Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Phosphine Mediated Reaction of Cyclic 1,2-Diones and 3-Alkyl Allenoates: An Efficient Protocol for Benzannulation Applicable to the Synthesis of Polycyclic Aromatic Hydrocarbons

Anu Jose,[a] Jayakrishnan A. J.,[a] Balaraman Vedhanarayanan,[a] Rajeev S. Menon,[b] Sunil Varughese,[a] Eringathodi Suresh[c] and Vijay Nair*[a]

[a] Chemical Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum 695 019, India

E-mail: vijaynair_2001@yahoo.com

[b] Medicinal Chemistry and Pharmacology Division, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500 007, India

[c] Analytical Department and Centralized Instrument Facility, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Bhavnagar 364 002, India.

Contents

1. General remarks

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 500 (^{1}H) and 126(^{13}C) MHz respectively on Bruker Avance DPX-500S MHz NMR spectrometer. Chemical shifts (δ) are reported relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. Coupling constant (*J*) is reported in Hertz (Hz). Mass spectra were recorded under HRMS (ESI) using Thermo Scientific Exactive Orbitrap mass spectrometer. IR spectra were recorded on a Bruker Alpha-T FT-IR spectrophotometer. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra on a SPEX-Fluorolog F112X spectrofluorimeter. Allenoates,[1] cycloheptane 1,2-dione,[2] and 3-bromoacenaphthene[3] were prepared using known

---

[1] R. W. Lang; H.-J. Hansen *Org. Synth. Coll. Vol.* **1990**, *7*, 232; **1984**, *62*, 202.

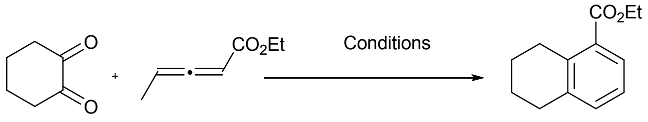
[2] Vogel's Textbook of Practical Organic Chemistry, Fifth Edition, Longman Group UK Ltd. **1989**, P.629.

[3] Z. Konga; H. Zhoua; J. Cuia; T. Maa; X. Yanga; L. Sunb, J. Photochem. Photobiol., A, **2010**, *213*, 152.

literature procedures. Gravity column chromatography was performed using silica gel and mixtures of petroleum ether-ethyl acetate were used for elution.

2. Optimization Studies

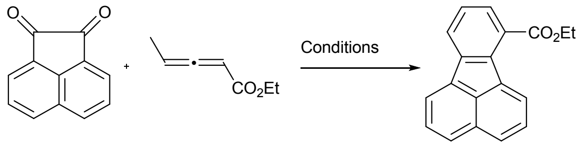
Table S1: Condition optimization for the benzannulation of cycloalkane1,2-dione



Entry	Phosphine	Allenoate (equiv)	Solvent	Temp (^{o}C)	Time (h)	Yield (%)
1	PPh$_3$(1.5 equiv)	1.5	THF	rt	3	41
2	PPh$_3$ (0.5 equiv)	1.5	THF	rt	12	12
3	PPh$_3$ (1.5 equiv)	1.5	THF	65	2	18
4	PPh$_3$ (1.5 equiv)	1.5	DCM	rt	3	31
5	PPh$_3$ (1.5 equiv)	1.5	Toluene	rt	3	33
6	PPh$_3$ (1.5 equiv)	1.5	CH$_3$CN	rt	5	14
7	PPh$_3$(1.5 equiv)	1.5	THF	rt	3	76[a]
8	PPh$_3$ (2.5 equiv)	2.5	THF	rt	3	84
9	PBu$_3$ (2.5 equiv)	2.5	THF	rt	24	trace
10	P(2-CH$_3$C$_6$H$_4$)$_3$ (2.5 equiv)	2.5	THF	rt	24	-
11	TDMPP[b] (2.5 equiv)	2.5	THF	rt	24	-
12	P(C$_6$F$_5$)$_3$ (2.5 equiv)	2.5	THF	rt	24	-
13	P(Cy)$_3$ (2.5 equiv)	2.5	THF	rt	24	<5

[a]Isolated yield of **3a** when both reagents were simultaneously added dropwise. [b]TDMPP = tris(2,6-dimethoxyphenyl)phosphine.

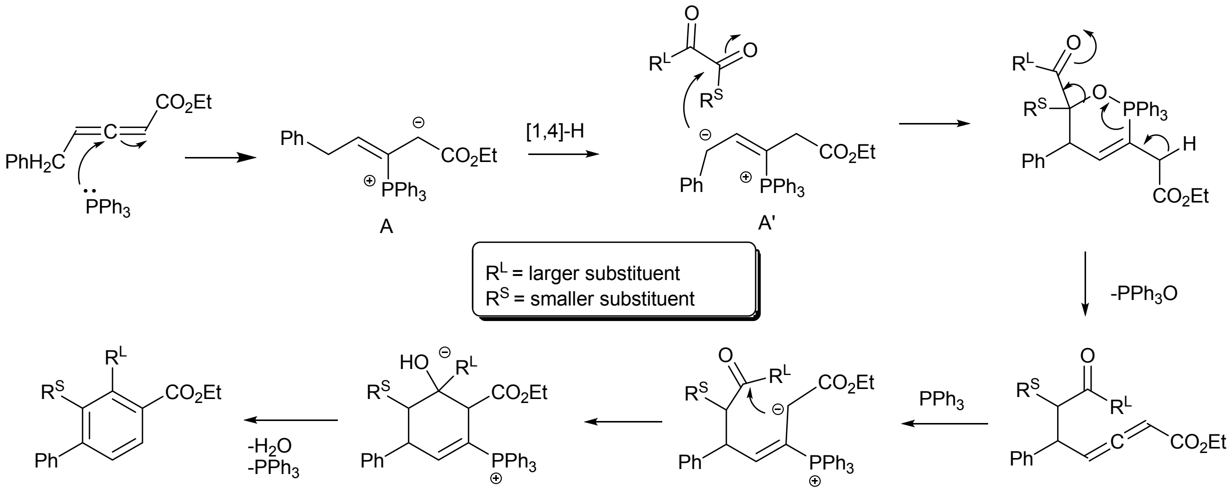
Table S2: Condition Optimization for the Benzannulation of Quinones



Entry	Phosphine	Allenoate (equiv)	Solvent	Time (h)	Temp	Yield (%)
1	PPh$_3$ (1.5 equiv)	1.5	THF	3	rt	29
2	PPh$_3$ (1.5 equiv)	1.5	Toluene	5	rt	34
3	PPh$_3$ (1.5 equiv)	1.5	DCM	3	rt	41
4	PPh$_3$ (2.5 equiv)	2.5	DCM	1	rt	82
5	TDMPP (2.5 equiv)	2.5	DCM	24	rt	-
6	P(Cy)3 (2.5 equiv)	2.5	DCM	24	rt	<5

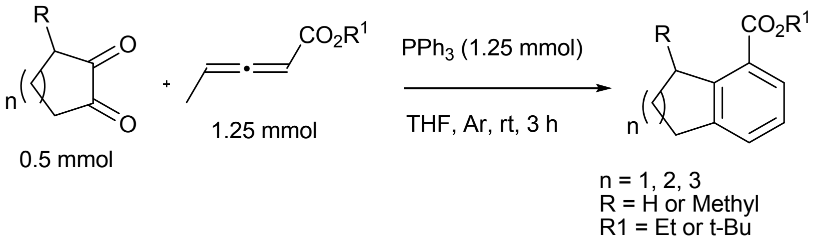
TDMPP = tris(2,6-dimethoxyphenyl)phosphine

3. Mechanistic Postulate for the formation of 6g



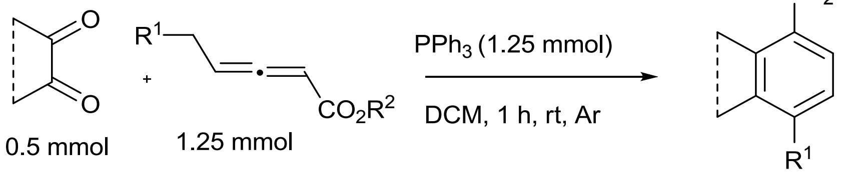
4. General Experimental procedure for the Benzannulation Reaction

(a) General procedure for the benzannulation of cycloalkane1,2-diones



The dione (0.5 mmol) and the allenoate (1.25 mmol) were taken in a round bottom flask in dry THF (3 ml) under argon atmosphere. Triphenylphosphine (1.25 mmol) was added to this mixture and stirred at room temperature for 3 h. After the completion of the reaction, as indicated by TLC, the crude mixture was concentrated and purified by column chromatography on silica gel using hexane: ethyl acetate (98:2) as the eluent to afford the benzannulated product.

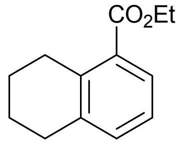
(b) General procedure for the benzannulation of quinones



The quinone (0.5 mmol) and the allenoate (1.25 mmol) were taken in a round bottom flask in dry DCM (3 ml) under argon atmosphere. Triphenylphosphine (1.25 mmol) was added to this mixture and stirred at room temperature for 1 h. After the completion of the reaction, as indicated by TLC, the crude mixture was concentrated and purified by column chromatography on silica gel using hexane: ethyl acetate (98:2) as the eluent to afford the benzannulated product.

5. Characterization data for compounds

Ethyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate (3a)



Yield: (86 mg, 84%), colourless oil.

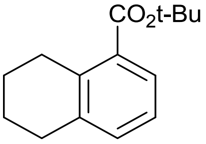
IR (film) ν_{max}: 1719, 1259, 1135 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.32 (q, *J* = 7.0 Hz, 2H), 3.06 – 3.04 (m, 2H), 2-82 – 2.80 (m, 2H), 1.80 – 1.78 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 167.9, 138.4, 138.1, 132.8, 130.6, 127.8, 124.9, 60.4, 30.2, 27.7, 23.2, 22.5, 14.4 ppm.

HRMS (ESI-MS) calcd for $C_{13}H_{16}O_2Na^+$ 227.1048; Found: 227.1050.

tert-Butyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate (3b)



Yield: (95 mg, 82%), colourless oil.

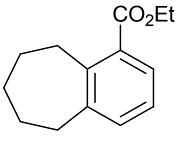
IR (film) ν_{max}: 1711, 1279, 1133 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 3.02 – 3.00 (m, 2H), 2.80 – 2.78 (m, 2H), 1.79-1.77 (m, 4H), 1.58 (s, 9H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 167.9, 138.4, 138.1, 132.8, 130.59, 127.8, 124.9, 60.4, 30.2, 27.7, 23.2, 22.5, 14.4 ppm.

HRMS (ESI-MS) calcd for $C_{15}H_{20}O_2Na^+$ 255.1361; Found: 255.1353.

Ethyl 6,7,8,9-tetrahydro-5H-benzo[7]annulene-1-carboxylate (3c)



Yield: (41 mg, 38%), colourless oil.

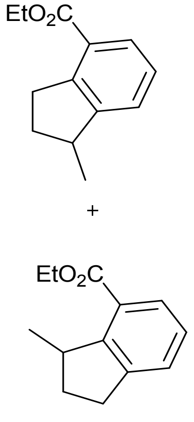
IR (film) ν_{max}: 1715, 1293, 1131 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.19 (d, *J* = 6.5 Hz1H), 7.08 (t, *J* = 7.5 Hz, 1H), 4.34 (q, *J* = 7.0 Hz, 2H), 3.02 – 3.00 (m, 2H), 2.86 – 2.84 (m, 2H), 1.86 – 1.81 (m, 2H), 1.71 – 1.63 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 169.1, 144.8, 143.1, 131.6, 131.5, 127.0, 125.3, 60.7, 36.2, 32.1, 30.9, 27.9, 27.2, 14.3 ppm.

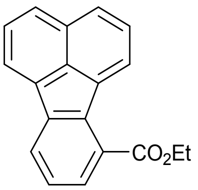
HRMS (ESI-MS) calcd for $C_{14}\ H_{18}O_2Na^+$ 241.1205; Found: 241.1198.

Ethyl 1-methyl-2,3-dihydro-1H-indene-4-carboxylate & Ethyl 3-methyl-2,3-dihydro-1H-indene-4-carboxylate (3d & 3d[1])



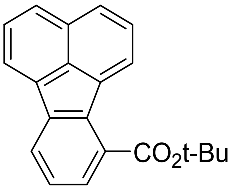
Yield: (31 mg, 30%), colourless oil.
IR (film) ν_{max}: 1719, 1262, 1131 cm^{-1}.
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82 – 7.78 (m, 1.64H), 7.34 (m, 1.64H), 7.22 (t, J = 7.5 Hz, 0.64H), 7.18 (t, J = 7.5 Hz, 1H), 4.38 – 4.33 (m, 3.28H), 3.92 – 3.89 (m, 1H), 3.36 (ddd, J_1 = 17.5 Hz, J_2 = 8.8 Hz, J_3 = 4.0 Hz, 0.64H), 3.21 – 3.01 (m, 2.28H), 2.81 (dd, J_1 = 16.0 Hz, J_2 = 9.0 Hz, 1H), 2.37 – 2.29 (m, 0.64H), 2.25 – 2.18 (m, 1H), 1.82 (ddt, J_1 = 12.3, J_2 = 7.8, J_3 = 1.5 Hz, 1H), 1.65 – 1.57 (m, 0.64H), 1.42 – 1.38 (m, 4.92H), 1.29 (d, J = 7.0 Hz, 1.92H), 1.19 (d, J = 7.0 Hz, 3H) ppm.
^{13}C NMR (126 MHz, CDCl$_3$): δ 167.0, 166.8, 151.4, 150.2, 146.2, 144.6, 128.7, 128.4, 128.1, 127.2, 126.7, 126.4, 126.2, 126.2, 60.4, 60.4, 39.6, 39.0, 34.2, 33.4, 32.4, 30.2, 20.1, 20.1, 14.4, 14.3 ppm.
HRMS (ESI-MS) calcd for $C_{13}H_{16}O_2Na^+$ 227.1048; Found: 227.1051.

