Supporting Information for

Calcium carbide as a dehydrating agent for the synthesis of carbamates, glycerol carbonate, and cyclic carbonates from carbon dioxide

Qiao Zhang,[a] Hao-Yu Yuan,[b] Xiao-Tao Lin, [ab] Norihisa Fukaya,[a] Tadahiro Fujitani,[a] Kazuhiko Sato,[a] and Jun-Chul Choi*[ab]

[a] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

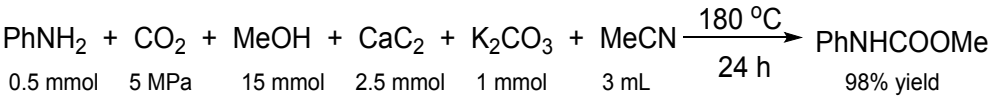
[b] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.

*Corresponding author. Email: junchul.choi@aist.go.jp. Tel: (+81) 029-861-9283.

Contents

Screening of reaction conditions of the synthesis of 1.

Standard reaction condition:



Tables S1−S4 investigated variation from standard condition.

Table S1. The influence of CaC_2

CaC_2	HPLC yield
1.25 mmol	73%
2.5 mmol	98%

Table S2. The influence of K_2CO_3

K_2CO_3	HPLC yield
0.05 mmol	39%
0.5 mmol	90%
1 mmol	98%
2 mmol	61%

Table S3. The influence of solvent

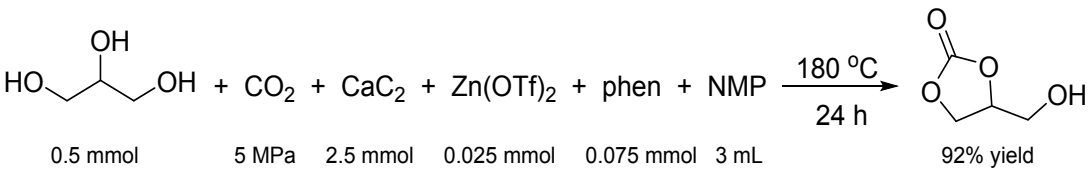
solvent	HPLC yield
MeCN	98%
DMAc	94%
NMP	90%
toluene	60%
MeOH	49%
MEK	48%
DMF	37%
THF	33%
PEG 400	26%
p-xylene	17%

Table S4. The influence of CO_2 pressure

CO_2 pressure	HPLC yield
1 MPa	80%
3 MPa	91%
5 MPa	98%

Screening of reaction conditions of the synthesis of glycerol carbonate.

Standard reaction condition:



Tables S5−S6 investigated variation from standard condition.

Table S5. The influence of CaC_2

CaC_2	^{1}H NMR yield
1.25 mmol	69%
2.5 mmol	92%

Table S6. The influence of CO_2 pressure

CO_2 pressure	^{1}H NMR yield
1 MPa	46%
3 MPa	72%
5 MPa	92%

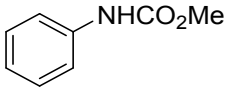
Table S7. The influence of high temperature (210 °C) on the yields.

Time (h)	^{1}H NMR yield
2	68%
4	91%

Table S8. Investigation of turnover numbers (TON).

$Zn(OTf)_2$ (mmol)	phen (mmol)	^{1}H NMR yield	TON
0.025	0.075	92%	18.4
0.005	0.015	49%	49

Product **1**.

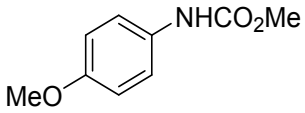


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.64 (s, 1H), 7.46 (d, 2H, J = 8.0 Hz), 7.28 (t, 2H, J = 7.4Hz), 6.98 (d, 1H, J = 7.4Hz), 3.67 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.5, 139.6, 129.2, 122.8, 118.6, 52.0.

GC−MS (m/z): 151 for $C_8H_{11}NO_3$.

Product **2**.

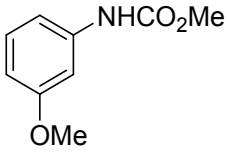


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.41 (s, 1H), 7.34 (d, 2H, J = 8.8 Hz), 6.85 (d, 2H, J = 7.6 Hz), 3.70 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 155.2, 154.6, 132.6, 120.3, 114.4, 55.6, 51.9.

GC−MS (*m*/*z*): 181 for $C_9H_{11}NO_3$.

Product **3**.

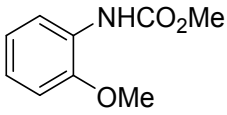


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.60 (s, 1H), 7.19−7.13 (m, 2H), 7.01 (d, 2H, J = 8.0 Hz), 6.57 (d, 1H, J = 8.0 Hz), 3.71 (s, 3H), 3.65 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 159.6, 153.9, 140.3, 129.5, 110.5, 107.6, 104.1, 54.9, 51.6.

GC−MS (*m*/*z*): 181 for $C_9H_{11}NO_3$.

Product **4**.

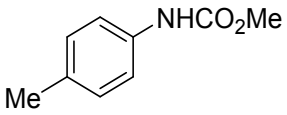


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.40 (s, 1H), 7.63 (d, 1H, J = 7.6 Hz), 7.08−6.99 (m, 2H), 6.93−6.88(m, 1H), 3.79 (s, 3H), 3.64 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.7, 150.6, 127.5, 124.7, 122.2, 120.7, 111.7, 56.0, 52.1.

GC−MS (*m*/*z*): 181 for $C_9H_{11}NO_3$.

Product **5**.

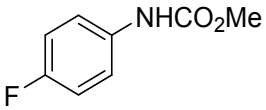


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.50 (s, 1H), 7.32 (d, 2H, J = 8.0 Hz), 7.07 (d, 2H, J = 7.6 Hz), 3.64 (s, 3H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.1, 136.6, 131.2, 129.2, 118.3, 51.5, 20.4.

GC−MS (*m*/*z*): 165 for $C_9H_{11}NO_2$.

Product **6**.

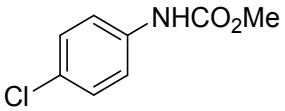


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.68 (s, 1H), 7.47−7.43 (m, 2H), 7.14−7.10 (m, 2H), 3.65 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 159.2, 156.9. 154.5, 136.0, 120.3, 115.9, 115.7, 52.1.

GC−MS (*m*/*z*): 169 for $C_8H_8NO_2F$.

Product **7**.

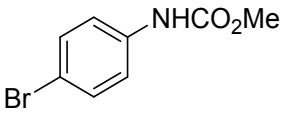


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.77 (s, 1H), 7.49−7.47 (m, 2H), 7.35−7.32 (m, 2H), 3.67 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.4, 138.6, 129.1, 126.5, 120.1, 52.2.

GC−MS (*m*/*z*): 185 for $C_8H_9NO_2Cl$.

Product **8**.

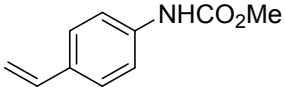


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.78 (s, 1H), 7.47−7.41 (m, 4H), 3.66 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.3, 139.0, 131.9, 120.4, 114.3, 52.2.

GC−MS (*m*/*z*): 231 for $C_8H_9NO_2Br$.

Product **9**.

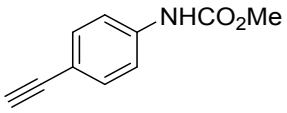


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.72 (s, 1H), 7.46−7.38 (m, 4H), 6.69−6.62 (m, 1H), 5.71 (d, 2H), 5.15 (d, 2H), 3.67 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.0, 139.0, 136.2, 131.5, 126.7, 118.2, 112.5, 51.7.

GC−MS (*m*/*z*): 177 for $C_{10}H_{11}NO_2$.

Product **10**.

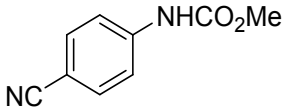


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.88 (s, 1H), 7.47 (d, 2H, J = 8.8 Hz), 7.40 (d, 2H, J = 8.8 Hz), 4.06 (s, 1H), 3.68 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.3, 140.3, 132.9, 118.3, 115.7, 84.1, 80.0, 52.3.

GC−MS (*m*/*z*): 175 for $C_{10}H_9NO_2$.

Product **11**.

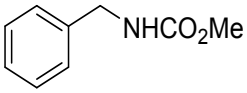


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.20 (s, 1H), 7.75 (d, 2H, J = 8.8 Hz), 7.63 (d, 2H, J = 8.8 Hz), 3.71 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.2, 144.1, 133.8, 119.6, 118.5, 104.5, 52.5.

GC−MS (*m*/*z*): 176 for $C_9H_8N_2O_2$.

Product **12**.

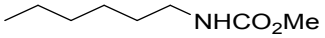


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.71 (s, 1H), 7.39−7.36 (m, 2H), 7.31−7.27 (m, 3H), 4.24 (d, 2H), 3.61 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 157.4, 140.3, 128.7, 127.5, 127.2, 51.8, 44.3.

GC−MS (*m*/*z*): 165 for $C_9H_{11}NO_2$.

Product **13**.

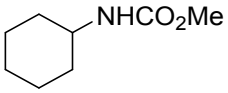


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.09 (s, 1H), 3.50 (s, 3H), 2.95 (q, 2H, J = 6.2 Hz), 1.37−1.24 (m, 8H), 0.86 (t, 3H, J = 7.2 Hz).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 157.1, 51.5, 31.4, 29.9, 29.6, 26.6, 22.5, 14.4.

GC−MS (*m*/*z*): 159 for $C_8H_{17}NO_2$.

Product **14**.

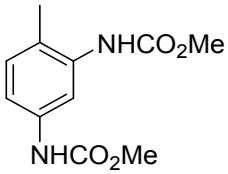


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.99 (s, 1H), 3.49 (s, 3H), 3.24−3.22 (m, 1H), 1.74−1.64 (m, 4H), 1.55−1.51 (m, 1H), 1.24−1.08 (m, 5H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 155.8, 50.9, 49.4, 32.7, 25.1, 24.6.

GC−MS (*m*/*z*): 157 for $C_8H_{15}NO_2$.

Product **15**.

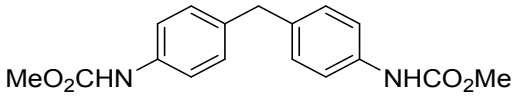


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.52 (s, 1H), 8.79 (s, 1H), 7.49 (s, 1H), 7.17 (d, 1H, J = 8.0 Hz), 7.07 (d, 1H, J = 8.0 Hz), 3.65 (s, 6H), 2.12 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 155.2, 154.4, 137.6, 136.9, 130.7, 126.1, 115.5, 115.4, 52.1, 52.0, 17.5.

GC−MS (*m*/*z*): 174 for the corresponding isocyanate.

Product **16**.

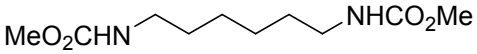


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.54 (s, 2H), 7.34 (d, 4H, J = 8.0 Hz), 7.10 (m, 4H), 3.78 (s, 2H), 3.63 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 154.4, 137.5, 135.9, 129.3, 118.8, 52.0.

GC−MS (*m*/*z*): 250 for the corresponding isocyanate.

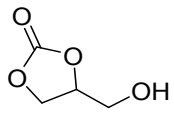
Product **17**.



^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.10 (s, 2H), 3.51 (s, 6H), 2.96−2.94 (m, 4H), 1.37 (s, 4H), 1.23 (s, 4H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 157.1, 51.6, 29.8, 26.4.

Product **18**.

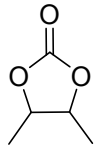


^{1}H NMR (DMSO-d_6, 400 MHz) δ 5.27 (t, J = 5.6 Hz, 1H), 4.83-4.77 (m, 1H), 4.50 (dd, J = 8.4 Hz, 8.6 Hz, 1H), 4.29 (dd, J = 8.3 Hz, 8.1 Hz, 1H), 3.70-3.63 (m, 1H), 3.55-3.48 (m, 1H).

^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 155.6, 77.5, 66.2, 61.1.

GC-MS (*m/z*): 118 for $C_4H_6O_4$.

Product **19**.

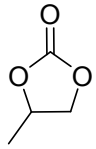


^{1}H NMR ($CDCl_3$, 400 MHz) cis-isomer: δ 4.89-4.78 (m, 2H), 1.39-1.33 (m, 6H); trans-isomer: δ 4.27-4.37 (m, 2H), 1.48-1.43 (m, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 154.6, 79.9, 76.0, 18.4, 14.4.

GC-MS (*m/z*): 116 for $C_5H_8O_3$.

Product **20**.

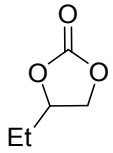


^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.90-4.80 (m, 1H), 4.55 (dd, J = 8.8 Hz, 7.7 Hz, 1H), 4.02 (dd, J = 8.7 Hz, 7.3 Hz, 1H), 1.49 (t, J=6.3 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 155.0, 73.5, 70.6, 19.5.

GC-MS (*m/z*): 102 for $C_4H_6O_3$.

Product **21**.

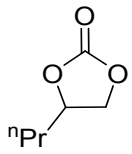


^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.70-4.62 (m, 1H), 4.52 (t, J = 8.2 Hz, 1H), 4.08 (dd, J = 8.4 Hz, 7.0 Hz, 1H), 1.90-1.70 (m, 1H), 1.04 (t, J = 7.4 Hz, 3H).

^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ 155.1, 78.0, 69.0, 27.0, 8.5.

GC-MS (*m/z*): 116 for $C_5H_8O_3$.

Product **22**.

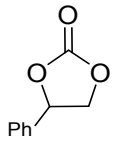


^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.75-4.67 (m, 1H), 4.52 (t, *J* = 8.3 Hz, 1H), 4.06 (dd, *J* = 8.7 Hz, 7.3 Hz, 1H), 1.86-1.76 (m, 1H), 1.71-1.60 (m, 1H), 1.56-1.35 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 155.1, 69.4, 35.9, 17.8, 13.6.

GC-MS (*m/z*): 131 for $C_6H_{10}O_3$.

Product **23**.



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.41 (m, 3H), 7.38-7.34 (m, 2H), 5.68 (dd, *J* = 8.0 Hz, 8.8 Hz, 1H), 4.80 (dd, *J* = 8.4 Hz, 9.4 Hz, 1H), 4.35 (dd, *J* = 8.0 Hz, 8.8 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 154.8, 135.8, 129.8, 129.3, 125.9, 78.0, 71.2.

GC-MS (*m/z*): 164 for $C_9H_8O_3$

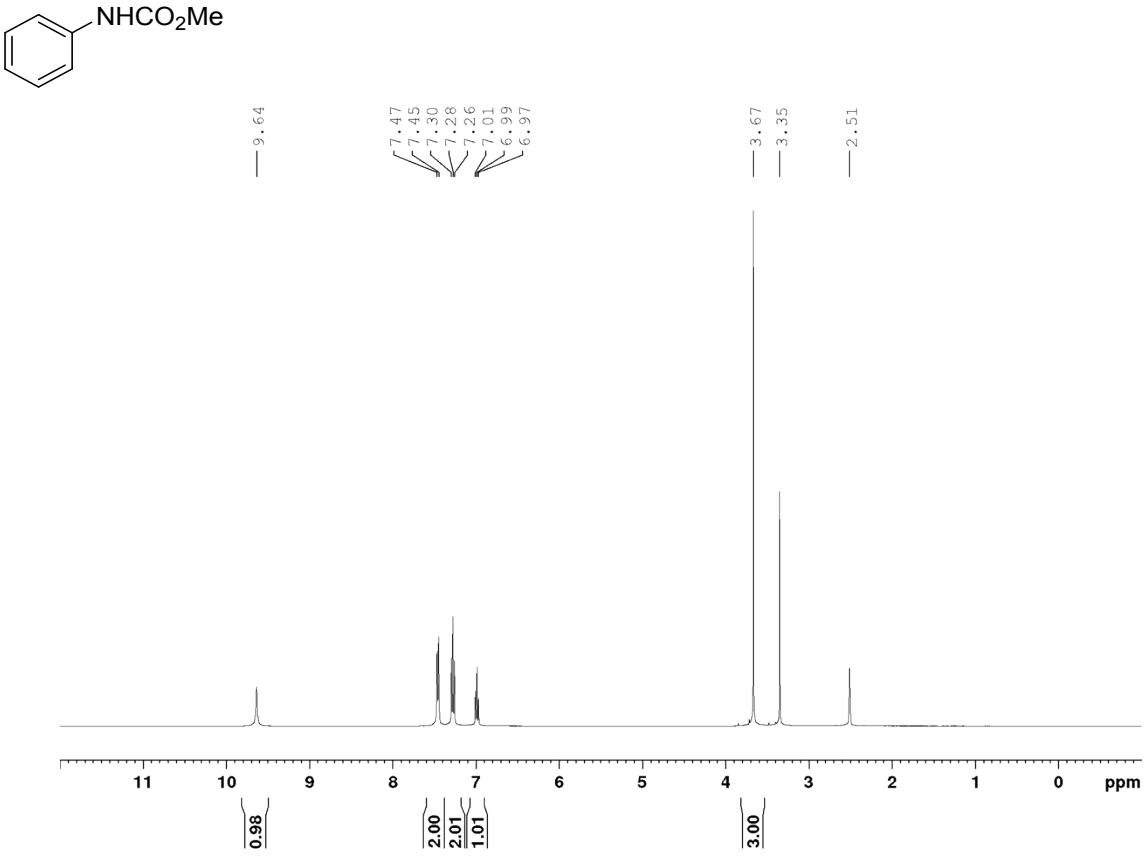


Figure S1. ^{1}H NMR (400 MHz, DMSO-d_6) of product **1**.

