Supporting Information for

Direct Synthesis of Carbamate from CO_2 Using a Task-Specific Ionic Liquid Catalyst

Qiao Zhang,[a] Hao-Yu Yuan,[b] Norihisa Fukaya,[a] Hiroyuki Yasuda[a] and Jun-Chul Choi*[ab]

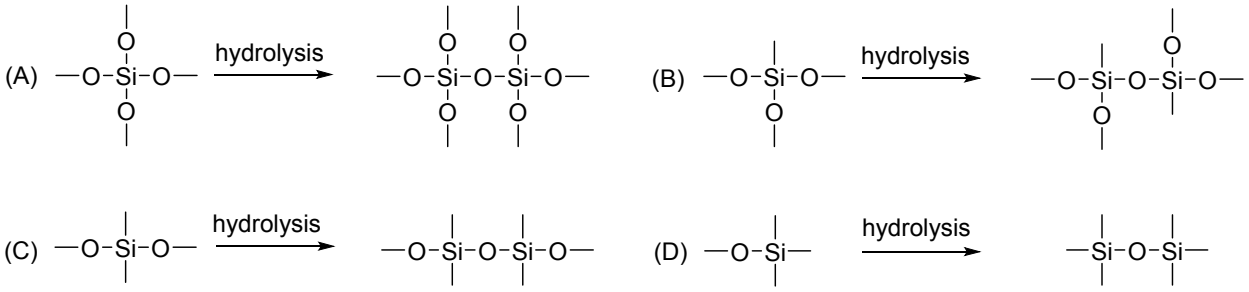
[a] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

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

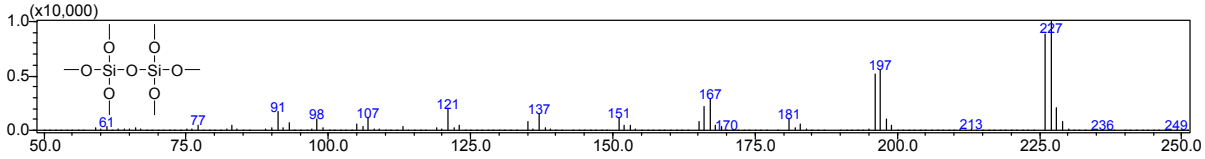
*Corresponding author. Email: junchul.choi@aist.go.jp. Tel: (+81) 029-861-9283.

Contents

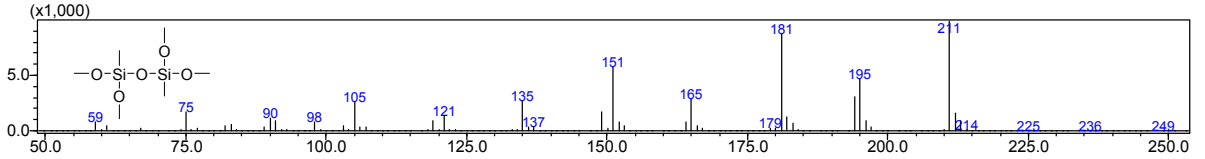
I. GC-MS determination of the hydrolysis products of silicate esters.



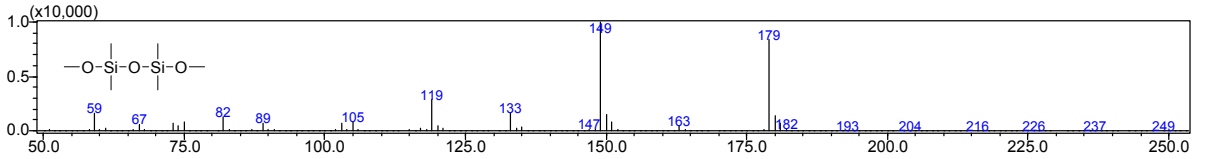
Scheme S1. Hydrolysis of silicate esters.



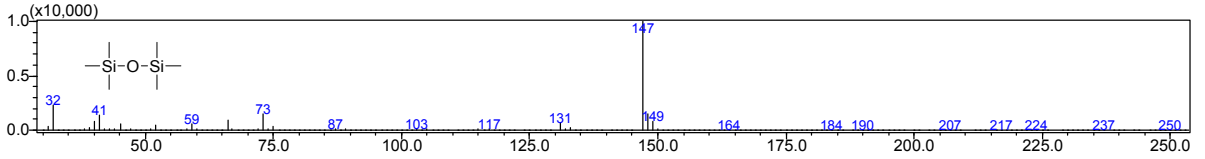
(A)



(B)



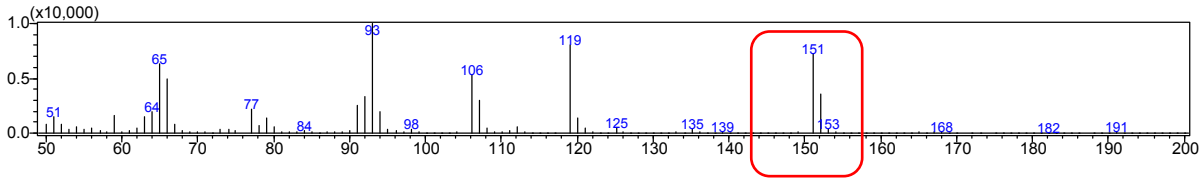
(C)



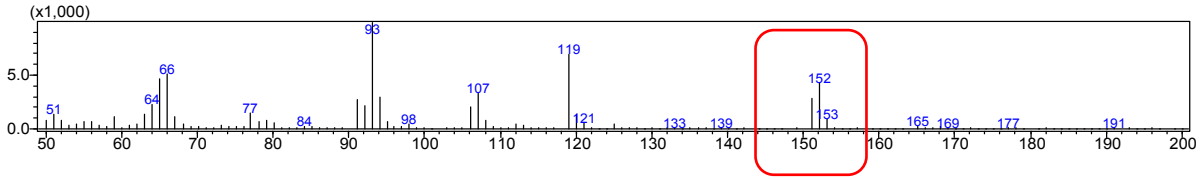
(D)

Figure S1. Supplementary GC-MS spectra for Figure 2: characterization of hydrolysis products from silicate esters. Spectra are consistent with database from Wiley Subscription Services.

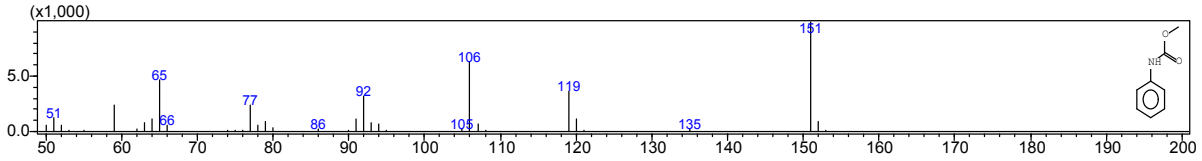
II. Supplementary GC-MS spectra for Figure 6.



(A)



(B)



(C)

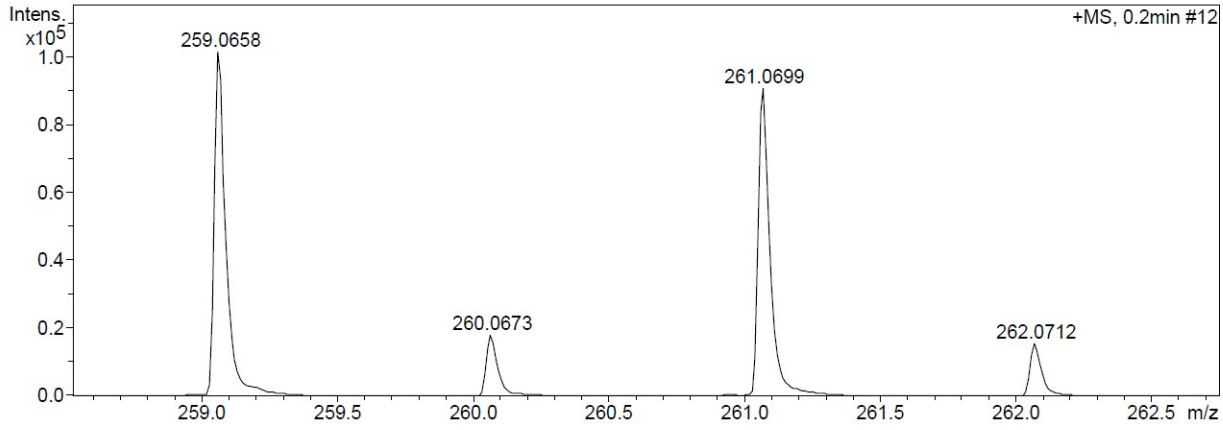
Figure S2.

(A) Supplementary GC-MS spectra for Figure 6A (extended *m*/*z* range);

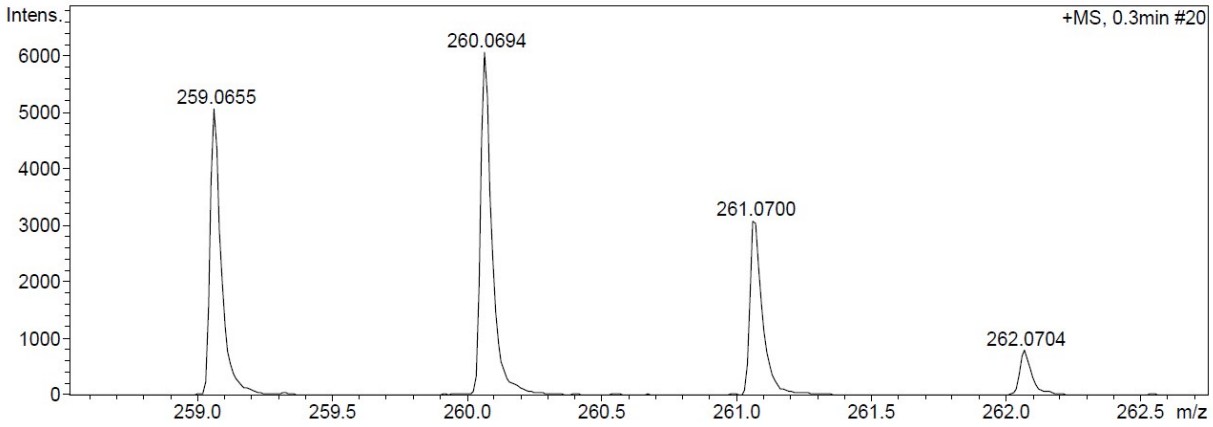
(B) Supplementary GC-MS spectra for Figure 6B (extended *m*/*z* range);

(C) Standard GC-MS spectra of **1**.