Ethyl fluoranthene-7-carboxylate (6a)



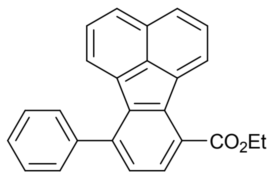
Yield: (112 mg, 82%), pale yellow solid. mp 60-62 °C.
IR (film) ν_{max}: 1721, 1263 cm^{-1}.
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.85 (d, J = 7.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.97 - 7.94 (m, 2H), 7.88 (t, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 4.52 (q, J = 7.0 Hz, 2H), 1.50 (t, J = 7.0 Hz, 3H) ppm.
^{13}C NMR (126 MHz, CDCl$_3$): δ 167.4, 140.9, 138.9, 135.5, 132.8, 129.8, 129.6, 128.4, 127.7, 127.5, 127.3, 127.3, 127.2, 126.7, 124.6, 119.8, 61.0, 14.5 ppm.
HRMS (ESI-MS) calcd for $C_{19}H_{14}O_2Na^+$: 297.0892; Found: 297.0895.
Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.17; H, 4.91 %.

tert-Butyl fluoranthene-7-carboxylate (6b)



Yield: (98 mg, 65%), pale yellow oil.
IR (film) ν_{max}: 1709, 1277, 1126 cm^{-1}.
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.81 (d, J = 7.5 Hz, 1H), 8.02 (d, J = 7.0 Hz, 1H), 7.92 (d, J = 7.0 Hz, 1H), 7.87 - 7.83 (m, 3H), 7.67 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 1.71 (s, 9H) ppm.
^{13}C NMR (126 MHz, CDCl$_3$): δ 166.8, 140.8, 138.6, 135.6, 135.6, 132.8, 129.8, 129.4, 129.1, 128.4, 127.5, 127.3, 127.3, 127.2, 126.6, 124.2, 119.7, 81.3, 28.4 ppm.
HRMS (ESI-MS) calcd for $C_{21}H_{18}O_2Na^+$: 325.1205; Found: 325.1198.

Ethyl -10-phenylfluoranthene-7-carboxylate (6c)



Yield: (172 mg, 98%), yellow solid, mp 94-96 ^{o}C

IR (film) ν_{max}: 1718, 1234, 1116 cm^{-1}.

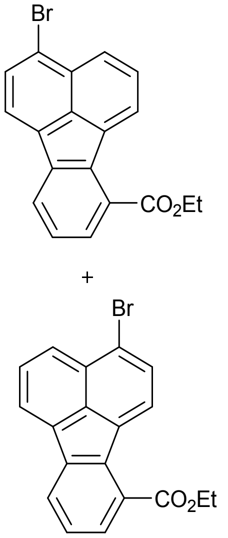
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.84 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.50 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 4.55 (q, *J* = 7.0 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 142.2, 140.5, 139.2, 138.0, 135.3, 134.9, 132.9, 129.7, 129.0, 128.8, 128.7, 128.7, 128.1, 127.9, 127.2, 126.3, 123.2, 61.1, 14.5 ppm.

HRMS (ESI-MS) calcd for $C_{25}H_{18}O_2Na^+$: 373.1205; Found: 373.1187.

Anal. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.42; H, 5.01 %.

Ethyl 3-bromofluoranthene-7-carboxylate & Ethyl 4-bromofluoranthene-7-carboxylate & Ethyl 4-bromofluoranthene-7-carboxylate (6d & 6d^1)



Yield: (124 mg, 70%), yellow solid

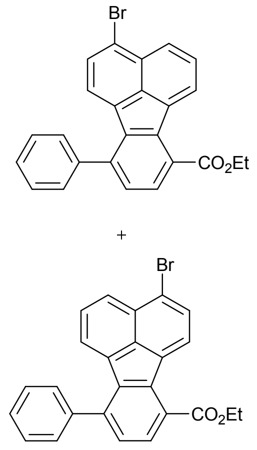
IR (film) ν_{max}: 1719, 1435, 1260, 1118 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (d, *J* = 7.0 Hz, 0.74H), 8.63 (d, *J* = 7.5 Hz, 1H), 8.01-7.97 (m, 1.74H), 7.95 – 7.91 (m, 3.48H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 0.74H), 7.68 (t, *J* = 7.5 Hz, 0.74H), 7.64 – 7.60 (m, 1.74H), 7.38 – 7.33 (m, 1.74H), 4.52 – 4.47 (m, 3.48H), 1.51 – 1.48 (m, 5.22H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.8, 166.8, 140.5, 140.1, 138.6, 138.4, 135.7, 135.6, 135.1, 135.1, 133.8, 133.7, 131.6, 130.5, 129.9, 129.9, 129.5, 129.5, 128.4, 128.3, 128.2, 127.2, 127.0, 126.9, 126.9, 126.6, 124.7, 124.5, 123.3, 122.6, 120.3, 120.1, 61.0, 14.5 ppm.

HRMS (ESI-MS) calcd for $C_{19}H_{13}BrO_2$ Na^+ 374.9997; Found: 375.0003 $(M+Na)^+$, 376.9982 $(M+2+Na)^+$

Ethyl 3-bromo-10-phenylfluoranthene-7-carboxylate & Ethyl 4-bromo-10-phenylfluoranthene-7-carboxylate (6e & 6e^1)



Yield: (139 mg, 65%), yellow solid.

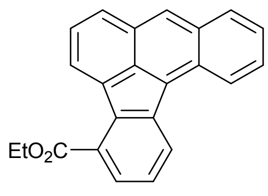
IR (film) ν_{max}: 1719, 1422, 1249, 1122 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.85 (d, *J* = 7.5 Hz, 0.84H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 0.84H), 7.96 – 7.92 (m, 2.84H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 0.84H), 7.54 – 7.48 (m, 9.2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.27 – 7.22 (m, 2.68H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 0.84H), 4.55 – 4.50 (m, 3.68H), 1.51 – 1.48 (m, 5.52H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.3, 167.2, 142.4, 142.2, 140.2, 140.1, 138.8, 138.7, 137.6, 137.3, 135.6, 135.2, 135.0, 134.7, 134.1, 134.1, 131.4, 130.5, 129.5, 129.4, 129.4, 129.4, 129.3, 129.0, 129.0, 128.8, 128.7, 128.7, 128.3, 128.2, 128.0, 127.9, 127.2, 126.4, 126.3, 123.8, 123.6, 123.5, 122.6, 61.2, 14.5 ppm.

HRMS (ESI-MS) calcd for $C_{25}H_{17}BrO_2Na^+$ 451.0310; Found: 451.0304 (M+Na)$^+$, (M+2+Na)$^+$ 453.0284.

Ethyl benzo[a]aceanthrylene-4-carboxylate (6f)



Yield: (83 mg, 51%), orange solid, mp 96-100 °C

IR (film) ν_{max}: 1719, 1248, 1126 cm^{-1}.

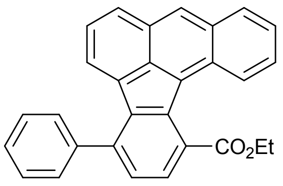
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.92 (d, *J* = 7.0 Hz, 1H), 8.81 (d, *J* = 8.5 Hz, 1H), 8.63 (d, *J* = 7.5 Hz, 1H), 8.52 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.73– 7.67 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 4.56 (q, *J* = 7.0 Hz, 2H), 1.52 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 167.7, 141.9, 138.1, 135.0, 134.0, 131.1, 130.7, 129.3, 128.8, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 126.8, 124.7, 123.8, 61.1, 14.5 ppm.

HRMS (ESI-MS) calcd for $C_{23}H_{16}O_2Na^+$: 347.1048; Found: 347.1050.

Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 84.95; H, 4.71 %.

Ethyl 4-phenylbenzo[a]aceanthrylene-1-carboxylate (6g)



Yield: (76 mg, 38%), orange yellow solid, mp 145-150 °C

IR (film) ν_{max}: 1712, 1244, 1101 cm^{-1}.

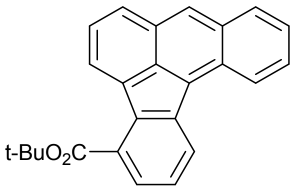
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.51 (s, 1H), 8.13 (t, *J* = 10.0 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.58 – 7.52 (m, 4H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 6.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 1.03 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 170.5, 141.4, 140.5, 138.5, 137.2, 135.4, 134.5, 131.7, 131.0, 130.3, 129.9, 129.4, 128.9, 128.9, 128.7, 128.3, 128.1, 128.1, 127.6, 127.4, 127.0, 126.5, 125.8, 124.8, 124.1, 61.4, 13.7 ppm.

HRMS (ESI-MS) calcd for $C_{29}H_{20}O_2Na^+$: 423.1361; Found: 423.1366.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.98; H, 5.03. Found: C, 86.82; H, 4.89 %.

***tert*-Butyl benzo[a]aceanthrylene-4-carboxylate (6h)**



Yield: (81 mg, 46%), orange solid, mp 125-130 °C

IR (film) ν_{max}: 1713, 1277, 1128 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.87 (d, *J* = 7.0 Hz, 1H), 8.82 (d, *J* = 9.0 Hz, 1H), 8.60 (d, *J* = 7.5 Hz, 1H), 8.53 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.55 – 7.50 (m, 2H), 1.74 (s, 9H) ppm.

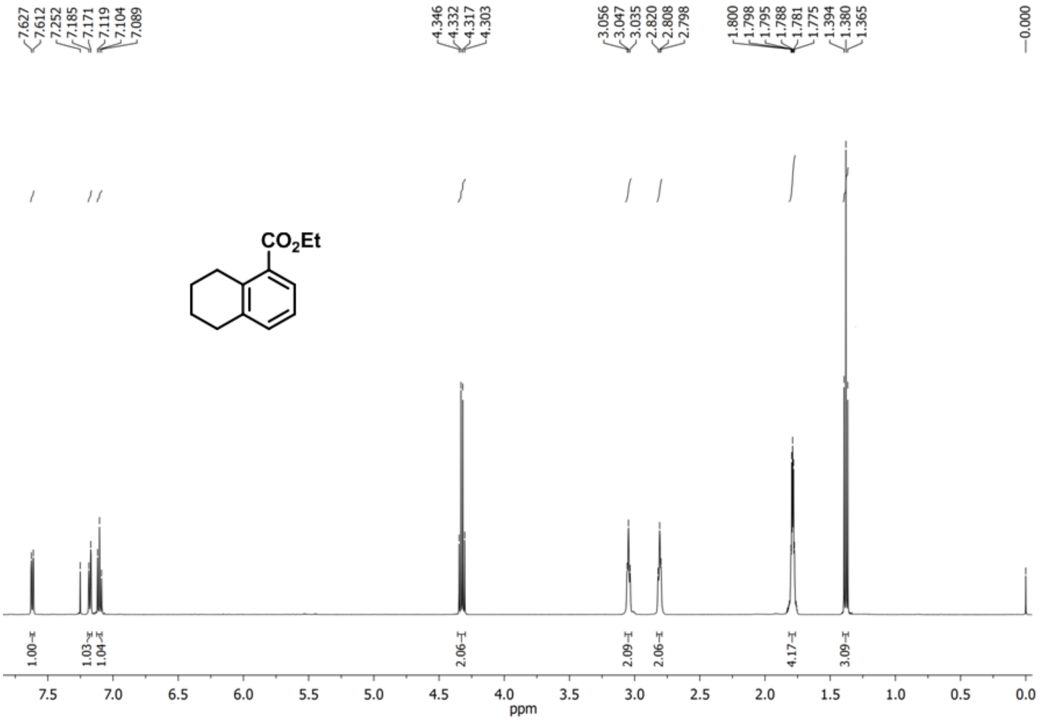
^{13}C NMR (126 MHz, CDCl$_3$): δ ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.4, 141.8, 137.6, 135.2, 134.1, 131.2, 130.7, 129.6, 129.4, 128.8, 128.2, 128.1, 128.0, 127.8, 127.8, 127.7, 127.5, 127.0, 126.4, 124.8, 123.9, 81.6, 28.4 ppm.

HRMS (ESI-MS) calcd for $C_{25}H_{20}O_2$+Na$^+$: 375.1361; Found: 375.1356.

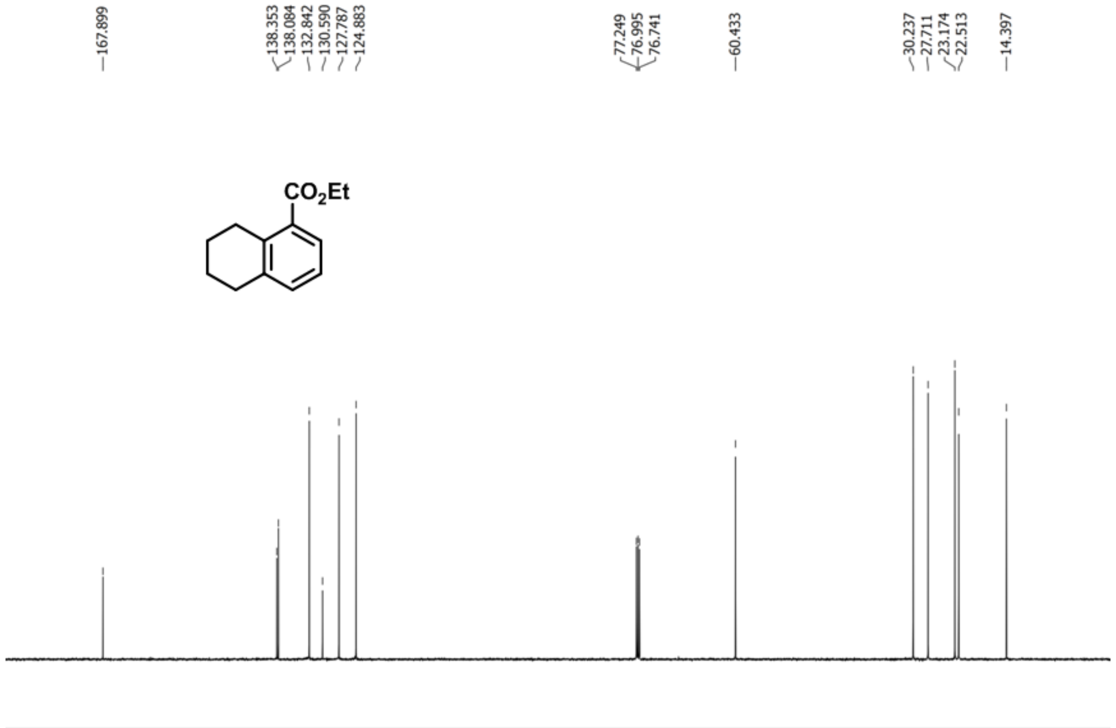
Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 84.97; H, 5.54 %.

