Supplementary Information

A Practical Guide for X–H Insertion Reactions with Sulfoxonium Ylides

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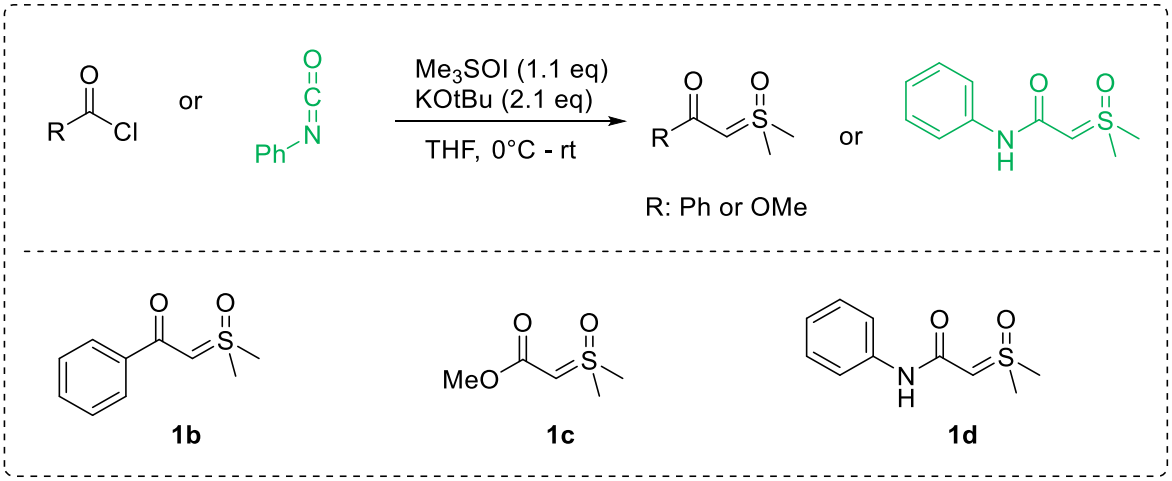
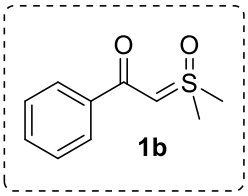
Synthesis of starting materials

Preparation of sulfoxonium ylides without substitutes



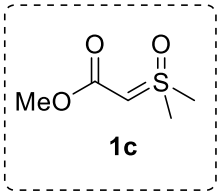
Scheme S1. Ylides without substitutes.

2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (**1b**)[1]



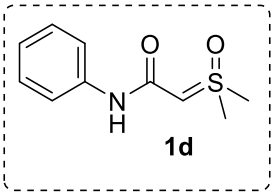
Pale yellow solid; 735 mg; 55% yield; MP: 117-119 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.46-7.34 (m, 2H), 4.98 (s, 1H), 3.51 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 182.5, 139.0, 130.9, 128.3, 126.7, 68.4, 42.6. The spectroscopic data were in good agreement with the literature data.[2]

Methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (**1c**)[2]



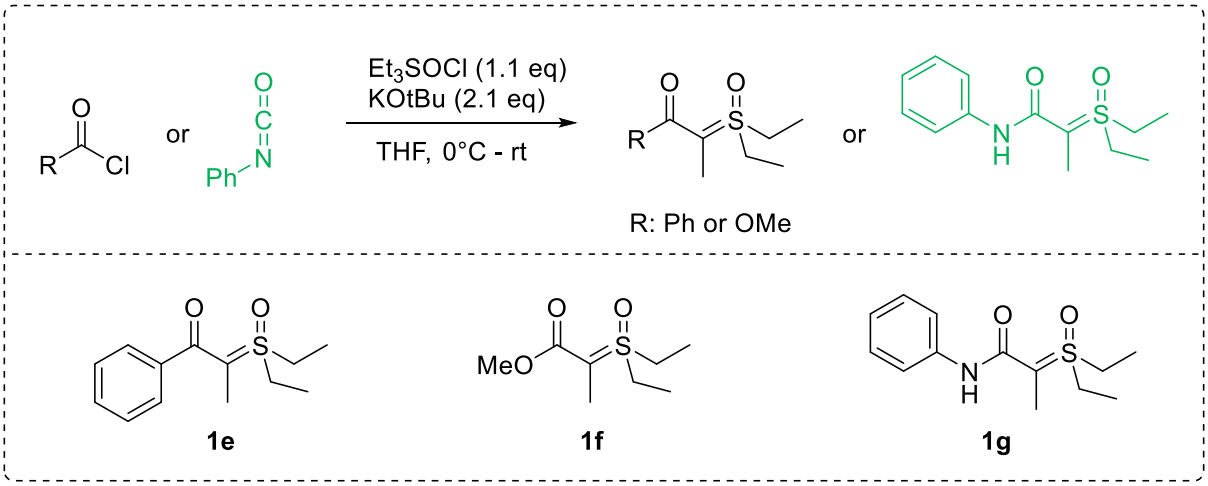
White solid; 315 mg; 44% yield; MP: 107-109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (s, 1H), 3.61 (s, 3H), 3.37 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 178.5, 54.8, 50.2, 42.4. The spectroscopic data were in good agreement with the literature data.[3]

2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-*N*-phenylacetamide (**1d**)[3]



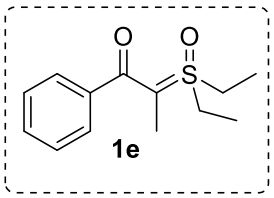
White solid; 375 mg; 50% yield; MP: decomposition over 185 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 7.47-7.38 (m, 2H), 7.17-7.08 (m, 2H), 6.83-6.75 (m, 1H), 4.11 (s, 1H), 3.30 (s, 6H); ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 165.8, 141.4, 128.3, 120.5, 117.9, 59.0, 41.3. The spectroscopic data were in good agreement with the literature data.[3]

Preparation of α-alkylated sulfoxonium ylides



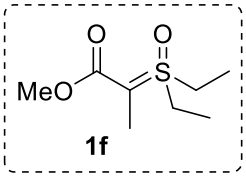
Scheme S2. *α*-Alkylated ylides.

2-(Diethyl(oxo)-λ^6-sulfaneylidene)-1-phenylpropan-1-one (**1e**)



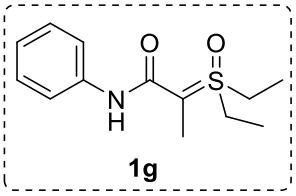
Crystalline solid; 198mg; 78% yield; MP: 74-75 °C; IR ν_{max} / cm^{-1} 3446, 2976, 2935, 2875, 1672, 1595, 1580, 1514, 1449, 1375, 1330, 1308, 1232, 1202, 1182, 1051, 1020, 1182, 1051, 1020, 1000, 988, 957, 945, 782, 758, 721, 688; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.49 (m, 2H), 7.40-7.31 (m, 3H), 4.32 (dq, *J* 13.3, 7.6 Hz, 2H), 3.32 (dq, *J* 13.2, 7.2 Hz, 2H), 1.98 (s, 3H), 1.38 (t, *J* 7.4 Hz, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 182.7, 141.6, 129.1, 128.0, 127.5, 68.0, 46.4, 11.5, 5.1; HR-MS (FTMS+pESI): *m/z* calcd. for $[C_{13}H_{19}O_2S + H]^+$: 239.1100, found: 239.1099.

Methyl 2-(diethyl(oxo)-λ^6-sulfaneylidene)propanoate (**1f**)[3]



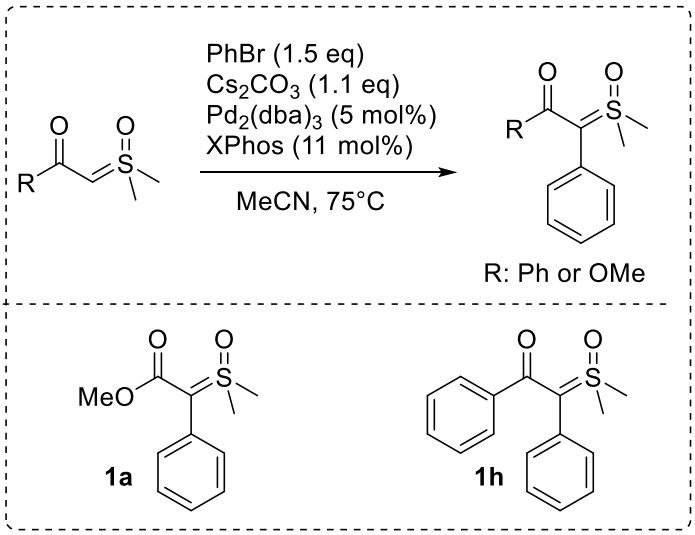
White wax; 410 mg; 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (d, *J* 12.4 Hz, 2H), 3.58 (s, 3H), 3.15 (dq, *J* 14.2, 7.2 Hz, 2H), 1.78 (s, 3H), 1.28 (t, *J* 7.4 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 50.0, 46.2, 44.4, 8.0, 5.0. The spectroscopic data were in good agreement with the literature data.[4]

2-(Diethyl(oxo)-l6-sulfaneylidene)-*N*-phenylpropanamide (**1g**)



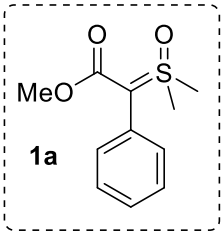
Pale yellow solid; 379 mg; 15% yield; MP: 105-108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.38 (m, 1H), 7.31-7.21 (m, 1H), 6.96 (tt, *J* 7.4, 1.2 Hz, 1H), 4.05 (dq, *J* 13.3, 7.6 Hz, 1H), 3.23 (dq, *J* 14.1, 7.1 Hz, 1H), 1.92 (s, 2H), 1.30 (t, *J* 7.4 Hz, 4H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.00, 139.69, 128.81, 122.28, 119.47, 47.07, 8.42, 6.75, 4.85; HR-MS (FTMS + pESI): *m/z* calcd. for $[C_{13}H_{20}NO_2S + H]^+$: 254.1209, found 254.1206.

Preparation of α-arylated sulfoxonium ylides



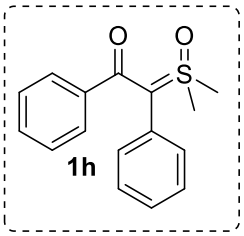
Scheme S3. *α*-Arylated ylides.

Methyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-2-phenylacetate (**1a**)[2]



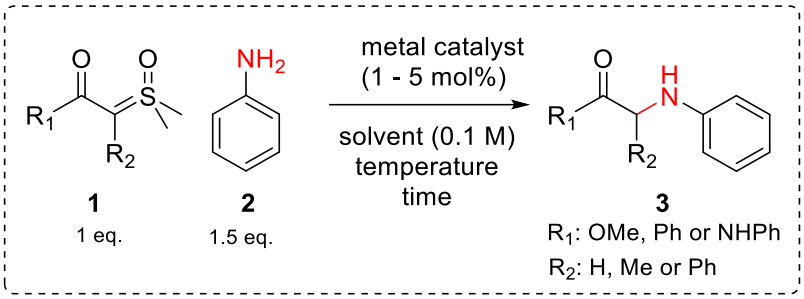
White solid; 40.5 mg; 67% yield; MP: 179-181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.21 (m, 2H), 3.61 (s, 1H), 3.41 (s, 2H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.8, 133.8, 132.5, 128.6, 127.3, 70.3, 50.6, 43.3. The spectroscopic data were in good agreement with the literature data.[2]

2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1,2-diphenylethan-1-one (**1h**)[3]



Yellow solid; 113 mg; 38% yield; MP: 174-176 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.34 (m, 1H), 7.25-7.19 (m, 2H), 7.19-7.12 (m, 2H), 3.63 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 183.2, 140.3, 134.9, 132.2, 129.5, 128.8, 128.4, 127.6, 127.4, 86.9, 43.2. The spectroscopic data were in good agreement with the literature data.[3]

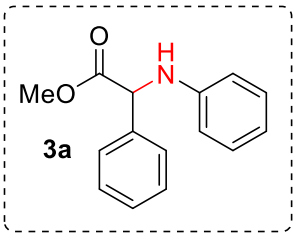
General procedure for N–H insertion reactions



Scheme S4. Procedure for N–H insertions.

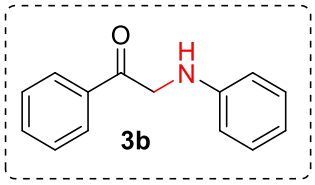
To a 4-mL vial, ylide **1** (0.1 mmol, 1 equiv.) and metal catalyst (1-5 mol%) were added sequentially. After exchanging the atmosphere to argon, solvent (PhMe or CH_2Cl_2, 0.1 M) was added, followed by distilled aniline **2** (0.15 mmol, 1.5 equiv.) via syringe, and the reaction mixture was stirred at determined temperature (rt or 80 °C). After the total consumption of the corresponding ylide or the stipulated reaction time (16 or 40 h), the reaction mixture was filtered through a short plug of silica gel, concentrated and purified via silica gel chromatography.

Methyl 2-phenyl-2-(phenylamino)acetate (**3a**)[4]



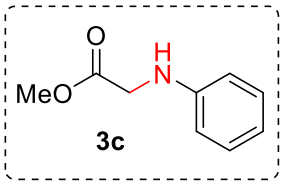
White solid; 23.8 mg; 98% yield ($[Ir(cod)Cl]_2$, toluene, 80 °C, 16 h); MP: 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.47 (m, 2H), 7.44-7.28 (m, 3H), 7.18-7.09 (m, 2H), 6.76-6.67 (m, 1H), 6.62-6.54 (m, 2H), 5.10 (d, *J* 5.8 Hz, 1H), 4.96 (d, *J* 5.9 Hz, 1H), 3.74 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 146.1, 137.8, 129.4, 129.0, 128.4, 127.4, 118.3, 113.5, 60.9, 52.9. The spectroscopic data were in good agreement with the literature data.[4]

1-Phenyl-2-(phenylamino)ethan-1-one (**3b**)



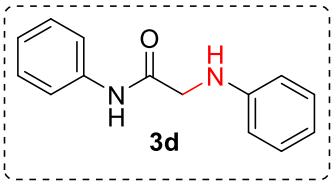
Yellow solid; 16.6 mg; 78% yield ($[Ir(cod)Cl]_2$, CH_2Cl_2, rt, 40 h); MP: 94-96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.00 (m, 2H), 7.66-7.59 (m, 1H), 7.56-7.48 (m, 2H), 7.26-7.19 (m, 2H), 6.79-6.68 (m, 3H), 4.93 (s, 1H), 4.62 (s, 2H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 195.2, 147.3, 135.1, 134.0, 129.5, 129.0, 127.9, 118.0, 113.2, 50.5. The spectroscopic data were in good agreement with the literature data.[4]

Methyl phenylglycinate (**3c**)



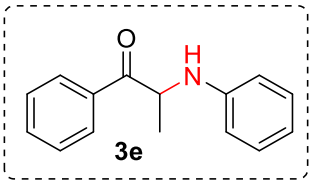
Yellowish oil; 12.2 mg; 73% yield ($[Ir(cod)Cl]_2$; CH_2Cl_2; rt; 16 h); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 6.76 (tt, *J* 7.3, 1.1 Hz, 1H), 6.65-6.57 (m, 2H), 4.27 (s, 1H), 3.93 (s, 2H), 3.79 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 147.1, 129.5, 118.4, 113.2, 52.4, 45.9. For product **3c**, the prolonged exposure to air at longer times leads to a degradation, so shortly after the purification, the product was stored at a refrigerator under Ar. The spectroscopic data were in good agreement with the literature data.[5]

N-Phenyl-2-(phenylamino)acetamide (**3d**)



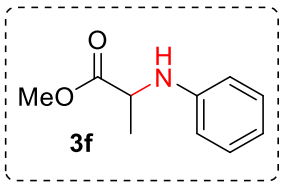
White solid; 15.6 mg; 69% yield ([Ir(cod)Cl]$_2$, PhMe, 80 °C, 16 h); MP: 107-109 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.95 (s, 1H), 7.65-7.57 (m, 2H), 7.33-7.26 (m, 2H), 7.14-7.01 (m, 3H), 6.63-6.54 (m, 3H), 5.96 (t, *J* 6.1 Hz, 1H), 3.85 (d, *J* 6.1 Hz, 2H); ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 169.3, 148.3, 138.8, 128.9, 128.7, 123.3, 119.2, 116.4, 112.3, 47.3.

