Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Unveiling the Catalytic Nature of Palladium-N-Heterocyclic Carbene Catalysts in the α-Alkylation of Ketones with Primary Alcohols

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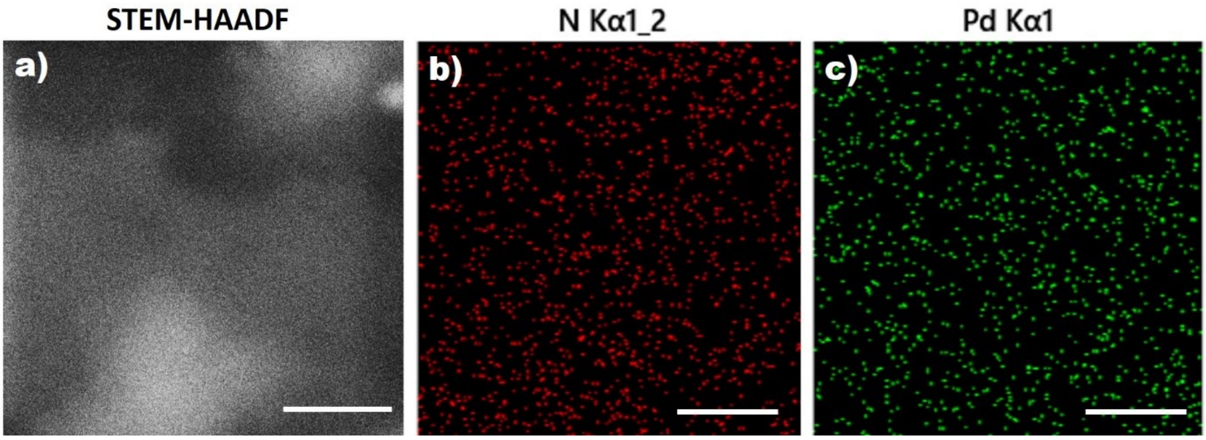

Figure S1. a) STEM-HAADF image, and associated EDX elemental mapping images for b) nitrogen and c) palladium atoms

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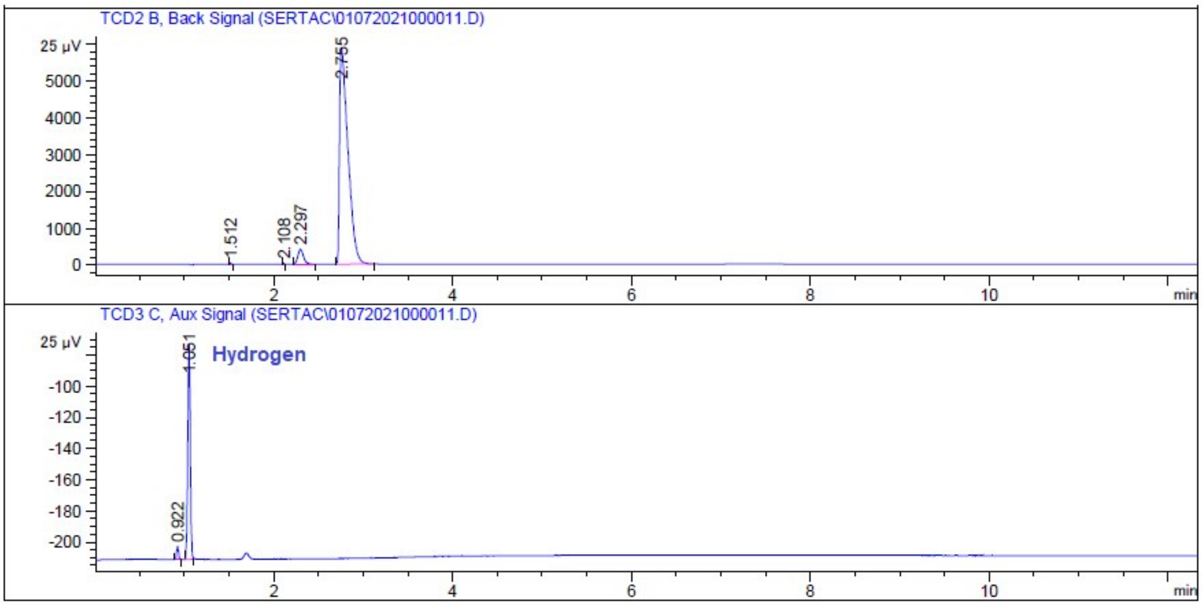

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4.217		-	-	-		CO

Totals : 88.18000

Signal 3: TCD3 C, Aux Signal

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Totals : 1.45669

Figure S2. GC traces to confirm H_2 evolution.

Analytical data for compounds 5a-u.

5a.[1,2] Yield 172 mg (82%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.35-7.21 (m, 5H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.0, 141.2, 136.8, 132.9, 128.5, 128.4, 128.3, 127.9, 126.0, 40.3, 30.0.

5b.[1-4] Yield 214 mg (89%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.97 (d, *J* = 8.4 Hz, 2H), 7.55 (t, 7,4Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.4, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.6, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.3, 157.9, 136.8, 133.2, 132.9, 129.3, 128.5, 127.9, 113.9, 55.2, 40.6, 29.2.

5c.[2,3] Yield 179 mg (80%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.03 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.25-7.18 (m, 4H), 3.33 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.8, 137.9, 136.6, 135.2, 132.7, 128.9, 128.3, 128.1, 127.8, 40.2, 29.4, 20.8.

5d.[1] Yield 212 mg (84%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.04 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.29-7.25 (m, 4H), 3.36 (t, *J* = 7.6 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 3.01-2.94 (m, 1H), 1.34 (d, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.9, 146.4, 138.4, 136.6, 132.8, 128.3, 128.2, 127.8, 126.3, 40.3, 33.5, 29.5, 23.9.

5e.[3] Yield 264 mg (95%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.96 (d, *J* = 8.0 Hz, 2H), 7.57-7.54 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 7.4 Hz, 2H), 3.14 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.5, 145.4, 136.7, 133.2, 128.8, 128.6, 128.0, 125.4, 39.8, 29.8.

5h.[3,5,6] Yield 293 mg (92%). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 4.14-4.05 (m, 9H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.4, 136.9, 132.9, 128.5, 128.0, 88.0, 68.5, 68.1, 67.3, 40.3, 24.1.

5i.[2] Yield 151 mg (63%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.21-7.19 (m, 2H), 6.92-6.85 (m, 2H), 3.82 (s, 3H), 3.27 (t, *J* = 7.8 Hz, 2H), 3.06 (t, *J* = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.9, 157.4, 136.8, 132.8, 130.1, 129.4, 128.4, 128.0, 127.4, 120.4, 110.1, 55.1, 38.8, 25.6.

5j.[1,3,4] Yield 156 mg (60%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.09 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.78-7.76 (m, 1H), 7.57-7.50 (m, 3H), 7.46-7.42 (m, 4H), 3.57 (t, J = 7.8 Hz, 2H), 3.42 (t, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.1, 137.2, 136.8, 133.8, 133.0, 131.5, 128.8, 128.5, 127.9, 126.9, 126.0, 126.0, 125.5, 125.5, 123.4, 39.6, 27.0.

5k.[1,2] Yield 139 mg (60%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.95 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 2.95 (t, J = 7.4 Hz, 2H), 1.76-1.69 (m, 2H), 1.38-1.26 (m, 12H), 0.87 (t, J = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 200.5, 137.0, 132.8, 128.5, 128.0, 38.6, 31.8, 29.4, 29.4, 29.3, 29.2, 24.3, 22.6, 14.1.

5l.[1-4] Yield 228 mg (95%). White solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.95 (d, J = 8.8 Hz, 2H), 7.32-7.19 (m, 5H), 6.93 (d, J = 9.2 Hz, 2H), 3.86 (s, 3H), 3.26 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 197.8, 163.4, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.7, 55.4, 40.1, 30.3.

5m.[1,3] Yield 193 mg (86%). White solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.89 (d, J = 8.0 Hz, 2H), 7.34-7.23 (m, 7H), 3.29 (t, J = 7.8 Hz, 2H), 3.09 (t, J = 7.8 Hz, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.7, 143.7, 143.1, 134.3, 129.2, 128.4, 128.3, 128.1, 126.0, 40.2, 30.1, 21.5.

5n.[1,3,4] Yield 253 mg (91%). White solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.05 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.34-7.21 (m, 5H), 3.33 (t, J = 7.4 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.2, 140.8, 139.5, 134.5, 134.2, 128.6, 128.4, 128.3, 126.3, 125.7, 40.7, 29.9.

5p.[1-3] Yield 179 mg (69%). White solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.47 (s, 1H), 8.06 (dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 7.6 Hz, 2H), 7.63-7.54 (m, 2H), 7.37-7.31 (m, 4H), 7.27-7.22 (m, 1H), 3.45 (t, J = 7.8 Hz, 2H), 3.16 (t, J = 7.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.1, 141.3, 135.5, 134.1, 132.4, 129.6, 129.5, 129.0, 128.5, 128.4, 128.4, 127.7, 126.7, 126.1, 123.8, 40.5, 30.2.

5q.[5,6] Yield 270 mg (85%). Yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.32-7.22 (m, 5H), 4.77 (s, 2H), 4.48 (s, 2H), 4.08 (s, 5H), 3.05-3.03 (m, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 203.0, 141.6, 128.6, 128.4, 126.1, 79.0, 72.2, 69.6, 69.2, 41.4, 30.1.

5r.[1,2,4] Yield 130 mg (55%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.08 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.33-7.21 (m, 7H), 3.51 (dd J_1 = 17.6 Hz, J_2 = 4 Hz, 1H), 2.99-2.86 (m, 2H), 2.79-2.62 (m, 2H), 2.14-2.08 (m, 1H), 1.84-1.74 (m, 1H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 199.3, 144.0, 140.0, 133.2, 132.4, 129.2, 128.7, 128.3, 127.5, 126.5, 126.1, 49.4, 35.6, 28.6, 27.6.

5s.[7] Yield 104 mg (69%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.06 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.18 (q, J = 8.4 Hz, 4H), 3.34 (t, J = 7.8 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.8, 145.6, 139.8, 138.1, 135.6, 135.5, 129.2, 128.9, 128.6, 128.2, 128.1, 127.2, 127.1, 40.6, 29.7, 21.0.

5t.[8] Yield 102 mg (68%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.91 (d, J = 8.0 Hz, 2H), 7.58 (dd, J_1 = 18.4 Hz, J_2 = 7.2 Hz, 4H), 7.45 (t, J = 7.4 Hz, 2H), 7.37-7.33 (m, 3H), 7.27 (d, J = 8.4 Hz, 2H), 3.34 (t, J = 7.8 Hz, 2H), 3.13 (t, J = 7.8 Hz, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.7, 143.8, 140.9, 140.4, 139.0, 134.3, 129.2, 128.8, 128.7, 128.1, 127.2, 127.0, 126.9, 40.2, 29.7, 21.6.

5u.[9] Yield 133 mg (79%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.06 (d, J = 8.0 Hz, 2H), 7.69 (d, J= 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.50-7.41 (m, 5H), 7.39-7,32 (m, 3H), 3.39 (t, J = 6.0 Hz, 2H), 3.15 (t, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 198.7, 145.7, 141.0, 140.4, 139.8, 139.1, 135.5, 128.9, 128.8, 128.7, 128.6, 128.2, 127.2, 127.1, 127.0, 40.4, 29.8.

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1. Traces of ^{1}H and ^{13}C NMR spectra and HRMS analysis of complexes

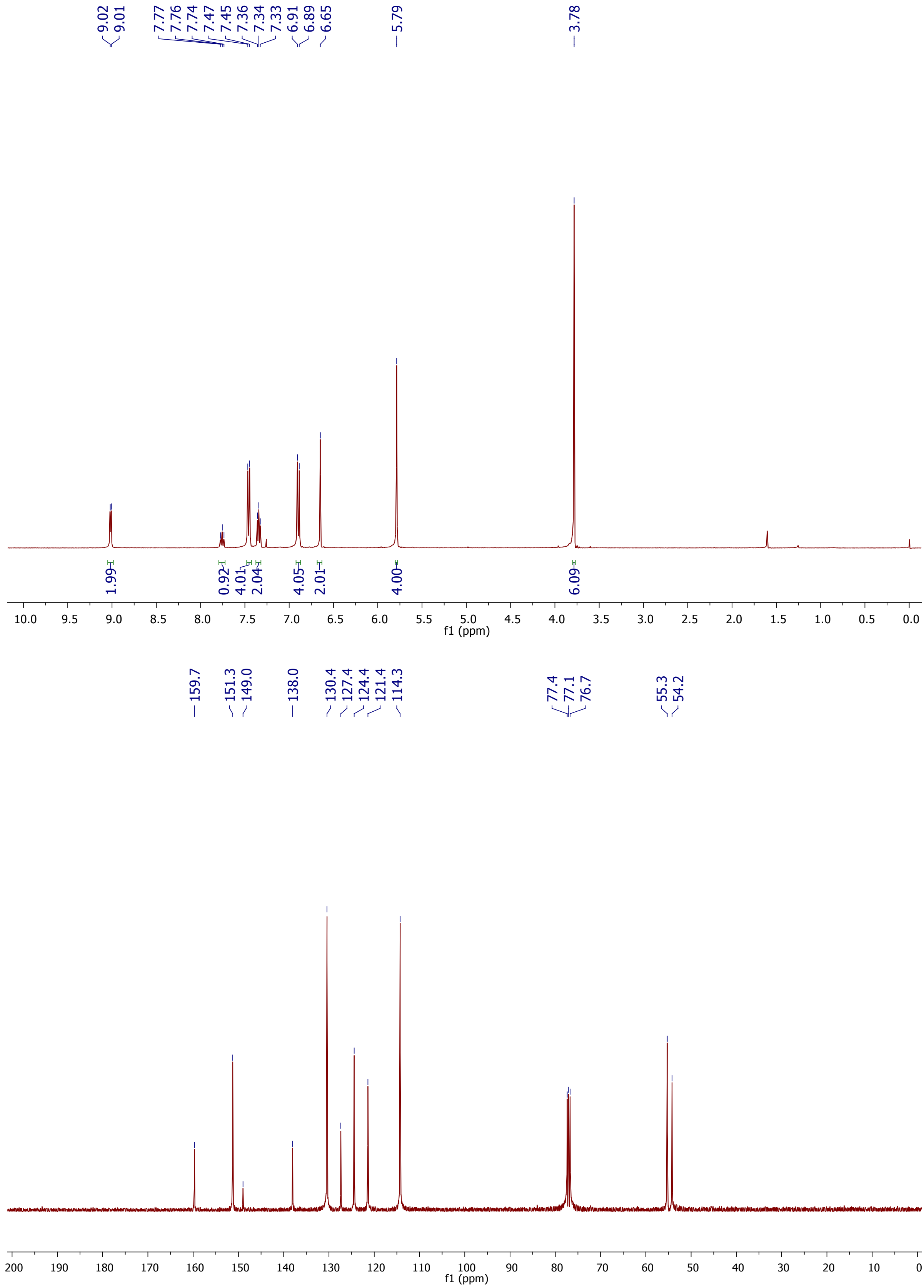


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **2a**.