6. ^{1}H and ^{13}C NMR spectra of compounds

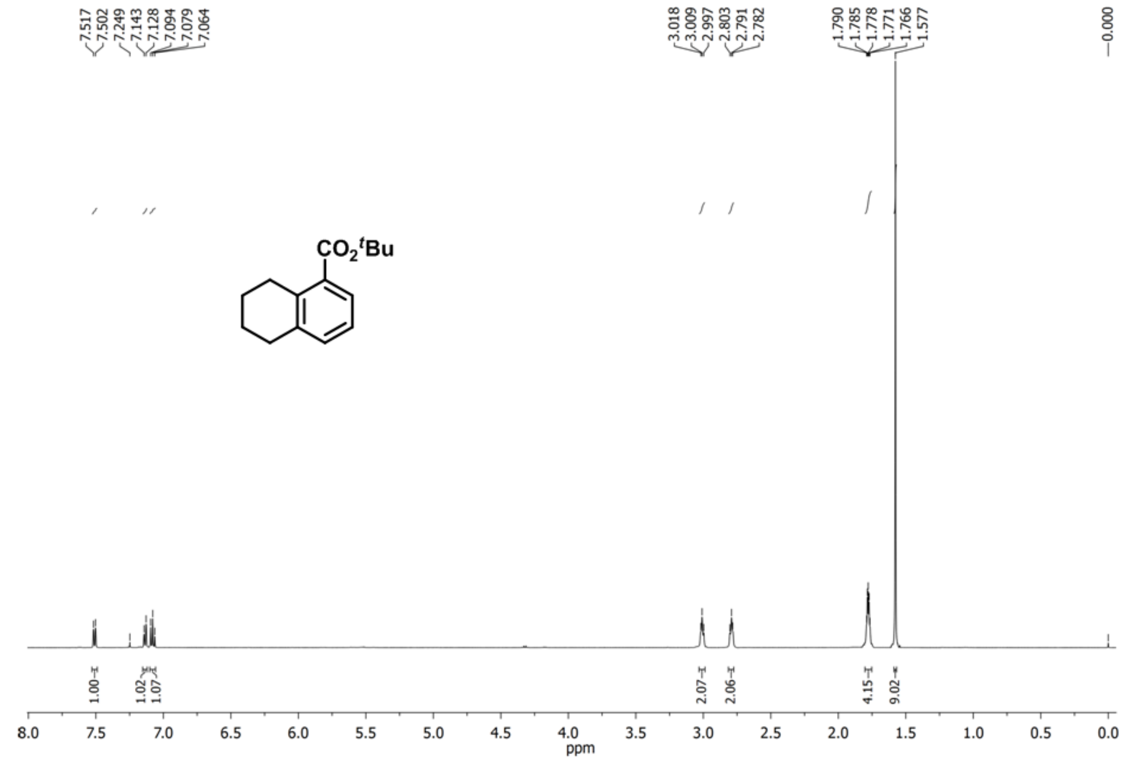
^{1}H NMR (500 MHz) of Compound 3a



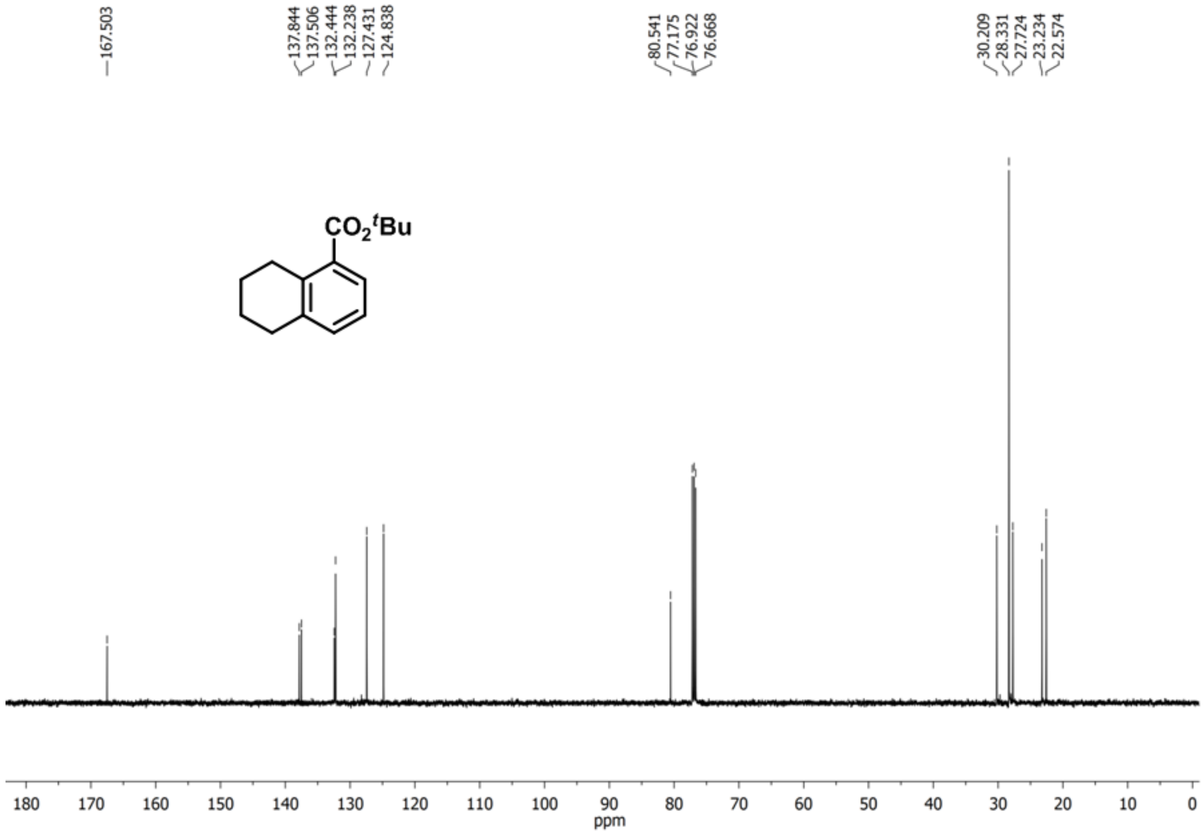
^{13}C NMR (126 MHz) of Compound 3a



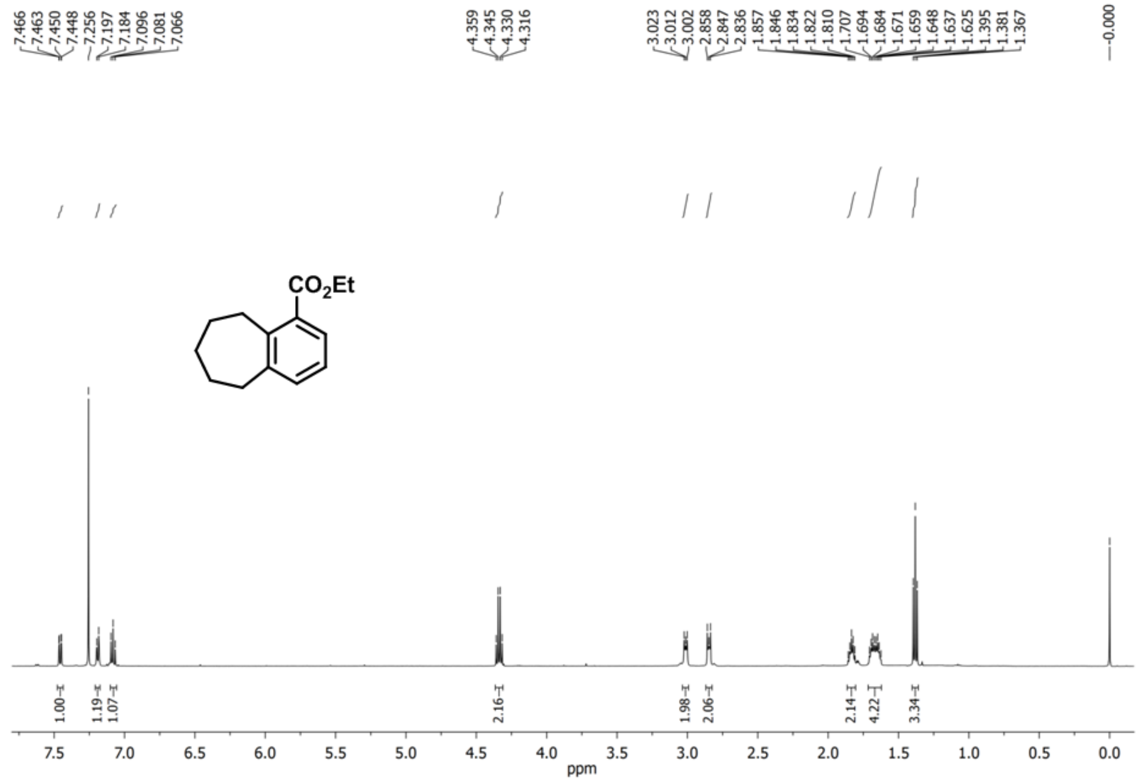
^{1}H NMR (500 MHz) of Compound 3b



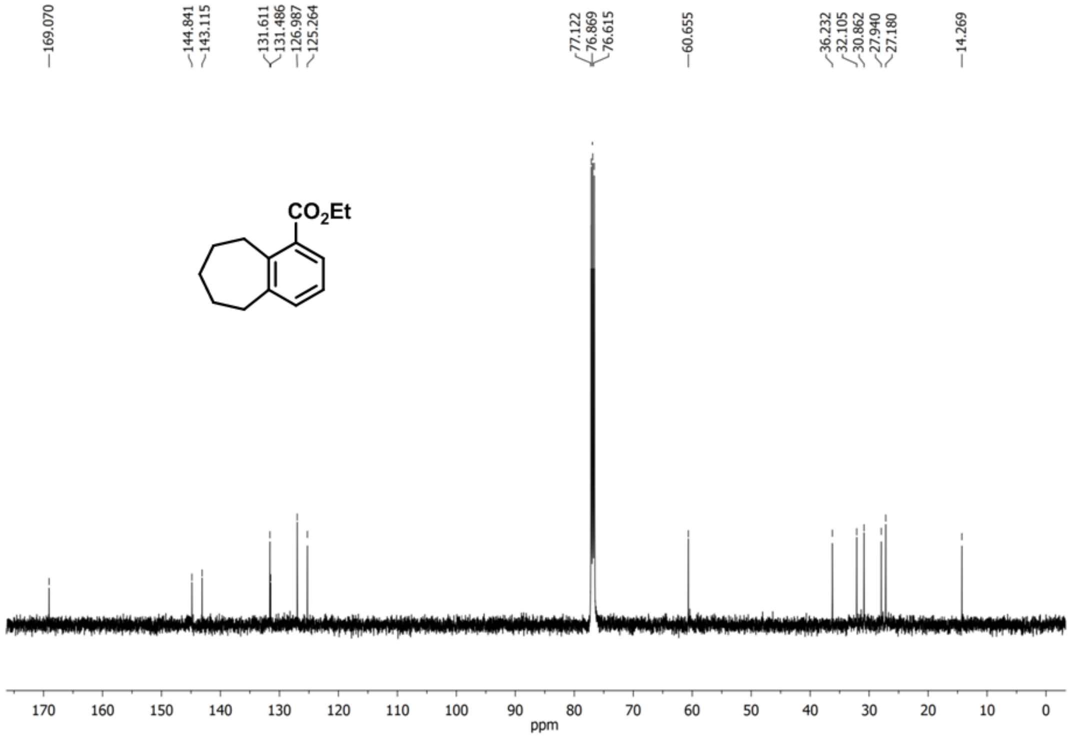
^{13}C NMR (126 MHz) of Compound 3b



