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Supporting Information

Multi C–H Functionalization Reactions of Carbazole Heterocycles via Gold-Catalyzed Carbene Transfer Reactions

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General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, TCI, abcr, Fluorochem and Carl Roth. Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR were recorded on a Varian AV600/AV400, Agilent DD2 400, Bruker Avance III 300 MHz, Bruker Avance III 400 MHz, or Bruker Avance III 600 MHz Cryo NMR spectrometer in $CDCl_3$. ^{13}C-NMR spectra were recorded at 298 K with proton decoupling. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). Data is expressed in parts per million (ppm) downfield shift relative to the internal reference. HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV. IR spectra were recorded on a Perkin Elmer-100 spectrometer or a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Elemental analysis was performed on an Elementar VarioEL instrument.

Important Safety Note

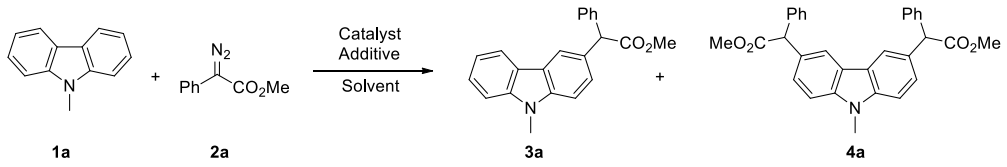
Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

General procedure for the Gold(I) catalyzed multi C-H functionalization reaction (GP)

In an oven dried reaction tube *N*-protected carbazole (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.0 mg, 6 mol-%) were dissolved in 3 mL of dry degassed DCM. The respective diazoalkane (4 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. The completion of the reaction was indicated by the colour change of the reaction mixture from dark orange to black. Solvent was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (*n*-hexane : EtOAc) to afford the desired multi C-H functionalized product as a mixture of diastereoisomers and single regioisomer in terms of site of the C-H functionalization.

Reaction Optimization

Table S1.



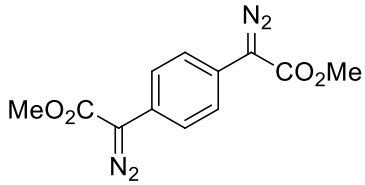
Entry[a]	Catalyst	Additive	Solvent	Total volume (mL)	(3a/4a) Yield %[d]
1	$Pd(OAc)_2$	PPh_3	DCM	2	11 / n.d
2	$Rh_2(OAc)_4$	-	DCM	2	51 / 17
3	$Rh_2(esp)_2$	-	DCM	2	42 / 26
4	$CuPF_6(MeCN)_4$	bipy	DCM	2	19 / n.d.
6	(Ipr)AuCl	$AgSbF_6$	DCM	2	16 / 46
7	(IMes)AuCl	$AgSbF_6$	DCM	2	10 / 49
8	(Xphos)AuCl	$AgSbF_6$	DCM	2	8 / 69[e]
9	(*t*Bu-XPhos)AuCl	$AgSbF_6$	DCM	2	23 / 50
10	(JohnPhos)AuCl	$AgSbF_6$	DCM	2	13 / 61
11	$(tBu_3P)AuNTf_2$	-	DCM	2	42 / 16
11	$dppf(AuCl)_2$	$AgSbF_6$	DCM	2	41 / 31
12	$(L_1)AuCl$	$AgSbF_6$	DCM	2	<5 / 76[e]
13	$(L_1)AuCl$	$AgBF_4$	DCM	2	7 / 32
14	$(L_1)AuCl$	$AgPF_6$	DCM	2	17 / 44
15	**$(L_1)AuCl$**	**$AgSbF_6$**	**DCM**	**4**	**<5 / 84[e]**
16	$(L_1)AuCl$	$AgSbF_6$	$CHCl_3$	4	<5 / 74[e]
17	$(L_1)AuCl$	$AgSbF_6$	THF	4	9 / 48
18	$(L_1)AuCl$	$AgSbF_6$	1,4-dioxane	4	18 / 9
19	$(L_1)AuCl$	$AgSbF_6$	Toluene	4	12 / 19
20	$(L_1)AuCl$	$AgSbF_6$	EtOAc	4	20 / 27
21	$(L_1)AuCl$	$AgSbF_6$	DMF	4	13 / 7
22[b]	$(L_1)AuCl$	$AgSbF_6$	DCM	4	<5 / 86[e]
23[c]	$(L_1)AuCl$	$AgSbF_6$	DCM	4	13 / 43

Reaction Condition: [a] 9-methyl-9*H*-carbazole **1a** (0.2 mmol, 1.0 equiv.), 5 mol-% catalyst, 6 mol-% additive were dissolved in 1.5 mL or 3 mL of dry degassed solvent. Methyl 2-diazo-2-phenylacetate **2a** (0.8 mmol, 4.0 equiv.) was dissolved in 0.5 mL or 1 mL of dry degassed solvent (solvent volume was used as mentioned in the table) and added to the reaction mixture slowly over 60 min and stirred additional 2 h at RT under argon atmosphere; [b] 1.2 mmol (6.0 equiv.) of methyl 2-diazo-2-phenylacetate **2a** was used; [c] Methyl 2-diazo-2-phenylacetate **2a** (0.8 mmol, 4.0 equiv.) was added in one portion; [d] ^{1}H NMR yield, 0.2 mmol mesitylene was used as an internal standard; [e] Isolated yield.

IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, **IMes** = 1,3-dimesitylimidazol- 2-ylidene; **XPhos** = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl, **tBu-XPhos** = 2-di-*tert*-butyl(2′,4′,6′-triisopropylbiphenyl)phosphine, **JohnPhos** = (1,1′-biphenyl-2-yl)di-*tert*-butylphosphine, **dppf** = 1,1'- bis(diphenylphoshino)ferrocene, $\mathbf{L_1}$ = tris(2,4-di-*tert*.-butylphenyl)phosphite.

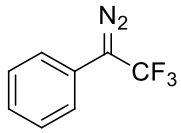
Characterization data of compounds

Dimethyl 2,2'-(1,4-phenylene)bis(2-diazoacetate) (11)



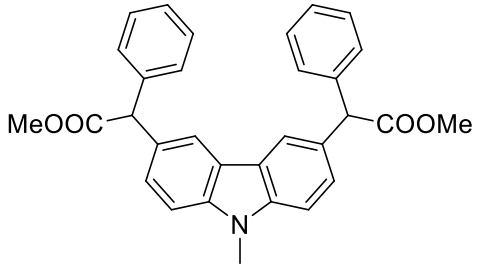
DBU (12.6 mmol, 2.8 equiv.) was added to a solution of the dimethyl 2,2'-(1,4-phenylene)diacetate (1.0 g, 4.5 mmol, 1.0 equiv.) and *p*-tosyl azide (9.9 mmol, 2.2 equiv.) in 40 mL MeCN at 0 °C. The reaction mixture was stirred over night while slowly warming up to room temperature. The reaction mixture was quenched with sat. NH_4Cl solution and extracted with DCM. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica column chromatography (*n*-hexane : EtOAc – 40:1 → 20:1) and the desired product was obtained as an orange solid (63%, 776 mg).
^{1}H NMR (300 MHz, Chloroform-*d*): δ = 7.52 (s, 4H), 3.89 (s, 6H) ppm.
^{13}C NMR (76 MHz, Chloroform-*d*): δ =165.5, 124.4, 122.8, 52.0 ppm.
IR (neat): 3236, 3100, 3031, 2961, 2848, 2587, 2385, 2478, 2085, 1927, 1695, 1595, 1595, 1514, 1435, 1340, 1284, 1236, 1188, 1151, 1046, 901, 833, 734 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{12}H_{10}O_4N_4Na^+$:297.0594; Found: 297.0593.

(1-diazo-2,2,2-trifluoroethyl)benzene (13)



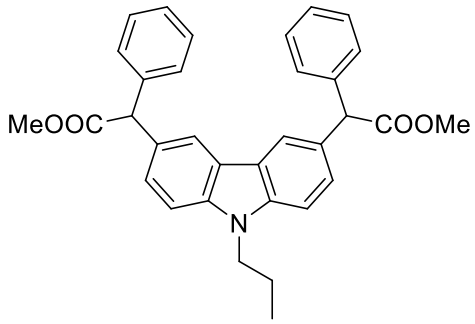
Diazo 14 was prepared according to the literature procedure: G. Pisella, A. Gagnebin, J. Waser, *Chem. Eur.J.* **2020**, *26*, 10199 –10204.
^{1}H NMR (300 MHz, Chloroform-*d*): δ = 7.44 – 7.36 (m, 1H), 7.23 – 7.17 (m, 1H), 7.10 (dq, *J* = 7.8, 1.0 Hz, 1H) ppm.
^{19}F NMR (282 MHz, Chloroform-*d*): δ = -57.41 ppm.

Dimethyl 2,2'-(9-methyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4a)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (84%, 80 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.05 (br, 2H), 7.47 – 7.44 (m, 2H), 7.41 – 7.32 (m, 10H), 7.31 – 7.26 (m, 2H), 5.25 (s, 2H), 3.83 (s, 3H), 3.80 (s, 6H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 140.6, 139.5, 129.2, 128.58, 128.56, 127.1, 126.6, 122.8, 120.5, 108.6, 57.0, 52.3, 29.1 ppm.
IR (KBr): 3458, 3031, 2961, 2912, 2804, 2638, 2263, 2081, 1876, 1726, 1481, 1448, 1281, 1234, 1152, 1079, 991, 900, 815, 736, 699 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{31}H_{27}NNaO_4^+$: 500.1832; Found: 500.1840.

Dimethyl 2,2'-(9-propyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4b)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (82%, 83 mg).

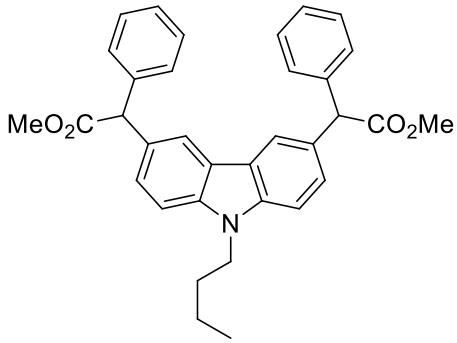
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.08 – 8.05 (m, 2H), 7.46 – 7.40 (m, 3H), 7.39 – 7.34 (m, 9H) 7.32 – 7.25 (m, 2H), 5.26 (s, 2H), 4.24 (t, *J* = 7.1 Hz, 2H), 3.81 (s, 6H), 1.91 (heptet, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.6, 140.1, 139.5, 129.0, 128.5, 127.1, 126.5, 122.8, 120.51, 120.50, 108.9, 57.0, 52.3, 44.7, 22.3, 11.8 ppm.

IR (neat): 3026, 2950, 2644, 2252, 2088, 1872, 1729, 1603, 1487, 1452, 1271, 1223, 1193, 1151, 1075, 1005, 908, 800, 730, 696 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{33}H_{31}NNaO_4^+$: 528.2145; Found: 528.2146.

Dimethyl 2,2'-(9-butyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4c)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (75%, 78 mg).

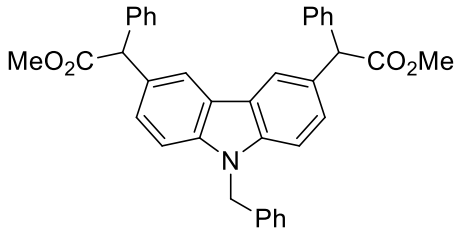
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.08 – 8.05 (m, 2H), 7.46 – 7.43 (m, 2H), 7.42 – 7.35 (m, 10H), 7.32 – 7.27 (m, 2H), 5.26 (s, 2H), 4.27 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 6H), 1.89 – 1.78 (m, 2H), 1.46 – 1.36 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.6, 140.1, 139.5, 129.1, 128.5, 127.1, 126.5, 122.8, 120.5, 108.9, 57.0, 52.3, 43.0, 31.2, 20.5, 13.8 ppm.

IR (KBr): 3495, 3030, 2953, 2874, 2165, 1969, 1885, 1734, 1604, 1487, 1454, 1331, 1155, 1007, 921, 886, 802, 732, 698 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{34}H_{34}NO_4^+$: 520.2482; Found: 520.2489.

Dimethyl 2,2'-(9-benzyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4d)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless foam (81%, 90 mg).

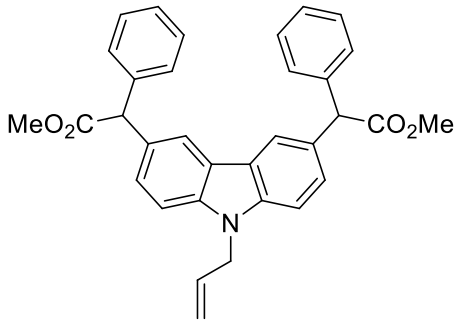
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.11 (s, 2H), 7.44 – 7.41 (m, 6H), 7.38 (t, *J* = 7.6 Hz, 4H), 7.35 – 7.26 (m, 7H), 7.19 – 7.16 (m, 2H), 5.47 (s, 2H), 5.27 (s, 2H), 3.82 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 140.3, 139.4, 137.0, 129.6, 128.8, 128.63, 128.60, 127.5, 127.1, 126.8, 126.5, 123.1, 120.5, 109.1, 57.0, 52.3, 46.7 ppm.

IR (KBr): 3480, 3021, 2957, 2877, 2169, 1981, 1887, 1735, 1606, 1486, 1441, 1402, 1332, 1209, 1154, 1007, 923, 909, 881, 829, 736, 662 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{37}H_{31}NNaO_4^+$: 576.2145; Found: 576.2151.

Dimethyl 2,2'-(9-allyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4e)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (87%, 88 mg).

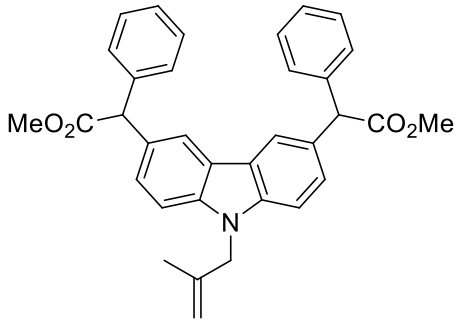
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.09 – 8.07 (m, 2H), 7.48 – 7.27 (m, 14H), 6.03 – 5.94 (m, 1H), 5.26 (s, 2H), 5.21 – 5.16 (m, 1H), 5.11 – 5.06 (m, 1H), 4.90 – 4.86 (m, 2H), 3.81 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 140.0, 139.5, 132.2, 129.4, 128.6, 128.5, 127.1, 126.6, 123.0, 120.5, 117.0, 109.0, 57.0, 52.3, 45.4 ppm.

IR (KBr): 3485, 3027, 2950, 2164, 1965, 1878, 1732, 1605, 1487, 1325, 1275, 1192, 1153, 1078, 1006, 922, 847, 803, 728, 699 cm^{-1}.

HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd. for $C_{33}H_{29}NNaO_4^+$: 526.1988; Found: 526.1996.

Dimethyl 2,2'-(9-(2-methylallyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4f)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (68%, 70 mg).

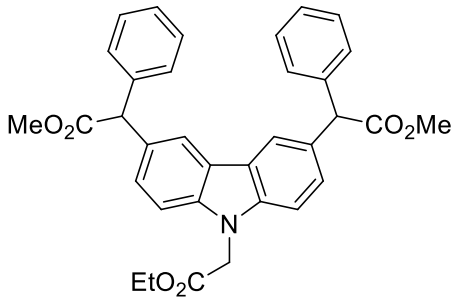
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.06 (d, *J* = 1.7 Hz, 2H), 7.49 – 7.24 (m, 14H), 5.25 (s, 2H), 4.93 – 4.87 (m, 1H), 4.78 (s, 2H), 4.76 – 4.69 (m, 1H), 3.80 (s, 6H), 1.73 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.5, 140.3, 140.1, 139.4, 129.3, 128.5, 127.1, 126.6, 122.9, 120.4, 112.3, 109.1, 57.0, 52.3, 49.1, 20.0 ppm.

IR (neat): 3502, 3026, 2981, 2950, 2340, 2253, 2084, 1881, 1731, 1604, 1490, 1433, 1371, 1322, 1236, 1193, 1152, 1043, 1006, 905, 846, 802, 729, 697 cm^{-1}.

HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd. for $C_{34}H_{31}O_4NNa^+$: 540.2145; Found: 540.2140.

Dimethyl 2,2'-(9-(2-ethoxy-2-oxoethyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4g)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) as a colorless gel (78%, 86 mg).

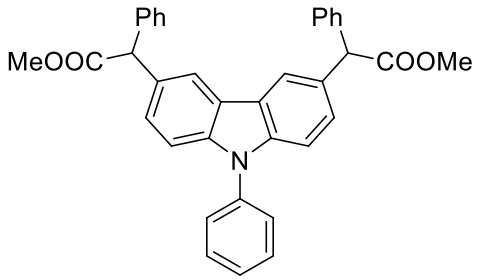
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.08 – 8.04 (m, 2H), 7.46 – 7.43 (m, 2H), 7.41 – 7.34 (m, 8H), 7.32 – 7.27 (m, 4H), 5.25 (s, 2H), 4.96 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.4, 168.3, 140.1, 139.3, 130.0, 128.6, 128.5, 127.1, 126.9, 123.3, 120.7, 108.6, 61.7, 56.9, 52.3, 44.8, 14.1 ppm.

IR (KBr): 3454, 3027, 2951, 2163, 2041, 1878, 1732, 1606, 1488, 1434, 1272, 1192, 1153, 1076, 1009, 922, 880, 802, 731, 700 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{34}H_{31}NNaO_6^+$: 572.2043; Found: 572.2048.

Dimethyl 2,2'-(9-phenyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4h)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (66%, 71 mg).

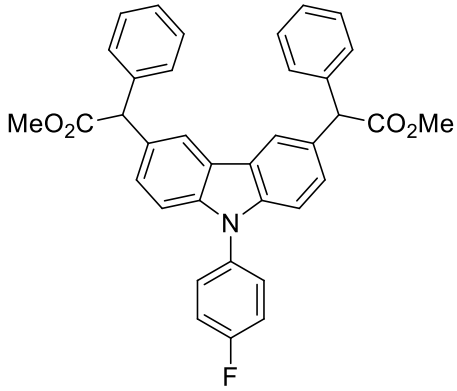
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.09 (s, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.41 – 7.33 (m, 12H), 7.31 – 7.27 (m, 3H), 5.25 (s, 2H), 3.80 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.4, 140.5, 139.3, 137.5, 130.3, 129.8, 128.6, 128.5, 127.5, 127.1, 126.9, 126.8, 123.4, 120.4, 110.0, 56.9, 52.3 ppm.

IR (KBr): 3059, 3027, 2939, 2842, 2669, 2081, 1997, 1892, 1732, 1605, 1493, 1265, 1234, 1279, 1231, 1158, 1011, 921, 831, 816, 728, 662 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{36}H_{29}NNaO_4^+$: 562.1988; Found: 562.1981.

Dimethyl 2,2'-(9-(4-fluorophenyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4i)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (75%, 84 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.13 (s, 2H), 7.52 – 7.48 (m, 2H), 7.44 – 7.40 (m, 6H), 7.38 (t, *J* = 7.6 Hz, 4H), 7.34 – 7.27 (m, 6H), 5.29 (s, 2H), 3.83 (s, 6H) ppm.

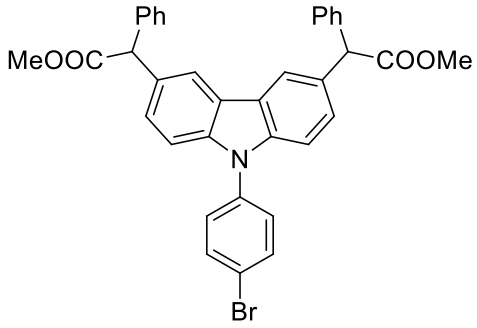
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 161.7 (d, *J* = 247.1 Hz), 140.6, 139.3, 133.4 (d, *J* = 3.5 Hz), 130.5, 128.8 (d, *J* = 8.5 Hz), 128.6, 128.5, 127.2, 127.0, 123.3, 120.5, 116.9 (d, *J* = 22.9 Hz), 109.8, 57.0, 52.4 ppm.

^{19}F NMR (565 MHz, Chloroform-*d*): δ = -113.24 – -113.42 (m) ppm.

IR (KBr): 3877, 3452, 3062, 3028, 2951, 2844, 2666, 2325, 2254, 2087, 1992, 1895, 1733, 1603, 1509, 1459, 1282, 1231, 1154, 1008, 908, 837, 810, 729 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{36}H_{28}FNNaO_4^+$: 580.1894; Found: 580.1901.

Dimethyl 2,2'-(9-(4-bromophenyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4j)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless gel (85%, 105 mg).