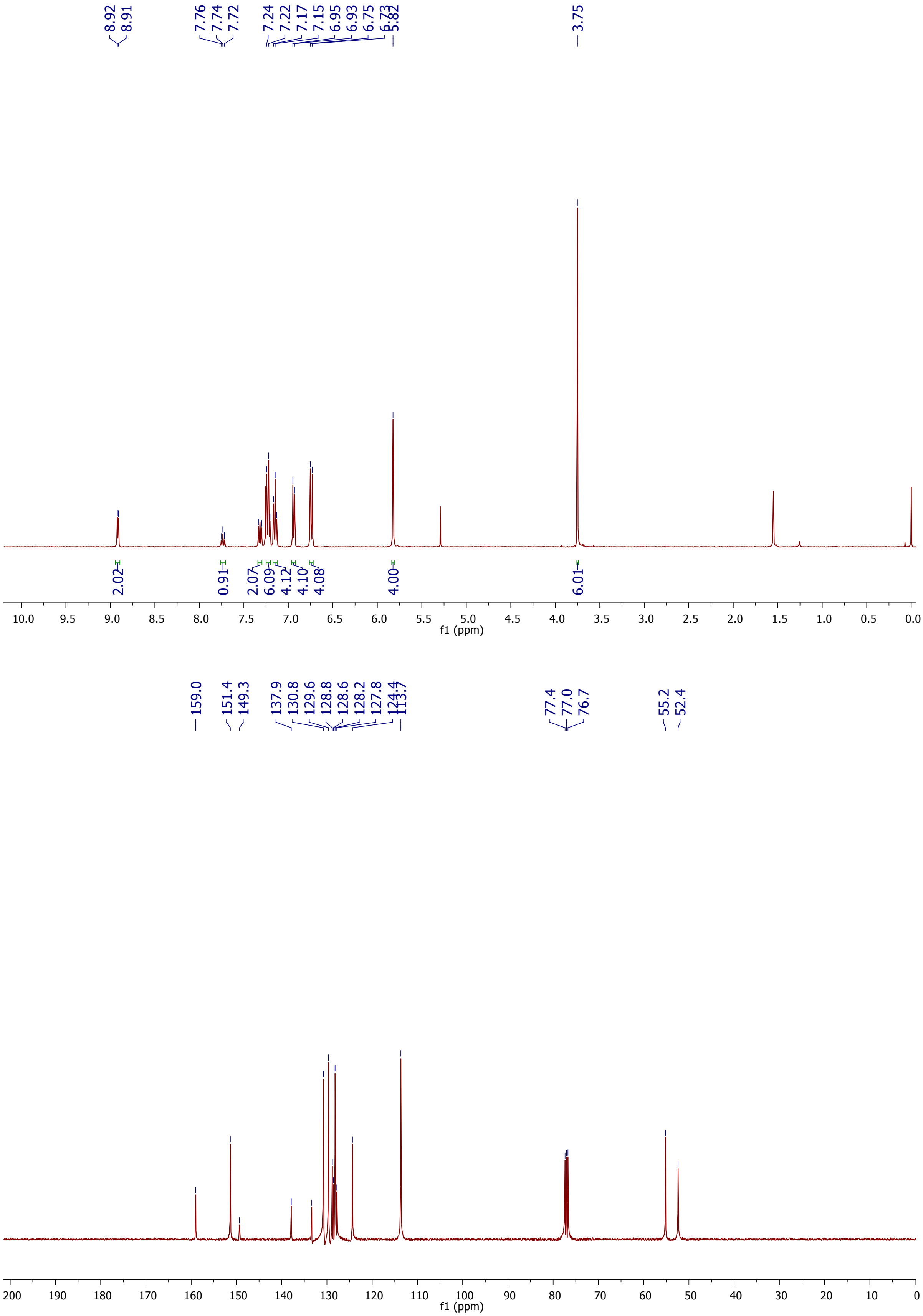


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **2b**.

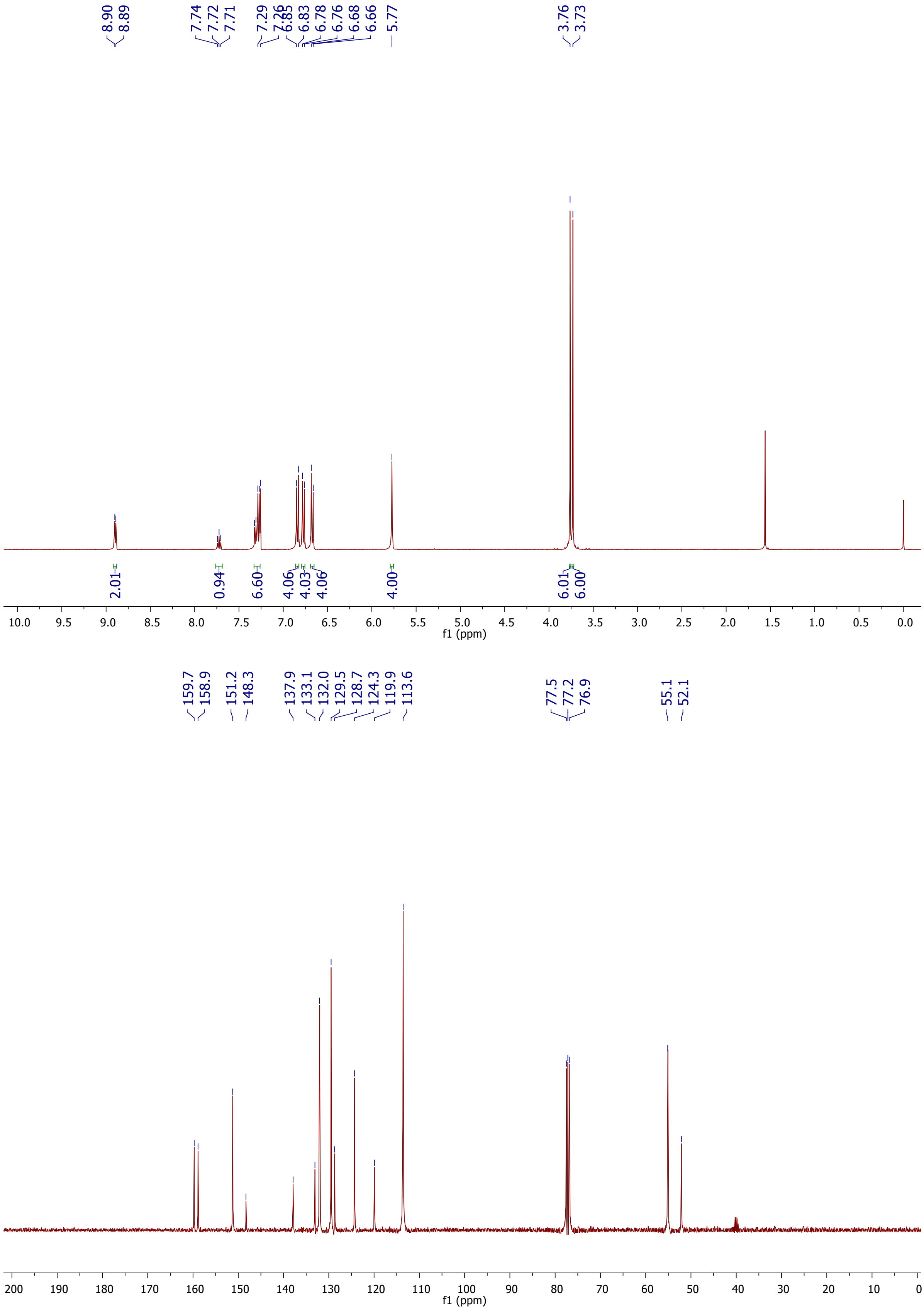


Figure S5. ^{1}H and ^{13}C NMR spectra of compound **2c**.

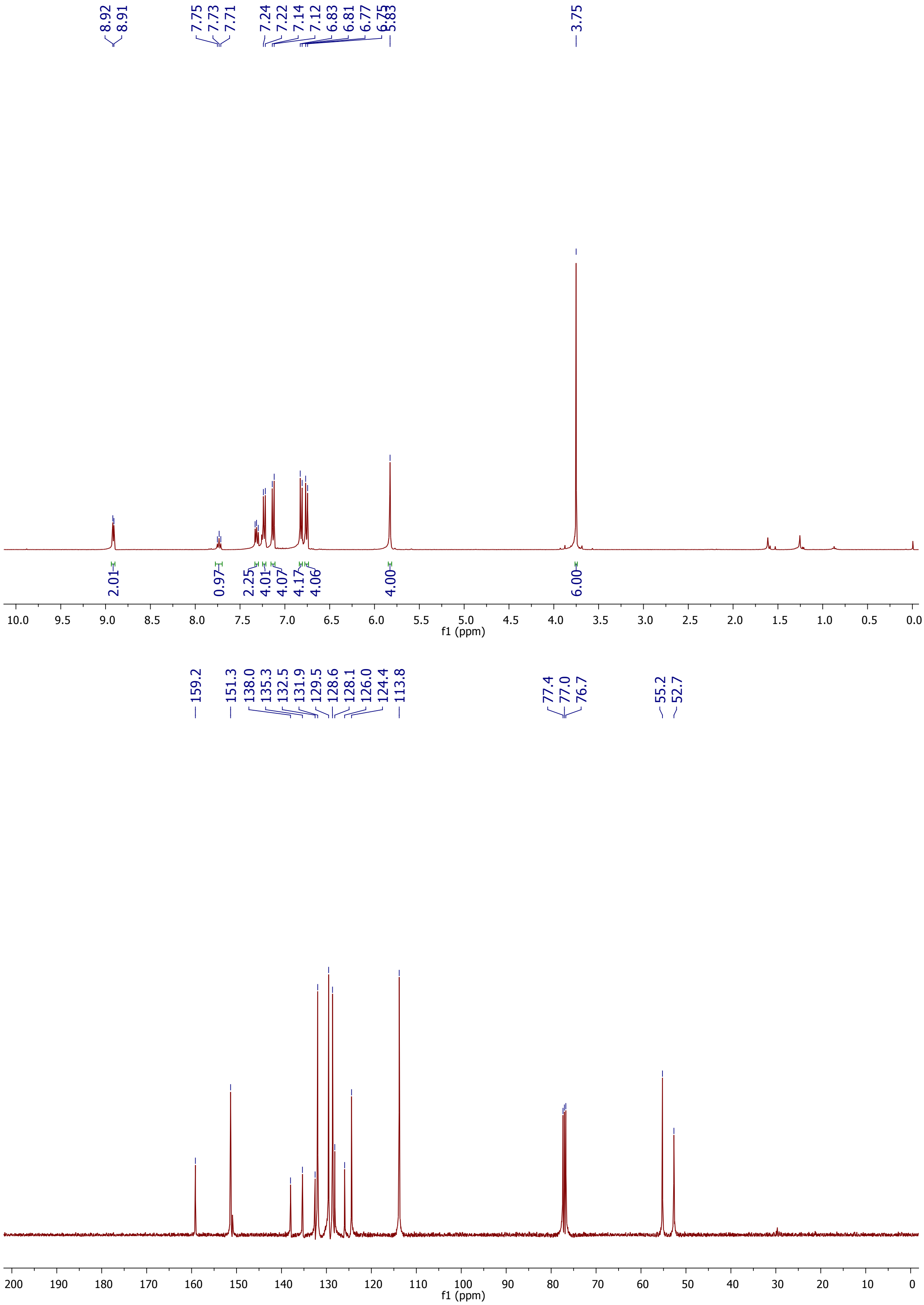


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **2d**.

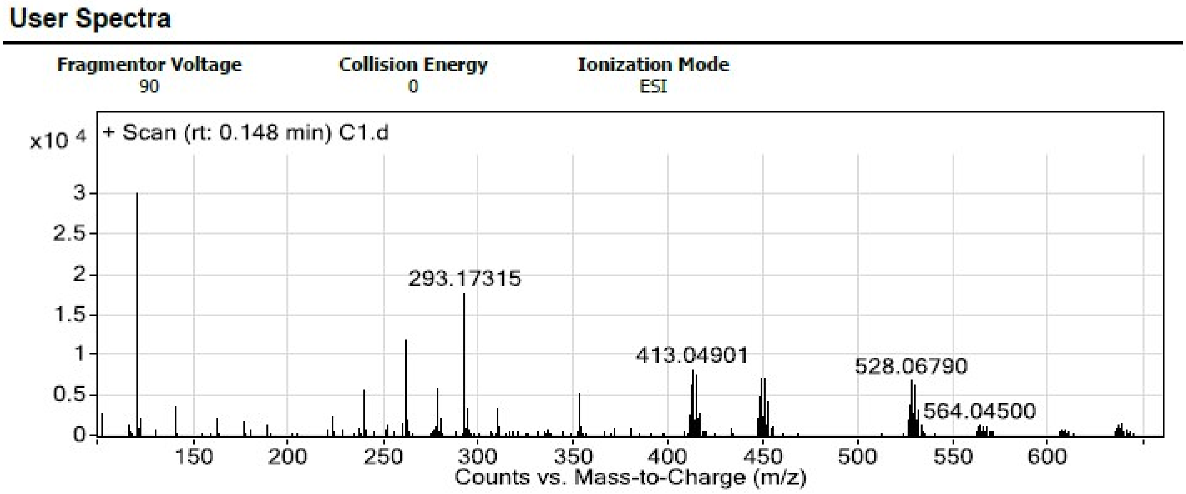


Figure S7. HRMS analysis report of compound **2a**.

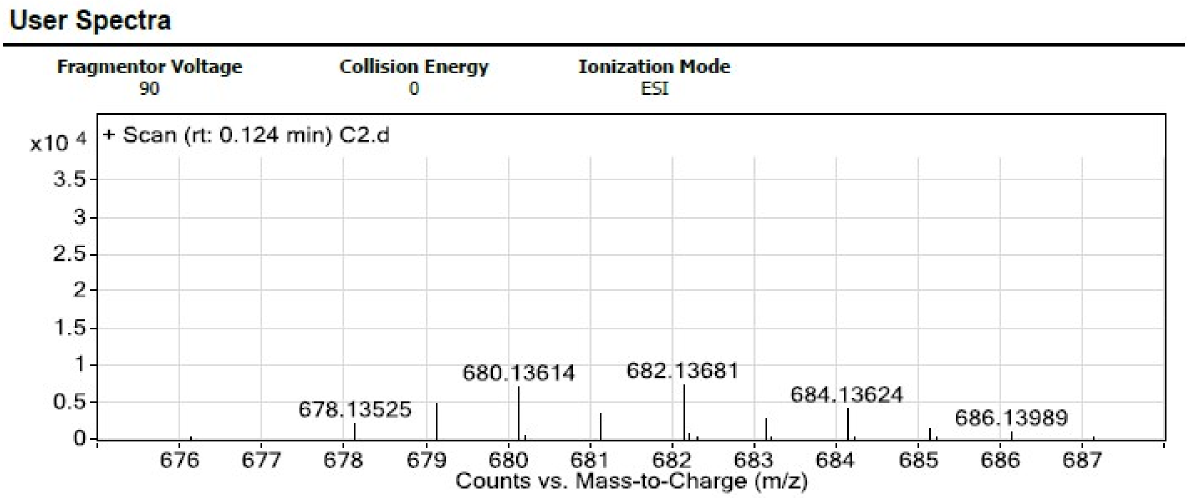


Figure S8. HRMS analysis report of compound **2b**.