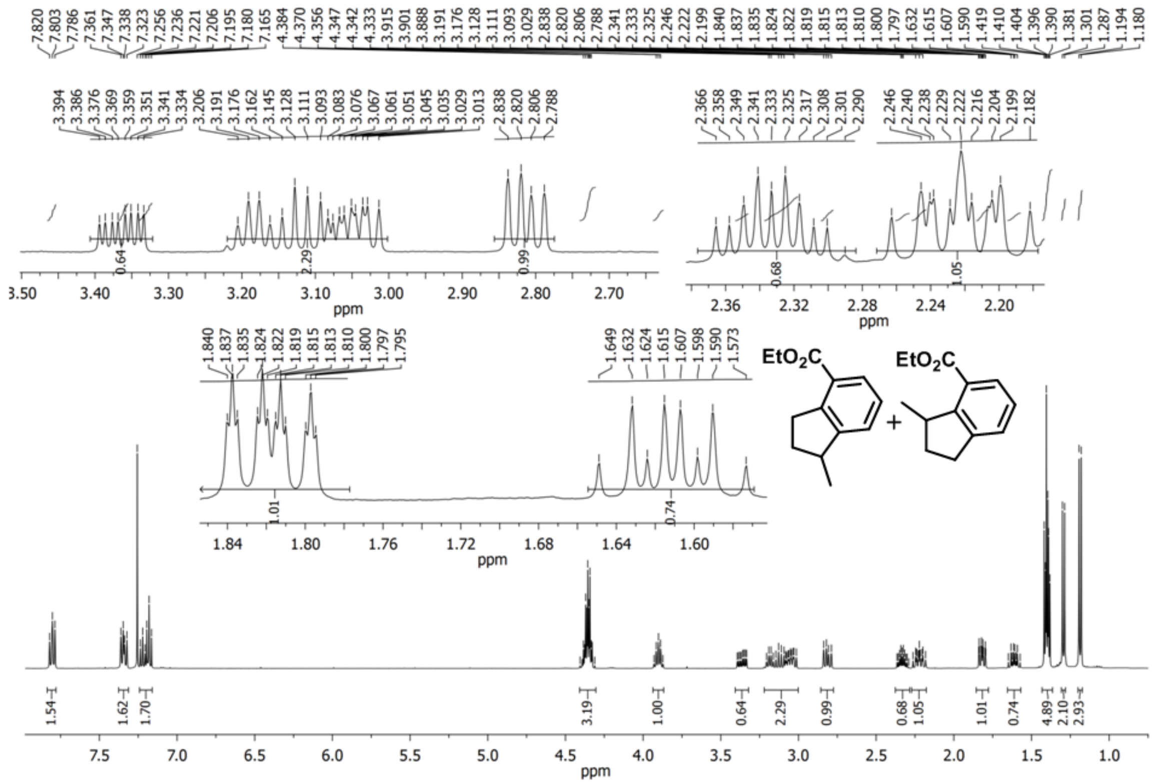
^{1}H NMR (500 MHz) of Compound 3c



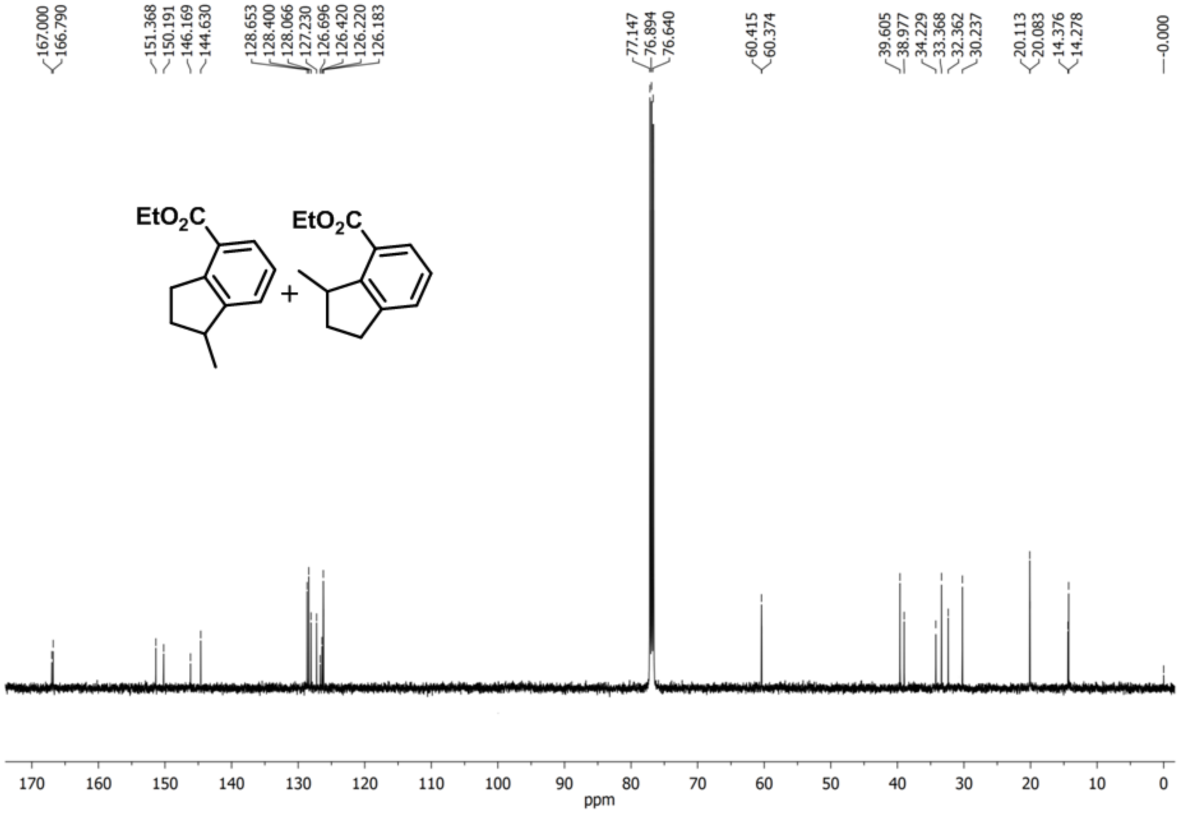
^{13}C NMR (126 MHz) of Compound 3c



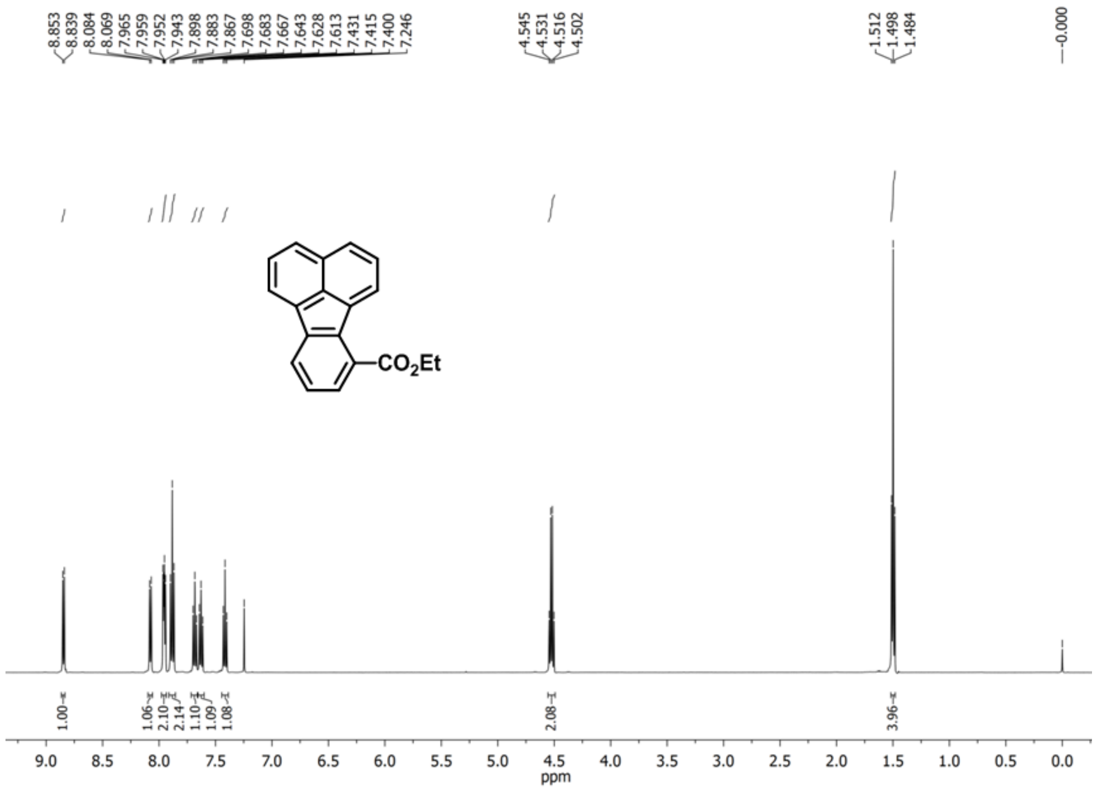
^{1}H NMR (500 MHz) of Compounds 3d & 3d^1



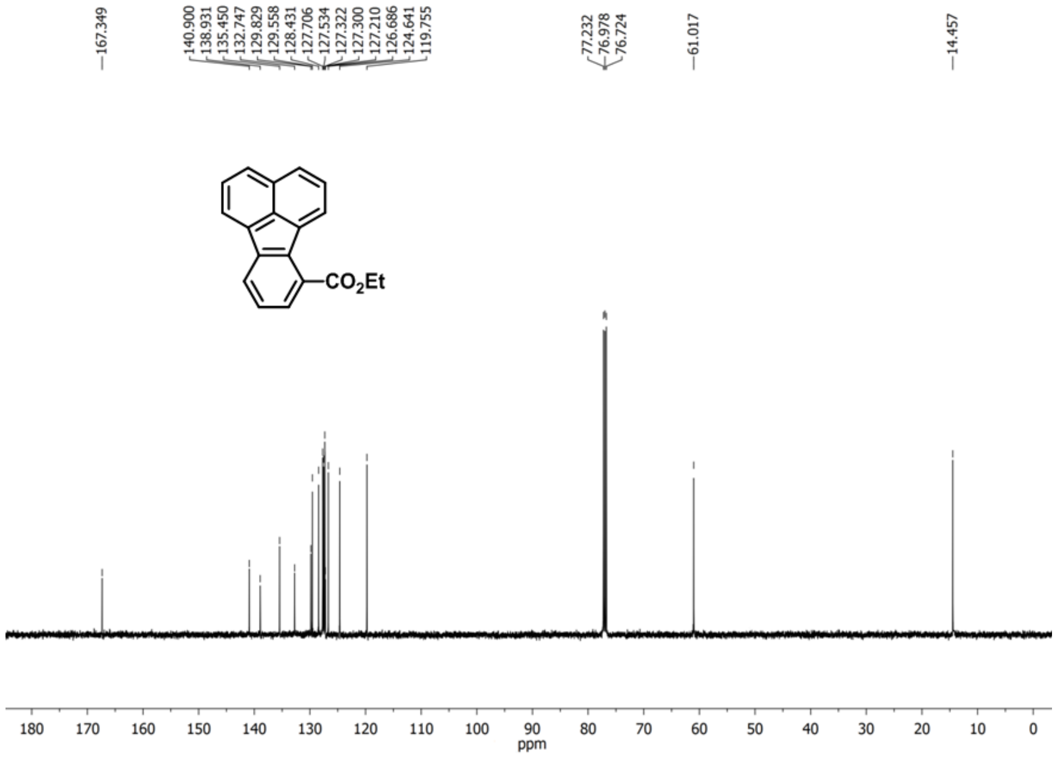
^{13}C NMR (126 MHz) of Compounds 3d & 3d^1



