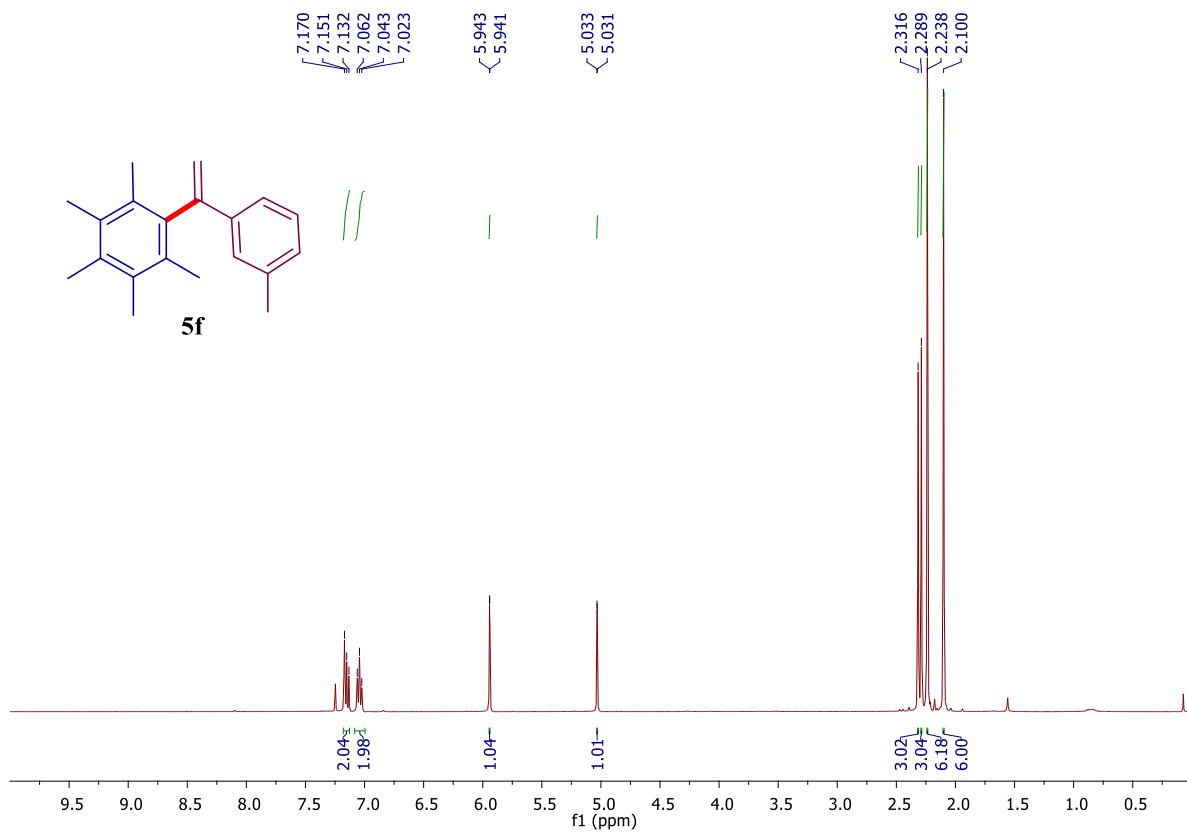
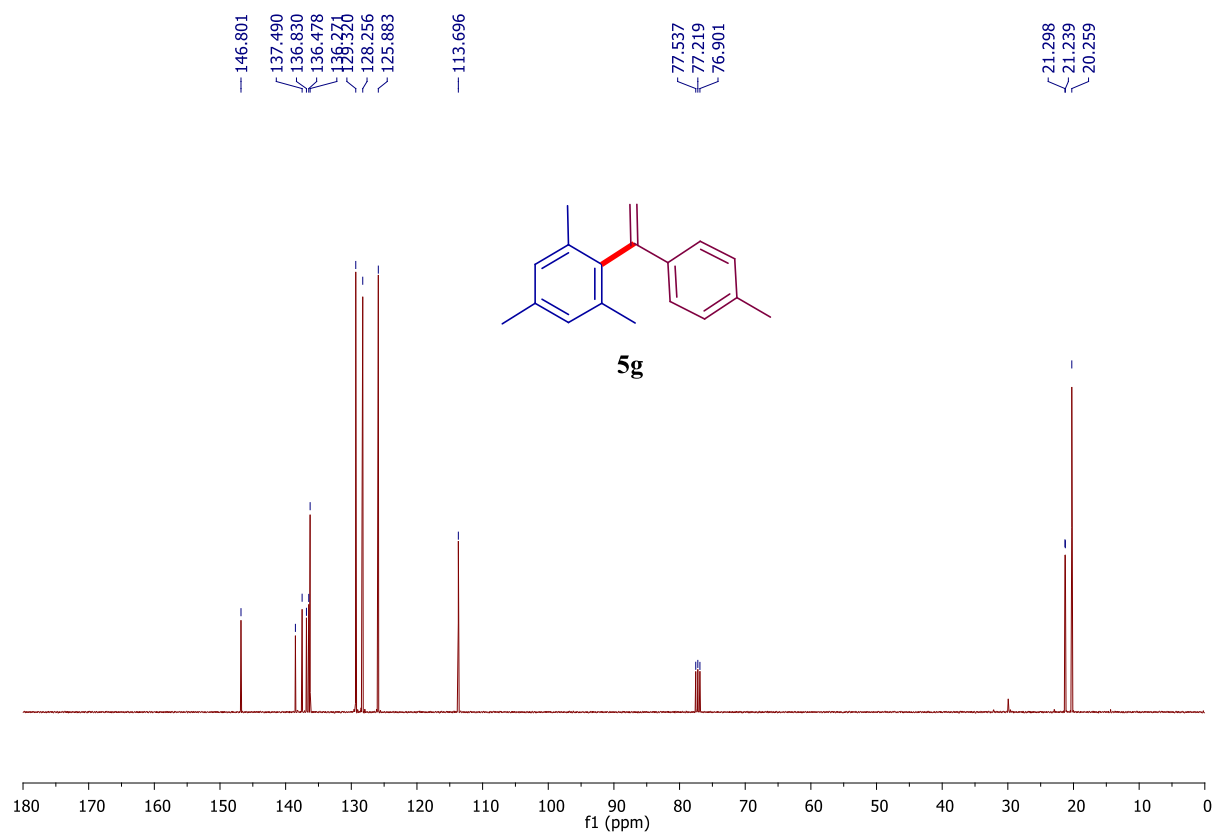
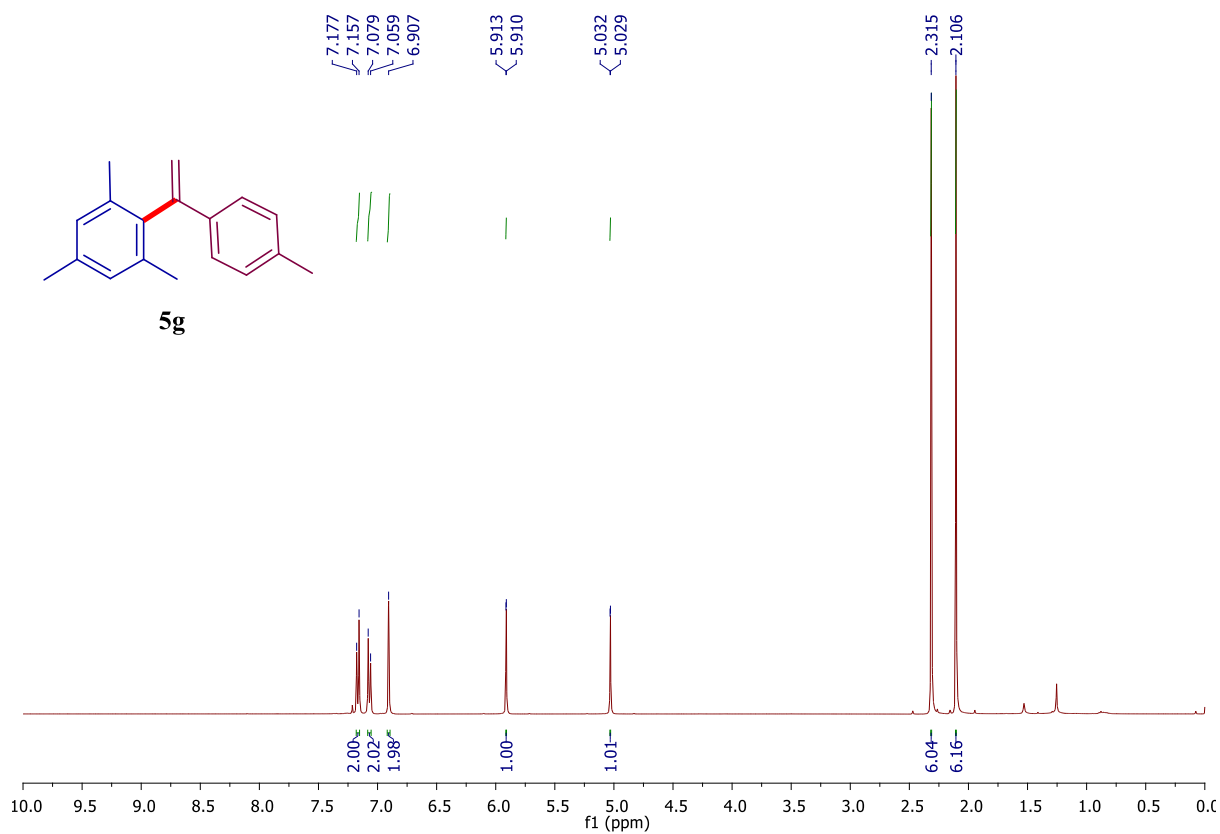


