



REGULAR ARTICLE

A simple synthetic strategy to π -conjugated spirofluorenes

SAMBASIVARAO KOTHA*^{ORCID} and RASHID ALI

Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400 076, India
E-mail: srk@chem.iitb.ac.in

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Abstract. We have developed a simple synthetic strategy to spirofluorene derivatives *via* ring-closing metathesis and Suzuki–Miyaura cross-coupling reactions as key steps. To this end, we have used readily available starting materials to generate a library of spirofluorene derivatives under mild reaction conditions.

Keywords. Spirofluorene derivatives; ring-closing metathesis; Suzuki–Miyaura cross-coupling reaction; Grubbs' catalyst.

1. Introduction

Advances in the molecular design of optoelectronics have resulted in the growth of organic electronics.¹ In this regard, π -conjugated aromatics have been widely used as organic semiconductors in the context of organic light-emitting diodes (OLEDs) as well as organic thin film transistors (OTFTs).² Functionalized fluorenes with imidazole or diphenylamine units are useful as electron donors and cyanoacrylic acid as an electron acceptor in dye-sensitized solar cells (DSSCs).³ The fluorene-based π -conjugated oligomers have also been shown to exhibit multiphoton-excited blue photoluminescence and lasing properties. Additionally, spirofluorenes are found to be useful for optoelectronic materials.⁴ Recently, some attention has been paid toward the synthesis of ladder-type oligomers and polymers with rigid spiro linkage in their structures.⁵ Fluorene containing oligomers with spiro linkages have been shown to exhibit high fluorescence and hole-transporting abilities.⁶ Moreover, spirobifluorenes exhibit good thermal stability and color stability.⁷ Although a number of reports are available for the synthesis of spirofluorenes,⁸ there is a continuous need to develop new and simple strategies for these molecules.

Synthetic organic chemistry has benefited by the development of new metathetic catalysts and new

retrosynthetic paths.⁹ In this regard, there is an opportunity to generate interesting spiro frameworks by employing these catalysts. Although several reports are devoted to spirocycles,¹⁰ more opportunities exist to construct the spirocyclic frameworks containing heterocycles and functional carbocycles in their structures. To this end, the synthesis of various spirotruxene derivatives by using RCM strategy as key steps, were demonstrated recently, and a number of photophysical properties of π -conjugated spirotruxene derivatives have been studied.¹¹ In view of these applications, we are interested in designing spiro fluorene derivatives *via* ring-closing metathesis¹² (RCM) and Suzuki coupling¹³ as key steps.

2. Experimental

2.1 Materials, analytical measurements and general synthetic procedures

All commercially accessible reagents were used without further purification and reactions involving air-sensitive catalysts or reagents were performed in degassed solvents. Analytical thin layer chromatography (TLC) was performed on (7.5 × 2.5 cm) glass plates coated with Acme's silica gel GF 254 (containing 13% calcium sulfate as a binder) by using a suitable mixture of EtOAc and petroleum ether for development. Column chromatography was performed by using Acme's silica gel (100–200 mesh) with an appropriate mixture of EtOAc

*For correspondence

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and petroleum ether. The coupling constants (J) are given in hertz (Hz) and chemical shifts are denoted in parts per million (ppm) downfield from internal standard, tetramethylsilane (TMS). The abbreviations, s, d, t, q, m, dd and td, refer to the singlet, doublet, triplet, quartet, multiplet, doublet of doublets, and a triplet of doublets respectively. Grubbs' catalysts were purchased from Sigma Aldrich. Infrared (IR) spectra were recorded on Nicolet Impact-400 FT IR spectrometer in CHCl_3 . Proton nuclear magnetic resonance (^1H NMR, 500 MHz) spectra and carbon nuclear magnetic resonance (^{13}C NMR, 125 MHz) spectra were recorded on a Bruker spectrometer. The high-resolution mass measurements were carried out by using electrospray ionization (ESI, Q-TOF) spectrometer. Melting points were recorded on a Veego melting point apparatus.

