Gold(I)-Catalysed Cascade Reactions in the Synthesis of 2,3-Fused Indole Derivatives

Authors: Ana Gimeno, Alejandra Rodríguez, Ana B. Cuenca, Carmen Ramírez de Arellano, Mercedes Medio-Simón and Gregorio Asensio

Departamento de Química Orgánica, Universidad de Valencia,

Avda. Vicente Andrés Estellés, s/n
Burjassot, Valencia 46100.

Gregorio.asensio@uv.es

Supporting Information

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General Remarks

General Methods

Chemicals were purchased from commercial suppliers and used as delivered. All reactions were carried out in oven-dried resealable test tubes or Schlenk tubes under an atmosphere of Argon. Solvents were refluxed and freshly distilled from desiccants. *N,N*-dimethylformamide and deuterated solvents were purchased from Aldrich and used without further purification. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the spectrometers Bruker DPX-300, Bruker AVANCE-400 or Bruker DRX-500. Chemical shifts are given in ppm and coupling constants in Hz. In the ^{1}H and ^{13}C spectra chemical shifts are reported relative to deuterated solvents ($CDCl_3$: 7.26 / 77.16 ppm; CD_2Cl_2: 5.32 / 54.00 ppm; Acetone-d_6: 2.05 / 29.84 ppm; DMF-d_7: 2.75 / 29.76 ppm; THF-d_8: 1.73 / 25.37 ppm). ^{31}P chemical shifts are given in δ ppm relative to H_3PO_4 (5% solution) as an external standard. The following abbreviations were used for ^{1}H-NMR to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet), bs (broad singlet). High Resolution Mass Spectra were determined on a TRIPLETOFT5600 (ABSciex, USA) spectrometer. Analytical thin

layer chromatography was carried out using commercial aluminium sheets pre-coated (0.2mm layer thickness) with silica gel 60 F254 (E. Merck), and visualization was effected with shorts wavelength UV light (254nm). Reactions were monitored by GC. Product purification by flash chromatography was performed using E. Merck Silica gel (230-400 mesh). Melting points were measured in a Cambridge Instrument Apparatus.

Materials

2-haloanilines derivatives, alkynes and alkenes were commercially available and were used without further purification. All the commercial reagents and Gold/Silver catalysts were purchased from Aldrich or Strem Chemical Co. The following non-commercially available starting materials were prepared according to literature procedures: 2-iodo-4-methoxyaniline[1]

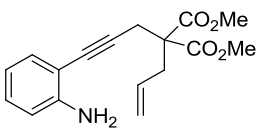
Synthesis of Starting Materials

Preparation of enynes

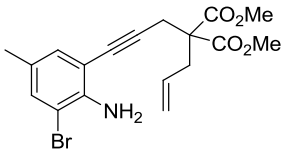
The following non-commercially enynes were prepared according to described literature procedures: dimethyl 2-allyl-2-(prop-2-ynyl)malonate,[2] Dimethyl 2-(2-methylallyl)-2-(prop-2-ynyl)malonate,[3] *N*-allyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide,[4] hept-1-en-6-yne,[5] 3-(prop-2-ynyloxy)prop-1-ene,[6] dimethyl 2-(but-3-enyl)-2-(prop-2-ynyl)malonate,[7] *N*-(but-3-enyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide,[8] 4-(prop-2-ynyloxy)but-1-ene,[9] dimethyl 2-cinnamyl-2-(prop-2-ynyl)malonate,[10] hex-1-en-5-yn-3-yl acetate[11].

Preparation of 2-aniline-enynes 1, 4 and 7. General procedure A

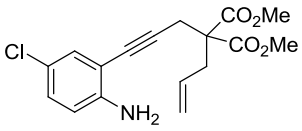
CuI (10 mol%), $Pd(PPh_3)_2Cl_2$ (5 mol %) were suspended in iPr_2NH (0.5 M) under Argon. The corresponding 2-haloaniline (1.3 eq) and enyne (1 eq) were successively added and the reaction mixture was stirred at room temperature until all the enyne was consumed. Next, the mixture was diluted with dichloromethane and filtered over Celite®. The solvent was removed under reduced pressure and the 2-aniline-enyne was isolated by silica gel column chromatography.



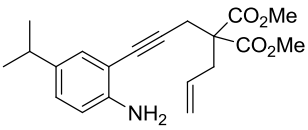
Dimethyl 2-allyl-2-(3-(2-aminophenyl)prop-2-ynyl)malonate (1a). Compound **1a** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 20:1). Yield: 90%. Yellow dense oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (ddd, 1H, J^3_{HH} = 7.6 Hz, J^4_{HH} = 1.5 Hz, J^5_{HH} = 0.3 Hz), 7.07 (ddd, 1H, J^3_{HH} = 8.2 Hz, J^4_{HH} =7.3 Hz, J^5_{HH} =1.6 Hz), 6.69 – 6.58 (m, 2H), 5.67 (ddt, 1H, $J^3_{HHtrans}$ = 17.5 Hz, J^3_{HHcis} = 10.0 Hz, J^3_{HH} = 7.4 Hz), 5.24 – 5.12 (m, 2H), 3.75 (s, 6H), 3.07 (s, 2H), 2.87 (dt, J^3_{HH} = 7.4 Hz, J^4_{HH} = 1.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 148.1, 131.9, 131.5, 129.2, 119.9, 117.4, 114.1, 107.5, 89.1, 80.4, 57.2, 52.7, 36.7, 24.0. HRMS (TOF) calc. for $C_{17}H_{20}NO_4$ $[M+H]^+$ 302.1387, found 302.1390.



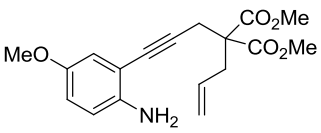
Dimethyl 2-allyl-2-(3-(2-amino-3-bromo-5-methylphenyl)prop-2-ynyl)malonate (1b). Compound **1b** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 50:1). Yield: 70%. White solid, m.p.: 79-81 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, 1H, J^4_{HH} = 1.3 Hz), 6.98 (d, 1H, J^4_{HH} 1.3 Hz), 5.65 (ddt, 1H, $J^3_{HHtrans}$ = 17.4 Hz, J^3_{HHcis} = 10.0 Hz, J^3_{HH} =7.4 Hz), 5.24-5.12 (m, 2H), 4.54 (bs, 2H), 3.76 (s, 6H), 3.05 (s, 2H), 2.86 (dt, 2H, J^3_{HH} = 7.5 Hz, J^4_{HH} = 0.9 Hz), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 143.5, 133.1, 131.5, 131.5, 127.4, 120.1, 108.5, 108.3, 89.7, 80.1, 57.2, 52.9, 36.8, 24.0, 19.9. HRMS (TOF) calc. for $C_{18}H_{20}BrNO_4$ $[M+H]^+$ 394.0648, found 394.0633.



Dimethyl 2-allyl-2-(3-(2-amino-5-chlorophenyl)prop-2-ynyl)malonate (1c). Compound **1c** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 20:1). Yield: 95%. Yellow dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, 1H, J^4_{HH} = 2.5 Hz), 7.01 (dd, 1H, J^3_{HH} = 8.6 Hz, J^4_{HH} =2.5 Hz), 6.57 (d, 1H, J^3_{HH} = 8.6 Hz), 5.64 (ddt, 1H, $J^3_{HHtrans}$ = 17.4 Hz, J^3_{HHcis} = 10.0 Hz, J^3_{HH} = 7.4 Hz), 5.25 – 5.10 (m, 2H), 4.14 (bs, 2H), 3.75 (s, 6H), 3.04 (s, 2H), 2.84 (d, 2H, J^3_{HH} = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 146.8, 131.4, 131.1, 129.3, 121.6, 120.1, 115.2, 108.8, 90.3, 79.3, 57.1, 52.8, 36.8, 23.9. HRMS (TOF) calc. for $C_{17}H_{19}ClNO_4$ $[M+H]^+$ 336.0997, found 336.0993.

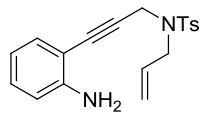


Dimethyl 2-allyl-2-(3-(2-amino-5-isopropylphenyl)prop-2-ynyl)malonate (1d). Compound **1d** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 20:1). Yield: 93%. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, 1H, J^4_{HH} = 2.1 Hz), 6.96 (dd, 1H, J^3_{HH} = 8.4 Hz, J^4_{HH} = 2.1 Hz), 6.61 (d, 1H, J^3_{HH} = 8.1 Hz), 5.67 (ddt, 1H, $J^3_{HHtrans}$ = 17.7 Hz, J^3_{HHcis} = 10,2 Hz, J^3_{HH} = 7.5 Hz), 5.24-5.13 (m, 2H), 4.10 (bs, 2H), 3.76 (s, 6H), 3.07 (s, 2H), 2.88 (dt, 2H, J^3_{HH} = 7.2 Hz, J^4_{HH} = 1.2 Hz), 2.75 (sept, 1H, J^3_{HH} = 6.9 Hz), 1.18 (d, 6H, J^3_{HH} = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 146.1, 138.1, 131.6, 129.5, 127.6, 120.0, 114.3, 107.5, 88.7, 80.8, 57.3, 52.8, 36.8, 33.0, 24.0, 24.0. HRMS (TOF) calc. for $C_{20}H_{26}NO_4$ $[M+H]^+$ 344.1856, found 344.1855.

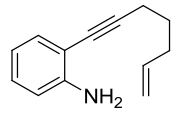


Dimethyl 2-allyl-2-(3-(2-amino-5-methoxyphenyl)prop-2-ynyl)malonate (1e). Compound **1e** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 10:1). Yield: 92%. Orange dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, 1H, J^4_{HH} = 2.8 Hz), 6.72 (dd, 1H, J^3_{HH} = 8.7 Hz, J^4_{HH} = 2.9 Hz), 6.61 (d, 1H, J^3_{HH} = 8.7 Hz), 5.66 (ddt, 1H, $J^3_{HHtrans}$ = 17.4 Hz, J^3_{HHcis} = 10.0 Hz, J^3_{HH} = 7.5 Hz), 5.18 (m, 2H), 3.76 (s, 6H), 3.71 (s, 3H), 3.06 (s, 2H), 2.87(dt, 2H, J^3_{HH} = 7.2 Hz, J^4_{HH} = 0.9 Hz).^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 151.7, 142.3, 131.6, 120.0,

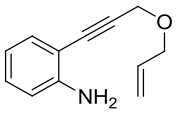
116.8, 116.1, 115.7, 108.4, 89.3, 80.5, 57.2, 55.8, 52.8, 36.8, 24.0. HRMS (TOF) calc. for $C_{18}H_{21}NO_5$ $[M+H]^+$ 332.1492, found 332.1503.



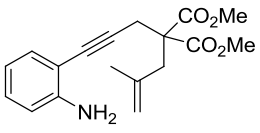
N-allyl-N-(3-(2-aminophenyl)prop-2-ynyl)-4-methylbenzenesulfonamide (1f). Compound **1f** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 5:1). Yield: 83%. Yellow dense oil. ^{1}H NMR (300 MHz,) δ 7.77 (d, 2H, J^3_{HH} = 8.4 Hz), 7.27 (d, 2H, J^3_{HH} = 8.0 Hz), 7.08 (ddd, 1H, J^3_{HH} = 8.2 Hz, J^3_{HH} = 7.3 Hz, J^4_{HH} =1.6 Hz), 6.90 (dd, 1H, J^3_{HH} = 7.7 Hz, J^4_{HH} =1.5 Hz), 6.66 – 6.56 (m, 2H), 5.79 (ddt, 1H, $J^3_{HHtrans}$ = 16.4 Hz, J^3_{HHcis} =10.0 Hz, J^3_{HH} = 6.4 Hz), 5.32 (dq, 1H, J^3_{HH} = 17.1 Hz, J^2_{HH} = J^4_{HH} = 1.5 Hz), 5.26 (dq, 1H, J^3_{HH} = 10.0 Hz, J^2_{HH} = J^4_{HH} = 1.2 Hz), 4.34 (s, 2H), 3.90 (d, 2H, J^3_{HH} = 6.4 Hz), 2.35 (s, 3H).^{13}C NMR (75 MHz,) δ 147.9, 143.6, 135.9, 132.2, 132.1, 129.8, 129.6, 127.7, 119.8, 117.5, 114.2, 106.8, 87.0, 82.4, 49.3, 36.9, 21.4. HRMS (TOF) calc. for C19H21N_2O_2S $[M+H]^+$ 341.1318, found 341.1315.



2-(hept-6-en-1-ynyl)aniline (1g). Compound **1g** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 200:1). Yield: 96%. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (dd, 1H, J^3_{HH} = 8.1 Hz, J^4_{HH} = 1.5 Hz), 6.99 (td, 1H, J^3_{HH} = 7.7 Hz, J^4_{HH} = 1.5 Hz), 6.59 (d, 1H, J^3_{HH} = 7.8 Hz), 6.57 (td, 1H, J^3_{HH} = 6.3 Hz, J^4_{HH} = 1.2 Hz) 5.75 (ddt, 1H, $J^3_{HHtrans}$ = 16.9 Hz, J^3_{HHcis} = 10.2 Hz, J^3_{HH} = 6.7 Hz), 5.04 - 4.89 (m, 2H), 4.06 (bs, 2H), 2.40 (t, 2H, J^3_{HH} = 7.1 Hz), 2.18 - 2.10 (m, 2H), 1.64 (quint, 2H, J^3_{HH} = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 137.9, 132.1, 129.0, 117.9, 115.4, 114.2, 109.0, 95.4, 77.4, 33.0, 28.2, 19.1. HRMS (TOF) calc. for $C_{13}H_{16}NO$ $[M+H]^+$ 186.1277, found 186.1277.

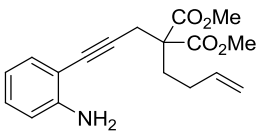


2-(3-(allyloxy)prop-1-ynyl)aniline (1h). Compound **1h** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 20:1). Yield: 70%. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, 1H, J^3_{HH} = 8.1 Hz, J^4_{HH} = 1.5 Hz), 7.12 (ddd, 1H, J^3_{HH} = 9.3 Hz, J^3_{HH} = 6.9 Hz, J^4_{HH} = 1.6 Hz), 6.72 – 6.64 (m, 2H), 5.96 (ddt, 1H, $J^3_{HHtrans}$ = 17.3 Hz, J^3_{HHcis} =10.4 Hz, J^3_{HH} =5.8 Hz), 5.35 (dq, 1H, J^3_{HH} = 17.3 Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz), 5.25 (ddt, 1H, J^3_{HH} =10.4 Hz, J^2_{HH} = 1.7 Hz, J^4_{HH} =1.2 Hz), 4.44 (s, 2H), 4.22 (bs, 2H), 4.15(dt, 2H, J^3_{HH} = 6 Hz, J^4_{HH} = 1.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 134.0, 132.4, 129.8, 117.8, 117.7, 114.2, 107.2, 90.3, 82.9, 70.6, 58.0. HRMS (TOF) calc. for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1070, found 188.1068.

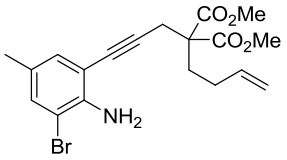


Dimethyl 2-(3-(2-aminophenyl)prop-2-ynyl)-2-(2-methylallyl)malonate (1i). Compound **1i** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 20:1). Yield: 78%. Orange dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, 1H, J^3_{HH} = 7.6 Hz, J^4_{HH} =1.5 Hz), 7.08 (ddd, 1H, J^3_{HH} = 8.2, J^3_{HH} =7.4, J^4_{HH} =1.6 Hz), 6.65 (dd, 1H, J^3_{HH} = 8.1 Hz, J^4_{HH} =0.6 Hz), 6.63 (td, 1H, J^3_{HH} = 7.5, J^4_{HH} =1.1 Hz), 4.95-4.92 (m, 1H), 4.88 (m, 1H), 4.25 (bs, 2H), 3.76 (s, 6H), 3.11 (s, 2H), 2.91 (s, 2H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

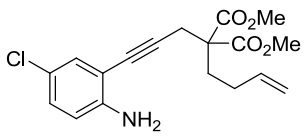
171.0, 148.3, 139.8, 132.1, 129.4, 117.6, 116.5, 114.2, 107.8, 89.6, 80.8, 56.9, 52.9, 39.9, 24.2, 23.3. HRMS (TOF) calc. for $C_{18}H_{22}NO_4$ $[M+H]^+$ 316.1543, found 316.1549.



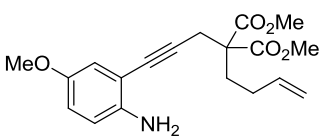
Dimethyl 2-(3-(2-aminophenyl)prop-2-ynyl)-2-(but-3-enyl)malonate (1j). Compound **1j** was prepared according to the general procedure A (eluents:Hexane: ethyl acetate = 10:1). Yield: 87%. Yellow dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (ddd, 1H, J^3_{HH} = 7.5 Hz, J^4_{HH} = 1.5 Hz, J^4_{HH} = 0.3 Hz), 7.08 (ddd, 1H, J^3_{HH} = 8.2 Hz, J^3_{HH} = 7.3 Hz, J^4_{HH} = 1.6 Hz), 6.68-6.59 (m, 2H), 5.79 (ddt, 1H, $J^3_{HHtrans}$ = 16.6 Hz, J^3_{HHcis} = 10.2 Hz, J^3_{HH} = 6.4 Hz), 5.06 (dq, 1H, J^3_{HH} = 17.1 Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz), 4.98 (dq, 1H, J^3_{HH} = 10.2 Hz, J^2_{HH} = J^4_{HH} = 1.2 Hz), 4.23 (bs, 2H), 3.76 (s, 6H), 3.11 (s, 2H), 2.28-2.18 (m, 2H), 2.08-1.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 148.1, 137.1, 132.0, 129.3, 117.5, 115.3, 114.1, 107.6, 89.1, 80.3, 57.0, 52.8, 31.5, 28.3, 24.3. HRMS (TOF) calc. for $C_{18}H_{22}NO_4$ $[M+H]^+$ 316.1543, found 316.1536.



Dimethyl 2-(3-(2-amino-3-bromo-5-methylphenyl)prop-2-ynyl)-2-(but-3-enyl)malonate (1k). Compound **1k** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 30:1). Yield: 70%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, 1H, J^4_{HH} = 1.4 Hz), 6.97 (d, 1H, J^4_{HH} = 1.3 Hz), 5.78 (ddt, 1H, $J^3_{HHtrans}$ = 16.7 Hz, J^3_{HHcis} = 10.2 Hz, J^3_{HH} = 6.5 Hz), 5.05 (dq, 1H, J^3_{HH} = 17.1 Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz), 4.98 (ddd, 1H, J^3_{HH} = 10.2 Hz, J^2_{HH} = 2.9 Hz, J^4_{HH} = 1.2 Hz), 4.53 (s, 2H), 3.76 (s, 6H), 3.10 (s, 2H), 2.25-2.18 (m, 2H), 2.16 (s, 3H), 2.06-1.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 143.6, 137.2, 133.3, 131.6, 127.5, 115.6, 108.6, 108.5, 89.8, 80.2, 57.1, 53.0, 31.7, 28.5, 24.4, 20.0. HRMS (TOF) calc. for $C_{19}H_{23}BrNO_4$ $[M+H]^+$ 408.0805, found 408.0802.

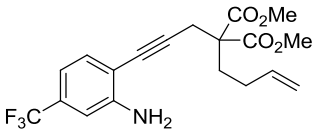


Dimethyl 2-(3-(2-amino-5-chlorophenyl)prop-2-ynyl)-2-(but-3-enyl)malonate (1l). Compound **1l** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 20:1). Yield: 90%. Yellow dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, 1H, J^4_{HH} = 2.5 Hz), 6.99 (dd, 1H J^3_{HH} = 8.6 Hz, J^4_{HH} = 2.5 Hz), 6.55 (d, 1H, J^3_{HH} = 8.6 Hz), 5.77 (ddt, 1H, $J^3_{HHtrans}$ = 16.6 Hz, J^3_{HHcis} = 10.2 Hz, J^3_{HH} = 6.4 Hz,), 5.04 (dq, 1H, J^3_{HH} = 17.1 Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz), 4.97 (ddd, 1H, J^3_{HH} = 10.2 Hz, J^2_{HH} = 2.9 Hz, J^4_{HH} = 1.3 Hz), 4.26 (bs, 2H), 3.74 (s, 6H), 3.08 (s, 2H), 2.25-2.15 (m, 2H), 2.06-1.95 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 147.0, 137.1, 131.2, 129.4, 121.7, 115.5, 115.3, 108.9, 90.4, 79.3, 57.0, 52.9, 31.6, 28.4, 24.3. HRMS (TOF) calc. for $C_{18}H_{21}ClNO_4$ $[M+H]^+$ 350.1154, found 350.1159.

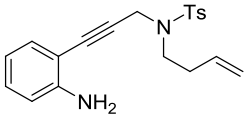


Dimethyl 2-(3-(2-amino-5-methoxyphenyl)prop-2-ynyl)-2-(but-3-enyl)malonate (1m). Compound **1m** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 10:1). Yield: 90%. orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (d, 1H, J^4_{HH} = 2.8 Hz), 6.71 (dd, 1H, J^3_{HH} = 8.7 Hz, J^4_{HH} = 2.9 Hz), 6.60 (d, 1H, J^3_{HH} = 8.7 Hz), 5.79 (ddt,

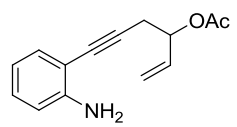
1H, $J^3_{HHtrans}$ = 16.6 Hz, J^3_{HHcis} = 10.2 Hz, J^3_{HH} = 6.4 Hz), 5.05 (dq, 1H, J^3_{HH} = 17.1 Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz,), 4.98 (ddd, 1H, J^3_{HH} = 10.2 Hz, J^2_{HH} = 2.9 Hz, J^4_{HH} = 1.3 Hz), 3.94 (bs, 2H), 3.75 (s, 6H), 3.71 (s, 3H), 3.10 (s, 2H), 2.27 - 2.17 (m, 2H), 2.08 - 1.96 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 151.8, 142.5, 137.3, 117.0, 116.2, 115.8, 115.5, 108.5, 89.3, 80.5, 57.2, 56.0, 52.9, 31.6, 28.5, 24.4. HRMS (TOF) calc. for $C_{19}H_{24}NO_5$ $[M+H]^+$ 346.1649, found 346.1664.



Dimethyl 2-(3-(2-amino-4-(trifluoromethyl)phenyl)prop-2-ynyl)-2-(but-3-enyl)malonate (1n). Compound **1n** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 20:1). Yield: 80%. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, 1H, J^3_{HH} = 7.9 Hz), 6.86 (s, 1H), 6.83 (d, J^3_{HH} = 8.8Hz, 1H), 5.78 (ddt, 1H, $J^3_{HHtrans}$ = 15.0 Hz, J^3_{HHcis} = 9.0 Hz, J^3_{HH} = 6.0 Hz), 5.05 (dq, 1H, J^3_{HH} =17.1Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz), 4.98 (ddd, 1H, J^3_{HH} = 10.2 Hz, J^2_{HH} = 2.9 Hz, J^4_{HH} = 1.2 Hz, 4.48 (bs, 2H), 3.75 (s, 6H), 3.11 (s, 2H), 2.27 - 2.18 (m, 2H), 2.08 - 1.96 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 148.5, 137.1, 132.5, 131.1 (q, J^2_{CF} = 32.0 Hz), 124.1 (q, J^1_{CF} = 272.3 Hz), 115.6, 113.8 (q, J^3_{CF} = 3.8 Hz), 110.5 (q, J^3_{CF} = 3.9 Hz), 91.5, 79.4, 57.1, 52.9, 31.7, 28.4, 24.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.15. HRMS (TOF) calc. for $C_{19}H_{21}NO_4F_3$ $[M+H]^+$ 384.1417, found 384.1401.



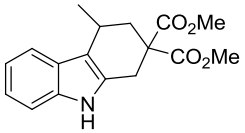
***N*-(3-(2-aminophenyl)prop-2-ynyl)-*N*-(but-3-enyl)-4-methylbenzenesulfonamide (1o)**. Compound **1o** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 10:1). Yield: 85%. Yellow dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H, J^3_{HH} = 8.3 Hz), 7.6 (d, 2H, J^3_{HH} = 8.3 Hz), 7.08 (ddd, 1H, J^3_{HH} = 8.2 Hz, J^3_{HH} =7.4 Hz, J^4_{HH} =1.6 Hz), 6.91 (dd, 1H, J^3_{HH} = 7.7 Hz, J^4_{HH} =1.3 Hz), 6.62 (d, 1H, J^3_{HH} = 8.2 Hz), 6.60 (td, 1H, J^3_{HH} = 7.5 Hz, J^4_{HH} =1.1 Hz), 5.79 (ddt, 1H, $J^3_{HHtrans}$ = 17.0 Hz, J^3_{HHcis} = 10.2 Hz, J^3_{HH} = 6.8 Hz), 5.13 (dq, J^3_{HH} = 17.1 Hz, J^2_{HH} = J^4_{HH} = 1.6 Hz), 5.07 (ddd, J^3_{HH} = 10.2 Hz, J^2_{HH} = 2.9 Hz, J^4_{HH} = 1.2 Hz, 4.39 (s, 2H), 3.93 (bs, 2H), 3.34 (t, 2H, J^3_{HH} = 7.2 Hz), 2.43 -2.36 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.7, 136.1, 134.7, 132.4, 130.0, 129.7, 127.8, 117.8, 117.4, 114.4, 106.9, 87.2, 82.6, 46.0, 37.5, 32.5, 21.6. HRMS (TOF) calc. for $C_{20}H_{23}N_2O_2S$ $[M+H]^+$ 355.1475, found 355.1489.



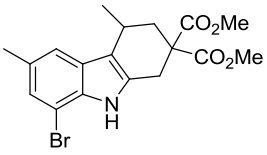
6-(2-aminophenyl)hex-1-en-5-yn-3-yl acetate (1p). Compound **1p** was prepared according to the general procedure A (eluents: Hexane: ethyl acetate = 30:1). Yield: 54%. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (dd, 1H, J^3_{HH} = 7.5 Hz, J^4_{HH} = 1.5 Hz), 7.09 (ddd, 1H, J^3_{HH} = 8.2 Hz, J^3_{HH} = 7.4 Hz, J^4_{HH} = 1.6 Hz), 6.68 – 6.62 (m, 2H), 5.95 (ddd, 1H, $J^3_{HHtrans}$ = 17.2 Hz, J^3_{HHcis} = 10.5 Hz, J^3_{HH} = 6.2 Hz), 5.49 (qt, 1H, J^3_{HH} = 6.2 Hz, J^4_{HH} =1.2 Hz), 5.39 (dt, 1H, J^3_{HH} = 17.2 Hz, J^4_{HH} = 1.3 Hz), 5.29 (dt, 1H, J^3_{HH} = 10.5 Hz, J^4_{HH} = 1.2 Hz), 4.20 (bs, 2H), 2.82 (d, 2H, J^3_{HH} = 6.2 Hz), 2.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 148.1, 135.2, 132.1, 129.4, 118.0, 117.8, 114.3, 108.1, 90.1, 79.5, 72.6, 25.8, 21.3. HRMS (TOF) calc. for $C_{14}H_{16}NO_2$ $[M+H]^+$ 230.1176, found 230.1173.

Representative general procedure for the gold(I)-catalyzed synthesis of annulated indoles derivatives 3a-3p.

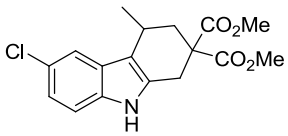
An oven dried resealable test tube with a Teflon stirring bar was charged with the 1,X-enynes **1** (0.3 mmol) in dried DMF (0.125M). Subsequently, [Au(JohnPhos)(NCMe)]SbF_6 (5 mol%) were added. The tube was sealed with a Teflon screw-cap and placed in an oil bath at 60 ºC (80 ºC). As indicated extra 5 mol% [Au(JohnPhos)(NCMe)]SbF_6 was added after 8 h of reaction. The reaction was heated at this temperature until consumption of the starting material. Next, the mixture was cooled to room temperature, diluted with dichloromethane (2-3 mL), and filtered over Aluminium oxide activated. The solvent was removed under reduced pressure and the annulated indoles were isolated by silica gel column chromatography.



Dimethyl 4-methyl-3,4-dihydro-1*H*-carbazole-2,2(9*H*)-dicarboxylate (3a). (eluents: Hexane: ethyl acetate = 10:1). Yield: 91%. Yellow dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (bs, 1H), 7.50 (dm, 1H, J^3_{HH} = 7.5 Hz), 7.22 - 7.16 (m, 1H), 7.08 - 6.94 (m, 2H), 3.71 (s, 3H), 3.58 (s, 3H), 3.35 (dt, 1H, J^2_{HH} = 16.2 Hz, J^4_{HH} = 1.5 Hz), 3.11 - 3.05 (m, 2H), 2.64 (ddd, 1H, J^2_{HH} = 13.3 Hz, J^3_{HH} = 5.4 Hz, J^4_{HH} = 1.7 Hz), 1.80 (dd, 1H, J^2_{HH} = 13.4, J^3_{HH} = 10.1 Hz), 1.37 (d, J^3_{HH} = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 171.0, 136.5, 130.7, 127.0, 121.3, 119.6, 119.3, 113.5, 110.9, 54.7, 53.1, 52.9, 38.7, 29.5, 26.1, 21.3. HRMS (EI) calc. for $C_{17}H_{19}NO_4$ $[M]^+$ 301.1314, found 301.1302.

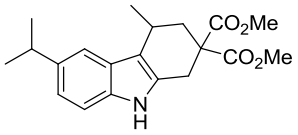


Dimethyl 8-bromo-4,6-dimethyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate (3b). (eluents: Hexane: ethyl acetate = 10:1). Yield: 75%. Pale yellow solid, m.p.: 195-197 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (bs, 1H), 7.28 (s, 1H), 7.10 (s, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 3.47 (dt, 1H, J^2_{HH} = 16.5 Hz, J^4_{HH} = 1.6 Hz,), 3.18 (dd, 1H, J^2_{HH} = 14.2 Hz, J^4_{HH} = 3.9 Hz), 3.18 – 3.05 (m, 1H), 2.71 (ddd, 1H, J^2_{HH} = 13.4 Hz, J^3_{HH} = 5.6 Hz, J^4_{HH} = 1.9 Hz), 2.41 (s, 3H), 1.86 (dd, 1H, J^2_{HH} = 13.5 Hz, J^3_{HH} = 10.2 Hz), 1.42 (d, 3H, J^3_{HH} = 6.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 170.9, 133.3, 131.6, 130.1, 128.2, 124.9, 118.6, 114.2, 104.0, 54.6, 53.2, 53.0, 38.5, 29.5, 26.2, 21.4, 21.2. HRMS (TOF) calc. for $C_{18}H_{21}NO_4Br$ $[M+H]^+$ 394.0648, found 394.0641.

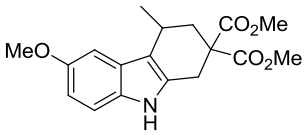


Dimethyl 6-chloro-4-methyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate (3c). (eluents: Hexane: ethyl acetate = 10:1). Yield: 81%. Pale yellow solid, m.p.: 192-194 ºC. ^{1}H NMR (300 MHz, $CDCl_3$)

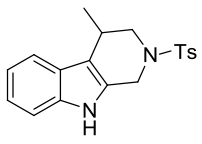
δ 7.97 (s, 1H), 7.55 (d, 1H, J^4_{HH} = 2.0 Hz), 7.21 (dd, 1H, J^3_{HH} = 8.6 Hz, J^4_{HH} = 0.5 Hz), 7.09 (dd, 1H, J^3_{HH} = 8.6 Hz, J^4_{HH} = 2.0 Hz), 3.82 (s, 3H), 3.71 (s, 3H), 3.45 (dt, 1H, J^2_{HH} = 14.8 Hz, J^4_{HH} = 1.7 Hz), 3.18 (dd, 1H, J^2_{HH} = 16.2 Hz, J^4_{HH} = 2.0 Hz), 3.19-3.08 (m, 1H), 2.74 (ddd, 1H, J^2_{HH} = 13.5 Hz, J^3_{HH} = 5.5 Hz, J^3_{HH} = 1.8 Hz), 1.91 (dd, 1H, J^2_{HH} = 13.5 Hz, J^3_{HH} = 10.2 Hz), 1.45 (d, 3H, J^3_{HH} = 6.7 Hz ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 170.9, 134.8, 132.3, 128.0, 125.0, 121.5, 119.1, 113.4, 111.8, 54.6, 53.1, 53.0, 38.5, 29.5, 26.0, 21.1. HRMS (TOF) calc. for $C_{17}H_{19}NO_4Cl$ $[M+H]^+$ 336.0997, found 336.0963.



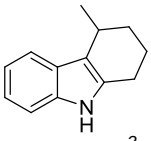
Dimethyl 6-isopropyl-4-methyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate (3d). (eluents: Hexane: ethyl acetate = 5:1). Yield: 78%. Pale yellow solid, m.p.: 64-66 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (bs, 1H), 7.41 (d, 1H, J^4_{HH} = 0.9 Hz), 7.21 (d, 1H, J^3_{HH} = 8.3 Hz), 7.03 (dd, 1H, J^3_{HH} = 8.4 Hz, J^4_{HH} = 1.6 Hz), 3.79 (s, 3H), 3.67 (s, 3H), 3.42 (dt, 1H, J^2_{HH} = 14.7 Hz, J^4_{HH} = 1.7 Hz), 3.24-3.11 (m, 2H), 3.00 (hept, 1H, J^3_{HH} = 7.0 Hz), 2.72 (ddd, 1H, J^2_{HH} = 13.4 Hz, J^3_{HH} = 5.4 Hz, J^4_{HH} = 1.7 Hz), 1.88 (dd, 1H, J^2_{HH} = 13.4 Hz, J^3_{HH} = 10.1 Hz), 1.47 (d, 3H, J^3_{HH} = 6.7 Hz), 1.31 (d, 6H, J^3_{HH} = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 171.0, 140.0, 135.0, 130.8, 127.0, 120.3, 116.7, 113.3, 110.7, 54.7, 53.1, 52 9, 38.7, 34.4, 29.5, 26.1, 24.9, 24.8, 21.3.HRMS (TOF) calc. for $C_{20}H_{26}NO_4$ $[M+H]^+$ 344.1856 found 344.1844.