Figure S38. ¹³C NMR Spectrum of **5d** in CDCl₃.







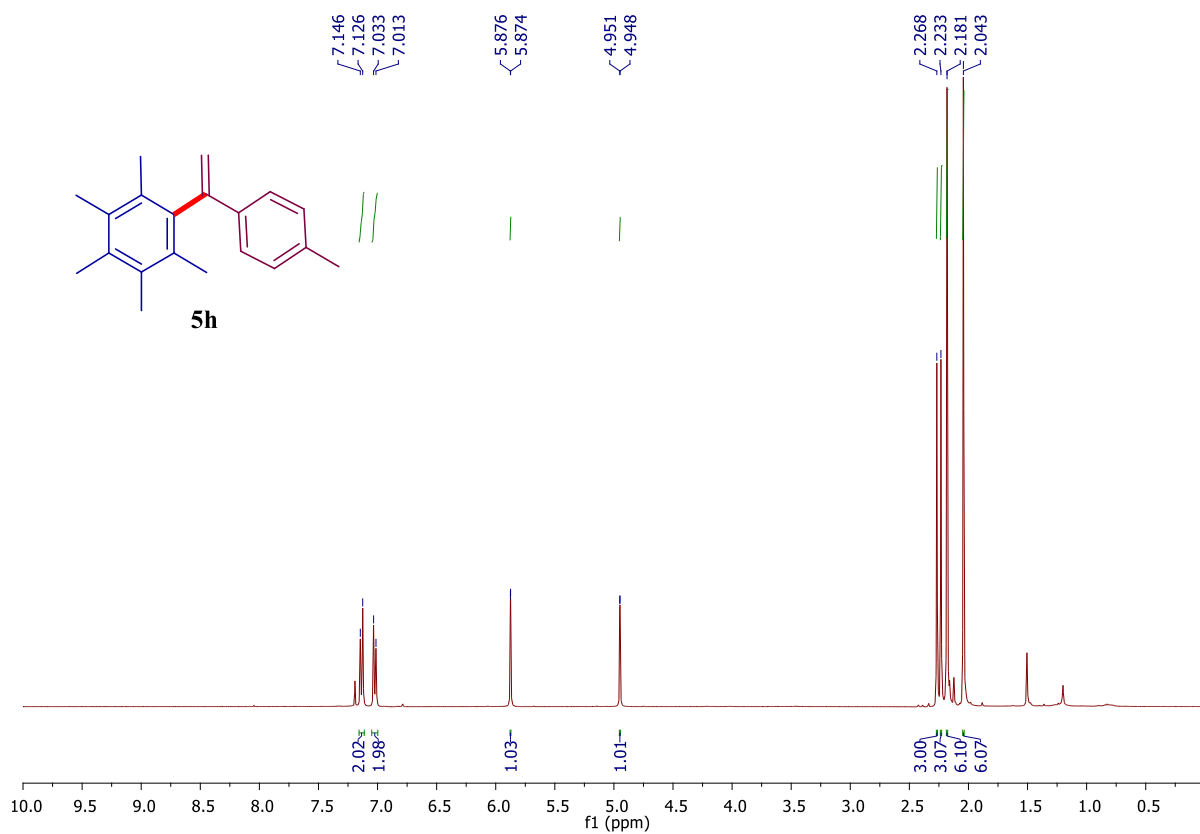


Figure S45. ¹H NMR Spectrum of **5h** in CDCl₃.

