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Supporting Information

for

A New Approach to Arylhydrazides via the Reaction of Mitsunobu Reagent with Arynes: Further Application to Access Diverse Nitrogen-containing Heterocycles in One Pot

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1. General

All isolated compounds were characterized on Bruker 400 and JEOL 400 MHz spectrometers in the $CDCl_3$, CD_3OD or $(CD_3)_2CO$. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^1H NMR and 77.16 for ^{13}C NMR), methanol (δ 3.31 for ^1H NMR) and acetone (δ 2.05 for ^1H NMR and 29.84 for ^{13}C NMR). High resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof). All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel. Anhydrous THF, PhMe were distilled over sodium benzophenone ketyl under Ar. All other solvents and reagents were used as obtained from commercial sources without further purification.

2. General Experimental Procedure

2.1 General Procedure for the Preparation of Arylhydrazines 3a-3j

To a solution of benzyne precursor **1a** (149 mg, 0.500 mmol) and diisopropyl azodicarboxylate (**2a**, 212 mg, 1.05 mmol) in CH_3CN (2.5 mL) were added 18-Crown-6 (330 mg, 1.25 mmol) and Ph_3P (275 mg, 1.05 mmol) at rt. After 10 mins, CH_3CN (2.5 mL, containing H_2O 4.32 g/L) and CsF (152 mg, 1.00 mmol) were added successively. The mixture was heated to 50 ^oC and kept for 4 h. The solvent was removed under reduced pressure and the residue was diluted with EtOAc (50 mL) and washed with H_2O three times. The organic layer was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by flash chromatography to respectively give **3a** (116 mg, 83%) as a light yellow oil and **4a** as a light yellow oil (4 mg, 3%).

Other Arylhydrazines were prepared following the similar method: **1** (0.5 mmol), azodicarboxylate/PPh_3 (2.1 equiv.), CsF (2.0 equiv.), 18-Crown-6 (2.5 equiv.), H_2O (1.2 equiv.), solvent (5 mL), 50 ^oC.

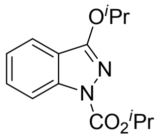
2.2 General Procedure for the Preparation of Heterocycles 5a-5c

5a & 5c To a solution of benzyne precursor **1a** (149 mg, 0.500 mmol) and azodicarboxylate **2c** (242 mg, 1.05 mmol) in CH_3CN (2.5 mL) were added 18-Crown-6 (330 mg, 1.25 mmol) and Ph_3P (275 mg, 1.05 mmol) at rt. After 10 min, CH_3CN (2.5 mL, containing H_2O 4.32 g/L) and CsF (152 mg, 1.00 mmol) were added successively. The mixture was heated to 50 ^oC and kept for 4 h. The solvent was removed under reduced pressure.

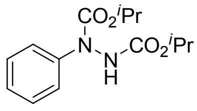
To a solution of the above residue and cycloheptanone (2.0 equiv.) or acetylacetone (2.0 equiv.) in AcOH (5.0 mL) was added $ZnCl_2$ (68 mg, 0.5 mmol) at rt. The mixture was heated to 130 ^oC and kept for 12 h. The solvent was removed under reduced pressure and the residue was diluted with EtOAc and washed with H_2O three times. The organic layer was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography to respectively give **5a** (52 mg, 56% for 3 steps) as a white solid or **5c** (55 mg, 64% for 3 steps) as a yellow oil.

5b 1-tetralone (2.0 equiv.) was used as the ketone. In accordance with the above operation, for the second step, the mixture was stirred under O_2, heated at 130 ^oC and kept for 24 h. The solvent was removed under reduced pressure and the residue was diluted with EtOAc and washed with H_2O three times. The organic layer was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography to give **5b** (58 mg, 53% for 4 steps) as a white solid.

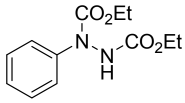
3. Characterization Data of the Products



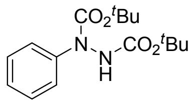
4a (4 mg, Y = 3%, R_f = 0.64 (PE:EA = 5:1)) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 6.4 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 5.36 (q, J = 6.0 Hz, 1H), 5.29 (q, J = 6.0 Hz, 1H), 1.49 (d, J = 6.4 Hz, 6H), 1.46 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 150.7, 141.0, 129.7, 123.1, 120.2, 118.1, 114.8, 72.6, 71.6, 22.2, 22.1; ESI-HRMS *m/z* Calcd. for $C_{14}H_{18}N_2O_3$ + Na (M+Na): 285.1210, found 285.1214.



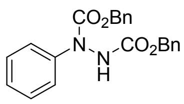
3a (116 mg, Y = 83%, R_f = 0.32 (PE:EA = 5:1) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (br s, 2H), 7.33-7.29 (m, 2H), 7.18-7.15 (m, 2H), 5.05-4.94 (m, 2H), 1.26 (d, J = 6.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 154.5, 141.9, 128.6, 126.0, 124.0, 70.9, 70.1, 22.0, 22.0; ESI-HRMS *m/z* Calcd. for $C_{14}H_{20}N_2O_4$ + Na (M+Na): 303.1315, found 303.1314.



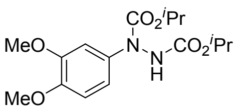
3b (97 mg, Y = 77%, R_f = 0.16 (PE:EA = 5:1)) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.35-7.31 (m, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.15 (br s, 1H), 4.28-4.18 (m, 4H), 1.27 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 155.1, 141.8, 128.8, 126.5, 124.4, 63.1, 62.4, 14.6; ESI-HRMS *m/z* Calcd. for $C_{12}H_{16}N_2O_4$ + Na (M+Na): 275.1002, found 275.1003.



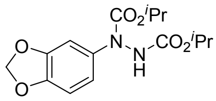
3c (111 mg, Y = 72%, R_f = 0.49 (PE:EA = 5:1)) as a light yellow solid. m.p. 105-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (br s, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 6.91-6.74 (m, 1H), 1.49 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 153.7, 142.2, 128.5, 125.6, 123.8, 82.3, 81.5, 28.3, 28.2; ESI-HRMS *m/z* Calcd. for $C_{16}H_{24}N_2O_4$ + Na (M+Na): 331.1628, found 331.1629.



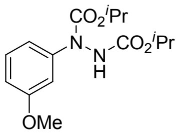
3d (133 mg, Y = 71%, R_f = 0.27 (PE:EA = 5:1)) as a light yellow oil. ^{1}H NMR (300 MHz, CD_3OD) δ 7.32-7.21 (br s, 15H), 5.18 (s, 2H), 5.12 (s, 2H); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.26 (br s, 16H), 5.21 (s, 2H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 154.8, 141.5, 135.7, 135.6, 128.8, 128.7, 128.6, 128.6, 128.4, 128.3, 128.0, 126.6, 124.5, 68.5, 68.0; ESI-HRMS *m/z* Calcd. for $C_{22}H_{20}N_2O_4$ + Na (M+Na): 399.1315, found 399.1316.



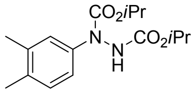
3e (142 mg, Y = 83%, R_f = 0.30 (PE:EA =2:1)) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (br s, 1H), 6.95-6.93 (m, 2H), 6.81-6.79 (m, 1H), 5.04-4.96 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 1.28-1.25 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.8, 148.6, 147.5, 135.2, 116.8, 110.7, 109.2, 70.6, 69.9, 56.0, 55.8, 22.0, 22.0; ESI-HRMS *m/z* Calcd. for $C_{16}H_{24}N_2O_6$ + Na (M+Na): 363.1527, found 363.1528.



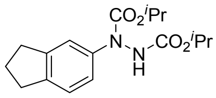
3f (113 mg, Y = 70%, R_f = 0.24 (PE:EA = 5:1)) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (br s, 1H), 6.94 (br s, 1H), 6.86 (br s, 1H), 6.74-6.72 (m, 1H), 5.95 (s, 2H), 5.03-4.93 (m, 2H), 1.27-1.23 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.7, 147.5, 146.1, 136.0, 118.4, 107.7, 106.9, 101.5, 70.8, 69.9, 22.0, 21.9; ESI-HRMS *m/z* Calcd. for $C_{15}H_{20}N_2O_6$ + Na (M+Na): 347.1214, found 347.1213.



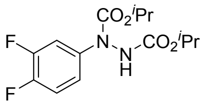
3g (The regioselectivity was confirmed through comparison of the ^{13}C-NMR of **3g** with analogous *m*-methoxylarylhydrazide. See **Fig. S35**) (94 mg, Y = 60%, R_f = 0.25 (PE:EA = 5:1)) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.0 Hz, 1H), 7.09-7.02 (m, 3H), 6.72 (d, *J* = 7.6 Hz, 1H), 5.02-4.97 (m, 2H), 3.77 (s, 3H), 1.26 (d, *J* = 5.6 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.1, 154.3, 143.0, 129.2, 116.0, 111.8, 109.7, 70.9, 70.1, 55.4, 22.0, 22.0; ESI-HRMS *m/z* Calcd. for $C_{15}H_{22}N_2O_5$ + Na (M+Na): 333.1421, found 333.1420.



3h (131 mg, Y = 85%, R_f = 0.33 (PE:EA = 5:1)) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (br s, 1H), 7.12 (br s, 2H), 7.08-7.06 (m, 1H), 5.05-4.96 (m, 2H), 2.23 (s, 3H), 2.22 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.7, 139.6, 136.8, 134.7, 129.7, 125.5, 121.8, 70.7, 69.9, 22.0, 22.0, 19.9, 19.3; ESI-HRMS *m/z* Calcd. for $C_{16}H_{24}N_2O_4$ + Na (M+Na): 331.1628, found 331.1629.

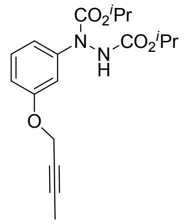


3i (141 mg, Y = 88%, R_f = 0.32 (PE:EA = 5:1)) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (br s, 1H), 7.18 (br s, 1H), 7.15 (br s, 2H), 5.03-4.96 (m, 2H), 2.87 (q, *J* = 7.2 Hz, 4H), 2.10-2.02 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.8, 144.7, 142.4, 140.1, 124.1, 122.7, 120.8, 70.6, 69.8, 32.9, 32.4, 25.6, 22.0, 22.0; ESI-HRMS *m/z* Calcd. for $C_{17}H_{24}N_2O_4$ + Na (M+Na): 343.1628, found 343.1630.

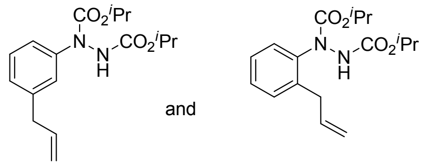


3j (67 mg, Y = 42%, R_f = 0.29 (PE:EA = 5:1)) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (br s, 1H), 7.18 (br s, 1H), 7.13-7.06 (m, 1H), 6.87-6.75 (m, 1H), 5.05-4.97 (m, 2H), 1.28 (d, *J* =

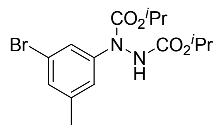
6.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 154.1, 151.4 (J = 13.5Hz), 148.1 (J = 13.6 Hz), 138.3 (dd, J = 7.5, 3.0 Hz), 119.5, 116.8 (J = 18.0 Hz), 113.5, 71.5, 70.6, 22.0, 22.0; ESI-HRMS *m/z* Calcd. for $C_{14}H_{18}F_2N_2O_4$ + Na (M+Na): 339.1127, found 339.1128.



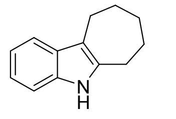
3k (The regioselectivity was confirmed through comparison of the ^{13}C-NMR of **3k** with analogous *m*-alkoxylarylhydrazide like **3g**) (108 mg, Y = 62%, R_f = 0.22 (PE:EA = 5:1)) as a light yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 8.4 Hz, 1H), 7.08 (br s, 2H), 6.85-6.64 (m, 2H), 5.06-4.96 (m, 2H), 4.63 (q, J = 2.1 Hz, 2H), 1.86 (t, J = 2.1 Hz, 3H), 1.28 (d, J = 6.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.1, 154.3, 143.0, 129.3, 116.5, 112.4, 110.7, 84.0, 74.0, 71.1, 70.2, 56.7, 22.1, 22.1, 3.8; ESI-HRMS *m/z* Calcd. for $C_{18}H_{24}N_2O_5$+ Na (M+Na): 371.1577, found 371.1574.



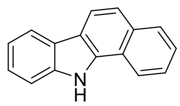
3l (ratio of *o*:*m* **=** 1:4 according to the integrals of allylic hydrogens. The minor isomer was further confirmed through the transformation of E1cB eliminative cleavage of the N-N′-bond reported by Magnus (*Org. Lett.* **2009**, *11*, 5646), and the crude ^1H-NMR of which could be found in **Fig. S36**. It could be easily compared with known compounds. See **Fig. S37 and Fig. S38**) (112 mg, Y = 70%, R_f = 0.33 (PE:EA = 5:1)) as a yellow oil. ^1H NMR (300 MHz, $(CD_3)_2CO$) δ 8.83 (s, 0.80H), 8.50 (s, 0.20H), 7.59-7.20 (m, 4H), 7.07-6.97 (m, 1H), 6.04-5.90 (m, 1H), 5.24-4.83 (m, 4H), 3.51 (d, J = 6.0 Hz, 0.40H) 3.39 (d, J = 6.0 Hz, 1.6H), 1.42-1.09 (m, 12H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 156.8, 154.8, 143.6, 141.0, 138.2, 129.1, 127.6 (minor isomer), 126.3, 124.4, 121.9, 116.1, 40.6, 22.2, 22.2; ESI-HRMS *m/z* Calcd. for $C_{17}H_{24}N_2O_4$ + Na (M+Na): 343.1628, found 343.1622.



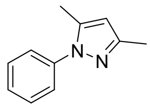
3m (The regioselectivity was readily observed from the ^1H-NMR of **3m**) (DIAD/PPh_3 (4.2 equiv.) were used instead, 50 mg, Y = 27%, R_f = 0.37 (PE:EA = 5:1)) as a yellow oil. ^1H NMR (300 MHz, $(CD_3)_2CO$) δ 8.71 (s, 1H), 7.39 (s, 1H), 7.18 (s, 1H), 7.05 (s, 1H), 4.85-4.74 (m, 2H), 2.19 (s, 3H), 1.13 (d, J = 3.9 Hz, 6H), 1.11 (d, J = 4.2 Hz, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 156.8, 154.5, 144.7, 141.2, 129.3, 123.6, 123.0, 121.8, 71.1, 70.0, 22.2, 22.2, 21.2; ESI-HRMS *m/z* Calcd. for $C_{15}H_{21}BrN_2O_4$ + Na (M+Na): 395.0577, found 395.0575.



5a (52 mg, Y = 56%, R_f = 0.66 (PE:EA = 5:1)) as a white solid. m.p. 133-134 °C. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.68 (s, 1H), 7.48-7.45 (m, 1H), 7.27-7.24 (m, 1H), 7.09-7.06 (m, 2H), 2.85-2.80 (m, 4H), 1.90-1.87 (m, 2H), 1.80-1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 137.5, 134.4, 129.4, 120.7, 119.1, 117.8, 113.8, 110.3, 31.9, 29.6, 28.8, 27.6, 24.8; ESI-HRMS *m/z* Calcd. for $C_{13}H_{15}N$ + H (M+H): 186.1277, found 186.1278.



5b (58 mg, Y = 53%, R_f = 0.51 (PE:EA = 5:1)) as a white solid. m.p. 222-223 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) *δ* 11.28 (s, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.68-7.59 (m, 3H), 7.56-7.52 (m, 1H), 7.41 (td, *J* = 7.2, 1.2 Hz, 1H), 7.28-7.24 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) *δ* 140.1, 136.3, 133.4, 129.6, 126.3, 126.0, 125.5, 124.8, 122.5, 122.3, 120.5, 120.5, 120.3, 120.2, 118.9, 112.2; ESI-HRMS *m/z* Calcd. for $C_{16}H_{11}N$ + H (M+H): 218.0964, found 218.0965.