III. Supplementary HR-MS spectra for Figure 9.



(A)



(B)

Figure S3.

(A) Supplementary HR-MS spectrum (MH^+) for Figure 9B (with ^{17}O labeled H_2O).

(B) Supplementary HR-MS spectrum (MH^+) for Figure 9C (with ^{18}O labeled H_2O).

IV. Supplementary ^{1}H NMR spectra for Figure 6.

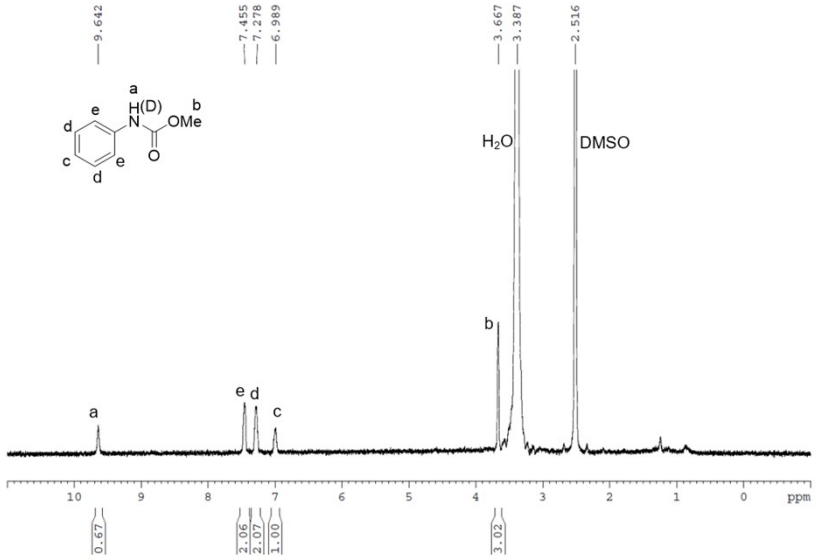


Figure S4. Supplementary ^{1}H NMR spectrum (400 MHz, DMSO-d_6) for Figure 6A. Reaction conditions: 1 mmol aniline, 2 mmol TMOS, 1 mmol [DBUD][OAc], 5 MPa CO_2, 24 h, 150°C. The comparison between "a" and "c" indicated that 33% H in "a" have been exchanged.

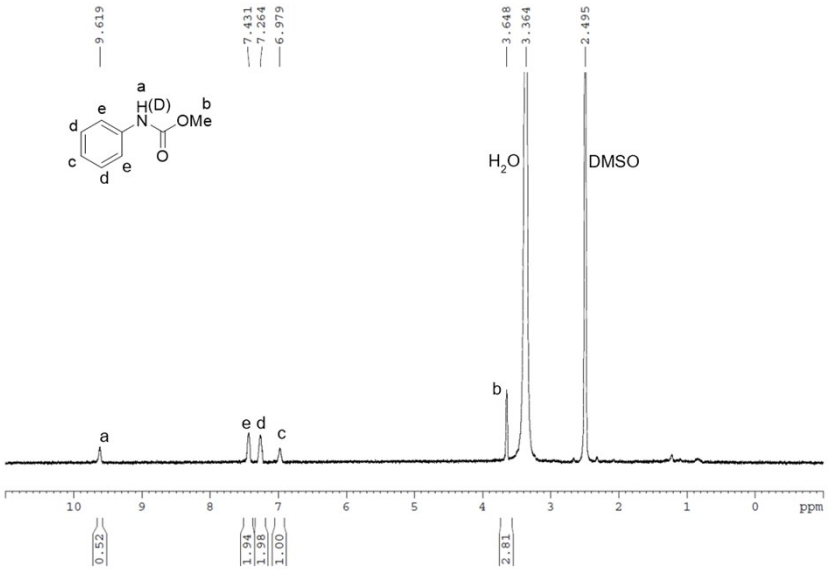


Figure S5. Supplementary ^{1}H NMR spectrum (400 MHz, DMSO-d_6) for Figure 6B. Reaction conditions: 1 mmol aniline-d_2, 2 mmol TMOS, 1 mmol [DBUH][OAc], 5 MPa CO_2, 24 h, 150°C. The comparison between "a" and "c" indicated that 52% D in "a" have been exchanged.

V. ^{1}H NMR chemical shifts of the NH_2 group of aniline with the addition of [DBNH][OAc] and [TBDH][OAc].

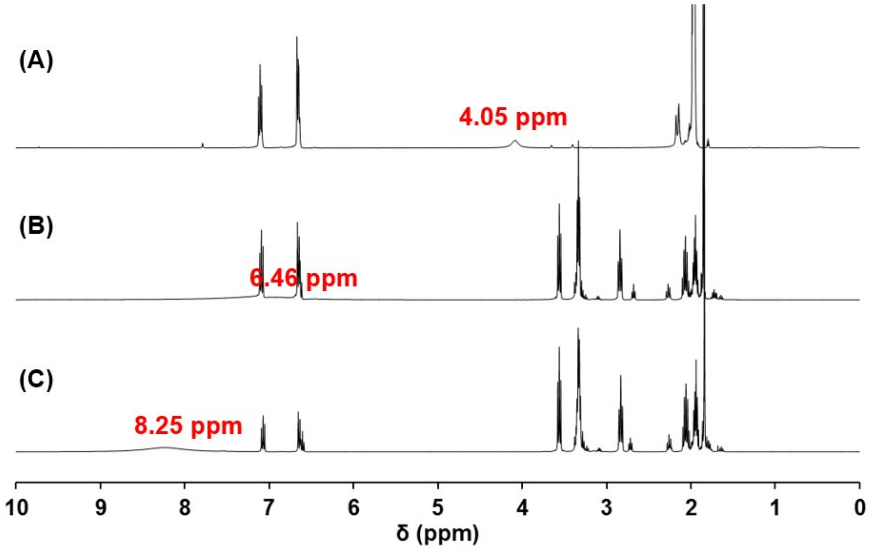


Figure S6. ^{1}H NMR (400 MHz, CD_3CN) analysis NH_2 group of (A) 1.0 M aniline; (B) 1.0 M aniline and 1.0 M [DBNH][OAc]; (C) 1.0 M aniline and 2.0 M [DBNH][OAc].

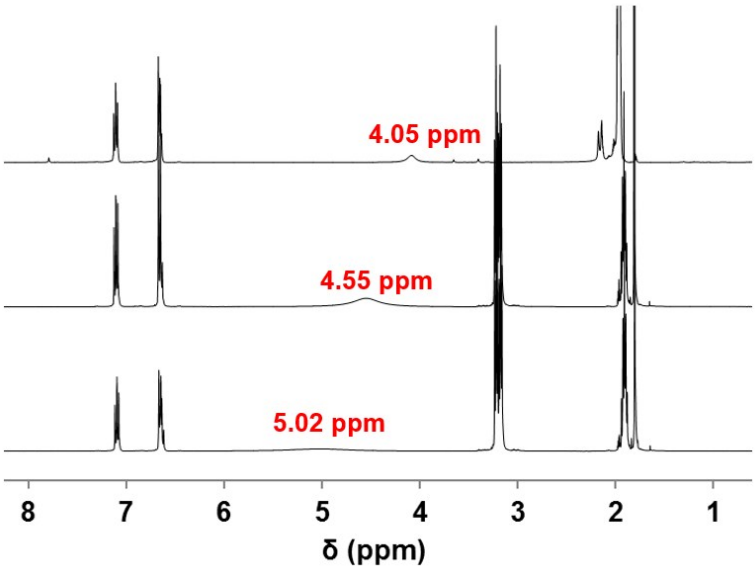


Figure S7. ^{1}H NMR (400 MHz, CD_3CN) analysis NH_2 group of (A) 1.0 M aniline; (B) 1.0 M aniline and 1.0 M [TBDH][OAc]; (C) 1.0 M aniline and 2.0 M [TBDH][OAc].

VI. An example of HPLC graph.

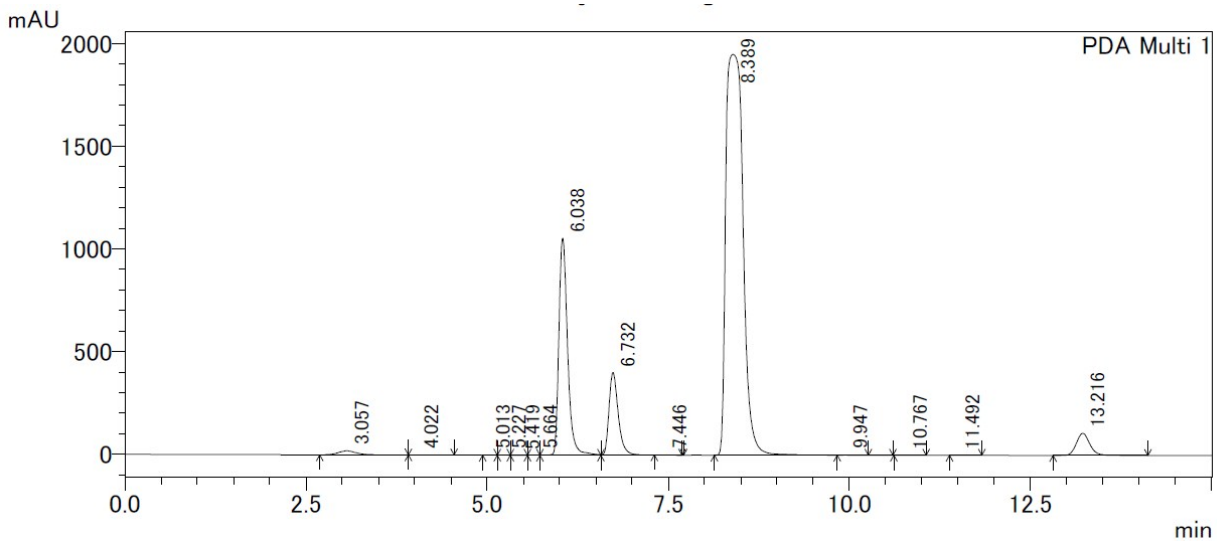
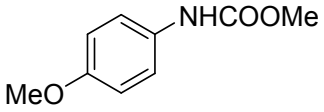


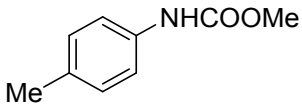
Figure S8. An example of HPLC graph.

compound	mass (mg)	retention time (min)	peak area
aniline	25	6.038	8746349
N-phenyl methylcarbamate	20	6.732	3556951
1,3-diphenylurea	20	8.389	32272237
toluene	25	13.216	1384971

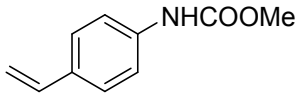
VII. ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, and MS data for isolated products.