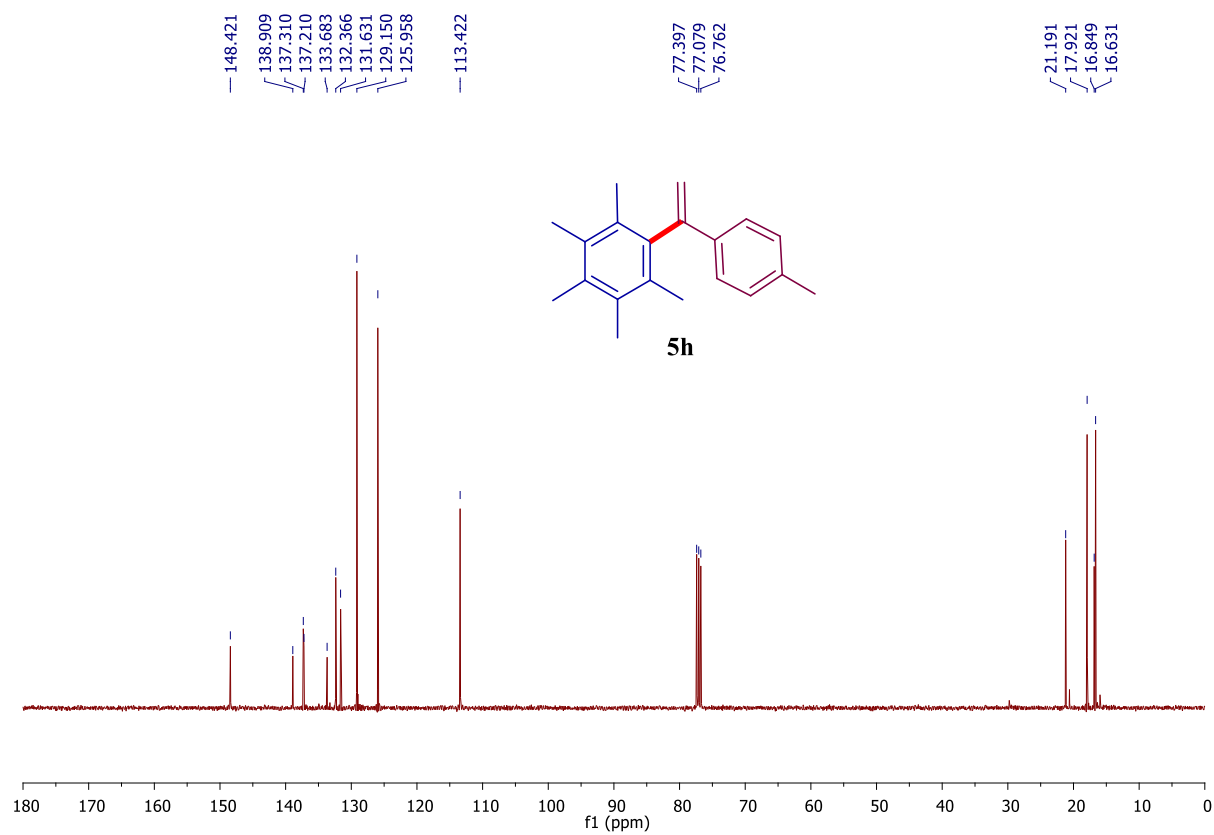


Figure S46. ¹³C NMR Spectrum of **5h** in CDCl₃.