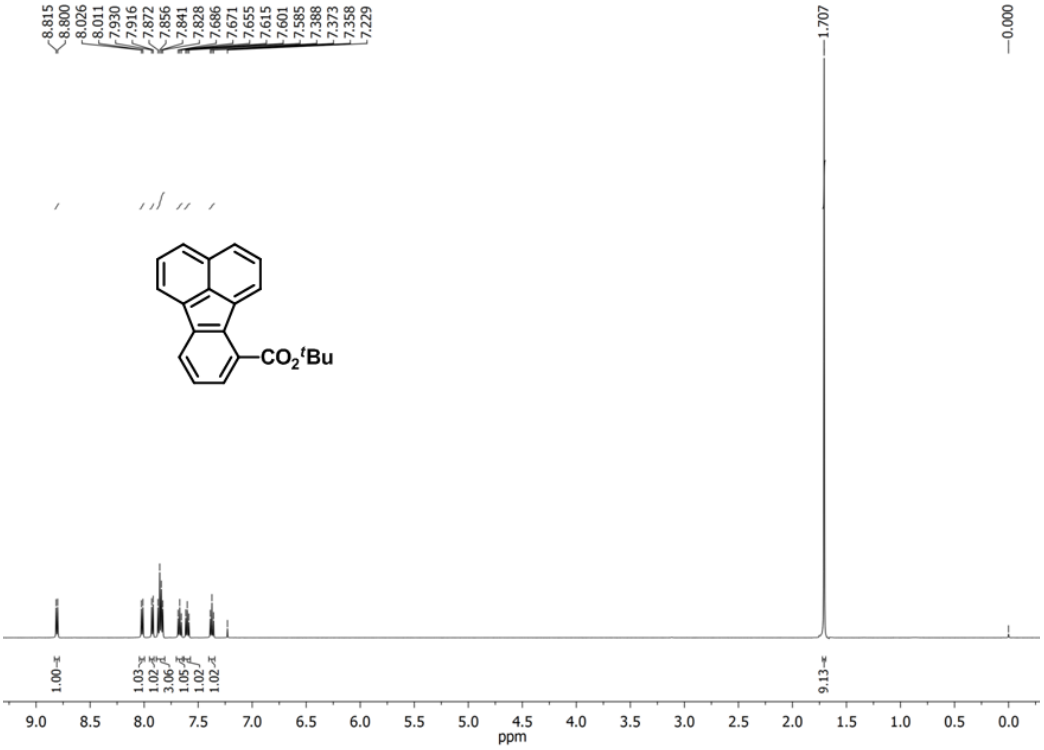
^{1}H NMR (500 MHz) of Compound 6a



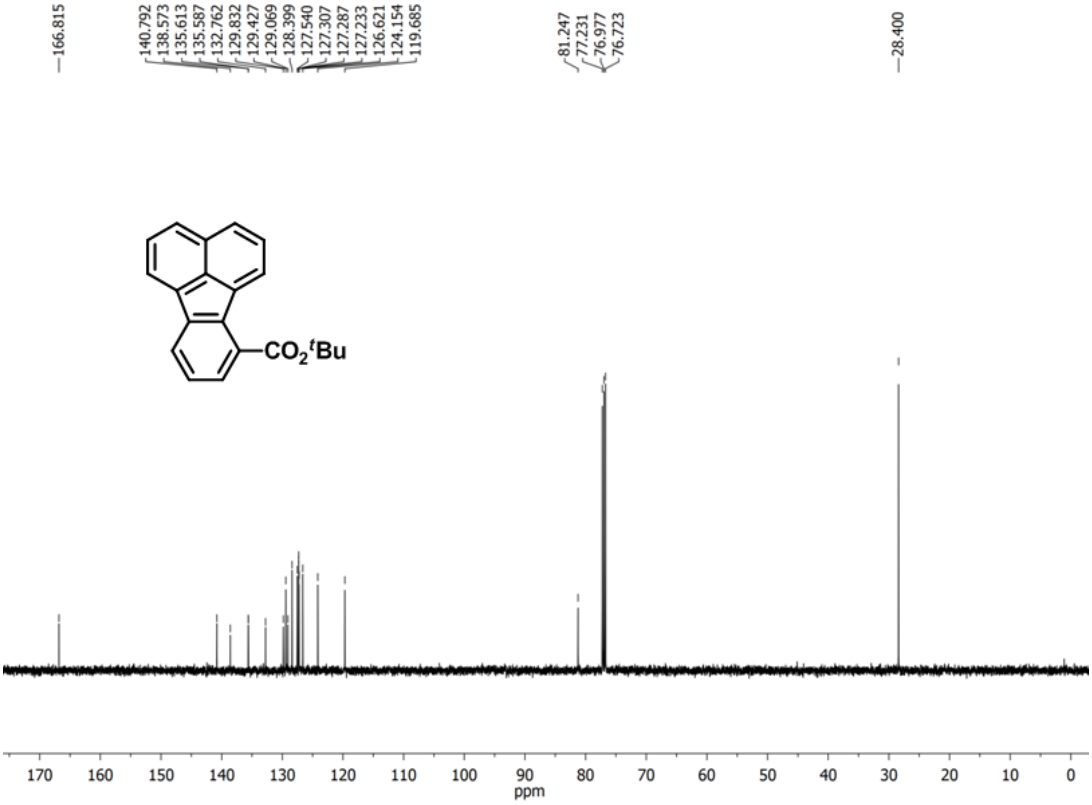
^{13}C NMR (126 MHz) of Compound 6a



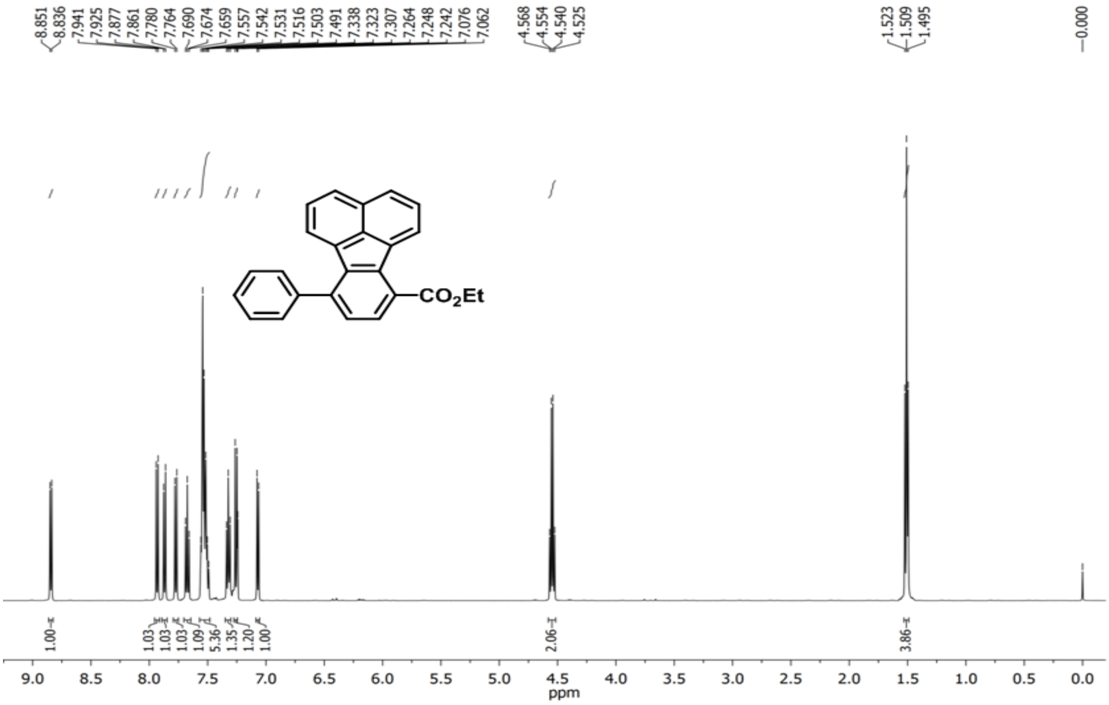
^{1}H NMR (500 MHz) of Compound 6b



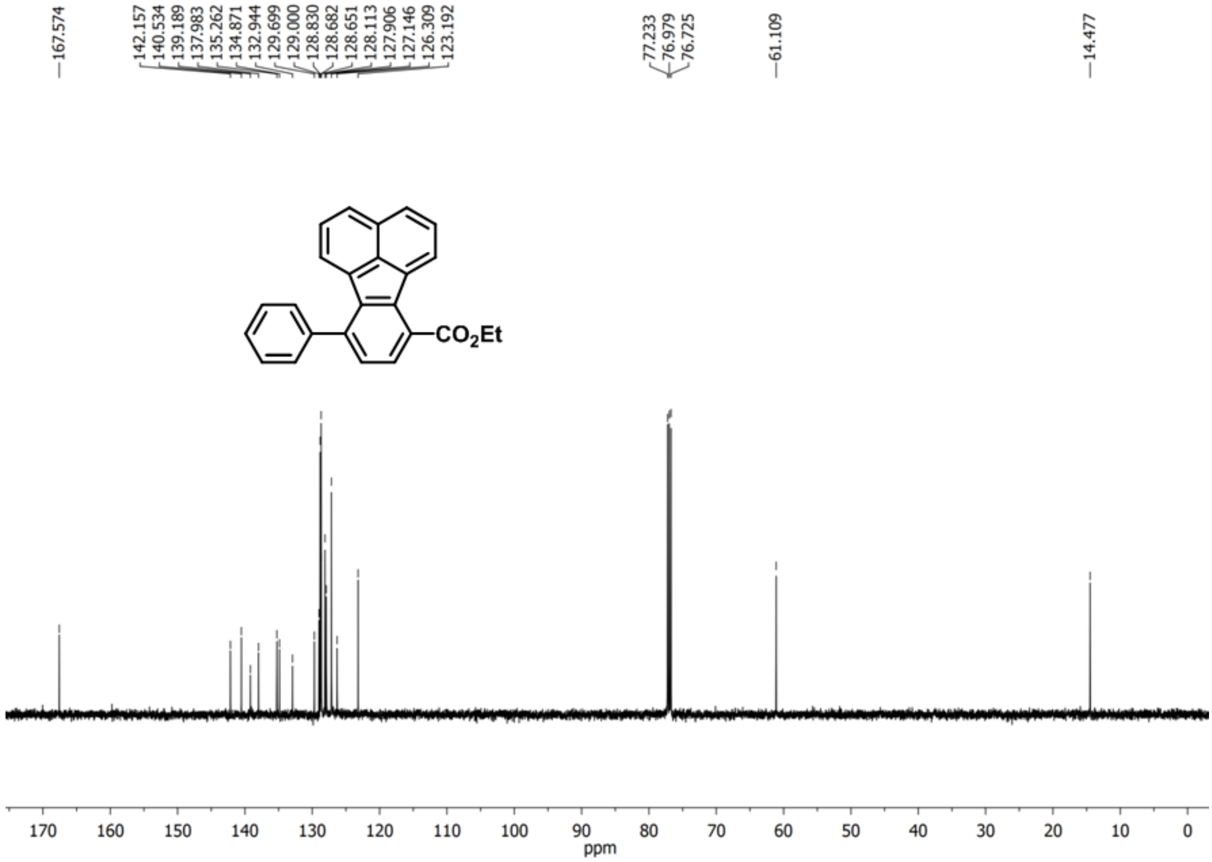
^{13}C NMR (126 MHz) of Compound 6b



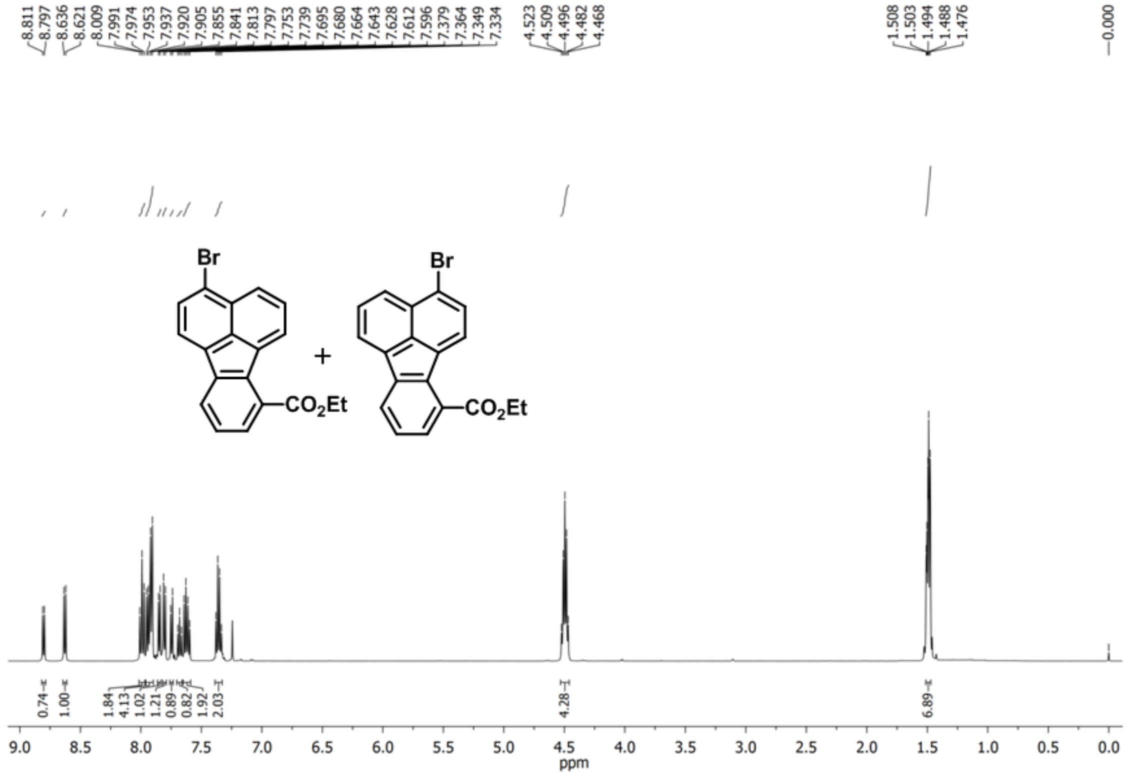
^{1}H NMR (500 MHz) of Compound 6c



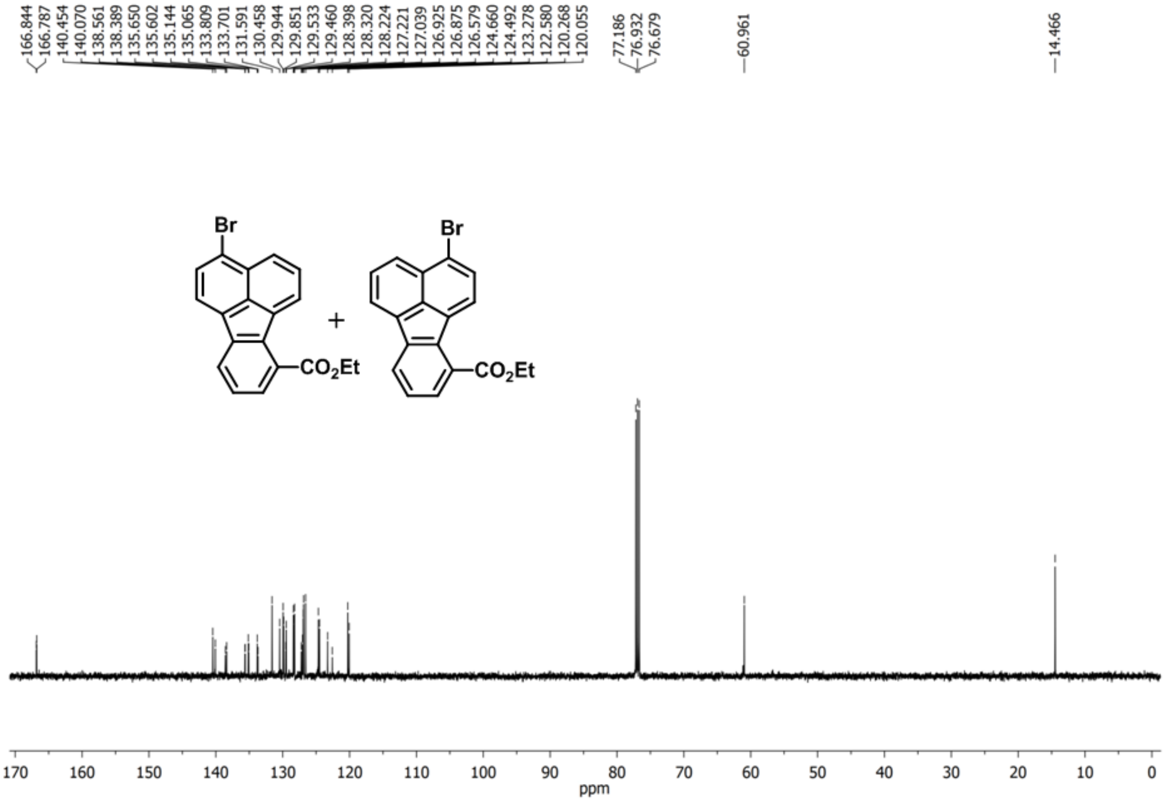
^{13}C NMR (126 MHz) of Compound 6c



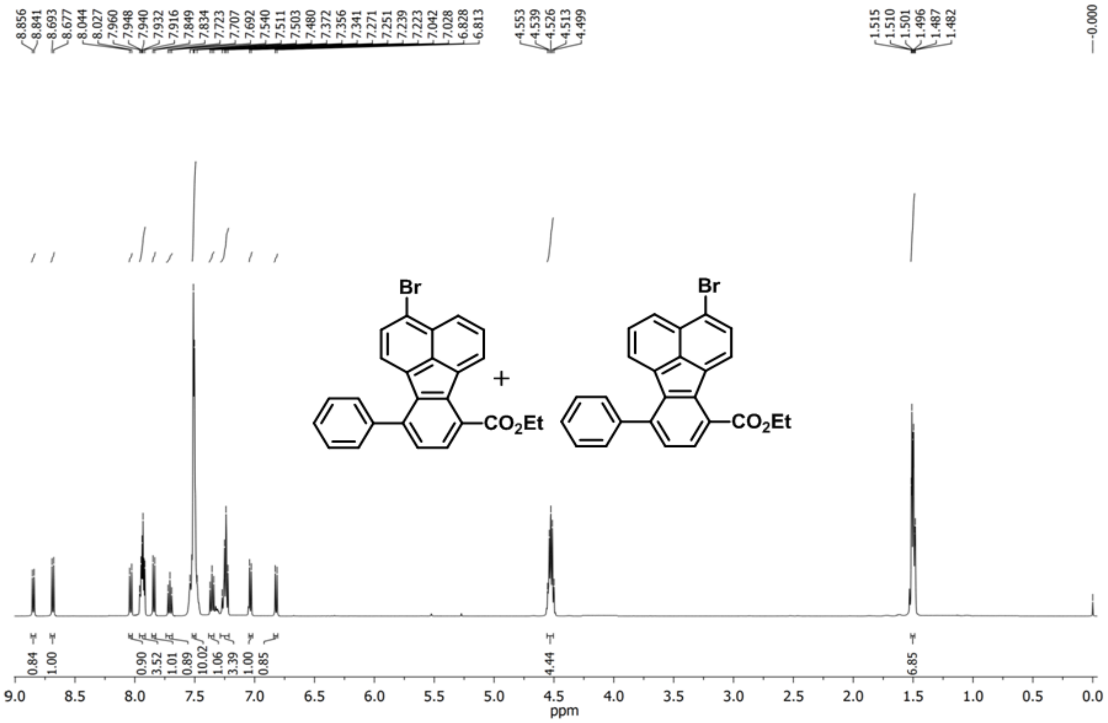
^{1}H NMR (500 MHz) of Compounds 6d & 6d^1