5c (55 mg, Y = 64%, R_f = 0.53 (PE:EA = 5:1)) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43-7.42 (m, 4H), 7.34-7.32 (m, 1H), 5.99 (s, 1H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 149.0, 140.0, 139.4, 129.0, 127.3, 124.8, 107.0, 13.6, 12.4; ESI-HRMS *m/z* Calcd. $C_{11}H_{12}N_2$ + H (M+H): 173.1073, found 173.1074.

4. NMR spectra

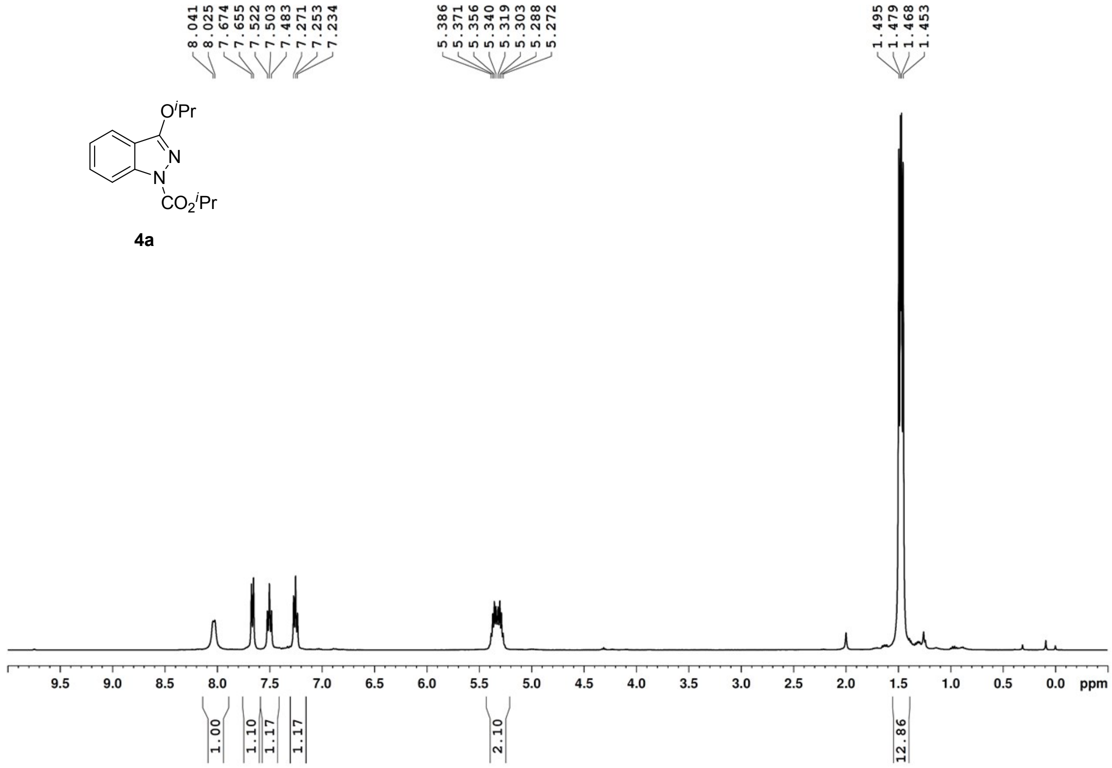


Fig. S1. ^{1}H NMR of compound **4a** (400 MHz, $CDCl_3$).

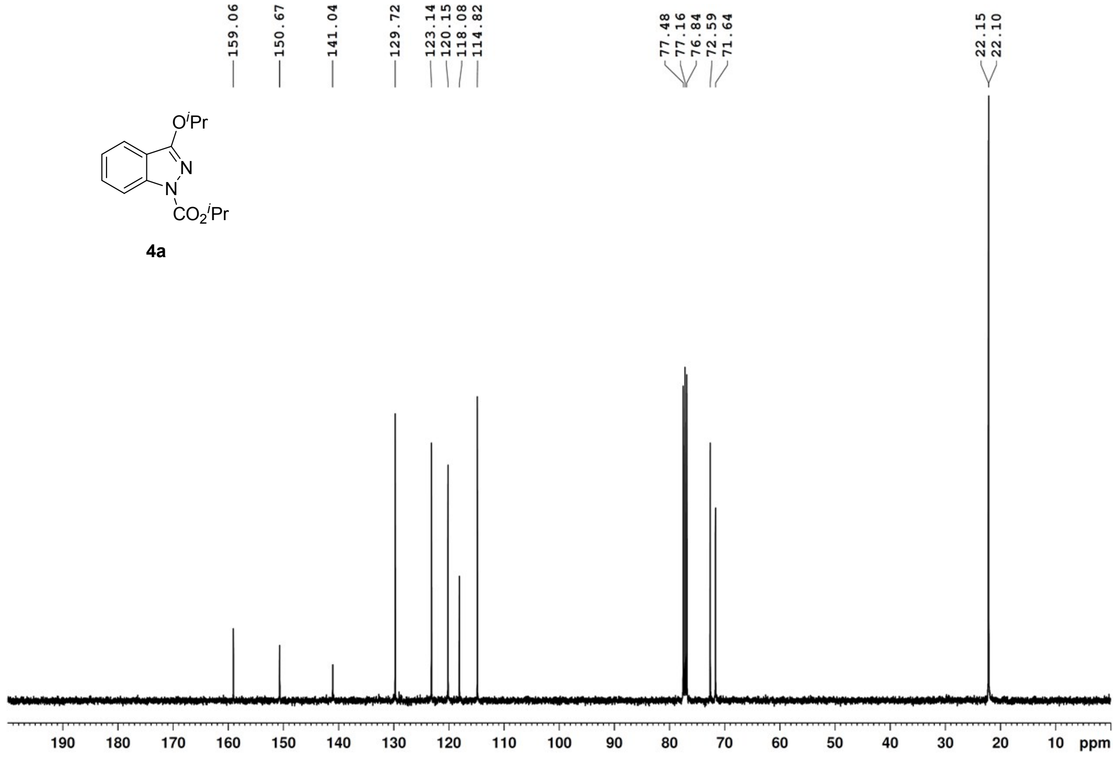


Fig. S2. ^{13}C NMR of compound **4a** (100 MHz, $CDCl_3$).

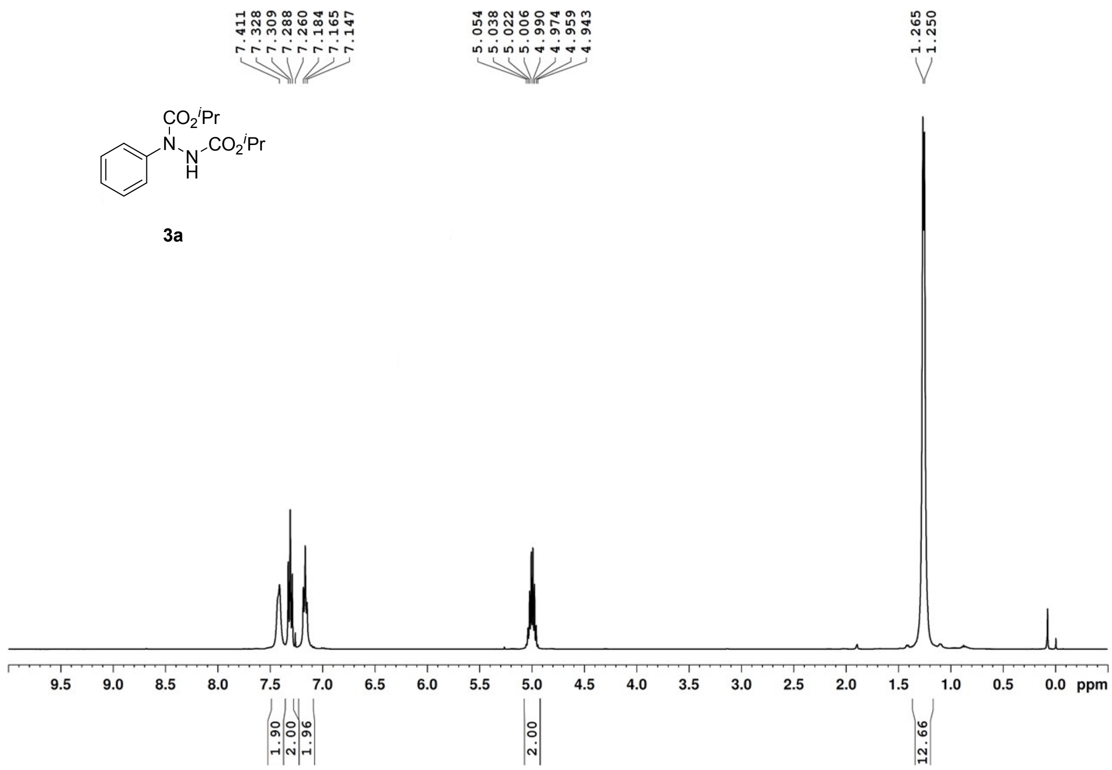


Fig. S3. [1]H NMR of compound **3a** (400 MHz, $CDCl_3$).

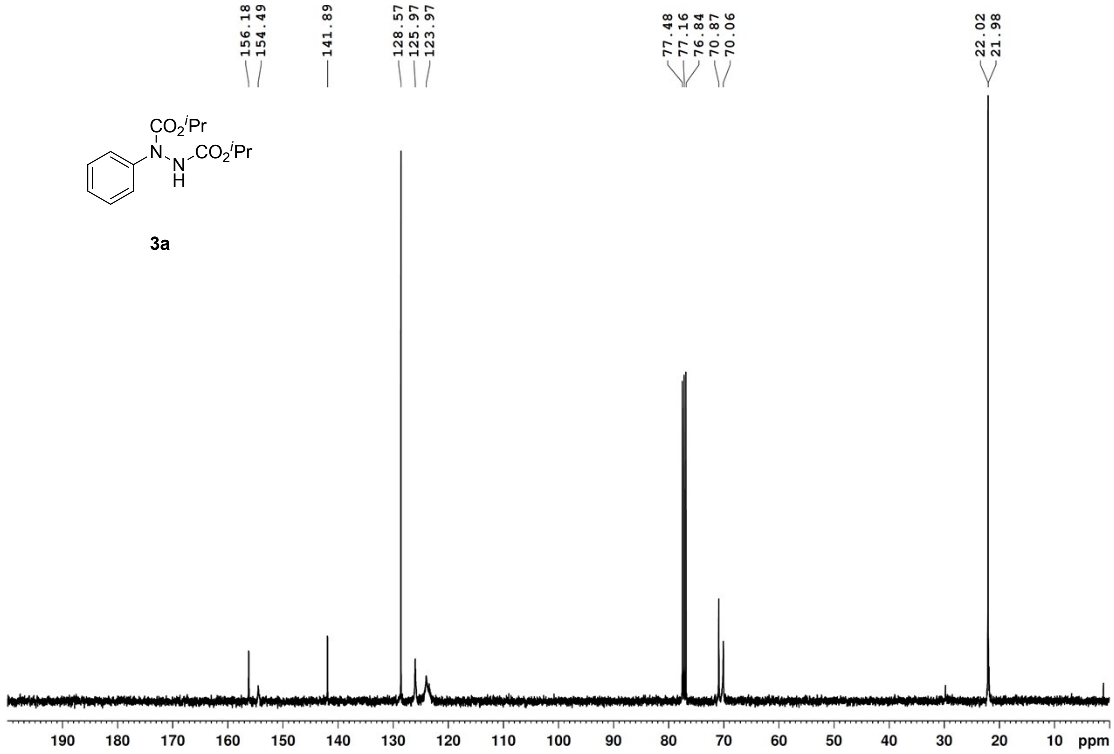


Fig. S4. [13]C NMR of compound **3a** (100 MHz, $CDCl_3$).

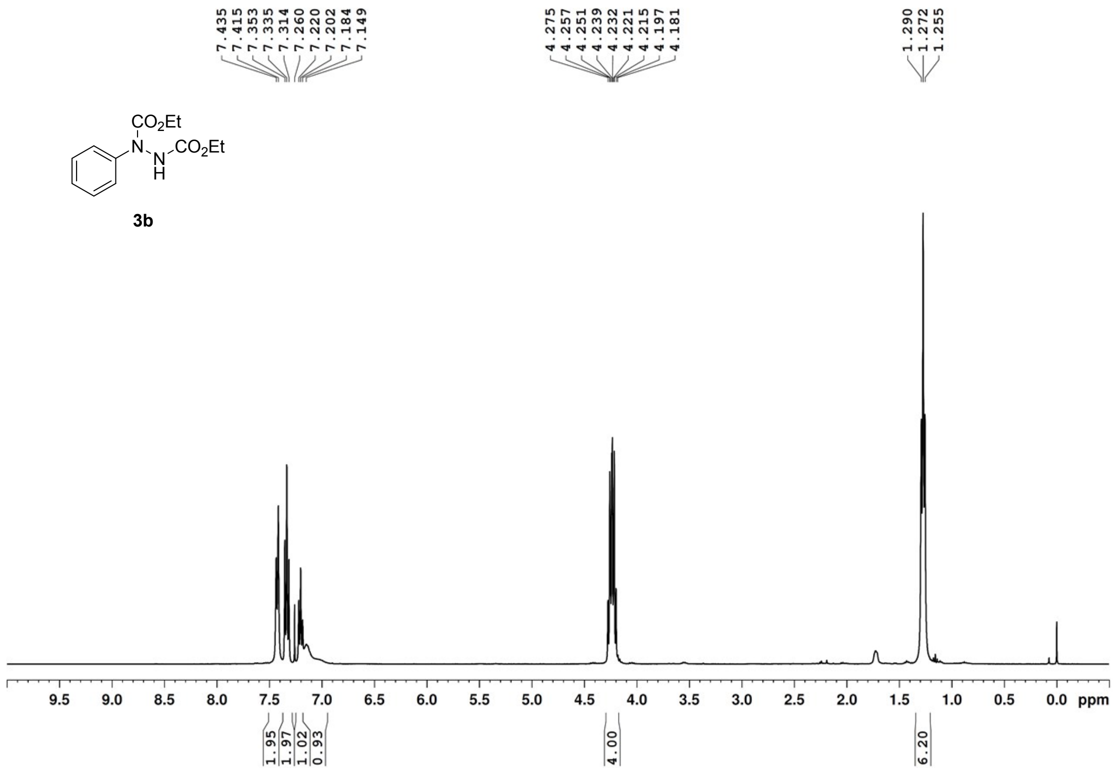


Fig. S5. ^{1}H NMR of compound **3b** (400 MHz, $CDCl_3$).

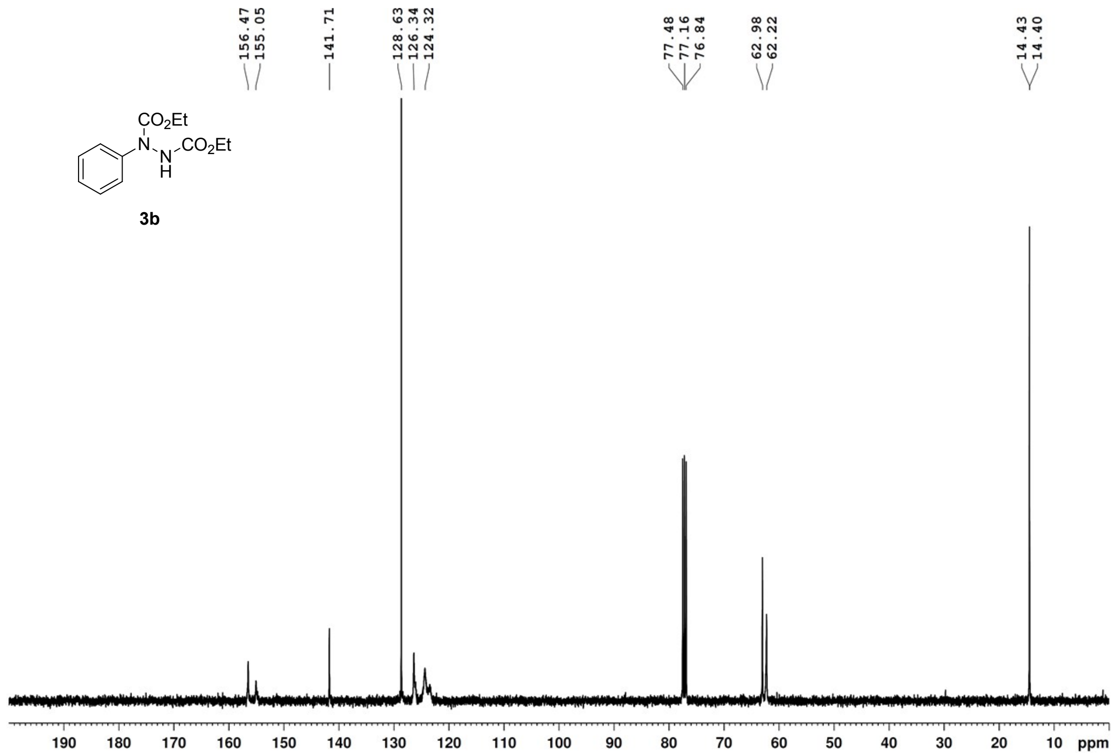


Fig. S6. ^{13}C NMR of compound **3b** (100 MHz, $CDCl_3$).