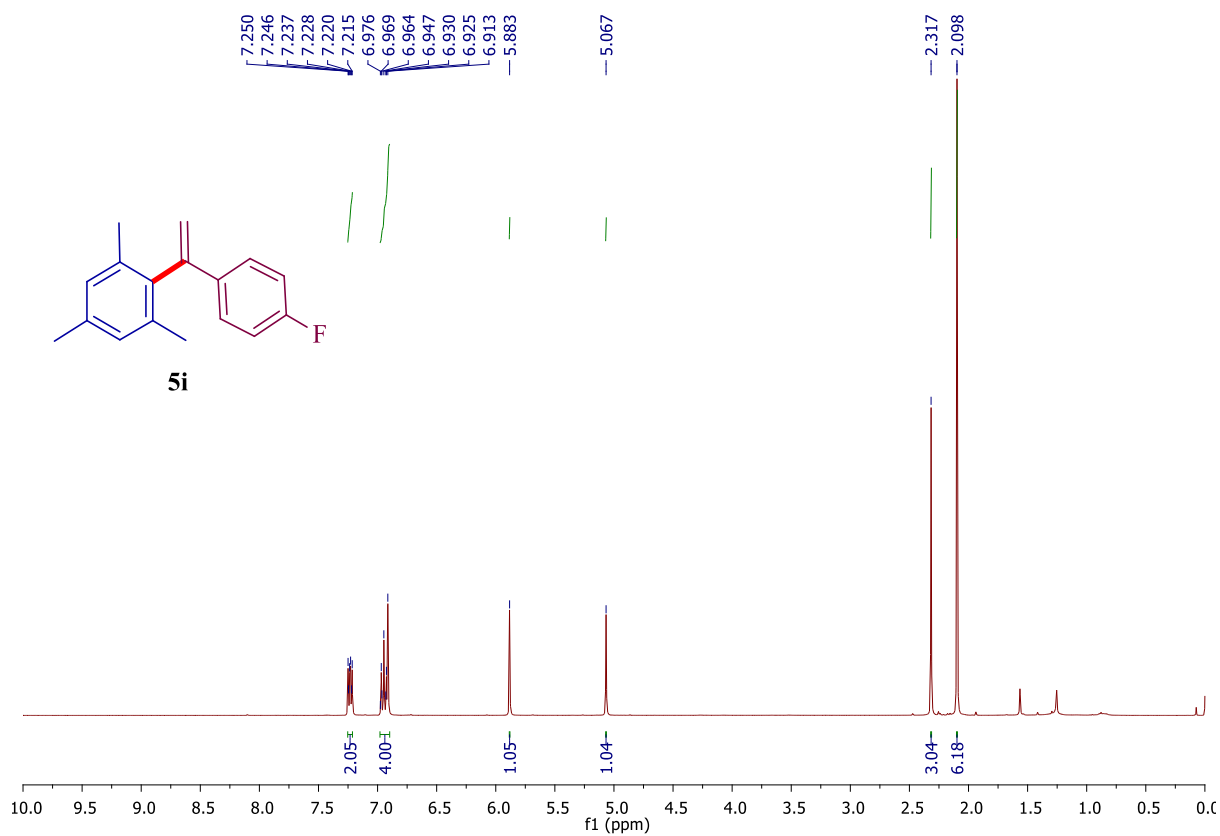


Figure S47. ¹H NMR Spectrum of **5i** in CDCl₃.