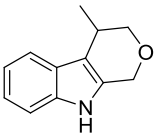
Dimethyl 6-methoxy-4-methyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate (3e). (eluents: Hexane: ethyl acetate = 5:1). Yield: 90%. Pale yellow solid, m.p.: 105-107 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (bs, 1H), 7.16 (dd, 1H, J^3_{HH} = 8.7 Hz, J^4_{HH} = 0.5 Hz), 7.03 (d, 1H, J^4_{HH} = 2.4 Hz), 6.77 (dd, 1H, J^3_{HH} = 8.7 Hz, J^4_{HH} = 2.4 Hz), 3.84 (s, 3H), 3.78 (s, 4H), 3.66 (s, 3H), 3.40 (dt, 1H, J^2_{HH} = 14.7 Hz, J^4_{HH} =1.7 Hz), 3.19-3.09 (m, 2H), 2.70 (ddd, 1H, J^2_{HH} = 13.3 Hz, J^3_{HH} = 5.4 Hz, J^4_{HH} = 1.6 Hz,), 1.87 (dd, 1H, J^2_{HH} = 13.4 Hz, J^3_{HH} = 10.0 Hz), 1.43 (d, 3H, J^3_{HH} = 6.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 171.0, 153.8, 131.7, 127.4, 113.3, 111.4, 110.7, 102.5, 56.2, 54.7, 53.1, 52.9, 38.6, 29.6, 26.1, 21.1. HRMS (TOF) calc. for $C_{18}H_{22}NO_5$ $[M+H]^+$ 332.1492 found 332.1498.



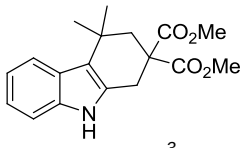
4-methyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3f). (eluents: Hexane: ethyl acetate = 5:1). Yield: 90%. Pale yellow solid, m.p.: 80-83 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (bs, 1H), 7.77 - 7.70 (m, 2H), 7.52 (d, 1H, J^3_{HH} = 7.7 Hz), 7.30 (m, 3H), 7.18 - 7.04 (m, 2H), 4.40 (d, 1H, J^2_{HH} = 14.4 Hz), 4.18 (d, 1H, J^2_{HH} = 14.4 Hz), 3.38 - 3.14 (m, 3H), 2.42 (s, 3H), 1.38 (d, 3H, J^3_{HH} = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 136.5, 133.8, 129.9, 128.2, 127.8, 126.3, 122.0, 119.8, 118.8, 113.6, 111.2, 51.3, 43.8, 28.1, 21.7, 18.9. HRMS (TOF) calc. for $C_{19}H_{21}N_2O_2S$ $[M+H]^+$ 341.1318 found 341.1308.



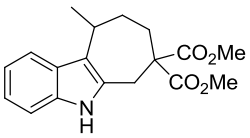
4-methyl-2,3,4,9-tetrahydro-*1H*-carbazole (3g). (eluents: Hexane: ethyl acetate = 20:1). Yield: 91%. Colorless dense oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (bs, 1H), 7.57 (d, 1H, J^{3}_{HH} = 7.6 Hz), 7.28 (d, 1H, J^{3}_{HH} = 7.7 Hz,), 7.08 (ddt, 2H, J^{3}_{HH} = 8.0 Hz, J^{3}_{HH} = 7.2 Hz, J^{4}_{HH} =4.1 Hz), 3.14-3.10 (m, 1H), 2.73-2.67 (m, 2H), 2.03-1.94 (m, 2H), 1.87-1.77 (m, 1H), 1.62-1.58 (m, 1H), 1.38 (d, 3H, J^{3}_{HH} = 6.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 133.9, 127.6, 120.9, 119.1, 118.8, 115.2, 110.6, 32.3, 27.3, 23.6, 21.4, 20.6. HRMS (TOF) calc. for $C_{13}H_{15}N$ $[M+H]^+$ 186.1277 found 186.1274.



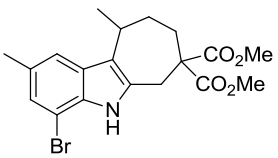
4-methyl-1,3,4,9-tetrahydropyrano[3,4-b]indole (3h). (eluents: Hexane: ethyl acetate = 20:1). Yield: 48%. Yellow dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (bs, 1H), 7.62 - 7.56 (m, 1H), 7.36 - 7.30 (m, 1H), 7.21 - 7.07 (m, 3H), 4.80 (t, 2H, J^{3}_{HH} = 1.4 Hz), 4.02 (dd, 1H, J^{2}_{HH} = 11.1 Hz, J^{3}_{HH} = 4.5 Hz), 3.67 (dd, 1H, J^{2}_{HH} = 11.1 Hz, J^{3}_{HH} = 5.3 Hz), 3.24- 3.08 (m, 1H), 1.38 (d, 3H, J^{3}_{HH} = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 131.3, 126.8, 121.7, 119.7, 118.9, 113.1, 111.1, 72.6, 63.9, 28.4, 18.0. HRMS (TOF) calc. for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1070 found 188.1063.



Dimethyl 4,4-dimethyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate (3i). (eluents: Hexane: ethyl acetate = 20:1). Yield: 80%. White solid, m.p.: 133-135 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.65 (d, 1H, J^{3}_{HH} = 7.7 Hz), 7.29 (d, 1H, J^{3}_{HH} = 7.6 Hz), 7.14 (t, 1H, J^{3}_{HH} = 7.1 Hz), 7.09 (t, 1H, J^{3}_{HH} = 7.4 Hz), 3.77 (s, 6H), 3.23 (s, 2H), 2.45 (s, 2H), 1.44 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 136.6, 129.6, 126.0, 121.1, 119.9, 119.1, 116.7, 111.1, 53.3, 52.8, 44.4, 31.7, 30.1, 29.2. HRMS (TOF) calc. for $C_{18}H_{22}NO_4$ $[M+H]^+$ 316.1543 found 316.1544.

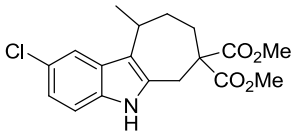


Dimethyl 10-methyl-6,8,9,10-tetrahydrocyclohepta[*b*]indole-7,7(*5H*)-dicarboxylate (3j).(eluents: Hexane: ethyl acetate = 10:1). Yield: 90%. Pale yellow solid, m.p.: 134-136 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (bs, 1H), 7.52-7.46 (m, 1H), 7.27- 7.23 (m, 1H), 7.14- 7.02 (m, 2H), 3.76 (s, 3H), 3.61 (s, 3H), 3.47- 3.32 (m, 2H), 3.35- 3.23 (m, 1H), 2.51 (ddd, 1H, J^{2}_{HH} = 14.6 Hz, J^{3}_{HH} =10.7 Hz, J^{3}_{HH} = 2.2 Hz), 2.26 (ddd, 1H, J^{2}_{HH} = 14.6 Hz, J^{3}_{HH} = 7.8 Hz, J^{3}_{HH} = 1.0 Hz), 2.10-1.80 (m, 2H), 1.31 (d, 3H, J^{3}_{HH} = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 171.3, 135.1, 130.3, 128.5, 121.2, 119.1, 118.1, 117.4, 110.7, 57.0, 53.0, 52.7, 32.7, 30.6, 30.2, 29.8, 20.3. HRMS (TOF) calc. for $C_{18}H_{22}NO_4$ $[M+H]^+$ 316.1543 found 316.1549.

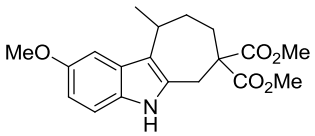


Dimethyl 4-bromo-2,10-dimethyl-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate (3k). (eluents: Hexane: ethyl acetate = 20:1). Yield: 80%. White solid, m.p.: 175-177 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.20 (s, 1H), 7.11 (s, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 3.41 (d, 1H, J^{2}_{HH} = 15.2 Hz), 3.37 (d, 1H, J^{2}_{HH} = 15.3 Hz), 3.28-3.17 (m, 1H), 2.49 (ddd, 1H, J^{2}_{HH} = 14.4 Hz, J^{3}_{HH} = 11.1 Hz, J^{3}_{HH} = 1.8 Hz), 2.41 (s, 3H), 2.27 (dd, 1H, J^{2}_{HH} = 14.4 Hz, J^{3}_{HH} = 7.4 Hz), 2.02-1.93 (m, 1H), 1.86 (ddd, 1H, J^{2}_{HH} = 14.7

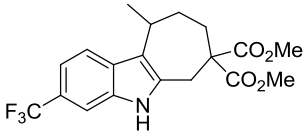
Hz, J^3_{HH} = 8.3 Hz, J^3_{HH} = 1.8 Hz), 1.29 (d, J^3_{HH} = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 171.1, 132.1, 131.4, 130.1, 129.7, 124.9, 118.3, 117.1, 103.9, 56.8, 53.1, 52.7, 32.8, 30.5, 30.1, 29.9, 21.4, 20.2. HRMS (TOF) calc. for $C_{19}H_{23}BrNO_4$ $[M+H]^+$ 408.0805 found 408.0813.



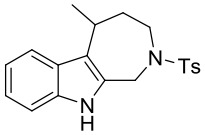
Dimethyl 2-chloro-10-methyl-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate (3l). (eluents: Hexane: ethyl acetate = 10:1). Yield: 77%. White solid, m.p.: 58-60 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (bs, 1H), 7.45 (d, 1H, J^4_{HH} = 2.0 Hz), 7.15 (dd, 1H, J^3_{HH} = 8.5 Hz, J^5_{HH} =0.4 Hz), 7.04 (dd, 1H, J^3_{HH} = 8.6, J^4_{HH} = 2.0 Hz), 3.77 (s, 3H), 3.62 (s, 3H), 3.41 (d, 1H, J^2_{HH} = 15.2 Hz), 3.34 (d, 1H, J^2_{HH} = 15.4 Hz), 3.29-3.15 (m, 1H), 2.51 (ddd, 1H, J^2_{HH} =14.6 Hz, J^3_{HH} =10.6, J^3_{HH} = 2.3 Hz), 2.26 (ddd, 1H, J^2_{HH} = 14.6 Hz, J^3_{HH} = 7.7 Hz, J^3_{HH} = 1.4 Hz), 2.04- 1.81 (m, 2H), 1.30 (d, 3H, J^3_{HH} = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 171.3, 133.5, 132.0, 129.6, 124.9, 121.4, 117.6, 117.3, 111.7, 56.9, 53.1, 52.7, 32.8, 30.5, 30.1, 29.7, 20.2. HRMS (TOF) calc. for $C_{18}H_{21}ClNO_4$ $[M+H]^+$ 350.1154 found 350.1136.



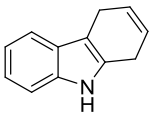
Dimethyl 2-methoxy-10-methyl-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate (3m). (eluents: Hexane: ethyl acetate = 5:1). Yield: 82%. Pale yellow solid, m.p.: 175-177 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (bs, 1H), 7.16 (dd, 1H, J^3_{HH} = 8.7 Hz, J^4_{HH} = 0.3 Hz), 6.95 (d, 1H, J^4_{HH} = 2.4 Hz), 6.78 (dd, 1H, J^3_{HH} = 8.7 Hz, J^4_{HH} = 2.4 Hz), 3.85 (s, 3H), 3.77 (s, 3H), 3.62 (s, 3H), 3.42 (d, 1H, J^2_{HH} = 15.1 Hz), 3.32 (dd, 1H, J^2_{HH} = 15.2 Hz, J^4_{HH} = 0.7 Hz), 3.26- 3.19 (m, 1H), 2.50 (ddd, 1H, J^2_{HH} = 14.6, J^3_{HH} = 10.8 Hz, J^3_{HH} = 2.0 Hz), 2.26 (dd, 1H, J^2_{HH} = 14.6 Hz, J^3_{HH} = 6.9 Hz), 2.05-1.81 (m, 2H), 1.31 (d, 3H, J^3_{HH} = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 171.3, 154.0, 131.3, 130.3, 128.9, 117.3, 111.4, 111.0, 100.5, 56.9, 56.1, 53.0, 52.7, 32.8, 30.5, 30.2, 29.8, 20.2. HRMS (TOF) calc. for $C_{19}H_{24}NO_5$ $[M+H]^+$ 346.1649 found 346.1657.



Dimethyl 10-methyl-3-(trifluoromethyl)-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate (3n). (eluents: Hexane: ethyl acetate = 5:1). Yield: 76%. Pale yellow solid, m.p.: 152-154 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 7.55 (d, 1H, J^3_{HH} = 8.3 Hz), 7.48 (t, 1H, J^4_{HH} = 0.9 Hz), 7.28 (dd, 1H, J^3_{HH} = 8.4 Hz, J^4_{HH} = 1.1 Hz), 3.79 (s, 3H), 3.65 (s, 3H), 3.43 (s, 2H), 3.38-3.26 (m, 1H), 2.55 (ddd, 1H, J^2_{HH} = 14.6 Hz, J^3_{HH} = 10.5 Hz, J^3_{HH} = 2.4 Hz), 2.30 (ddd, 1H, J^2_{HH} = 14.7 Hz, J^3_{HH} = 7.5 Hz, J^3_{HH} = 2.1 Hz), 2.06-1.84 (m, 2H), 1.32 (d, 3H, J^3_{HH} = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 171.4, 133.9, 133.5, 130.7, 125.5 (q, J^1_{CF} = 269.3 Hz), 123.1 (q, J^2_{CF} = 31.5 Hz), 118.3, 115.9 (q, J^3_{CF} = 3.0 Hz), 108.2 (q, J^3_{CF} = 4.5 Hz), 56.9, 53.2, 52.8, 32.9, 30.5, 30.2, 29.7, 20.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.47. HRMS (TOF) calc. for $C_{19}H_{21}F_3NO_4$ $[M+H]^+$ 384.1417 found 384.1425.



5-methyl-2-tosyl-1,2,3,4,5,10-hexahydroazepino[3,4-b]indole (3o). (eluents: Hexane: ethyl acetate = 10:1). Yield: 80%. Yellow solid, m.p.: 95-97 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (bs, 1H), 7.62 (d, 1H, J^3_{HH} = 8.3 Hz), 7.46 (d, 1H, J^3_{HH} = 7.6 Hz), 7.22 (d, 1H, J^3_{HH} = 7.8 Hz), 7.17 (d, 1H, J^3_{HH} = 8.0 Hz), 7.12 (td, 1H, J^3_{HH} = 6.8 Hz, J^4_{HH} =1.2 Hz), 7.07 (td, 1H, J^3_{HH} = 7.4 Hz, J^4_{HH} = 1.2 Hz), 4.71 (d, 1H, J^2_{HH} = 15.8 Hz), 4.46 (d, 1H, J^2_{HH} = 15.8 Hz), 3.70 (dt, 1H, J^2_{HH} = 14.0 Hz, J^3_{HH} = 4.0 Hz), 3.54 (ddd, 1H, J^2_{HH} = 13.5 Hz, J^3_{HH} = 11.1 Hz, J^3_{HH} = 2.5 Hz), 3.39-3.26 (m, 1H), 2.35 (s, 3H), 2.15-2.04 (m, 1H), 1.95-1.84 (m, 1H), 1.25 (d, 1H, J^3_{HH} = 7.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.1, 135.0, 130.5, 129.8, 128.1, 127.22, 121.8, 119.5, 118.4, 118.3, 111.1, 46.3, 45.7, 33.6, 28.6, 21.6, 19.9. HRMS (TOF) calc. for $C_{20}H_{22}N_2O_2S$ $[M+H]^+$ 355.1475 found 355.1464.

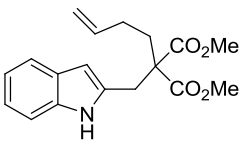


4,9-dihydro-1H-carbazole (3p). (eluents: Hexane: ethyl acetate = 50:1). Yield: 81%. White solid, m.p.: 142-144 ºC. ^{1}H NMR (400 MHz, Acetone) δ 9.83 (bs, 1H), 7.41 (d, 1H, J^3_{HH} = 7.7 Hz,), 7.32 (dt, 1H, J^3_{HH} = 7.9 Hz, J^4_{HH} = 0.8 Hz), 7.05 (td, 1H, J^3_{HH} = 7.5 Hz, J^4_{HH} = 1.2 Hz), 6.98 (td, 1H, J^3_{HH} = 7.4 Hz, J^4_{HH} = 1.1 Hz), 6.05-6.00 (m, 1H), 5.95-5.89 (m, 1H), 3.47-3.34 (m, 4H). ^{13}C NMR (101 MHz, Acetone) δ 137.3, 132.2, 128.2, 123.8, 121.5, 119.4, 118.3, 111.4, 106.9, 24.9, 23.9. HRMS (TOF) calc. for $C_{12}H_{12}N$ $[M+H]^+$ 170.0964 found 170.0962.

Preparation of Intermediates and Indole-Gold Compexes

Procedure for the gold(I)-catalyzed synthesis of indole 3b.

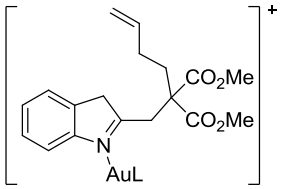
An oven dried resealable test tube with a Teflon stirring bar was charged with the 2-aniline-enyne **2b** (0.5 mmol) in dried EtOH (0.125M). Subsequently, $NaAuCl_4 \cdot 2H_2O$ (5 mol %) were added. The tube was sealed with a Teflon screw-cap and placed in an oil bath at 60 ºC. The reaction was heated at this temperature until consumption of the starting material. Next, the mixture was cooled to room temperature, diluted with dichloromethane (2-3 mL), and filtered over Aluminium oxide activated. The solvent was removed under reduced pressure and indole **3b** was isolated by silica gel column chromatography (eluents: Hexane: ethyl acetate = 20:1).



Dimethyl 2-((1H-indol-2-yl)methyl)-2-(but-3-enyl)malonate. Yield: 87%. Pale yellow solid, m.p.: 72-74 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (bs, 1H), 7.53 (d, 1H, J^3_{HH} = 7.8 Hz), 7.32 (dd, 1H, J^3_{HH} = 8.0 Hz, J^4_{HH} = 0.8 Hz), 7.17-7.04 (m, 2H), 6.25 (d, 1H, J^4_{HH} = 1.4 Hz), 5.87-5.65 (m, 1H), 5.10-4.92 (m, 2H), 3.70 (s, 6H), 3.37 (s, 2H), 2.07-2.06 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 137.2, 136.3, 133.7, 128.3, 121.5, 120.1, 119.6, 115.5, 110.8, 102.8, 58.8, 52.8, 33.5, 32.9, 28.8. HRMS (TOF) calc. for $C_{18}H_{22}NO_4$ $[M+H]^+$ 316.1543 found 316.1535.

Synthesis of indole-gold complex 4.

An oven dried resealable test tube with a Teflon stirring bar was charged under argon with [Au(JohnPhos)(NCMe)]SbF_6 (0.1 mmol) and compound **3a** (0.1 mmol) in dried CH_2Cl_2 (1 mL). The tube was sealed with a Teflon screw-cap and the reaction was stirred at room temperature for 1 h. Then the solvent was removed under vacuum, and the solid residue was washed with diethyl ether to give complex **4** as a white solid (98%).

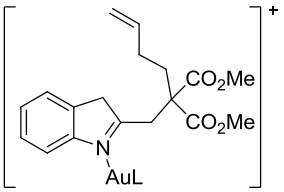


L = JohnPhos

Complex 4. m.p.: 78-80 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02-7.95 (m, 1H), 7.69-7.62 (m, 3H), 7.54-7.45 (m, 2H), 7.36 (d, 1H, J^3_{HH} = 7.5 Hz), 7.33-7.28 (m, 1H), 7.21 (dd, 2H, J^3_{HH} = 8.2 Hz, J^4_{HH} = 1.2 Hz), 7.02 (t, 2H, J = 7.8 Hz), 6.72 (t, 1H, J^3_{HH} = 7.5 Hz), 5.74 (bs, 1H), 5.03 (m, 2H), 3.91 (s, 2H), 3.72 (s, 6H), 3.37 (s, 2H), 2.12-1.95 (m, 4H), 1.53 (d, 18H, J^3_{PH} = 16.1 Hz). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 186.5, 170.7, 151.1, 149.4 (d, J^1_{PC} = 12.3 Hz), 144.2 (d, J^2_{PC} = 6.1 Hz), 136.9, 134.3 (d, J^3_{PC} = 3.5 Hz), 133.9 (d, J^2_{PC} = 7.6 Hz), 132.2 (d, J^4_{PC} = 2.0 Hz), 129.9, 129.2, 128.7, 128.4 (d, J^3_{PC} = 7.5 Hz), 127.5, 125.4, 124.8, 124.4, 120.4, 119.4, 116.3, 57.9, 53.8, 45.1, 41.7, 38.8 (d, J^1_{PC} = 26.6 Hz), 35.5, 31.3 (d, J^2_{PC} = 5.9 Hz), 29.42. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 58.7.HRMS (TOF) calc. for $C_{38}H_{48}AuNO_4P$ $[M]^+$ 810.2981 found 810.2972.

Synthesis of indole-gold complexes 5 and 6.

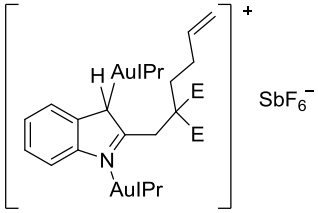
An oven dried resealable test tube with a Teflon stirring bar was charged under argon with [Au(IPr)]SbF_6 (0.1 mmol) (generated from a stoichiometric mixture of [AuCl(IPr)] and $AgSbF_6$) and compound **3a** (0.1 mmol) in dried CH_2Cl_2 (1 mL). The tube was sealed with a Teflon screw-cap and the reaction was stirred at room temperature for 1 h. Then the solvent was removed under vacuum, and the solid residue was washed with diethyl ether to give complex **5** as a violet solid in quantitative yield.



L = IPr

Complex 5. m.p.: 88-90 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (t, 2H, J^3_{HH} = 7.8 Hz), 7.51 (s, 2H), 7.47 (dd, 1H, J^3_{HH} = 7.4 Hz, J^4_{HH} = 1.0 Hz), 7.44 (d, 4H, J^3_{HH} = 7.8 Hz), 7.33 (td, 1H, J^3_{HH} = 7.6 Hz, J^4_{HH} = 1.0 Hz), 7.17 (td, 1H, J^3_{HH} = 7.9 Hz, J^3_{HH} = 1.1 Hz), 6.32 (d, 1H, J^3_{HH} = 7.9 Hz,), 5.85-5.72 (m, 1H), 5.16-5.05 (m, 2H), 3.75 (s, 2H), 3.60 (s, 6H), 3.00 (s, 2H), 2.66-2.52 (m, 4H), 1.87-1.78 (m, 2H), 1.77-1.70 (m, 2H), 1.30 (d, J^3_{HH} = 6.9 Hz, 12H), 1.29 (d, J^3_{HH} = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 188.3, 171.2, 170.4, 151.3, 146.7, 137.0, 134.3, 134.1, 131.9, 128.5, 128.4, 125.4, 125.1, 125.1, 118.3, 116.3, 57.8, 53.6, 45.0, 41.1, 35.7, 29.5, 29.1, 24.9, 24.4. HRMS (TOF) calc. for $C_{45}H_{57}AuN_3O_4$ $[M]^+$ 900.4009 found 900.3990.

Complex 6



Attempts to crystallize complex **5** from a dichloromethane-pentane solution at low temperature allowed to isolate the diaurated species **6** derived from [Au(IPr)]SbF6)

X-ray Data

a) b)

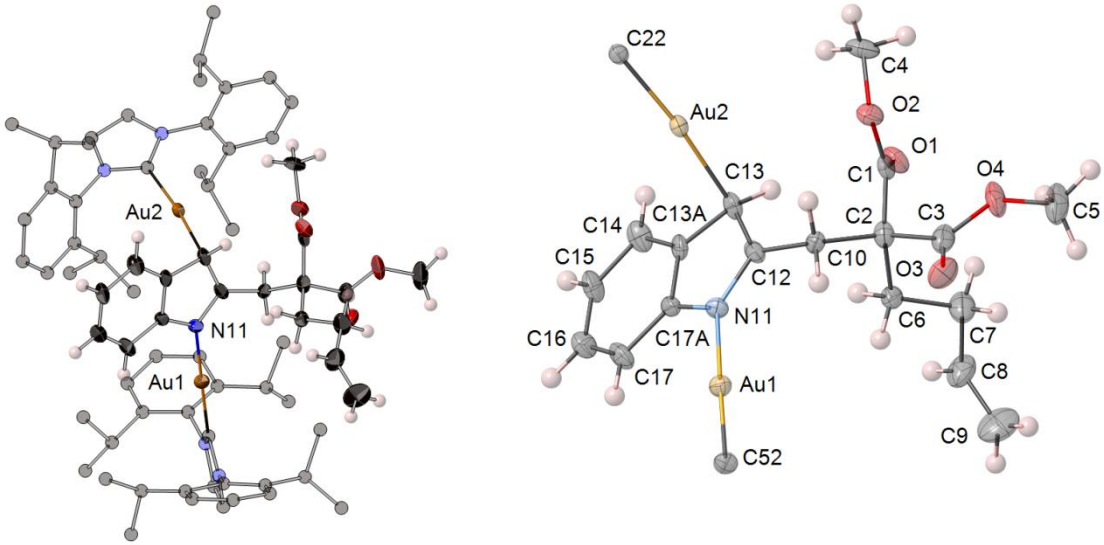
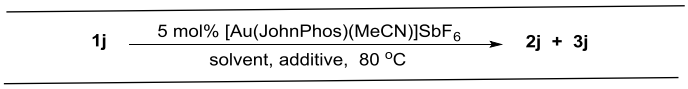


Figure 1. Thermal ellipsoid plot (50% probability level) for **6**: (a) IPr ellipsoids and hydrogen atoms omitted, (b) labelling scheme with IPr ligands [C(22) and C(52)] omitted. Selected bond lengths (Å) and angles (º): Au(1)-N(11) 2.044(7), Au(1)-C(52) 1.978(8), Au(2)-C(13) 2.122(8), Au(2)-C(22) 2.016(7), N(11)-C(12) 1.325(9), N(11)-C(17A) 1.382(10), C(12)-C(13) 1.429(12), C(13)-C(13A) 1.483(10), C(13A)-C(17A) 1.382(11), C(13A)-C(14) 1.410(11), C(14)-C(15) 1.392(11), C(15)-C(16) 1.387(13), C(16)-C(17) 1.377(12) , C(17)-C(17A) 1.413(10), C(52)-Au(1)- N(11) 178.0(3), C(22)-Au(2)-C(13) 173.8(3), C(12)-N(11)-C(17A) 107.1(7), C(12)-N(11)-Au(1) 129.8(6), C(17A)-N(11)-Au(1) 123.0(5), N(11)-C(12)-C(13) 113.5(7), C(12)-C(13)-C(13A) 101.4(7) , C(12)-C(13)-Au(2) 105.6(5), C(13A)-C(13)-Au(2) 105.5(5), C(17A)-C(13A)-C(14) 120.1(7), C(17A)-C(13A)-C(13) 107.1(7), C(14)-C(13A)-C(13) 132.8(8), C(15)-C(14)-C(13A) 118.7(8), C(16)-C(15)-C(14) 120.4(8), C(17)-C(16)-C(15) 121.8(8), C(16)- C(17)-C(17A) 117.9(8), C(13A)-C(17A)-N(11) 110.4(6), C(13A)-C(17A)-C(17) 121.0(8), N(11)-C(17A)-C(17) 128.6(8).

Table 3. Solvent and acid additive effect on the [Au(JohnPhos)(MeCN)]SbF_6 catalysed cascade formation of cycloheptaindole **3j** from **1j**

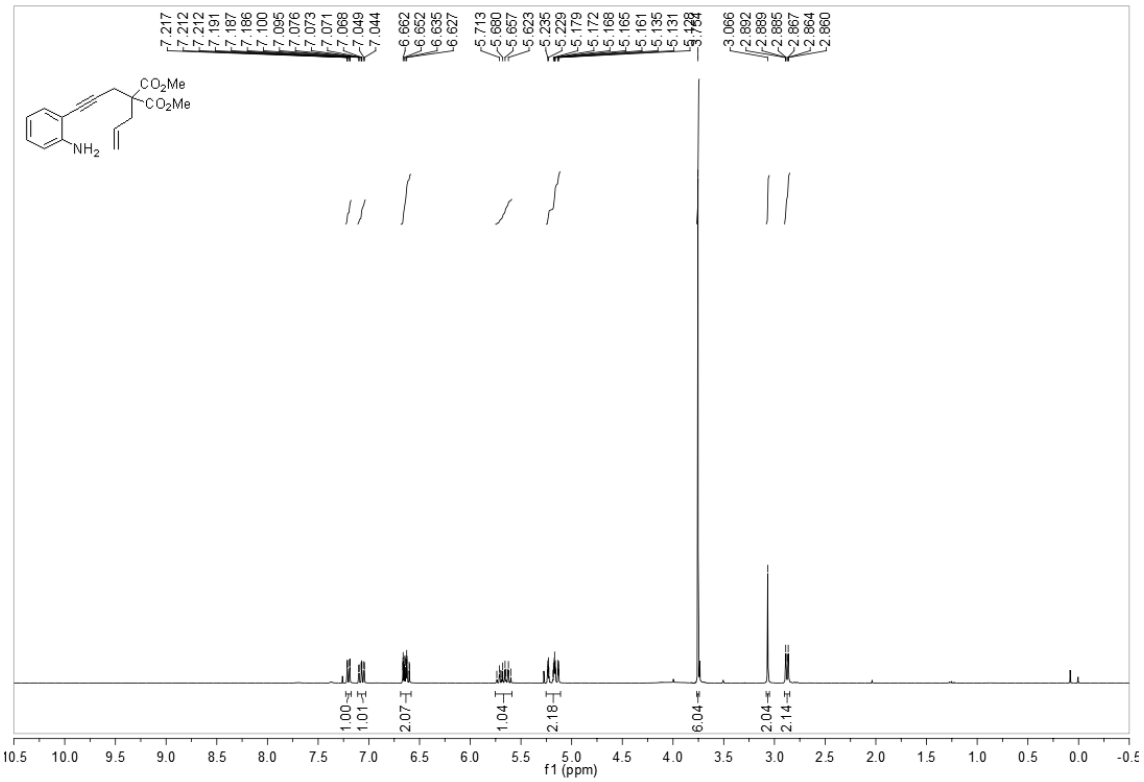


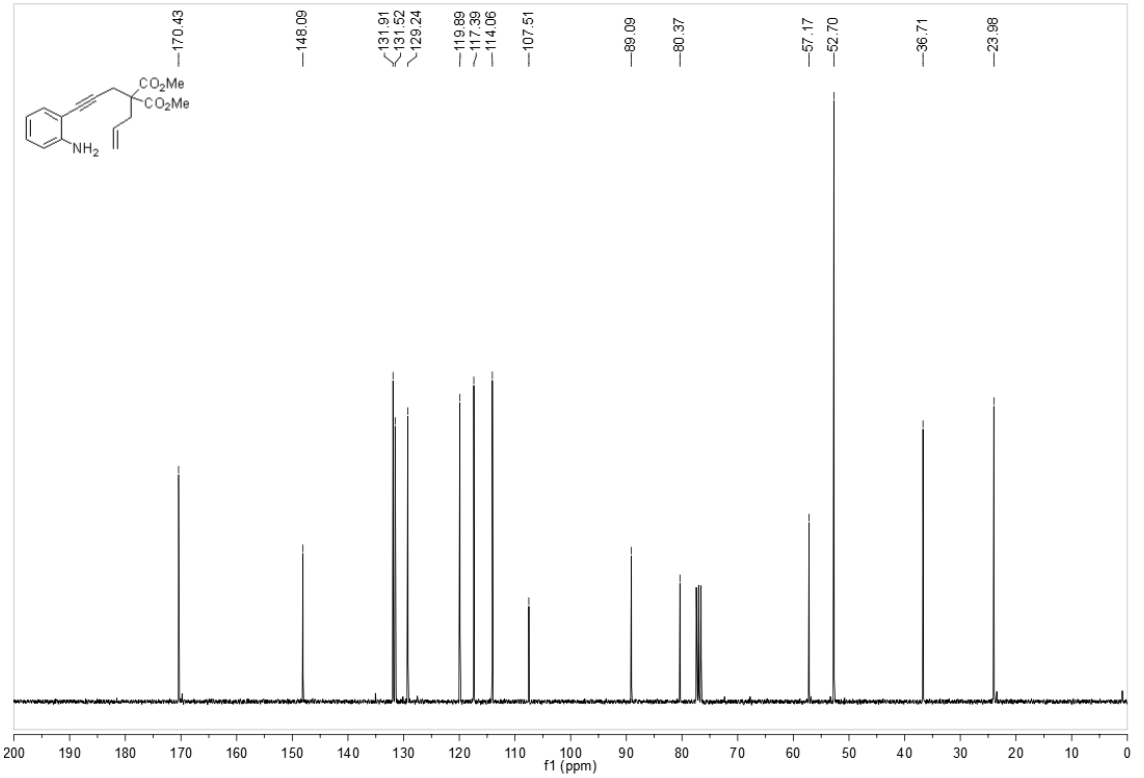
Entry	Solvent	Additive[a]	t (h)	**2j**(%)	**3j**(%)
1	DCM	none	30	>95	-
2	1,2-DCE	none	30	>95	-
3	Toluene	none	30	>95	-
4	THF	none	30	92	8
5	DMA	none	30	37	63
6	DMF	none	30	36	64
7	EtOH	none	30	50	50
8	HFIP	none	30	>95	-
9	DMF/HFIP[b]	none	30	-	>95
10	DMF	AcOH	45	38	72
11	DMF	BzOH	45	14	86
12	DMF	*p*-$NO_2C_6H_4CO_2H$	45	5	95
13	DMF	TfOH	45	55	45
14	DMF	*p*-TsOH	45	55	45