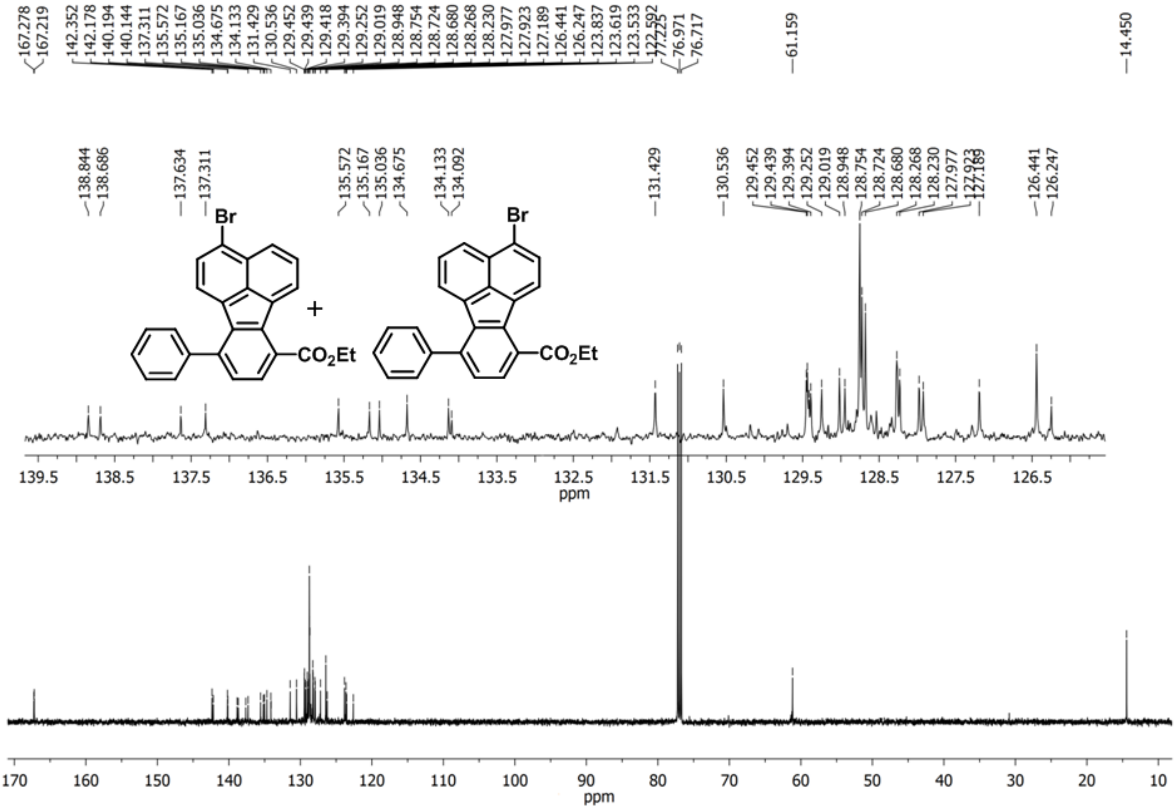
^{13}C NMR (126 MHz) of Compound 6d & 6d^1



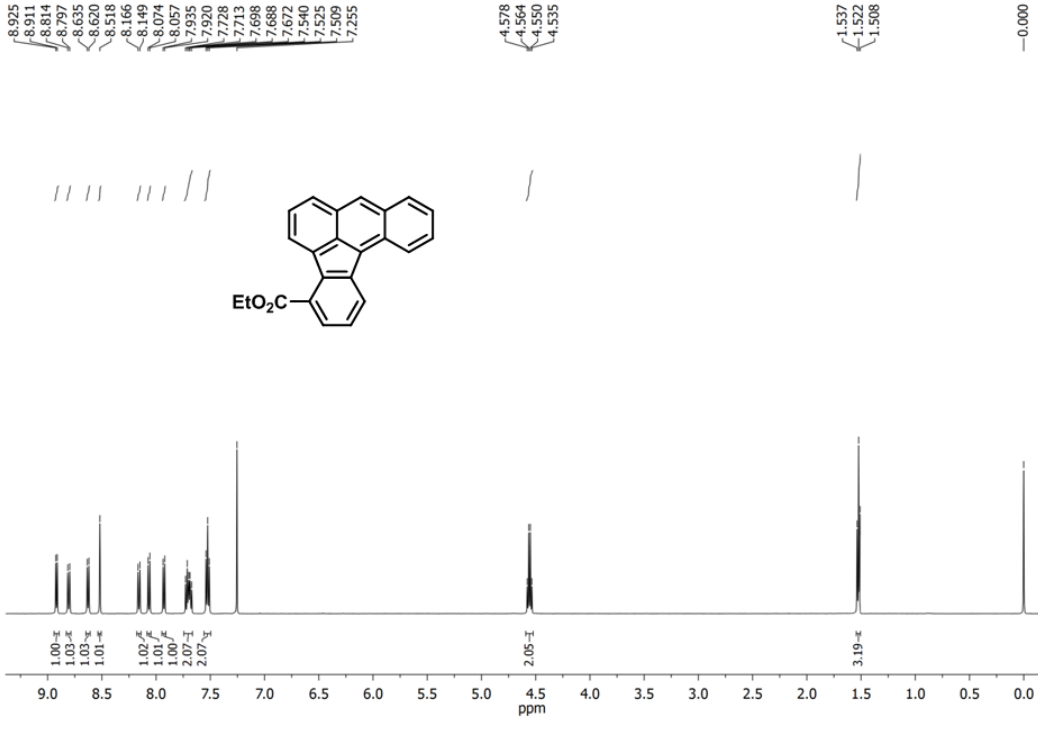
^{1}H NMR (500 MHz) of Compounds 6e & 6e^1



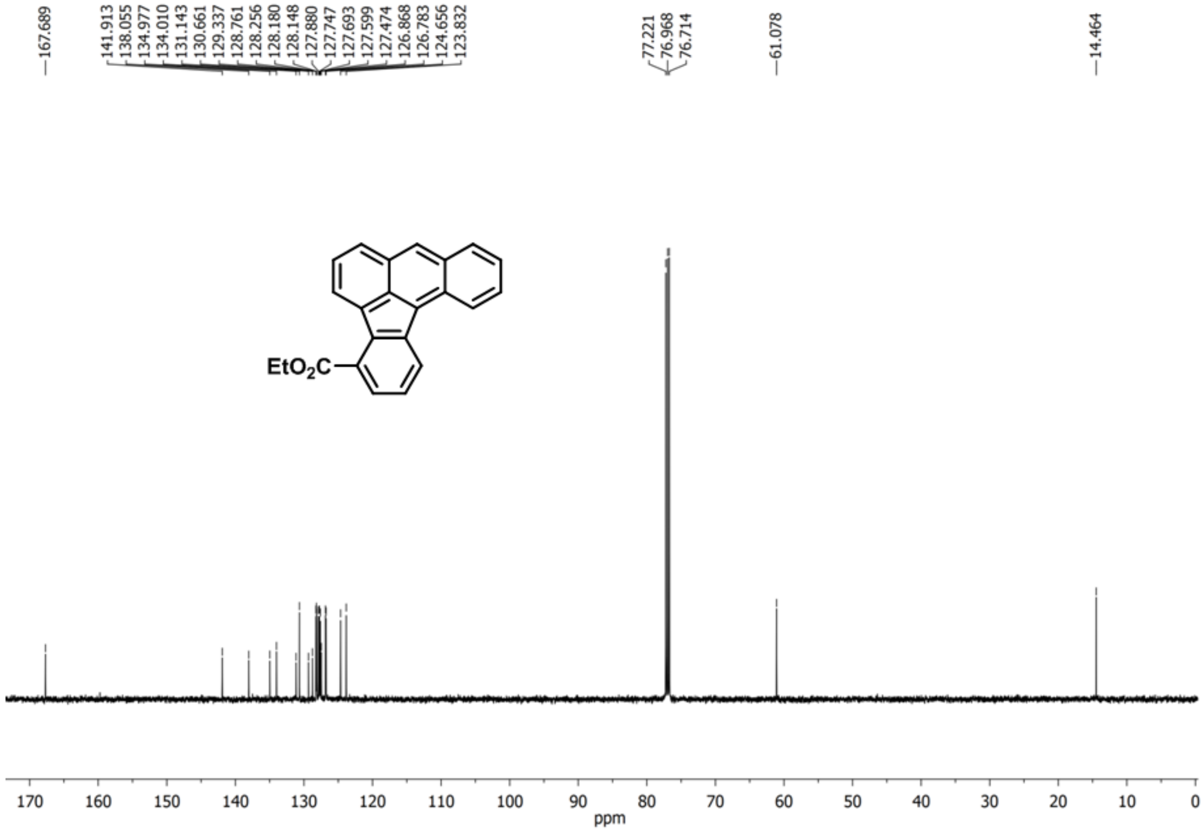
^{13}C NMR (126 MHz) of Compounds 6e & 6e^1