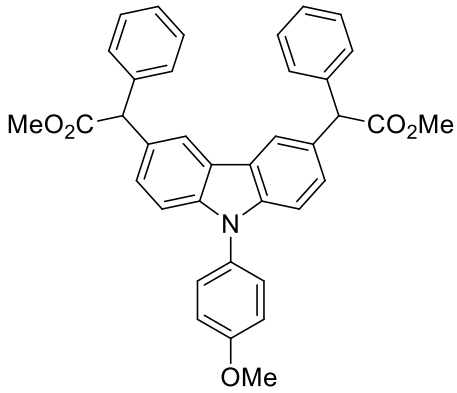
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.11 – 8.08 (m, 2H), 7.79 – 7.69 (m, 2H), 7.49 – 7.25 (m, 16H), 5.26 (s, 2H), 3.81 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.4, 140.2, 139.2, 136.6, 133.1, 130.7, 129.6, 128.6, 128.5, 127.2, 127.0, 123.5, 121.0, 120.6, 109.8, 56.9, 52.3 ppm.

IR (neat): 3026, 2948, 2299, 2079, 1893, 1730, 1602, 1489, 1318, 1267, 1230, 1192, 1151, 1068, 1008, 913, 808, 733, 696 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{36}H_{28}O_4NBrNa^+$: 640.1093; Found: 640.1098.

Dimethyl 2,2'-(9-(4-methoxyphenyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4k)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) as a colorless foam (86%, 98 mg).

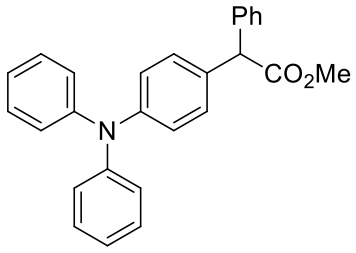
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.12 – 8.10 (m, 2H), 7.45 – 7.35 (m, 12H), 7.33 – 7.28 (m, 4H), 7.14 – 7.10 (m, 2H), 5.28 (s, 2H), 3.93 (s, 3H), 3.82 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 158.9, 141.0, 139.4, 130.0, 128.6, 128.5, 128.4, 127.1, 126.8, 123.1, 120.4, 115.1, 109.9, 57.0, 55.6, 52.3 ppm.

IR (KBr): 3454, 3027, 2951, 2839, 2669, 2324, 2254, 2059, 1892, 1733, 1604, 1512, 1487, 1459, 1291, 1243, 1192, 1154, 1079, 1028, 1009, 908, 831, 809, 729, 701 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{37}H_{32}NO_5^+$: 570.2275; Found: 570.2266.

Methyl 2-(4-(diphenylamino)phenyl)-2-phenylacetate (5a)



In an oven dried reaction tube triphenylamine (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (5 mol-%) and $AgSbF_6$ (6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazolkane **2a** (1.5 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 40:1 → 20:1); the product **5a** was obtained as colorless gel (67%, 53 mg).

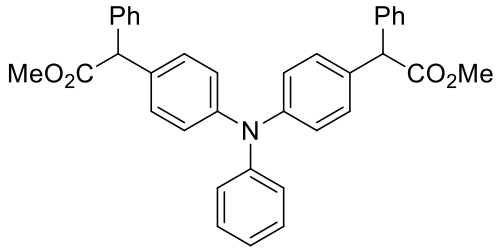
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.37 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.28 – 7.22 (m, 4H), 7.20 – 7.17 (m, 2H), 7.12 – 7.09 (m, 4H), 7.05 – 7.01 (m, 4H), 4.99 (s, 1H), 3.78 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.1, 147.6, 146.9, 138.8, 132.4, 129.3, 129.2, 128.6, 128.5, 127.2, 124.4, 123.5, 122.8, 56.4, 52.3 ppm.

IR (KBr): 3458, 3031, 2954, 2791, 2163, 2098, 2021, 1973, 1891, 1731, 1601, 1431, 1312, 1271, 1221, 1181, 1142, 919, 817, 731, 692 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{27}H_{23}NNaO_2^+$: 416.1621; Found: 416.1629.

Dimethyl 2,2'-((phenylazanediyl)bis(4,1-phenylene))bis(2-phenylacetate) (5b)



The titled compound was synthesized according to the general procedure-GP. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) as a colorless foam (54%, 59 mg).

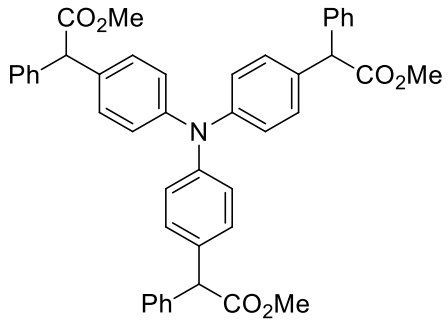
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.36 (d, *J* = 4.4 Hz, 8H), 7.32 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H), 7.20 – 7.17 (m, 4H), 7.12 – 7.08 (m, 2H), 7.04 – 7.00 (m, 5H), 4.99 (s, 2H), 3.77 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.1, 147.4, 146.7, 138.7, 132.6, 129.3, 129.2, 128.6, 128.5, 127.2, 124.5, 123.8, 123.0, 56.4, 52.3 ppm.

IR (KBr): 3031, 2953, 2792, 2851, 2278, 2164, 2021, 2001, 1979, 1892, 1732, 1607, 1315, 1272, 1195, 1141, 1077, 1005, 923, 881, 813, 736, 697 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{36}H_{32}NO_4^+$: 542.2325; Found: 542.2331.

Trimethyl 2,2',2''-(nitrilotris(benzene-4,1-diyl))tris(2-phenylacetate) (5c)



In an oven dried reaction tube triphenylamine (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (5 mol-%) and $AgSbF_6$ (6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (6.0 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) and the product **5a** was obtained as colorless foam (79%, 109 mg).

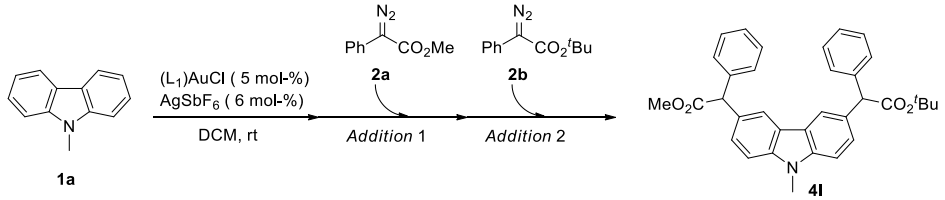
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.39 – 7.35 (m, 12H), 7.33 – 7.28 (m, 3H), 7.20 – 7.16 (m, 6H), 7.05 – 7.00 (m, 6H), 5.00 (s, 3H), 3.78 (s, 9H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.0, 146.5, 138.7, 132.9, 129.4, 128.6, 128.5, 127.3, 124.1, 56.4, 52.3 ppm.

IR (neat): 3456, 3030, 2950, 2850, 2165, 2022, 1979, 1899, 1732, 1602, 1502, 1434, 1314, 1275, 1194, 1149, 1078, 1006, 921, 880, 814, 738, 698 cm^{-1}.

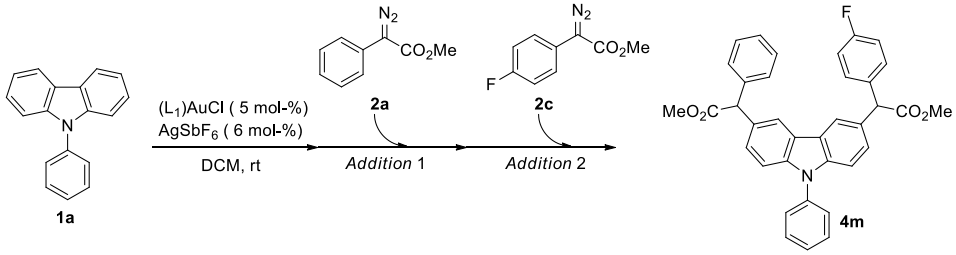
HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{45}H_{40}NO_6^+$: 690.2850; Found: 690.2854.

Stepwise one pot protocol for the introduction of two different carbenes and the synthesis of *tert*-butyl 2-(6-(2-methoxy-2-oxo-1-phenylethyl)-9-methyl-9*H*-carbazol-3-yl)-2-phenylacetate (4l)



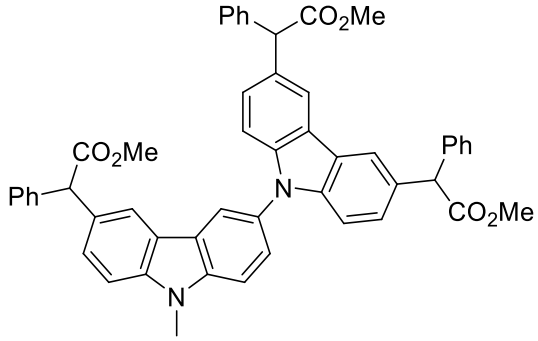
In an oven dried reaction tube 9-methyl-9*H*-carbazole (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (5 mol-%) and $AgSbF_6$ (6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (1.5 equiv.) was dissolved in 0.5 mL of dry degassed DCM and added to the reaction mixture for first 30 minutes and then diazoalkane **2b** in 0.5 mL DCM was added to the reaction mixture over another 30 mins via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) and the product **4l** was obtained as colorless gel (77%, 80 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.09 – 7.93 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.31 (m, 10H), 7.30 – 7.24 (m, 2H), 5.25 (s, 1H), 5.12 (s, 1H), 3.83 (s, 3H), 3.80 (d, *J* = 1.4 Hz, 3H), 1.49 (s, 9H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 172.3, 140.57, 140.52, 140.1, 139.5, 129.9, 129.16, 129.15, 128.58, 128.55, 128.53, 128.4, 127.1, 126.8, 126.7, 126.5, 126.4, 122.8, 122.7, 120.5, 120.47, 120.44, 108.6, 108.5, 81.1, 58.0, 57.0, 52.3, 29.1, 28.0 ppm.
IR (KBr): 3490, 3051, 2951, 2873, 2166, 2099, 1963, 1881, 1732, 1601, 1482, 1330, 1298, 1153, 1131, 928, 817, 739, 696, 661 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{34}H_{33}NNaO_4^+$: 542.2301; Found: 542.2307.

Stepwise one protocol for the introduction of two different carbenes and the synthesis of methyl 2-(4-fluorophenyl)-2-(6-(2-methoxy-2-oxo-1-phenylethyl)-9-phenyl-9*H*-carbazol-3-yl)acetate (4m)



In an oven dried reaction tube 9-phenyl-9*H*-carbazole (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (5 mol-%) and $AgSbF_6$ (6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (1.5 equiv.) was dissolved in 0.5 mL of dry degassed DCM and added to the reaction mixture for first 30 minutes and then diazoalkane **2c** in 0.5 mL DCM was added to the reaction mixture over another 30 mins via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) and the product **4m** was obtained as colorless gel (81%, 90 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.10 (s, 1H), 8.07 (s, 1H), 7.63 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.33 (m, 10H), 7.32 – 7.27 (m, 1H), 7.05 (t, *J* = 8.7 Hz, 2H), 5.27 (s, 1H), 5.23 (s, 1H), 3.81 (s, 6H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 173.4, 161.9 (d, *J* = 245.8 Hz), 140.5, 139.3, 137.4, 135.1 (d, *J* = 3.5 Hz), 130.4, 130.1 (d, *J* = 7.8 Hz), 129.9, 128.6, 128.5, 127.6, 127.1, 127.0, 126.9, 126.68, 126.67, 123.4, 123.3, 120.4 (d, *J* = 1.9 Hz), 120.3 (d, *J* = 1.7 Hz), 115.4 (d, *J* = 20.9 Hz), 110.1, 110.0, 56.9, 56.1, 52.4, 52.3 ppm.
^{19}F NMR (565 MHz, Chloroform-*d*): δ = -115.60 – -115.67 (m) ppm.
IR (KBr): 3884, 3451, 3024, 2949, 2431, 2199, 2179, 2089, 1998, 1891, 1733, 1601, 1478, 1311, 1261, 1239, 1189, 1150, 1061, 1001, 912, 876, 738, 691 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{36}H_{28}FNNaO_4^+$: 580.1894; Found: 580.1890.

Trimethyl 2,2',2''-(9-methyl-9*H*-[3,9'-bicarbazole]-3',6,6'-triyl)tris(2-phenylacetate) (6)



In an oven dried reaction tube 9-methyl-9*H*-3,9'-bicarbazole (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.10 mg, 6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (6.0 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 1:1) and the product **6** was obtained as colorless foam (76%, 120 mg).

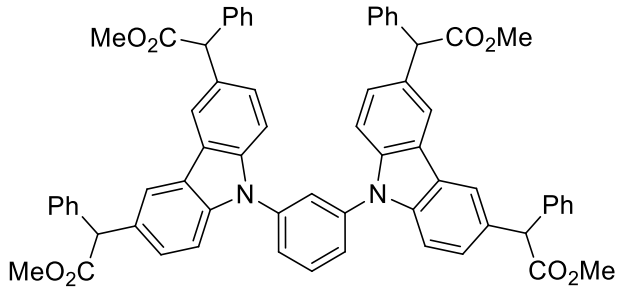
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.16 (s, 1H), 8.12 (s, 2H), 8.01 (s, 1H), 7.56 (s, 2H), 7.54 – 7.50 (m, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 4H), 7.40 – 7.33 (m, 10H), 7.32 – 7.26 (m, 5H), 5.27 (s, 2H), 5.25 (s, 1H), 3.95 (s, 3H), 3.82 (s, 6H), 3.79 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 173.4, 141.5, 140.9, 140.5, 139.5, 139.3, 129.9, 129.8, 128.7, 128.6, 128.59, 128.53, 127.24, 127.20, 127.1, 126.7, 125.2, 123.6, 123.1, 122.5, 120.6, 120.45, 120.44, 119.5, 110.0, 109.5, 109.0, 57.0, 56.9, 52.3, 29.4 ppm.

IR (KBr): 3455, 3027, 2944, 2252, 1881, 1731, 1603, 1488, 1333, 1239, 1151, 1008, 907, 806, 725 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{52}H_{42}N_2NaO_6^+$: 813.2935; Found: 813.2935.

Tetramethyl 2,2',2'',2'''-(9,9'-(1,3-phenylene)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (7)



In an oven dried reaction tube 1,3-di(9*H*-carbazol-9-yl)benzene (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.10 mg, 6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (8.0 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) and the product **7** was obtained as colorless foam (67%, 134 mg).

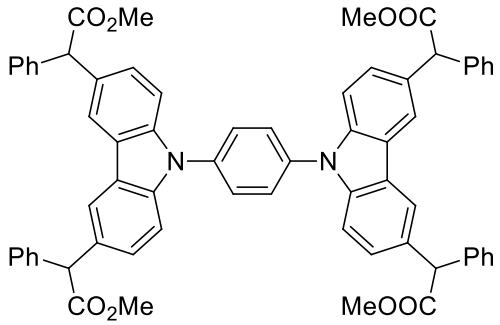
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.10 (s, 4H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.65 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 4H), 7.43 – 7.34 (m, 20H), 7.32 – 7.28 (m, 4H), 5.26 (s, 4H), 3.81 (s, 12H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.4, 140.1, 139.29, 139.29, 131.3, 130.8, 128.6, 128.5, 127.2, 127.1, 125.7, 124.9, 123.6, 120.6, 109.8, 56.9, 52.3 ppm.

IR (KBr): 3454, 3203, 3061, 3028, 2949, 2845, 2659, 2327, 2255, 2180, 2118, 1991, 1879, 1808, 1732, 1597, 1488, 1455, 1315, 1232, 1193, 1150, 1079, 1006, 907, 804 cm^{-1}.

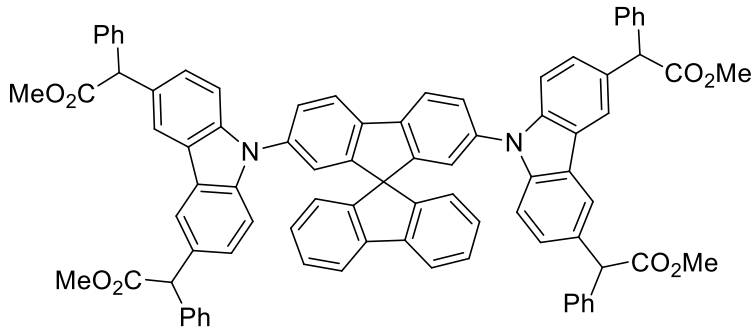
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{66}H_{52}N_2NaO_8^+$: 1023.3615; Found: 1023.3620.

Tetramethyl 2,2',2'',2'''-(9,9'-(1,4-phenylene)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (8)



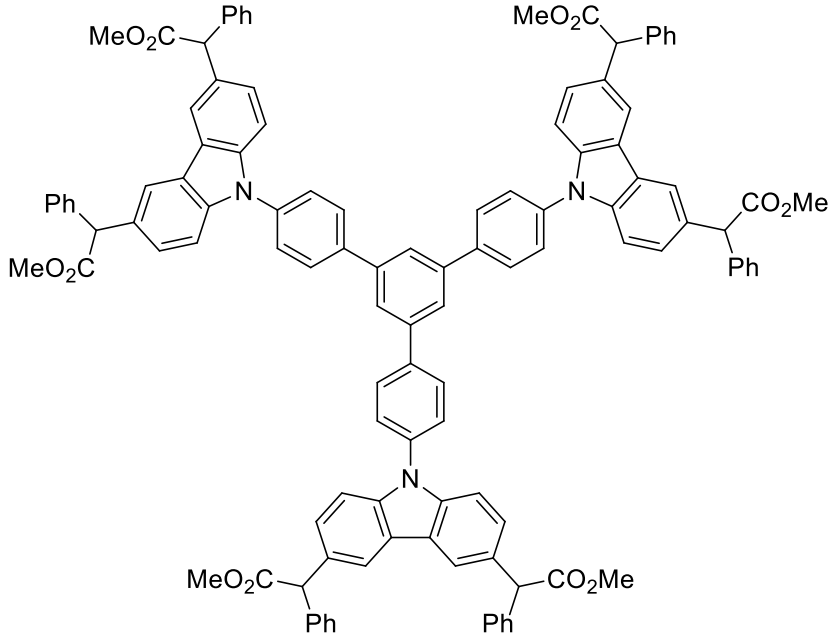
The titled compound was synthesized according to the procedure used for the synthesis of **7**. And was obtained after silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) as a colorless foam (78%, 156 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.15 – 8.14 (m, 4H), 7.78 (s, 4H), 7.51 (d, *J* = 8.5 Hz, 4H), 7.46 (dd, *J* = 8.6, 1.7 Hz, 4H), 7.44 – 7.41 (m, 8H), 7.39 (t, *J* = 7.6 Hz, 8H), 7.34 – 7.30 (m, 4H), 5.30 (s, 4H), 3.84 (s, 12H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.4, 140.3, 139.3, 136.5, 130.8, 128.6, 128.5, 128.2, 127.2, 127.1, 123.6, 120.6, 110.0, 57.0, 52.4 ppm.
IR (KBr): 3448, 3201, 3069, 2998, 2947, 2845, 2658, 2327, 2118, 1992, 1878, 1807, 1731, 1598, 1568, 1483, 1451, 1311, 1291, 1237, 1008, 905, 804, 789, 639 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{66}H_{52}N_2NaO_8^+$: 1023.3615; Found: 1023.3619.

Tetramethyl 2,2',2'',2'''-(9,9'-(9,9'-spirobi[fluorene]-2,7-diyl)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (9)



In an oven dried reaction tube 2,7-di(9*H*-carbazol-9-yl)-9,9'-spirobi[fluorene] (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.10 mg, 6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (8.0 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) and the product **9** was obtained as gray foam (74%, 183 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.10 (d, *J* = 8.1 Hz, 2H), 8.02 (s, 4H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.41 – 7.33 (m, 18H), 7.32 – 7.26 (m, 8H), 7.24 – 7.17 (m, 6H), 6.98 – 6.94 (m, 4H), 5.22 (s, 4H), 3.79 (s, 12H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.4, 151.3, 147.4, 141.7, 140.1, 140.0, 139.3, 137.1, 130.3, 128.6, 128.5, 128.3, 128.1, 127.1, 126.8, 126.4, 123.6, 123.3, 122.5, 121.3, 120.4, 109.9, 66.0, 56.9, 52.3 ppm.
IR (KBr): 3449, 3203, 3029, 2949, 2841, 2325, 2253, 2176, 2117, 2031, 1984, 1942, 1875, 1805, 1732, 1604, 1479, 1349, 1232, 1192, 1150, 1078, 1007, 809, 759, 727 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{85}H_{63}N_2O_8^+$: 1239.4578; Found: 1239.4561.

Tetramethyl 2,2',2'',2'''-(9,9'-(5'-(4-(3,6-bis(2-methoxy-2-oxo-1-phenylethyl)-9*H*-carbazol-9-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (10)



In an oven dried reaction tube 9,9'-(5'-(4-(9*H*-carbazol-9-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(9*H*-carbazole) (0.2 mmol, 1.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.10 mg, 6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **2a** (10.0 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 4:1 → 2:1) and the product **10** was obtained as colorless foam (63%, 213 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.12 (s, 6H), 8.03 (s, 3H), 8.02 – 7.98 (m, 6H), 7.73 – 7.66 (m, 6H), 7.47 (d, *J* = 8.5 Hz, 6H), 7.44 – 7.40 (m, 18H), 7.37 (t, *J* = 7.6 Hz, 12H), 7.32 – 7.28 (m, 6H), 5.28 (s, 6H), 3.82 (s, 18H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.4, 141.8, 140.4, 140.0, 139.3, 137.2, 130.5, 128.8, 128.6, 128.5, 127.3, 127.2, 127.0, 125.4, 123.5, 120.6, 110.0, 57.0, 52.3 ppm.