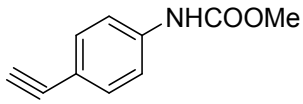
Product **1a**. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.27 (d, 2H, J = 7.2 Hz), 6.84 (d, 2H, J = 8.8 Hz), 6.63 (s, 1H), 3.77 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (100MHz, DMSO-d_6): δ 154.7, 154.1, 132.1, 119.8, 113.9, 55.1, 51.4. GC-MS: 181.



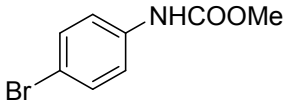
Product **1b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2H, J = 7.2 Hz), 7.11 (d, 2H, J = 8.0 Hz), 6.50 (s, 1H), 3.77 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 136.5, 131.1, 129.0, 118.2, 51.4, 20.2. GC-MS: 165.



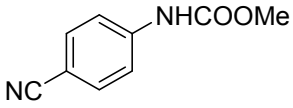
Product **1c**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.68 (s, 1H), 7.43 (d, 2H, J = 8.8 Hz), 7.38 (d, 2H, J = 8.4 Hz), 6.65 (dd, 1H, J = 17.6 Hz, ^{2}J = 11.2 Hz), 5.69 (d, 1H, J = 17.6 Hz), 5.14 (dd, 1H, J = 10.8 Hz, ^{2}J = 0.8 Hz), 3.66 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 138.9, 136.1, 131.4, 126.6, 118.1, 112.3, 51.6. GC-MS: 177.



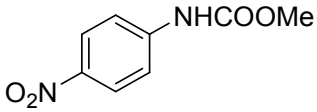
Product **1d**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, 2H, J = 8.4 Hz), 7.35 (d, 2H, J = 8.4 Hz), 6.62 (s, 1H), 3.79 (s, 3H), 3.03 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.8, 139.8, 132.4, 130.5, 117.9, 115.2, 112.4, 83.6, 79.5, 51.8. GC-MS: 175.



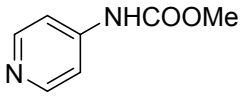
Product **1e**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.78 (s, 1H), 7.41-7.47 (m, 4H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 138.6, 131.5, 131.7, 120.0, 113.9, 51.7. GC-MS: 231.



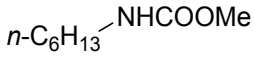
Product **1f**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.16 (s, 1H), 7.74 (d, 2H, J = 8.8 Hz), 7.63 (d, 2H, J = 8.8 Hz), 3.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.7, 143.6, 133.3, 119.1, 118.0, 104.0, 52.0. GC-MS: 176.



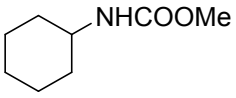
Product **1g**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H), 8.21 (dd, 2H, J = 7.2 Hz, ^{2}J = 2.0 Hz), 7.69 (dd, 2H, J = 7.2 Hz, ^{2}J = 2.0 Hz), 3.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.7, 145.7, 141.7, 125.1, 117.6, 52.2.



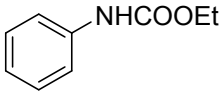
Product **1h**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.09 (s, 1H), 8.38 (dd, 2H, J = 5.2 Hz, ^{2}J = 1.6 Hz), 7.43 (dd, 2H, J = 4.8 Hz, ^{2}J = 1.6 Hz), 3.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.7, 150.2, 146.0, 112.2, 52.0. GC-MS: 152.



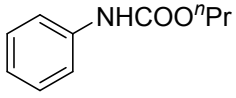
Product **1i**. ^{1}H NMR (400 MHz, DMSO-d_6): 7.03 (s, 1H), 3.51 (s, 3H), 2.95 (q, 2H, J = 6.4 Hz), 1.23-1.39 (m, 8H), 0.86 (t, 3H, J = 2.8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.6, 51.1, 50.6, 31.0, 29.4, 25.9, 22.0, 13.9. GC-MS: 159.



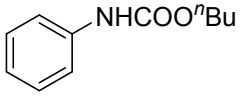
Product **1j**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.99 (s, 1H), 3.49 (s, 3H), 3.23 (m, 1H), 1.63-1.74 (m, 4H), 1.53 (d, 2H, J = 12.8 Hz), 1.11-1.27 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.8, 50.9, 49.4, 33.7, 25.1, 24.6. GC-MS: 157.



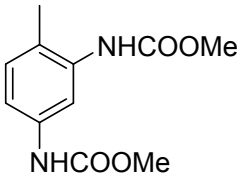
Product **1k**. ^{1}H NMR (400MHz, DMSO-d_6): δ 9.60 (s, 1H), 7.46 (d, 2H, J = 8.4 Hz), 7.26 (t, 2H, J = 7.6 Hz), 6.97 (t, 1H, J = 7.6 Hz), 4.11 (q, 2H, J = 6.8 Hz), 1.24 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 153.5, 139.2, 128.7, 122.3, 118.1, 60.1, 14.5. GC-MS: 165.



Product **1l**. ^{1}H NMR (400MHz, DMSO-d_6): δ 9.60 (s, 1H), 7.46 (d, 2H, J = 7.6 Hz), 7.26 (t, 2H, J = 8.0 Hz), 6.97 (t, 1H, J = 7.6 Hz), 4.03 (t, 2H, J = 6.4 Hz), 1.63 (quint, 2H, J = 7.6 Hz), 0.93 (t, 3H, J = 7.6 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 153.6, 139.2, 128.7, 122.3, 118.1, 65.6, 21.9, 10.3. GC-MS: 179.



Product **1m**. ^{1}H NMR (400MHz, DMSO-d_6): δ 9.58 (s, 1H), 7.46 (d, 2H, J = 7.6 Hz), 7.26 (t, 2H, J = 7.6 Hz), 6.97 (t, 1H, J = 7.6 Hz), 4.07 (t, 2H, J = 6.4 Hz), 1.60 (quint, 2H, J = 7.6 Hz), 1.38 (sext, 2H, J = 7.6 Hz), 0.91 (t, 3H, J = 7.6 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 153.6, 139.2, 128.7, 122.2, 118.1, 63.8, 30.6, 18.6, 13.6. GC-MS: 193.



Product **1n**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.25 (s, 1H), 7.08 (d, 1H, J = 8.0 Hz), 6.54 (br s, 1H), 6.37 (br s, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.7, 153.9, 137.2, 136.4, 130.2, 125.5, 115.0, 114.8, 51.6, 51.5, 17.1. GC-MS: 174 for corresponding isocyanate.

VIII. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for isolated products.

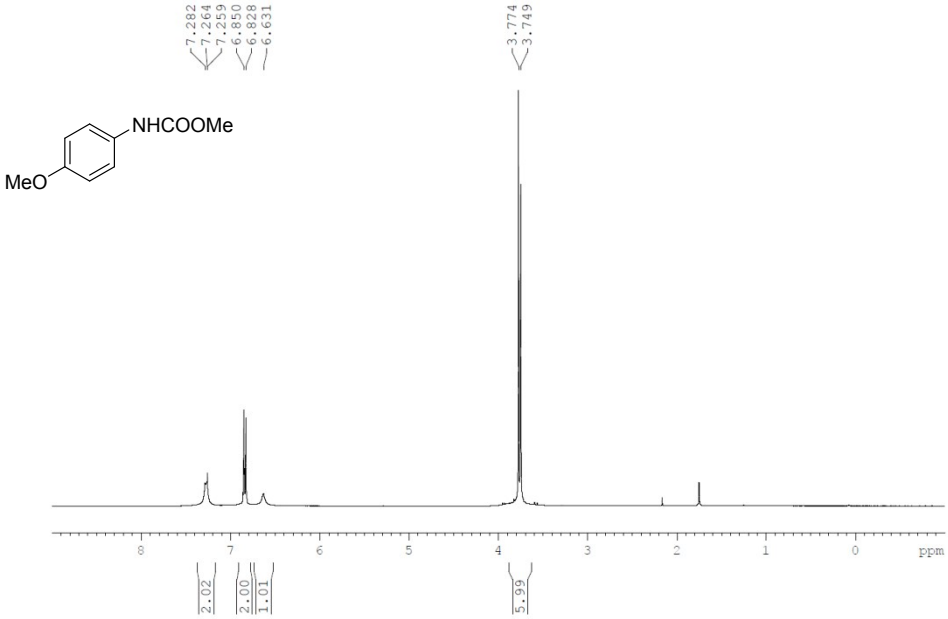


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of **1a**.

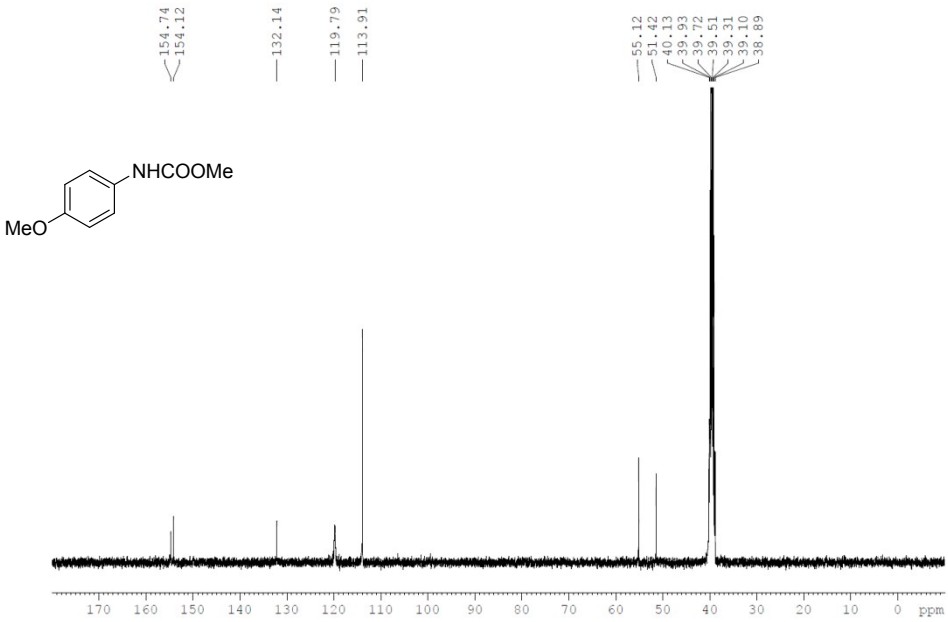


Figure S10. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **1a**.