1-Phenyl-2-(phenylamino)propan-1-one (**3e**)



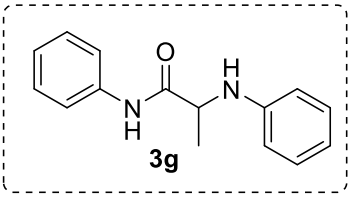
White solid; 21.8 mg; 97% yield ([Ir(COD)Cl]$_2$, CH_2Cl_2, rt, 16 h); MP: 95-97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-7.99 (m, 2H), 7.65-7.58 (m, 1H), 7.55-7.47 (m, 2H), 7.22-7.15 (m, 2H), 6.76-6.66 (m, 3H), 5.14 (q, *J* 6.9 Hz, 1H), 4.69 (s, 1H), 1.49 (d, *J* 6.9 Hz, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 200.8, 146.7, 134.8, 133.8, 129.5, 129.0, 128.6, 118.0, 113.6, 53.5, 19.7. The spectroscopic data were in good agreement with the literature data.[6]

Methyl phenylalaninate (**3f**)[4]



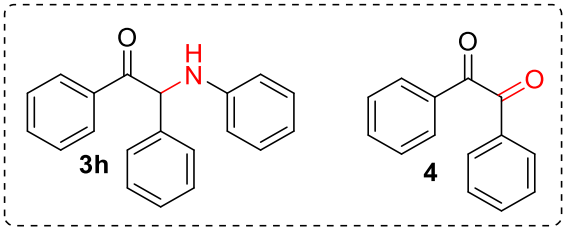
Colorless oil; 17.5 mg; 97% yield ([Ir(COD)Cl]$_2$, CH_2Cl_2, rt, 16 h); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.14 (m, 2H), 6.75 (tt, *J* 7.3, 1.1 Hz, 1H), 6.64-6.58 (m, 2H), 4.15 (d, *J* 6.2 Hz, 2H), 3.73 (s, 3H), 1.48 (d, *J* 6.3 Hz, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.2, 146.7, 129.5, 118.5, 113.5, 52.4, 52.1, 19.1. The spectroscopic data were in good agreement with the literature data.[4]

N-Phenyl-2-(phenylamino)propanamide (**3g**)[7]



White solid; 53% yield ([Ir(COD)Cl]$_2$, toluene, 80 °C, 16 h); MP: 134-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.58-7.45 (m, 2H), 7.33-7.27 (m, 2H), 7.25-7.19 (m, 2H), 7.15-7.06 (m, 1H), 6.85 (tt, *J* 7.4, 1.1 Hz, 1H), 6.75-6.64 (m, 2H), 3.95-3.92 (s, 1H), 3.87 (qd, *J* 7.0, 2.4 Hz, 1H), 1.60 (d, *J* 7.0 Hz, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.33, 146.44, 137.46, 129.55, 128.96, 124.41, 119.83, 119.81, 114.00, 56.41, 19.83. The spectroscopic data were in good agreement with the literature data.[8]

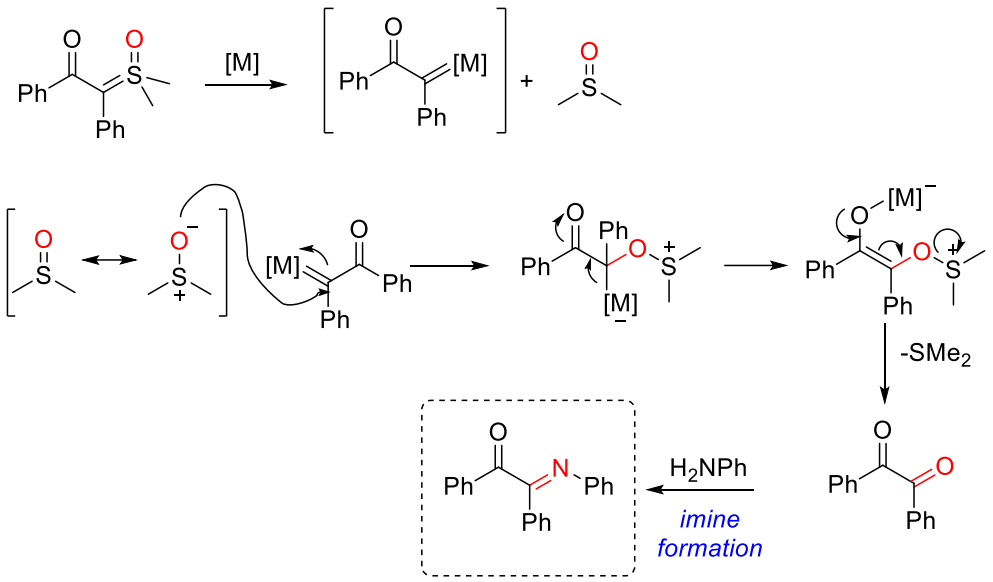
1,2-Diphenyl-2-(phenylamino)ethan-1-one (**3h**+**4**)[3]



Yellow solid; 28% yield; **3h** + 10% yield **4** (yield determined by qNMR due to co-elution issues during purification); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* 7.1 Hz, 2H), 7.79-7.73 (m, 1H), 7.49-7.41 (m, 2H), 7.17-7.09 (m, 1H), 6.96-6.85 (m, 2H). The spectroscopic data were in good agreement with the literature data.[3]

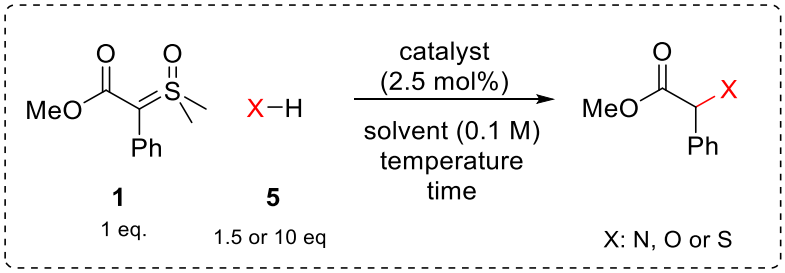
The formation of 1,2-dicarbonyl compounds from α-substituted sulfoxonium ylides is also observed as reported by Burtoloso *et al*.[3,7] In that case, the reaction is promoted by iodine, although the nucleophilic attack of DMSO to the electrophilic carbon leads to the formation of the observed product.

In our case, one possibility of the mechanism occurs via nucleophilic attack of DMSO at metal carbene, followed by the metal enolate formation and the regeneration of ketone, leading to SMe_2 extrusion via Kornblum-type oxidation. The subsequent attack of aniline leads to the formation of the observed imine (Scheme S1).



Scheme S5. Proposal mechanism for imine generation.

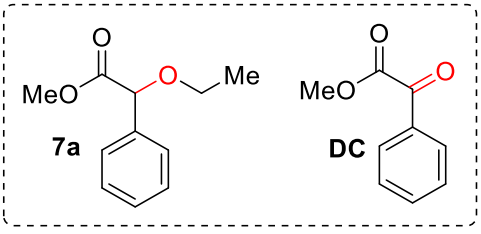
General procedure for the X–H insertion reactions



Scheme S6. Procedure for X–H insertions.

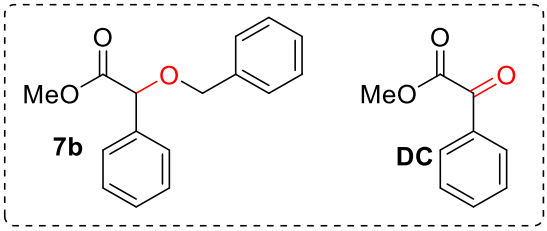
To a 4 mL vial, **1** (22.6 mg; 0.1 mmol; 1 eq), metal catalyst (2.5 mol%) were added, followed by addition of X–H (0.15 mmol; 1.5 eq or 1 mmol; 10 eq) and solvent (PhMe or CH_2Cl_2; 1 mL; 0.1 M) under Ar. The reaction mixture was stirred at 80 °C until the consumption of the starting material, or after 40 h. After elapsed time, the crude was filtered on silica gel, the solvent was removed under reduced pressure and purification by column chromatography led to the product.

Methyl 2-ethoxy-2-phenylacetate (**7a** + **DC**)



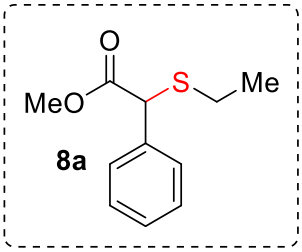
Colorless oil; 4 mg (ratio **7a**:**DC** 54:46); yield determined by qNMR due to co-elution issues during purification; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.40-7.31 (m, 3H), 3.72 (s, 3H), 3.61 (dq, *J* 9.2, 7.0 Hz, 1H), 3.52 (dq, *J* 9.1, 7.0 Hz, 1H), 1.29 (t, *J* 7.0 Hz, 3H). The spectroscopic data were in good agreement with the literature data.[8]

Methyl 2-(benzyloxy)-2-phenylacetate (**7b**+**DC**)



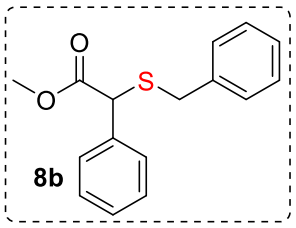
Colorless oil; 10 mg (ratio **7b**:**DC** 4:6); yield determined by qNMR due to co-elution issues during purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.42 (m, 2H), 7.39-7.30 (m, 8H), 4.92 (s, 1H), 4.58 (d, 1H), 4.57 (d, 1H), 3.69 (s, 3H). The spectroscopic data were in good agreement with the literature data.[9] DC: methyl 2-oxo-2-phenylacetate.

Methyl 2-(ethylthio)-2-phenylacetate (**8a**)



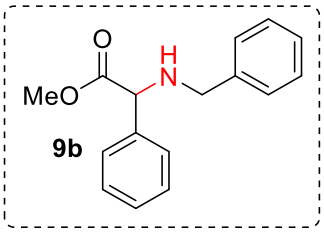
Colorless oil; 17.85 mg; 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2H), 7.37-7.26 (m, 3H), 4.60 (s, 1H), 3.72 (s, 3H), 2.60-2.52 (m, 1H), 2.52-2.45 (m, 1H), 1.21 (t, *J* 7.4 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 136.1, 128.6, 128.5, 128.1, 52.7, 51.9, 26.0, 14.1. The spectroscopic data were in good agreement with the literature data.[10]

Methyl 2-(benzylthio)-2-phenylacetate (**8b**)



Yellowish oil; 25.8 mg; 94% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.38-7.24 (m, 8H), 4.44 (s, 1H), 3.79 (d, *J* 13.5 Hz, 1H), 3.70 (s, 3H), 3.64 (d, *J* 13.5 Hz, 1H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.1, 137.1, 135.8, 129.0, 128.7, 128.6, 128.6, 128.2, 127.3, 52.7, 51.5, 36.2. The spectroscopic data were in good agreement with the literature data.[11]

Methyl 2-(benzylamino)-2-phenylacetate (**9b**)



Colorless oil; 17.7 mg; 69% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.21 (m, 10H), 4.40 (s, 1H), 3.73 (d, J 2.2, 2H), 3.68 (s, 3H), 2.24 (s, 1H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.6, 139.6, 138.1, 128.9, 128.6, 128.5, 128.3, 127.7, 127.3, 64.5, 52.4, 51.5. The spectroscopic data were in good agreement with the literature data.[12]

^{1}H and ^{13}C NMR spectra

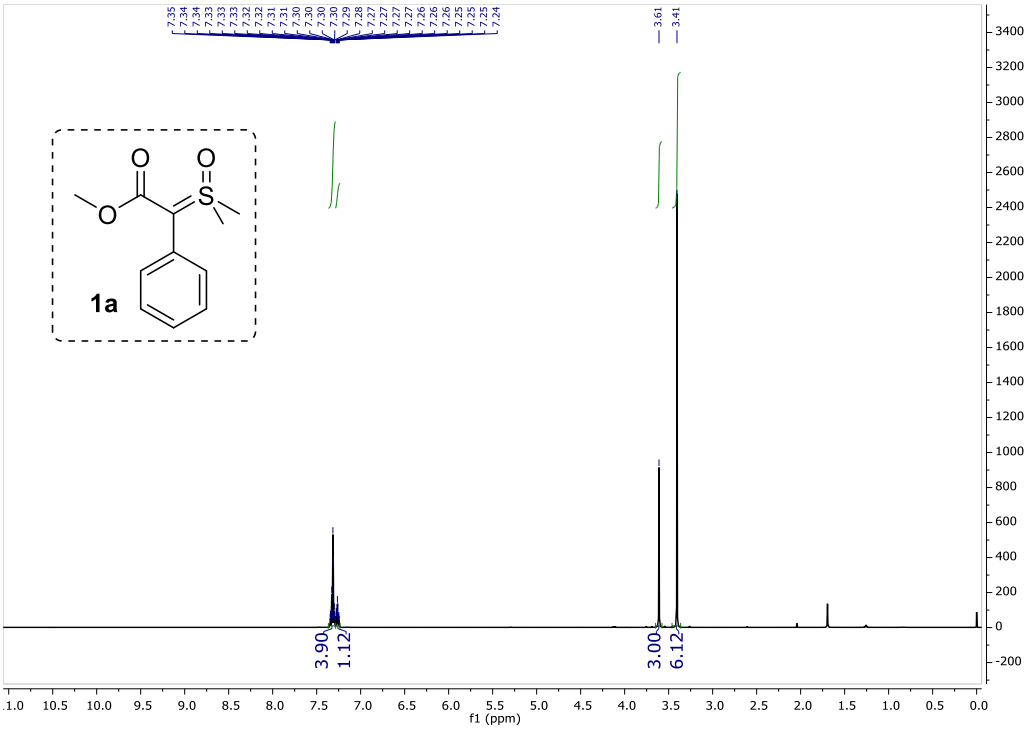


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-2-phenylacetate (**1a**).

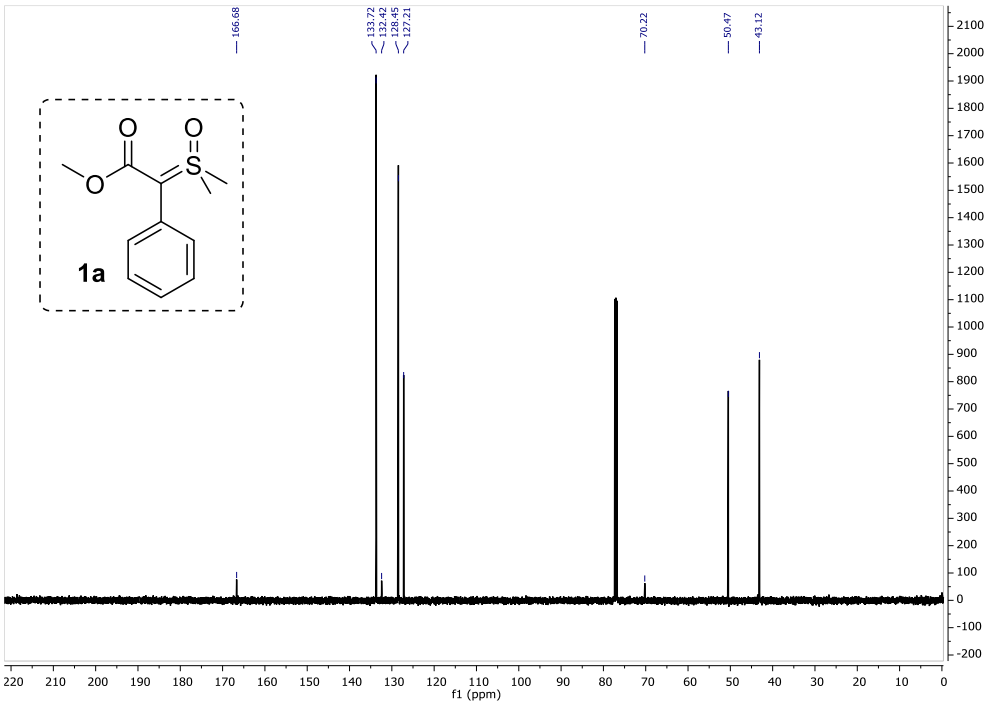


Figure S2. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-2-phenylacetate (**1a**).

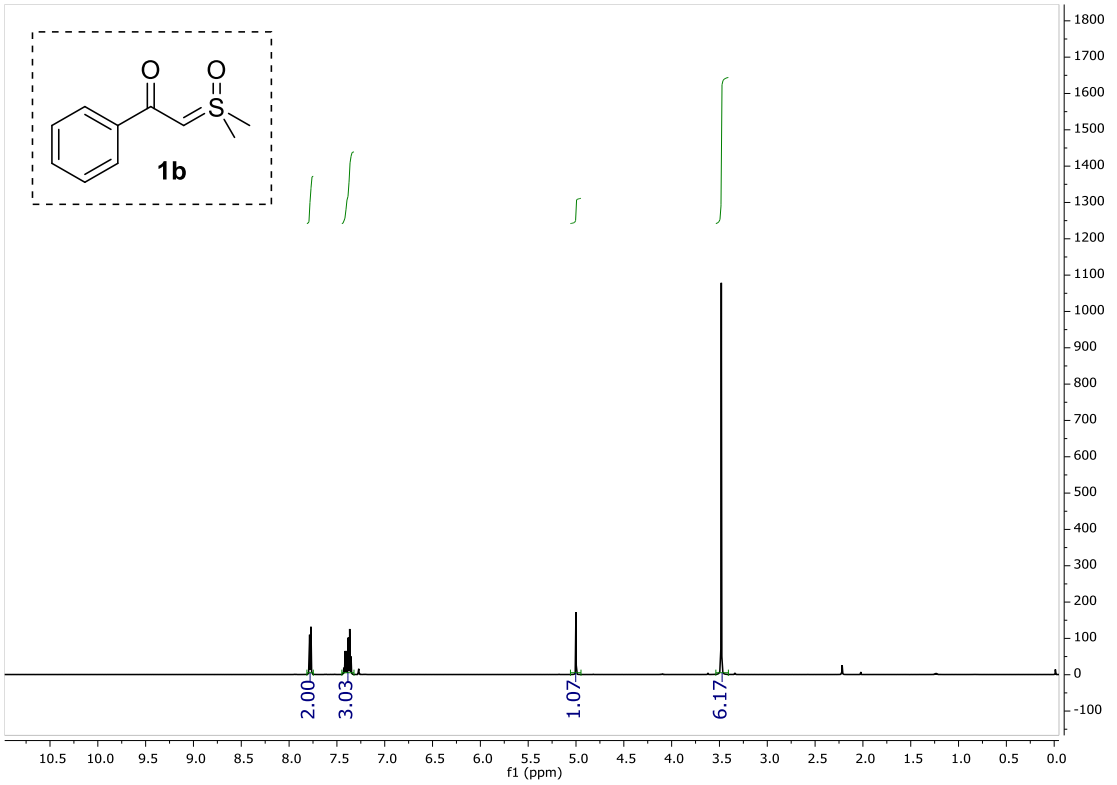


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) of 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-phenylethan-1-one (**1b**).