2.2 General procedure for RCM sequence of 3

The solution of compound **3** in CH_2Cl_2 (25 mL) was degassed with nitrogen for 15 min. Then, G-I catalyst (5 mol%) was added, and the reaction mixture was stirred at room temperature for 12 h. At the completion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using appropriate mixtures of EtOAc-petroleum ether to afford the expected RCM product **4**.

2.3 General procedure for the Suzuki–Miyaura cross-coupling reaction of 4

To a solution of bromo derivative **4** in THF/toluene/water (1:1:1, each 10 mL) were added Na_2CO_3 (3.0 equiv) and arylboronic acid (2.0 equiv). The reaction mixture was degassed with nitrogen for 15–20 min. $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) was then added and the reaction mixture was heated at 100°C . At the end of the reaction (18–26 h, TLC monitoring), the reaction mixture was diluted with water and the organic layer was extracted with CH_2Cl_2 . The organic layer was washed with water as well as brine and dried over Na_2SO_4 . The solvent was removed on a rotavapour and the crude product was purified by silica gel column chromatography using appropriate mixtures of EtOAc-petroleum ether to afford the desired cross-coupling product **5**.

2.3a *2',7'-Diphenylspiro[cyclopentane-1,9'-fluoren]-3-ene* (**5a**): White solid; yield = 88% (43 mg, starting from 50 mg of **4**); reaction time = 12 h; M.p. $293\text{--}295^\circ\text{C}$; R_f = 0.58 (silica gel, 10% EtOAc-petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 3.02 (s, 4H), 6.06 (s, 2H), 7.36–7.39 (m, 2H), 7.48 (d, J = 7.60 Hz, 4H), 7.61 (dd, J_1 = 1.55 Hz, J_2 = 7.80 Hz, 2H), 7.67 (d, J = 8.05 Hz, 4H), 7.76–7.79 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 46.64, 55.71, 120.16, 121.37, 126.45, 127.35, 128.94, 130.55, 138.51, 141.03, 141.70, 156.46; IR (CHCl_3): ν_{max} = 1216, 1266, 1417, 1448, 1604, 2850, 2927, 3019 cm^{-1} ; HRMS (ESI, Q-TOF) calculated for $\text{C}_{29}\text{H}_{22}\text{Na}$ $[\text{M}+\text{Na}]^+$ 393.1614 found: 393.1616.

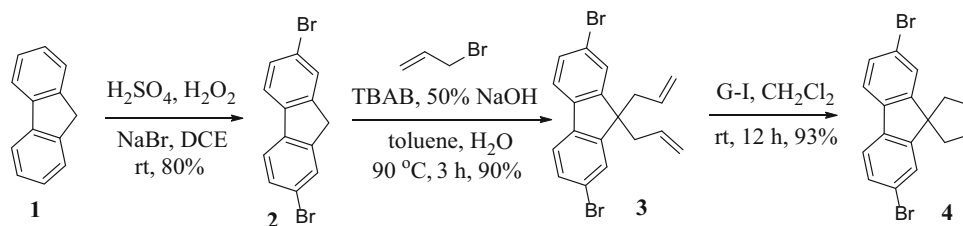
2.3b *1,1'-(Spiro[cyclopentane-1,9'-fluoren]-3-en-2',7'-diyl)bis(4,1-phenylene)bis(ethan-1-one)* (**5b**): White solid; yield = 79% (48 mg, starting from 50 mg of **4**); reaction time = 26 h; M.p. 267°C (decomposed); R_f = 0.44 (silica gel, 10% EtOAc-petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 2.65 (s, 6H), 3.01 (s, 4H), 6.07 (s, 2H), 7.64 (d, J = 7.40 Hz, 2H), 7.73–7.81 (m, 8H), 8.04 (d, J = 8.10 Hz, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 26.86, 46.56, 55.81, 120.54, 121.48, 126.75, 127.38, 129.13, 130.57, 135.94, 139.20, 139.89, 146.14, 155.67, 197.94; IR (CHCl_3): ν_{max} = 1266, 1361, 1596, 1677, 2857, 2925, 3020 cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{33}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$ 455.2006 found: 455.2005.