IR (KBr): 3648, 3452, 3200, 3029, 2947, 2846, 2654, 2325, 2246, 2182, 2070, 2015, 1984, 1957, 1877, 1801, 1732, 1603, 1513, 1485, 1457, 1358, 1324, 1233, 1192, 1150, 1008, 810, 735, 698 cm^{-1}.

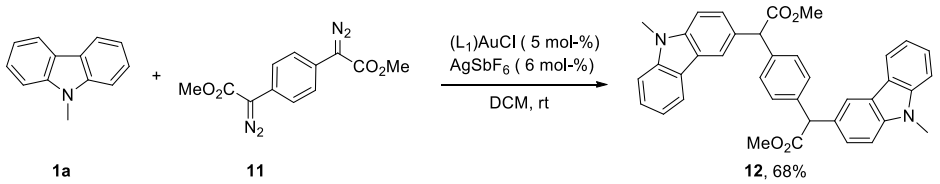
Elemental analysis:

calculated (%) for [M] C, 80.97; H, 5.19; N, 2.49. Found: C, 79.81; H, 5.26; N, 2.36.

The discrepancy of the C-value was observed for multiple samples that were synthesized separately and was consistently reproduced. This results most likely from impurities of $CDCl_3$ present within the sample, NMR samples do not suggest the inclusion of ethyl acetate or water.

calculated (%) for [M+0.25 $CDCl_3$] C, 79.73; H, 5.12; N, 2.44.

Dimethyl 2,2'-(1,4-phenylene)bis(2-(9-methyl-9*H*-carbazol-3-yl)acetate) (12)



1a **11** **12**, 68%

In an oven dried reaction tube 9-methyl-9*H*-carbazole **1a** (0.8 mmol, 4.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.10 mg, 6 mol-%) were dissolved in 1.5 mL of dry degassed DCM. Diazoalkane **11** (0.2 mmol, 1.0 equiv.) was dissolved in 1.5 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 9:1 → 4:1) and the product **12** was obtained as colorless solid (64%, 74 mg).

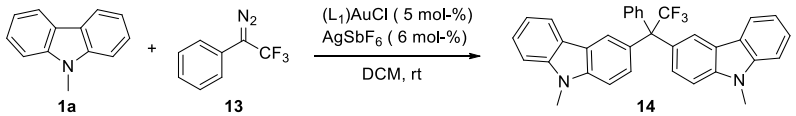
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.09 – 8.05 (m, 4H), 7.52 – 7.44 (m, 4H), 7.41 – 7.38 (m, 2H), 7.38 – 7.34 (m, 6H), 7.25 – 7.21 (m, 2H), 5.23 (s, 2H), 3.84 (d, *J* = 2.5 Hz, 6H), 3.78 (d, *J* = 2.8 Hz, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.5, 141.3, 140.2, 138.3, 128.9, 128.7, 126.4, 125.8, 122.9, 122.6, 120.4, 120.3, 118.9, 108.5, 108.4, 56.6, 52.3, 29.1 ppm.

IR (neat): 3278, 2947, 2879, 2246, 2081, 1728, 1657, 1599, 1482, 1432, 1323, 1276, 1247, 1193, 1146, 1005, 905, 853, 799, 723 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{38}H_{32}O_4N_2Na^+$: 603.2254; Found: 603.2253.

3,3'-(2,2,2-trifluoro-1-phenylethane-1,1-diyl)bis(9-methyl-9*H*-carbazole) (14)



1a **13** **14**

In an oven dried reaction tube 9-methyl-9*H*-carbazole **1a** (0.4 mmol, 2.0 equiv.), (tris(2,4-di-*tert*. butylphenyl)phosphite)AuCl (8.80 mg, 5 mol-%) and $AgSbF_6$ (4.10 mg, 6 mol-%) were dissolved in 3 mL of dry degassed DCM. Diazoalkane **13** (0.2 mmol, 1.0 equiv.) was dissolved in 1 mL of dry degassed DCM and added to the reaction mixture over 60 minutes via syringe pump. The reaction mixture was stirred for additional 2 h at room temperature under argon atmosphere. Solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : EtOAc – 40:1 → 20:1) and the product **14** was obtained as colorless gel (61%, 63 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.92 – 7.90 (m, 4H), 7.51 – 7.47 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.35 (m, 7H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.21 – 7.17 (m, 2H), 3.90 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 141.7, 141.4, 140.1, 131.5, 130.2, 128.7 (d, *J* = 286.6 Hz), 128.0, 127.8, 127.5, 125.8, 122.8, 122.3, 122.1, 120.4, 119.0, 108.5, 107.8, 65.4 (q, *J* = 23.9 Hz), 29.1 ppm.

^{19}F NMR (282 MHz, Chloroform-*d*): δ = -57.92 ppm.

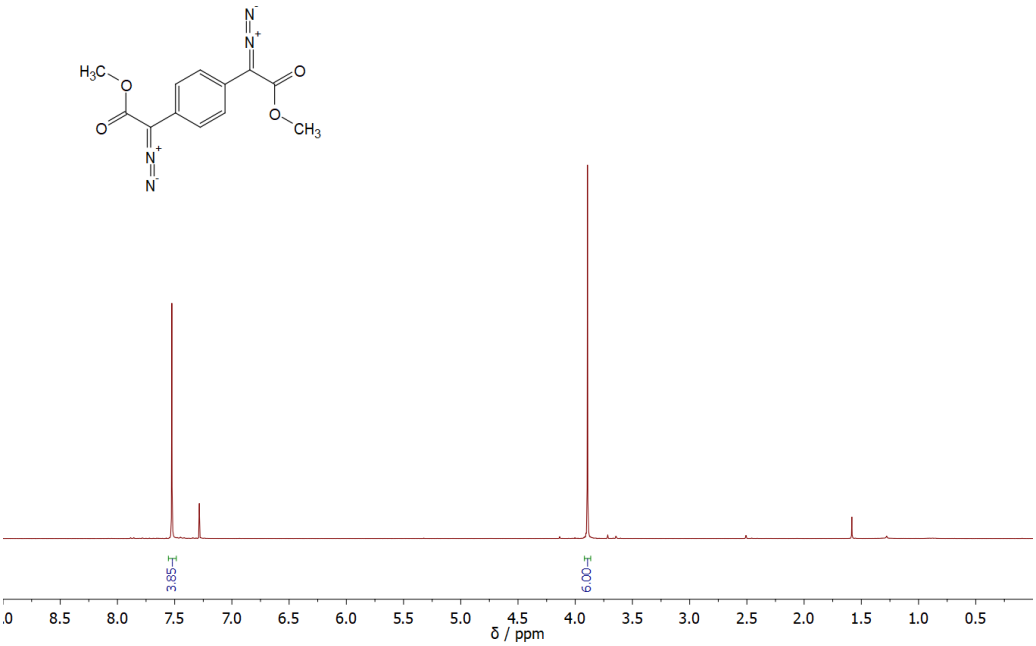
IR (KBr): 3393, 3056, 2925, 2651, 2509, 2322, 2187, 2058, 2004, 1894, 1764, 1687, 1600, 1480, 1325, 1227, 1136, 1019, 943, 894, 800, 662 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{26}F_3N_2^+$: 519.2042; Found: 519.2043.

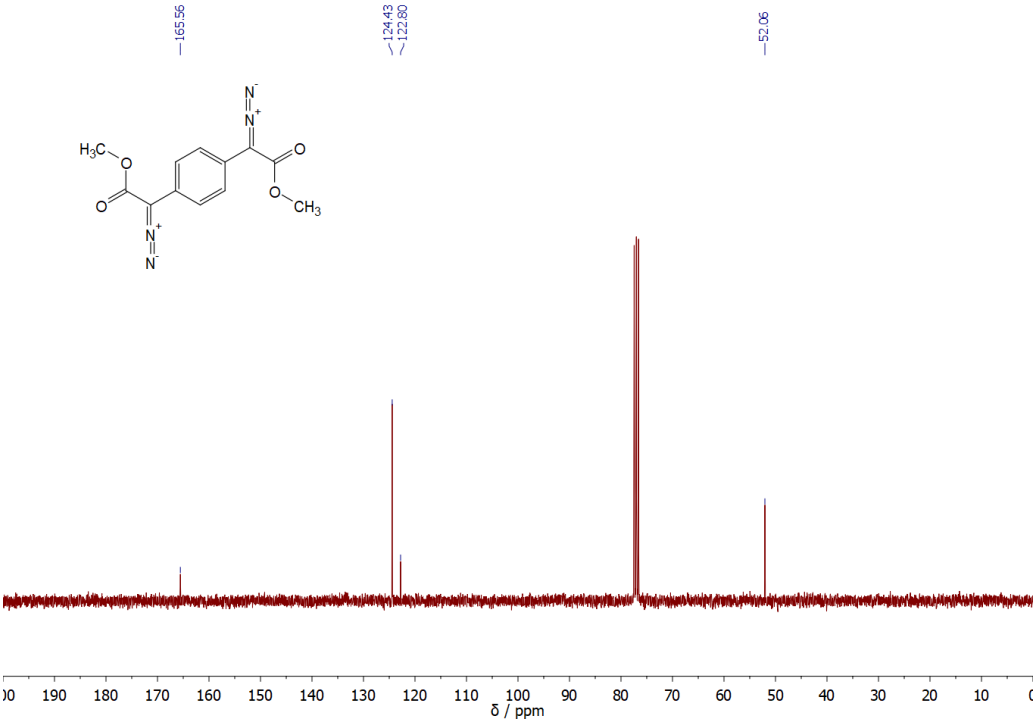
Spectra of compounds

Dimethyl 2,2'-(1,4-phenylene)bis(2-diazoacetate) (11)

^{1}H NMR (300 MHz, Chloroform-*d*):

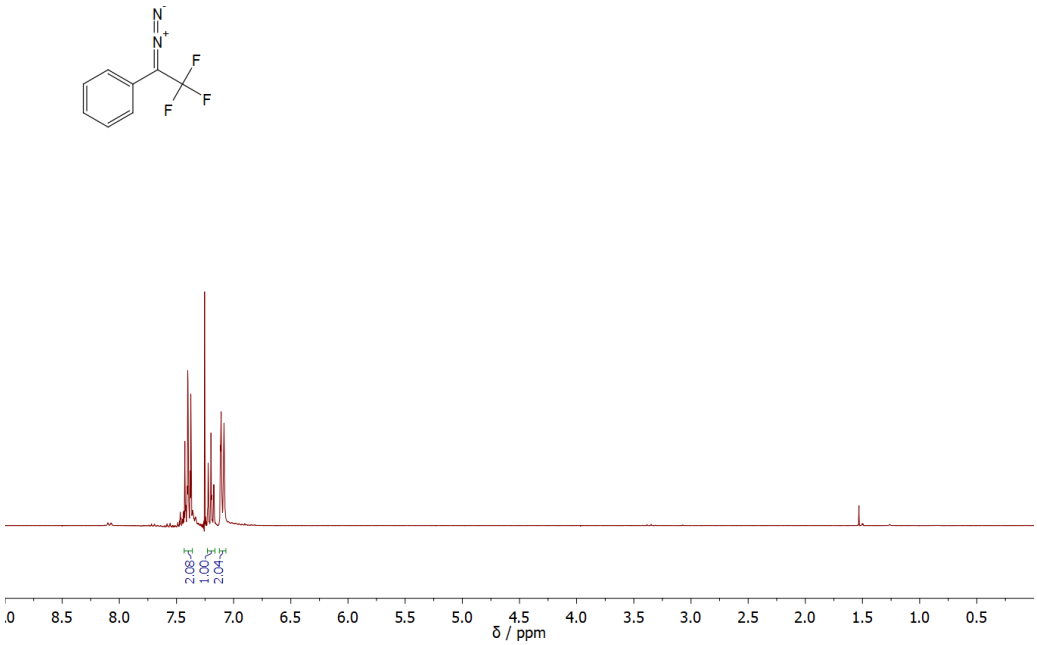


^{13}C NMR (76 MHz, Chloroform-*d*):

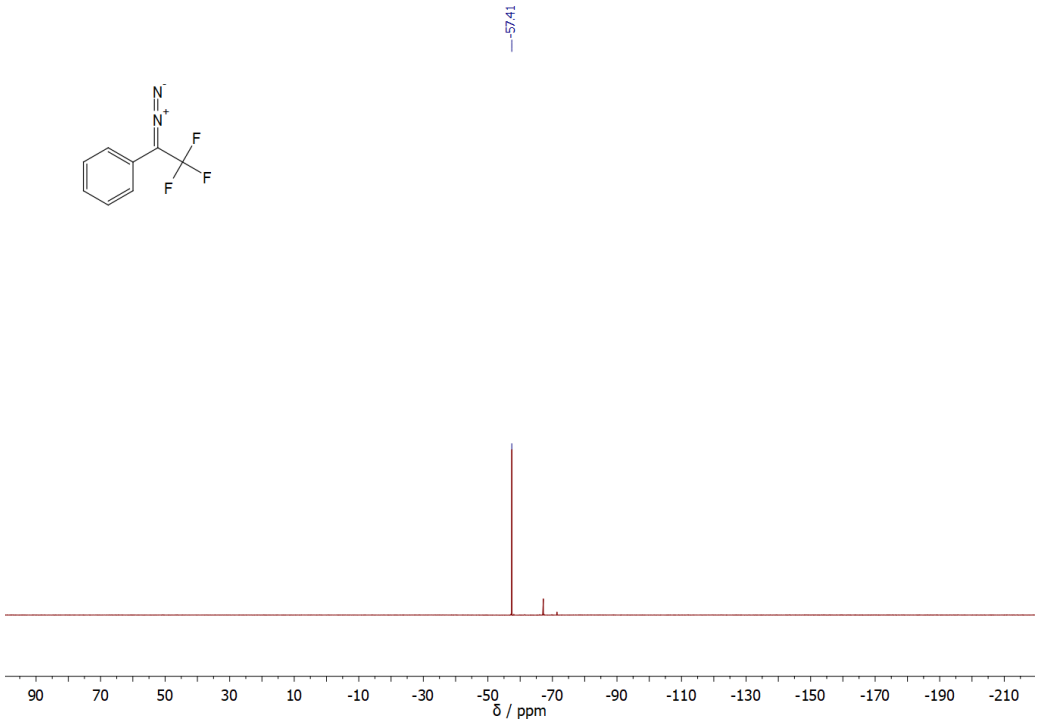


(1-diazo-2,2,2-trifluoroethyl)benzene (13)

^{1}H NMR (300 MHz, Chloroform-*d*):

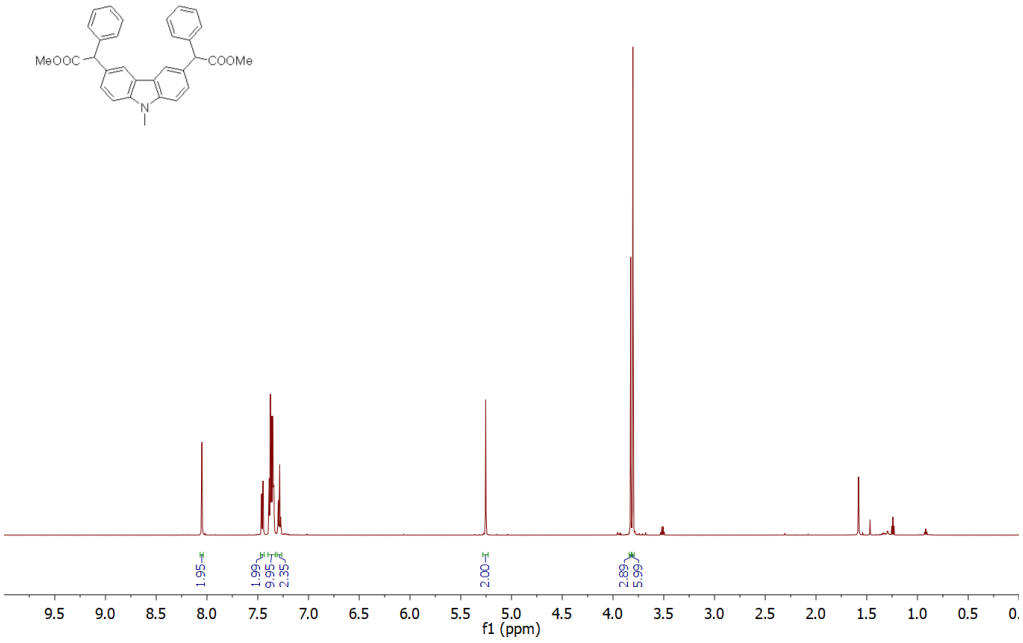


^{19}F NMR (282 MHz, Chloroform-*d*):

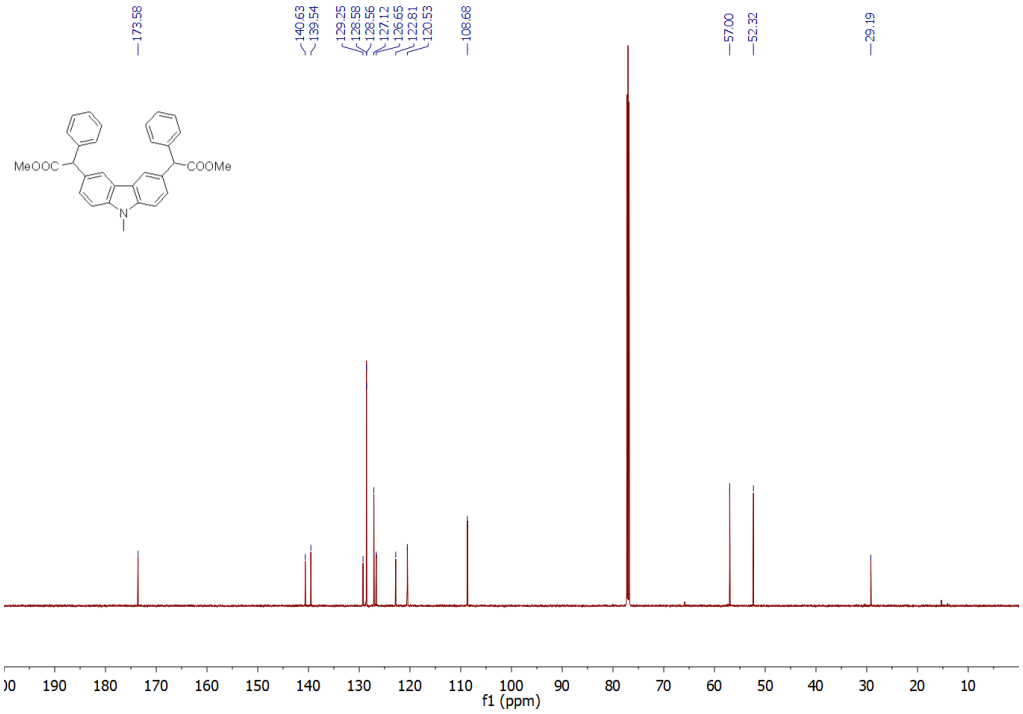


Dimethyl 2,2'-(9-methyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4a)

^{1}H NMR (600 MHz, Chloroform-*d*):

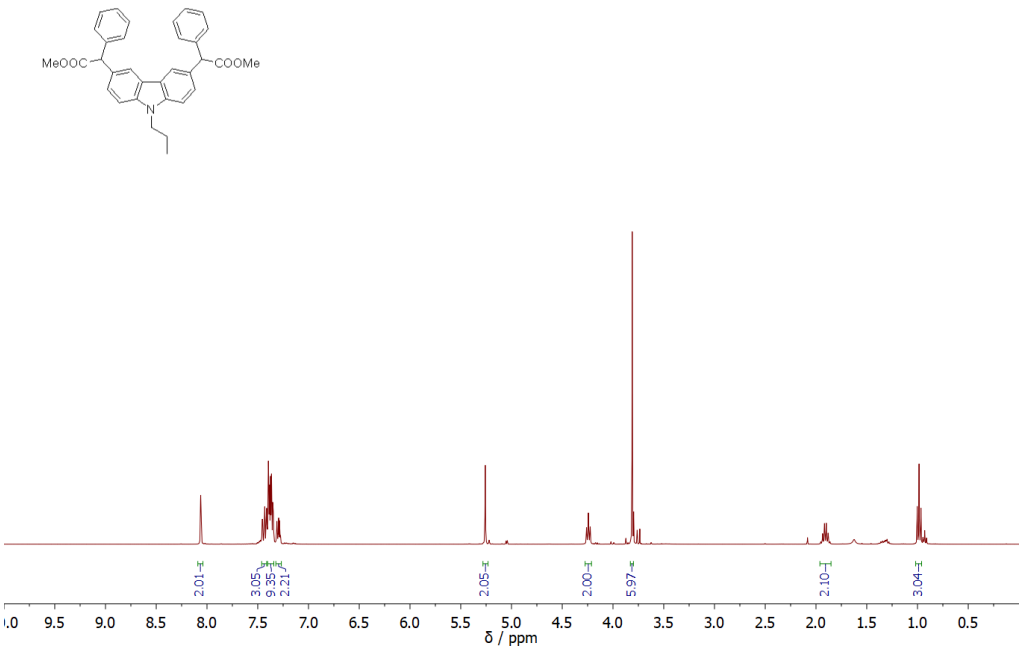


^{13}C NMR (151 MHz, Chloroform-*d*):