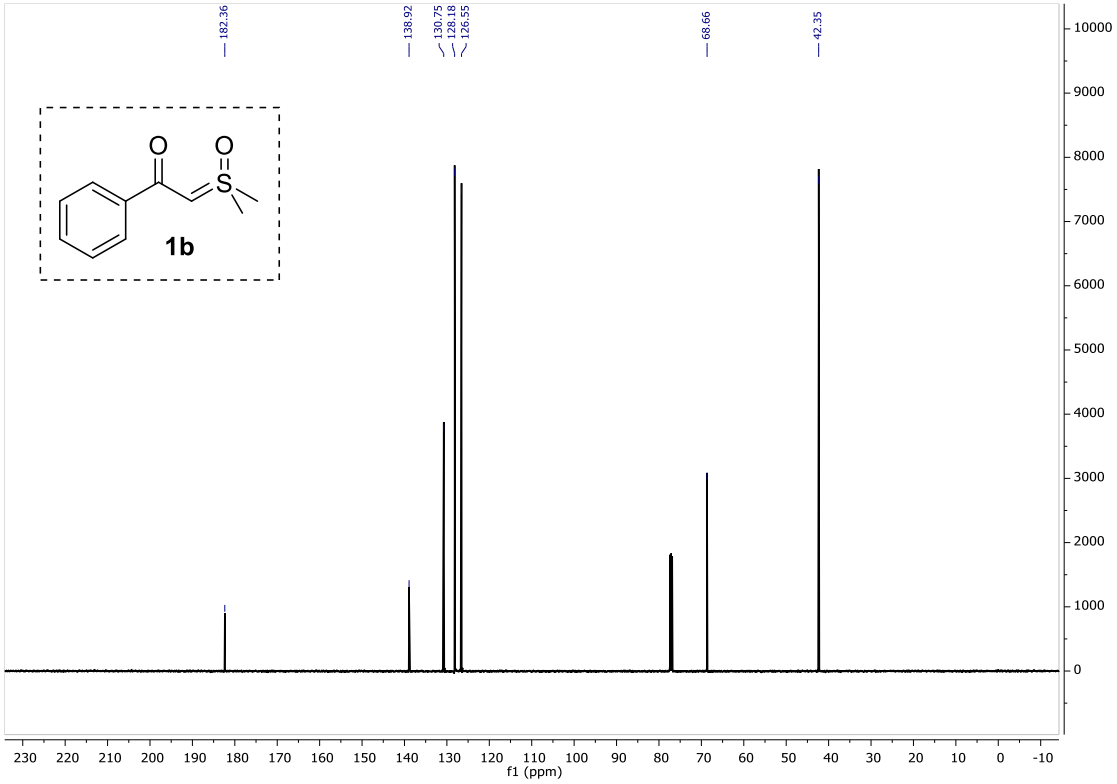


Figure S4. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-phenylethan-1-one (**1b**).

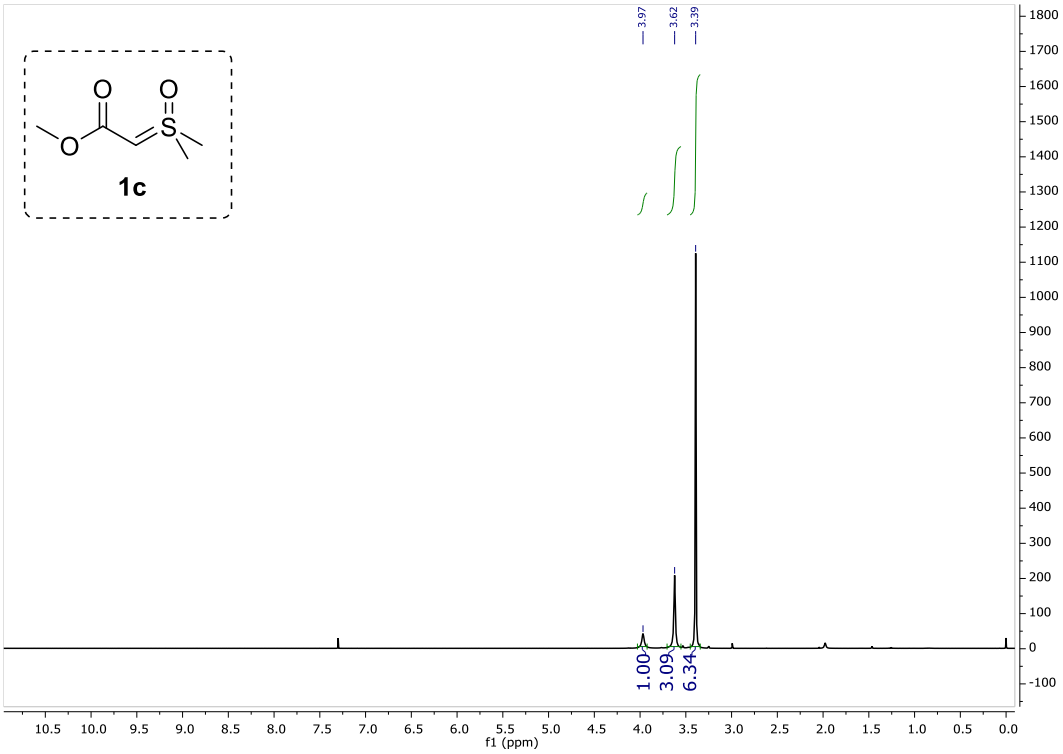


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)acetate (**1c**).

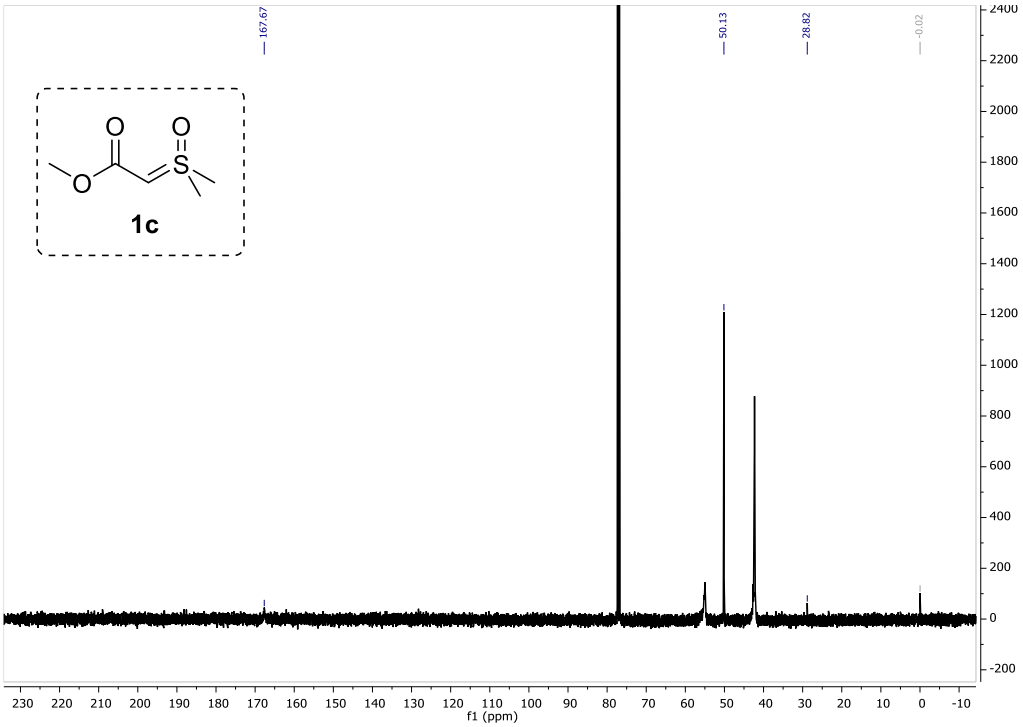


Figure S6. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)acetate (**1c**).

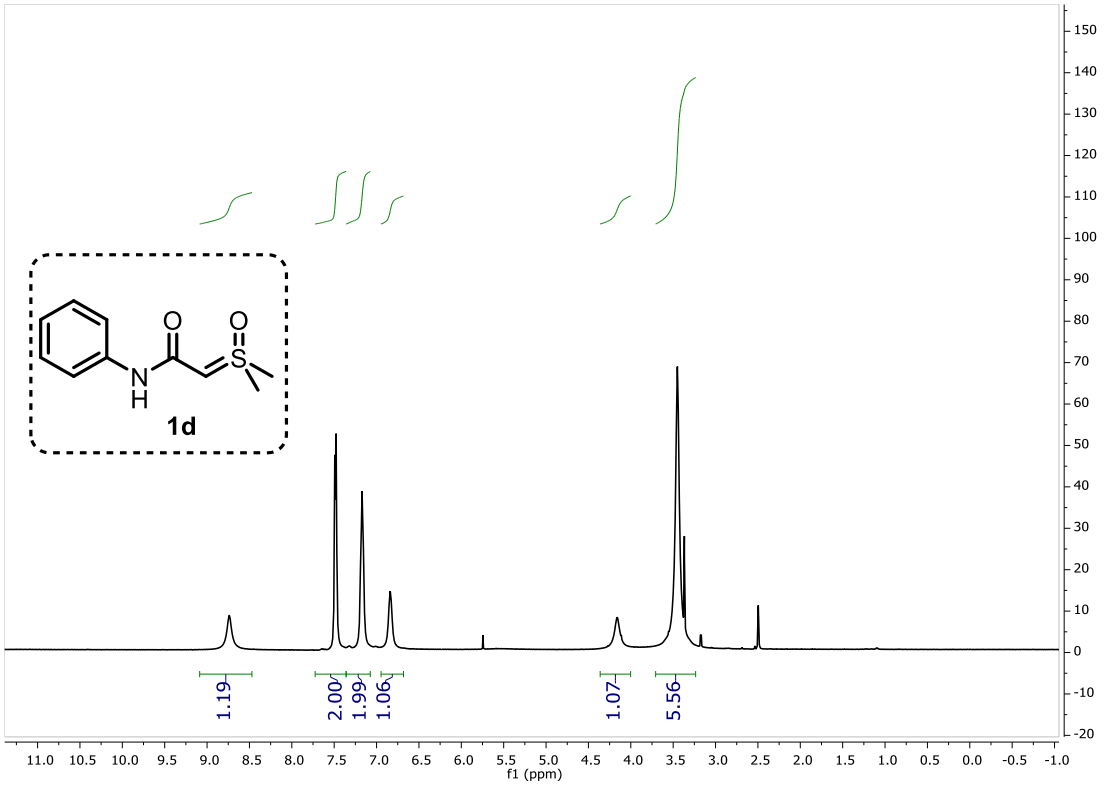


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-(dimethyl(oxo)- λ^6-sulfaneylidene)acetate (**1c**).

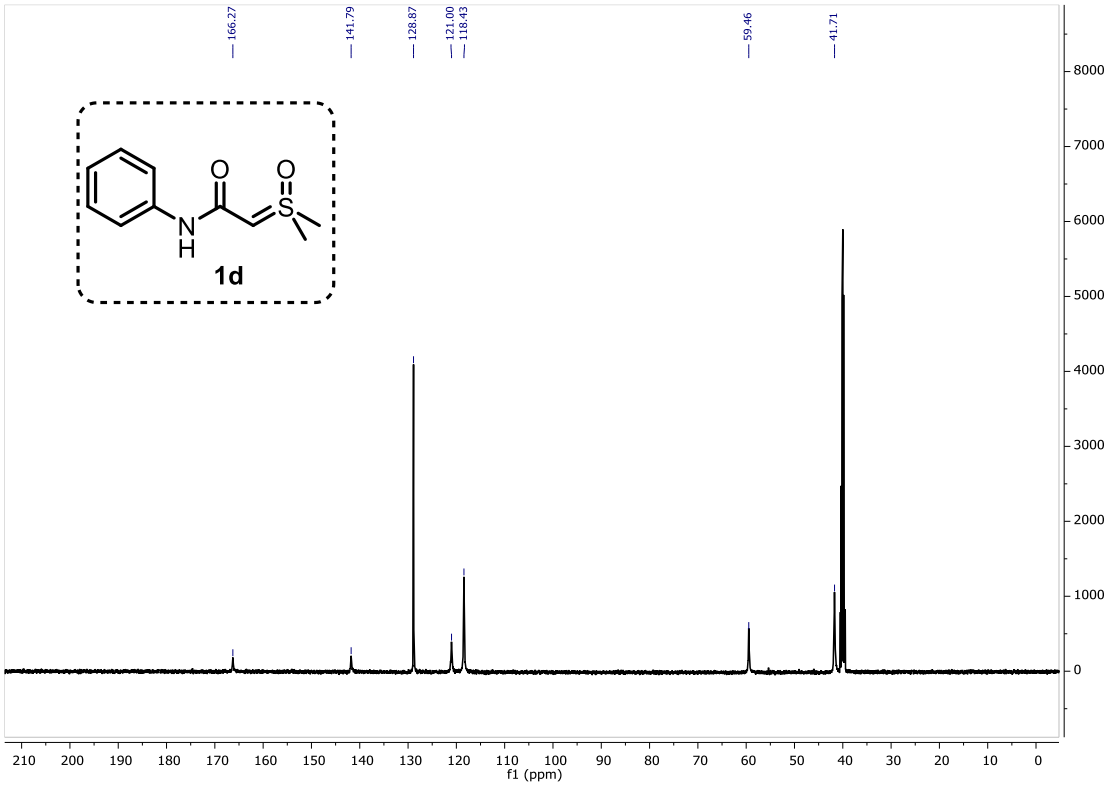


Figure S8. ^{13}C {^{1}H} NMR (125 MHz, DMSO–d_6) of 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-N-phenylacetamide (**1d**).

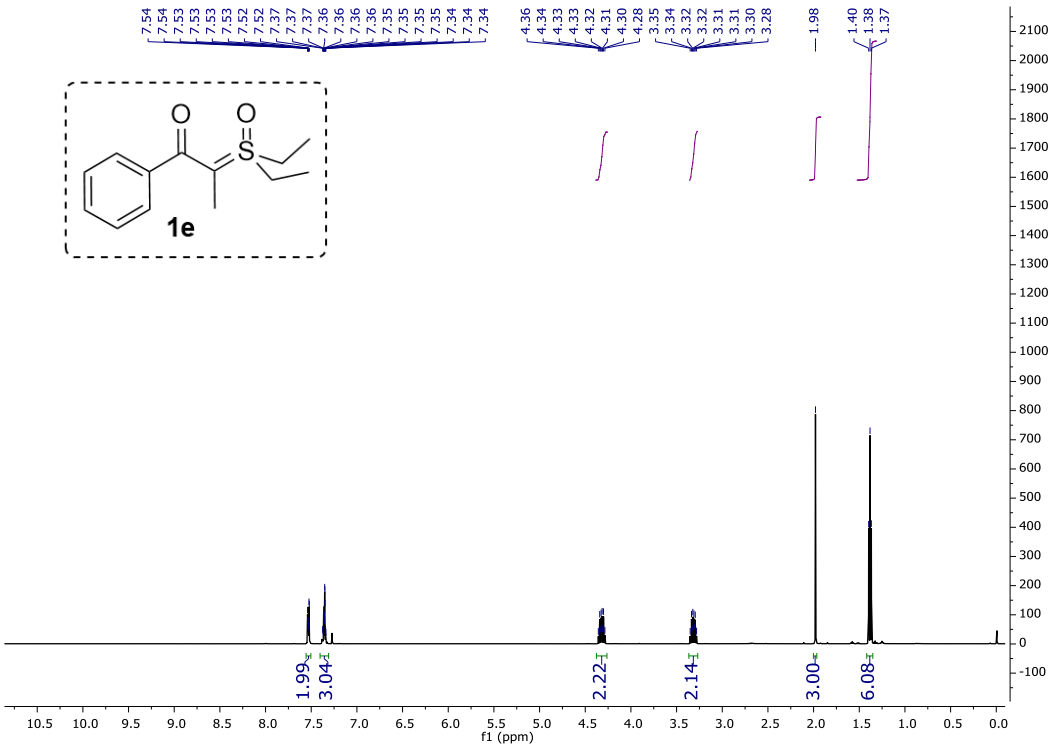


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) of 2-(diethyl(oxo)- λ^6-sulfaneylidene)-1-phenylpropan-1-one (**1e**).