2.3b' *1-(4-(2'-Bromospiro[cyclopentane-1,9'-fluoren]-3-en-7'-yl)phenyl)ethan-1-one* (**5b'**): White solid; yield = 11% (6 mg, starting from 50 mg of **4**); reaction time = 26 h; M.p. $155\text{--}157^\circ\text{C}$; R_f = 0.58 (silica gel, 10% EtOAc-petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 2.64 (s, 3H), 3.87–2.99 (m, 4H), 6.02 (s, 2H), 7.48 (dd, J_1 = 1.75 Hz, J_2 = 7.40 Hz, 1H), 7.58–7.61 (m, 2H), 7.66 (d, J = 1.68 Hz, 1H), 7.70–7.74 (m, 4H), 8.03 (d, J = 8.44 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.84, 46.30, 55.85, 120.35, 121.39, 121.50, 121.89, 126.05, 126.76, 127.35, 129.11, 130.41, 130.47, 135.97, 137.88, 138.84, 139.94, 146.03, 154.76, 197.87; IR (CHCl_3): ν_{max} = 1352, 1464, 1599, 1687, 2842, 2928, 3016 cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{25}\text{H}_{20}\text{BrO}$ $[\text{M}+\text{H}]^+$ 415.0692 found: 415.0696.

2.3c *2',7'-Di(thiophen-3-yl)spiro[cyclopentane-1,9'-fluoren]-3-ene* (**5c**): Creamy solid; yield = 87% (35 mg, starting from 40 mg of **4**); reaction time = 24 h; M.p. $133\text{--}134^\circ\text{C}$; R_f = 0.68 (silica gel, 10% EtOAc-petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 2.97 (s, 4H), 6.04 (s, 2H), 7.39–7.41 (m, 2H), 7.43–7.45 (m, 2H), 7.48 (dd, J_1 = 1.20 Hz, J_2 = 7.75 Hz, 2H), 7.59 (dd, J_1 = 1.50 Hz, J_2 = 7.85 Hz, 2H), 7.70–7.72 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 46.61, 55.62, 120.12, 120.24, 120.61, 125.76, 126.36, 126.66, 130.56, 135.57, 138.37, 142.87, 155.43; IR (CHCl_3): ν_{max} = 1225, 1452, 1601, 2850, 2922, 3033 cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{25}\text{H}_{19}\text{S}_2$ $[\text{M}+\text{H}]^+$ 383.0923 found: 383.0925.

2.3d *5,5'-(Spiro[cyclopentane-1,9'-fluoren]-3-en-2',7'-diyl)bis(furan-2-carbaldehyde)* (**5d**): Brown sticky solid; yield = 75% (24 mg, starting from 30 mg of **4**); reaction time = 20 h; M.p. $103\text{--}106^\circ\text{C}$; R_f = 0.41 (silica gel, 10% EtOAc-petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 2.96 (s, 4H), 6.07 (s, 2H), 7.89 (d, J = 3.75 Hz, 2H), 7.40 (d, J = 3.56 Hz, 2H), 7.81 (dd, J_1 = 1.50 Hz, J_2 = 7.90 Hz, 4H), 7.96 (d, J = 1.15 Hz, 2H), 9.65 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 46.32, 55.73, 108.07, 119.47, 120.72, 125.05, 128.96, 130.47, 140.27, 152.12, 155.79, 159.98, 177.28; IR (CHCl_3): ν_{max} = 1390, 1455, 1515, 1670, 2850, 2924 cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{27}\text{H}_{19}\text{O}_4$ $[\text{M}+\text{H}]^+$ 407.1278 found: 407.1272.