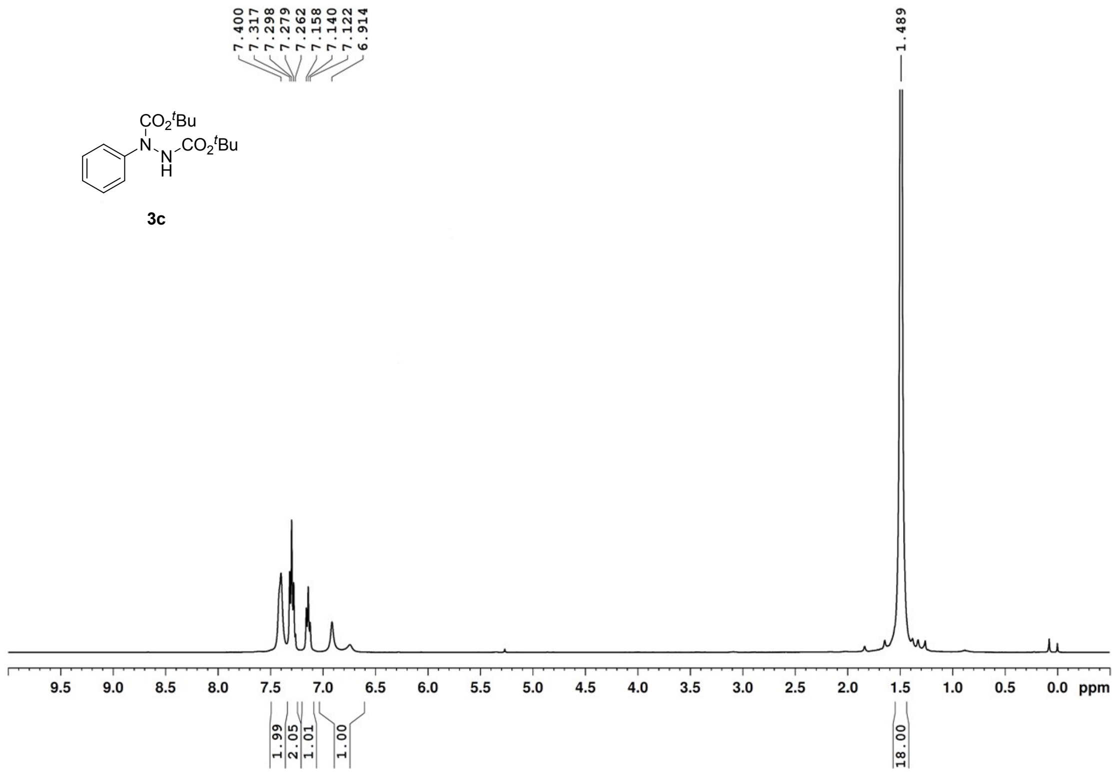


Fig. S7. ^{1}H NMR of compound **3c** (400 MHz, $CDCl_3$).

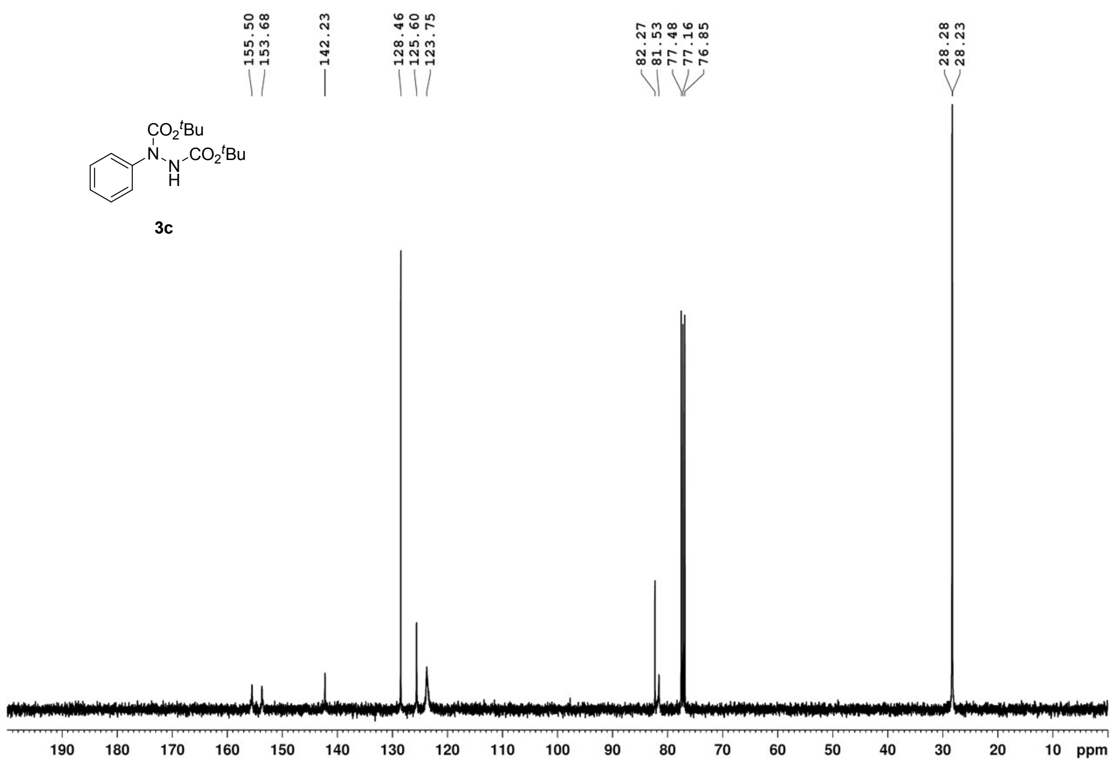


Fig. S8. ^{13}C NMR of compound **3c** (100 MHz, $CDCl_3$).

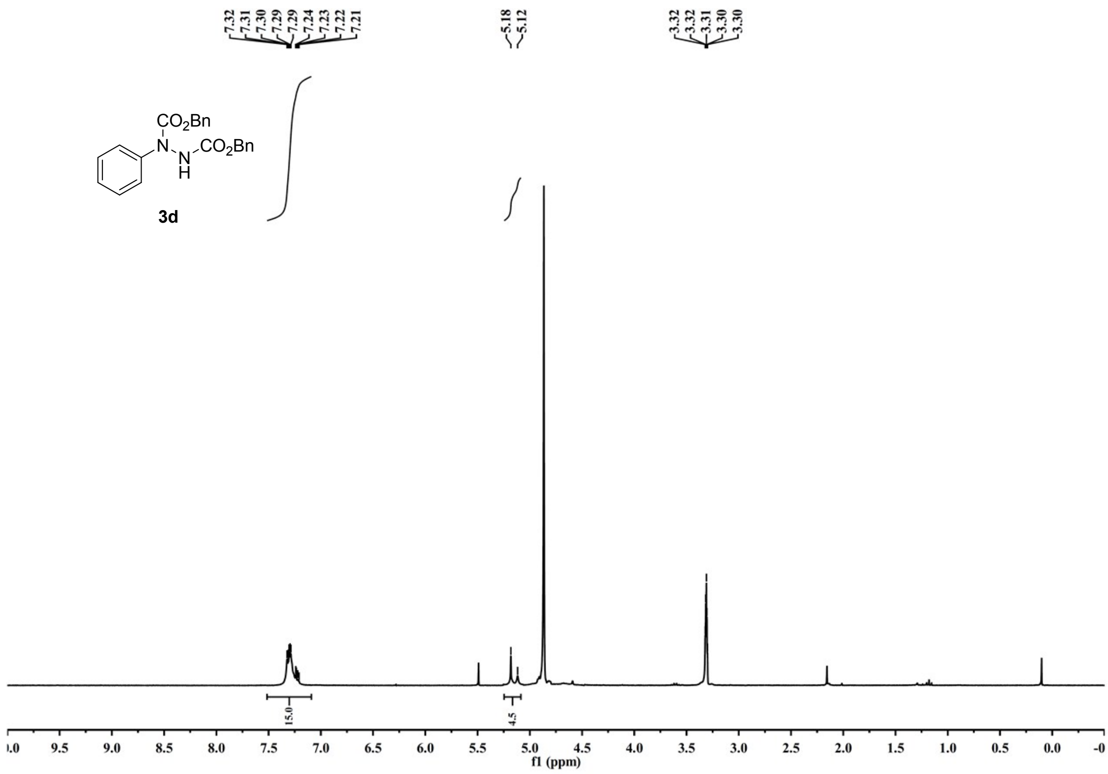


Fig. S9. ^{1}H NMR of compound **3d** (300 MHz, CD_3OD).

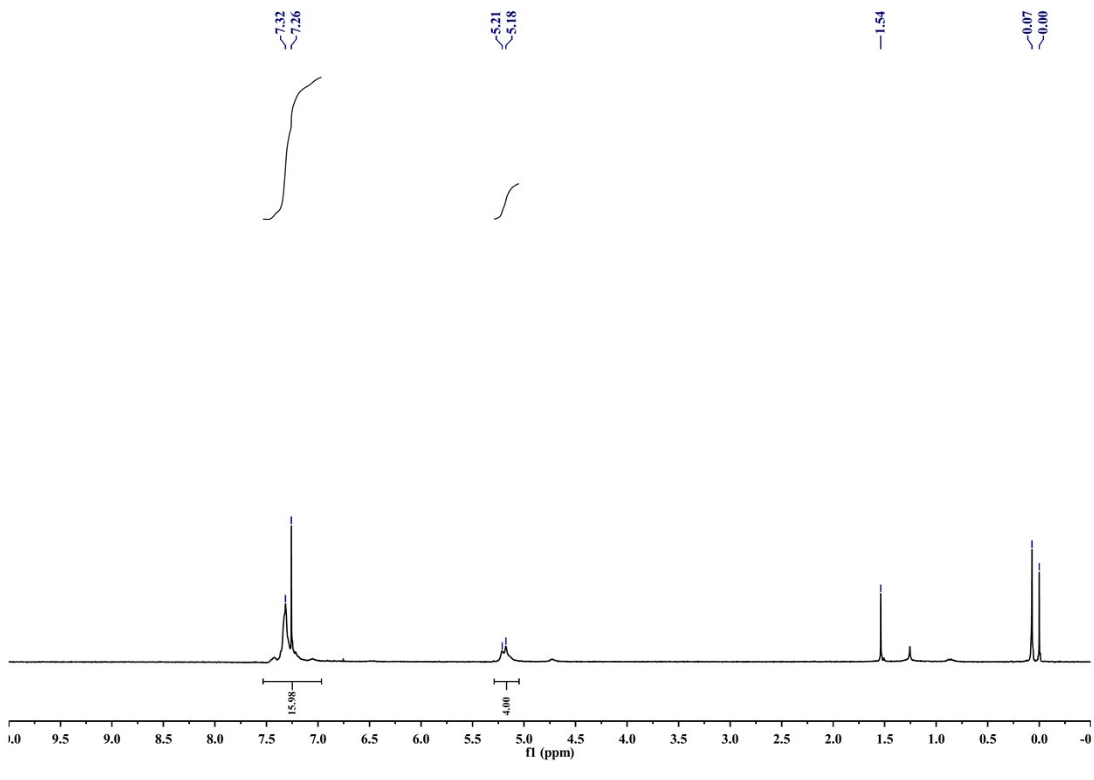


Fig. S9'. ^{1}H NMR of compound **3d** (300 MHz,$CDCl_3$).

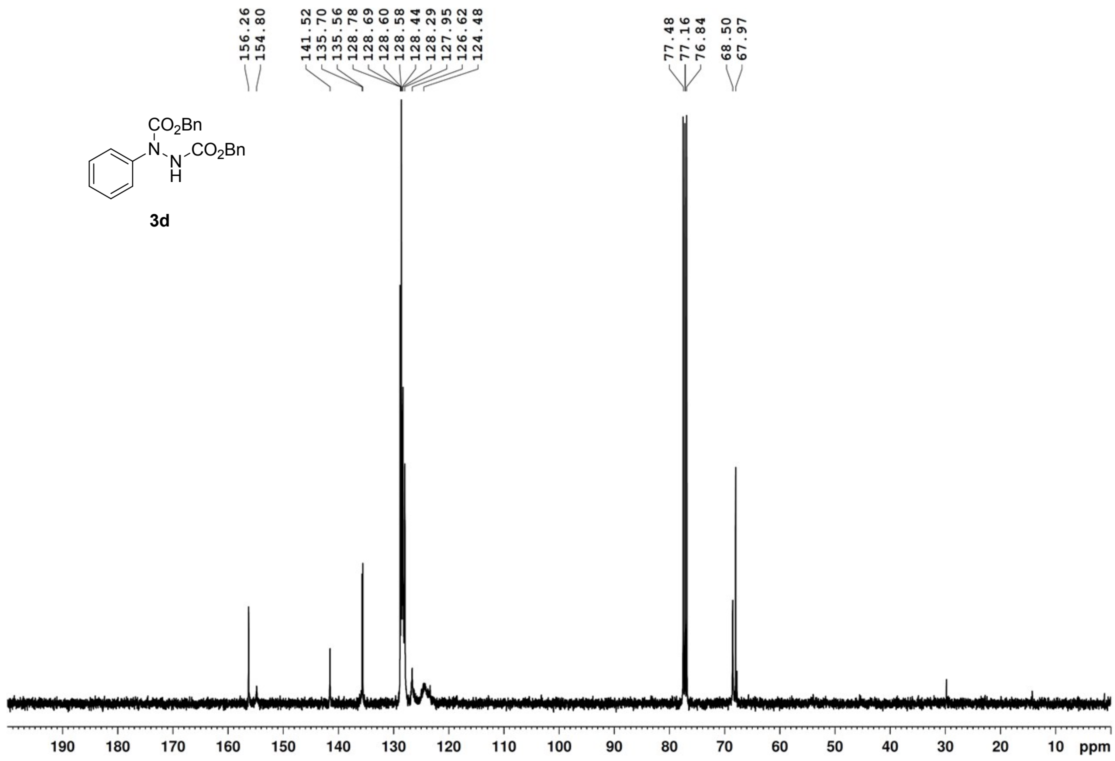


Fig. S10. ^{13}C NMR of compound **3d** (100 MHz, $CDCl_3$).