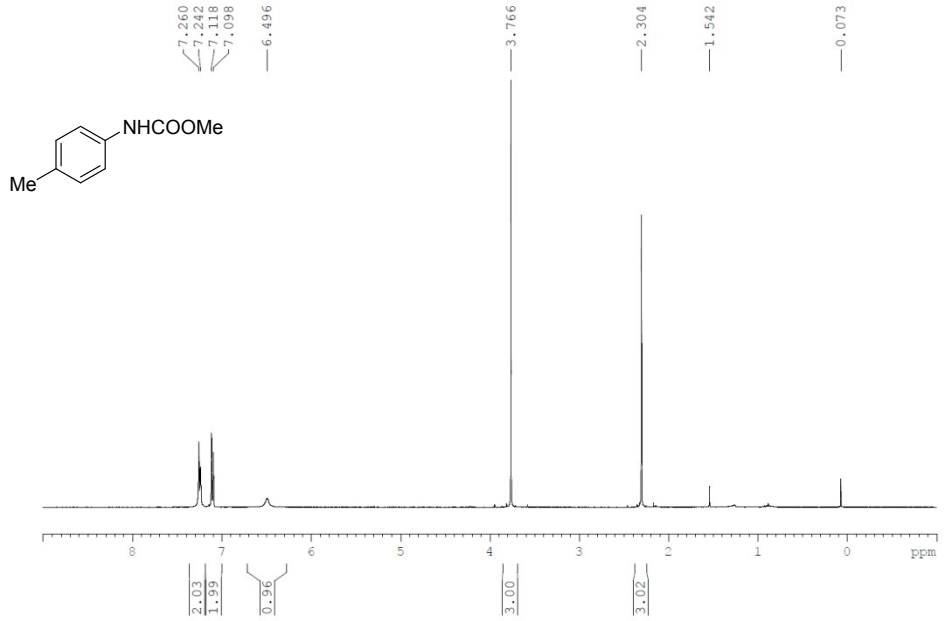


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of **1b**.

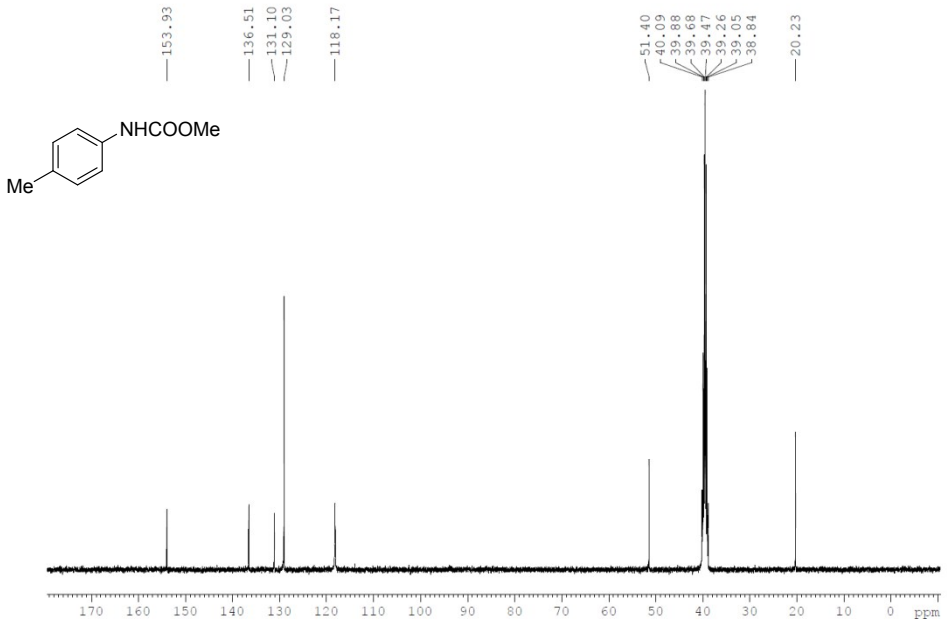


Figure S12. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **1b**.

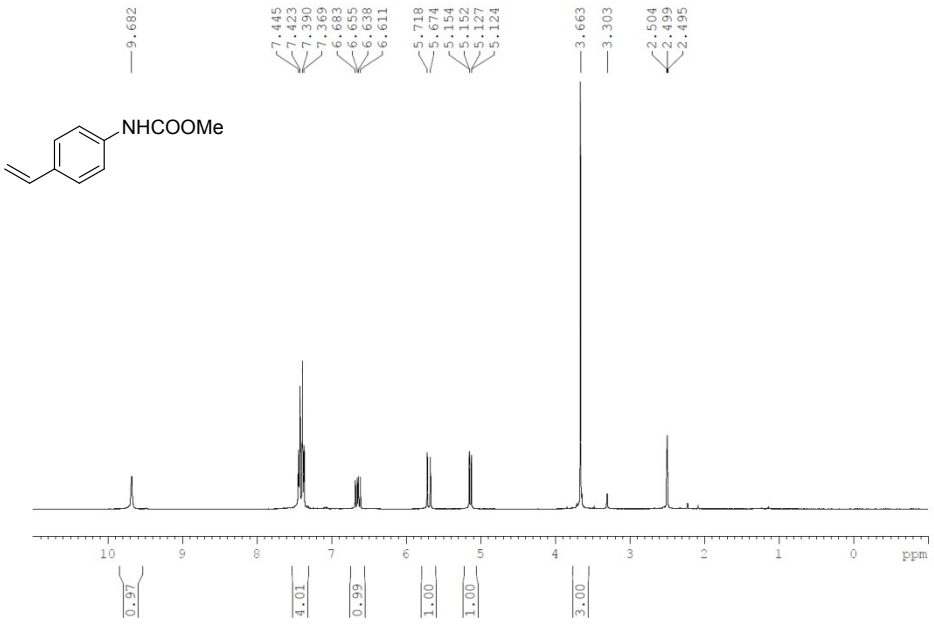


Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6) of **1c**.

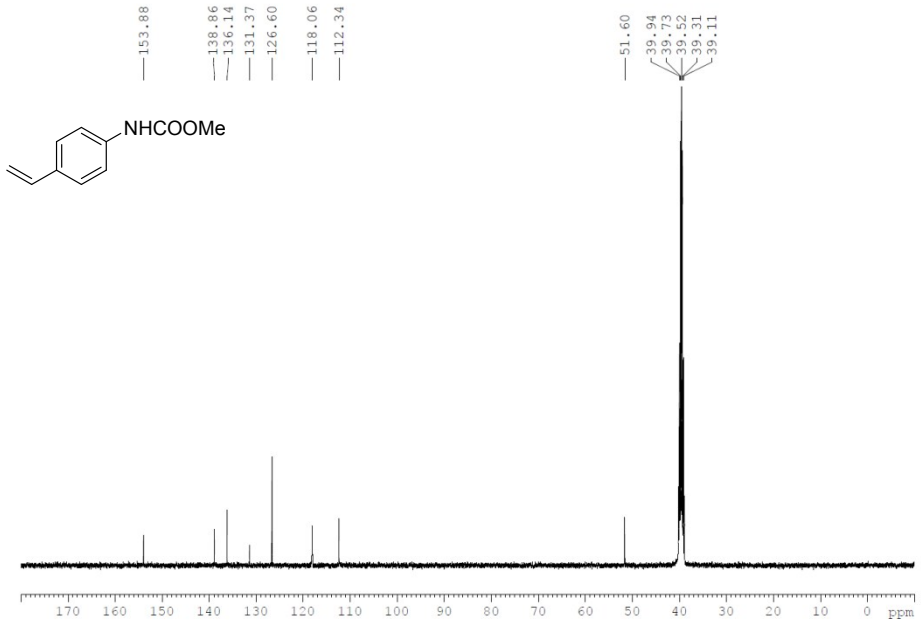


Figure S14. ^{13}C{^{1}H} NMR of (100 MHz, DMSO-d_6) **1c**.

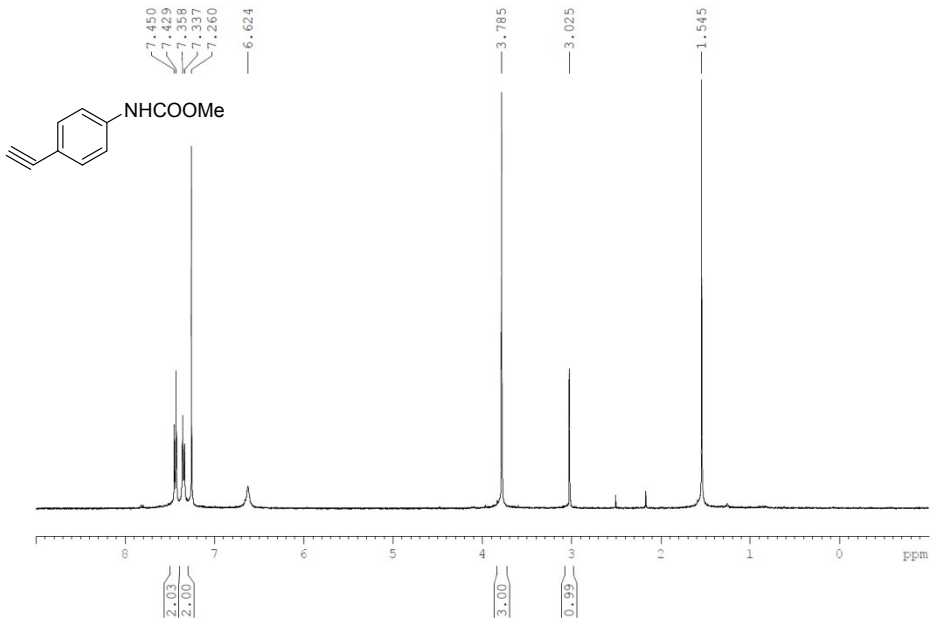


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of **1d**.