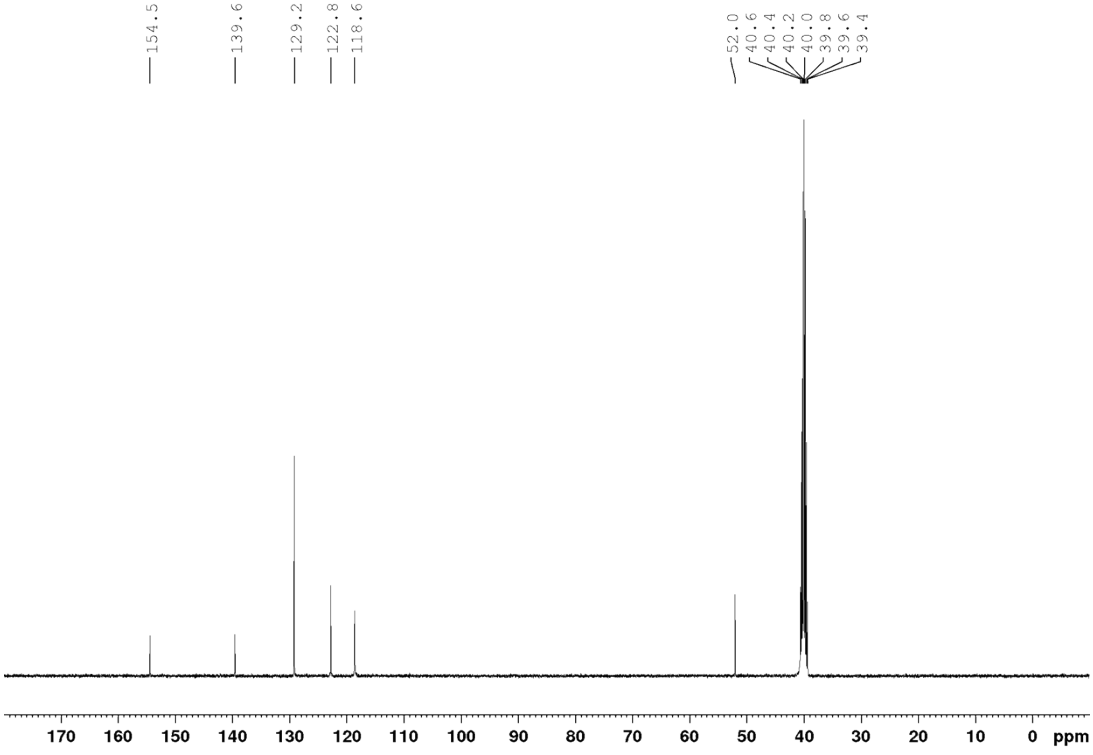


Figure S2. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **1**.

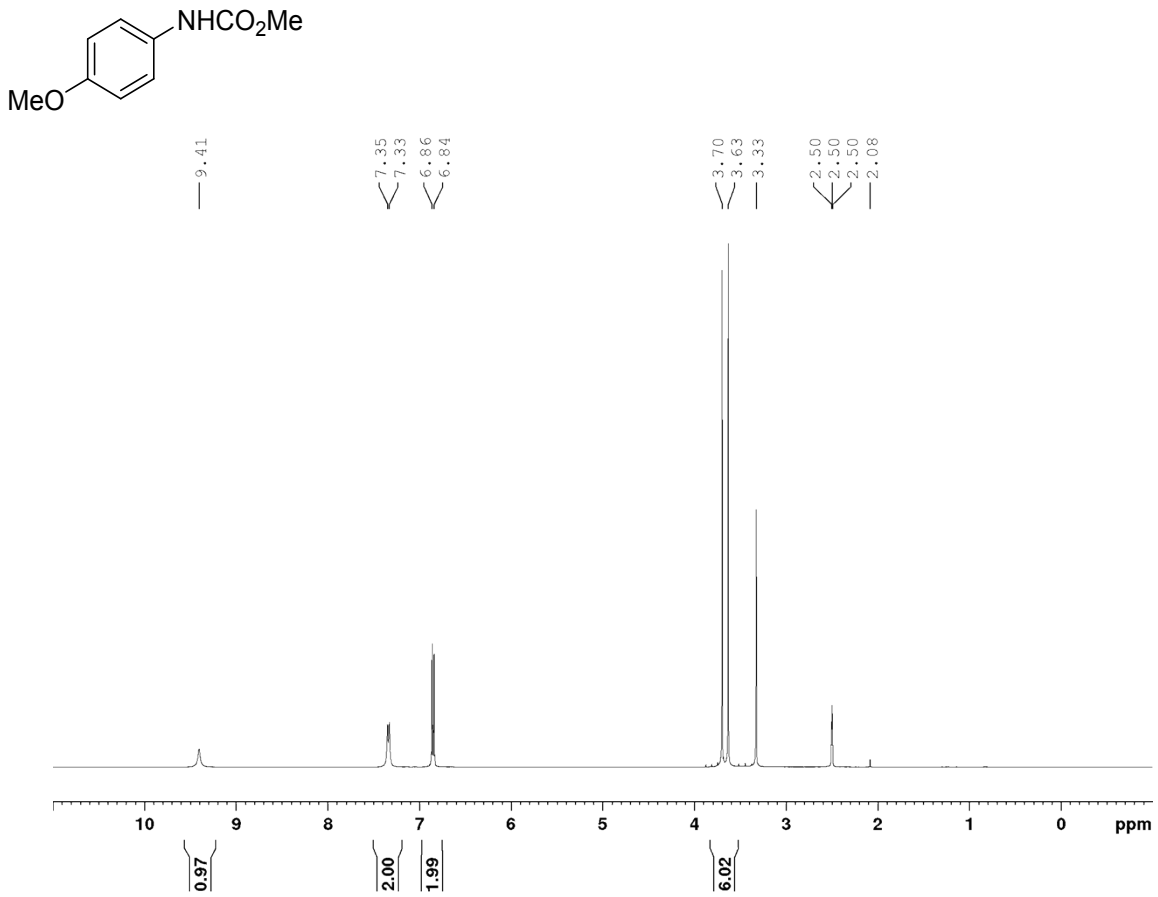


Figure S3. ^{1}H NMR (400 MHz, DMSO-d_6) of product **2**.

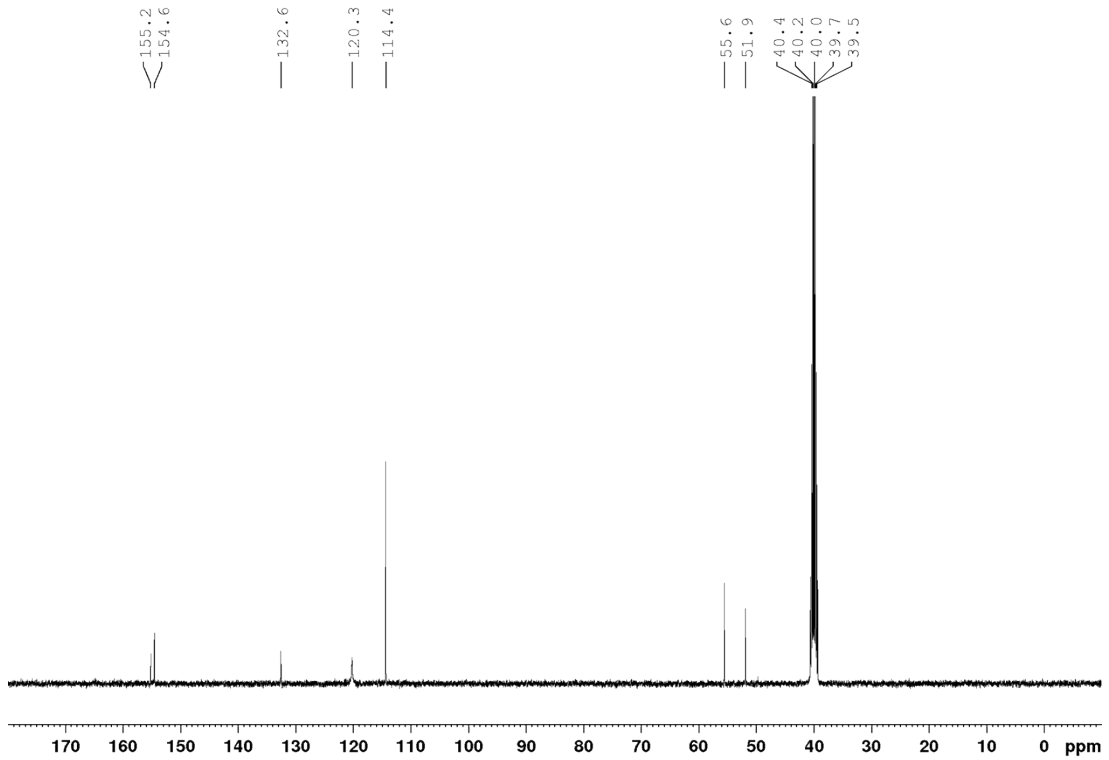
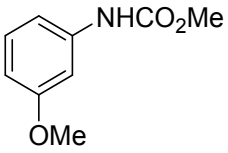


Figure S4. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **2**.



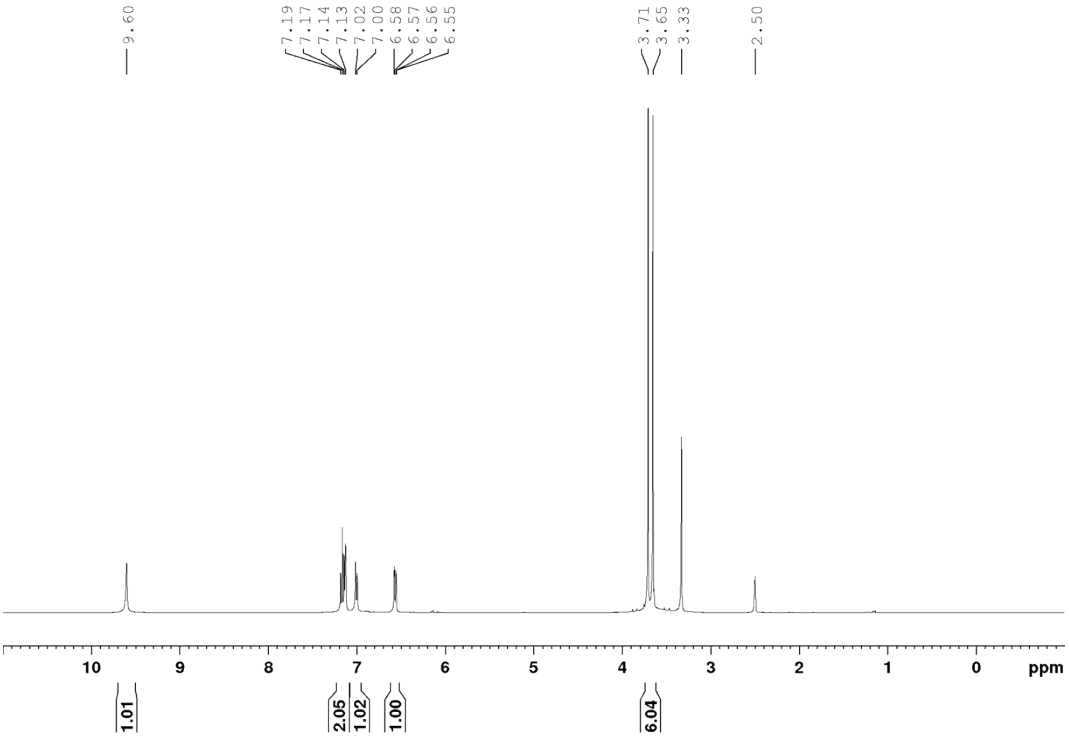


Figure S5. ^{1}H NMR (400 MHz, DMSO-d_6) of product **3**.

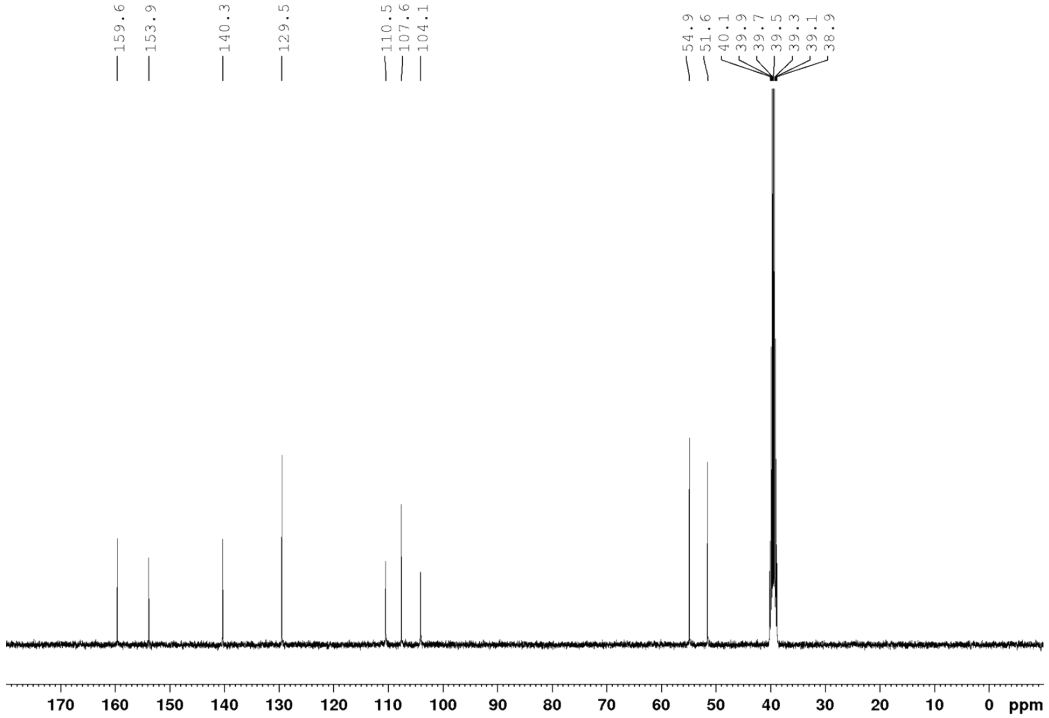


Figure S6. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **3**.

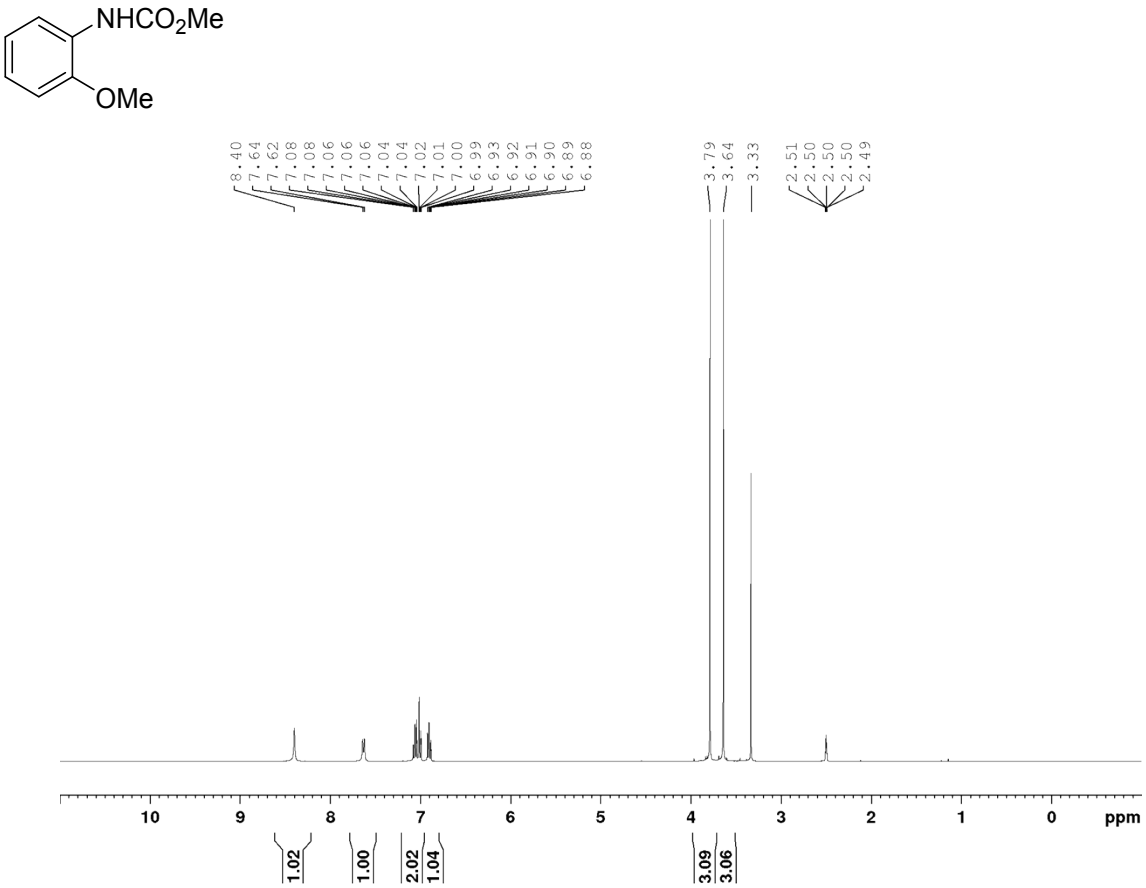


Figure S7. ^{1}H NMR (400 MHz, DMSO-d_6) of product **4**.

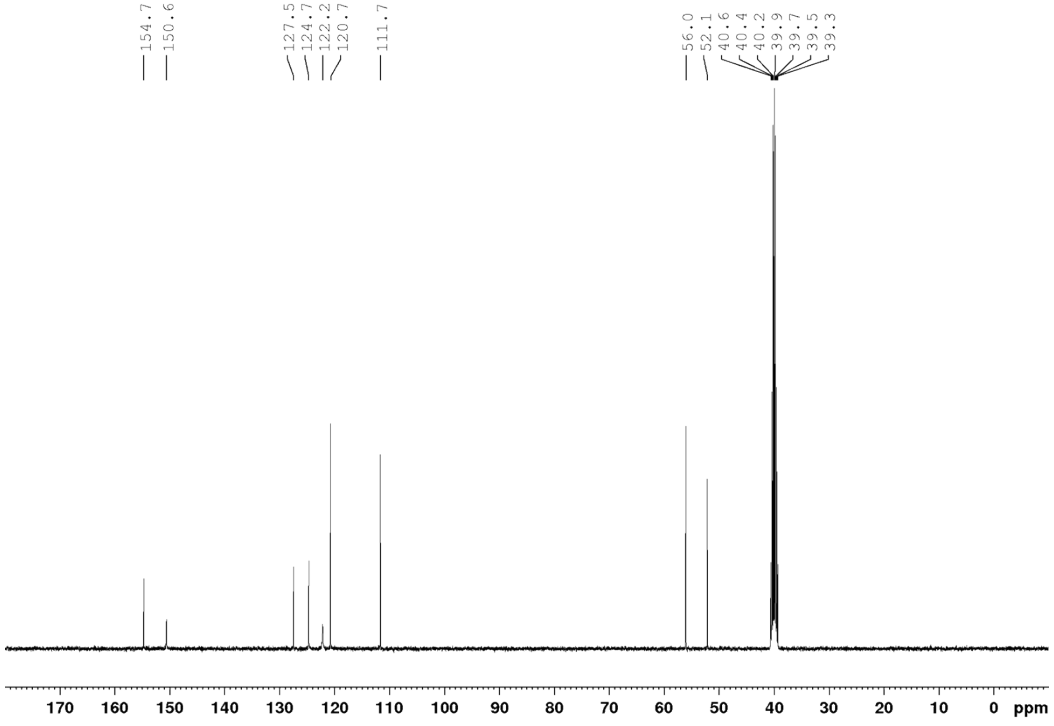


Figure S8. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **4**.