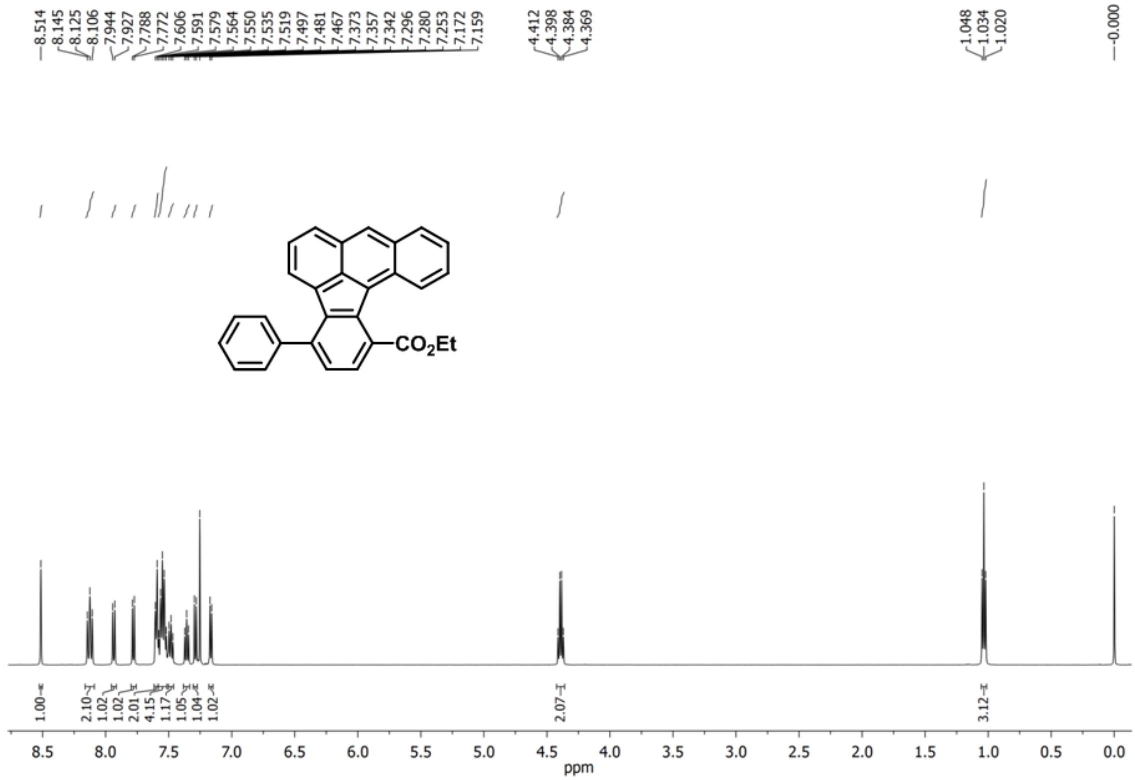
^{1}H NMR (500 MHz) of Compound 6f



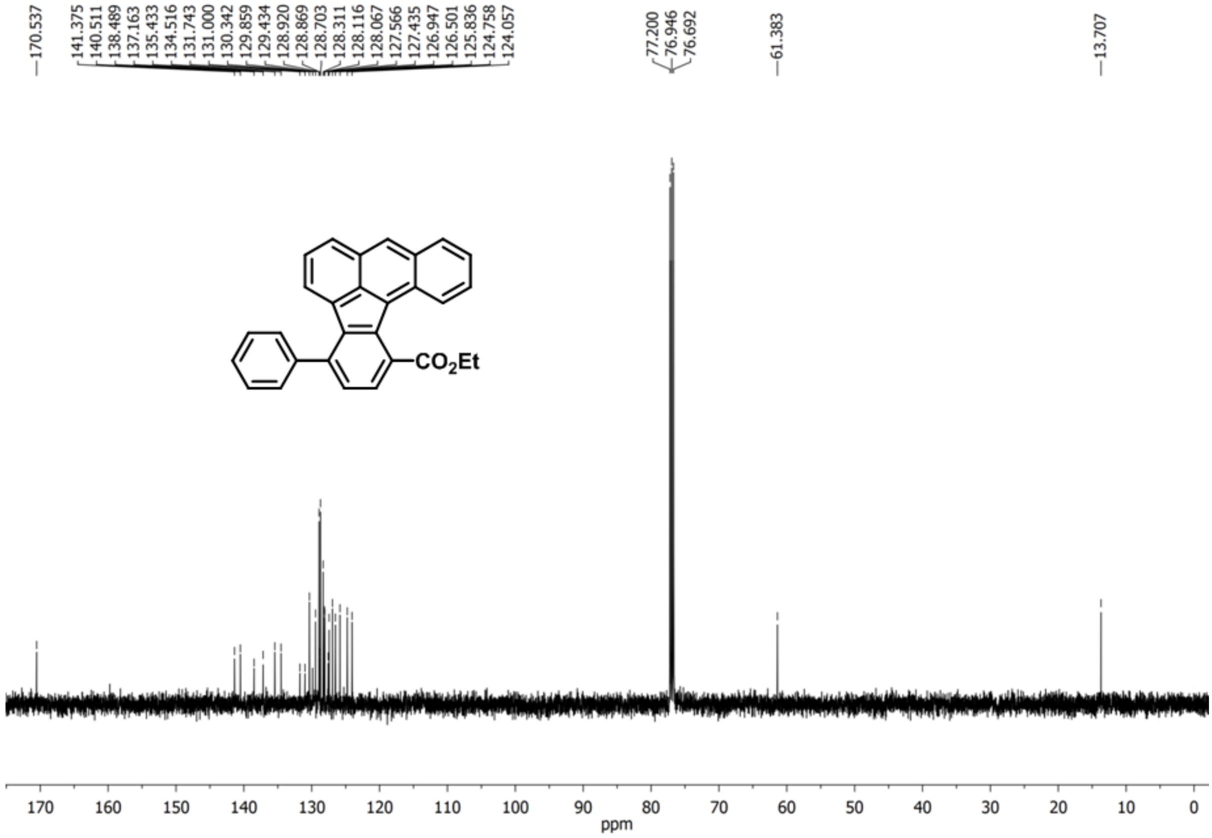
^{13}C NMR (126 MHz) of Compound 6f



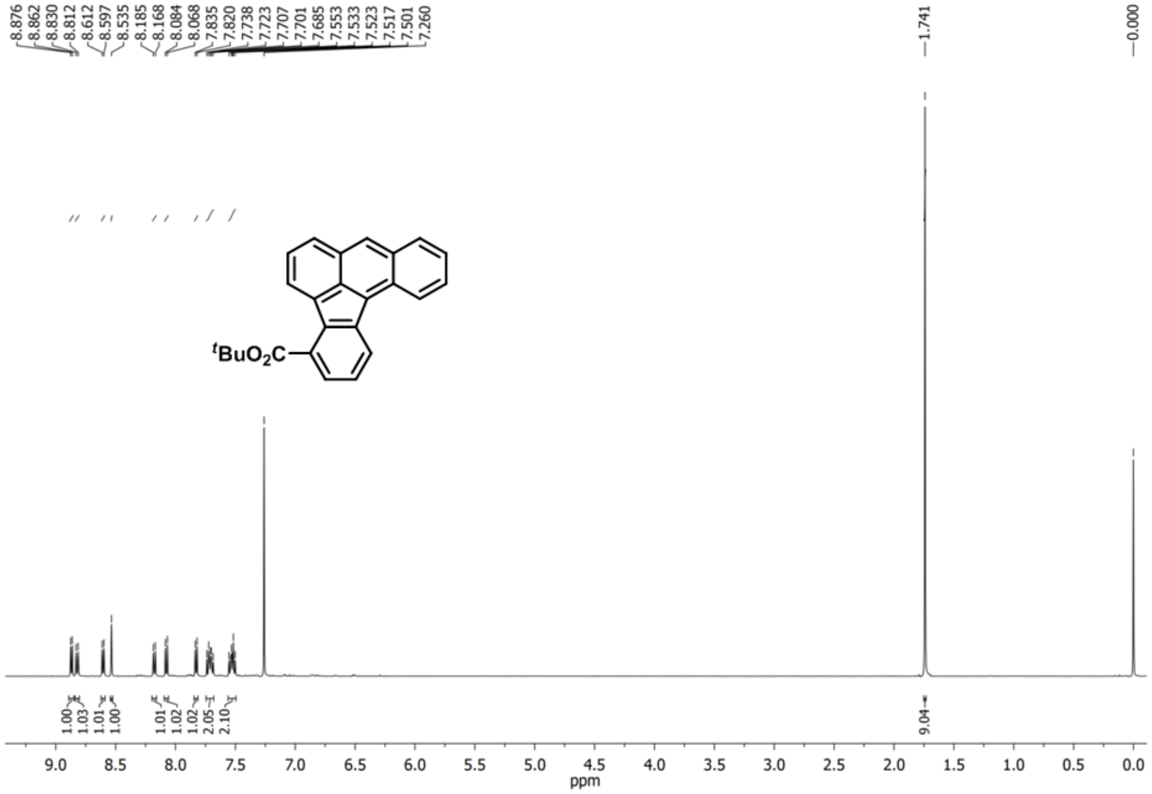
^{1}H NMR (500 MHz) of Compound 6g



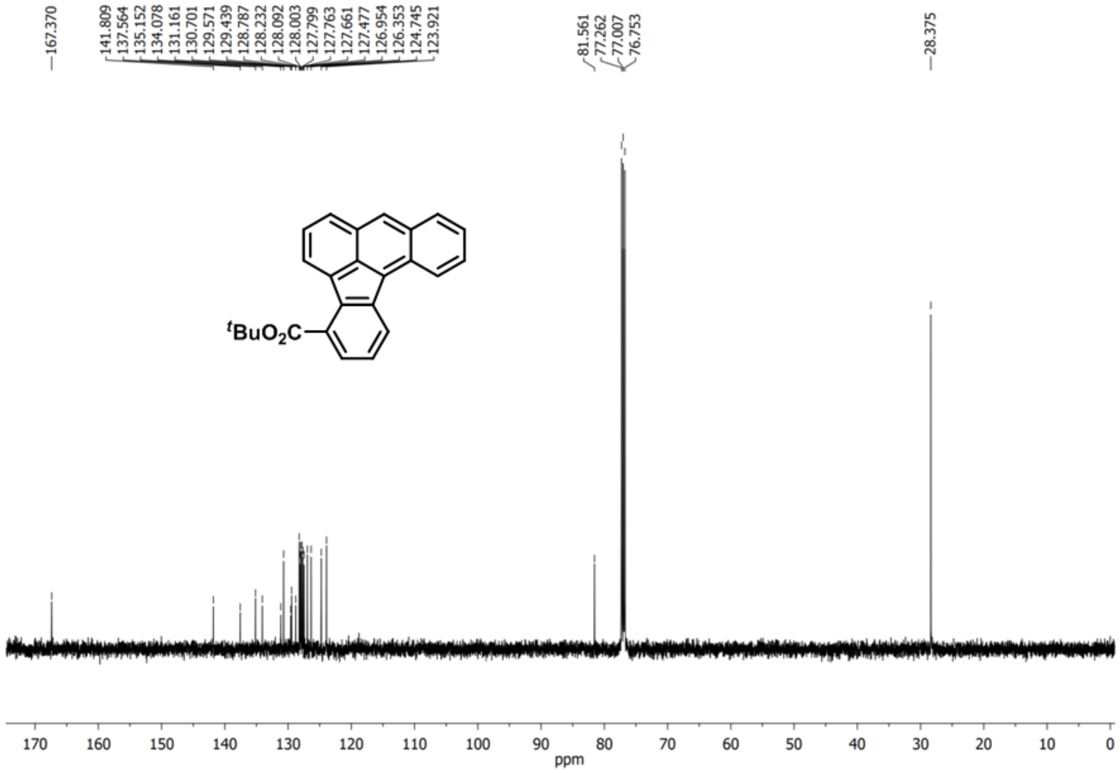
^{13}C NMR (126 MHz) of Compound 6g



^{1}H NMR (500 MHz) of Compound 6h

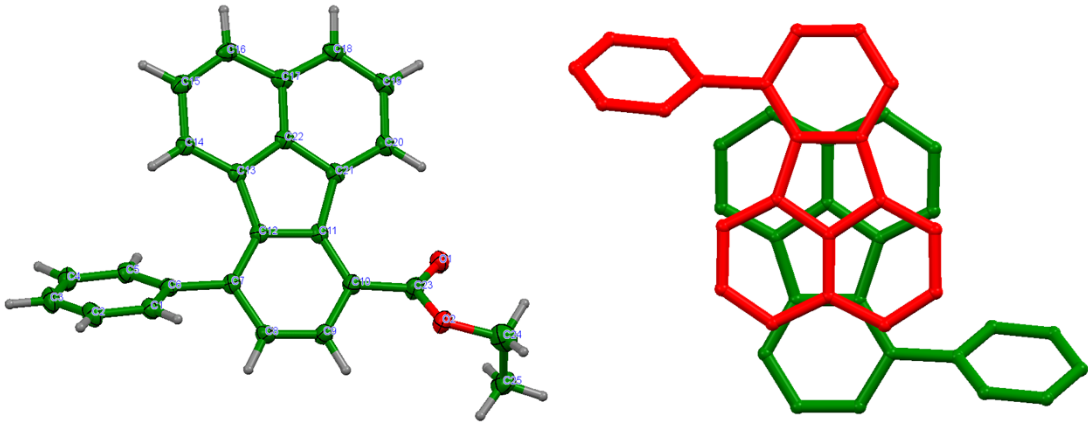


^{13}C NMR (126 MHz) of Compound 6h



7. ORTEP and crystal packing of compounds 6c, 6g and 6h

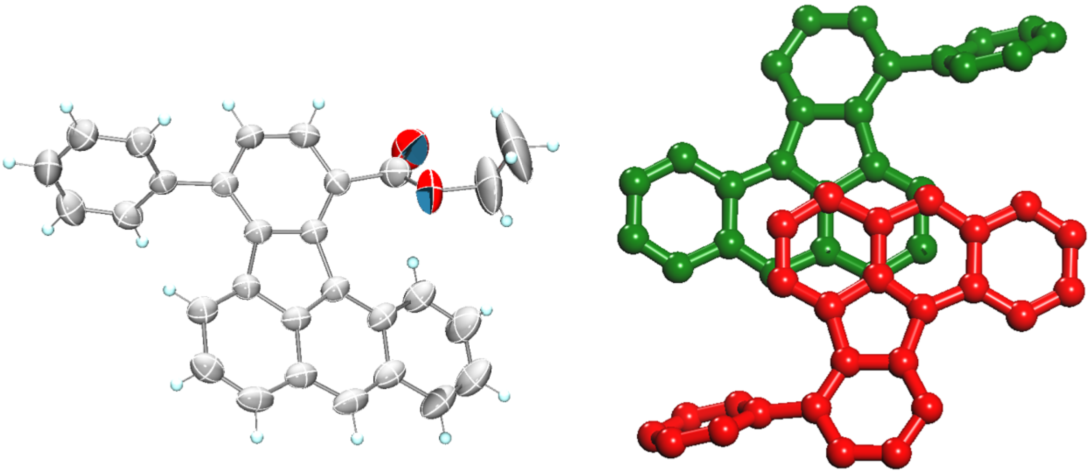
Compound 6c (CCDC No. 960560)



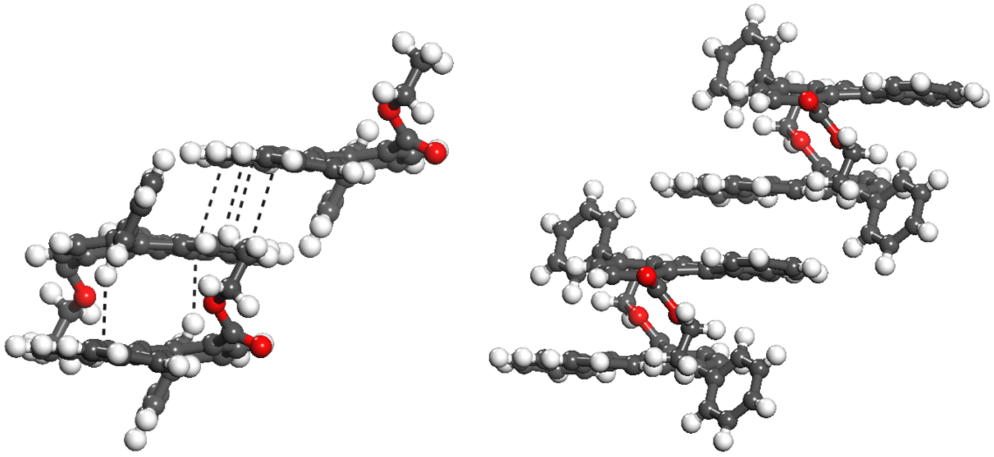
(a) (b)

Fig. S1: Compound **6c**: (a) ORTEP (50% probability factor for the thermal ellipsoids; only the major occupancy site for the disordered –O–C_2H_5 moiety is shown for clarity); (b) π-overlap (average π–π distance of 3.73 Å and the dimers are connected through C–H…π interaction).

Compound 6g (CCDC No. 960136)



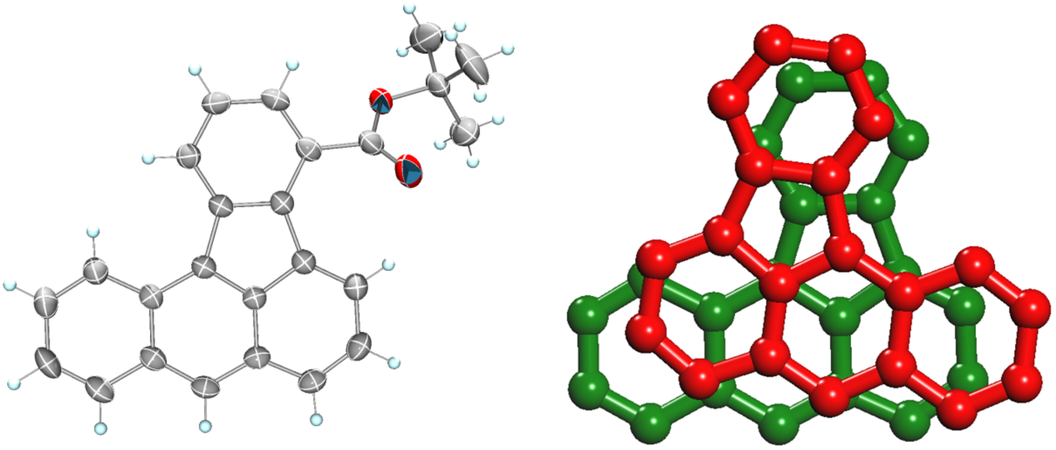
(a) (b)



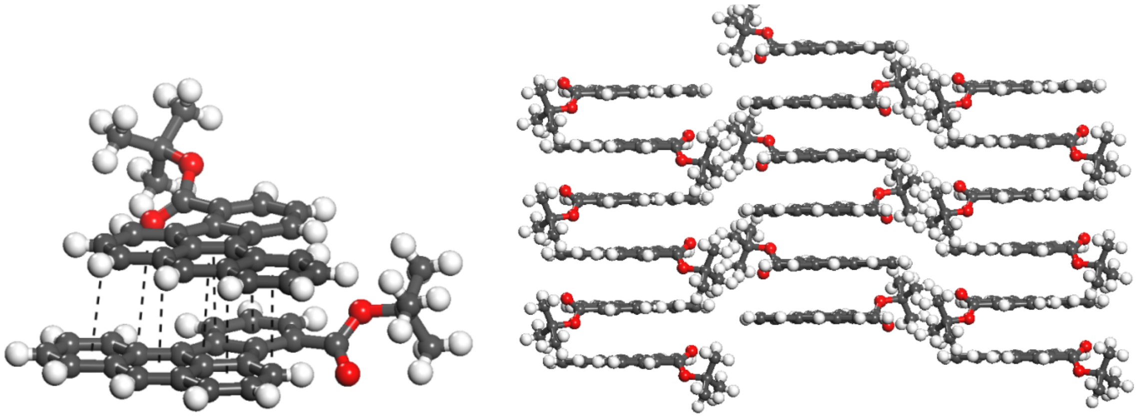
(c) (d)

Fig. S2: compound **6g**: (a) ORTEP (50% probability factor for the thermal ellipsoids). (b) ring overlap. (c), (d) *π–π* stacking (head to tail stacking with edge to edge contact. Average *π*-*π* distance is 3.38 Å).