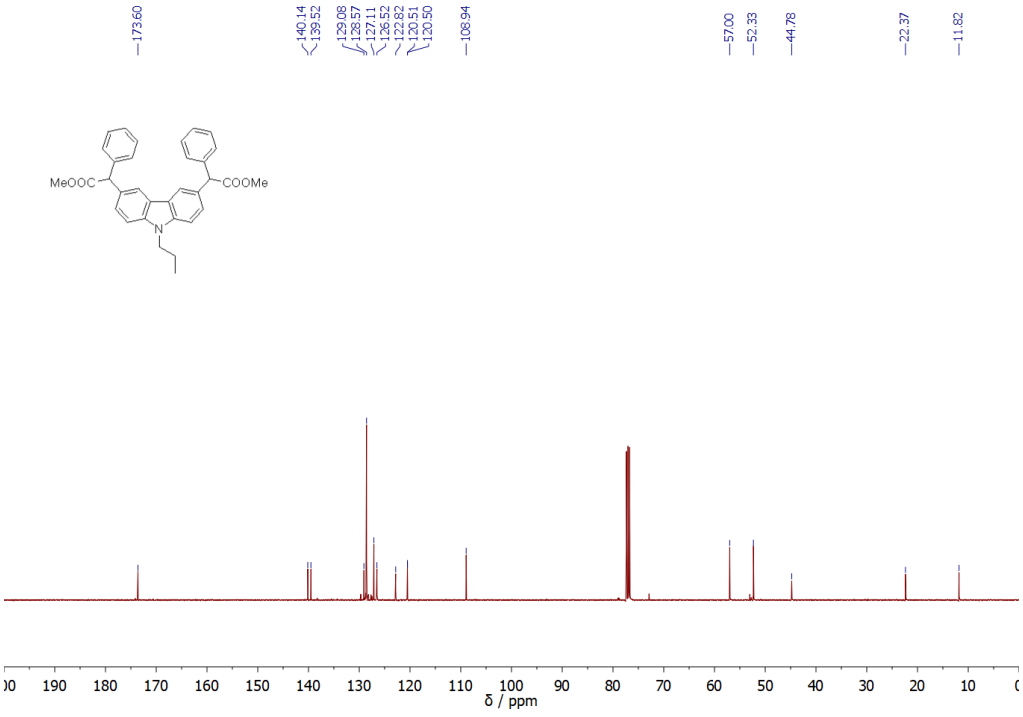


Dimethyl 2,2'-(9-propyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4b)

^{1}H NMR (400 MHz, Chloroform-*d*):

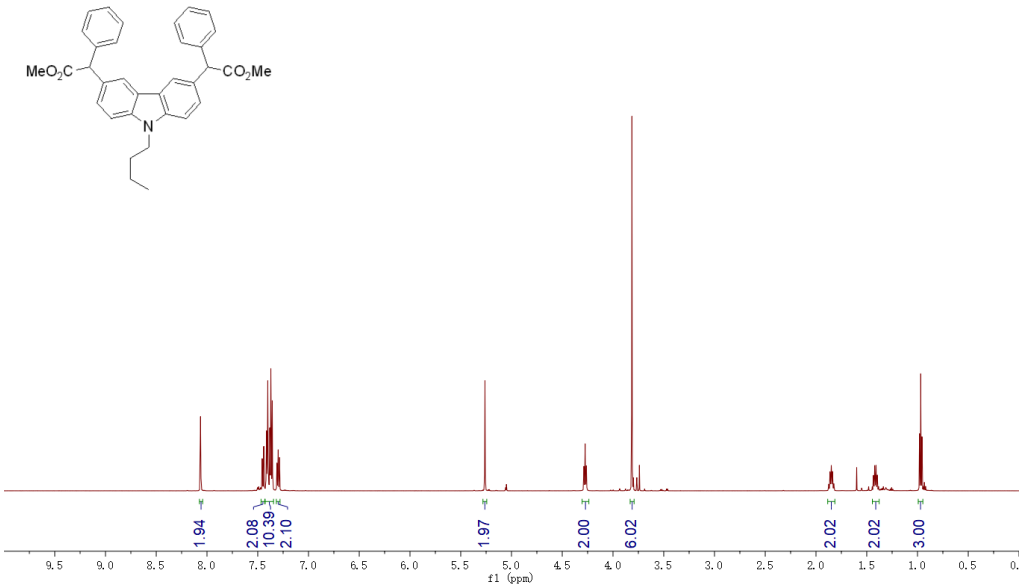


^{13}C NMR (101 MHz, Chloroform-*d*):

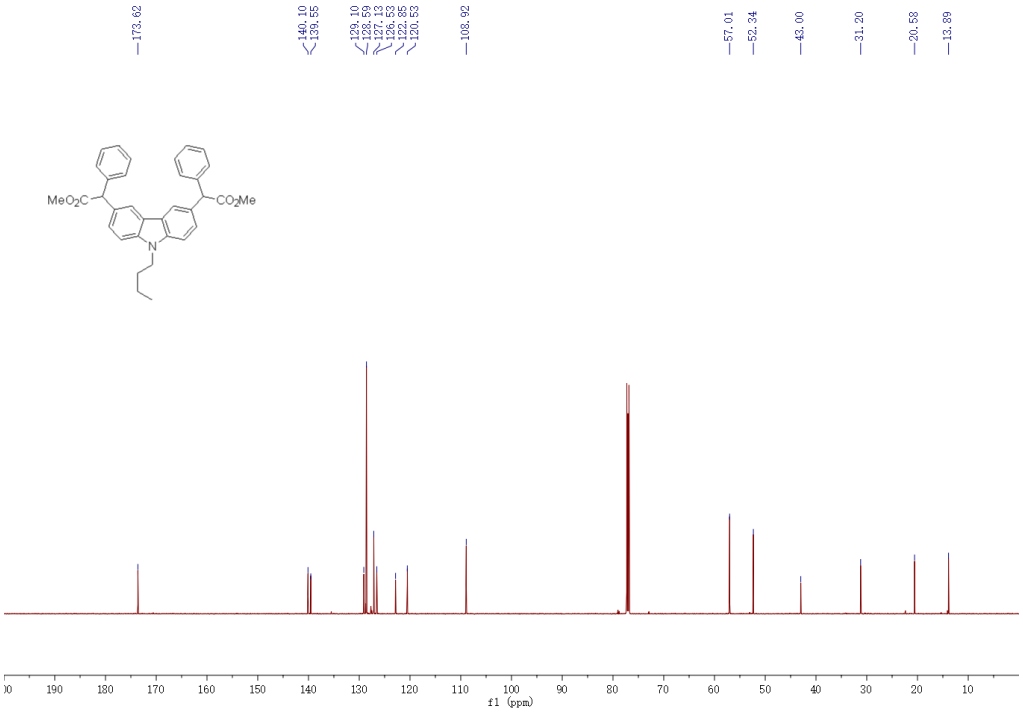


Dimethyl 2,2'-(9-butyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4c)

^{1}H NMR (600 MHz, Chloroform-*d*):

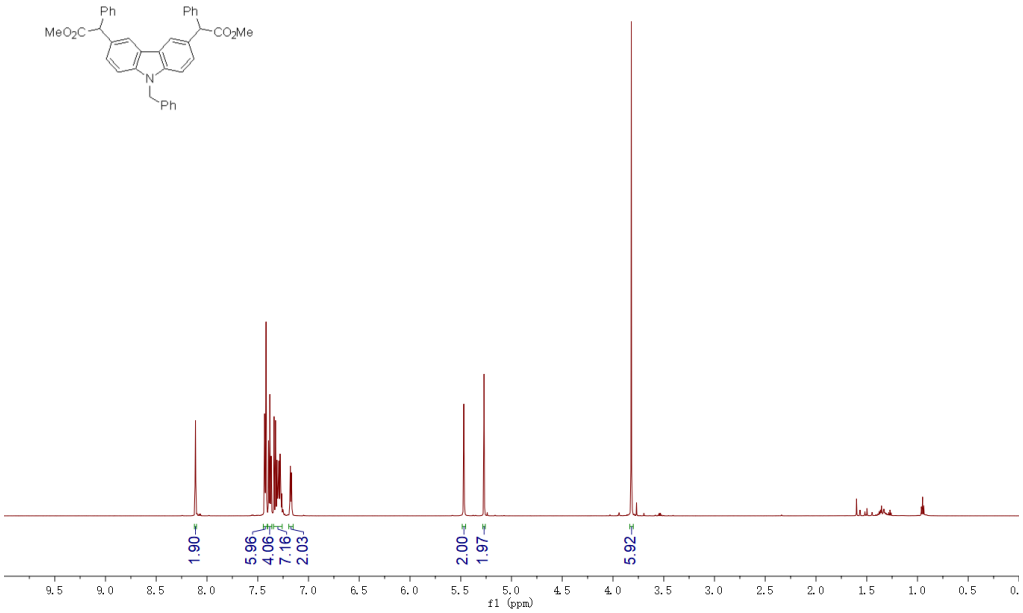


^{13}C NMR (151 MHz, Chloroform-*d*):

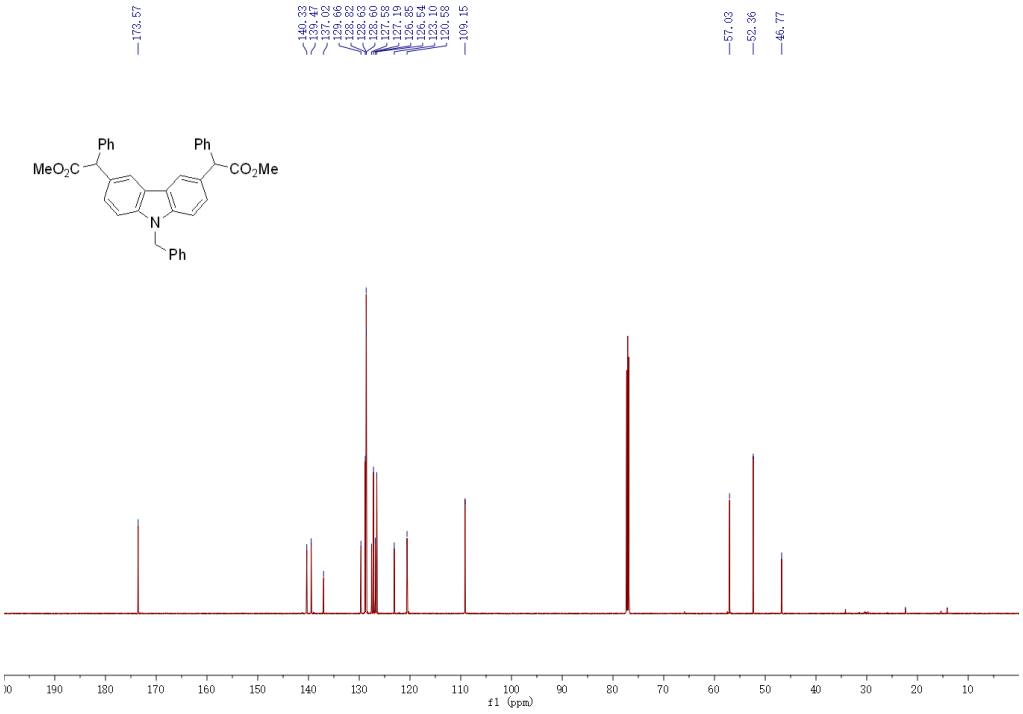


Dimethyl 2,2'-(9-benzyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4d)

^{1}H NMR (600 MHz, Chloroform-*d*):

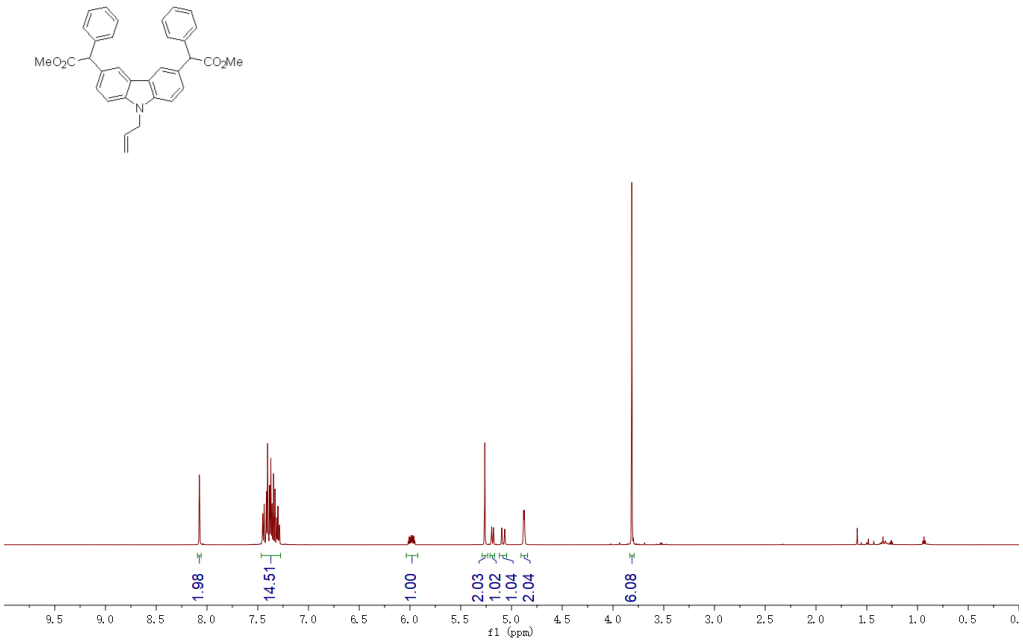


^{13}C NMR (151 MHz, Chloroform-*d*):

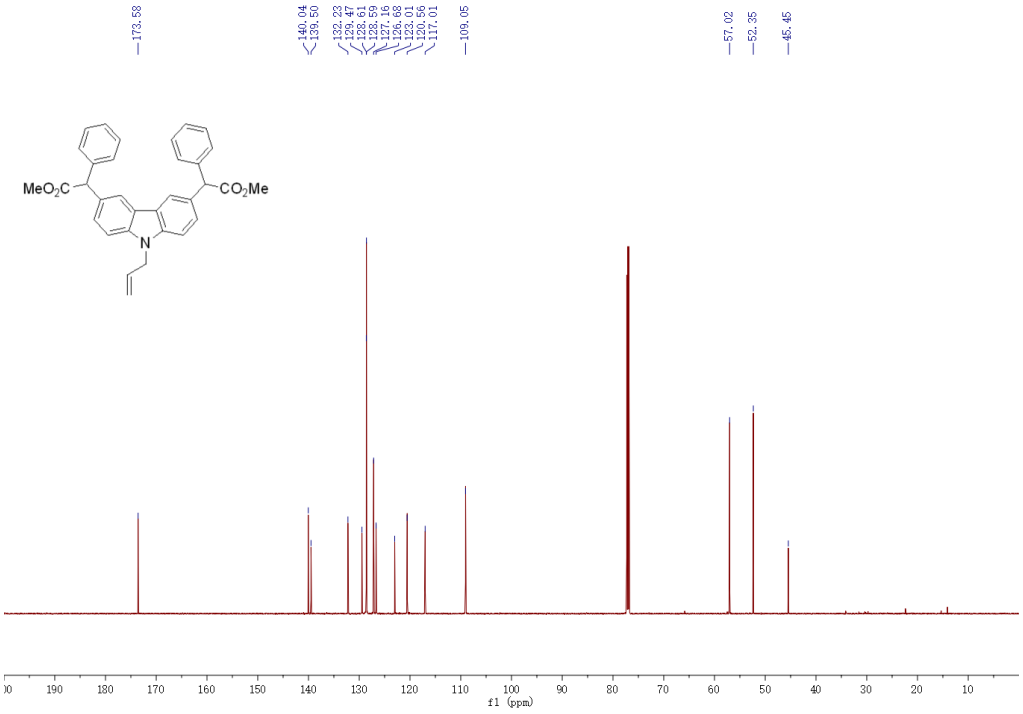


Dimethyl 2,2'-(9-allyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4e)

^{1}H NMR (600 MHz, Chloroform-*d*):

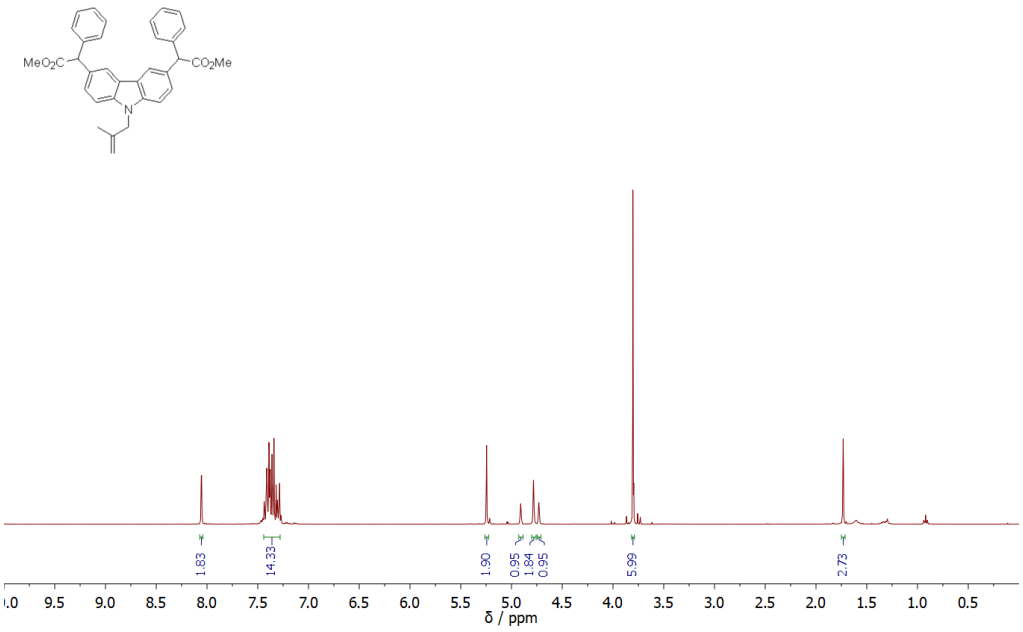


^{13}C NMR (151 MHz, Chloroform-*d*):

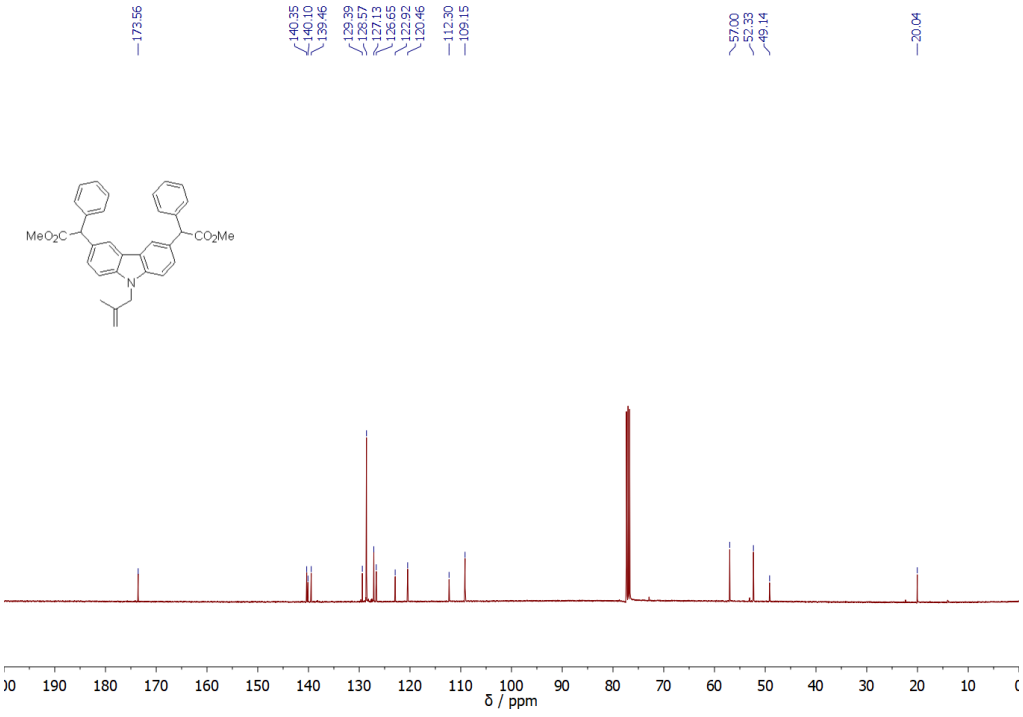


Dimethyl 2,2'-(9-(2-methylallyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4f)