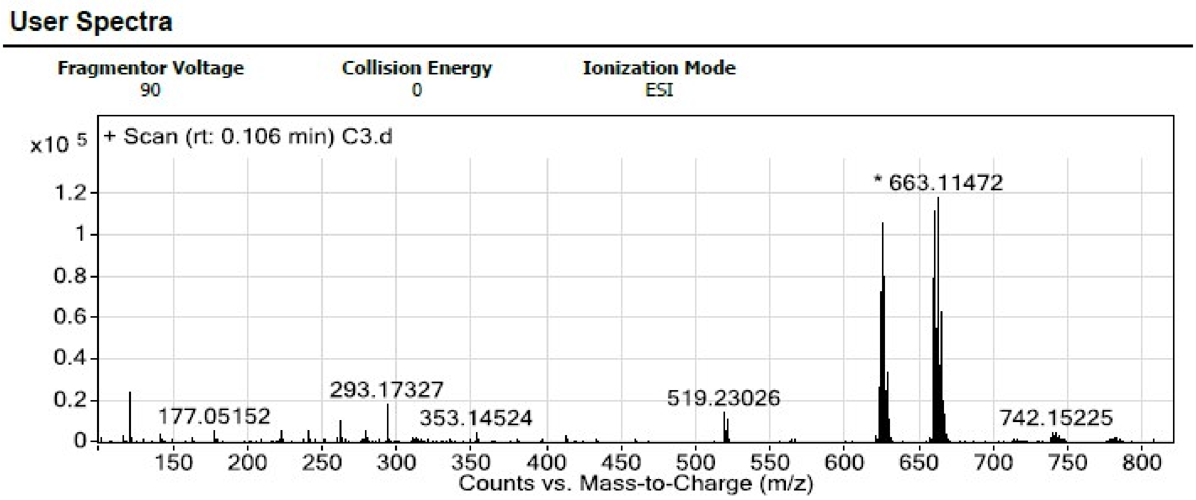


Figure S9. HRMS analysis report of compound **2c**.

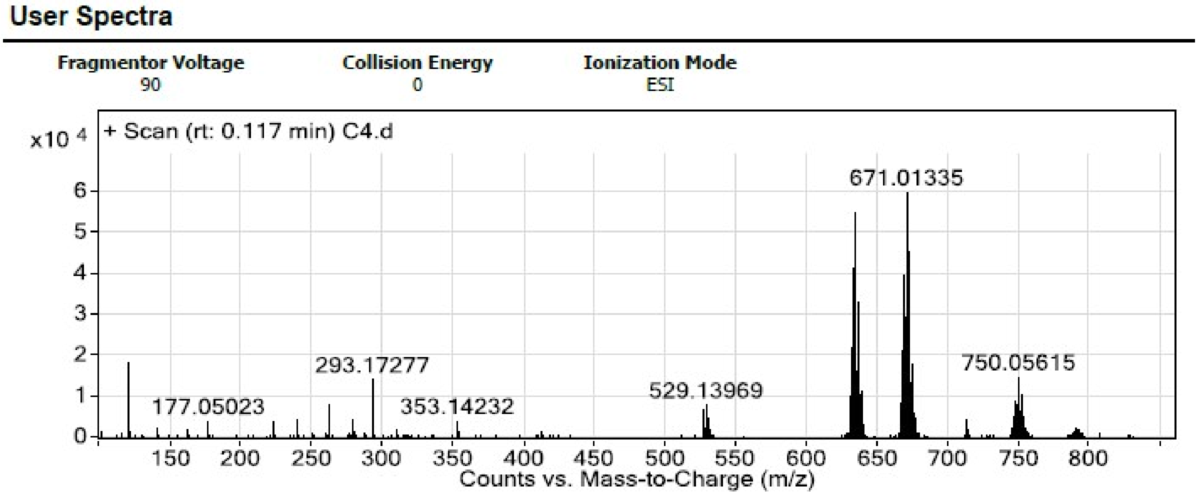
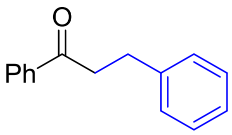
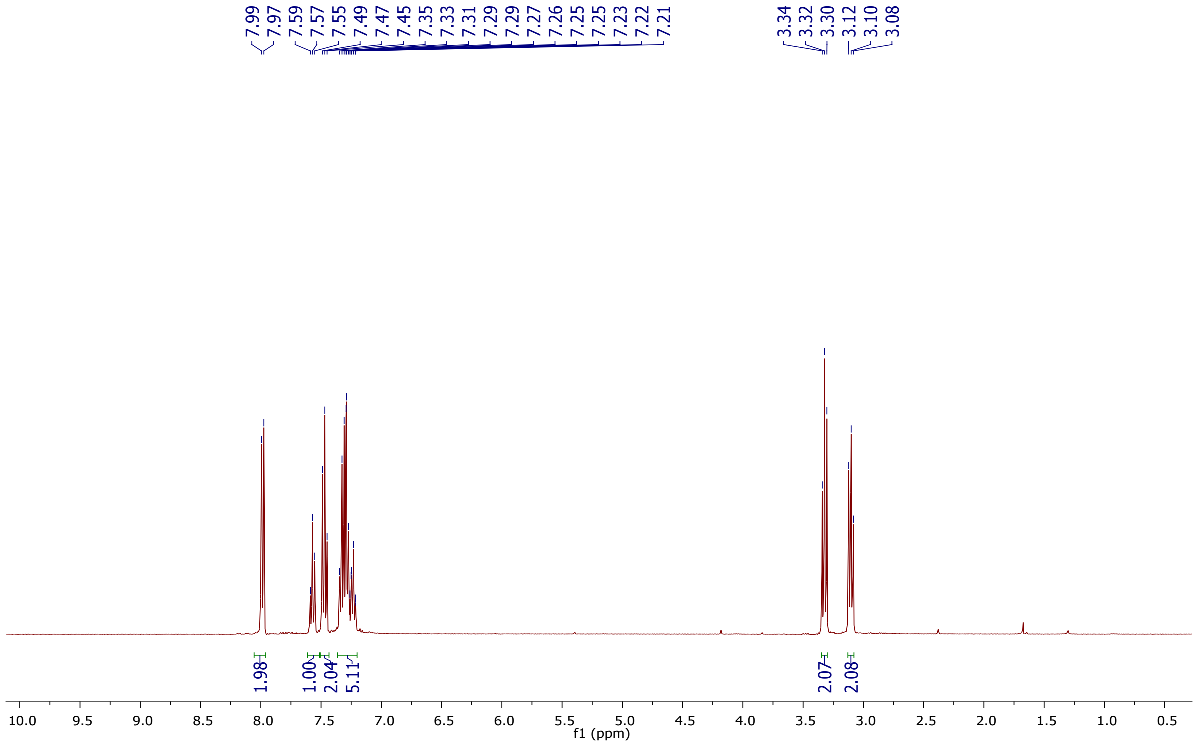


Figure S10. HRMS analysis report of compound **2d**.

2. Traces of ^{1}H and ^{13}C NMR spectra of products





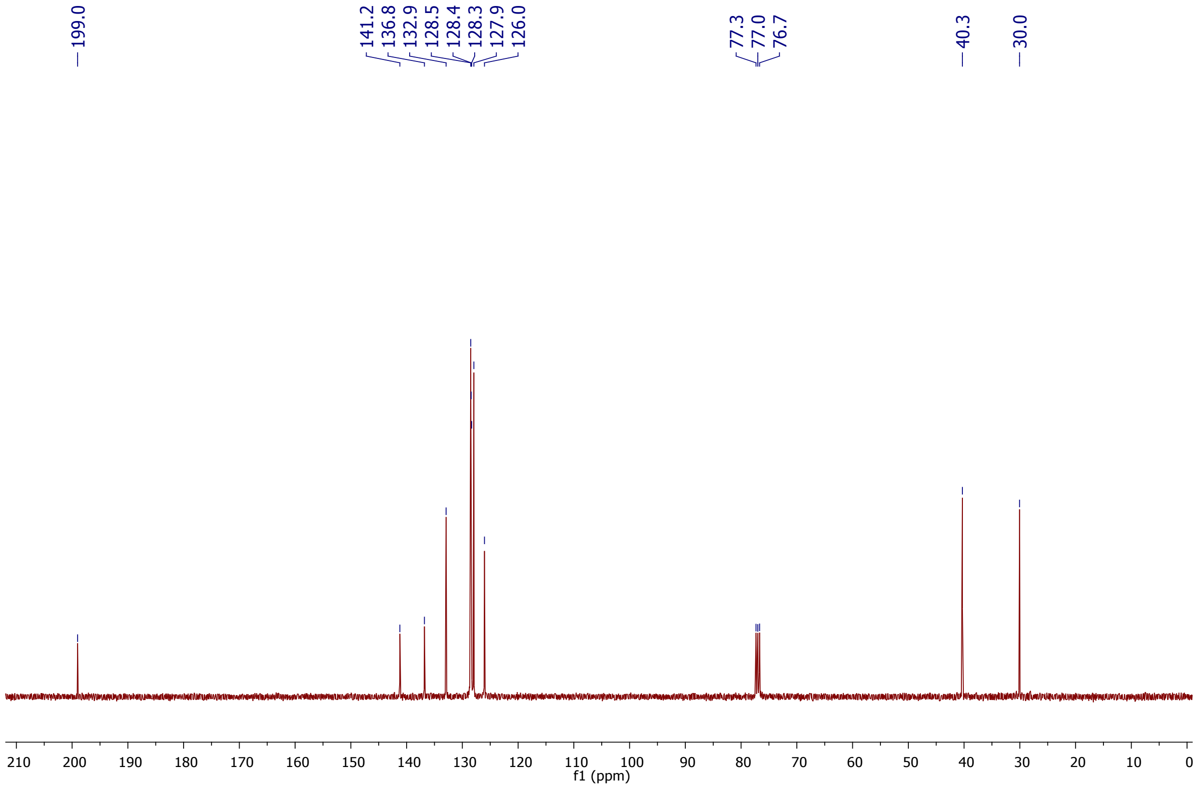


Figure S11. ^{1}H and ^{13}C NMR spectra of **5a**.

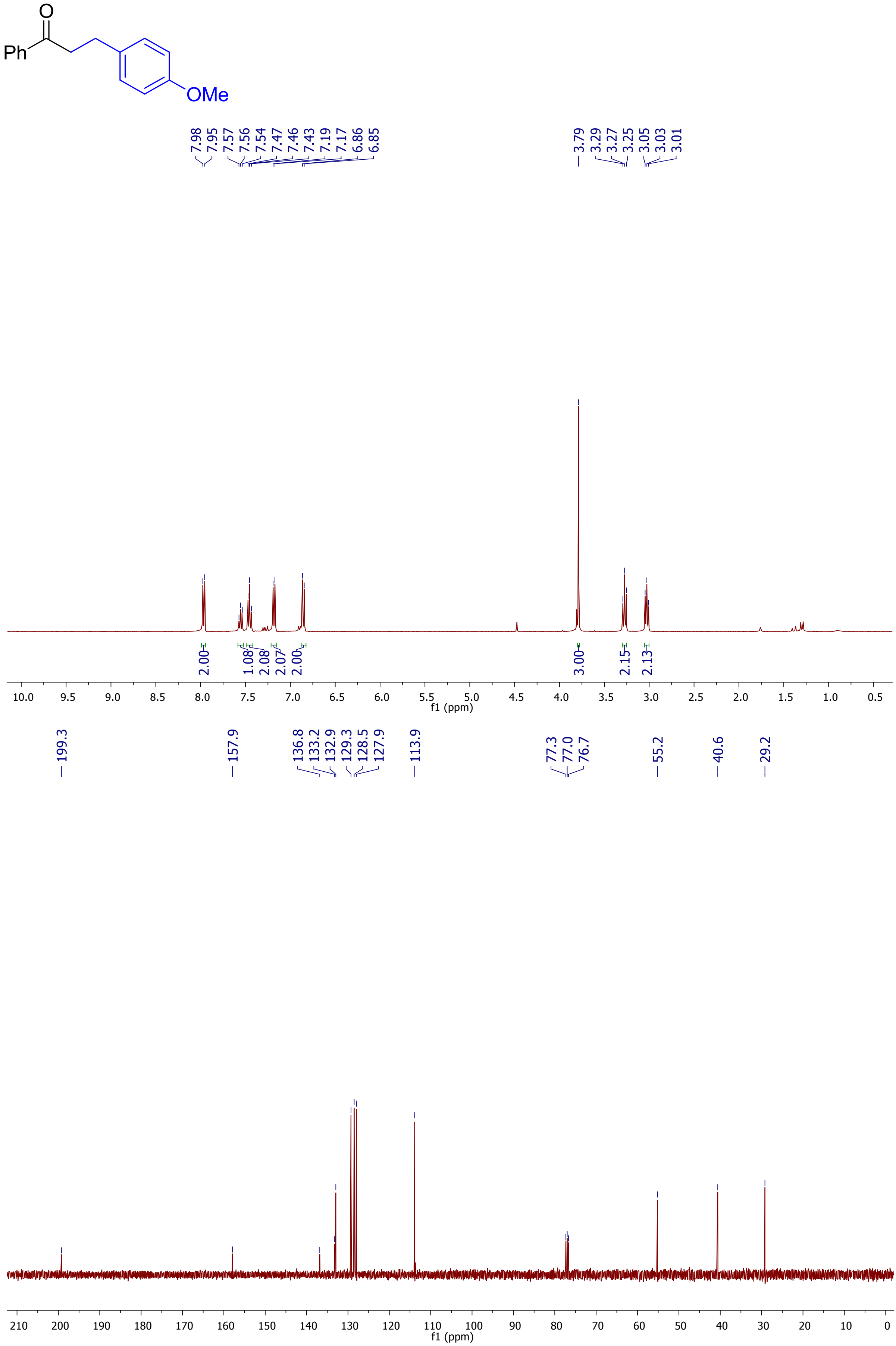


Figure S12. ^{1}H and ^{13}C NMR spectra of **5b**.