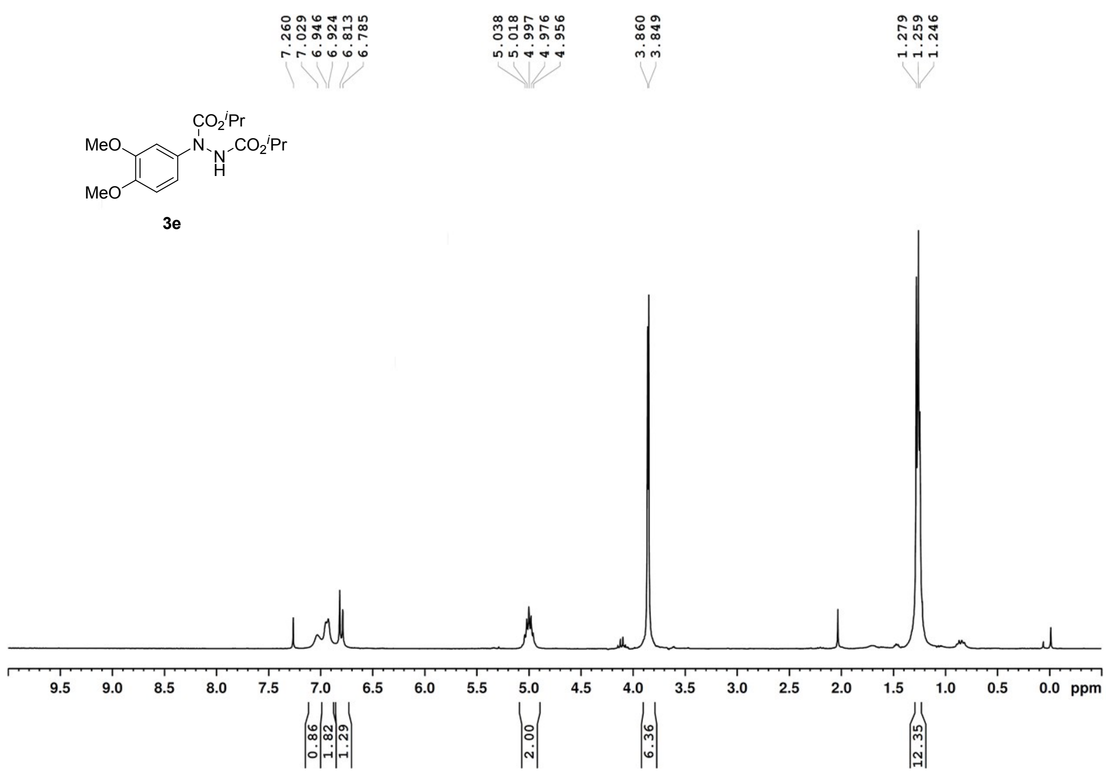


Fig. S11. ^{1}H NMR of compound **3e** (300 MHz, $CDCl_3$).

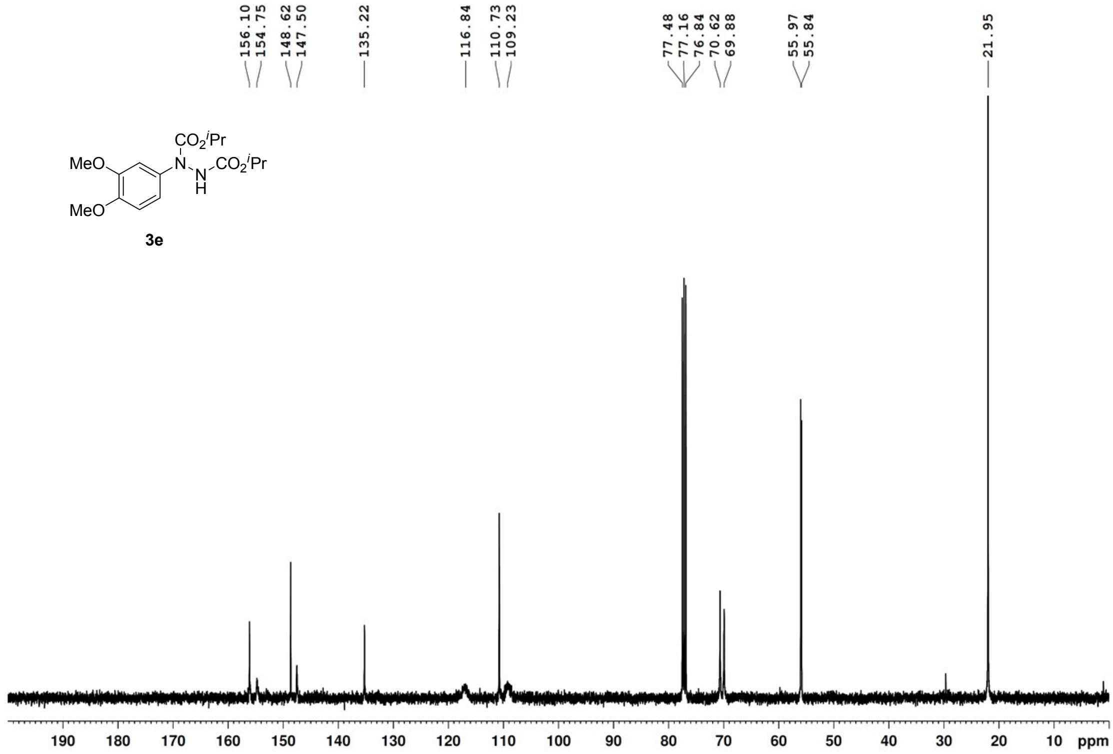


Fig. S12. ^{13}C NMR of compound **3e** (100 MHz, $CDCl_3$).

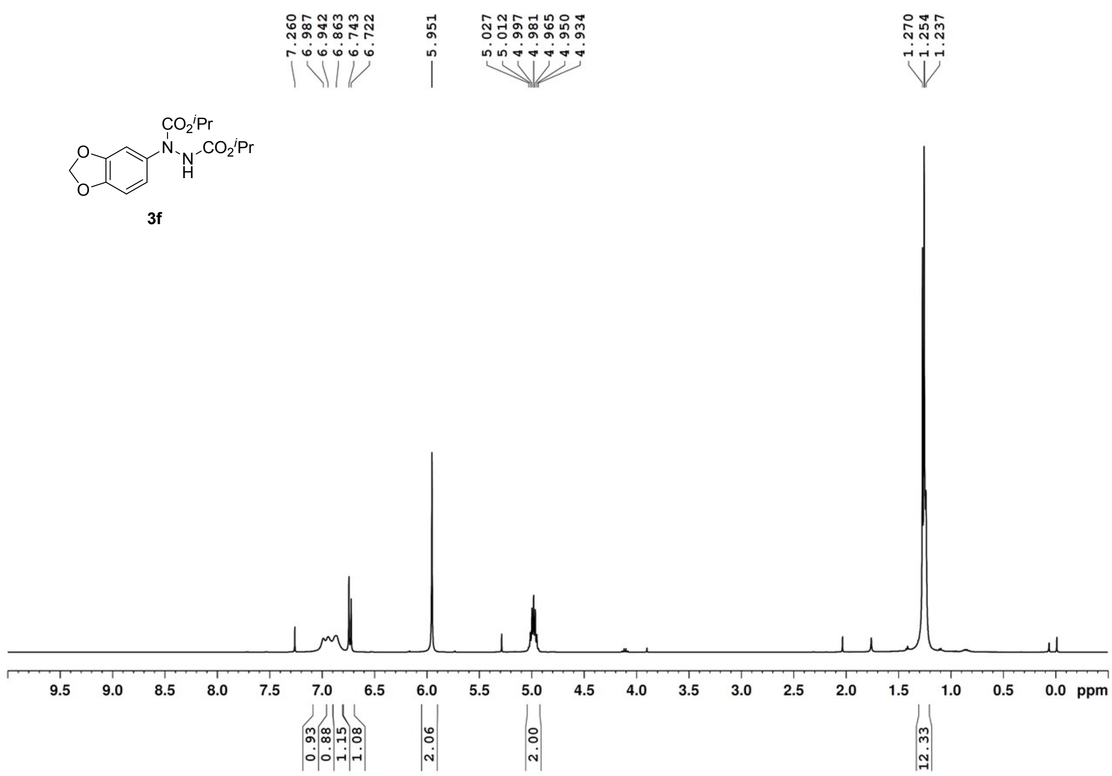


Fig. S13. ^{1}H NMR of compound **3f** (400 MHz, $CDCl_3$).

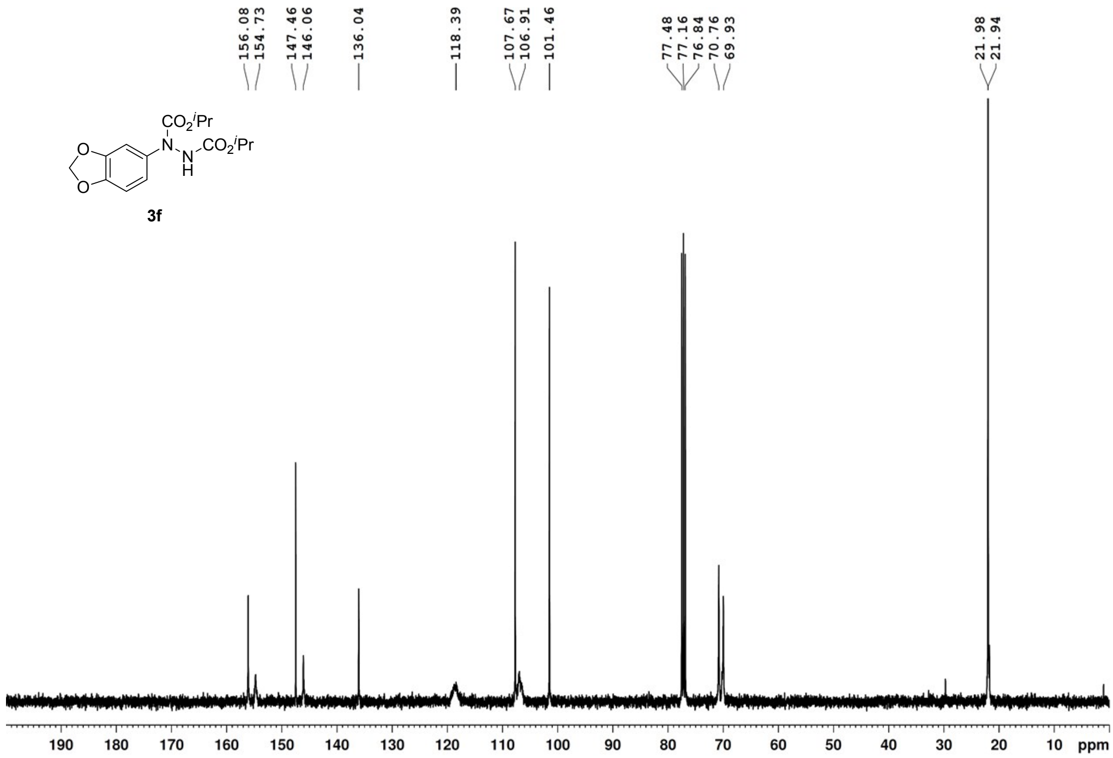


Fig. S14. ^{13}C NMR of compound **3f** (100 MHz, $CDCl_3$).

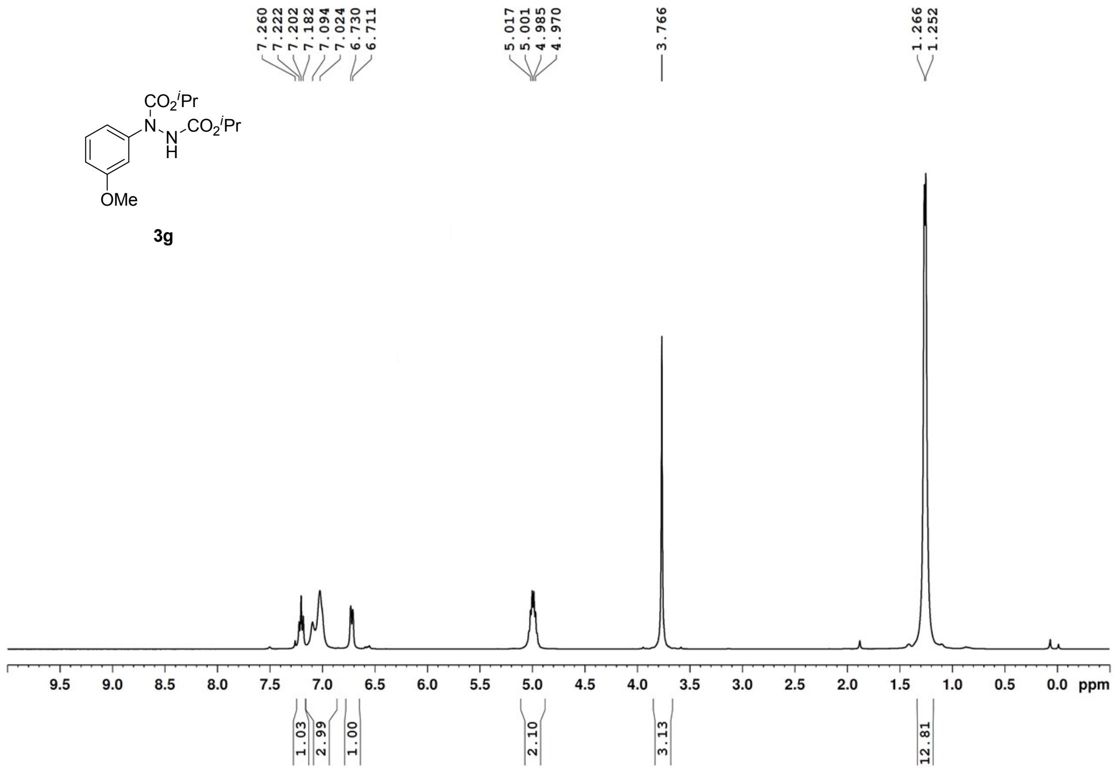


Fig. S15. ^{1}H NMR of compound **3g** (400 MHz, $CDCl_3$).

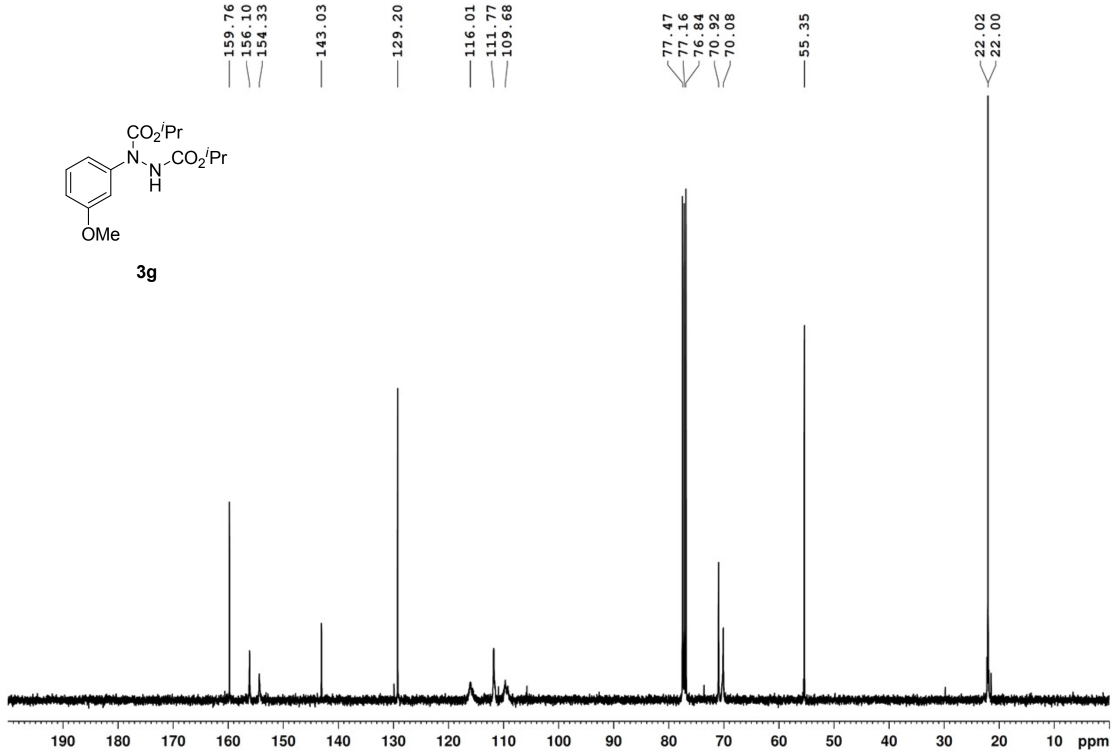


Fig. S16. ^{13}C NMR of compound **3g** (100 MHz, $CDCl_3$).