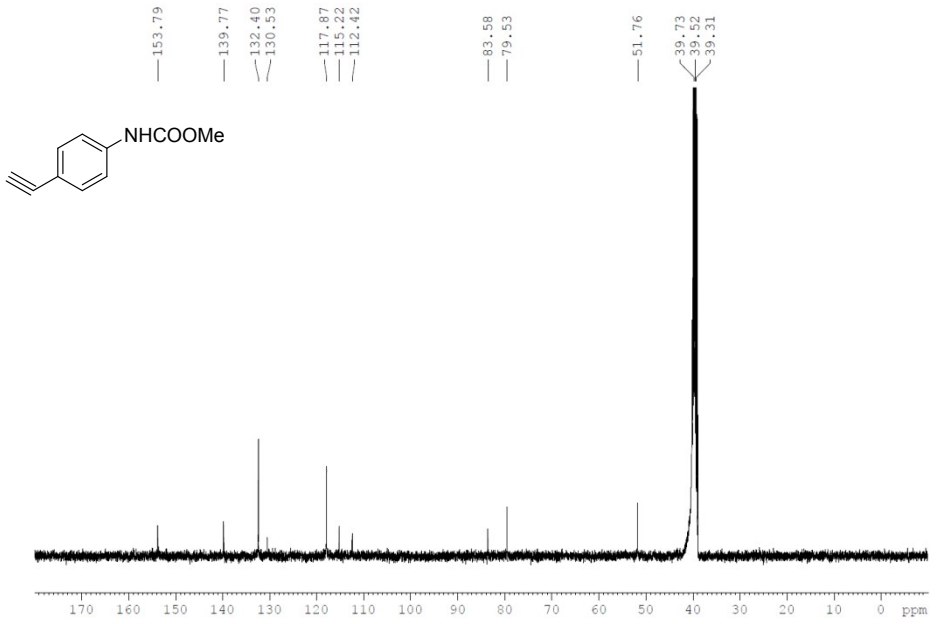


Figure S16. $^{13}C\{^{1}H\}$ (100 MHz, DMSO-d_6) NMR of **1d**.

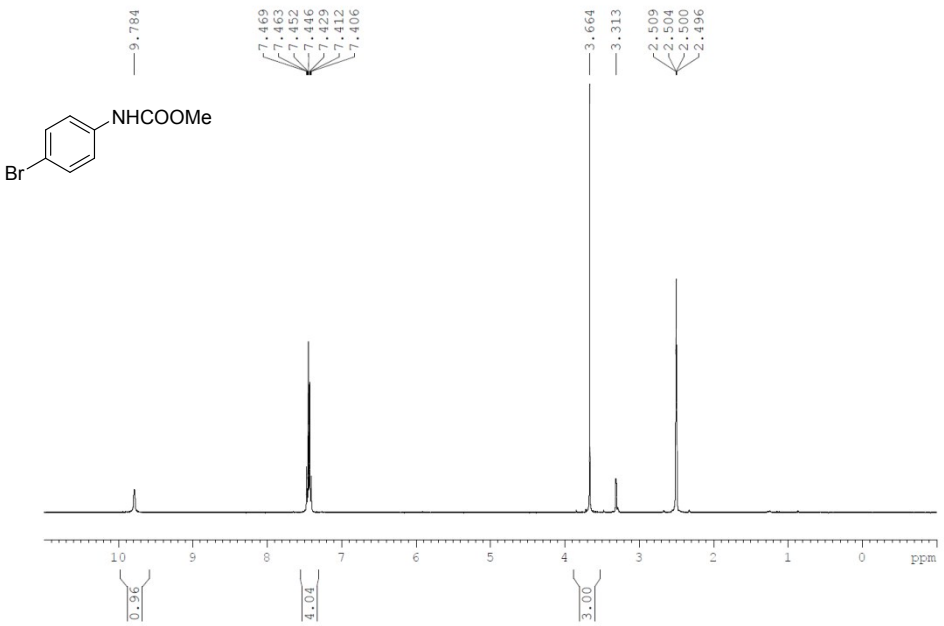


Figure S17. ^{1}H NMR (400 MHz, DMSO-d_6) of **1e**.

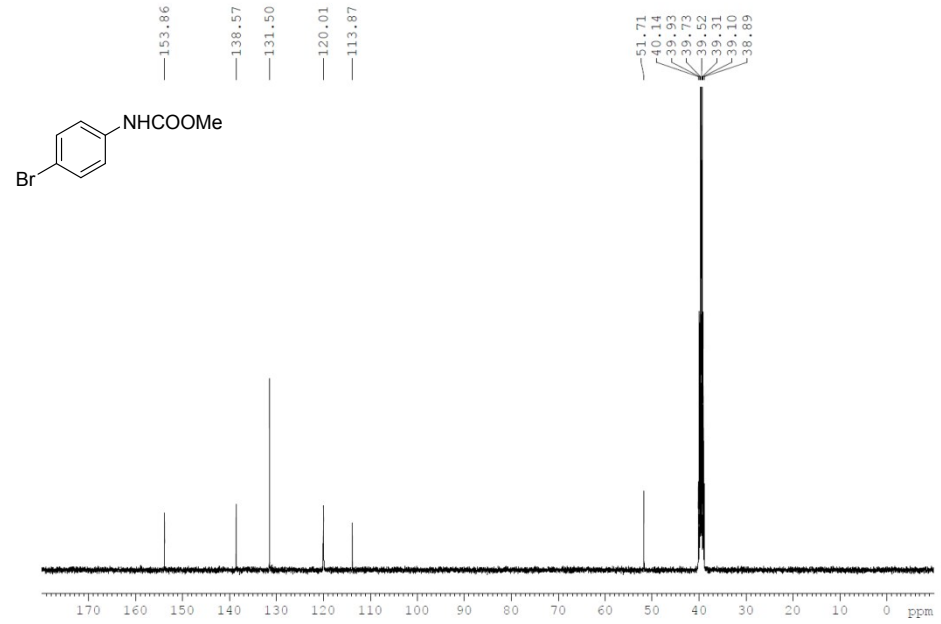


Figure S18. $^{13}C\{^{1}H\}$ (100 MHz, DMSO-d_6) NMR of **1e**.

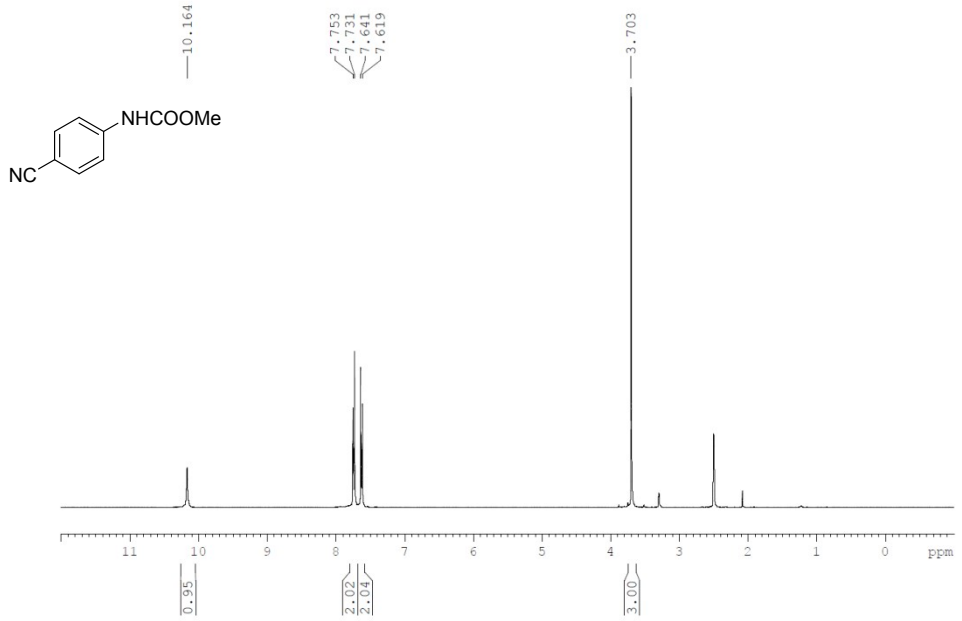


Figure S19. ^{1}H NMR (400 MHz, DMSO-d_6) of **1f**.

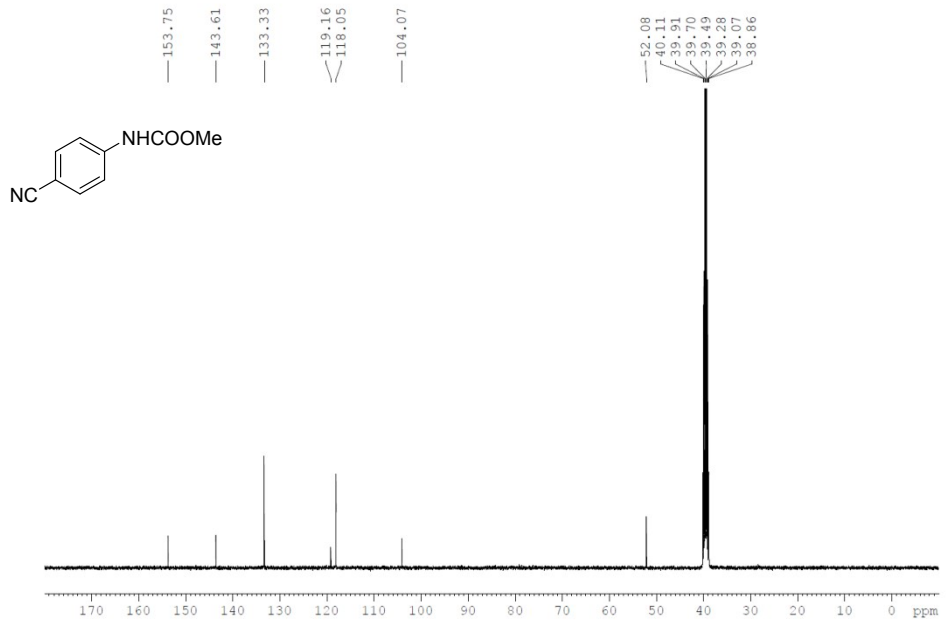


Figure S20. ^{13}C{^{1}H} (100 MHz, DMSO-d_6) NMR of **1f**.