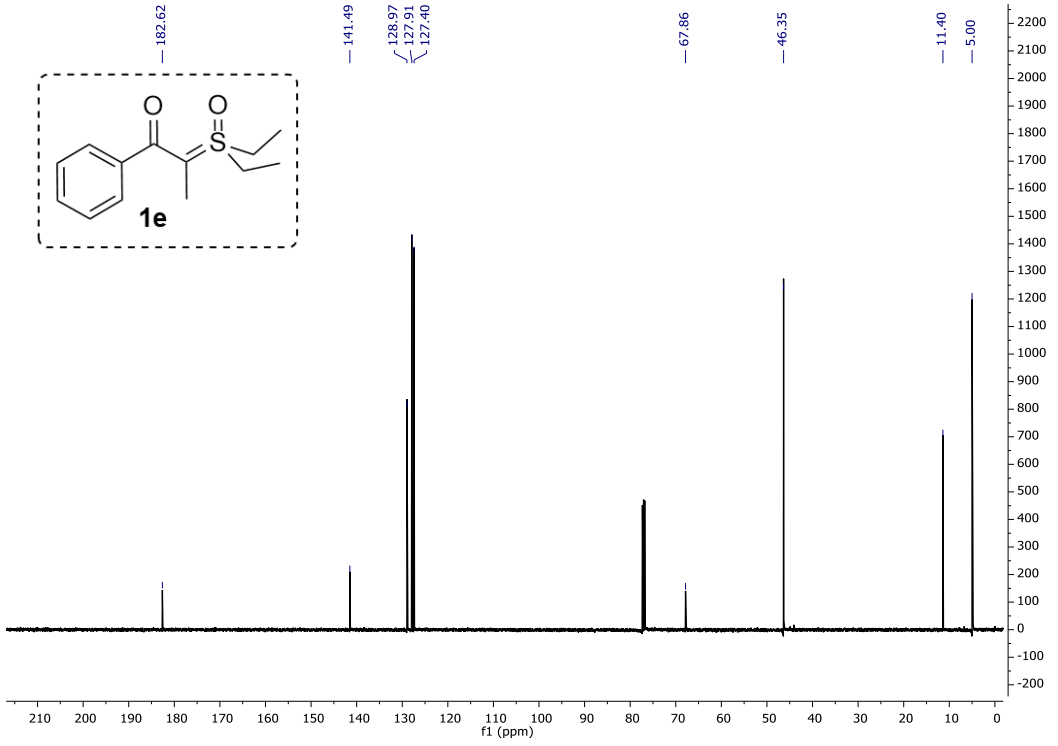


Figure S10. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of 2-(diethyl(oxo)- λ^6-sulfaneylidene)-1-phenylpropan-1-one (**1e**).

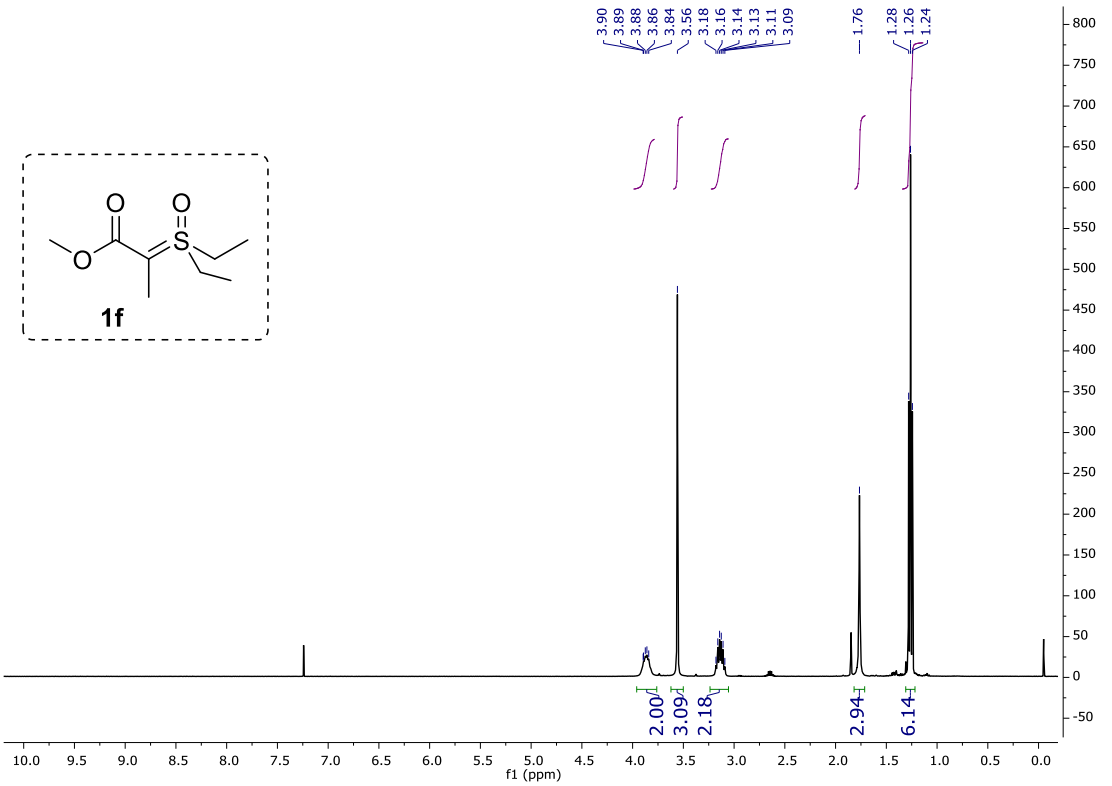


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-(diethyl(oxo)- λ^6-sulfaneylidene)propanoate (**1f**).

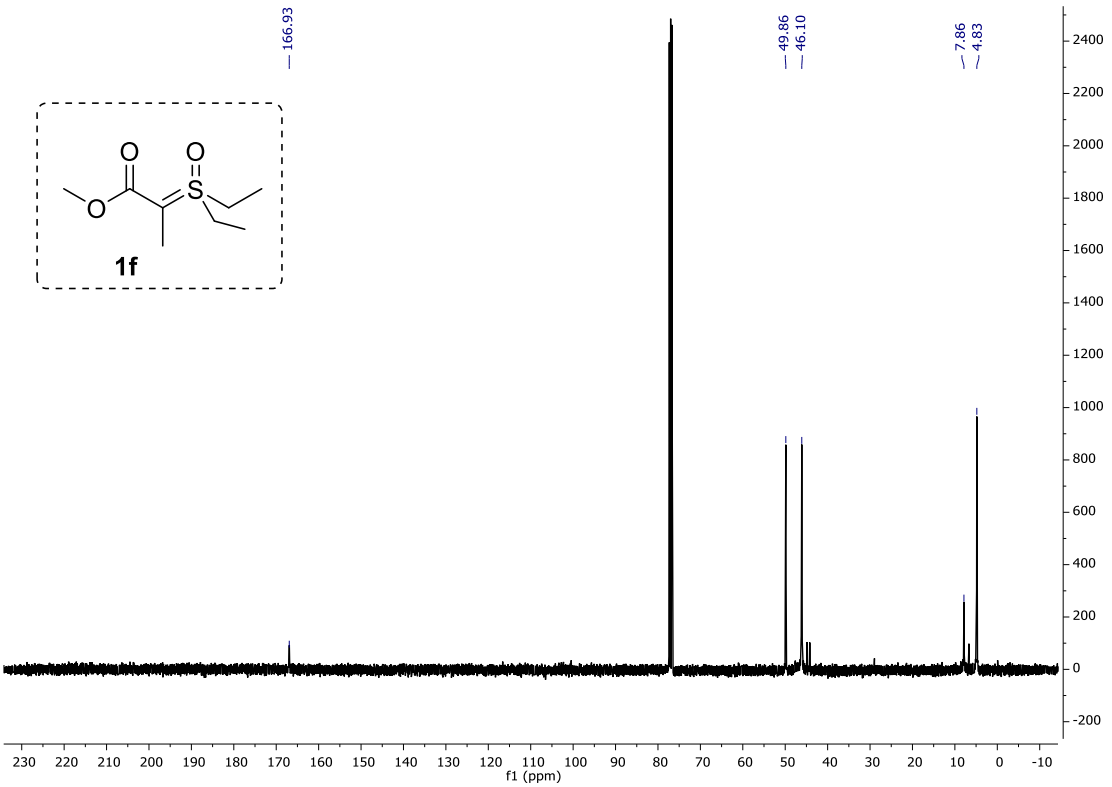


Figure S12. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of methyl 2-(diethyl(oxo)- λ^6-sulfaneylidene)propanoate (**1f**).

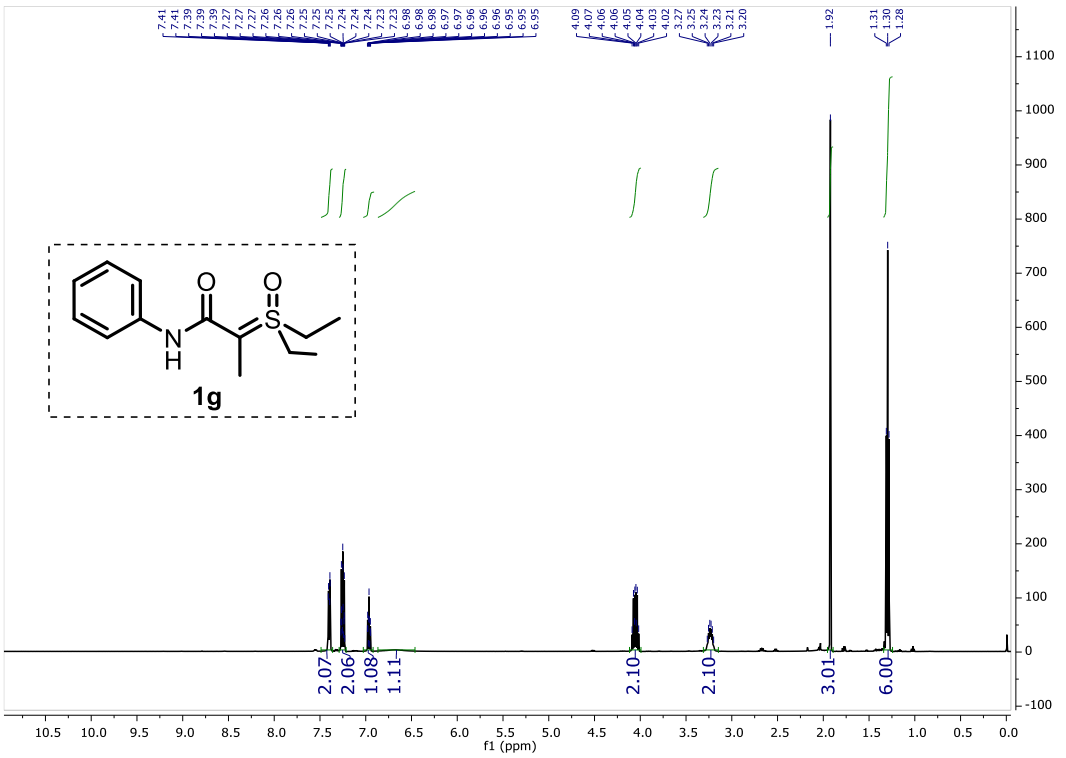


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) of 2-(diethyl(oxo)-λ^6-sulfaneylidene)-N-phenylpropanamide (**1g**).

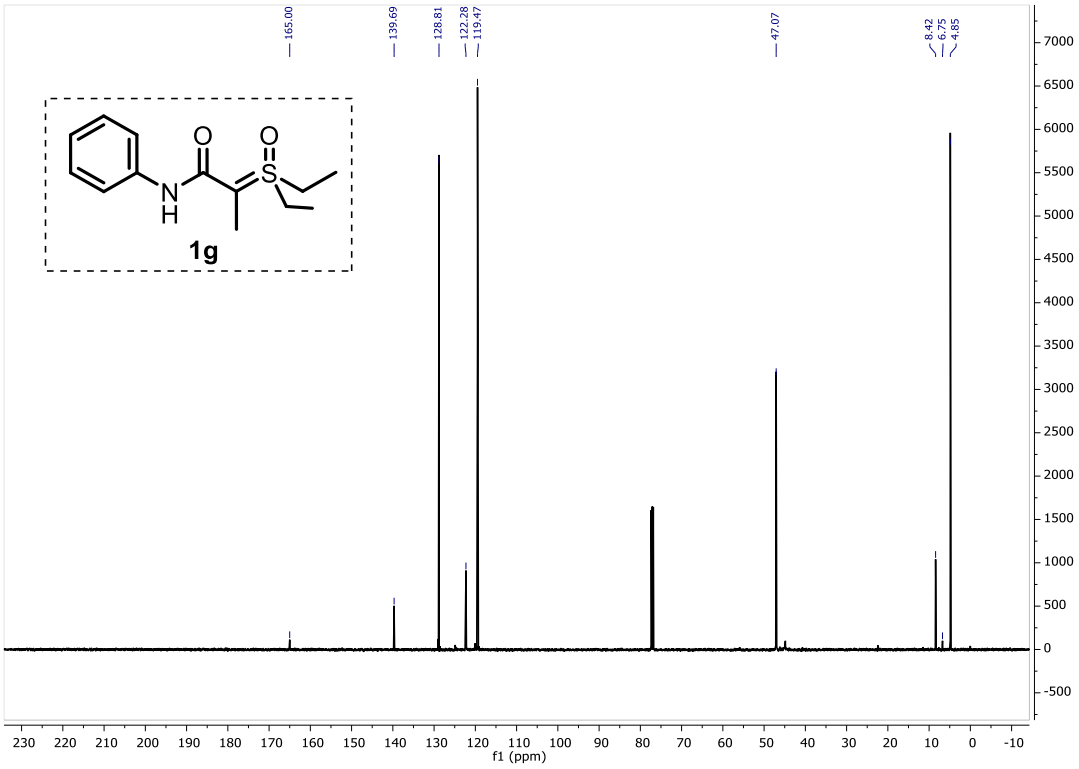


Figure S14. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of 2-(diethyl(oxo)-λ^6-sulfaneylidene)-N-phenylpropanamide (**1g**).

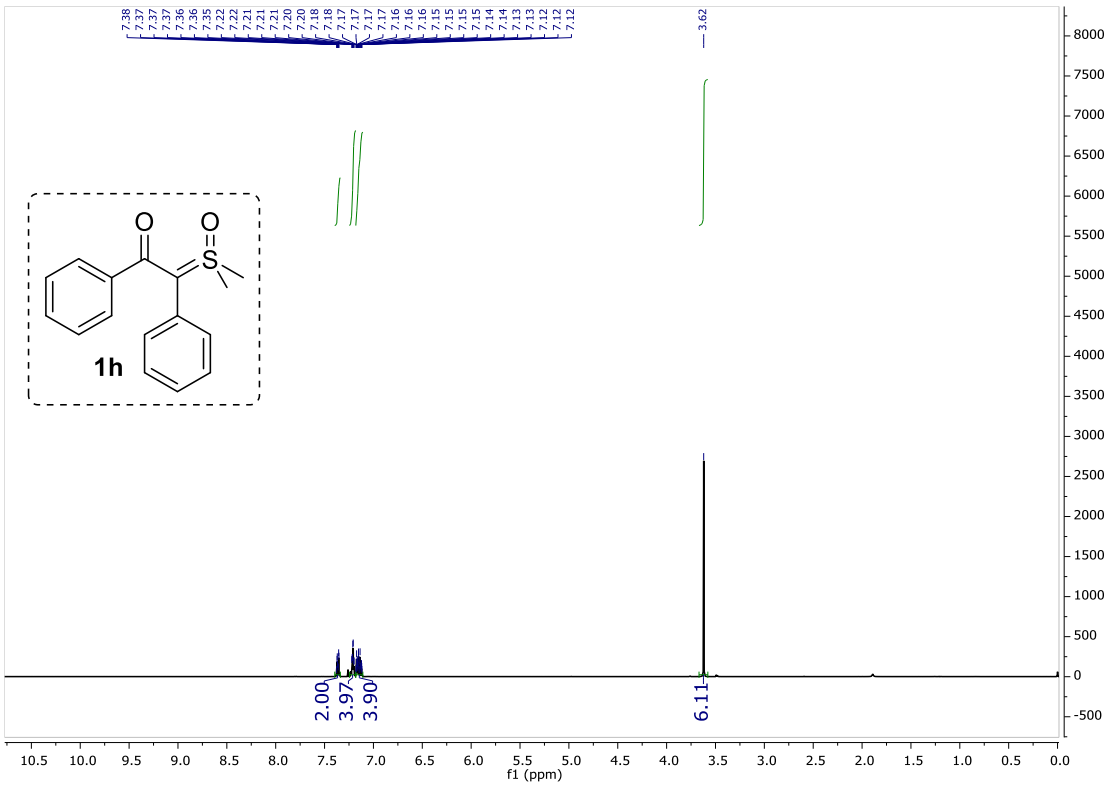


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) of 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,2-diphenylethan-1-one (**1h**).