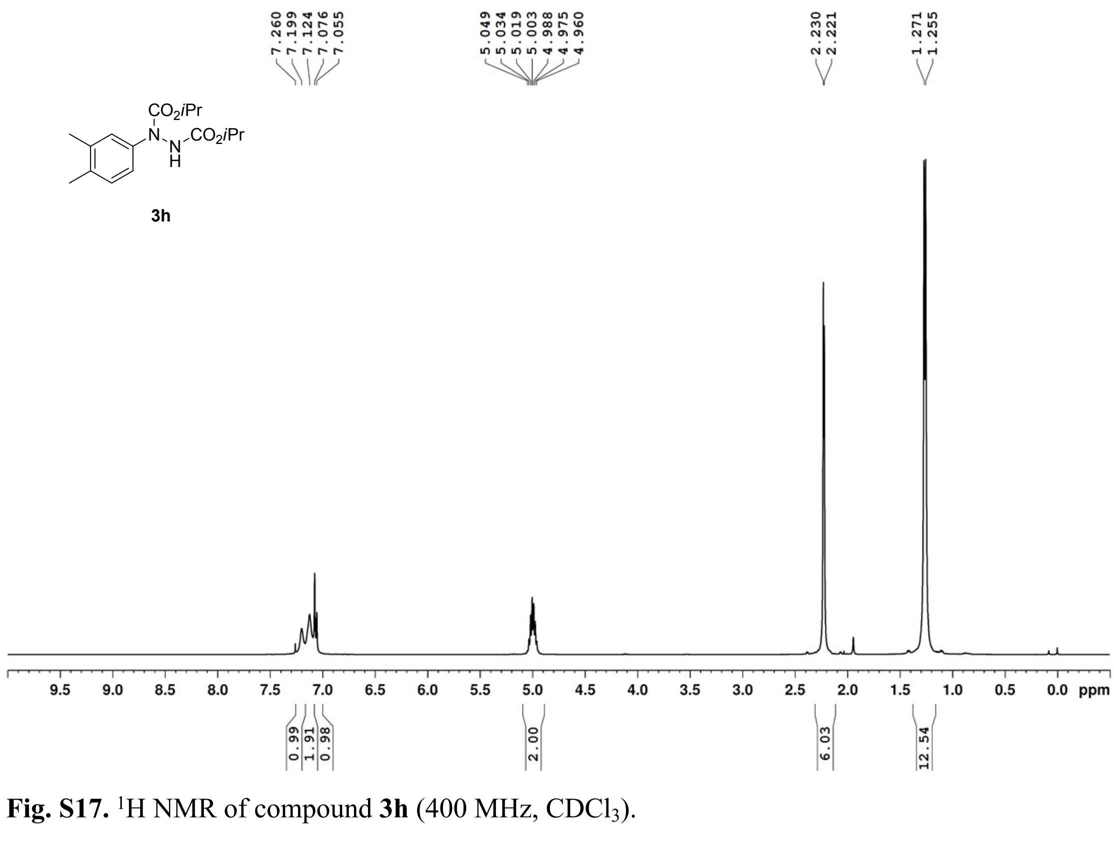


Fig. S17. ^{1}H NMR of compound **3h** (400 MHz, $CDCl_3$).

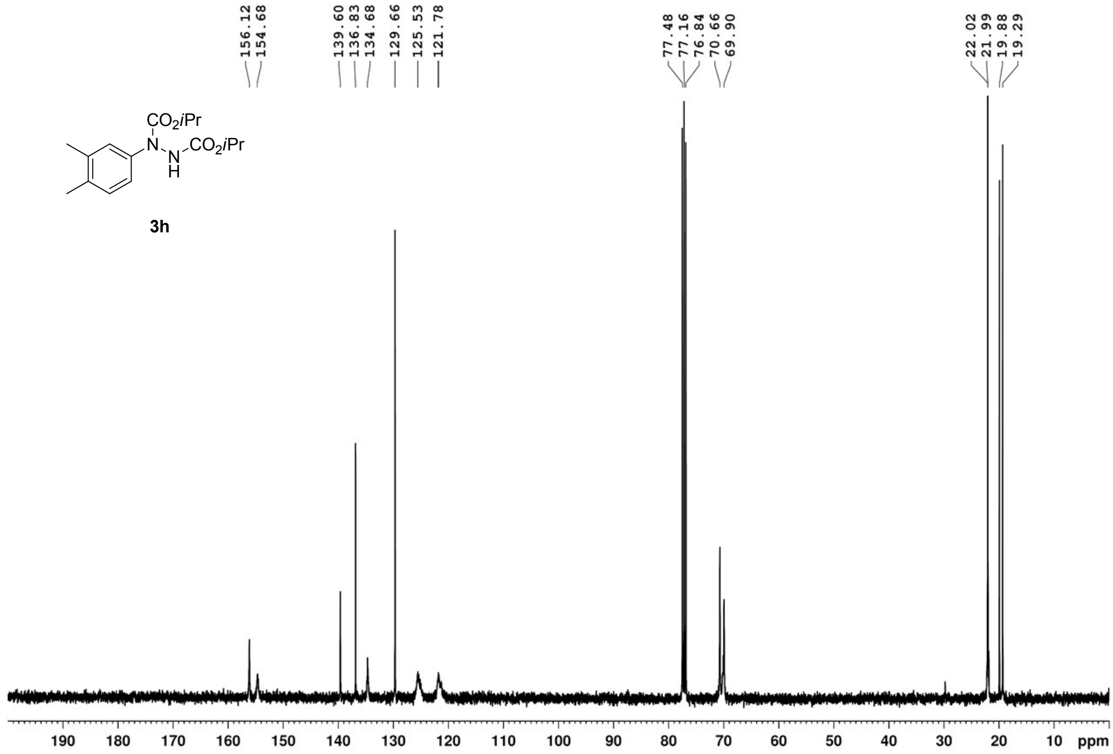


Fig. S18. ^{13}C NMR of compound **3h** (100 MHz, $CDCl_3$).

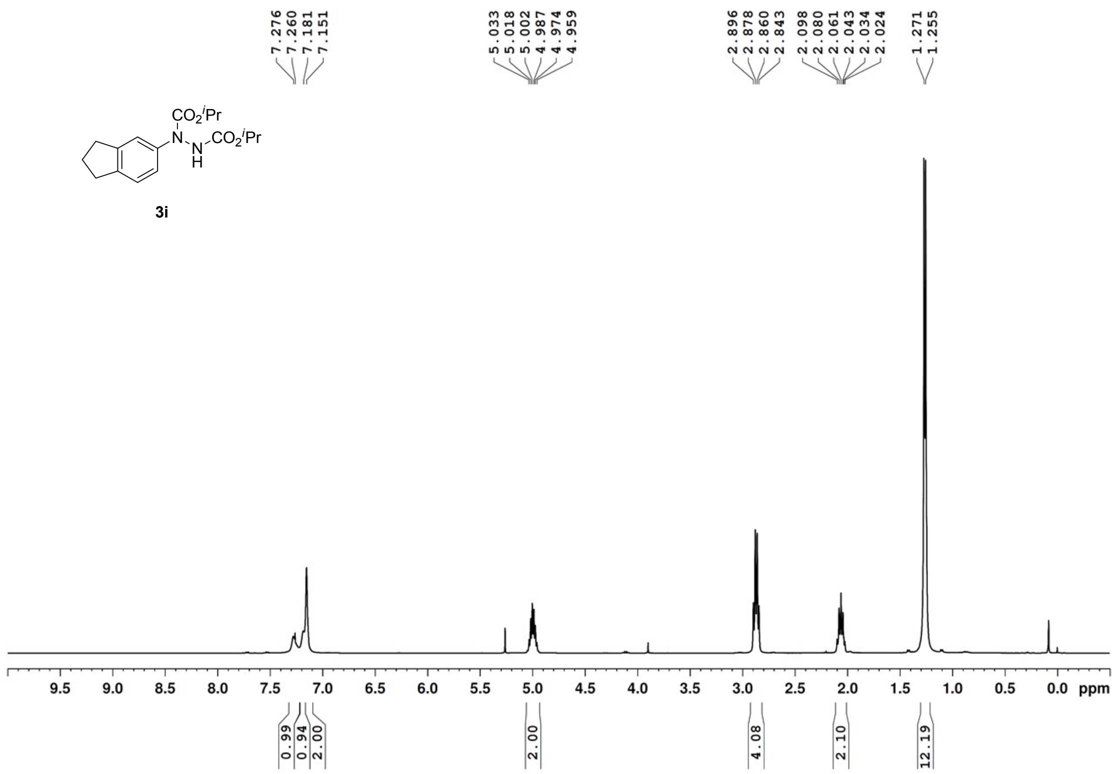


Fig. S19. ^{1}H NMR of compound **3i** (400 MHz, $CDCl_3$).

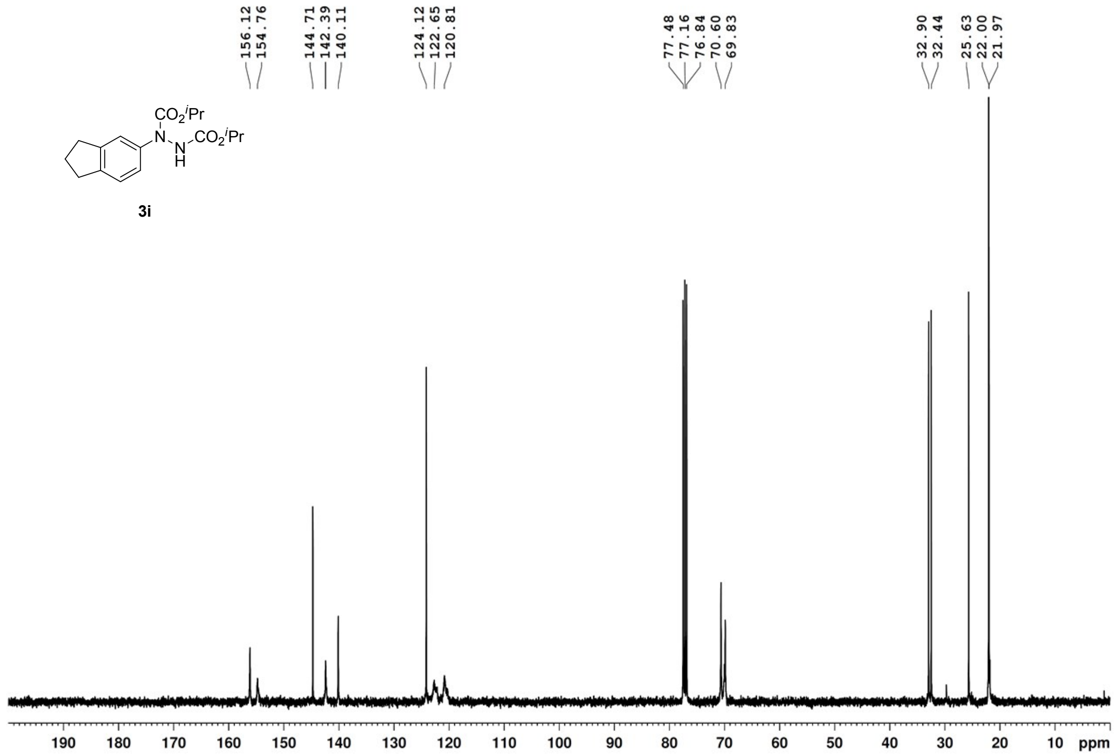


Fig. S20. ^{13}C NMR of compound **3i** (100 MHz, $CDCl_3$).

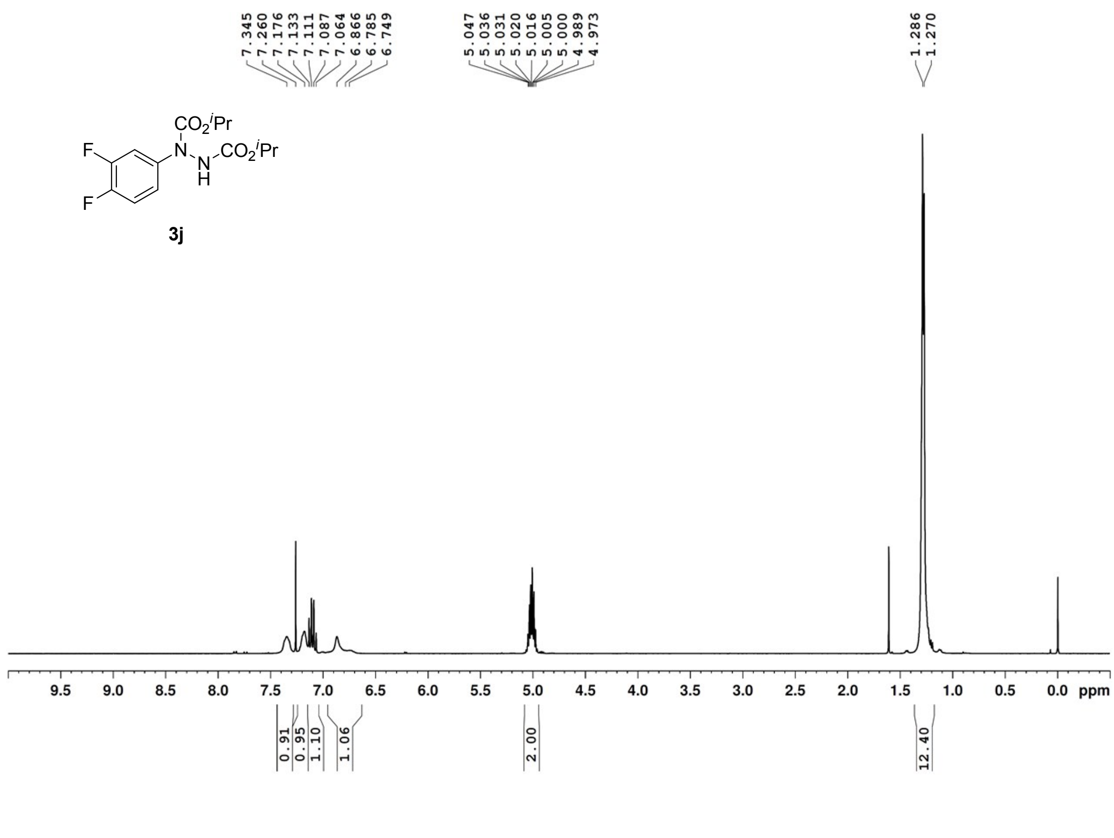


Fig. S21. ^{1}H NMR of compound **3j** (400 MHz, $CDCl_3$).