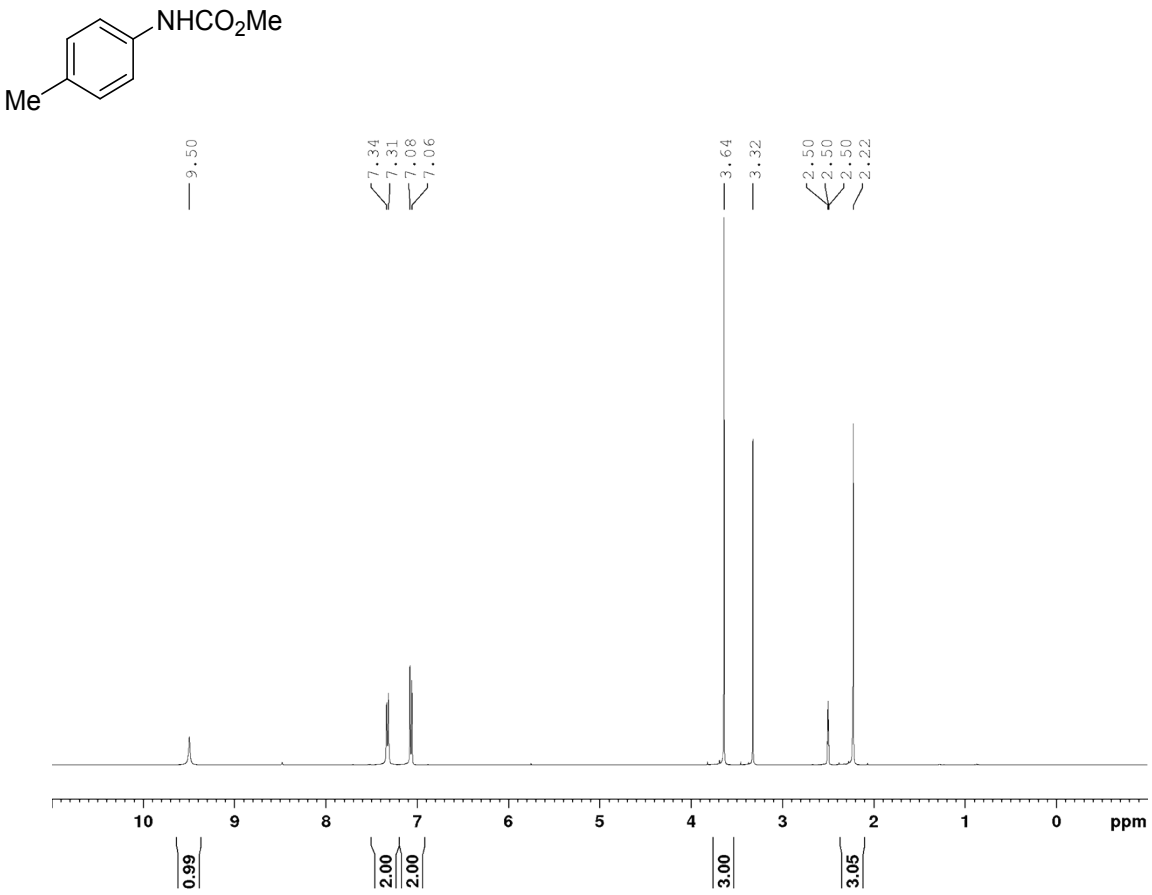


Figure S9. ^{1}H NMR (400 MHz, DMSO-d_6) of product **5**.

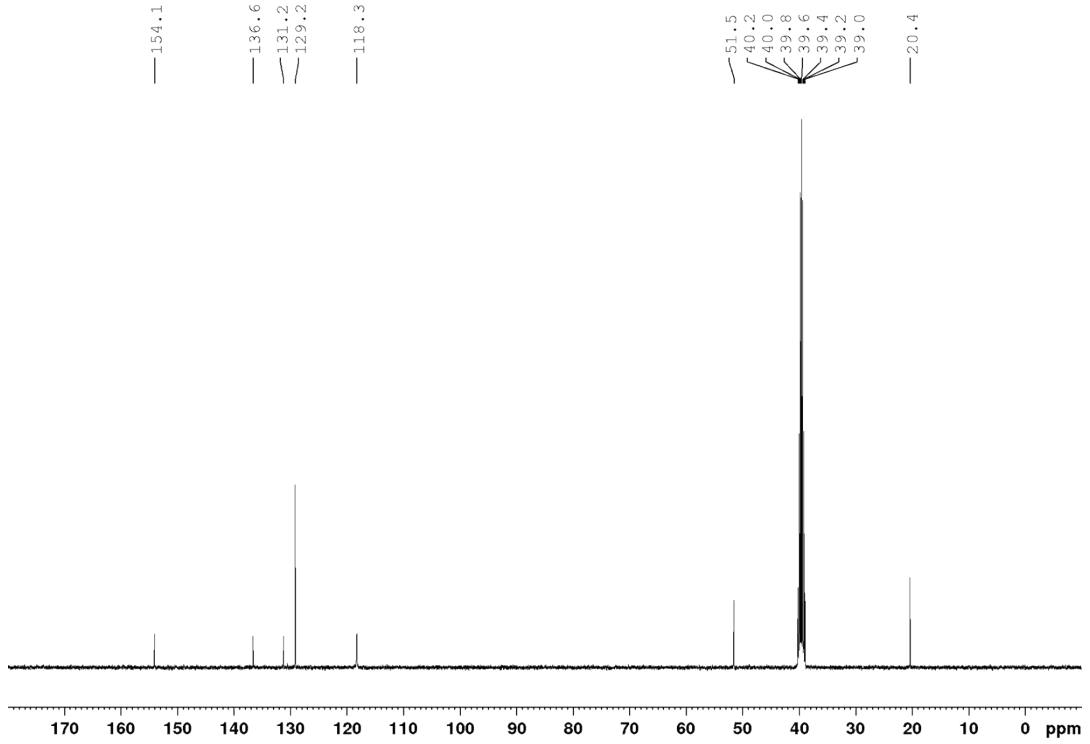


Figure S10. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **5**.

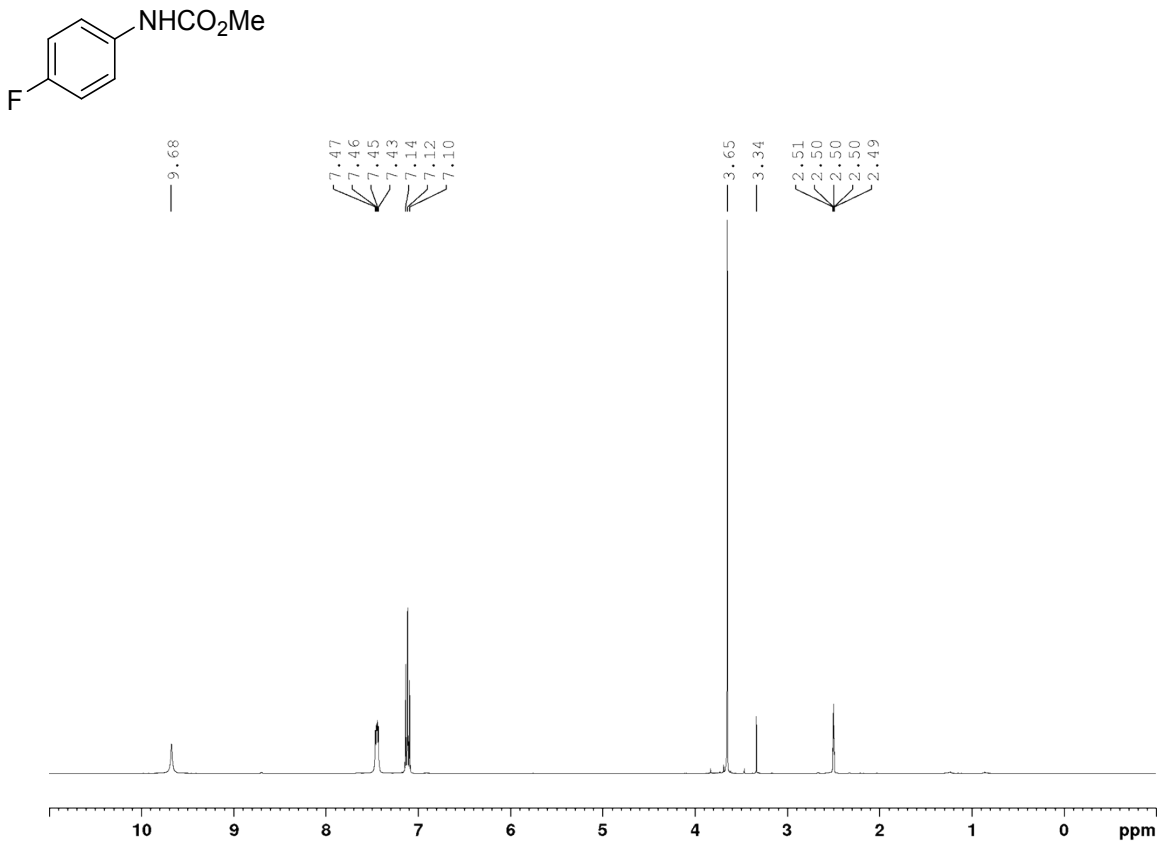


Figure S11. ^{1}H NMR (400 MHz, DMSO-d_6) of product **6**.

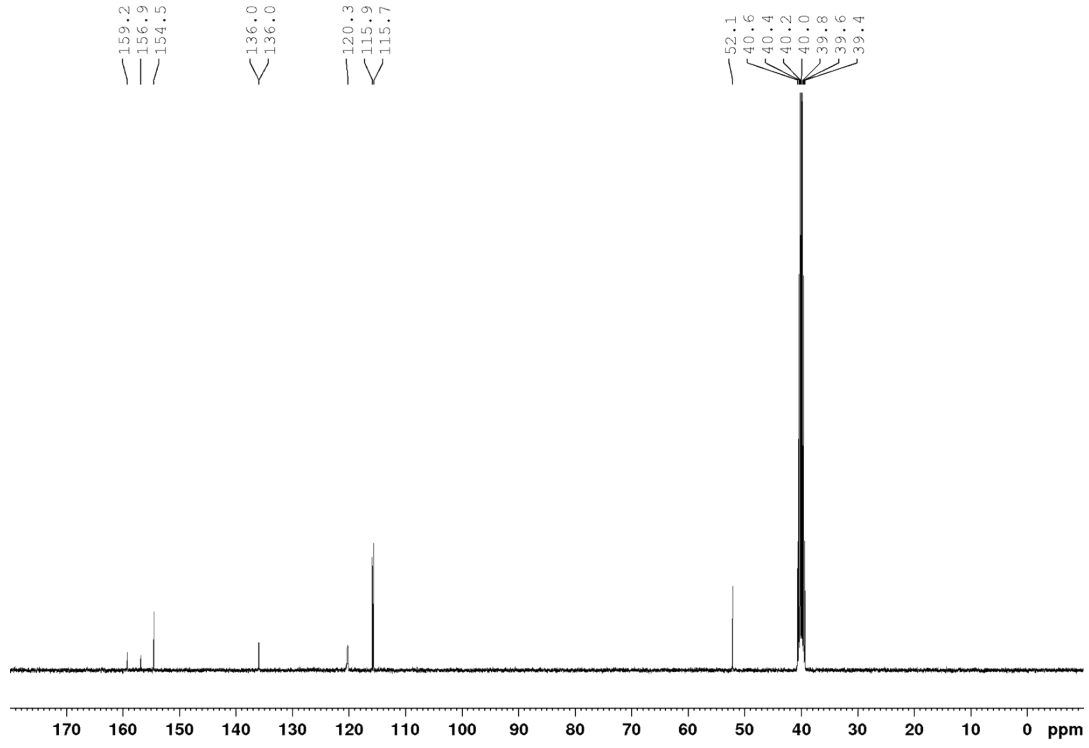
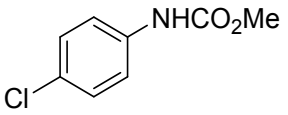


Figure S12. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **6**.



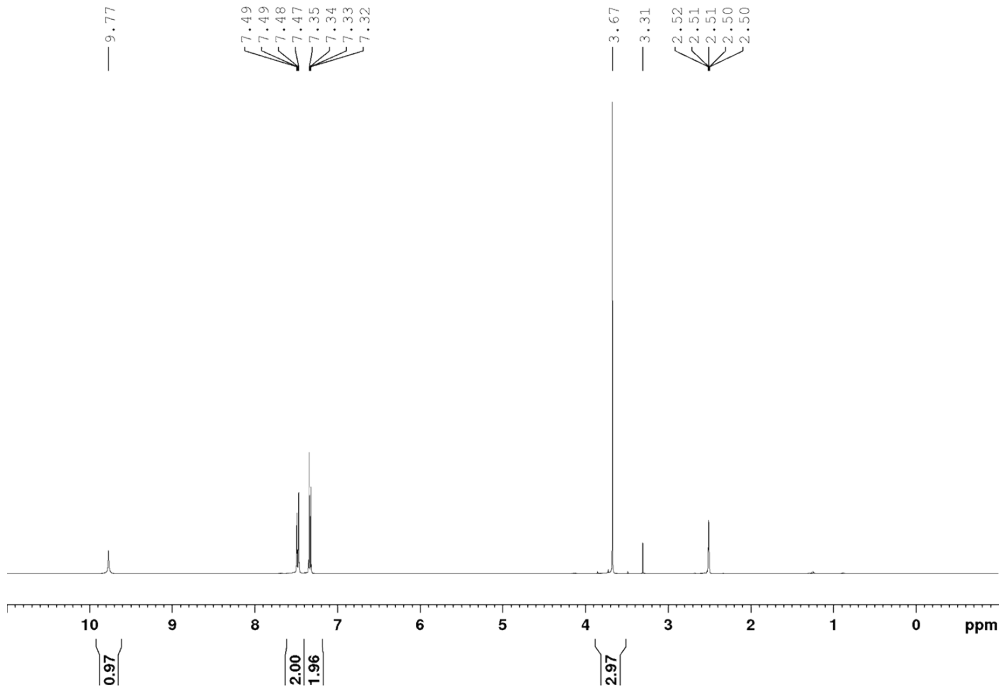


Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6) of product **7**.

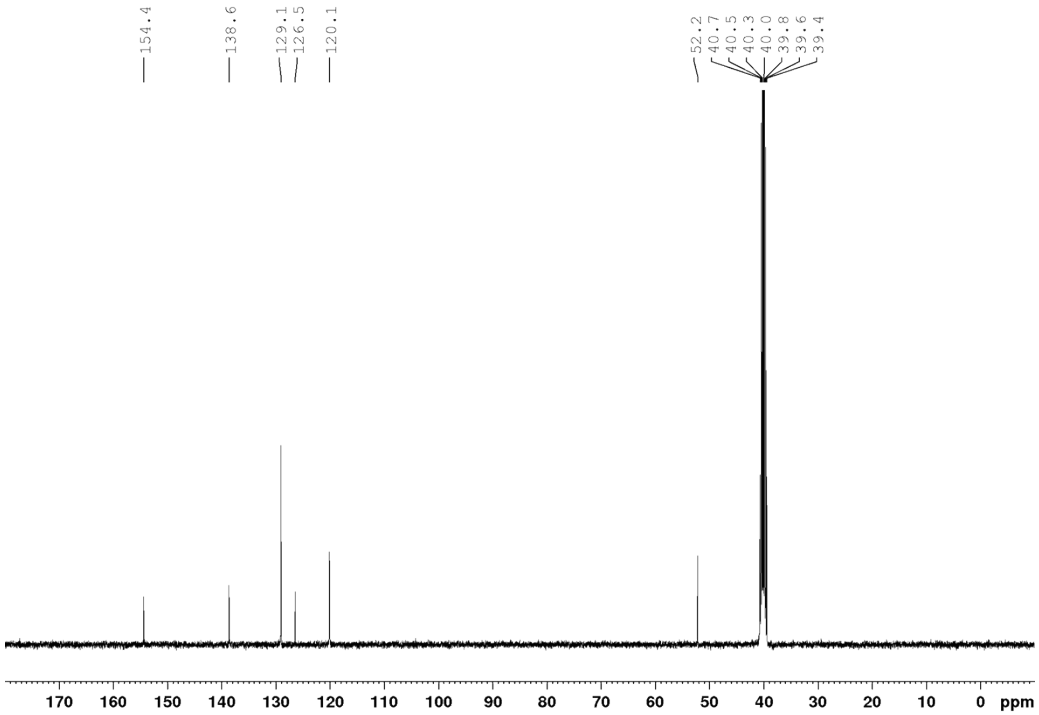


Figure S14. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **7**.