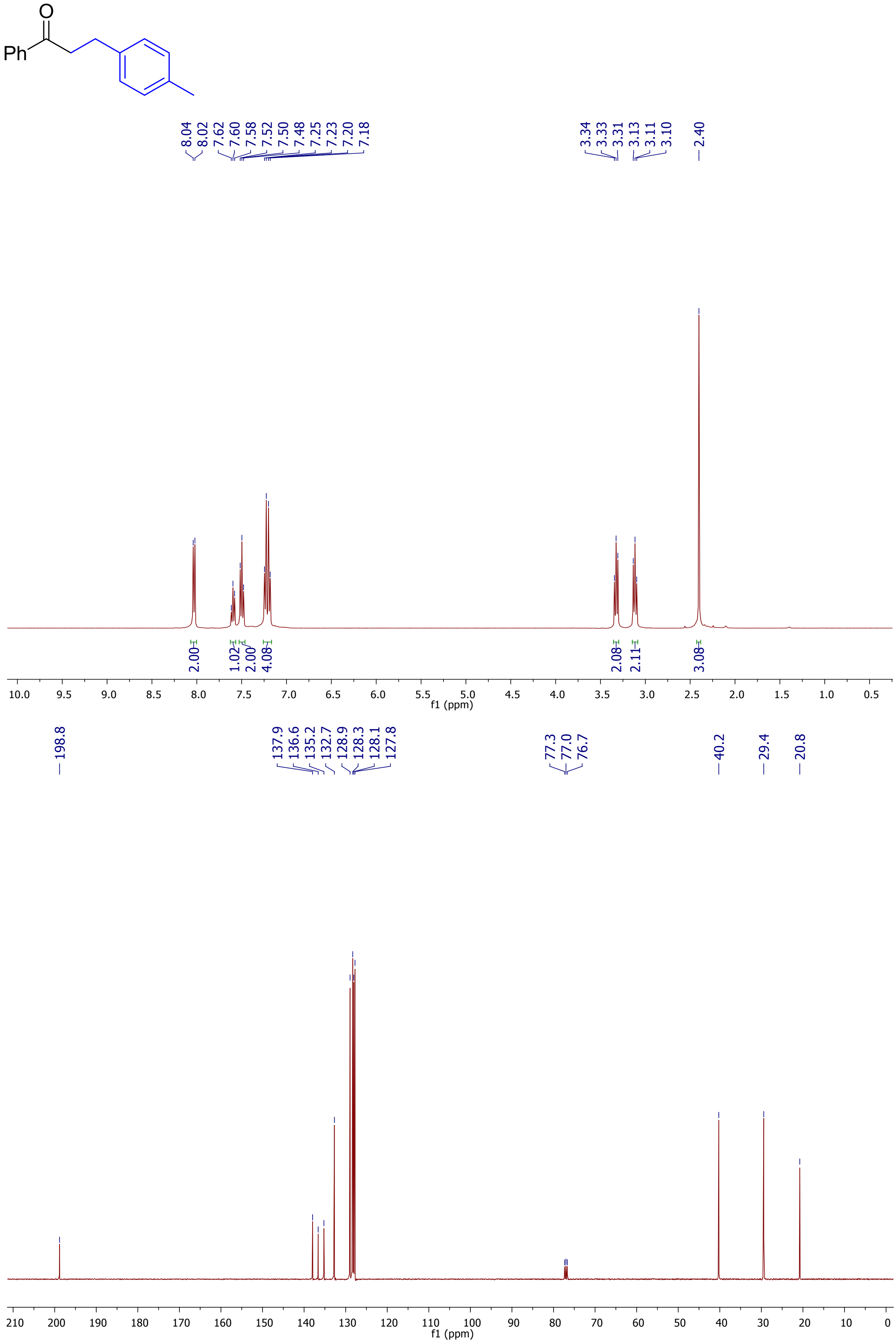
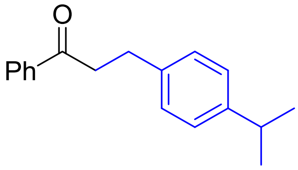
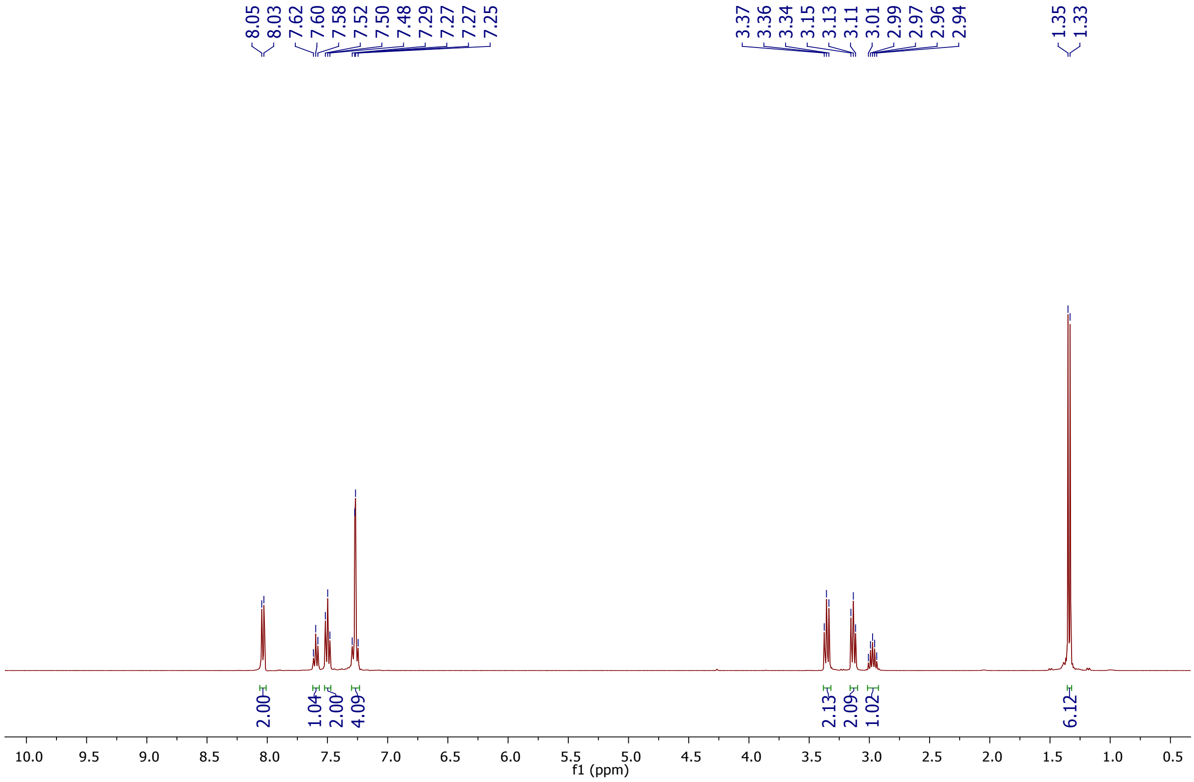


Figure S13. ^{1}H and ^{13}C NMR spectra of **5c**.





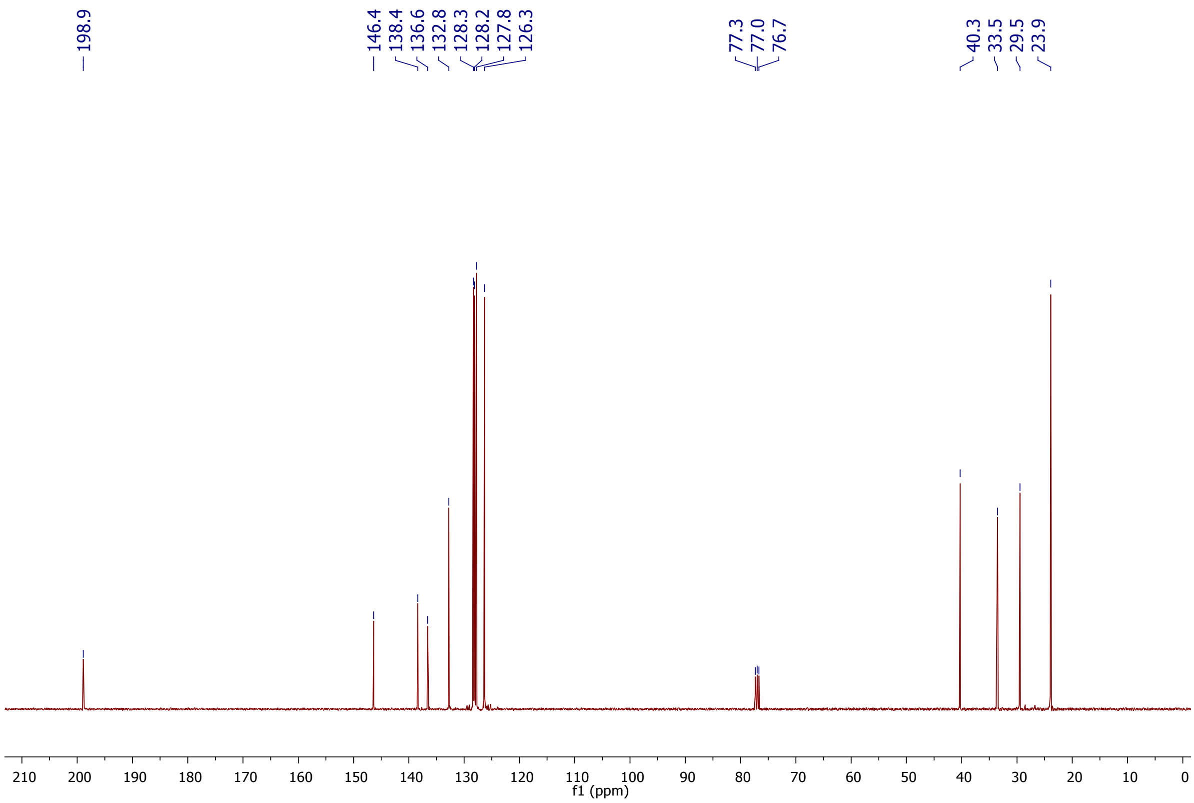


Figure S14. ^{1}H and ^{13}C NMR spectra of **5d**.

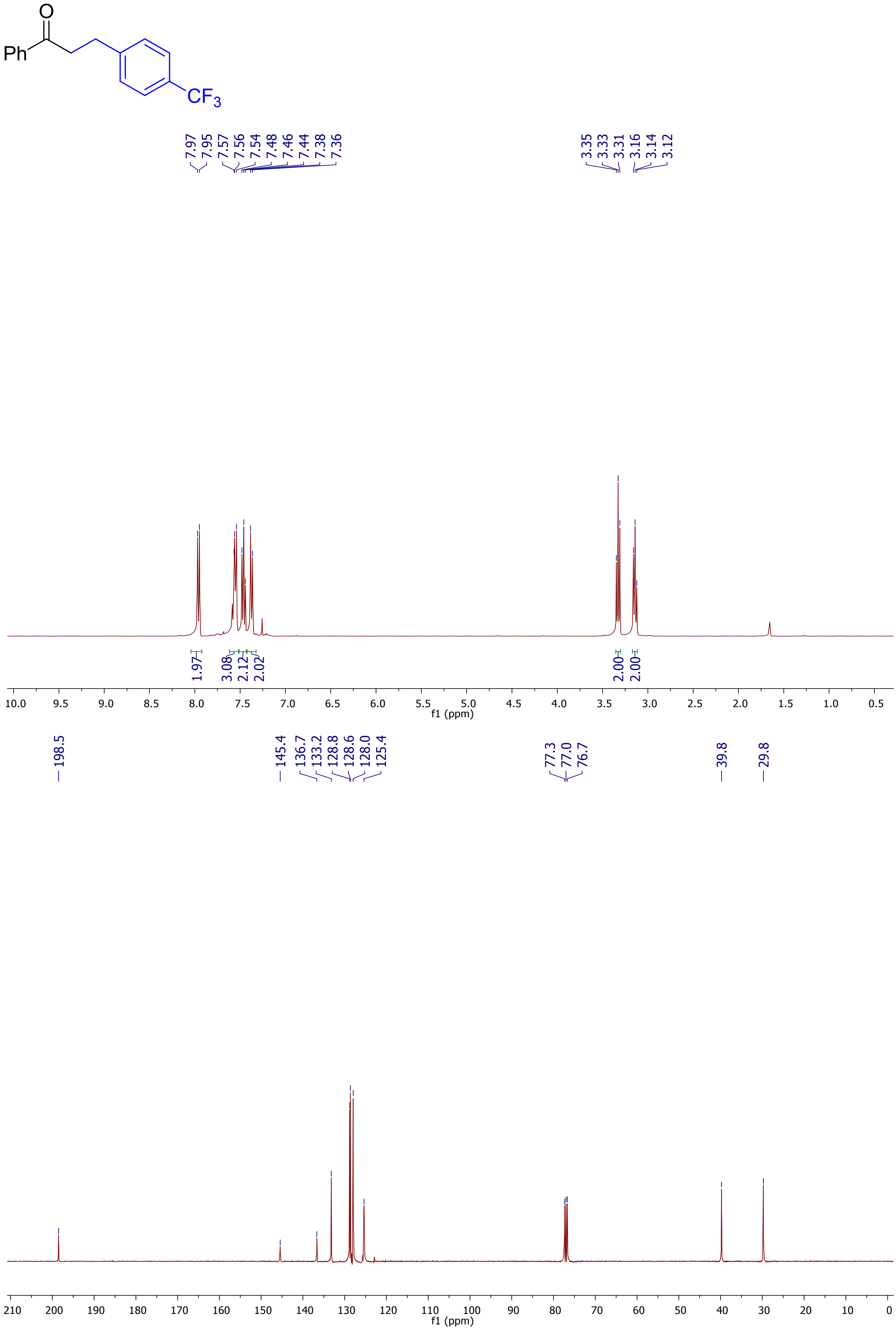


Figure S15. ^{1}H and ^{13}C NMR spectra of **5e**.

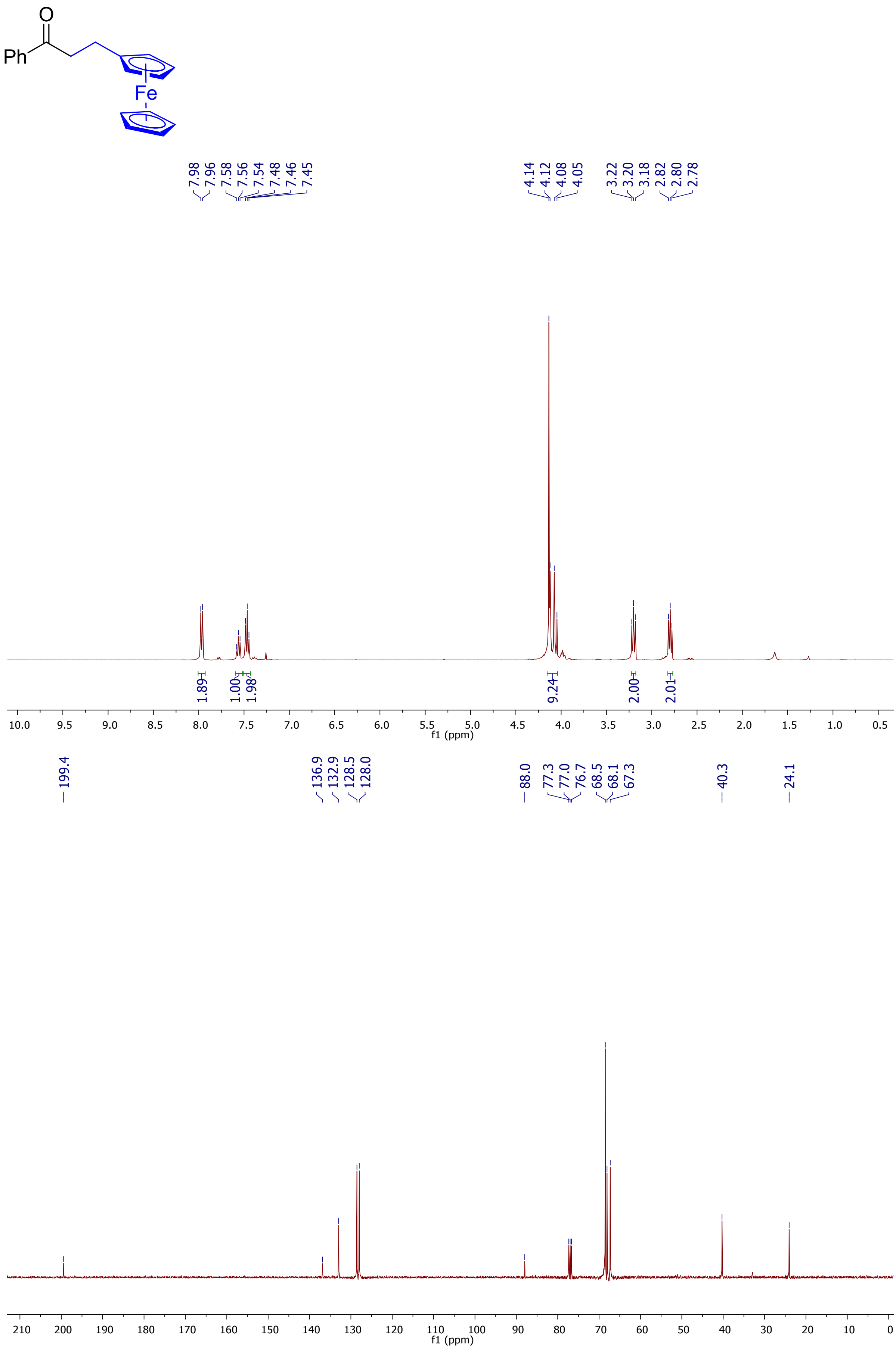


Figure S16. ^{1}H and ^{13}C NMR spectra of **5h**.