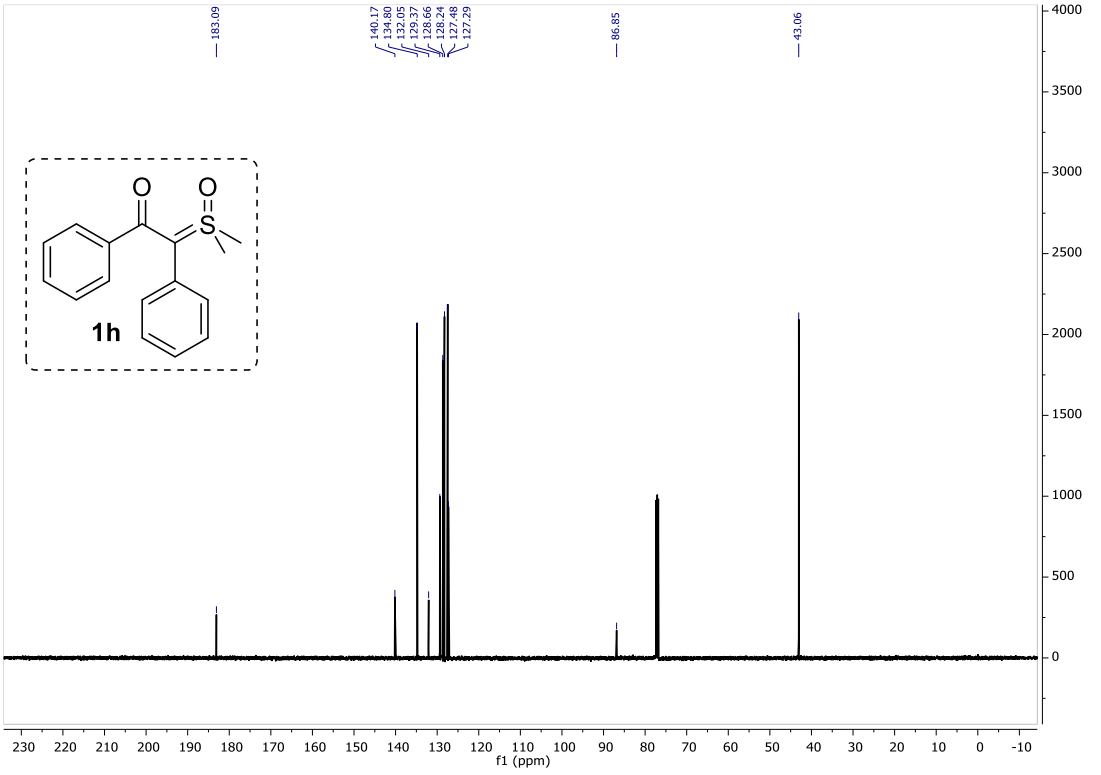


Figure S16. ^{13}C {^{1}H} NMR of (125 MHz, $CDCl_3$) 2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,2-diphenylethan-1-one (**1h**).

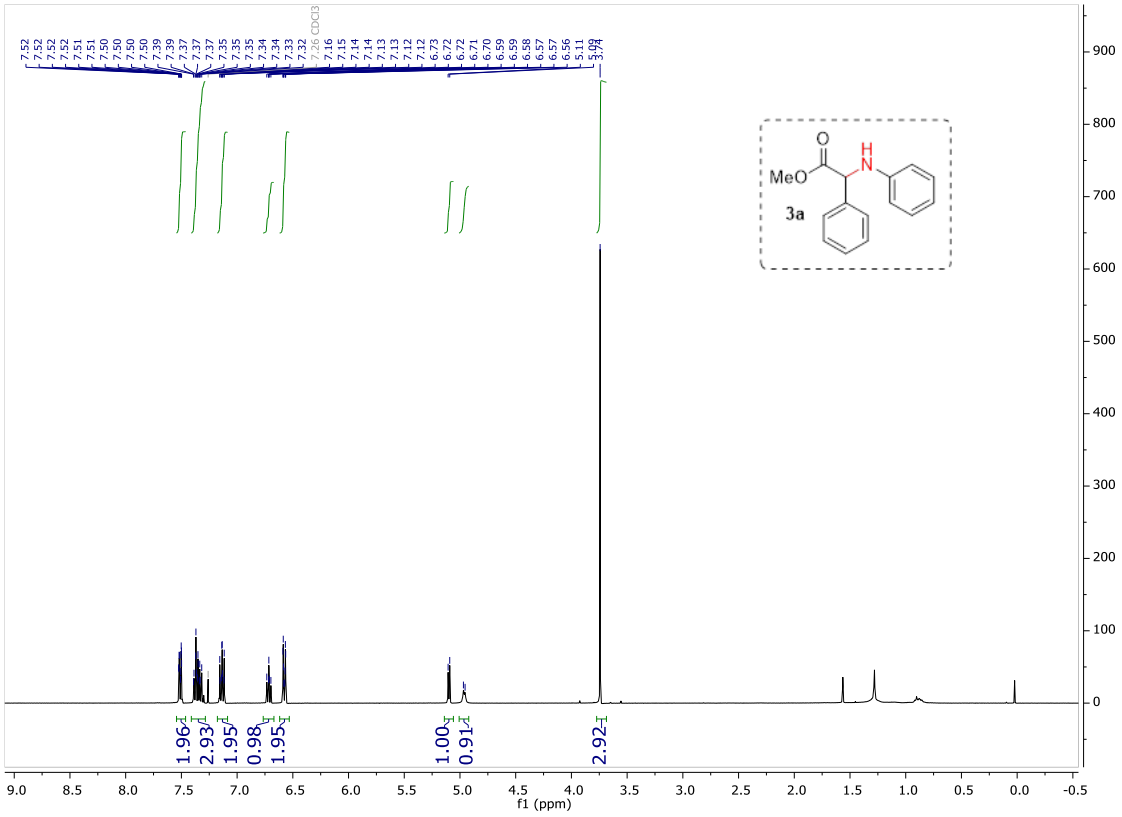


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2-phenyl-2-(phenylamino)acetate (**3a**).

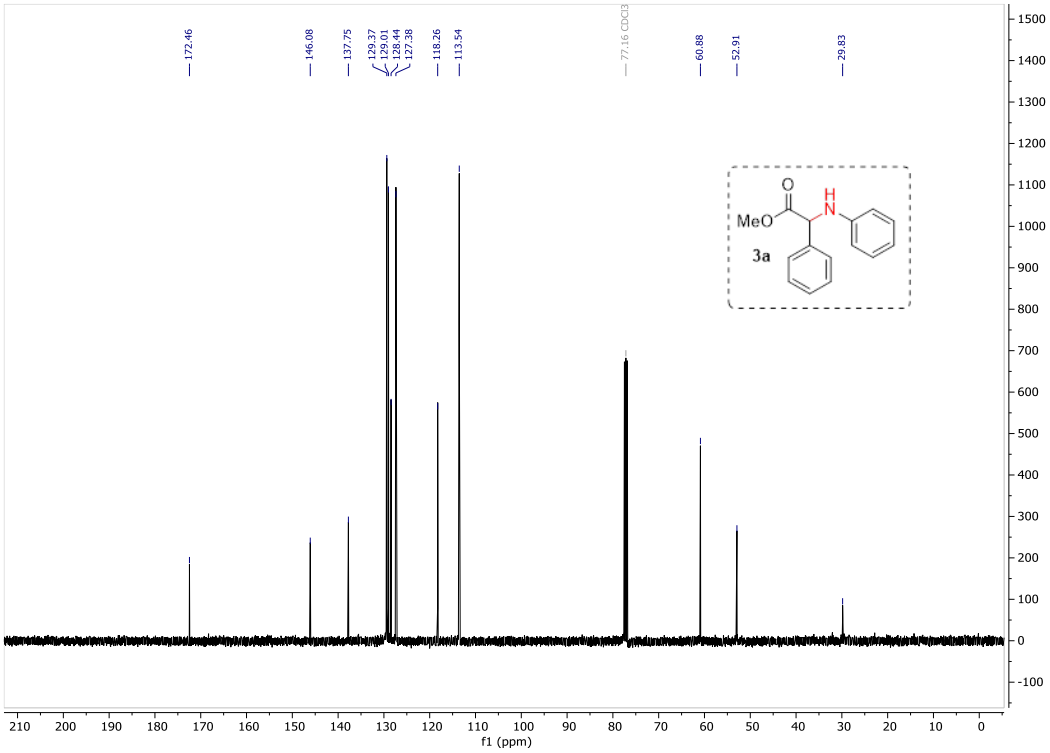


Figure S18. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of methyl 2-phenyl-2-(phenylamino)acetate (**3a**).

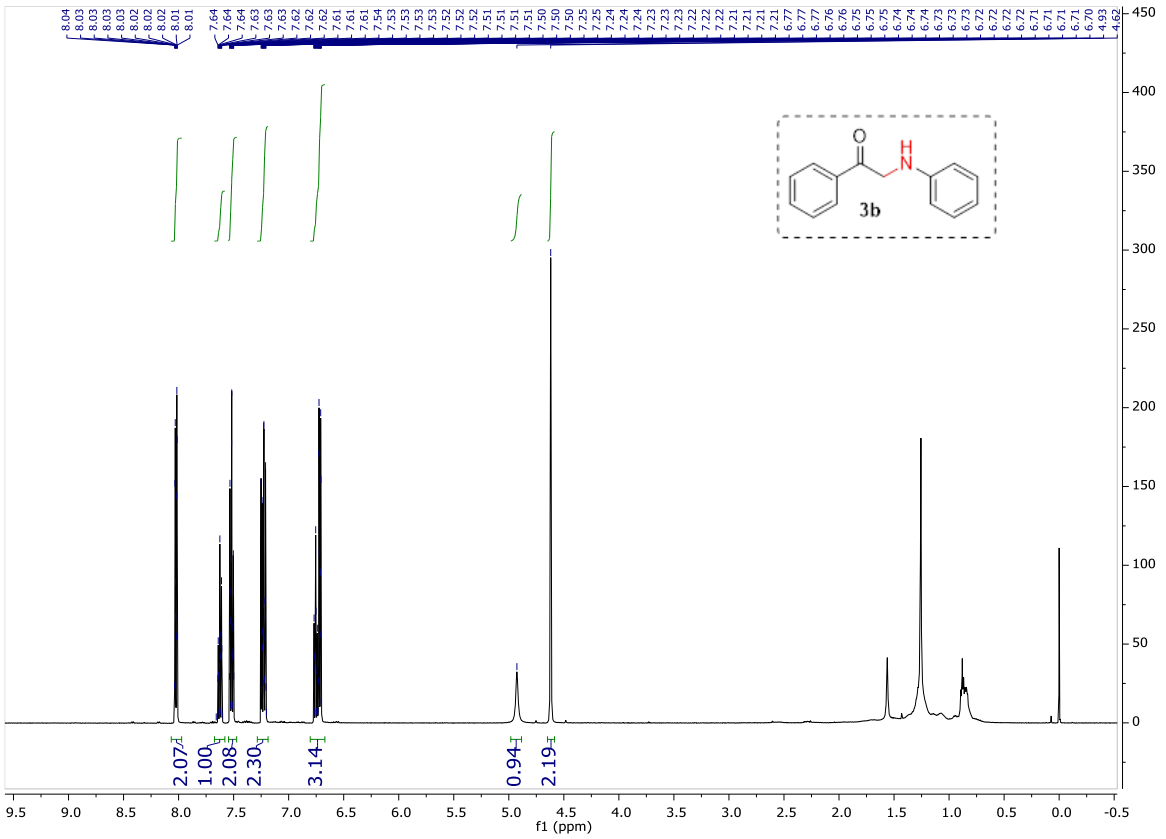


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-phenyl-2-(phenylamino)ethan-1-one (**3b**).

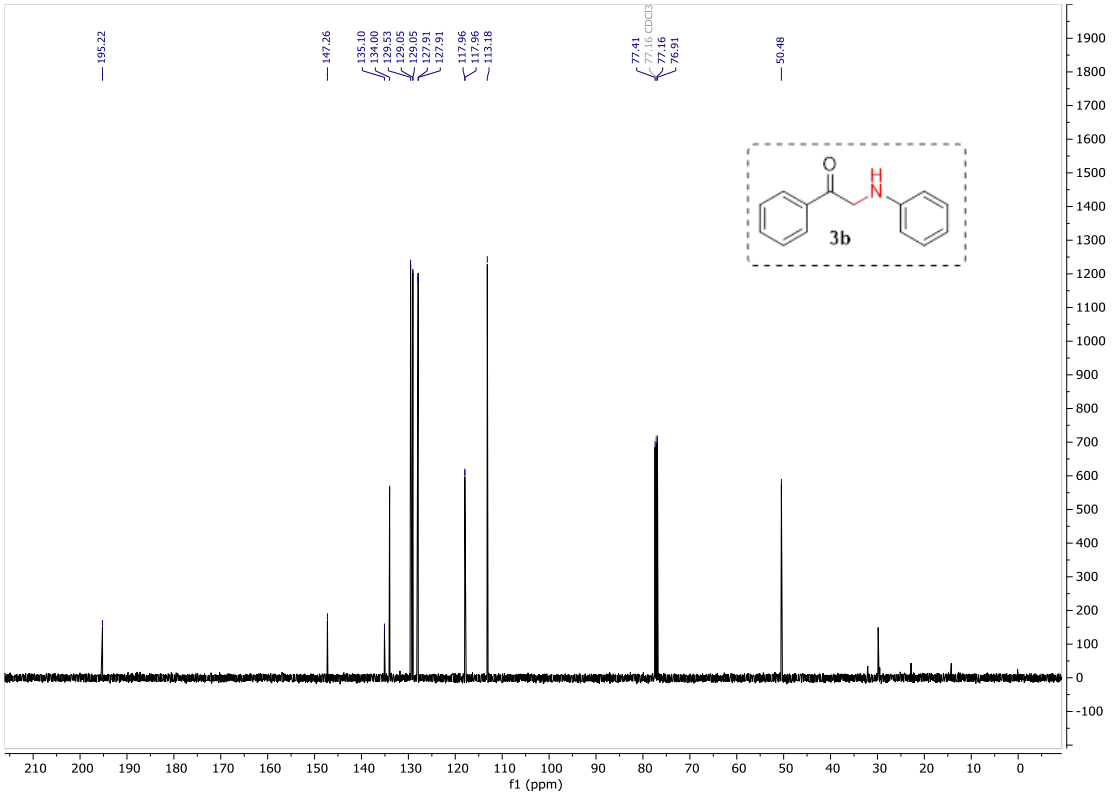


Figure S20. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) of 1-phenyl-2-(phenylamino)ethan-1-one (**3b**).

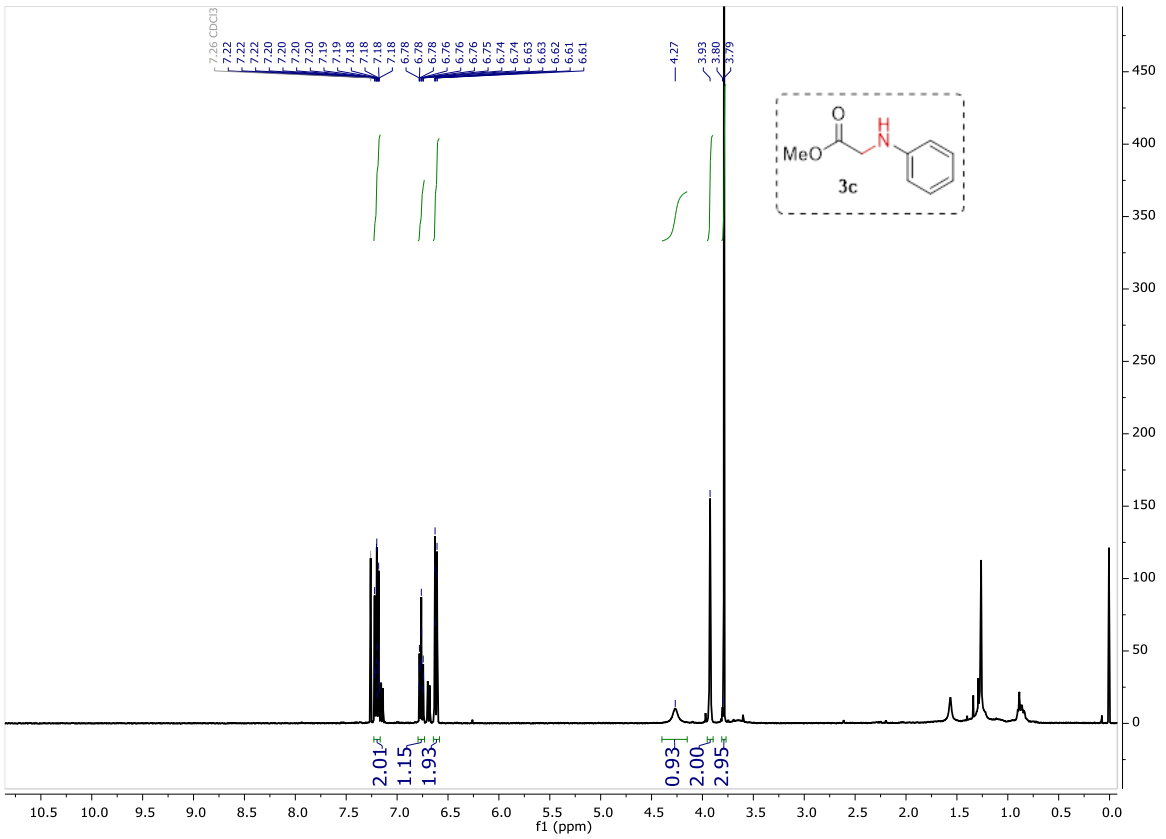


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl phenylglycinate (**3c**).