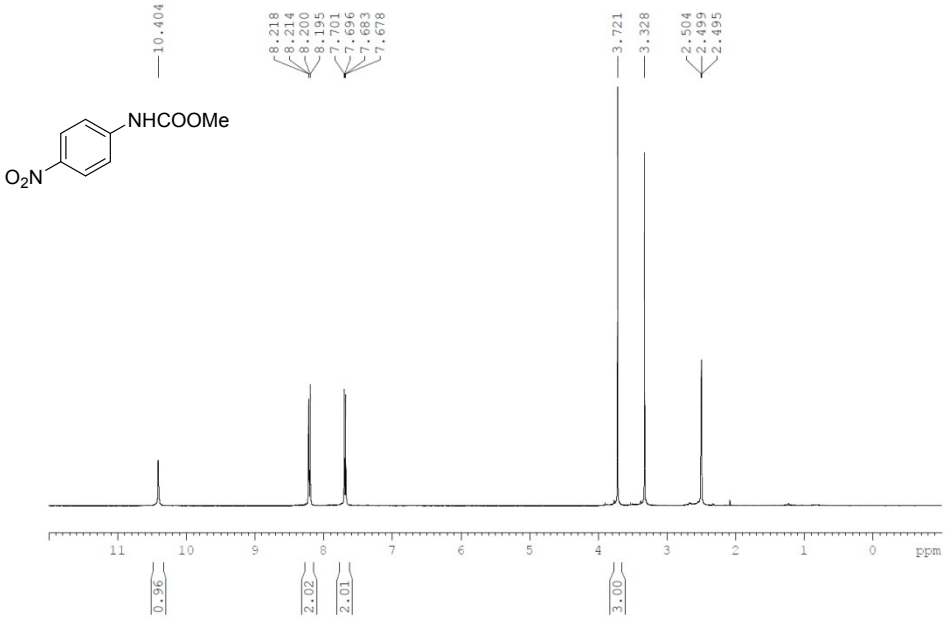


Figure S21. ^{1}H NMR (400 MHz, DMSO-d_6) of **1g**.

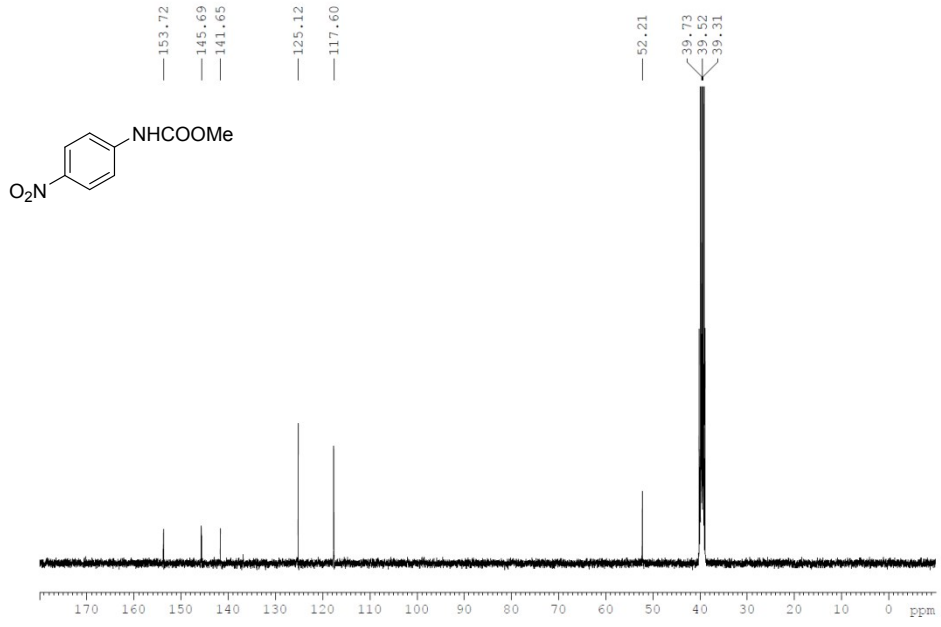


Figure S22. $^{13}C\{^{1}H\}$ (100 MHz, DMSO-d_6) NMR of **1g**.

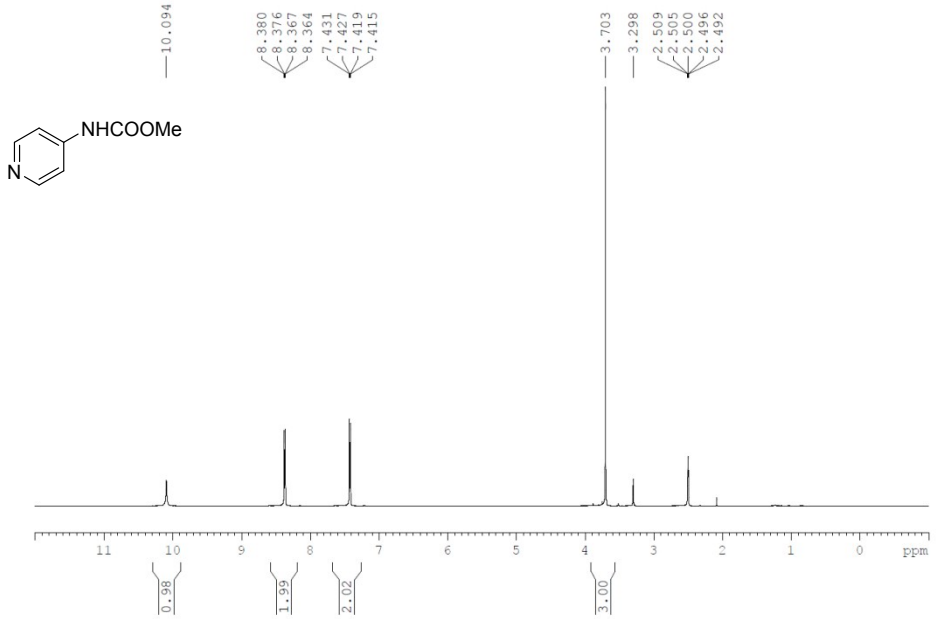


Figure S23. ^{1}H NMR (400 MHz, DMSO-d_6) of **1h**.

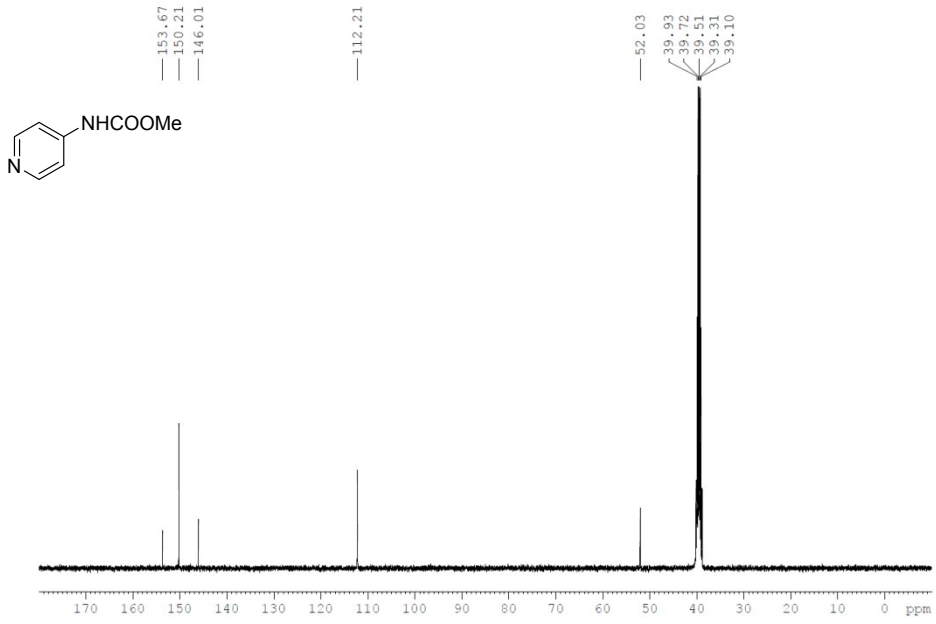


Figure S24. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **1h**.

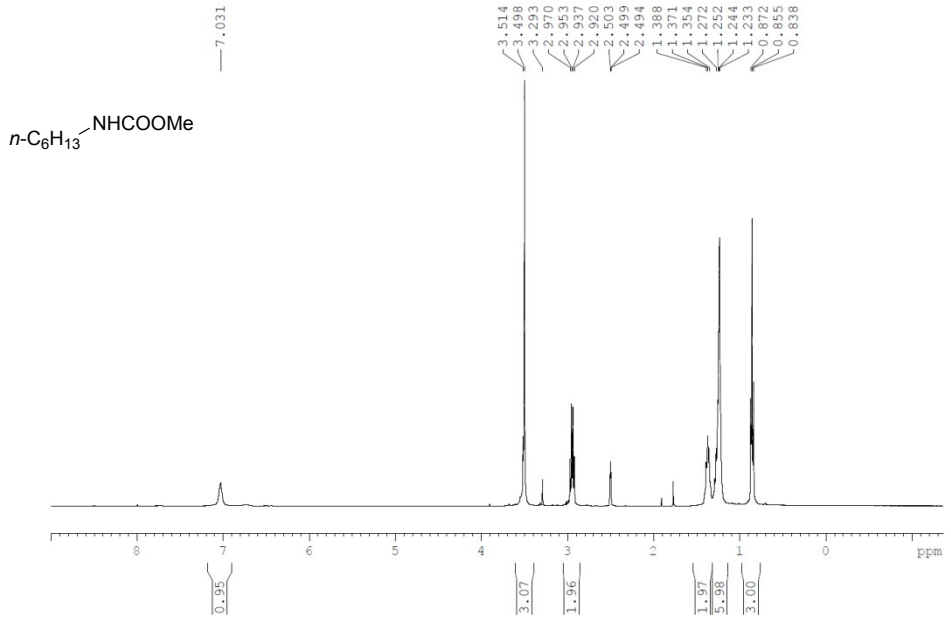


Figure S25. ^{1}H NMR (400 MHz, DMSO-d_6) of **1i**.

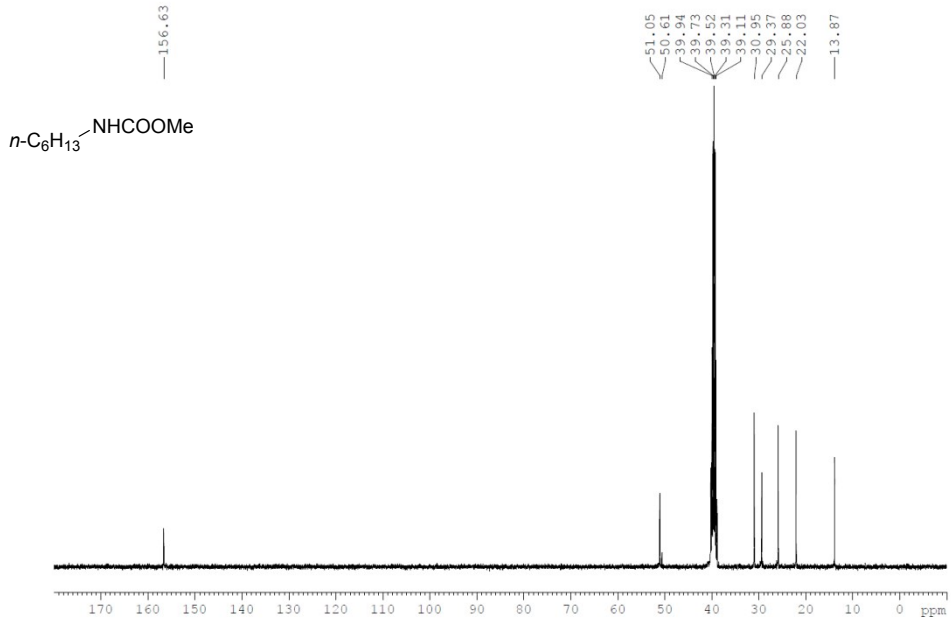


Figure S26. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **1i**.