^{1}H NMR (400 MHz, Chloroform-*d*):

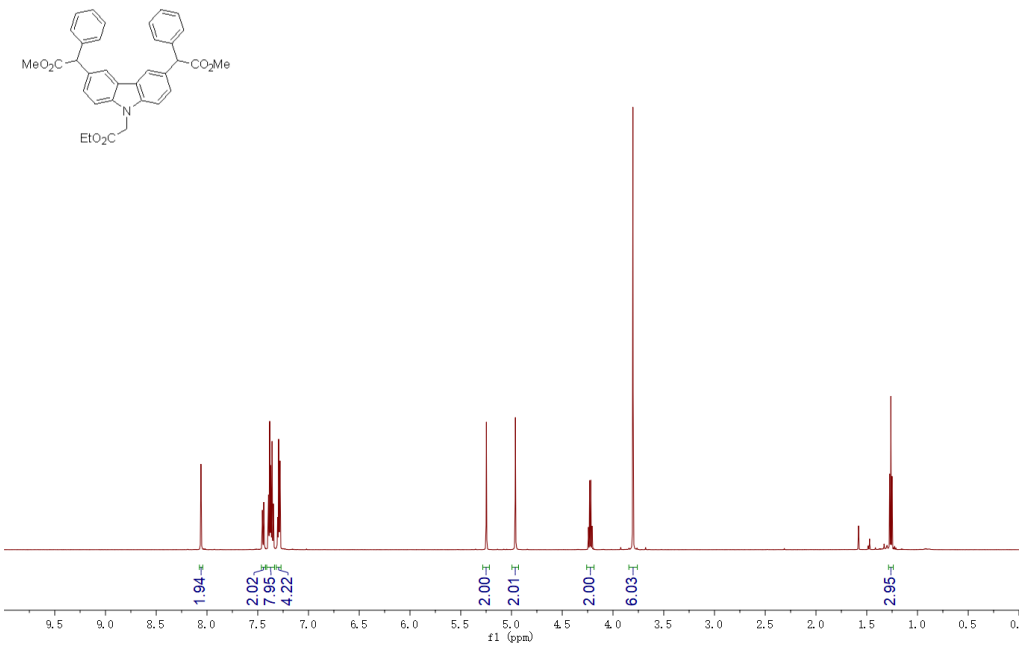


^{13}C NMR (101 MHz, Chloroform-*d*):

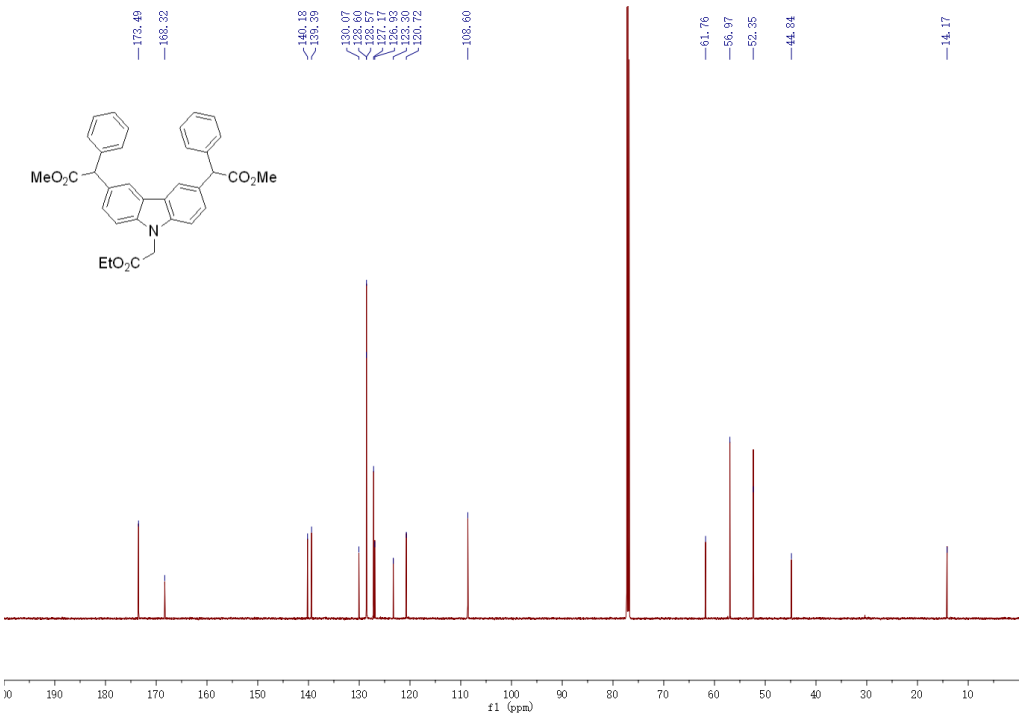


Dimethyl 2,2'-(9-(2-ethoxy-2-oxoethyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4g)

^{1}H NMR (600 MHz, Chloroform-*d*):

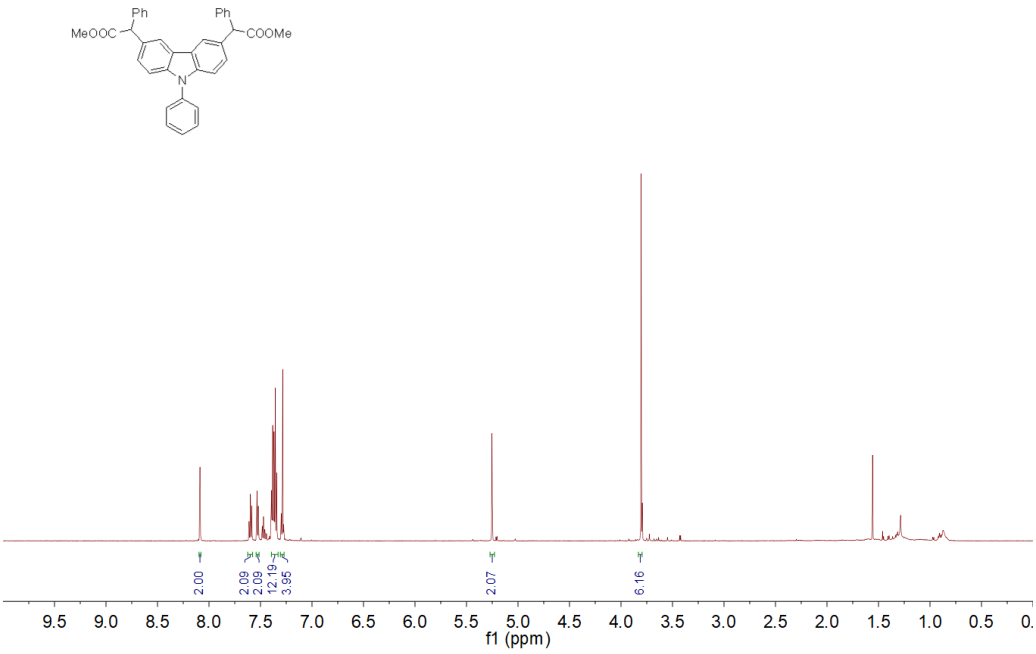


^{13}C NMR (151 MHz, Chloroform-*d*):

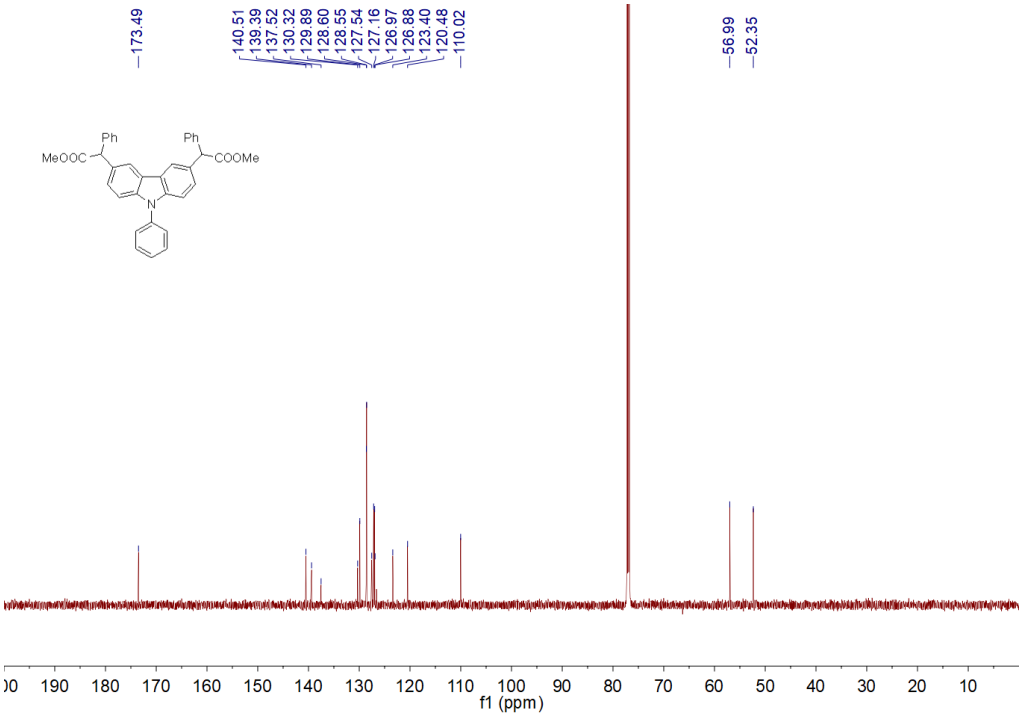


Dimethyl 2,2'-(9-phenyl-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4h)

^{1}H NMR (600 MHz, Chloroform-*d*):

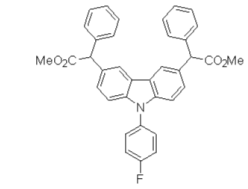


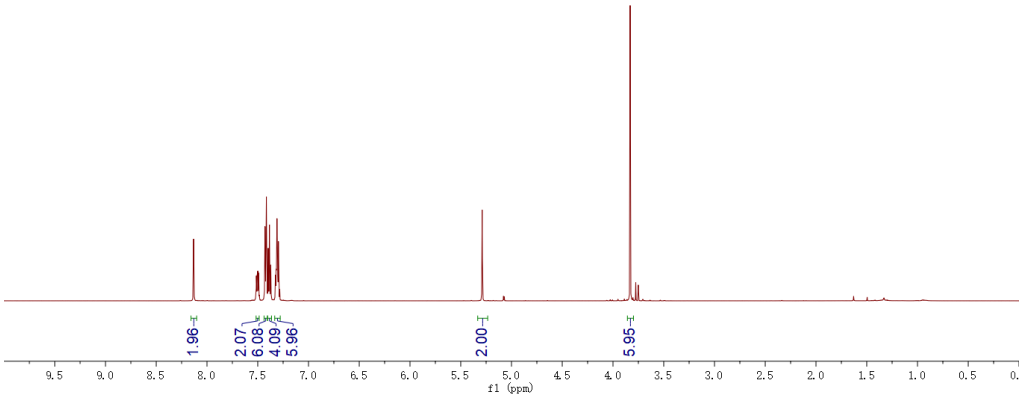
^{13}C NMR (151 MHz, Chloroform-*d*):



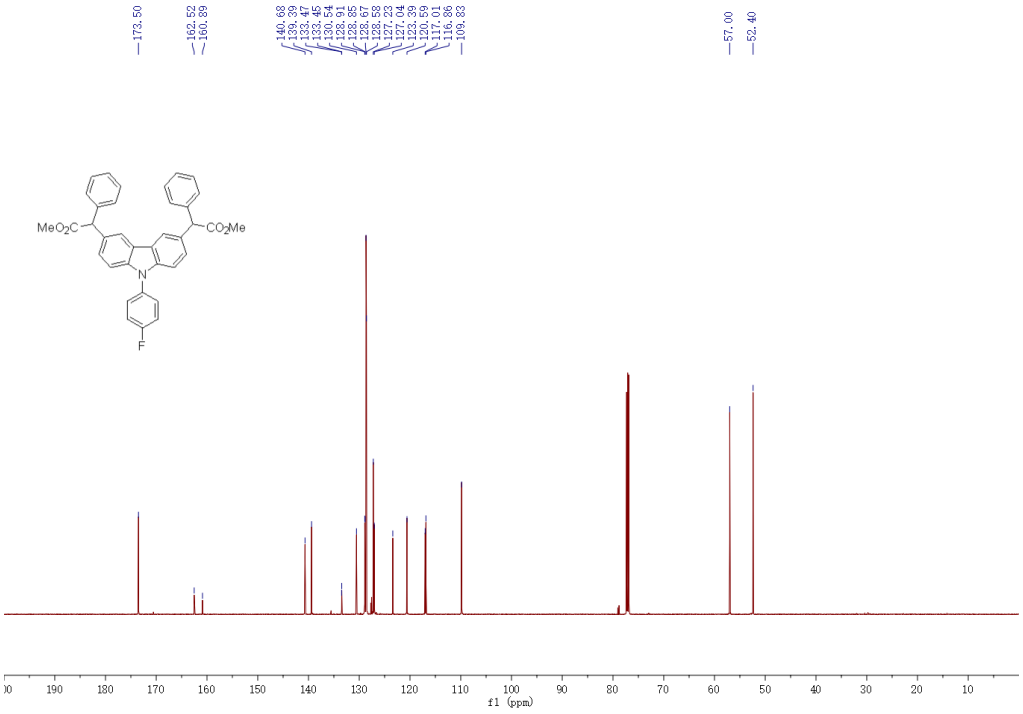
Dimethyl 2,2'-(9-(4-fluorophenyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4i)

^{1}H NMR (600 MHz, Chloroform-*d*):

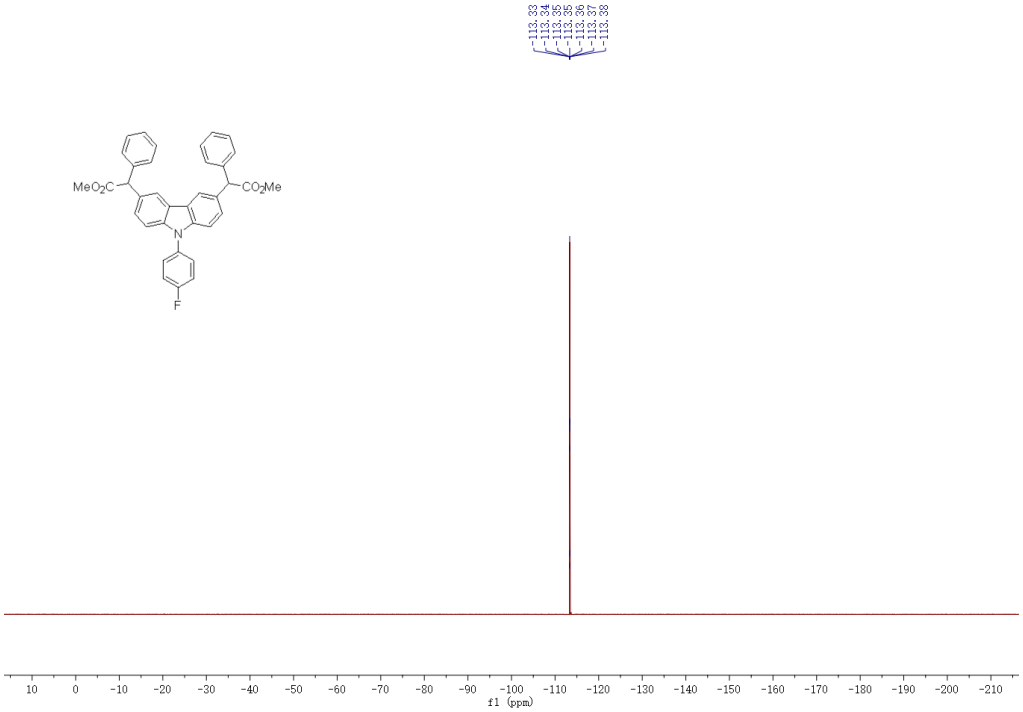




^{13}C NMR (151 MHz, Chloroform-*d*):

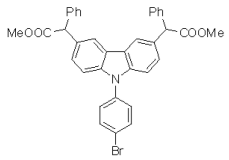


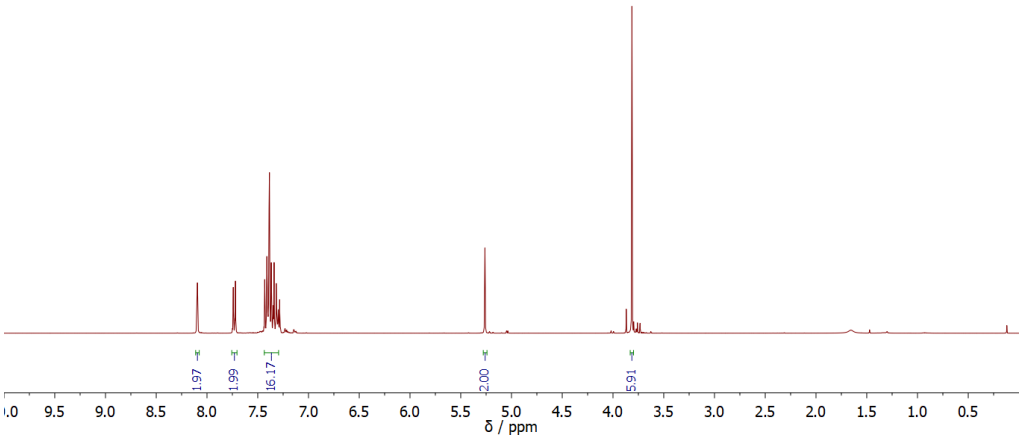
^{19}F NMR (565 MHz, Chloroform-*d*):



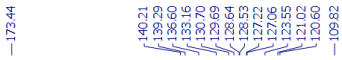
Dimethyl 2,2'-(9-(4-bromophenyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4j)

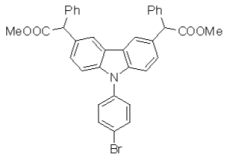
^{1}H NMR (400 MHz, Chloroform-*d*):

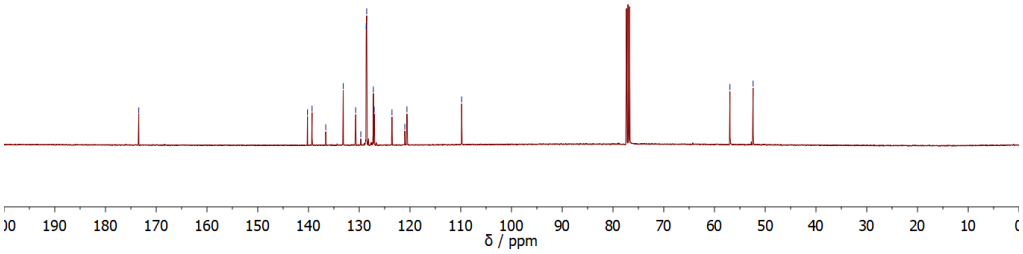




^{13}C NMR (101 MHz, Chloroform-*d*):