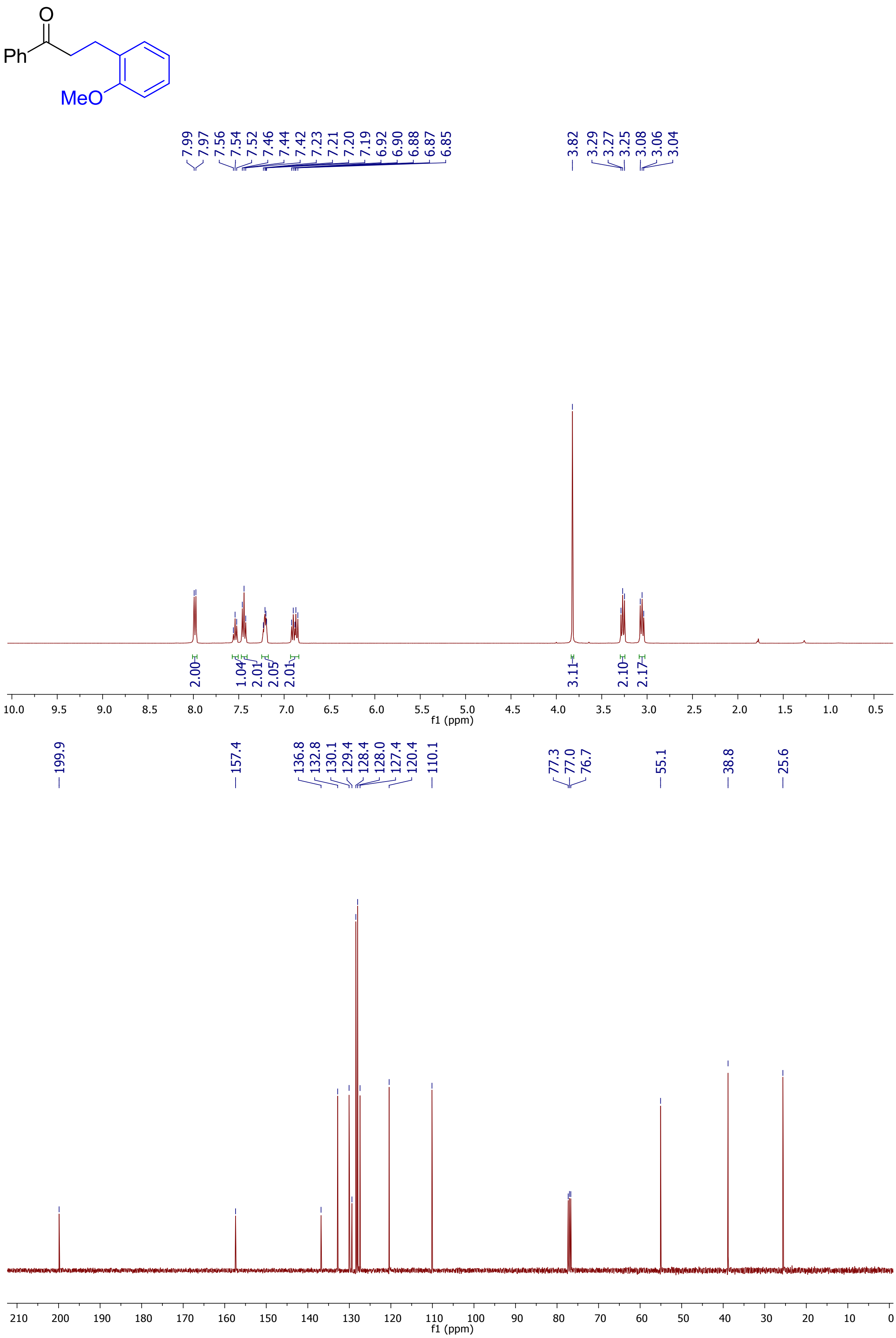
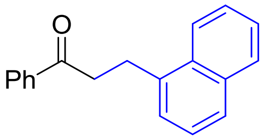
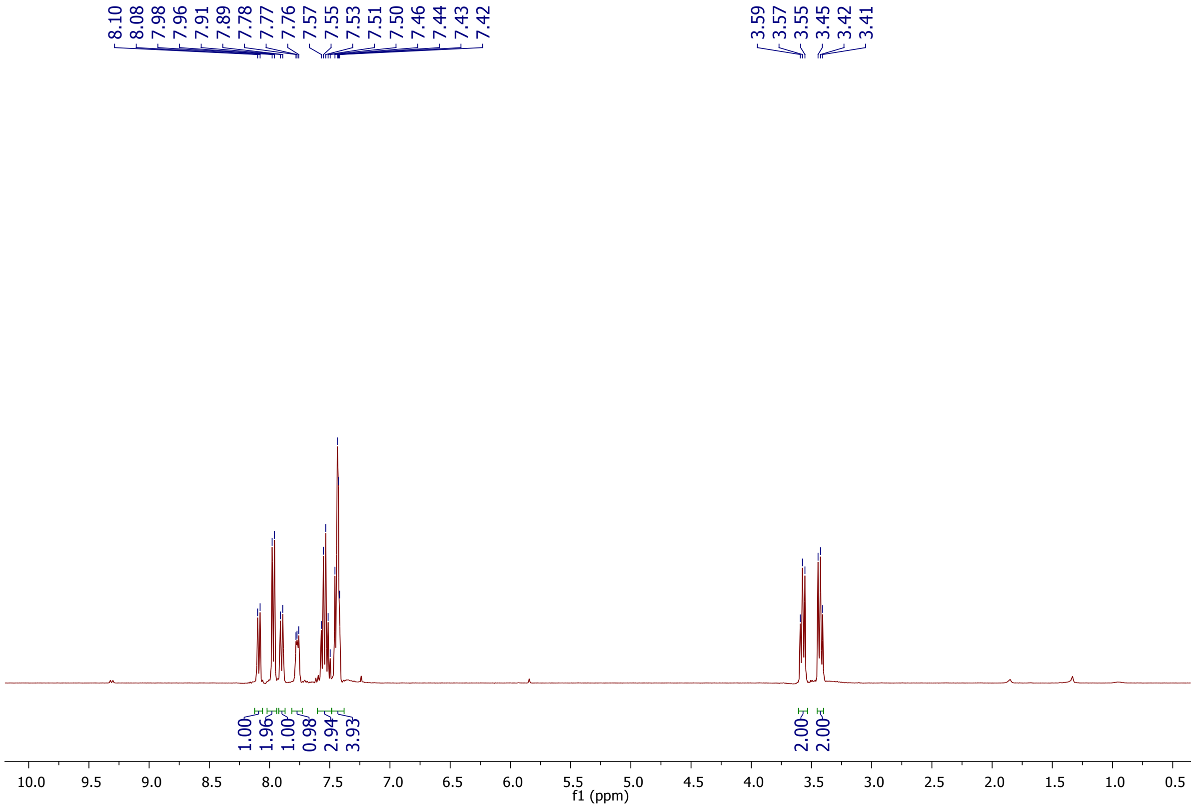


Figure S17. ^{1}H and ^{13}C NMR spectra of **5i**.





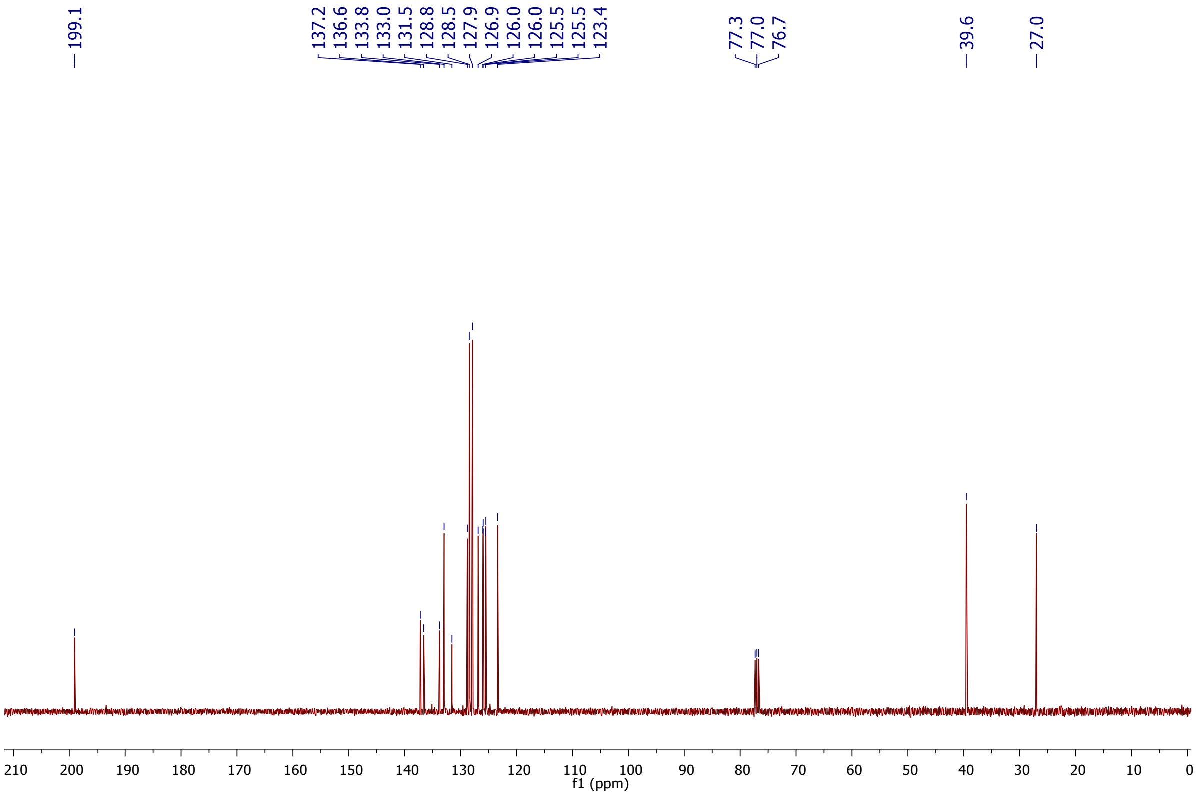
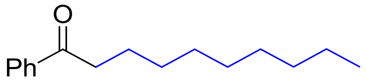
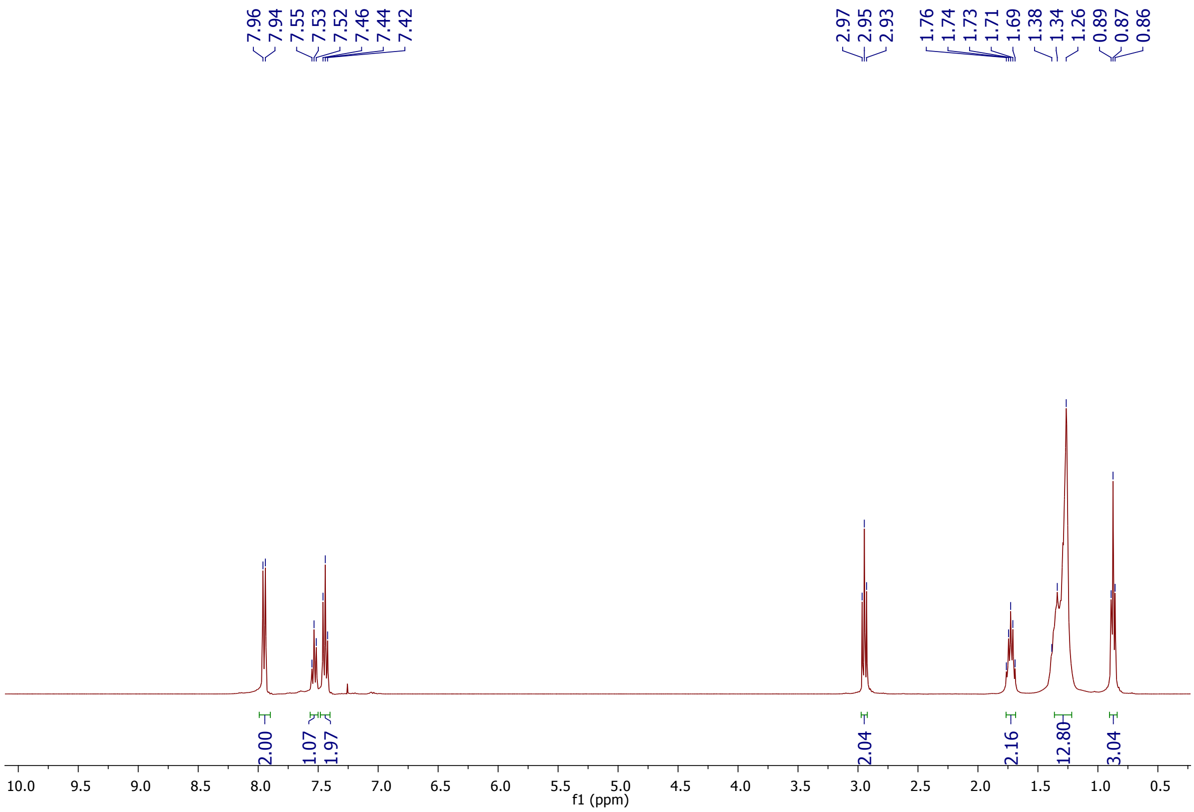


Figure S18. ^{1}H and ^{13}C NMR spectra of **5j**.