[a)]7.5 mol% of the corresponding acid were added. [b)]50% *v*/*v* mixture

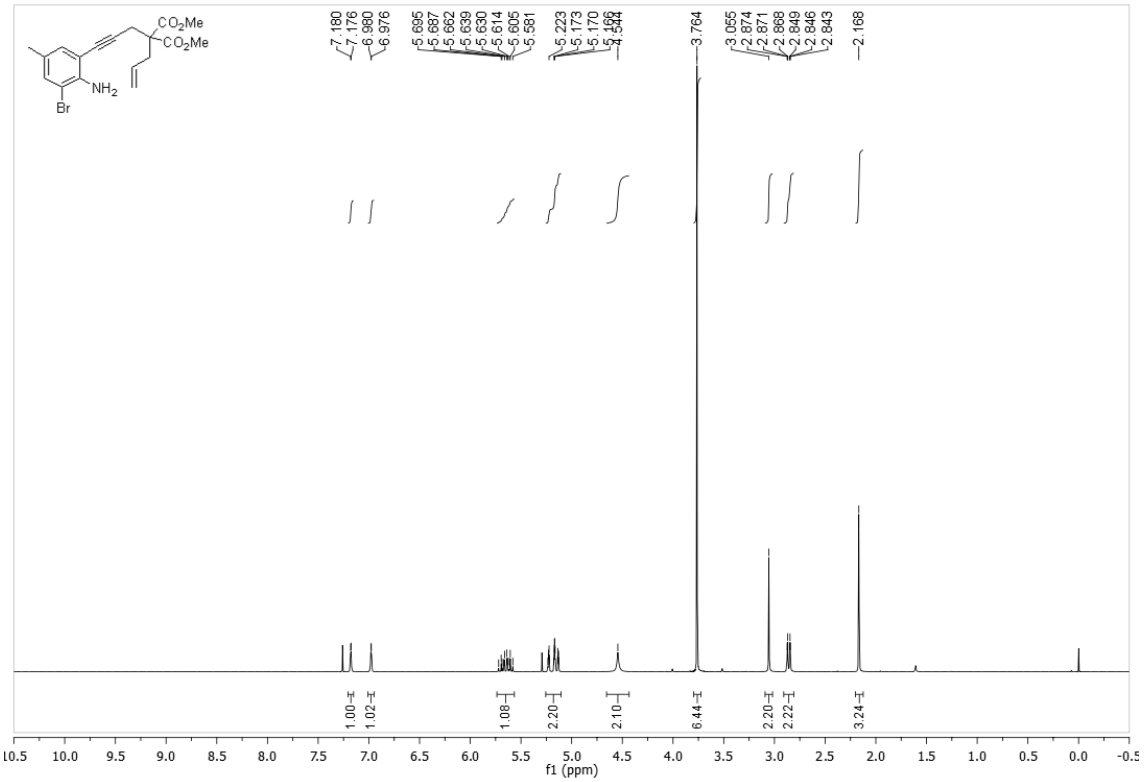
NMR Spectra of New Compounds

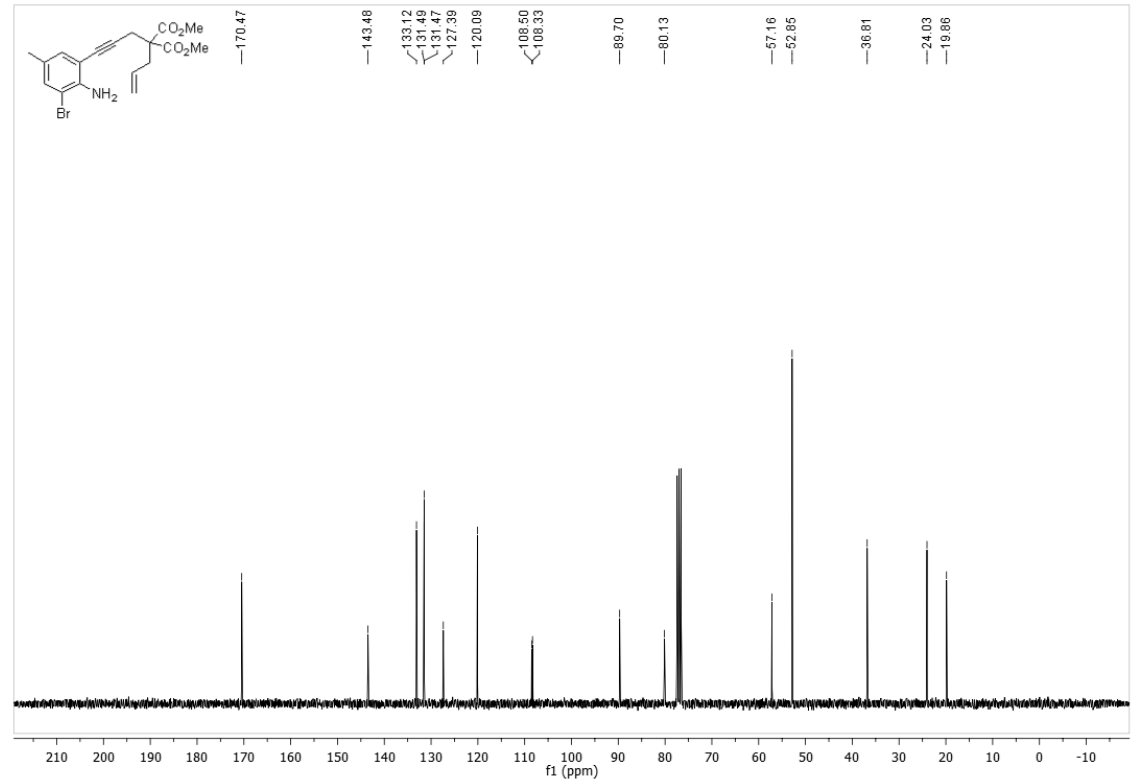
Dimethyl 2-allyl-2-(3-(2-aminophenyl)prop-2-ynyl)malonate



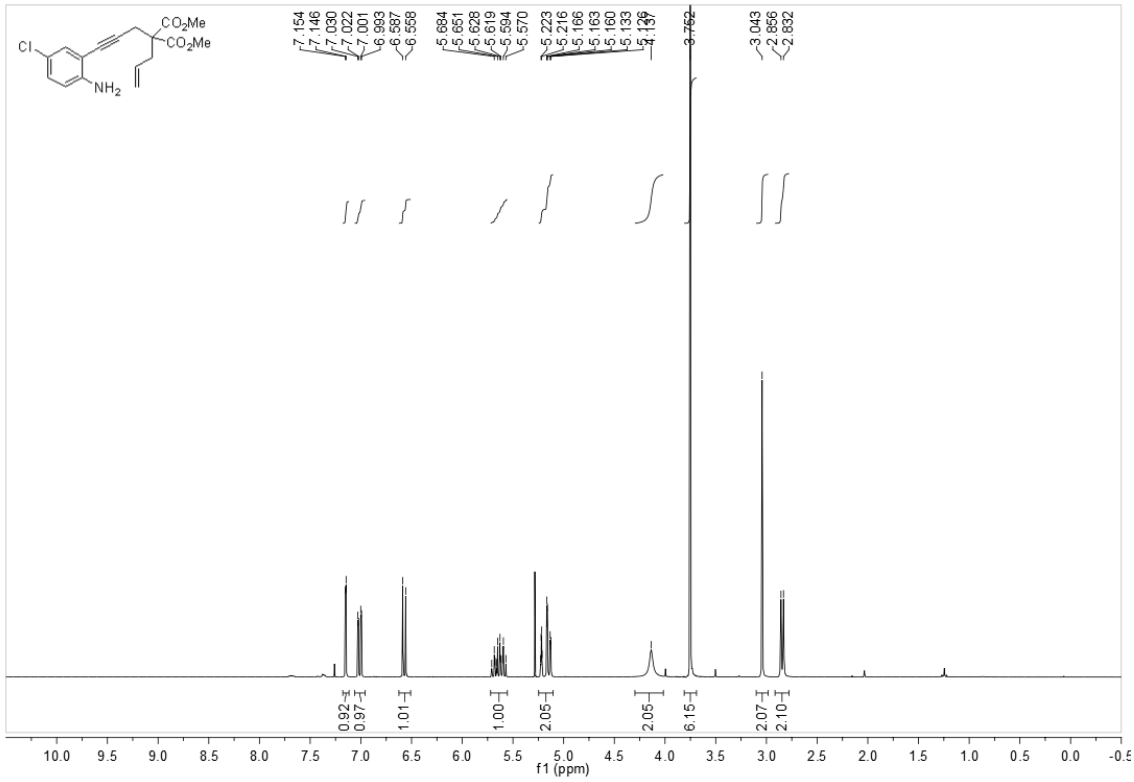


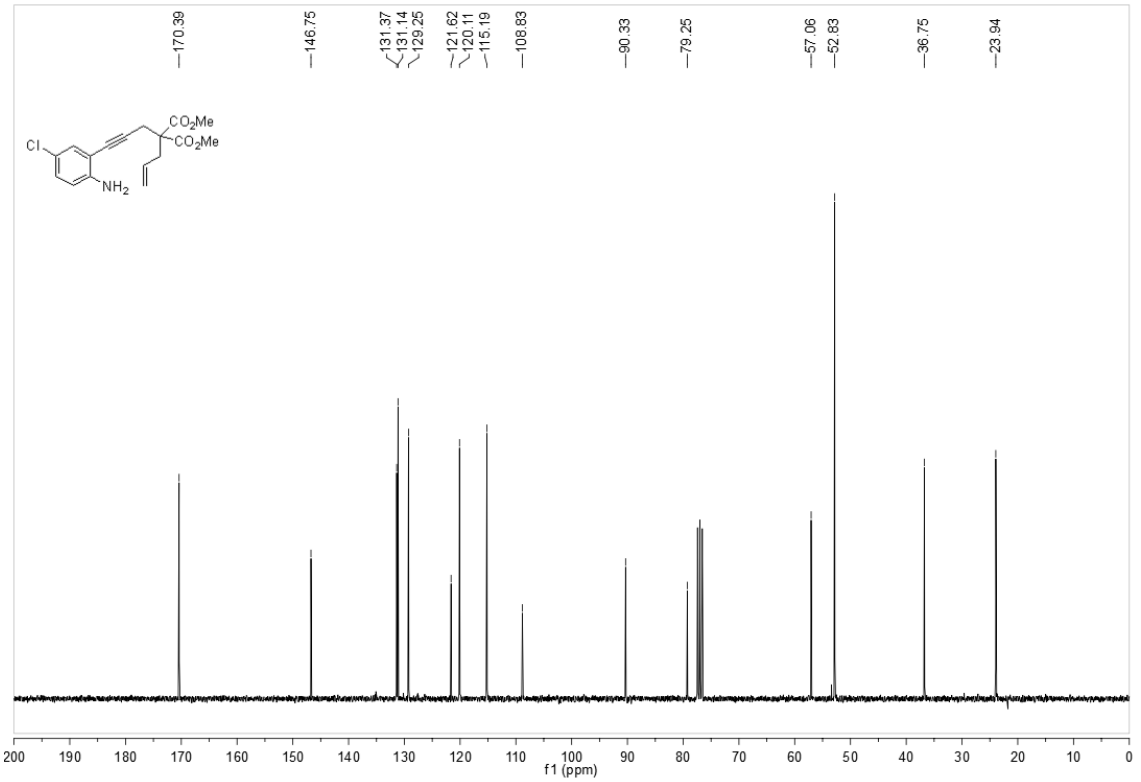
Dimethyl 2-allyl-2-(3-(2-amino-3-bromo-5-methylphenyl)prop-2-ynyl)malonate



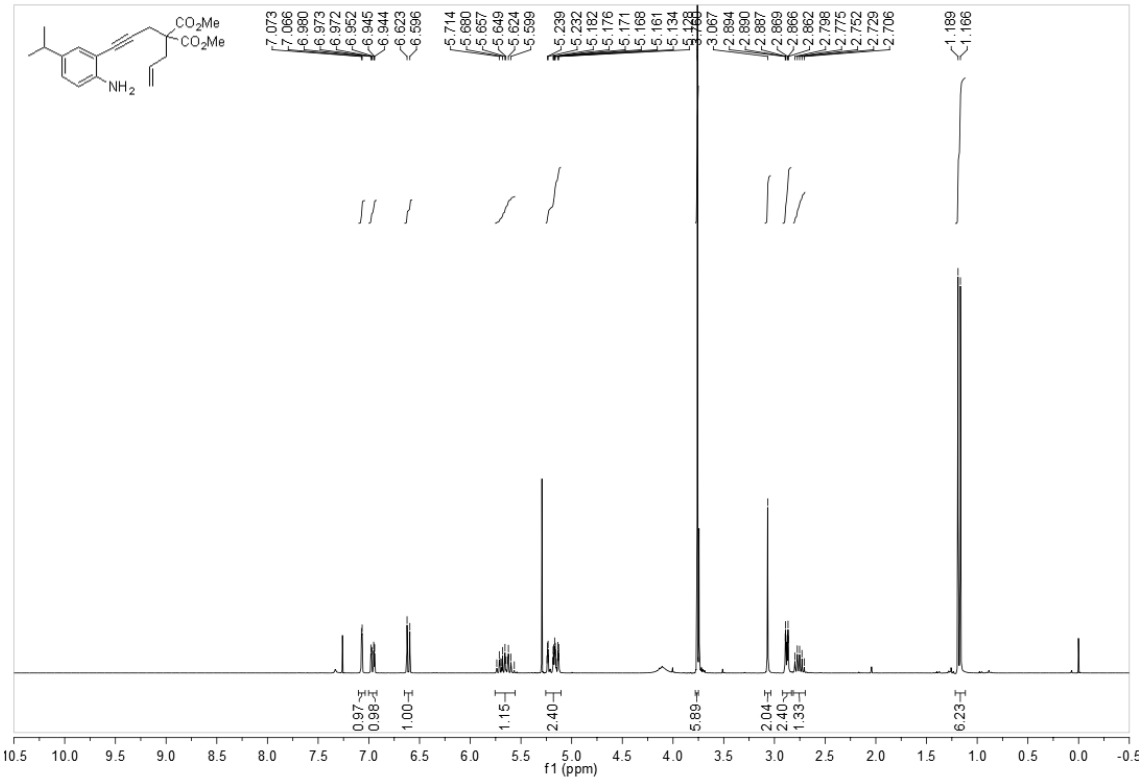


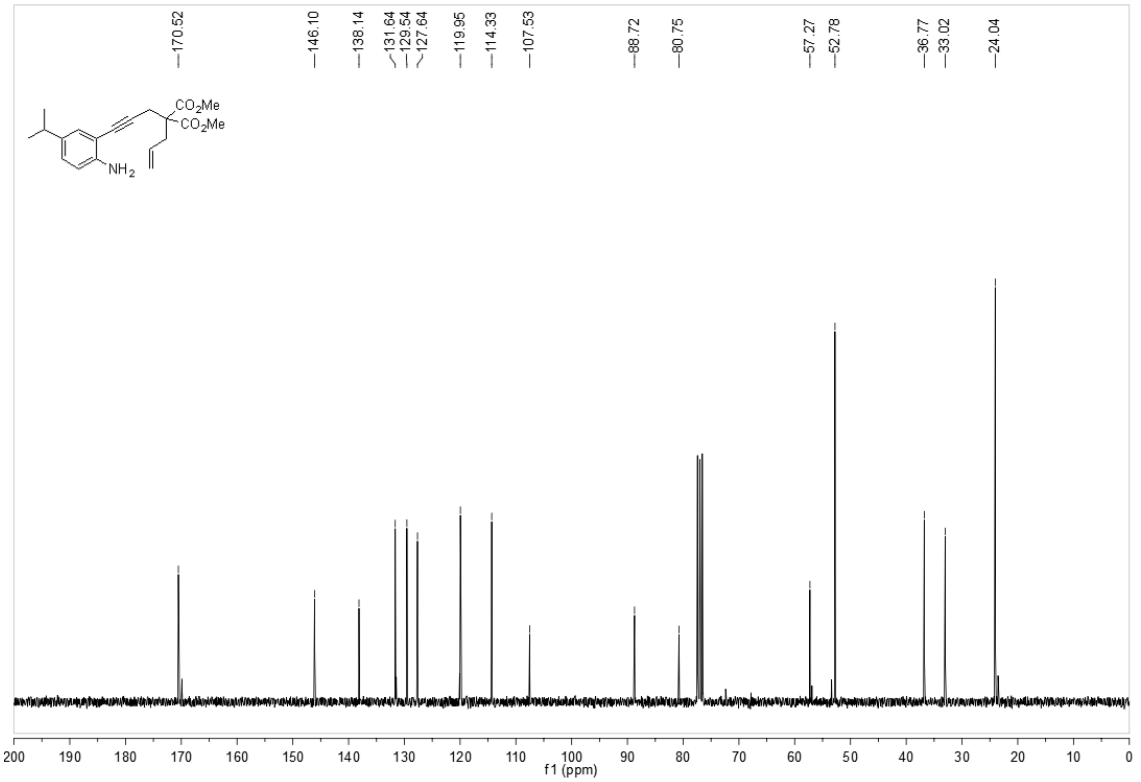
Dimethyl 2-allyl-2-(3-(2-amino-5-chlorophenyl)prop-2-ynyl)malonate



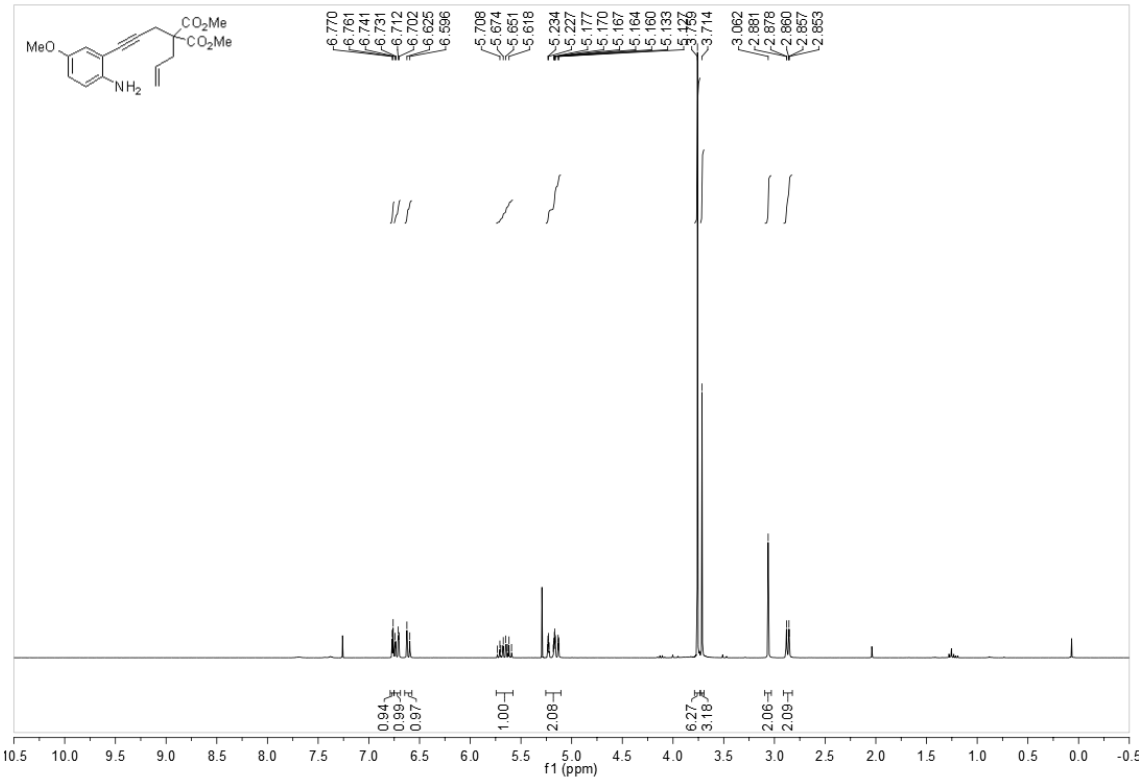


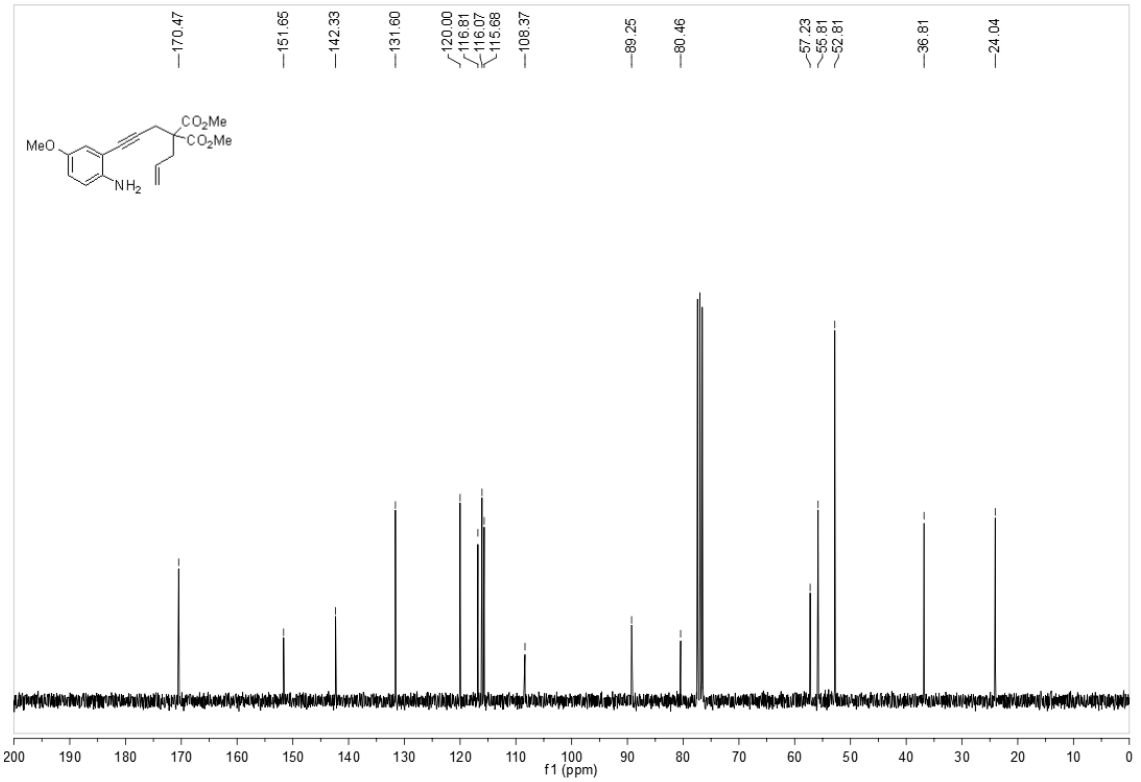
Dimethyl 2-allyl-2-(3-(2-amino-5-isopropylphenyl)prop-2-ynyl)malonate



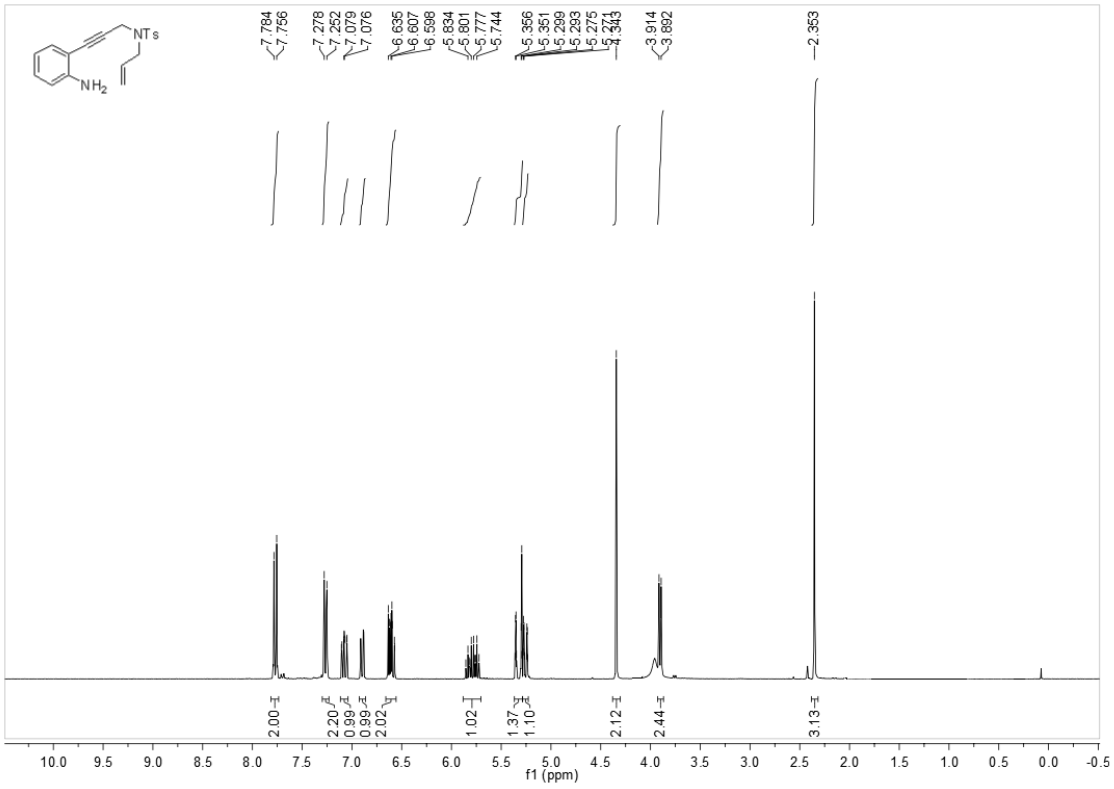


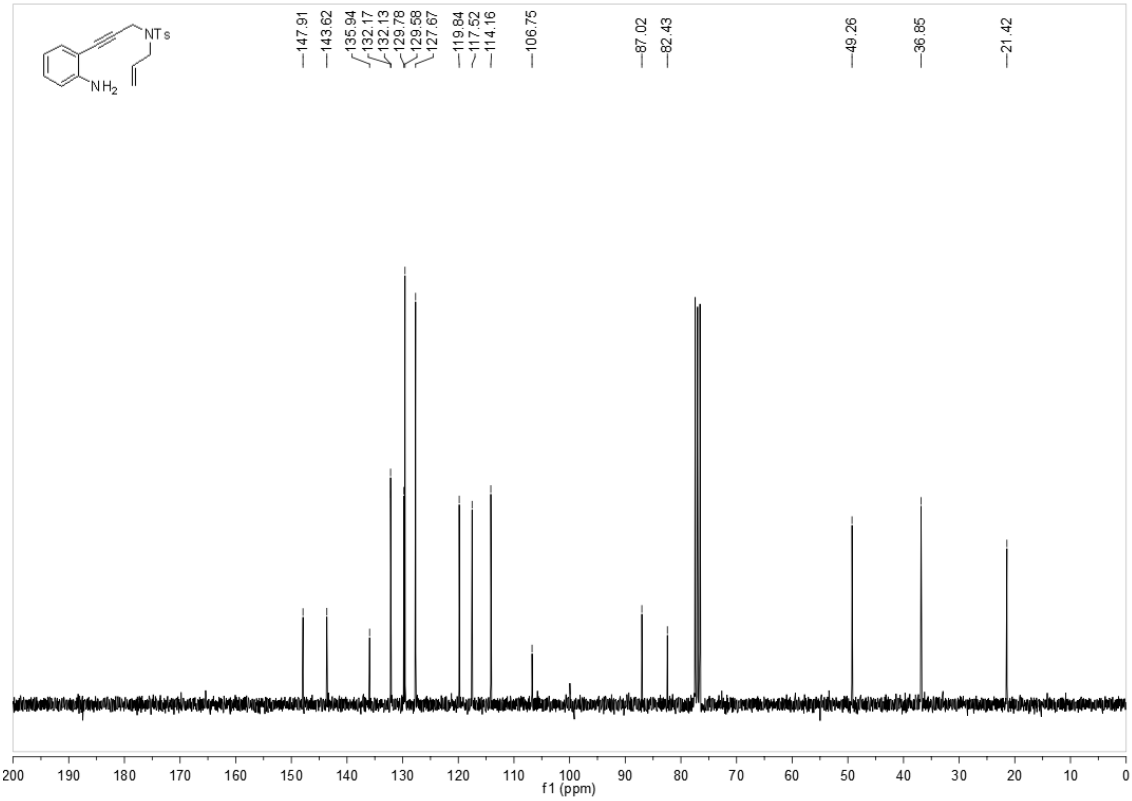
Dimethyl 2-allyl-2-(3-(2-amino-5-methoxyphenyl)prop-2-ynyl)malonate



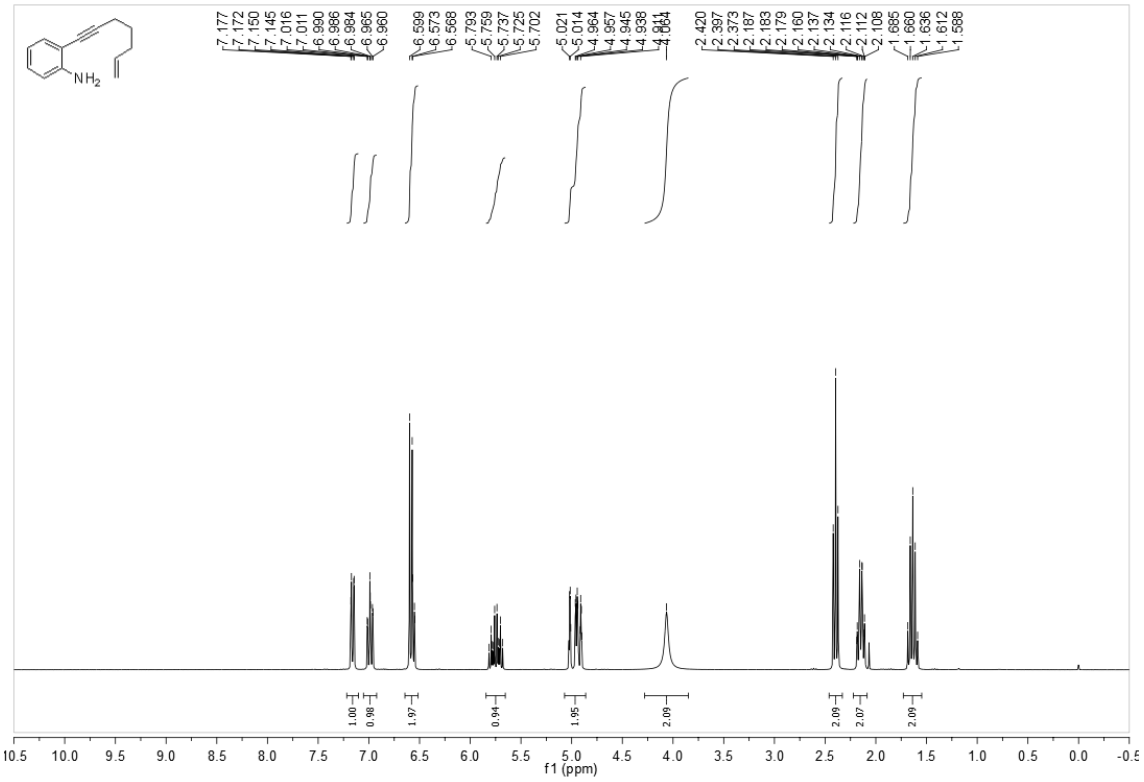


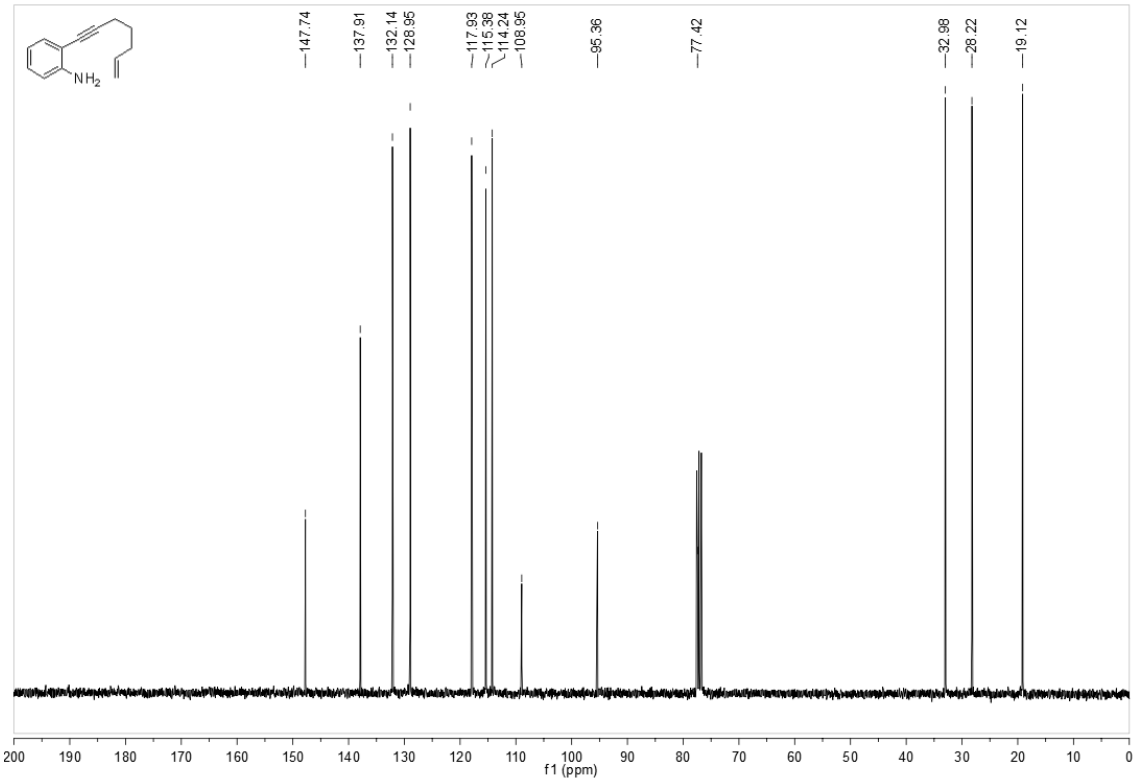
N-allyl-N-(3-(2-aminophenyl)prop-2-ynyl)-4-methylbenzenesulfonamide