2.3e *4,4'-(Spiro[cyclopentane-1,9'-fluoren]-3-en-2',7'-diyl)dibenzonitrile* (**5e**): Creamy solid; yield = 68% (38



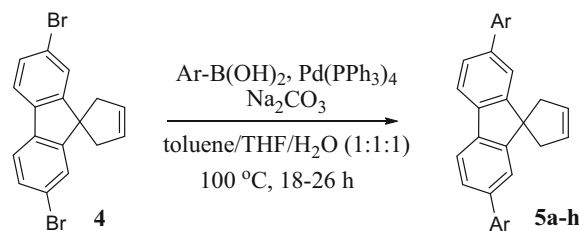
Scheme 1. Synthesis of dibromo building block **4**.

mg, starting from 50 mg of **4**); reaction time = 26 h; M.p. 245–247 °C; $R_f = 0.47$ (silica gel, 10% EtOAc-petroleum ether); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 2.99 (s, 4H), 6.06 (s, 2H), 7.60 (dd, $J_1 = 1.45$ Hz, $J_2 = 7.85$ Hz, 2H), 7.74 (s, 10H), 7.82 (d, $J = 7.85$ Hz, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 46.52, 55.84, 110.96, 119.15, 120.75, 121.46, 126.77, 127.89, 130.54, 132.79, 139.30, 139.40, 145.95, 155.79; IR (CHCl_3): $\nu_{\text{max}} = 1601, 2220, 2850, 2921$ cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{31}\text{H}_{20}\text{N}_2\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 443.1519 found: 443.1517.

2.3f 2',7'-Bis(4-methoxyphenyl)spiro[cyclopentane-1,9'-fluorene]-3-ene (**5f**): White solid; yield = 85% (24 mg, starting from 25 mg of **4**); reaction time = 24 h; M.p. 214–216 °C; $R_f = 0.62$ (silica gel, 10% EtOAc-petroleum ether); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.00 (s, 4H), 3.88 (s, 6H), 6.06 (s, 2H), 7.03 (d, $J = 8.70$ Hz, 4H), 7.55 (dd, $J_1 = 1.60$ Hz, $J_2 = 7.85$ Hz, 2H), 7.60 (d, $J = 8.70$ Hz, 4H), 7.71–7.74 (m, 4H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 46.67, 55.52, 55.64, 114.37, 120.02, 120.84, 125.94, 128.31, 130.54, 134.26, 138.01, 140.47, 155.39, 159.24; IR (CHCl_3): $\nu_{\text{max}} = 1242, 1430, 1460, 1515, 1608, 2915, 3010$ cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{31}\text{H}_{26}\text{KO}_2$ [$\text{M}+\text{K}$] $^+$ 469.1564 found: 469.1568.

2.3g 4,4'-(Spiro[cyclopentane-1,9'-fluorene]-3-en-2',7'-diyl)dibenzaldehyde (**5g**): White solid; yield = 93% (53 mg, starting from 50 mg of **4**); reaction time = 20 h; M.p. 260–262 °C; $R_f = 0.39$ (silica gel, 10% EtOAc-petroleum ether); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.01 (s, 4H), 6.07 (s, 2H), 7.65 (d, $J = 7.85$ Hz, 2H), 7.80–7.83 (m, 8H), 7.96 (d, $J = 8.15$ Hz, 4H), 10.06 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 46.52, 55.79, 120.62, 121.55, 126.87, 127.81, 130.46, 130.54, 135.27, 139.33, 139.74, 147.47, 155.71, 192.06; IR (CHCl_3): $\nu_{\text{max}} = 1210, 1303, 1600, 1696, 2810, 2850, 2916, 3040$ cm^{-1} HRMS (ESI, Q-TOF) calculated for $\text{C}_{31}\text{H}_{22}\text{NaO}_2$ [$\text{M}+\text{Na}$] $^+$ 449.1512 found: 449.1518.

2.3h 2',7'-Bis(4-(trifluoromethyl)phenyl)spiro[cyclopentane-1,9'-fluorene]-3-ene (**5h**): White solid; yield = 74% (50 mg, starting from 50 mg of **4**); reaction time = 18 h; M.p. 125–126 °C; $R_f = 0.58$ (silica gel, 10% EtOAc-petroleum ether); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.02 (s, 4H), 6.07 (s, 2H), 7.57–7.62 (m, 6H), 7.33 (d, $J = 1.25$ Hz, 2H), 7.81 (d, $J = 7.85$ Hz, 4H), 7.87 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 46.60, 55.84, 120.55, 121.41, 124.07, 126.67, 129.43, 130.58, 130.67, 138.97, 139.81, 142.44, 155.72; IR (CHCl_3): $\nu_{\text{max}} = 1217, 1300, 1335, 1438, 1612, 2847, 2925, 3055$ cm^{-1}



Scheme 2. Synthesis of spirofluorene building blocks **5a–h**.