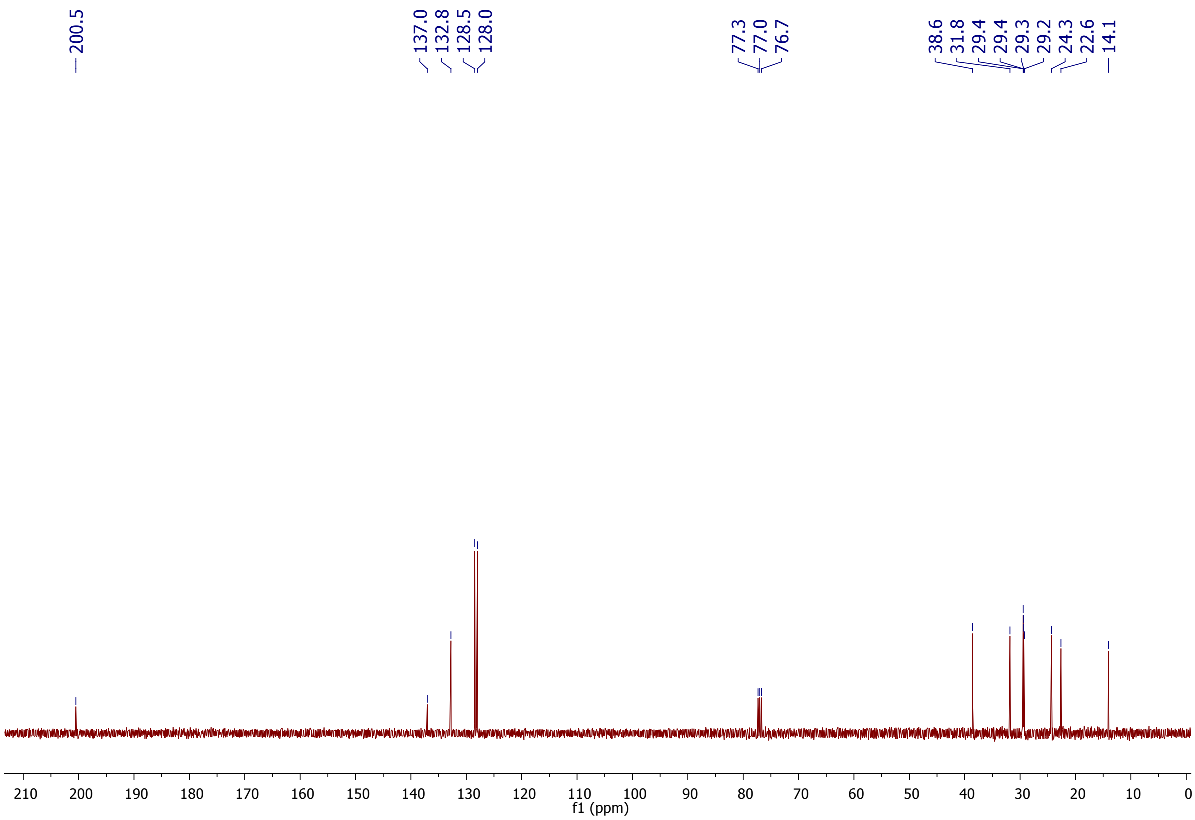
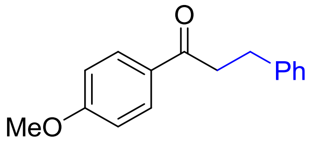
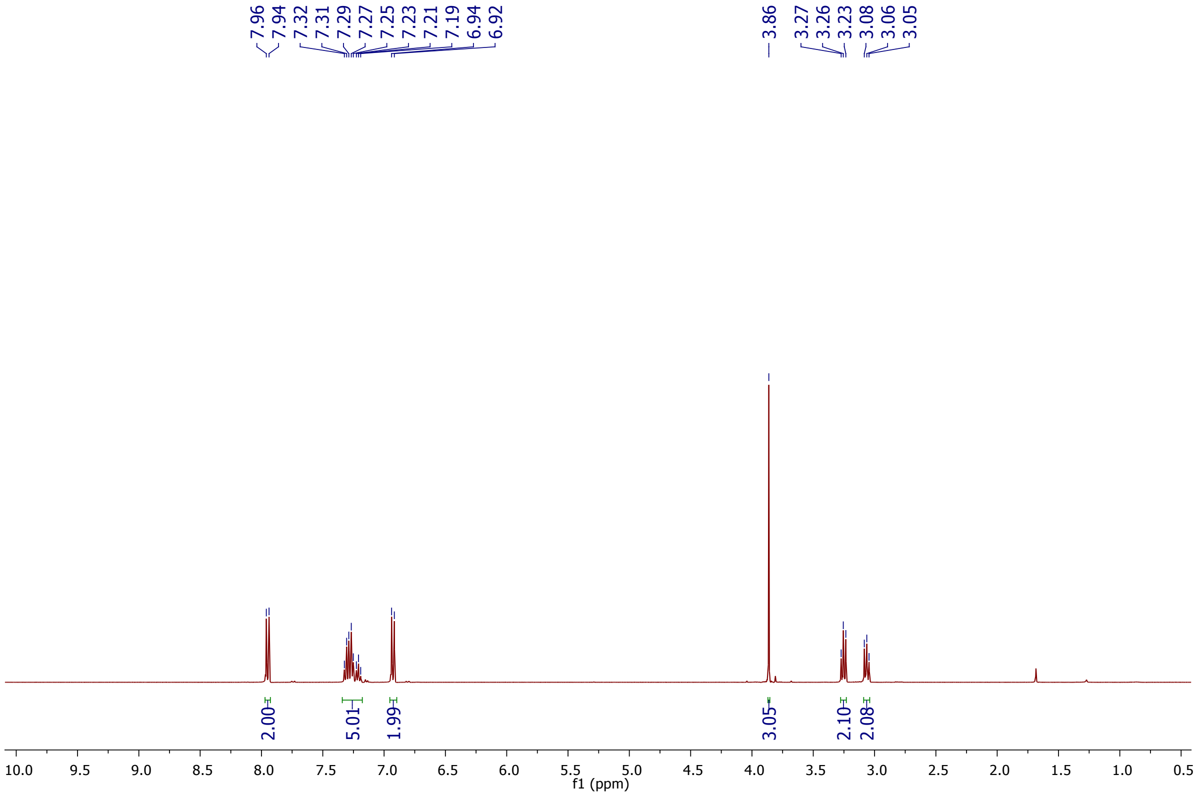


Figure S19. ^{1}H and ^{13}C NMR spectra of **5k**.





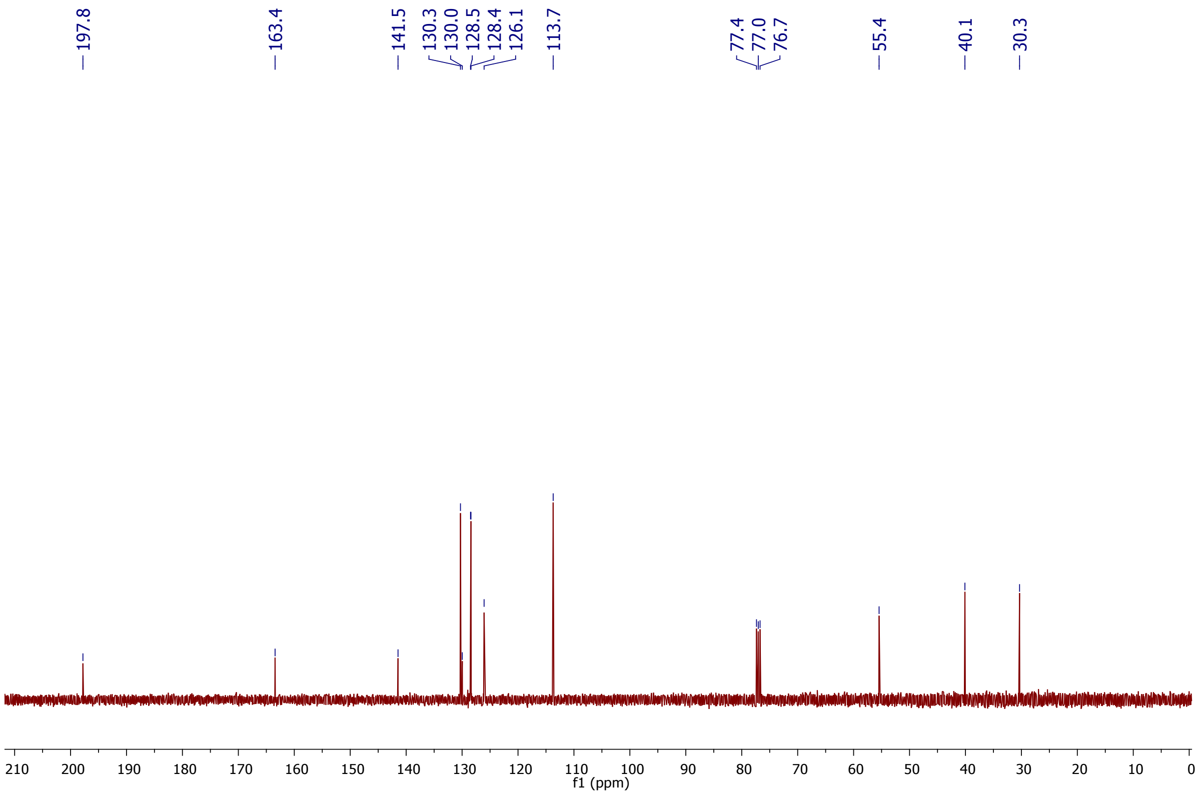
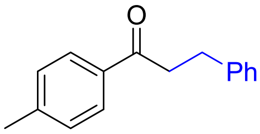
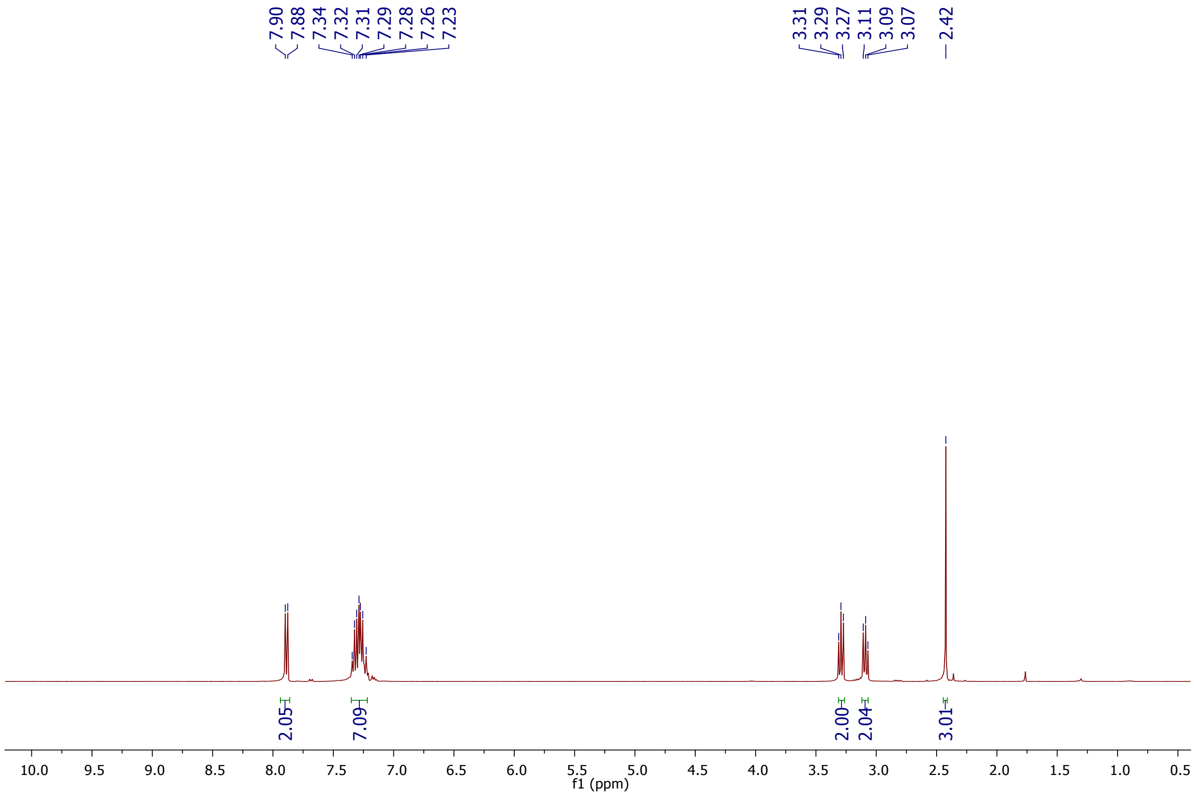


Figure S20. ^{1}H and ^{13}C NMR spectra of **5l**.





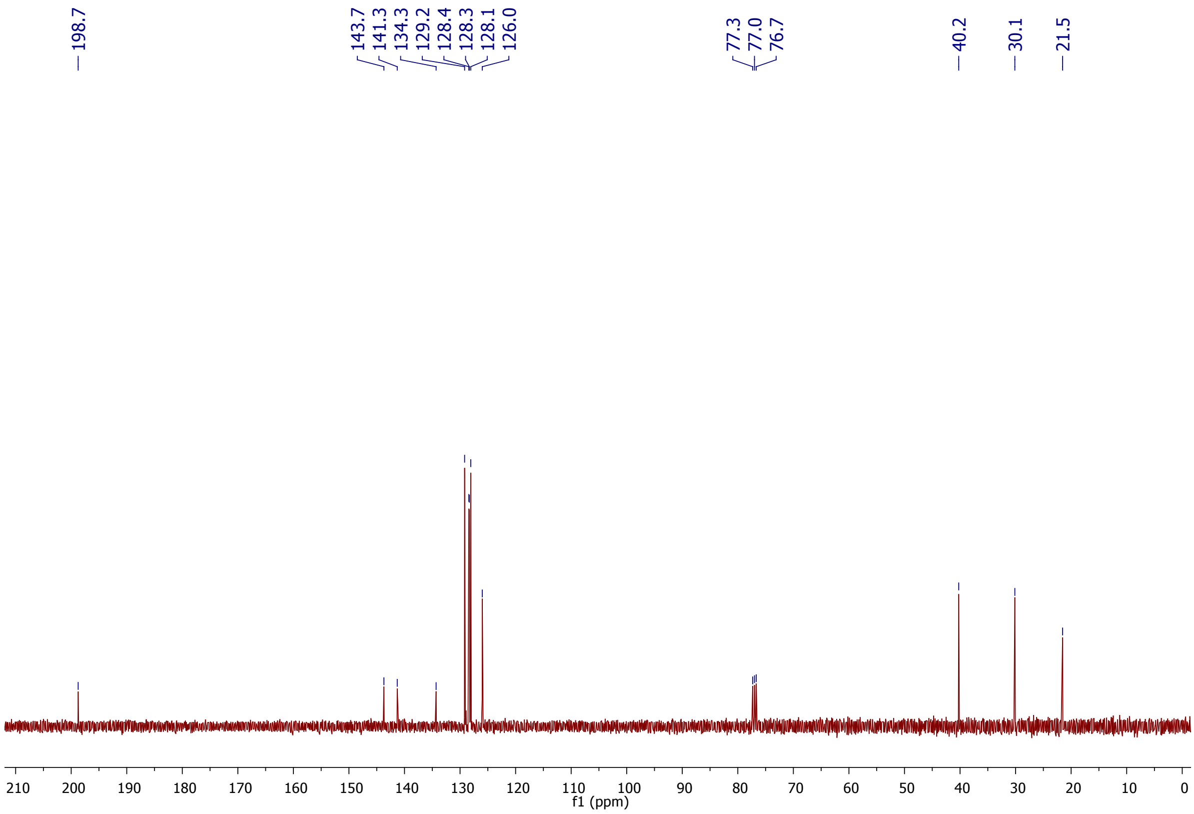


Figure S21. ^{1}H and ^{13}C NMR spectra of **5m**.