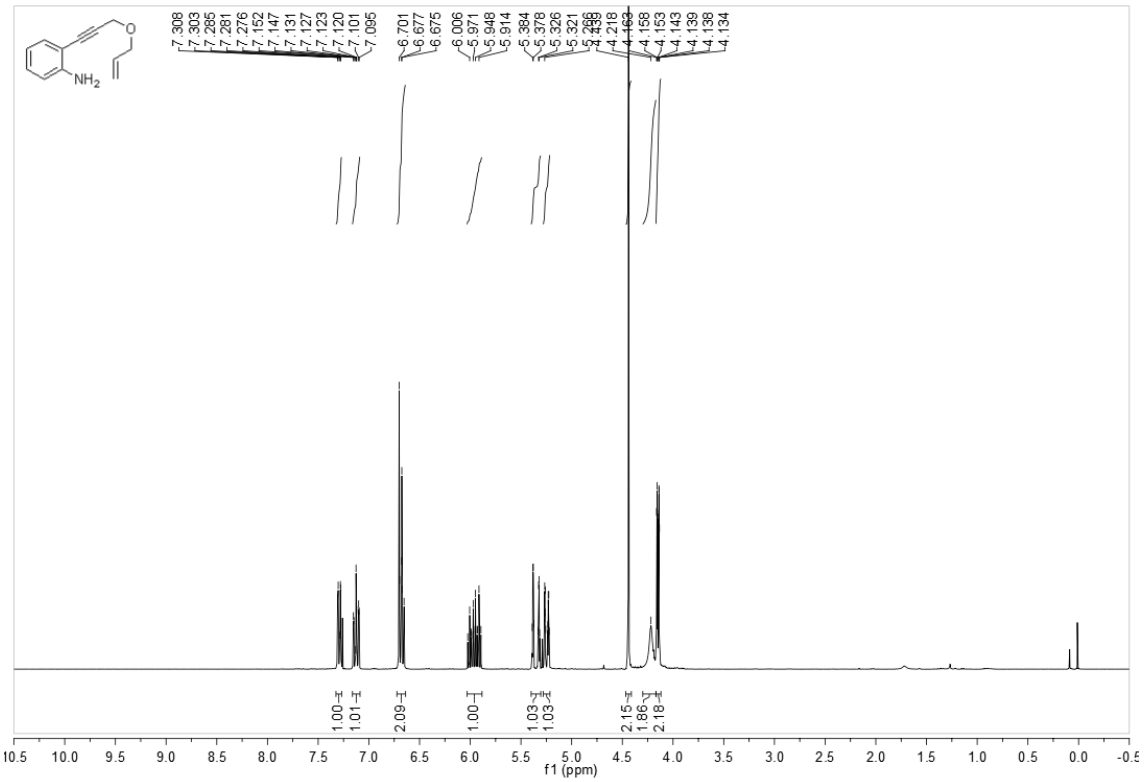


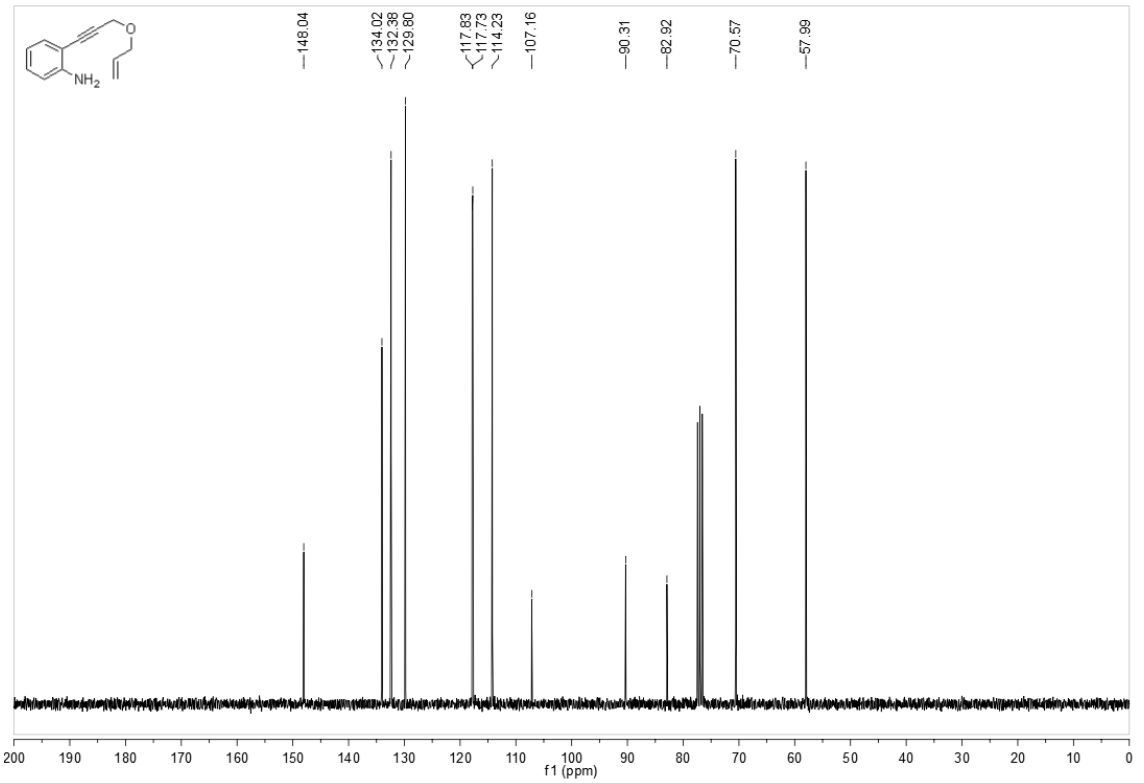
2-(hept-6-en-1-ynyl)aniline



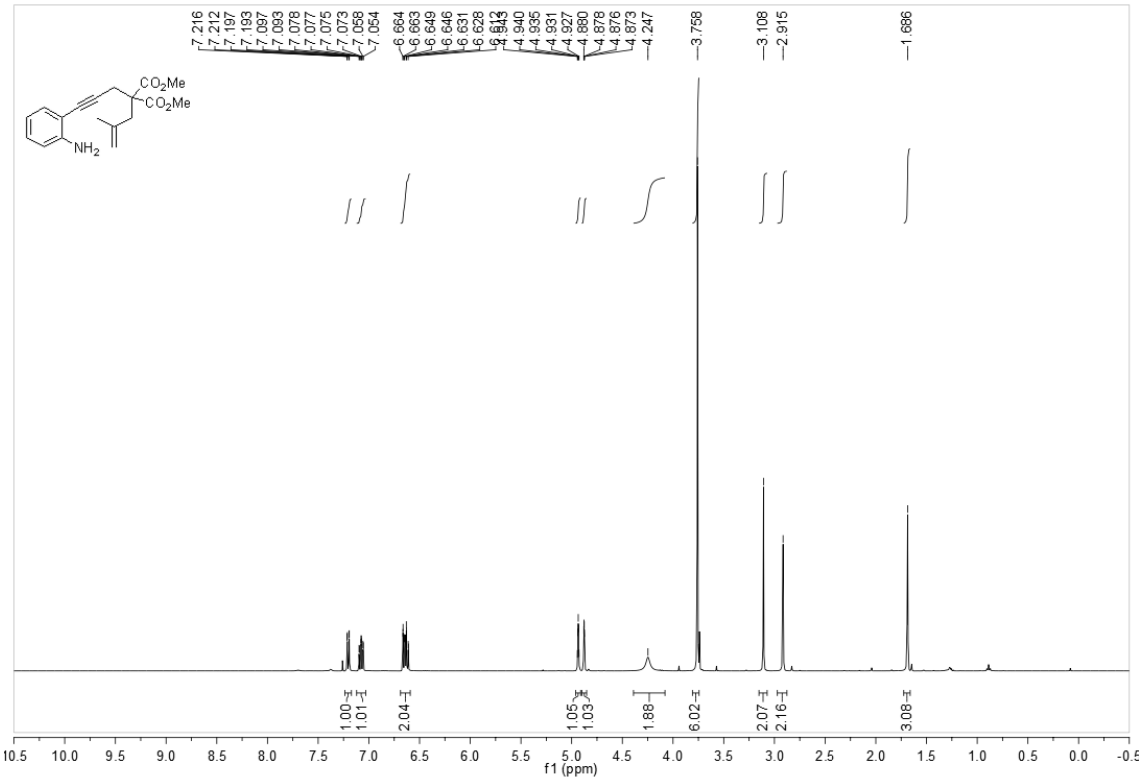


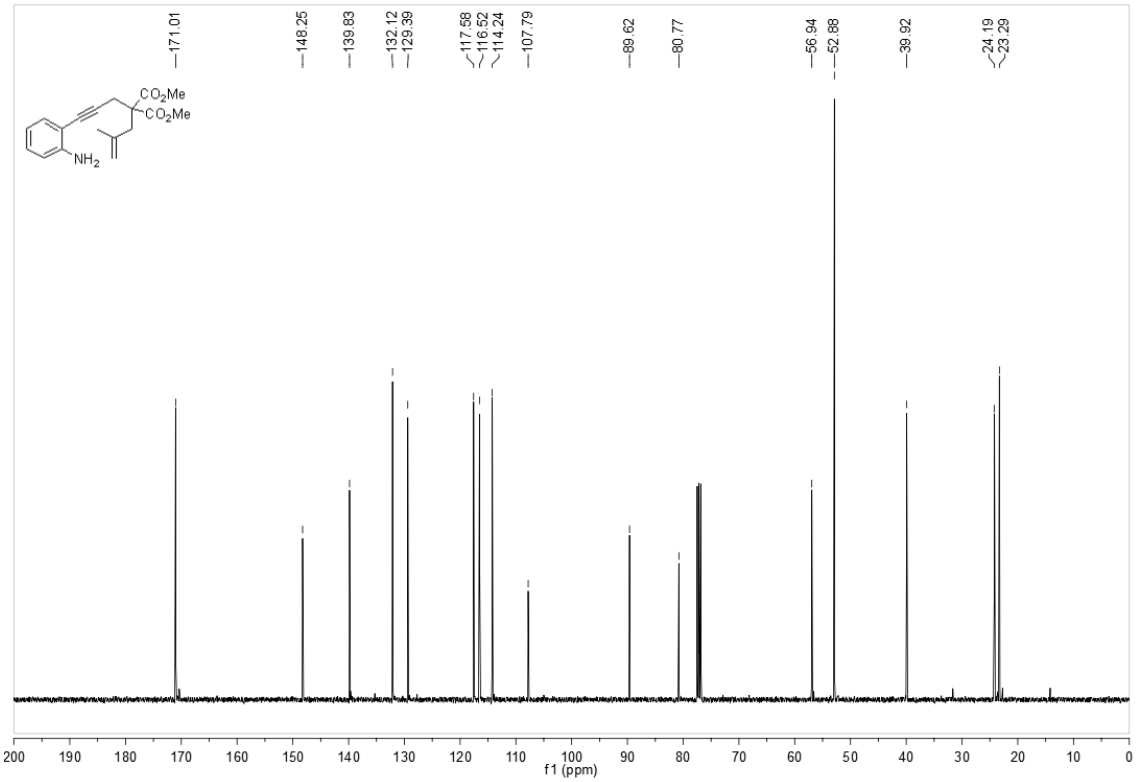
2-(3-(allyloxy)prop-1-ynyl)aniline



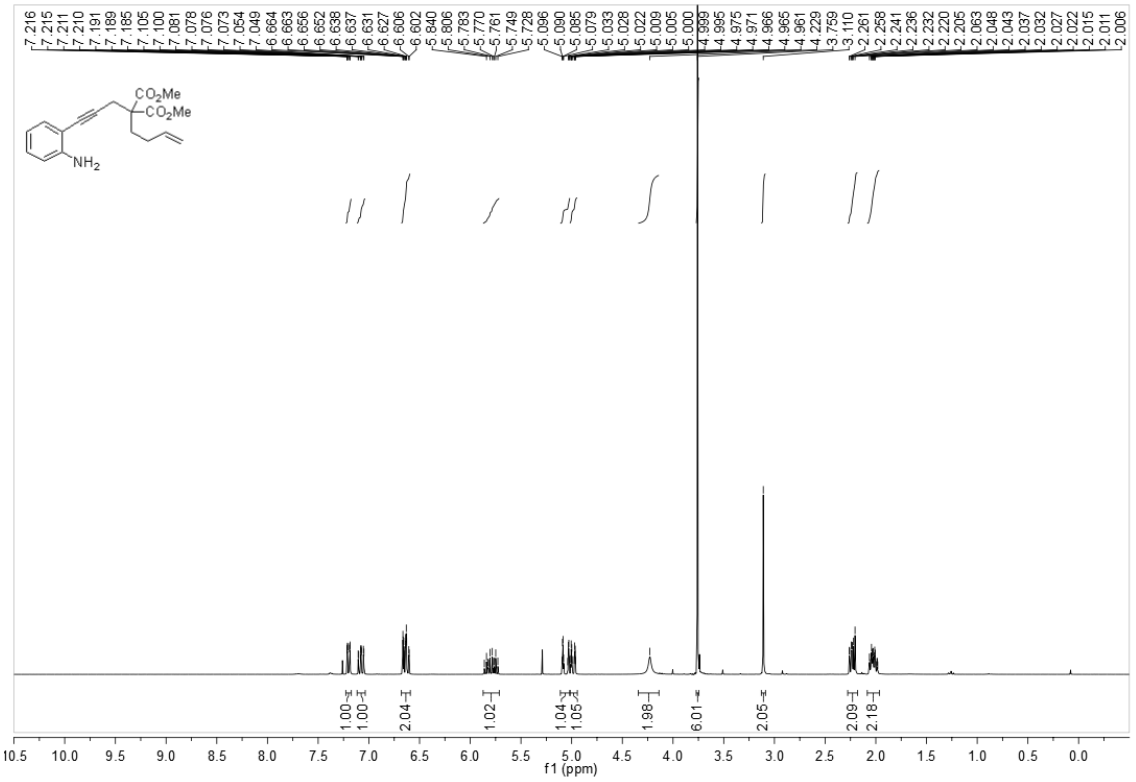


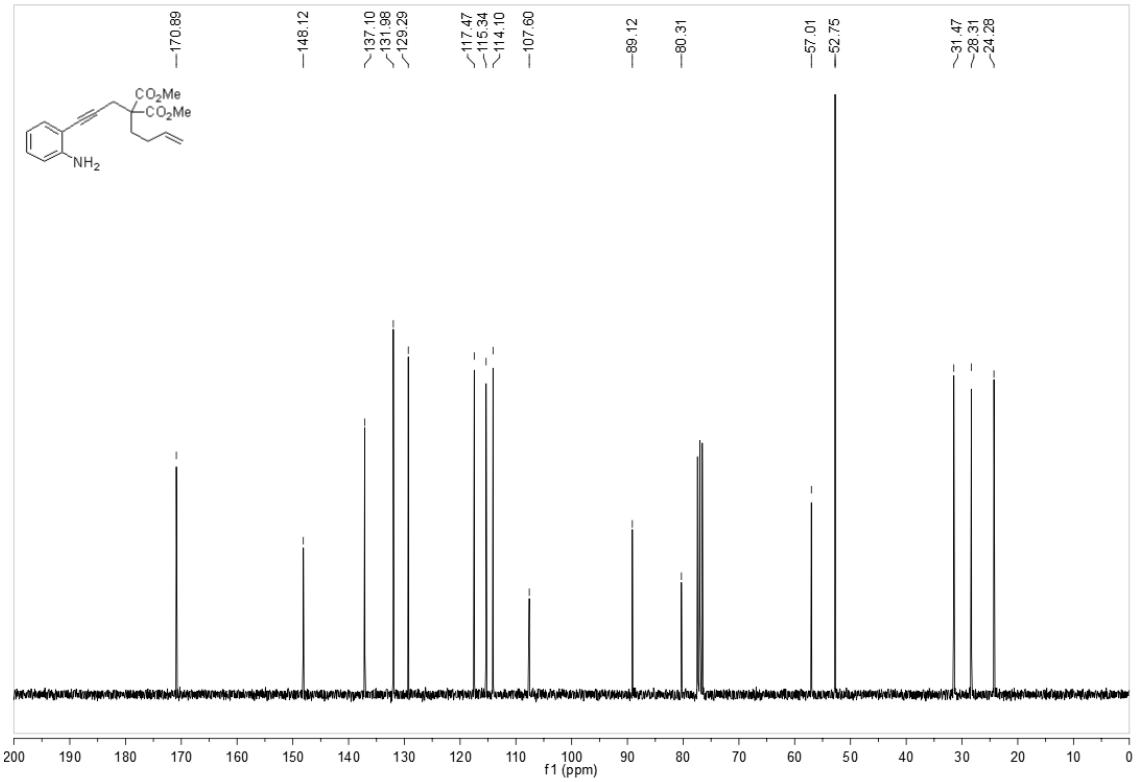
Dimethyl 2-(3-(2-aminophenyl)prop-2-ynyl)-2-(2-methylallyl)malonate



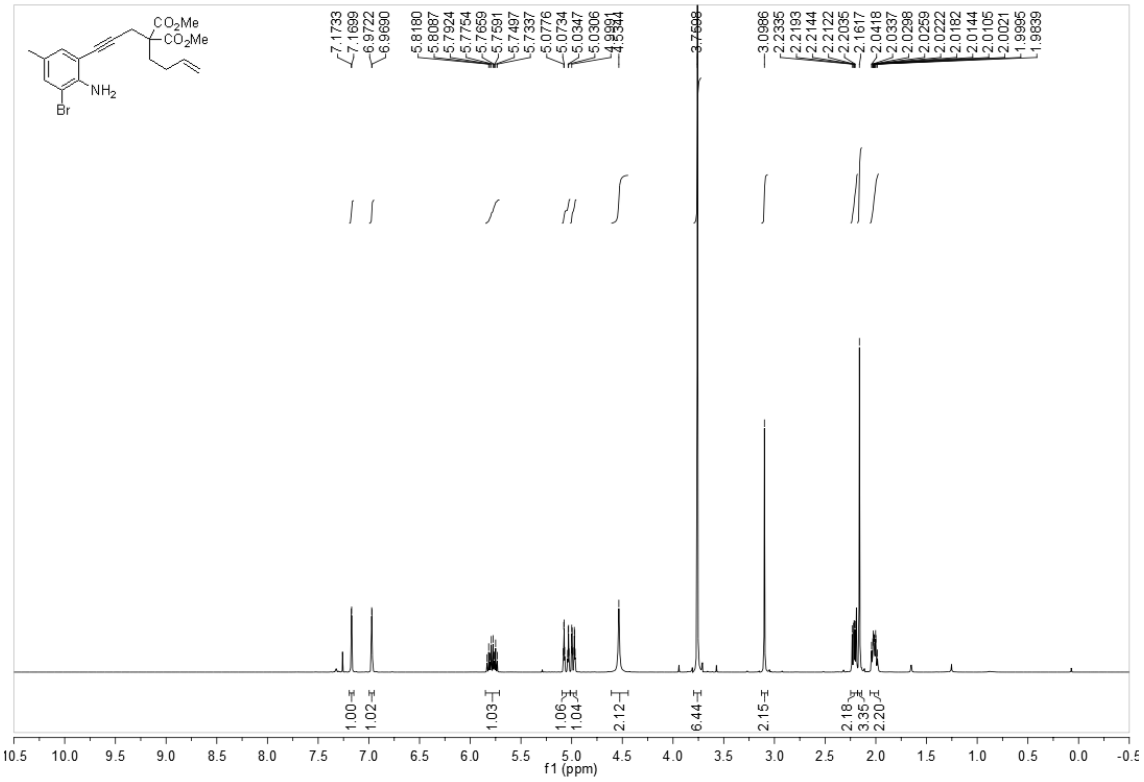


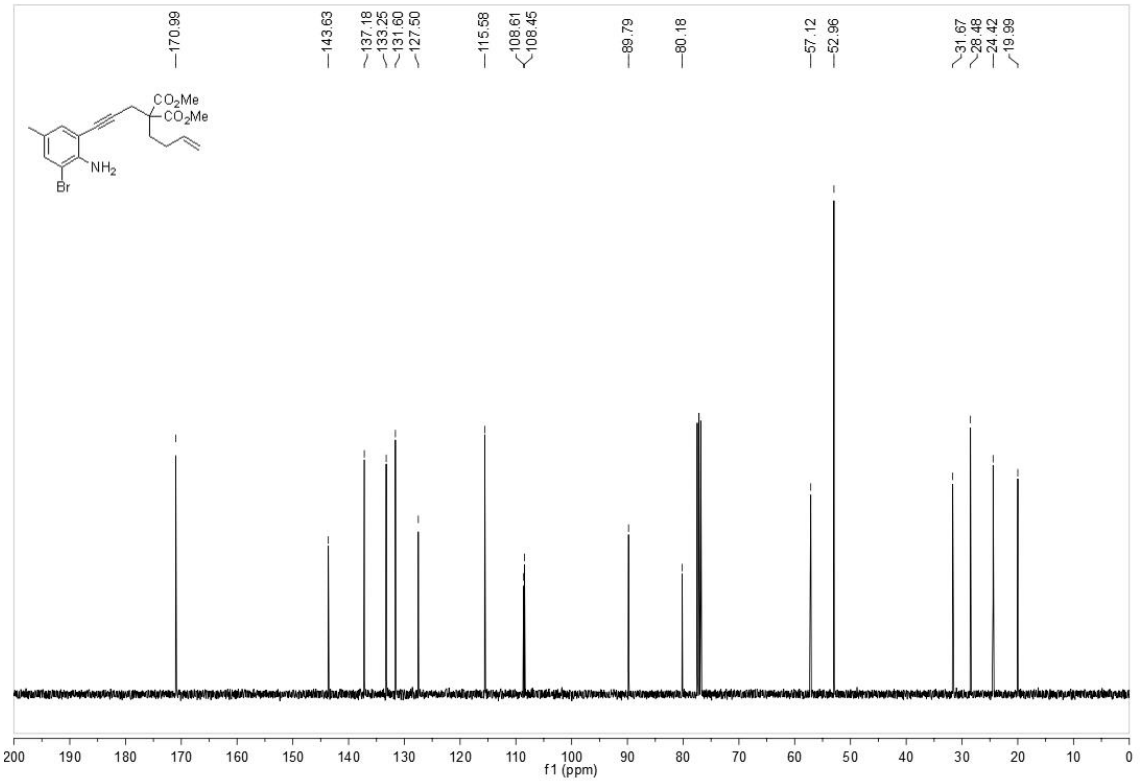
Dimethyl 2-(3-(2-aminophenyl)prop-2-ynyl)-2-(but-3-enyl)malonate



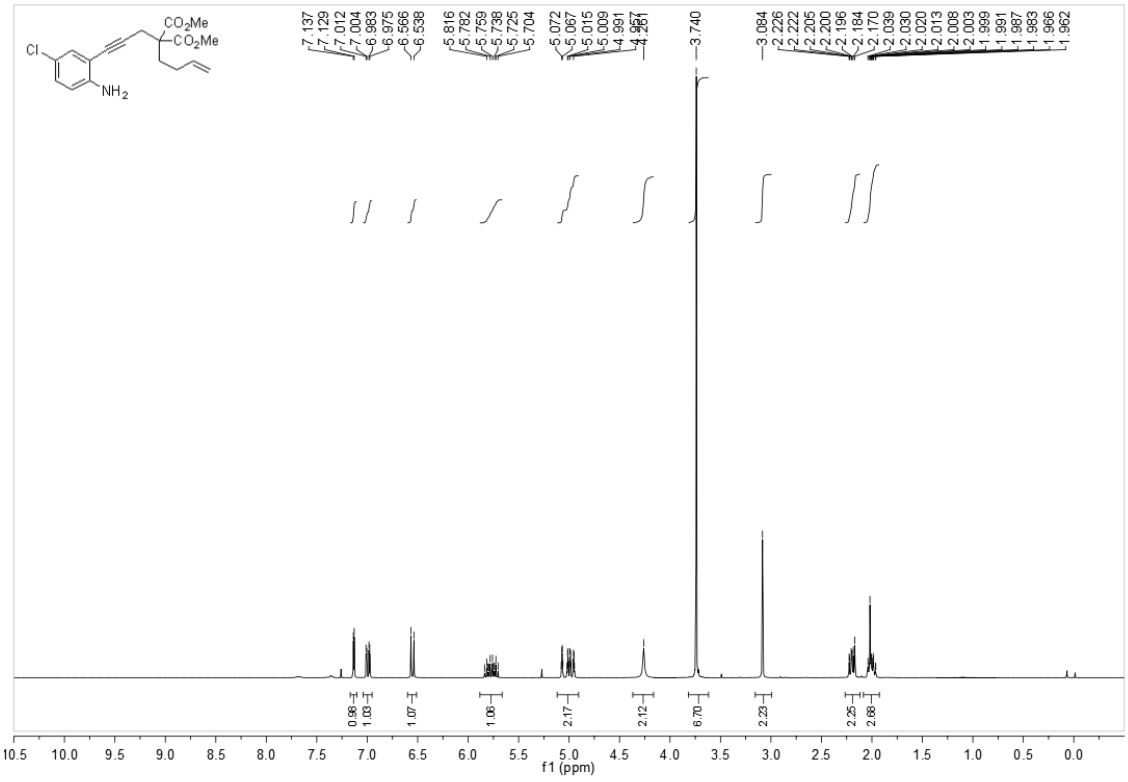


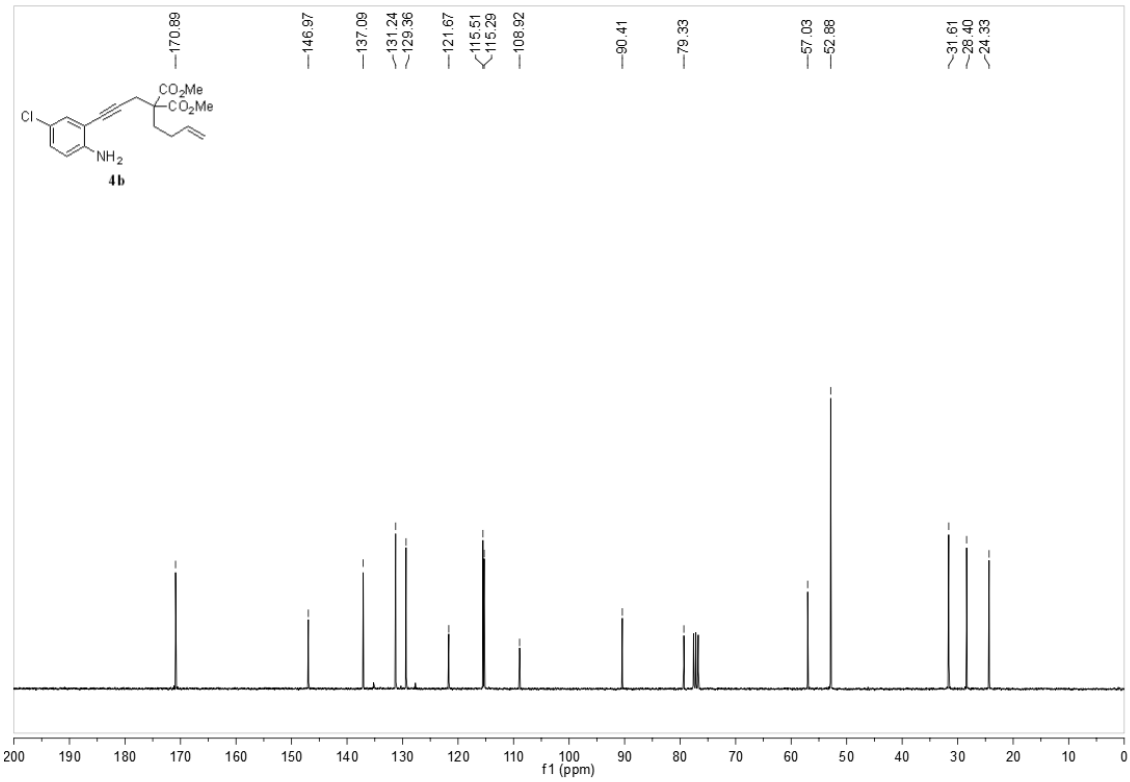
Dimethyl 2-(3-(2-amino-3-bromo-5-methylphenyl)prop-2-ynyl)-2-(but-3-enyl)malonate



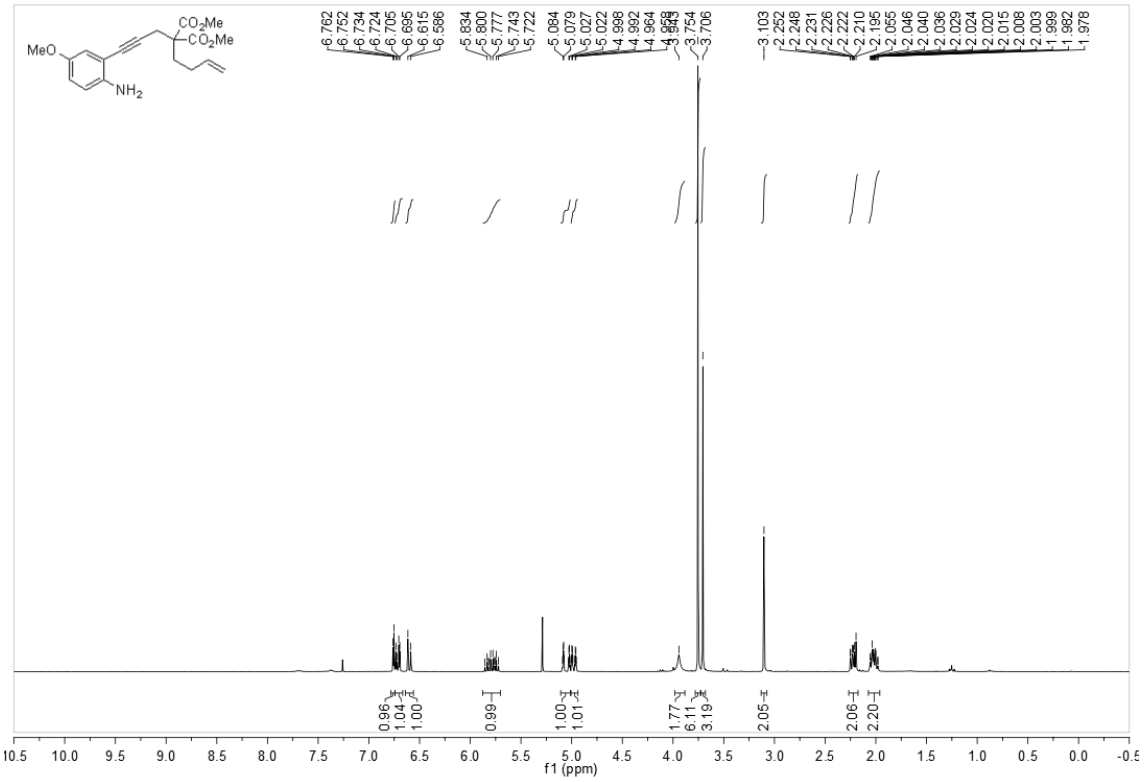


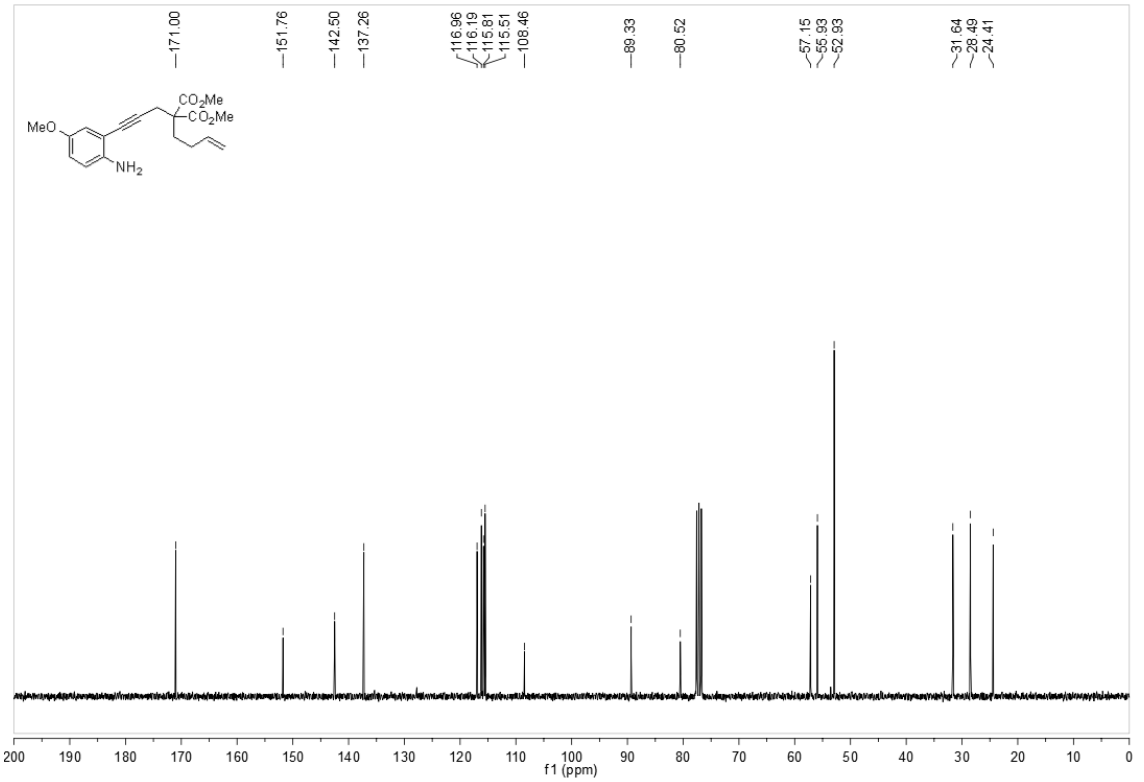
Dimethyl 2-(3-(2-amino-5-chlorophenyl)prop-2-ynyl)-2-(but-3-enyl)malonate