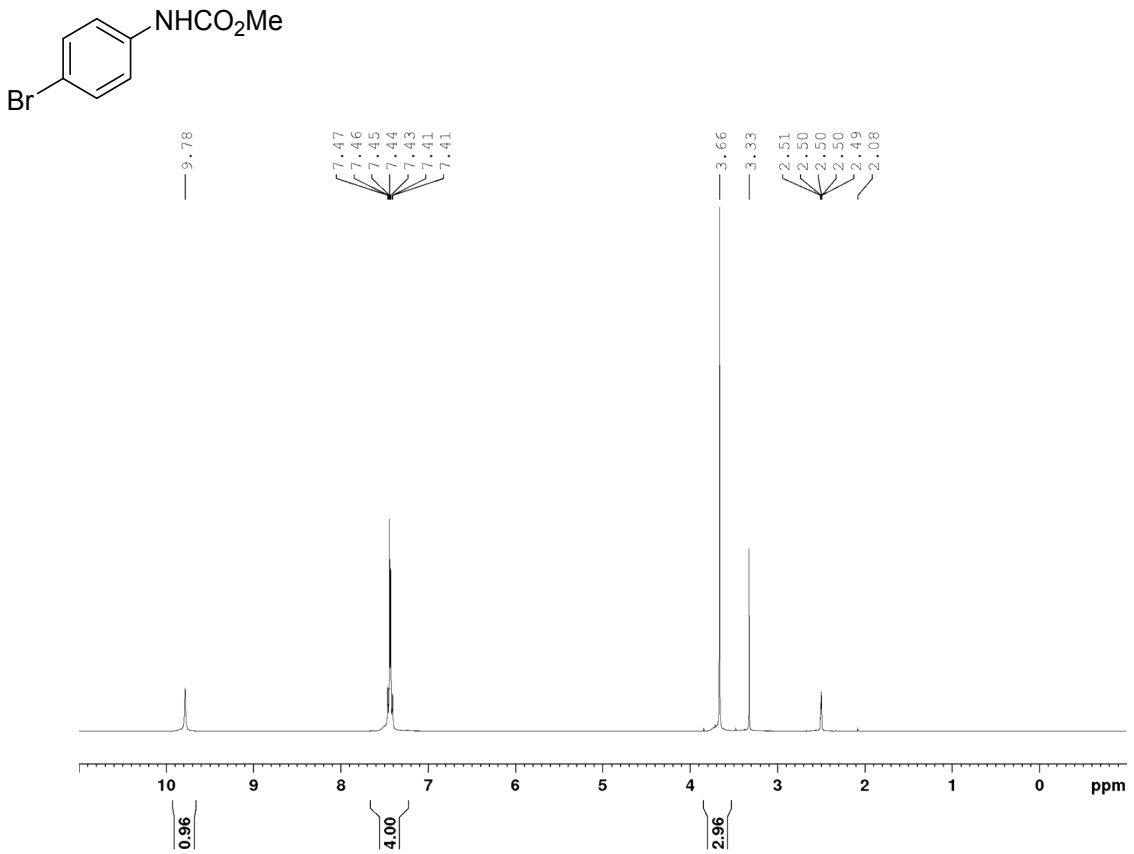


Figure S15. ^{1}H NMR (400 MHz, DMSO-d_6) of product **8**.

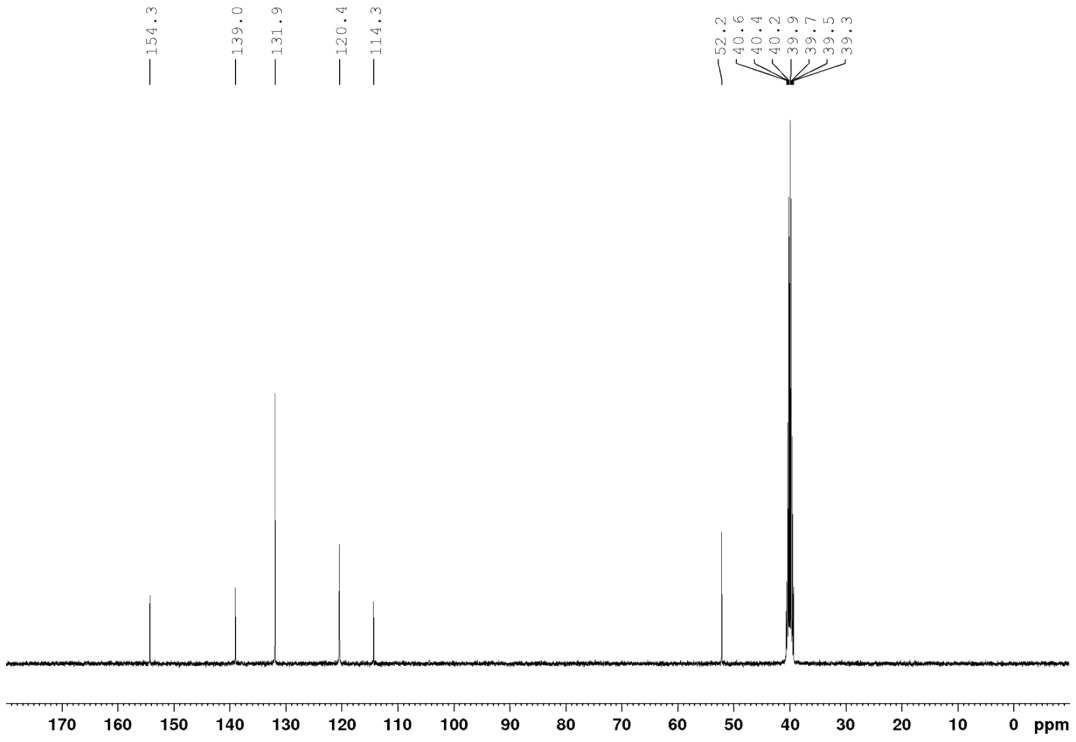


Figure S16. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **8**.

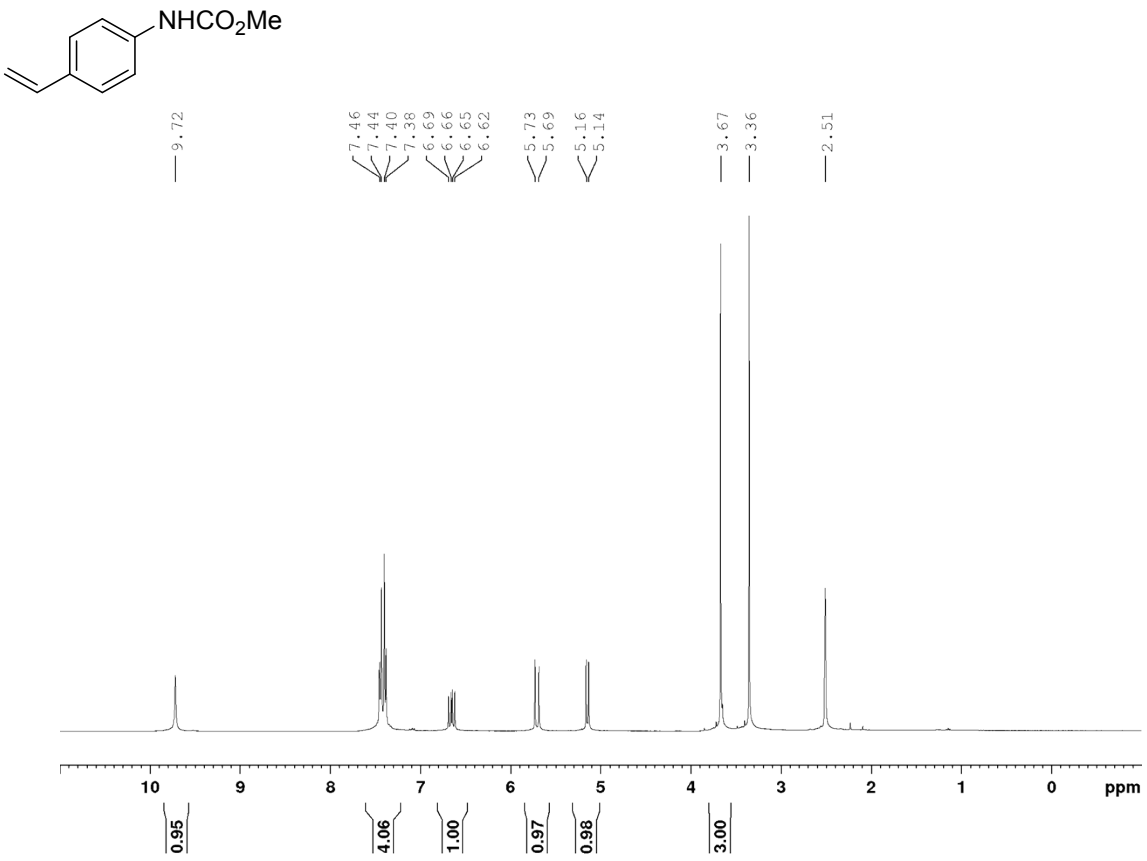


Figure S17. ^{1}H NMR (400 MHz, DMSO-d_6) of product **9**.

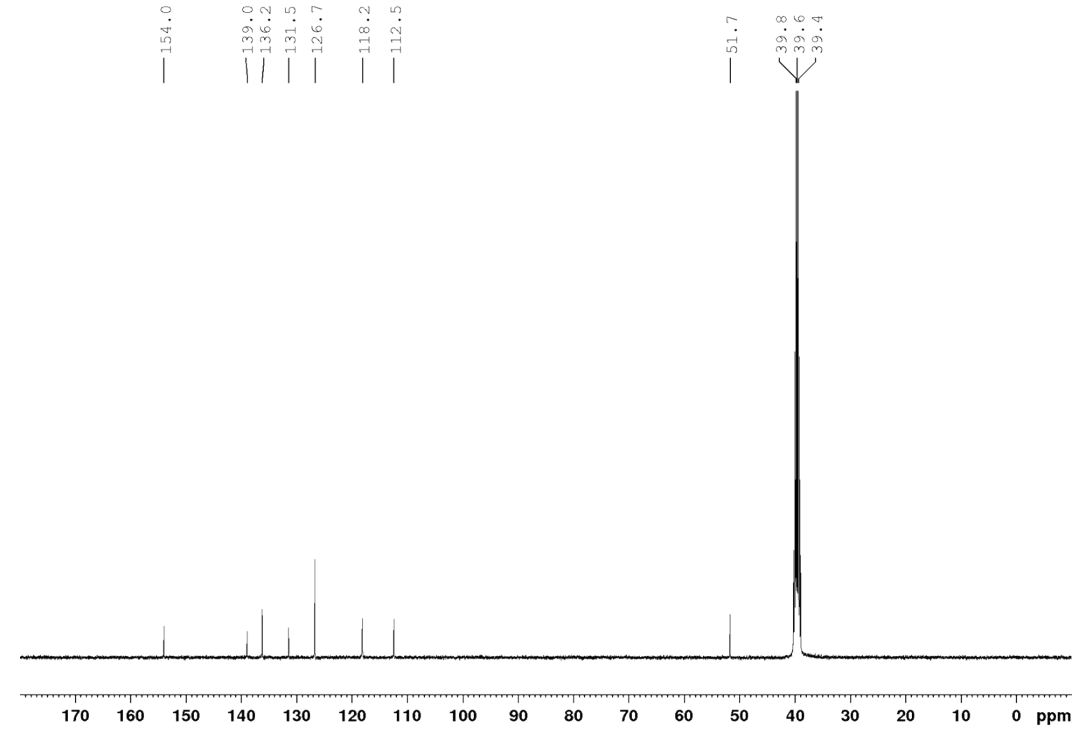


Figure S18. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **9**.

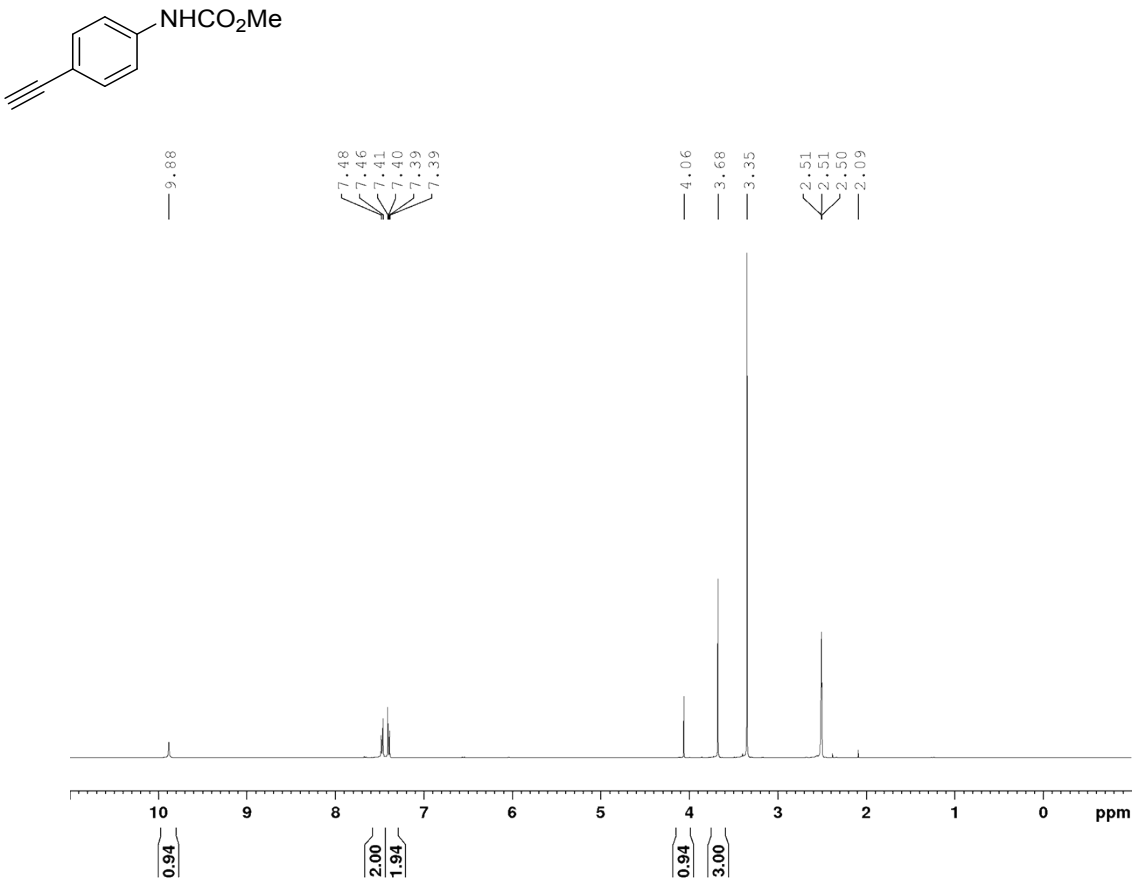


Figure S19. ^{1}H NMR (400 MHz, DMSO-d_6) of product **10**.

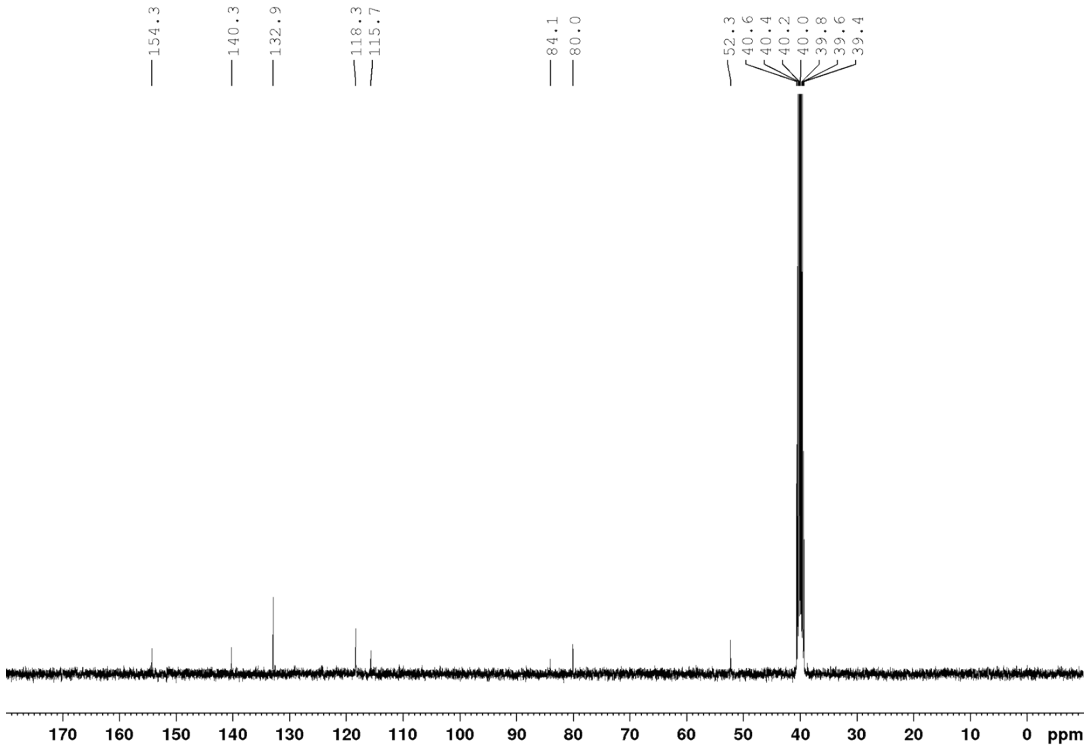


Figure S20. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **10**.

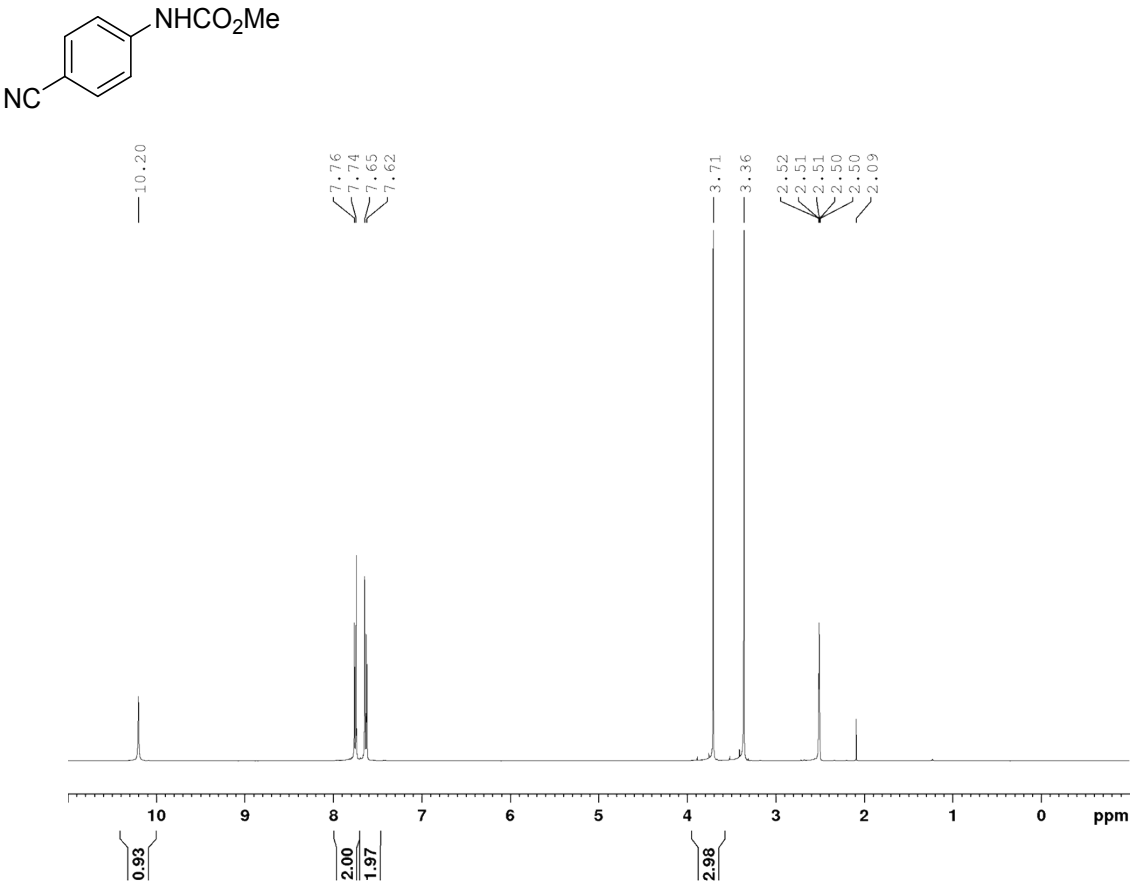


Figure S21. ^{1}H NMR (400 MHz, DMSO-d_6) of product **11**.