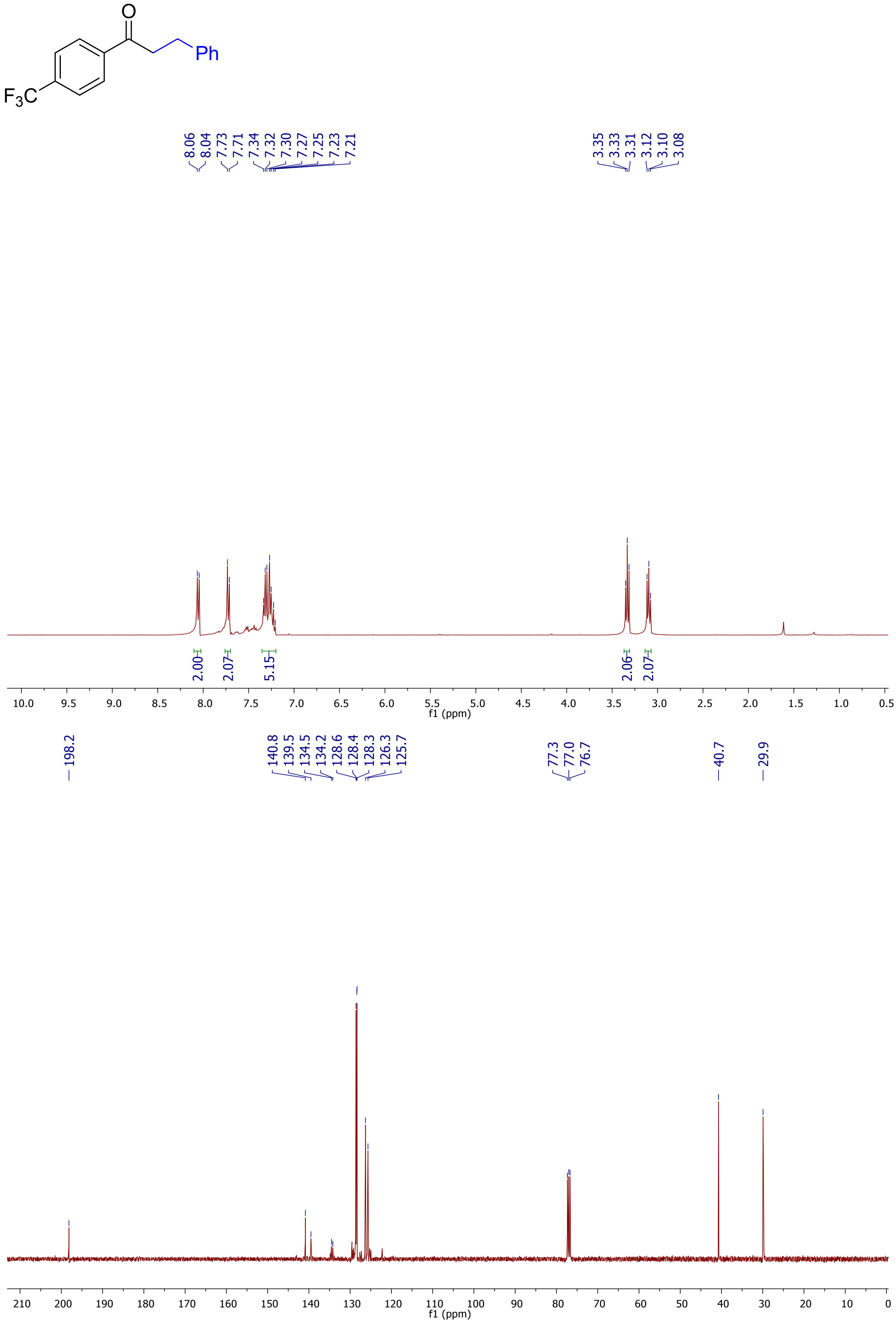


Figure S22. ¹H and ¹³C NMR spectra of **5n**.

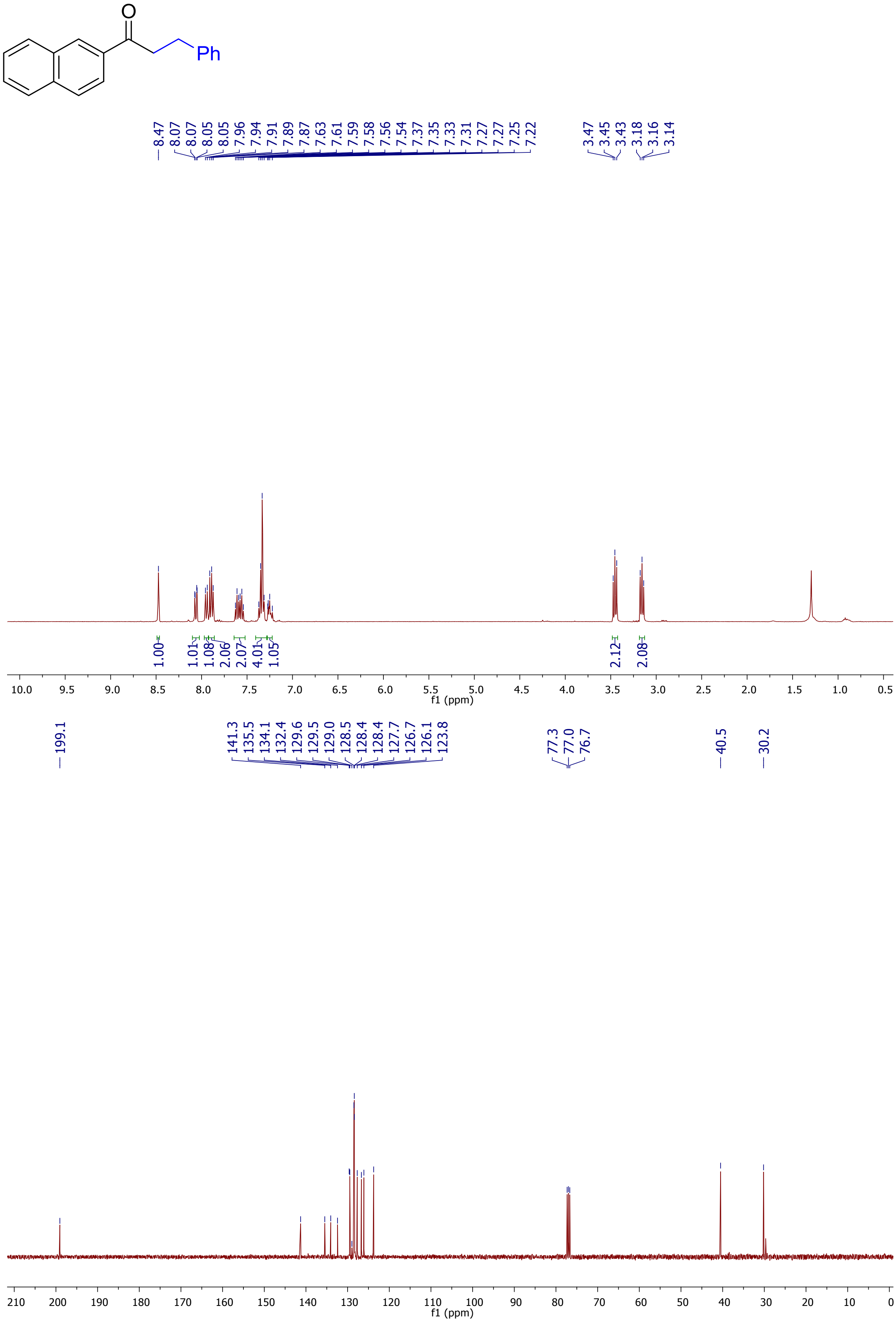


Figure S23. ^{1}H and ^{13}C NMR spectra of **5p**.

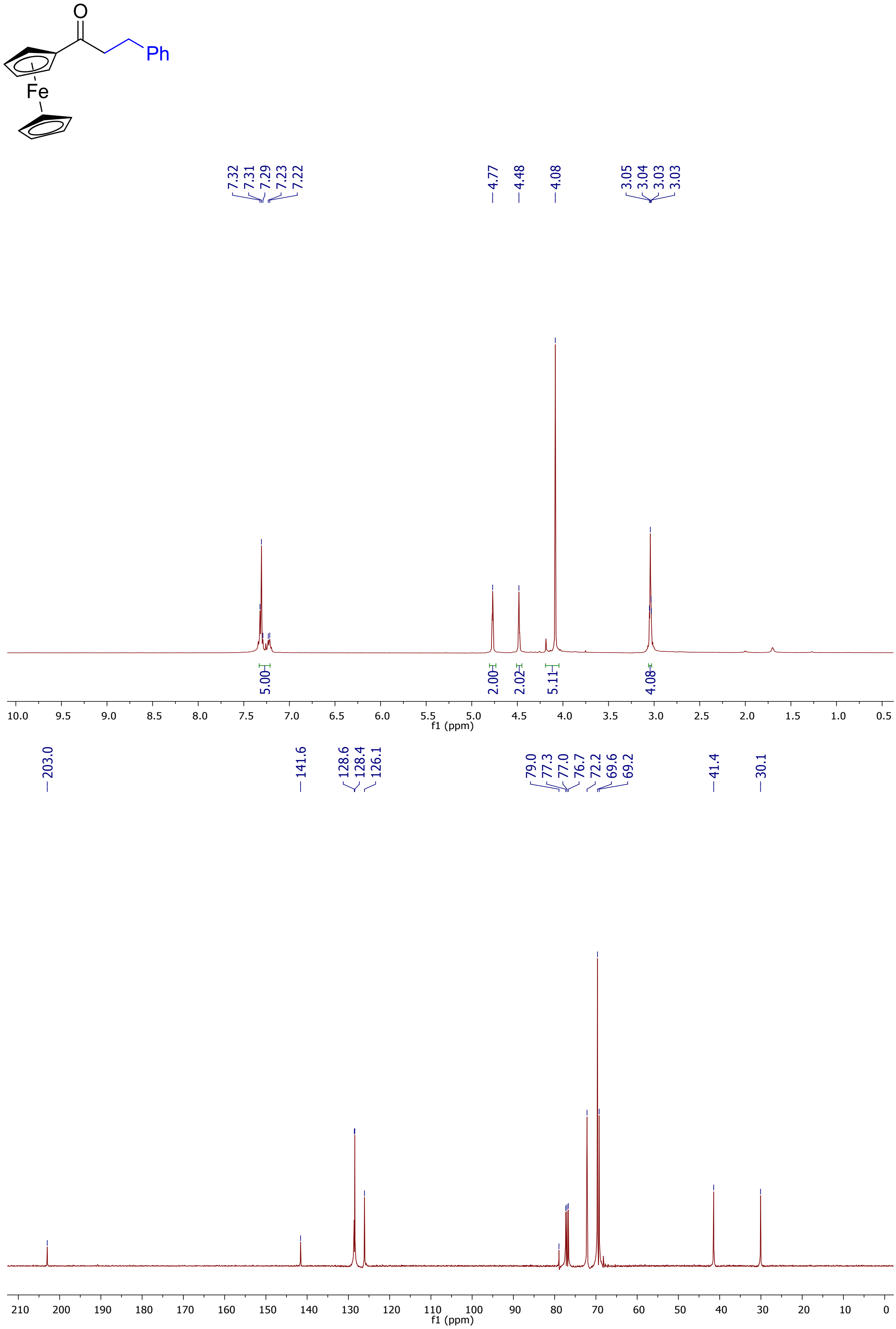


Figure S24. ^{1}H and ^{13}C NMR spectra of **5q**.

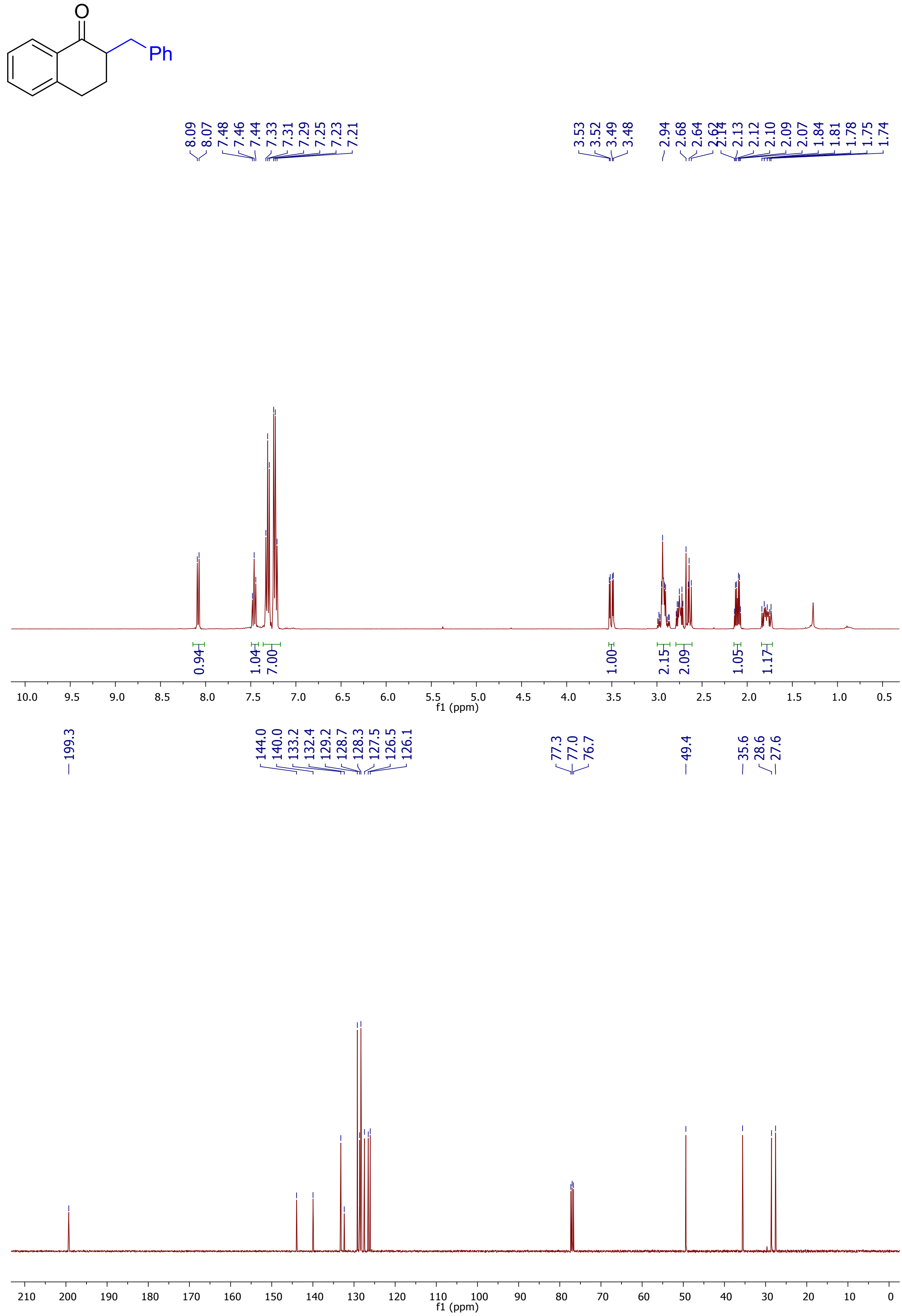


Figure S25. ^{1}H and ^{13}C NMR spectra of **5r**.