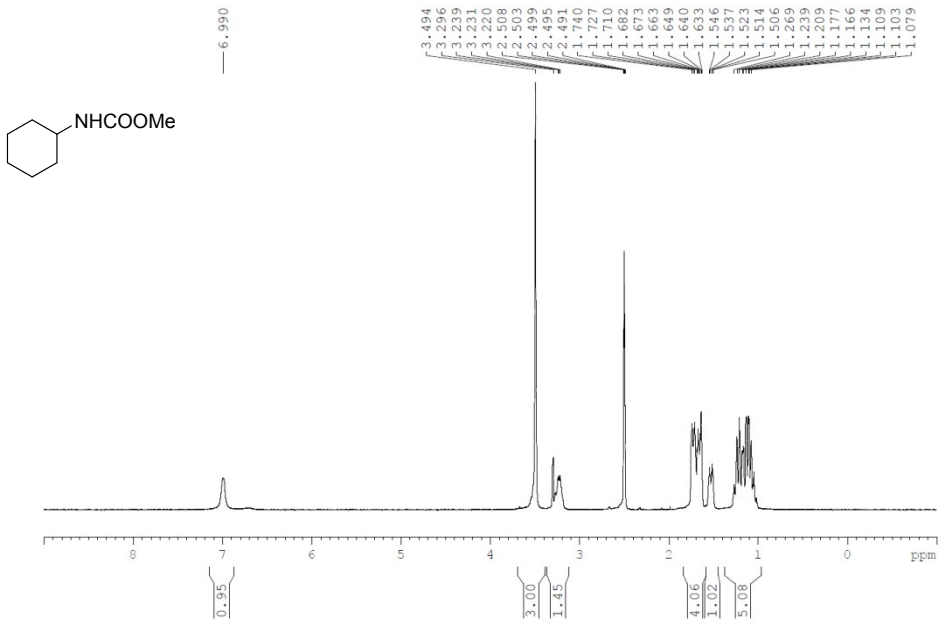


Figure S27. ^{1}H NMR (400 MHz, DMSO-d_6) of **1j**.

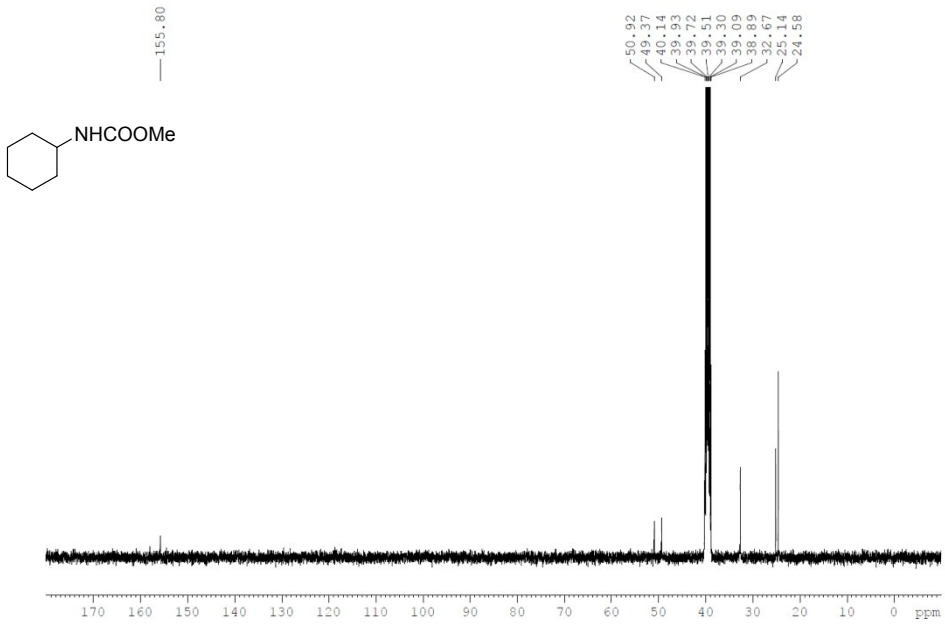


Figure S28. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **1j**.

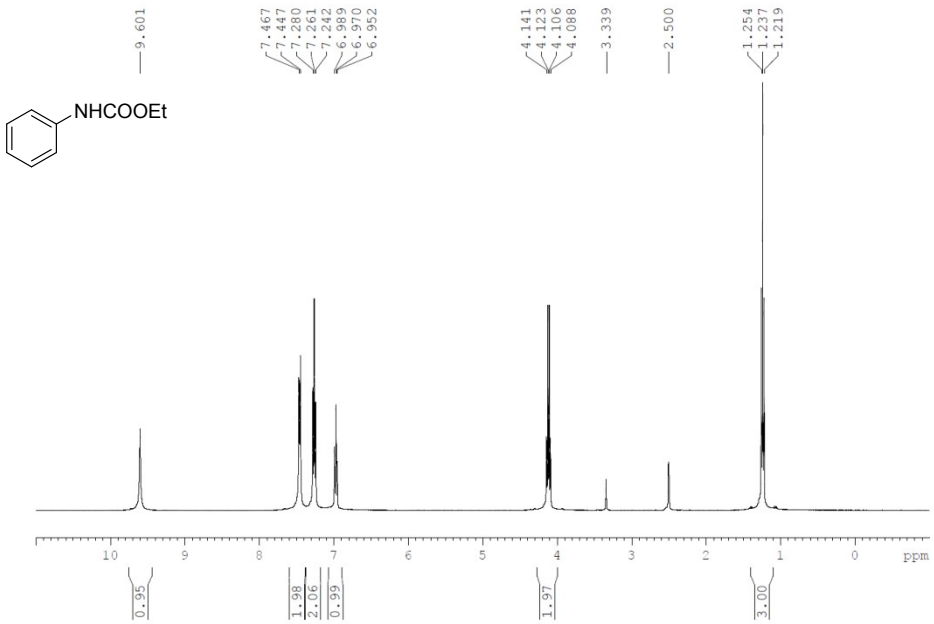


Figure S29. ^{1}H NMR (400 MHz, DMSO-d_6) of **1k**.

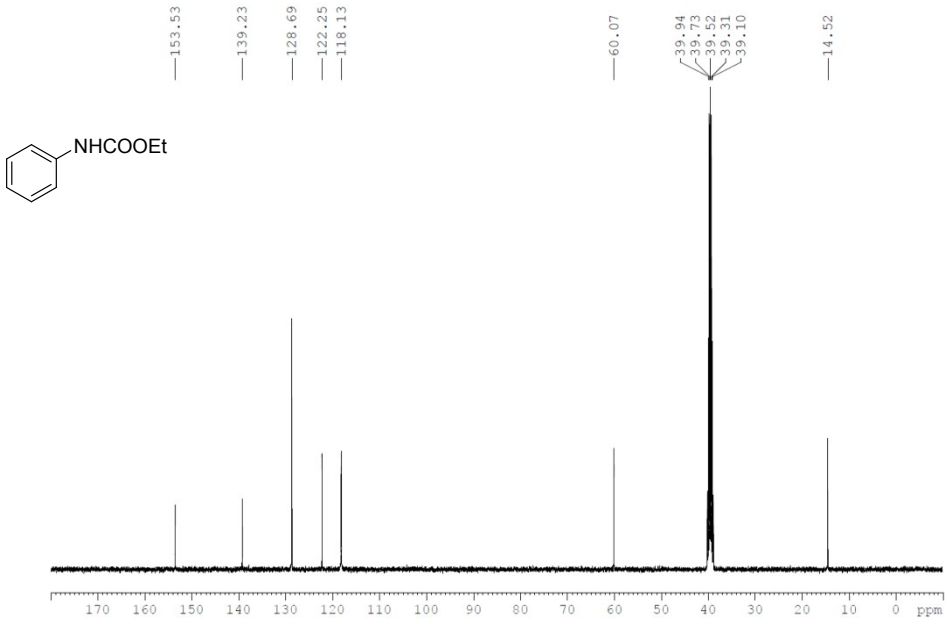


Figure S30. ^{13}C NMR of (100 MHz, DMSO-d_6) **1k**.

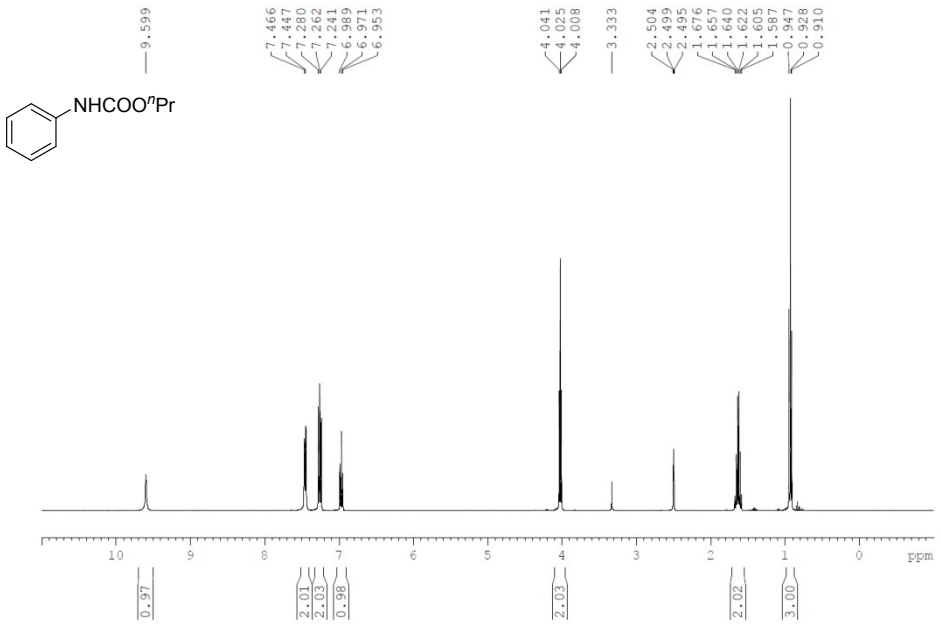


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of **1l**.