HRMS (ESI, Q-TOF) calculated for $\text{C}_{31}\text{H}_{20}\text{KF}_6$ [$\text{M}+\text{K}$] $^+$ 545.1243 found: 545.1246.

3. Results and Discussion

Our group has been actively involved in the development of new synthetic strategies towards the development of spirocycles. To this end, we now report a new approach to diverse spirofluorenes. Our journey started with the preparation of known 2,7-dibromofluorene **2** by employing the known procedure.¹⁴ Then, the dibromo compound **2** was subjected to di-allylation in the presence of 50% aq. NaOH, leading to dibromo diallyl derivative **3** in 90% yield. Later, RCM sequence in the presence of Grubbs's first generation catalyst (G-I) yielded the spirofluorene derivative **4** in excellent yield (Scheme 1). Having the spiro building block **4** in hand, it was subjected to Suzuki-Miyaura (SM) cross-coupling reaction with simple and commercially-available phenylboronic acid in the presence of palladium catalyst [$\text{Pd}(\text{PPh}_3)_4$] and toluene:THF:water (1:1:1) as the solvent system to deliver the cross-coupling product **5a** in 88% yield (Scheme 2, Figure 1). Later, the scope of the methodology was expanded by preparing various other spiro derivatives including some interesting heterocyclic rings embedded in spirofluorene frame in good to excellent yields. As can be seen in Figure 1, we also synthesized some molecules containing polar functional groups such as carbonyl, formyl and cyano, which can be further manipulated to generate diverse interesting heterocycles. In case of **5b**,