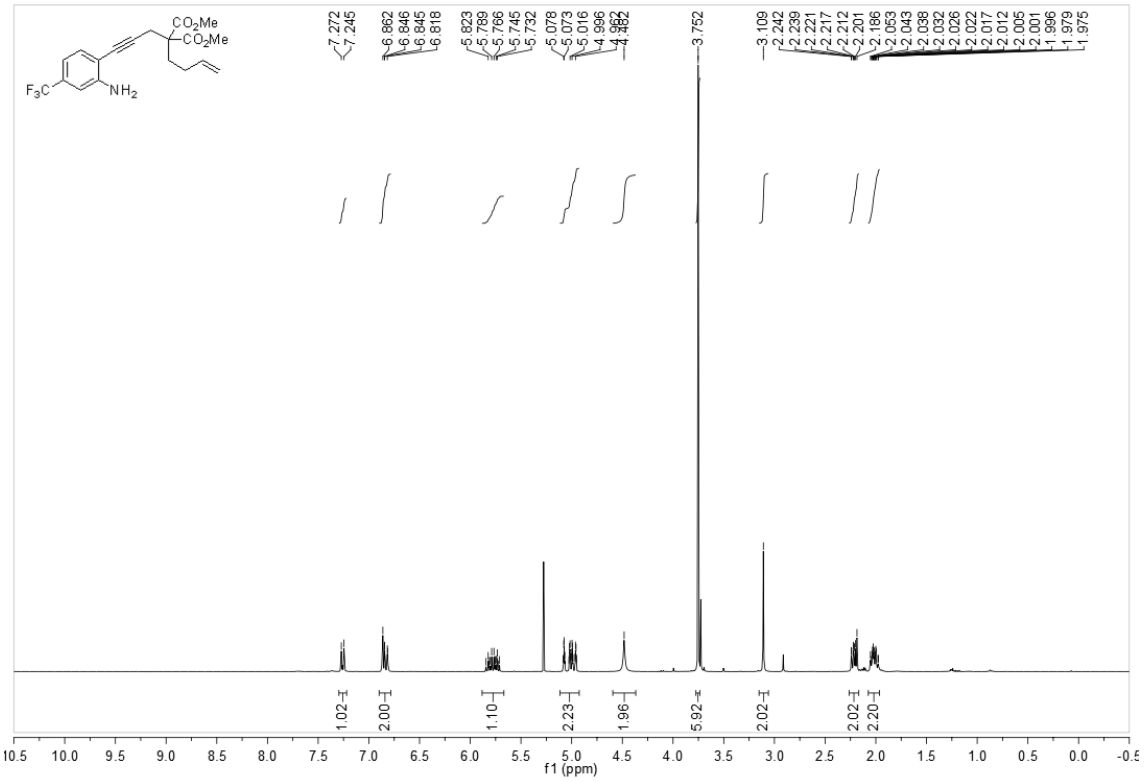


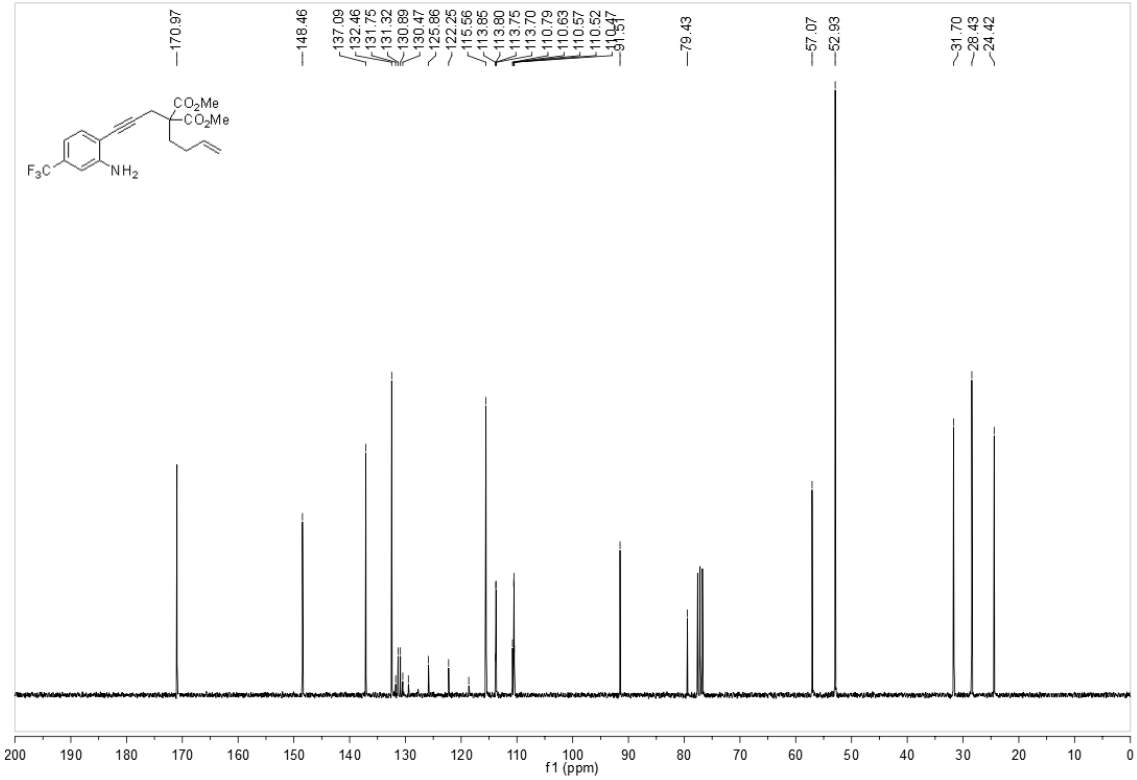
Dimethyl 2-(3-(2-amino-5-methoxyphenyl)prop-2-ynyl)-2-(but-3-enyl)malonate

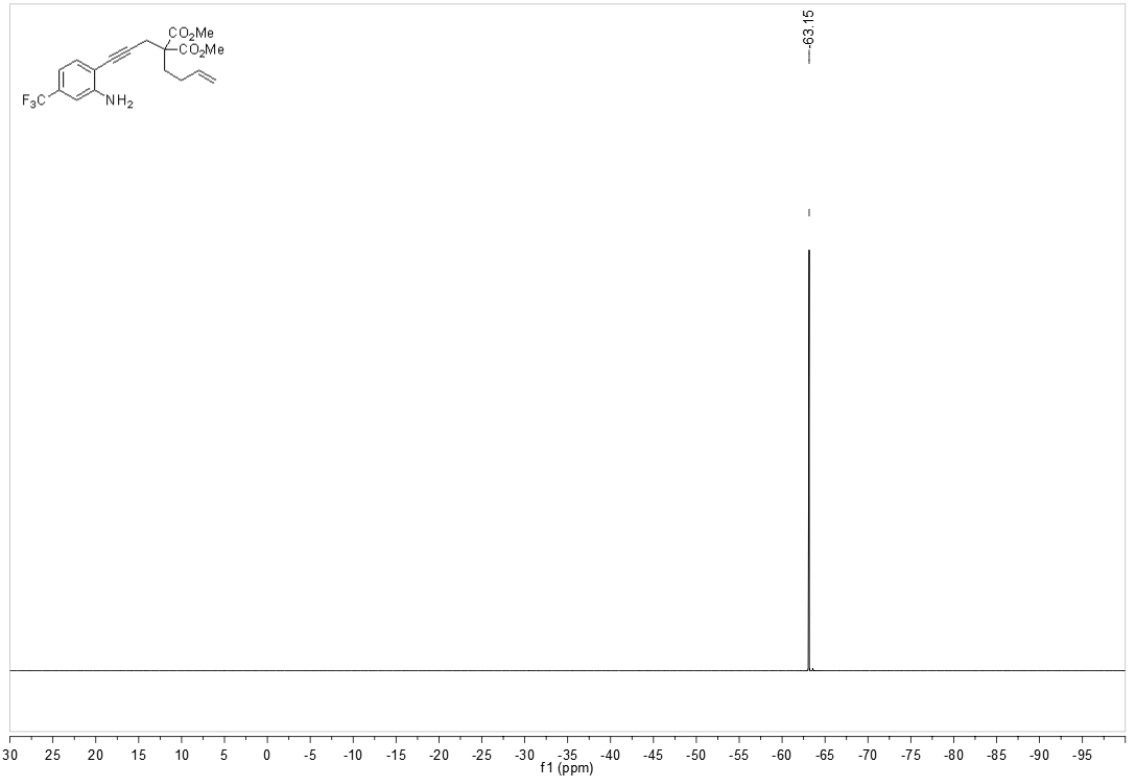




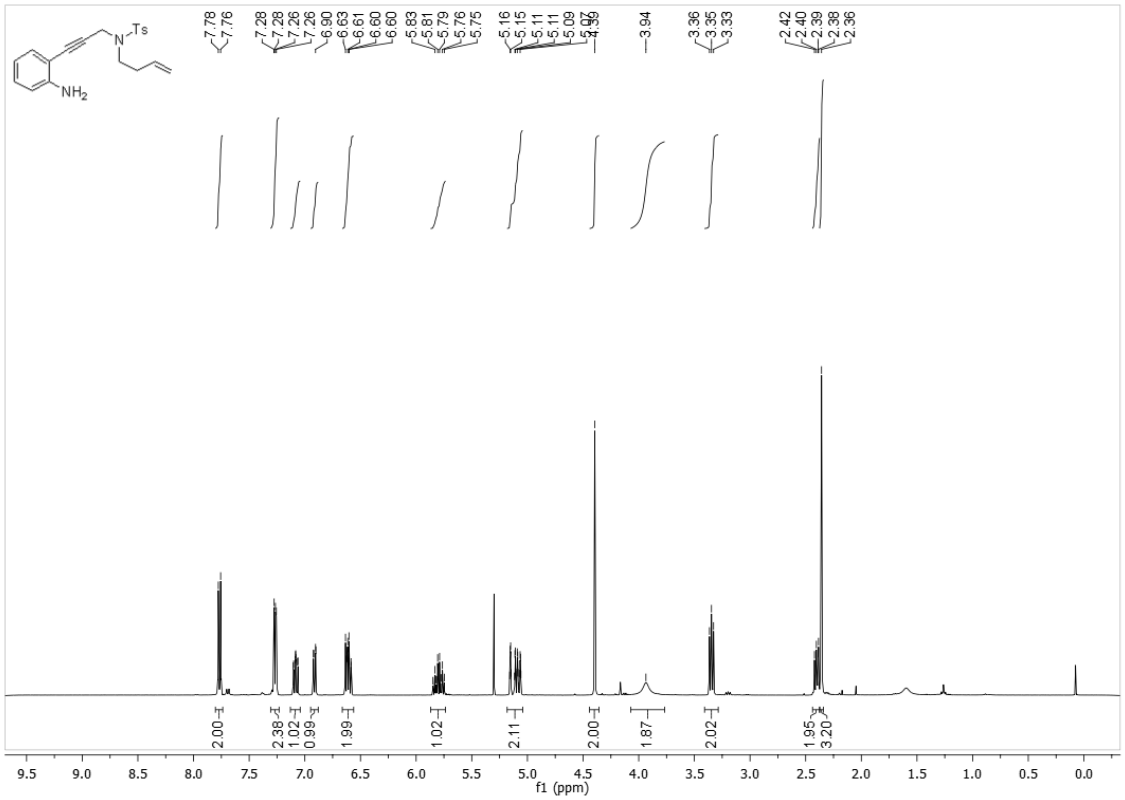
Dimethyl 2-(3-(2-amino-4-(trifluoromethyl)phenyl)prop-2-ynyl)-2-(but-3-enyl)malonate

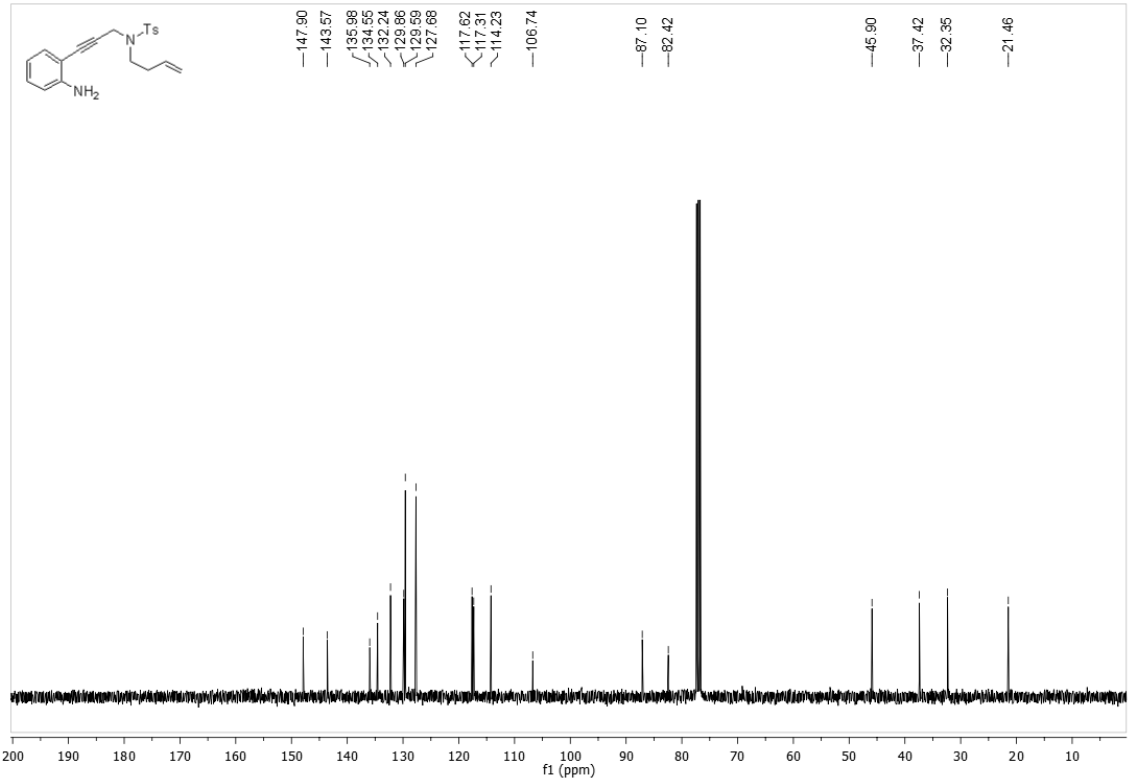




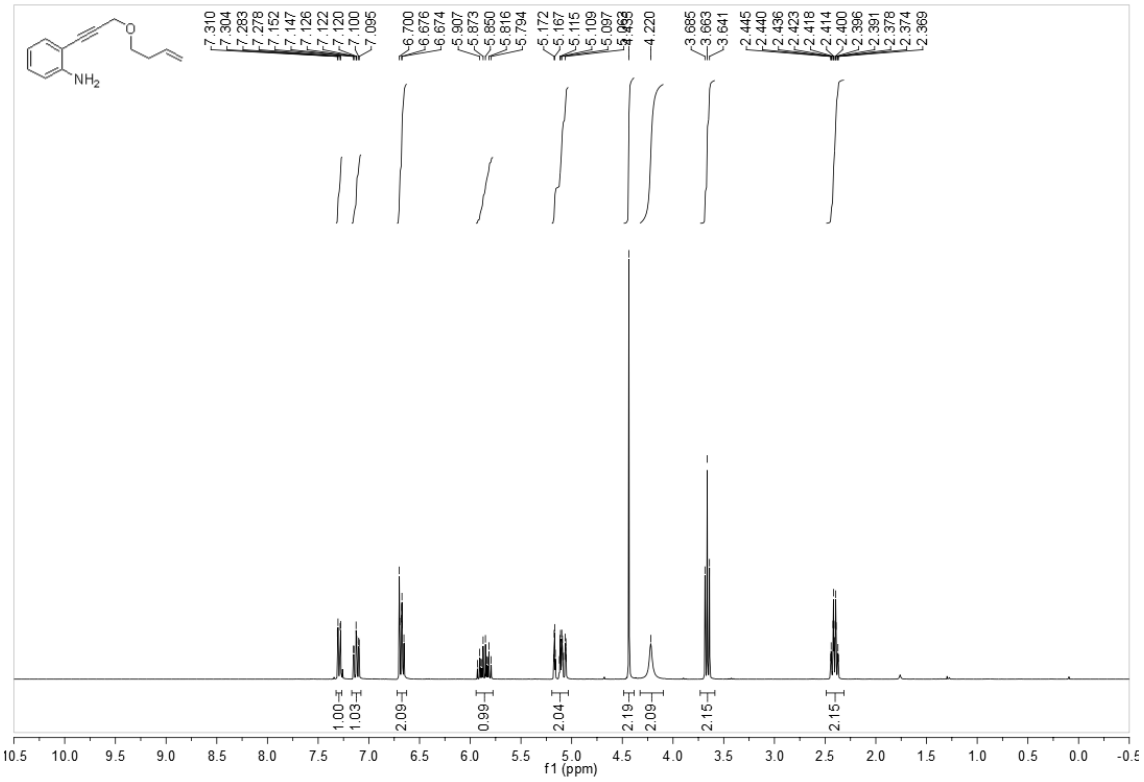

CO2Me
CO2Me
F3C
NH2
-63.15
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

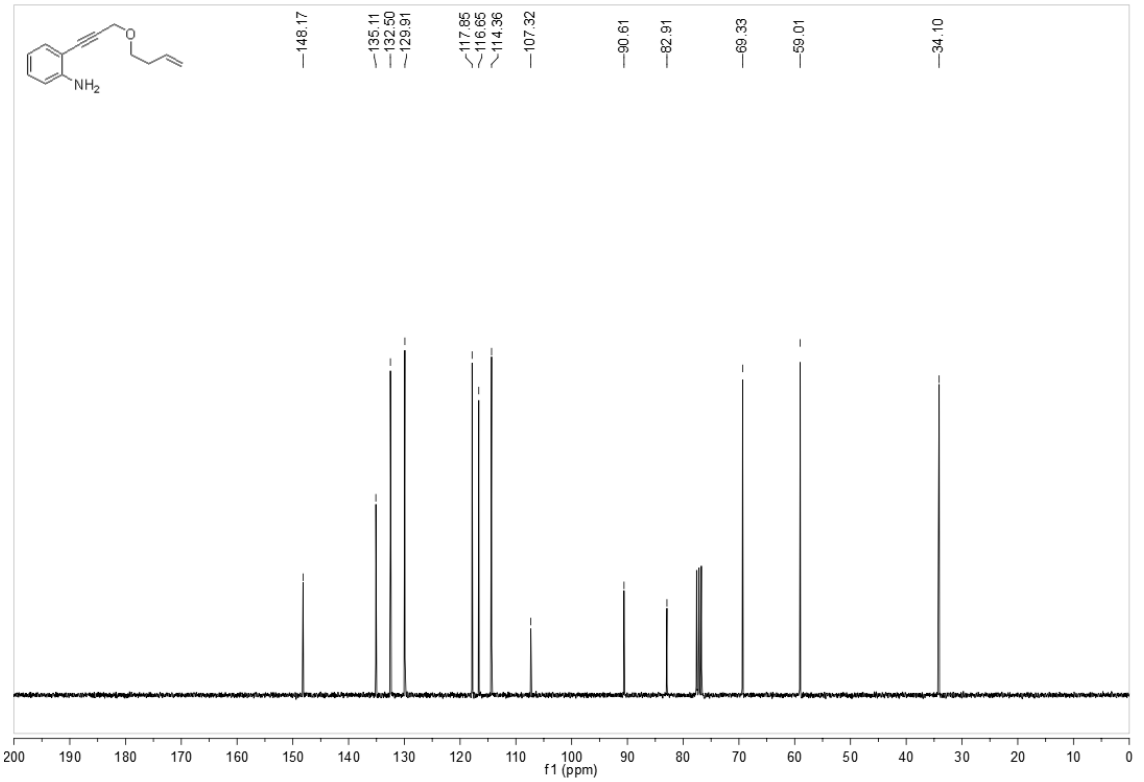
***N*-(3-(2-aminophenyl)prop-2-ynyl)-*N*-(but-3-enyl)-4-methylbenzenesulfonamide**



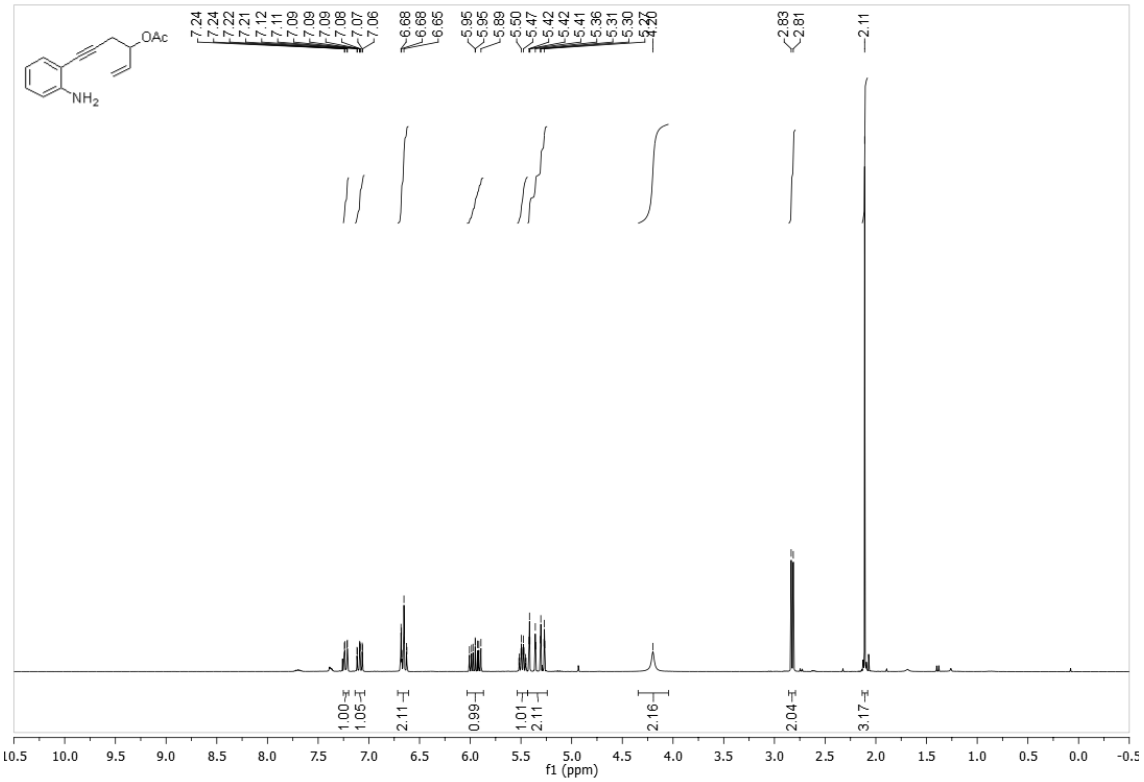


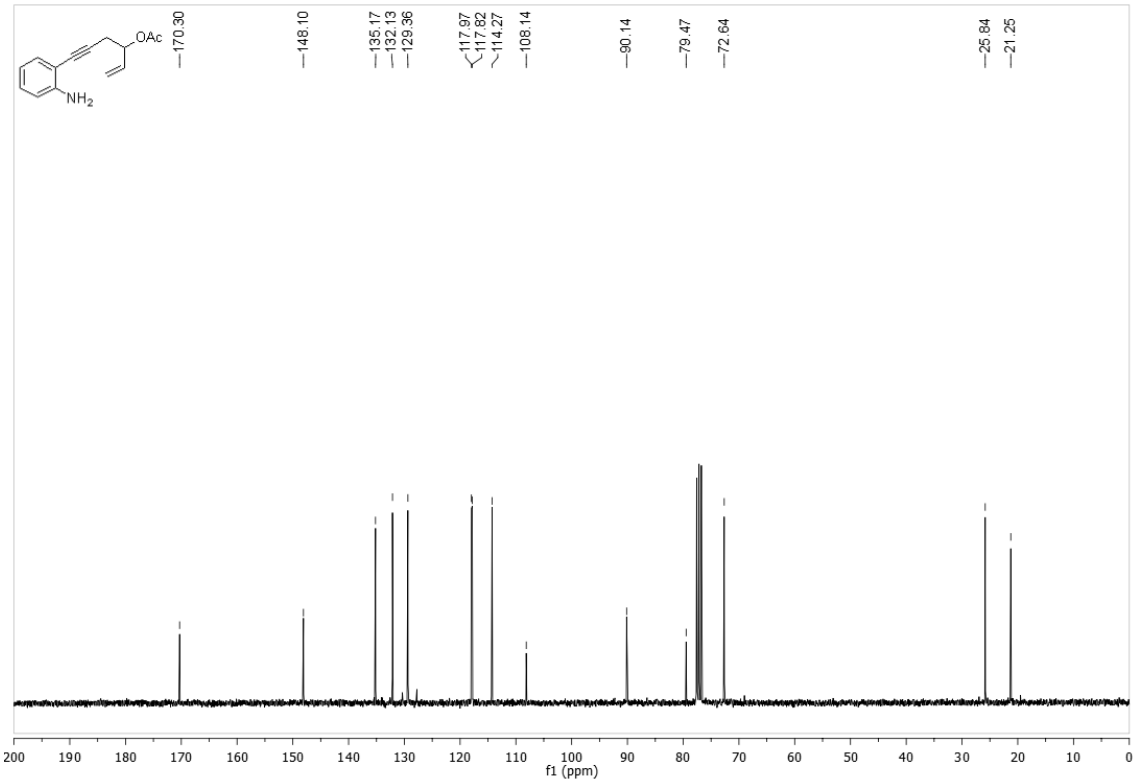
2-(3-(but-3-enyloxy)prop-1-ynyl)aniline



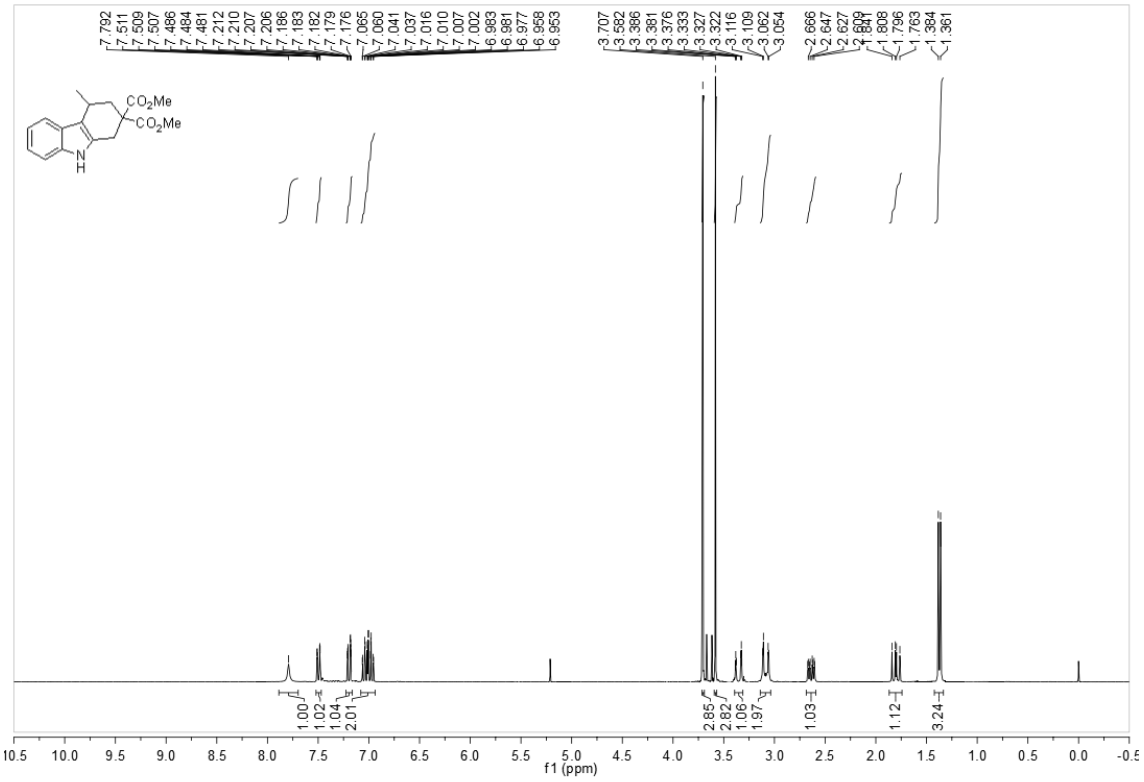


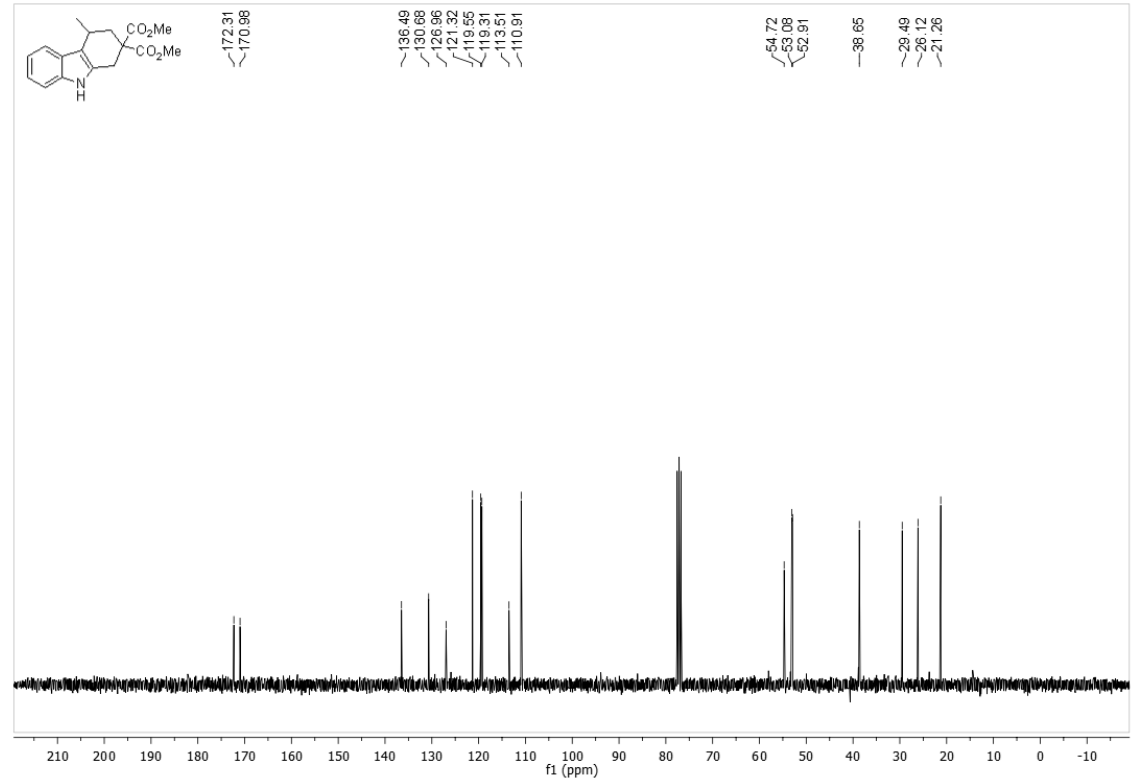
6-(2-aminophenyl)hex-1-en-5-yn-3-yl acetate



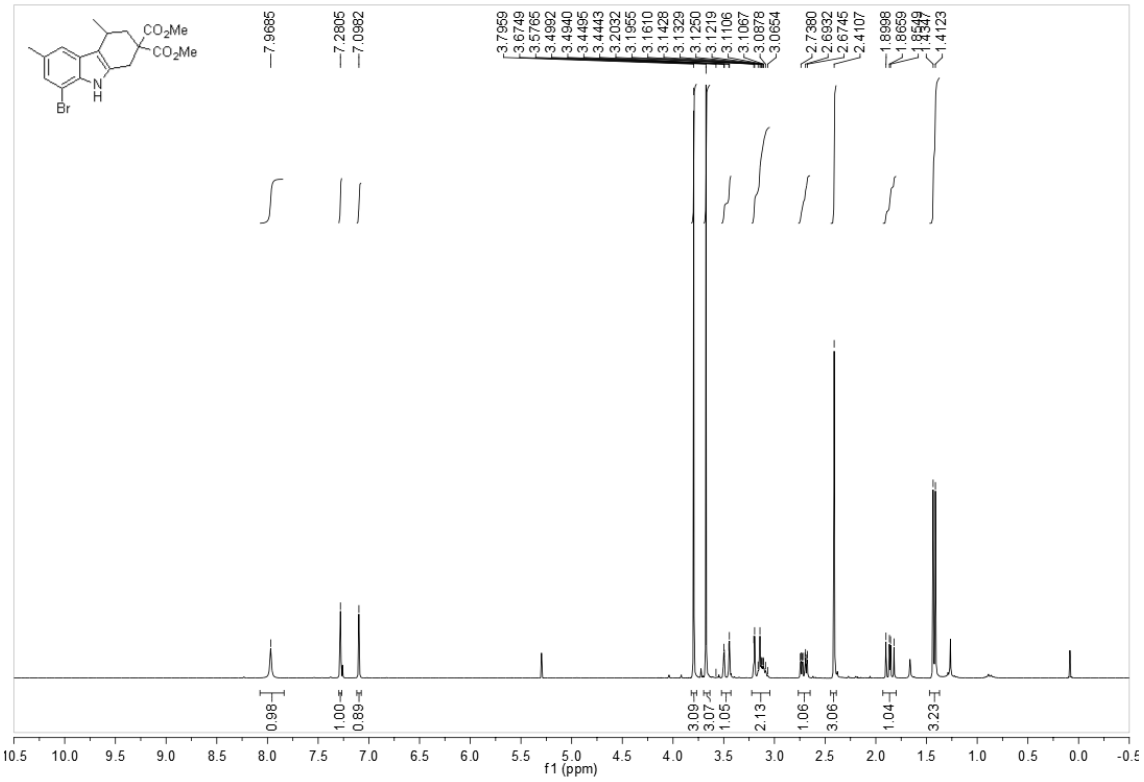


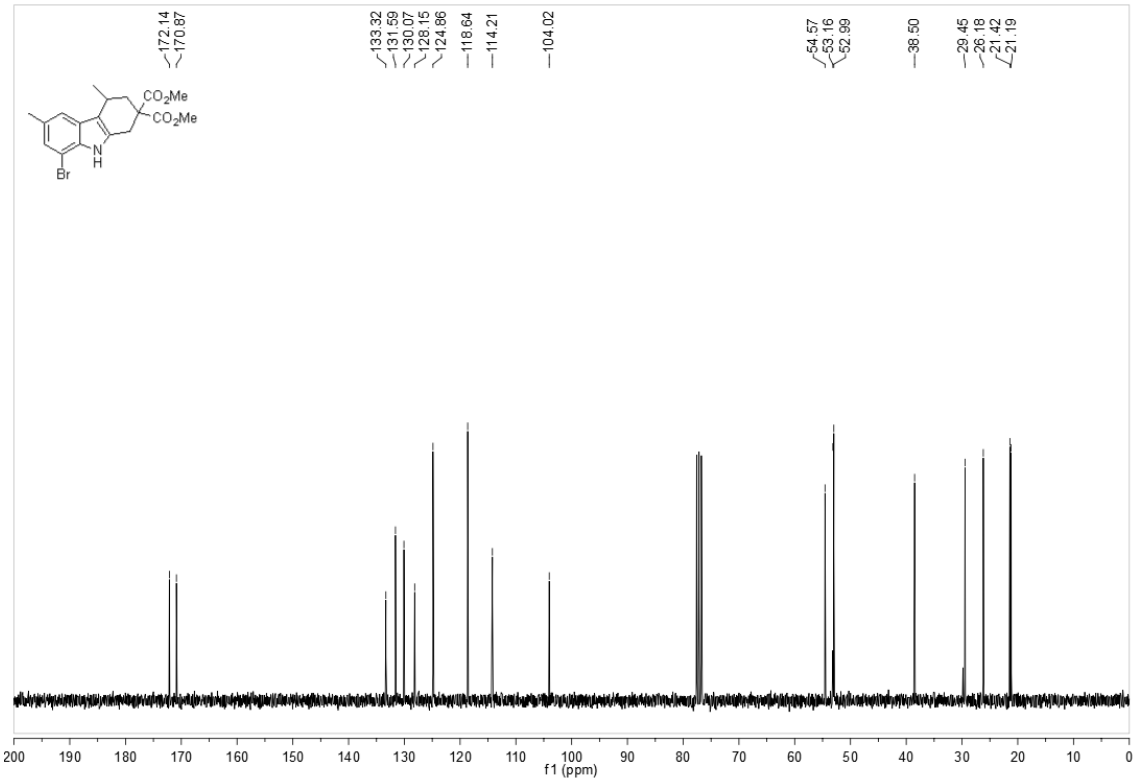
Dimethyl 4-methyl-3,4-dihydro-1*H*-carbazole-2,2(9*H*)-dicarboxylate