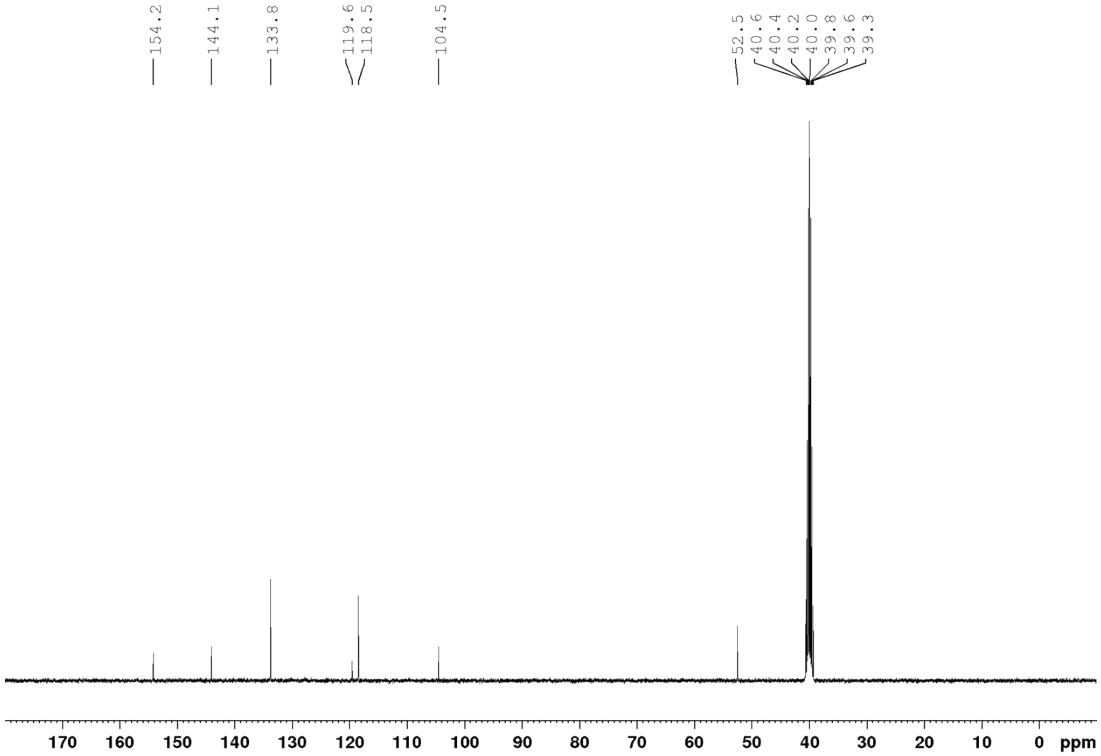


Figure S22. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **11**.

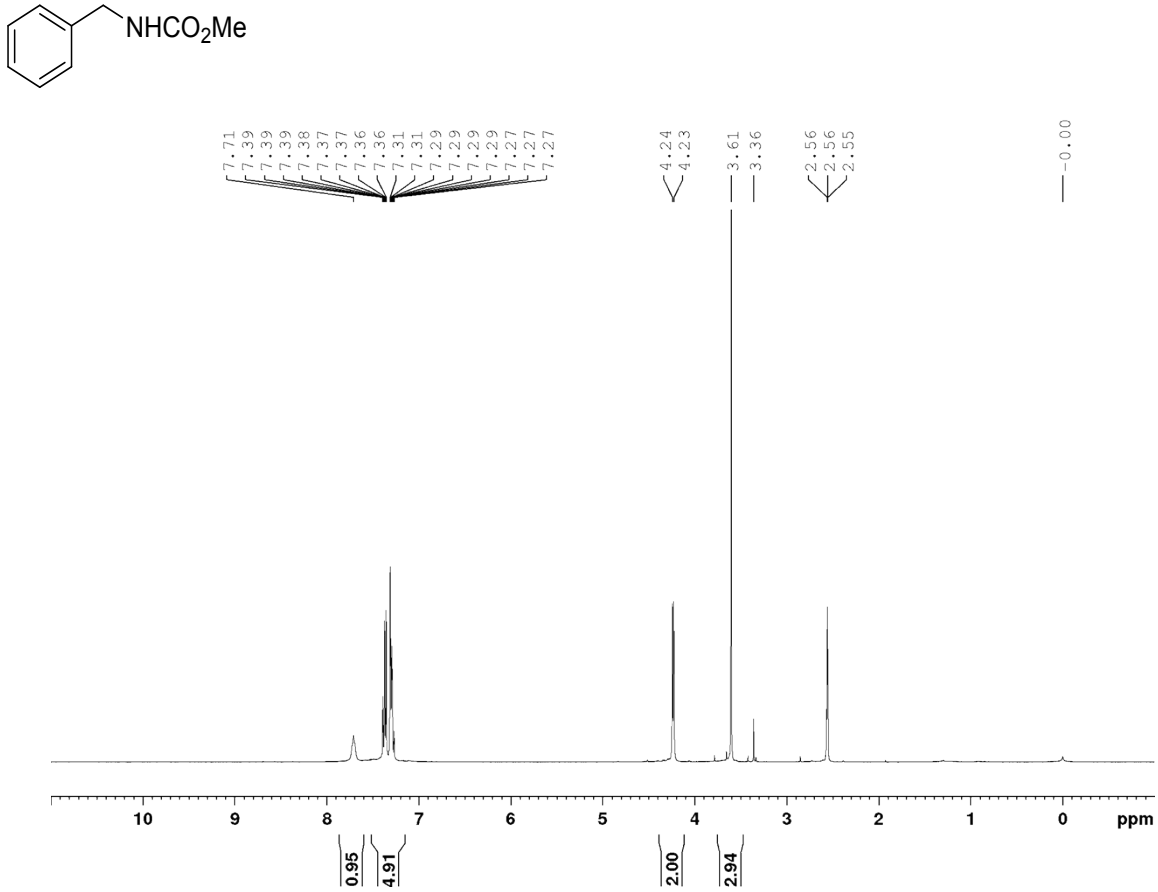


Figure S23. ^{1}H NMR (400 MHz, DMSO-d_6) of product **12**.

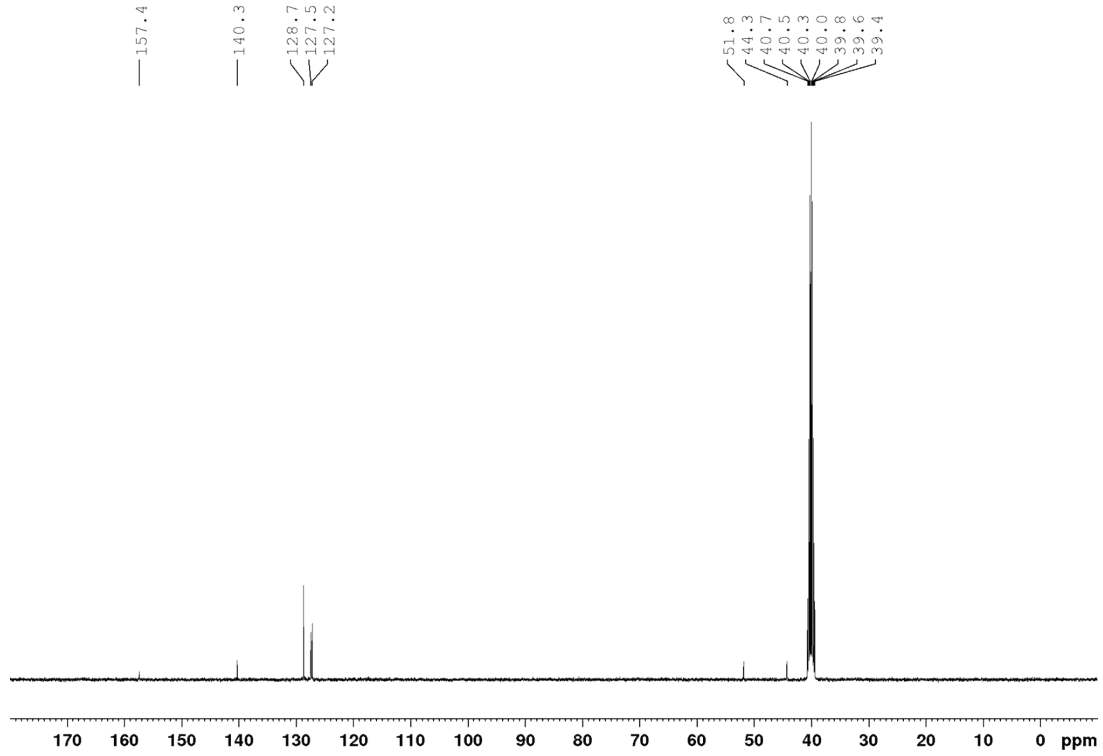


Figure S24. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **12**.

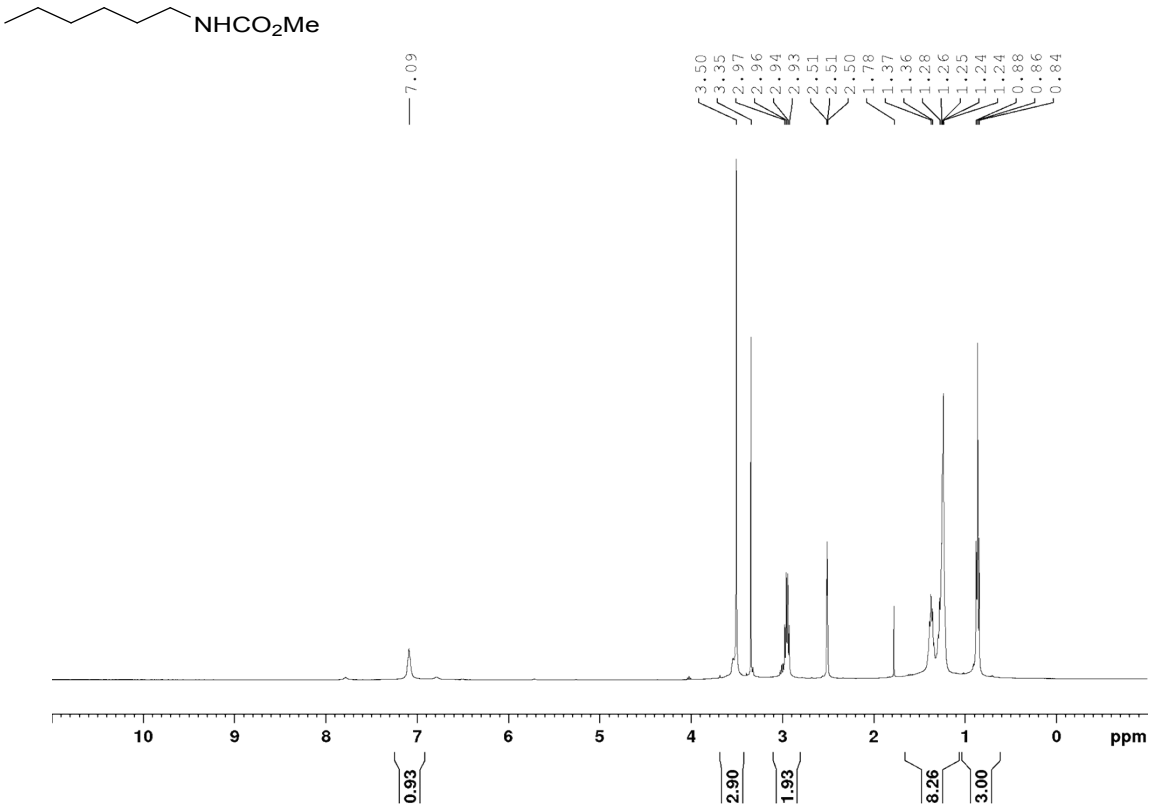


Figure S25. ^{1}H NMR (400 MHz, DMSO-d_6) of product **13**.

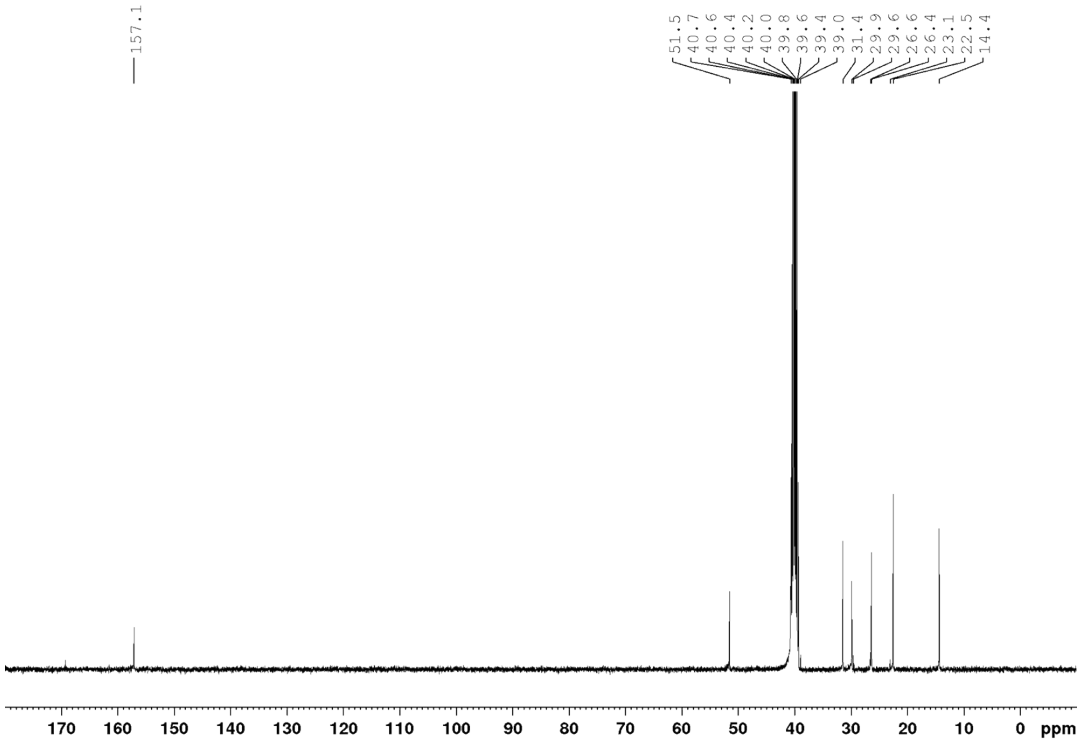


Figure S26. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **13**.

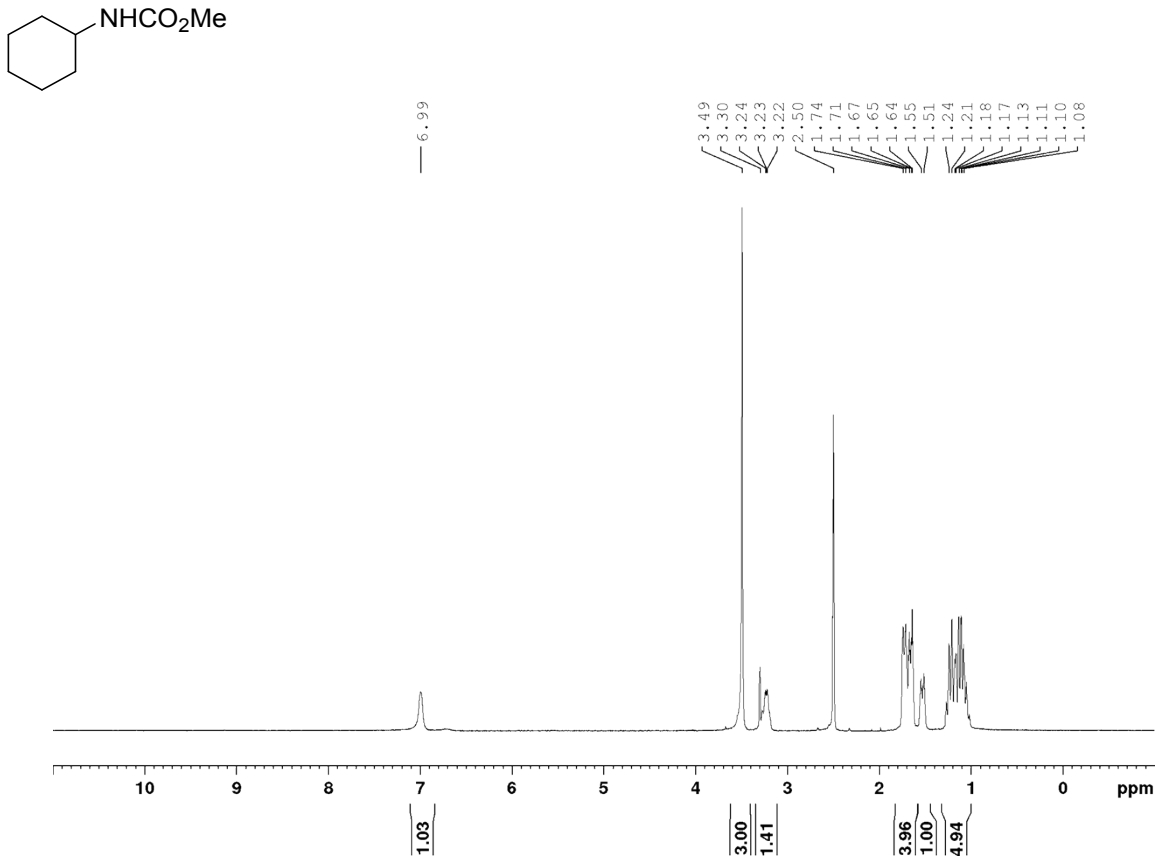


Figure S27. ^{1}H NMR (400 MHz, DMSO-d_6) of product **14**.