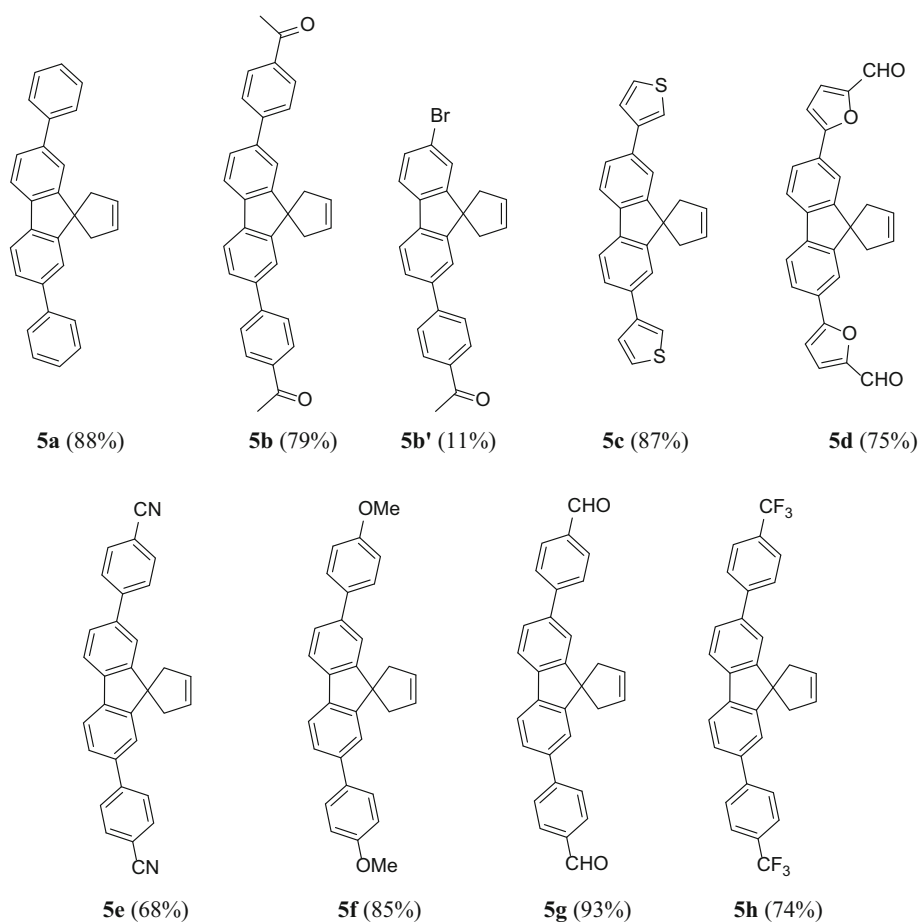


Figure 1. Structures of cross-coupling products assembled in our strategy.

Suzuki-Miyaura cross-coupling with 4-acetyl phenylboronic acid gave mono-cross-coupling product **5b'** in 11% yield along with **5b** (79%) (Figure 1). Some of these mono cross-coupling products can be further synthetically manipulated to generate highly functionalized fluorene derivatives suitable for material science applications.

4. Conclusions

We have demonstrated a simple strategy to the synthesis of spirofluorenes *via* RCM and SM cross-coupling reactions as key steps under operationally simple reaction conditions. The scope of this methodology has also been expanded by synthesizing spirofluorene derivatives containing heterocycles. The methodology developed and the molecules prepared here may find applications in material science.

Supplementary Information (SI)

Copies of the original spectra ($^1\text{H NMR}$, $^{13}\text{C NMR}$) of all the molecules reported in the experimental section are included

in Supplementary Information. Supplementary Information is available at www.ias.ac.in/chemsci.

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References

- (a) Saragi T P I, Spehr T, Siebert A, Fuhrmann-Lieker T and Salbeck J 2007 Spiro compounds for organic optoelectronics *Chem. Rev.* **107** 1011; (b) Qi H, Chang J, Abdelwahed S H, Thakur K, Rathore R and Bard A J 2012 Electrochemistry and electrogenerated chemiluminescence of π -stacked poly(fluorene)methylene oligomers. Multiple, interacting electron transfers *J. Am. Chem. Soc.* **134** 16265; (c) Rodríguez J G, Tejedor J L,