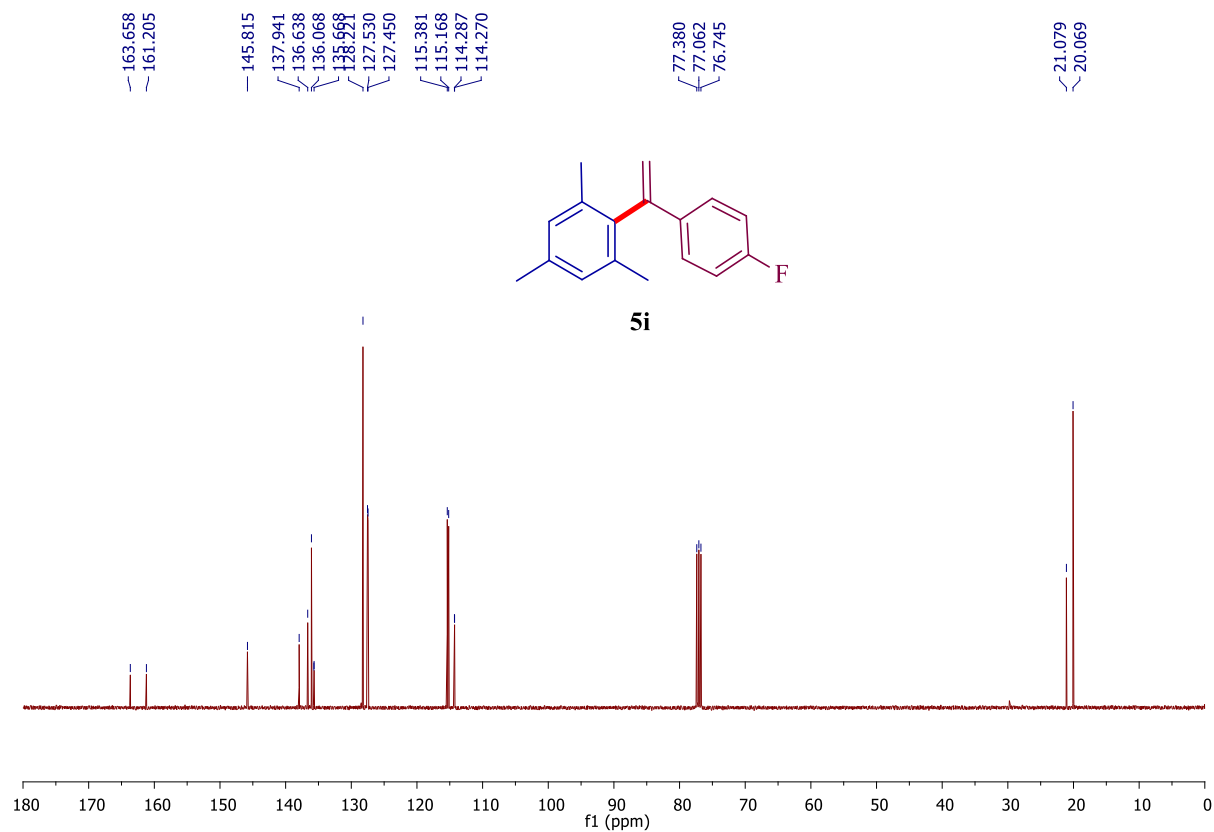
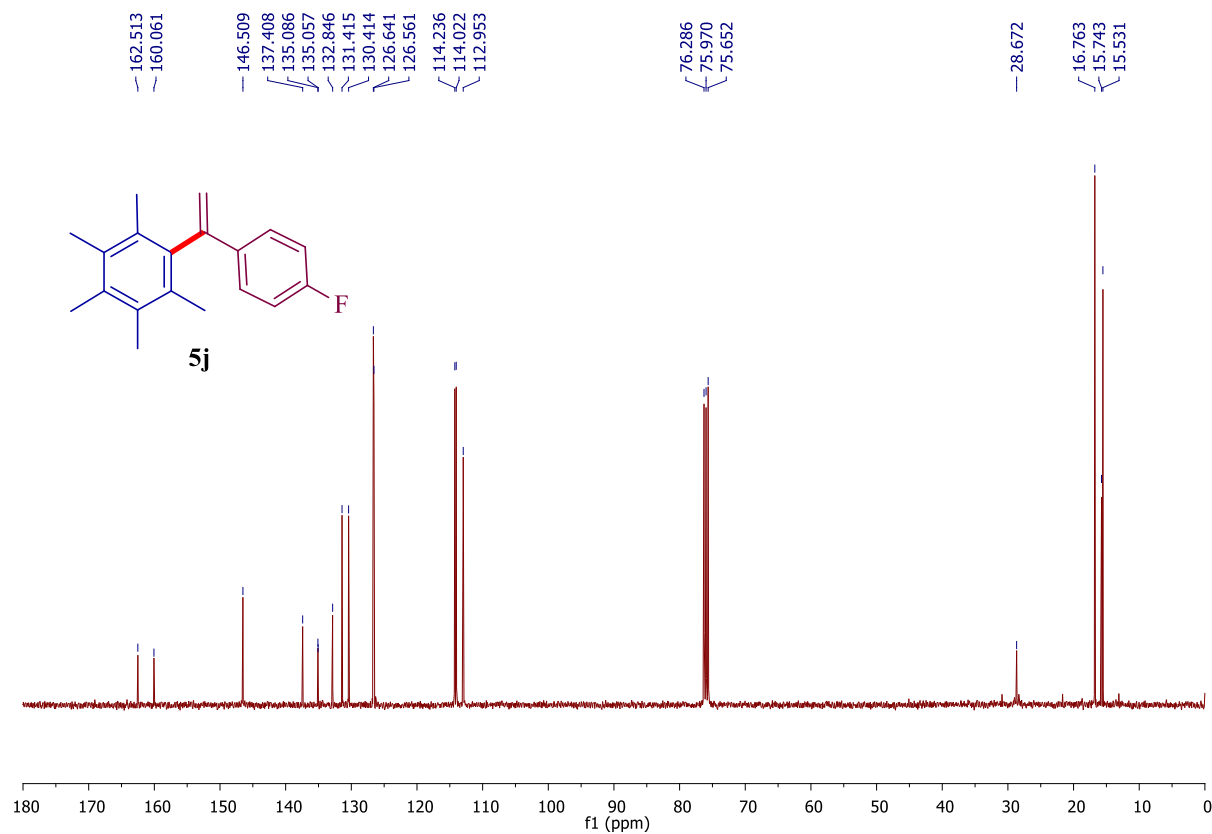
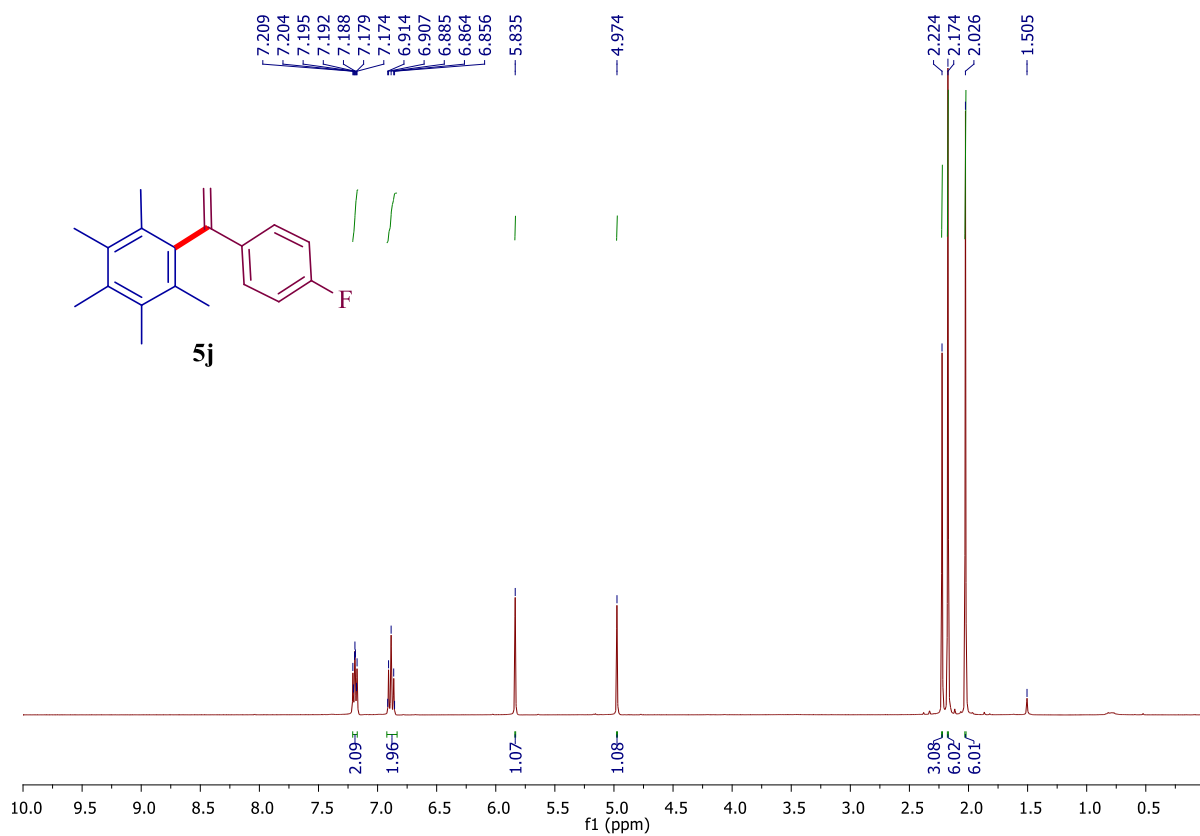