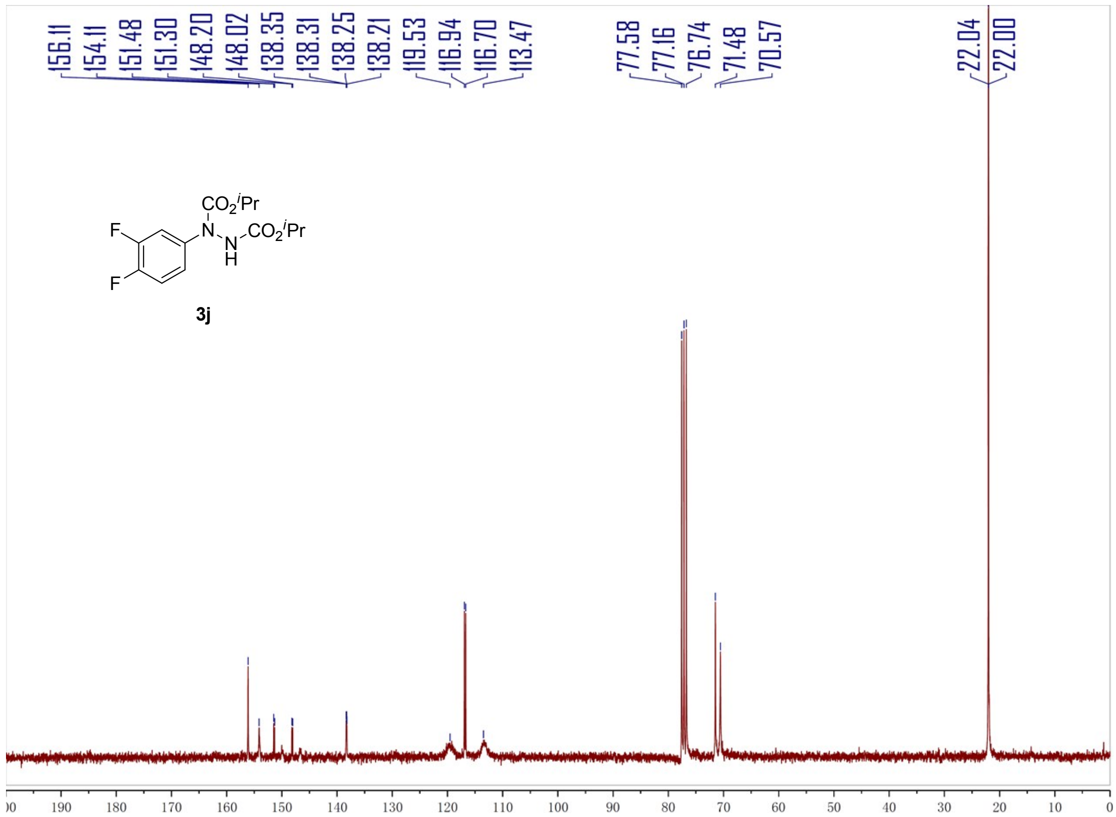


Fig. S22. ^{13}C NMR of compound **3j** (75 MHz, $CDCl_3$).

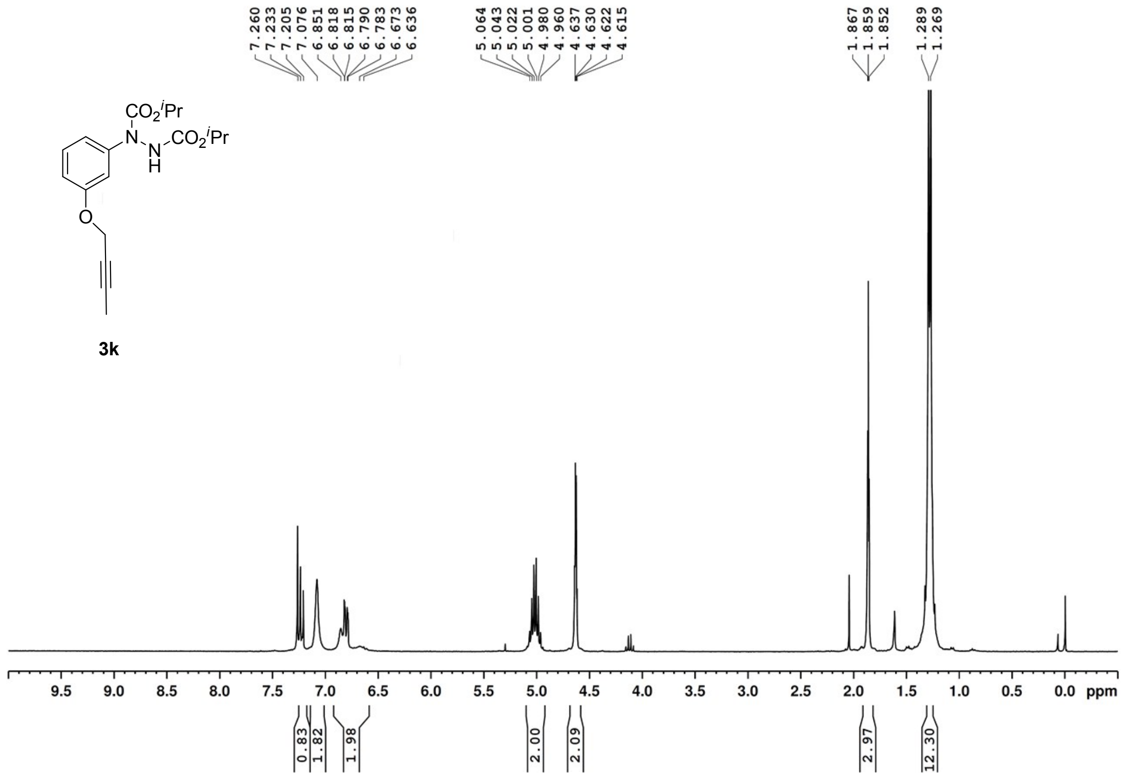


Fig. S23. ^{1}H NMR of compound **3k** (300 MHz, $CDCl_3$).

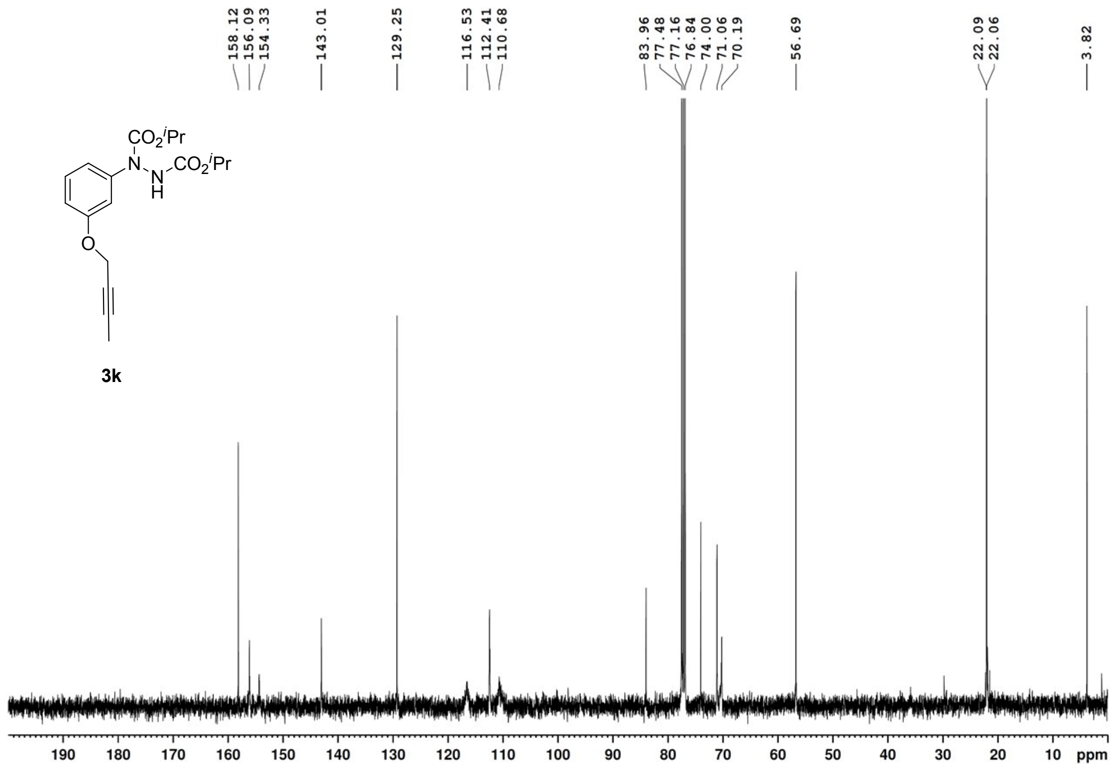


Fig. S24. ^{13}C NMR of compound **3k** (100 MHz, $CDCl_3$).

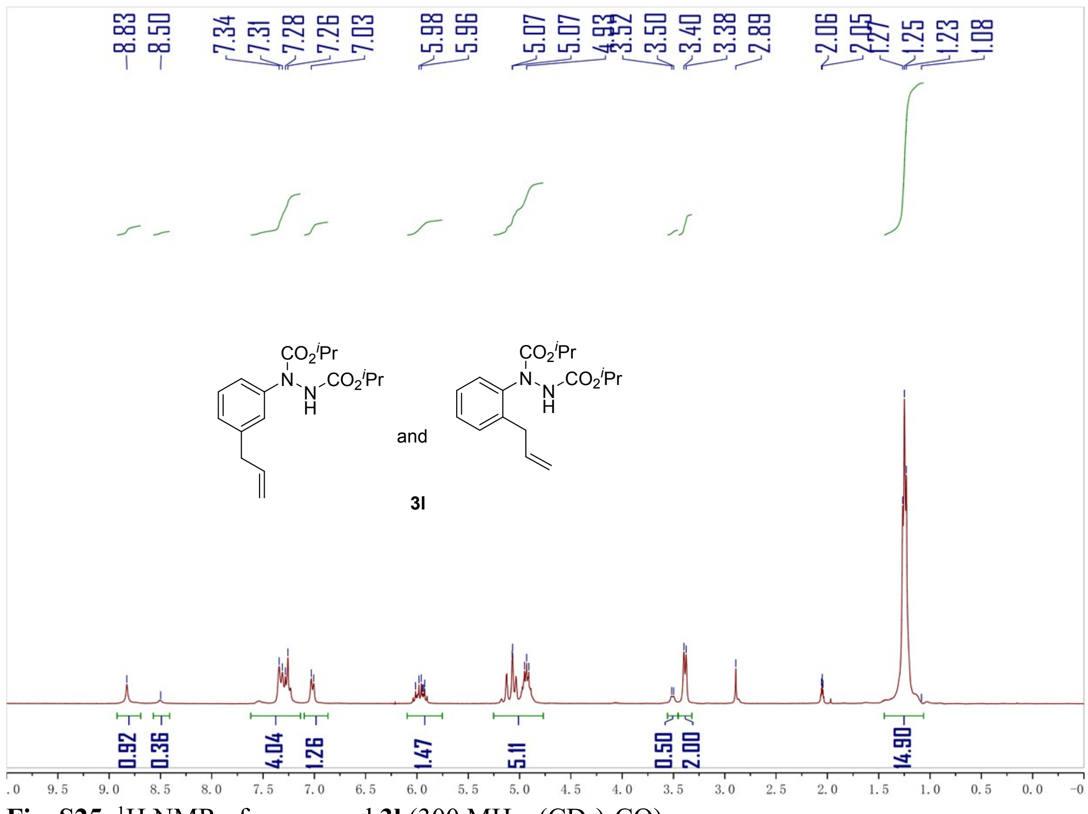


Fig. S25. ^{1}H NMR of compound **3l** (300 MHz, $(CD_3)_2CO$).

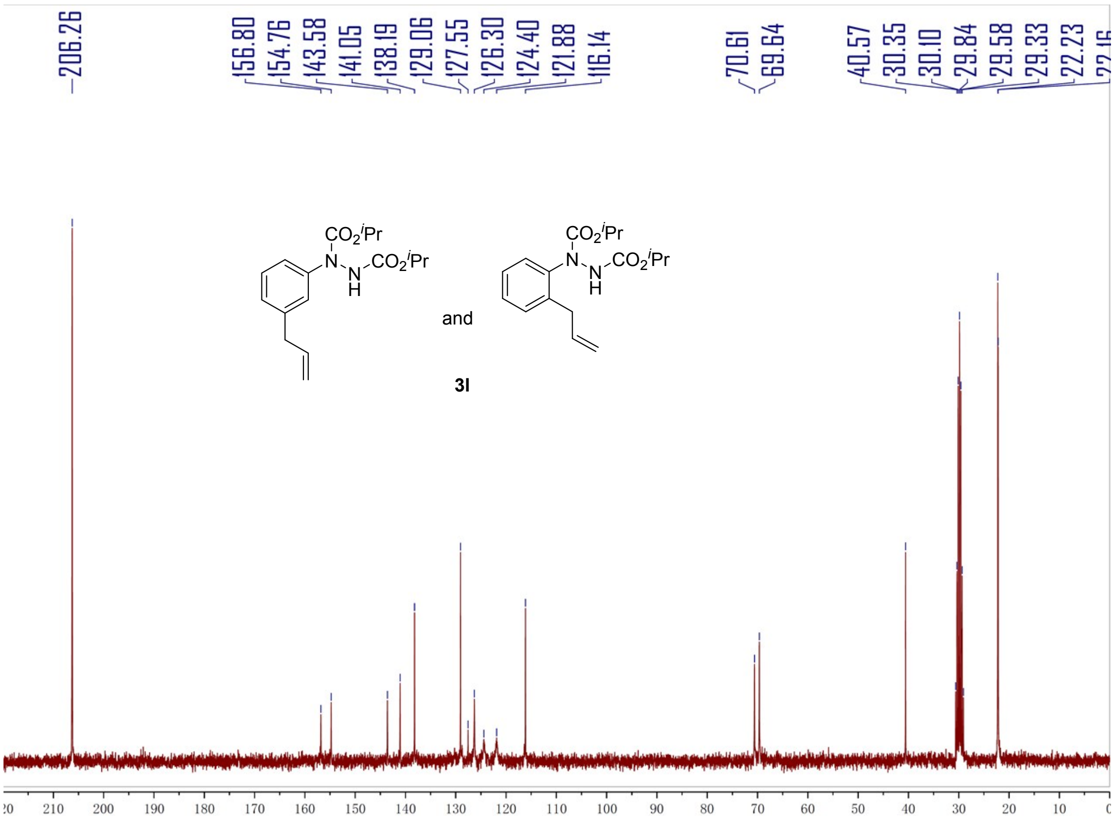


Fig. S26. ^{13}C NMR of compound **3l** (75 MHz, $(CD_3)_2CO$).

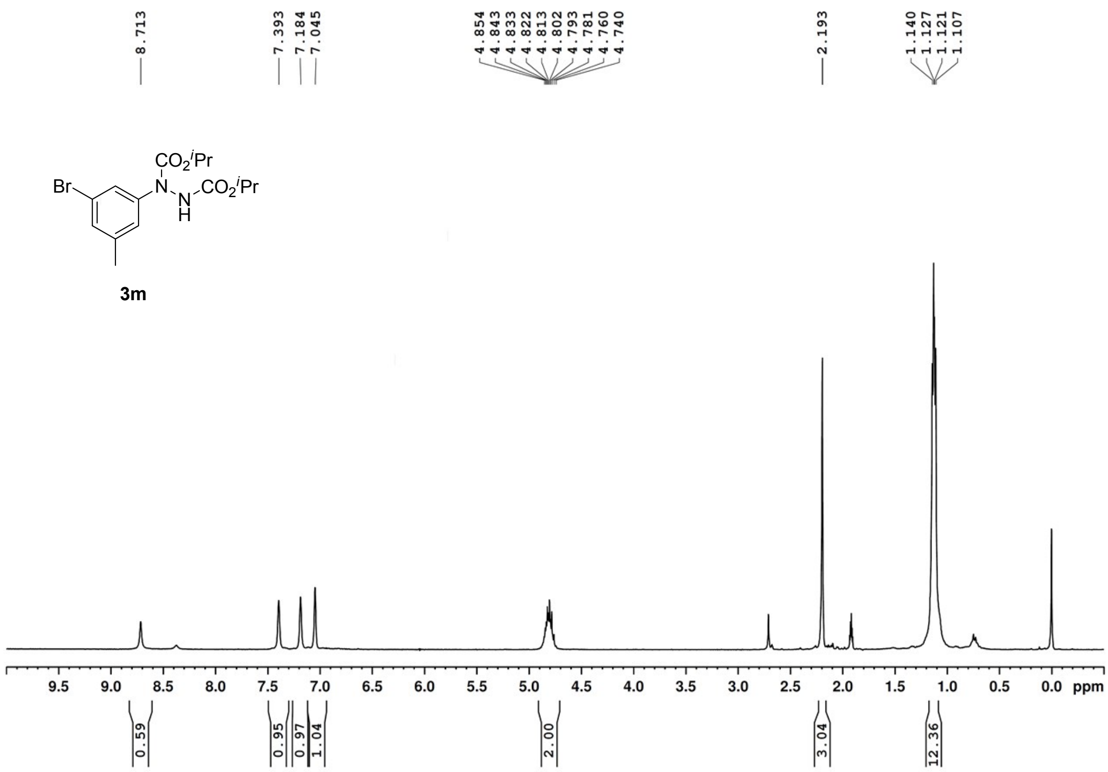


Fig. S27. ^{1}H NMR of compound **3m** (300 MHz, $(CD_3)_2CO$).