Compound 6h (CCDC No. 960137)



(a) (b)



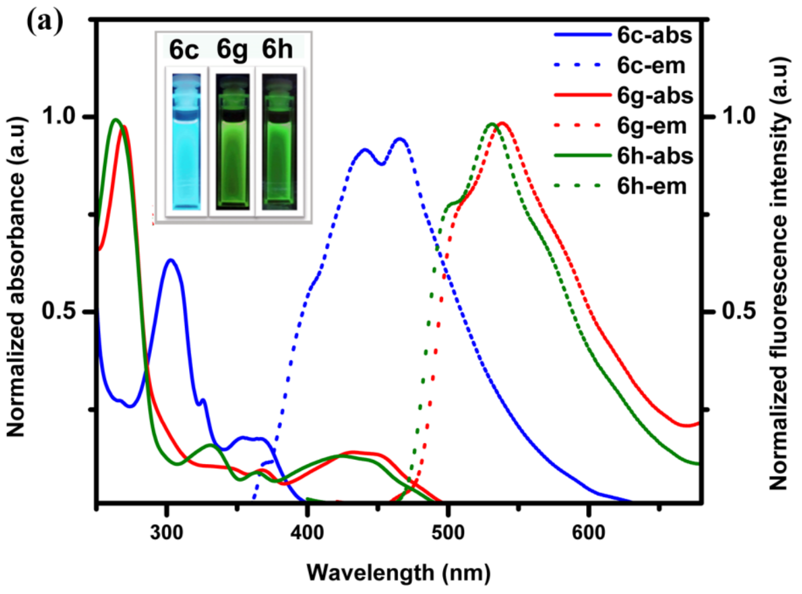
(c) (d)

Fig. S3: Compound **6h**: (a) ORTEP (50% probability factor for the thermal ellipsoids); (b) π overlap (c), (d) extended 1D-π-stacking (average π-π distance of 3.50 Å).

8. Photophysical studies

Absorption and fluorescence spectra of 6c, 6g & 6h

Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra on a SPEX-Fluorolog F112X spectrofluorimeter. The solution state studies were carried out in a 1 mm quartz cuvette. The samples of film state experiments were prepared by dropcasting 1 mmol chloroform solution of all compounds on quartz plate and dried at room temperature.



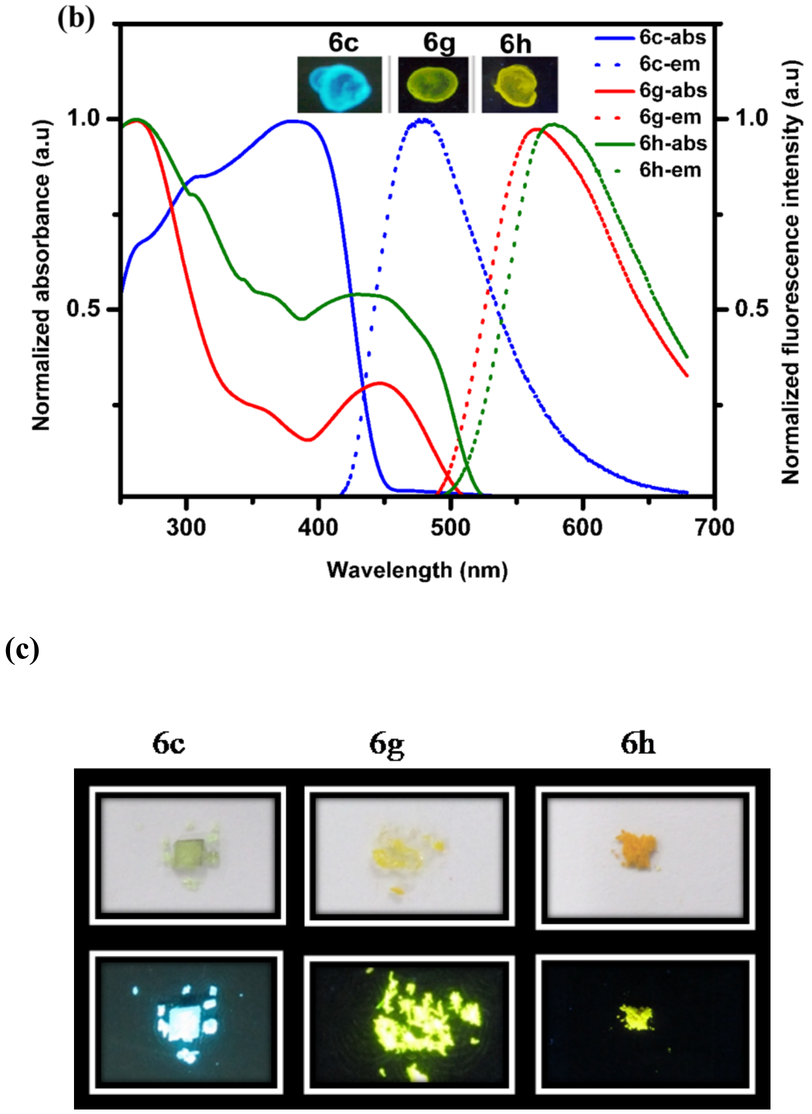


Fig. S4. Normalized absorption and fluorescence spectra of **6c**, **6g** & **6h** in (chloroform) solution state (a) and in film (b); Corresponding material images under UV light are provided as insets; (c) Photographs of **6c**, **6g** and **6h** in solid state under day light and UV(365 nm). Note: abs – absorption; em – emission.

Flourescence Quantum Yield in the Solution State

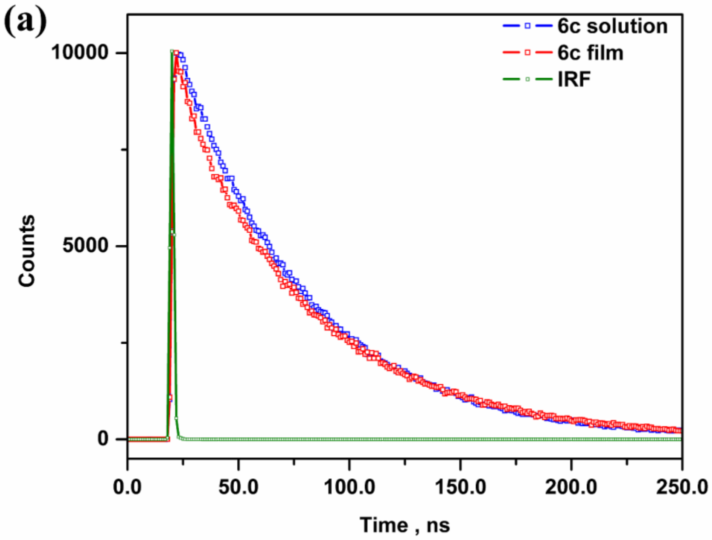
Relative fluorescence quantum yields (±5% error) were determined using quinine sulphate (ϕ_f = 0.546 in 0.1M H_2SO_4) and fluorescein (ϕ_f = 0.79 in 0.1M NaOH) as standards. For fluorescence quantum yield measurement the absorbance at the excitation wavelength was adjusted at 0.1. Fluorescence decay profile of 6c (monitored at 450 nm), 6g and 6h (monitored at 535 nm) in chloroform with excitation wavelength of 335 nm. The experiments were done using optically matching solutions and the quantum yield is calculated using the following equation,

$$\Phi_s = \Phi_r\,(A_r F_s / A_s F_r)\,(\eta_s^2 / \eta_r^2)$$

where, A_s and A_r are the absorbance of the sample and reference solutions respectively at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities and η is the refractive index of the solvents used.

Time Correlated Single Photon Counting (TCSPC)

Fluorescence was measured using IBH (FluoroCube) time-correlated picosecond single photon counting (TCSPC) system. Solutions were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 335 nm (NanoLED-11) with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (DataStation Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) software). The fluorescence lifetime values were determined by deconvoluting the instrument response function with mono and triexponential decay using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as $\chi 2$ (<1.2) as well as the visual inspection of the residuals. All measurements were carried out in a 1 mm cuvette using a front face sample holder (5000U-04).



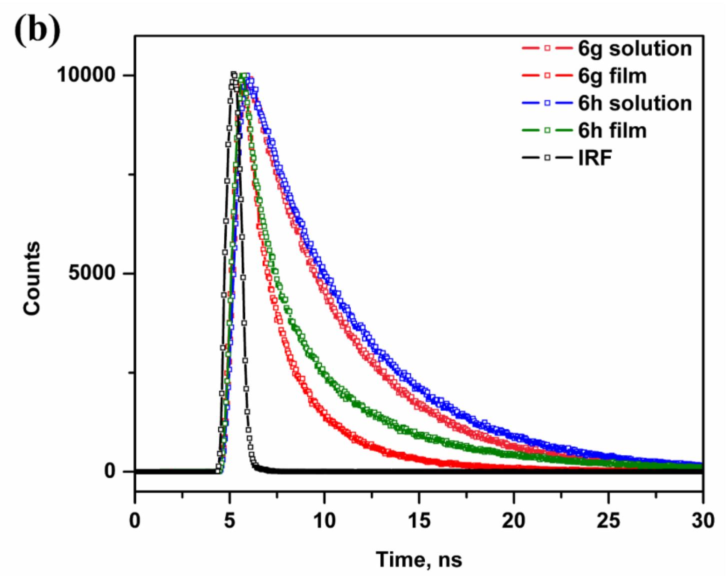


Fig. S5: Fluorescence decay profile of (a) **6c** (at 450 nm) and (b) **6g** and **6h** (at 535 nm) with excitation wavelength of 335 nm.

Table S3: Photophysical data

Compound	$\lambda_{max;abs}$ (nm)		$\lambda_{max;em}$ (nm)		Lifetime (ns)		Relative quantum yield[c]
	Solution (Chloroform)	Film	Solution (Chloroform)	Film	Solution (Chloroform)	Film	
6c	303, 361[a]	(250-450)[b]	404,[a] 439, 465	480	27.9	28.5	0.88
6g	267, 440	267, 440	503,[a] 538, 572[a]	563	4.9	0.63 (18.65%), 2.2 (59.08%), 5.1 (22.26%)	0.63
6h	262, 430	265, 430	501,[a] 528, 562[a]	578	5.1	2.77 (41.85%), 7.7 (46.88%), 0.46 (11.27%)	0.66

[a]Shoulder peaks, [b]broad band, [c]fluorescence quantum yields in chloroform (Φ_s) relative to quinine sulphate ($\phi_f = 0.546$ in 0.1 M H_2SO_4) and fluorescein ($\phi_f = 0.79$ in 0.1 M NaOH) for **6c** and **6g**, **6h** respectively.

9. Discussion

Solution state absorption spectrum of **6c** displays λ_{max} = 303 nm and a less resolved shoulder at 361 nm. In solid state (film), the absorption peaks show a marginal red-shift along with broadening (Fig. S4). Emission spectrum of **6c** (in chloroform solution) comprised of one shoulder band at 404 nm and two bands around 439, 465 nm when excited at 350 nm. In film, a broad emission spectrum with emission maximum centred at 480 nm was observed. The structured nature of emission peaks in solution however appears less resolved in film. The observed spectral characteristics can be understood in the context of crystal packing. Fluoranthene **6c** shows the formation of a weak *π*-dimer motif with an average inter-aromatic plane distance of 3.73 Å. The dimers are further connected through C–H···*π* interactions (Fig.

S1). Compared to the solution state, the fluorescence lifetime of **6c** is slightly longer (27.9 vs 28.5 ns) and this may be attributed to the formation of the weak π-dimer in the solid state.

In the solid state, planar benzo[a]aceanthrylene moiety in **6g** enhances the extended conjugation while the phenyl substituent at C4 adopts a twisted conformation. Edge-to-edge π-overlap (π-π distance 3.38 Å) makes the intermolecular electron conjugation less effective (Fig. S2). However, the increased intramolecular effective conjugation length (ECL) due to the melding of more aromatic rings leads to redder emission (λ_{max} = 538 nm) with respect to **6c** (Fig. S4). Interestingly, the effective emission color in solid state as well as in solution is green with only $\Delta\lambda_{em}$ = 25 nm; this corroborates well with the structural observations wherein the structure shows only weak edge-to-edge π interaction (3.38 Å). Because of this less efficient stacking, the lifetime of the transient species is comparable to that of solution. The multiple contributing factors in this decay curve may be attributed to the restricted intramolecular rotations induced by the constrained environment in solid state. However **6h** with more effective face-to-face extended stacking (1D-π-stacking and with an average π-π distance of 3.50 Å) exhibits longer lifetime in solid state. Rest of the spectral features are akin to **6g** (Fig. S3).

Notably, the emission wavelength in all the aforementioned compounds in solid state showed only marginal red-shift as compared to the solution state, and hence it can be assumed that emission characteristics is mainly determined by the intramolecular electronic conjugation rather than the stacking effect. The bulky substituents in the periphery of the aromatic core apparently deter the close stacking of the planar aromatics; this steric effect also avoids aggregation caused quenching (ACQ) and leads to comparable emission behavior of the compounds both in solution as well as aggregated states. However, the weak π-stacking in solid state enables the formation of possible transient species with longer lifetime, as evident from the lifetime studies (Fig. S5).