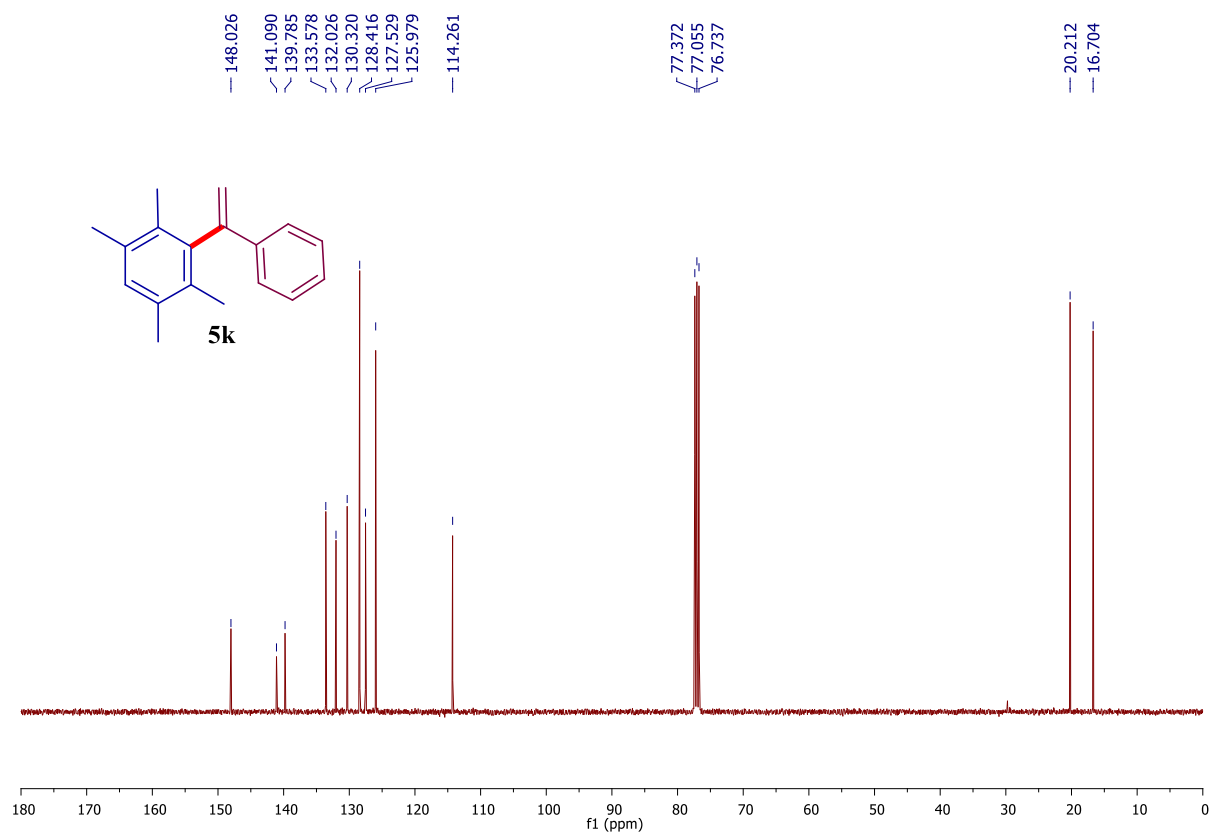
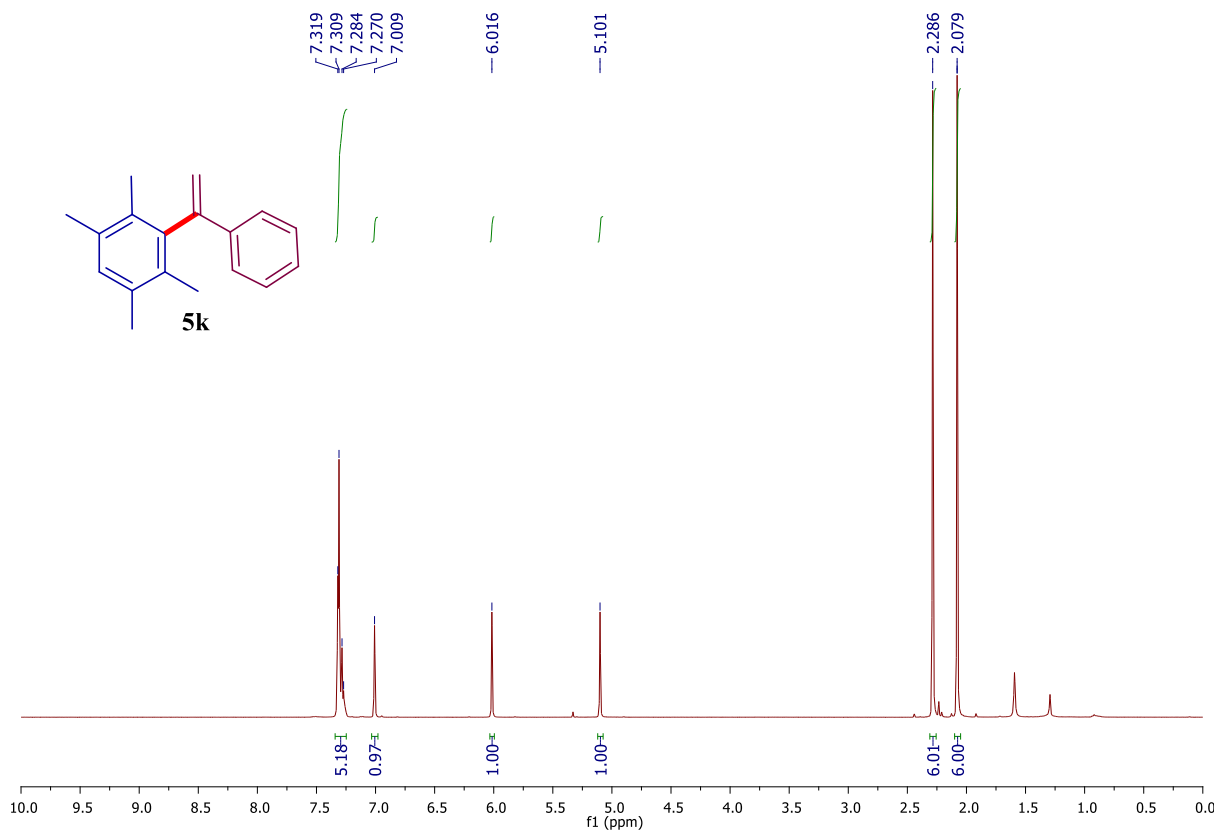