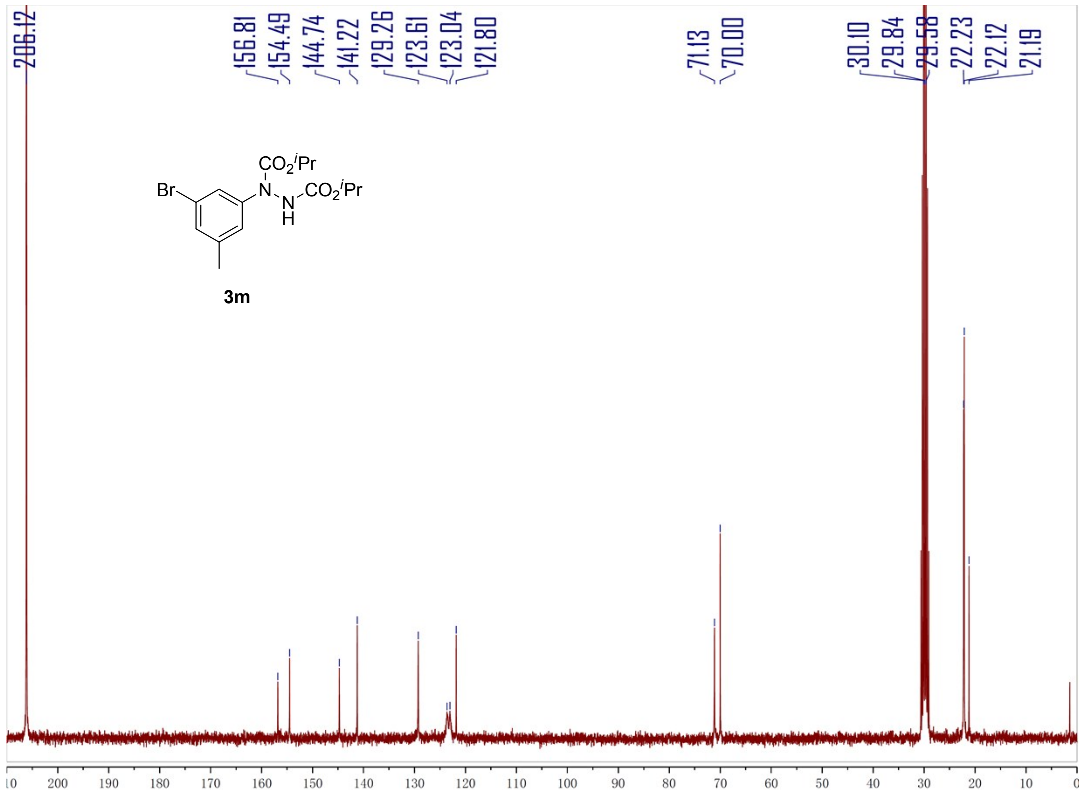


Fig. S28. ^{13}C NMR of compound **3m** (75 MHz, $(CD_3)_2CO$).

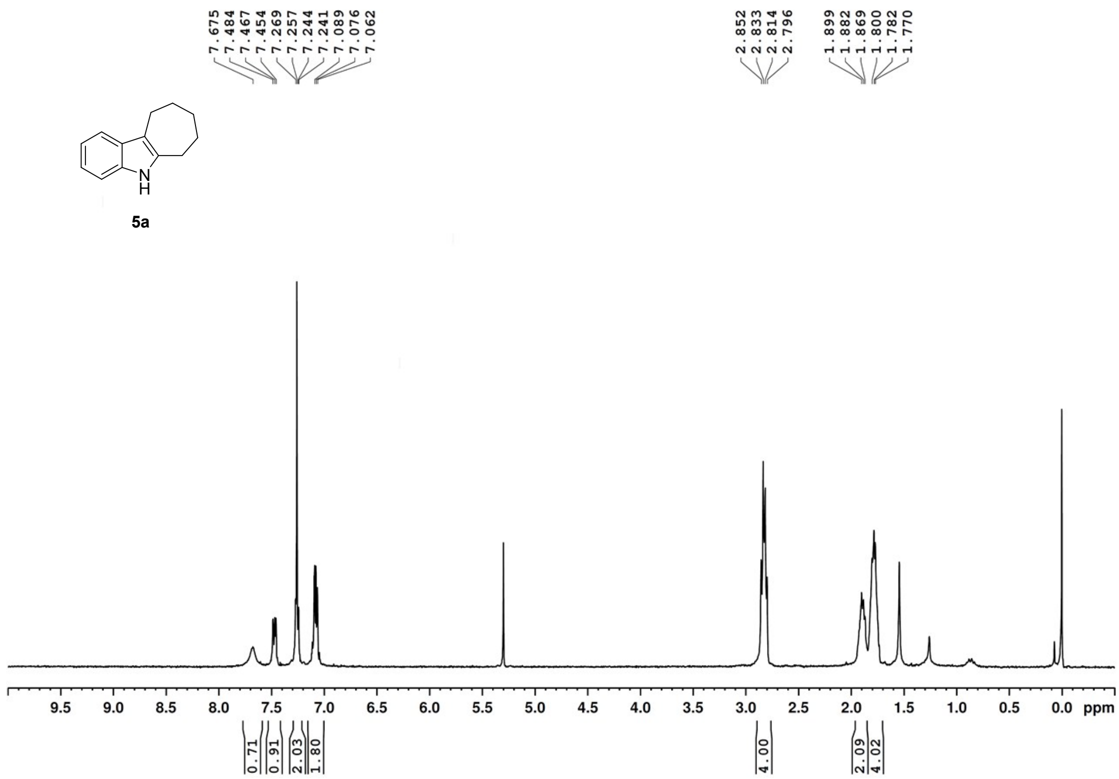


Fig. S29. ^{1}H NMR of compound **5a** (300 MHz, $CDCl_3$).

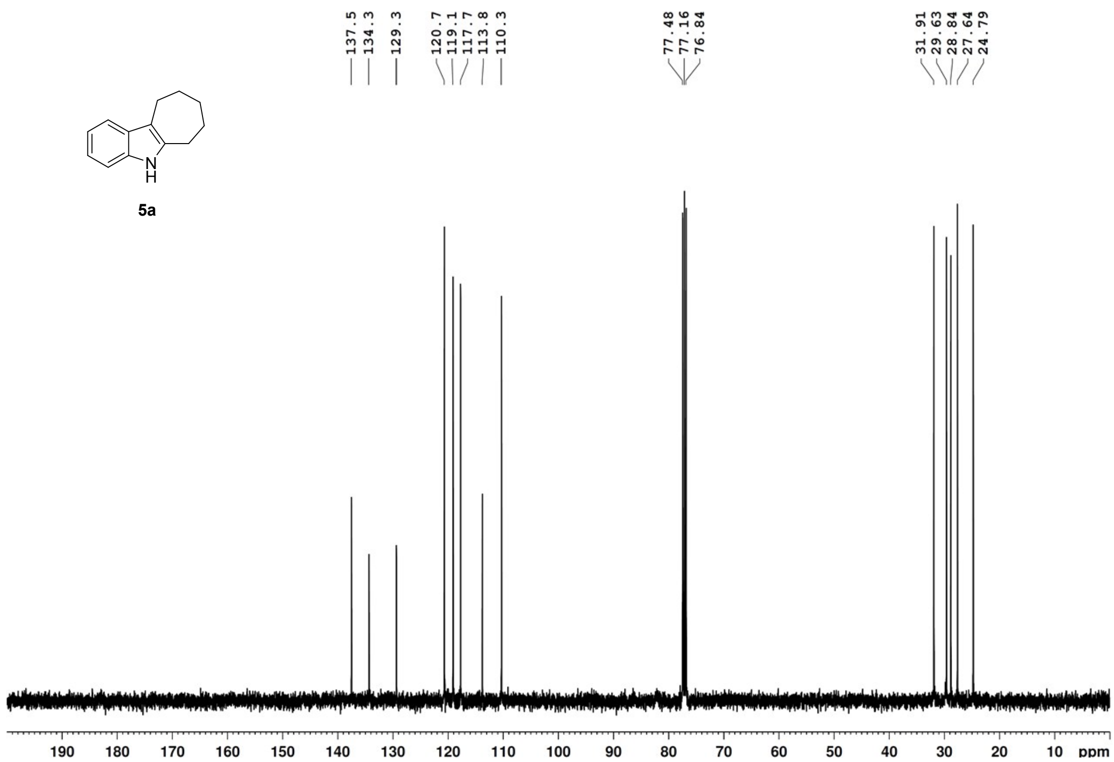


Fig. S30. ^{13}C NMR of compound **5a** (100 MHz, $CDCl_3$).

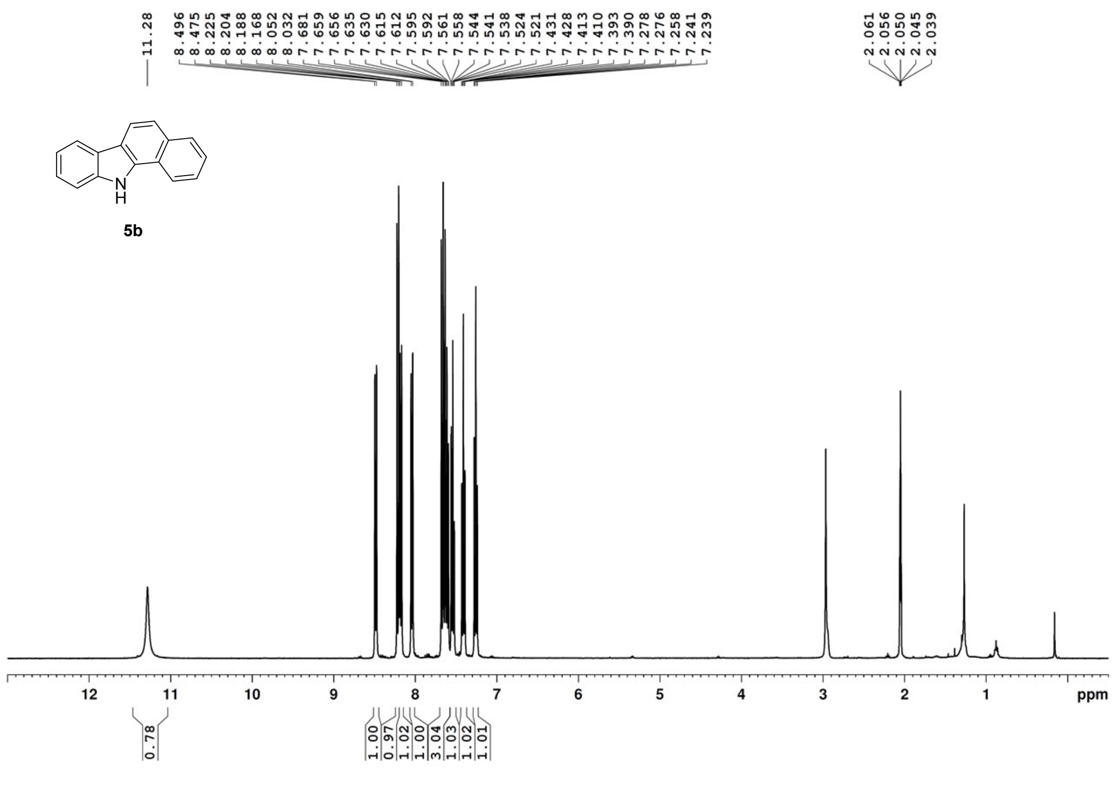


Fig. S31. ^{1}H NMR of compound **5b** (400 MHz, $(CD_3)_2CO$).

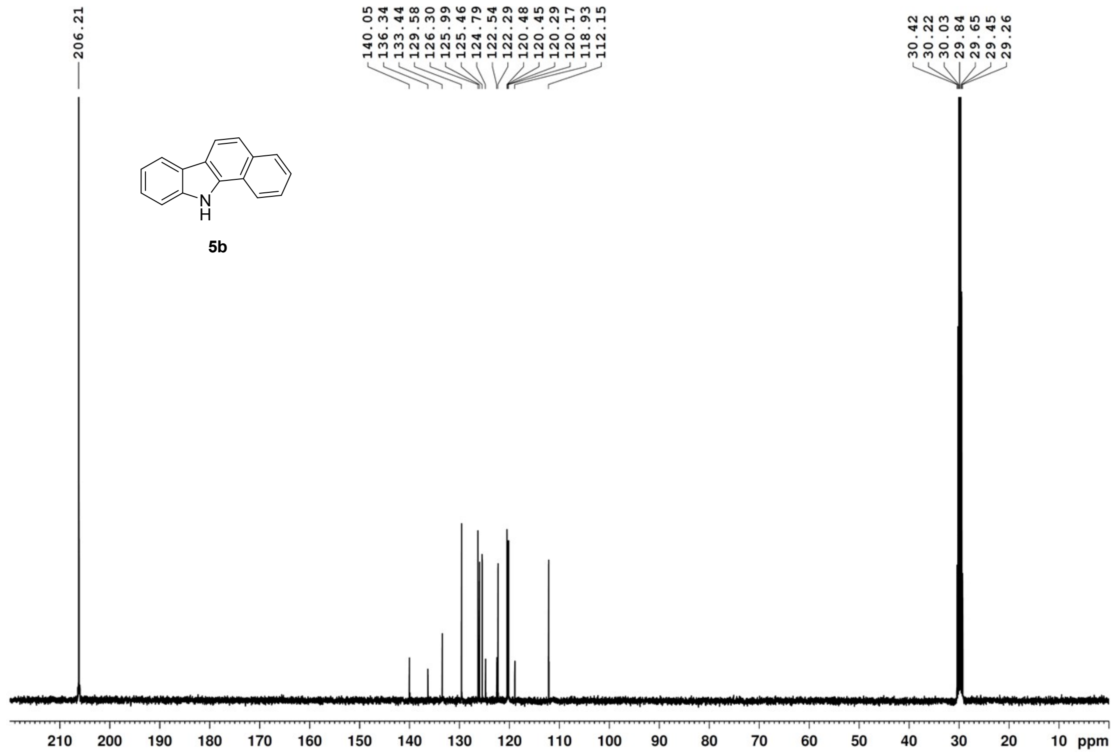


Fig. S32. ^{13}C NMR of compound **5b** (100 MHz, $(CD_3)_2CO$).