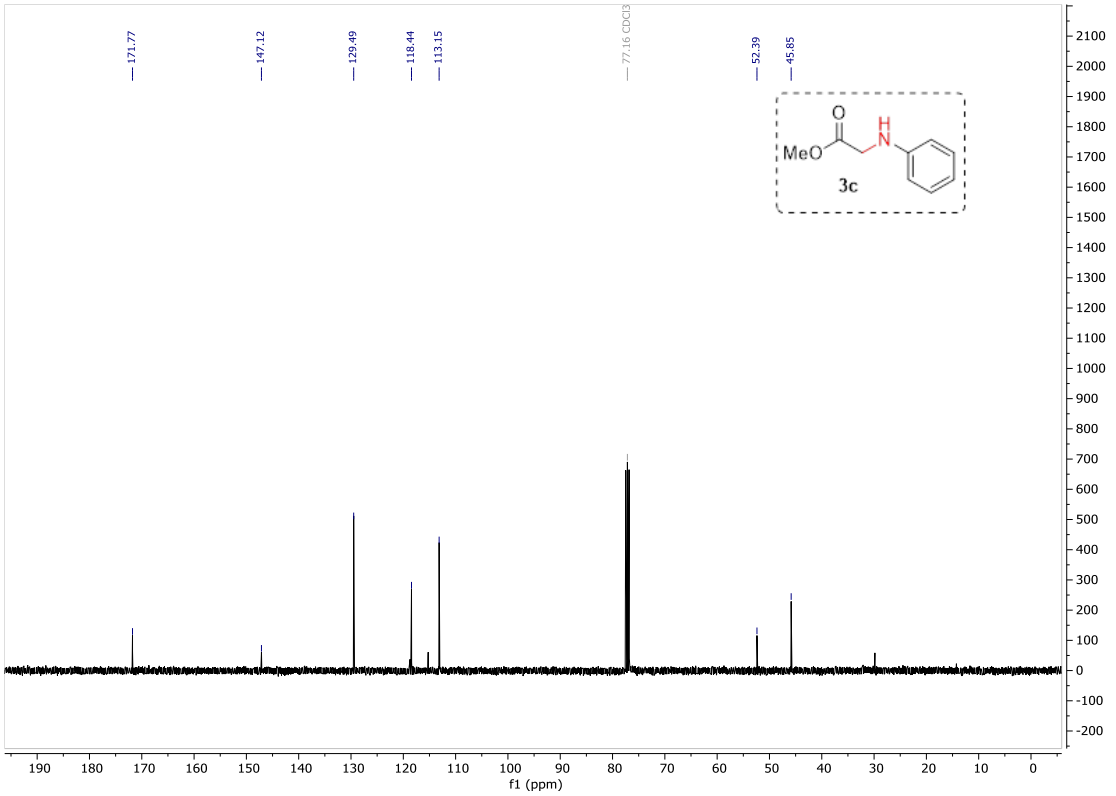


Figure S22. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of methyl phenylglycinate (**3c**).

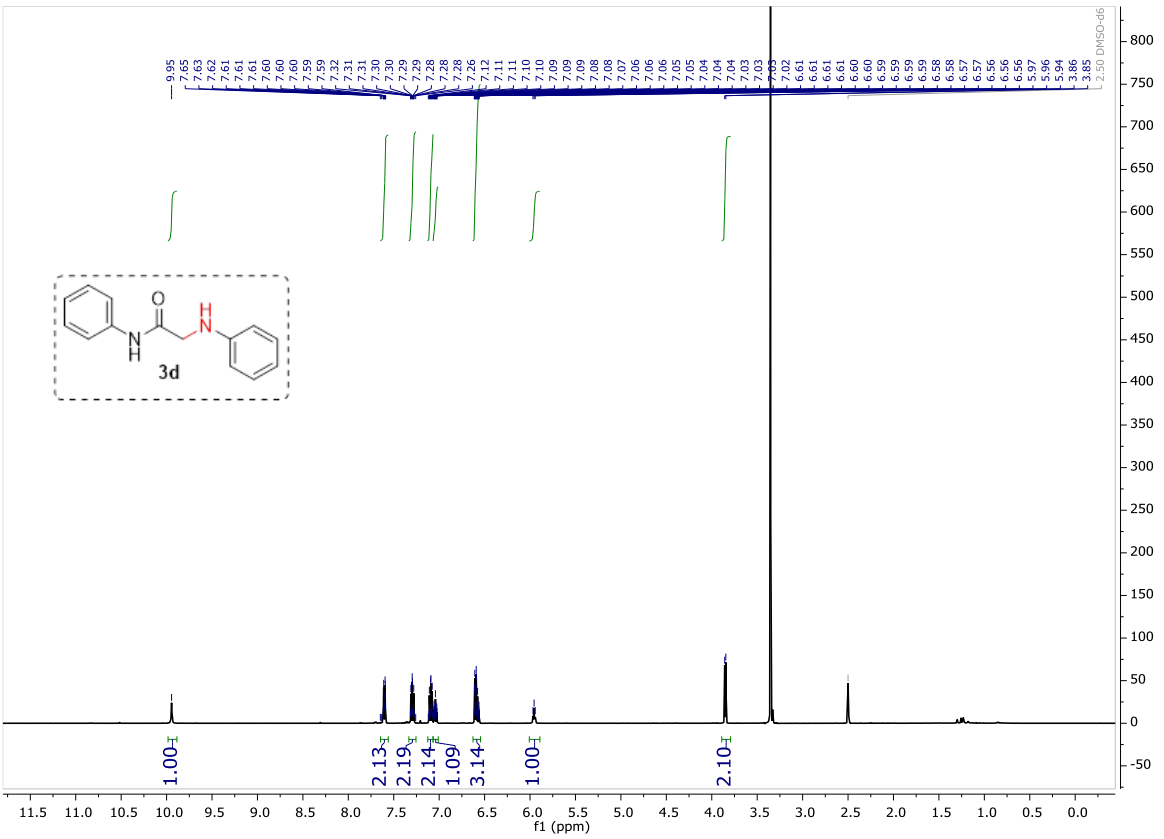


Figure S23. ^{1}H NMR (500 MHz DMSO-d_6) of N-phenyl-2-(phenylamino)acetamide (**3d**).

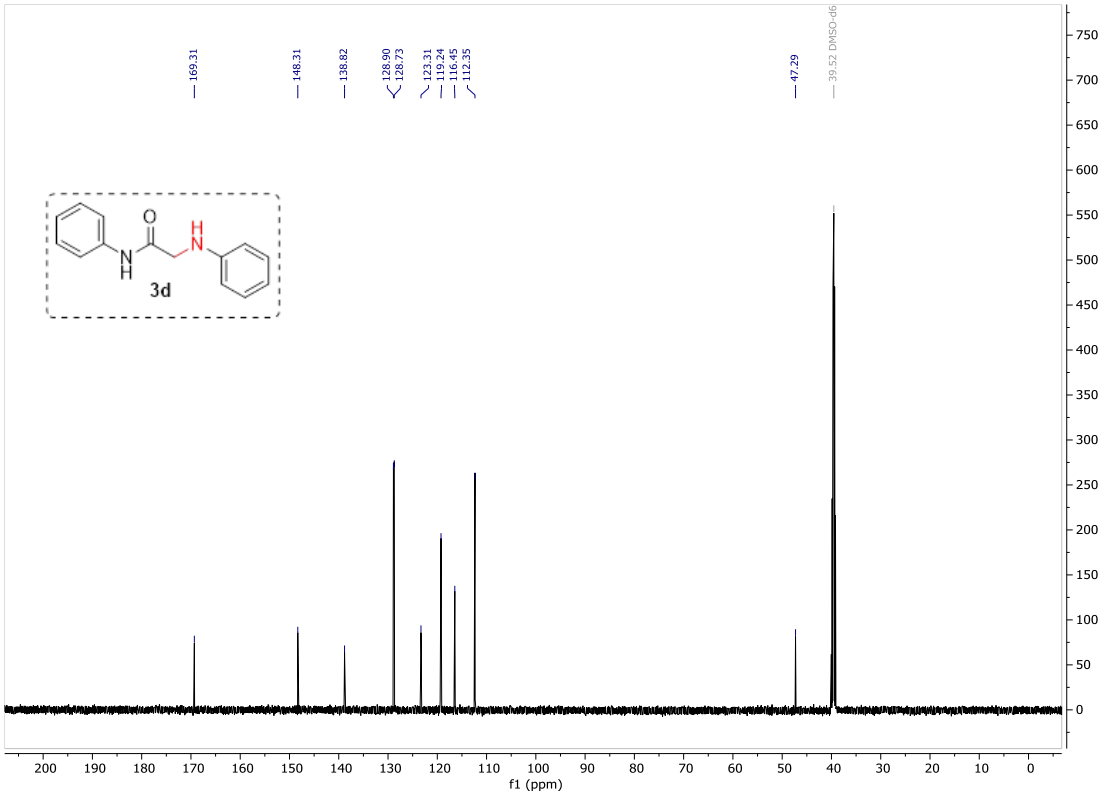


Figure S24. ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) of N-phenyl-2-(phenylamino)acetamide (**3d**).

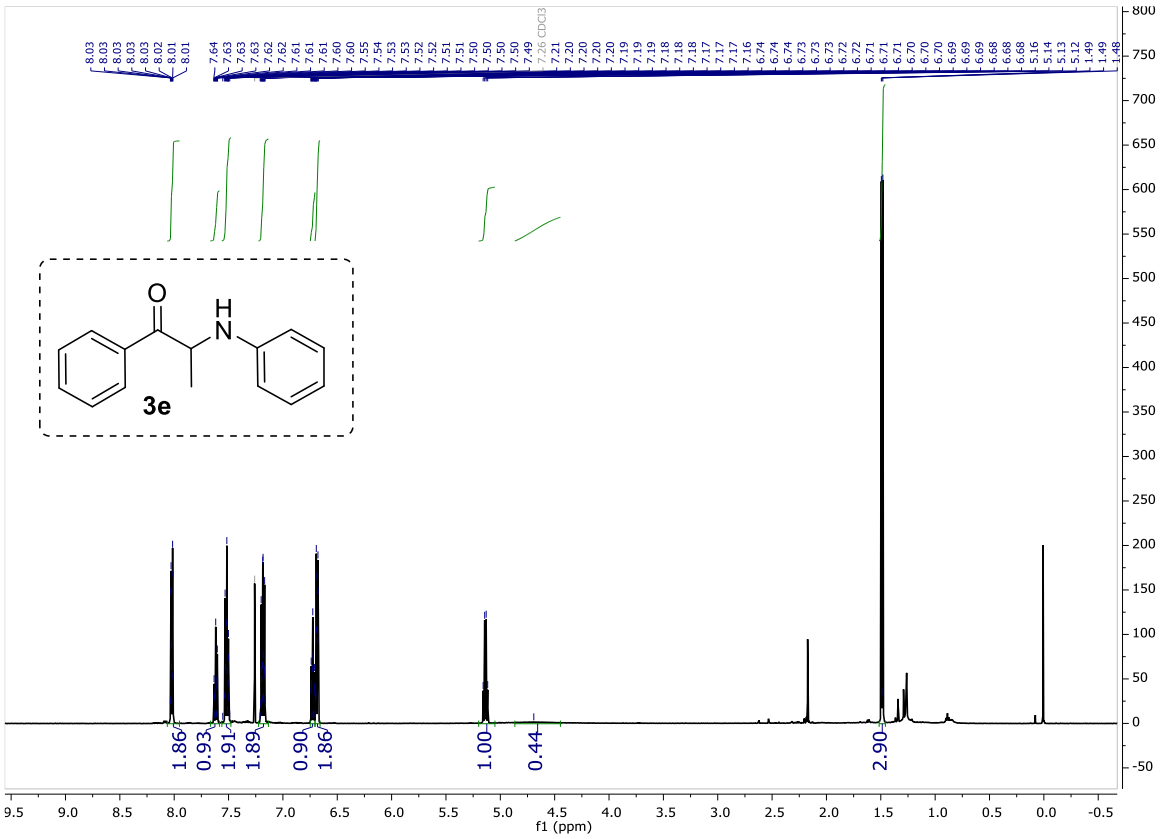


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-phenyl-2-(phenylamino)propan-1-one (**3e**).

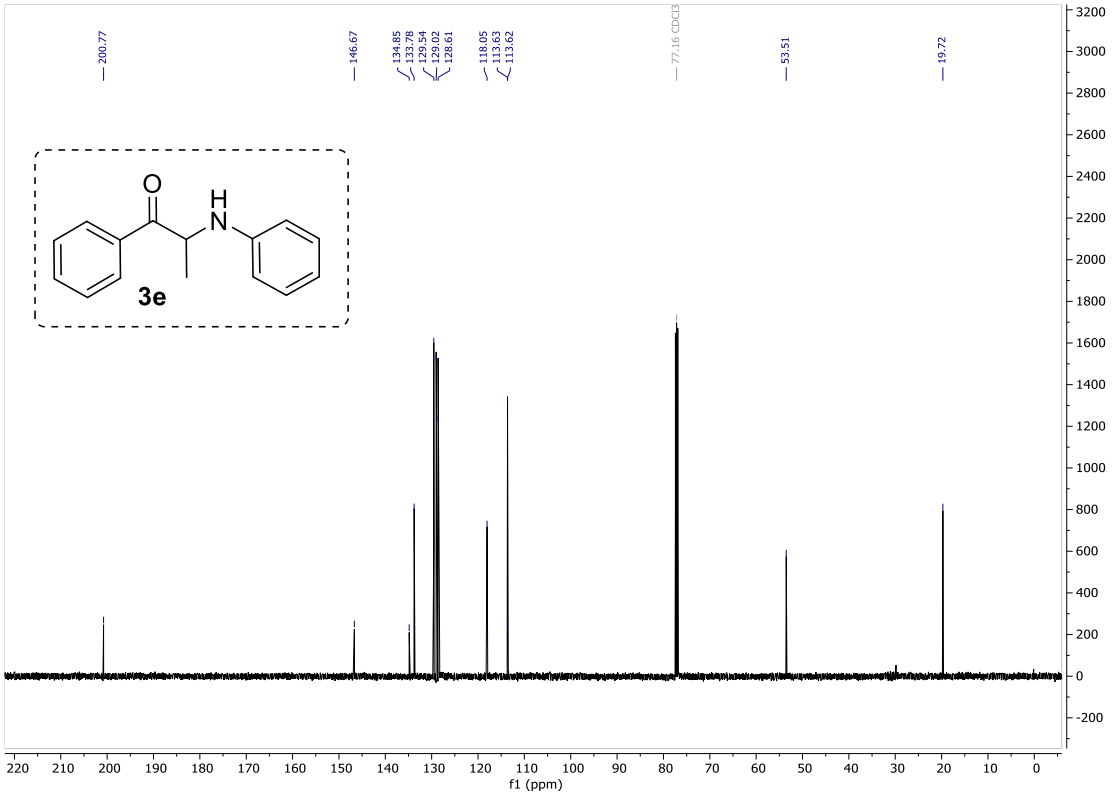


Figure S26. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) of 1-phenyl-2-(phenylamino)propan-1-one (**3e**).

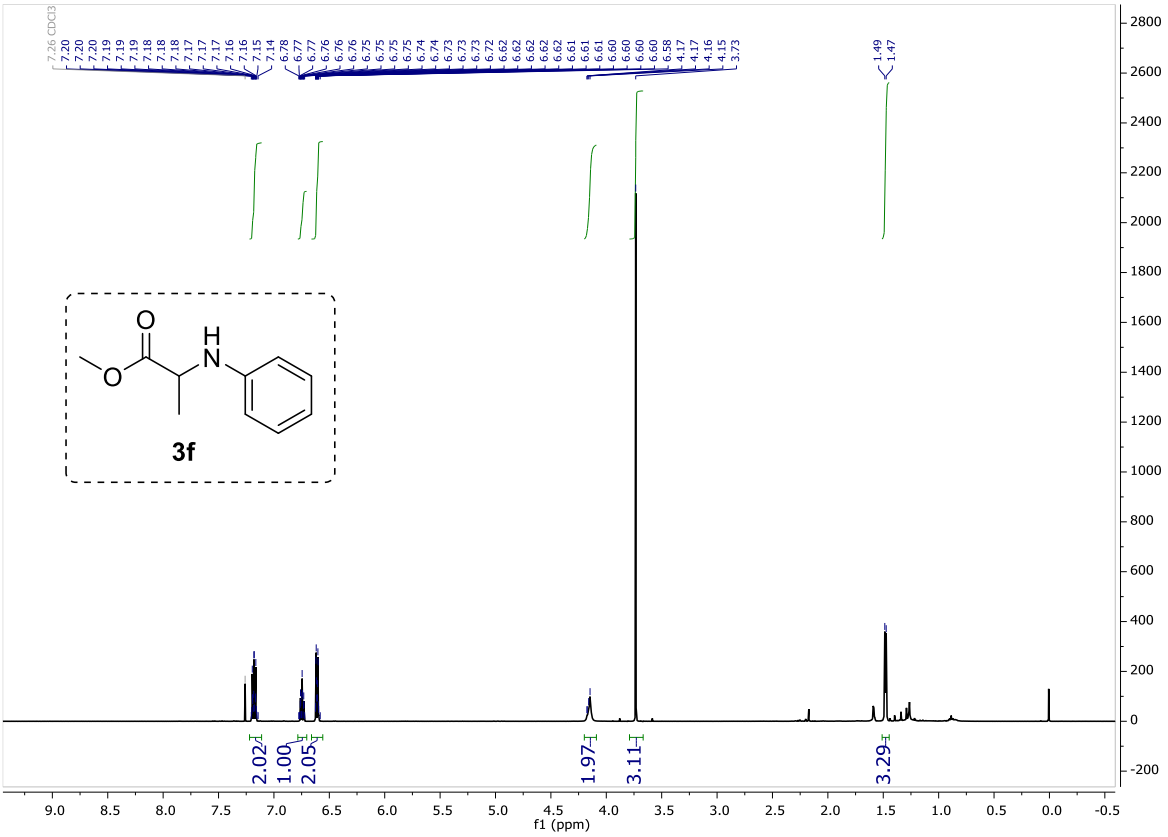


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl phenylalaninate (**3f**).