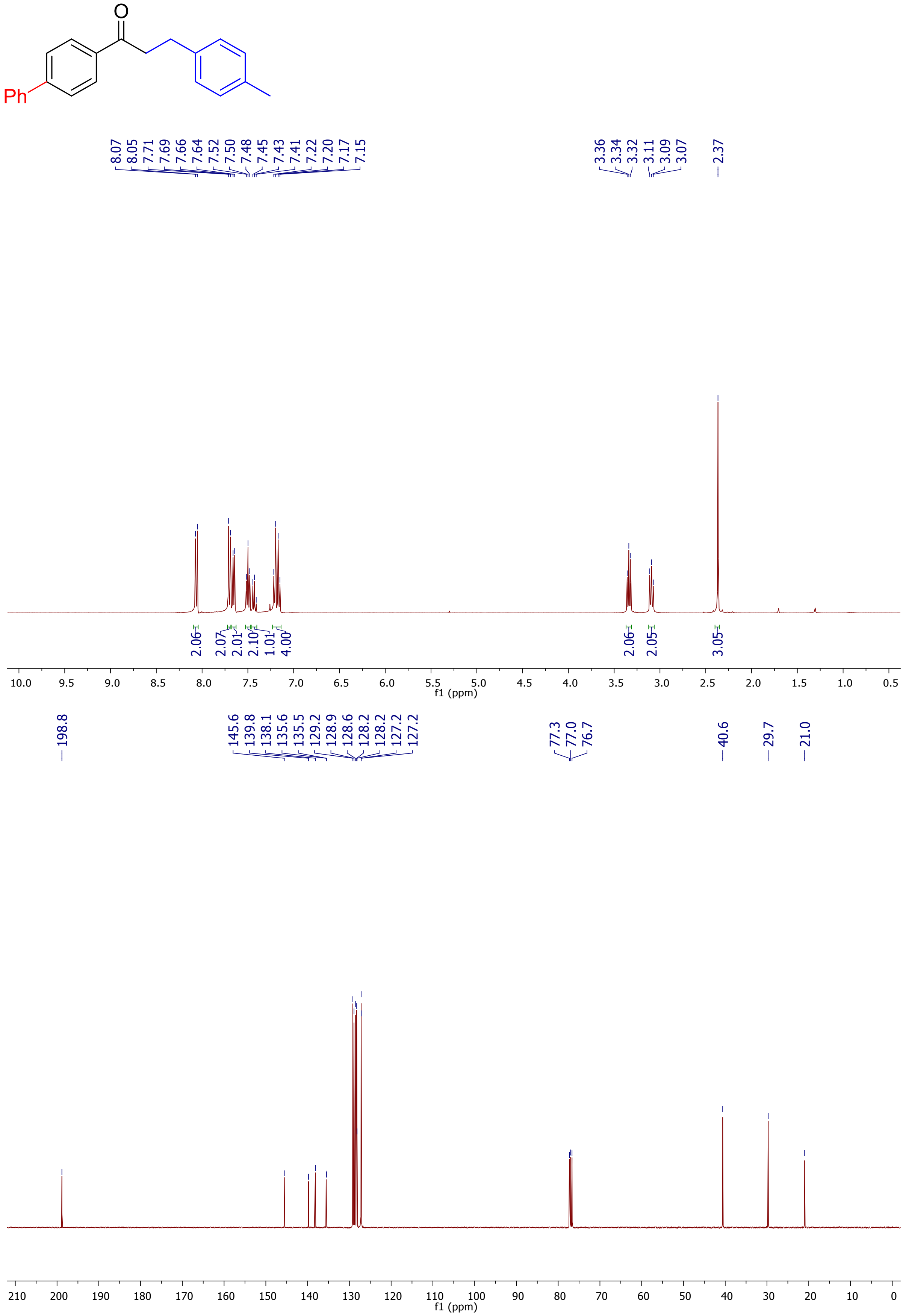
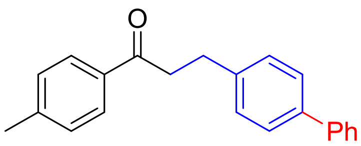
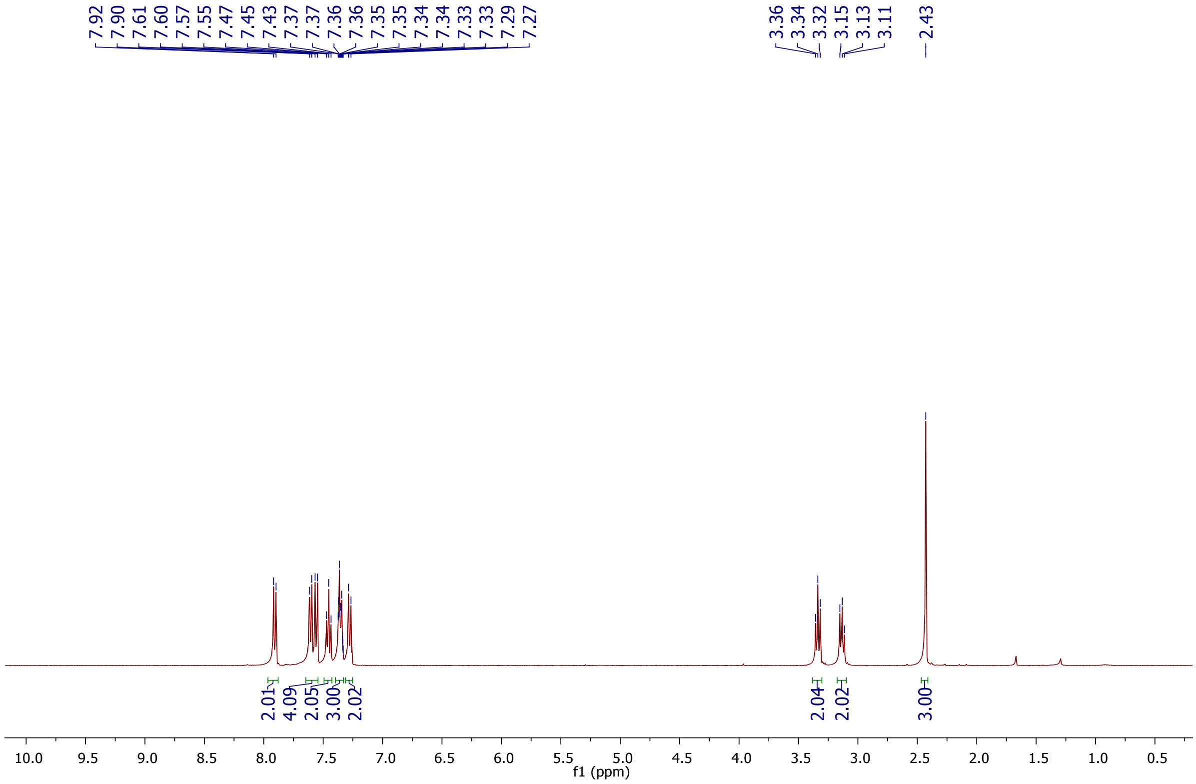


Figure S26. ^{1}H and ^{13}C NMR spectra of **5s**.





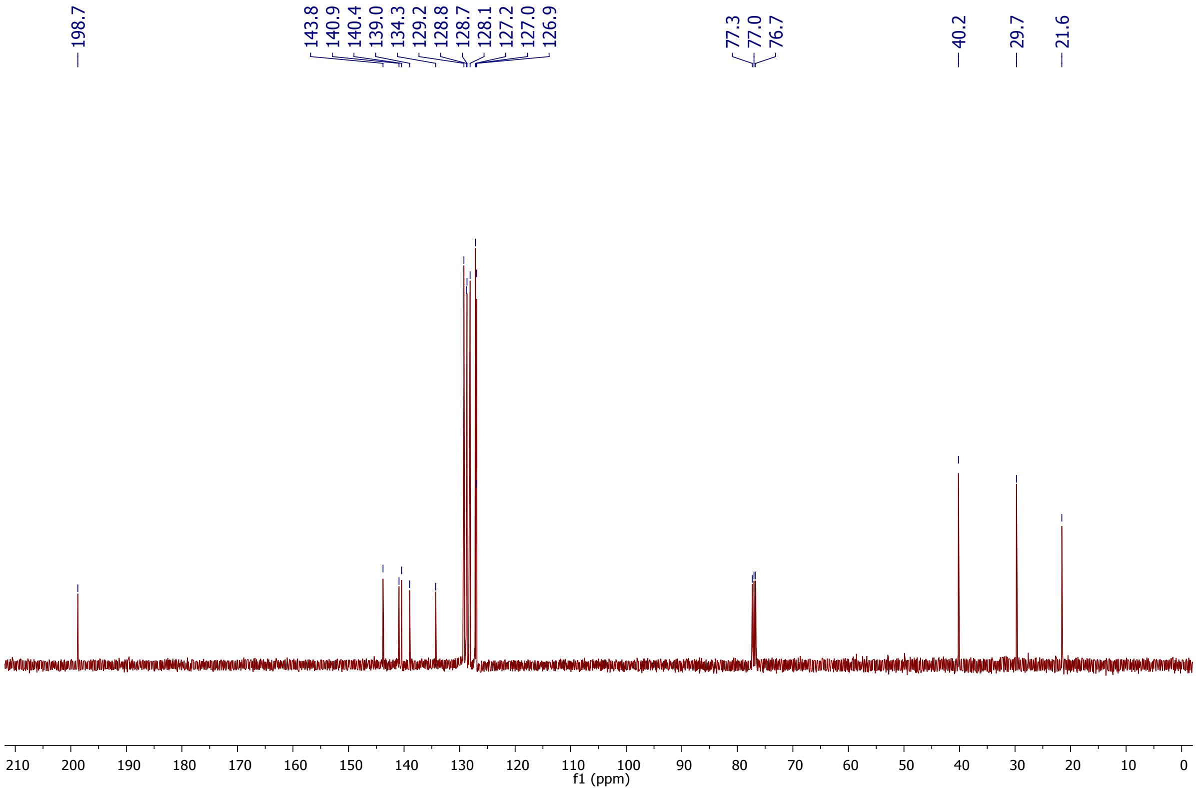
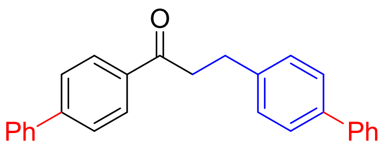
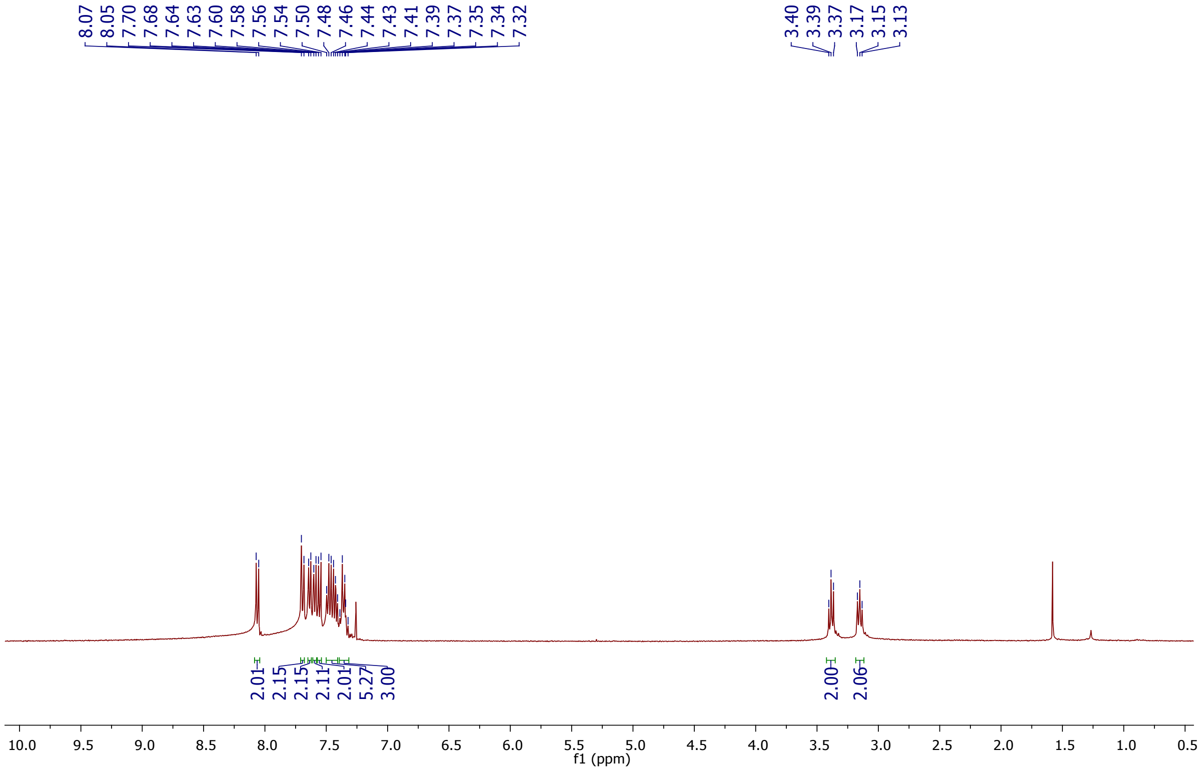


Figure S27. ^{1}H and ^{13}C NMR spectra of **5t**.





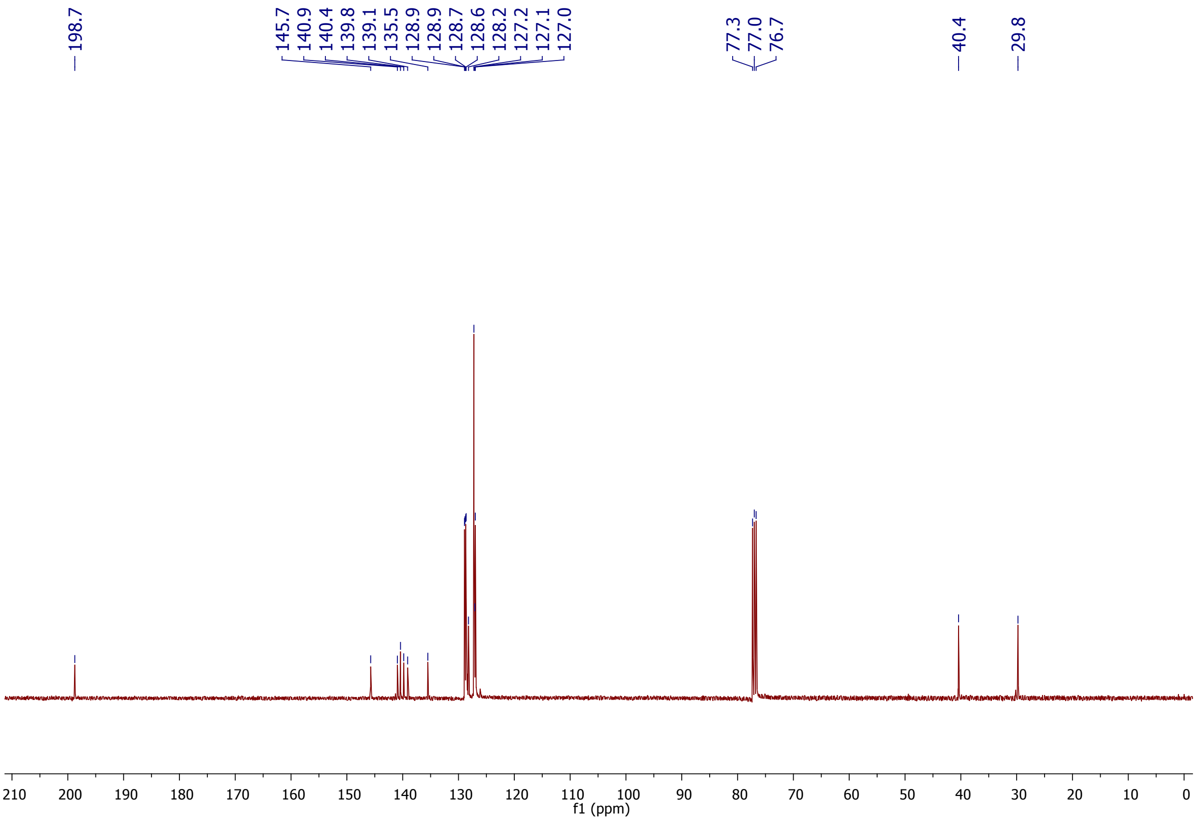


Figure S28. ^{1}H and ^{13}C NMR spectra of **5u**.