Figure S48. ¹³C NMR Spectrum of **5i** in CDCl₃.





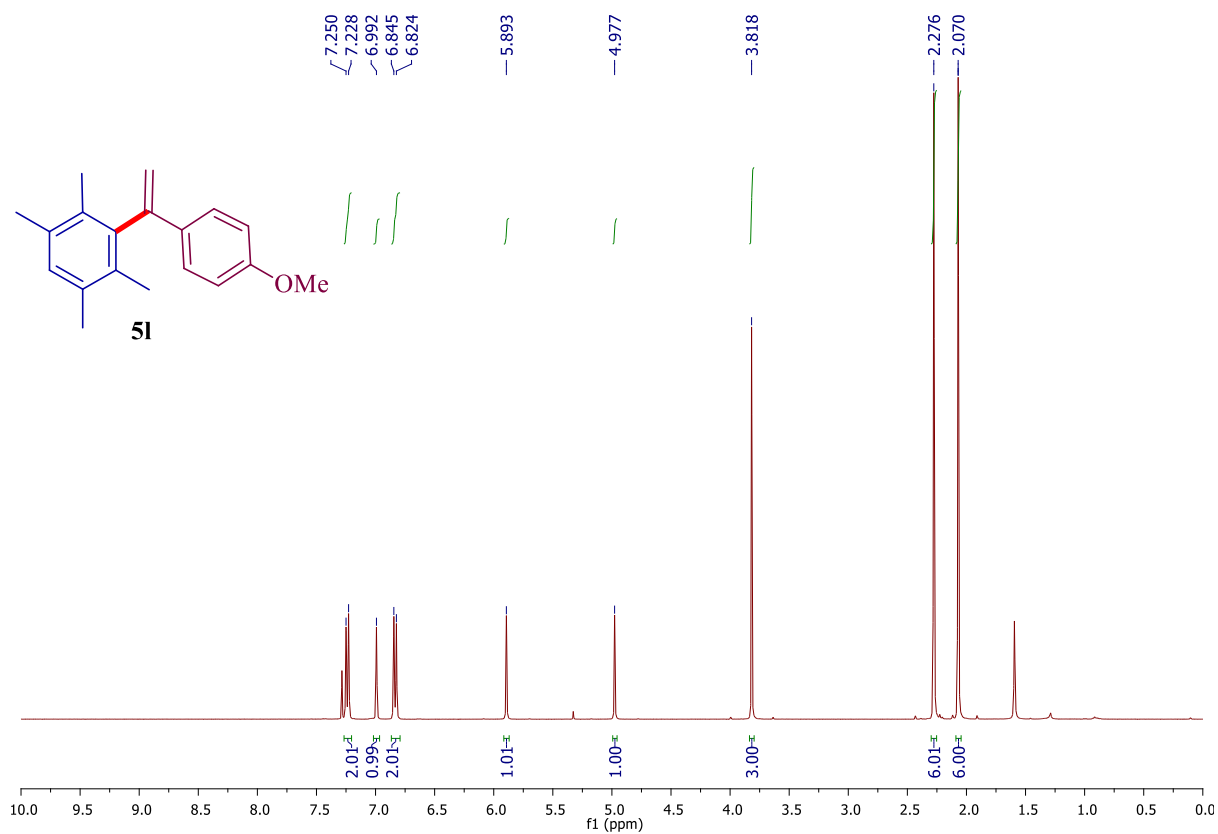


Figure S53. ¹H NMR Spectrum of **51** in CDCl₃.

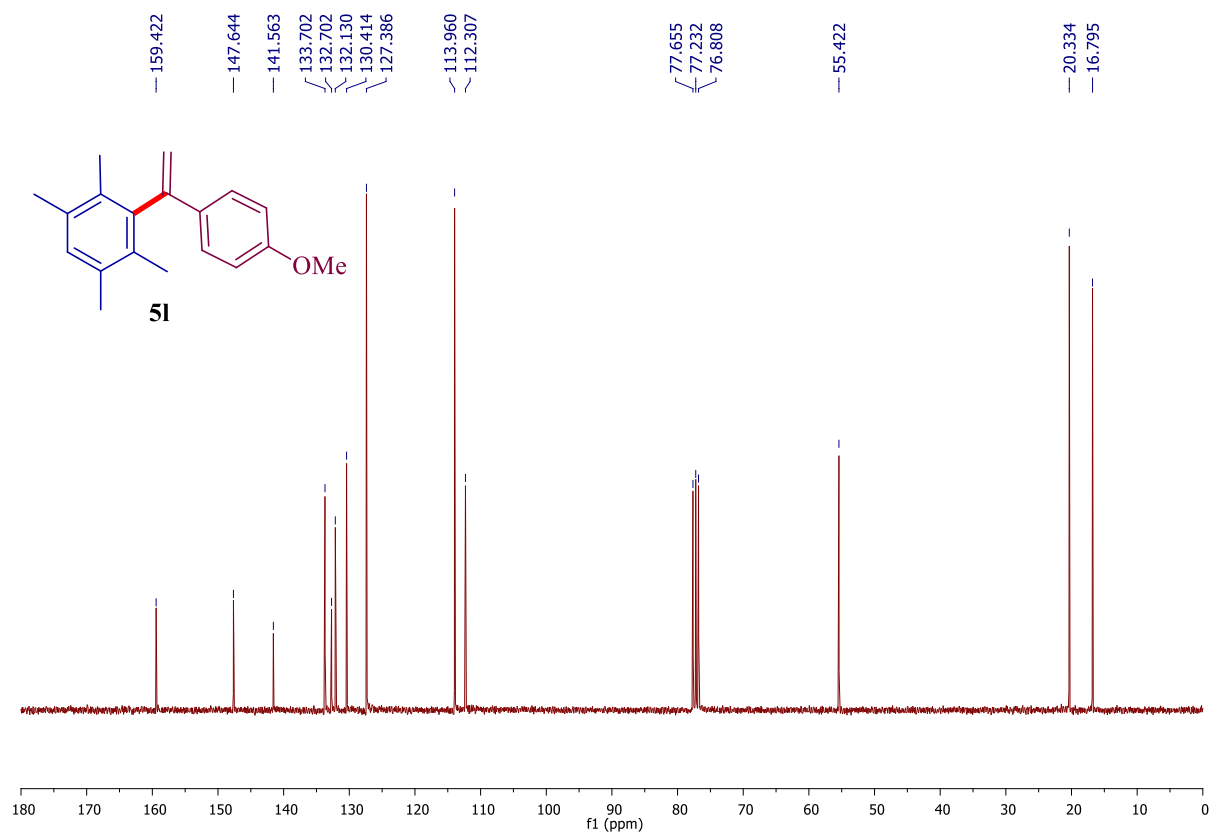


Figure S54. ¹³C NMR Spectrum of **51** in CDCl₃.