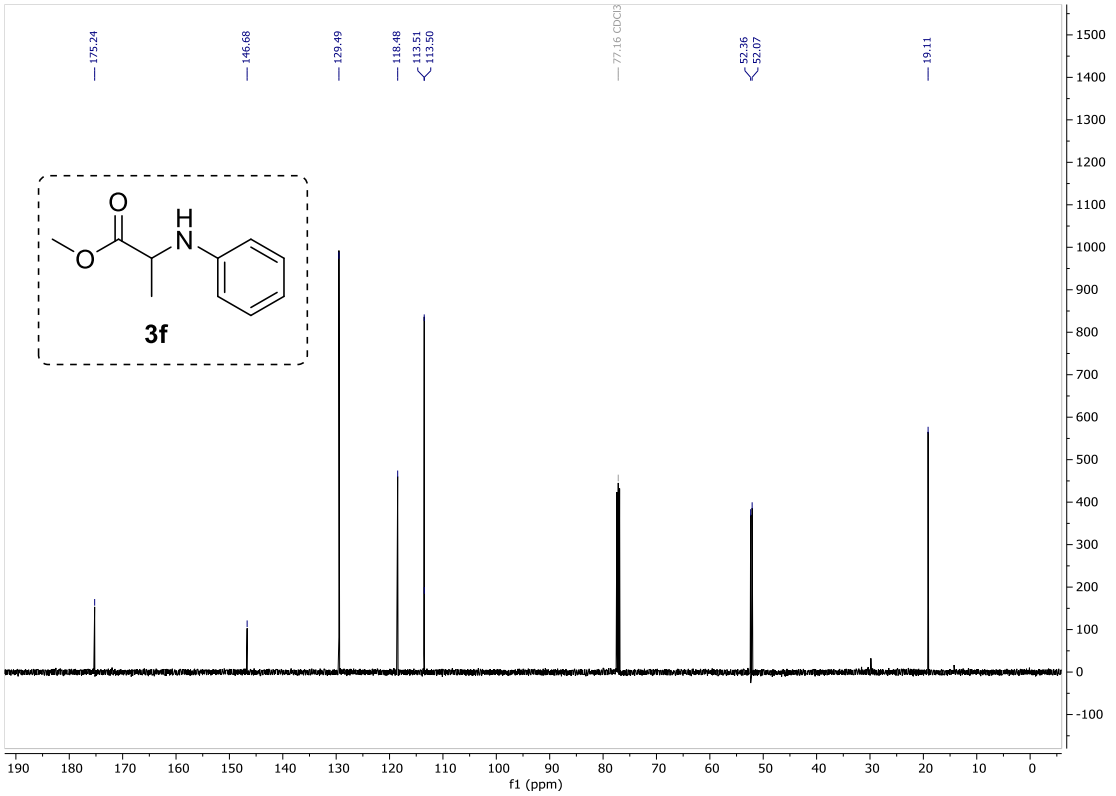


Figure S28. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) of methyl phenylalaninate (**3f**).

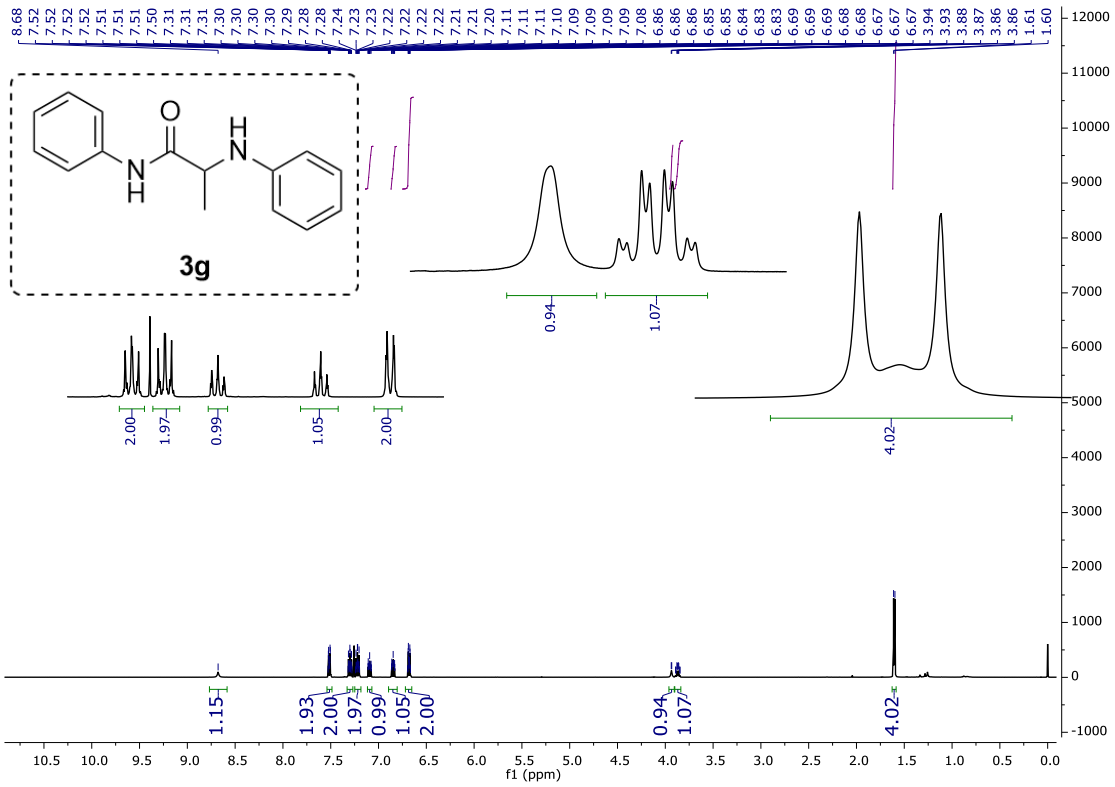


Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-phenyl-2-(phenylamino)propan-1-one (**3g**).

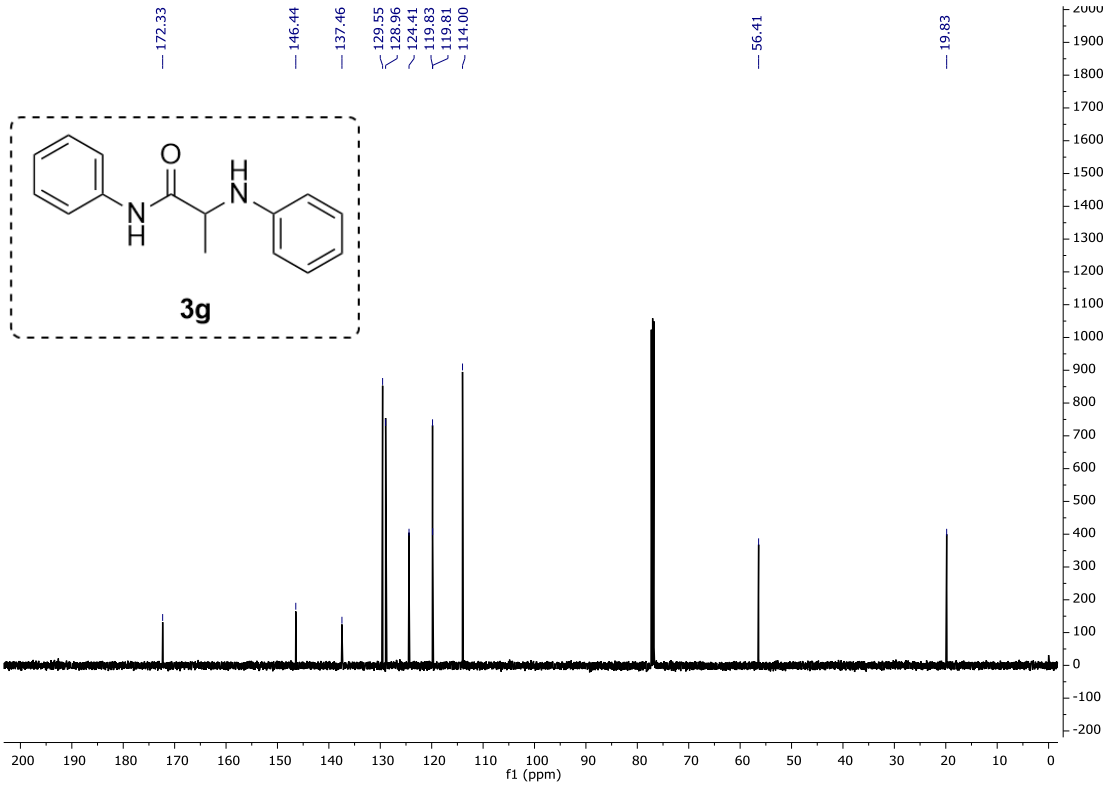


Figure S30. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) of 1-phenyl-2-(phenylamino)propan-1-one (**3g**).

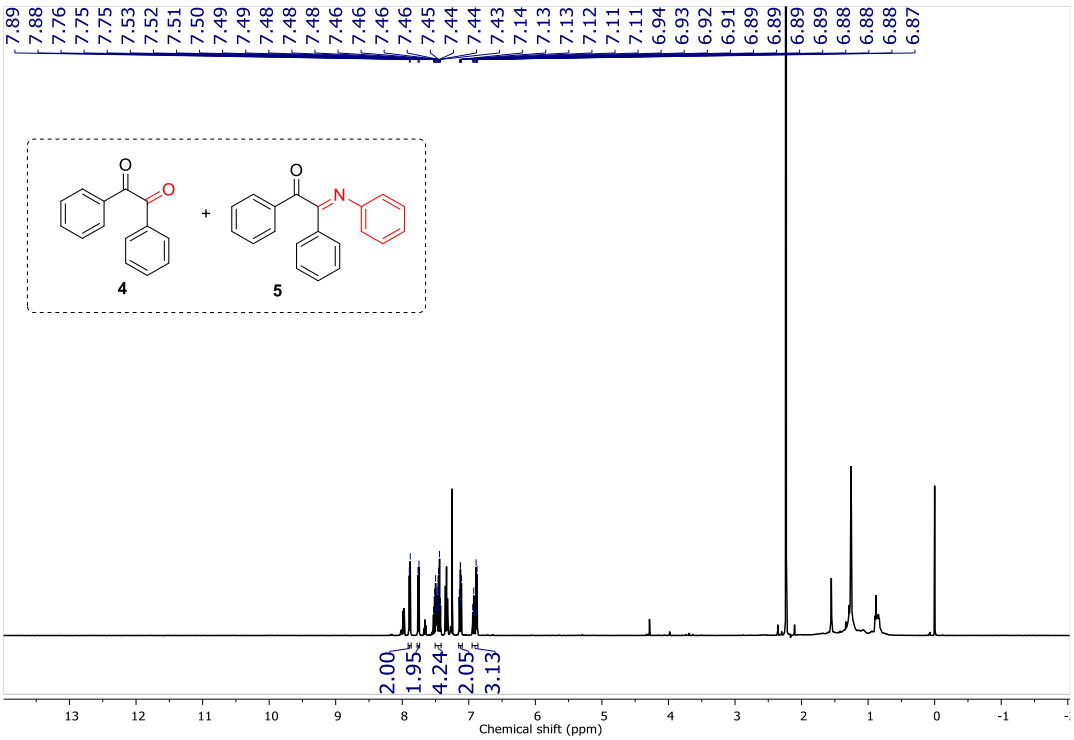


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) of 1,2-diphenyl-2-(phenylamino)ethan-1-one (**4** + **5** mixture).

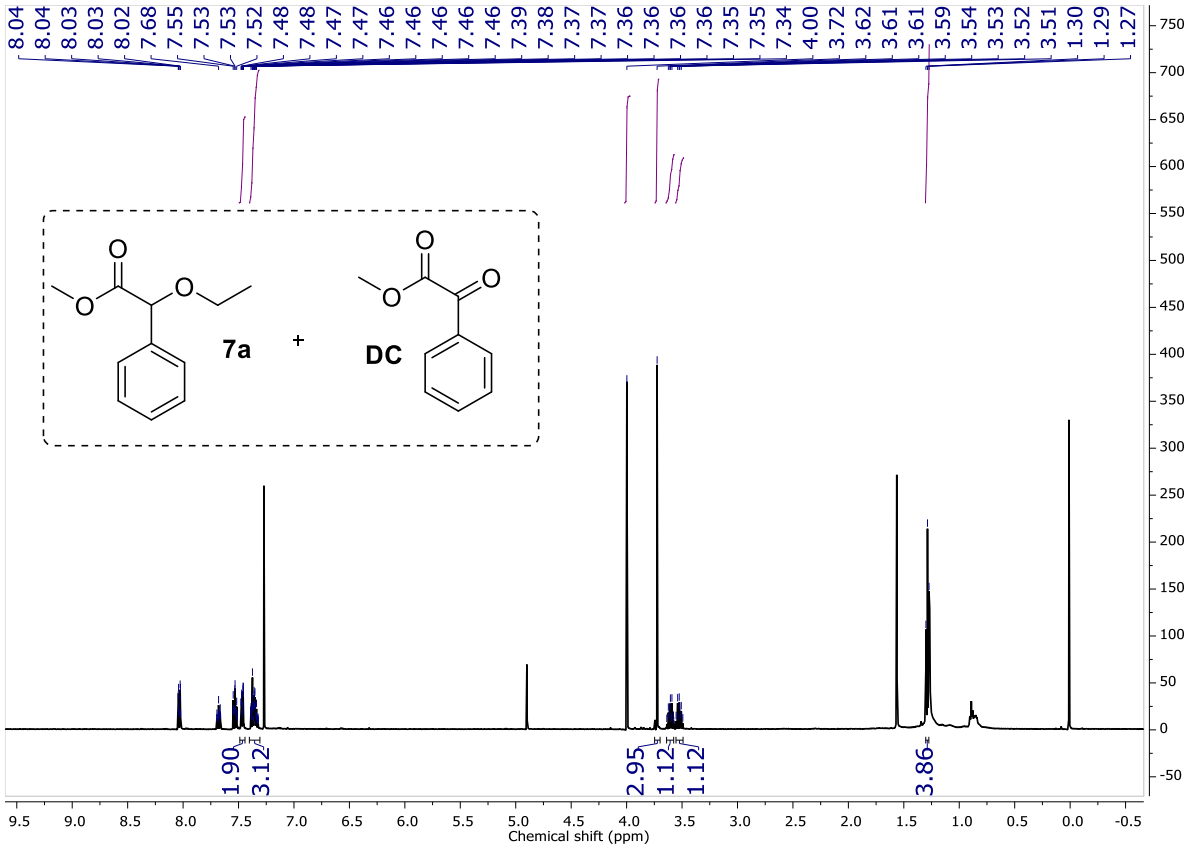


Figure S32. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) of methyl 2-ethoxy-2-phenylacetate (**7a** + **DC** mixture).

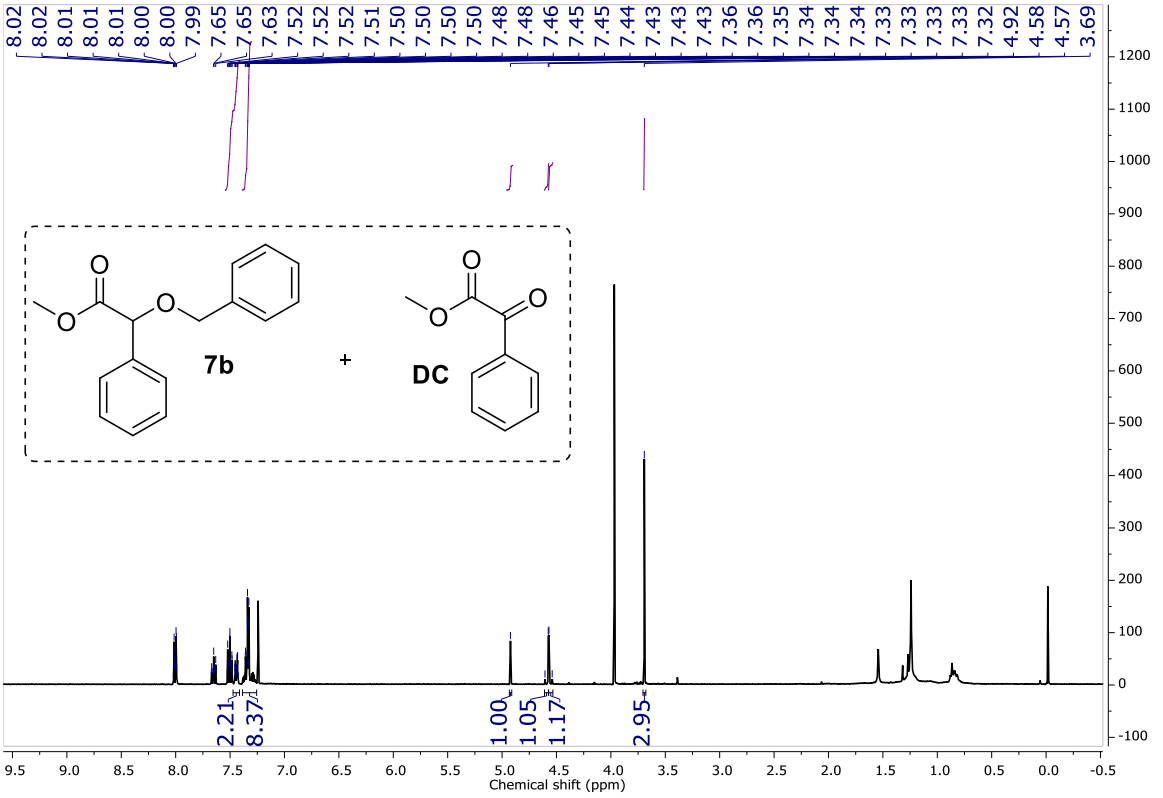


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2-(benzyloxy)-2-phenylacetate (**7b** + **DC**).