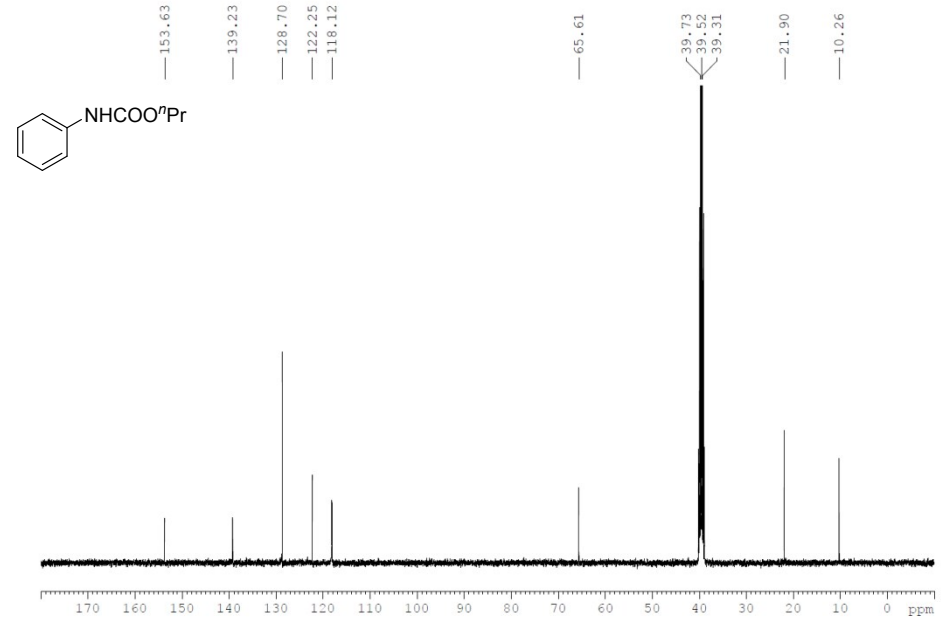


Figure S32. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **1l**.

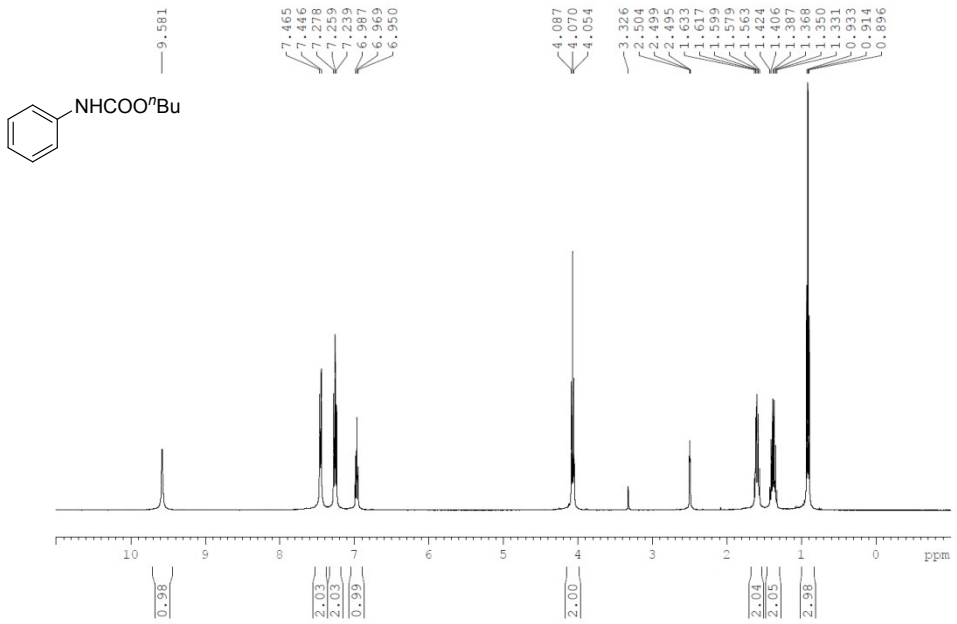


Figure S33. ^{1}H NMR (400 MHz, DMSO-d_6) of **1m**.

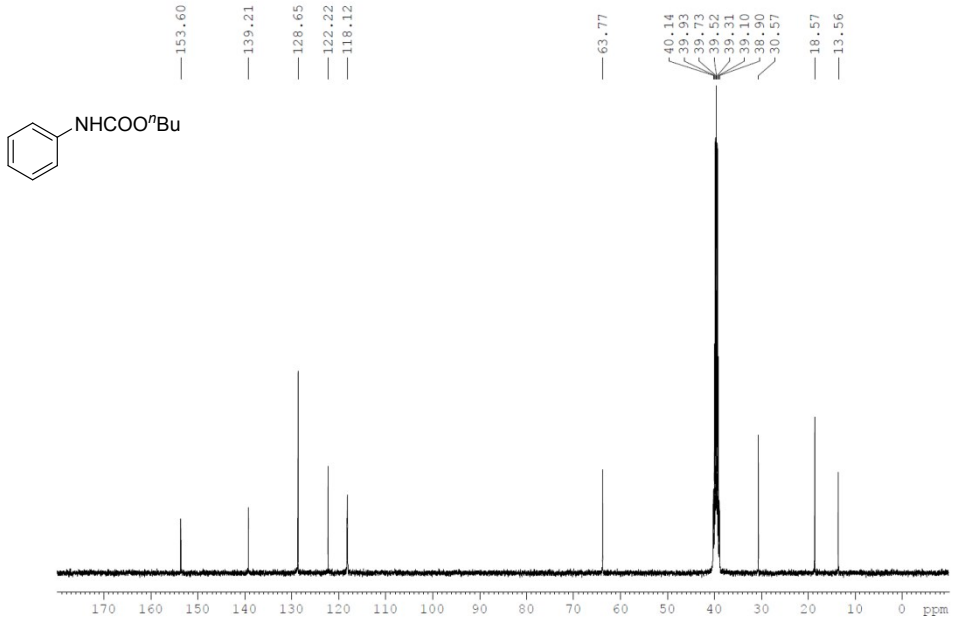


Figure S34. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **1m**.

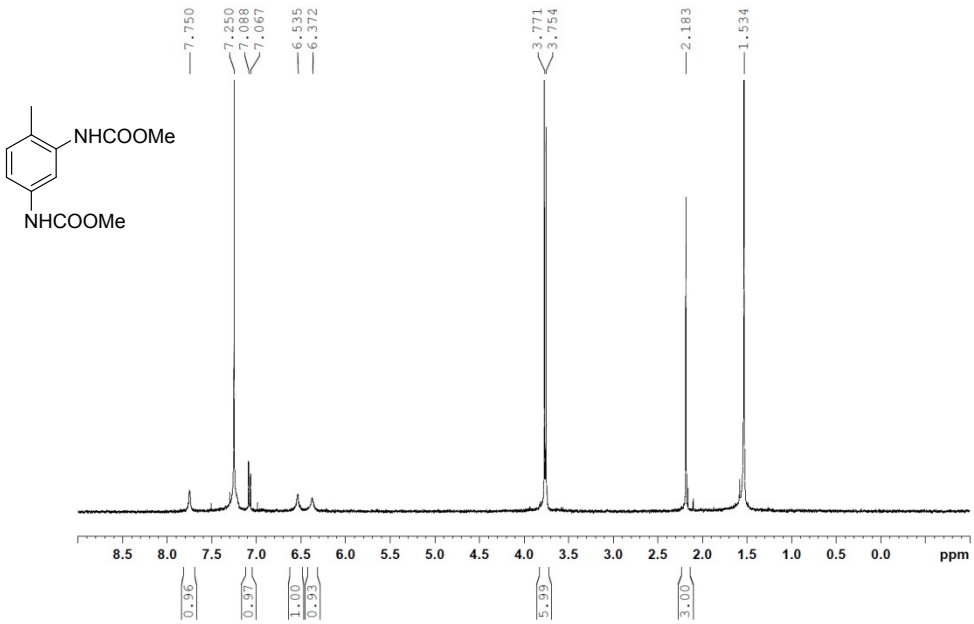


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of **1n**.

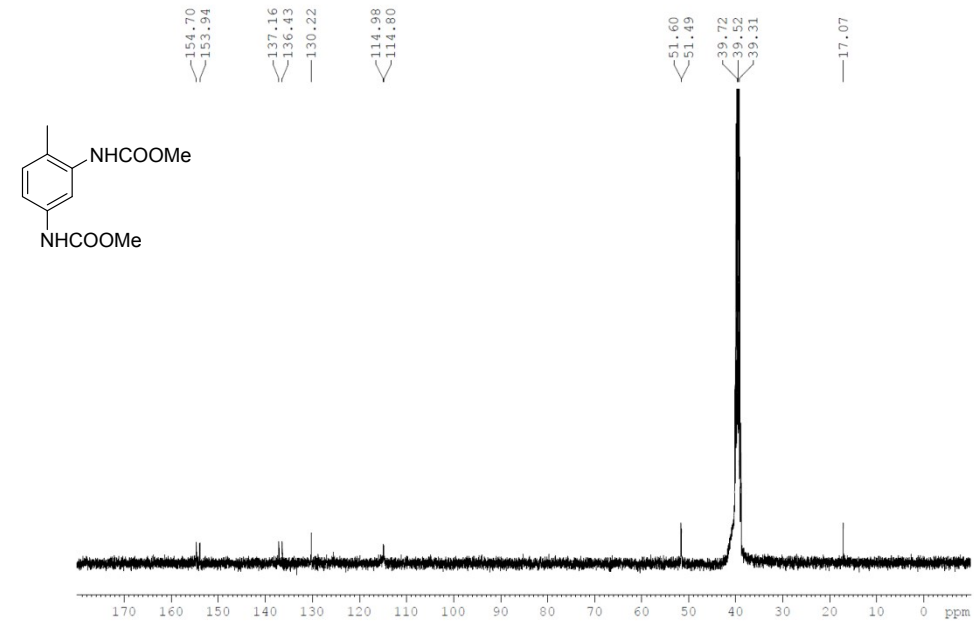


Figure S36. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **1n**.