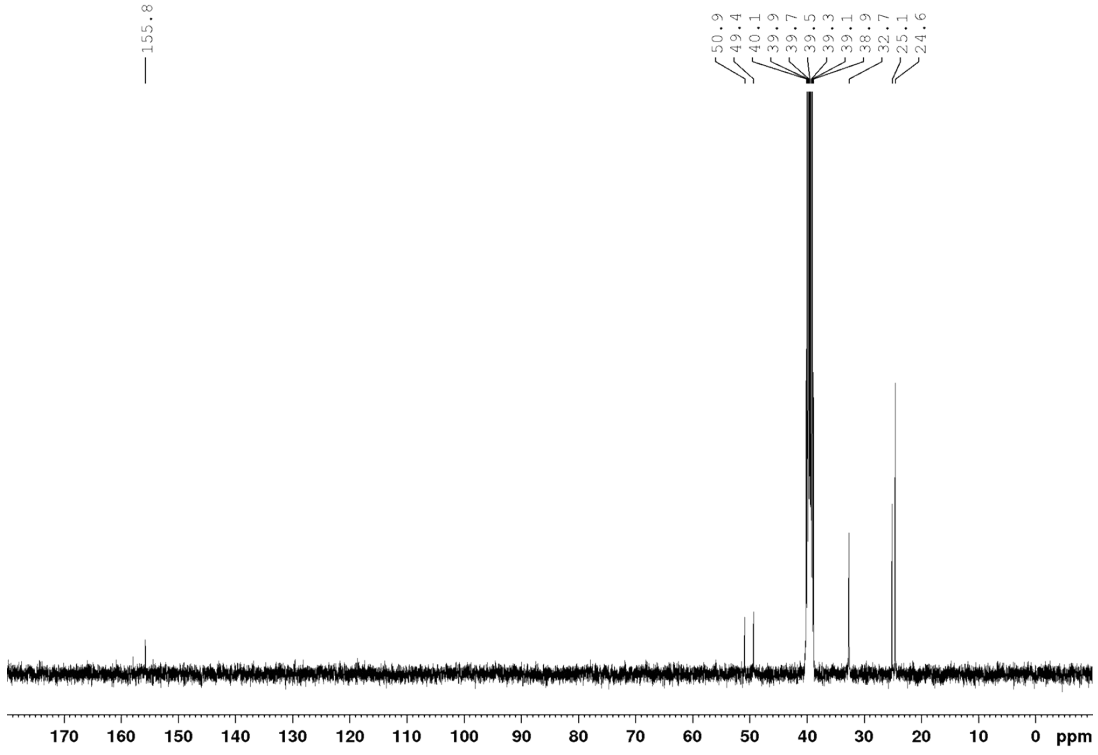


Figure S28. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **14**.

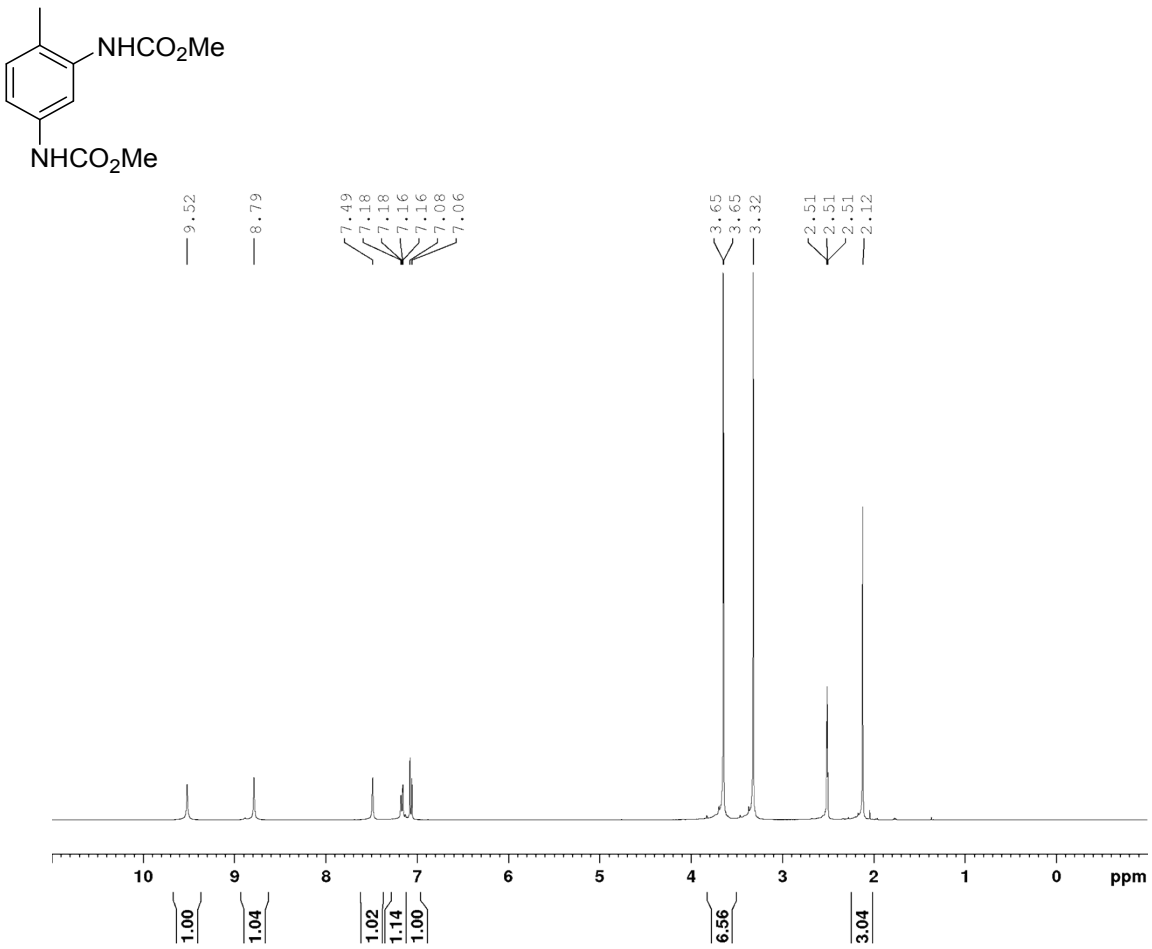


Figure S29. ^{1}H NMR (400 MHz, DMSO-d_6) of product **15**.

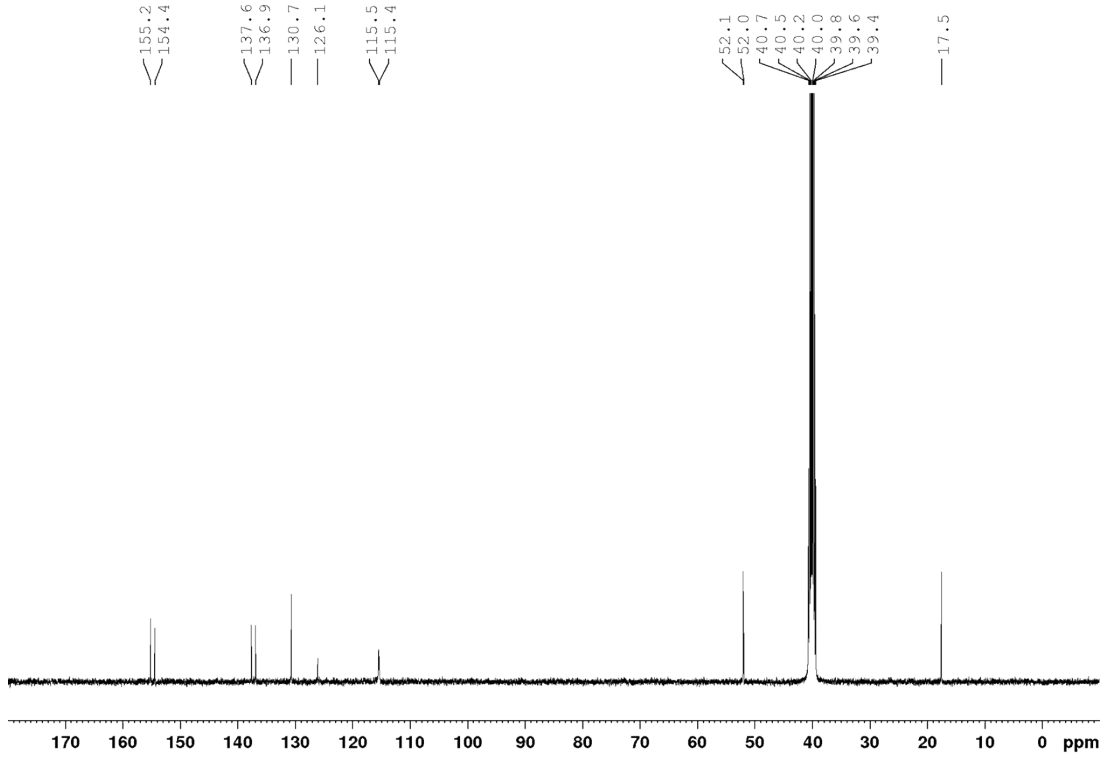


Figure S30. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **15**.

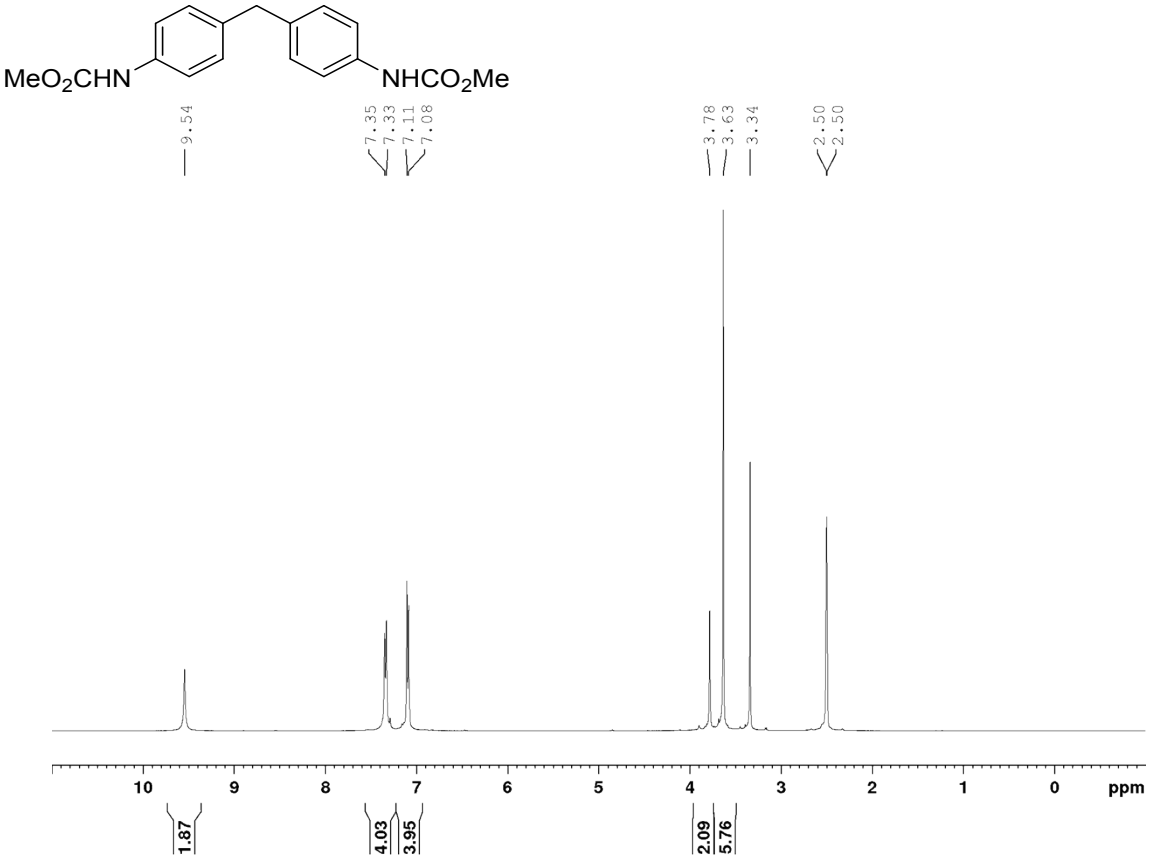


Figure S31. ^{1}H NMR (400 MHz, DMSO-d_6) of product **16**.

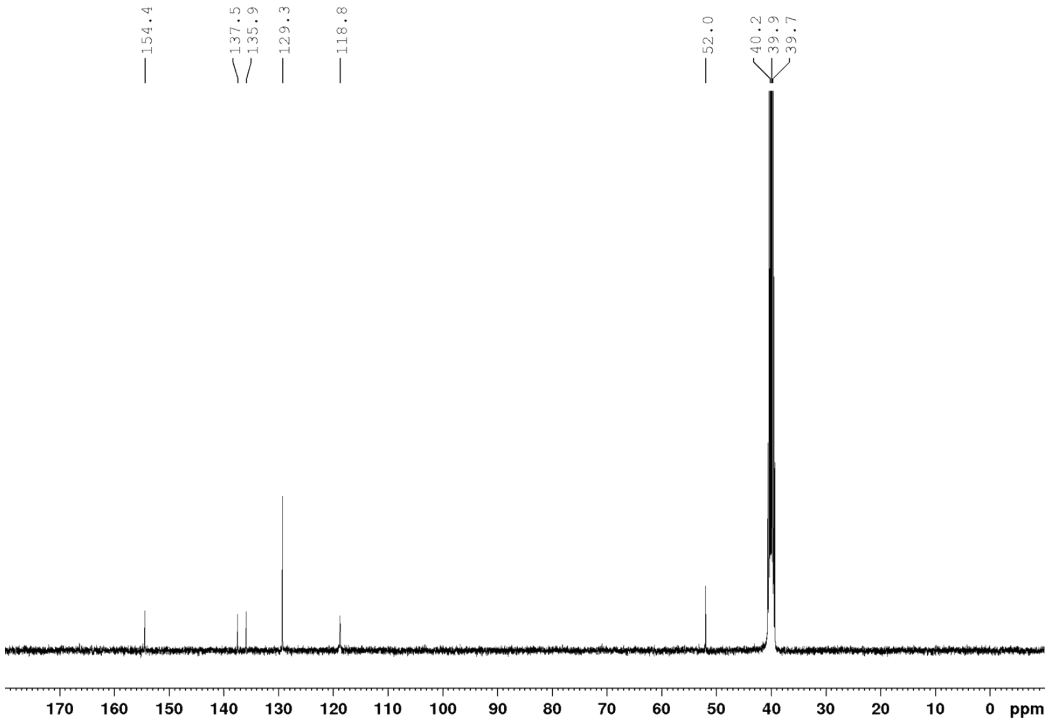
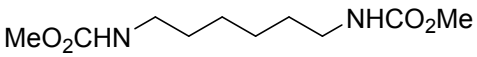


Figure S32. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **16**.



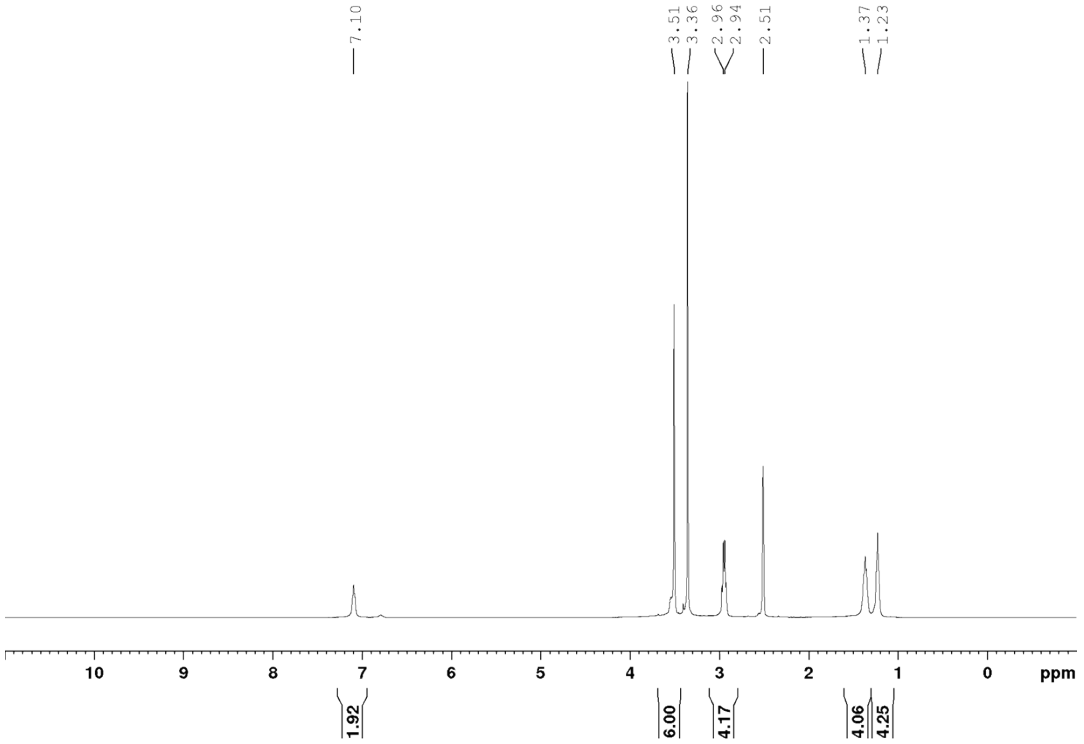


Figure S33. ^{1}H NMR (400 MHz, DMSO-d_6) of product **17**.