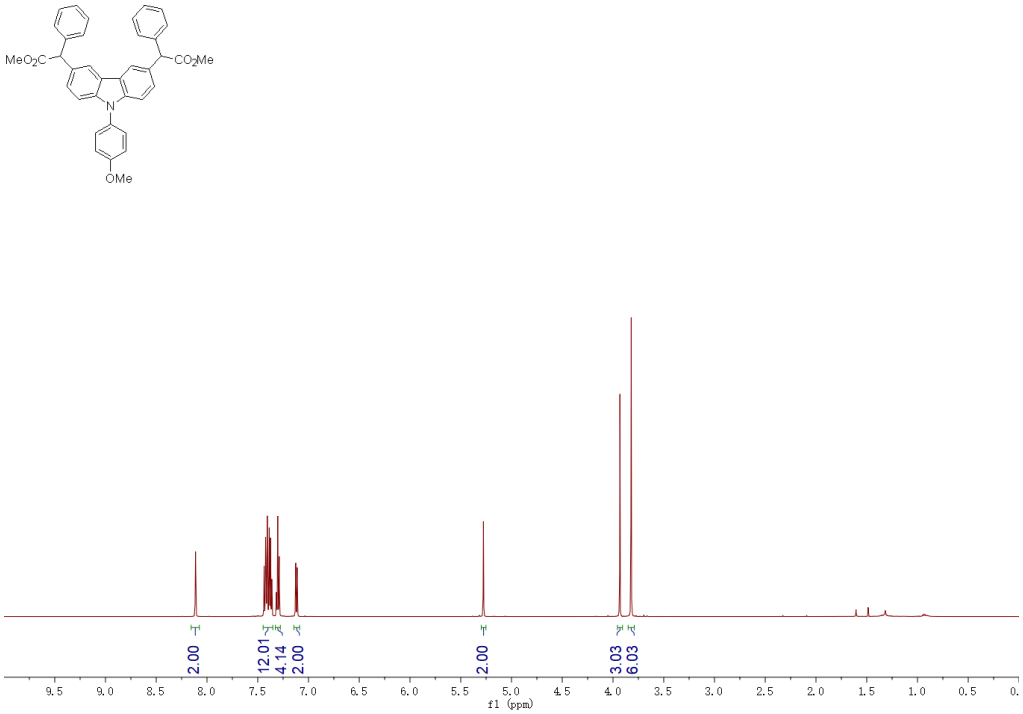




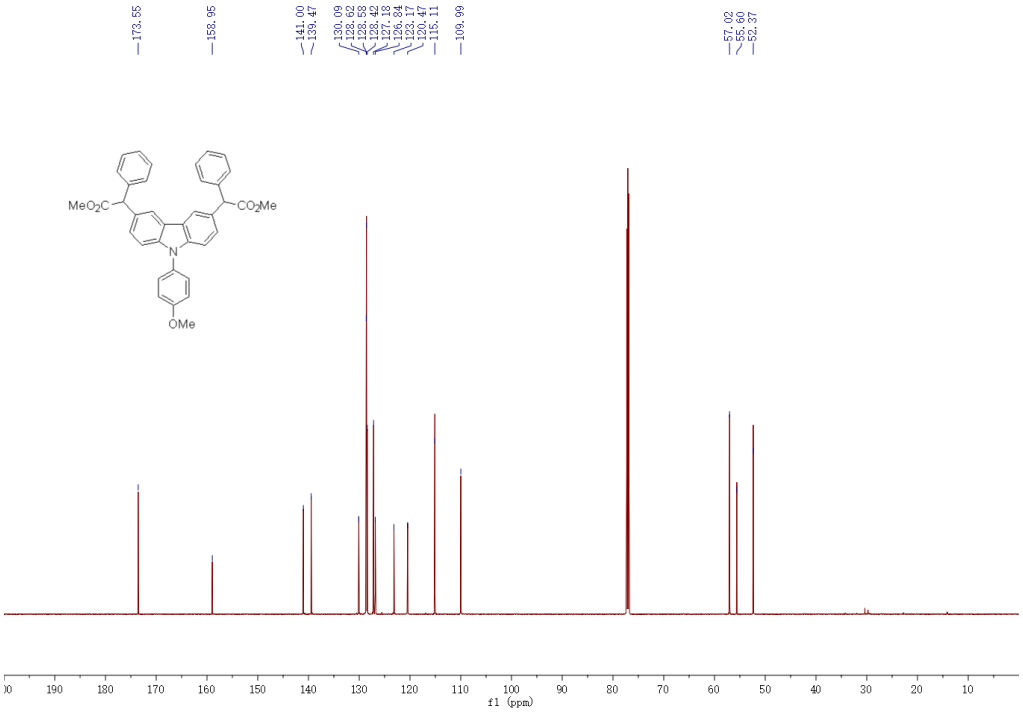


Dimethyl 2,2'-(9-(4-methoxyphenyl)-9*H*-carbazole-3,6-diyl)bis(2-phenylacetate) (4k)

^{1}H NMR (600 MHz, Chloroform-*d*):

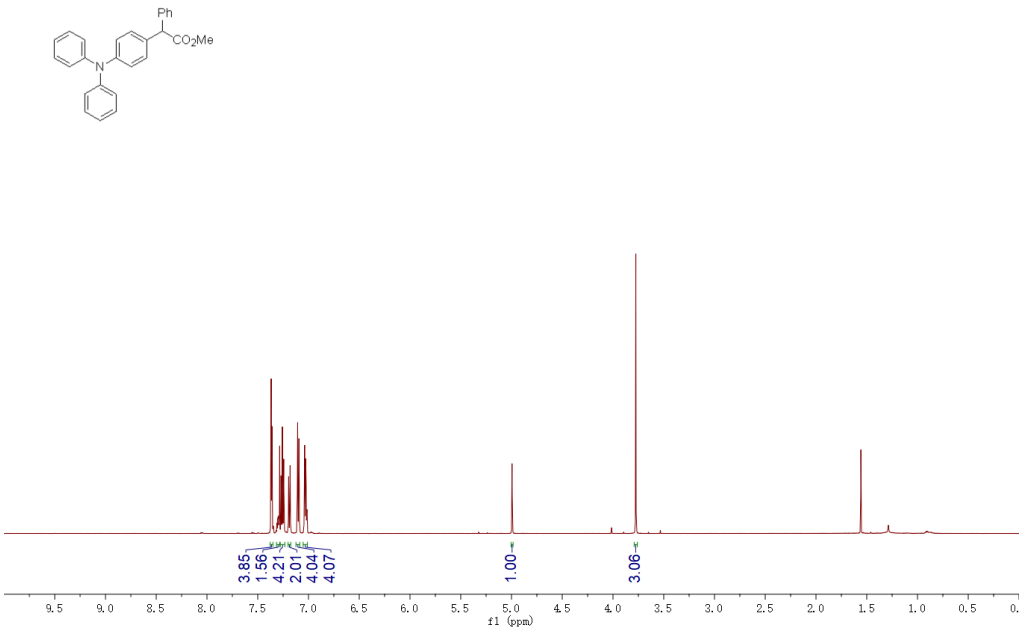


^{13}C NMR (151 MHz, Chloroform-*d*):

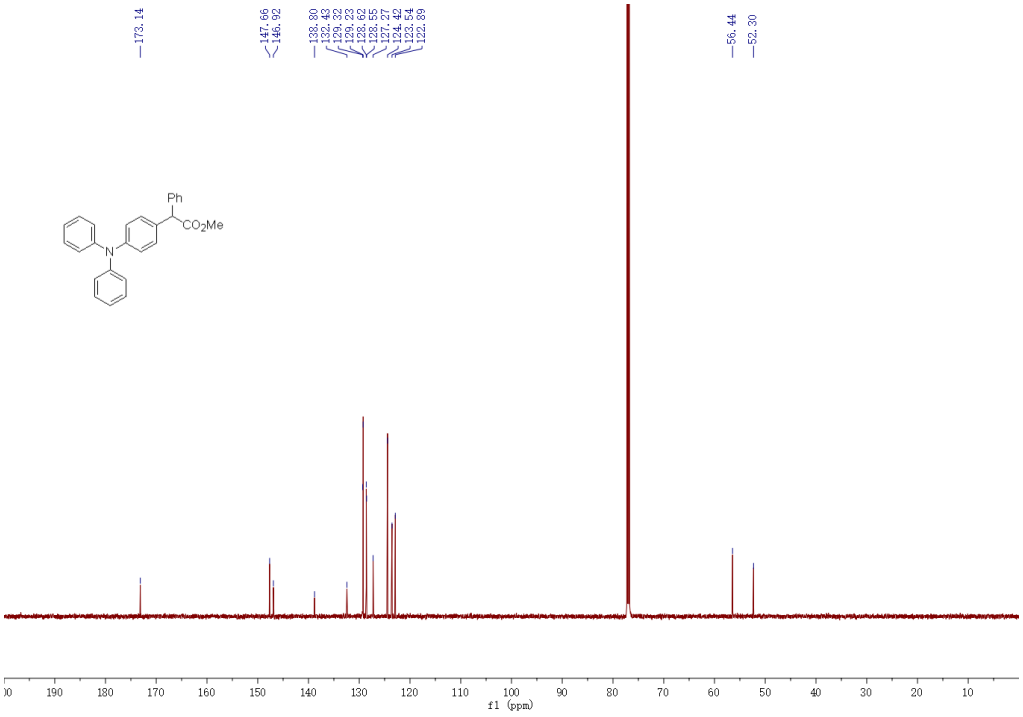


Methyl 2-(4-(diphenylamino)phenyl)-2-phenylacetate (5a)

^{1}H NMR (600 MHz, Chloroform-*d*):

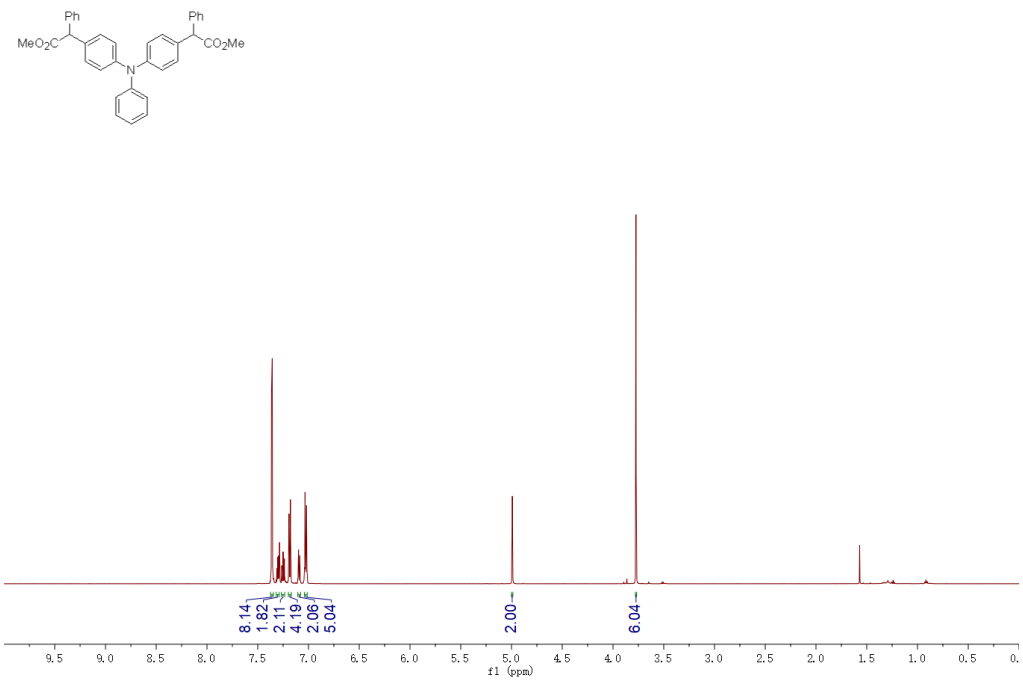


^{13}C NMR (151 MHz, Chloroform-*d*):

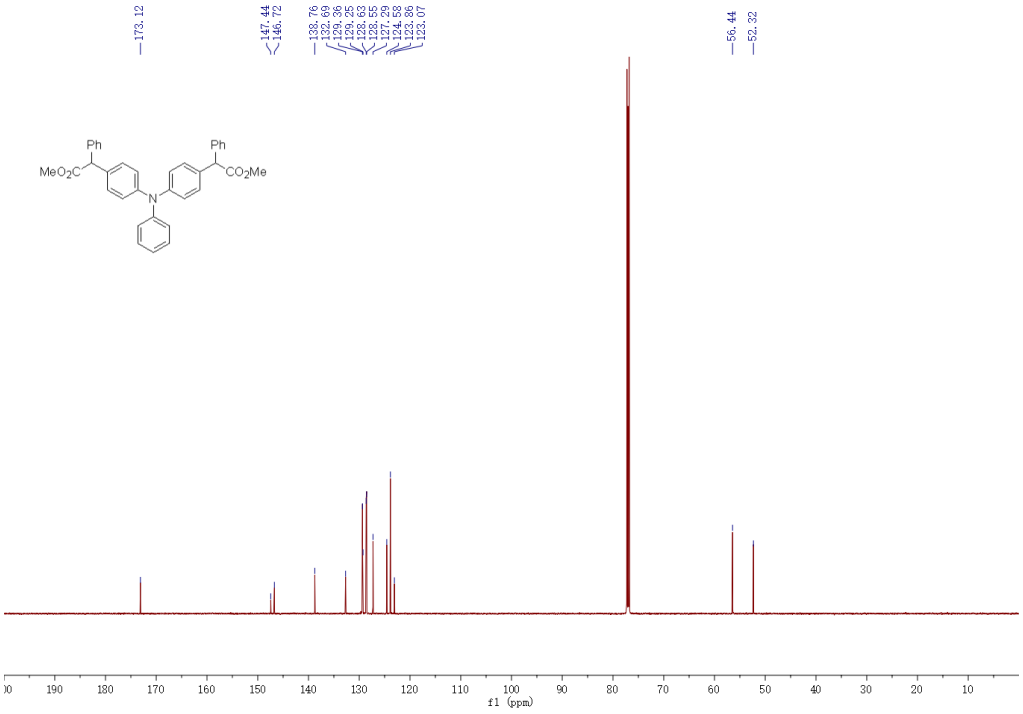


Dimethyl 2,2'-((phenylazanediyl)bis(4,1-phenylene))bis(2-phenylacetate) (5b)

^{1}H NMR (600 MHz, Chloroform-*d*):

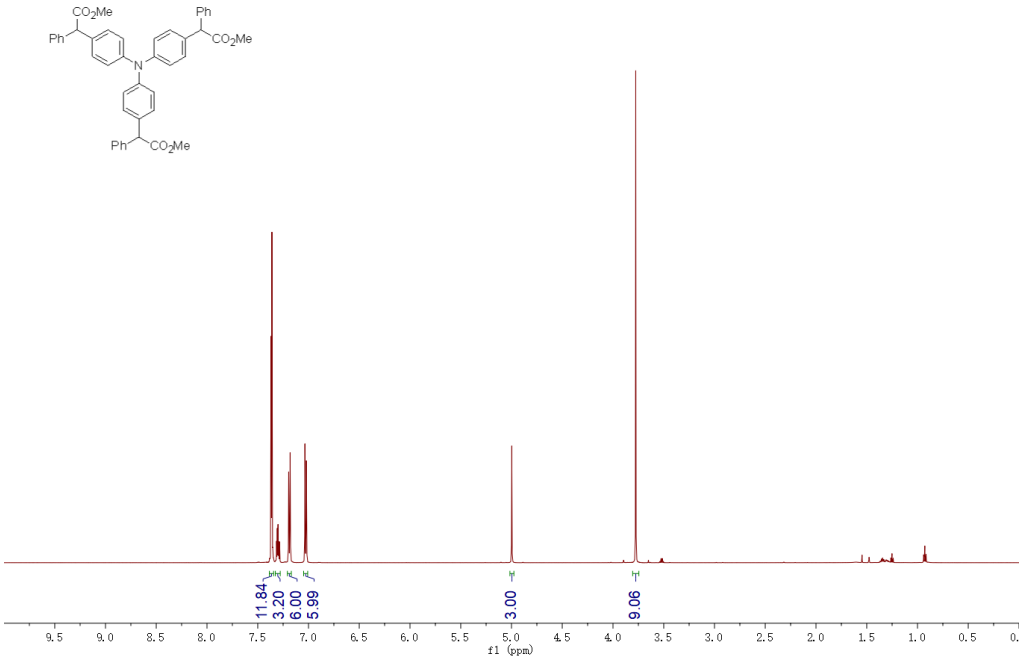


^{13}C NMR (151 MHz, Chloroform-*d*):

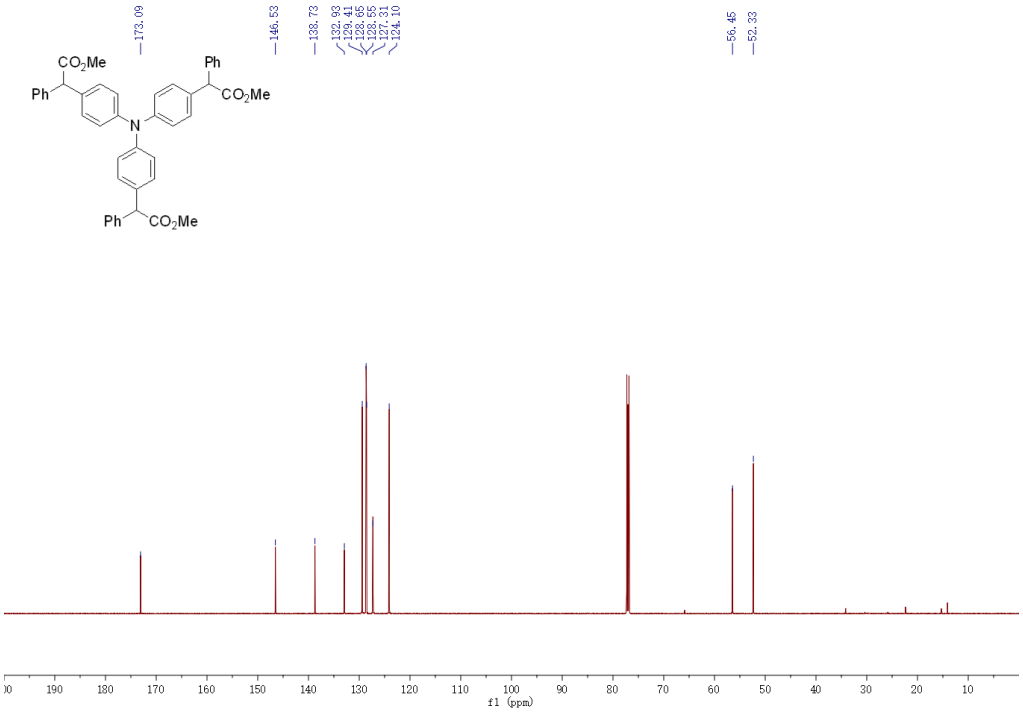


Trimethyl 2,2',2''-(nitrilotris(benzene-4,1-diyl))tris(2-phenylacetate) (5c)

^{1}H NMR (600 MHz, Chloroform-*d*):

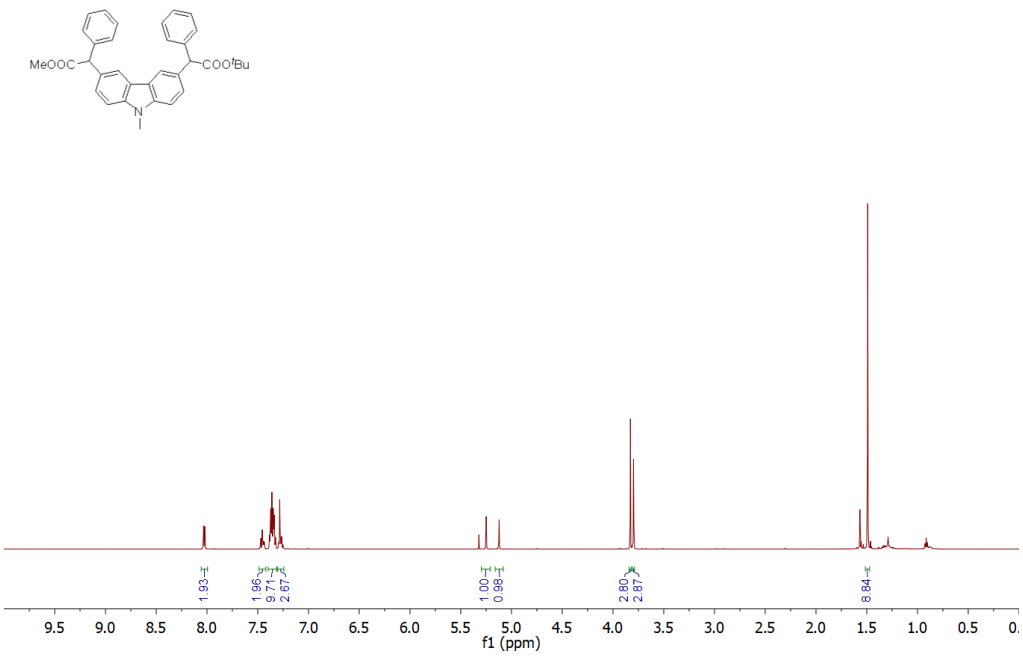


^{13}C NMR (151 MHz, Chloroform-*d*):

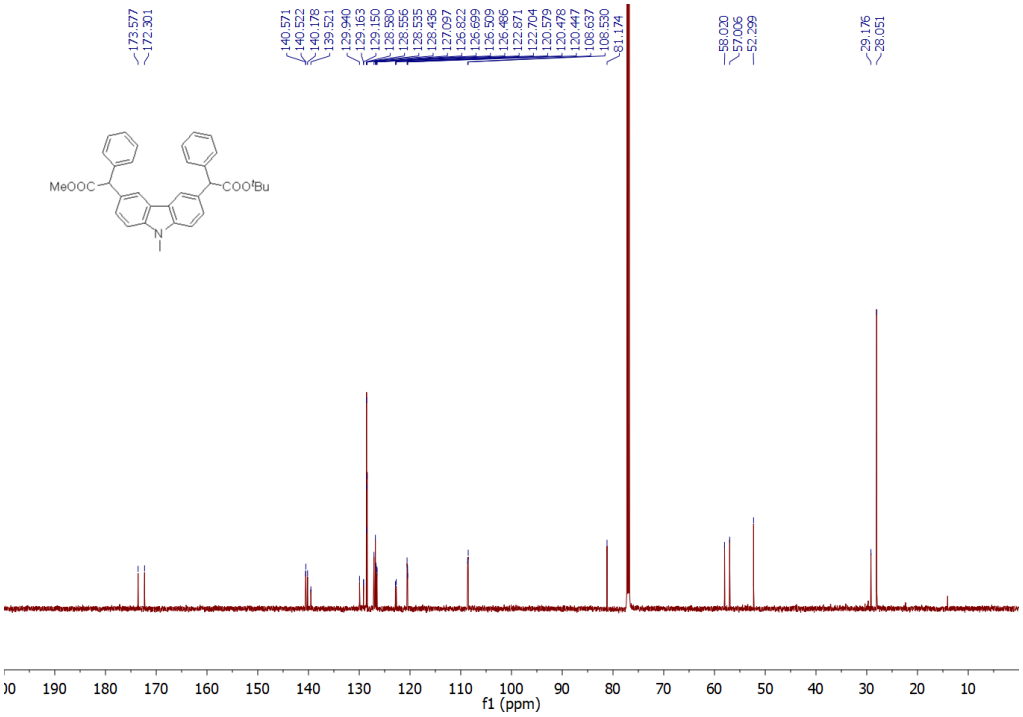


***tert*-butyl 2-(6-(2-methoxy-2-oxo-1-phenylethyl)-9-methyl-9*H*-carbazol-3-yl)-2-phenylacetate (4l)**

^{1}H NMR (600 MHz, Chloroform-*d*):