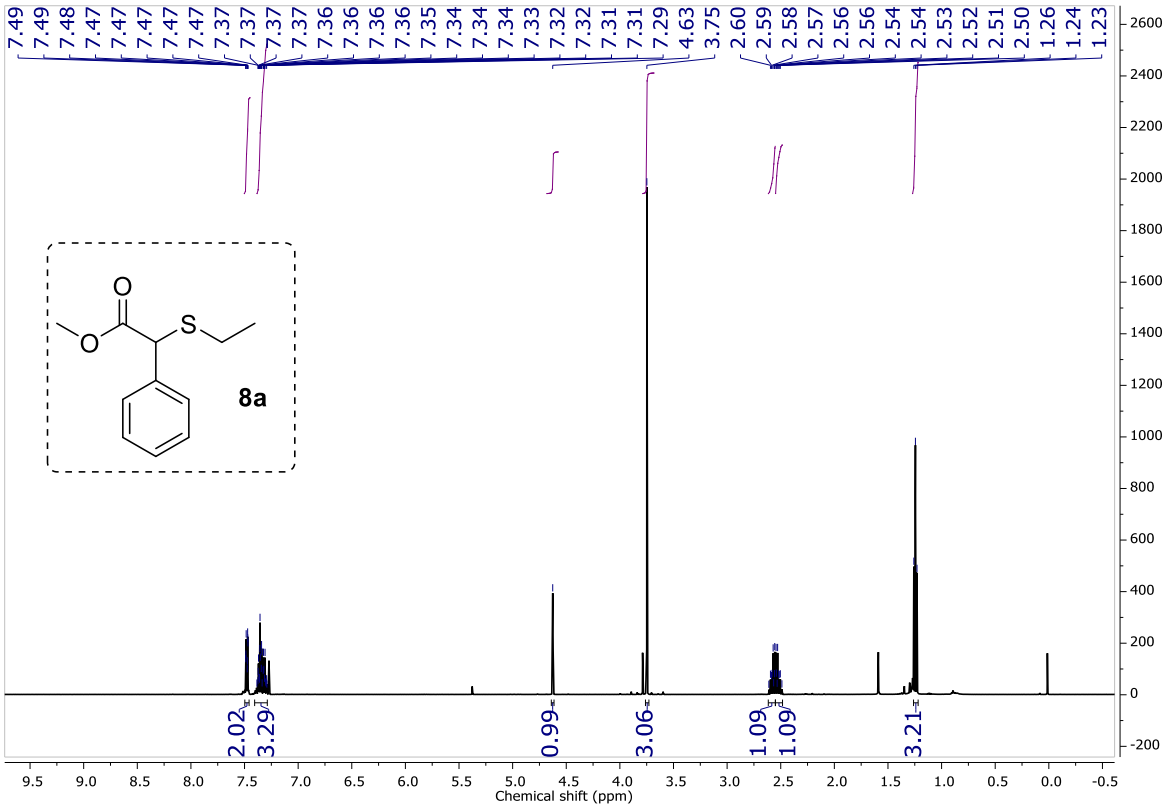


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2-(ethylthio)-2-phenylacetate (**8a**).

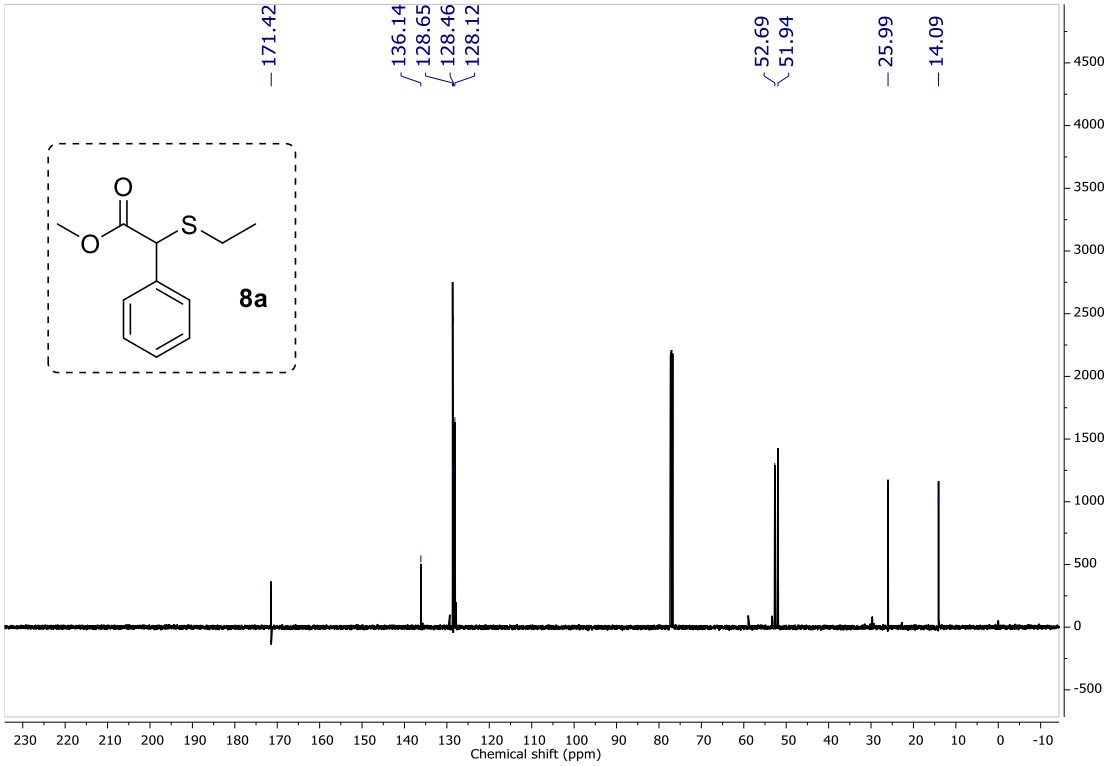


Figure S35. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) of methyl 2-(ethylthio)-2-phenylacetate (**8a**).

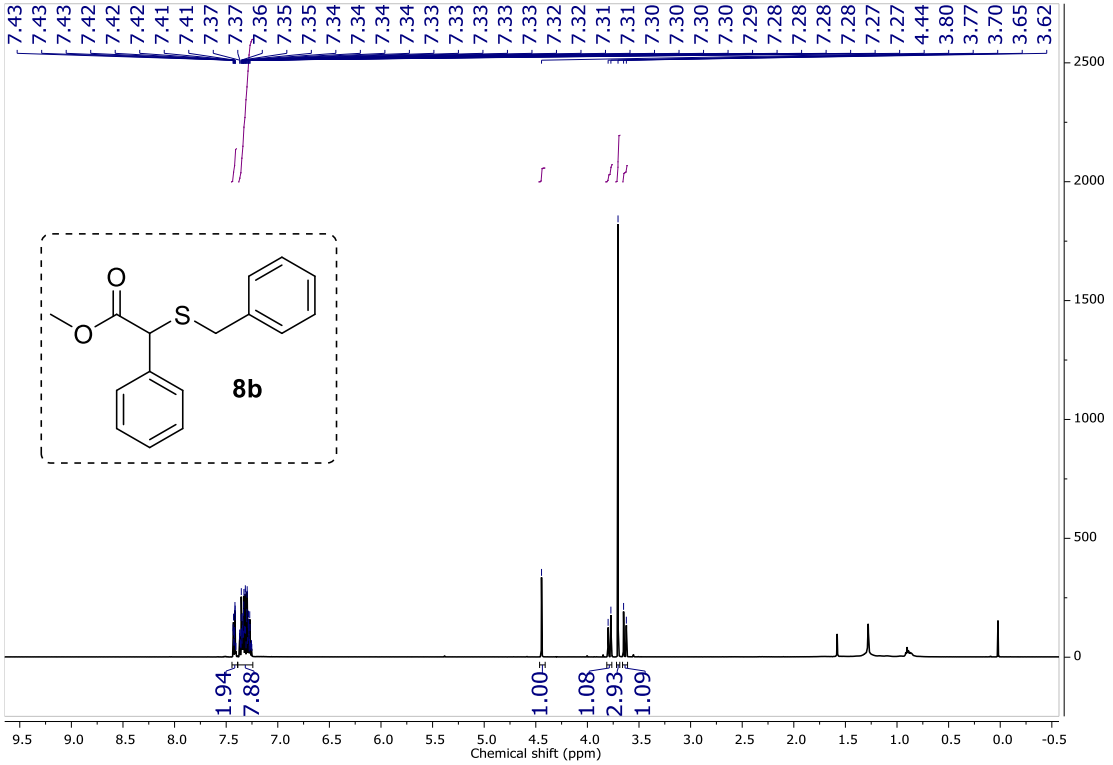


Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-(benzylthio)-2-phenylacetate (**8b**).

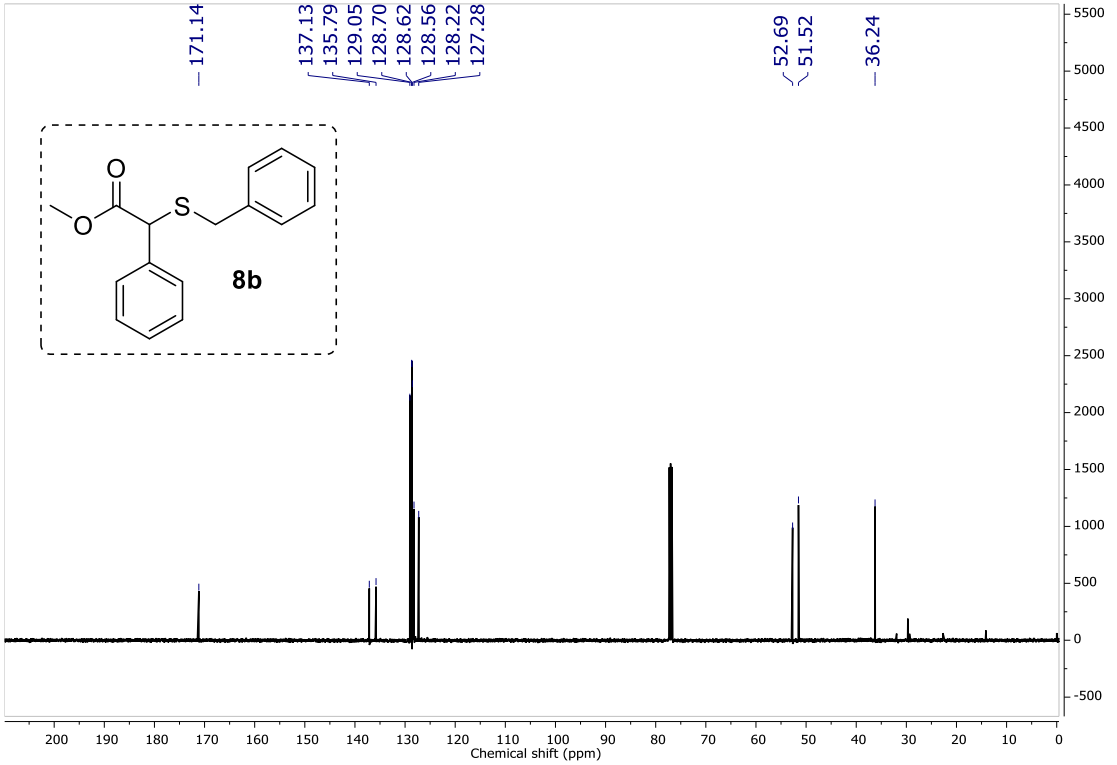


Figure S37. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of methyl 2-(benzylthio)-2-phenylacetate (**8b**).

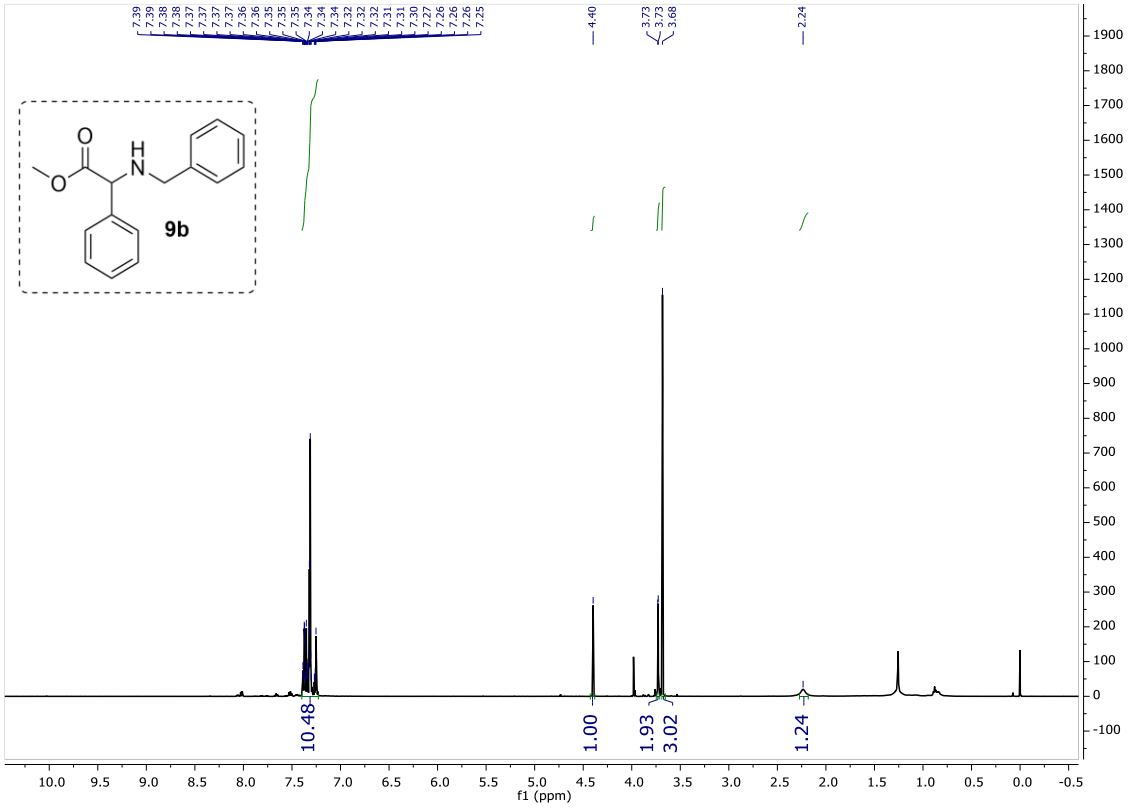


Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-(benzylamino)-2-phenylacetate (**9b**).

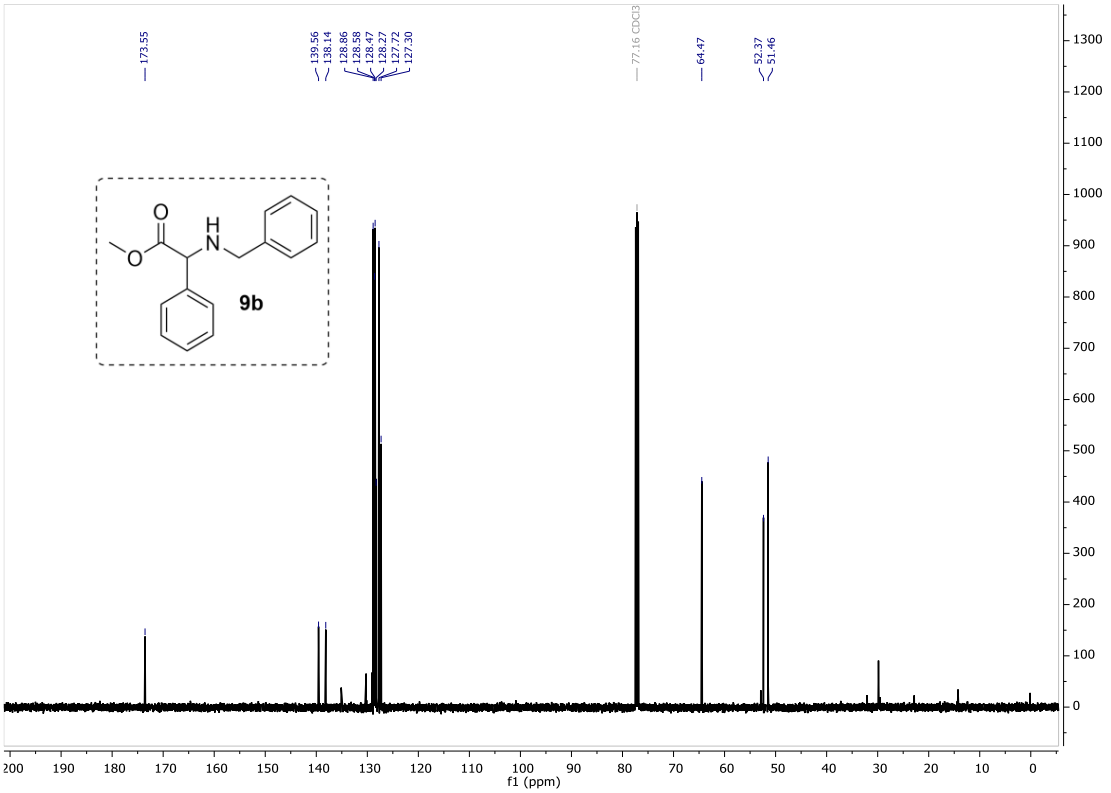


Figure S39. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) of methyl 2-(benzylamino)-2-phenylacetate (**9b**).

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