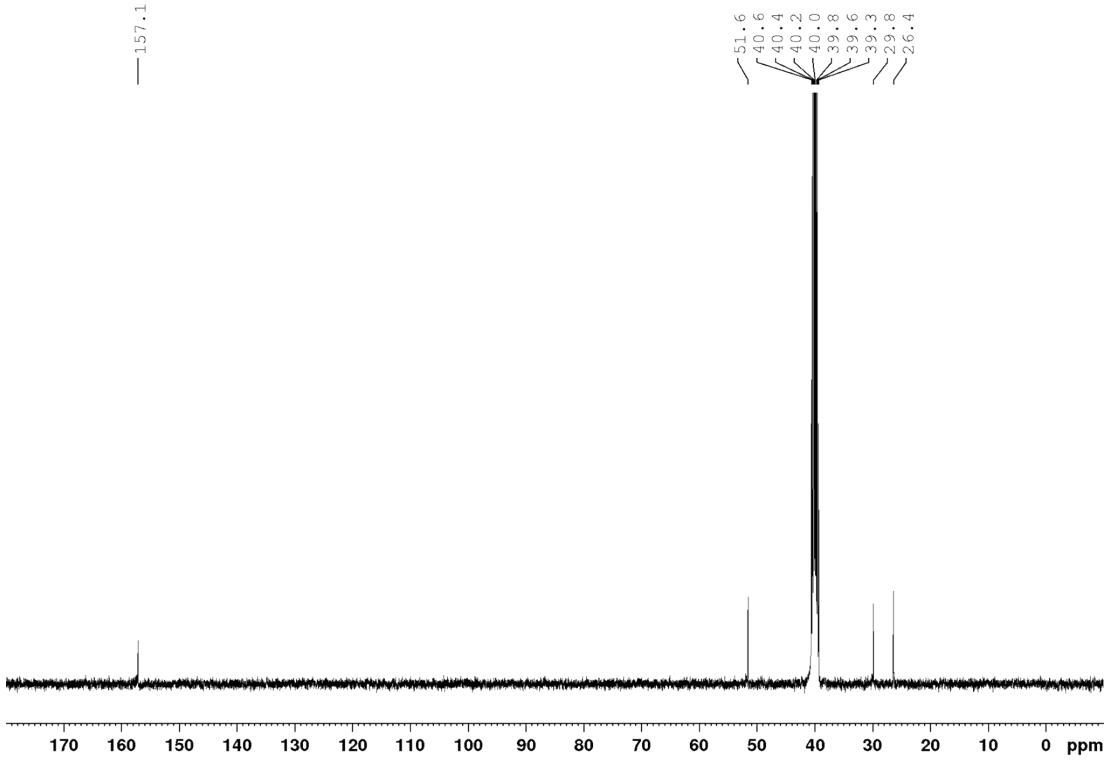


Figure S34. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **17**.

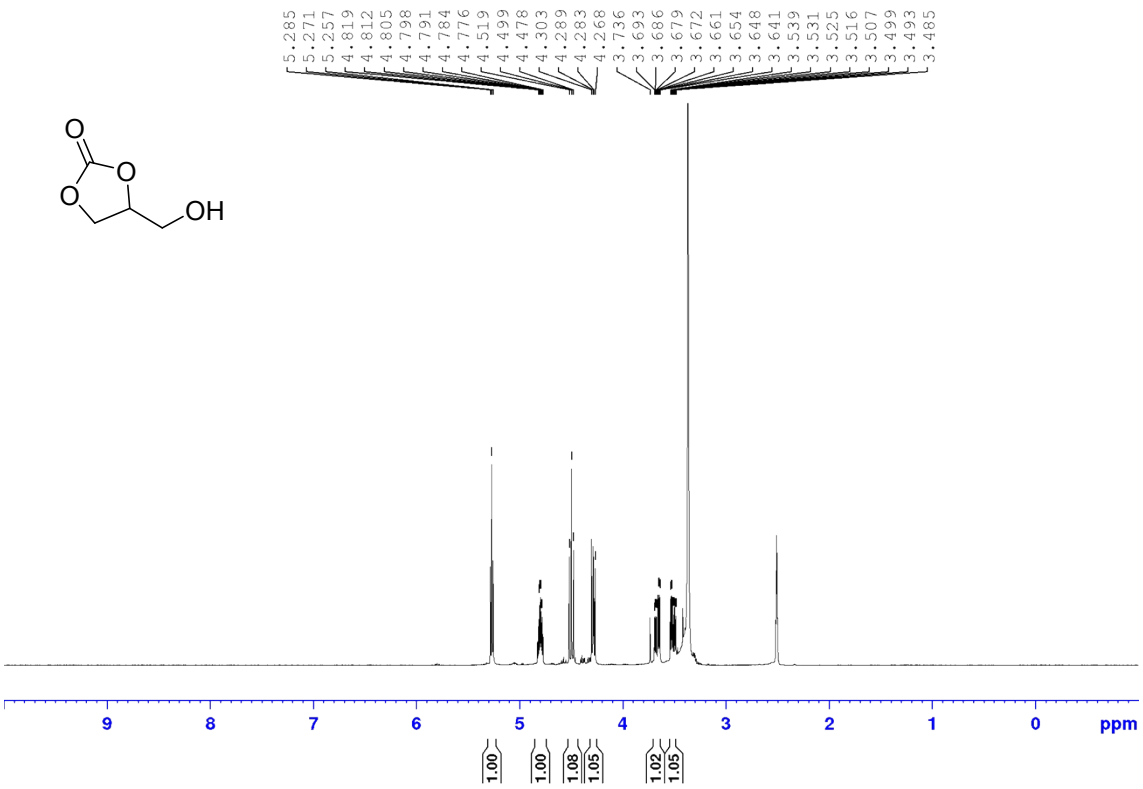


Figure S35. ^{1}H NMR (400 MHz, DMSO-d_6) of product **18**.

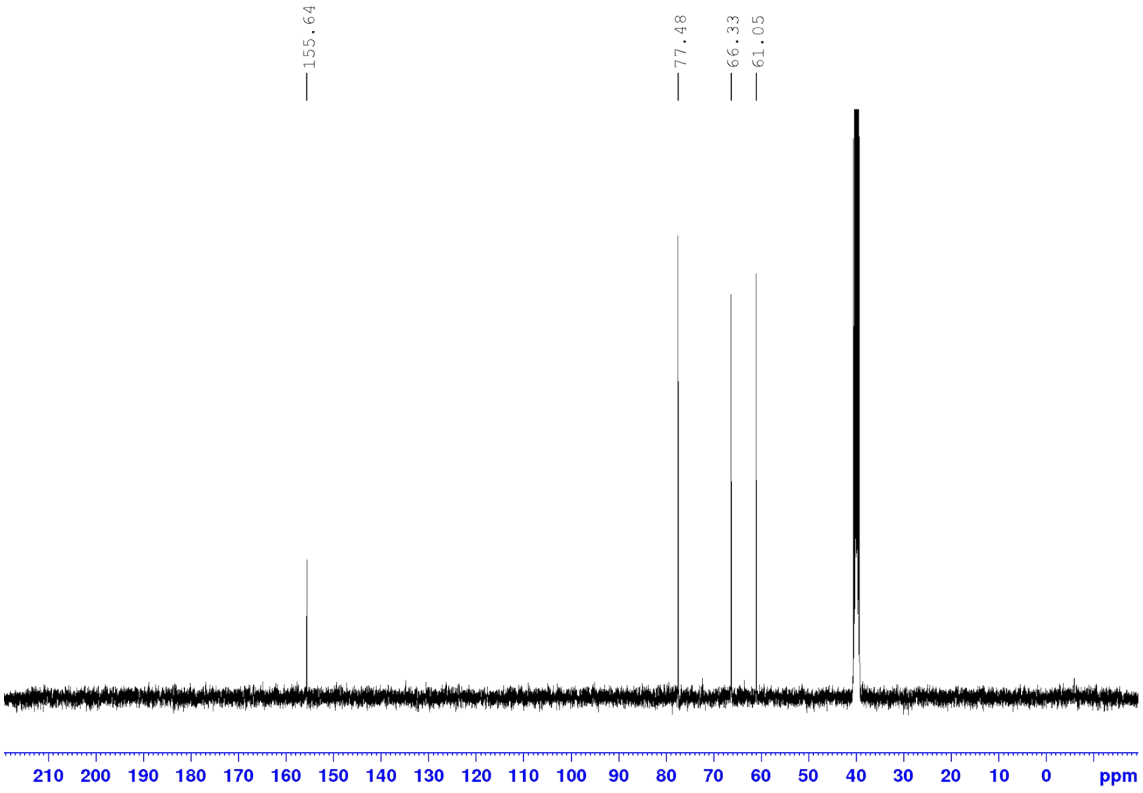


Figure S36. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of product **18**.

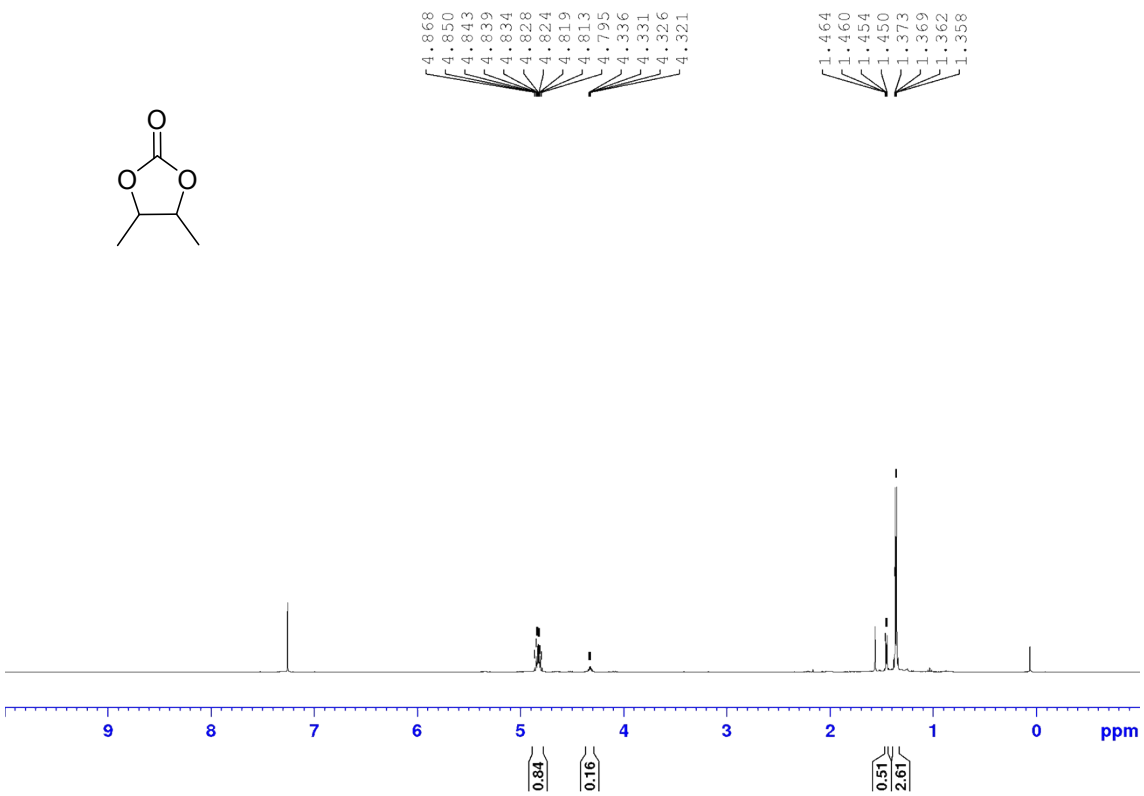


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of product **19**.

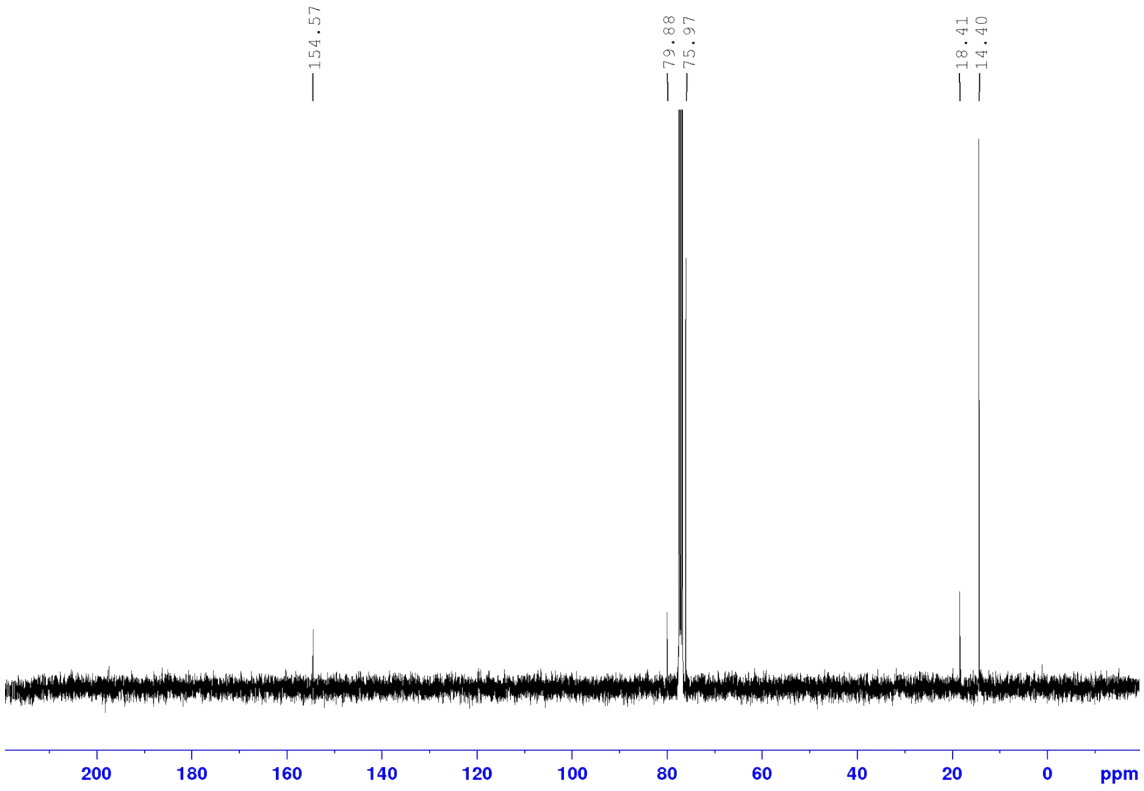


Figure S38. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of product **19**.

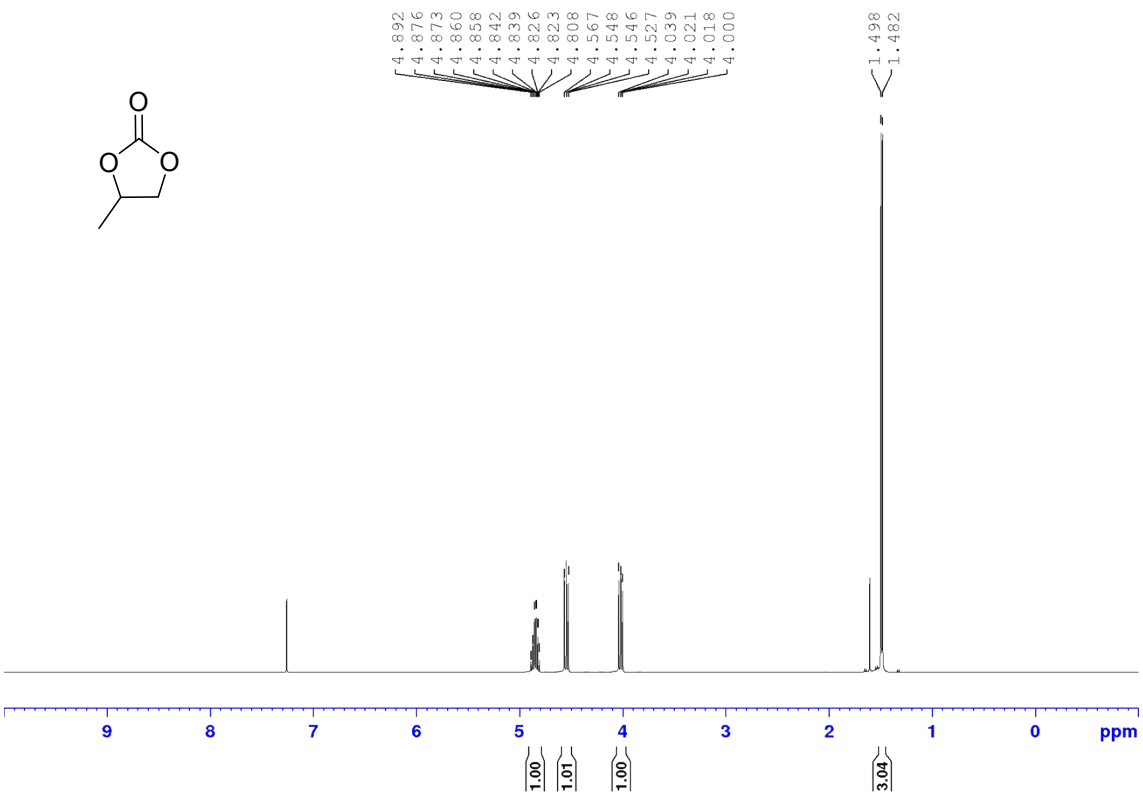


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of product **20**.

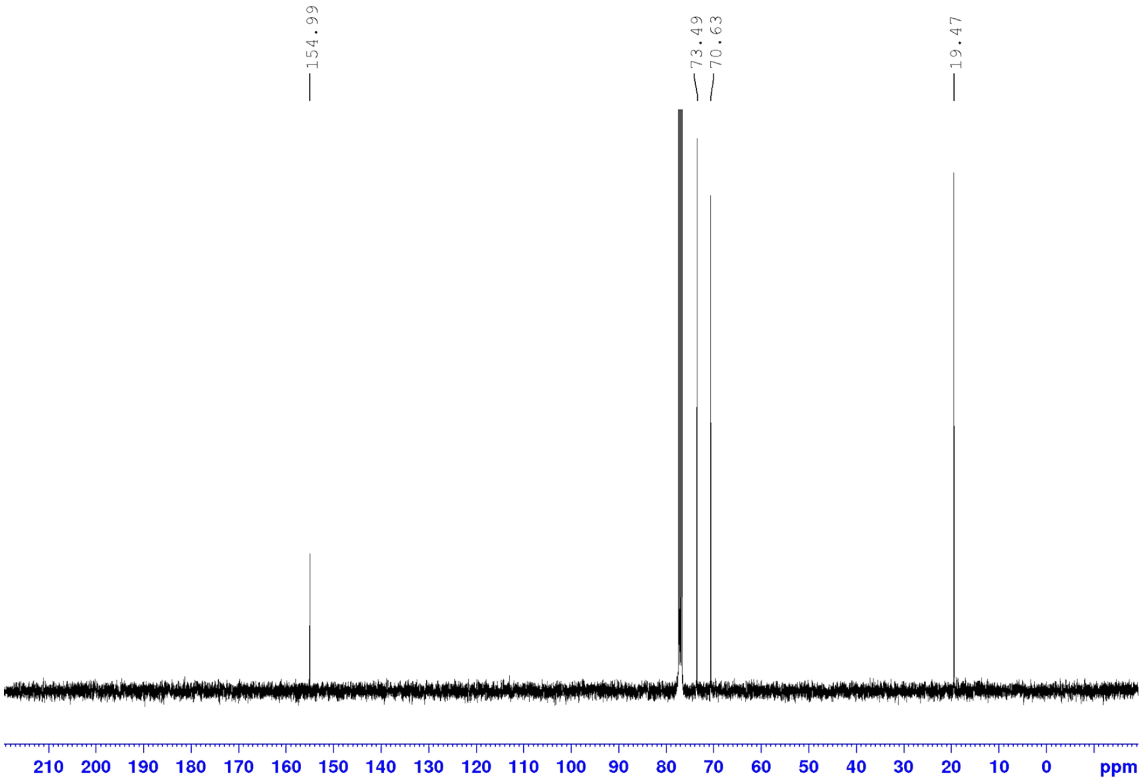


Figure S40. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of product **20**.