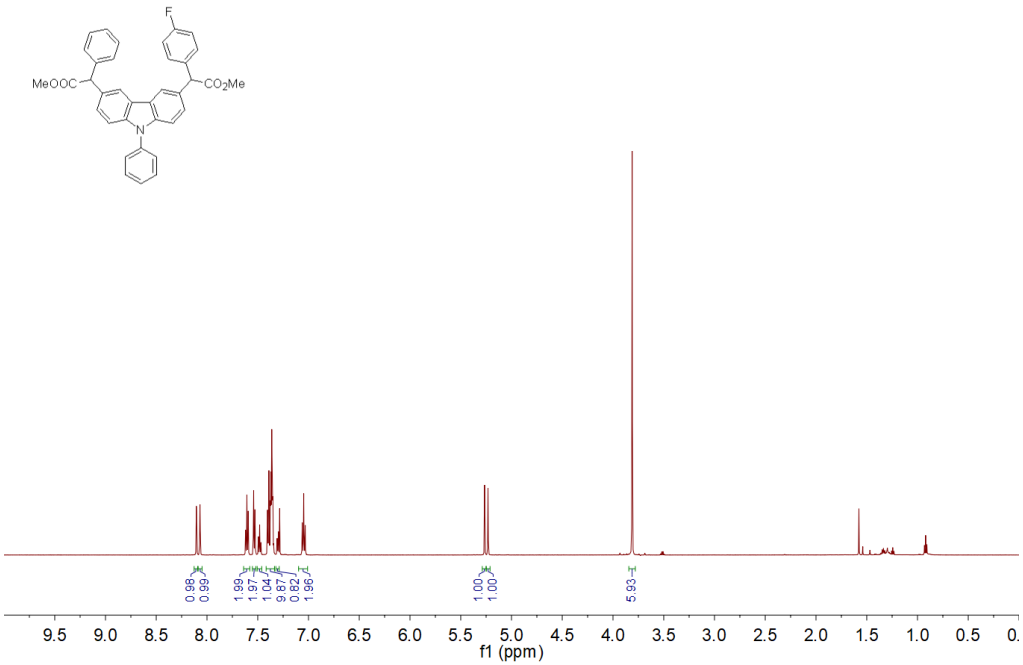


^{13}C NMR (151 MHz, Chloroform-*d*):

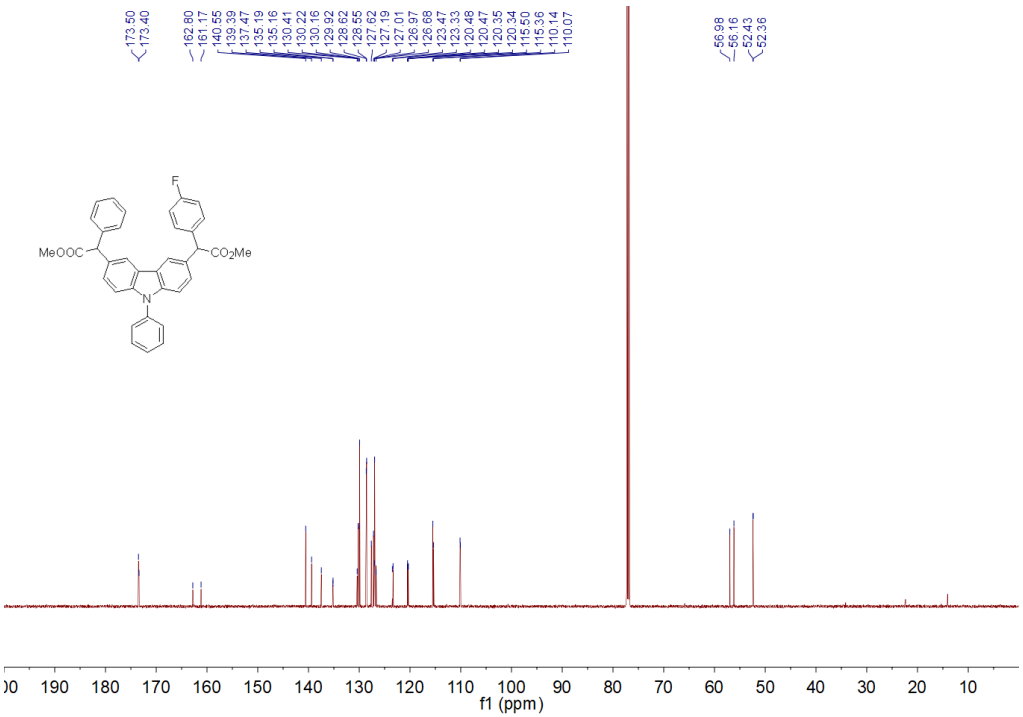


Methyl 2-(4-fluorophenyl)-2-(6-(2-methoxy-2-oxo-1-phenylethyl)-9-phenyl-9*H*-carbazol-3-yl)acetate (4m)

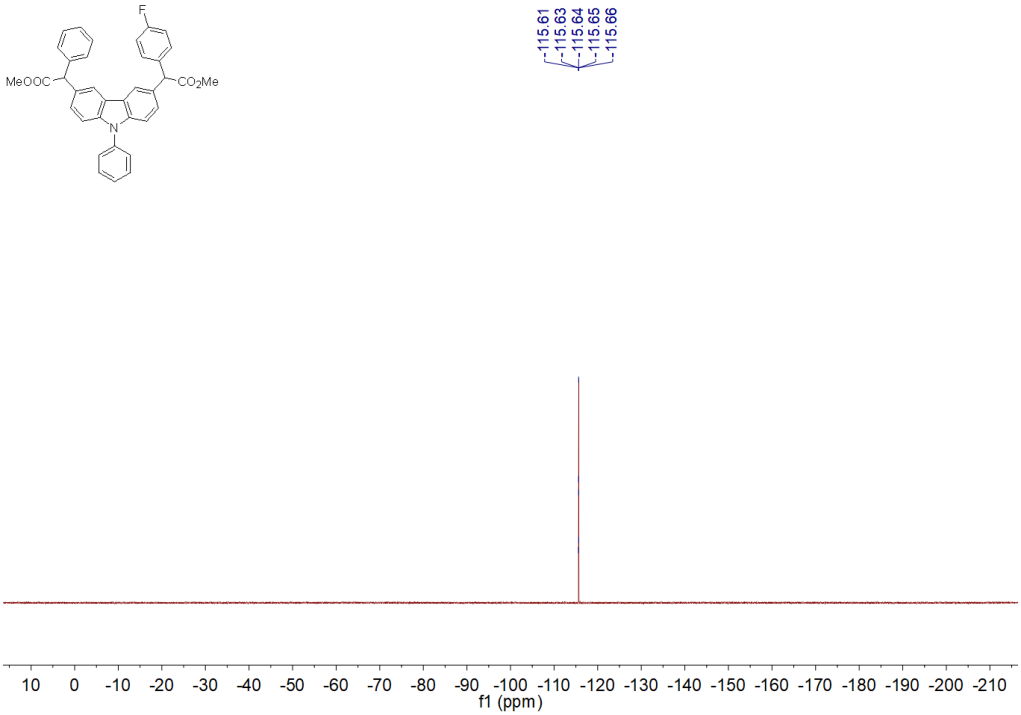
^{1}H NMR (600 MHz, Chloroform-*d*):



^{13}C NMR (151 MHz, Chloroform-*d*):

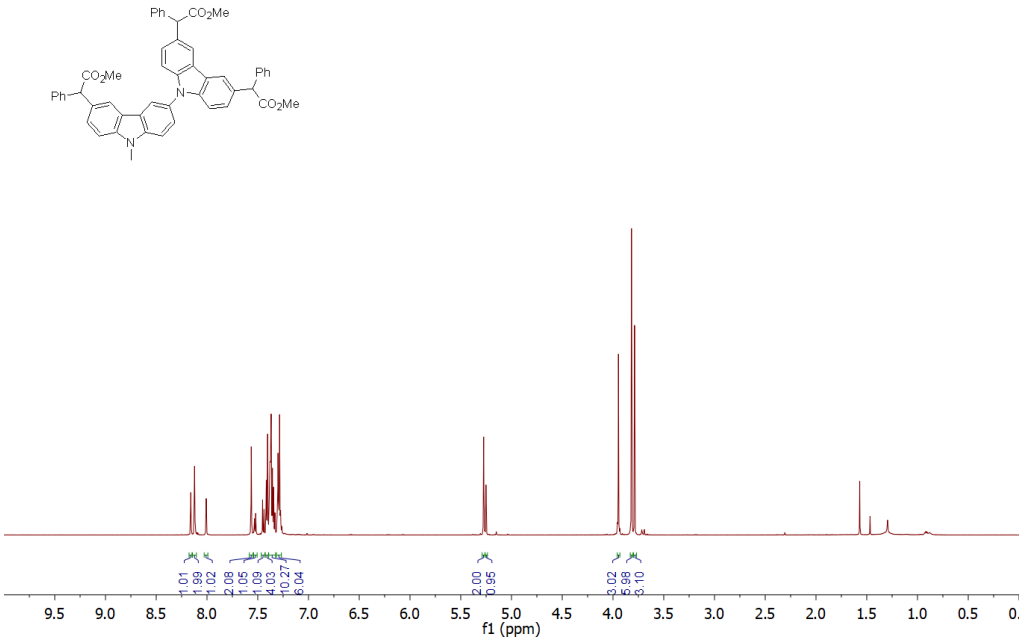


^{19}F NMR (565 MHz, Chloroform-*d*):

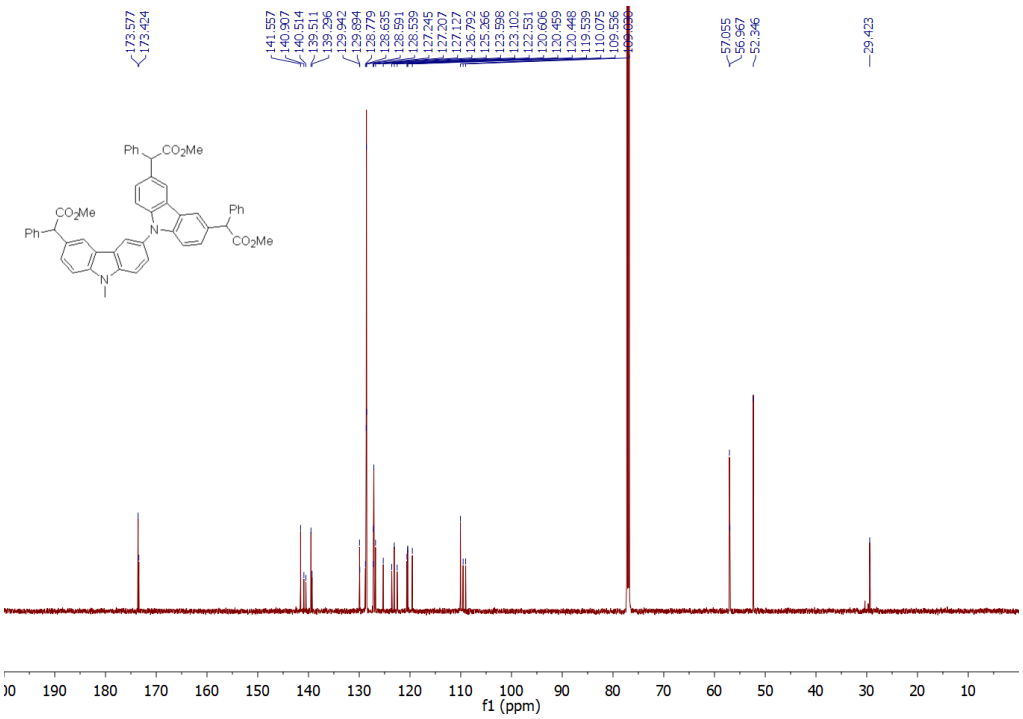


Trimethyl 2,2',2''-(9-methyl-9*H*-[3,9'-bicarbazole]-3',6,6'-triyl)tris(2-phenylacetate) (6)

^{1}H NMR (600 MHz, Chloroform-*d*):

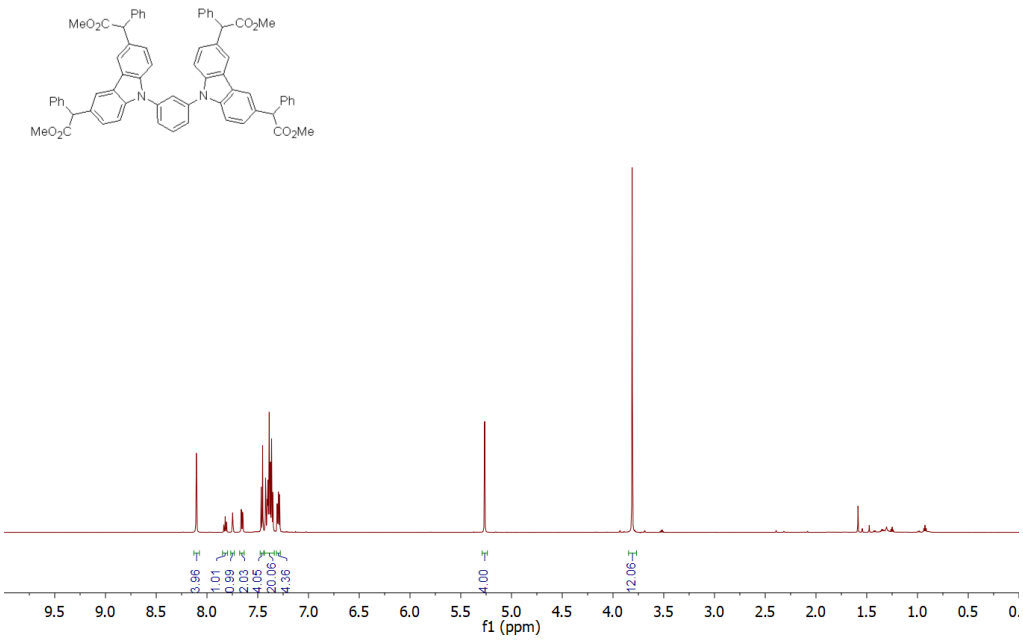


^{13}C NMR (151 MHz, Chloroform-*d*):

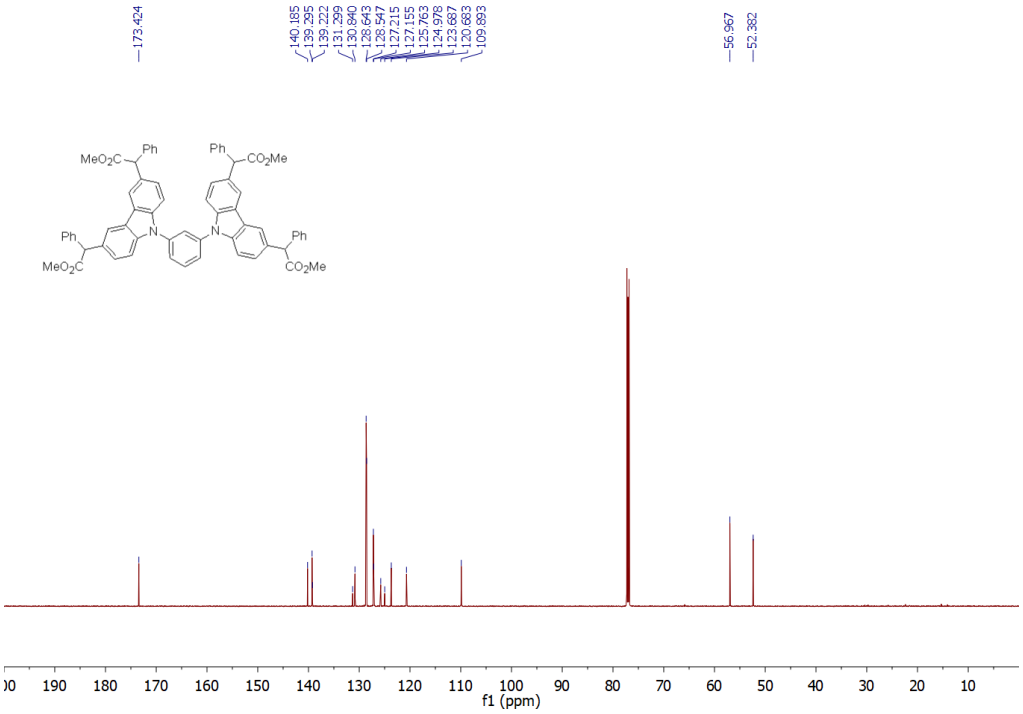


Tetramethyl 2,2',2'',2'''-(9,9'-(1,3-phenylene)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (7)

^{1}H NMR (600 MHz, Chloroform-*d*):

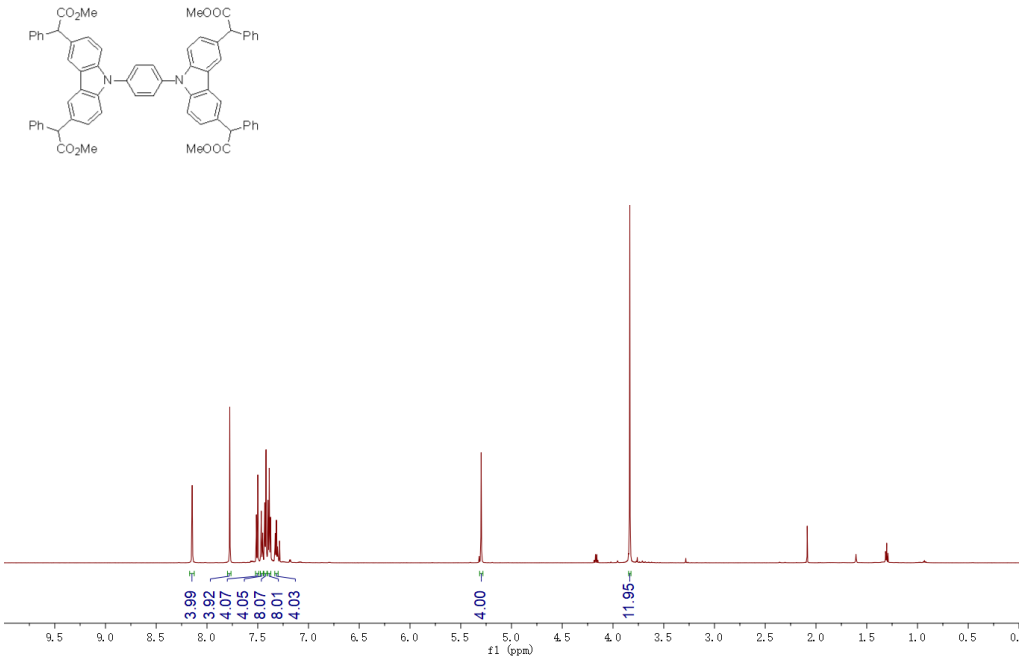


^{13}C NMR (151 MHz, Chloroform-*d*):