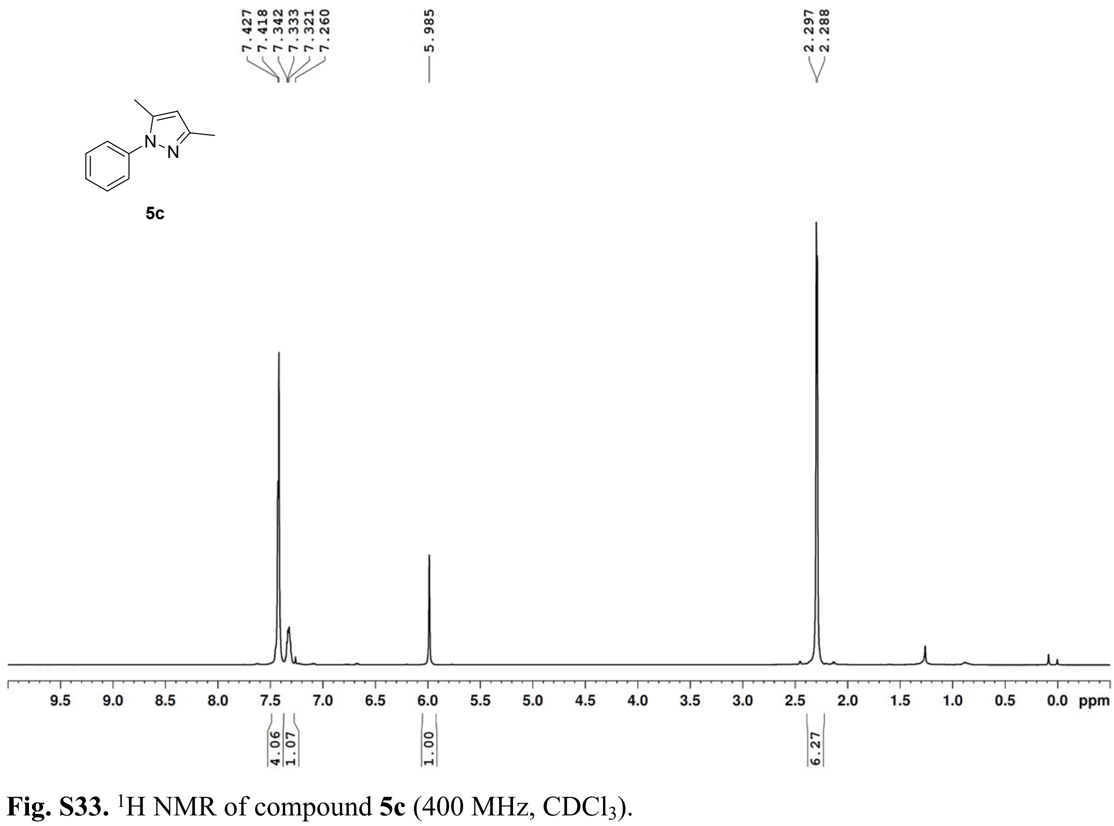


Fig. S33. ^{1}H NMR of compound **5c** (400 MHz, $CDCl_3$).

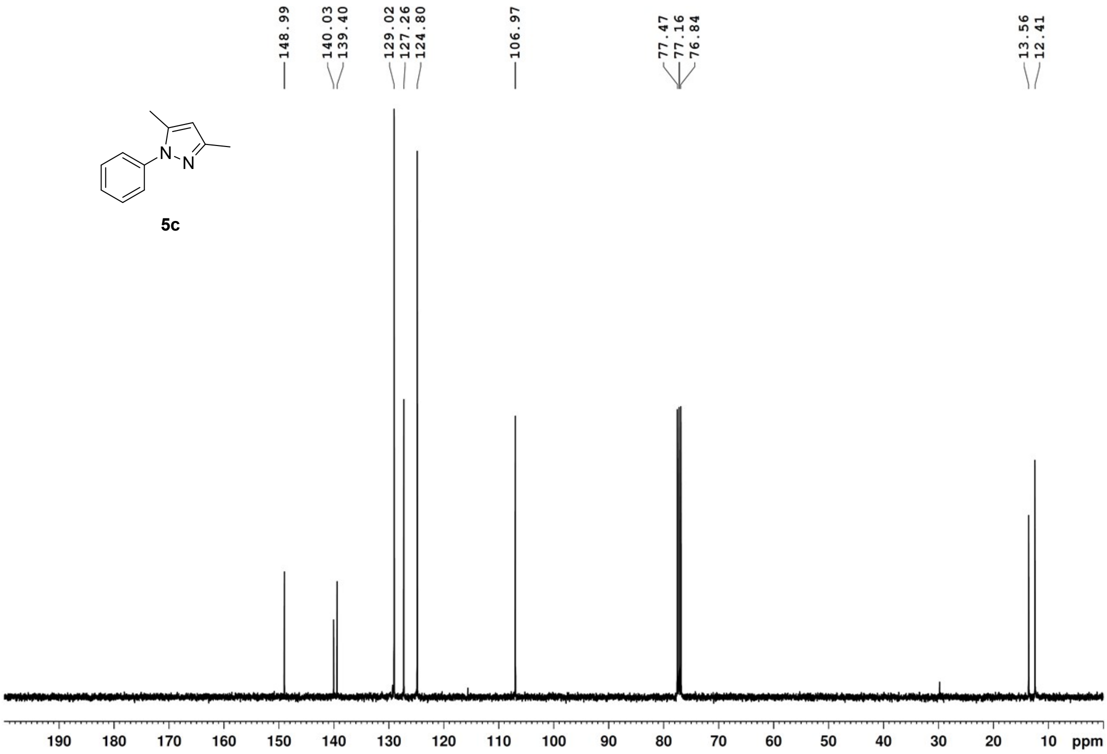


Fig. S34. ^{13}C NMR of compound **5c** (100 MHz, $CDCl_3$).

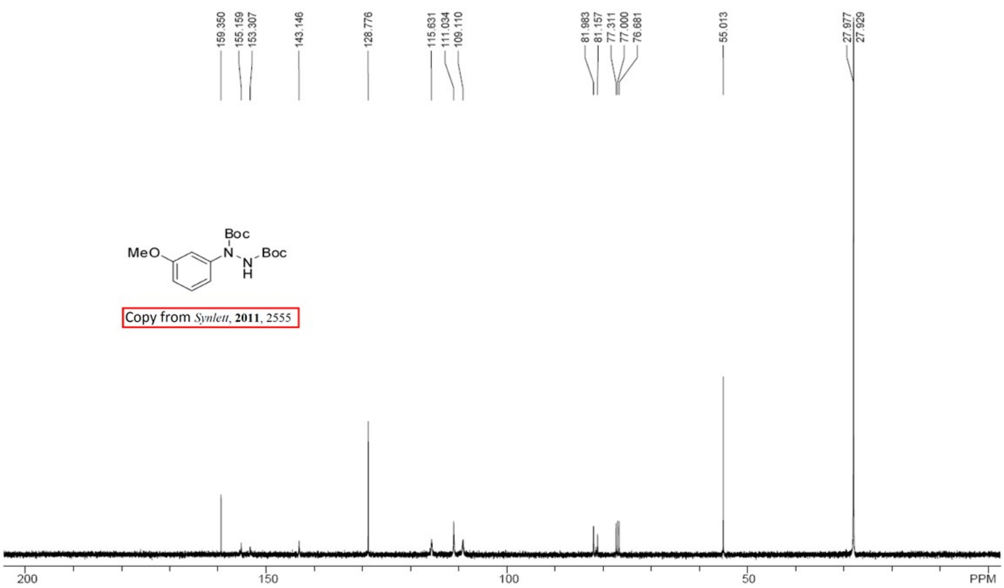


Fig. S35. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 155.2, 153.3, 143.1, 126.8, 115.6, 111.0, 109.1, 82.0, 81.2, 55.0, 28.0, 27.9.

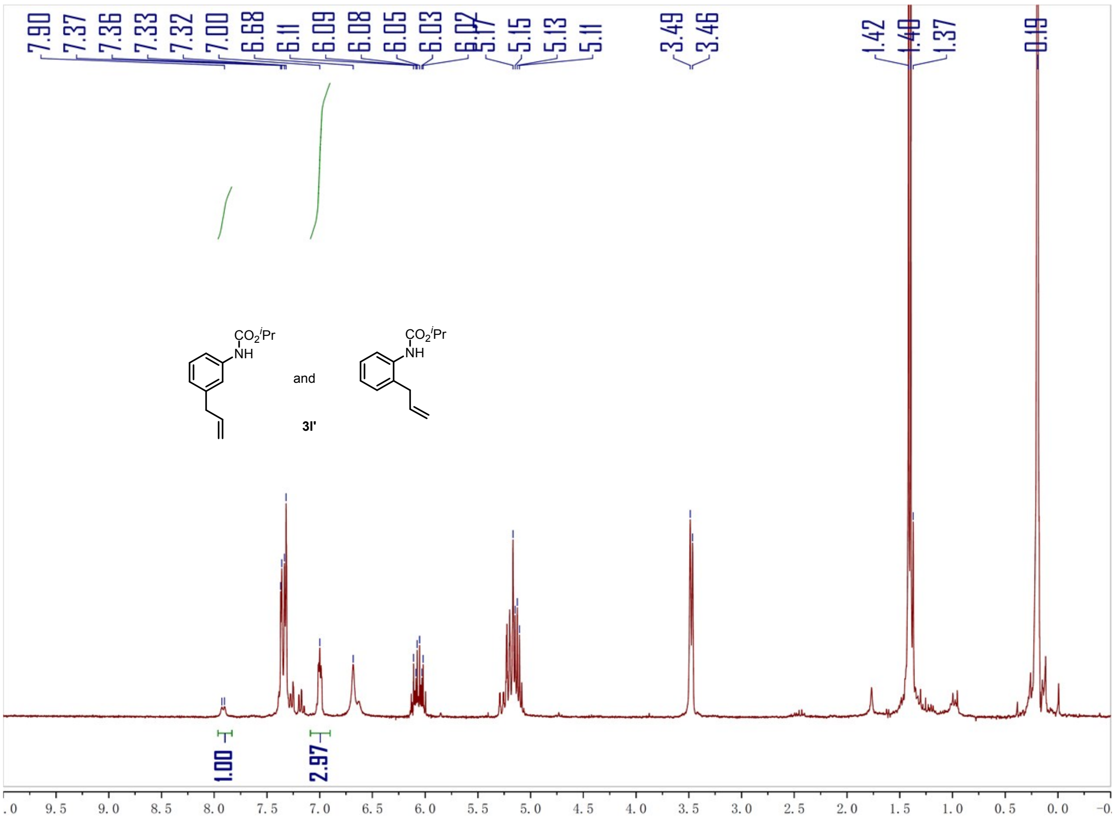


Fig. S36. ^{1}H NMR (300 MHz, $CDCl_3$)

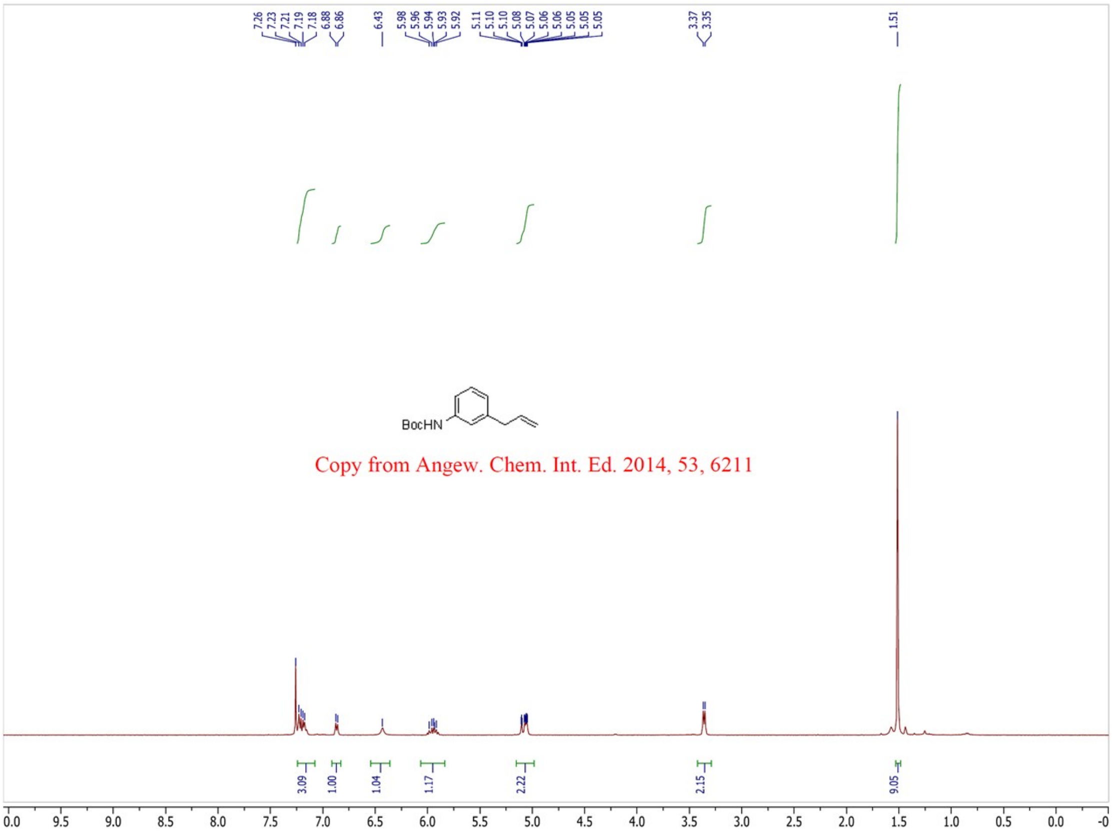


Fig. S37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.15 (m, 3H), 6.88 (d, J = 7.2 Hz, 1H), 6.44 (s, 1H), 5.96 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.17-4.97 (m, 2H), 3.37 (d, J = 6.7 Hz, 2H), 1.52 (s, 9H).

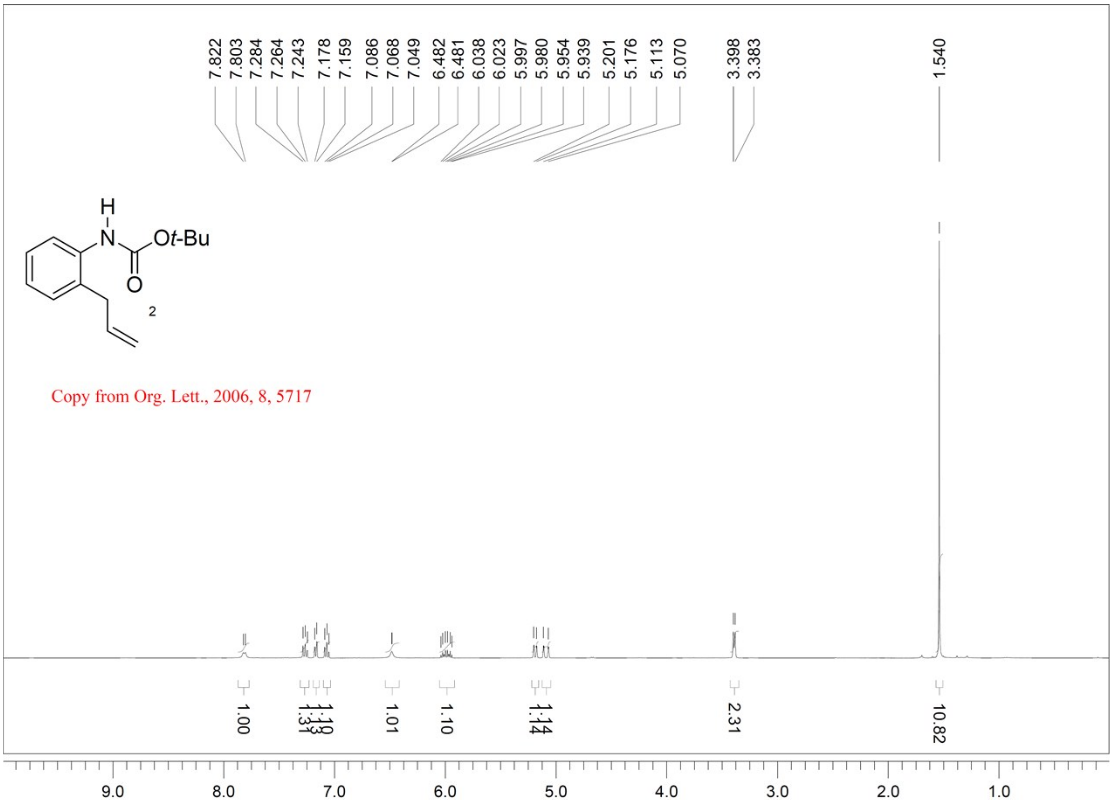


Fig. S38. [1]H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7Hz, 1H), 7.26 (t, J = 8Hz, 1H), 7.17 (d, J = 7Hz, 1H), 7.07 (t, J = 7Hz, 1H), 6.48 (s (br), 1H), 5.99 (ddt, J = 17, 10, 6 Hz, 1H), 5.20-5.17 (m, 1H), 5.11-5.07 (m, 1H), 3.39 (d, J = 6 Hz, 2H), 1.54 (s, 9H).