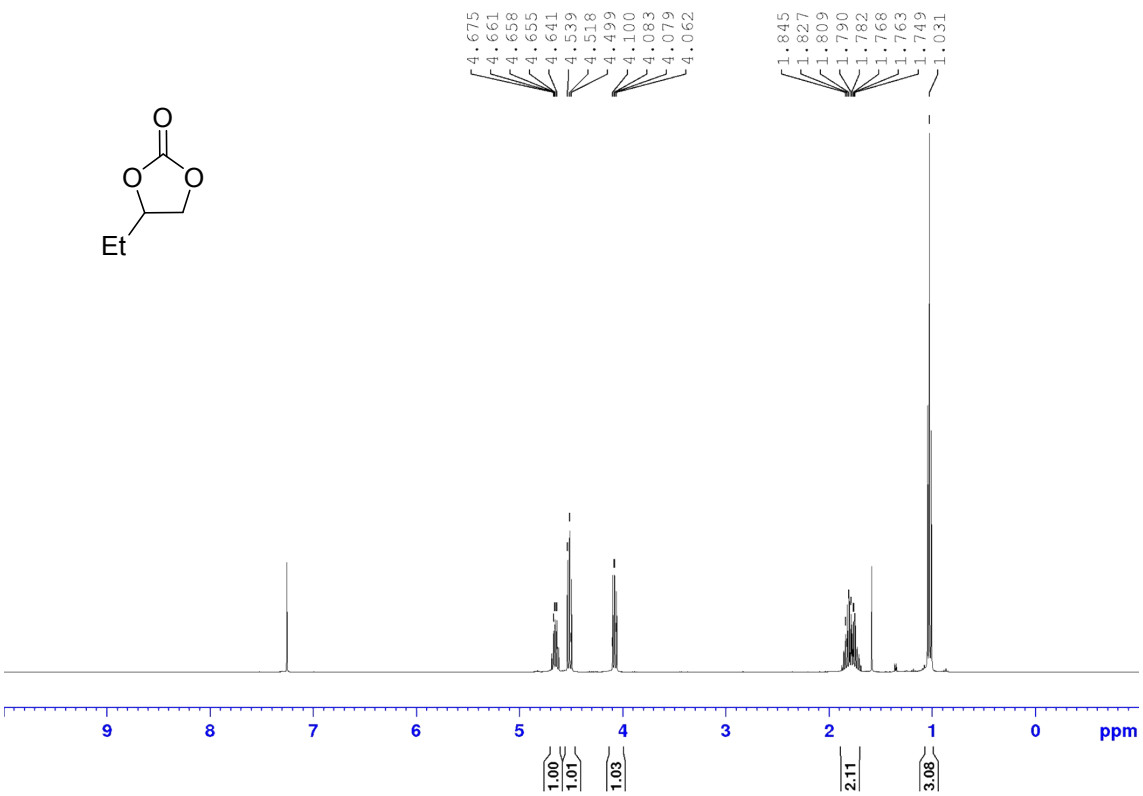


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of product **21**.

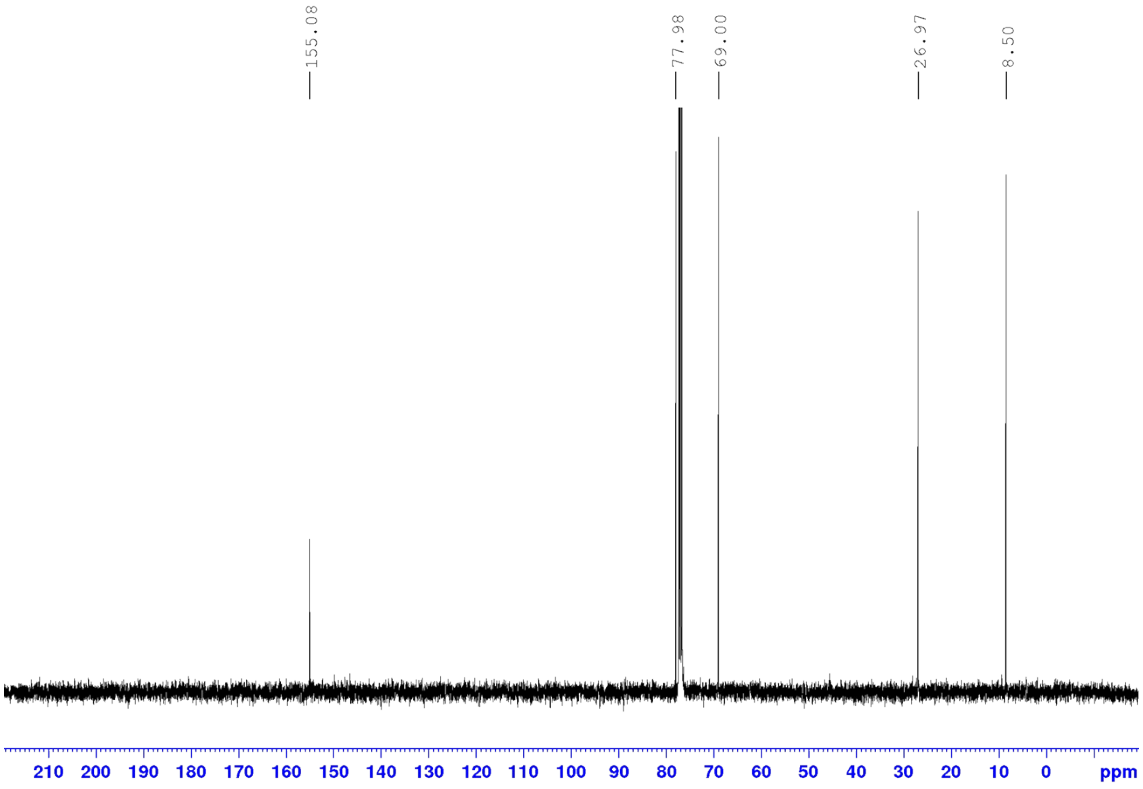


Figure S42. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of product **21**.

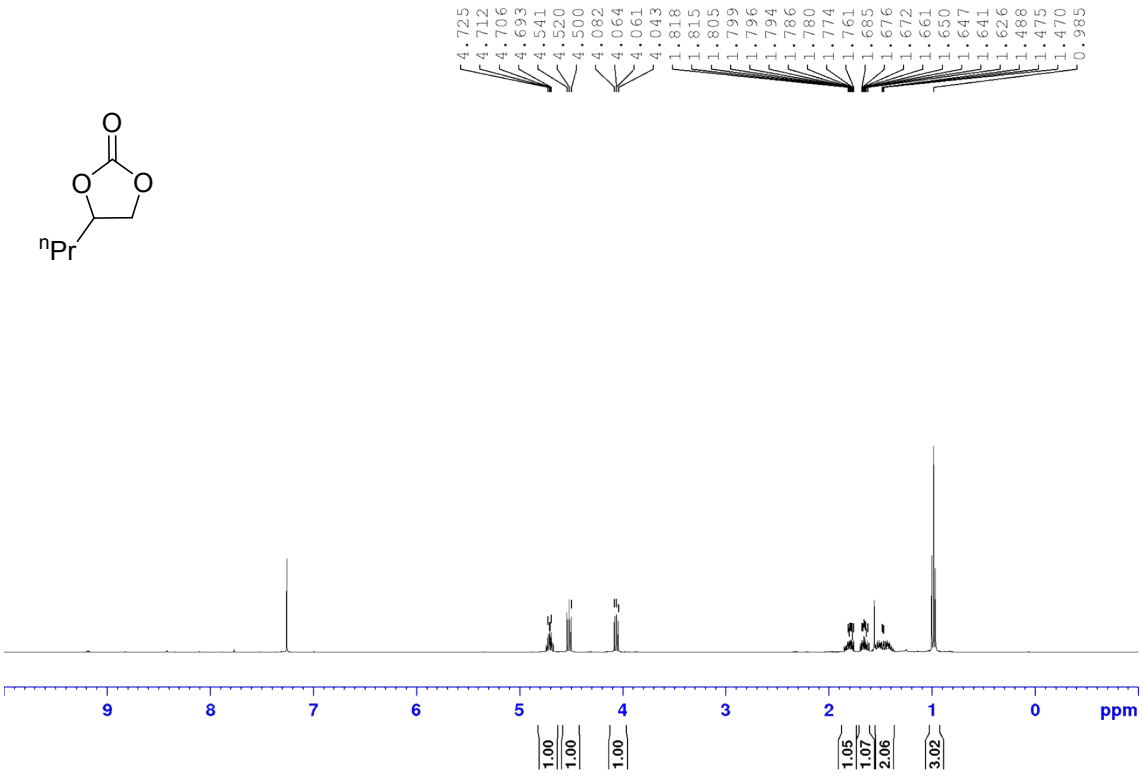


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of product **22**.

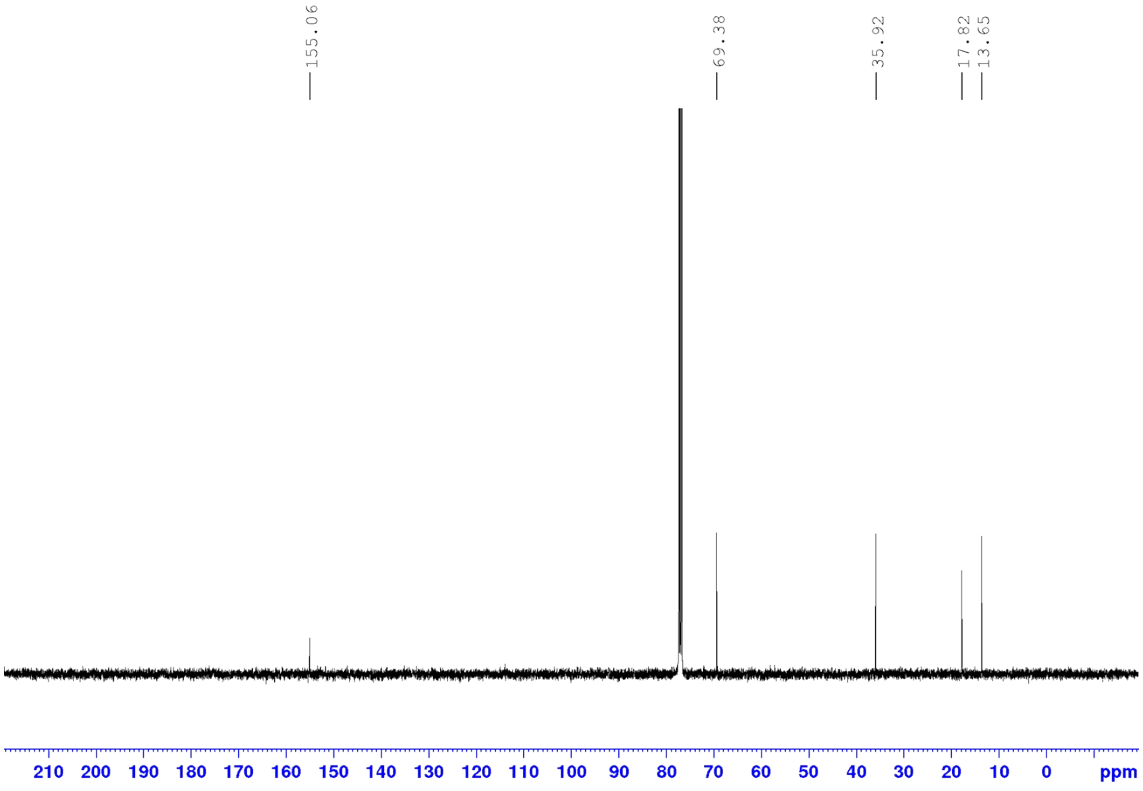


Figure S44. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of product **22**.

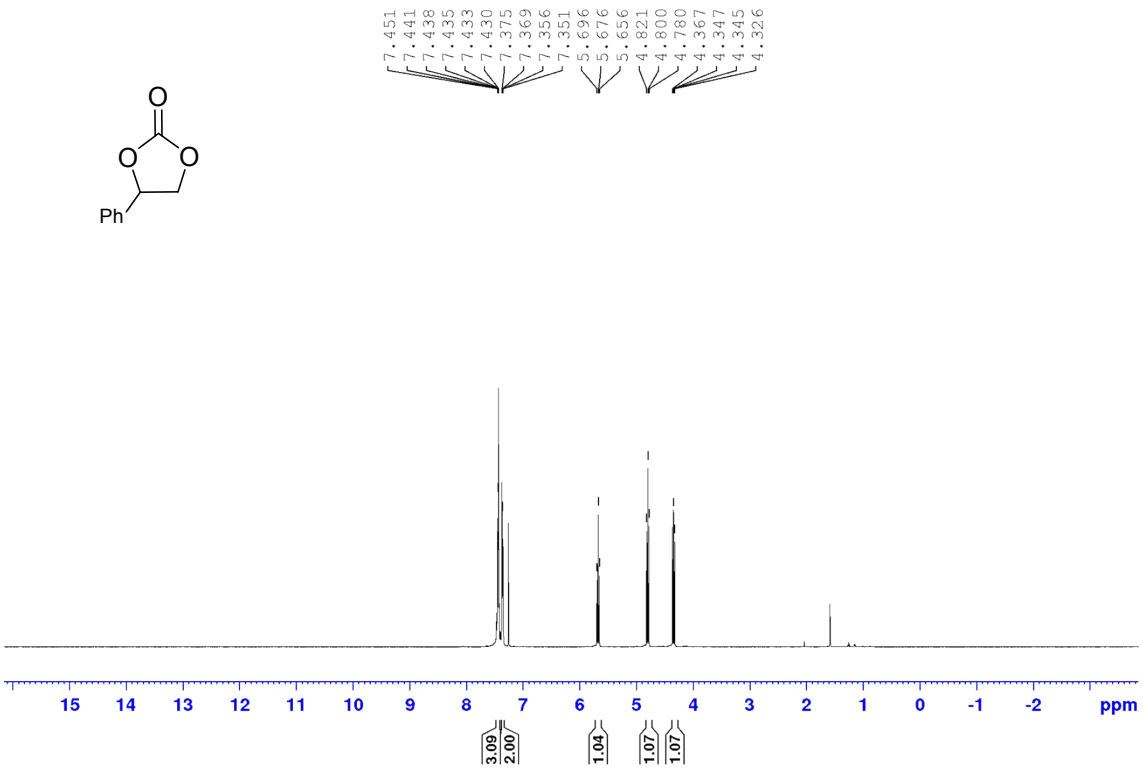


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of product **23**.

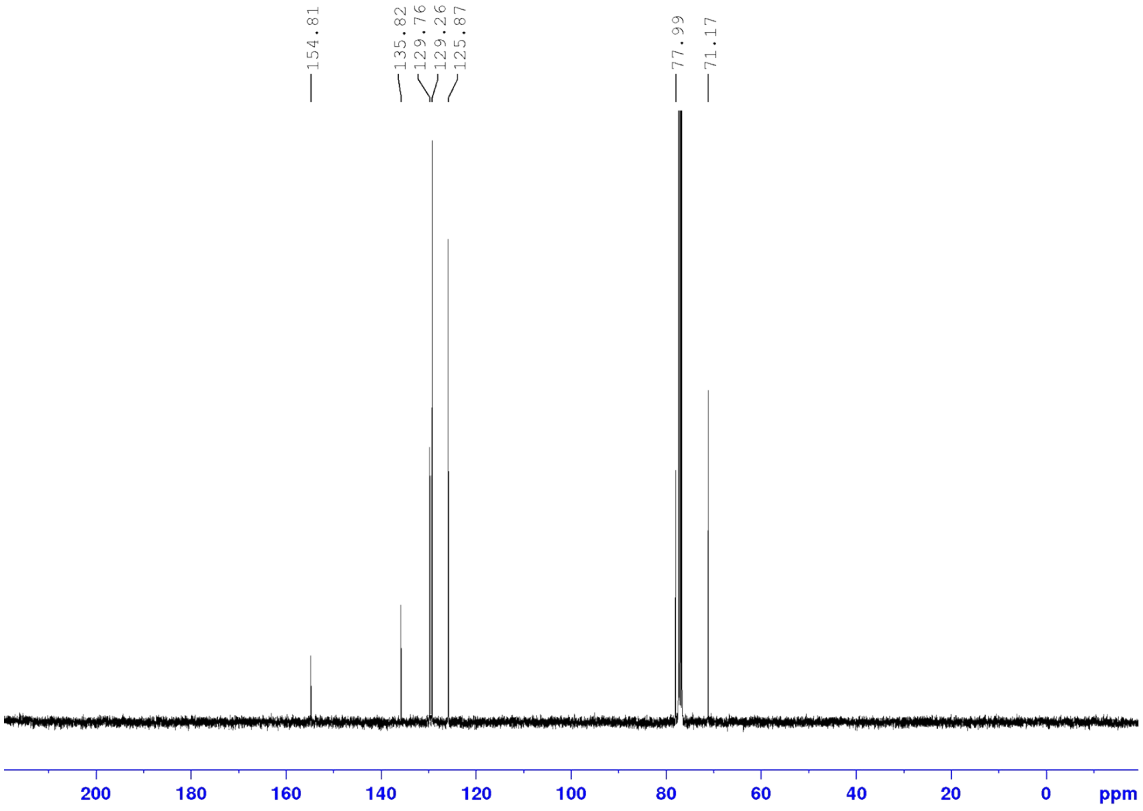


Figure S46. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of product **23**.