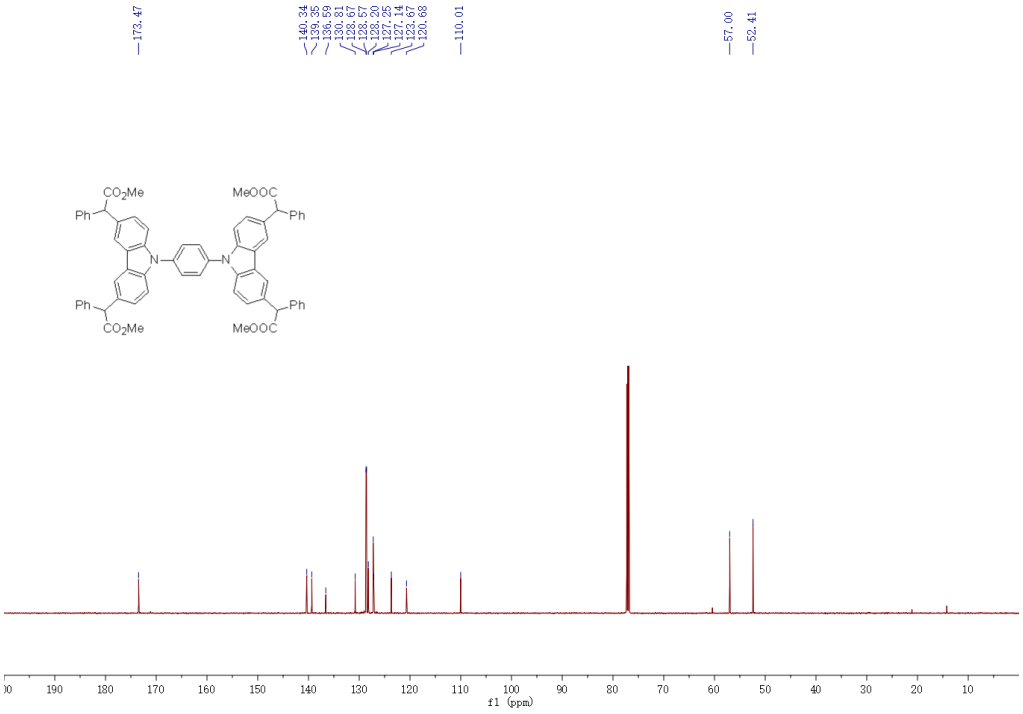


Tetramethyl 2,2',2'',2'''-(9,9'-(1,4-phenylene)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (8)

^{1}H NMR (600 MHz, Chloroform-*d*):

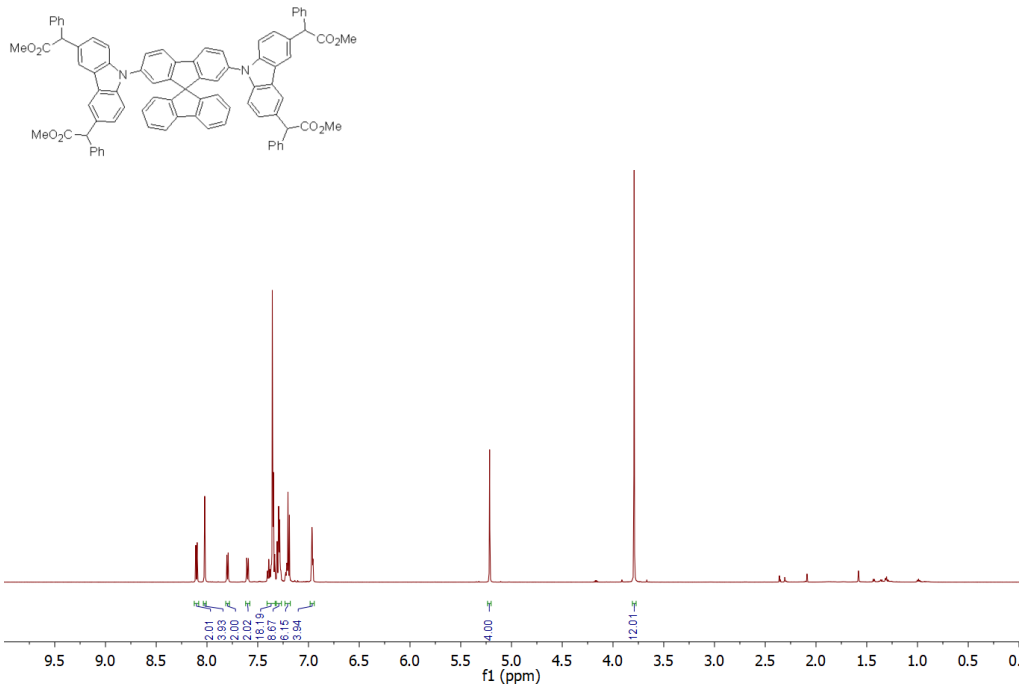


^{13}C NMR (151 MHz, Chloroform-*d*):

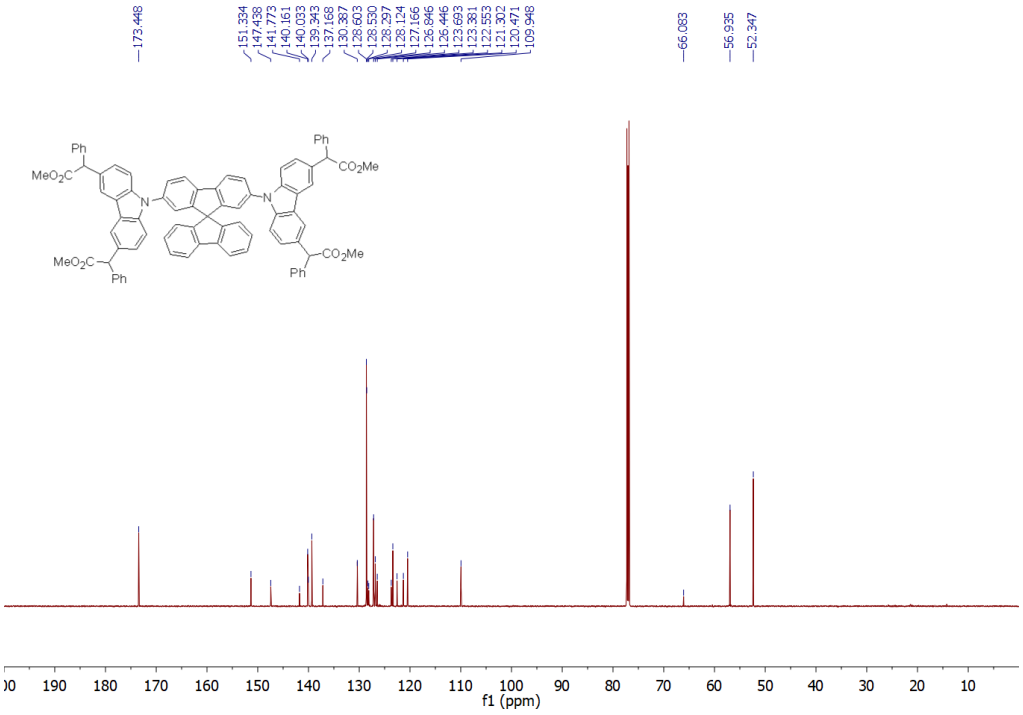


Tetramethyl 2,2',2'',2'''-(9,9'-(9,9'-spirobi[fluorene]-2,7-diyl)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (9)

^{1}H NMR (600 MHz, Chloroform-*d*):

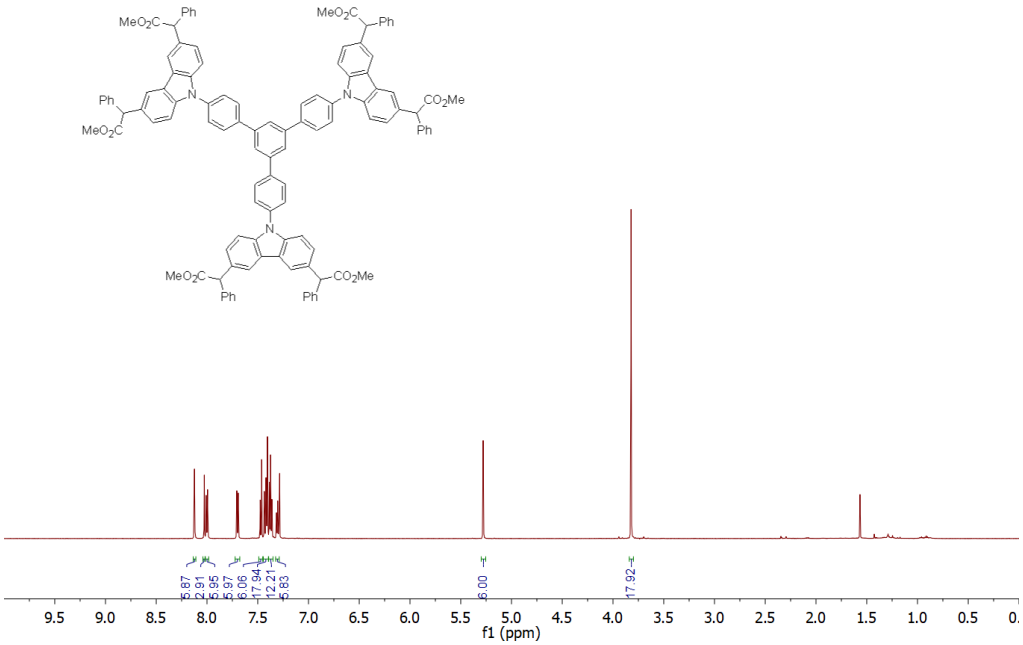


^{13}C NMR (151 MHz, Chloroform-*d*):

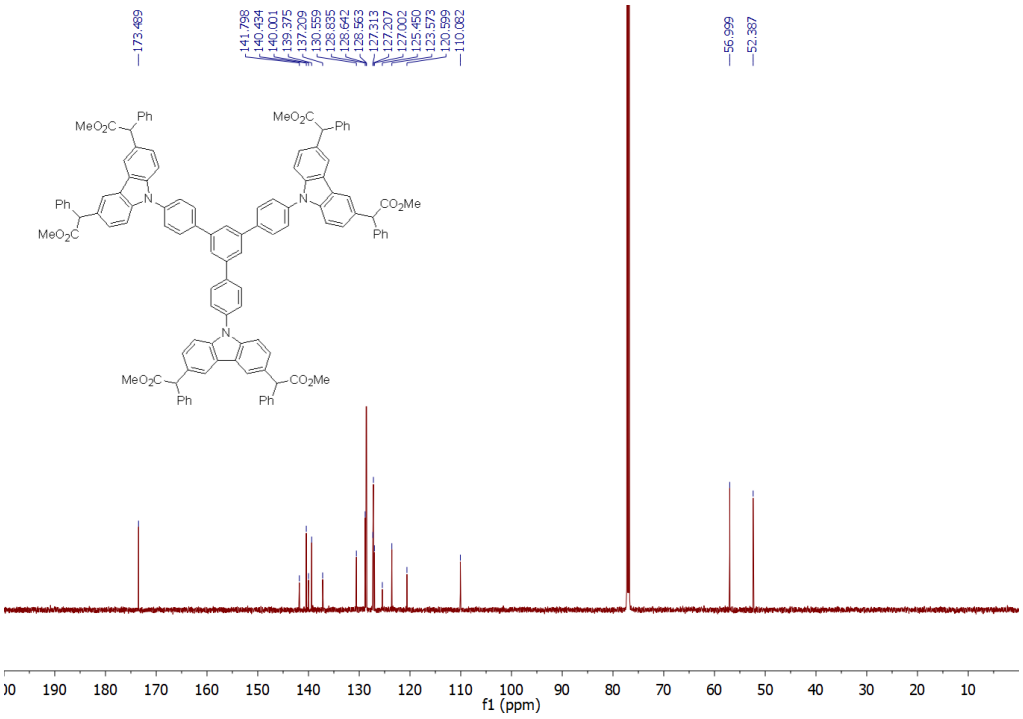


Tetramethyl 2,2',2'',2'''-(9,9'-(5'-(4-(3,6-bis(2-methoxy-2-oxo-1-phenylethyl)-9*H*-carbazol-9-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(9*H*-carbazole-9,6,3-triyl))tetrakis(2-phenylacetate) (10)

^{1}H NMR (600 MHz, Chloroform-*d*):

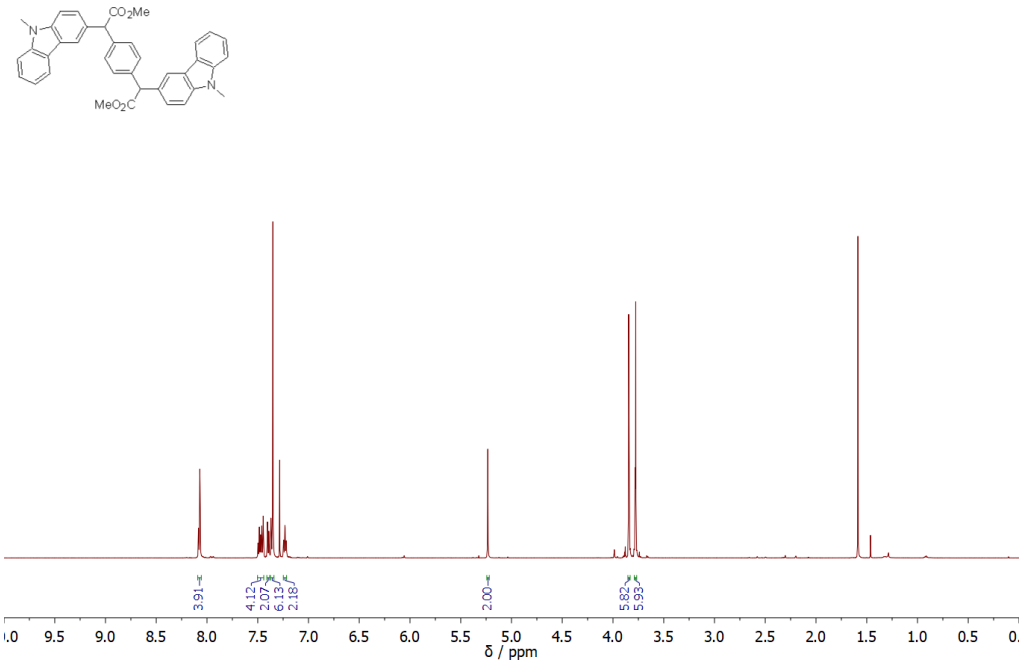


^{13}C NMR (151 MHz, Chloroform-*d*):

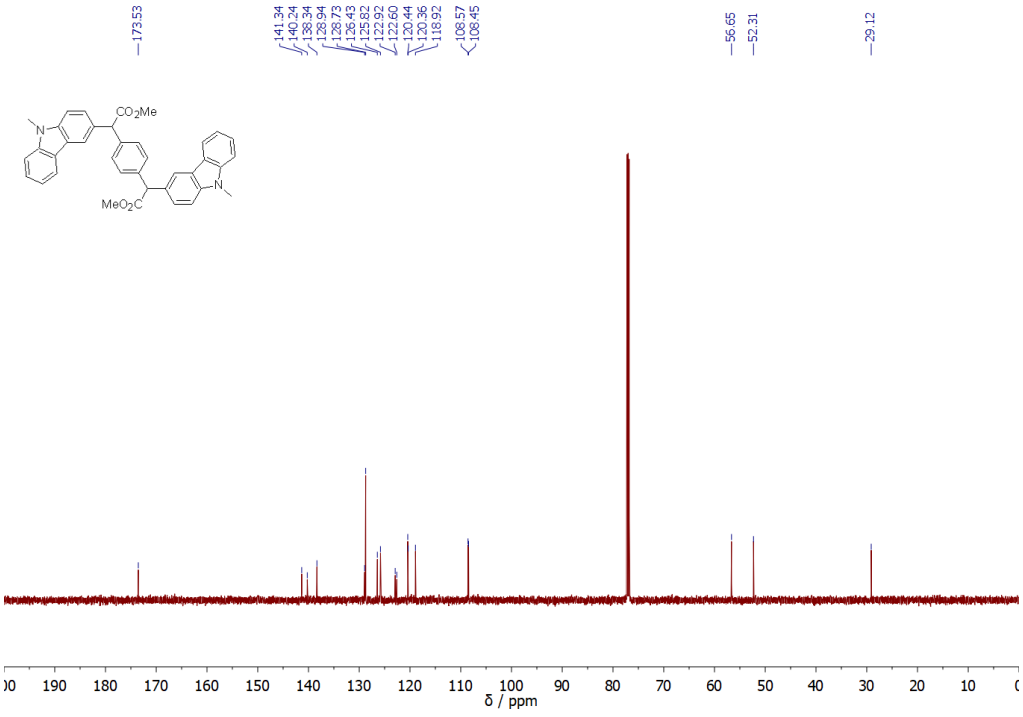


Dimethyl 2,2'-(1,4-phenylene)bis(2-(9-methyl-9*H*-carbazol-3-yl)acetate) (12)

^{1}H NMR (600 MHz, Chloroform-*d*):

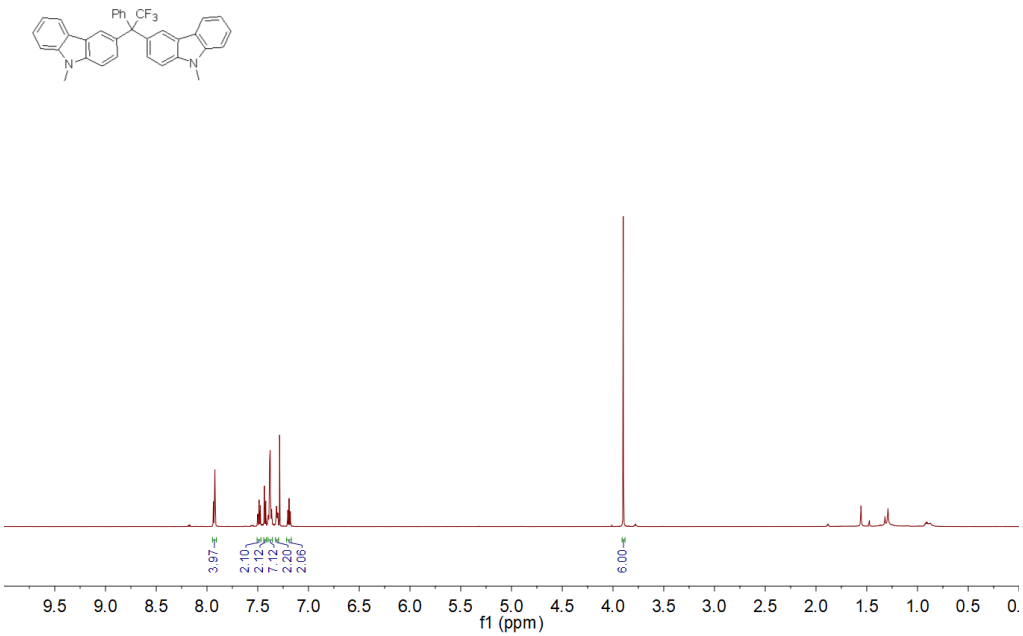


^{13}C NMR (151 MHz, Chloroform-*d*):

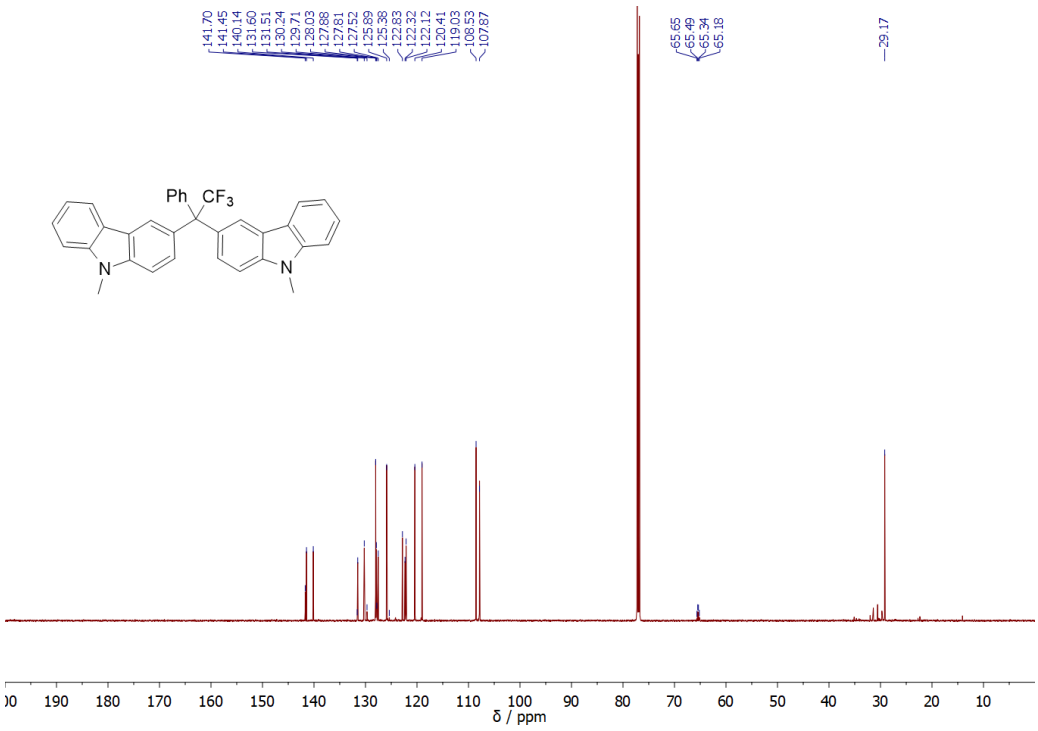


3,3'-(2,2,2-trifluoro-1-phenylethane-1,1-diyl)bis(9-methyl-9*H*-carbazole) (14)

^{1}H NMR (600 MHz, Chloroform-*d*):



^{13}C NMR (151 MHz, Chloroform-*d*):



^{19}F NMR (282 MHz, Chloroform-*d*):