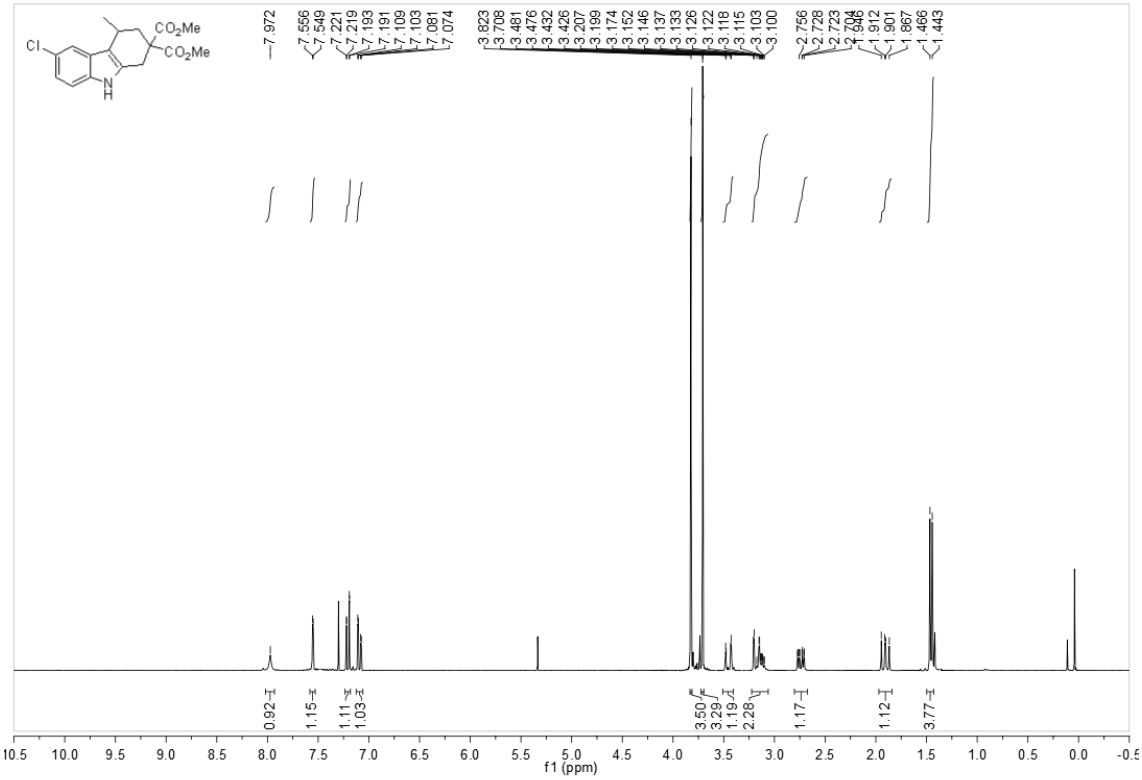


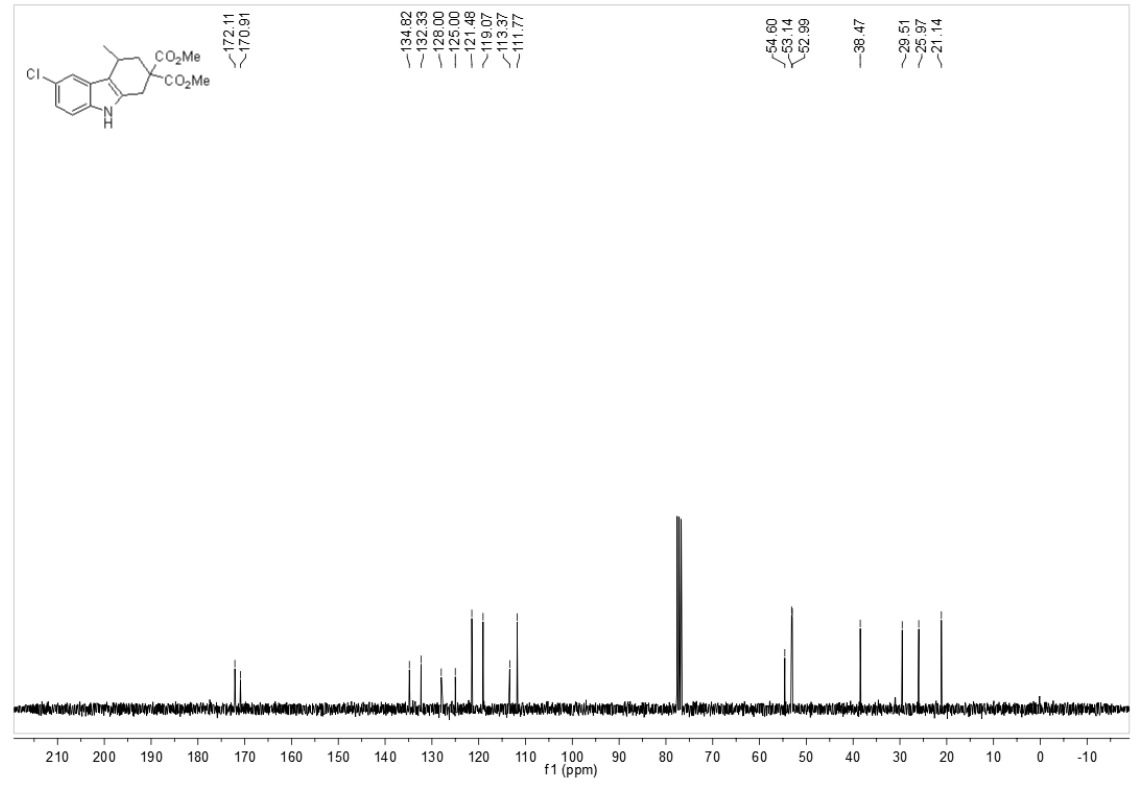
Dimethyl 8-bromo-4,6-dimethyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate



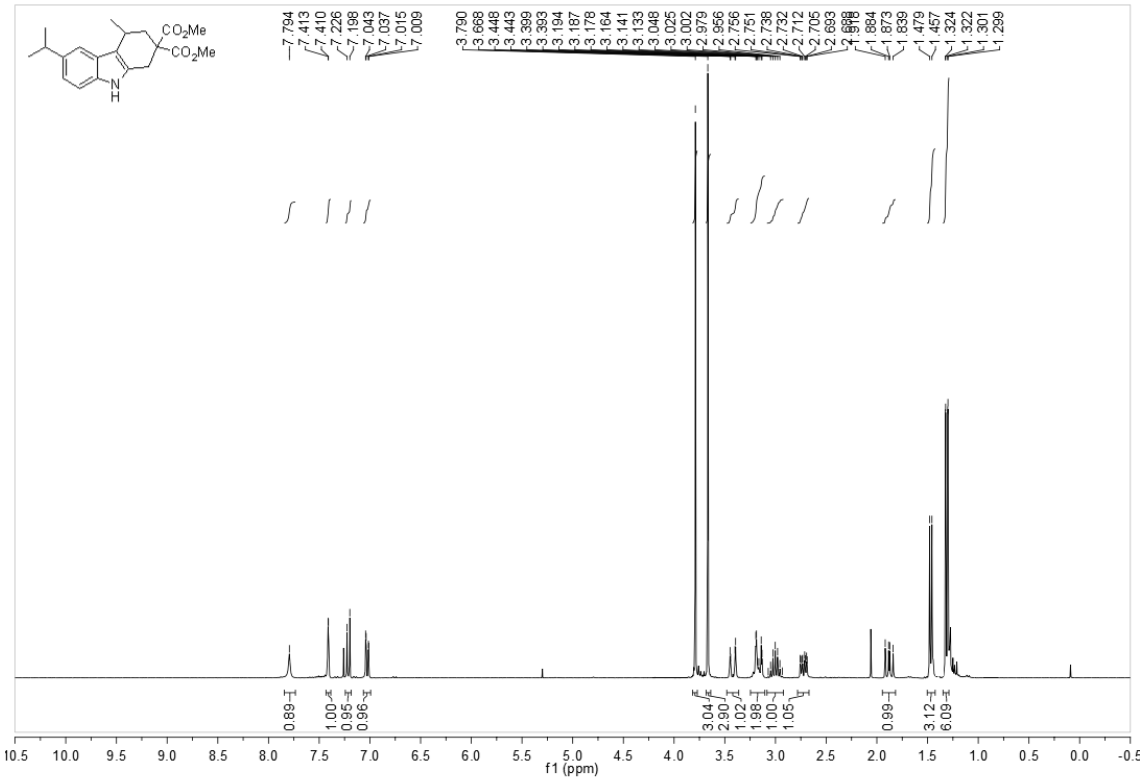


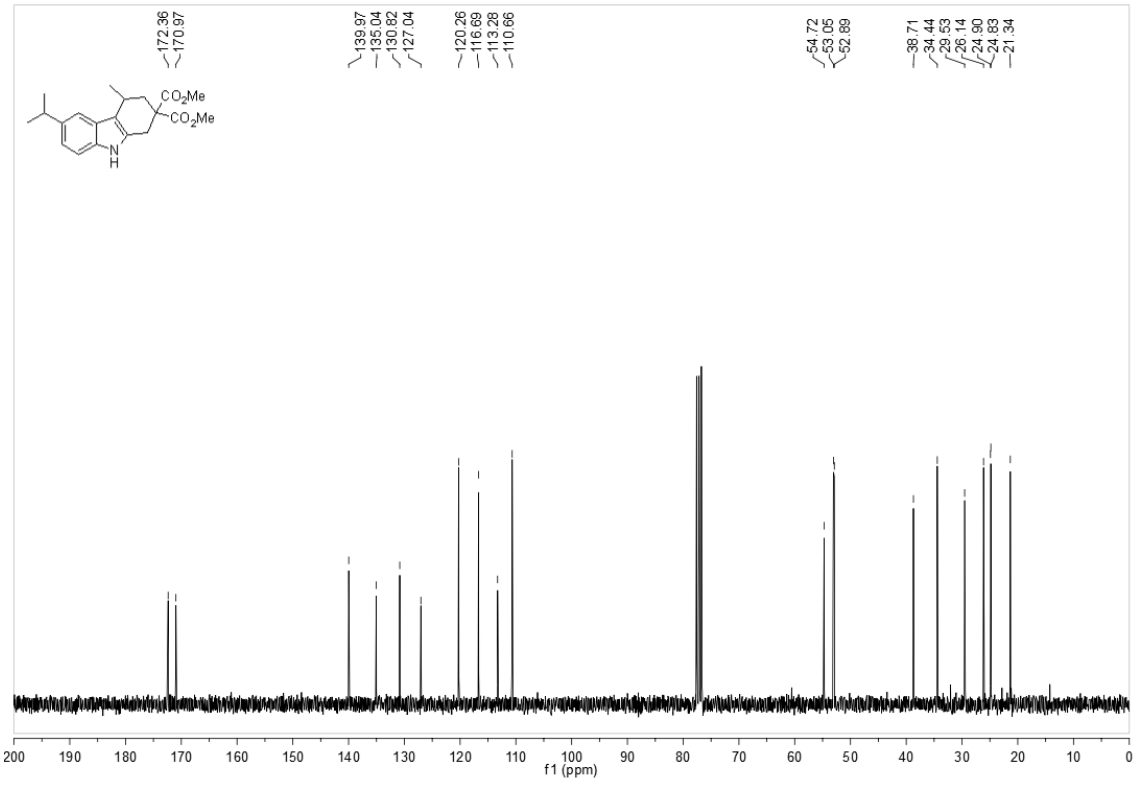
Dimethyl 6-chloro-4-methyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate



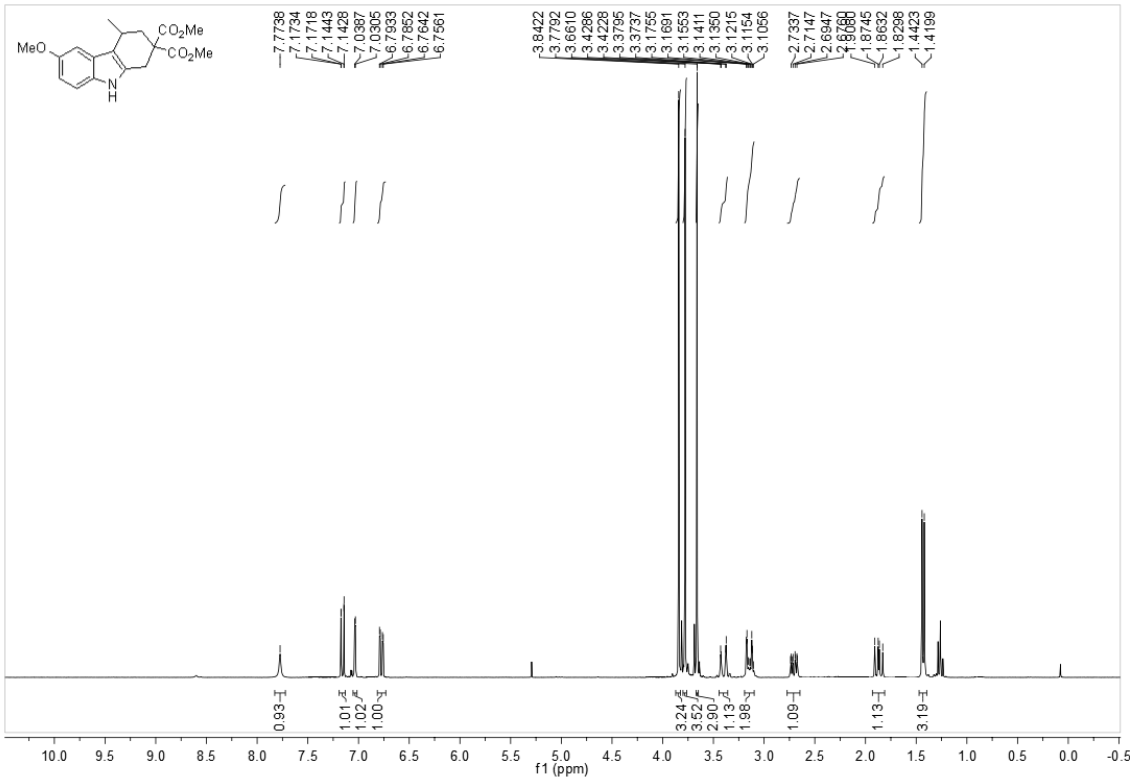


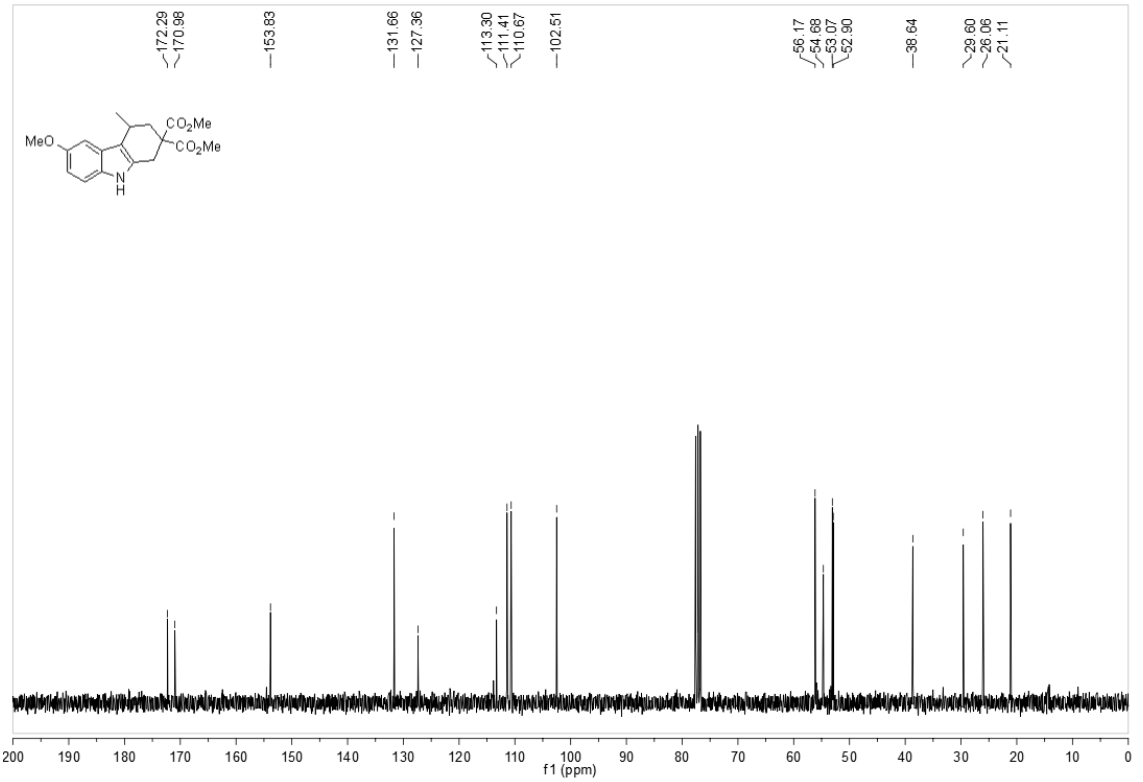
Dimethyl 6-isopropyl-4-methyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate



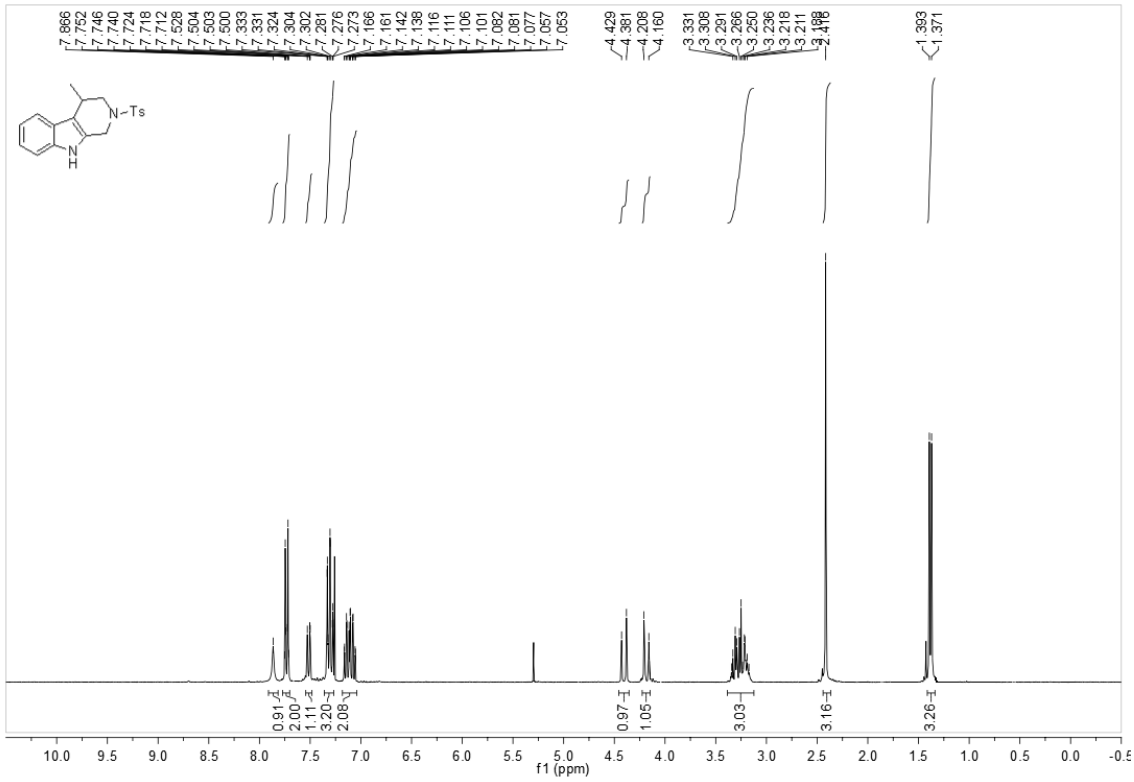


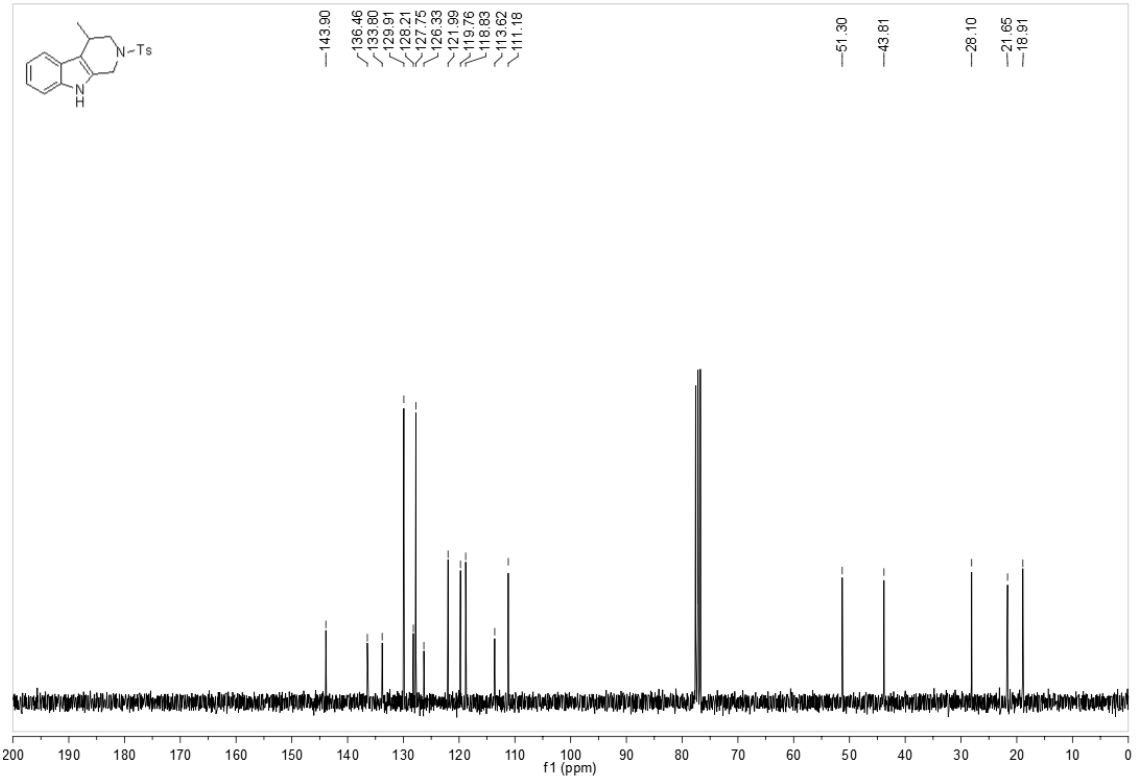
Dimethyl 6-methoxy-4-methyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate



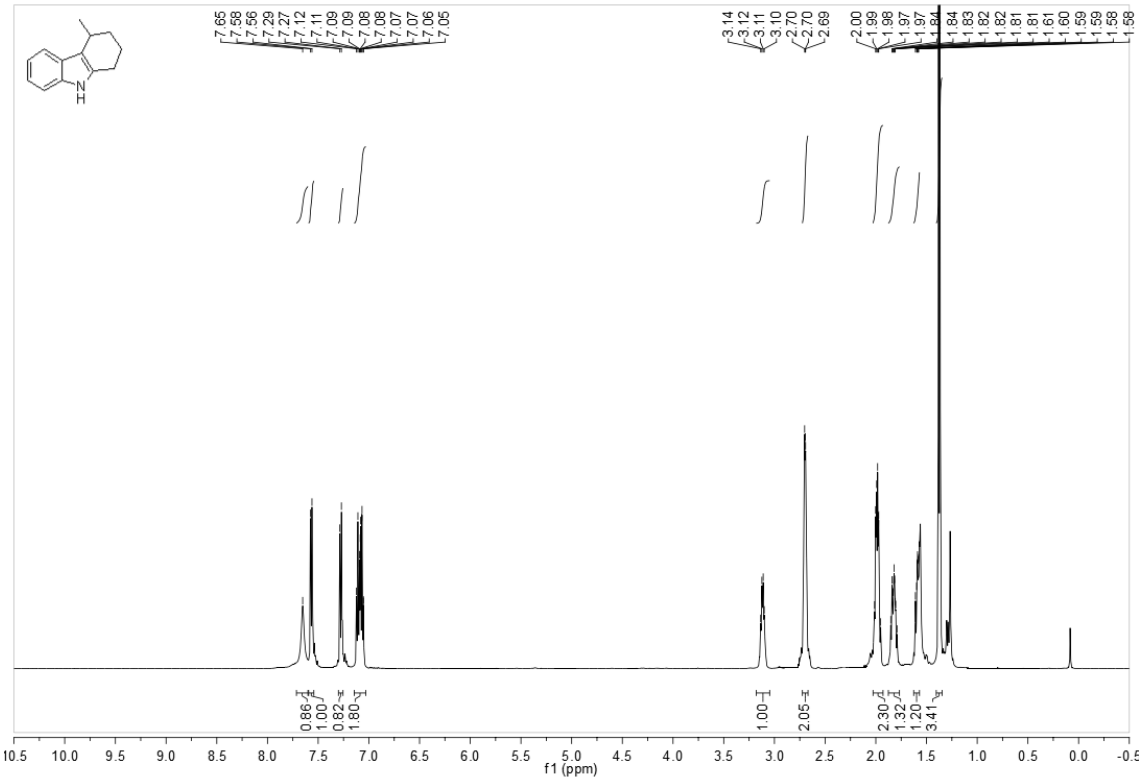


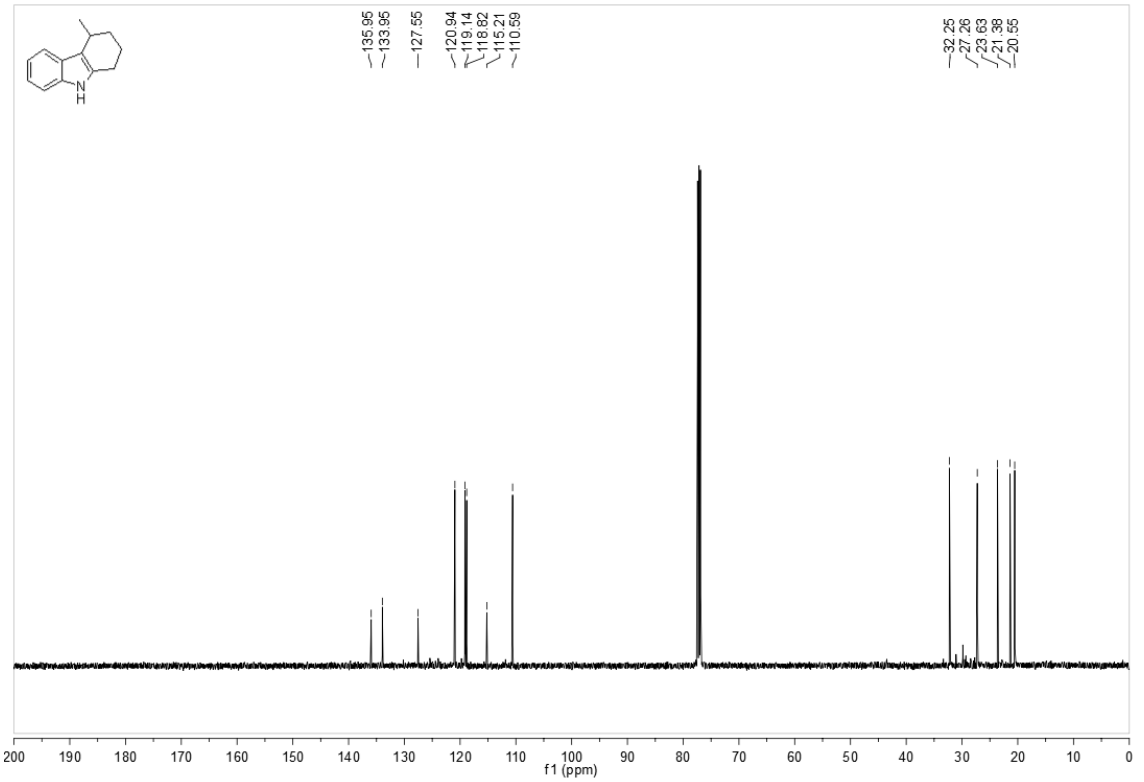
4-methyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole



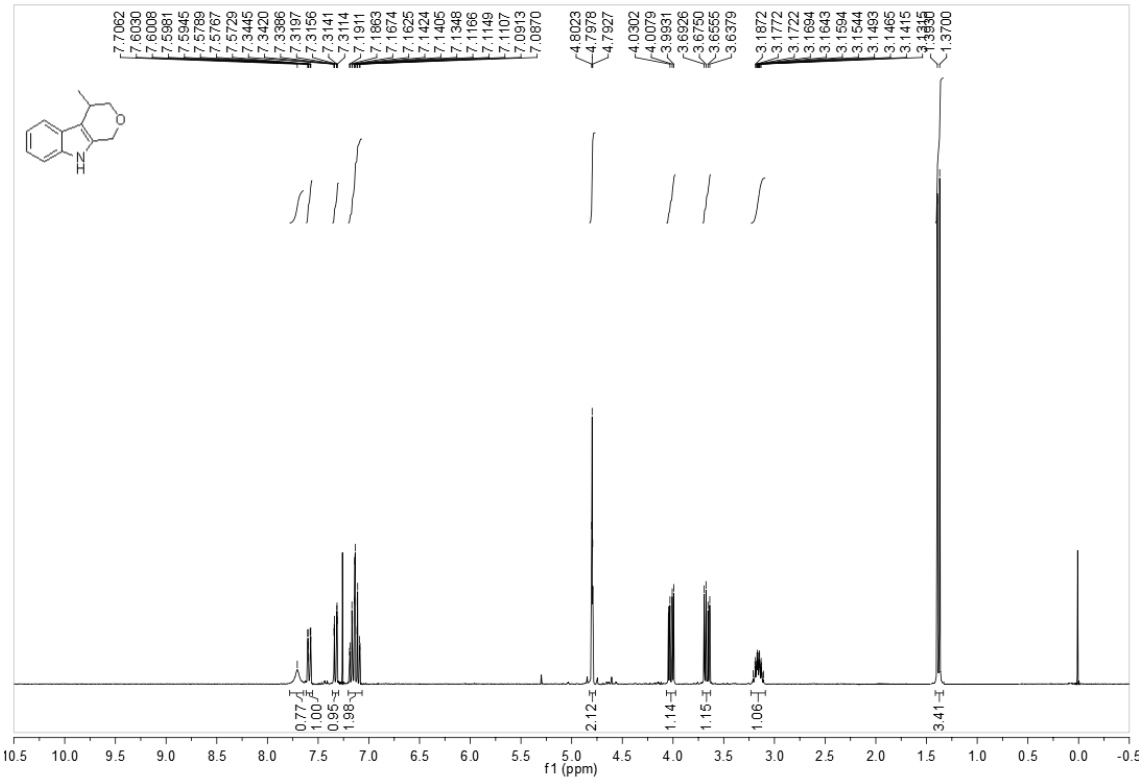


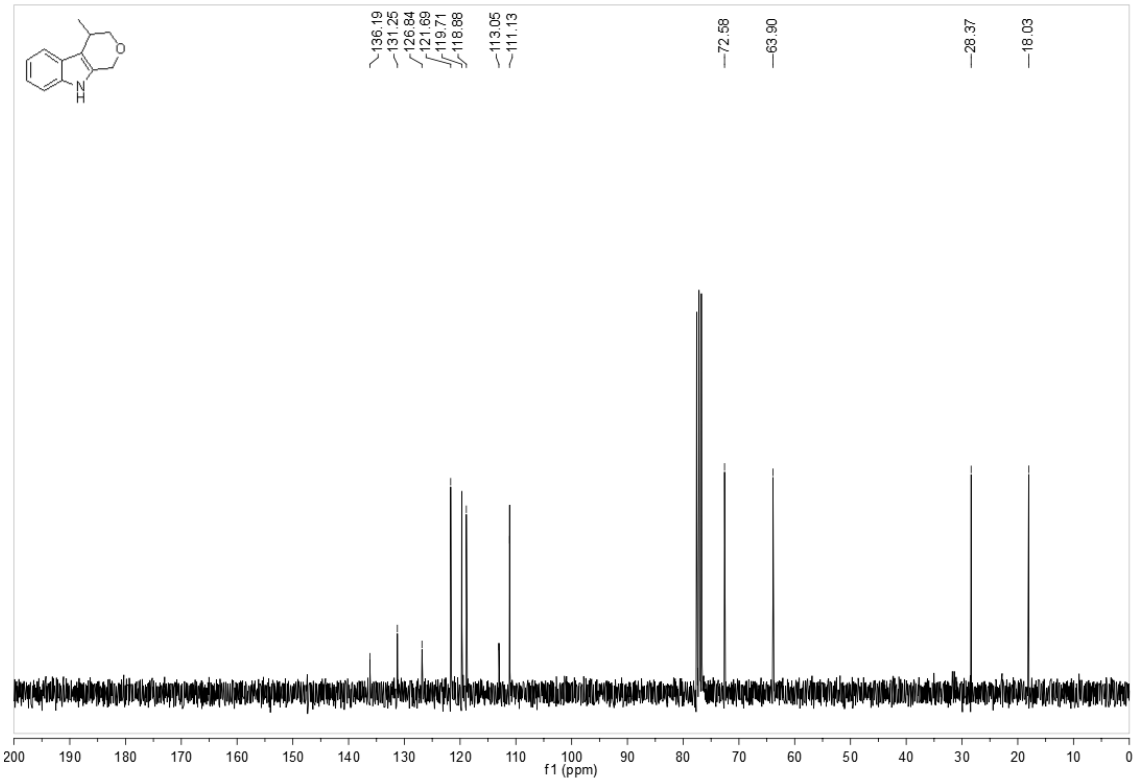
4-methyl-2,3,4,9-tetrahydro-*1H*-carbazole