- Parra T L and Díaz C 2006 Synthesis of conjugated 2,7-bis(trimethylsilylethynyl)-(phenylethynyl)_nfluorene-9-one and 9-(p-methoxyphenyl)-9-methyl derivatives: Optical properties *Tetrahedron* **62** 3355; (d) Hadizad T, Zhang J, Wang Z Y, Gorjanc T C and Py C 2005 A general synthetic route to indenofluorene derivatives as new organic semiconductors *Org. Lett.* **7** 795
- (a) Reisch H, Wiesler U, Scherf U and Tuytuykov N 1996 Poly(indenofluorene) (PIF), a novel low band gap polyhydrocarbon *Macromolecules* **29** 8204; (b) Inaoka S and Advincula R 2002 Synthesis and oxidative cross-linking of fluorene-containing polymers to form conjugated network polyfluorenes: Poly(fluorene-9,9-diyl-*alt*-alkan- α , ω -diyl) *Macromolecules* **35** 2426; (c) Wong K T, Chen R T, Fang F C, Wu C C and Lin Y T 2005 4,5-Diazafluorene-incorporated ter(9,9-diarylfuorene): A novel molecular doping strategy for improving the electron injection property of a highly efficient OLED blue emitter *Org. Lett.* **7** 1979; (d) Wong K T, Chen Y M, Lin Y T, Su H C and Wu C C 2005 Non-conjugated hybrid of carbazole and fluorene: A novel host material for highly efficient green and red phosphorescent OLEDs *Org. Lett.* **7** 5361; (e) Liu X-Y, Tang X, Zhao D, Song B, Ding L, Fan J and Liao L-S 2018 A series of spirofluorene-based host materials for efficient phosphorescent organic light-emitting diodes *Org. Electron.* **61** 70
 - (a) Kumar D, Thomas K R J, Lee C P and Ho K C 2014 Organic dyes containing fluorene decorated with imidazole units for dye-sensitized solar cells *J. Org. Chem.* **79** 3159; (b) Marzari G, Durantini J, Minudri D, Gervaldo M, Otero L, Fungo F, Pozzi G, Cavazzini M, Orlandi S and Quici S 2012 Fluorous molecules for dye-sensitized solar cells: Synthesis and characterization of fluorene-bridged donor/acceptor dyes with bulky perfluoroalkoxy substituents *J. Phys. Chem. C* **116** 21190
 - (a) Liu F, Xie L-H, Tang C, Liang J, Chen Q-Q, Peng B, Wei W, Cao Y and Huang W 2009 Facile synthesis of spirocyclic aromatic hydrocarbon derivatives based on *o*-halobiaryl route and domino reaction for deep-blue organic semiconductors *Org. Lett.* **11** 3850; (b) Seo J A, Lee C-W and Gong M-S 2013 Synthesis of New Spiro[benzo[c]fluorene-7,9'-fluorene] dimers and their optical properties *Bull. Korean Chem. Soc.* **34** 1414
 - Jiang Z, Yao H, Liu Z, Yang C, Zhong C, Qin J, Yu G and Liu Y 2009 Bent ladder-type hexaphenylene with carbazole core and spiro linkage as stable and efficient blue emitter *Org. Lett.* **11** 4132
 - Jiang Z, Liu Z, Yang C, Zhong C, Qin J, Yu G and Liu Y 2009 Multifunctional fluorene-based oligomers with novel spiro-annulated triarylamine: Efficient, stable deep-blue electroluminescence, good hole injection, and transporting materials with very high T_g *Adv. Funct. Mater.* **19** 3987
 - (a) Yu W L, Pei J, Huang W and Heeger A J 2000 Spiro-functionalized polyfluorene derivatives as blue light-emitting materials *Adv. Mater.* **12** 828; (b) Shen W J, Dodda R, Wu C C, Wu F I, Liu T H, Chen H H, Chen C H and Shu C F 2004 Spirobifluorene-linked bisanthracene: An efficient blue emitter with pronounced thermal stability *Chem. Mater.* **16** 930
 - (a) Wu Y, Li J, Fu Y and Bo Z 2004 Synthesis of extremely stable blue light emitting poly(spirobifluorene)s with Suzuki polycondensation *Org. Lett.* **6** 3485; (b) Wong K T, Chen H F and Fang F C 2006 Novel spiro-configured PET chromophores incorporating 4,5-diazafluorene moiety as an electron acceptor *Org. Lett.* **8** 3501; (c) Omer K D, Ku S Y, Cheng J Z, Chou S H, Wong K T and Bard A J 2011 Electrochemistry and electrogenerated chemiluminescence of a spirobifluorene-based donor(triphenylamine)-acceptor (2,1,3-benzothiadiazole) molecule and its organic nanoparticles *J. Am. Chem. Soc.* **133** 5492; (d) Shen W J, Dodda R, Wu C C, Wu F I, Liu T H, Chen H H, Chen C H and Shu C F 2004 Spirobifluorene-linked bisanthracene: An efficient blue emitter with pronounced thermal stability *Chem. Mater.* **16** 930; (e) Zhu Y-Q and Dong L 2015 One-pot synthesis of polysubstituted spirofluorene-indene via Ru(II)-catalyzed [3 + 2]annulation and intramolecular Friedel-Crafts cyclization *J. Org. Chem.* **80** 9973
 - (a) Grubbs R H 2004 Olefin metathesis *Tetrahedron* **60** 1117; (b) Fürstner A 2000 Olefin metathesis and beyond *Angew. Chem. Int. Ed.* **39** 3012; (c) Kotha S and Dipak MK 2012 Strategies and tactics in olefin metathesis *Tetrahedron* **68** 397; (d) Kotha S and Sreenivasachary N 2001 Catalytic metathesis reaction in organic synthesis *Indian J. Chem.* **40B** 763; (e) Kotha S, Meshram M and Tiwari A 2009 Advanced approach to polycyclics by a synergistic combination of enyne metathesis and Diels-Alder reaction *Chem. Soc. Rev.* **38** 2065; (f) Diver S T and Giessert A J 2004 Enyne metathesis (Enyne bond reorganization) *Chem. Rev.* **104** 1317; (g) Mori M 2010 Recent progress on enyne metathesis: Its application to syntheses of natural products and related compounds *Materials* **3** 2087; (h) Kotha S, Meshram M, Khedkar P, Banerjee S and Deodhar D 2015 Recent applications of ring-rearrangement metathesis in organic synthesis *Beilstein J. Org. Chem.* **11** 1833; (i) R H Grubbs 2003 (Ed.) *Handbook of Metathesis* Vol. 1–3 (Weinheim: Wiley-VCH); (j) Cossy J, Arseniyadis S and Meyer C 2010 (Eds.) *Metathesis in Natural Product Synthesis: Strategies, Substrates and Catalysts* (Weinheim: Wiley-VCH); (k) Shramm M P, Reddy D S and Kozmin S A 2001 Siloxyalkyne-alkene metathesis: Rapid access to highly functionalized enones *Angew. Chem. Intl. Ed.* **40** 4274; (l) Malik C K and Ghosh S 2007 Domino metathesis involving ROM-RCM of substituted norbornenes. Rapid access to densely functionalized tricyclic bridged and condensed ring systems *Org. Lett.* **9** 2537
 - (a) Kotha S, Panguluri N R and Ali R 2017 Design and synthesis of spirocycles *Eur. J. Org. Chem.* 5316; (b) Kotha S, Deb A C, Lahiri K and Manivannan E 2009 Selected synthetic strategies to spirocyclics *Synthesis* 165
 - (a) Kotha S, Ali R, Panguluri N R, Datta A and Kannaujiya K K 2018 Synthesis and photophysical properties of star-shaped blue green emitting π -conjugated spirotruxenes *Tetrahedron Lett.* **59** 4080; (b) Kotha S, Ali R, Panguluri N R and Deb A C 2018 Design and synthesis of spirotruxene and spirofluorene derivatives *Indian J. Chem.* **57** 1489