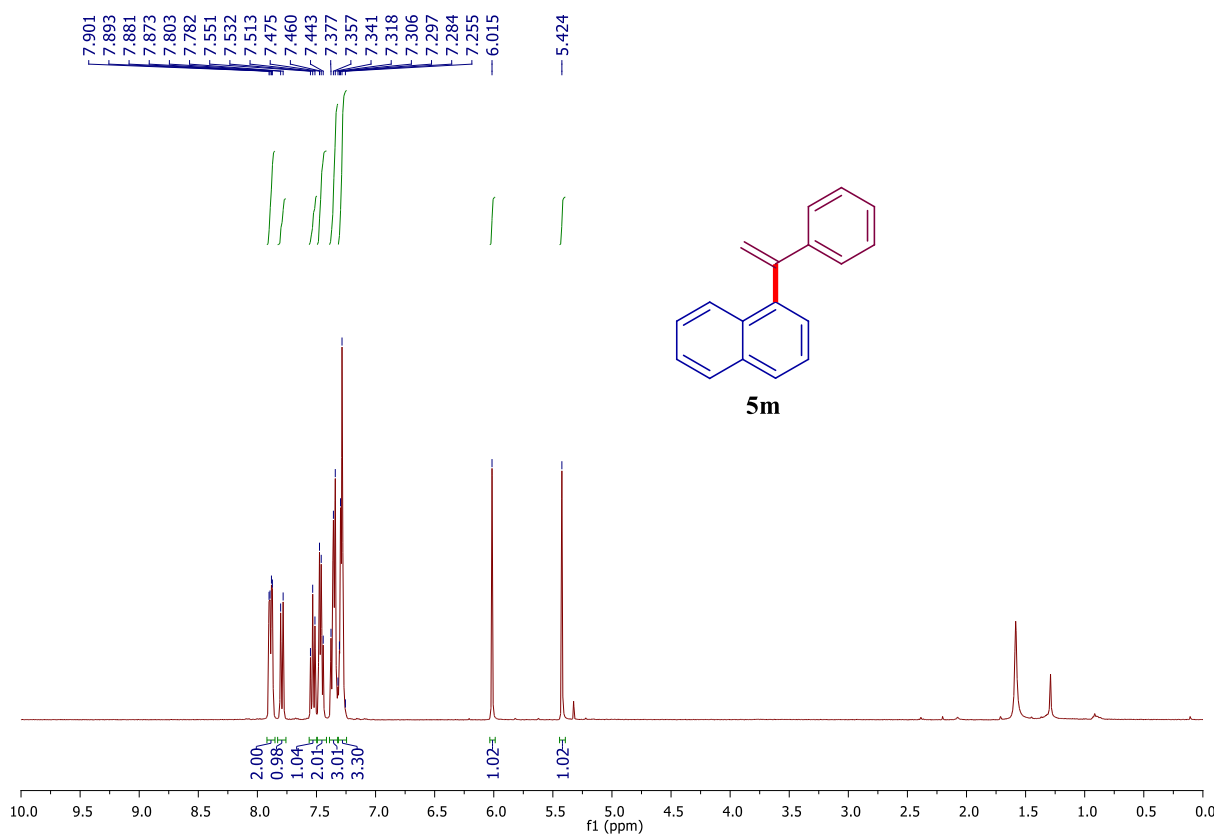


Figure S55. ¹H NMR Spectrum of **5m** in CDCl₃.

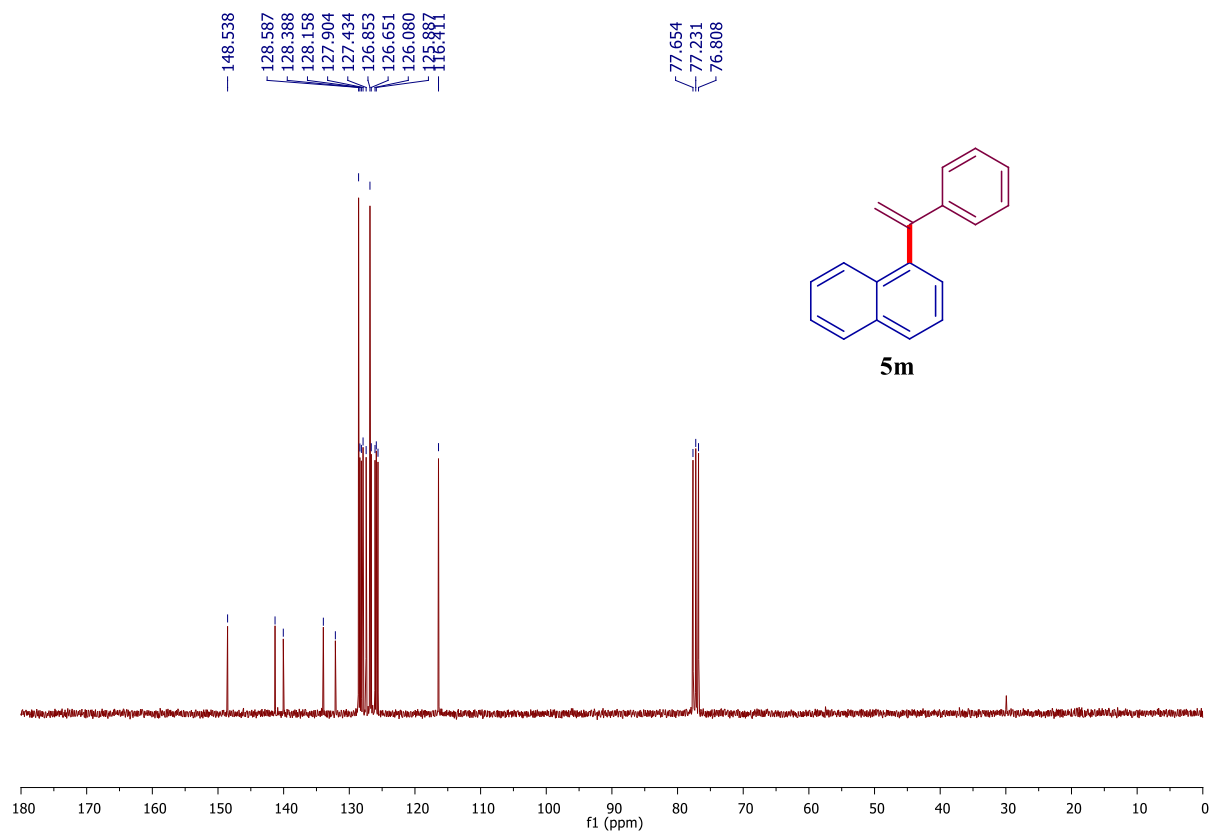


Figure S56. ¹³C NMR Spectrum of **5m** in CDCl₃.