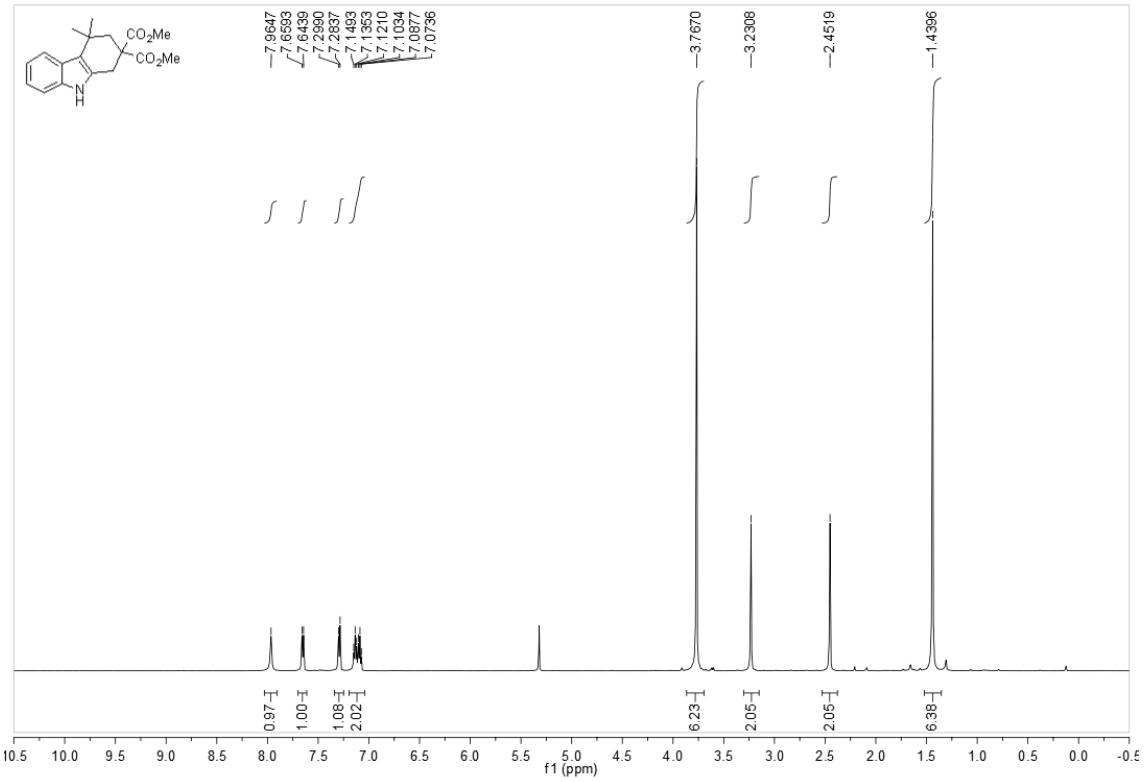


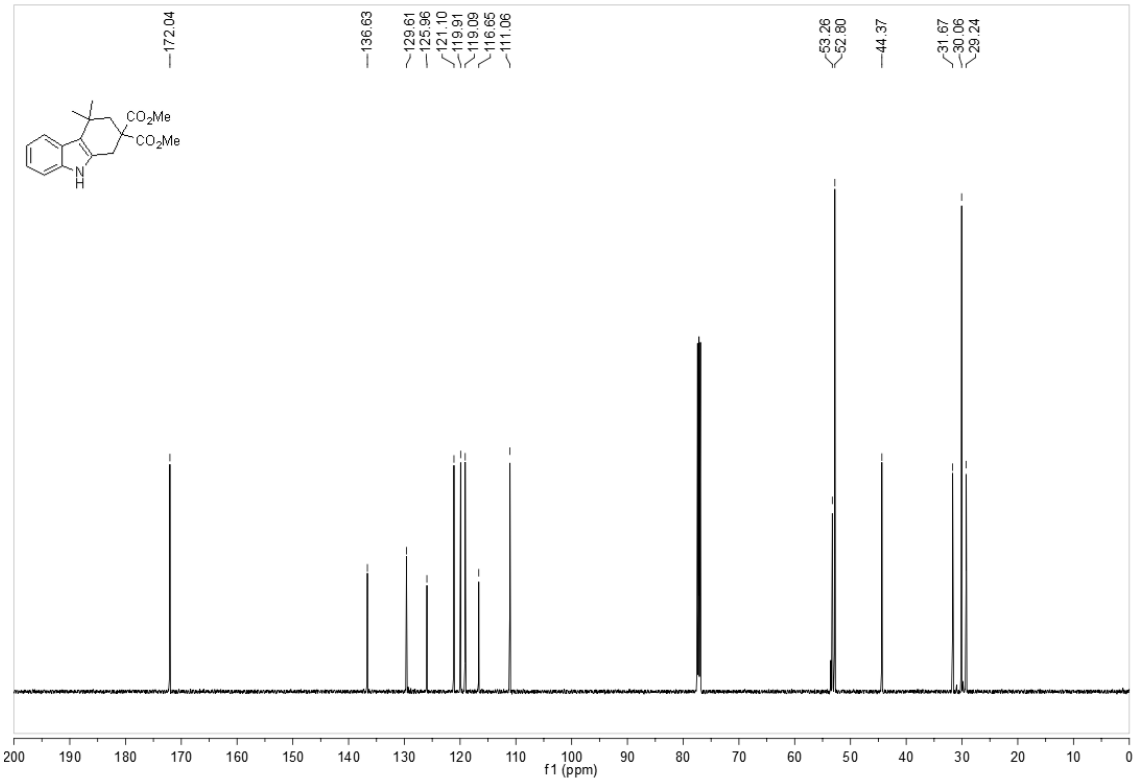
4-methyl-1,3,4,9-tetrahydropyrano[3,4-b]indole



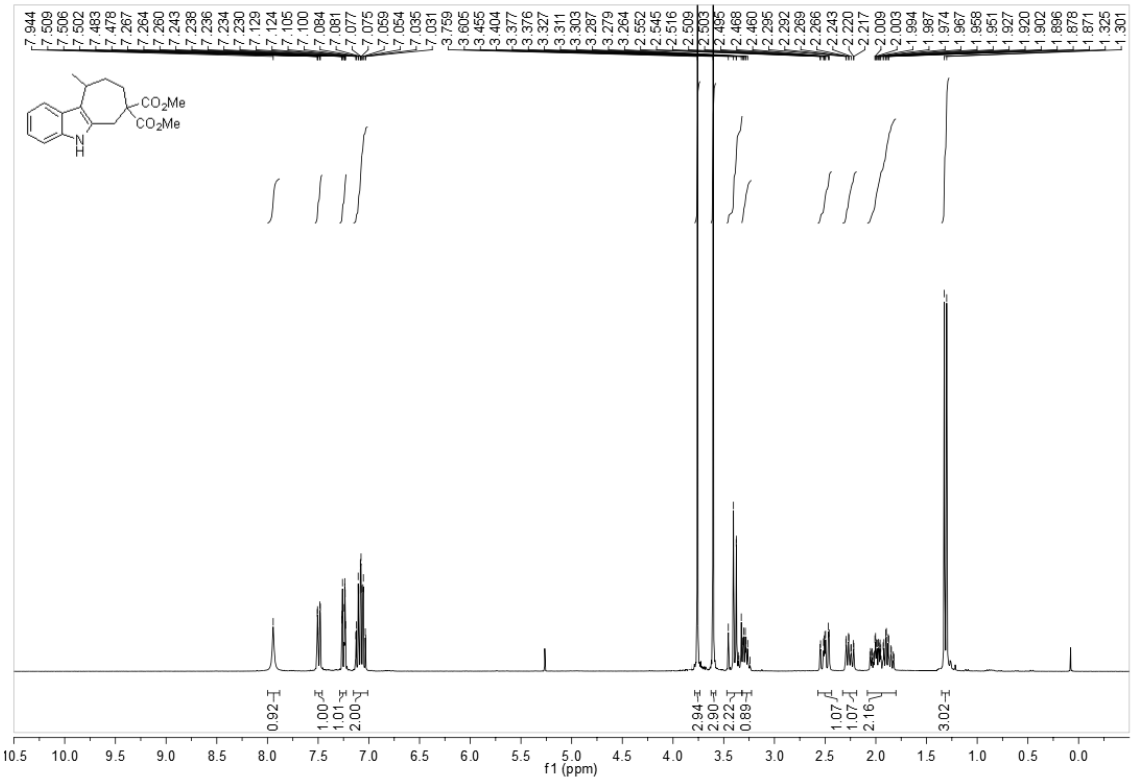


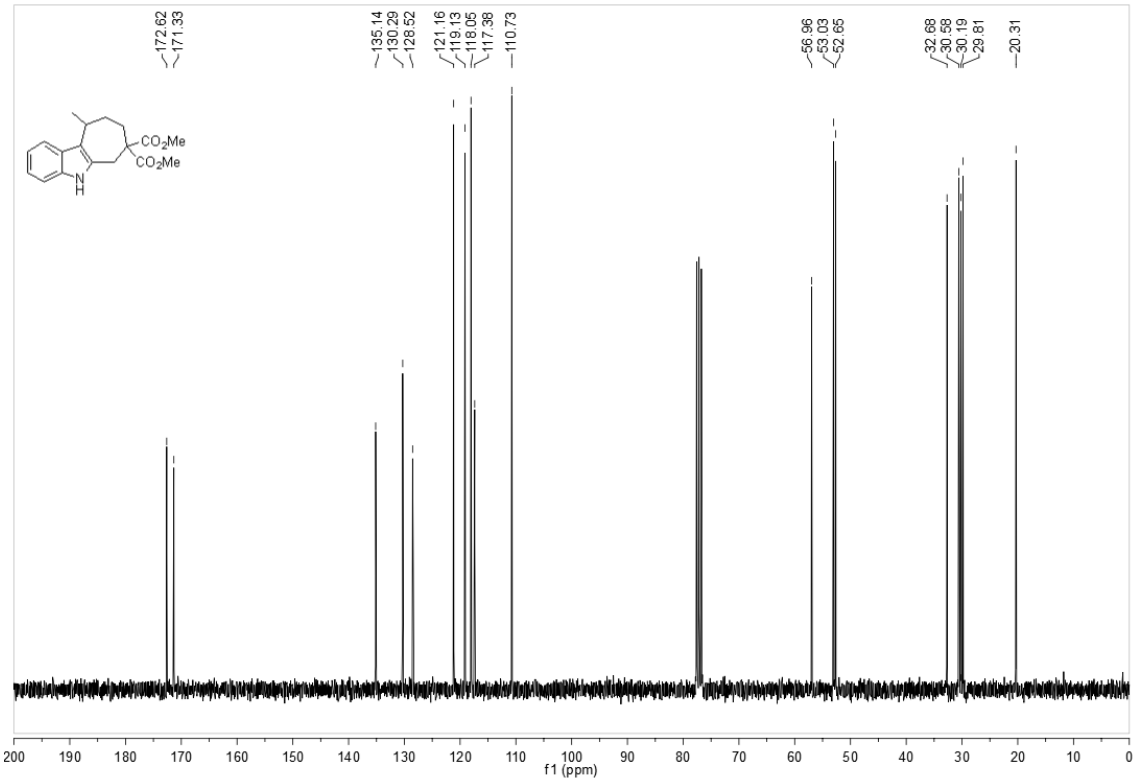
Dimethyl 4,4-dimethyl-3,4-dihydro-1H-carbazole-2,2(9H)-dicarboxylate



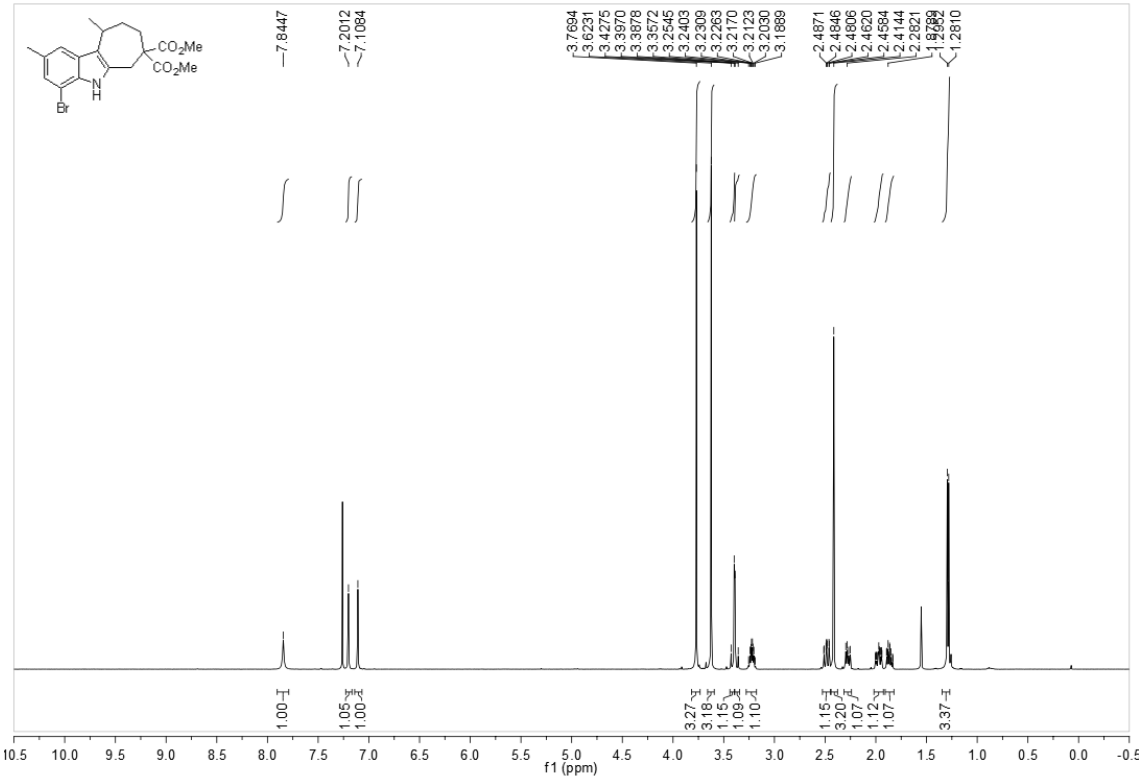


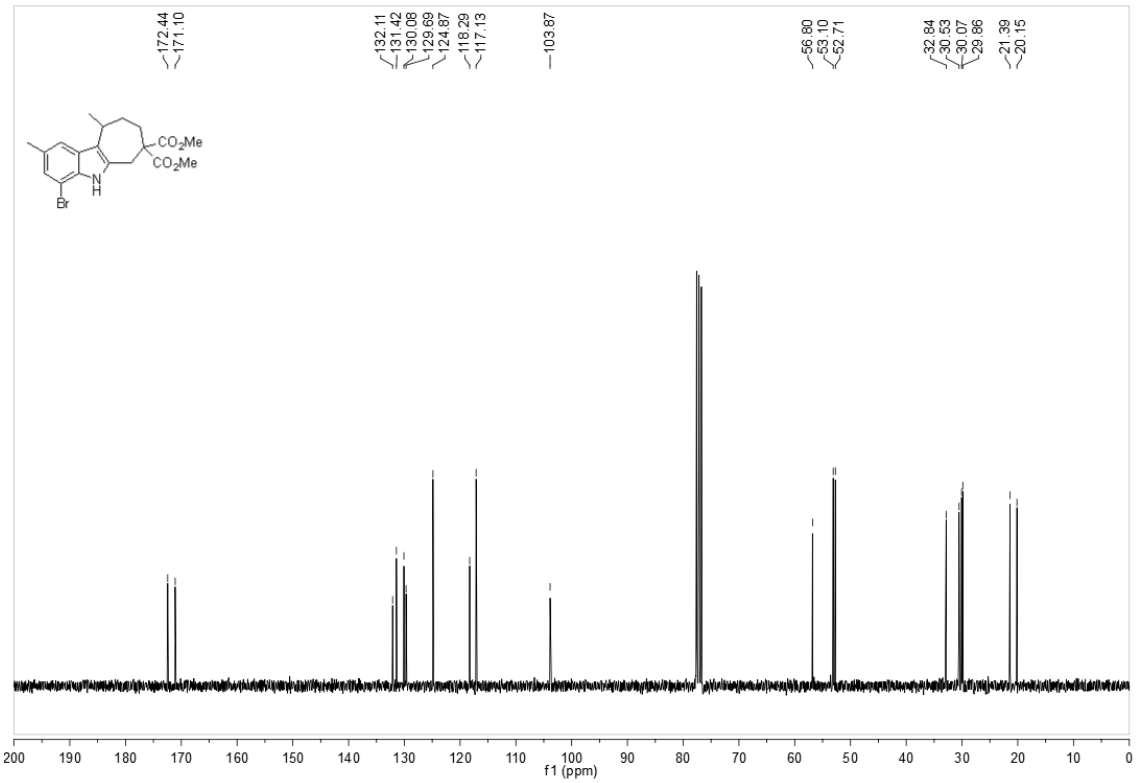
Dimethyl 10-methyl-6,8,9,10-tetrahydrocyclohepta[*b*]indole-7,7(*5H*)-dicarboxylate



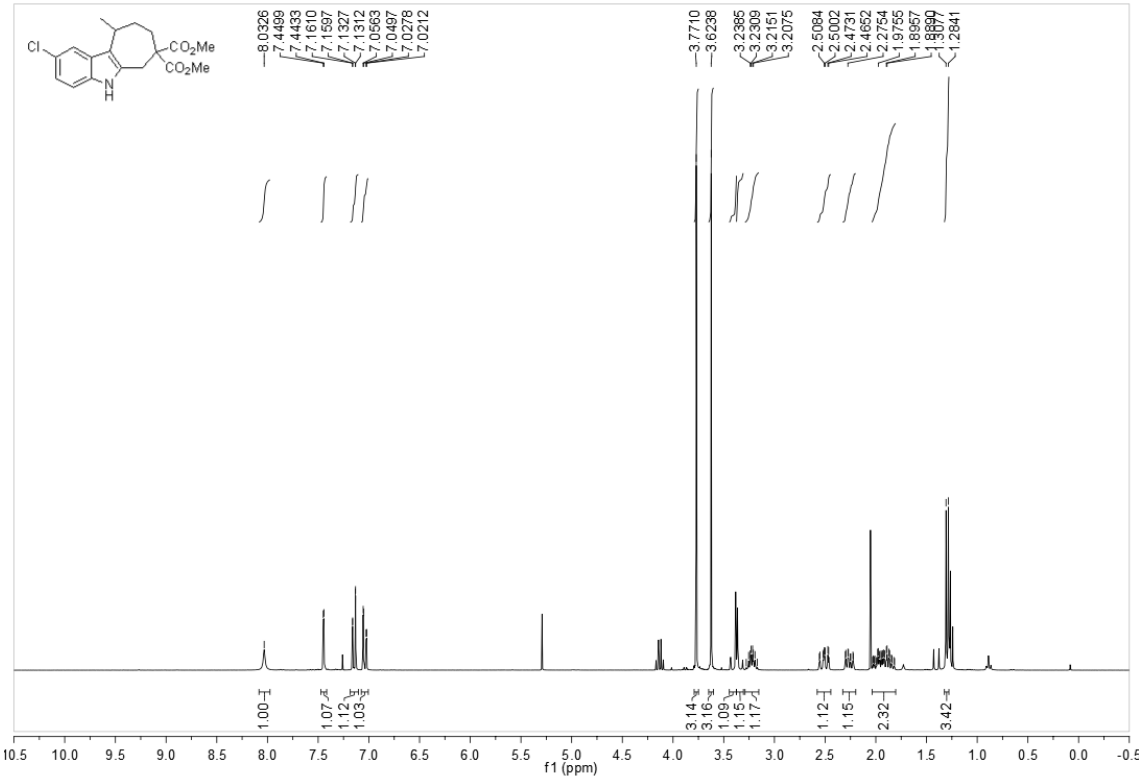


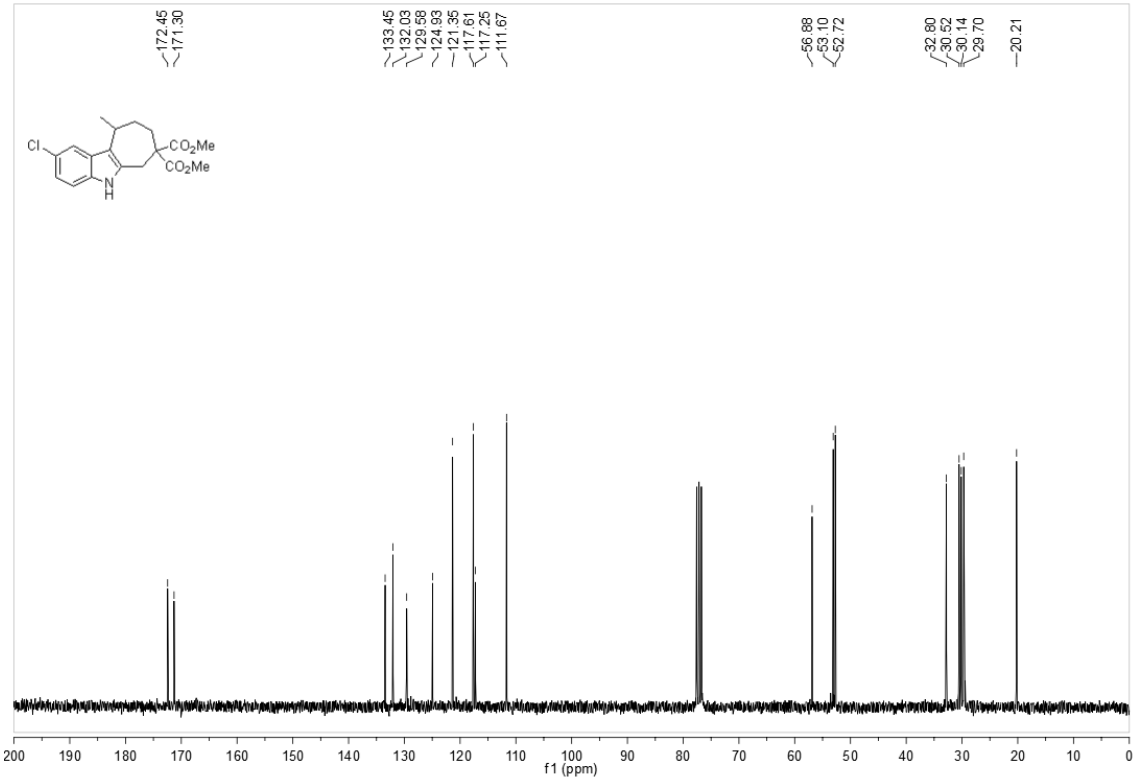
Dimethyl 4-bromo-2,10-dimethyl-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate



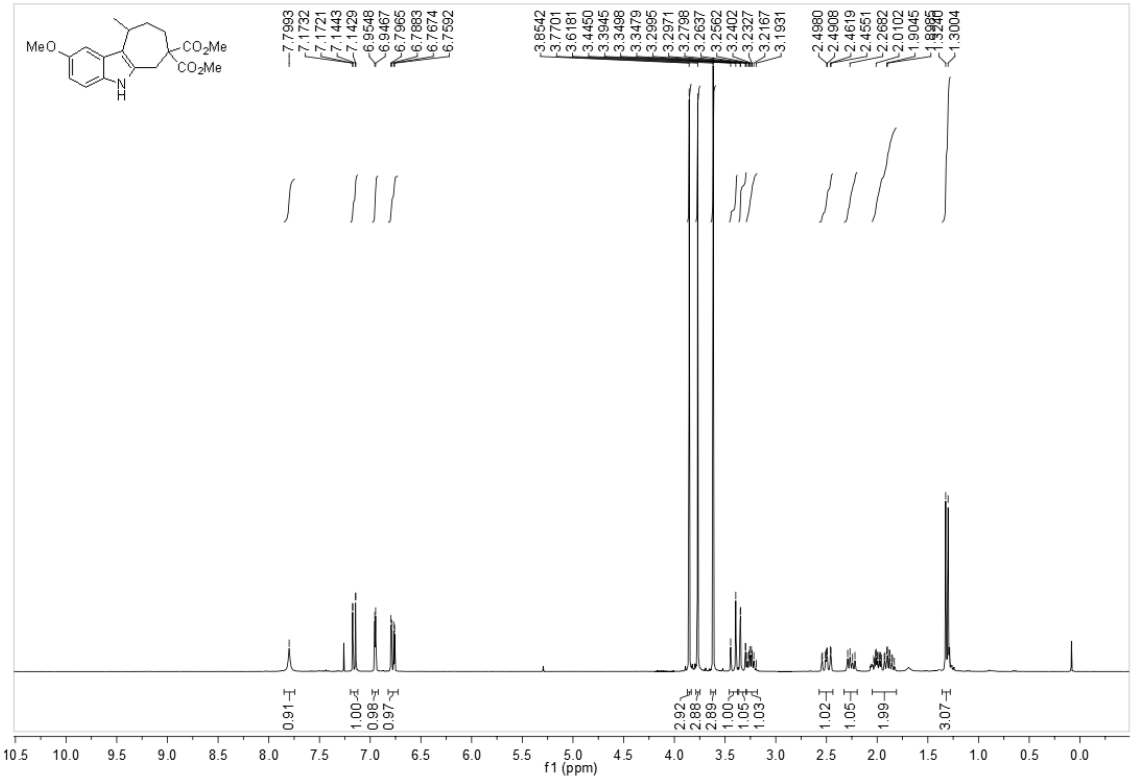


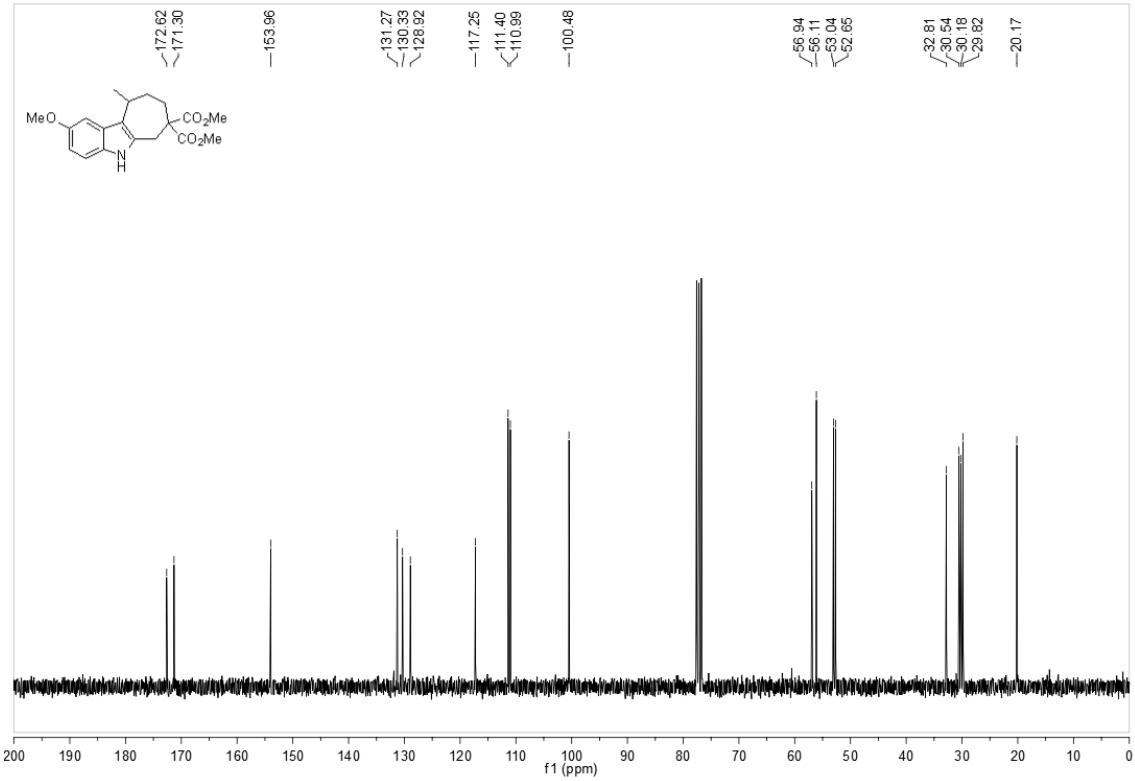
Dimethyl 2-chloro-10-methyl-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate



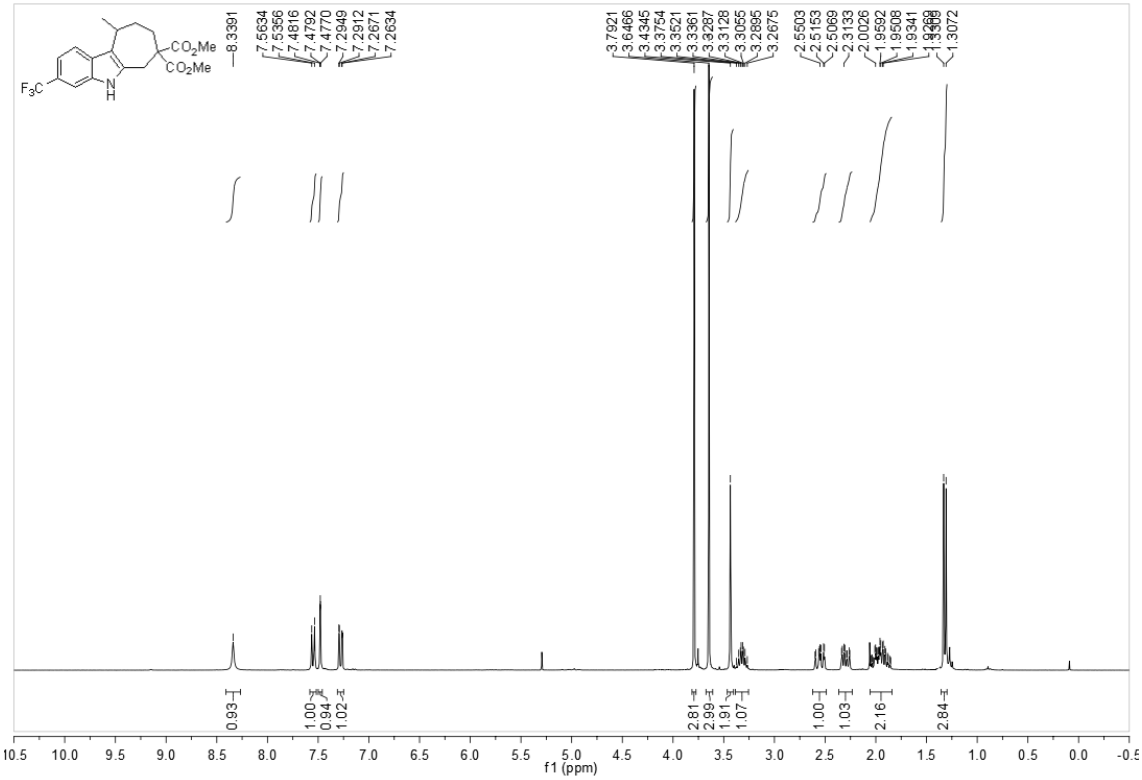


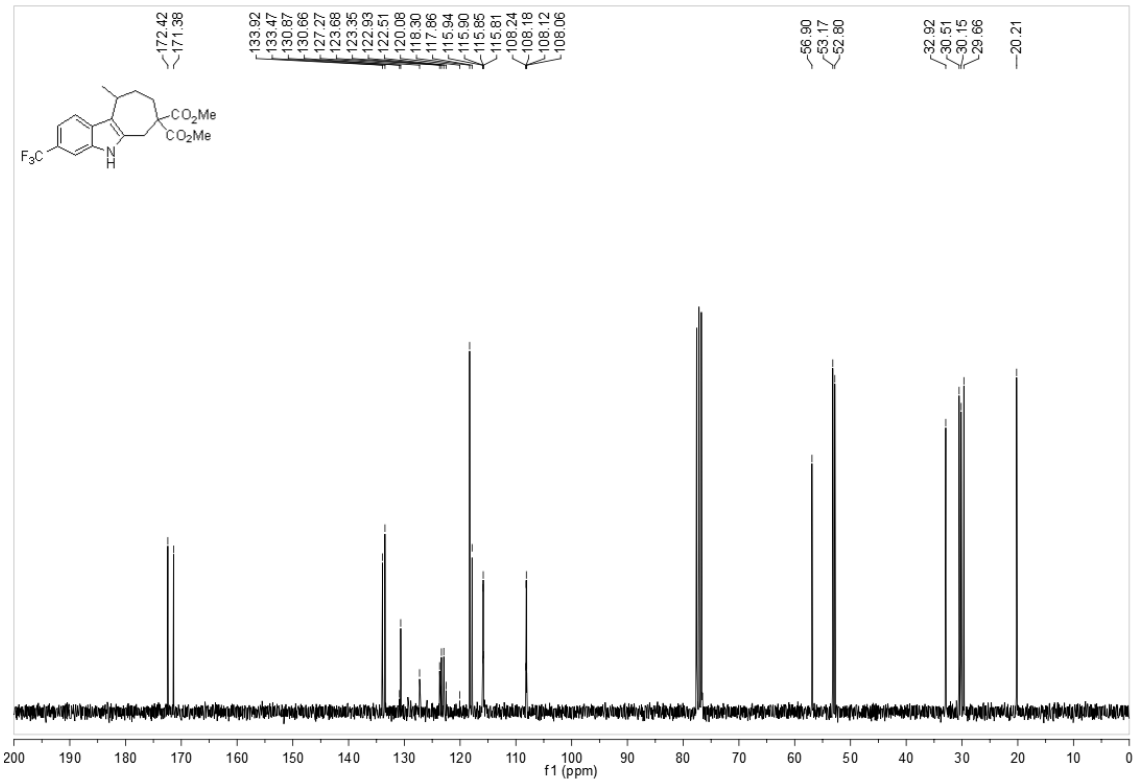
Dimethyl 2-methoxy-10-methyl-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate

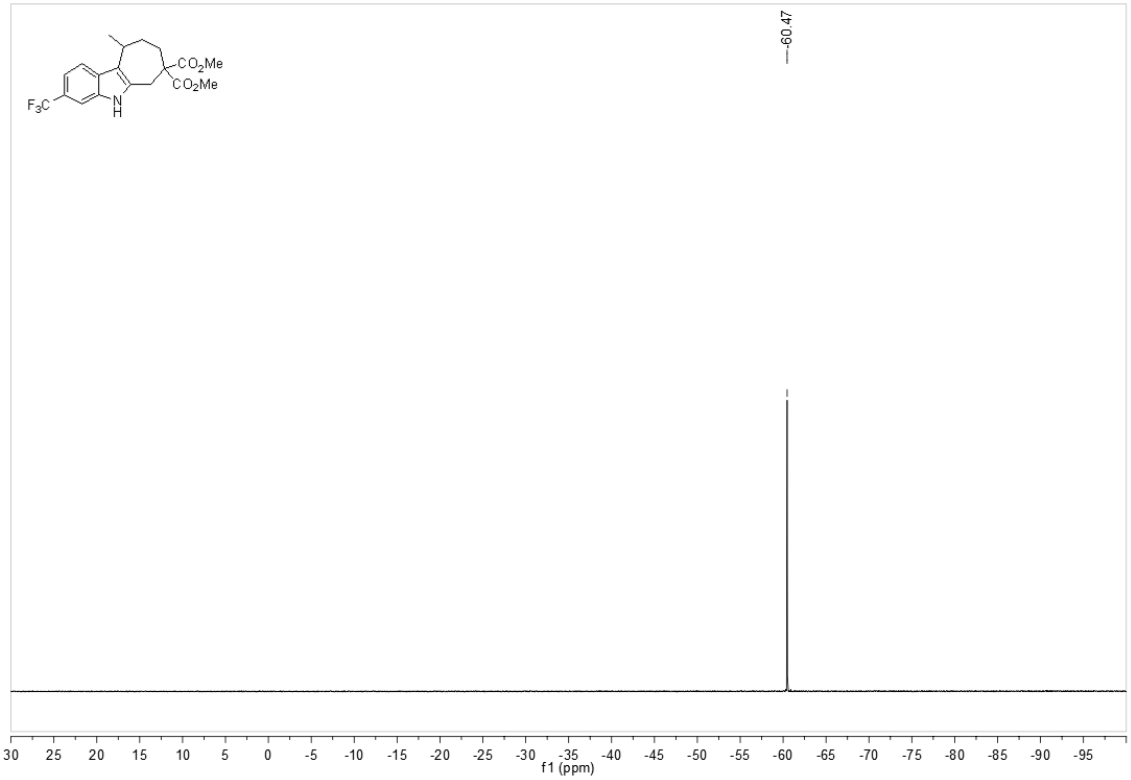




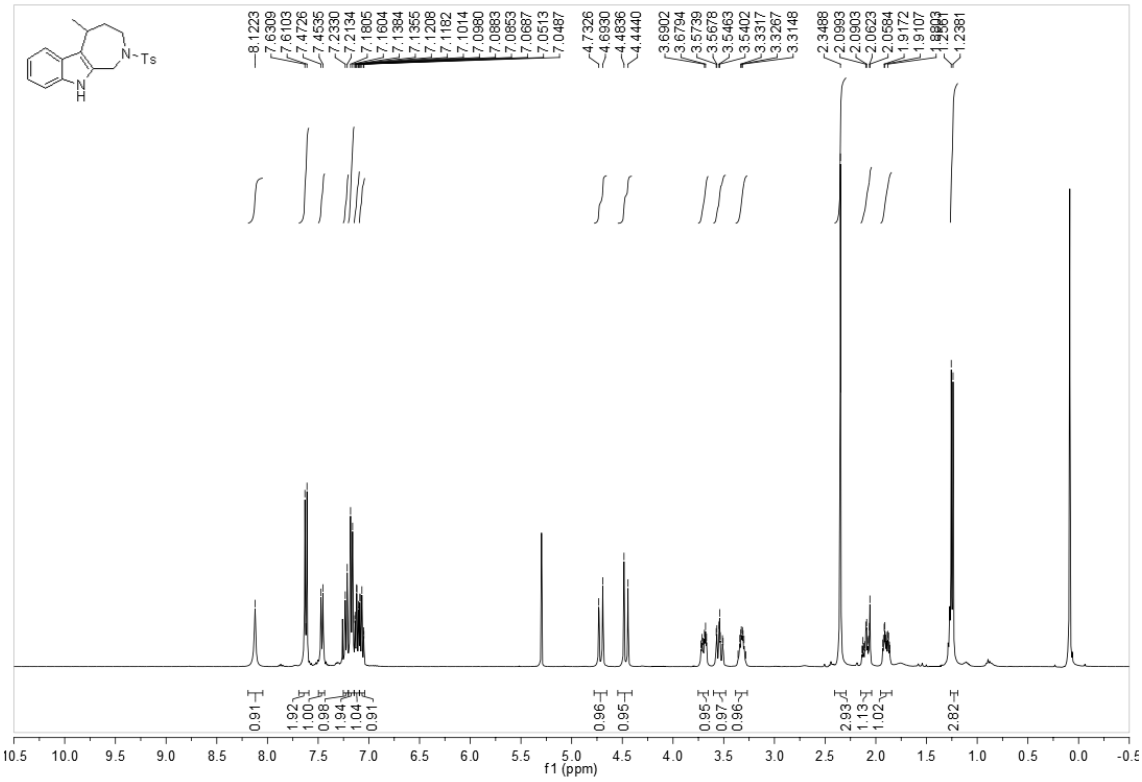
Dimethyl 10-methyl-3-(trifluoromethyl)-6,8,9,10-tetrahydrocyclohepta[b]indole-7,7(5H)-dicarboxylate

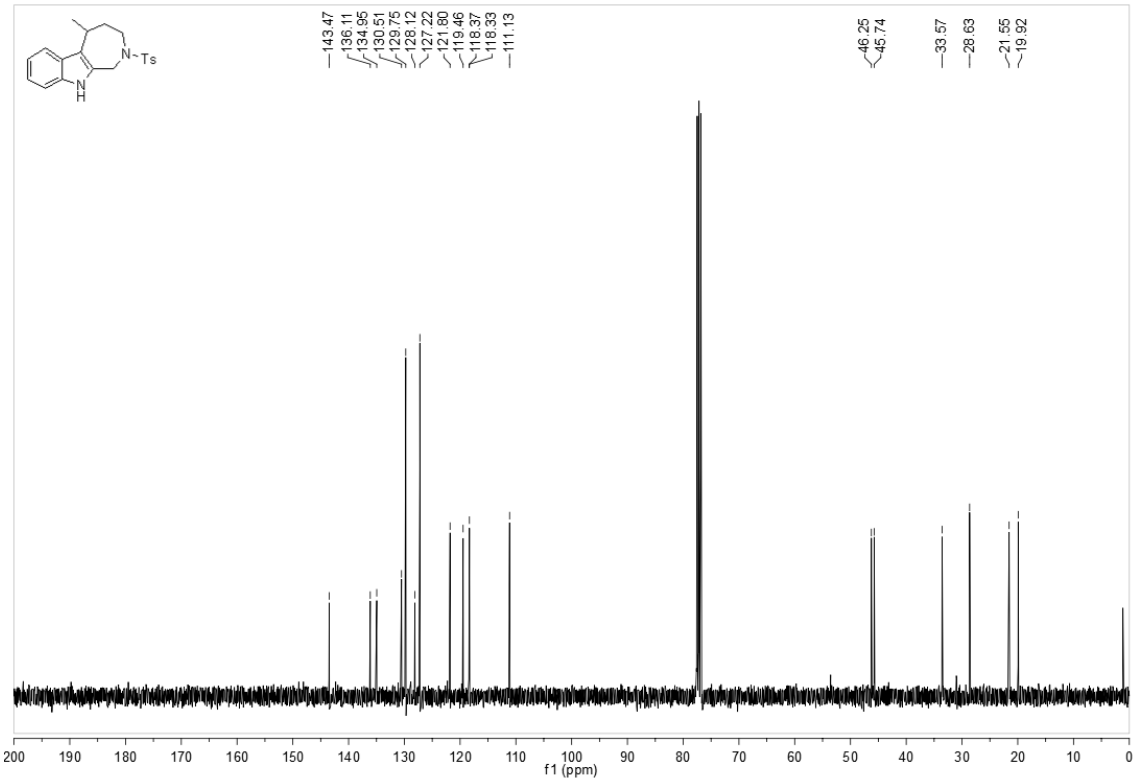




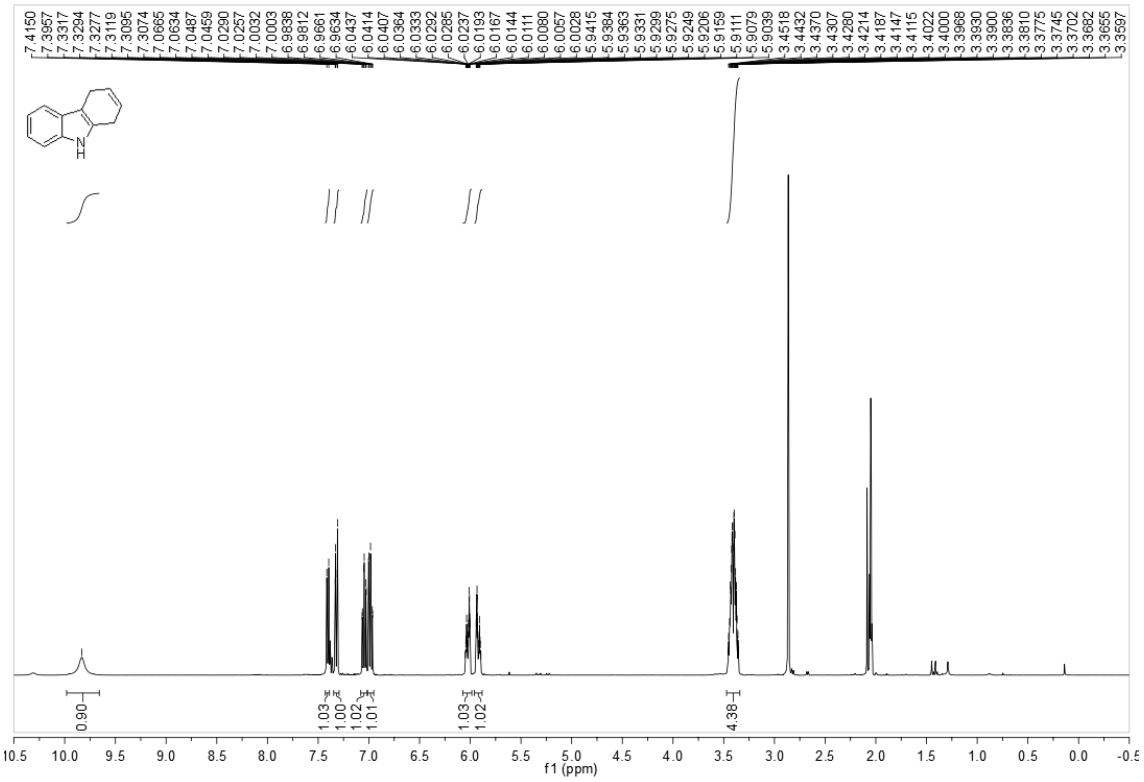

-60.47
CO2Me
CO2Me
F3C
N
H
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

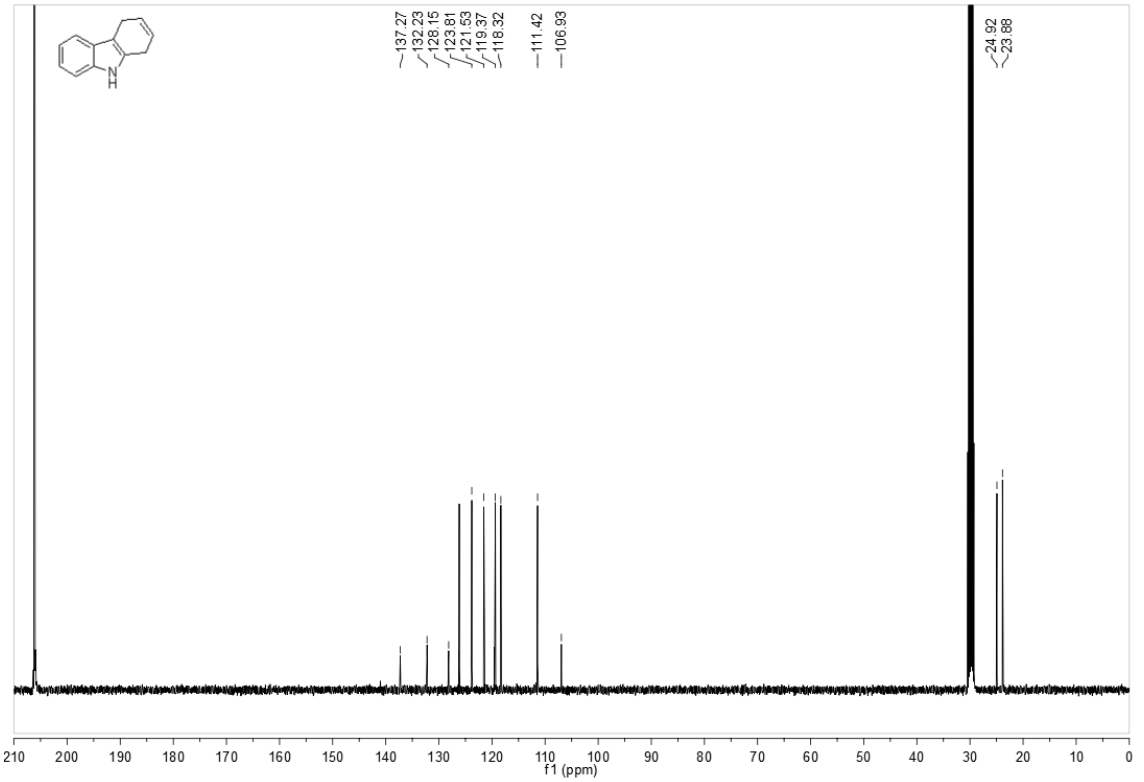
5-methyl-2-tosyl-1,2,3,4,5,10-hexahydroazepino[3,4-b]indole



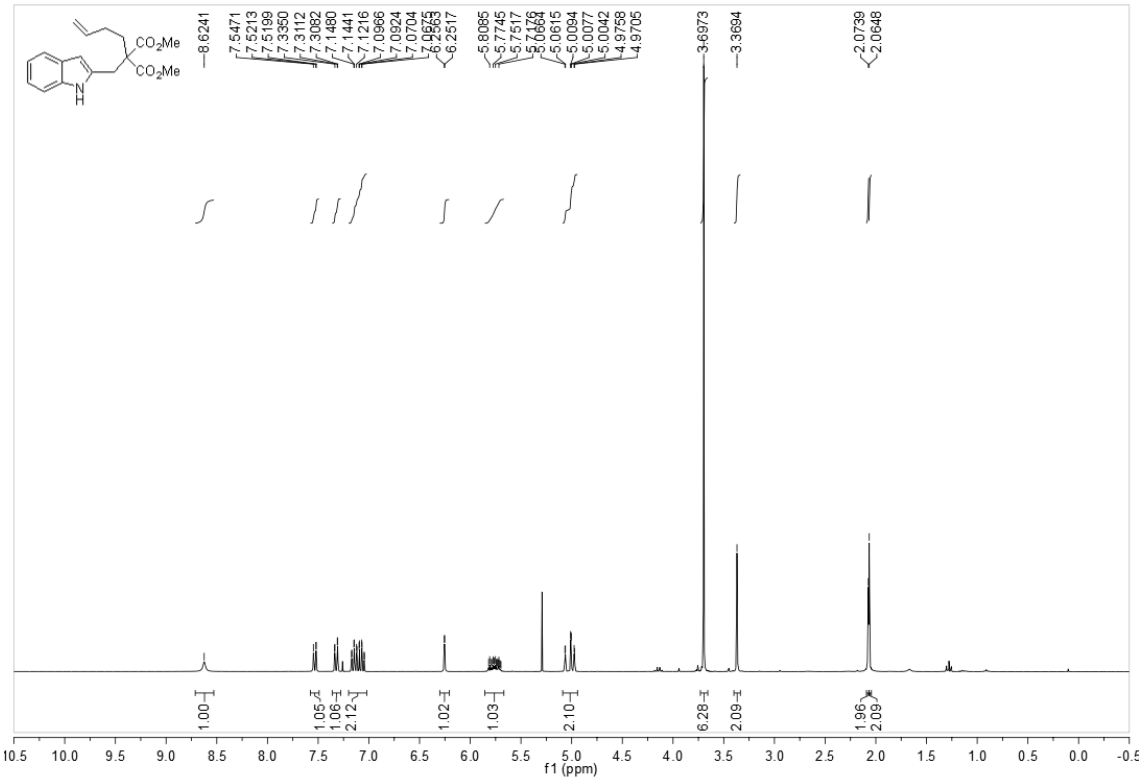


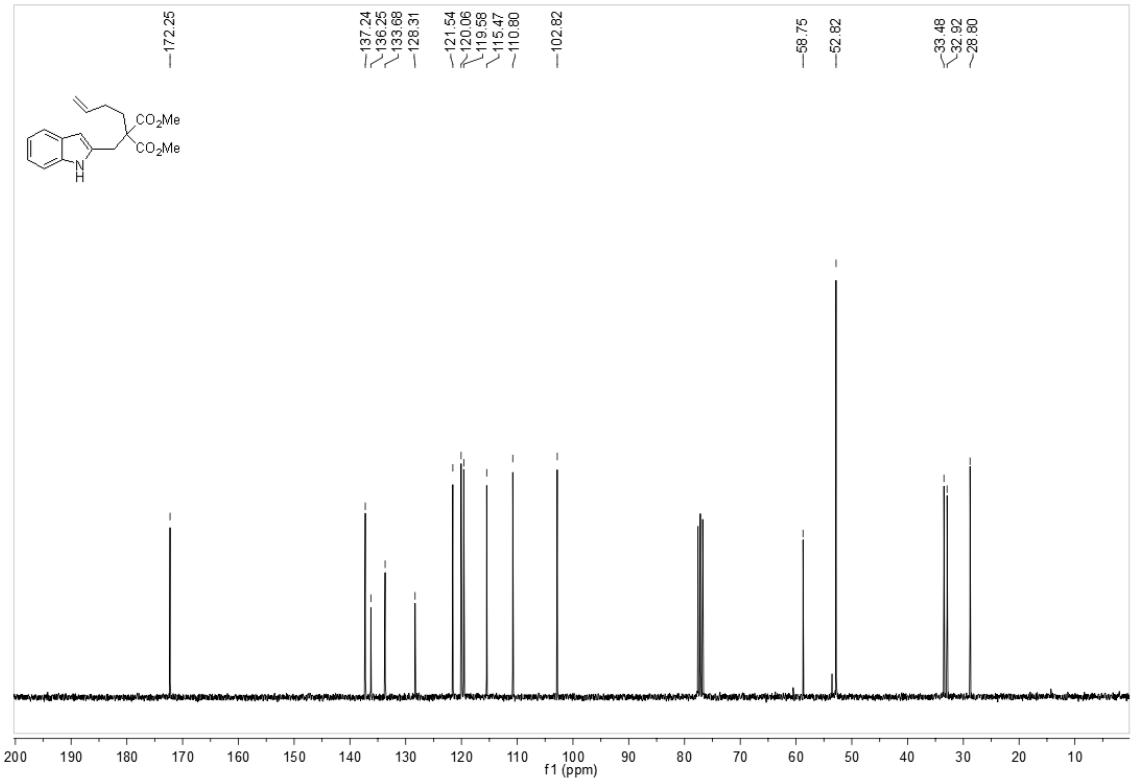
4,9-dihydro-1H-carbazole



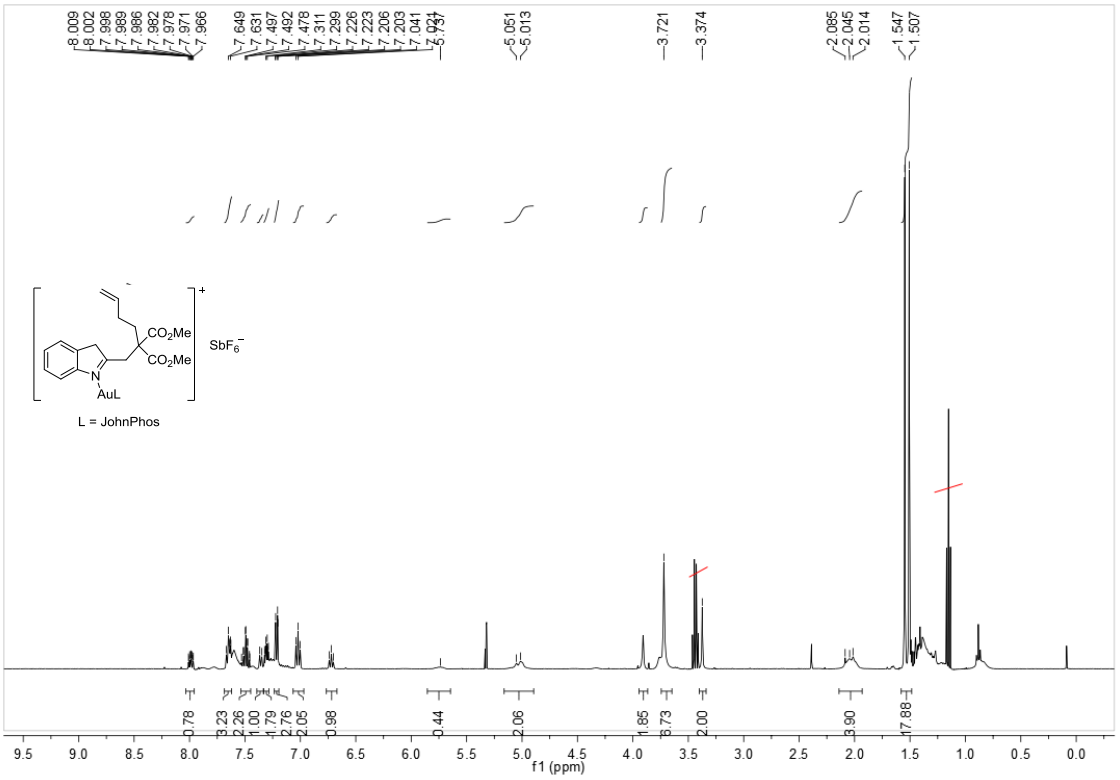


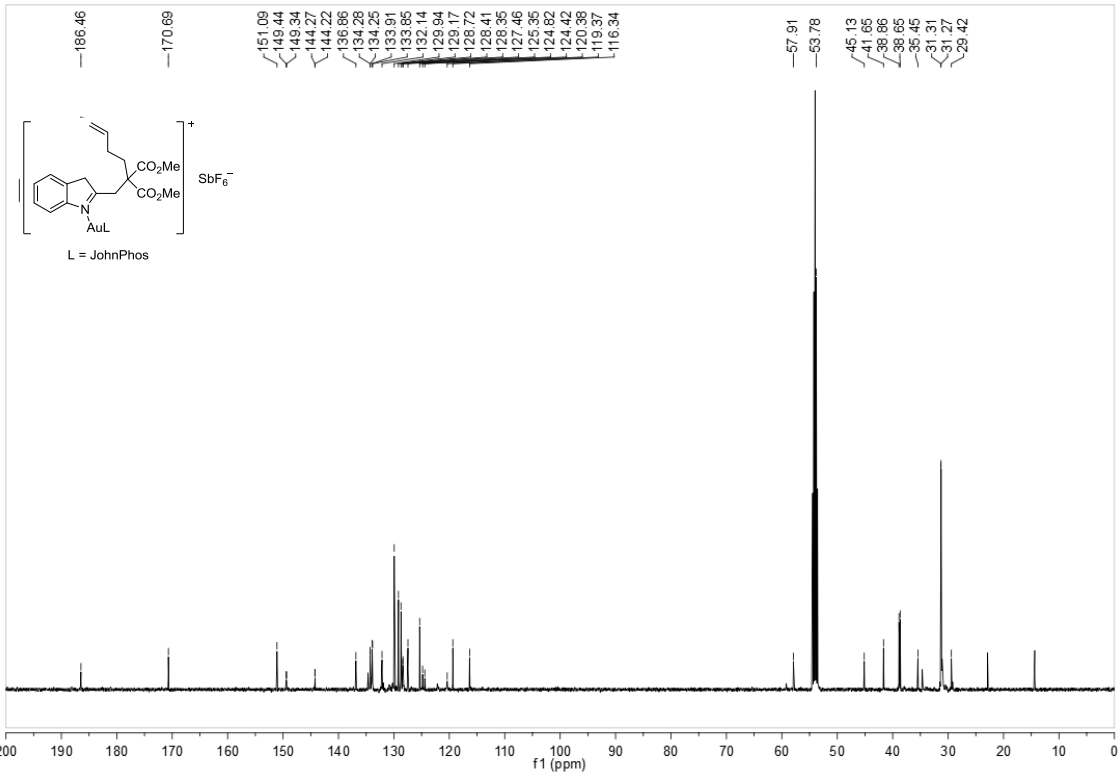
Dimethyl 2-((1H-indol-2-yl)methyl)-2-(but-3-enyl)malonate

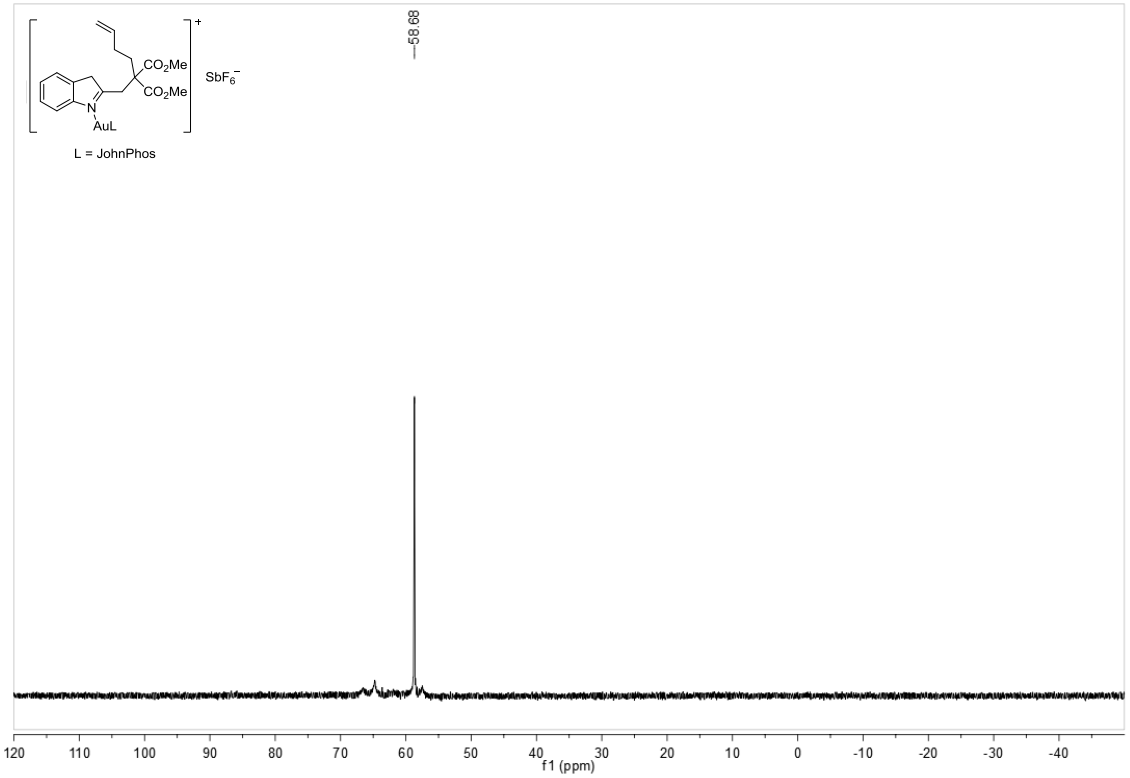




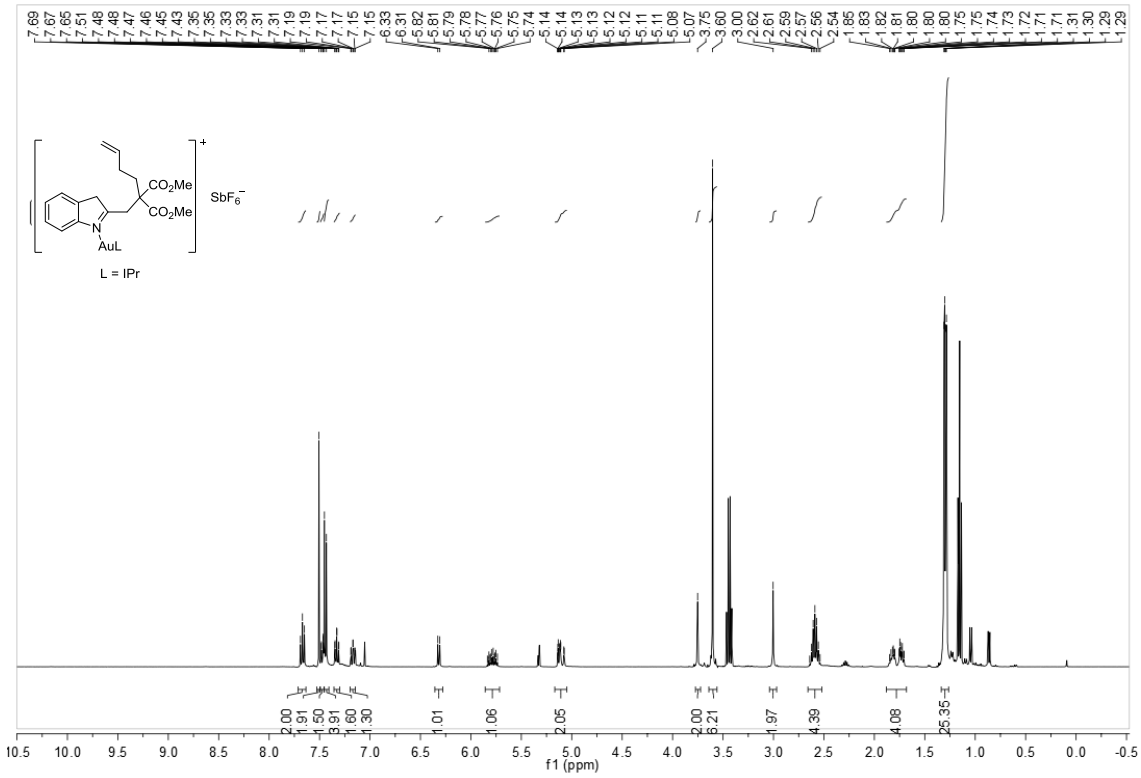
Complex 4

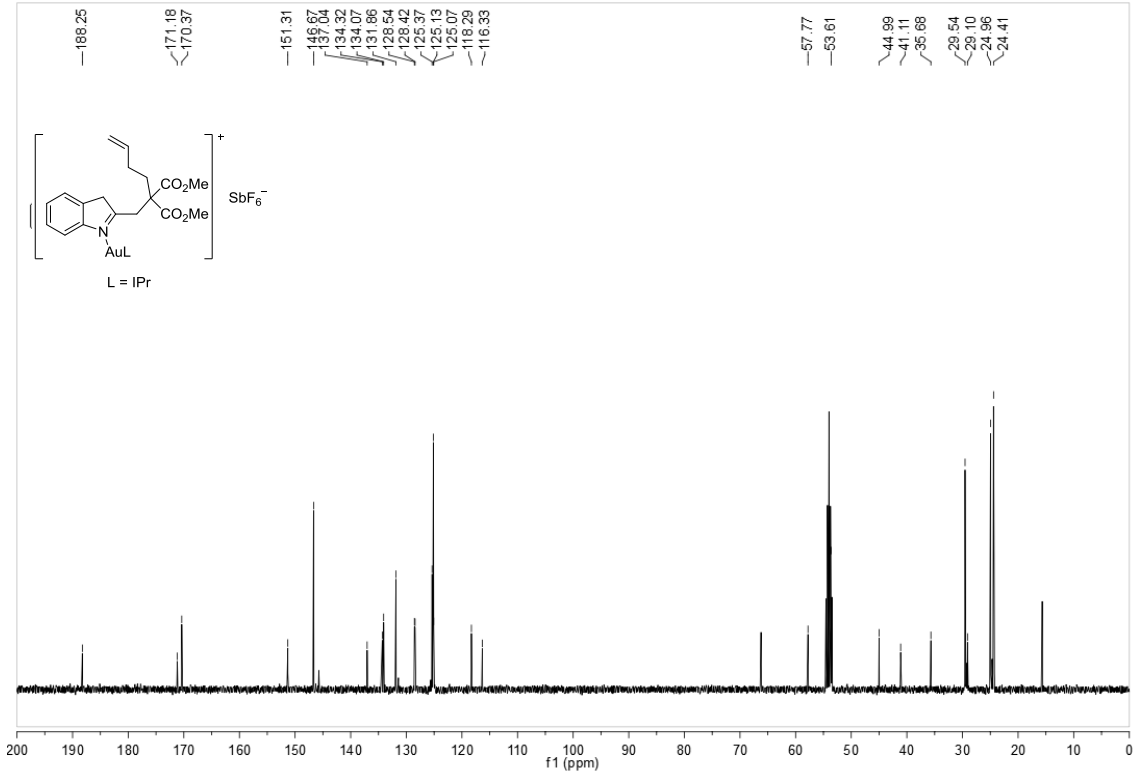

8.009
8.002
7.998
7.989
7.986
7.982
7.978
7.971
7.966
7.649
7.631
7.497
7.492
7.478
7.311
7.299
7.226
7.223
7.206
7.203
7.041
7.031
5.737
5.051
5.013
3.721
3.374
2.085
2.045
2.014
1.547
1.507
CO2Me
CO2Me
SbF6−
N
AuL
L = JohnPhos
0.78
3.23
2.26
1.00
1.79
2.76
2.05
0.98
0.44
2.06
1.85
6.73
2.00
3.90
17.88
f1 (ppm)


186.46
170.69
151.09
149.44
149.34
144.27
144.22
136.86
134.28
134.25
133.91
133.85
132.14
129.94
129.17
128.72
128.41
128.35
127.46
125.35
124.62
124.42
120.38
119.37
116.34
57.91
53.78
45.13
41.65
38.86
38.65
35.45
31.31
31.27
29.42
CO2Me
CO2Me
SbF6−
N
AuL
L = JohnPhos
f1 (ppm)


58.68
CO2Me
CO2Me
SbF6−
N
AuL
L = JohnPhos
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

Complex 5


CO2Me
CO2Me
SbF6−
AuL
L = IPr
f1 (ppm)


CO2Me
CO2Me
SbF6−
AuL
L = IPr
f1 (ppm)

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[1] 2-iodo-4-methoxyaniline was prepared from 5-methoxy-2-nitroaniline in two steps accordind to the procedures described in: S. W. Dantale and B. C. G. Söderberg, *Tetrahedron*, 2003, ***59***, 5507.
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[4] *N*-allyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide was prepared according to the procedure described in: F. Monnier, C. Vovard-Le Bray, D. Castillo, V. Aubert, S. Dérien, P. H. Dixneuf, L. Toupet, A. Lenco and C. Meall, *J. Am. Chem. Soc*. 2007, **129**, 6037 and the properties were consistent with previously reported data: K. T. Sylvester and P. J. Chirik, *J. Am. Chem. Soc*. 2009, **131**, 8772.
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[7] B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.* 2005, **127**, 17644.
[8] *N*-(but-3-enyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide was prepared according to the procedure described in: F. Monnier, C. Vovard-Le Bray, D. Castillo, V. Aubert, S. Dérien, P. H. Dixneuf, L. Toupet, A. Lenco and C. Meall, *J. Am. Chem. Soc*. 2007, **129**, 6037 and the properties were consistent with previously reported data: Y. Kavanagh, C. M. Chaney, J. Muldoon and P. Evans, *J. Org. Chem*. 2008, **73**, 8601.
[9] Y. Kavanagh, C. M. Chaney, J. Muldoon and P. Evans, *J. Org. Chem*. 2008, **73**, 8601.
[10] See ref. 1*.*
[11] C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer and A. M. Echavarren *J. Org. Chem.*, 2008, **73**, 7721.