12. (a) Kotha S, Manivannan E, Ganesh T, Sreenivasachary N and Deb A 1999 Spiro-annulation *via* ring closing metathesis reaction *Synlett* 1618; (b) Kotha S, Meshram M and Dommaraju Y 2018 Design and synthesis of polycycles, heterocycles, and macrocycles *via* strategic utilization of ring-closing metathesis *Chem. Rec.* **18** 1613; (c) Rao H S P, Rafi S, Kumar P R, Guravaiah C and Muthanna N 2012 On the stereochemistry of the olefinic double bond in 13-membered heterocyclic rings accessible by ring-closing metathesis reaction *Tetrahedron Lett.* **53** 6877
13. (a) Kotha S, Lahiri K and Kashinath D 2002 Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis *Tetrahedron* **58** 9633; (b) Kotha S and Lahiri K 2007 Expanding the diversity of polycyclic aromatics through a Suzuki–Miyaura cross-coupling strategy *Eur. J. Org. Chem.* 1221; (c) Kotha S and Mandal K 2009 A Retrospective on the design and synthesis of novel molecules through a strategic consideration of metathesis and Suzuki–Miyaura cross-coupling *Chem. Asian J.* **4** 354; (d) Kotha S, Meshram M and Chakkapalli C 2018 Synergistic approach to polycycles through Suzuki–Miyaura cross coupling and metathesis as key steps *Beilstein J. Org. Chem.* **14** 2468; (e) Kotha S, Behera M and Shah V R 2005 A Simple Synthetic Approach to Allylated Aromatics *via* the Suzuki–Miyaura Cross-Coupling Reaction *Synlett* 1877
14. Zhang X, Bu L, Qu Y, Wang L, Geng Y and Wang F 2009 Novel spiro-fluorenes from tandem radical addition for liquid crystalline monodisperse conjugated oligomers *J. Mater. Chem.* **19** 399